



nanomaterials

Special Issue Reprint

Advanced Nanomaterials and Energetic Application

Experiment and Simulation

Edited by
Weiqiang Pang, Djalal Trache and Kaili Zhang

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Advanced Nanomaterials and Energetic Application: Experiment and Simulation

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Guest Editors

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About the Editors

Weiqliang Pang

Weiqliang Pang is currently a professor at the National Key Laboratory of Energetic Materials at Xi'an Modern Chemistry Research Institute. For many years, he has been engaged in research on energetic materials, solid propellants, micro/nano-metallic fuels, and explosion mechanics. He has published more than 200 peer-reviewed papers in journals such as *Progress in Energy and Combustion Science*, *Combustion and Flame*, *Defence Technology*, etc. He has Guest-Edited a number of Special Issues in journals such as *Nanomaterials*, *FirePhysChem*, and the *Chinese Journal of Explosives and Propellants*. His main research interests include the preparation and combustion characteristics of nano-energetic materials (nEMs), solid propellant preparation and characterization, and the ignition and combustion of energetic materials.

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Editorial

Advanced Nanomaterials and Energetic Application: Experiment and Simulation

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In recent years, significant advancements have been made in the exploitation, combustion, ignition, and application of innovative nano-metric energetic materials (nEMs), including solid fuels, energetic combustion catalysts, metal particles, thermites, energetic composites, and more, thanks to new technological developments in the field of nano-scale science and technology. Utilizing innovative nEMs and their composites in various chemical propulsion systems is beneficial because of their high heat of formation, high specific surface area, high reactive activation, and high energy density. However, although the extremely high heat release rates and tailored burning rates of innovative nEMs are attractive features, their production of high energy in their combustion processes and high combustion efficiency in industry applications presents a great challenge to many engineers and scientists. Various techniques have recently been developed to overcome these intrinsic difficulties. Fundamental research investigations have also been conducted to explore the detailed physicochemical processes associated with the preparation, combustion, and application of innovative nEMs. In particular, state-of-the-art rocket propulsion systems have benefited greatly from the development of innovative nEMs in recent years, especially in terms of prospective nEMs for future rocket fuels and the fabrication of propellants, explosives, and pyrotechnics.

This Special Issue presents the compiled results of the most recent developments of innovative nEMs, which include nano-sized metal fuels, nano-sized combustion catalysts, nano-sized energetic composite nano-sized oxidizers, nano-sized thermites, and more, to be used in simulations, ignition, and combustion, with a particular focus on energetic application technology in chemical propulsion systems. This effort focuses on the design and investigation of novel high-tech nEMs for metal fuels, oxidizers, combustion catalysts, thermites, and further additives for solid, liquid, gelled, hybrid, electro-controlled, and propellant systems. On the one hand, considerable effort is exerted to improve and perfect the propulsion systems themselves, which are designed exclusively for the nano-metric ingredients that they work with. On the other hand, researching new nano-metric ingredients for chemical propulsion represents a challenge. In recent years, in the realm of nano-metric energetic material ingredients for chemical propellants, great progress has been made in the development of propellants, explosives, and pyrotechnics. Yet, despite the impressive progress witnessed in the field of nano-EMs during the last century, it must be admitted that the rate of progress is much slower than in other fields, such as polymer chemistry, electronics, and computers, due to the various constraints and restrictions that nano-EM

scientists encounter when developing a new nEM. These include safety, stability (thermal, storage, etc.), cost, and other considerations.

To accelerate the potential applications, various works have focused on the physical and chemical characteristics through theory, experiments, and simulations. The aim of this issue is to present a comprehensive knowledge on the synthesis, characterization, combustion, mechanical, detonation, and safety of nEMs. This Special Issue *Advanced Nanomaterials and Energetic Application: Experiment and Simulation* explores innovative nEMs and nEM ingredients, as well as the experiment and simulation of formulations. It collects contributions spanning the recent progress and data of nEMs in chemical propulsion and applications. Attention has been paid to the design, model, properties, and state-of-the-art nature of this class of thermochemical propulsion devices. A total of 15 papers were selected for publication, following a standard peer review process, which represent the most recent achievements of famous research groups. The participation of young authors with novel or innovative concepts was particularly encouraged, and they were of course supported by the assistance of their supervisors.

Aluminum powder is the most commonly used metal fuel in the explosives industry, and is widely used in explosives and propellants. The application of aluminum powder in explosives can greatly improve the detonation heat and work power, as well as the damage efficiency of the ammunition. Aluminum-containing explosives are widely used in ammunition for air defense weapons, ground targets, and underwater weapons. The application of aluminum powder in propellants can significantly increase their combustion heat and improve the specific impulse of rocket engines.

The research progress in the preparation technology, reactivity, and application of nano-aluminum in explosives and propellants is systematically reviewed here, and the reactivity differences between nano-aluminum powder and micro-aluminum powder are compared [1]. It has been established that nano-sized aluminum exhibits a significantly higher reactivity than its micron-sized counterpart, as evidenced by its lower ignition threshold, enhanced combustion behavior, and greater reaction completeness. These characteristics result in a more pronounced impact both on the detonation performance of mixed explosives and on the combustion efficiency of propellant formulations.

As the global energy transition accelerates and the integration of renewable energy into power grids presents new challenges, the development of electrochemical energy storage materials which are capable of delivering both high power density and high energy density has become a priority in energy research. Since the emergence of two-dimensional transition metal carbides and nitrides (MXenes), these materials have been of great interest due to their tunable interlayer spacing, excellent hydrophilicity, high electrical conductivity, compositional versatility, and chemically rich surface characteristics. More than 100 different MXene combinations can be calculated theoretically, but only more than 40 have been successfully synthesized through experiments. Among the many synthesized and reported MXene materials, vanadium-based carbide MXenes, represented by V_2CT_x and $V_4C_3T_x$, show excellent application prospects in energy storage and have become a key focus for researchers. In this review, the structure, characteristics, and preparation methods of vanadium-based MXene precursors in the MAX phase, and their applications in supercapacitors, are discussed. The key challenges currently associated with vanadium-based materials and their heterostructures are highlighted, and an outline of the promising future research directions is presented [2].

Metal and metalloid powders are widely used in high-energy compositions (HECs) and solid propellants (SPs), with the effect of increasing their energetic characteristics in the combustion chamber. The particle size distribution, protective coatings of the particles, and heat of combustion of the metal powders influence both the ignition and combustion

parameters of the HECs, as well as the characteristics of the propulsion systems [3]. The effect of Al-B, Fe-B, and Ti-B (Me-B) mixture ultrafine powders (UFPs) on the ignition and combustion characteristics of a model HEC, which is based on a solid oxidizer and a polymer combustible binder, was investigated. The Me-B mass ratios in the mixture UFPs corresponded to the phase composition of the borides AlB_2 , FeB , and TiB_2 . It was found that by replacing the aluminum UFP with Al-B, Fe-B, and Ti-B UFPs in the HECs, the exponent (n) in the correlations of the ignition delay time $t_{\text{ign}}(q)$ and burning rate $u(p)$ changed. The maximum burning rate and n over the pressure range of 0.5–5.0 MPa were obtained for the HEC with Al-B UFPs due to the increase in the heat release rate near the sample surface during the joint combustion of the Al and B particles.

Aluminum (Al) powder is a metal fuel used ubiquitously in solid propellants, and its practical energy release significantly impacts the performance of solid propellants. The enhanced energy release is a consequence of the increased energy in Al powder and its improved combustion efficiency. To enhance the energy release of Al powder in solid propellants, poly (difluoroaminomethyl-3-methylethoxybutane) (PDF), which has difluoroamino (NF_2), was utilized to improve the energy and promote combustion efficiency. Al with three distinct powder sizes (29 μm , 13 μm , and 1–3 μm) was coated with PDF using the solvent/non-solvent method, which led to the formation of Al/PDF composites. The morphology and characteristics of this Al/PDF were characterized [4], and the results demonstrated that all powder sizes of Al/PDF had core-shell structures, and that the NF_2 in the PDF layer on the Al surface maintained its original structure. Al/PDF exhibited greater hydrophobicity. NF_2 prompted Al/PDF, with better catalysis upon ammonium perchlorate (AP) decomposition. Compared to the Al powder, the ignition delay time of the Al/PDF was significantly reduced. For the mixed samples of Al/PDF and AP, NF_2 shortened the ignition delay time, improved the combustion stability, extended the combustion duration, and formed volatile fluorine compounds. These findings underscore the effect of NF_2 in Al/PDF composites, which enhance the energy release of Al and offer promising potential applications.

Due to the increase in the application of antibacterial nanomaterials (NMs), the potential for their ingestion by humans has also increased. Evidence shows that NMs can induce dysbiosis in the gut microbiota in vivo. Despite this, in vitro investigation of the antibacterial activity of NMs on gut-relevant, commensal bacteria has been neglected, with studies predominantly assessing NM toxicity against pathogenic bacteria. Thus, the current study investigates the antibacterial activity of copper oxide (CuO) NMs to *Escherichia coli* K12, *Enterococcus faecalis*, and *Lactobacillus casei*, using a combination of approaches to evaluate the importance of reactive oxygen species (ROS) production as a mechanism of toxicity [5]. The data suggest that CuO NMs have antibacterial activity against gut-relevant bacteria, with evidence that NM-mediated ROS production may contribute to reductions in bacterial viability, which suggests that the use of a combination of assays provides a robust assessment of the antibacterial properties of ingested NMs. In particular, it is recommended that plate counts and OD measurements be prioritized in future screenings of the antibacterial properties of NMs.

Progress and innovation in material science increasingly rely on the development of next-generation materials that integrate multi-functionality, sustainability, and responsiveness to external stimuli, like heat, light, or mechanical stress. These features are essential to meeting the escalating demands for high-performance materials in advanced applications, including flexible electronics, advanced sensing technologies, and smart integrated platforms. Composite films based on phosphorylated polyvinyl alcohol (PVA-P), $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, and cholesteryl acetate (ChLC) were designed and characterized to explore their potential in flexible electronic applications [6]. The incorporation of phosphate groups and

ChLC in these films enhanced the intermolecular interactions, which was confirmed by FTIR spectroscopy. Morphological and optical analyses revealed a transition from homogeneous to phase-separated structures with birefringent textures in ChLC-rich films. Thermal studies demonstrated their improved stability and increased glass transition and melting temperatures, particularly in samples with higher ChLC contents. Mechanical and dielectric evaluations, meanwhile, highlighted the tunability of the stiffness, flexibility, permittivity, and dielectric losses depending on the MXene and ChLC ratios. These multifunctional films exhibit flame-retardant behavior and show promise for use in stimuli-responsive, sustainable electronic devices, such as flexible displays and sensors.

Vaterite particles, naturally occurring mineral forms of polycrystalline calcium carbonate (CaCO_3), are both biocompatible and biodegradable, making them promising candidates for targeted drug delivery. Biocompatible vaterite microspheres, which are renowned for their porous structure, are promising carriers for magnetic nanoparticles (MNPs) in biomedical applications such as targeted drug delivery and diagnostic imaging. Having precise control over the magnetic moment of individual microspheres is crucial for these applications. This study employs wide-field quantum diamond microscopy to map the stray magnetic fields of individual vaterite microspheres (3–10 μm) which are loaded with Fe_3O_4 MNPs of varying sizes (5 nm, 10 nm, and 20 nm) [7]. By analyzing over 35 microspheres under a 222 mT external magnetizing field, the peak-to-peak stray field amplitudes of $41 \pm 1 \mu\text{T}$ for 5 nm and 10 nm superparamagnetic MNPs were measured, and these measurements reflect their comparable magnetic response. Finite-element simulations confirm variations in the MNP distribution and magnetization uniformity within the vaterite matrix. This high-resolution magnetic imaging approach yields critical insights into MNP-loaded vaterites, enabling their optimized synthesis and magnetically controlled systems for precision therapies and diagnostics.

The complex dielectric permittivity has been studied with waves of millimeter wavelengths for both rare earth manganate and titanate and for LiCoPO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ orthophosphate composites. The measurements were performed in the 26 to 38 GHz range by determining the transmission and reflection coefficients through a plate [8]. The authors discuss the non-monotonic frequency dependence observed in both the real and imaginary components of the permittivity. In addition, the structural and phase compositions of the nanocomposites were examined to support the interpretation of the electromagnetic behavior.

Semiconductor bridges (SCBs), which represent a novel category of pyrotechnic devices, have garnered significant attention in both military and civilian sectors due to their distinctive operating principles and broad application potential. The complex burst characteristic parameters of SCBs were subjected to dimensionality reduction using principal component analysis (PCA), which enabled accurate evaluations of the output performance of SCBs. The accuracy and reliability of the PCA method were also validated. A 100 μF tantalum capacitor was used to excite the SCB, while a digital oscilloscope recorded the characteristic parameters of the SCB explosion [9]. The experimental results demonstrate that the critical burst time of the SCB decreases with the rising voltage, with the critical burst energy decreasing first and then increasing with the rising voltage. The total burst time and total burst energy of SCBs all decrease first and then increase with the rise in voltage. The SCB was utilized to ignite lead styphnate (LTNR) under varying circuit conditions, and the characteristic parameters obtained were analyzed using PCA to obtain comprehensive scores. The consistency between the two sets of scores validated the accuracy and reliability of PCA in assessing the SCB's output capability.

Improving the energy release and safety of composite solid propellants is a key focus in energetic materials research. Graphene, with its excellent thermal conductivity

and lubrication properties, is a promising additive. The propellants' performance can be enhanced by graphene's large surface area and excellent thermal and electrical conductivity, which promote AP decomposition and combustion, combined with its lubricating effect, which enhances safety. However, excessive graphene may hinder these benefits. The Al@AP core-shell particles doped with graphene were prepared via an in situ deposition method. The structure, thermal decomposition, combustion, and safety performance of the graphene-doped Al@AP samples were investigated [10]. The results showed that AP effectively coated the aluminum to form a typical core-shell structure, with graphene uniformly loaded into the framework. Closed-bomb and laser ignition tests revealed that the pressure rise rates and combustion intensity increased with the graphene content up to 1.0 wt.%, but beyond that they declined. Additionally, graphene significantly improved safety by reducing the sensitivity to impact and friction. This study provides balanced design criteria for graphene-doped Al@AP as a solid propellant.

Very-low-frequency (VLF, frequency range 3–30 kHz) radio waves play a crucial role in long-distance underwater navigation and communication due to their stable propagation characteristics and low attenuation rates. However, the applications of traditional VLF transmitter antennas (e.g., T-shaped antennas, umbrella antennas, etc.) are restricted by their wavelength limitations, their large physical dimensions (which usually reach several square kilometers), and the need to lay a large-area ground network. As a result, the construction of miniaturized VLF antennas is a current research hotspot. Research and experiments have been conducted to create some feasible solutions which promote the miniaturization of VLF antennas, such as mechanical antennas and magnetic resonant coupled antennas. In order to break through the difficulties of very-low-frequency (VLF) miniaturized antenna which have a small power capacity and low radiation efficiency, this paper proposes a high-radiation-field-strength magnetic loop antenna based on a nanocrystalline alloy magnetic core. A high-permeability nanocrystalline toroidal core ($\mu_r = 50,000$, $B_s = 1.2$ T) is used to optimize the thickness-to-diameter ratio ($t = 0.08$) and to increase the effective permeability to 11,000. The Leeds wires, characterized by their substantial carrying capacity, are manufactured through a toroidal winding process [11].

Terahertz technology covers a broad spectrum of application prospects in a range of fields, such as communication, the military, and medicine, and the use of metamaterials is important for further developments of terahertz technology. Ning et al. [12] proposed a multi-mode switchable ultra-wideband terahertz absorber based on patterned graphene and VO₂. They designed a graphene pattern which was composed of a large rectangle, rotated 45° in the center, and four identical small rectangles in the periphery, as well as a VO₂ layer pattern composed of four identical rectangular boxes, with small rectangles embedded in the dielectric layer. The absorption mechanism was revealed by using the relative impedance theory and the electric field distribution, along with local plasma resonance analysis.

Prelithiation is widely considered one of the most promising strategies to compensate for the loss of active substances and to improve the initial Coulombic efficiency in silicon-based anodes for advanced high-energy-density batteries. However, because of their unstable solid electrolyte interface (SEI) layer and low initial Coulombic efficiency, they expand in volume during prelithiation and react with moisture, making commercialization a difficult process. A strategy using lithium bis(fluorosulfonyl)imide (LiFSI) treatment to eliminate redundant lithium was developed and LiF-based inorganic compounds on the surface of the prelithiated electrode were generated [13]. This technique not only increases the battery's energy density but also its cycle stability, resulting in superior capacity retention and a longer cycling life.

Gallium oxide (Ga_2O_3), an ultra-wide bandgap semiconductor, is an ideal material for solar-blind photodetectors, but challenges, such as its low responsivity and response speed, persist. One-dimensional (1D) Ga_2O_3 nanorods were designed to achieve high photodetection performance [14]. Through modulating the source concentration, pH value, temperature, and reaction time, 1D $\beta\text{-Ga}_2\text{O}_3$ nanorods were controllably fabricated using a cost-effective hydrothermal method, followed by post-annealing. The findings highlight the potential of 1D Ga_2O_3 nanostructures to be used in high-performance solar-blind ultraviolet photodetectors, paving the way for future integrable deep ultraviolet optoelectronic devices.

With the continuation of industrialization, the problem of water resource pollution has become increasingly serious, and the mismatch between the supply of and demand for water resources in China has thus become more acute. Therefore, solving the problem of water pollution and improving the water ecological environment are particularly important to enhance the utilization rate of water resources. Chi et al. [15] synthesized graphene oxide (GO)/zinc oxide (ZnO)/silver (Ag) composite materials and investigated their photocatalytic degradation performance with ciprofloxacin (CIP) under visible light irradiation. The GO/ZnO/Ag composites, which had different ratios, were prepared via an impregnation and chemical reduction method and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). This catalyst effectively degraded ciprofloxacin under light irradiation, showing the potential for its use in water purification applications.

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Review

Preparation Technology, Reactivity and Applications of Nano-Aluminum in Explosives and Propellants: A Review

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Abstract

Aluminum powder is the most commonly used metal fuel in the industry of explosives and propellants. The research progress in preparation technology, reactivity and application of nano-aluminum in explosives and propellants is systematically reviewed in this paper. The preparation technology of nano-aluminum powder includes mechanical pulverization technology (such as the ball milling method and ultrasonic ablation method, etc.), evaporation condensation technology (such as the laser induction composite heating method, high-frequency induction method, arc method, pulsed laser ablation method, resistance heating condensation method, gas-phase pyrolysis method, wire explosion pulverization method, etc.), chemical reduction technology (such as the solid-phase reduction method, solution reduction method, etc.) and the ionic liquid electrodeposition method, each of which has its own advantages. Some new preparation methods have emerged, providing important reference value for the large-scale production of high-purity, high-quality nano-aluminum powder. The reactivity differences between nano-aluminum powder and micro-aluminum powder are compared in the thesis. It is clear that the reactivity of nano-aluminum powder is much higher than that of micro-aluminum powder in terms of ignition performance, combustion performance and reaction completeness, and it has a stronger influence on the detonation performance of mixed explosives and the combustion performance of propellants. Nano-aluminum powder is highly prone to oxidation, which seriously affects its application efficiency. In addition, when aluminum powder oxidizes or burns, a surface oxide layer will be formed, which hinders the continued reaction of internal aluminum powder. In addition, nano-aluminum powder may deteriorate the preparation process of explosives or propellants. To improve these shortcomings, appropriate coating or modification treatment is required. The application of nano-aluminum powder in mixed explosives can improve many properties of mixed explosives, such as detonation velocity, detonation heat, peak value of shock wave overpressure, etc. Applying nano-aluminum powder to propellants can significantly increase the burning rate and improve the properties of combustion products. It is pointed out that the high reactivity of nano-aluminum powder makes the preparation and storage of high-purity nano-aluminum powder extremely difficult. It is recommended to increase research on the preparation and storage technology of high-purity nano-aluminum powder.

Keywords: nano-aluminum; preparation technology; reactivity; application; explosives and propellants

1. Introduction

Aluminum powder is the most commonly used metal fuel in the explosives industry, which is widely used in explosives and propellants. The application of aluminum powder in explosives can greatly improve the detonation heat and work power, as well as the damage efficiency of ammunition. Aluminum-containing explosives are widely used in ammunition for air defense weapons, ammunition for ground targets and ammunition for underwater weapons [1–5]. The application of aluminum powder in propellants can significantly increase their combustion heat and improve the specific impulse of rocket engines [6–10].

The biggest problem in the application of aluminum powder in explosives and propellants is that it is difficult for aluminum powder to react completely because of the formation of surface oxide layer, so its high combustion calorific potential cannot be fully realized. Ultrafining and nanocrystallizing micro-aluminum powder are important methods to improve the combustion completeness of aluminum powder. High-purity and high-quality nano-aluminum powder is necessary for effectively utilizing the energy characteristics of explosives and propellants. Therefore, it is very important to prepare high-purity and high-quality nanometer aluminum powder. In addition, the reactivity difference between nano-aluminum powder and micro-aluminum powder is compared in this paper.

Because nano-aluminum powder is easily oxidized, its application efficiency is seriously affected. In addition, when aluminum powder is oxidized or burned, it will form a surface oxide layer, which will prevent the internal aluminum powder from continuing to react. In addition, nano-aluminum powder will deteriorate the preparation process of explosives or propellants [11]. Appropriate coating or modification treatment is needed in order to improve these shortcomings. The latest research progress in nano-aluminum powder modification technology is also introduced in this paper, aiming to provide technical support for workers in the explosives and propellants industry.

Finally, the influence of nano-aluminum powder on the properties of explosives and propellants is also expounded.

2. Preparation Technology of Nano-Aluminum

2.1. Mechanical Pulverization Technology

2.1.1. Ball Milling Method

The ball milling process utilizes the collision, impact and friction of milling balls to crush materials. Ball milling is the most commonly used mechanical pulverization technology. The shape, hardness and ratio of the milling balls, their ratio to the materials, the fill ratio of the ball milling chamber, the ball milling medium, the rotating speed and the ball milling time all affect the final product quality. The ball milling chamber can be divided into the impact area, milling area, inert area, falling area, empty throwing area and throwing area, as shown in Figure 1. Among these, the movement direction and high relative speed of the medium in the throwing area, impact area, empty throwing area and milling area will change sharply, which plays a key role in milling and crushing [12].

Yuan [13] prepared nanometer aluminum powder by the high-energy ball milling method. Anhydrous ethanol was used as the liquid medium and polyvinylpyrrolidone (PVP) as the modifier. The particle size analysis results showed that the yield of aluminum powder below 100 nm was about 22.85%. Jiang [14] prepared nano-aluminum powder by the ball milling method. Raw material aluminum powder with an average particle size of 40 microns was ground under nitrogen protection and protected by a coating agent to prevent oxidation. X-ray diffraction (XRD) test results showed that the average grain size of the prepared aluminum nanoparticles was between 25 nm and 30 nm, and the average particle size was 27.8 nm. Wang [15] prepared nano-aluminum powder with self-designed

NP-V typed nano-powder production equipment. According to the X-ray diffraction (XRD) pattern, the particle size of the nanometer aluminum powder was mainly distributed in the range of 20~200 nm, the average particle size (D_n) was 98.9 nm, and the crystal size was 36.1 nm. The aluminum content, calculated according to energy spectrometry measurements, was 87.44%. Kumar [16] prepared nano-aluminum powder particles by a low-temperature milling method. It was observed that the microcrystal size of the low-temperature milling powder changed from 10 to 15 nm after 390 min of ball milling. The authors believe that the low-temperature milling process can produce high-activity aluminum powder with a particle size of about 10 nm in batches, which has important application value. Yu [17] prepared nano-aluminum powder by the ball milling method. Raw material aluminum powder with a particle size of 4~8 microns was milled in gas-phase or liquid-phase acetonitrile (ACN) under the protection of argon. The analysis results showed that about 95% of the particles were in the mass range of 50~100 nm. The authors suggested that an important factor in the effective size reduction of aluminum powder is the ability of the milling reactants to reach the crack tip quickly, and that small-molecule reactants (such as ACN) are more effective in promoting size reduction than large end-sealed molecules. Furthermore, the team in Ref. [18] also prepared nano-aluminum powder by ball milling in an ammonia and monomethylamine (MMA) atmosphere, efficiently producing nano-aluminum powder particles about 100 nm in size. Therefore, the milling medium is very important for the production of high-quality nano-aluminum powder. Salas [19] prepared nanometer aluminum powder by wet milling. The aluminum powder used was 99.8% pure, and the milling ball was an yttrium-stabilized zirconia (YSZ) ball with a diameter of 3.0 mm. Aluminum nanoparticles made from aluminum powder are produced by wet mechanical milling through a combination of different milling conditions, such as the ball-powder ratio (BPR) and the amount of solvent used. It was found that the particle size of nano-aluminum powder is about 10 nm under optimized conditions.

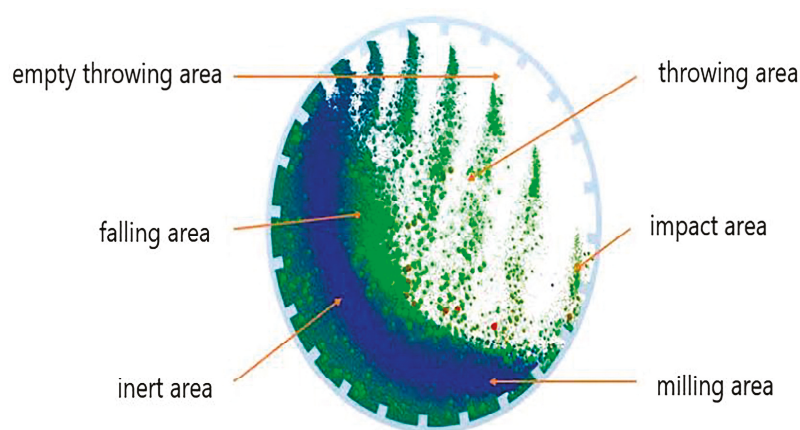


Figure 1. Division of movement area in ball mill chamber. Division of movement area in ball mill chamber [12]. Reproduced with permission from *Nonferrous Metals (Mineral Processing Section)* Editorial Office, 2024.

The analysis shows that the temperature, the material and size of the ball, the medium of the ball mill and the milling time have a significant influence on the quality of the product. Due to the different ball milling conditions adopted by different researchers, it cannot be inferred that specific ball milling conditions are optimal.

2.1.2. Ultrasonic Ablation (Scrub) Method

The ultrasonic ablation (scrub) method is an emerging method for preparing some nano materials. It uses the energy-driven screw movement of an ultrasonic device to

grind aluminum powder into nanoscale aluminum powder, as shown in Figure 2. Hahnrouzi [20] creatively proposed a new ultrasonic ablation (scrub) technique to prepare aluminum nanoparticles. The ultrasonic amplitude transformer bar is composed of three parts: a sandwich transducer (Langevin type), a titanium-reinforced amplitude transformer bar and a titanium screw. Ultrasonic waves are longitudinal waves that cause the titanium screw to move back and forth within a range of about 145 nm, quickly producing nanometer aluminum powder of nearly the same size. Ultrasonic ablation technology has many advantages, such as a fast process, green synthesis, no need for any other chemical precursors, homogeneous and pure products (without any solvent), stable particles, unique morphology and a narrow size distribution. Whenever the ultrasonic device is turned on, the production of nano-aluminum powder starts immediately, and all target foils can be converted into nano-aluminum powder in a matter of minutes. The particle size and preparation efficiency of aluminum powder can be changed by changing the power of the ultrasonic device and displacing the titanium amplifier and screw. No additional elements were detected in multiple analyses. Therefore, this novel method has important application value for the preparation of nano-aluminum powder.

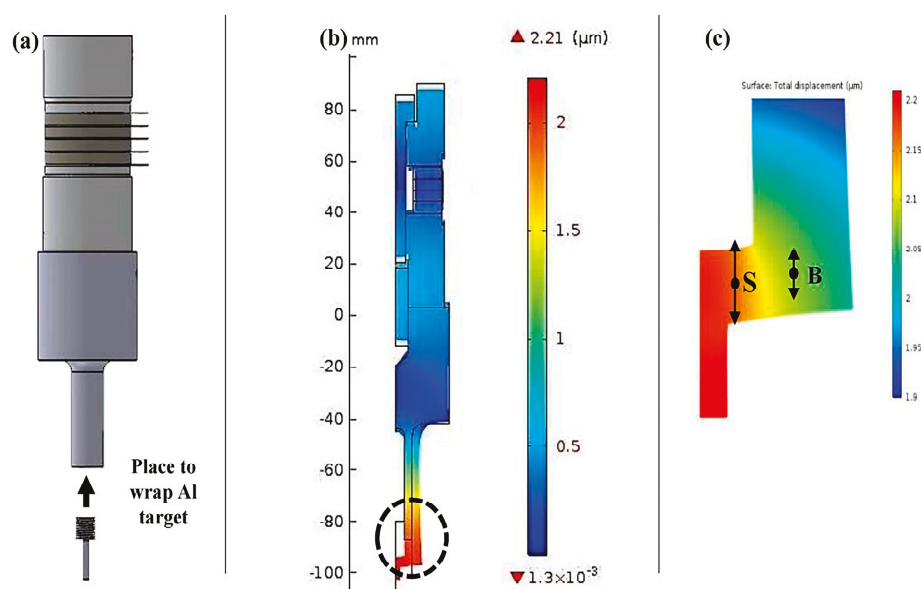


Figure 2. Transducer simulation. (a) Schematic of the transducer; (b) FEM analyses of the horn; (c) magnified dashed circle in (b). The arrows show the screw displacement (S) and the booster displacement (B) [20]. Reproduced with permission from Elsevier, 2019.

Because ultrasonic ablation has many advantages that traditional techniques cannot match, the analysis results show that this technology has the potential to replace the existing technology and is worthy of further study.

2.2. Evaporation–Condensation Technology

Evaporation–condensation technology is utilized to prepare nano-aluminum powder using induction coils, plasma, arcs and other means to evaporate aluminum into gas, followed by cooling in an inert medium. Nano-scale aluminum powder can be obtained by controlling the appropriate process parameters.

2.2.1. Laser Induction Composite Heating Method

Nano-scale aluminum powder was prepared by Chen [21,22] using the laser induction composite heating method. This method involves the use of high-frequency induction currents to heat and melt the metal material as a whole to reach a higher temperature,

followed by laser heating evaporation and condensation. The particle size of the prepared nano-aluminum powders ranged from 15 nm to 35 nm, with an average particle size of 30 nm. The active aluminum content was measured by the X-ray diffraction K-value method [23], and the measured activity of the aluminum powder was between 40.7% and 54.5%. Duan [24] prepared nano-aluminum powder by laser induction composite heating technology, and the particle size of the prepared nano-aluminum powder was about 50 nm. The content of active aluminum reached 75.19%, based on non-aqueous solvent redox titration. Zhang [25,26] used the laser induction composite heating method to prepare carbon-coated nano-aluminum powder in situ under the protection of a methane and argon atmosphere in order to prevent oxidation of the prepared nano-aluminum powder. The prepared products had a core-shell structure, were mostly spherical, and had an average particle size of 20~40 nm.

2.2.2. High-Frequency Induction Method

Wang and Guo [27–29] prepared nano-aluminum powder through evaporation and condensation by heating with high-frequency induction coils, followed by passivation with air to prepare nano-aluminum powder protected by a passivating layer. Transmission electron microscopy (TEM), field emission scanning electron microscopy (SEM) and X-ray diffraction (XRD) results showed that the particle sizes of the prepared nano-aluminum powder ranged from 15 nm to 60 nm, and the surface of the nano-aluminum powder was coated with alumina film 3 nm to 5 nm thick.

2.2.3. Arc Method

The arc method, or arc discharge method, vaporizes aluminum rods or wires through a high-density current pulse to generate nano-scale aluminum particles. An aluminum rod or wire can be used as a moving anode or a stationary cathode. The medium can be water, alcohol, nitrogen or liquid nitrogen. The particle size and crystal type of the prepared nano-aluminum powder can be controlled [30] by adjusting the current and cooling medium. Liang [31] prepared high-purity nano-aluminum powder by the direct current arc plasma evaporation method and characterized the sample with a specific surface area analyzer and scanning electron microscope (SEM). The raw material used was a 99.91% pure aluminum block, and the working gases were argon with over 99.99% purity and 99.5% hydrogen. The preparation process was as follows: the raw metal aluminum block was placed in a crucible and vaporized by arc heating. Inert gas, driven by a high-pressure vacuum fan, blew the aluminum vapor into the collection system and passivation system for cyclone collection. After gas and fog separation, nano-scale aluminum powder was obtained. Fan [32] prepared nanometer aluminum powder by the direct current arc method. The aluminum powder was analyzed by transmission electron microscopy (TEM), and the average particle size of the aluminum powder was 88 nm. The activity of the aluminum powder was tested by the gas volumetric method, and the test result was 72.35%. Chen [33] used the direct current arc hydrogen plasma method to prepare nano-aluminum powder under a 1.0 kPa CH₄ and 2.5 kPa Ar atmosphere. The specific surface area of the nanometer aluminum powder was measured by the BET multilayer gas adsorption method, and the calculated particle size was 373.8 nm. Zhuang [34] prepared highly active nano-aluminum powder by the DC arc plasma method. The micro-aluminum powder used was of analytical-grade purity. The aluminum powder was prepared by current arc plasma equipment under the protection of inert gas, collected and sealed with anhydrous ethanol to isolate the air and then modified by a KH-550-typed coupling agent. The prepared nano-Al powder was regular spherical or quasi-spherical, and the particle size distribution was between 20 and 100 nm.

Compared with the traditional evaporation–condensation method, the arc preparation process for nano-powder is environmentally friendly. The prepared powder products have high purity, small average particle sizes and controllable shapes and sizes, making it a nanomaterial preparation method with great application potential.

2.2.4. Pulsed Laser Denudation

Pulsed laser denudation [35] is another kind of evaporation method. The high-purity aluminum target is first heated to its boiling point by a laser pulse, forming atoms containing the vapor of the plasma target. Then, the plasma expands adiabatically and cools by gas to generate nanometer-sized aluminum powder particles. Many factors affect the quality of the prepared aluminum powder, including the laser energy, laser wavelength, laser pulse width, liquid medium type and denudation time. Huang [36] used a high-frequency nanosecond pulse power supply to produce high-energy nanosecond pulses with a maximum voltage of about 3000 V to impact aluminum targets and prepare nano-scale aluminum particles. It was found that the particle size of the prepared nano-aluminum powder decreased with increases in the flow rate of the cooled inert gas. The particle size of the metal nanoparticles also decreased gradually with decreases in discharge frequency. The particle size of nanometer aluminum powder prepared under optimized conditions was about 52.9 nm. Mathe [37] prepared nano-aluminum powder by applying laser plasma impact to an aluminum block. The particle size of the aluminum powder reached 50 nm. The aluminum powder was also passivated by air and palmitic acid in order to avoid excessive oxidation of the aluminum powder.

2.2.5. Resistance Heating Condensation Method

Ma [38] prepared nanometer aluminum powder by the high-efficiency vacuum resistance heating and condensation method. The raw material used was aluminum with a purity greater than 95%. The aluminum powder was placed in a high-pressure vapor deposition system, heated to a certain temperature by high-efficiency resistance in a vacuum environment. The aluminum underwent a liquefaction process, and then rapidly evaporated and vaporized. Nanometer aluminum powder with an average particle size of 80 nm was obtained after gas-phase condensation and cold deposition.

2.2.6. Wire Explosive Crushing Method

The wire explosion method [39] is another physical method for preparing nanomaterials. First, the explosion chamber is pumped to a high vacuum, and then filled with high-purity inert gas to a certain pressure. The voltage of the accumulator is adjusted to keep the whole system in a stable state. An aluminum wire is fed into the explosion chamber through a wire feeding device to control its explosion frequency. The aluminum wire explodes instantaneously through plasma discharge, forming a highly dispersed aluminum powder that can reach the nanometer scale. This method still uses high temperatures generated by currents to explode an aluminum wire and prepare aluminum powder, and the process involves passing a large current through the wire, resulting in joule heating, conductor temperature rise, liquid phase heating, melting, and finally reaching the boiling point and overheating. Then, the liquid phase becomes a gas phase [40,41], so this technique can still be classified as an evaporation condensation method. Zeng [42] prepared nano-aluminum powder by the wire explosion method. The preparation system is first filled with argon gas of 99.99% purity at standard atmospheric pressure. The high-voltage discharge causes the aluminum wire to explode 120 times per minute. Then, the air is extracted and filtered for separation. The diameter of the aluminum wire used was 0.35 mm, and the purity was higher than 99.99%. Transmission electron microscopy (TEM) analysis showed that most of the final prepared aluminum powder particles had diameters of about 50 nm.

Fan [32] prepared nano-aluminum powder by the electric explosion method. The prepared aluminum powder particles were nearly spherical with an average size of 81 nm, according to transmission electron microscopy (TEM) analysis. The activity of the aluminum powder was tested by the gas volumetric method, and the test result was 71.02%. Lv [43] studied the reaction kinetics of preparing nanometer aluminum powder by the electric explosion method. The results showed that deposition energy can be preferentially converted not only into the internal energy of the material but also into explosive kinetic energy. The metal wire goes through mechanical fragmentation, phase explosion, dual-mechanism explosion and supercritical explosion with increases in the deposition energy. The particle size of the explosive product decreases and the gas rate increases with increases in deposition energy. Zhao [44] prepared aluminum powder by the wire explosion method. The electron temperature of aluminum wire electroexplosive (EEW) plasma in argon was 1~2 eV, and the electron density was about $10^{19}/\text{cm}^3$. The author mainly discussed the mechanism of the process, but did not share the specific particle size of the prepared product. Antony [45] prepared nano-aluminum powder by the wire explosion method. Wire explosions were carried out in different environments, namely argon (Ar), helium (He) and nitrogen (N_2) at 25, 50 and 100 kPa pressures. The average diameter of the final prepared aluminum powder was in the range of 30~45 nm. Li [46] prepared nano-aluminum powder by the wire explosion method. The experimental system consisted of a 50 kA, 5 μs pulse current generator, aluminum wire electric explosion (EEW), a gas circulation system and a particle collection system. It was observed that, using different diameters of aluminum powder, almost all Al nanoparticles were basically spherical, with average particle sizes of 80.2 nm and 91.5 nm, respectively, without and with a 3.5 cm shunt gap. The average particle size of the nanoparticles decreased with increases in deposition energy. Energy transferred from the capacitor to the explosive aluminum during the partial reheating process may affect the characteristics of the nanoparticles, reducing their average particle size.

The evaporation–condensation process is relatively simple, produces easily separable products and is suitable for industrial large-scale production. However, the cost of equipment and production are relatively high compared with the ball milling method.

2.3. Chemical Reduction Technology

2.3.1. Gas-Phase Pyrolysis Method

Kaplowitz [47] prepared nano-aluminum powder by gas-phase pyrolysis. The raw material used was TiBAl. Aluminum volatilizes during heating under an Ar atmosphere. The particle size of the prepared nano-aluminum powder can reach 87 nm, and the purity is about 64%. Although the quality of nano-aluminum powder prepared by this method is not excellent, it provides a unique idea for preparing nano-aluminum powder.

2.3.2. Solid-Phase Chemical Reduction Method

Li [48] prepared nano-aluminum powder by the solid-phase chemical reduction method. The process control agent used was 1 wt% sorbitan anhydride trioleate (Span-85). Nanometer aluminum powder (n-Al) was prepared by chemically reacting lithium aluminum hydride with anhydrous aluminum chloride at a molar ratio of 3:1 in a ball mill. The results of scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM) showed that the prepared nano-aluminum powders were basically spherical. It can be seen from the particle size distribution diagram that the particle size of the nano-aluminum powder was mainly distributed between 45 and 65 nm, with less agglomeration. Chu [49] designed a new preparation method for nanometer aluminum powder. First, 200 mg aluminum powder (99%) with high purity was reacted with naphthalene in tetrahydrofuran (THF) solution under the protection of an inert gas

to form an intermediate, and then the product was filtered and transferred to a special reaction bottle, where the intermediate was heated under vacuum and then cooled to room temperature. The particle sizes of the prepared nano-aluminum powder ranged between about 30 and 45 nm. Beaudette [50] proposed a new method for preparing nano-aluminum powder, producing 11 nm aluminum powder particles by plasma excitation of AlCl_3 and Ar.

At present, the preparation efficiency of this method is low and needs to be optimized, but it provides a new idea for preparing nanometer aluminum powder.

2.3.3. Solution Chemical Reduction Method

The solution chemistry method [51] can generate nano-scale aluminum powder by chemically reacting oxidant and reducing agent in solution. AlLiH_4 is commonly used to react with aluminum chloride and can also be prepared by reacting with oxidants and other aluminum-containing reducing agents. Li [52] prepared a series of nano-sized aluminum powders with different particle sizes by the solution chemical reduction method. AlCl_3 and LiAlH_4 were used as raw materials, the solvents used were mesitylene, toluene, pyridine and *N*-methylpyrrolidone. Redox reactions occurred at different temperatures. In addition, different concentrations of organic amines were used to control the preparation process. The results of SEM analysis showed that the particle sizes of the aluminum powder prepared by changing the preparation conditions were between 20 and 100 nm. Li [53] prepared nano-aluminum powder by the solution chemical reduction method. Nano-aluminum powders were prepared under inert gas protection using toluene as the solvent and anhydrous AlCl_3 , $\text{N}(\text{Et})_3$ and LiAlH_4 as the raw materials. The results of SEM and TEM analysis showed that the prepared aluminum nanoparticles were spherical and the particle size ranged from 80 nm to 120 nm. The results of gas volumetric analysis showed that the average content of active aluminum was 75.5%. Wang [54] used 1,3,5-tritylene as the solvent, anhydrous AlCl_3 and LiAlH_4 as the raw materials, and triphenyl phosphorus as the coating agent to effectively protect the aluminum powder from oxidation. The reaction was heated to 164 °C under magnetic stirring. TEM analysis showed that the average particle size of the prepared nano-aluminum powder was 70 nm. The particle size of the prepared aluminum powder can reach 20~30 nm when oleamine is used as the coating agent. In order to improve the quality of the prepared nano-aluminum powder, Wang also used anhydrous AlCl_3 and LiAlH_4 as raw materials to prepare the precursor $4\text{AlH}_3 \cdot \text{Et}_2\text{O}$ in a mixed solution of ether and toluene, then catalyzed the decomposition to prepare nano-aluminum powder. The particle size of the prepared nano-aluminum powder was about 20~30 nm when oleamine was used as the coating agent. The particle size was also more uniform. Yu [55] catalyzed the decomposition of AlH_3 in tetrahydrofuran solution with titanium isopropyl alcohol as the catalyst, obtaining colloidal stable monodisperse aluminum nanospheres with uniform sizes in the range of 85~200 nm. E Xiu [56] also used this method to prepare nano-aluminum powder, with particle sizes of about 16 nm under optimized conditions. McClain [57] prepared nano-aluminum powder by the solvent reduction method, easily synthesizing high-purity aluminum nanocrystals with a controllable size range from 70 to 220 nm in diameter. Size control was achieved by simply modifying the proportion of solvent in the reaction solution. Li [58] prepared nano-sized aluminum powder particles by the template method. Small aluminum nanoparticles (approximately 10 nm in diameter) were easily synthesized by catalytic decomposition of aluminane precursors using nanoscale cavities in a perfluorinated monomer membrane (Nafion-117, DuPont, Wilmington, DE, USA) as a template. This template synthesis may represent a new way to stabilize aluminum nanoparticles and related high-energy nanomaterials, providing a new idea for the preparation of a new type of template material—nanometer aluminum powder composite materials. Klein [59] proposed a thermal

decomposition method starting with triisobutyl aluminum (TIBAL) as a precursor. TIBAL is refluxed at a high boiling point with diphenyl ether as the solvent and nickel, ruthenium or silver as the seed for metal nanoparticles. The resulting particle size was about 100 nm. Klein [60] also prepared nano-aluminum powders using $\text{H}_3\text{AlNMe}_2\text{Et}$ or H_3AlNEt_3 as the precursor, alcohol salts of Ti (such as $\text{Ti}(\text{OiPr})_4$) as the catalyst and non-polar solvents such as toluene as the reaction medium. The optimal duration for complete conversion was less than 15 min, and the optimal temperature was between 90 and 100 °C. Under optimized conditions, the particles of the prepared aluminum powder are less than 100 nm in size and basically spherical. Ghanta [61] synthesized nano-aluminum powder by the chemical method. Aluminum acetylacetonate $[\text{Al}(\text{acac})_3]$ was reduced by lithium aluminum hydride (LiAlH_4) in tritoluene at 165 °C with particle sizes between 50 and 250 nm. Cui [62] chemically synthesized nano-aluminum powders with triphenylphosphine (PPh_3) shells. The raw materials used were AlCl_3 and LiAlH_4 , the solvent was tritylene and the reaction temperature was 164 °C. The results of transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) showed that the size of the prepared nano-aluminum powder ranged from 50 nm to 120 nm. Thomas [63] prepared 1,2-epoxy-9-decene terminated nano-aluminum powder by the chemical method. Nanometer aluminum powder was prepared by decomposing AlH_3 in toluene. Transmission electron microscopy confirmed that these spherical nanostructures (25 nm in diameter) embedded in a covalently bound polymer matrix acted as a preventive barrier against water/air ($\text{H}_2\text{O}/\text{O}_2$) degradation, allowing the nano-aluminum powder to remain highly active for 6 weeks.

Some researchers have used the chemical reduction method to prepare nano-aluminum powder. The advantages of this method are that it is flexible and can be used for specific scenarios [63], such as significantly improving polymer properties. However, the process is complex, product separation is relatively difficult and the cost is high, so it is more suitable for laboratory-scale preparation and not suitable for large-scale mass production.

2.4. Ionic Liquid Electrodeposition Method

Ionic liquid is a room-temperature molten electrolyte, usually composed of imidazole, pyridine, other model cations and organic/inorganic anions. This special structure gives ionic liquids advantages such as a low melting point, high conductivity, a wide electrochemical window, non-volatility, non-flammability, etc. Recent studies have shown that the electrodeposition method can realize the preparation of nanoparticles in some ionic liquids. This new preparation process for nano-aluminum operates at low temperatures, has low energy consumption, provides good safety and has unique technical advantages over the traditional process. Figure 3 shows the microscopic electrodeposition process of aluminum on an electrode surface [64].

Nano-aluminum powder coating can be directly deposited onto accelerant or energetic material through a suitable process to increase the closeness of their contact, thereby increasing the reactivity of the aluminum. Abbott [65] prepared a nanometer aluminum powder coating. The effects of toluene and lithium chloride in $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ ionic liquid prepared by 1-butyl-3-methylimidazole chloride ($[\text{Bmim}]\text{Cl}$) on the morphology of nanometer aluminum powder coating were studied. The results showed that bright nanometer aluminum powder coating can be obtained by electrodeposition after adding toluene. Li and Wang [66,67] studied the effects of potassium chloride, choline chloride, tetramethylammonium chloride and toluene on the morphology of coating in $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ plasma liquid. The results showed that proper addition of choline chloride, tetramethylammonium chloride or toluene in ionic solution produces smooth and fine nanometer aluminum powder coatings. Yin and Liu [68,69] used a similar ionic system to prepare nano-aluminum powder. $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ and $[\text{Amim}]\text{Cl}/\text{AlCl}_3$ systems

were used to successfully prepare nano-aluminum powder deposition layers by the low-temperature electrodeposition process. In addition, studies in this area [70–74] have used different systems to prepare deposited nano-aluminum with different specifications.

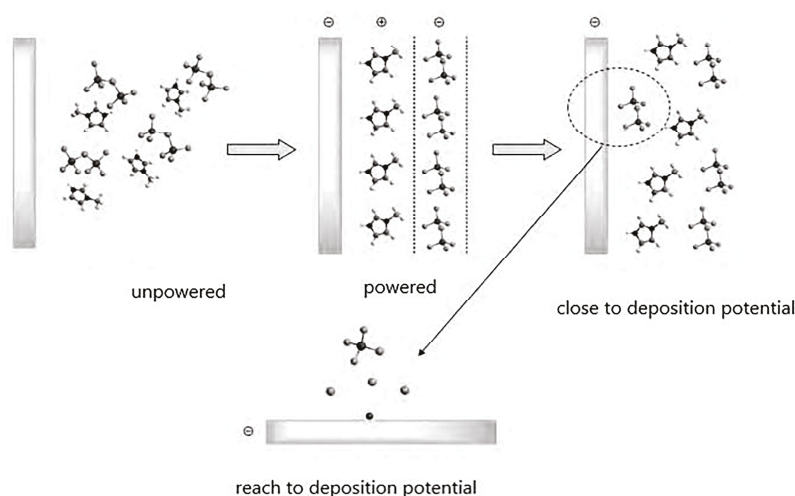


Figure 3. Electrodeposition process of aluminum on electrode surface [64]. Reproduced with permission from *Nonferrous Metals (Extractive Metallurgy)*, Editorial Office, 2017.

The particle liquid electrodeposition method is used to deposit nano-aluminum powder onto materials, enhancing the binding between the aluminum and the applied material. It can be inferred that more complete aluminum reaction can occur under redox reactions. This method of preparing nano-aluminum is very rare in the propellants and explosives industries. More research is still ongoing.

In conclusion, the existing preparation technologies and methods for nano-aluminum include physical and chemical methods. Table 1 presents a comparison of the advantages and disadvantages of different preparation methods for nano-aluminum powder.

Table 1. Advantages and disadvantages of different preparation methods for nano-aluminum powder.

Preparation Methods		Product Average Granularity	Product Purity	Manufacturability	Equipment Cost	Feasibility of Industrial Production	Environmental Friendliness
physical methods	mechanical pulverization method						
	ball milling method	low to medium to excellent	low to medium to good	easy	cheap	feasible	environmentally friendly
	ultrasonic ablation (scrub) method	excellent	good	difficult	high costs	needs to be researched deeply	environmentally friendly
	laser induction compound heating method	medium to excellent	low to medium	medium to difficult	high costs	feasible	environmentally friendly
	evaporation–condensation method						
	high-frequency induction method	medium to excellent	low to medium	medium to difficult	high costs	feasible	environmentally friendly
	arc Method	low to medium to excellent	low to medium to good	medium to difficult	high costs	feasible	environmentally friendly

Table 1. Cont.

Preparation Methods		Product Average Granularity	Product Purity	Manufacturability	Equipment Cost	Feasibility of Industrial Production	Environmental Friendliness
chemical methods	pulsed laser denudation	good	medium to good	medium to difficult	high costs	feasible	environmentally friendly
	resistance heating condensation method	good	medium to good	medium to difficult	medium to high costs	feasible	environmentally friendly
	wire explosive crushing method	low to medium	low to medium	low to medium	cheap to medium	feasible	environmentally friendly
	gas-phase pyrolysis method	medium to good	low to medium	medium	cheap	suitable for the laboratory scale	waste
	solid-phase chemical reduction method	medium to good	low to medium	medium	cheap	suitable for the laboratory scale	waste
	solution chemical reduction method	medium to excellent	medium	medium	cheap	suitable for the laboratory scale	waste liquid
	ionic liquid electrodeposition method	nanofilms	good	medium	medium	feasible	waste liquid

From the advantages and disadvantages of different preparation methods for nano-aluminum powder in Table 1, physical methods and the ionic liquid electrodeposition method are more suitable for industrial production. The ball milling method is better in terms of process simplicity and production cost, and the ultrasonic ablation method and ionic liquid electrodeposition method are better in terms of the quality of prepared products. The appropriate preparation method can be selected according to product use and production cost.

3. Reactivity Differences Between Nano-Aluminum and Micro-Aluminum

The explosives and propellant industries mainly use aluminum powder with an average particle size of 5~10 μm . If the average particle size of aluminum powder is reduced to 100 nanometers, the specific surface area will increase by 2500~10,000 times, which undoubtedly has a significant impact on its reactivity. Researchers have also conducted in-depth studies on the differences in reactivity between nano-scaled aluminum powder and micrometer-scaled aluminum powder.

There are two main indexes to determine the efficiency of aluminum powder in explosives and propellants. One is related to chemical thermodynamics, that is, under what conditions aluminum powder begins to react. The other is related to chemical kinetics, the reaction rate and degree of aluminum powder under set conditions.

3.1. Properties of Nano-Aluminum Powder

The conditions under which aluminum powder begins to react can be investigated using ignition tests and thermal analysis, with the test results demonstrating the difference in reaction activity between nano-aluminum powder and micron-sized aluminum powder.

3.1.1. Differences Between Nano-Aluminum Powder and Micron-Sized Aluminum Powder in Ignition Tests

Ignition performance determines whether the redox reaction can proceed effectively and is an important characteristic to determine whether a material is practical. Wang [75]

studied the difference in ignition ability between nano-aluminum powder and micro-aluminum powder. Nano-aluminum powder with an average diameter of 80 nm and micro-aluminum powder with an average diameter of 7 μm were placed in 3 wt% polyacrylamide aqueous solution. First, the sample was placed in a quartz tube, and a certain voltage was applied to both ends of the ignition column to heat the resistance wire for ignition. The results showed that the nano-aluminum powder was ignited when the pressure was greater than 1 MPa, and the micro-aluminum powder was ignited when the pressure was greater than 2.5 MPa. This indicates that the ignition activity of nano-aluminum powder is significantly higher than that of micro-aluminum powder. Chen [76] studied the ignition characteristics of several aluminum powders. The results showed that the minimum ignition energy for 35 nm aluminum powder and 100 nm aluminum powder was less than 1 mJ, however, the minimum ignition energy for 40 μm aluminum powder was 59.7 mJ. Therefore, the ignition performance of nano-aluminum powder is far superior to that of micro-aluminum powder. In addition, the lower explosion thresholds for 35 nm, 100 nm and 40 μm aluminum powders are 40 g m^{-3} , 50 g m^{-3} and 65 g m^{-3} , respectively. Therefore, the smaller the particle size of aluminum powder, the lower the ignition threshold. Li [77] studied the differences in combustion characteristics between micro-aluminum powder and nano-aluminum powder. The average particle size of the micro-aluminum powder was 5 μm , and the thickness of the oxide shell was about 6.7 nm. The average particle sizes of the nano-aluminum powder were 80 nm and 120 nm, and the thickness of the oxide shells were about 1.5 nm and 1.2 nm respectively. The ignition and combustion performance of aluminum powder with different sizes was experimentally studied using a CO_2 laser ignition device. The experiment was carried out in a power density range of 50.3~267.6 W/cm^2 . Figure 4 shows the relationship between the ignition delay time and the heat flux q , and Table 2 shows photos of the ignition and combustion process of the above samples at the same heat flux ($q = 123.3 \text{ W/cm}^2$). Lx-1 to Lx-6 represent aluminum with particles of 5 μm , 80 nm, 120 nm, 5 μm (25 wt%) + 80 nm (75 wt%), 5 μm (50 wt%) + 80 nm (50 wt%) and 5 μm (75 wt%) + 80 nm (25 wt%), respectively. Figure 4 and Table 2 show that the ignition delay times of aluminum powder with different particle sizes and proportions decreased with increases in laser heat flux. At the same time, under the same heat flux, the ignition delay time of the micro-aluminum powder was much longer than that of the nano-aluminum powder. With the increase in nano-aluminum powder content, the combustion flame became brighter and brighter, and the range of spot diameter gradually increased. When only nano-aluminum powder was used, the flame was the brightest and the spot diameter of fire was the largest, indicating that the combustion was the most intense. When only micro-aluminum powder was used, the flame was the darkest and the spot diameter of fire was the smallest, indicating that the combustion was the slowest. Jin [78,79] studied the differences in ignition characteristics between micro-aluminum powder and nano-aluminum powder. Three particle sizes of micro-aluminum powder were selected, which were 2.9, 6.1 and 10.8 μm . Three particle sizes of 56.0, 74.4 and 93.4 nm were also selected for the nano-aluminum powder. The ignition test results showed that the ignition delay times for the micro-aluminum particles were 3.56 ms, 5.87 ms and 8.03 ms, respectively, and the ignition delay times increased with increases in particle size. The ignition delay times for the nano-aluminum were 2.08 ms, 1.84 ms and 1.81 ms, respectively, and the ignition delay time decreased with increases in particle size. The combustion process of nano-aluminum with different particle sizes was measured by synchronous data acquisition using a high-speed camera and infrared thermal imager, and 93.4 nm nano-aluminum powder and 10.8 μm micro-aluminum powder were selected. The results showed that it took 800 ms for the nano-aluminum to reach the highest temperature, and 2375 ms for the micro-aluminum, so the temperature rise rate of

the nano-aluminum was much faster than that of micro-aluminum. Martin et al. [80–84] obtained the same research results through similar research methods. Similar results were found by Uhlenhake [85], where 20 wt.% of n Al and μ Al particles were mixed in PVDF, and discs was manufactured by melting wire manufacturing technology. The nAl/PVDF printing disc ignited at a minimum ignition power (MIP) of 4.1 W, while the μ Al/PVDF disc needed 9.5 W to ignite.

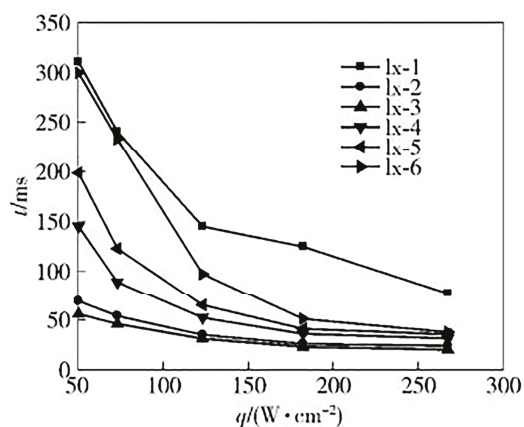
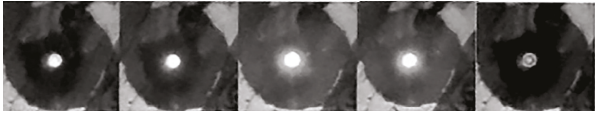
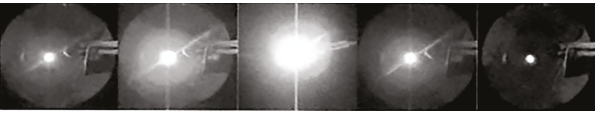
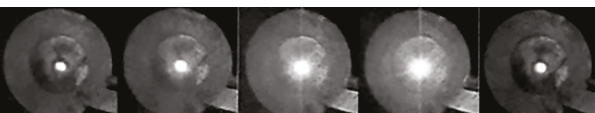
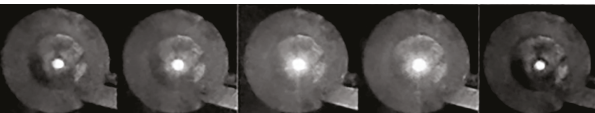


Figure 4. Ignition delay times for aluminum powders with different sizes and proportions as a function of laser heat flux density [77]. Reproduced with permission from *Acta Armamentarii*, Editorial Office, 2014.

Table 2. Ignition and combustion processes for aluminum powders with different sizes and proportions ($q = 123.3 \text{ W/cm}^2$) [77]. Reproduced with permission from *Acta Armamentarii*, Editorial Office, 2014.

Samples	The Photos of Ignition and Combustion Processes
lx-1	
lx-2	
lx-3	
lx-4	
lx-5	
lx-6	

3.1.2. Differences in Nano-Aluminum Powder and Micron-Sized Aluminum Powder Based on Thermal Analysis

Thermal stability represents whether the chemical properties of materials are stable in a certain environment, which is closely related to the storage performance and reaction performance of materials. The thermal behavior of aluminum powder can be characterized by differential scanning calorimetry (DSC), thermogravimetric–differential thermal analysis (TG-DTA) and gas phase analysis combined with thermogravimetric analysis (TGA); it can also be characterized by heating rate calorimetry (ARC). Wang [86] studied the influence of nano-aluminum powder and micro-aluminum powder on the thermal stability of mixed explosives. Three kinds of aluminum powders with particle sizes of 40 nm, 3 μm and 35 μm were selected, and the effective aluminum contents were 84.24%, 90.57% and 93.29%, respectively. Octagon (HMX)-based mixed explosive was prepared, and the content of aluminum powder was 35 wt%. Differential scanning calorimetry (DSC) analysis showed that the smaller the particle size of aluminum powder, the lower the initial reaction temperature and peak reaction temperature. The activation energy was calculated using the Kissinger method, and the apparent activation energies of three kinds of mixed explosives were 331.2 kJ mol^{−1}, 421.7 kJ mol^{−1} and 480.9 kJ mol^{−1}, respectively. Therefore, the apparent activation energy also decreased with decreases in aluminum particle size. The results showed that the smaller the particle size of aluminum powder, the easier it is to react. Lu [87] also obtained similar results. The thermogravimetric (TG) curve showed that the weight and thermal flow of nano-aluminum powder increased sharply, indicating that the reaction rate of nano-aluminum powder was much faster than micron-grade aluminum. Chang [88] studied the reactivity differences between micro-aluminum powder and nano-aluminum powder. After screening, the particle size of micro-aluminum powder was 10–20 μm , and the average particle size of nano-aluminum powder was 100 nm. The results of dust explosion experiments of nano-particles showed that they exhibited a lower minimum explosible concentration (MEC) than those of micron particle dust clouds. The MEC value for micro-aluminum powder is 510 g cm^{−3}, while for nano-aluminum powder it is 190 g cm^{−3}. TGA results showed that the nanoparticles of aluminum were almost completely oxidized below 1500 K. In contrast, the reaction amount of microparticles of aluminum was less than a quarter, as shown in Figure 5. Therefore, the reactivity of nano-aluminum powder is much higher than that of micro-aluminum powder. In order to understand the differences in the reaction behavior between micro- and nano-aluminum powder in the temperature range of 25–1500 °C and in the environment of O₂ and CO₂, Zhou [89] conducted thermal tests on 50 nm and 1.5 μm aluminum powders. The experimental results show that the reaction of 50 nm and 1.5 μm aluminum powders with O₂ mainly occurred at 530–575 °C and 775–1500 °C, respectively. The reactions of 50 nm and 1.5 μm aluminum powders with CO₂ mainly occurred at 445–955 °C and 590–1130 °C, respectively, in a CO₂ environment. The results showed that nano-aluminum powder is more reactive than micro-aluminum powder and needs a lower reaction temperature.

In Figure 5, different stages represent different polymorphic phase evolution of alumina [77]. Stage I corresponds to the formation of a regular polycrystalline layer $\gamma\text{-Al}_2\text{O}_3$ from amorphous Al₂O₃. Stage II indicates that the growth of $\gamma\text{-Al}_2\text{O}_3$ layer is accompanied by phase transformation, and it becomes other transitional polymorphs, such as $\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$, but its density is very close to $\gamma\text{-Al}_2\text{O}_3$, and this transformation will not significantly affect the oxidation rate; At the end of this stage, stable and more dense $\alpha\text{-alumina}$ begins to form. At stage III, the oxide layer is completely converted to $\alpha\text{-Al}_2\text{O}_3$.

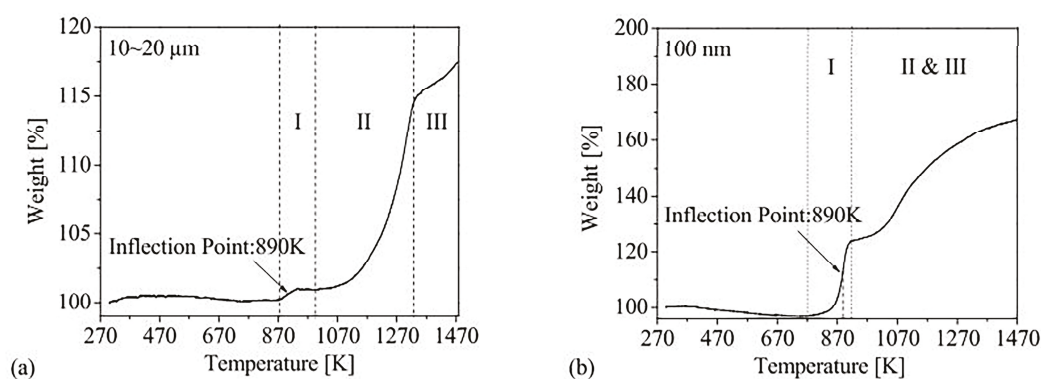


Figure 5. TGA results: (a) 10–20 μm Al particles; (b) 100 nm Al particles [88]. Reproduced with permission from Elsevier, 2020.

Regarding the reactivity differences between nano-aluminum powder and micro-aluminum powder, Li [77] stated that the ignition and combustion mechanisms of nano-aluminum particles are completely different from those of micro-aluminum powder. An evaporation process occurs during the combustion process of micro-aluminum powder. In contrast, there is no gasification process during the process of ignition and temperature rise in nano-aluminum powder, but it directly reaches the oxidation stage, resulting in complete ignition. Compared with micro-aluminum powder, nano-aluminum powder requires less energy for ignition combustion, which significantly shortens the ignition delay time. The surface oxide layer hinders the evaporation of aluminum powder and its reaction with external oxygen, so the thickness of the surface oxide layer has a very significant influence on ignition. Other researchers [79,80] think that there may be a minimum value (critical point) between 93.4 nm and 2.9 μm for sub-micron-grade aluminum powder, at which the ignition delay time is minimized and the ignition performance is optimal. Bockmon [90] also obtained similar research results.

3.2. Difference in Reaction Completeness Between Nano-Aluminum Powder and Micro-Aluminum Powder

Whether there is a significant difference in the reaction completeness between nano-aluminum powder and micro-aluminum powder directly determines the application prospects of nano-aluminum powder, as well as its future development. Chen [91] studied the performances of composite explosives containing micro-aluminum powder and nano-aluminum powder to metal-plate acceleration. Three kinds of aluminum powders with average particle sizes of 50 nm, 5 μm and 50 μm were selected. The content of aluminum powder in mixed explosives was 20 wt%, and LiF was used for comparison. The results showed that the reactivity of the 50 nm aluminum powder was obviously better than that of the 5 μm and 50 μm aluminum powders, especially in the early stage of the reaction, no matter driving a 0.54 mm copper plate or a 1.00 mm copper plate, as shown in Figure 6. In tests driving a 1 mm copper plate, the reactivity of all three aluminum powders was higher than that of driving a 0.54 mm copper plate, which shows that the reaction of aluminum powder in the detonation of aluminum-containing explosives is not only affected by the size of the aluminum powder but also closely related to the explosive loading conditions. Small-sized aluminum powder and strong constraint conditions are more favorable for aluminum to participate in the reaction. Yan [92] studied the differences in explosion characteristics between micro-aluminum powder and nano-aluminum powder induced by shock waves. The experiment was completed in an explosion shock tube. The results showed that the ignition delay time of nano-aluminum powder was less when the shock Mach number was the same. When the shock Mach number was greater than 2.5, the ignition delay time of the nano-aluminum powder decreased sharply. XPS results showed

that the oxide layer on the surface of the nano-aluminum powder product was 35 nm thick and the oxidation degree was 92%. The thickness of oxide layer on the surface of the micro-aluminum powder product was 30 nm, and the oxidation degree was 65%. Therefore, the reaction degree of the nano-aluminum powder was higher than that of the micro-aluminum powder. Zhu [93] studied the exothermic behavior of an Al/AP (ammonium perchlorate) system. Three kinds of aluminum powders with a D50 of 40 nm, 2.6 μm and 10.7 μm were used. The results of DSC analysis showed that the smaller the particle size of the aluminum powder, the lower the peak temperature of exothermic peak and the higher the heat generated by the system, indicating that nano-aluminum powder reacts more easily and completely under the same conditions. Galfetti [94] studied the differences in combustion products of propellants containing two kinds of aluminum powder. The average particle sizes of the aluminum powder were 150 nm and 30 μm , respectively, with a formula composition of Al/AP/HTPB(hydroxyl-terminated polybutadiene) = 15/68/17. The results showed that when environmental pressure of $P = 0.1$ MPa was applied, the proportion of unburned aluminum in the combustion products was normalized to the aluminum mass contained in the propellant sample, with $(21.4 \pm 8.5)\%$ for the propellant containing 150 nm aluminum powder and $(35.1 \pm 5.9)\%$ for the propellant containing 30 μm aluminum powder. When the pressure increased to 3 MPa, the two samples decreased to $(17.1 \pm 3.1)\%$ and $(29.9 \pm 7.9)\%$, respectively. The results showed that the formula containing nano-aluminum had higher combustion efficiency.

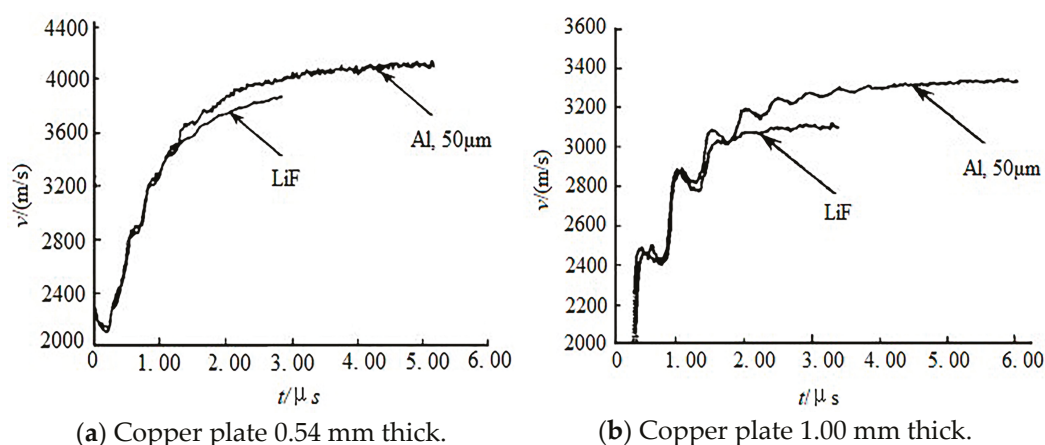


Figure 6. Free surface velocity of two kinds of copper plates [90]. Reproduced with permission from *Explosion and Shock Waves*, Editorial Office, 1999.

3.3. Surface Coating and Modification of Nano-Aluminum Powder

Nano-aluminum powder has several obvious defects. Firstly, nano-aluminum powder is easily oxidized, which seriously affects its storage and application efficiency. Secondly, due to the large specific surface area, the relatively thicker surface oxide layer prevents the internal aluminum powder from continuing to react. Thirdly, nano-aluminum powder often deteriorates the preparation process of explosives or propellants. These defects can be significantly improved by using a proper coating or modification process.

According to the different bonding properties between nano-aluminum powder and auxiliary materials, coating and modification can be divided into physical processes and chemical processes. Different coating and modified materials will have different effects on various properties of nano-aluminum powder.

3.3.1. Protecting the Activity of Nano-Aluminum Powder

A large number of studies have shown that coating and modification can effectively protect the activity of nano-aluminum powder and increase its application potential.

Luo [95] coated nano-aluminum powder with different contents of polyethylene glycol (PEG). The results of differential scanning calorimetry (DSC) showed that the peak temperature of thermal decomposition of the coated samples was delayed to some extent compared with the uncoated samples, but the specific temperature difference in the delayed position was not specified, which indicates that PEG has a certain protective effect on the activity of nano-aluminum powder. Hao [96] used hydroxyl-terminated polybutadiene–toluene diisocyanate (HTPB-TDI) to coat nano-aluminum powder with an average particle size of 80 nm and an activity of more than 99.99%. The results of transmission electron microscopy (TEM) showed that the coating was intact, indicating potential for long-term storage of high-activity nano-aluminum powder. Zhang [97] prepared Al/PS microcapsules by coating nano-aluminum powder with polystyrene (PS) and analyzed the activity of aluminum powder in microcapsules stored for different durations. The results showed that the contents of active aluminum were 76.07%, 76.06% and 74.81%, respectively, after newly prepared, sealed and stored in an oxygen tank for 30 days under natural conditions, indicating that nano-aluminum powder coated with PS can maintain its activity for a long time. In contrast, uncoated nano-aluminum powder was stored naturally under the same conditions, and the proportion of active aluminum was only 42.3%. Zha [98] used octadecylamine (ODA) as a raw material to prepare carbon-coated nano-composite particles. After being stored in air for one month, the active aluminum content decreased from 88.5% to 87.9%, and the activity changed little, indicating that carbon coating can effectively prevent further oxidation of nano-aluminum powder. Li [99] prepared nano-aluminum powder by the redox method and coated it with paraffin wax and perfluorotetradecanoic acid, respectively. The storage test results showed that the activity of the newly prepared composite particle aluminum powder was 80.8%, and after being stored in air for two months, the active aluminum contents decreased by 1.7% and 3.8%, respectively, indicating that both paraffin wax and perfluorotetradecanoic acid can effectively maintain the activity of nano-aluminum powder. Kwon [100] used boron to coat nano-aluminum powder and stored it in air with humidity of 70% for one year. The active aluminum content of composite particles decreased from 84% to 82%, which is very low, indicating that boron had a very good coating effect. Because boron coating can increase the combustion heat of nano-aluminum powder at the same time [101–104], this material may have very good application prospects. Hammerstroem [105] coated nano-aluminum powder with epoxy resin. The results of XRD, TG and other tests showed that the active aluminum content of nano-aluminum powder prepared under optimized conditions was as high as 94%, which may have application prospects. Liu [106] used trimethylolpropane triacrylate ($(\text{CH}_2=\text{CHCOOCH}_2)_3\text{CCH}_2\text{CH}_3$) (TMPTA) as monomer raw material to coat nano-aluminum powder and successfully prepared nano-Al/PTMPTA composite particles. The results showed that the dispersion, corrosion resistance and thermal stability of the composite particles were greatly improved, and the content of active aluminum powder was about 90%. After two months of testing, the activity of nano-aluminum powder was basically unchanged after coating, while the activity of naturally passivated nano-aluminum powder had decreased by 48%. Mathe [37] studied the influence of accelerated aging on palmitic acid-coated nano-aluminum powder. Even in an environment with 90% humidity and 60 °C for 10 h, the activity of the coated aluminum powder changed little, while that of the uncoated aluminum powder decreased by about 10 percentage points.

The above research results show that the oxidation rate of nano-aluminum powder after coating modification can be greatly reduced using suitable coating materials and processes. Specifically, using boron powder to coat nano-aluminum powder and PTMPTA to coat nano-aluminum powder can improve the energy of aluminum powder or have an excellent coating effect, indicating stronger application prospects.

3.3.2. Improving the Reactivity of Nano-Aluminum Powder

The reactivity of nano-aluminum powder has a very important influence on its application efficiency in explosives and propellants. Zhang [107] prepared carbon-coated nano-aluminum powder by the laser induction composite heating method. The prepared core-shell structure material had a particle size range of 20–60 nm and a shell thickness of 3–8 nm. Differential thermal analysis (DTA) showed that the core-shell structure material began to emit heat at 400 °C, which is far lower than the melting point of aluminum (660 °C) and more than 100 °C earlier than alumina-coated nano-aluminum powder. Yao [108] used perfluorotetradecanoic acid to coat nano-aluminum powder with an average particle size of 50 nm and a purity of more than 98.0%, and the coating agent content was 10 wt%. Laser ignition testing was carried out and compared with uncoated aluminum powder. It was found that, compared with uncoated aluminum powder, when the laser heat flux was low, the ignition delay time of coated aluminum powder was shorter, the combustion reaction was more intense, and the flame brightness was higher. The combustion test also showed that coated aluminum powder burned more fully. Wang [109] prepared nano-aluminum powder (nAl) coated with ammonium perchlorate (AP) by the recrystallization method, and the content of the coating agent was 10–30 wt%. It was found that when the heating rate was high, AP decomposed violently, the ignition temperature of the composites with optimized formula was about 200 °C lower than that of pure nano-aluminum powder and the weight loss rate was higher than that of uncoated nano-aluminum powder. Hao [110] prepared a nano-aluminum/perfluorooctanoic acid (Fx) composite with a core-shell structure (nAl@Fx). The results of differential scanning calorimetry (DSC) showed that the instantaneous heat flux of the nAl@Fx composites was 155 W/g at 633 °C, which is much higher than that of nAl at 573 °C. The combustion test results showed that the maximum combustion flame temperature of nAl@F-x composite reached 1366 °C, which was higher than the 1198 °C recorded for the raw nAl. Wang [111] prepared nAl/PFSA nano-composite energetic materials. The average particle size of the nAl was 50 nm, with aluminum powder content of 30 wt%, and it was compared with an Al/PTFE system with the same mass ratio. The results of differential scanning calorimetry (DSC) showed that the exothermic reaction of the nAl/PFSA system was 2675 J/g, which was about three times of that of the nAl/PTFE system, and the initial reaction temperature was 370 °C, which was much lower than that of the nAl/PTFE system (463.8 °C). The combustion-supporting effect of PFSA on aluminum powder is better than PTFE. Nitrocellulose (NC) has high energy. Wang [112] prepared Al/NC composites by the electrostatic spraying method, using aluminum powder with a particle size smaller than 50 nm, containing about 70% active aluminum and 10% NC. The results of the ignition test showed that the Al/NC composite particles prepared by the electrostatic spraying method burned more violently than untreated nano-Al particles, resulting in dazzling fire, and the ignition delay time was sharply reduced from 14 ms to 0.3 ms. Luo [95] studied the influence of polyethylene glycol (PEG) and fluorocarbon surfactant TF3721 (F-C surfactant) coating on the reaction characteristics of aluminum powder. The aluminum powder used was nano-scale, and the active aluminum content was 89.70%. The original text did not specify the proportion of combustion improver. The combustion test results showed that compared with pure n-Al, PEG/n-Al composite particles and F-C/n-Al composite particles had better combustion performance, and pure n-Al could not be ignited directly. The ignition delay time of the PEG/n-Al composite particles was 0.95 s, and that of the F-C/n-Al composite particles was 1.20 s. The burning rate of the PEG/n-Al composite particles was 0.050 cm s⁻¹, and that of the F-C/n-Al composite particles was 0.065 cm s⁻¹. Therefore, the F-C/n-Al composite particles had a higher burning rate, and the burning phenomenon was more intense. Therefore, both PEG and F-C have a certain degree of combustion-supporting

effects. Zhu [113] studied the combustion-supporting effect of KBH_4 coating on aluminum powder. The average particle size of aluminum powder used was 50 nm, and the purity was 80.8%. It was found that when the content of KBH_4 was 3%, the initial ignition temperature was 429 °C, which was 8.54% lower than that of pure aluminum powder. The highest combustion temperature was 1404 °C, which was 1.52% higher than that of pure aluminum powder. The results showed that KBH_4 had a certain combustion-supporting effect on aluminum powder. Zeng [3] modified aluminum nanoparticles by in situ grafting onto high-energy glycidyl azide polymer (GAP) and prepared composites. The diameter of the aluminum powder used was about 50 nm, and its activity was 93.6%. GAP was grafted onto the surface of nano-aluminum to form an $-\text{O}-(\text{CO}-\text{NH})$ chemical bond. The thickness of GAP shells can be adjusted by changing the relative ratio of reactants. On this basis, $(\text{Al}@\text{GAP})/\text{fluorine}$ composites were prepared. The ignition test results showed that GAP could shorten the ignition time of aluminum powder, while the $(\text{Al}@\text{GAP})/\text{fluorine}$ composite had a shorter ignition time and more intense flame intensity. Mulamba [114] used polytetrafluoroethylene (PTFE) to coat nano-aluminum powder with an average particle size of 80 nm. The results of the combustion test showed that the burning rate of nano-aluminum powder coated with PTFE was significantly improved because Al_2O_3 on the surface of aluminum powder can react exothermically with tetrafluoroethylene. Cheng [115] prepared nickel-coated nano-Al composite particles by electroless plating using a redox reaction between nickel acetate ($\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$) and sodium hydroxide (NaOH) in the medium containing nano-aluminum powder. Thermogravimetric analysis (TG) showed that the oxidation initiation temperature of the composite particles was 190~260 °C earlier than that of the raw material nano-aluminum powder. Qiu [116] also prepared nickel-coated nano-Al composite particles by a similar method and obtained similar results. Kaplowitz [117] coated Fe_3O_4 on nano-aluminum by gas-phase inversion and formed thermite with CuO . T-Jump ignition test results showed that the ignition temperature of the thermite coated with aluminum powder was 973 K, while that of the thermite formed without aluminum powder was 1076 K, which indicates that nano-aluminum powder coated with Fe_3O_4 has higher reactivity. Yang [118] prepared nano-aluminum (n-Al)@polyvinylidene fluoride (PVDF) microspheres by electrospray deposition. The average particle size of the aluminum powder was 50 nm, and the contents of PVDF were 5, 10 and 15 wt%, respectively. Combustion tests and thermogravimetric-differential scanning calorimetry analysis showed that the combustion performance of n-Al@PVD was better than that of n-Al, and the exothermic process was more intense (sharper exothermic peak). Li [119] synthesized fluorinated polydopamine (PF) and coated it with nano-aluminum powder to prepare core-shell composite materials. The combustion rate (196.4 mm s^{-1}) of the optimized formula was 8.1 times and 3.6 times than that of the original n-Al (24.2 mm s^{-1}) and the physical mixed sample (54.7 mm s^{-1}), respectively. He [120] used an energetic metal-organic framework (EMOF) as a metal-oxide precursor and as the oxidant in conventional nano-thermite to prepare metastable nano-composite material n-Al@EMOFs. The average particle size of the aluminum powder in the material was 80 nm. EMOF is the reaction product of 5,5-bitetrazole-1,1-diol dihydrate (DHBT) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The results showed that the ignition temperature of n-Al@EMOFs was 301.5 °C, which is much lower than the 578 °C recorded for nano-aluminum. This indicates that this structure has a good combustion-supporting effect on aluminum powder.

Ruesch [121] studied three kinds of composite propellants of the AP/Al/HTPB system, with different aluminum particle sizes (31 μm , 4.5 μm and 80 nm, respectively), and propellant without aluminum for comparison, burning in air at 1 atm. It was found that the propellant with the smallest particle (nano-aluminum) had the highest average temperature, and the temperature changed much less with changes in the measurement position. This

indicates that the nano-aluminum not only reacted more easily than the micro-aluminum, but also the propellant system containing nano-aluminum burned more stably.

The large number of studies mentioned above clearly show that proper coating and modification materials can significantly increase the chemical reactivity of nano-aluminum powder and greatly improve the application possibilities of nano-aluminum powder in explosives.

3.3.3. Increasing the Reaction Degree of Nano-Aluminum Powder

The reaction extent of aluminum powder is the most critical indicator of its performance in explosives. It is evident that the higher the reaction extent, the more aluminum powder can leverage its energy advantage. Yan [122] used fluororubber F2602 with fluorine content of 66% to coat nanoscale aluminum powder, with the mass fractions of 5, 10, and 15%. fluororubber. Differential scanning calorimetry (DSC) studies found that the heat release rate of the uncoated sample was 6451 J/g, while the heat release rates of the three coated samples were 6902, 7892 and 9259 J/g, representing increases of 6.99, 22.34 and 43.53% over the uncoated sample, respectively. The results showed that as the content of fluororubber increased, the total heat release also increased significantly. Lv [123] prepared Al/PTFE core-shell-structured composite materials using chemical vapor deposition technology, with an aluminum powder particle size of 150–200 nm and an effective aluminum content of 85.3%. The results showed that the combustion heat of the Al/PTFE composite material increased by 4.1% compared to the raw nano-scale aluminum powder when tested using the oxygen bomb method. Sun [124] prepared an Al@PVDF core-shell-structured composite by electrostatic spraying with an average particle size of 69 nm, and compared it to samples prepared by mechanical mixing. The results showed that fluorinated materials improved the combustion performance of nano-aluminum powders. The PVDF-coated nano-aluminum composite particles prepared by electrostatic spraying had a higher heat release rate and more complete combustion compared to the composite prepared by mechanical mixing. Chang [125] prepared aluminum/fluorinated acrylic ester (Al/PFDMA) composite particles and aluminum/polyvinylidene fluoride (Al/PVDF) composite particles. TG/DSC analysis showed that when the polymer content was 20 wt%, the reaction heats of Al/PVDF and Al/PFDMA composite particles were 11,908 J/g and 8203 J/g, which were 68% and 15% higher than that of the raw nano-aluminum (7066 J/g). The burning rates of propellants made from these two materials were also significantly increased. Kim et al. [126,127] coated nano-aluminum powder with polytetrafluoroethylene (PTFE), which was used as both a protective layer and an oxidation promoter. The results showed that, compared with pure aluminum, the weight calorific value of the composite increased from 0.88 kJ/g to 4.80 kJ/g, more than four times. The team also prepared an Al/PVDF composite, and the exothermic enthalpy was about twice that of uncoated Al particles. Wang [128] proposed an effective surface-activation strategy for nano-aluminum powder to improve the combustion performance and energy output of nano-aluminum-based energetic materials. By coating the aluminum powder with perfluorododecanoic acid, a porous AlF_3 shell was formed on the surface of the nano-Al particles. The energy output and combustion reaction rate of the $\text{C}_{11}\text{F}_{23}\text{COOH}$ -coated PTFE/nano-aluminum were 6304 J/g and 670 m/s, 3.0 and 2.6 times than that of PTFE/uncoated-nano-aluminum. Campbell [129] coated aluminum powder with perfluorotetradecanoic acid (PFTD) to prepare Al/PFTD composites with different proportions, with an average particle size 1.6 μm . Ignition tests showed that when the PFTD content was 9 wt%, the maximum temperature could reach 1826 °C, far higher than the maximum temperature of pure aluminum powder at 1310 °C. Jiang's team [130,131] modified graphene by adopting perfluorooctyltriethoxysil-functionalized graphene oxide (CFGO) and selected aluminum powder with a nominal particle size of 70 nm and an active aluminum content of 72.5 wt% to prepare nAl/CFGO (80/20 wt%)

composites. Constant-volume ignition tests showed that nAl/CFG0 exhibited the most intense combustion and the highest combustion temperature, with peak pressure and a pressure rise rate more than seven times and six times higher than those of the original nano-aluminum powder, respectively. In addition, the research team modified nanoscale Al with perfluoroalkyl silanes, and similar research results were obtained. Wang [132] prepared aluminum powder composites coated with fluororubber F2311. The aluminum powder was prepared by the electroexplosive method with an average particle size of about 200 nm. The results showed that compared with the raw nano-Al material, the apparent activation energy of Al/F2311 was reduced by 4 kJ/mol, and the temperature of the first exothermic peak was advanced by about 10 °C. Furthermore, the heat release was nearly twice that of the raw nano-aluminum material. Moreover, the research results of Huang [133] also showed that when using fluororubber F2314 as a binder to prepare n-Al/CL-20 microspheres, F2314 promoted the oxidation reaction of aluminum powder, resulting in higher heat release. Uhlenhake [134] prepared Al/THV composites (THV is a terpoly of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride), with an average particle size of 80 nm and a of 70 wt% Al content. The Al/THV composites were then incorporated into the AP/HTPB propellant system. When the composite material accounted for 5 wt%, the burning rate was 2.1 times than that of the original propellant. When the composite material accounted for 15 wt%, the burning rate was 4.7 times than that of the original propellant. Additionally, the team also prepared Al/PVDF films, which showed similar effects [135]. Tang [136] used fluorinated polyurethane (FPU) as a binder to prepare energetic composites containing aluminum nanoparticles (with an average particle of 100 nm). The explosion calorimetry test showed that when the fluorine content in the composite was only 3.70 wt%, the explosion calorimetry of the composite increased from 1685 kJ kg⁻¹ for the non-fluorinated system to 3222 J kg⁻¹, an increase of 91.2%. The authors calculated that if the additional heat of explosion was solely due to the formation of AlF₃, it would only be 482 kJ kg⁻¹. Therefore, the fluorine in the fluorinated materials not only undergoes oxidation reactions but also acts as a catalyst. When the fluorine contents in the composite were increased to 4.55, 5.24, 3.2 and 6.79%, the explosion calorimetry rates were 2973, 2926, 3032 and 3037 kJ kg⁻¹, respectively, and did not continue to increase with the fluorine content. It can be inferred that fluorine acts as a catalyst.

A large number of studies have shown that suitable coating and modification materials have a great influence on the reaction degree of nano-aluminum powder, and suitable materials can even increase the heat release of raw aluminum powder by several times.

The combustion mechanism of aluminum powder is significant for its practical application. Chen and his team [137] explored the combustion mechanism of single micron-sized aluminum particles using a numerical model. The research results showed that the diffusion coefficient of oxidizers, the activation energy of surface kinetics and the evaporation coefficient (α) of aluminum impact the particle temperature the most. The burning time is most sensitive to the activation energy of surface kinetics. For some important issues, such as the combustion mechanism, combustion thermodynamics and combustion kinetics of nano-aluminum particles, the particle sizes and effective aluminum contents of aluminum powder used by different researchers have varied significantly. Additionally, most researchers have not shared the effective aluminum content used, making it difficult to obtain convincing views. Therefore, this article will not discuss this topic in detail.

4. Differences in Energy Release Characteristics Between Nano-Aluminum Powder and Micro-Aluminum Powder in Explosives and Propellants

4.1. Differences in Energy Release Characteristics Between Nano-Aluminum Powder and Micro-Aluminum Powder in Explosives

Many researchers have studied the differences in nanometer aluminum powder and micro-aluminum in mixed explosives. Liu [138] studied the reactivity differences between micro-aluminum powder and nano-aluminum powder in mixed explosives by the flyer push test. The results showed that the initial reaction time of small particles was earlier than that of large particles. Cao [139] studied the influence of nano-aluminum powder on the detonation velocity of RDX-based explosives. The results showed that the detonation velocity of samples containing nano-aluminum powder was higher than those of containing micron-sized aluminum powder when the content of aluminum powder was below 10%. Liu [140] studied the influence of nano-aluminum powder on explosive detonation pressure. The average particle size of the aluminum powder was 170 nm, the main explosive was RDX and 5 wt% wax was used as the binder and desensitizer. The results showed that when the content of nano-aluminum powder was 5 wt% and 10 wt%, the explosion pressure was higher than that of the composite without aluminum powder. In addition, Brousseau [141] studied three percentages of aluminum, namely 0%, 20% and 30%. The results showed that the explosive charge containing nano aluminum powder had higher detonation velocity than that containing micro-aluminum particles. With increases in the charge diameter, the detonation velocity difference decreased. Bai [142] carried out flyer experiment driven by the explosion of mixed explosives containing aluminum powder with different particle sizes. Three kinds of aluminum powders with particle sizes of 50 nm, 5 μ m and 50 μ m were selected. The results showed that the free surface velocity of the flyer was higher for aluminized explosives containing aluminum powder with a particle size of 50 nm than that of aluminized explosives containing aluminum powder with particle sizes of 5 μ m and 50 μ m when driving a copper plate. Wang [143] studied the influence of nano-aluminum on the metal driving ability of RDX-based mixed explosives by cylinder tests. The total amount of aluminum powder in the composite was 20 wt%. The particle size of the nano-aluminum powder was 100 nm~200 nm, which was used to replace the micro-aluminum powder in the composite. The results showed that the expansion force of detonation products increased by 10.2% and 5.5%, respectively, after the aluminum powder in the composite was replaced by 5 wt% and 10 wt% nano-aluminum powder. The author stated that the addition of nano-aluminum powder may be beneficial to adjust the rupture time of warhead shells and improve the energy utilization efficiency of charge. Huang [144] prepared explosive composites containing nano-aluminum but did not specify the particle size or effective aluminum content of nano-aluminum. The composition was HMX/micro-aluminum/nano-aluminum/binder = 57/28/5/10, and it was compared with the composite without nano-aluminum (HMX/micro-aluminum/binder = 57/33/10). The contrast formula only ignited cotton yarn 3 m away from the explosion center, while the formula containing nano-aluminum ignited the cotton yarn 5~7 m away, and the arson effect of the composite containing nano-aluminum powder was significantly improved. Elert [145] replaced micron aluminum powder with nano-aluminum powder in an explosive composite (the specific composition was not announced for confidentiality reasons), and the plate dent test showed that the dent volume on the witness plate was about twice that of the original composite. Huang [146] studied the influence of nano-aluminum on the shock wave overpressure in an air explosion test of mixed explosives. The average particle size of the nano-aluminum was 91.7 nm, and flammable fine aluminum powder was used for comparison. The test results showed that the peak value of shock wave overpressure of the

sample containing nano-aluminum was much higher than that of the sample containing micro-aluminum for all the test data at all distances. This indicates that nano-aluminum has obvious advantages. Simić [147] studied the influence of nano-aluminum powder on the overpressure and impulse of air explosion shock waves. The explosive formula was HMX/AP/Al/HTPB = 45/15/20/20. Two kinds of aluminum powders with average particle sizes of 5 μm and 70 nm were selected. One composite was only micro-aluminum powder, while the other was 50% nano-aluminum powder. The air explosion test results showed that the composite with micro-aluminum powder had a lower overpressure peak in the far-field shock waves than that of the mixed aluminum powder composite. For impulse, the composite with mixed aluminum powder was higher than the micro-aluminum powder composite at all measuring points. The above experiments showed that nano-aluminum powder had a better supporting effect on shock waves. Fang [148] studied the influence of nano-aluminum powder on the explosive power of fuel–air explosives. The micro-aluminum powder used was flaky aluminum powder with a diameter of about 18 μm , a thickness of less than 1 μm and an effective aluminum content of 85%. The d_{50} of nano-aluminum powder was 100 nm, and the effective aluminum content was 88%. The results are shown in Table 3. The peak value and the maximum rising rate of explosion pressure were 0.82 MPa and 1.75 MPa s^{-1} , respectively when pure micro-aluminum powder was used for the test. When adding 5% and 10% nano-aluminum powder, the peak explosion pressure increased to 1.02 MPa and 1.30 MPa, respectively, with increases of 24.4% and 58.5%. Additionally, the maximum pressure rise rates increased to 3.16 MPa s^{-1} and 3.56 MPa s^{-1} , with increases of 80.6% and 103.4%, indicating the addition of nano-aluminum powder had a significant effect. Under the same ignition energy and the same environmental conditions, the maximum overpressure of fuel–air explosives showed an obvious increasing trend with increases in aluminum powder content. Nano-aluminum powder can replace some micron-sized aluminum powder, which can increase the peak explosion pressure and the rising rate of explosion pressure, improving the power of mixed explosives. Feng [149] studied the effects of nano-aluminum powder on the underwater explosion energy of RDX-based mixed explosives. The particle size of the micro-aluminum powder was 4–5 μm , and the particle size of the nano-aluminum powder was 60–80 nm. The results showed that when the total contents of aluminum powder were 30% and 35%, the total energy of underwater explosion of explosives was higher than that of explosives containing only micro-aluminum powder when mixed with nano-aluminum powder. Niu [150,151] studied the effect of nano-aluminum on the underwater explosion energy of RDX-based explosives. The average particle size of micro-aluminum powder was about 5 μm , and the average particle size of nano-aluminum powder was about 150 nm. It was found that when the total mass fraction of aluminum powder was 30%, if the mass ratio of micro-aluminum to nano-aluminum was 50:50, the total energy of underwater explosion was higher than that of the composite containing micro-aluminum alone. Therefore, nano-aluminum powder changes the energy output structure of underwater explosions of mixed explosives. Liu [152,153] studied the degree of participation of nano-aluminum powder and micro-aluminum powder in C-J surface reactions with a CL-20/Al formula system. Three kinds of aluminum powder, 200 nm, 2–3 μm and 16–18 μm in size, were used. The ratio of the reaction product particle velocity to the C-J plane particle velocity at 1 μs was tested. The results showed that the degree of 200 nm aluminum powder in the system participating in the C-J surface reaction was significantly higher than that in the other two systems, and the reaction start time of aluminum powder with a smaller particle size was earlier than that of aluminum powder with a larger particle size.

Table 3. Explosion parameters of micro/nano-aluminum mixture [149].

No.	Concentration of Aluminum Dust/g·m ⁻³	Nano-Aluminum Content/%	Maximum Pressure/MPa	(dp/dt) _{max} /MPa·s ⁻¹
1 [#]	344	0	0.82	1.75
2 [#]	342	5	1.02	3.16
3 [#]	342	10	1.30	3.56
4 [#]	343	15	1.16	3.12

4.2. Differences in Energy Release Characteristics Between Nano-Aluminum Powder and Micro-Aluminum Powder in Propellants

Many studies have compared the differences between nano-aluminum powder and micro-aluminum powder regarding their propellant properties, including ignition performance, combustion performance, and particle size effects.

Jiang [154] studied the influence of nano-aluminum powder on the ignition performance of propellants. The average particle size of the nano-aluminum powder was 83 nm, and the average particle size of the ordinary aluminum was 13 μ m. The research showed that the ignition threshold of the propellant containing nano-aluminum powder was several orders of magnitude smaller than that of the propellant containing ordinary micro-aluminum powder, and adding nano-aluminum powder significantly shortened the ignition delay time of the propellant. Hao [155] also showed that the smaller the particle size of aluminum powder, the shorter the ignition delay time of AP/HTPB composite solid propellants containing nano-aluminum powder. Additionally, Meda [156] prepared propellants with aluminum powders of different particle sizes. The research showed that the smaller the particle size of the aluminum powder, the lower the ignition temperature of the propellant and the shorter the ignition delay time.

Wang [157,158] studied the influence of nano-aluminum powder on the combustion performance of propellants and adopted four kinds of aluminum powder with average particle sizes of 50 nm and 100 nm, respectively: long ellipsoid, with average sizes of 53.35 nm and 105.11 nm; and flat ellipsoid, with average sizes of 55.56 nm and 110.88 nm, respectively. The composite consisted of 80–85 wt% aluminum powder, 12–17 wt% oxidant, 2 wt% binder and 1 wt% catalyst. The density of the prepared nano-aluminum powder column was about 1.8–2.0 g cm⁻³, and the column size was $\varnothing 20$ mm $\times$ 150 mm. It was found that the burning time of the propellant column containing 50 nm aluminum powder was obviously shorter than that of the propellant column containing 100 nm aluminum powder. When the aspect ratio was 10, the maximum burning rate of the flat ellipsoid particles was only 1.3×10^{-13} kg s⁻¹, while that of the long ellipsoid particles was as high as 3.0×10^{-13} kg s⁻¹, which is about 2.3 times that of the flat ellipsoid particles. Li [159] replaced 3 wt% micro-aluminum powder with nano-aluminum powder to prepare a propellant. It was found that the static burning rate of the sample increased by 22.0% at 7 MPa and 8.1% at 15 MPa. However, the dynamic burning rate increased by 14.3% when the engine was tested at 7 MPa, and increased by 9.8% when it was tested at 15 MPa. The static burning rate pressure index of the sample was 0.11 (7–15 MPa), which is 31.0% lower than that of the original sample. The dynamic burning rate pressure index obtained in the engine test was 0.22, which was 12.0% lower than that of the original sample. Ramakrishnan [160] studied the influence of aluminum powder with different particle sizes on the combustion performance of propellants. The average particle sizes of the aluminum powder were 18 μ m, 250 nm, and 100 nm, respectively, and they were tested in the range of 0.2–3.1 MPa. The research showed that the combustion rates of propellants containing nano-aluminum were 2–5 times than that of propellants containing micro-aluminum. Zhang

and others [161–166] applied nano-aluminum powder to propellants, which increased the burning rate of the propellants and reduced the pressure index. Galfetti [167] studied the AP/Al/HTPB solid rocket propellant system, and found that the aluminized composite solid rocket propellant containing nano-aluminum particles had a faster combustion rate than the control propellant containing the same mass percentage of micro-aluminum particles. When 20%, 50% and 100% nano-aluminum powder replaced micro-aluminum powder, the combustion rate increased by about 40%, 60% and 100%, respectively. This increase was mainly determined by the strong energy released by the oxidation of ultrafine particles near the combustion surface. In addition, the analysis of condensed combustion products showed that when the propellant formula contained nanoparticles, the combustion process was more efficient, and nano-aluminum particles reduced the unburned metal content in the condensate and increased the alumina content. This indicates that the reaction of nano-aluminum powder is more complete. Watson [168] obtained similar results. For an Al/MoO₃ composite system, the peak burning rate of Al/MoO₃ composite containing 50 nm Al particles was 960 m/s, while that of the same system containing 1–3 µm Al was only 244 m/s. James [169] studied the influence of nano-aluminum powder on propellant retrogression rate, and the particle sizes of the aluminum powder used were 100 nm and 20–30 µm, respectively. The composition of the system was Al/AP/HTPB = 10/70/20. It was found that the retrogression rate of the system containing nano-aluminum powder was higher than that of the propellant system containing micro-aluminum powder. Jiang [154] observed the agglomeration of combustion products of propellants containing nano-aluminum powder. After the combustion test, it was observed that the residue of propellants containing nano-aluminum powder was small and white, or mixed with a little gray, and the residue of propellants containing micro-aluminum powder was large and dark, indicating that nano-aluminum powder could burn more fully than micro-aluminum powder. Galfetti [94] found that the average size of combustion products of propellants containing 150 nm aluminum powder was 6.6 µm, while that of propellants containing 30 µm aluminum powder was 13 µm. Liu [170,171] used micro-aluminum powder with different particle sizes and obtained similar results. The particle size of agglomerates decreased with increases in the aluminum powder particle size.

Peuker [172] applied aluminum powder with different particle sizes to explosives and obtained the following conclusions: (1) Aluminum particles with particle sizes ranging from 3 to 40 µm enhance primary blasting, and the blasting driving effect does not strongly depend on particle size. (2) The quasi-static pressure measurement showed that the oxygen in the air was enough to completely oxidize aluminum powder within 10 µm. (3) In the absence of external oxygen, aluminum is usually only oxidized to 50%, but the aluminum powder with the smallest particle size (3 µm) was almost completely oxidized. These research results indicate that different application scenarios and different systems of propellants and mixed explosives may be brought into full play by using aluminum powder with different particle sizes under different environmental conditions.

The influences of nano-aluminum particles on the properties of explosives and propellants are summarized in Table 4.

Compared with micro-aluminum powder, nano-aluminum powder has higher reaction activity and a more complete reaction, so nano-aluminum powder has good application prospects. However, the high reactivity of nano-aluminum powder makes the preparation and storage of high-purity nano-aluminum powder extremely difficult; therefore, further research on preparation and storage technologies is extremely important to ensure that this material can play a greater role in many fields as soon as possible.

Table 4. Influences of nano-aluminum particles on the energy release characteristics of explosives and propellants.

Applications	Test Method	Results	References
explosives	flyer push test	The initial reaction time of small particles was earlier than that of large particles.	[138]
	detonation velocity	The detonation velocity of samples containing nano-aluminum powder was higher than those of containing micron-sized aluminum powder when the content of aluminum powder was below 10%.	[139]
	detonation pressure	When the content of nano-aluminum powder was 5 wt% and 10 wt%, the explosion pressure was higher than that of the composite without aluminum powder.	[140]
	flyer experiment	The free surface velocity of flyer was higher for aluminized explosives containing aluminum powder with a particle size of 50 nm than that of aluminized explosives containing aluminum powder with particle sizes of 5 μm and 50 μm .	[141]
	cylinder test	The expansion force of detonation products increased by 10.2% and 5.5%, respectively, after the aluminum powder in the composite was replaced by 5 wt% and 10 wt% nano-aluminum powder.	[142]
	arson effect	The arson effect of the composite containing nano-aluminum powder was better than composite containing micro-aluminum powder.	[144]
	plate dent test	The dent volume of the composite with nano-aluminum on the witness plate was about twice that of the original composite.	[145]
	air explosion test	The peak value of shock wave overpressure of the sample containing nano-aluminum was much higher than that of the sample containing micro-aluminum for all the test data at all distances.	[146]
		The impulse of the composite with nano-aluminum powder was higher than that of micro-aluminum powder at all measuring points.	[147]
	explosion chamber experiment	The peak value and the maximum rising rate of explosion pressure of composites with nano-aluminum were better than those of composites without nano-aluminum.	[148]
propellants	underwater tests	The total energy of underwater explosion was higher than that of the composite containing micro-aluminum alone.	[149–151]
	C-J surface reaction tests	The degree of aluminum powder in the system containing nano-aluminum powder participating in C-J surface reaction was significantly higher than that in systems containing micro-aluminum powder, and the reaction start time of aluminum powder with a small particle size was earlier than that of aluminum powder with a large particle size.	[152,153]
	ignition tests	The ignition threshold of propellant containing nano-aluminum powder was several orders of magnitude smaller than that of propellant containing ordinary micro-aluminum powder, and adding nano-aluminum powder can significantly shorten the ignition delay time of propellant. The smaller the particle size of aluminum powder, the shorter the ignition delay time, and the lower the ignition temperature of the propellant.	[154–156]
	combustion rate experiment	The combustion rate and retrogression rate of propellant containing nano-aluminum were much faster than those of propellant containing micro-aluminum.	[157–169]
		The residue of propellants containing nano-aluminum powder was small and white, or mixed with a little gray, and the residue of propellants containing micro-aluminum powder was large and dark, indicating that nano-aluminum powder could burn more fully than micro-aluminum powder.	[95,154,170,171]

5. Conclusions

In summary, there are many ways to prepare nano-aluminum, such as mechanical crushing methods (including the ball milling method and ultrasonic ablation method, etc.), evaporation–condensation methods (including the laser induction composite heating method, high frequency induction method, arc method, pulse laser ablation method, resistance heating condensation method, gas phase pyrolysis method, wire explosion crushing method, etc.), chemical reduction methods (including the solid phase reduction method, solution reduction method, etc.) and ionic liquid electrodeposition methods. Each of these methods has its advantages and disadvantages, but many researchers have only provided the particle size of the nano-aluminum powder prepared by their team, and not the effective aluminum content. In fact, the effective aluminum content has a very important effect on the application of mixed explosives and propellants.

Some innovative nano-aluminum preparation methods, such as low-temperature ball milling, the ultrasonic ablation (scrub) method to prepare nano-aluminum powder and the template method to prepare nano-aluminum powder and active organic composite materials, may have very promising application value, and further research has been suggested.

The reaction activity and completeness of aluminum powders with different particle sizes are significantly different. A large number of studies from the perspective of ignition performance and combustion performance show that the reaction activity of nano-aluminum powder is much higher than that of micro-aluminum powder. Many studies on reaction completeness show that nano-aluminum powder achieves significantly higher reaction completeness than micro-aluminum powder.

As far as the characteristics of nano-aluminum powder are concerned, coating or modifying nano-aluminum powder can provide many advantages, such as protecting the activity of nano-aluminum powder, improving the reactivity of nano-aluminum powder and increasing the reaction heat of nano-aluminum powder.

The application of nano-aluminum powder in mixed explosives can improve many properties of mixed explosives, such as the detonation velocity, detonation heat and the peak overpressure of shock waves. The application of nano-aluminum powder to propellants can significantly improve the burning rate and the agglomeration of combustion products.

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Abbreviation

A	
Accelerating rate calorimetry	ARC
Acetonitrile	ACN
B	
Ball–powder ratio	BPR
C	
Perfluoroalkyl-functionalized graphene oxide	CFGO

D	
Direct current	DC
5,5-bitetrazole-1,1-diol dihydrate	DHBT
Differential scanning calorimetry	DSC
E	
Aluminum wire electroexplosive	EEW
Energetic metal–organic framework	EMOF
F	
Fluorinated acrylic ester	AI/PFDMA
Fluorinated polyurethane	FPU
H	
Hydroxyl-terminated polybutadiene	HTPB
Hydroxyl-terminated polybutadiene-toluene Diisocyanate	HTPB-TDI
M	
Minimum explosible concentration	MEC
Monomethylamine	MMA
N	
Nitrocellulose	NC
O	
Octadecylamine	ODA
P	
Perfluorosulfonic acid	PFSA
Perfluorotetradecanoic acid	PFTD
Polydopamine	PF
Polyethylene glycol	PEG
Polyvinylpyrrolidone	PVP
Polystyrene	PS
Polytetrafluoroethylene	PTFE
Poly(trimethylolpropane triacrylate)	PTMPTA
Polyvinylidene fluoride	PVDF
S	
Scanning electron microscopy	SEM
Tetrahydrofuran	THF
T	
Thermogravimetric	TG
Thermogravimetric analysis	TGA
Trimethylolpropane triacrylate	$\text{CH}_2 = \text{CHCOOCH}_2\text{CCH}_2\text{CH}_3\text{TMPTA}$
Transmission electron microscopy	TEM
Triisobutyl aluminum	TIBAL
Thermogravimetric–differential thermal analysis	TG-DTA
X	
X-ray diffraction	XRD
Y	
Yttrium-stabilized zirconia	YSZ

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Review

Vanadium-Based MXenes: Types, Synthesis, and Recent Advances in Supercapacitor Applications

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Abstract

Since the discovery of two-dimensional transition metal carbides and nitrides (MXenes), MXenes have attracted widespread research in the academic community due to their advantages, such as adjustable interlayer spacing, excellent hydrophilicity, conductivity, compositional diversity, and rich surface chemical composition. More than 100 different MXene combinations can be calculated theoretically, but only more than 40 have been successfully synthesized through experiments. Among the many synthesized and reported MXene materials, vanadium-based carbide MXenes, represented by V_2CT_x and $V_4C_3T_x$, show excellent application prospects in energy storage and have become the focus of researchers. In this review, we mainly discuss the structure, characteristics, and preparation methods of vanadium-based MXene precursors in the MAX phase and their applications in supercapacitors. Finally, we propose the main challenges existing at the current stage of vanadium-based materials and their heterostructures and provide a perspective on future research directions.

Keywords: two-dimensional material; V_2CT_x ; $V_4C_3T_x$; derivatives; supercapacitor applications

1. Introduction

In addressing global energy transition and the challenges of renewable energy grid integration, developing new electrochemical energy storage materials that combine high power density and high energy density has become a vital frontier topic in energy science [1–3]. As a core component of the electrochemical energy storage system, supercapacitors, with their ultra-fast charge transfer kinetics and cycle life, hold an essential position in transient power supply scenarios such as smart grid peak shaving and electromagnetic catapult systems [4,5]. However, due to the limitation of the double-layer physical adsorption energy storage mechanism, there is an order of magnitude difference in their intrinsic energy density compared to battery systems. This key performance shortcoming seriously constrains their application prospects in large-scale energy storage fields [6].

The breakthrough progress in two-dimensional nanomaterials has provided a new theoretical framework for the design of energy storage materials. Following the successful synthesis of the two-dimensional carbonaceous material graphene [7], two-dimensional material systems represented by transition metal chalcogenides (such as MoS_2 , WS_2) [8–10]

and layered double hydroxides (such as NiCo-LDH) [11,12], due to their unique quantum confinement effect and surface pseudocapacitance characteristics, have sparked continuous research enthusiasm in the field of energy storage [13,14]. Notably, MXenes (transition metal carbides/nitrides), as new members of the two-dimensional material family, since their successful preparation in 2011 through hydrofluoric acid etching of MAX phase precursors [15], have achieved significant progress in structural regulation strategies and energy storage application research [16–18]. The synthesis of these materials follows specific topological chemical rules: by selectively removing the weakly bonded “A” atom layer (typically Al, Si elements) from the MAX phase, $M_{n+1}X_nT_x$ structures ($n = 1–3$) with alternating stacking are obtained, where M represents transition metals like Ti and V, X is C or N atoms, and T_x denotes surface terminating functional groups (–O, –OH, –F, etc.) [19–21]. As shown in Figure 1a,b, the unique metal-like conductivity and large interlayer spacing of MXenes make them possess rapid ion transport capabilities and a high Faraday pseudocapacitance contribution rate, becoming an ideal electrode material system for constructing the next generation of high-performance supercapacitors [22–27].

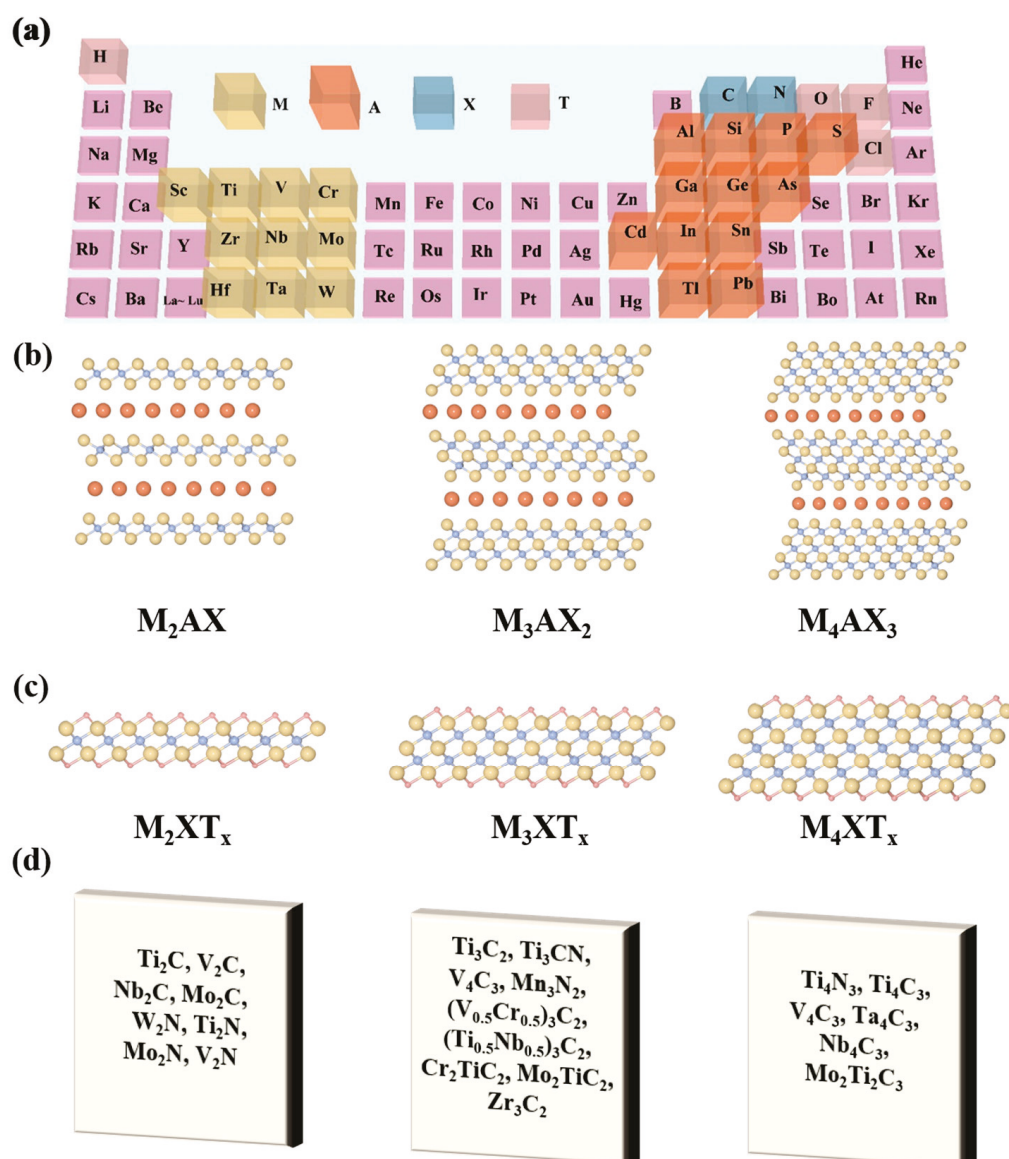


Figure 1. (a) Fragment of the periodic table of elements, the “M”, “A”, “X” and “T” elements in MAX phases. (b) The structure of a MAX phase and (c) the corresponding MXA. (d) A typical MXene.

MAX phase materials have a typical hexagonal close-packed crystal structure, and their unit cells consist of alternating stacked MX hexagonal layers and A atomic layers [28–30]. Depending on the difference in the value of n in the chemical formula ($n = 1, 2, 3$), the layered structures of derived MXenes ($M_{n+1}X_nT_x$) can present different stacking configurations such as 3, 5, and 7 layers [31–35]. Theoretical predictions show over a hundred possible combinations in the MXenes family, but only 40 have been synthesized experimentally (Figure 1d). Based on atomic arrangement features, MXenes can be divided into two major structural types: a solid solution phase (random distribution of multiple metals) and an ordered phase (ordered interlayer of transition metals) [36,37]. Among them, M_2X -type MXenes can be classified into single-metal and bimetallic systems according to the composition of the metal layer. The increase in the number of metal layers will cause a compression effect on the interlayer spacing, and this structural evolution will directly affect the ion diffusion barrier, the number of electrochemical active sites, and the mechanical properties of the material [38]. By precisely controlling the surface chemical composition and interlayer spacing of MXenes, the conductivity, mechanical strength, and electrochemical activity performance parameters can be effectively optimized.

Current research mainly focuses on the Ti_3AlC_2 -phase-derived Ti-based MXene system, while vanadium-based MXenes (V-MXenes) possess unique redox reversibility ($V^{2+}/V^{3+}/V^{4+}$) and ultra-high theoretical specific capacity. However, they face technical bottlenecks such as controllable etching and efficient exfoliation due to the difficulty in regulating surface functional groups and strong interlayer coupling [39]. Among the reported vanadium-based MXenes, V_2CT_x and $V_4C_3T_x$ have become a hot topic in energy storage research due to their distinct interlayer channel characteristics. In response to the challenges in their preparation techniques, the academic community has proposed a series of synthesis strategies, including in situ etching with hydrofluoric acid, fluoride salt-assisted etching (such as NaF/LiF system), and electrochemical gradient etching [40]. It is worth emphasizing that the multivalent nature of vanadium endows V-MXenes with excellent charge storage kinetics. By compositing with conductive polymers or transition metal oxides to form heterogeneous interfaces, the composite materials' specific capacitance and cyclic stability can be significantly improved. Simultaneously, metal–organic framework materials (MOFs), carbon nanofibers (CNFs), and layered double hydroxides can also be supercapacitor materials. V-based MXenes and MOFs show significant differences in structure and performance. V-based MXenes, as a two-dimensional transition metal carbide, are obtained by etching the MAX phase with hydrofluoric acid and have conductivity like metals and tunable interlayer spacing. Still, they have a lower specific surface area and are easily oxidized. On the other hand, MOFs are three-dimensional porous crystals constructed from metal clusters and organic ligands. They have a higher specific surface area and porosity but inherently poor conductivity [41]. Therefore, due to their high conductivity, V-based MXenes perform prominently in supercapacitors and zinc-ion battery electrode modifications. At the same time, MOFs are more advantageous in gas storage and catalysis due to their designable pore channels. Using the electrospinning method, CNFs can be massively produced with a porous/hollow structure. Typically, V-based MXene is combined with CNFs to utilize its porous structure to buffer volume expansion, resulting in long-term stability characteristics in supercapacitors [42]. Its high flexibility can enhance device bendability, expanding its application field. Layered double hydroxides (LDHs) generally comprise divalent or trivalent metal layered hydroxide nanosheets with interchangeable anions between layers, maintaining interlayer equilibrium through electrostatic interactions. Using V-based MXene as a conductive substrate to form a composite can accelerate the charge transfer kinetics of LDHs and reduce the overpotential of the oxygen evolution reaction (OER), and the synergistic active sites between the LDH nanosheets

can provide an efficient catalytic center, enhancing the catalytic reaction efficiency [43]. Moreover, the ultra-thin two-dimensional layered structure of V-based MXene can significantly inhibit the agglomeration of LDHs, increasing its specific surface area. The interlayer confinement effect of LDHs can also slow the oxidation of MXenes by anchoring $-OH/-O$ functional groups. Therefore, constructing a heterostructure combining V-based MXene with LDHs can synergistically leverage both advantages, showing immense industrial application potential in supercapacitors.

The specific challenges of the HF-free synthesis route for V-MXene are as follows: Firstly, vanadium-based MXenes are generally prepared from the precursor V_2AlC to produce V_2C . The bond energy of V-Al is significantly higher than that of Ti-Al, making it difficult for traditional HF-free etchants to break effectively, leading to residual Al layers [25]. Secondly, vanadium elements are easily oxidized to higher valence states (V^{4+}/V^{5+}), especially in oxygen-containing environments, forming inactive oxides (such as V_2O_5), and the terminal functional groups of V-based MXenes prepared by the HF-free method ($T_x = Cl/Br$) are unstable in air. Finally, the etched accordion-structured V-based MXene generally requires the use of intercalants (TBAOH/TMAOH) to exfoliate and obtain single or few-layer MXenes [24–26], thereby increasing their exposed active sites and promoting their significant electrochemical performance.

This review systematically analyzes the preparation of the chemical system of vanadium-based MXenes, focusing on the reaction mechanisms and process characteristics of core synthesis technologies such as hydrofluoric acid etching, fluoride salt-assisted etching, and electrochemical etching. It deeply explores the optimization mechanisms of its electrochemical performance by strategies such as interlayer distance regulation engineering, surface termination functional group regulation, and heterostructure construction. A comprehensive review of the latest research progress of V-MXenes in supercapacitors reveals their unique advantages in high-power energy storage devices. Finally, it also looks forward to the potential research directions of V-MXenes in precise and controllable synthesis and multi-scale structure regulation.

2. Basic Properties of V-MXene

V-based MXenes possess multivalent characteristics, excellent conductivity, large specific surface area, adjustable interlayer spacing, and good chemical stability, endowing them with broad application potential in energy storage. Through rational design and functionalization of V-based MXenes, these materials can play a significant role in electrode materials, energy storage devices, and other fields, especially demonstrating outstanding electrochemical performance in battery and supercapacitor applications due to their unique structural advantages.

2.1. Multi-Valence Characteristics

The unique advantage of vanadium-based MXenes stems from the multivalent nature (+2 to +4) of the vanadium element, which enables a multi-electron transfer mechanism during electrochemical energy storage, significantly enhancing charge storage capacity [44]. In alkali metal-ion batteries and supercapacitors, the reversible redox reactions of vanadium effectively enhance the energy density and cyclic stability of electrode materials through synergistic transitions between different valence states. This characteristic is universal in vanadium-based compound systems; typical representatives include layered vanadium oxides, two-dimensional chalcogenides, and polyanion-type compounds. Their diverse crystal structures provide abundant active sites for ion storage [45].

As essential members of the vanadium-based material system, V_2C and V_4C_3 , with their unique two-dimensional layered structure and the multivalent characteristics of vanadium elements (reversibility of $V^{2+}/V^{3+}/V^{4+}$ redox), have shown significant advantages in the field of energy storage and catalysis [28]. Their structural features are the following: the V-C layers obtained by selective etching of MAX phases (such as V_2AlC) are stacked by van der Waals forces, with surface modifications of $-O$, $-OH$, $-F$, etc., terminating groups, and interlayer stacking can be suppressed through intercalation engineering or heterogeneous compounding to optimize ion diffusion dynamics, while the multivalent state characteristics of vanadium provide high-density pseudocapacitive active sites through reversible oxidation reactions (such as $V^{3+} \leftrightarrow V^{4+}$), endowing the material with high specific capacity and catalytic activity [37,38]. In addition, the synergistic effect of structure and valence state (such as surface amination enhancing potassium ion adsorption, heterogeneous interface accelerating charge transfer) will further strengthen its performance advantages. Still, it is necessary to overcome the bottlenecks of poor oxidation stability and dependence on hydrofluoric acid during preparation [44,45].

Vanadium trioxide (V_2O_3) exhibits a unique metal–insulator phase transition behavior. This material has a rhombohedral crystal structure, and its electronic properties undergo significant changes with temperature: it exhibits quasi-metallic conductivity at high temperatures. It transforms into an insulating state at low temperatures, accompanied by antiferromagnetic order. This phase transition characteristic is closely related to the special electron configuration of vanadium ions, making it of great application value in intelligent thermal control devices and phase change memory. Meanwhile, the open framework structure of V_2O_3 is conducive to ion implantation/extraction dynamics, combined with its intrinsic high conductivity, making it an ideal candidate for lithium/sodium ion battery anode materials [46]. It is worth noting that this material also performs prominently in catalysis, especially in the purification of nitrogen oxides and organic synthesis reactions, highlighting its multifunctional characteristics in the energy-environment intersection. Vanadium monoxide (VO), as a typical metallic conductive oxide, has the +2 oxidation state of vanadium in its cubic crystal system, endowing the material with unique electronic structure characteristics. The material has both quasi-metallic conductivity and excellent thermal stability [47]. Its chemical characteristics show a significant reductive tendency: stepwise oxidation reactions can occur in an oxidizing environment to form high-valent oxides, react with acidic media to form vanadium salt compounds, and maintain structural stability under alkaline conditions. This special chemical activity gives it significant application potential in high-temperature electrode materials and functional coatings.

Vanadium sulfide (V_2S_3) exhibits differentiated structural features and functional advantages in the vanadium-based sulfide system. In the three-dimensional framework of V_2S_3 , vanadium atoms and sulfur ligands form an octahedral coordination configuration; its semiconducting properties and abundant redox active sites provide an ideal reaction interface for electrochemical energy storage. In contrast, the layered monoclinic system of vanadium sulfide promotes rapid ion diffusion through expanded sulfur–vanadium–sulfur interlayers; its intrinsic magnetism and high conductivity synergistically enhance the charge transfer rate [48]. The outstanding performance of these two types of sulfides in alkali metal ion storage systems stems from the synergistic effect of the high polarizability of chalcogen elements and weak van der Waals forces between layers, which not only ensures cyclic stability but also displays unique advantages in hydrogen evolution reactions (HERs) and oxygen reduction reactions (ORRs) [49].

2.2. High Surface Area and Conductivity

The preparation of vanadium-based MXenes follows the principle of topological chemical etching, which is achieved by selectively removing the Al atom layer from the ternary layered MAX phase (such as V_2AlC , V_4AlC_3). The resulting two-dimensional material comprises a V-X ($X = C/N$) covalent bond network, with surface modifications of $-OH$, $-O$, $-F$, and other termination groups. The layers are held together by weak van der Waals forces, forming a peelable structure [40]. This unique chemical bonding method endows the material with dual characteristics: covalent and metallic bonds ensure structural stability. At the same time, the adjustable interlayer distance (through intercalation engineering) provides diffusion channels for ion transport [50].

Through intercalation engineering strategies (such as dimethyl sulfoxide, tetrabutylammonium hydroxide solution, or KCl intercalation), the interlayer spacing can be controlled and the interlayer interaction weakened. Combined with subsequent liquid phase exfoliation, the controlled preparation of mono/few-layer MXene nanosheets can be achieved [51]. After exfoliation, the specific surface area of the material significantly increases, exposing numerous active edge sites and interlayer storage space, effectively promoting the reversible embedding/desorption of ions such as Li^+ and Na^+ . Notably, the electronic structure of MXenes has both metallic and semiconductor characteristics: The strong V-C/N covalent bond forms a highly conductive substrate. At the same time, the surface terminal groups regulate the interfacial electrochemical activity through charge redistribution. In energy storage applications, this structural feature gives the material metal-like conductivity and structural stability. The expanded interlayer channels significantly reduce the ion diffusion barrier, demonstrating excellent rate performance and cyclic stability in fast energy storage devices such as supercapacitors.

2.3. Surface Functionalization and Heterostructures

The surface termination group ($-OH$, $-F$, $-O$) engineering of vanadium-based MXenes is the core strategy for its functional modification. By directionally modifying the surface chemical environment through liquid phase intercalation or gas phase post-treatment technology, the interface compatibility between the material and the electrolyte can be significantly optimized: oxygen-containing groups enhance hydrophilicity to promote the infiltration of aqueous electrolytes. At the same time, fluorination treatment improves the structural stability under organic systems. This surface chemical regulation reduces the ion migration barrier (the diffusion coefficient increases by two to three orders of magnitude). It activates the pseudocapacitive behavior of edge sites by inducing local charge redistribution.

The heterostructure design further expands the performance boundaries of MXenes: The composites with conductive polymers (such as 3,4-ethylenedioxythiophene) can construct a three-dimensional ion/electron dual continuous transport network [52]; coupling with transition metal oxides (such as MnO_2) achieves a synergistic effect of double-layer storage and Faraday reaction [53]. This structure–function integrated design endows it with the advantages of high conductivity substrate and adjustable active sites, showing a triple-gain effect in the field of energy storage: the porous interlayer channels accelerate the diffusion kinetics of multivalent ions (Zn^{2+} , Al^{3+}); the multivalent state transition of vanadium ($V^{2+}/V^{3+}/V^{4+}$) provides high-density redox active sites; and the surface terminal groups and heterogeneous interfaces synergistically regulate the charge storage mechanism [54].

The integration of such characteristics makes V-MXenes an ideal platform for innovative energy storage devices: achieving high reversible capacity in zinc-ion capacitors, suppressing sulfide shuttle in lithium–sulfur battery systems, and possessing bending cycle

stability in the field of flexible supercapacitors. Through cross-scale structural engineering and precise control of surface interfaces, this material system demonstrates the value of innovation from basic research to industrial applications.

3. Synthesis Methods of V-MXene

Many studies have been published on the synthesis of MXene, mainly based on the layered ternary MAX phase, using chemical etching techniques to remove the A elements, thus forming a layered MXene structure. Subsequent intercalation and exfoliation processes result in few-layer or monolayer MXene sheets with more active sites. The preparation method of V-MXene is through a top-down synthesis approach. Generally, V_2AlC is used as a precursor, and an accordion structure is obtained by etching out the “Al” layer. The scalability of V-based MXene in industrial applications has achieved significant breakthroughs in recent years. Its high conductivity and theoretical capacity demonstrate considerable potential in energy storage. However, the traditional hydrofluoric acid etching method is limited for large-scale applications due to its high toxicity and the product’s oxidation tendency. Solid solution design and cation intercalation modification techniques have significantly improved the material’s cyclic stability and environmental adaptability [53]. For instance, interlayer ion regulation and heterogeneous interface optimization can significantly extend the lifespan of devices and enhance their low-temperature performance. Moreover, the current development bottlenecks focus on developing green synthesis processes (such as fluoride-free etching agents) and cost control of precursor raw materials. In the future, it is necessary to combine emerging technologies such as artificial intelligence to optimize material structural parameters and collectively promote industrialization in areas like flexible energy storage and wearable devices. The primary etching methods currently include hydrofluoric acid (HF), mixed-acid, hydrothermal, and other methods. In this section, commonly used etching methods are discussed.

3.1. Mixed-Acid Etching

The direct etching method with hydrofluoric acid has defects such as incomplete layered dissolution and insufficient exposure of active sites when preparing V-based MXene, which significantly restricts the improvement of its energy storage performance. Systematic research by Matthews et al. [55] shows that using a mixture of HF/HCl can dramatically improve the interlayer stripping effect compared to the traditional hydrofluoric acid system. This conclusion is verified through characterization methods such as XRD and SEM (Figure 2a). The etching process uses 12 mL of 48% HF and 8 mL of 12M HCl mixed acid to prepare the typical “accordion” layered structure (Figure 2b,c). SEM characterization further confirms (Figure 2d–f) that the mixed-acid etched samples show a more significant interlayer expansion effect and regular two-dimensional flake structure, providing optimized diffusion channels for ion transport. Wu et al. [51] used the mixed-acid etching method to prepare few-layer or single-layer V-based MXene, increasing active sites, and combined it with carbon nanotube (CNT) composite technology to build a two-dimensional/one-dimensional V_2CT_x /CNT electrode. In this electrode, the three-dimensional network of CNTs suppresses the aggregation between MXene layers, reducing the charge transfer resistance to 32% of pure MXene and increasing the surface capacitance of the composite electrode to $246.88 \text{ mF cm}^{-2}$ (0.5 mA cm^{-2}). These studies indicate that mixed-acid etching optimizes the interlayer structure, exposure of active sites, and charge transfer dynamics of MXene, providing an essential direction for developing high-energy storage performance MXene-based electrodes.

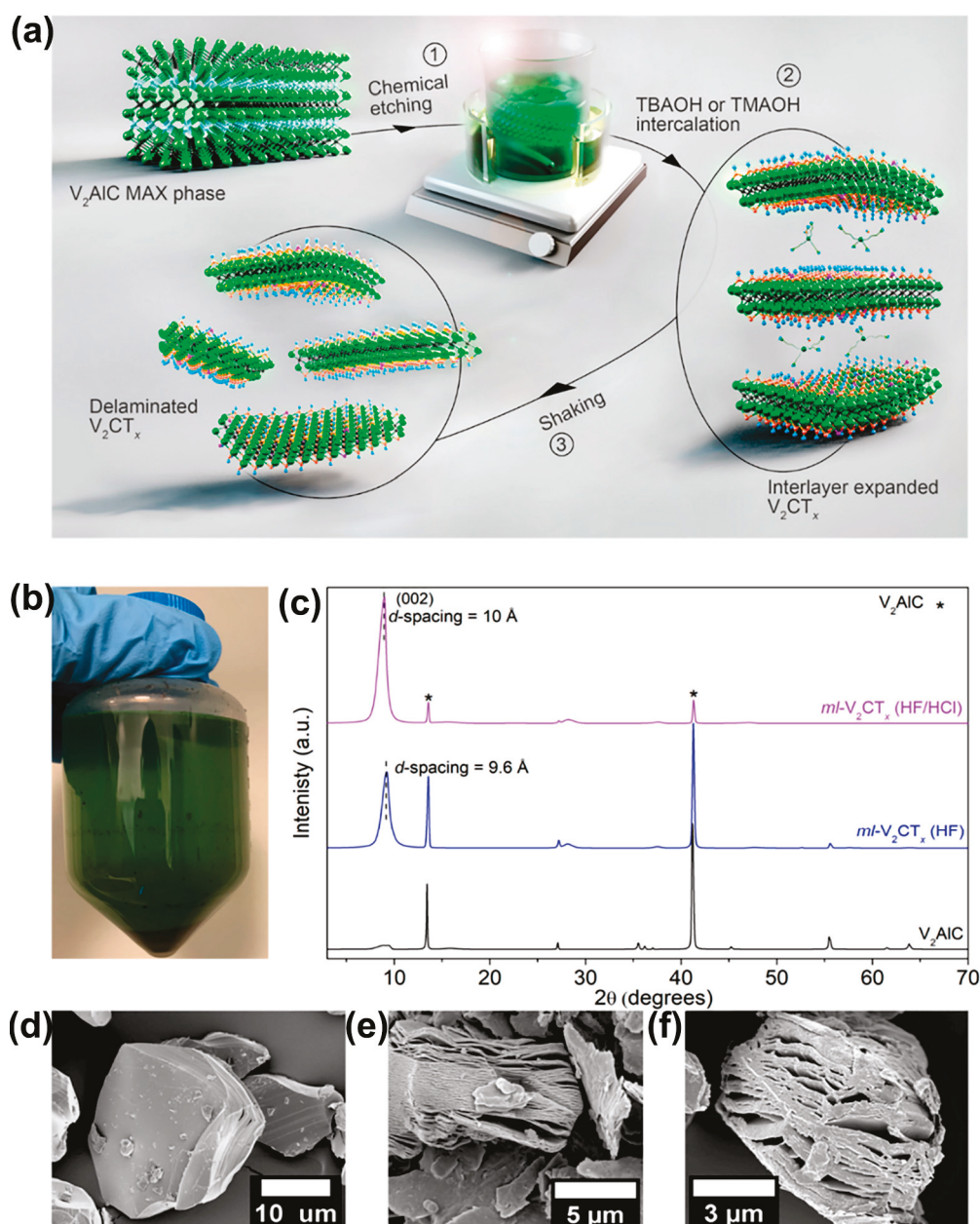


Figure 2. (a) Schematic of the MXene synthesis process. (b) Optical image of the supernatant after the first washing. (c) XRD of the MAX phase and multilayer V_2CT_x with different etching solutions. (d) V_2AlC MAX phase. (e) HF-etched multilayer V_2CT_x . (f) Mixed-acid etched multilayer V_2CT_x SEM images [55]. Copyright 2021, ACS Publications.

3.2. Hydrothermal Etching Method

Although the hydrofluoric acid etching method can effectively generate MXene materials, its high corrosiveness, safety risks, and environmental impact make most current research use hydrofluoric-acid-free preparations. Researchers have developed a new method for synthesizing Ti_3C_2 MXene, using a mixture of lithium fluoride (LiF) and hydrochloric acid (HCl) as an in situ-generated HF etching agent [56]. The advantage of this method is that Li^+ ions can be embedded between the Ti_3C_2 layers during the etching process, increasing the interlayer distance, thus improving the ion diffusion rate and electrochemical specific capacity. The research team of Guo et al. [57] further explored other combinations of fluoride salts and hydrochloric acid as etching agents. Yet, results showed that ammonium fluoride (NH_4F) and hydrochloric acid (HCl) required a reaction at 140 °C for 24 h in a Teflon-lined stainless steel autoclave to obtain pure MXene. Different MXene materials have

different etching temperatures and selections for fluoride salts. Liu et al. [58] synthesized high-purity V_2C MXene by etching V_2AlC with sodium fluoride and hydrochloric acid at 90 °C for 72 h for lithium-ion batteries. Zhao et al. [50] etched multilayer/few-layer V_2CT_x MXene by the hydrothermal method, and the process is shown in Figure 3a. A two-dimensional V_2CT_x MXene material with an interlayer expanded accordion morphology was successfully prepared by selective chemical etching of the Al atom layer in the V_2AlC precursor using a mixed solution of hydrochloric acid (HCl) and sodium fluoride (NaF). Subsequently, the V_2CT_x nanosheets were uniformly assembled on the surface of a flexible conductive substrate using the electrophoretic deposition (EPD) process to construct a high-performance flexible electrode (Figure 3b). Furthermore, a Zinc-Ion Hybrid Capacitor (ZIHC) was designed and assembled based on the electrode. Its energy storage mechanism (Figure 3c) can be analyzed as follows: During charging and discharging, zinc ions (Zn^{2+}) diffuse through the electrolyte to the interlayer of V_2CT_x and reversibly react with the surface functional groups (such as $-O$, $-F$, etc.) in a pseudocapacitive reaction; at the same time, anions in the electrolyte (such as SO_4^{2-}) form a double-layer adsorption at the electrode/electrolyte interface, thus achieving efficient energy storage and release. This synergistic mechanism combines the fast kinetic characteristics of double-layer capacitance with the high energy density advantages of pseudocapacitance.

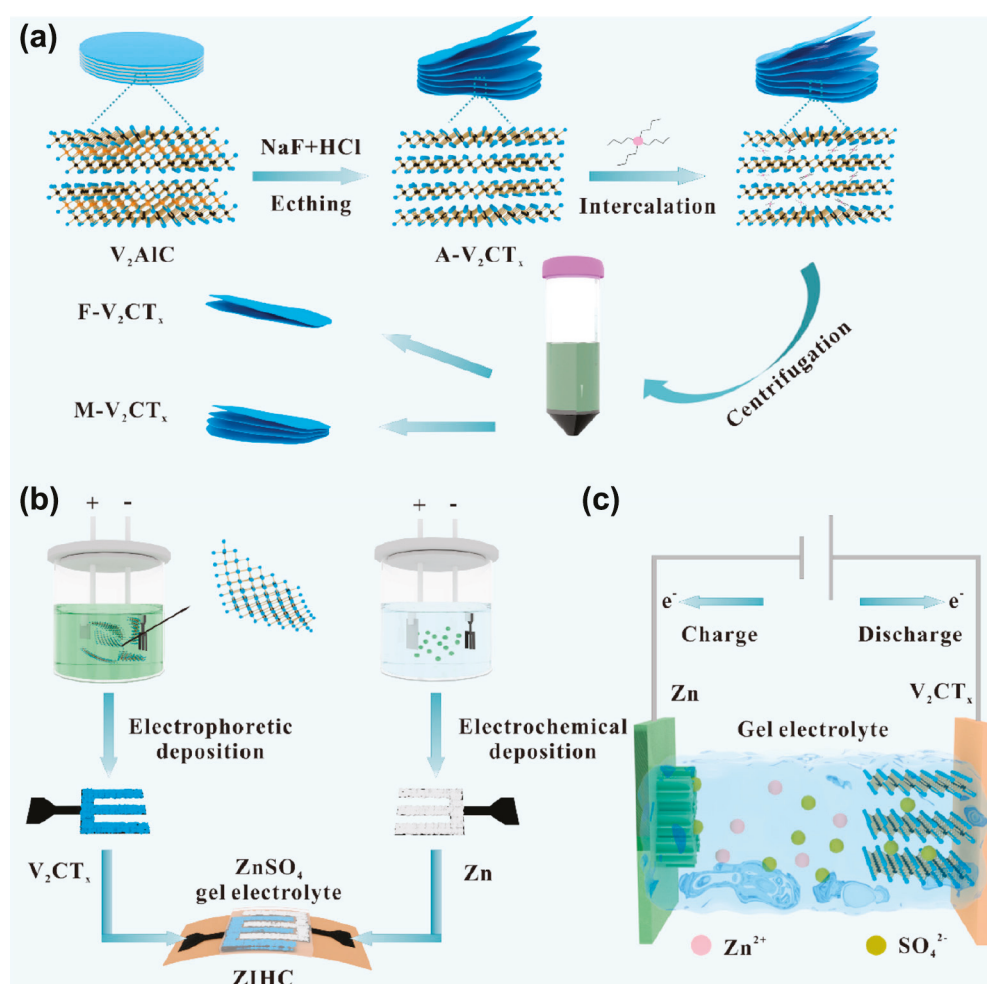


Figure 3. The fabrication process and mechanism of ZIHC based on V_2CT_x . (a) Controllable synthesis of layered V_2CT_x nanosheets. (b) Assembly strategy of flexible ZIHC devices. (c) The synergistic energy storage mechanism of ZIHC [50]. Copyright 2022, Elsevier.

The traditional sodium fluoride/hydrochloric acid system struggles to achieve single-layer exfoliation of V_2CT_x MXene, a technical bottleneck that was broken by the team led by Guan et al. [59]. Research shows that the etching time significantly regulates the layered structure by using a LiF/HCl mixed solution to gradient temporally hydrothermally etch the V-based MXene precursor (90 °C, 72~144 h). SEM analysis indicates that as the etching time is extended from 72 h to 144 h, (Figure 4) the selective etching efficiency of the Al atomic layer improves, and the interlayer spacing gradually expands. Short etching times (72 h) tend to cause localized holes and non-uniform exfoliation defects, while gradually increasing the etching time results in the material forming an “accordion” like structure. However, at 144 h, collapse in the structure is evident, but the interlayer interface is stable at 120 h. This result reveals that extending the etching time can promote the diffusion of the etching agent and orderly deslipping of the Al layer, thereby enhancing the structural regularity and potential energy storage applications of the two-dimensional nanosheets. Thus, the two-dimensional nanosheets’ structural regularity and potential energy storage applications are enhanced. The preparation scheme of the V-MXenes is shown in Table 1.

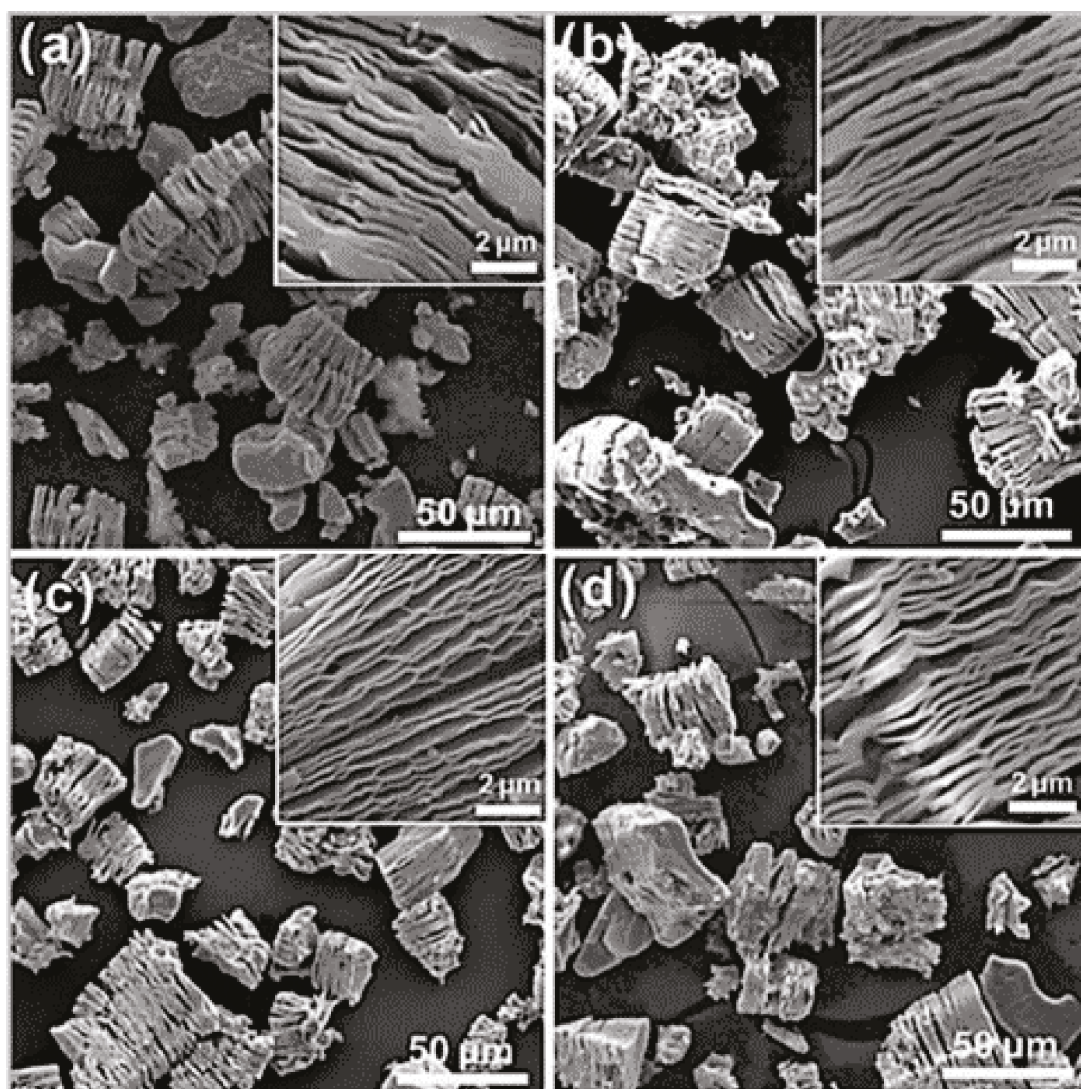


Figure 4. SEM images of V_2AlC etched with LiF and HCl at 90 °C for (a) 72 h, (b) 96 h, (c) 120 h, and (d) 144 h V_2C MXene. The insets show a high-magnification SEM [59]. Copyright 2020, IOP Science.

Table 1. Summary of the preparation schemes of V-MXenes.

Material	Etching Method	Synthesis Time	Synthesis Temperature	Capacity	Reference
V ₂ CT _x	NaF + HCL (6 M)	7 day	90 °C	0.1 mA cm ⁻² 54.12 mF cm ⁻²	[50]
V ₂ CT _x	LiF + HCL	120 h	90 °C	2 mV s ⁻¹ 164 F g ⁻¹	[59]
V ₂ CT _x	LiF + HCL (6 M)	24 h	35 °C	2 mV s ⁻¹ 1473 F cm ⁻³	[60]
V ₂ CT _x	50% HF	92 h	25 °C	5 mV s ⁻¹ 1200 F g ⁻¹	[61]
V ₂ CT _x	48% HF	120 h	70 °C	2 mV s ⁻¹ 1842 F g ⁻¹	[62]
V ₂ CT _x	LiF + HCL (12 M)	72h	90 °C	1 A g ⁻¹ 827.45 C g ⁻¹	[63]
V ₂ CT _x	LiF + HCL (12 M)	72 h	90 °C	1 A g ⁻¹ 1658.2 F g ⁻¹	[64]
V ₄ C ₃ T _x	40% HF	3 day	25 °C	5 mV s ⁻¹ 330 F g ⁻¹	[65]
V ₄ C ₃ T _x	40% HF	96 h	55 °C	2 mV s ⁻¹ 209 F g ⁻¹	[66]

The possible reactions in the synthesis process of V₂CT_x MXene are as follows:



4. Application of V-MXene in Supercapacitors

Vanadium-based MXene (V-MXene) has shown broad application prospects in various fields due to its unique structure and excellent physicochemical properties, especially in energy storage, catalysis, electrochemical sensing, and environmental protection. Energy storage is mainly used in supercapacitor electrode materials, lithium-ion batteries, and sodium-ion batteries. The capacity decay of V-based MXene during cycling can be principally attributed to the material's structural collapse and volume expansion. During the electrochemical reaction process, accompanied by the ion insertion/extraction, the volume of the electrode material will change. If the structure collapses, the interlayer distance of V-based MXene will become smaller, affecting the ion insertion/extraction kinetic rate [58]. At the same time, the number of active sites will decrease. Secondly, the surface functional groups of V-based MXene may have side reactions with the electrolyte, affecting the material performance, and there may be irreversible phase changes during cycling, leading to capacity decay [59]. Currently, researchers mainly alleviate the volume expansion through structural strategy engineering to construct layered heterostructures and form solid solution structures, as well as enhance the electronic conductivity of the host material (V-based MXene) through surface modification, such as composites with carbon materials, to suppress the capacity decay during cycling. Zhao et al. [50] constructed a few-layer V₂CT_x-based flexible zinc ion hybrid capacitor (ZIHC) through electrophoretic deposition technology. Its unique two-dimensional exfoliated structure exposed a high density of surface-active sites (Figure 5a) and shortened the diffusion path of Zn²⁺, enabling the device to achieve a capacitance of 54.12 mF cm⁻² under 2M ZnSO₄, 0.1 mA cm⁻². After 8000 cycles, the capacity retention rate was 81.48% (Figure 5b–d). The material maintained stable electrochemical performance under extreme mechanical deformation (bending angle 0~150°, multi-axis bending load cycle), confirming its intrinsic flexible characteristics and structural tolerance (Figure 5e). This excellent mechanical–electrochemical coupling

stability broke through the performance bottleneck of traditional energy storage materials under dynamic service environments, providing a key material basis for the development of flexible/stretchable energy devices that can withstand complex deformations (such as implantable medical devices, bright fabric integrated systems), highlighting the strategic value of MXene-based materials in the next generation of wearable electronics. Wu et al. [51] further broke through performance limits through a heterogeneous composite strategy: using low-temperature ($0\sim5\text{ }^{\circ}\text{C}$) gradient etching combined with carbon nanotube (CNT) composite technology, they constructed a two-dimensional/one-dimensional $\text{V}_2\text{CT}_x/\text{CNT}$ electrode. In this, the three-dimensional network of CNTs inhibited the inter-layer agglomeration of MXene (Figure 5f), reducing the charge transfer resistance to 32% of pure MXene and synergizing the pseudocapacitive active sites of MXene, increasing the composite electrode surface capacitance to 246.88 mF cm^{-2} (0.5 mA cm^{-2}). After 10,000 cycles (3.2 mA cm^{-2}), the capacity retention rate was $>90\%$ (Figure 5h).

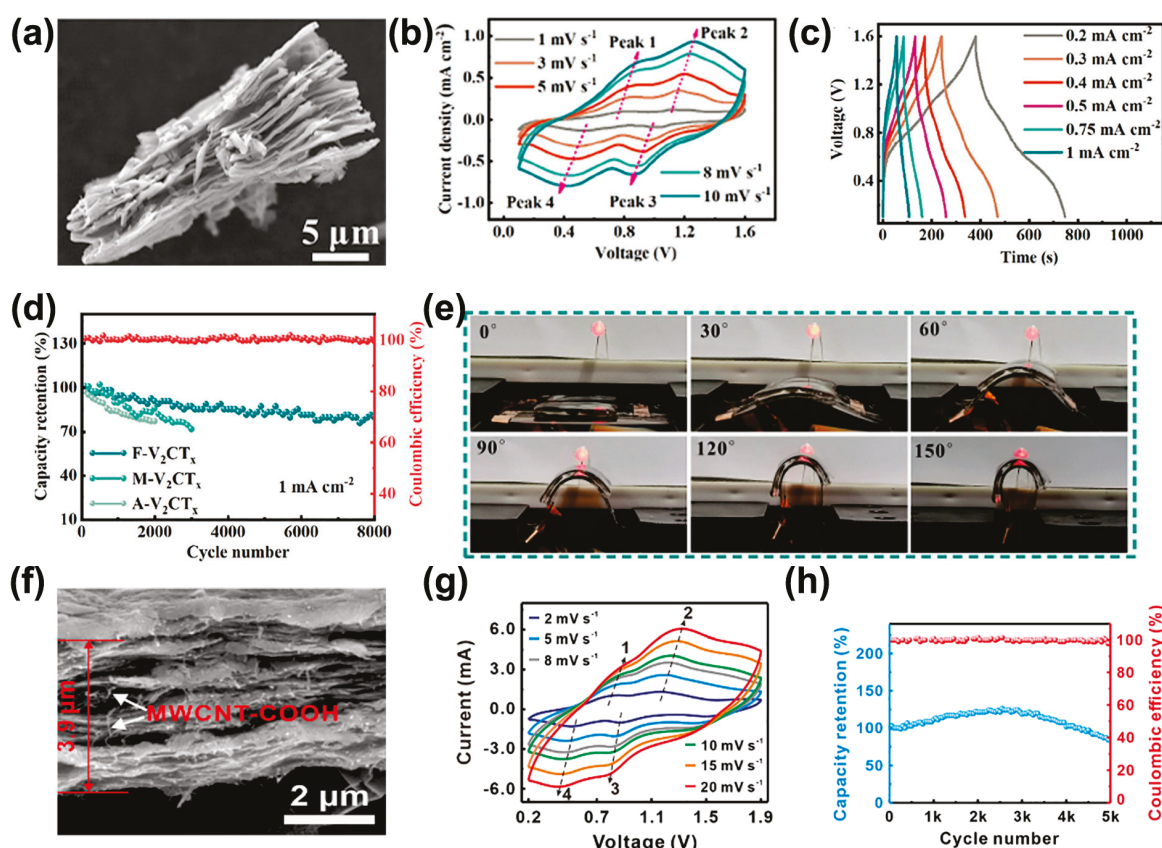


Figure 5. (a) SEM of V_2CT_x . (b) CV curves of ZIHC at 1 to 10 mV s^{-1} scan rate. (c) GCD curves of ZIHC at various current densities ($0.2\sim1\text{ mA cm}^{-2}$). (d) Long-term cycling performance of A-ZIHC, M-ZIHC and F-ZIHC at 1 mA cm^{-2} . (e) Digital images of the F-ZIHC powering an LED lamp under different bending states [50]. Copyright 2023, Elsevier. (f) SEM of $\text{V}_2\text{CT}_x/\text{CNT}$ cathode. (g) CV curves of V/C-ZIMSC at $2.0\sim20.0\text{ mV s}^{-1}$ scan rate. (h) Cycling stability of V/C-ZIMSC at 3.2 mA cm^{-2} [51]. Copyright 2024, Elsevier.

V_2CT_x has applications not only in ZnSO_4 electrolyte. Majid et al. [60] used $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x colloidal solutions to induce self-assembly through a saturated sodium chloride solution. The fabricated free-standing and binder-free MXene heterostructure film showed characteristic redox peaks, which led to more stable capacitance across the entire testing range. The modified MXene structure has a high volumetric capacity of about 1473 F cm^{-3} in $3\text{M H}_2\text{SO}_4$ electrolyte, with a maximum volumetric power and energy density of 0.03 W cm^{-3} and 12.3 Wh cm^{-3} , respectively, and no capacity decay after 50,000 cycles.

The self-assembly of two 2D materials has a stable structural state, and Rizwan et al. [61] prepared V_2CT_x by etching with hydrofluoric acid (HF) as mentioned above. They also prepared $ZrO_2-V_2CT_x$ via a hydrothermal method at 80 °C for 12 h. Introducing zirconium oxide reduces the electrostatic attraction between V_2CT_x flakes, but the overall structure remains unchanged (Figure 6). In $ZrO_2-V_2CT_x$, zirconium provides accessible diffusion sites and accelerates diffusion dynamics to drive pseudocapacitive behavior, exhibiting 447 F g^{-1} at a scan rate of 5 mV s^{-1} in $3\text{M H}_2\text{SO}_4$ electrolyte using plastic Swagelok test cells. Moreover, under 1 A g^{-1} testing for 10,000 charge/discharge tests, the Coulombic efficiency is close to 100%, indicating that the electrode durability and stability significantly improved after the self-assembly of zirconium oxide and V_2CT_x . This represents another breakthrough in the electrochemical stability of V-based MXene materials.

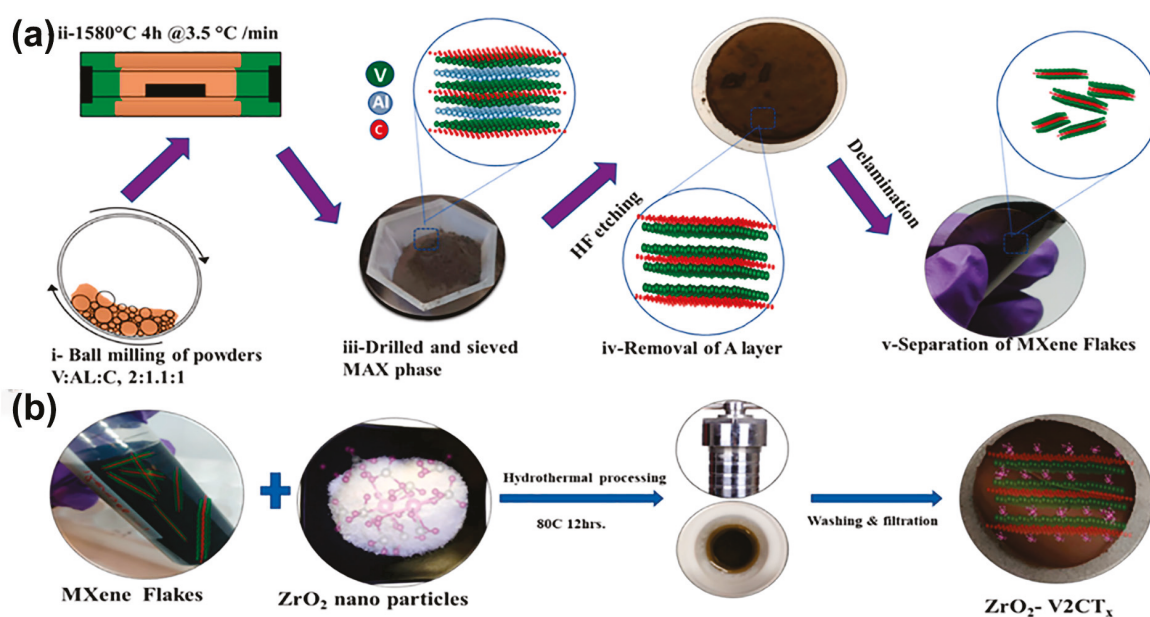


Figure 6. (a) Synthesis of MAX and MXene flakes. (b) Schematic illustration for the synthesis of $ZrO_2-V_2CT_x$ composites [61]. Copyright 2022, Elsevier.

V_2CT_x materials exhibit excellent energy storage effects in acidic electrolytes, and some researchers have also studied them in alkaline electrolytes. Yadav et al. [62] innovatively developed a metal–organic framework (MOF)-assisted synthesis strategy, successfully preparing a vanadium carbide composite material ($V_2CT_x@C$) with a three-dimensional carbon network confinement structure. Through the topological structure reconstruction induced by the MOFs template, the initially stacked V_2CT_x MXene nanosheets were dissociated and reassembled into a nano-disk array rich in carbon matrix, achieving optimization of three key structures: specific surface area, electronic conductivity, and effective contact area of the electrode. Yu's team [63] successfully constructed a $2D@3D\ V_2CT_x@NiCoMn-OH-20$ nanocomposite with a hierarchical heterostructure, which innovatively integrates the dual-function characteristics of supercapacitors and electrochemical sensors. The ZIF-67 precursor was uniformly anchored on the surface of V_2CT_x nanosheets through an electrostatic self-assembly strategy, and the active component distribution environment was accurately controlled by combining anion exchange reactions to achieve molecular-level coupling of the three-dimensional porous framework with the two-dimensional layered matrix. Structural characterization confirmed that this heterostructure effectively suppressed the interlayer stacking of the two-dimensional nanosheets, increasing the specific surface area to $385\text{ m}^2\text{ g}^{-1}$, and constructed continuous ion transport channels. The optimized $V_2CT_x@NiCoMn-OH-20$ electrode exhibited a high specific capacity of 827.45 C g^{-1} at a

current density of 1 A g^{-1} , a 2.7-fold increase compared to a single component and a capacity retention rate of 88.44% after 10,000 cycles (Figure 7), which is attributed to the buffering effect of V-O-Co bond cooperation on structural stress at the heterogeneous interface. The assembled symmetrical supercapacitor achieved an energy density of 88.35 Wh kg^{-1} and a power density of 750 W kg^{-1} .

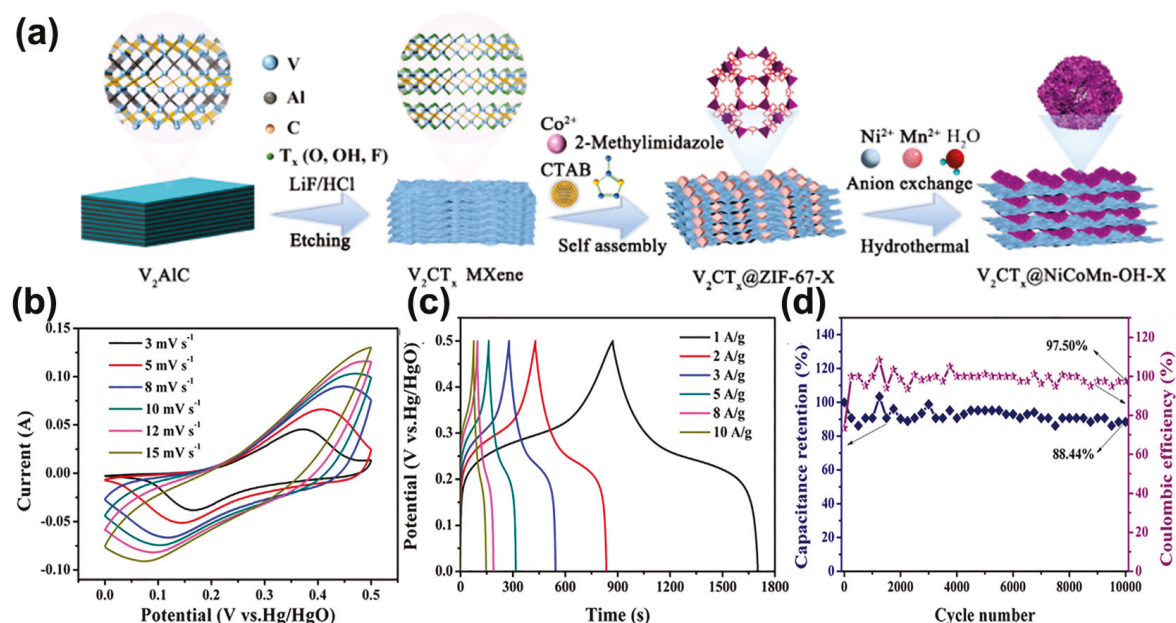


Figure 7. (a) Schematic illustration for the synthesis of $\text{V}_2\text{CT}_x\text{@NiCoMn-OH}$ composites. (b) CV curves at different scan rates in 3M KOH electrolyte. (c) GCD curves at various current densities and (d) cycling stability and Coulombic efficiency at 20 A g^{-1} for 10,000 cycles [63]. Copyright 2023, Elsevier.

Based on the study of the structural characteristics and energy storage mechanisms of V_2CT_x MXene, we further focused on the research of higher-order homologous material $\text{V}_4\text{C}_3\text{T}_x$, exploring the effects of the complete addition of transition metal layers on its specific surface area, conductivity, and electrochemical performance. Wang et al. [65] successfully prepared two-dimensional multilayer V_4C_3 MXene material by selectively removing Al layers from V_4AlC_3 precursor through a topological chemical etching strategy, achieving a specific capacitance of 209 F g^{-1} at a scan rate of 2 mV s^{-1} . Subsequently, Cheng et al. [67] addressed the issues of easy oxidation of the MXene surface and the stacking limitations of its layered structure by adopting poly-o-phenylenediamine (PoPD) modified vanadium carbide MXene ($\text{N-V}_4\text{C}_3\text{T}_x$). Using an in situ oxidant-free polymerization and redox synergistic process (the preparation process is shown in Figure 8), PoPD nanoparticles were uniformly anchored onto the surface of $\text{N-V}_4\text{C}_3\text{T}_x$ nanosheets, forming a three-dimensional conductive network composite system. Through proportional optimization, it was found that the optimal ratio of $\text{N-V}_4\text{C}_3\text{T}_x$ and PoPD powder is 1:4 (abbreviated as NP14). The strong chemical bonding between the amino group ($-\text{NH}_2$) and the $-\text{O}/-\text{F}$ groups on the MXene surface inhibits the stacking of nanosheets, constructing continuous electron transport channels and increasing the electrical conductivity of the material. The composite electrode achieved a specific capacitance of 676.5 F g^{-1} at a current density of 1 A g^{-1} , which is 2.48 times higher than that of the pure $\text{V}_4\text{C}_3\text{T}_x$ electrode, and after 10,000 cycles, it still maintained a capacity retention rate of 95%. This is attributed to the synergistic effect of the π - π conjugated system of PoPD and the nitrogen-containing functional groups on the MXene surface, reducing the charge transfer resistance by 68%. As a negative electrode material, $\text{N-V}_4\text{C}_3\text{T}_x$ exhibited a high reversible capacity of 561.2 mAh g^{-1} at 0.1 A g^{-1} and still maintained 382.4 mAh g^{-1} at a high rate of 2 A g^{-1} .

Its performance advantage stems from the synergistic effect of the pseudocapacitance contribution induced by N doping and the interlayer expansion effect of MXene (Figure 9). Through a molecular interface design strategy, this work overcame the dual bottlenecks of limited capacity and insufficient cycle stability of MXene materials, providing a new paradigm for developing high-cost performance energy storage devices.

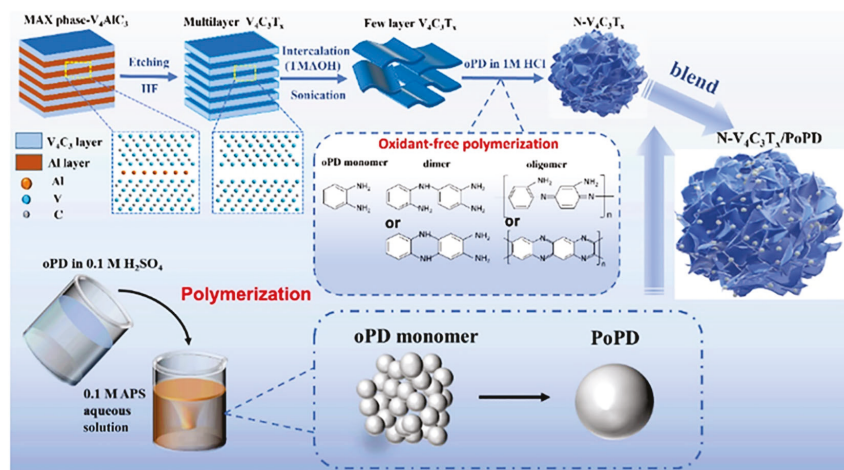


Figure 8. Schematic diagram of the preparation of $V_4C_3T_x$ and the preparation of $N-V_4C_3T_x$ /PoPD mixture [67]. Copyright 2023, ACS Publications.

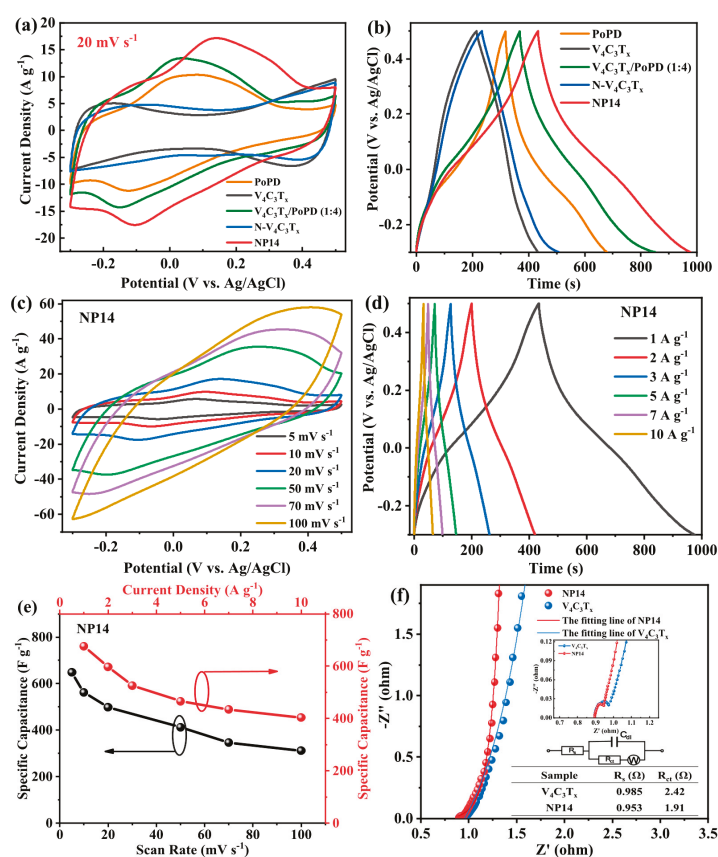


Figure 9. (a) CV curves of $V_4C_3T_x$, $N-V_4C_3T_x$, PoPD, $V_4C_3T_x$ /PoPD (1:4), and NP14 electrodes in 1 M H_2SO_4 electrolyte. (b) GCD curves of $V_4C_3T_x$, $N-V_4C_3T_x$, PoPD, $N-V_4C_3T_x$ /PoPD (1:4), and NP14 electrodes at 1 A g^{-1} . (c) Specific capacitance of the NP14 electrode at different scan rates. (d) GCD curves of the NP14 electrode at different current densities. (e) Plots of specific capacitance versus scan rate and current density of the NP14 electrode. (f) Nyquist plots of $V_4C_3T_x$ and NP14 electrodes [67]. Copyright 2023, ACS Publications.

The two-dimensional, multi-layered V_4C_3 MXene material is not limited to acidic electrolytes but exhibits good energy storage performance in alkaline KOH electrolytes. Table 2 outlines the applications of V-MXenes and modified supercapacitor electrode materials. Researchers [68–76] developed a high-performance $V_4C_3T_x@NiO$ -RGO heterostructure hydrogel and a defect-engineered DRGO hydrogel through a multi-step synergistic assembly strategy. They integrated them to create a high-energy density asymmetric supercapacitor (ASC). Using the hydrothermal method, NiO nanoplates with high pseudocapacitance characteristics were uniformly deposited on the surface of highly conductive $V_4C_3T_x$ to form a face-to-face heterogeneous interface with strong chemical bonding. Combined with the graphene oxide self-assembly strategy, a three-dimensional interconnected network was constructed, effectively inhibiting the stacking of nanoplates. As a result, the material exhibited an ultra-high specific capacitance of 191.6 F g^{-1} at 0.5 A g^{-1} and 123.5 F g^{-1} at 10 A g^{-1} (Figure 10).

Table 2. Review of the application of V-MXenes and modified supercapacitor electrode materials.

Electrode Material	Electrolyte	Potential Window	Capacitance	Scan Rate/Current Density	Reference
V_2CT_x	2 M Zn_2SO_4	0.1~1.6	54.12 mF cm^{-2}	0.1 mA cm^{-2}	[50]
V_2CT_x/CNT	2 M Zn_2SO_4	0.2~1.9	$246.88 \text{ mF cm}^{-2}$	0.5 mA cm^{-2}	[51]
V_2C	1 M Na_2SO_4	−0.3~−0.9	164 F g^{-1}	2 mV s^{-1}	[59]
V_2CT_x	3 M H_2SO_4	−0.4~0.2	1473 F cm^{-3}	2 mV s^{-1}	[60]
V_2CT_x/ZrO_2	3 M H_2SO_4	−0.5~0.3	1200 F g^{-1}	5 mV s^{-1}	[61]
$V_2CT_x@C$	1 M H_2SO_4	0.0~1.2	551 F g^{-1}	2 A g^{-1}	[62]
$V_2CT_x@NiCoMn-OH$	3 M KOH	0.0~0.5	827.45 C g^{-1}	1 A g^{-1}	[63]
$V_2CT_x/Co-LDH$	6 M KOH	−0.1~0.4	1005 F g^{-1}	1 A g^{-1}	[64]
$V_4C_3T_x$	1 M H_2SO_4	−0.4~0.4	330 F g^{-1}	5 mV s^{-1}	[65]
V_4C_3	1 M H_2SO_4	−0.3~0.1	209 F g^{-1}	2 mV s^{-1}	[66]
$V_4C_3T_x/POPD$	1 M H_2SO_4	−0.2~0.4	676.5 F g^{-1}	1 A g^{-1}	[67]
$V_4C_3T_x@NiO-RGO$	1 M KOH	−1.0~0.8	1021 F g^{-1}	0.5 A g^{-1}	[68]
$V_2CT_x/Ti_3C_2T_x$	1 M H_2SO_4	−0.6~0.2	365 F g^{-1}	1 A g^{-1}	[69]
V_2C	1 M Na_2SO_4	−1.0~−0.2	120 F g^{-1}	2 mV s^{-1}	[70]
V_2CT_x	2 M Zn_2SO_4	−0.9~0.3	481 F g^{-1}	1 A g^{-1}	[71]
$V_2CT_x@Si$	1 M Zn_2SO_4	0~1.0	557 F g^{-1}	1 A g^{-1}	[72]
V_2CT_x	1 M LiOH	−1.4~0.8	386 F g^{-1}	2 mV s^{-1}	[73]
$V_2CT_x/NiV-LDH$	6 M KOH	0.0~0.5	1658.2 F g^{-1}	1 A g^{-1}	[74]
$V_4C_3T_x$	1 M H_2SO_4	−0.3~0.3	210 F g^{-1}	10 mV s^{-1}	[75]
$NiCoAl-LDH/V_4C_3T_x$	1 M KOH	−0.1~0.5	627 F g^{-1}	1 A g^{-1}	[76]

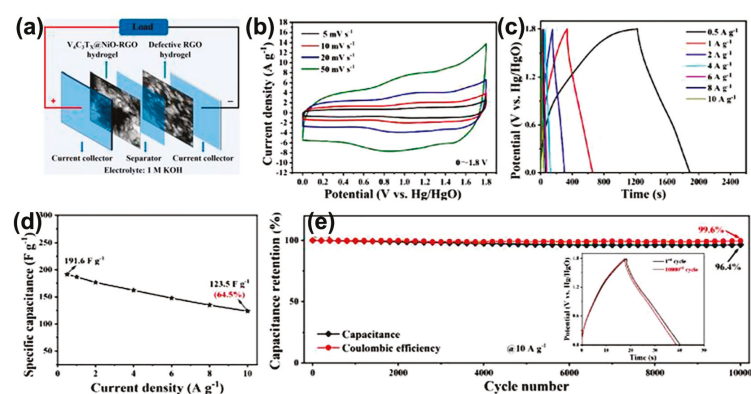


Figure 10. (a) The schematic illustration of the construction of the ASC device. (b) CV curves of the ASC at different scan rates in the voltage window of 0~1.8 V. (c) GCD curves of the ASC at different scan rates in the voltage window of 0~1.8 V. (d) Specific capacitance calculated from GCD curves at various current densities. (e) Cyclability and Coulombic efficiency at 10 A g^{-1} [68]. Copyright 2023, Royal society of chemistry.

5. Conclusions and Prospects

5.1. Conclusions

This paper reviews the characteristics, preparation methods, and applications of vanadium-based MXene in the field of supercapacitors. V-MXene, with its multivalent state characteristics, high conductivity, large specific surface area, and adjustable inter-layer spacing, demonstrates great potential in the energy storage field. Through different etching methods and surface functionalization, researchers can effectively enhance the electrochemical performance of V-based MXene, making its application prospects broad in areas such as supercapacitors and batteries. However, the preparation and application of V-based MXene still face many challenges, such as the generation of by-products during the etching process, poor cyclic stability of the material, and optimization of electrochemical performance. In practice, it still needs to be clarified how the structure of the MXenes, the chemical functional groups on the surface, and the long-term stability in various applications can be better controlled. Moreover, research based on vanadium-based MXene composite materials and heterostructures will also be an important direction for future development. Through synergistic effects with other functional materials, there is hope to enhance its application in energy storage further.

5.2. Prospects

In conclusion, V-based MXenes hold significant promise for supercapacitor applications due to their unique structure and favorable surface functionality. However, several challenges remain. With careful structural design and surface modification, we believe these obstacles can be overcome, expanding the use of V-based MXenes beyond supercapacitor electrodes. Future research should focus on the following directions:

1. Enhancing synthesis efficiency and purity: Developing more efficient and green synthesis processes, reducing by-product generation, and optimizing reaction conditions to obtain high-purity V-based MXene.
2. Structure and function optimization: Explore different surface modification and functionalization strategies to enhance the stability, conductivity, and reactivity of the material, further improving its electrochemical performance.
3. Composite materials and heterostructures: By compounding with other two-dimensional materials or nanomaterials, novel heterostructures are developed. Utilizing the built-in electric field within the heterojunction can accelerate electron transfer and expose more electrochemical sites at the grain boundaries, thereby synergistically enhancing the electrochemical performance.
4. Large-scale production and practical applications: advancing the fabrication technologies of V-based MXene materials at industrial scales, paving the way for their energy storage and conversion applications.

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Article

Combustion of High-Energy Compositions (HECs) Containing Al-B, Ti-B and Fe-B Ultrafine Powders (UFPs)

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Abstract: Metal and metalloid powders are widely used in high-energy compositions (HECs) and solid propellants (SPs), increasing their energetic characteristics in the combustion chamber. The particle size distribution, protective coatings of the particles and heat of combustion of the metal powders influence the ignition and combustion parameters of the HECs as well as the characteristics of the propulsion systems. Boron-based metallic fuels achieve high-energy potentials during their combustion. The effect of Al-B, Fe-B and Ti-B (Me-B) mixture ultrafine powders (UFPs) on the ignition and combustion characteristics of a model HEC based on a solid oxidizer and a polymer combustible binder was investigated. The Me-B mass ratios in the mixture UFPs corresponded to the phase composition of the borides AlB_2 , FeB and TiB_2 . It was found that replacing the aluminum UFP with Al-B, Fe-B and Ti-B UFPs in the HECs changed the exponent (n) in the correlations of the ignition delay time $t_{ign}(q)$ and burning rate $u(p)$. The maximum burning rate and n over the pressure range of 0.5–5.0 MPa were obtained for the HEC with Al-B UFPs due to the increase in the heat release rate near the sample surface during the joint combustion of the Al and B particles.

Keywords: ultrafine metal; high-energy composition; ignition; combustion; heat release; kinetics; burning rate

1. Introduction

1.1. Ultrafine Powders of Metal

Ultrafine metals and metalloids (such as lithium, beryllium, magnesium, aluminum, titanium, iron, nickel, copper, boron, silicon and their alloys with various crystal structures) are used in a wide range of industries, including non-ferrous metallurgy, aerospace, microelectronics, energy, automotive, chemical, medical and military [1–4]. Their unique properties make them indispensable for the creation of high-performance and durable materials (hard alloys, ceramic, magnetic and composite materials), additives to lubricants, superconductors, filters, hybrid fuels (HFs) and solid propellants (SPs) [5–8]. There are several advantages of ultrafine powders (UFPs) over micron powders, including improving mechanical properties, high specific surface areas (SSAs) and reactivities, lower ignition temperature, melting and evaporation temperatures, ensuring a high combustion completeness and a uniformity of heat released in the production of ceramic and synthetic materials. However, their energetic application is limited by their disadvantages, including a tendency to aggregate particles, pyrophoricity and storage and transport complexities.

There are several methods for producing UFPs of metals, metalloids and their compounds that are used on laboratory and industrial scales. The particles' shape and size, the SSA and the active metal content depend on the production methods (mechanical, physical or chemical) [9–11]. The mechanical methods are based on the application of pressure, friction, vibration and other mechanical effects on the material. Ball milling, vibrating ball milling and horoscope milling are commonly used. The particles' shape obtained in ball milling is irregular and their surface is smooth. Gas-jet milling provides a finer grinding of the basic material when the action of a gas jet under pressure (air, inert gases) is fed into the working chamber through nozzles at the speed of sound or at supersonic speed. In the chamber, the initial particles collide with a metal wall or with each other. In jet milling, for example, porous metal structures obtained by electrochemical methods can be ground. The fraction of fine particles can be increased by applying cryogenic grinding technology. The physical methods for producing metal UFPs are based on the evaporation and subsequent condensation of the elements and their compounds. Heating and evaporation are carried out by plasma, laser, electric arc discharge, ionization, high-frequency currents or electron irradiation. The supersaturated steam is created by evaporating the material from a heated melt surface which is quickly cooled by the jet supply of coolant, flowing through nozzles and expanding. When cooled, the vapor droplets are solidified to form an aerosol system containing solid particles that can be captured by various methods. One of the main methods for producing metal UFPs, which produces nano-sized particles in large quantities, is the method of electrical explosion of a metal wire [12,13] placed between two electrodes. This method is also used for producing bimetallic nano-sized particles [14], which expands the applications of UFPs. The electrical explosion of a wire (EEW) is carried out by supplying a powerful high-voltage nanosecond electric current pulse with a density of 10^6 – 10^9 A cm^{−2} to a conductor (a metal wire with a diameter of 0.1–1.0 mm). The wire is heated to a melting point, melted and then destroyed by an explosion. When the explosion products expand, nanoparticles are formed in the gas atmosphere. The ultra-fast quenching of the electrical explosion products of a conductor at a rate of up to 10^7 K s^{−1} provides powders with particle sizes less than 0.5 μm. The chemical methods for producing metals (or oxides) are mainly based on reducing chemical reactions, catalytic and thermal decomposition of metal-organic compounds, hydrides or metal salts, electrolysis of metal salts and solvothermal and molten salt synthesis [15,16]. These methods allow the synthesis of nano-sized particles over a narrow size range and with high product purity, but they are expensive.

1.2. Use of Metal UFPs in SPs and HECs

Incorporating metal UFPs into SPs, HFs and high-energy compositions (HECs) presents significant benefits in heat release efficiency, ignition and combustion characteristics. The heat of combustion is an important characteristic in the context of metal use in HECs and SPs. Boron (B) and aluminum borides (AlB₂, AlB₁₀, AlB₁₂) have high heat of combustion per unit mass or volume (~ 58.1 kJ g^{−1} and 43.0–53.5 kJ g^{−1} or ~ 136.0 kJ cm^{−3} and 122.0–135.9 kJ cm^{−3}, respectively) with a complete oxidation of particles, which makes it the most energy-efficient metal [17–23]. The high-energy potential of B powder is difficult to achieve in fast-reacting fuel systems due to the presence of an oxide layer (B₂O₃) on the particles' surface, causing slow and incomplete combustion. One of the main reasons for incomplete B combustion is slow thermal oxidation due to the formation of a liquid B₂O₃ layer on the particles' surface, which reduces the diffusion rate of the oxidizer in the B core. The thickness of the B₂O₃ cover decreases during its evaporation (1860 °C) and heterogeneous surface reactions. The oxidizer from the environment diffuses through the molten B₂O₃ and B diffuses from inside the particle, which is a complex chemical

and physical process. The oxidation of the B particle occurs in several stages, starting with the formation of the intermediate gaseous products BO and BO₂, which diffuse outward. In a hydrogen- or steam-containing gas medium, the heat of combustion of B is low due to the formation of boric acid (HBO₂) [18,19,24–26]. The decrease in particle size in UFP B reduces the ignition delay time (t_{ign}) and the ignition temperature (T_{ign}) during intensive heating, increasing the degree of B oxidation [20]. Aluminum (Al) is the most common component due to its mid-level heat of combustion and density, relative safety, absence of toxic combustion products and low cost. Therefore, Al powders are widely used in SPs and pyrotechnic, explosive and high-energy systems. The heat of combustion of Al is $\sim 31.0 \text{ kJ g}^{-1}$, slightly higher than the heat of combustion of magnesium (Mg) and similar to that of carbon (C) ($\sim 27.0 \text{ kJ g}^{-1}$ and 32.8 kJ g^{-1} , respectively). However, the density of Al is 2.70 g cm^{-3} (at 20°C), which is higher than that of Mg (1.74 g cm^{-3}) and C (2.27 g cm^{-3}), so the volumetric heat of combustion is higher than the others (83.7 kJ cm^{-3}). Al combustion occurs in a gaseous oxidizing medium, which contributes to its increase in temperature and the rate of chemical reactions near the fuel or SP surface. The T_{ign} and burning time (t_b) of Al depends on the particles' size, the passivation coating on the particles' surface and the temperature, pressure and composition of the gaseous medium. The oxide coating slows down the intensity of ignition and the combustion processes of powder. In the equation of the ignition delay time $t_{\text{ign}}(q) = a \cdot q^{-n}$ for the heat flux density (q), the exponent (n) for Al and AlB_n micron powders is equal to ~ 2.0 . For aluminum (Alex) and B UFPs, the n is significantly smaller (1.5 and 1.0, respectively) due to rapid heating and a possible change in the ignition mechanism of Alex and B UFPs. The t_{ign} and the ignition energy for Alex and B UFPs are less dependent on the heat flux and significantly less (6–10 times) than those of micro-scale metals under intensive laser heating ($65\text{--}190 \text{ W cm}^{-2}$ in air). The combustion of micro-sized aluminum (μAl) particles is satisfactorily described by a generalized correlation of the burning time, $t_b(D) = c \cdot D^n \cdot X_{\text{eff}}^{-1.0} \cdot p^{-0.1} \cdot T^{-0.2}$, to the particle initial diameter (D) and the effective oxidizer concentration $X_{\text{eff}} = C_{\text{O}_2} + 0.6C_{\text{H}_2\text{O}} + 0.22C_{\text{CO}_2}$ as well as the pressure (p) and temperature (T) of the gas medium, obtained on the basis of more than 400 experimental values of the burning time of μAl particles, with the indicators $c = 0.00735$, $n = 1.80$ (M. Beckstead) and $c = 0.00213$, $n = 1.72$ (A. Braconnier). The burning time of Alex is slightly dependent on the initial particle diameter ($n = 0.15\text{--}0.34$). It is obvious that the pressure, temperature and oxidizer concentration of the gas medium have a greater influence [6,20,27–32]. When igniting Alex (with a heating rate above 10^6 K s^{-1}) or when burning Al, Al-Li and Al-Mg agglomerate particles, the melting and dispersive boiling mechanism of the droplet core (microexplosive combustion of the particle) can be realized [33–36], which contributes to the particles' size reduction, the reduction of condensed combustion products (CCPs) and the more efficient combustion of SPs in the combustion chamber. Therefore, the study of the kinetics, mechanisms and completeness of combustion of Al particles under different conditions is still relevant and has practical significance.

A small amount of additives (up to 2 wt.% of B, Al, titanium (Ti), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo) and tungsten (W) powders or their oxides) catalyzes the combustion process for HECs based on AP [11,37–39]. The most effective additives are UFPs of Fe, Cu and Zn. The introduction of Fe, Ni, Cu, or Zn UFPs has been found to reduce the t_{ign} of HECs and the power exponent in the correlations of the $t_{\text{ign}}(q)$ and $u(p) = b \cdot p^n$ on pressure. With an increase in the SSA of the metal powder, the number of active centers and oxygen vacancies on the surface of the particles increases sharply, which intensifies the thermal decomposition of AP and the combustion process of the HECs. Metal borides, such as AlB₂, AlB₁₂, FeB and TiB₂, also intensify the physical and chemical processes and increase the u of HECs and HFs [18–22,37,40–43].

In this work, the effect of Al-B, Fe-B and Ti-B (Me-B) mixture UFPs on the ignition and combustion characteristics for a model HECs based on a solid oxidizer and a polymer combustible binder were carried out. The mass ratios of the Me-B mixture in the UFPs corresponded to the phase composition of the borides AlB_2 , FeB and TiB_2 .

2. Materials and Methods

2.1. Ultrafine Powders of B, Al, Fe and Ti

Mechanical mixtures of UFPs of Al-B (mass ratio of 55.5/44.5%), Fe-B (83.7/16.3%) and Ti-B (68.9/31.1%) were used as high-energy metal fuels. Commercial Al, Fe and Ti powders were obtained by an EEW method in argon and passivated ("Advanced Powder Technologies" LLC, Tomsk, Russia). Amorphous B powder B-99A was produced in "Aviabor" LLC (N. Novgorod, Russia). All powders had a protective coating on the particle surface, therefore Al and B powders were stored in air, and Ti and Fe powders were stored in liquid hexane C_6H_{14} . The protective layer on the particles' surface is usually formed by controlled oxidation of the metal particles (in an argon and oxygen environment). In some cases, nitrogen can be used for passivation of Ti nano-scale particles to create a nitride surface layer or wetting with liquid hexane for the protective layer formation.

2.2. Ignition of HECs with Me UFPs

The model HEC samples contained 64.6 wt.% AP of two grades (particle size less than 50 μm (0.6 mass fraction) and 160–315 μm (0.4 mass fraction)), 19.7 wt.% SKDM-80 butadiene rubber and 15.7 wt.% metal UFP. The production of mixed HECs was carried out by mixing and continuous pressing. The ignition characteristics of the HECs containing metal UFPs with a sample diameter of 10 mm and a height of 5 mm were measured by using an experimental testbed in which a continuous CO_2 laser with an adjustable power from 10 to 200 W was used as an external heating source [44]. The thermal power and heat flux density on the sample surface was measured with a thermal laser power sensor (FL400A-BB-50, Ophir Optronics Solutions). The thermal decomposition onset time of the HECs was measured with the reactive force sensor of the outflow of gas products from the sample surface when it was heated by laser. The t_{ign} of the HECs was determined by the difference in electrical signals from the photodiodes, recorded via an analog-to-digital converter (L-card E-14-440) on a laptop at the beginning of the heating of the HEC sample and at the time of the appearance of glow and flame near the sample surface. The ignition criterion for t_{ign} measurement was the beginning of the formation of a visible flame zone, whose propagation lead to self-sustaining combustion of the HECs when the laser radiation was switched off.

2.3. Combustion of HECs with Me UFPs

The steady burning rate (u) of the HEC samples with a diameter of 10 mm and a height of 30 mm at excess pressures of 0.5–5.0 MPa was measured by using the burning-wire method and a constant-pressure bomb with nitrogen [45]. Measured with an oscilloscope, the burning time of a known sample height was used to calculate the u . Before the experiment, the lateral surface of the cylindrical HECs were reinforced with a double layer of insulating tape. The outflow of gases and CCPs occurred on the end surface of the HECs, which made it possible to capture condensed products using sieves and filters.

3. Results and Discussion

3.1. SEM and Particle Size of UFPs of B, Al, Fe and Ti

The SEM images of B, Al, Ti and Fe powders obtained using a TESCAN MIRA 3 LMU, Brno, Czech Republic, scanning electron microscope (SEM) are presented in Figure 1.

The powders used had spherical particles with a protective layer. Boron particles tend to aggregate and form larger micro-sized particles (1–2 μm) with a high SSA of 9–15 $\text{m}^2 \text{g}^{-1}$. The average diameter and SSA of the B particles were 210–230 nm and 8.6 $\text{m}^2 \text{g}^{-1}$ and for Al, Fe and Ti were 90–110 nm and 15.5, 7.7 and 13.8 $\text{m}^2 \text{g}^{-1}$, respectively (the manufacturer's data).

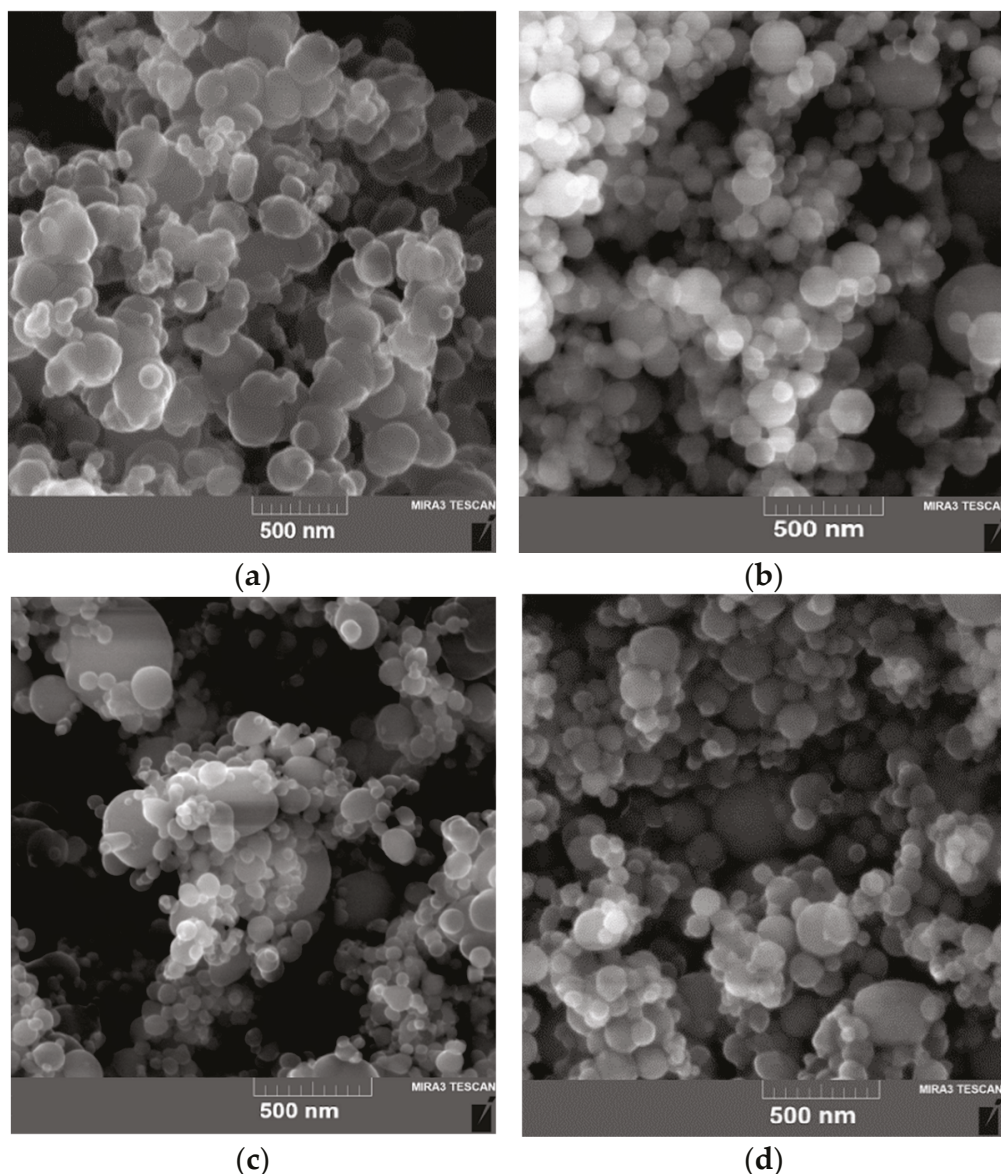


Figure 1. SEM images of UFPs: (a) amorphous B; (b) Al (Alex); (c) Ti; (d) Fe.

3.2. The t_{ign} of HECs with Me UFPs

The thermal decomposition onset time, the T_{ign} and t_{ign} for the HECs with Me UFPs were determined at the fixed heat flux density q . The heat flux density range used for the end surface sample heating was $q = 65\text{--}210 \text{ W cm}^{-2}$. The T_{ign} of HECs, measured using a Jade J530 SB thermal imaging camera, was over the temperature range of 350–650 $^{\circ}\text{C}$ and mainly depended on the heating rate and heat flux density of the laser radiation. The measured t_{ign} of the HECs (points) as a function of the heat flux density are presented in Figure 2. The lines represent the generalized correlations $t_{\text{ign}}(q) = a \cdot q^{-n}$.

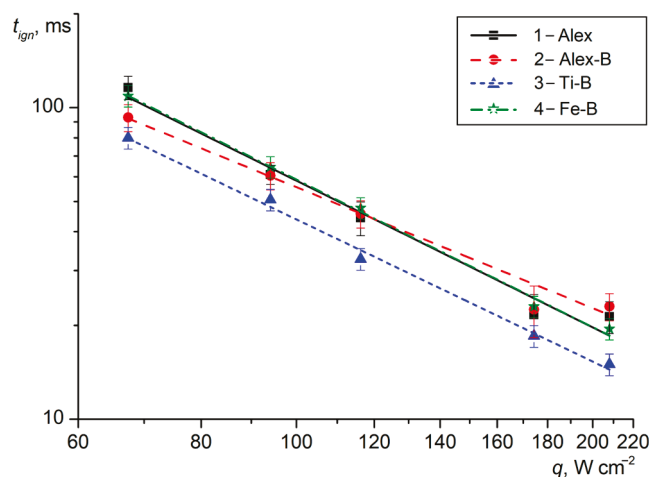


Figure 2. The t_{ign} of the HECs with Me UFPs vs. the heat flux density.

Note that the t_{ign} for HEC-1 with Alex decreased from 116 to 18 ms as q increased from 65 to 210 W cm⁻². The n exponent in $t_{ign}(q)$ was at its maximum and equal to 1.60. At $q = 67$ W cm⁻², the period of time between heating the sample surface to ~340 °C and the beginning of the formation of gas products during the HEC-1 thermal decomposition was ~60 ms. When the sample surface was heated to ~400–420 °C ($t = 100$ –105 ms), the outflow rate of the gas products increased and a luminous spot with a diameter of 3 mm was formed on the sample surface. After 1–1.5 ms, the ignition of the gas products with Al particles was recorded with the subsequent formation of a flame zone ($t = 108$ –112 ms) near the sample surface. The maximum flame propagation rate was ~8.5 m s⁻¹. The Al particles with a high SSA on the HEC-1 sample surface intensified the physical and chemical processes due to the additional heat release during their oxidation, the increase in the rate of the oxidation reactions in the flame zone and the reduction in the time to the steady burning of the sample. Moreover, when the burning Al-agglomerated particles were expelled from the flame zone into the air and their surface was sharply cooled, a thin oxide layer was formed, which increased the excess pressure in the encapsulated core (accumulation of gaseous AlO and AlO₂ suboxidized at the boundary of the inner surface of the oxide layer) and the probability of the micro-explosive combustion of the particles in the final stage [36]. The burning time of the Al particle fragments was significantly reduced due to a decrease in their particles size and the increase in the SSA.

When Alex was replaced with Me-B UFP in the HECs, the t_{ign} of the samples changed over the entire range of q under consideration. However, the greatest efficiency in reducing the t_{ign} was achieved by HEC-3 with Ti-B, for which the t_{ign} values were reduced by 20–27% compared to the base HEC-1 with Alex. At the same time, the exponent n was reduced to 1.52. At $q = 67$ W cm⁻², the time to reach a sample surface temperature of 340 °C was reduced to ~50 ms and after 15 ms, a luminous spot on the HEC-3 surface with a subsequent outflow of gas products, including Ti and B burning particles ($t = 66$ –72 ms), was recorded. When the sample surface was heated to 490 °C (~78–80 ms), the appearance of a flame was registered near the HEC surface. The propagation rate of the flame zone was ~6.5 m s⁻¹. The fast ignition and micro-explosive combustion of Ti particles with a characteristic star formation (similar to those observed for micro-size particles [46,47]) promotes the thermal oxidation of B particles and the development of flame processes with increasing temperature and gas outflow rate from the HEC surface.

The use of Al-B UFPs in HEC-2 reduced the t_{ign} by 6–16% over the heat flux density range of 65–100 W cm⁻² compared with the t_{ign} of HEC-1. As the values of q increased up to 150–210 W cm⁻², the t_{ign} increased by 5–14%. The exponent n in $t_{ign}(q)$ was at a

minimum and equal to 1.34. The heating time of the sample surface layer to a temperature of 340 °C was ~56 ms. The flame appearance was recorded after ~37 ms. The rate of flame zone propagation reached 6.5 m s⁻¹. Reducing the concentration of Al particles by replacing them with B particles on the sample surface increased the rate of flame formation and the achievement of the stable combustion of HEC-2 at $q < 120 \text{ W cm}^{-2}$.

In the case of using Fe-B UFPs in HEC-4, the ignition time had similar values (difference was less than 3%) in comparison to the t_{ign} of HEC-1 with Alex. The n exponent was 1.57. The heating time of the surface layer to a temperature of 340 °C was ~50 ms. When a luminous spot appeared on the sample surface, an intense stream of thermal decomposition gas products ($t = 65\text{--}70 \text{ ms}$) with small particles from the surface were recorded. The flame formation near the surface of the HEC-4 sample ($t = 100\text{--}105 \text{ ms}$) occurred when the surface was heated to a temperature of 430 °C. However, the maximum propagation rate of the flame zone was ~8.6 m s⁻¹. Iron particles with an oxide cover catalyzed the thermal decomposition of the oxidizer crystals and increased the outflow rate of gas products from the sample surface, forming a flame zone with the maximum length and high-temperature process. Additional heat release during the oxidation of the B particles in a flame increased the rate of the chemical reactions and the HEC-4 combustion stability.

Thus, the ignition efficiency by using Me-B UFPs in HECs can be represented as a series: at $q = 65 \text{ W cm}^{-2}$, $[t_{\text{ign}} \text{ HEC-3, Ti-B}] < [t_{\text{ign}} \text{ HEC-2, Al-B}] < [t_{\text{ign}} \text{ HEC-4, Fe-B}] \approx [t_{\text{ign}} \text{ HEC-1, Alex}]$ and at $q = 210 \text{ W cm}^{-2}$, $[t_{\text{ign}} \text{ HEC-3, Ti-B}] < [t_{\text{ign}} \text{ HEC-1, Alex}] < [t_{\text{ign}} \text{ HEC-4, Fe-B}] < [t_{\text{ign}} \text{ HEC-2, Al-B}]$.

3.3. Ignition Kinetics of HECs with Me UFPs

The kinetic parameters of reactions in the HEC condensed phase (activation energy (E) and pre-exponential factor (z)) were obtained at high heating rates of the HEC surface based on the experimentally determined t_{ign} at given initiating q [48]. These parameters are necessary in calculating the time and energy characteristics of ignition and combustion of HEC, provided that the main reactions in the sample reaction layer take into account a set of reaction mechanisms that can change with variation in the heating rate, pressure, reactants physical state and other conditions. Moreover, with rapid heating of the surface (more than $1000 \text{ K} \cdot \text{s}^{-1}$) and combustion of the HEM in the high-temperature reaction zone, as a rule, physical and chemical processes are accompanied by melting, evaporation and diffusion mass transfer. These processes are characterized by their own time, which should also be taken into account when determining the boundaries of the kinetic parameters. The $t_{\text{ign}}(q)$ correlation and the calculation method of the formal kinetic parameters of ignition [38] are applied to identify E , the thermal effect of the exothermic reactions with z ($Q \cdot z$), the ignition temperature T_{ign} on the sample surface and also the heat release rate (W) in condensed phase when the HECs is exposed to a radiant heat flux (Table 1). The T_{ign} is calculated analytically based on experimentally determined t_{ign} at given q , the thermal conductivity coefficient (λ), specific heat capacity (c), and density (ρ) for HECs. Replacing Alex with Al-B, Ti-B and Fe-B UFPs in HECs causes a significant decrease in the heat release rate in the thermal layer surface (up to 30–35%), while the T_{ign} on the reaction surface remains in the range $T_{\text{ign}} = 461\text{--}566 \text{ K}$, depending on the active heat flux q .

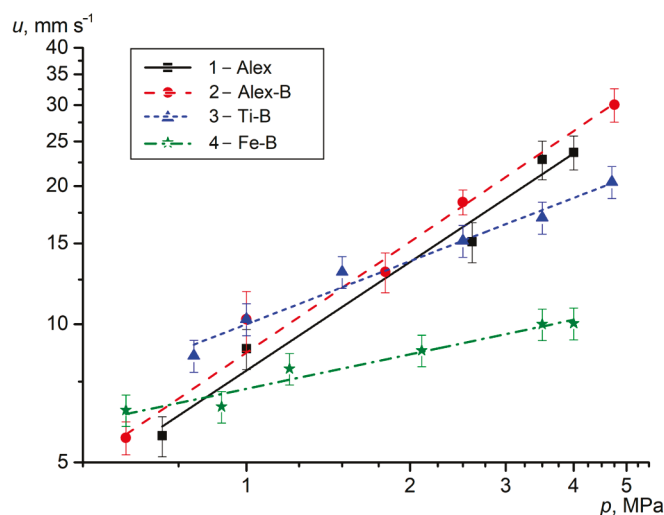
Table 1. Calculated kinetic parameters of HEC ignition.

HECs	E , kJ mol^{-1}	$Q \cdot z$, W g^{-1}	T_{ign}^* , K at $q = 60\text{--}200 \text{ W cm}^{-2}$	W^{**} , kW g^{-1} at T_{ign}
1. Alex	119.0	$1.82 \cdot 10^{16}$	503–546	7.9–75.0
2. Al-B	56.8	$5.17 \cdot 10^9$	490–575	4.6–35.7
3. Ti-B	57.0	$1.51 \cdot 10^{10}$	461–536	5.3–42.1
4. Fe-B	81.2	$1.58 \cdot 10^{12}$	503–566	5.8–50.7

* $T_{\text{ign}} = 0.287 \cdot q \cdot (t_{\text{ign}}/(\lambda c \rho))^{0.5} + T_0$; ** $W = Q \cdot z \exp(-E/RT)$.

3.4. The u of HECs with Me UFPs

The u is an important characteristic for HECs and SPs affecting the outflow rate of combustion products from the HECs surface and the outflow rate of combustion gas products from the engine nozzle. The u of the HECs is measured at different excess pressures p in a constant-pressure bomb. The average measured values (points) of the u for the HECs with Me UFPs as a function of pressure are presented in Figure 3. The experimental data were used in obtaining the burning rate law as $u(p) = b \cdot p^n$.

**Figure 3.** The u of the HECs with Me UFPs vs. the pressure.

The u of the HEC-1 with Alex increases from 4.7 to 27.5 mm s^{-1} with the chamber pressure rising from 0.5 to 5.0 MPa, while exponent n in $u(p)$ correlation is equal to 0.77. The use of Al-B UFP in the HEC-2 increases the u by 7–18% (as a p function), but n is the maximum and equal to 0.81. Replacing Alex with Ti-B UFP in the HEC-3 causes an increase in the u by 10–55% over the pressure range of 0.5–1.5 MPa and decrease in the u by 6–24% over the pressure range of 2.5–5.0 MPa due to decreasing exponent n to 0.45. Note that the minimum exponent $n = 0.25$ is obtained for the HEC-4 with Fe-B UFP, the u of which is lower than that of the base HEC-1 with Alex by 9–61% as a function of pressure. However, at a low pressure ($p = 0.5$ MPa), the u of HEC-4 is 6.1 mm s^{-1} and 30% higher than that for u base HEC-1.

Thus, the use of Al-B UFP in the HEC-2 increases the u to 5.0–32.3 mm s^{-1} with a pressure change from 0.5 to 5.0 MPa due to the high reactivity, intense energy release of Al particles and an increase in the burning rate of B particles in the reaction layer and gas decomposition products near the combustion surface. A comparative analysis with published data of the u for the same component HEC compositions with micro-sized AlB_2 and AlB_{12} powders [21] show that the u of HEC-2 with Al-B UFP is 1.4–3.7 times higher and the exponent n is 80% higher at the same pressure range. The use of highly reactive

Al and B nano-sized particles increases their oxidation and heat release degree, and the temperature on the HEC combustion surface. Accordingly, the HEC-2 with Al-B UFP has greater sensitivity to pressure change in the combustion chamber. The use of Ti-B and Fe-B UFPs in the HEC-3 and HEC-4 increases the u to 7.3 mm s^{-1} (by 55%) and 6.1 mm s^{-1} (by 30%) at $p = 0.5 \text{ MPa}$ (in compare with u HEC-1). However, the combustion efficiency for these HECs decreases with increasing chamber pressure due to the possible relative reduction of the heat release rate and temperature on the HEC reaction layer surface.

As previously noted, the metal and B combustion is a multi-stage physical and chemical process that depends on the initial diameter and protective coating of the particles, temperature, pressure and oxidizer concentration of the gas medium. The combustion mode of metals may differ depending on external conditions, the boiling point of the metal and the evaporation temperature of the oxide coating of the particles. The combustion of Al particles occurs in the diffusion mode during the destruction or melting of the oxide coating and the active aluminum evaporation. Their combustion intensity mainly depends on the initial particle diameter and the thickness of the oxide coating. The high reactivity of the Al nanoparticles increases the heat release rate in the condensed phase (Table 1) and the burning rate of the HEC (Figure 3). An p increase in the chamber helps to increase the u of the HEC, reduce the width of the chemical reaction zone and the reaction time of metal particles with reagents on the surface. Particles of Ti, Fe and B burn more slowly in the heterogeneous mode due to their high boiling and evaporation temperatures. An increase in the SSA and possible micro-explosive combustion of particles (in the final stages Ti or under certain conditions Fe) contributes to the intensification of heterogeneous reactions on the surface and a decrease in the burning time of the particles. With temperature increase on the particle surface, the evaporation rate of the oxide coatings and the diffusion of the gas oxidizer increases, which intensifies the burning process and increases the completeness of particle combustion. When replacing Alex with Ti, Fe or B, the heat release rate in the reaction layer of the HEC is reduced by 40–50% (Table 1), while the u of propellants can either increase (HEC-2 with Al-B) or decrease (HEC-3 with Ti-B and HEC-4 with Fe-B) at p above 2 MPa, due to the possible influence of the heat release rate of reagents in the gas phase and changes in the HEC surface temperature.

4. Conclusions

The use of metal and metalloid UFPs in HECs makes it possible to regulate the t_{ign} and the u for SPs, ensuring their complete combustion in the chamber. The nature of the metal and the protective layer on the metal particles affects their reaction efficiency in the oxidizing medium and the combustion intensity of the B particles, which allows them to realize their energy potential in the combustion chamber. The experimental study of the ignition and combustion of HECs containing AP, a butadiene rubber and ultrafine Me-B mixture fuel demonstrates the effect of changing the exponent n in the correlations with the $t_{\text{ign}}(q)$ and $u(p)$ for SPs.

Replacing Alex with Al-B UFP (mass ratio of 55.5/44.5%) in HEC-2 reduced the t_{ign} by 6–16% over the heat flux density range of $65\text{--}100 \text{ W cm}^{-2}$ and increased the u by 7–18% over the pressure range of 0.5–5.0 MPa due to the increase in the heat release rate near the sample surface during the joint combustion of the Al and B particles. The exponent n in the $u(p)$ correlation was at the maximum and was equal to 0.81 (80% more than that of HECs with AlB_2 micron powder).

The use of Ti-B UFP (mass ratio of 68.9/31.1%) in HEC-3 reduced the t_{ign} by 20–27% (over the heat flux density range of $65\text{--}210 \text{ W cm}^{-2}$) compared to the base HEC-1 with Alex. Micro-explosive and rapid combustion of Ti particles promoted the thermal oxidation of the B particles and the development of flame processes with increasing temperature and

gas outflow rate from the HEC-3 surface. The u increased by 10–55% over the pressure range of 0.5–1.5 MPa and decreased by 6–24% over the pressure range of 2.5–5.0 MPa due to decreasing the exponent n to 0.45.

In the case of using Fe-B UFP (mass ratio of 83.7/16.3%) in HEC-4, the t_{ign} had similar values (difference was less than 3%) in comparison to the t_{ign} of HEC-1 with Alex. Iron nano-sized particles catalyzed the thermal decomposition of AP and increased the outflow rate of gas decomposition products from the sample surface, forming a flame zone with the maximum length. Additional heat release during the oxidation of the B particles in the flame increased the rate of chemical reactions and combustion stability. The exponent n in the $u(p)$ correlation was at the minimum and was equal to 0.25.

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Article

Miraculous Al/PDF Composites Using NF₂ to Enhance the Energy Release of Al, Prepared Through an Efficient Method

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Abstract: To enhance the energy release of Al powder in solid propellant, ploy (difluoroaminomethyl-3-methylethoxybutane) (PDF), which has difluoroamino (NF₂), was utilized to improve energy and promote combustion efficiency. In this study, Al with three distinct powder sizes (29 μm, 13 μm, and 1–3 μm) was coated with PDF using the solvent/non-solvent method, leading to the formation of Al/PDF composites. The morphology and characteristics of Al/PDF were then characterized. The results demonstrated that all powder sizes of Al/PDF had core-shell structures, and NF₂ of the PDF layer on the Al surface maintained the original structure. The TG curves indicated the amount of the PDF layer related to the powder sizes. Furthermore, Al/PDF exhibited greater hydrophobicity. NF₂ prompted Al/PDF, with better catalysis on ammonium perchlorate (AP) decomposition. Compared to Al powder, the ignition delay of Al/PDF was significantly shortened. For mixed samples of Al/PDF and AP, NF₂ shortened the ignition delay, improving combustion stability, extending the combustion duration, and forming volatile fluorine compounds. These findings underscore the effects of NF₂ in Al/PDF composites, which enhances the energy release of Al and holds promising potential applications.

Keywords: NF₂; Al powder; PDF; composites; coating; energy release

1. Introduction

Aluminium (Al) powder is the ubiquitous metal fuel used in solid propellants, and its practical energy release significantly impacts the performance of solid propellants [1–3]. The enhanced energy release is a consequence of the increased energy in Al powder and its improved combustion efficiency [4,5]. Based on the above, enhanced Al energy release, especially combustion efficiency, has garnered significant research interest [6–10]. Of these, it is feasible to address the objectives mentioned above through Al and the special functional materials of combined composites. Fluorinated materials [11–14] are incorporated with Al as composites, which are in the form of fluorinated polymers such as perfluoro tetra decanoic acid (PFTD), polyvinylidene fluoride (PVDF), or polytetrafluoroethylene (PTFE) [15–19]. These make AlF₃, formed during the solid propellant reaction, easier to decompose and volatilize, and during the decomposition, it is highly reactive with Al and Al₂O₃, allowing a pre-ignition reaction (PIR); thus, the fluorinated materials improve the combustion efficiency of the Al powder. Regrettably, however, these fluorinated materials are not energetic, resulting in a possible reduction of Al's energy release. Meanwhile, compounds like nitrocellulose (NC), ammonium perchlorate (AP), and glycidyl azide polymer (GAP) [20,21] can introduce energetic groups for the Al powder, increasing the energy [22,23]. This enhancement of the energy of Al powder is unable to improve its combustion efficiency but is equally significant for solid propellants. Nevertheless, considering the performance of solid propellants, it is preferable to combine Al powders with energetic

fluorinated materials, which have all the functions of the two methods mentioned above. However, research on concise and effective methods to incorporate target groups on the surface of Al powder to meet the above requirements is still in its infancy.

Difluoroamino (NF_2) has a theoretical density of 2.303 g/cm^3 and an enthalpy of formation of -32.7 kJ/mol [24]. The N-F bond has higher reactivity than the C-F bond, with the F in NF_2 appearing in the form of the oxidant. When NF_2 is introduced into the structure of the compound, the energy level of the compound can be significantly enhanced and, thus, can be used as a potential oxidant or binder in solid propellants [24,25]. Notably, the HF produced by NF_2 during decomposition has a low relative molecular mass and a bond energy as high as 565 kJ/mol . The released energy of Al and F during the reaction is approximately 56.10 kJ/g , which is approximately twice that (30.98 kJ/g) of Al and oxygen [26,27]. At the same time, the F in NF_2 is a good combustion aid in improving the combustion efficiency of Al powders, which is as effective as F in fluorinated polymers [27,28]. Therefore, NF_2 combines the functions and advantages of the F elemental group and the energy group, which provides a good breakthrough for solving the above problems. The emergence of NF_2 offers a novel solution to the issues mentioned above if incorporated into the Al powder and reacts with Al. Poly (difluoroaminomethyl-3-methylethoxybutane) (PDF) [27] is a kind of difluoroamino polymer with an active telohydroxyl group ($-\text{OH}$) and can facilitate interaction with the Al powder; thus, PDF serves as an NF_2 material and is combined with Al powder to synthesize Al/PDF composites.

The oxide layer on the surface of Al powder protects and isolates the external chemical reaction, thus hindering the direct bonding of PDF with the Al surface. It must be removed as much as possible through a low-concentration alkali solution. At the same time, the alkali solution is able to hydroxylate the Al surface, making PDF easier to bond with Al. NF_2 with strong reactivity can quickly occur reaction, and it is necessary to prevent NF_2 from other reactions that may lead to its structural destruction, thus rendering NF_2 useless. According to previous studies and our previous work on the similar metal fuel boron [29], the coating is a common and efficient method for functional materials added for Al, which can enhance the specific surface area of Al powder and improve its surface reactivity with no drastic change in morphology [10,23]. In this study, Al/PDF composites were prepared through surfactants and the solvent/non-solvent method [2], which can react rapidly and efficiently, and isocyanate was used with PDF linked with the Al powder. We successfully incorporated NF_2 of PDF on Al powder with three different powder sizes ($29 \mu\text{m}$, $13 \mu\text{m}$, and $1\sim3 \mu\text{m}$), and Al/PDF was synthesized. Furthermore, the structure, morphology, and hydrophobicity of Al/PDF were investigated. It has been confirmed that NF_2 of PDF significantly improves the total performance of Al powder. More importantly, this verifies the facilitating effect of NF_2 on the ignition of Al/PDF and the catalytic behavior of Al/PDF on AP.

2. Experimental Section

2.1. Materials

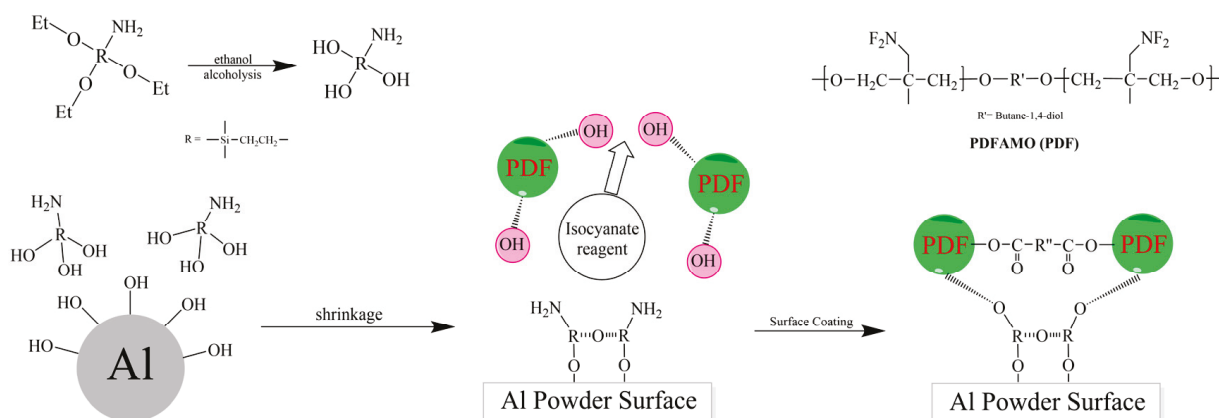
Aluminium (Al) powders with sizes of approximately $29 \mu\text{m}$, $13 \mu\text{m}$, and $1\sim3 \mu\text{m}$ were acquired from the Shanghai Academy of Spaceflight Technology (Shanghai, China). 95% ethanol, ethyl acetate, and hexane, all of analytical purity, were brought from Wohua Chemical Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH) and (3-aminopropyl) triethoxysilane (KH-550), all of the analytical grades, were provided by Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Analytically-pure methylidynetri-p-phenylene triisocyanate (20% in $\text{C}_6\text{H}_5\text{Cl}$) was purchased from Macklin (Shanghai, China). Ammonium perchlorate (AP) with a particle size of approximately $150 \mu\text{m}$ was purchased by the Xi'an Modern Chemistry Research Institute. PDF was synthesized using Li's et al. [27] method. The molecular mass (M_n) of PDF was 3600 g/mol , with a polydispersity index (M_w/M_n) of 1.6.

2.2. Pretreatment of Al Powder

The pretreatment of Al powder involves adding the Al powder of each powder size (29 μm , 13 μm , 1–3 μm) to 0.01 mol/l of NaOH solution to remove the oxide layer. The above-treated Al powder was thoroughly dispersed in ethanol and then KH-550 was added. After ultrasonic dispersion for 1 h, the suspension of Al powder was magnetically stirred at 60 °C for 2 h under nitrogen (N_2). At the end of the reaction, the Al powder was filtered and dried in a vacuum oven at 60 °C for 12 h.

2.3. Preparation of Al/PDF Composites

In this study, we prepared Al/PDF with various powder sizes using the solvent/non-solvent method. A schematic of the preparation process is shown in Scheme 1. In a typical step, 2 g of pretreated Al powder was dispersed in 50 mL of ethyl acetate, followed by the addition of 10% wt PDF, and then ultrasonic dispersion for 30 min. The mixture was then slowly added to 250 mL of hexane containing methylidyne tri-*p*-phenylene tri-isocyanate with vigorous magnetic stirring under N_2 . It is important to note that the temperature of the hexane was 60 °C, and the mixture was added at a rate of 1 mL/min. After the addition of the mixture, the temperature was reduced to room temperature (20 °C). The precipitated PDF adhered to the surface of the Al powder and formed the desired coating with the help of the methylidyne tri-*p*-phenylene tri-isocyanate. After the addition of the mixture, the reaction was carried out for 2 h at room temperature. Subsequently, the coated Al powders were filtered, washed twice with hexane, and dried under vacuum at 60 °C. It is worth noting that the coating technique was similar for each powder size.



Scheme 1. Schematic diagram of the preparation process of Al/PDF.

2.4. Characterizations and Measurements

The surface chemical structure of Al/PDF was measured by Fourier transform infrared (FTIR) (NICOLETIS 20, Thermo Fisher Scientific, Waltham, MA, USA) with a range of 4000 to 500 cm^{-1} . The surface morphology of Al/PDF was observed by field emission scanning electron microscope (FESEM) (FEI QUANTA 400 FEG, Oxford Instruments, Abingdon, Oxfordshire, UK) and transmission electron microscope (TEM) (JEM-2100F, Akishima, Tokyo, Japan). The X-ray diffraction (XRD) patterns of the samples were conducted on Smartlab 9 (Rigaku, Akishima-shi, Tokyo, Japan) ($2\theta = 10\text{--}90^\circ$). Additionally, the elemental state of Al/PDF was conducted by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA).

The static contact angle of the samples (Al or Al/PDF) was measured using a surface tensiometer (SDC-100, Dongguan, China). A hydraulic machine was used to press each sample (500 mg) into a wafer (10 mm in diameter) at 10 MPa, then the pressed sample was treated on the test bed of the surface tensiometer in turn, using 4 μL of deionized water drops each test. Each sample was tested five times, and the average was taken as the reference value. Thermogravimetric analysis (TGA) (SDTA851E, Mettler Toledo, Zurich,

Switzerland) and differential scanning calorimetry (DSC) (DSC3, Mettler Toledo, Zurich, Switzerland) with the heating rate of 10 K/min, and a temperature range of 50~500 °C under N₂ atmosphere. TGA was used to examine the thermal mass loss of Al or Al/PDF (weighed 0.6~0.8 mg), and DSC was tested the exothermic characteristics of the mixed sample of Al and AP, Al/PDF, and AP. The mass ratio of DSC samples (AP:Al or Al/PDF) was 9: 1, and weighed 0.6~0.8 mg. Pyrolysis–gas chromatography/mass spectrometry (PY-GC/MS) analyzed volatile compounds of mixed samples (AP and Al/PDF), and the pyrolysis temperatures were set as 300 °C and 500 °C, respectively. The mass ratio of AP:Al/PDF was 9:1, and around 0.2 mg samples were placed in the Frontier 3030D pyrolyzer interfaced with a GC/MS (QP2010ULTTA, Shimadzu, Kyoto, Japan). The relevant parameters were set as follows: He as the carrier gas, pyrolysis and GC/MS interfaces were kept at 300 °C, the GC was temperature-programmed from 40 °C (for 2 min) to 140 °C at 10 K/min, and from 140 °C to 300 °C at 20 K/min, and the electron impact mode (70 eV) for m/z 10~550.

For Al or Al/PDF laser ignition and combustion, each sample (Al or Al/PDF) was weighed to 20 mg and then put into the quartz tube (diameter: 3 mm, length: 5 mm). For mixed samples laser ignition and combustion, each sample was mixed with a ratio of 65: 35 (AP: Al or Al/PDF) [29,30], weighed to 20 mg, and put into the quartz tube (diameter: 3 mm, length: 5 mm). At the end of the combustion of the mixed samples, the residues were collected and then characterized by FESEM using the above method. A high-speed camera recording (Photron, FASTTXAM Mini UX100, Tokyo, Japan) performed at 1000 fps was employed to detect the above ignition and combustion process. The parameters of the laser ignition device provided by Nanjing University of Science and Technology were set as voltage: 220 V $\pm$ 10%; laser power: 40 W; laser spot: 5 mm; light duration: 1 s [30].

3. Result and Discussion

3.1. Structure and Morphology of Al/PDF

Al/PDF with powder sizes of 29 μ m, 13 μ m, and 1~3 μ m are shown in Figure 1, where spectra are compared with the Al without coating and PDF layer. The FTIR spectra revealed significant changes in the Al/PDF with different powder sizes compared to the uncoated Al powder. Moreover, the intensity of the characteristic peaks of the Al/PDF weakened as the powder size decreased. Notably, Al/PDF with a size of 29 μ m exhibited the most apparent characteristic peaks (Figure 1a,b). Generally, the characteristic peaks of all Al/PDF were identified. The N-H stretching vibration [31] was found at nearly 3450 cm^{-1} (Figure 1a,c,e), the N-H bending vibration [32] at nearly 1530~1500 cm^{-1} (Figure 1a,c), and the C=O [31] bond at approximately 1715 cm^{-1} (Figure 1a,c), demonstrating the isocyanate reaction with the -OH of PDF and the formation of carbamate in Al/PDF (29 μ m and 13 μ m). The characteristic peak at around 1100 cm^{-1} was caused by the C-O-C [28] in the main chain segment of the binder. The characteristic peaks located at nearly 1015 cm^{-1} and 900 cm^{-1} (Figure 1b,d) were due to N-F [28,33] bond vibrations. Meanwhile, the characteristic peak at nearly 800 cm^{-1} (Figure 1b,d) was attributed to the C-N [28,34] bond vibration, which verified that NF₂ of Al/PDF with sizes of 29 μ m and 13 μ m was not damaged during the reaction. Notably, several Al/PDF peaks with a powder size of 1~3 μ m (Figure 1e) were not evident, particularly the N-H bending vibration (1530~1500 cm^{-1}), C=O bond characteristic peak (~800 cm^{-1}), N-F bond characteristic peak (~1015 cm^{-1} and ~900 cm^{-1}), and C-N bond characteristic peak (~800 cm^{-1}). However, in contrast, a more substantial characteristic peak existed at approximately 965 cm^{-1} , which is presumed to overlap with peaks occurring after the shift of several of the above characteristic groups. Nevertheless, this requires further characterization.

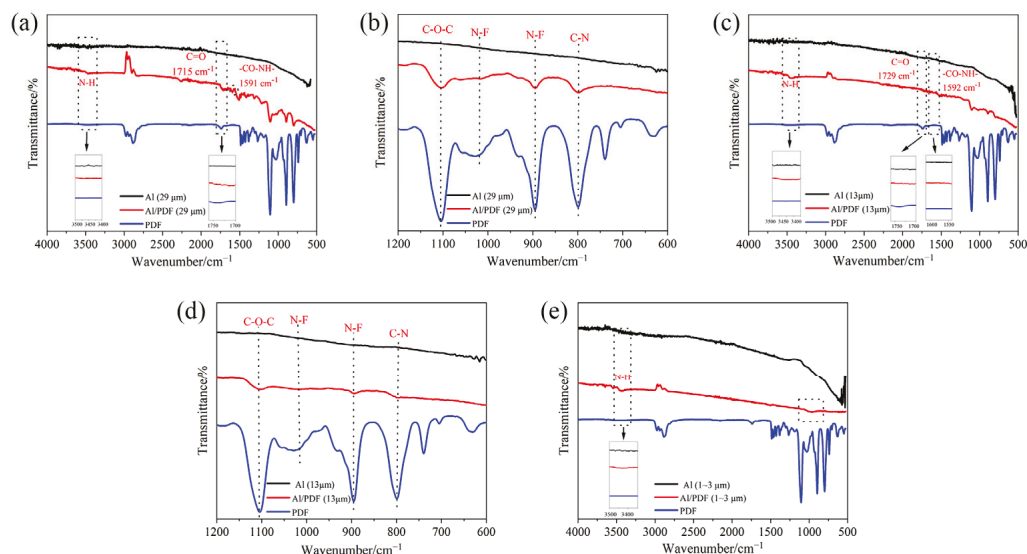


Figure 1. FTIR spectra: (a) full spectra of Al/PDF (29 μm); (b) 1200–600 cm^{-1} of Al/PDF (29 μm); (c) full spectra of Al/PDF (13 μm); (d) 1200–600 cm^{-1} of Al/PDF (13 μm); (e) full spectra of Al/PDF (1–3 μm).

Furthermore, the morphology of Al powder and Al/PDF with different powder sizes was analyzed through FESEM. Figure 2 describes the morphologies. As described in Figure 2d–f, all Al/PDFs exhibited a spherical shape, with the PDF layer cladding stacked on the surface. The Al/PDF surfaces were smoother and flatter than the Al surfaces, which had rougher and sharper protrusions. Compared to Al/PDF with powder sizes of 29 μm and 13 μm , the 1–3 μm Al/PDF presented slight agglomeration. A typical mapping analysis was performed to investigate the distribution of PDF on the Al powder further. The element mapping results (Figure 2g–l) for Al/PDF and Al revealed the generation of the N and F elements after the coating, and these elements were evenly distributed on the Al sphere. By combining the images of the FTIR spectra, it could be verified that NF_2 retained the original structure and was uniformly distributed on Al/PDF composites successfully. Figure 3 displays the TEM image of Al/PDF (1–3 μm). As indicated in Figure 3b,c, Al/PDF (1–3 μm) presented a typical core-shell structure, with the transparent film-like substance PDF adhering to the periphery of the Al powder. Based on the morphological characterization, it can be concluded that NF_2 was distributed on the Al/PDF composites, and the thin coating layers of PDF formed core-shell structures. Additionally, the FTIR spectra of Al/PDF (1–3 μm) were validated and complemented by the TEM images.

Figure 4 depicts the XRD diffraction pattern of Al/PDF with different powder sizes. It was observed from Figure 4 that there was no significant change in the strong peak position of Al/PDF composites in comparison to the XRD standard spectra of Al powder. Besides, the angles of the five diffraction peaks in the three Al/PDF composites were maintained at 38.46° , 44.73° , 65.09° , 78.26° , and 82.45° . This finding aligned with the diffraction peaks of standard Al, and the corresponding diffraction crystal planes were (111), (200), (220), (311), and (222), respectively [17,14]. Notably, the crystal structure was a face-centered cubic structure, suggesting that the positions of the diffraction peaks were unchanged after adding PDF for Al powder.

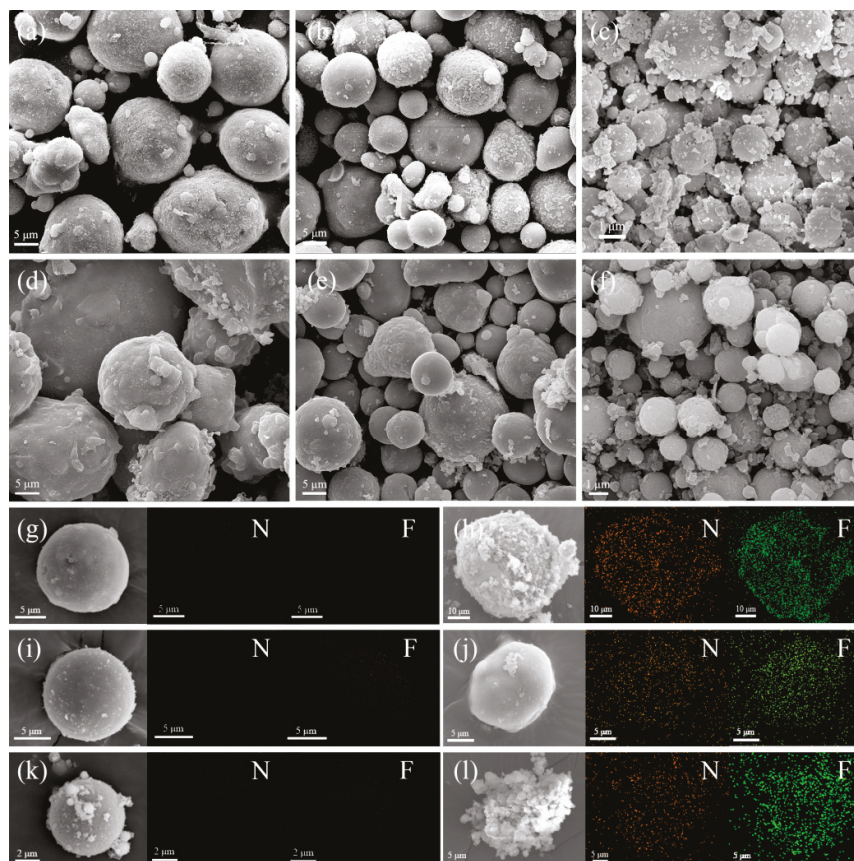


Figure 2. FESEM images: (a) Al (29 μm); (b) Al (13 μm); (c) Al (1~3 μm); (d) Al/PDF (29 μm); (e) Al/PDF (13 μm); (f) Al/PDF (1~3 μm), and mapping images: (g) Al (29 μm); (h) Al/PDF (29 μm); (i) Al (13 μm); (j) Al/PDF (13 μm); (k) Al (1~3 μm); (l) Al/PDF (1~3 μm).

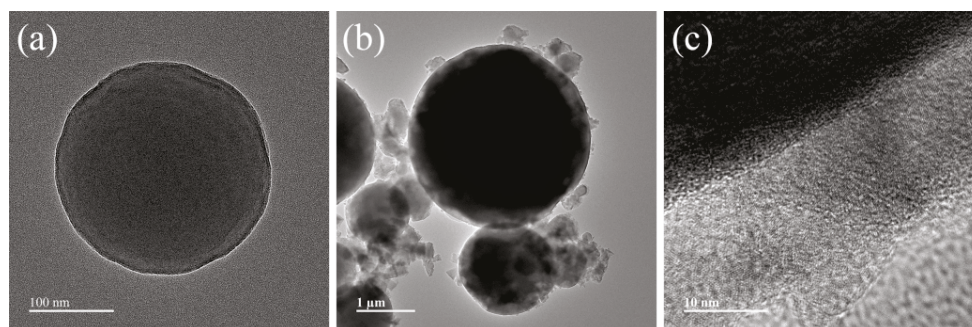


Figure 3. TEM images: (a) Al (1~3 μm); (b,c) Al/PDF composites (1~3 μm).

Figure 5 demonstrates the XPS spectra of Al powder and Al/PDF composites of different powder sizes. These spectra were used to analyze the elements and states of the surface. The Al powder primarily consists of Al, O, and C, in which O and C elements result from the oxide layer. Correspondingly, more evident peaks of N and F elements can be observed in 29 μm Al/PDF, 13 μm Al/PDF, and 1~3 μm Al/PDF, which implies the presence of the PDF coating layer on the Al powder surface. The spectrum of C 1s (see Figure 5d–f) of Al/PDF displays signal peaks at ~284.4 eV, 284.8 eV, ~286.2 eV, ~286.6 eV, and ~289 eV positions after splitting, corresponding to C-H [5], C-C [5,7,9], C-O [5,9,35], C-N [33], and C=O [5,7,9,35] bonds, respectively. Meanwhile, the O 1s spectra (Figure 5g–i) of Al/PDF display signal peaks at 531.1~531.5 eV, 531.5~532 eV, and ~533 eV, which correspond to O-Al [7,36], O-C [36], and O=C [5,36] bonds, respectively. Combined with the analysis of the N element, the signal peak at 399.4 eV was -CO-NH- [19,33,37], confirming the occurrence of the curing reaction of PDF with the isocyanate groups of

methylidyne tri-*p*-phenylene tri-isocyanate on the surface of Al powder during the coating process. As depicted in the N 1s (~404.15 eV) [33,35] and F 1s (~686.55 eV) [35,38] spectra, element F still existed in the form of NF₂, and the structure of the N-F bond was not damaged. Combining the other characterization results it could be observed that NF₂ was not destroyed and routinely encapsulated through PDF on the surface of Al powder by curing with methylidyne tri-*p*-phenylene tri-isocyanate.

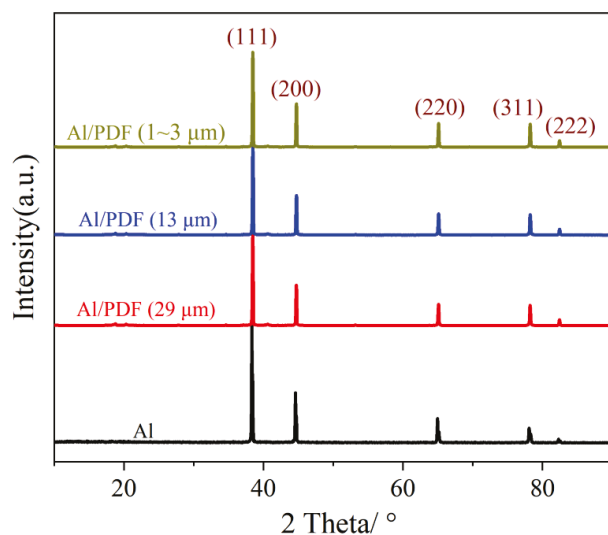


Figure 4. XRD pattern of Al/PDF composites with 29 μm , 13 μm , and 1~3 μm .

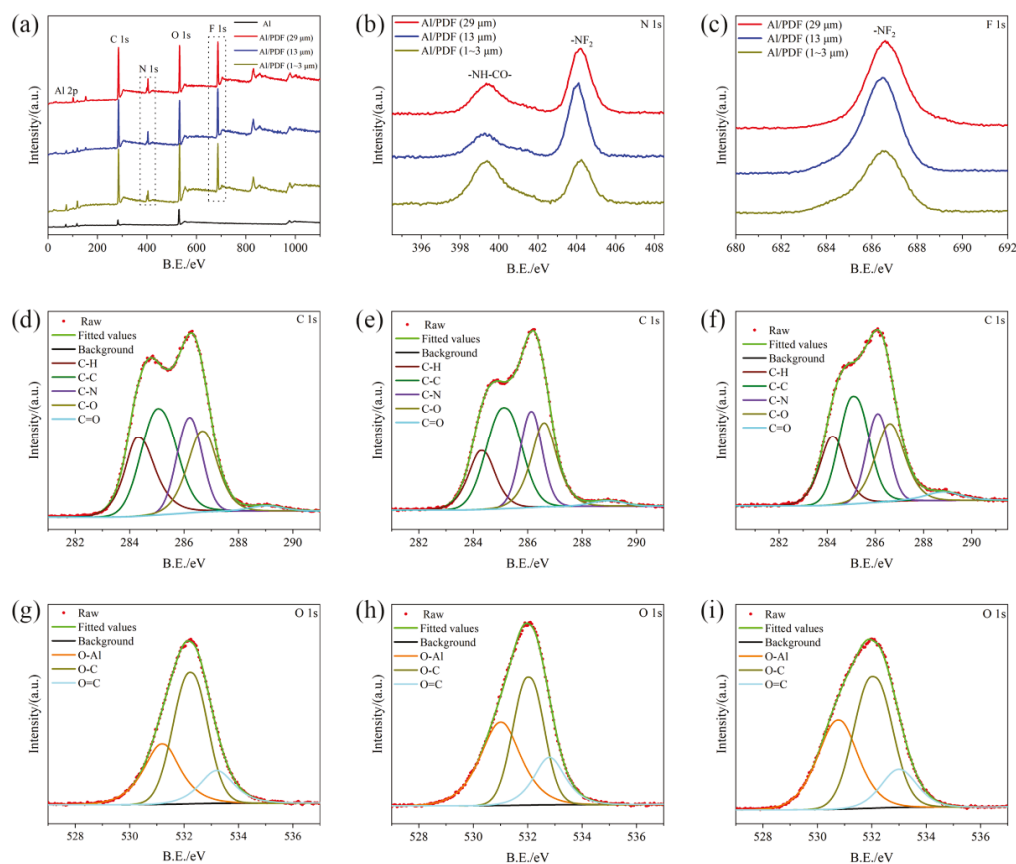


Figure 5. XPS wide scan and high-resolution scan spectra of Al/PDF composites: (a) full scan; (b) N 1s spectra; (c) F 1s spectra; (d,g) C 1s and O 1s spectra of Al/PDF (29 μm); (e,h) C 1s and O 1s spectra of Al/PDF (13 μm); (f,i) C 1s and O 1s spectra of Al/PDF (1~3 μm).

3.2. Characteristics of Al/PDF Composites

Figure 6a–f illustrates the contact angles of water on the Al powder and Al/PDF composites with different powder sizes. Moreover, the specific values of these contact angles are listed in Figure 6g. Notably, after pressing and forming the flat plane, deionized water can quickly spread out the surface of Al powder, with the contact angle dropping as the particle size decreases. Meanwhile, the contact angle of deionized water on Al/PDF composites significantly increased by 51.24° ($29\ \mu\text{m}$), 69.47° ($13\ \mu\text{m}$), and 75.96° ($1\sim3\ \mu\text{m}$). These results imply that Al/PDF composites generated greater hydrophobicity, thereby effectively protecting internal Al powder from moisture.

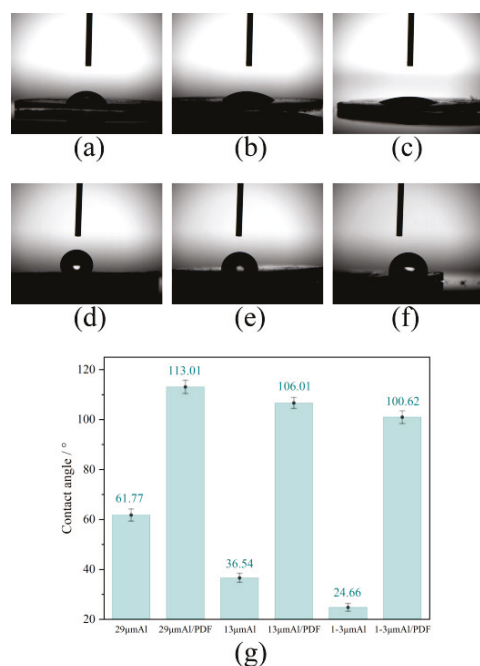


Figure 6. Photographs of static water contact angle measurement: (a) Al ($29\ \mu\text{m}$); (b) Al/PDF ($29\ \mu\text{m}$); (c) Al ($13\ \mu\text{m}$); (d) Al/PDF ($13\ \mu\text{m}$); (e) Al ($1\sim3\ \mu\text{m}$); (f) Al/PDF ($1\sim3\ \mu\text{m}$); and (g) static water contact angle.

To provide NF_2 for Al powder, an energetic fluorinated polymer PDF was bonded on Al powder. As exhibited in Figure 7, the actual amount of PDF layer can be roughly measured through PDF thermal decomposition [26,28,39] by TG analysis. The decomposition of PDF started at nearly $200\ ^\circ\text{C}$, leading to a mass loss of approximately 7.89 wt% ($29\ \mu\text{m}$), 8.56 wt% ($13\ \mu\text{m}$), and 9.29 wt% ($1\sim3\ \mu\text{m}$) in Al/PDF. This phenomenon is attributed to the surface energy of Al powders with different powder sizes. As the powder size decreases, the specific surface area increases, enabling a more significant amount of PDF to be bonded on Al powder.

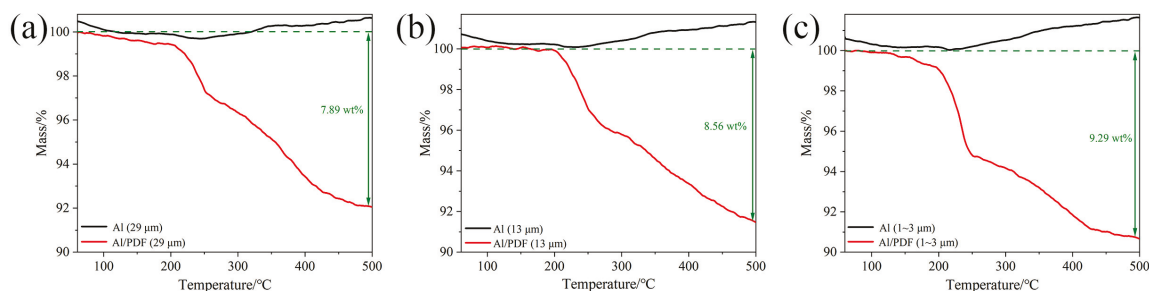


Figure 7. TG analysis of Al/PDF: (a) $29\ \mu\text{m}$; (b) $13\ \mu\text{m}$; (c) $1\sim3\ \mu\text{m}$.

Figure 8 shows the ignition and combustion processes of the Al powder and Al/PDF composites of different powder sizes. Figure S1a indicates the statistics of the ignition delay, and Figure S1b displays the combustion duration. Figure 8 describes that the ignition delay of Al/PDF was reduced by NF₂, with the ignition delay shorted 319 ms (29 μ m), 177 ms (13 μ m), and 157 ms (1~3 μ m), respectively. Notably, the NF₂ increased flame intensity and duration of combustion extended with 1708 ms (29 μ m), 2005 ms (13 μ m), and 1343 ms (1~3 μ m), respectively. These findings imply that NF₂ can assist in the combustion process of Al, thereby achieving the target of enhancing energy release. With decreasing powder size, the ignition delay of both Al and Al/PDF decreased together, the duration of combustion increased, and the combustion intensity improved. Furthermore, due to the significant role of NF₂ through PDF, 1~3 μ m Al/PDF was highlighted optimally. Facilitating minimum ignition delay and the most extended combustion duration.

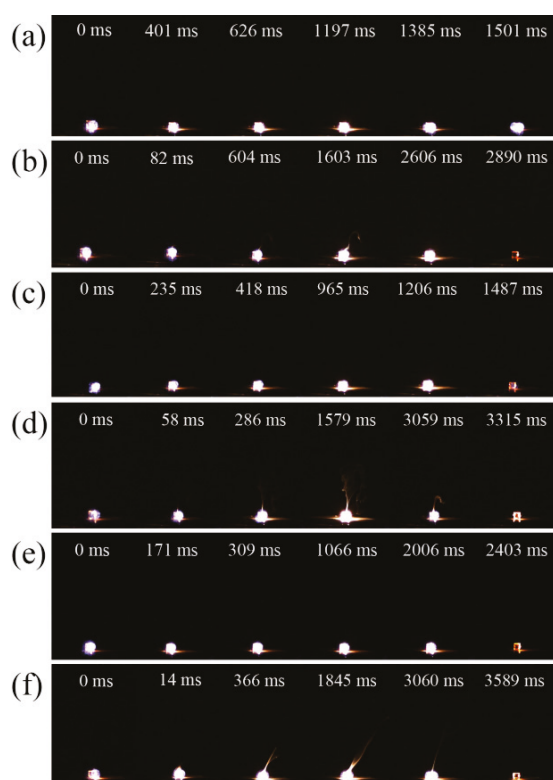


Figure 8. Combustion images after ignition: (a) Al (29 μ m); (b) Al/PDF (29 μ m); (c) Al (13 μ m); (d) Al/PDF (13 μ m); (e) Al (1~3 μ m); (f) Al/PDF (1~3 μ m).

3.3. The Catalytic Effect of Al/PDF on AP

Ammonium perchlorate (AP) is a common oxidant component in solid propellants. The burning rate of the solid propellant is closely related to the decomposition of AP [5]. Numerous studies have demonstrated that a reduction in the decomposition temperature of AP can increase the burning rate of the propellant. The catalytic effects of Al and Al/PDF samples of different powder sizes on the decomposition of AP were analyzed through DSC. Figure 9 reveals the DSC curves. As presented in Figure 9, the thermal decomposition of pure AP consists of the following three stages: an endothermic peak at 243.33 $^{\circ}$ C, which is attributed to the crystal transition, and two exothermic peaks at 298.50 $^{\circ}$ C and 403.12 $^{\circ}$ C, which correspond to the low-temperature and the high-temperature decomposition (THTD) of the AP exothermic process. Notably, all the Al-containing samples exhibit similar endothermic peaks as AP at nearly 243.5 $^{\circ}$ C. This indicates that the endothermic peak of AP is unaffected by the presence or absence of NF₂ in PDF. It is observed that after adding Al-contained samples for AP, all low-temperature exothermic peaks of AP weaken and shift closer to high-temperature exothermic peaks. This implies that the exothermic process

of AP changed from two separate phases to two consecutive phases, even nearly one phase. A more focused exothermic reaction favors further energy release between AP and Al in the solid propellant. Nevertheless, the peaks of THTD of AP catalyzed by Al are at 411.83 °C (29 μm), 399.67 °C (13 μm), and 405.50 °C (1~3 μm), respectively, in the absence of the catalytic effect of NF₂ in PDF. The increase in the temperature of high-temperature exothermic peaks lowered the catalysis for AP. In contrast, THTD peaks of AP catalyzed by Al/PDF composites are located at 384.75 °C (29 μm), 368.52 °C (13 μm), and 356.47 °C (1~3 μm). Compared to the absence of NF₂ of PDF, THTD was reduced by 27.08 °C (29 μm), 31.15 °C (13 μm), and 49.03 °C (1~3 μm), respectively. The Al/PDF composites can lower the decomposition temperature of AP more or less and promote the thermal decomposition of AP at high temperatures. Moreover, the catalytic effect of Al/PDF on AP increases with decreasing powder size.

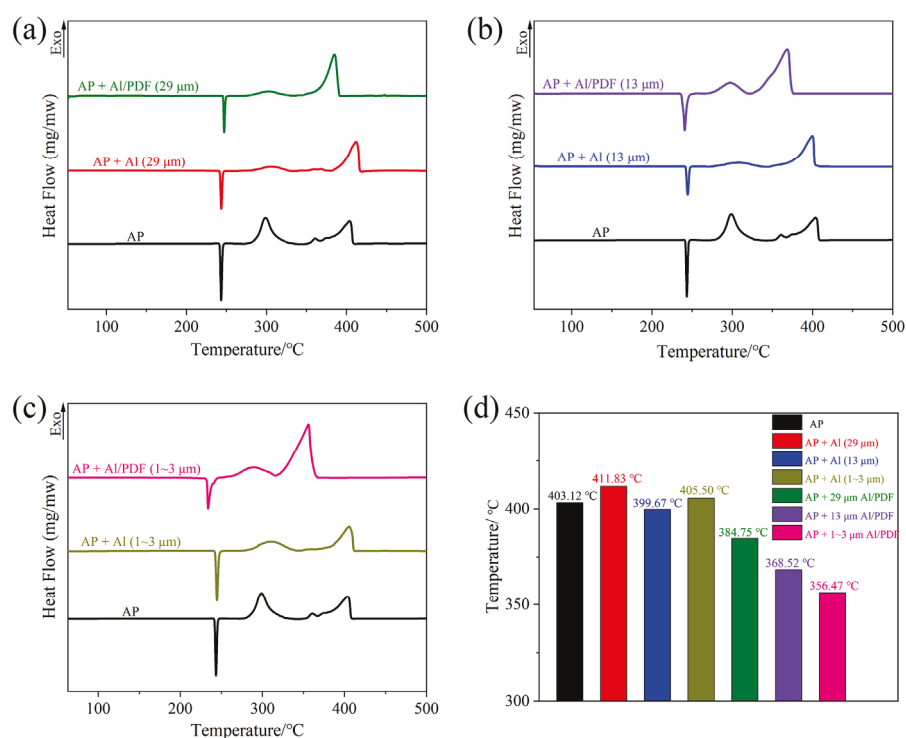


Figure 9. DSC curves of AP decomposition: (a) Al and Al/PDF with 29 μm ; (b) Al and Al/PDF with 13 μm ; (c) Al and Al/PDF with 1~3 μm , and (d) histogram of the corresponding THTD.

According to the aforementioned DSC results and discussions, the main pyrolysis volatiles of mixed samples consisting of AP and Al/PDF composites (29 μm , 13 μm , and 1~3 μm) were analyzed through PY-GC/MS system at 300 °C and 500 °C. Chromatograms mixed samples pyrolysis are indicated in Figures S2 and S3. The majority of peaks were identified using the NIST library and previous studies [40,41]. The main compounds identified are listed in Tables S1–S3. When the pyrolysis occurred at 300 °C, the pyrolysis products of Al/PDF and AP were detected to be dominated by elements C, O, and N, such as *N*-Methylethylenediamine (C₃H₁₂N₂) and glyoxylic acid (C₂H₂O₃), as well as some chlorine compounds such as 2-hexenedioic acid, 2,4-dichloro-5-oxo-(C₆H₄Cl₂O₅), ammonium chloride (NH₄Cl), and chlorobenzene (C₆H₅Cl). With the decrease of the powder size, a small amount of silicone compounds exist in the pyrolysis products of Al/PDF and AP with 1~3 μm powder. Presumably due to the strong reactivity of Al/PDF at this powder size, which reacted with tubes containing Si during the pyrolysis reaction with AP, resulting in such as dodecamethylcyclotrioxasiloxane (C₁₂H₃₆O₆Si₆), octadecamethylcyclononasiloxane (C₁₈H₅₄O₉Si₉), tetradecamethylheptasiloxane (C₁₄H₄₄O₇Si₇), and other compounds. When the pyrolysis was at 500 °C, the main products were aminoacetic acid (C₂H₅NO₂), alanin (C₃H₇NO₂), and 3-amino-2-methylpropanoic acid (C₄H₉NO₂). As the powder size de-

creased, some fluorine compounds and silicone compounds were detected. There is the generation of fluoro(trinitro)methane (CFN_3O_6) and dimethylphenylfluorosilane ($\text{C}_8\text{H}_{11}\text{FSi}$) in the pyrolysis of $13\text{ }\mu\text{m}$ Al/PDF with AP. Compounds such as dimethylphenylfluorosilane ($\text{C}_8\text{H}_{11}\text{FSi}$), fluoro(trinitro)methane (CFN_3O_6), and *N*-(Trifluoroacetyl)-*N'*-tetrakis(trimethylsilyl)norepinephrine ($\text{C}_{22}\text{H}_{42}\text{F}_3\text{NO}_4\text{Si}_4$) were monitored from the pyrolysis products of AP and $1\sim 3\text{ }\mu\text{m}$ Al/PDF. The organic volatiles generated from the pyrolysis of AP and Al/PDF at $300\text{ }^\circ\text{C}$ and $500\text{ }^\circ\text{C}$ are mainly compounds consisting of C, H, N, and O elements. Fluorine compounds and silicon compounds were more likely to be produced at $500\text{ }^\circ\text{C}$ rather than at $300\text{ }^\circ\text{C}$. In the pyrolysis of AP and Al/PDF, the powder sizes of $13\text{ }\mu\text{m}$ and $1\sim 3\text{ }\mu\text{m}$ Al/PDF pyrolysis the fluorine compounds with higher reactivity corroded the pyrolyzer tubes, leading to the production of silicon compounds.

Combined with the results and discussions of DSC and PY/GC-MS, the ignition and combustion tests were conducted on mixed samples of AP and Al to investigate the energy released from the combustion. Herein, the laser ignition and the combustion process of these mixed samples were recorded by the high-speed camera, and the images are recorded in Figure 10. The corresponding ignition delay and combustion duration data are depicted in Figure S1c,d, respectively. Notably, the mixed sample of $29\text{ }\mu\text{m}$ Al has a long ignition delay. However, the mixed sample of Al/PDF with the same powder size shortened the ignition delay from 583 ms to 45 ms. During the combustion process, the combustion duration was nearly doubled (499 ms extended to 838 ms), and the intensity of the trailing flame during the combustion process was considerably increased. Moreover, the NF_2 of Al/PDF enhanced the energy release during the combustion process with AP. Besides, the energy release of $13\text{ }\mu\text{m}$ Al/PDF and AP was promoted by NF_2 during the combustion process with AP, with the ignition delay shortened by 134 ms and the combustion duration extended by 365 ms. Although the ignition delay between $1\sim 3\text{ }\mu\text{m}$ Al and AP without NF_2 (16 ms) was close to the sample of Al/PDF (15 ms), severe deflagration occurred during the combustion process, leading to an unstable combustion state with a duration of only 266 ms. In contrast, the stability of $1\sim 3\text{ }\mu\text{m}$ Al/PDF and AP was significantly enhanced without any deflagration in the presence of NF_2 of PDF, and the ignition delay remained short. Thus, the stability of $1\sim 3\text{ }\mu\text{m}$ Al/PDF and AP was drastically enhanced without any deflagration phenomenon. Furthermore, the intensity of the tail flame is considerable, and the combustion duration is extended to 1153 ms. With the powder size of Al/PDF composites decreased, the ignition delay of the mixed samples was shortened, the burning time was increased, and the intensity of the tail flame was increased.

In order to further understand the reaction processes and changes after ignition, the combustion residues of Al (Al/PDF) and AP adhering to the walls of the quartz tubes were also investigated. These burned-out particles were collected and analyzed by SEM and EDS. The graph of SEM is exhibited in Figure 11, and the results of EDS are demonstrated in Figure S4. According to previous studies [42,43], the powder size of Al has a significant decisive influence on Al combustion characteristics. When large agglomerates are generated, combustion efficiency will be reduced. From Figure 11, it can be seen that the combustion of Al with AP after ignition in the case where there is no NF_2 produced agglomerates with the same or even larger particle size than the original ones, and with the increase of the particle size, there is still some unreacted Al powder in the residue, which also corresponds to the phenomenon in Figure 11a. All of the above indicates the incomplete oxidation of Al powder during the combustion reaction. According to the results of the characterization of EDS, the main components of the above residues are Al_2O_3 , Al powder incomplete with oxidation, and C-containing particles. After ignition, Al/PDF with different powder sizes provided NF_2 to the combustion reactions with AP, and the residues produced in these reactions changed significantly compared to Al without NF_2 . Although agglomeration of the residues still occurred, the particle sizes were significantly reduced compared to the state when no ignition occurred. This implies that NF_2 of Al/PDF improved the combustion and reaction efficiencies with AP, which corresponds to the combustion ignition diagrams of Figure 11. This is mainly due to the high reactivity of NF_2

of Al/PDF, which reacts violently with AP and Al on the surface, respectively. The high temperature generated during the combustion reaction induces the Al vapor to escape from the interior of Al and immediately react with the oxygen in the air to form nanoscale Al_2O_3 smoke particles that condense and attach to each other and finally form agglomeration (Figure 11d–f).

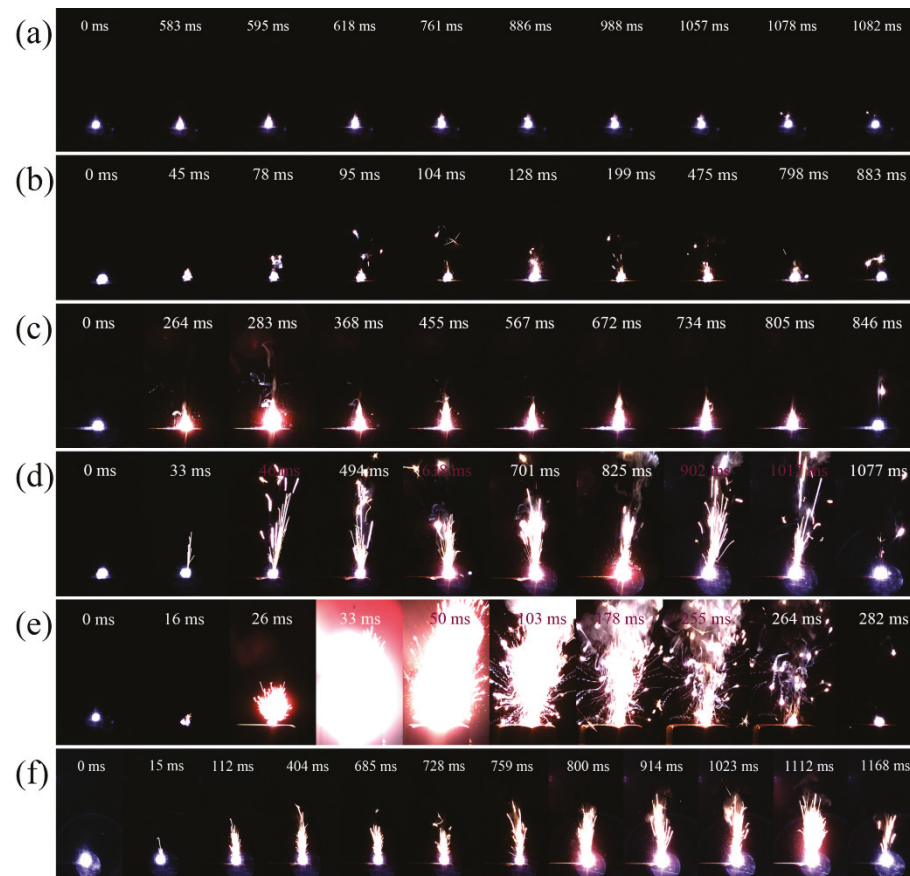


Figure 10. The combustion process of the mixture of AP after ignition: (a) Al (29 μm); (b) Al/PDF (29 μm); (c) Al (13 μm); (d) Al/PDF (13 μm); (e) Al (1~3 μm); (f) Al/PDF (1~3 μm).

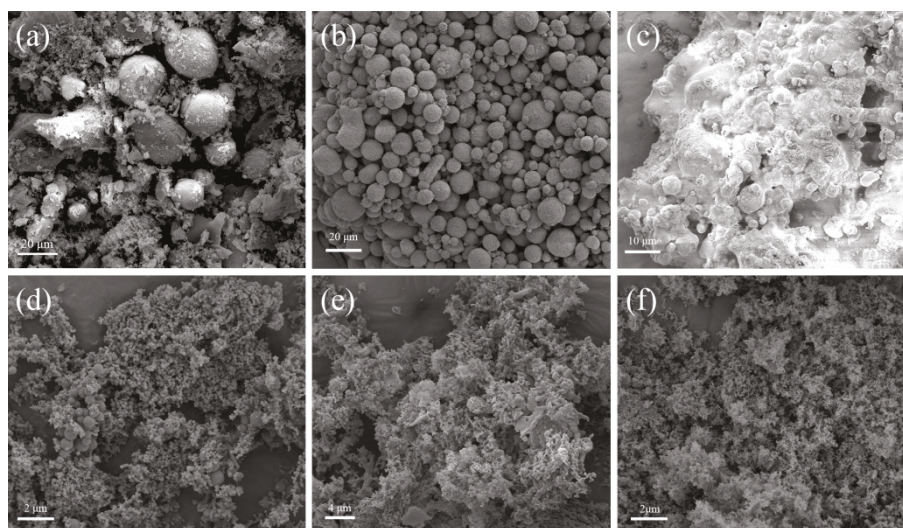


Figure 11. SEM images of collected combustion residues of mixtures of AP: (a) Al (29 μm); (b) Al (13 μm); (c) Al (1~3 μm); (d) Al/PDF (29 μm); (e) Al/PDF (13 μm); (f) Al/PDF (1~3 μm).

4. Conclusions

In summary, the Al/PDF composites with different powder sizes were efficiently synthesized through the solvent/non-solvent method. The corresponding characterization demonstrated that NF₂ with no damage and the PDF content of Al/PDF surface was found to be 7.89 wt% (29 μm), 8.56 wt% (13 μm), and 9.29 wt% (1~3 μm), respectively. Al/PDF has superior hydrophobicity than Al, with the static contact angle increasing by 51.24° (29 μm), 69.47° (13 μm), and 75.96° (1~3 μm). The NF₂ effect of energy release in Al/PDF was studied. The ignition delay of Al/PDF was shortened, and Al/PDF presented more excellent catalytic behavior than Al on AP in DSC curves. The joining of NF₂ in the ignition and combustion of Al/PDF and AP improved the combustion efficiency of Al by proving PY-GC/MS and combustion residues, which detected fluorinated gas compounds and residue particle sizes that were significantly reduced. More impressively, NF₂ of Al/PDF with a powder size of 1~3 μm presented impressive catalytic behavior on AP; the ignition delay and the combustion duration were 15 ms and 1153 ms, respectively. Most importantly, this study highlights the positive impact of NF₂ of Al/PDF composites, prepared through the rapid and efficient method, in enhancing Al energy release, with the ignition and combustion properties of Al/PDF improving significantly.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano14241980/s1>. Figure S1. Statistics of ignition combustion data: (a) ignition delay of Al and Al/PDF; (b) combustion duration of Al and Al/PDF; (c) ignition delay of mix samples (AP and Al or Al/PDF); (d) combustion duration of mix samples (AP and Al or Al/PDF), Figure S2. Chromatograms for AP and Al/PDF at 300 °C, Figure S3. Chromatograms for AP and Al/PDF at 500 °C, Figure S4. EDS of collected combustion residues of mixtures of AP: (a) Al (29 μm); (b) Al (13 μm); (c) Al (1~3 μm); (d) Al/PDF (29 μm); (e) Al/PDF (13 μm); (f) Al/PDF (1~3 μm), Table S1. The main chemical compounds of AP and Al/PDF (29 μm) by PY/GC-MS, Table S2. The main chemical compounds of AP and Al/PDF (13 μm) by PY/GC-MS, Table S3. The main chemical compounds of AP and Al/PDF (1~3 μm) by PY/GC-MS.

Author Contributions: Conceptualization, J.H. and W.Z.; Methodology, J.H. and W.Z.; Software, J.L. and Y.L.; Validation, J.H. and J.L.; Formal analysis, J.H.; Investigation, J.H.; Resources, W.Z. and R.P.; Data curation, J.H.; Writing—original draft, J.H.; Writing—review & editing, J.L., W.Z. and Y.L.; Visualization, J.L. and Y.L.; Supervision, W.Z. and R.P.; Project administration, W.Z. and R.P.; Funding acquisition, W.Z. and R.P. All authors have read and agreed to the published version of the manuscript.

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Article

Assessing Antibacterial Properties of Copper Oxide Nanomaterials on Gut-Relevant Bacteria In Vitro: A Multifaceted Approach

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Abstract

Due to the growth in the application of antibacterial nanomaterials (NMs), there is an increased potential for ingestion by humans. Evidence shows that NMs can induce dysbiosis in the gut microbiota in vivo. However, in vitro investigation of the antibacterial activity of NMs on gut-relevant, commensal bacteria has been neglected, with studies predominantly assessing NM toxicity against pathogenic bacteria. The current study investigates the antibacterial activity of copper oxide (CuO) NMs to *Escherichia coli* K12, *Enterococcus faecalis*, and *Lactobacillus casei* using a combination of approaches and evaluates the importance of reactive oxygen species (ROS) production as a mechanism of toxicity. The impact of CuO NMs (100, 200, and 300 µg/mL) on the growth and viability of bacterial strains was assessed via plate counts, optical density (OD) measurements, well and disc diffusion assays, and live/dead fluorescent imaging. CuO NMs reduced the viability of all bacteria in a concentration-dependent manner in all assays except the diffusion assays. The most sensitive methods were OD measurements and plate counts. The sensitivity of bacterial strains varied depending on the method, but overall, the results suggest that *E. coli* K12 is the most sensitive to CuO NM toxicity. The production of ROS by all bacterial strains was observed via DCFH-DA fluorescent imaging following exposure to CuO NMs (300 µg/mL). Overall, the data suggests that CuO NMs have antibacterial activity against gut-relevant bacteria, with evidence that NM-mediated ROS production may contribute to reductions in bacterial viability. Our findings suggest that the use of a combination of assays provides a robust assessment of the antibacterial properties of ingested NMs, and in particular, it is recommended that plate counts and OD measurements be prioritised in the future when screening the antibacterial properties of NMs.

Keywords: nanomaterials; antibacterial; copper oxide; in vitro; nanotoxicology; reactive oxygen species

1. Introduction

Nanomaterials (NMs) are defined as having at least one dimension < 100 nm [1]. The physicochemical (PC) properties of NMs (e.g., composition, size, and shape) determine their diverse functions (such as antibacterial activity) and have led to their utilisation in various applications such as pharmaceuticals, electronics, diagnostics, cosmetics, and textiles [2–8]. The food industry is a leading exploiter of nanotechnology as NMs can be utilised in agriculture, food processing, nutritional supplements, and packaging [9,10]. For example, titanium dioxide (TiO₂) particles (which have a nano component) can be used as

a pigment in foods [10]. Copper (Cu) NMs are used as pesticides, as they exhibit antifungal and antibacterial properties against many crop plant pests [11]. The antibacterial properties of NMs are also exploited in food contact materials. For example, silver (Ag), zinc oxide (ZnO), Cu, and TiO₂ NMs also function as antimicrobial agents in food packaging [10,12]. In addition, antibacterial NMs can be used in a clinical setting to treat bacterial infections and have been used in wound dressings, implant devices, as antibiotic delivery systems, and in antibacterial vaccines [13,14].

As industries continue to exploit NMs, increased human exposure via ingestion will inevitably occur [15]. For example, NMs can leach from food contact materials (e.g., food packaging) into food, and NMs may contaminate crops when used as pesticides, leading to their accidental ingestion. In addition, inhaled NMs may interact with the gastrointestinal tract (GIT) following mucociliary clearance from the lungs [16–18]. NMs may also be unintentionally ingested due to hand-to-mouth contact (e.g., in an occupational setting or due to their use in consumer products (e.g., wood preservatives) [19]. Furthermore, the increased use of NMs in several consumer products can lead to their release into the environment and contamination of drinking water [20,21]. While most existing studies focus on the antibacterial properties and toxicity of Ag NMs, there is comparatively limited research on other antibacterial nanomaterials such as copper oxide (CuO) [22–26]. This study, therefore, focuses on CuO NMs to address this knowledge gap.

Additionally, toxicology research has also primarily examined the effects of NMs following inhalation; however, as antibacterial NMs are likely to be ingested, they may have a detrimental impact on the gut microbiota to cause adverse health outcomes. Of concern is that ingestion of Cu by humans can disrupt the GIT, inducing abdominal pains, vomiting, and diarrhoea [27]. The gut microbiota is a diverse microbial community within the GIT and plays an essential role in maintaining human health [28,29]. Firmicutes and Bacteroidetes account for 90% of the gut microbiota, with Firmicutes encompassing ~200 different genera, namely, *Clostridium*, *Lactobacillus*, *Bacillus*, *Enterococcus*, and *Ruminococcus* [30]. The commensal bacteria within the gut microbiota are critical to specific host functions [30]. Commensals such as *Enterococcus* spp. and *Escherichia coli* (*E. coli*) colonise and regulate the digestive system and modulate immune responses; *Lactobacillus* spp. also enhance gut barrier integrity [30]. There is an indisputable link between dysbiosis of the gut microbiota and disease pathogenesis, namely, diabetes, liver disease, and obesity, among others [28,29].

Research has shown numerous NMs to have broad-spectrum antibacterial activity against both Gram-negative and Gram-positive bacteria. Ag and ZnO NMs are commonly assessed and have been observed to have antibacterial activity against many bacterial strains, such as *E. coli*, *Bacillus subtilis* (*B. subtilis*), *Pseudomonas aeruginosa* (*P. aeruginosa*), *Staphylococcus aureus* (*S. aureus*), *Salmonella enterica*, *Listeria monocytogenes*, and *Vibrio cholera* [31–40]. Studies have also reported Ag and ZnO NMs to have antibacterial behaviour against antimicrobial-resistant bacterial strains, including methicillin-resistant *S. aureus* (MRSA) and *E. coli* [41–43].

The assessment of antibacterial NMs on the gut microbiota in vivo has increased over recent years; for instance, Zhou et al. (2021) [44] used an in vitro approach to assess the effect of ZnO NMs on the microbial composition of human faecal samples. Following NM treatment, the relative abundance of the genera Firmicutes decreased and Actinobacteria increased with a reduction in bacterial viability overall. An in vivo study orally administered Ag NMs to mice, and 16s rRNA sequencing identified an alteration in the Bacteroidetes/Firmicutes ratio in the gut of NM-treated mice. Bacteroidetes increased from 73% to 85%, and Firmicutes decreased from 26% to 15%, both compared to the control. Notably, *Lactobacillus* in the gut also decreased following NM treatment [45]. Van den Brule

et al. (2016) [46] found mice that were orally exposed to food supplemented with Ag NMs over 28 days displayed an increased ratio of Bacteroidetes to Firmicutes in the gut bacterial community. Other NMs have also received attention for their antibacterial properties, including CuO and TiO₂, albeit to a lesser extent [11,13,22,23,47–49]. One in vivo study found the composition of the gut microbiota of zebrafish was altered following dietary intake of Ag and CuO NMs [24]. Similarly, Swart et al. (2020) [25] showed via DNA isolation, PCR, and 16s rRNA sequencing that earthworms treated with CuO NMs for 28 days presented a shift in the bacterial community of the gut. However, not all studies have found antibacterial NM to induce dysbiosis of commensal gut bacteria. For example, Sizentsov et al. (2018) [26] assessed the effects of Cu and CuO NMs on the probiotic strains *Enterobacterium*, *Lactobacillus*, and *Enterococcus* isolated from the pure intestinal cultures from broiler chickens. No significant alteration in the probiotic bacterial strains at low concentrations of NM exposure was observed, which is postulated to be due to the slow release of Cu ions [26]. Additionally, Pietroiusti et al. (2016) [50] found Cu complexed to chitosan NMs to have antibacterial activity against pathogenic *Salmonella* while not affecting commensal *Lactobacillus*. Wilding et al. (2016) [51] assessed microbial communities in mice via 16s rRNA sequencing 28 days post oral exposure to Ag NMs (20 and 110 nm in size and coated with PVP and citrate). The Ag NMs induced no changes in the structure, diversity, or composition of the gut microbiota. Due to conflicting findings across studies and a lack of assessments on commensal bacterial strains, it is necessary to further evaluate the potential impact of NMs on the gut microbiota.

There are many benefits to using in vitro studies to assess the antibacterial activity of NMs. They allow for the direct evaluation of the potential bactericidal or bacteriostatic effects of NMs, offer enhanced control over experimental conditions, and reduce ethical concerns. There are numerous methods for the assessment of the antibacterial properties of NMs, and some of the most common include disc and well diffusion, microtiter plate assays (e.g., qPCR, live/dead assay, and Alamar Blue assay), optical density (OD) measurements, fluorescent microscopy, and colony plate counts [38,52]. Using a battery of approaches provides a more robust toxicity assessment and allows for a comparison of the sensitivity of different methods as they assess the bacterial response via different mechanisms. In a recent in vitro study, CuO NMs were found to act as an antibacterial agent to a varying degree against pathogenic bacteria (*B. subtilis* > *E. coli* > *S. aureus* > *P. aeruginosa*) [22]. Masri et al. (2022) [22] observed that the methods employed to assess the antibacterial activity of CuO NMs varied in their sensitivity, finding plate counts (time kill assay) and OD measurements to be the most effective. Additionally, Masri et al. (2022) [22] used live/dead fluorescent imaging to assess the antibacterial activity of CuO NM, as it is sensitive and allows for a visual indication of bacterial viability. Similarly, Hossain et al. (2019) [53] utilised a multifaceted approach to assess the antibacterial activity of Ag NMs against both pathogenic and non-pathogenic bacteria in vitro. Plate counts, disc diffusion assays, and OD readings demonstrated Ag NMs to have antibacterial activity against all bacterial strains, with the highest activity against pathogenic *S. aureus*. Sirelkhatim et al. (2015) [52] investigated the antibacterial effect of ZnO NMs on *E. coli* via 24-h OD measurements, finding bacteriostatic inhibition to increase in a concentration-dependent manner. The lack of standard protocols available to assess antibacterial NMs has led to studies varying drastically in their experimental design; for example, NM concentrations, exposure duration, and experimental procedure (e.g., protocol, growth media, and bacterial strain) can influence antibacterial potency [22,26,54]. This makes it challenging to compare results between studies and may explain why there are such conflicting findings across studies.

In vitro techniques also allow for the assessment of the potential toxic mechanisms that underpin the antibacterial activity of NMs. The currently hypothesised molecular

mechanism by which NMs elicit their antibacterial properties includes oxidative stress, the release of toxic ions, and the direct interaction between NMs and the bacterial cell surface [23,34,36,53,55,56]. Numerous studies have highlighted the importance of oxidative stress as a main antibacterial mechanism of action (MOA) of NMs [23,32]. It is hypothesised that ROS and free radicals reduce bacterial cell viability by stimulating a loss of membrane integrity and by promoting pore formation of the bacterial membrane, causing cell lysis [57–59]. Studies suggest ROS generation is directly promoted by NM interactions with bacteria [23,60,61]. For example, Li et al. (2012) [23] observed that *E. coli* K12 viability (using plate counts) reduced to varying degrees depending on NM treatment ($\text{CuO} > \text{TiO}_2 > \text{ZnO} > \text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{Fe}_2\text{O}_3 > \text{CeO}_2$) and demonstrated a correlation between antibacterial activity and increased ROS generation [23]. Kim et al. (2007) [32] reported that Ag NMs generated free radicals, which inhibited the growth of *E. coli* and moderately reduced the growth of *S. aureus*. Zheng et al. (2017) [55] also assessed intracellular ROS production within *Staphylococcus epidermidis* (*S. epidermidis*), *S. aureus*, *B. subtilis*, and *P. aeruginosa* following gold (Au) NM treatment via the DCFH-DA assay, observing a correlation between the antimicrobial effect and ROS production. Overall, while many approaches are available to assess antibacterial NMs in vitro, there are limitations to their use. In vitro methods are still to be standardised, and their suitability and sensitivity for testing NMs still require evaluation [22].

The primary aim of the current study was to evaluate the antibacterial activity of CuO NMs to gut-relevant bacterial strains using a multifaceted approach. More specifically, the antibacterial activity of CuO NMs was investigated via application of a battery of tests, including viability (plate count) assays, optical density (OD) measurements, well and disc diffusion assays, and live/dead fluorescent imaging. By comparing the sensitivity of different assays, we aim to identify which approaches should be prioritised in the future when investigating the antibacterial activity of NMs in vitro. In addition, we aim to evaluate the contribution of ROS generation to the antibacterial properties of CuO NMs to improve the understanding of the mechanisms that drive antibacterial activity. The antibacterial activity of CuO NMs against key gut bacterial (commensal) strains was assessed, namely *Escherichia coli* K12 (*E. coli* K12), *Enterococcus faecalis* (*E. faecalis*), and *Lactobacillus casei* (*L. casei*) (Figure 1). *E. coli* was selected as a representative Gram-negative human gut commensal bacterium that constitutes 0.1–5% of the bacterial community [28]. *E. faecalis* is Gram-positive and was selected as another commensal bacterium of the human gut, which is known to be an opportunistic pathogen [62]. *L. casei* was selected as it is a probiotic commensal bacterium that is integral to host health [26]. By examining both Gram-positive and negative strains, we aim to identify whether Gram-positive or negative bacteria vary in their sensitivity to NM toxicity, as previous studies have found the antibacterial effect of NMs on different bacterial strains varies, with previous studies generally observing Gram-negative bacteria being more susceptible to antibacterial NMs than Gram-positive strains [56,63]. We hypothesise that CuO NMs will induce an antibacterial response and will reduce bacterial cell viability within all bacteria tested, with Gram-negative *E. coli* exhibiting greater sensitivity to NM toxicity. Furthermore, we anticipate that CuO NMs will elevate ROS levels in bacteria to reduce bacterial cell viability.

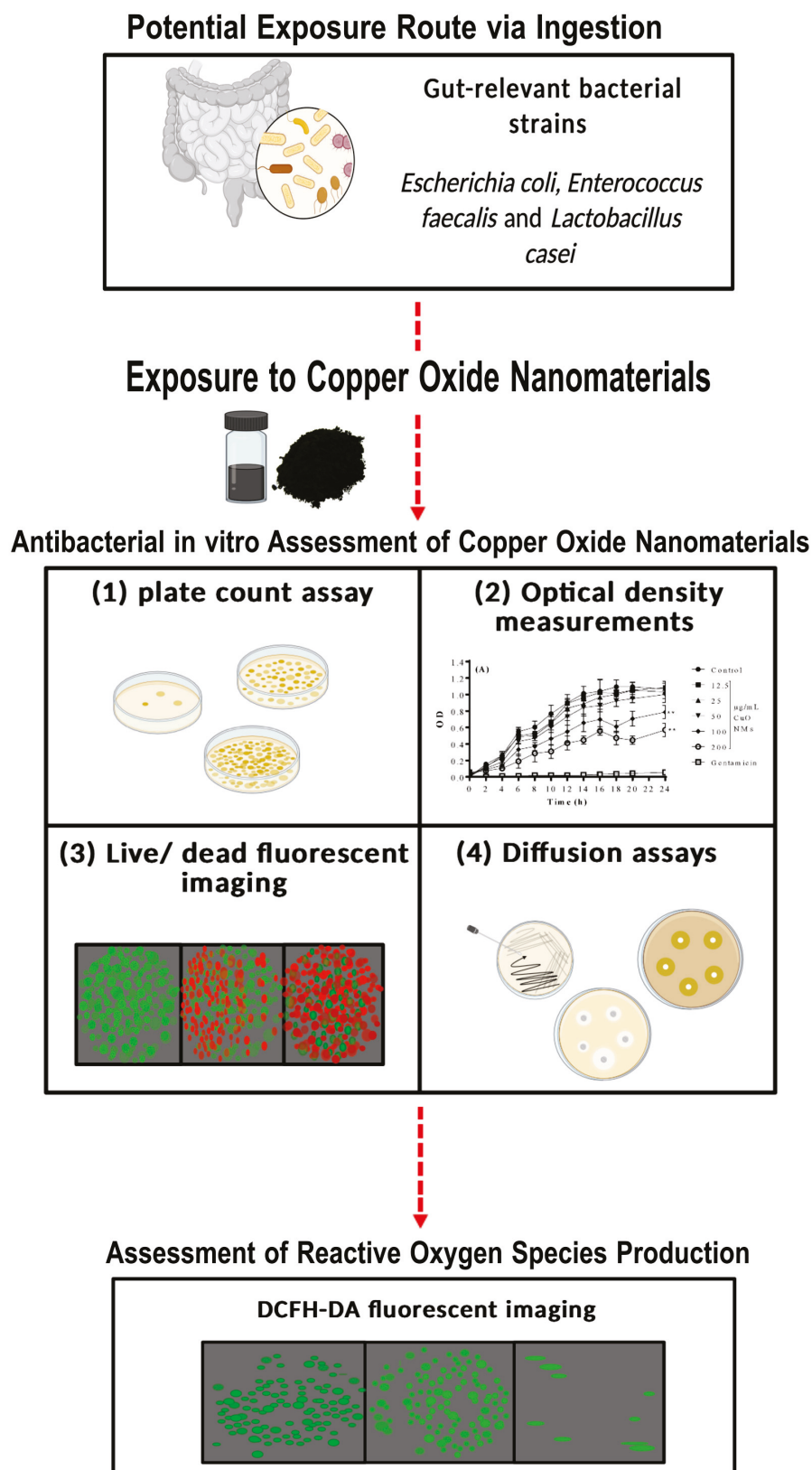


Figure 1. Schematic illustration of the experimental approach used within this study. Gut-relevant bacterial strains were exposed to CuO NMs, and bacterial viability was assessed using a combination of approaches. (1) Plate count assay, (2) optical density measurements, (3) live/dead fluorescent imaging, and (4) diffusion assays. Following this, fluorescent imaging employing a DCFH-DA probe was used to visualise the change in ROS levels in the bacterial cells after CuO NM treatment. Created in BioRender (2025, Edinburgh, UK).

2. Materials and Methods

2.1. CuO Nanomaterial Characterisation

CuO NMs were obtained from PlasmaChem, Gmbh (Berlin, Germany). The manufacturer information data sheet reported the NMs to range in size from 15 to 20 nm, have a specific surface area of 47 m²/g, and have a density of 6.3 g/cm³ employing the Brunauer–Emmett–Teller (BET) method [19]. Comprehensive characterisation of the CuO NMs used in this study has already been reported in previous research [64]. More specifically, the size and morphology of the CuO NMs were characterised by Gosens et al. (2016) [64,65]. Briefly, CuO NMs were analysed via transmission electron microscopy (TEM) (Hillsboro, Oregon, USA) and X-ray diffraction (XRD) (Philips, Eindhoven, Netherlands), with a primary particle size measured of 10 nm and 9.3 nm, respectively. Gosens et al. (2016) [64] and Pantano et al., 2018 [65] present the TEM images of the pristine CuO NMs in their study and demonstrate that the CuO particles agglomerate. Cu dissolution has been assessed previously via inductively coupled plasma optical emission spectrometry (ICP-OES) Faenza, Italy) and was measured at <1.5% at pH 7.4 and ~62% at pH 4.5 in Gamble's solution at 1 and 24 h [64,66]. In the present study, independent characterisation of NM PC properties was performed in sterile distilled water (50 µg/mL) via Dynamic Light Scattering (DLS, Malvern Zeta sizer Nano series) to assess the hydrodynamic diameter, zeta (ζ) potential, and polydispersity index (PDI) of a CuO NM suspension. Measurement of the hydrodynamic diameter reflects the size of nanomaterials in suspension. The PDI is a dimensionless measure of the particle size distribution, and the zeta (ζ) potential reflects the electrostatic surface charge of particles in suspension and is a key indicator of colloidal stability.

2.2. CuO Nanomaterial Preparation

CuO NM stock suspensions were prepared at a concentration of 1 mg/mL using sterile distilled water and bath sonicated (max capacity 1.5 L, ultrasonic power 36 W) for 15 min [22]. Stock suspensions were then diluted in distilled water, Mueller-Hinton broth (MHB), or Tryptone soya broth (TSB) to a concentration range of 100, 200, and 300 µg/mL. NM concentration selection was informed by existing studies [22,67].

2.3. Bacterial Models and Culture Conditions

Escherichia coli (*E. coli*) K12, *Enterococcus faecalis* (*E. faecalis*), and *Lactobacillus casei* (*L. casei*) were utilised as model organisms in this study. Stock cultures of *E. coli* K12 (NCTC 14582), *E. faecalis* (NCTC 775), and *L. casei* (NCTC 13764) were obtained from the National Collection of Type Cultures (NCTC). *E. coli* K12 and *E. faecalis* were cultured and grown in MHB and Mueller–Hinton agar (MHA). *L. casei* was cultured and grown in TSB and Mann, Rogosa, and Sharp agar (MRSA). The bacteria were cultured on a shaking incubator (250 rpm) at 37 °C overnight in aerobic conditions. MHA and MRSA (<20 mL) were poured into Petri dishes (100 mm D × 15 mm H) under sterile conditions (airflow hood) and left to dry. To ensure uniformity of bacteria within all experiments, standardisation of bacteria was performed. Evaluation of the number of CFU for each strain was completed by measuring turbidity at 600 nm using a UV/visible spectrophotometer (Edinburgh, UK). The bacterial suspensions were diluted to a final concentration of ~5.0 × 10⁵ CFU/10 µL in specific culture media (MHB or TSB) for all assays [22]. Culture media was utilised as a negative control and 10 µg/mL gentamicin as a positive control for all experiments.

2.4. Time Kill Assay (Plate Count)

Each bacterial inoculum (10 µL) was added to 190 µL of CuO NM suspensions (100–300 µg/mL) or the positive or negative controls in 1.5 mL Eppendorf tubes. The

bacterial samples were vortexed and then incubated at 37 °C in a shaking incubator (250 rpm) for 2 h. For each bacterial strain, 10 µL of the samples was then diluted via 10-fold serial dilution using sterile distilled water. Following this, 10 µL of each dilution for *E. coli* K12 and *E. faecalis* were plated onto the surface of MHA plates, and 10 µL of each dilution for *L. casei* were plated onto MRSA plates and incubated overnight at 37 °C. The viable bacteria colonies were then counted by CFUs [22].

2.5. Optical Density Measurement

Ten microlitres (10 µL) of each bacterial inoculum was exposed to 190 µL of CuO NM suspensions (100–300 µg/mL) or the positive or negative control in each well of a 96-well plate. To compensate for potential NM interference, NMs in specific culture media (100–300 µg/mL) in the absence of bacteria were also included as a control. The plate was then incubated at 37 °C for 24 h. To quantify the OD, absorption was measured at 600 nm at 2 h intervals for 24 h via UV–Vis spectroscopy (microplate reader) (FLUOstar Omega (version 5.10), BMG LABTECH, Aylesbury, UK). To account for the potential NM interference, OD values of NM interference control were subtracted from OD values in the presence of bacteria. This is essential for appropriate data interpretation, as the optical properties of NMs are known to interfere with results [68]. The data generated a bacterial growth curve for all bacteria strains [67,69].

2.6. Diffusion Assay (Well and Disc)

Diffusion assays were employed to assess the inhibition of bacterial growth via measurement of the zone of inhibition (ZOI) 24 h post-exposure. For both assays, MHA or MRSA Petri dishes were seeded with 100 µL of each bacterial suspension using a sterile cotton spreader. The plates were then dried at room temperature (RT) for 10–20 min. For the well diffusion assay, five wells (6 mm in diameter) were made in the agar plates via a sterile steel-core borer, and the well bases were sealed with 5 µL of molten agar. The wells were then loaded with 50 µL of CuO NMs (100–300 µg/mL) or the positive or negative control. The plates were then dried at RT for 30 min, followed by a 24 h incubation at 37 °C. The ZOI around each well was measured in mm to calculate the actual ZOI. Six mm was subtracted from the ZOI measurement to account for the diameter of the well [70]. For the disc diffusion (Kirby–Bauer) assay, Whatman filter paper antibiotic discs (6 mm) were gently placed on the agar plate. Following this, 10 µL of CuO NMs (100–300 µg/mL) or the negative or positive control were loaded onto paper discs. The plates were incubated for 24 h at 37 °C. The ZOI around each paper disc was measured in mm, and disc diameters (6 mm) were subtracted to calculate the actual ZOI [71].

2.7. Live/Dead Fluorescent Images

A commercially available kit (ThermoFisher (Waltham, MA, USA), LIVE/DEAD TMBa-cLight™ Bacterial Viability Kit, L7012) was employed as per the manufacturer's instructions to perform the live/dead imaging. In a 15 mL Falcon tube, 1 mL of bacterial cells were exposed to 300 µg/mL CuO NMs, positive or negative controls. Cells were then incubated for 2 h, followed by microscopy staining. Fluorescent microscopy was used to image the cells following staining with the live/dead stain using a Leica DM IRBE CLSM (Edinburgh, UK) (100× magnification).

2.8. DCFH-DA Fluorescent Images

The generation of intracellular ROS was qualitatively assessed via fluorescent microscopy. The bacterial strains (1 mL) were incubated in a 15 mL Falcon tube with 300 µg/mL CuO NMs, positive control (10 µM ($\sim 3.4 \times 10^{-5}\%$ w/w) hydrogen peroxide (H₂O₂)), or negative control (untreated cells) in specific culture media for 2 h. Then, the bacterial suspensions

were incubated with the 10 mM 2,7-dichlorodihydrofluorescein diacetate (DCFH₂-DA) probe diluted with methanol for 30 min in the dark. Following this, samples were mounted onto slides, and images were taken at 40× magnification using a Leica DM IRBE CLSM.

2.9. Statistical Analysis

Each experiment was performed as three independent replicates, and data are expressed as average $\pm$ standard error of the mean (SE). All statistical analyses were conducted with Minitab software [version 18]. Data for all assays were screened for normality using the Anderson–Darling test. Parametric data were analysed using an ANOVA, with a Tukey post hoc test identifying differences between the treatment groups. Non-parametric data were subjected to the Kruskal–Wallis test with a Kruskal–Wallis post hoc test. The results were considered statistically significant with a p value of ≤ 0.05 . Details of the statistical analysis performed for each assay are provided in the figure legends for all experiments.

3. Results

3.1. CuO NM Characterisation

The average hydrodynamic diameter of CuO NMs in sterile distilled water was 201.68 nm $\pm$ 4.3. The polydispersity index (PDI) was 0.31 $\pm$ 0.08, and the charge of the CuO particles was neutral with a ζ -potential of 0.005 mV $\pm$ 0.04. Our CuO NMs exhibited a PDI which indicates moderate polydispersity, which is not uncommon in metal oxide nanomaterial suspensions. These specific CuO NMs were selected to reflect a realistic and representative formulation of commercially available CuO NMs, rather than an idealised or artificially stabilised system. Their moderate PDI and neutral surface charge offer a relevant model for how such particles would potentially behave under practical exposure conditions.

3.2. Time Kill (Plate Count) Assay

The viability (plate count) assay found the bacteria to vary in their sensitivity to CuO NMs following a 2 h incubation. CuO NMs induced an antibacterial response in *E. coli* K12 in a concentration-dependent manner (Figure 2). The number of viable *E. coli* K12 was significantly reduced at all tested concentrations compared to the negative control (MHB for *E. coli* K12) ($p < 0.01$) (Figure 2). There was no significant decrease in the viability of *E. faecalis* or *L. casei*, compared to the control (Figure 2). Based on the results of this assay, the toxicity of CuO NMs to the bacteria can be ranked as follows (from most to least sensitive): *E. coli* K12 > *E. faecalis* = *L. casei*. All bacteria exposed to 10 μ g/mL of gentamicin exhibited 100% killing.

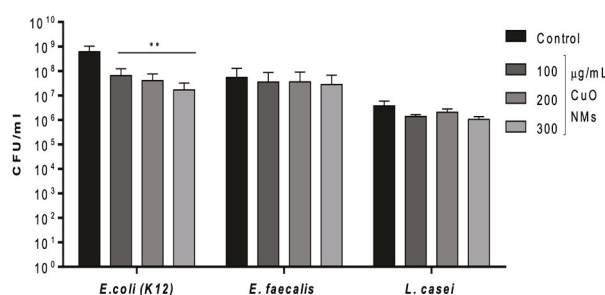


Figure 2. Bacterial growth following 2 h exposure to CuO NMs. *E. coli*, *E. faecalis*, and *L. casei* were treated with CuO NMs at concentrations of 100, 200, and 300 μ g/mL (in MHB or TSB). Viable cell counts were measured by culturing bacterial colonies on MHA (*E. coli* and *E. faecalis*) or MRSA (*L. casei*) plates. A negative control (MHB or TSB) and positive control (10 μ g/mL gentamicin) were also included. Data are expressed as the mean CFU/mL $\pm$ SE ($n = 3$). ANOVA with a post hoc Tukey test was performed with significance indicated by ** = $p < 0.01$ compared to the control.

3.3. OD Measurements

All bacteria exposed to the negative control were observed to have increased OD over time, which is indicative of bacterial growth (Figure 3). CuO NMs exhibited concentration- and time-dependent antibacterial activity against all bacteria, with the strongest growth inhibition observed at 24 h post-exposure (Table 1). Following 24 h of exposure to 300 µg/mL of CuO NMs, *L. casei* displayed the highest sensitivity, while *E. faecalis* showed greater resistance, presenting a 100% reduction and 50% reduction in cell viability, respectively (Figure 3B,C). The inhibition of *E. coli* K12 growth following exposure to 300 µg/mL CuO NM was reduced by 66% when compared to the control (Table 1). Treatment with gentamicin (10 µg/mL) effectively inhibited bacterial growth at all time points (Figure 3).

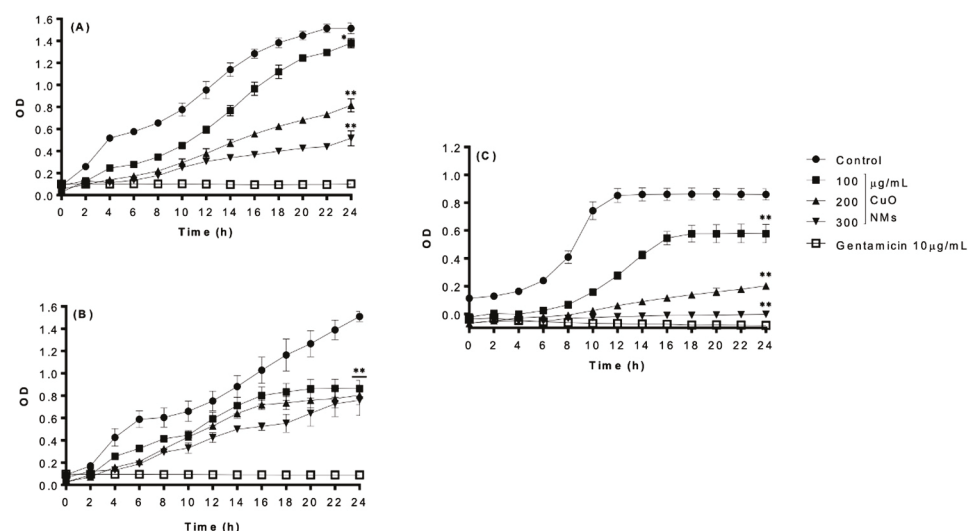


Figure 3. Bacterial growth following exposure to CuO NMs (OD Measurement). Bacterial growth curves of (A) *E. coli*, (B) *E. faecalis*, and (C) *L. casei* following exposure to CuO NMs at concentrations of 100, 200, and 300 µg/mL (in distilled water) for 24 h. Bacteria were also exposed to either 10 µg/mL gentamicin (positive control) or MHB (*E. coli* and *E. faecalis*) or TSB (*L. casei*) (negative control). OD measurements were made at 600 nm. Data are expressed as the mean OD ± SE (n = 3). Kruskal–Wallis or ANOVA with a post hoc Tukey test was performed with significance indicated by ** = $p < 0.01$ compared to the control, with significance indicated by * = $p < 0.05$ and ** = $p < 0.01$ compared to the control at 24 h.

Table 1. Percentage reduction in OD following CuO NM treatment compared to the control at 24 h post-exposure.

Bacteria	CuO NM (100 µg/mL)	CuO NM (200 µg/mL)	CuO NM (300 µg/mL)
<i>E. coli</i> K12	9%	46%	66%
<i>E. faecalis</i>	43%	47%	50%
<i>L. casei</i>	33%	76%	100%

3.4. Diffusion Assays

Interestingly, both the well and disc diffusion assays found CuO NMs to have no impact on bacterial growth, regardless of concentration or bacterial strain. Only gentamicin (10 µg/mL) exhibited inhibition of bacterial growth in both the well and disc diffusion assays (Figure 4). Disc diffusion inhibition zones measured were *E. coli* k12 = 4 ± 1.8 mm, *E. faecalis* = 7.5 ± 2 mm, and *L. casei* = 0.3 ± 1.6 mm. Well diffusion inhibition zones were *E. coli* K12 = 14 ± 1.4 mm, *E. faecalis* = 17 ± 2 mm, and *L. casei* = 4.6 ± 2 mm.

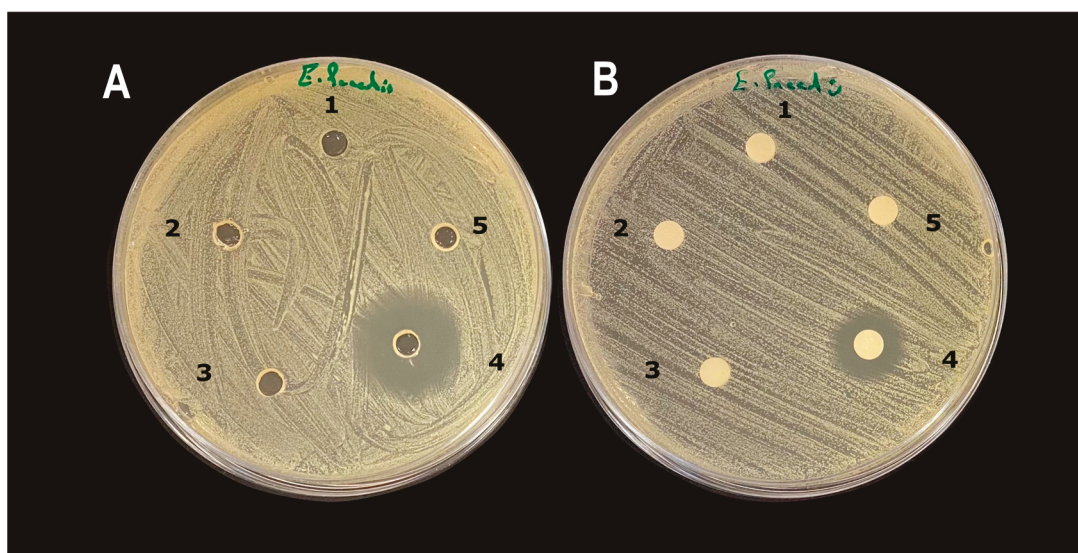


Figure 4. (A) Well diffusion assay and (B) disc diffusion assay inhibition zones of CuO NMs and gentamicin (10 µg/mL) on the growth of *E. faecalis*. (1) CuO NM 100 µg/mL; (2) CuO NM 200 µg/mL; (3) CuO NM 300 µg/mL; (4) gentamicin 10 µg/mL; (5) control (distilled water).

3.5. Live/Dead Fluorescent Microscopy

Fluorescent microscopy was performed to visualise the impact of CuO NMs on bacterial viability using the live/dead assay. The majority of control cells for all bacteria strains were viable (green), with very few or no dead (red) cells (Figure 5A,D,G). The bacterial cells exposed to gentamicin (10 µg/mL) in all bacterial models were almost all dead (Figure 5C,F,I). Following exposure to CuO NMs at a concentration of 300 µg/mL, a decrease in cell viability was observed for all bacteria, with an increased proportion of dead cells observed in all bacterial strains when compared to the control (Figure 5B,E,H). The images suggest *E. coli* K12 appears to be the most sensitive to the toxicity of the CuO NMs, as the highest proportion of dead cells is observed (Figure 5B).

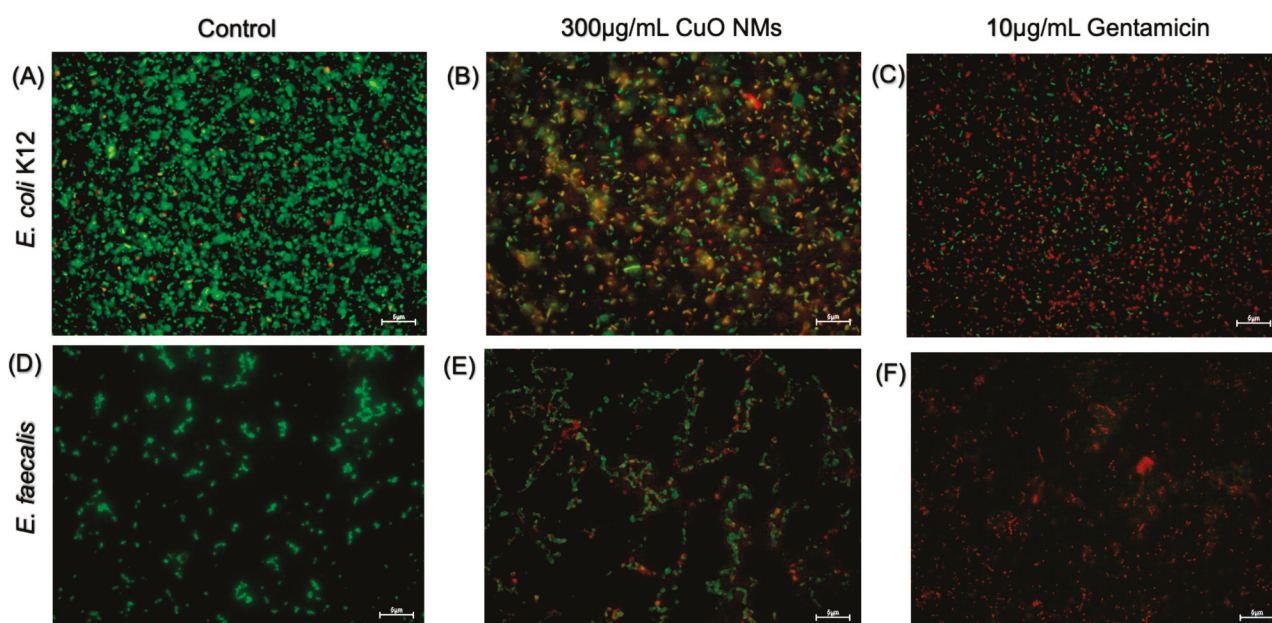


Figure 5. Cont.

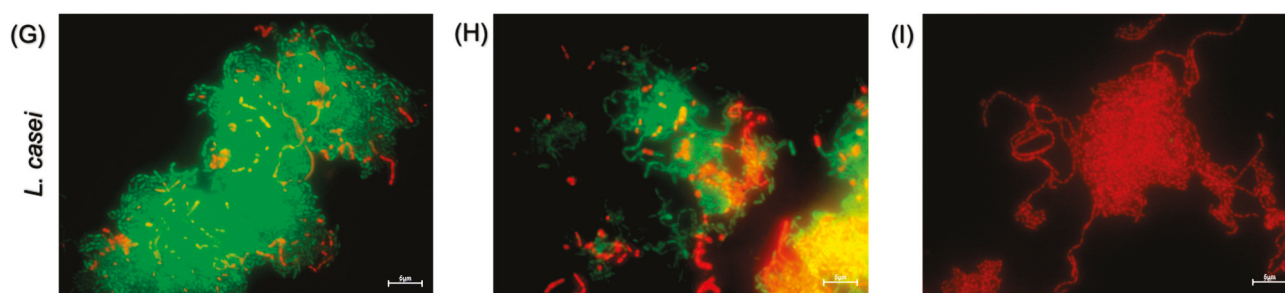


Figure 5. Imaging of live and dead cells following CuO NM exposure. Representative microscopic images of bacteria exposed to MHB or TSB (negative control), gentamicin 10 µg/mL (positive control), or CuO NMs for 2 h. *E. coli* K12; (A) Untreated control (MHB), (B) CuO NM 300 µg/mL, (C) gentamicin 10 µg/mL. *E. faecalis*; (D) untreated control (MHB), (E) CuO NM 300 µg/mL, (F) gentamicin 10 µg/mL. *L. casei*; (G) untreated control (TSB), (H) CuO NM 300 µg/mL, (I) gentamicin 10 µg/mL. Bacteria were stained using the live/dead stain to visualise dead (red) and viable (green) cells. Bacterial cells were imaged at 100× magnification using a Leica DM IRBE CLSM. The scale bar is 5 µm.

3.6. DCFH-DA Fluorescent Microscopy

The DCFH-DA fluorescent probe was used to visualise the impact of CuO NMs on intracellular ROS production. DCFH-DA is taken up by the cell via the cellular membrane. Following this, hydrolysis via cellular esterase converts the probe to DCFH. Intracellular ROS then oxidise DCFH, producing the highly fluorescent DCF molecule [63]. Therefore, the intensity of the DCF (green) fluorescence provides a visual indication of ROS within the bacterial cells. The majority of control cells for all bacteria models displayed weak to no fluorescence (Figure 6A,D,G). The bacterial cells exposed to the positive control (10 µM H₂O₂) in all bacterial models demonstrated the highest fluorescent intensity, thus inducing the greatest production of ROS (Figure 6C,F,I). The fluorescence of bacterial cells following exposure to 300 µg/mL CuO NMs appeared to increase compared to the control; however, not to the same extent as H₂O₂-treated cells (Figure 6B,E,H).

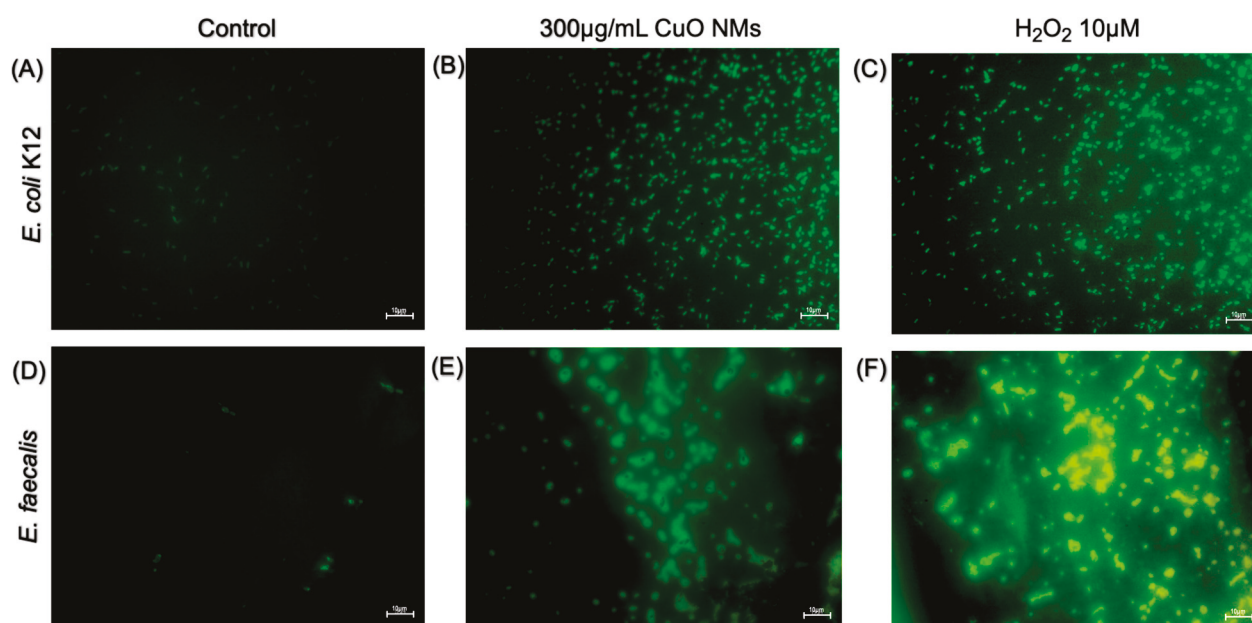


Figure 6. Cont.

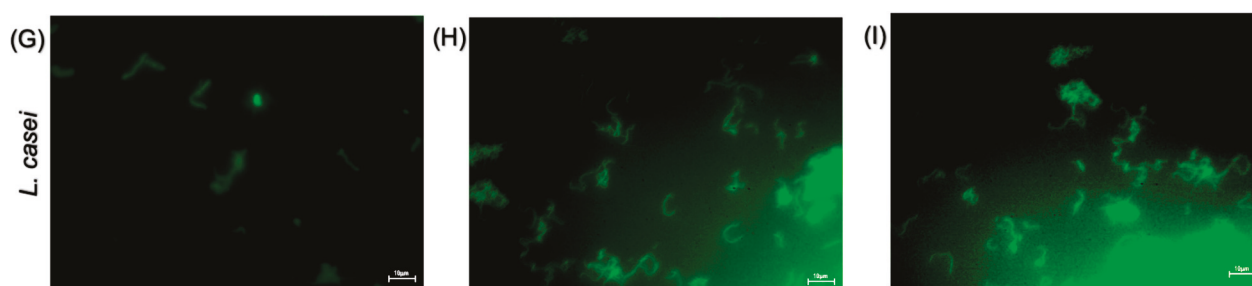


Figure 6. Imaging of intracellular ROS generation by bacterial cells following CuO NM exposure. Representative microscopic images of bacteria exposed to MHB or TSB (negative control), H₂O₂ (10 µM) (positive control), or CuO NMs (300 µg/mL) for 2 h. *E. coli* K12; (A) untreated control (MHB), (B) CuO NM, (C) H₂O₂ *E. faecalis*; (D) untreated control (MHB), (E) CuO NM 300 µg/mL, (F) H₂O₂ 10 µM. *L. casei*; (G) untreated control (TSB), (H) CuO NM 300 µg/mL, (I) H₂O₂ 10 µM. Bacteria were stained using the DCFH-DA probe to visualise ROS generation (green) in bacterial cells. Bacterial cells were imaged at 40× magnification using a Leica DM IRBE CLSM. The scale bar is 10 µm.

4. Discussion

4.1. Impact of CuO NMs on Commensal Gut Bacteria

It is well established that CuO NMs have antibacterial activity and are commonly exploited for this attribute [9,11]. Although increased accidental and intentional ingestion of antibacterial NMs is on the rise within the human population, assessment of their impact on gut resident bacteria using in vitro methods has been overlooked. The present study has found CuO NMs to induce an antibacterial response in both a concentration- and time-dependent manner against three gut-relevant bacteria: *E. coli* K12, *E. faecalis*, and *L. casei*. These findings align with previous in vitro studies; for example, Chatterjee et al. (2012) [72] observed Cu NMs have a bactericidal effect on *E. coli* K12 at a concentration of 7.5 µg/mL, with cell viability decreasing as NM concentration increased. Sizentsov et al. (2018) [26] also found Cu NMs to inhibit the growth of *Lactobacillus*, with increased toxicity at higher concentrations (30 µg/mL). In vivo studies have also found Cu NMs to induce dysbiosis of the gut microbiota. For example, Merrifield et al. (2013) [24] found alterations in bacterial community structure with disruption to commensal bacteria such as *Cetobacterium somerae* in zebrafish following 14 days of dietary intake of Cu NMs (500 mg/kg). Similarly, Cu NMs have been found to induce changes to the microbiome of broiler chickens following oral exposure for 28 days at a dosage of 1.7 mg/kg. Notably decreasing the presence of *Lactobacillus* by 9% when compared with the control [73]. In contrast to the current data, some in vitro studies have observed CuO NMs to have no antibacterial activity against *lactobacillus* even after prolonged exposure to a concentration of 30 µg/mL [26]. Discrepancies between studies are likely to emerge due to differences in the PC properties of the NMs being tested and their experimental design (e.g., NM concentration, media type, time point, and assay employed to assess toxicity).

The bacterial strains used in the current study varied in their sensitivity to CuO NM toxicity. This bacterial-dependent effect is likely due to the varying biochemical features and mechanisms of defence these microorganisms possess, namely surface charge, membrane permeability, and cell wall composition [74]. The current data presents Gram-negative *E. coli* K12 to be more sensitive to CuO NM toxicity when compared with the Gram-positive strains (*E. faecalis* and *L. casei*). This result is in concordance with the literature, with Ayaz Ahmed and Anbazhagan (2017) [63] finding CuO NMs to significantly inhibit the growth of Gram-negative *P. aeruginosa* and *E. coli*, whilst having a limited antibacterial action against Gram-positive *S. aureus*. The thick peptidoglycan layer of Gram-positive bacteria could limit the uptake of NMs and their toxic ions and thus may protect against NM toxicity [75]. Conversely, the anionic surface domains of Gram-negative bacteria may

allow for the binding of NMs [76]. Other studies have found the sensitivity of the bacteria against CuO NMs to be strain-specific and not solely dependent on the Gram type of the bacteria [22,72,74].

Overall, due to the conflicting nature of research assessing antibacterial NMs against gut bacteria, further studies are essential. To further determine if CuO NMs affect gut bacteria, studies should employ an array of (commensal) bacterial strains, e.g., *Lactobacillus* spp., *Bifidobacterium* spp., *Porphyromonas* spp., and *Clostridium* spp., which are resident in the gut. Additionally, future research should consider characterising the surface change of the bacteria by quantifying the ζ -potential via DLS as previously conducted by Halder et al. (2015) [77] or by fusing charged ligands to the bacteria to give them an artificial charge as previously conducted by Feng et al. (2015) [56]. Visualising and quantifying NM interactions with bacterial cells should also be prioritised in the future, as existing studies demonstrate that NMs will interact with the cell surface; for example, Sirelkhatim et al. (2015) [52] employed scanning electron microscopy (SEM) to visualise the interactions between ZnO NMs and *E. coli*, observing morphological changes in the bacteria. This will aid in determining if the biochemical features of the bacteria can influence their susceptibility to antibacterial NM.

4.2. Sensitivity of In Vitro Approaches

In vitro approaches are commonly used to assess the antibacterial effects of NMs, although most studies focus on pathogenic bacteria. Plate counts and diffusion assays are regularly employed to assess antibacterial properties [22]. The present study used a battery of assays that were identified to vary concerning their sensitivity. The plate counts conducted in the current study only found CuO NMs to have a significant antibacterial impact on *E. coli* K12 at all concentrations assessed. Surprisingly, the diffusion assays within the current study lacked sensitivity. Disc and well diffusion assays are commonly used assays and have previously been successfully used to assess the antibacterial activity of NMs [22,78]. The ineffectual response observed in this study may be due to the limited mobility of CuO NMs in agar and their inability to diffuse, which impedes their interaction with the bacterial cells [79]. Previous work assessing the antibacterial properties of CuO NMs has also shown limited results using this approach. For example, Masri et al. (2022) [22] found diffusion assays to detect CuO NM toxicity only at the highest concentrations tested (200 $\mu\text{g/mL}$), with small zones of inhibition (ZOI) measured. Similarly, in another study, *Lactobacillus* and *Enterococcus* strains exposed to CuO NM did not induce any inhibition of growth via the well diffusion assay [26].

OD measurements were successfully used in the present study to investigate the impact of CuO NMs on bacterial cell viability. A recent study also found the cell viability of *E. coli* and *B. subtilis* to be significantly reduced by CuO NMs (200 $\mu\text{g/mL}$) at 4, 8, and 24 h via OD readings [22]. A particular advantage of OD measurements is that they allow for the high throughput, continual assessment of bacterial growth inhibition over time. This is emphasised by the work of Dadi et al. (2019) [67], in which OD measurements were used to determine that *E. coli*, *S. aureus*, and *P. aeruginosa* are most sensitive to CuO NMs during the exponential growth phase. It is worth noting when using OD measurements, appropriate controls are essential, as the optical properties of NM are known to interfere with results [68]. Lastly, the live/dead fluorescent imaging approach found the viability of all bacterial models was reduced by CuO NM exposure, suggesting *E. coli* K12 was the most sensitive strain, which is in agreement with the other assays used. Similar results have also been observed by Masri et al. (2022) [22] using the same live/dead staining method. In the future, it is therefore recommended that plate counts and OD readings be prioritised

when assessing the antibacterial activity of NMs to streamline investigations, as they allow a rapid, efficient, and cheap assessment of toxicity.

4.3. Physiochemical Properties of CuO NMs

The PC properties of NMs (e.g., size, shape, charge, solubility, surface area) influence their interactions with cells and therefore their antibacterial activity [15,80]. As a consequence, the PC properties of NMs are characterised in parallel to assessing their toxicity to identify what PC properties confer toxicity. Furthermore, there is evidence that information provided by suppliers on NM PC properties is not always accurate [81–83] and thus it is prudent to perform an independent characterisation of the PC properties of NMs. The PC properties of the CuO NMs being investigated in our study have been extensively characterised previously [64–66], and so only limited characterisation of the PC properties of the NMs was performed in this study to avoid the duplication of existing research.

The size of NMs directly correlates to their reactivity, with toxicity typically increasing with decreasing particle size [15]. Azam et al. (2012) [84] found the antibacterial activity of CuO NMs to be dependent on particle size, with smaller particles (20 nm) inducing the greatest toxicity against both Gram-positive and Gram-negative bacterial strains. The primary particle size of the CuO NMs investigated in this study is ~10–20 nm [64,65]. However, the hydrodynamic diameter of the CuO NMs was found to be ~200 nm when suspended in water, which suggests that the CuO NMs were agglomerated. This finding is in agreement with other studies in the published literature that have used the same CuO NMs [22,85]. The agglomeration of NMs can influence their interaction with bacterial cells and therefore their toxic potency, and so future studies should conduct studies to visualise the interaction of CuO NMs with bacterial cells, and if deemed necessary, the dispersion protocol used could be modified to reduce the likelihood of NM agglomeration.

CuO NM dissolution is also known to influence their toxicity [86–88]. The solubility of the exact CuO NMs tested in our study has been investigated previously, with evidence that these NMs are highly soluble [64,66]. This suggests that ions rather than particle effects may drive the toxicity of the CuO NMs to bacteria. Indeed, there is evidence that Cu ions can be absorbed by bacterial cells and disrupt many biochemical functions [89,90] and promote intracellular ROS production, which supports our hypothesis [86]. Thus, future studies should therefore evaluate ion release from CuO NMs as it is essential to their antibacterial function using inductively coupled plasma-mass spectrometry (ICP-MS) or ICP-OES to monitor dissolution over time, as this will help distinguish between particle or ion effects [64,91]. In addition, an ionic control, such as copper sulphate, could be included in future experiments to help distinguish between particle- and ion-mediated antibacterial effects.

4.4. CuO NM-Mediated Intracellular ROS Production

It is well established in the literature that NMs mediate ROS production and stimulate oxidative stress [63,86]. The formation of ROS is widely hypothesised to be a key antibacterial mechanism of CuO NMs [13]. Within the present study, there is evidence that CuO NMs generate ROS in all bacterial strains, supporting this proposed MOA. Previous studies employing fluorescent imaging with DCFH-DA probes have found similar results, observing increased ROS production in *S. aureus*, *E. coli*, and *B. subtilis* following CuO NM exposure [63,92]. Given the growing evidence implicating ROS in NM-mediated antibacterial activity, future studies should consider incorporating the DCFH-DA assay to visualise and quantify ROS generation following NM exposure as a critical endpoint in NM toxicity evaluations.

4.5. Conclusions and Future Prospects

In conclusion, the obtained results suggest that CuO NMs induce a time- and concentration-dependent antibacterial response against gut-relevant bacteria. Among the assessed strains, Gram-negative *E. coli* K12 exhibited the greatest sensitivity to CuO NM toxicity. Following a mechanistic assessment of intracellular ROS production via fluorescent imaging using the DCFH-DA probe, all bacterial strains treated with CuO NM demonstrated an increase in ROS production.

Gaining a better understanding of the impact that ingested NMs have on the gut microbiota will help inform potential adverse health outcomes. Indeed, it has been proposed that the assessment of microbiota dysbiosis is a key component of the hazard assessment of ingested NMs [93]. Whilst a reliance has been placed on using in vivo models to assess this hazard outcome, to date, it is advised that in the future in vitro models be used to a greater extent. The use of a combination of assays provides a robust approach to assess the antibacterial properties of NMs in vitro, and it is therefore recommended that OD measurements and plate counts be prioritised in the future when assessing the antibacterial activity of NMs in vitro, as they are consistently identified as being the most sensitive assays. Our study, and those in the published literature, have considered the detrimental impact of CuO NMs on individual strains of bacteria in vitro [22,26]. Future studies should also consider assessing the antibacterial impact of NMs on communities of relevant gut bacteria in vitro to improve the physiological relevance of the test model. For example, a recent study employed an in vitro human gut simulator containing gut microbiota samples from healthy male volunteers to assess the impact of TiO₂ and Ag NMs on bacterial communities. TiO₂ NMs exhibited limited reductions in bacteria density, whereas antibacterial Ag NMs reduced community density by 62% [94]. Agans et al. (2019) [94] also observed no alteration in the community diversity after NM exposure, which may be an indication that although bacterial viability is reduced, gut dysbiosis does not occur. This approach would be beneficial to future assessment, as it allows the interplay between the bacterial strains to be evaluated and tracks the potential recovery of the community following NM exposure. Furthermore, it is prudent for future work to evaluate the antibacterial properties of NM under anaerobic conditions when assessing their impact on the gut microbiota to allow for a more physiologically relevant assessment of toxicity. Indeed, Xiu et al. (2012) [34] observed Ag NMs to be significantly more toxic when studies were conducted in the presence of oxygen.

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Article

Multifaceted Nanocomposites Combining Phosphorylated PVA, MXene, and Cholesteric Liquid Crystal: Design and Application Insights

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Abstract

In this study, composite films based on phosphorylated polyvinyl alcohol (PVA-P), $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, and cholesteryl acetate (ChLC) were designed and characterized to explore their potential in flexible electronic applications. The incorporation of phosphate groups and ChLC enhanced intermolecular interactions, as confirmed with FTIR spectroscopy. Morphological and optical analyses revealed a transition from homogeneous to phase-separated structures with birefringent textures in ChLC-rich films. Thermal studies demonstrated improved stability and increased glass transition and melting temperatures, particularly in samples with higher ChLC content. Mechanical and dielectric evaluations highlighted the tunability of stiffness, flexibility, permittivity, and dielectric losses depending on MXene and ChLC ratios. These multifunctional films exhibit flame-retardant behavior and show promise for use in stimuli-responsive, sustainable electronic devices such as flexible displays and sensors.

Keywords: phosphorylated PVA; MXene; cholesteric liquid crystal; multifunctional nanocomposites

1. Introduction

Progress and innovation in materials science increasingly rely on the development of next-generation materials that integrate multifunctionality, sustainability, and responsiveness to external stimuli such as heat, light, or mechanical stress [1–4]. These features are essential to meet the escalating demands for high-performance materials in advanced applications including flexible electronics [5,6], advanced sensing technologies [7,8], and smart integrated platforms [9,10]. This quest compels the engineering of materials that not only exhibit synergistic assemblage of thermal, mechanical, electrical, and optical properties but also support the Green Deal paradigms, by mitigating ecological footprints through biodegradable, recyclable, or renewable compositions [11,12]. To achieve such objectives, interdisciplinary approaches, forefront synthesis techniques, and nanoscale engineering

are required to tailor material architectures at the molecular and atomic levels, thereby optimizing performance while aligning with the principles of circular economy [13].

Polyvinyl alcohol (PVA), a synthetic polymer renowned for its multifaceted versatility, comes forth as an exemplary polymer matrix for such onward progress due to its exceptional mechanical robustness, inherent biodegradability, and remarkable chemical tunability [14]. Synthesized through the controlled hydrolysis of polyvinyl acetate, PVA possesses a linear macromolecular backbone abounding in hydroxyl groups, which facilitates further chemical functionalization and fosters extensive intermolecular hydrogen-bonding networks [15,16]. These attributes underpin the capacity of PVA to form transparent, mechanically stable, and homogeneous films. Furthermore, PVA's compatibility with an extended spectrum of additives, such as metallic nanoparticles [17,18], carbon-based nanostructures [19], and two-dimensional (2D) nanomaterials like graphene [20] or transition metal carbides (MXene) [21,22], recommends it as a platform of choice for engineering multifunctional nanocomposites [23]. However, pristine PVA lacks intrinsic flame resistance and high functional integration, which limits its application in high-performance electronics. To address these limitations, phosphorylation of PVA introduces phosphorus-containing groups that enhance thermal stability, flame retardancy, and mechanical integrity through stronger intermolecular interactions and crosslinking [24–28]. Nevertheless, phosphorylated PVA alone may not provide the necessary electrical functionality or structural reinforcement required for multifunctional devices.

The incorporation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, a 2D transition metal carbide with outstanding electrical conductivity and mechanical strength, offers a strategic pathway to enhance the functional capabilities of PVA-based systems [15,29,30]. The surface terminations of MXenes ($-\text{OH}$, $-\text{O}-$, $-\text{F}$) promote strong interfacial bonding with phosphorylated PVA, improving dispersion and structural coherence. Additionally, recent studies have highlighted MXene's ability to form ordered structures in dispersions, driven by its anisotropic two-dimensional (2D) morphology, surface chemistry, and inter-flake interactions [31–33]. This self-organization behavior, often observed in aqueous or polar solvent dispersions, results in liquid crystalline phases or aligned assemblies, which significantly influence the microstructural organization and properties of MXene-based composites [34–36].

Cholesteric liquid crystals (ChLCs) are a class of soft matter characterized by their distinctive helical molecular organization, which imparts unique optical and physical properties, making them a subject of increasing scientific interest across diverse fields [37,38]. Polymer-dispersed cholesteric liquid crystals (PDChLCs) constitute a sophisticated subset of liquid crystal (LC)/polymer composites, distinguished by their microphase-separated morphology, where ChLC droplets are homogeneously encapsulated within a porous polymer matrix [39,40]. Thanks to their facile preparation, excellent film-forming ability, and stable optical characteristics, polymer-dispersed liquid crystals (PDLCs) are widely employed in diverse applications, including switchable windows for energy-efficient buildings [41], reflective displays for low-power electronic devices, tunable microlenses, and optical shutters for privacy or light filtering [40].

Despite significant progress in developing individual PVA-based composites, MXene-polymer hybrids, or liquid crystal-polymer systems, the synergistic integration of phosphorylated PVA, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, and ChLCs remains largely unexplored. The research gap lies in understanding how these three distinct components interact at the molecular, interfacial, and macroscopic levels to generate materials with emergent, multifunctional behavior.

In this work, we propose a novel triadic hybrid system comprising phosphorylated PVA as the functional matrix, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as the conductive and reinforcing phase, and cholesteryl acetate as the optically active liquid crystal. This unique combination aims to overcome current limitations in polymer nanocomposites by enabling tunable optical,

dielectric, mechanical, and thermal properties within a sustainable platform. We investigate the structural organization, interfacial interactions, and resulting multifunctionality of these composites, with a view toward next-generation applications such as stimuli-responsive electronics, flexible sensors, and smart visual interfaces.

2. Materials and Methods

2.1. Materials

PVA powder ($M_w = 30,000\text{--}70,000$ Da, degree of hydrolysis = 87–90%) from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany) was utilized to prepare PVA-P via the controlled nucleophilic substitution reaction, wherein the hydroxyl (-OH) groups on the PVA backbone were reacted with the chlorine (-Cl) atoms of phenyl dichlorophosphate, following a protocol established in our previous publications [24,42]. Phenyl dichlorophosphate (purity = 98%) was sourced from TCI Europe (Zwijndrecht, Belgium). *N,N*-Dimethylformamide (DMF) was obtained from Sigma-Aldrich (Taufkirchen, Germany). Cholesteryl acetate and LiCl were purchased from Sigma-Aldrich (Steinheim, Germany). Ti_3AlC_2 MAX phase powder with a particle size $< 40\text{ }\mu\text{m}$ has been acquired from carbon (Ukraine). The minimally intensive layer delamination method MILD (via LiF-HCl etching) with in situ generation of HF, was applied to obtain $\text{Ti}_3\text{C}_2\text{T}_x$ multilayered MXene, while the delamination procedure used Li^+ as intercalant [43]. The preparation and characterization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene were described in our previous papers [34,35].

2.2. Fabrication of PVA-P Film (P0), PVA-P/MXene (P1, P2), and PVA-P/MXene/ChLC Composites (P3–P5)

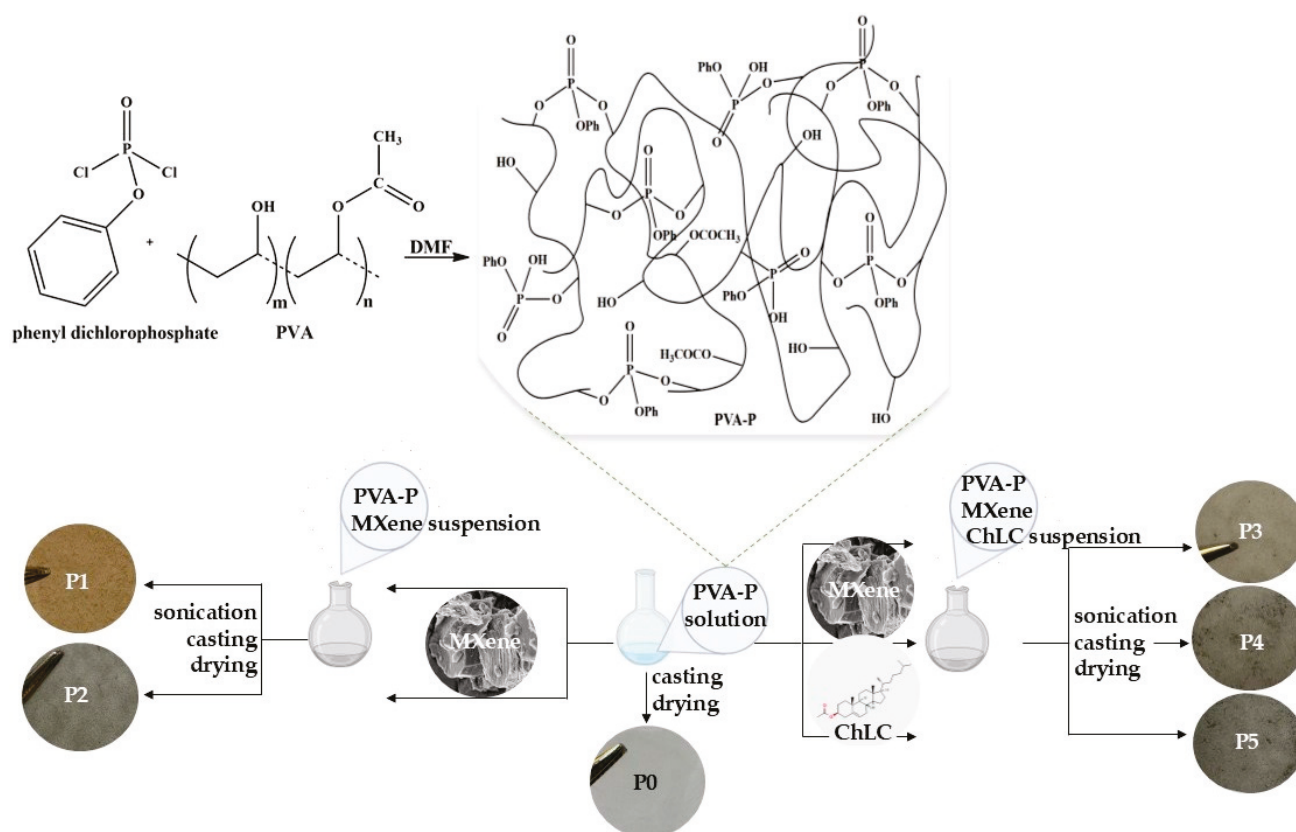
The resulting PVA-P, likely featuring phosphodiester linkages between the PVA backbone and phenyl phosphate groups (Scheme 1), introduces enhanced functionalities, including flame retardancy and thermal stability, critical for advanced applications. Post-reaction purification of PVA-P was performed through dialysis against distilled water over five days to remove unreacted phenyl dichlorophosphate, DMF, and low-molecular-weight byproducts. Then, the product was dried at $60\text{ }^\circ\text{C}$ under vacuum in an oven.

The PVA-P stock solution was prepared by dissolving phosphorylated PVA powder (PVA-P) at a 10% *w/v* concentration in double-distilled water, followed by continuous magnetic stirring at room temperature for 24 h to ensure complete dissolution and a homogeneous solution. The blank sample, denoted P0, was fabricated by casting a specific volume of the PVA-P stock solution onto a Petri dish and then drying it under ambient conditions (room temperature, $\sim 25\text{ }^\circ\text{C}$) for 72 h, yielding a transparent, mechanically stable film (Scheme 1). For composite samples P1 to P5, varying amounts of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene were incorporated into the PVA-P solution, according to Table 1.

Table 1. The composition of the PVA-P film, PVA-P/MXene, and PVA-P/MXene/ChLC composites.

Sample	PVA-P (mL) ¹	PVA-P (%) ²	MXene (mg)/%	ChLC (mg)/%
P0	5	100	-	-
P1	5	96	10/4	-
P2	5	92	20/8	-
P3	5	92	10/4	10/4
P4	5	82	10/3	50/15
P5	5	79	20/6	50/15

¹ A 5 mL solution PVA-P of concentration 10% *w/v*; ² mass percentage relative to the total solid content in the mixtures.



Scheme 1. Schematic representation regarding the preparation of PVA-P-based nanocomposites.

The MXene was uniformly dispersed through magnetic stirring for 30 min, promoting strong interfacial interactions with PVA-P's phosphate groups, which facilitate stable nanofiller dispersion. For samples P3 to P5, a cholesteryl acetate (ChLC) solution (1% *w/v*) in ethanol, a cholesteric liquid crystal derivative, was additionally introduced, and the mixtures underwent further stirring for 30 min to ensure homogeneity, followed by a 2-h degassing step using an ultrasonic bath at room temperature to eliminate entrapped air bubbles, which could otherwise compromise film uniformity and optical clarity (Scheme 1, Table 1). The degassed solutions were then cast onto Petri dishes in controlled volumes to form thin films, dried under ambient conditions for 72 h to achieve stable, defect-free films suitable for further characterization.

2.3. Methods

2.3.1. FTIR Investigation

The chemical structure and molecular interactions of the investigated phosphorylated polyvinyl alcohol (PVA-P)-based composite films, incorporating $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes and cholesteryl acetate (ChLC), were examined using Fourier Transform Infrared (FTIR) spectroscopy performed on a LUMOS Microscope FTIR spectrophotometer (Bruker Optik GmbH, Ettlingen, Germany), equipped with an attenuated total reflection (ATR) accessory, which enables direct, non-destructive examination of solid films by minimizing sample preparation. Spectra were acquired over a broad wavenumber range of $4000\text{--}500\text{ cm}^{-1}$, encompassing key vibrational modes such as O–H, C–H, P–O, and C=O stretches, with a spectral resolution of 4 cm^{-1} to achieve precise peak differentiation.

2.3.2. Morphology of PVA-P Film, PVA-P/MXene Films, and PVA-P/MXene/ChLC Composites

The surface morphology and microstructural characteristics of the phosphorylated polyvinyl alcohol (PVA-P)-based composite films, incorporating $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes and cholesteryl acetate (ChLC) (samples P1–P5), were analyzed using a Verios G4 UC Scanning Electron Microscope (SEM) (Thermo Scientific, Czech Republic), a high-resolution instrument optimized for nanoscale imaging. To mitigate charge accumulation and enhance electrical conductivity during electron beam exposure, the films were coated with a 6 nm layer of platinum using a Leica EM ACE200 Sputter Coater (Leica Mikrosysteme GmbH, Vienna, Austria). This ultrathin platinum coating ensures minimal interference with surface topography while providing sufficient conductivity to prevent imaging artifacts, enabling clear visualization of the composite's microstructural features. The SEM analysis was performed in high vacuum mode, which eliminates atmospheric interference and enhances resolution, utilizing a secondary electron detector (Everhart-Thornley detector, ETD) to capture topographical details with high contrast. An accelerating voltage of 5 kV was employed, balancing the need for sufficient electron penetration to reveal surface and near-surface features with the prevention of beam-induced damage to the polymer matrix.

2.3.3. Optical Microscopy (POM)

The surface appearance and optical characteristics of the samples P0–P5 were investigated with polarized optical microscopy, under perpendicular cross-polarizers, using a Zeiss Microscope Axio Imager A2M (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). This microscope was equipped with a Linkam Plate LTS420 (Honeyrock Lane, Salfords, UK), a precision temperature-controlled stage capable of maintaining stable thermal conditions (ranging from ambient temperature to 120 °C), which facilitated in situ observation of the films' optical behavior under varying temperatures, particularly relevant for assessing ChLC's thermotropic properties. The use of a 10× objective and a 10 °C/min heating-cooling rate enabled multi-scale imaging, capturing both macroscopic film uniformity and microscopic features, such as MXene dispersion, ChLC's chiral organization, and the PVA-P matrix's microstructure. Observations were conducted in polarized light modes, leveraging the Axio Imager A2M's polarizing capabilities to highlight the birefringence of ChLC's helical structure.

2.3.4. Thermogravimetric Analysis (TGA)

The thermal stability and decomposition behavior of the samples P0–P5 were rigorously evaluated using a Mettler Toledo TGA-SDTA851e thermogravimetric analyzer (Columbus, OH, USA), the experiments being conducted under a nitrogen atmosphere to prevent oxidative degradation. A gas flow rate of 20 mL·min^{−1} was maintained to provide a consistent inert environment, minimizing residual oxygen and facilitating the removal of volatile decomposition products. The measurements were performed under dynamic conditions with a heating rate of 10 °C/min, over a temperature range of 25–650 °C. Sample masses ranged from 2.34 mg to 3.89 mg.

2.3.5. Differential Scanning Calorimetry (DSC)

The thermal transitions of the films were investigated using a Mettler Toledo DSC 1 calorimeter (Mettler Toledo, Greifensee, Switzerland). The experiments were conducted under a nitrogen atmosphere with a flow rate of 150 mL·min^{−1}, ensuring an inert environment to prevent oxidative degradation. A heating rate of 10 °C·min^{−1} was applied, consistent with the thermogravimetric analysis (TGA) protocol previously described. The temperature range was from ambient conditions to 150 °C, a chosen range for polymer composites to capture key transitions such as T_g , T_m , and phase changes associated with chosen

ingredients, without exceeding much the onset of significant decomposition ($\sim 130^\circ\text{C}$ for PVA-P). Samples of masses ranging from 2.35 to 3.17 mg were prepared and placed in aluminum crucibles with perforated lids, a configuration designed to allow the release of volatile compounds (e.g., residual water or decomposition byproducts) while maintaining thermal contact with the calorimeter's sensors.

2.3.6. Mechanical Properties

The mechanical properties of the samples were systematically evaluated at room temperature using a Brookfield Texture PRO CT3[®] Texture Analyzer (Brookfield Engineering Laboratories Inc., Middleborough, MA, USA). The testing adhered to the ASTM D882-10 Standard Test Method [44] for tensile properties of thin plastics, ensuring standardized and reproducible results. Two distinct mechanical tests—uniaxial tensile testing and penetration testing—were conducted to assess the films' strength, stiffness, toughness, and resistance to puncture. Uniaxial tensile tests were performed using the TA-RCA module, specifically designed for thin films, on rectangular samples with dimensions of 40 mm length, 10 mm width, and ~ 0.10 mm thickness, reflecting the thin, flexible nature of the PVA-P-based films. A trigger load of 0.067 N was applied to initiate the test, ensuring accurate detection of the onset of deformation, while a tensile rate of 0.5 mm/s was maintained to provide controlled elongation, allowing precise measurement of stress–strain behavior. The Young's modulus (Y), a measure of the films' stiffness, was calculated from the slope of the stress–strain curves within the linear elastic region, specifically between 0.5% and 4% elongation, a range chosen to capture the initial elastic response while avoiding artifacts from sample alignment or slippage. The tests continued until specimen fracture, providing data on ultimate tensile strength (UTS), elongation at break, and other parameters. Penetration tests were conducted on rectangular samples measuring 15 mm $\times$ 15 mm, using a TA-FSF probe with a blunt head to simulate localized puncture resistance, a critical property for flexible electronic substrates exposed to mechanical stress. A penetration force of 44 N was applied at a test speed of 4 mm/s, allowing controlled deformation and accurate measurement of the force required to puncture the films. The tests terminated upon specimen fracture, providing insights into the films' toughness and resistance to mechanical failure. The penetration test results complement tensile data, highlighting the composites' suitability for applications requiring durability under localized stress, such as wearable electronics or protective coatings.

2.3.7. Electrical Properties

The dielectric properties of the phosphorylated polyvinyl alcohol (PVA-P)-based composite films, incorporating $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes and cholesteryl acetate (ChLC), were further characterized using a broadband dielectric spectrometer (Novocontrol Technologies, Montabaur, Germany), an instrument designed for high-precision measurement of dielectric permittivity, conductivity, and relaxation processes across a wide frequency range.

3. Results

3.1. FTIR Analysis

The formation of the P0 network was confirmed with FTIR spectroscopy, as shown in Figure 1. The FTIR spectrum of P0 exhibits a broad and intense absorption band centered at 3350 cm^{-1} , corresponding to the stretching vibrations of non-condensed hydroxyl groups still present along the macromolecular chain. Characteristic absorption bands of aliphatic C–H bonds are observed at 2923 and 2849 cm^{-1} (asymmetric and symmetric stretching vibrations), and at 1425 cm^{-1} (bending vibrations). A distinct band at 1728 cm^{-1} is attributed to residual acetate groups [45]. In addition, absorption bands around 1256 cm^{-1} are at-

tributed to alkyl phosphates $((\text{RO})_3\text{P}=\text{O})$, while weaker bands near 1320 cm^{-1} correspond to aryl phosphate groups $((\text{ArO})_3\text{P}=\text{O})$. Bands observed at approximately 1650 cm^{-1} suggest the presence of acid phosphate structures, such as $(\text{RO})_2(\text{HO})\text{P}=\text{O}$ and/or $(\text{ArO})_2(\text{HO})\text{P}=\text{O}$.

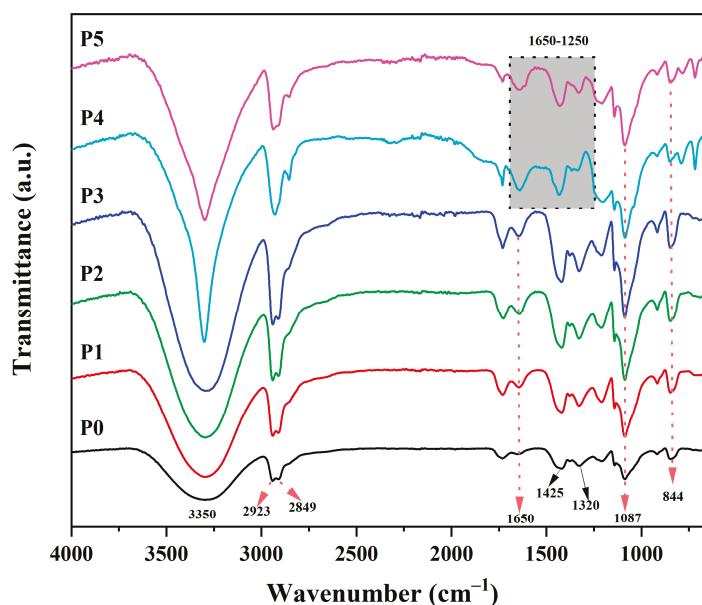


Figure 1. FTIR spectra of the investigated composite films.

Furthermore, bands at 1087 cm^{-1} and 844 cm^{-1} , associated with asymmetric and symmetric stretching of P–O–C linkages, respectively, confirm the formation of phosphate ester bonds. These spectral features collectively support the successful chemical crosslinking of PVA chains via phenyl dichlorophosphate condensation. Given its bifunctional nature, phenyl dichlorophosphate effectively facilitates network formation by introducing a variety of aryl and acid phosphate linkages, as illustrated schematically in Scheme 1. With the incorporation of MXene (samples P1 and P2), subtle shifts and increased definition in the O–H and phosphate-related regions suggest enhanced interaction between MXene and the PVA–P matrix, likely via hydrogen bonding and possible coordination with phosphate groups. Nonetheless, due to the presence of MXenes in the system—compounds rich in –OH, –F, and –O surface groups formed during exfoliation and intercalation—the FTIR spectra of P1 and P2 exhibit broadened O–H stretching bands, slightly shifted toward 3400 cm^{-1} (Figure S1, Supplementary Information). Additionally, the characteristic band at 1087 cm^{-1} becomes more intense, attributed to Ti–O or Ti–O–Ti stretching vibrations. A subtle signal around 619 cm^{-1} confirms the presence of Ti–F groups, further supporting the successful integration of MXene particles into the polymer matrix. Samples P3–P5, which contain both MXene and the liquid crystal additive ChLC, display further spectral changes. Thus, overlapped characteristic bands for $\text{Ti}_3\text{C}_2\text{T}_x$ MXene appeared at $\sim 3400\text{ cm}^{-1}$ (contribution of O–H from surface, Figure S1 Supplementary Information) along with the influences of O–H and C–H interactions coming from the polar, chiral structure of ChLC, which contains acetate and cholesterol side chains, these contributions being more relevant in the samples P4 and P5 when the content of ChLC increased. MXene’s characteristic Ti–O band at $\sim 1100\text{ cm}^{-1}$ shifts slightly in P3–P5, suggesting coordination or interaction with the phosphate groups of the PVA–P matrix $((\text{RO})_3\text{P}=\text{O}$ at 1256 cm^{-1}). The presence of ChLC appears to enhance these interactions, as evidenced by variations in the $1650\text{--}1250\text{ cm}^{-1}$ region, where additional contributions from ChLC’s functional groups (imine or aromatic phosphate moieties) are observed. These changes indicate that ChLC may act as a compatibilizer, facilitating stronger interfacial bonding between MXene and the phosphate groups of PVA–P.

3.2. Morphological Characteristics

Figure 2 displays SEM images of the cross-sectional morphology of composite films (P0–P5). At no MXene content and low MXene content (Figure 2a,b), the films exhibit smooth and uniform surfaces, indicating that the PVA-P matrix forms a continuous phase with well-dispersed MXene sheets. The absence of visible phase boundaries or agglomerates suggests strong compatibility and efficient dispersion at these concentrations.

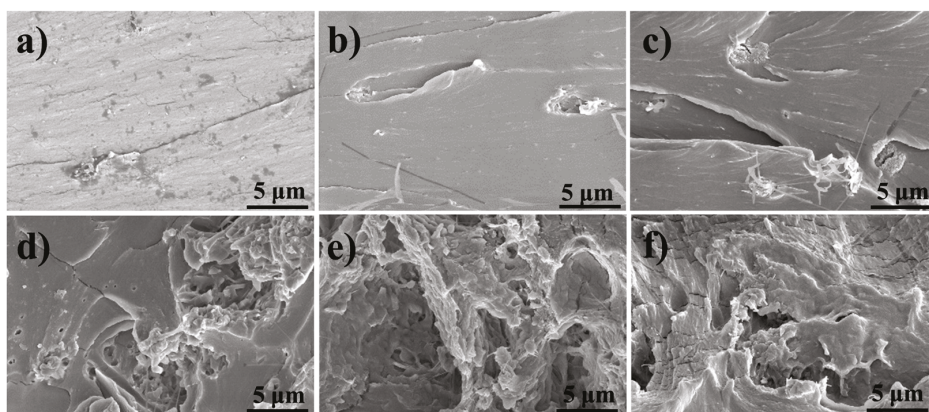


Figure 2. SEM images of the investigated composite films P0 (a), P1 (b), P2 (c), P3 (d), P4 (e), P5 (f).

As the MXene content increases (Figure 3c), layered and overlapping sheet structures become more apparent, reflecting the intrinsic lamellar morphology of MXene. While dispersion remains relatively uniform, the emergence of microvoids and localized accumulations indicates the initial stages of agglomeration at higher MXene loadings. With the incorporation of ChLC into the PVA-P/MXene composites (Figure 2d–f), the morphology changes markedly. The cross-sections display increased surface roughness, numerous voids, microcracks, and evidence of phase heterogeneity. These features suggest poor interfacial adhesion between ChLC and the PVA-P/MXene matrix, due to its scarce solubility in the host fluid, resulting in brittle fracture behavior and structural discontinuities. The observed morphological defects likely arise from phase separation and inadequate interaction at the polymer–ChLC interface, further compromising the mechanical integrity of the composite films. SEM images (Figure 2d–f) reveal that ChLC in P3–P5 is dispersed as phase-separated microdomains, with increased surface roughness, voids, and microcracks indicating poor interfacial adhesion due to ChLC's limited solubility in the polar PVA-P/MXene matrix.

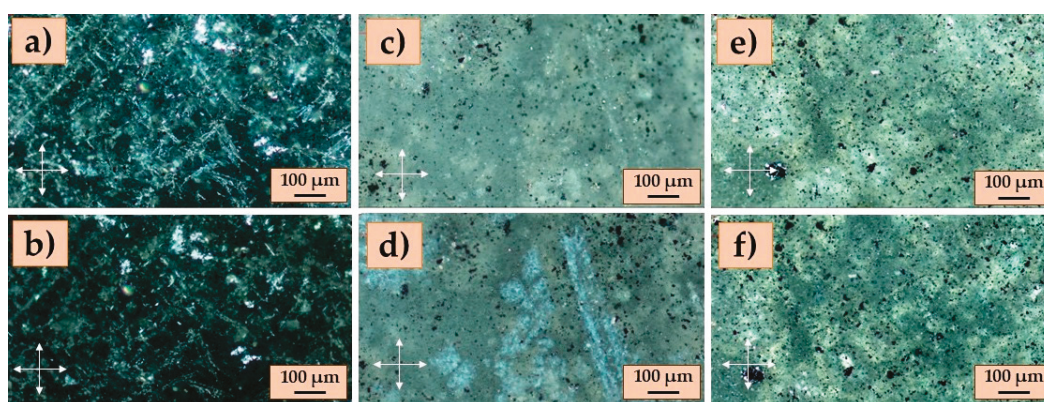


Figure 3. POM microphotographs taken for the samples containing ChLC during the first heating cycle: (a) P3 at 54.3 °C; (b) P3 at 120.1 °C; (c) P4 at 26.6 °C; (d) P4 at 107 °C; (e) P5 at 38.2 °C; and (f) P5 at 120.1 °C.

3.3. Optical Microscopy Observations

POM introspection of the blank sample, denoted P0, consisting solely of phosphorylated polyvinyl alcohol (PVA-P) without the incorporation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes or cholesteryl acetate (ChLC), exhibited expected transparency, under non-polarized mode, P0 appearing as a colorless, smooth, and uniform film with minimal light scattering, indicating a smooth, defect-free surface (Scheme 1, the inset for P0). However, under polarized light, sample P0 revealed a morphology characterized by acicular (needle-like) formations (Figure S2, Supplementary Information), suggesting the presence of internal ordering or oriented crystalline domains within the phosphorylated matrix. These effects can induce localized crystalline domains or oriented structures. Under polarized light, such domains may appear as acicular (needle-like) formations, which are not visible under non-polarized light due to the otherwise uniform and transparent nature of the film [46].

The microscopy observations upon samples having no content of ChLC (P1, P2) revealed surface morphologies with reduced transparency and increased light scattering due to MXene's dark, opaque appearance and nanoscale aggregation, observable along the whole microscopic view, as homogeneously dispersed granular formations, especially at higher loadings (Figures S3 and S4, Supplementary Information).

Figure 3 illustrates polarized optical microscopy images depicting the texture morphology of composite films P3, P4, and P5, which incorporate varying concentrations of cholesteryl acetate (ChLC), in conjunction with $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes within the phosphorylated polyvinyl alcohol matrix. The POM analysis revealed distinct temperature-dependent microstructural dynamics in these ChLC-containing composites. Above the glass transition temperature (T_g , 68–74 °C for P3–P5), heating induced subtle softening or enhanced polymer chain mobility, manifested as refined textural changes under polarized light, likely due to increased segmental flexibility within the PVA-P matrix, as corroborated by differential scanning calorimetry data.

The POM images of P3–P5 (Figure 3) show birefringent textures due to ChLC's chiral molecular structure, but lack characteristic cholesteric LC textures (fingerprint or focal conic patterns) [47,48]. This is attributed to ChLC's confinement within the rigid PVA-P/MXene matrix, which disrupts long-range helical ordering. Phase separation (SEM: voids, microcracks) and steric constraints from the phosphorylated network (FTIR: phosphate bands) limit ChLC to localized birefringent microdomains. The absence of a cholesteric-to-isotropic transition within the studied temperature range (DSC: $T_m = 112$ °C for P4) further stabilizes these domains, preserving birefringence without forming macroscopic cholesteric textures. The birefringent patterns exhibited amplified molecular mobility above 100 °C, reflecting the dynamic reorientation of ChLC's helical domains under thermal stimulation. However, within the investigated temperature range, higher than the ChLC isotropic transition, no phase transitions accompanied by perceptible color shifts or significant alterations in birefringence were observed, indicating that the cholesteric-to-isotropic phase transition of ChLC was not attained [49]. POM birefringent textures (Figure 3) confirm ChLC's anisotropic domains, but their non-uniformity suggests confined microdomains rather than a continuous liquid crystalline phase, with domain size increasing from P3 to P5 due to higher ChLC content. This thermal stability of the optical textures highlights the effective stabilization of ChLC within the PVA-P/MXene matrix, preserving its thermotropic optical functionality and reinforcing the composites' suitability for advanced electronic applications, such as stimuli-responsive displays, colorimetric sensors, or flexible photonic devices, where consistent birefringence under moderate thermal conditions is essential [50].

3.4. Thermal Stability and Decomposition Behavior

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were performed to investigate the thermal stability and decomposition mechanisms of the composite films (P0–P5). The thermal degradation profiles of the composite films are shown in Figure 4a,b, while detailed thermal parameters are summarized in Table 2. The TGA curves of samples P0 to P2 exhibited five distinct mass loss events, whereas P3 to P5 demonstrated six, reflecting the addition of ChLC and its contribution to thermal behavior. The first mass loss, observed around 105 °C for all samples, is attributed to the evaporation of physically adsorbed moisture. The second stage, occurring between 157–167 °C, corresponds to the removal of bound or intrinsic water, often retained within the polymer network or between layered components. The third stage, detected in the range of 201–210 °C, is likely associated with the initial thermal degradation of the polyvinyl alcohol (PVA) matrix, involving chain scission and elimination reactions leading to the formation of volatile products such as water, acetic acid, or other small molecules. This is consistent with earlier studies on partially hydrolyzed PVA [24,51]. In samples P3 to P5, which contain ChLC, an additional degradation event is observed in the range of 286–304 °C. This stage is attributed to the thermal decomposition of ChLC, involving the breakdown of its cholesteric units. In particular, the presence of aromatic or rigid mesogenic units (from ChLC) could locally increase the order of the system, contributing to nucleation phenomena or char formation during decomposition. However, the degradation stage observed between 286–304 °C for samples containing ChLC (P3–P5) is attributed to the thermal breakdown of cholesteryl acetate, which does not significantly enhance thermal stability but rather introduces an additional thermal event. The presence of this stage confirms the successful incorporation of ChLC into the composite matrix. The main decomposition step, between 336–373 °C, corresponds to the concurrent degradation of MXene and further breakdown of the PVA matrix, likely involving dehydroxylation processes and the decomposition of the MXene surface functional groups (e.g., –OH, –F, –O). A second major degradation stage, occurring between 444–450 °C, is attributed to the final decomposition of the polymer backbone, representing carbonization and chain scission of the remaining organic material. The main contributors to enhanced thermal stability appear to be the inorganic MXene sheets, whose barrier effect is reflected in the increased residual mass at 650 °C (Supplementary Note S1). The char yield values of up to 17.77% in samples with higher MXene content (e.g., P2 and P5) confirm this effect. This suggests that the thermal behavior is governed primarily by the filler content and its interaction with the polymer matrix rather than by extensive chemical crosslinking.

Table 2. Thermal data of the composite films (P0–P5).

Sample Code	TGA Data ¹									DSC Data ²	
	T_0	$T_{10\%}$	T_1	T_2	T_3	T_4	T_{max1}	T_{max2}	% Residue	T_g	T_m
P0	128	223	113	167	210	–	336	450	15.02	51	–
P1	115	242	108	162	201	–	373	448	13.53	74	–
P2	129	250	108	166	203	–	365	445	17.77	66	–
P3	109	216	112	161	205	286	373	446	12.25	74	–
P4	108	223	112	157	206	304	360	444	10.36	70	112
P5	108	216	106	157	203	292	364	444	11.71	68	113

¹ T_0 : initial decomposition temperature; $T_{10\%}$: decomposition temperature corresponding to 10% weight loss; T_{1-4} : different steps of weight loss rate; T_{max1} : first step of maximum weight loss rate; T_{max2} : second step of maximum weight loss rate; % residue at 650 °C; ² T_g : glass transition temperature; T_m : melting temperature; T : temperature values in °C.

The materials under investigation exhibited high Limiting Oxygen Index (LOI) values, which are key indicators of flame retardancy. The LOI values were estimated using the

linear equation $\text{LOI} = 17.5 + 0.4 \times \text{CY}$, where CY represents the char yield at 650 °C. Based on this relationship, the LOI values of the samples ranged from 22.18 to 24.61, with sample P2 showing the highest value (Figure 4c). The combination of these compounds significantly influences their thermal and flame-retardant properties. In particular, the incorporation of MXene into the PVA-P matrix enhances both thermal stability and flame retardancy [52].

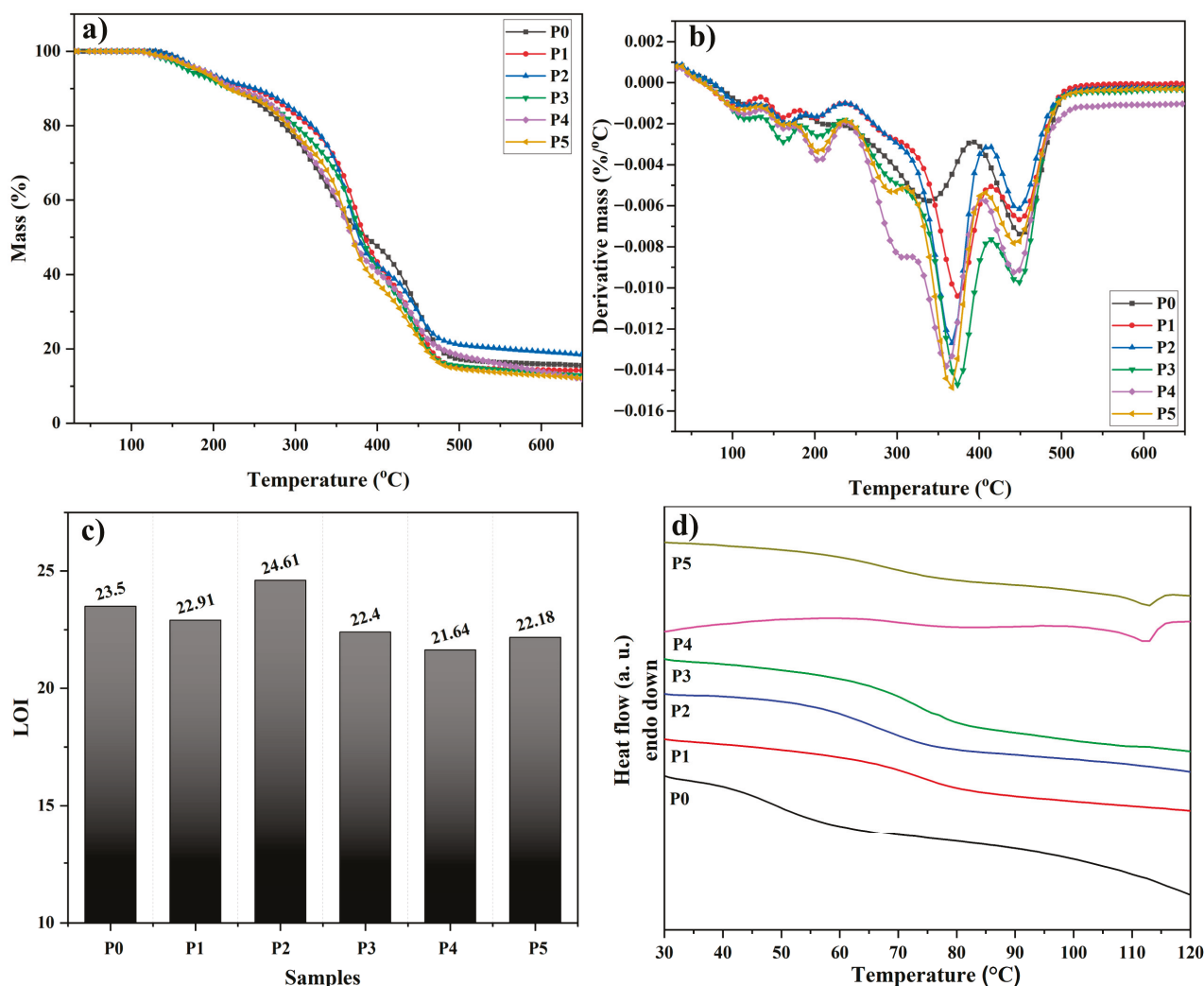


Figure 4. Thermogravimetric analysis (TG) (a) and derivative thermogravimetric (DTG) curves (b), calculated Limiting Oxygen Index (LOI) values derived from char yields at 650 °C (c), and Differential Scanning Calorimetry (DSC) curves of the samples of the investigated composite films (P0–P5) (d).

3.5. DSC Analysis

Differential scanning calorimetry (DSC) was employed to assess the thermal transitions of the phosphorylated polyvinyl alcohol (PVA-P)-based composite films (P0–P5), focusing on the glass transition temperature (T_g) and melting temperature (T_m), in accordance with light of polarized optical microscopy (POM) observations for samples P3–P5 containing cholesteryl acetate (ChLC) (Figure 4d). The DSC analysis revealed T_g values ranging from 51 °C for the blank PVA-P film (P0) to 74 °C for samples P1 and P3, which incorporate $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes and, in P3, ChLC. In P1, T_g increases from 51 °C (P0) to 74 °C due to MXene's 2D structure and strong interactions with PVA-P phosphate groups (FTIR: $\sim 3400\text{ cm}^{-1}$ O–H, $\sim 1100\text{ cm}^{-1}$ Ti–O, $\sim 1256\text{ cm}^{-1}$ P=O), restricting chain mobility. Despite ChLC's plasticizing potential, its low content in P3 forms ordered microdomains (POM: birefringent

textures) stabilized by the MXene–PVA–P network (FTIR: 1087, 844 cm^{-1} P–O–C). This balance offsets plasticization, keeping the glass transition at 74 °C, with MXene’s stiffening effect ($E = 5.88$ MPa in P3) counteracting ChLC’s mobility enhancement [29]. Further increasing the content of ChLC in P4 and 5, T_g drops to 70 and 68 °C, respectively, due to ChLC’s plasticizing effect, reduced crosslinking density, and possible phase separation, which together enhance polymer chain mobility and decrease thermal rigidity. The POM images of P3–P5, showing birefringent textures indicative of ChLC’s chiral helical structure, support these interactions, as the microphase-separated domains observed under polarized light, up to 120 °C suggest ordered ChLC integration that further constrains polymer chain dynamics, particularly above 100 °C where molecular mobility intensifies without altering birefringence [53,54]. Melting behavior was exclusively observed in samples P4 and P5, with T_m values of 112 °C and 113 °C, respectively, suggesting partial crystallinity induced by higher ChLC content, likely due to phase separation of ChLC’s helical domains, as evidenced by the stable birefringent textures in POM images that persist without color shifts or cholesteric-to-isotropic transitions within the tested range.

3.6. Mechanical Analysis

The mechanical properties of the composites in the series were performed, the mechanical behavior of the composites is shown in Figure 5, while the data are presented in Table 3 which provides insights into Young’s modulus (Y), ultimate tensile strength (σ_{ult}), fracture strain (ϵ_f), yield strain (ϵ_y), yield stress ($\sigma_{0.2\%}$), modulus of resilience (M_R), modulus of toughness (M_T), absorbed energy until fracture, and penetration force. These properties reflect the interplay of PVA–P’s phosphoester groups, MXene’s reinforcement, and ChLC’s chiral organization, as corroborated by FTIR, SEM, POM, TGA, and DSC analyses, informing their suitability for advanced applications.

Table 3. Mechanical properties of the P0–P5 composite films.

Sample	Y^1 MPa	σ_{ult}^2 MPa	ϵ_f^3 %	ϵ_y^4 %	$\sigma_{0.2\%}^5$ MPa	M_R^6 kJ/m ³	M_T^7 kJ/m ³	AE ⁸ kJ/m ³	PF ⁹ N
P0	4.85	40.18	49.00	8.27	33.5	168.25	1417.92	1586.17	24.48
P1	3.57	29.96	80.04	6.38	21.07	64.55	2021.69	2086.24	40.86
P2	3.85	33.47	76.48	8.00	29.41	117.97	2252.19	2370.16	44.59
P3	5.88	46.05	42.10	7.60	47.00	201.44	1608.01	1809.45	29.81
P4	1.63	16.96	24.11	2.00	5.65	5.85	311.31	317.76	23.31
P5	2.05	18.00	21.60	7.18	13.75	48.39	250.20	298.59	29.20

¹ Y : Young’s modulus (a measure of material stiffness or resistance to elastic deformation); ² σ_{ult} : ultimate tensile strength (the maximum stress a material can withstand while being stretched or pulled before it breaks); ³ ϵ_f : fracture strain or ductility (refers to the extent to which a material can stretch or elongate before it breaks); ⁴ ϵ_y : yield strain (the amount of strain (deformation) a material experiences at the yield point, which is when it begins to deform permanently under stress); ⁵ $\sigma_{0.2\%}$: yield stress (the amount of stress a material can withstand before it begins to permanently deform); ⁶ M_R : modulus of resilience (the energy a material can absorb elastically without permanent deformation); ⁷ M_T : modulus of toughness (the total energy absorbed before fracture, indicating overall toughness); ⁸ AE: absorbed energy (absorbed energy until fracture); ⁹ PF: penetration force (the force required to puncture the material).

The blank PVA–P sample with a Young’s modulus of 4.85 MPa, σ_{ult} of 40.18 MPa, and ϵ_f of 49.00%, exhibits moderate stiffness and strength, driven by phosphoester-induced hydrogen-bonding, but lower stiffness than pristine PVA (~500 MPa) due to plasticization. Its high M_R (168.25 kJ/m³) and M_T (1417.92 kJ/m³) indicate good resilience and toughness, suitable for flexible substrates, while a penetration force of 24.48 N reflects moderate puncture resistance.

By combining MXene/PVA–P mass ratios of 20 mg/g and 40 mg/g, respectively, in samples P1 and P2, the obtained results of P1 ($Y = 3.57$ MPa, $\sigma_{\text{ult}} = 29.96$ MPa) and

P2 ($Y = 3.85$ MPa, $\sigma_{ult} = 33.47$ MPa) showed reduced stiffness and strength compared to P0, despite MXene's high intrinsic modulus (~ 0.484 TPa), likely due to microagglomeration disrupting the PVA-P matrix. Higher ϵ_f (80.04% for P1, 76.48% for P2) and M_T (2021.69–2252.19 kJ/m³) indicate enhanced ductility and toughness, driven by MXene's layered structure. Penetration forces (40.86 N for P1, 44.59 N for P2) increase with MXene content, reflecting improved puncture resistance. These results are consistent with DSC's T_g increase to 74 °C, suggesting restricted chain mobility. The stress–strain curve of sample P3 (Figure 5a) shows an abnormal plateau region following the yield point, which is indicative of Lüders strain. This phenomenon, commonly associated with localized plastic deformation, may result from internal stress concentrations or heterogeneous filler distribution within the P3 composite. The observed behavior suggests that the P3 formulation facilitates strain localization before uniform plastic flow occurs, which differs from the deformation mechanisms seen in the other samples.

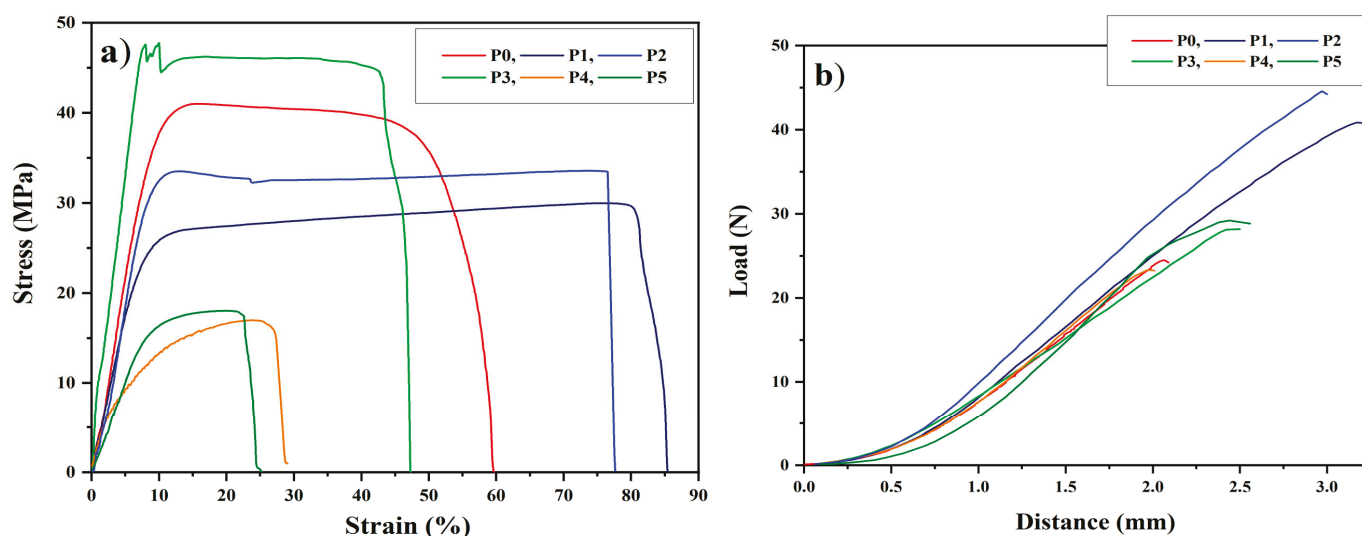


Figure 5. (a) The stress–strain curves and (b) load force as a function of distance curves for the studied composites.

By integrating further the third ingredient, ChLC, into the composite P3 in a MXene/ChLC/PVA-P/mass ratio of 20 mg/20 mg/g, the mechanical properties resulted in the highest stiffness ($Y = 5.88$ MPa) and strength ($\sigma_{ult} = 46.05$ MPa), with ϵ_f of 42.10%, indicating a synergistic MXene-ChLC effect. POM's birefringent textures confirm ChLC's helical domains, enhancing matrix order, while DSC's T_g of 74 °C and FTIR's C=O (~ 1730 cm^{−1}) bands suggest strong interfacial interactions. High M_R (201.44 kJ/m³) and penetration force (29.81 N) support its robustness for sensors or EMI shielding.

Finally, continuing to increase the content of MXene and ChLC, in P4 and P5, resulted in the lowest stiffness and strength (P4 ($Y = 1.63$ MPa, $\sigma_{ult} = 16.96$ MPa) and P5 ($Y = 2.05$ MPa, $\sigma_{ult} = 18.00$ MPa)) with reduced ϵ_f (24.11% and 21.60%) and M_T (311.31–250.20 kJ/m³), due to ChLC's plasticizing effect from phase-separated domains, as seen in POM and DSC's T_m (112–113 °C), indicating partial crystallinity. Penetration forces (23.31–29.20 N) remain comparable to P0, suggesting adequate puncture resistance for flexible displays. It is worth noting that while ChLC introduces chiral ordering that may act as a physical crosslinker at low concentrations (e.g., P3), higher loadings appear to plasticize the matrix and induce cavity formation, reducing mechanical strength. This dual behavior suggests that ChLC's role is highly dependent on its concentration and interaction with both the polymer and MXene phases.

3.7. Electrical Analysis

The dielectric characteristics of phosphorylated polyvinyl alcohol (PVA-P)-based composite films (P0–P5) containing $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes and cholesteryl acetate (ChLC) were assessed (Figure 6). Table 4 provides the real permittivity (ϵ'), imaginary permittivity (ϵ''), dielectric loss tangent ($\tan \delta$), and AC conductivity (σ) at 103 Hz. Due to polar phosphoester groups (FTIR: $\sim 1250\text{ cm}^{-1}$ P=O), which contribute to dipole polarization, and relatively high losses ($\tan \delta$) from amorphous chain relaxations (DSC: $T_g = 51\text{ }^\circ\text{C}$), P0 has moderate permittivity with $\epsilon' = 11.1$, $\epsilon'' = 5.55$, $\tan \delta = 0.498$, and $\sigma = 5.50 \times 10^{-9}\text{ S/cm}$. Because of its low conductivity, it can be used as a baseline dielectric matrix in an insulating polymer.

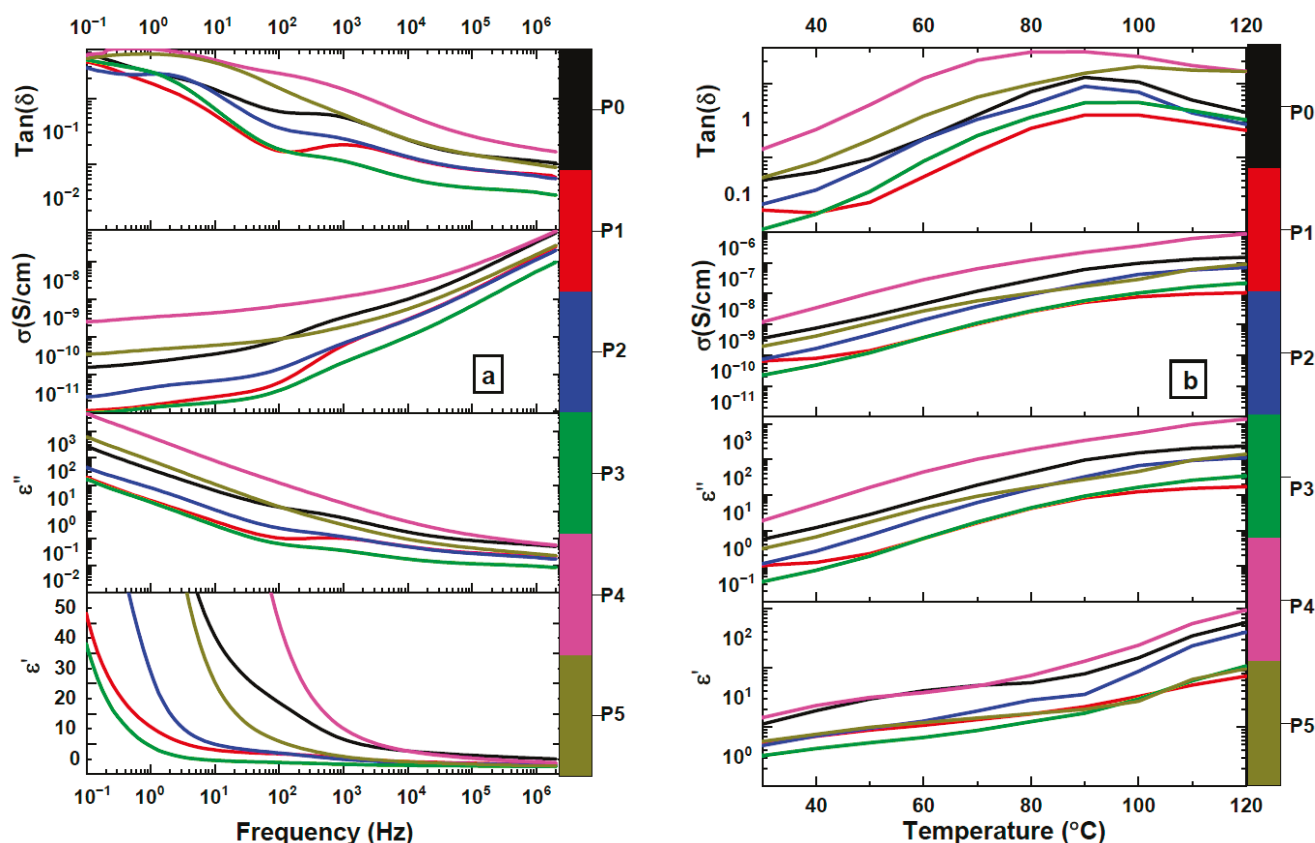


Figure 6. The dielectric permittivity (ϵ'), dielectric loss (ϵ''), conductivity (σ) and loss tangent ($\tan(\delta)$) of the composites as a function of frequency ranging from 10^{-1} Hz and 10^6 Hz at room temperature (a) and function of temperature between 30 $^\circ\text{C}$ and 120 $^\circ\text{C}$ at 103 Hz (b).

Table 4. The electrical properties of the PVA-P film, PVA-P/MXene, and PVA-P/MXene/ChLC composites.

Sample	ϵ' ^a	ϵ'' ^b	$\tan(\delta)$ ^c	σ ^d [S/cm]
P0	11.1	5.55	0.498	5.50×10^{-9}
P1	5.2	1.03	0.197	6.50×10^{-10}
P2	4.8	1.14	0.236	7.23×10^{-10}
P3	3.3	0.35	0.109	2.24×10^{-10}
P4	14.3	18.76	1.307	1.18×10^{-8}
P5	5.7	3.06	0.538	1.93×10^{-9}

^a dielectric permittivity; ^b dielectric loss; ^c loss tangent, and ^d conductivity.

A consistent dielectric response is supported by the smooth, isotropic shape of POM. Despite MXene's high conductivity ($\sim 7750\text{ S/cm}$), P1 ($\epsilon' = 5.2$, $\epsilon'' = 1.03$, $\tan \delta = 0.197$, $\sigma = 6.50 \times 10^{-10}\text{ S/cm}$) and P2 ($\epsilon' = 4.8$, $\epsilon'' = 1.14$, $\tan \delta = 0.236$, $\sigma = 7.23 \times 10^{-10}\text{ S/cm}$)

exhibit lower permittivity and losses when compared to P0. Reduced Young's modulus (3.57–3.85 MPa) indicates low MXene loadings or agglomeration (SEM: granular patterns), which restricts the development of conductive networks. Higher MXene content is reflected in the modest σ rise in P2, although low values still show poor percolation. T_g rising to 74 °C in DSC indicates little chain mobility, which lessens polarization. The lowest ϵ' (3.3), ϵ'' (0.35), $\tan \delta$ (0.109), and σ (2.24×10^{-10} S/cm) are found in P3 (PVA-P/MXene/ChLC), suggesting a minimal dielectric response. This is probably because balanced MXene/ChLC interactions enhance matrix order (POM: birefringent textures) and restrict dipole mobility (DSC: $T_g = 74$ °C). It is appropriate for low-loss dielectric applications such as capacitors due to its high Young's modulus (5.88 MPa), which indicates a stiff, ordered structure that reduces polarizability. P4 exhibits the highest ϵ' (14.3), ϵ'' (18.76), $\tan \delta$ (1.307), and σ (1.18×10^{-8} S/cm). This is due to the high ChLC content that induces phase-separated domains (POM: stable birefringence, DSC: $T_m = 112$ °C), which improves polarizability and conductive pathways. The elevated conductivity in P4 ($\sigma = 1.18 \times 10^{-8}$ S/cm) arises from the high ChLC content, which induces phase-separated domains (POM: stable birefringence, DSC: $T_m = 112$ °C). These domains enhance polarizability and create interfacial regions that facilitate charge transport via hopping or tunneling. Despite ChLC's insulating nature, its chiral, polar structure amplifies the local electric field, synergizing with MXene's conductive clusters to increase σ . This explains the higher dielectric response ($\epsilon' = 14.3$, $\epsilon'' = 18.76$) and losses ($\tan \delta = 1.307$) compared to P0–P3. The moderated values in P5 ($\epsilon' = 5.7$, $\epsilon'' = 3.06$, $\tan \delta = 0.538$, $\sigma = 1.93 \times 10^{-9}$ S/cm) point to an ideal ChLC/MXene ratio. Plasticization is indicated by low Young's moduli (1.63–2.045 MPa), which correlate with higher dielectric losses and make them perfect for flexible, high-permittivity devices such as EMI shielding.

The low conductivity in P1 and P2 reflects poor MXene plate interconnection due to low loadings or agglomeration (SEM: granular patterns), hindering percolating networks. In P4, high ChLC content partially disperses MXene plates, forming localized conductive clusters that increase σ (1.18×10^{-8} S/cm). Microcavities, potentially arising from agglomeration (P1, P2) or phase-separated interfaces (P4), reduce effective permittivity and increase losses by introducing air gaps or charge-trapping sites. In P3, the ordered matrix (POM: birefringent textures, high Young's modulus = 5.88 MPa) minimizes microcavities, ensuring low losses ($\tan \delta = 0.109$). These findings highlight the critical role of MXene dispersion and matrix morphology in optimizing dielectric performance.

These characteristics complement FTIR, SEM, POM, TGA, DSC, and mechanical investigations and indicate their suitability for electronic applications such as capacitive sensors or EMI shielding. They also show how the conductivity of MXene and the polar, chiral structure of ChLC affect the PVA-P matrix.

4. Discussion

This study demonstrates the successful development and comprehensive characterization of PVA-P-based nanocomposites incorporating MXene and cholesteryl acetate (ChLC), aimed at applications in advanced electronic devices. The integration of chemical, morphological, optical, thermal, mechanical, and dielectric analyses provides a holistic understanding of how MXene and ChLC modulate the matrix's structure and performance.

- FTIR confirmed effective crosslinking in PVA-P and revealed hydrogen bonding and coordination between MXene surface groups and phosphoester moieties. ChLC introduced additional interactions, contributing to a more complex bonding network.
- SEM and POM showed a progression from smooth morphologies (P0–P2) to phase-separated, birefringent structures (P3–P5), driven by ChLC's poor solubility and chiral organization. These optical features are stable up to 120 °C, making P3–P5 promising for stimuli-responsive and colorimetric applications.

- TGA and DSC analyses demonstrated enhanced thermal stability and higher glass transition and melting points in MXene- and ChLC-containing composites. Residual char and increased Tg suggest improved flame retardancy and restricted chain mobility.
- The composites exhibited tunable mechanical behavior. P3 showed optimal stiffness and strength due to MXene-ChLC synergy, while P4–P5 offered greater flexibility attributed to ChLC's plasticizing effect—favorable for flexible electronics.
- Dielectric analysis revealed P3's low losses and P4's high permittivity, driven by structural order and ChLC domains, respectively.

Overall, the PVA-P/MXene/ChLC composite films (P3–P5) demonstrate high efficacy for dielectric, mechanical, and photonic applications, driven by synergistic interactions among components. The triad achieves low dielectric loss ($\tan \delta = 0.109$, $\epsilon' = 3.3$ in P3) for capacitors, high permittivity ($\epsilon' = 14.3$, $\sigma = 1.18 \times 10^{-8}$ S/cm in P4) for EMI shielding, and balanced properties ($\epsilon' = 5.7$, Young's modulus = 1.63 MPa in P5) for flexible sensors. ChLC's chiral helical structure enhances polarizability and birefringence, while MXene's conductivity (~ 7750 S/cm) amplifies charge transport via interfacial polarization (FTIR: ~ 3400 cm^{-1} O–H, ~ 1100 cm^{-1} Ti–O shifts). ChLC improves MXene dispersion (SEM: reduced agglomeration in Figure 2d–f), and MXene stabilizes ChLC microdomains, mitigating phase separation. PVA-P's crosslinked matrix (FTIR: 1087, 844 cm^{-1} P–O–C) ensures structural stability, balancing MXene's rigidity (P3: 5.88 MPa) and ChLC's plasticization (P4, P5: 1.63–2.045 MPa). This synergy yields special efficacy, surpassing binary PVA-P/MXene (P1, P2: low $\epsilon' = 5.2$ –4.8, $\sigma = 10^{-10}$ S/cm) or PVA-P/ChLC systems (high losses, brittle fracture). The triad validates the hypothesis that combining a phosphorylated polymer, conductive MXene, and chiral ChLC can produce multifunctional composites with tailored properties for capacitors, EMI shielding, and photonic devices, offering a novel approach compared to prior polymer/LC or polymer/MXene systems.

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Article

Quantum Diamond Microscopy of Individual Vaterite Microspheres Containing Magnetite Nanoparticles

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Abstract

Biocompatible vaterite microspheres, renowned for their porous structure, are promising carriers for magnetic nanoparticles (MNPs) in biomedical applications such as targeted drug delivery and diagnostic imaging. Precise control over the magnetic moment of individual microspheres is crucial for these applications. This study employs widefield quantum diamond microscopy to map the stray magnetic fields of individual vaterite microspheres (3–10 μm) loaded with Fe_3O_4 MNPs of varying sizes (5 nm, 10 nm, and 20 nm). By analyzing over 35 microspheres under a 222 mT external magnetizing field, we measured peak-to-peak stray field amplitudes of 41 ± 1 μT for 5 nm and 10 nm superparamagnetic MNPs, reflecting their comparable magnetic response, and 12 ± 1 μT for 20 nm ferrimagnetic MNPs, due to distinct magnetization behavior. Finite-element simulations confirm variations in MNP distribution and magnetization uniformity within the vaterite matrix, with each microsphere encapsulating thousands of MNPs to generate its magnetization. This high-resolution magnetic imaging approach yields critical insights into MNP-loaded vaterite, enabling optimized synthesis and magnetically controlled systems for precision therapies and diagnostics.

Keywords: NV centers; vaterite; magnetic imaging; quantum sensors; nanoparticles

1. Introduction

Vaterite particles, a naturally occurring mineral form of polycrystalline calcium carbonate (CaCO_3), are both biocompatible and biodegradable, making them promising candidates for targeted drug delivery [1–5]. Their mesoporous spherical structure allows the embedding of diverse materials, such as metal nanoparticles or biomacromolecules [6,7]. The high loading capacity of these particles increases their potential for targeted and sustained drug delivery [8]. Additionally, upon exposure to solvents, vaterite undergoes a phase transition to calcite, facilitating the controlled release of the embedded materials [9]. When vaterite particles are loaded with magnetic nanoparticles, their applicability extends to medical imaging, targeted drug delivery, and hyperthermia [10]. MNPs such as magnetite (Fe_3O_4) embedded in vaterite microspheres enable controlled movement and displacement using magnetic fields, making them suitable for precision drug delivery. The

high porosity of vaterite microspheres allows them to host significant amounts of Fe_3O_4 , with a reported loading capacity of 11 mass% [11]. Research by N. Markina et al. [12] and B. V. Parakhonskiy et al. [13] has demonstrated their potential in magnetic separation, movement, and displacement for biomolecule detection. MNP-embedded vaterite particles with highly uniform composition and magnetic properties would greatly benefit these applications. Uniformly magnetized Fe_3O_4 -vaterite particles would allow more precise control over drug delivery and hyperthermia therapy. However, commercially available tools for quantitative magnetometry at the single-particle level with micrometer resolution are rather complex and rare. Advanced characterization techniques, while potentially useful, are often prohibitively expensive, require complex maintenance, or are simply nonexistent. To enable rapid screening and optimization of nanoparticles, customized tools need to be developed.

The magnetic properties of Fe_3O_4 MNPs have been extensively studied using various techniques, including vibrating sample magnetometry [14,15], superconducting quantum interference device (SQUID) [16,17], and Mössbauer spectroscopy [18,19]. These methods provide valuable insights into the bulk magnetic behavior of MNP ensembles. However, the magnetic field of MNPs within an individual vaterite particle remains largely unexplored. While techniques like micro-SQUID magnetometry [20], scanning magnetic microscopy [21], Brillouin light scattering [22], Lorentz electron microscopy [23], and magnetic force microscopy [24] offer the potential for single-particle magnetic imaging, they often face limitations in sensitivity for detecting the weak magnetic fields of individual particles or require specific, sometimes challenging, operating conditions.

Recently, widefield quantum diamond microscopy (QDM) has been developed to map magnetic fields with high sensitivity and submicron spatial resolution [25,26]. This technique relies on the optical detection of electron spin resonance from Nitrogen-Vacancy (NV) centers in diamond. The NV centers in a diamond have a well-characterized electronic structure that is sensitive to magnetic fields and can be examined using Optically Detected Magnetic Resonance (ODMR) spectroscopy under ambient conditions [26,27]. By depositing individual particles directly onto the diamond surface, optical spatial resolutions as fine as 400 nm can be achieved [26]. QDM has been used to map stray magnetic fields from ferrimagnetic [28,29], superparamagnetic [30,31], and paramagnetic MNPs [26,32]. While small magnetite nanoparticles are typically superparamagnetic at room temperature and generate strong signals near NV centers, this does not apply to larger Fe_3O_4 -functionalized vaterite microspheres, which produce weaker stray fields. In these microspheres, most MNPs are expected to be micrometers away from the NV layer. Since the dipole magnetic field rapidly decays with distance, studying the magnetic field associated with MNPs within individual vaterite particles remains both a challenge and an opportunity to explore more strategies for magnetically responsive platforms.

In this study, we used widefield QDM to investigate the stray magnetic fields (B_{str}) of Fe_3O_4 MNPs (5 nm, 10 nm, and 20 nm) embedded within vaterite microspheres. Applying an external magnetizing field of 222 mT, we mapped the stray fields and measured the peak-to-peak (PP) amplitudes of the magnetic signals from >35 individual vaterite microspheres, ranging in size from 5 to 10 μm . These measurements allowed us to correlate the observed stray fields with both the MNP and vaterite microsphere sizes, independently estimated using optical microscopy. Furthermore, we compared the measured magnetic maps with simulated maps generated by finite-element analysis of homogeneously magnetized microspheres. This comparison served to assess the uniformity of magnetization within the vaterite microspheres due to the embedded MNPs. Our study demonstrates a novel approach for investigating the magnetic fields of Fe_3O_4 MNPs in biogenic minerals such as vaterite, offering new insights into their magnetic properties and potential applications.

2. Experimental Methods

2.1. Synthesis of Fe₃O₄-Loaded Vaterite Microspheres

The Fe₃O₄ MNPs were synthesized via the co-precipitation method to achieve specific sizes (10 ± 2 nm and 20 ± 2 nm) while preserving their ferromagnetic properties via ultrasonication-assisted synthesis [33]. The particle sizes were confirmed using transmission electron microscopy (TEM). Additionally, 5, 10, and 20 nm particles dispersed in toluene with ultra-low dispersion were purchased from Merk, and those dispersed in DIW with PEG on their surface were obtained from NNCrystal Ltd., Fayetteville, AR, USA. The magnetization (M) of the Fe₃O₄ MNPs ranged from 1.55 to 2.59×10^6 A/m for 5 nm particles [34], 3.27 to 3.64×10^6 A/m for 10 nm particles [35], and 3.8 to 4.7×10^5 A/m for 20 nm particles [34]. The 5 nm and 10 nm Fe₃O₄ MNPs exhibited strong superparamagnetic behavior, whereas the 20 nm particles displayed ferrimagnetic properties with moderate magnetic susceptibility.

Vaterite particles were synthesized using a conventional co-precipitation reaction procedure with slight modifications. Briefly, a stock solution of 1 M calcium chloride (CaCl₂) and 1 M sodium carbonate (Na₂CO₃) solutions was mixed after dilution to 0.3 M with and without addition of polystyrene sulfonate 70k at 1 mg/mL, achieving a more polar surface and larger particles. Mixing of the solutions stopped after 1 min, and then the particles were washed with DI water followed by three EtOH washes. The sample was then dried or kept in EtOH for storage. Smaller particles were achieved through using controlled synthesis in ethylene glycol 85%, as shown previously [5]. The characterization of the resulting CaCO₃ particles, including their size and porosity, is described in detail by Barhum et al. [5]. The addition of MNPs to vaterite involved 15 min of vortexing, followed by 1 h of sonication, then another 15 min of vortexing and an additional 1 h of sonication. Then, the particle solutions were left for a few minutes to rest and the remaining MNPs in solution were removed, and EtOH was added then the particles were washed three times through centrifugation. The pore size, surface charges, and channel structure of the vaterite particles influenced the incorporation and distribution of Fe₃O₄ MNPs within them. Figure 1a depicts a schematic representation of the process by which a spherical, porous vaterite microsphere (dark gray) is loaded with Fe₃O₄ MNPs (black dots) from a suspension (gray). Prior to loading, the MNP and vaterite suspensions were sonicated for 1 minute to ensure uniform dispersion. Subsequently, the particles were rinsed with ethanol to remove residual water and dried at 60 °C for 3 h under air convection. The dried Fe₃O₄-vaterite powder (approximately 90 mg) was stored in polyethylene test tubes under ambient conditions. For magnetic imaging, the Fe₃O₄-vaterite microspheres were resuspended in 99.8% pure ethanol, vortexed for a few seconds, and drop-casted onto the surface of a diamond sensor.

High-resolution transmission electron microscopy imaging of the edge of a vaterite microsphere loaded with 10 nm Fe₃O₄ MNPs is shown in Figure 1b. The MNPs appear as dark spots within the microsphere, with an estimated density of 50–90 MNPs per 200 nm² area. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 1c) confirms the presence of iron (Fe) and oxygen (O) within the microsphere, alongside calcium (Ca) from the vaterite matrix, with the iron distribution appearing concentrated closer to the surface. An EDS line scan collected along the path marked by the white arrow in Figure 1c is shown in Figure 1d, revealing that calcium exhibits the highest intensity counts due to the vaterite matrix, while iron and oxygen show lower intensity counts. Notably, the iron signal displays a prominent peak near the surface, indicating that the Fe₃O₄ MNPs are primarily embedded closer to the microsphere's outer region. Figure 1e shows a scanning electron microscopy (SEM) image of an individual magnetic vaterite microsphere, highlighting its porous surface morphology. These microspheres are expected to possess

channel-like internal pore structures with sizes ranging from 30 to 50 nm, as supported by previous studies [36]. The synthesized vaterite particles are predominantly spherical, though some exhibit slight elongation, with diameters ranging from 2 μm , as observed in both the SEM image (Figure 1e) and the optical microscopy image of vaterite microspheres drop-casted onto a glass coverslip (Figure 1f). Microsphere batches showed monodisperse size distributions, as reflected by the polydispersity index values below 0.05 for all samples. This indicates good batch homogeneity in terms of particle diameter.

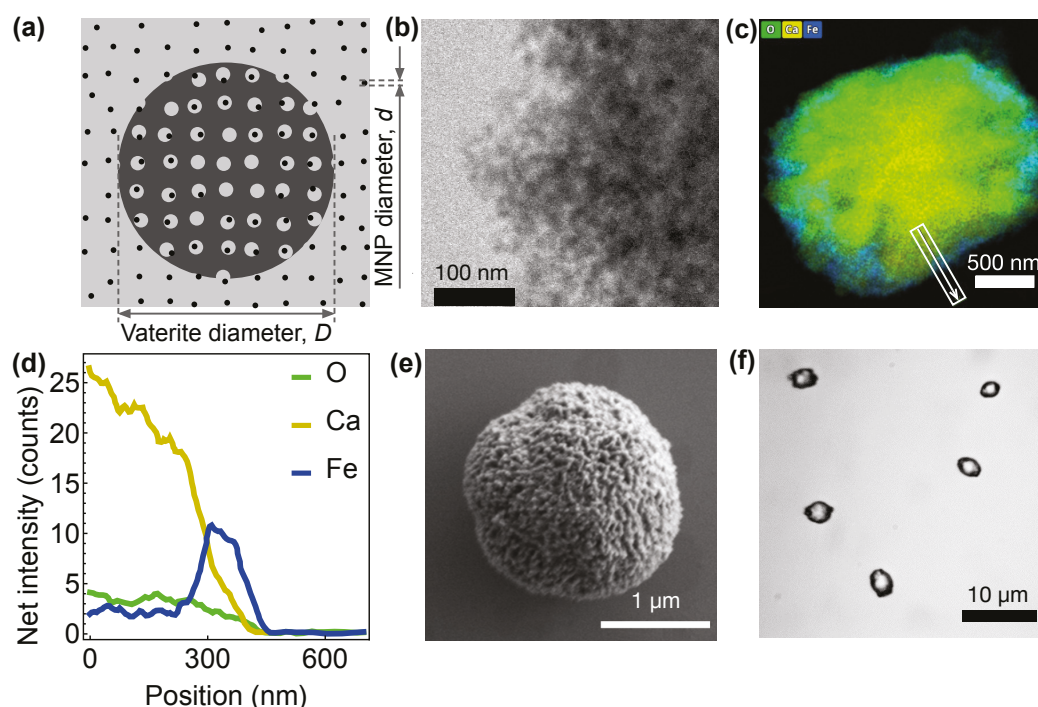


Figure 1. Characterization of vaterite microspheres loaded with Fe₃O₄ magnetic nanoparticles. (a) Schematic illustration of a porous vaterite microsphere (dark gray) loaded with Fe₃O₄ MNPs (black dots) dispersed within its structure from the surrounding suspension (gray). (b) High-resolution TEM image of the edge of a vaterite microsphere, revealing the presence of 10 nm Fe₃O₄ MNPs. (c) Energy-dispersive X-ray spectroscopy (EDS) elemental mapping of an entire magnetic vaterite microparticle. (d) Quantitative elemental analysis of the microsphere's surface collected along the arrow shown in (c), displaying the relative abundance of O, Ca, and Fe. (e) Scanning electron microscopy (SEM) image of a vaterite microsphere loaded with 20 nm Fe₃O₄ MNPs, highlighting its surface morphology. (f) Optical microscopy images of individual vaterite microspheres drop-casted onto a glass coverslip, observed using a 100 $\times$ oil immersion objective.

2.2. Quantum Diamond Microscopy

The custom-built widefield QDM is based on the design detailed in Ref. [26], with additional improvements for rapid inline data processing [37] and automated control [38] of an external magnetic field capable of reaching up to 222 mT. For convenience, we provide a concise overview of the measurement setup and highlight the modifications implemented to study magnetic microspheres.

The sensor employed in this study is fabricated from a high-pressure high-temperature type-Ib monocrystalline diamond (Sumitomo Electric) with dimensions of $2 \times 2 \times 0.06 \text{ mm}^3$, grown along the (110) crystal plane and featuring an initial nitrogen concentration of $\sim 100 \text{ ppm}$. NV centers were created by implanting $^4\text{He}^+$ ions at a dose of $10^{12} \text{ He}^+/\text{cm}^2$ and energies of 5 keV, 15 keV, and 33 keV to achieve a uniform vertical vacancy distribution. After implantation, the diamond underwent a two-step annealing process: first at 800 $^\circ\text{C}$ for 4 h, followed by a second step at 1100 $^\circ\text{C}$ for an additional 4 h. This treatment facilitated

the intracrystalline migration of vacancies and the formation of NV centers. This procedure is described in detail in Ref. [38] for the F1 sample, resulting in an NV center concentration of ~ 6 ppm and the formation of a ~ 200 nm NV layer near the diamond surface.

Figure 2a–c illustrate the principles of the ODMR technique utilizing negatively charged NV centers in diamond (Figure 2e). The electronic energy levels of the negatively charged NV center consist of a ground state (3A_2) and an excited state (3E), both of which are spin-triplet states (Figure 2a). The 3A_2 ground state exhibits a zero-field splitting of $D \approx 2.87$ GHz between the $m_s = |0\rangle$ and $m_s = |\pm 1\rangle$ spin sublevels, arising from electron spin–spin interactions. When the diamond is illuminated with 532 nm green light, electrons in the ground state are excited through vibronic levels of the lattice to the 3E state while preserving their spin projections. The excited triplet system can relax either radiatively ($^3E \rightarrow ^3A_2$), emitting fluorescence in the range of 600–800 nm, or nonradiatively via intermediate singlet states. Under continuous green light excitation, the unequal probabilities of nonradiative relaxation from different excited sublevels lead to optical spin polarization into the $m_s = |0\rangle$ ground-state sublevel. Electrons polarized in this state are more likely to undergo radiative relaxation, contributing maximally to the fluorescence intensity. However, when a microwave (MW) field with a frequency resonant to the $m_s = |0\rangle \leftrightarrow m_s = |\pm 1\rangle$ ground-state transition is applied, a significant portion of the spin population is pumped into the $m_s = |\pm 1\rangle$ sublevels. This results in a switch to nonradiative relaxation pathways under continuous green light excitation, leading to a decrease in fluorescence intensity. By sweeping the MW frequency around the resonant frequency, Lorentzian-shaped dips in the fluorescence intensity are observed (Figure 2b). Applying a bias magnetic field B_0 lifts the degeneracy of the $m_s = |\pm 1\rangle$ states due to the Zeeman effect. For a magnetic field $B_0 = B_{||}$ aligned along one of the NV axis orientations (e.g., the [111] crystallographic axis of the diamond), the transition frequencies f_+ and f_- of the $m_s = |0\rangle \leftrightarrow m_s = |\pm 1\rangle$ states shift linearly with the magnetic field (Figure 2c). These frequencies are given by $f_{\pm} = D \pm \gamma B_{||}$, where $\gamma \approx 28$ GHz/T is the electron gyromagnetic ratio. Since the zero-field splitting D is sensitive to temperature and strain [27], it is eliminated by measuring the frequency difference $f_+ - f_- = 2\gamma B_{||}$, which provides an absolute measure of the magnetic field $B_{||}$. For magnetic fields $B_{||} > 102.5$ mT, the ground-state spin level anti-crossing [39] must be considered, and the equation $2\gamma B_{||} = f_+ + f_-$ is used instead (Figure 2c). Thus, magnetic field $B_{||}$ is optically detected using the ODMR technique by observing the corresponding shifts in the fluorescence intensity dips (Figure 2b).

The QDM is operated on a standard vibration isolation optical table in a climate-controlled laboratory environment. Figure 2d shows a schematic representation of the epifluorescence QDM setup. MW frequencies f_+ and f_- are generated using a Stanford Research Systems SG384 frequency generator and delivered via two parallel copper wires (diameter = 0.11 mm). The studied Fe_3O_4 -vaterite microspheres are positioned in a ~ 0.3 mm wide gap between these wires. The diamond sensor is pressed against a glass coverslip (thickness = 100 μ m) by the MW wires. The coverslip is mounted on a three-axis motorized stage (Newport, Irvine, CA, USA, Picomotor 8742), which is controlled through a USB interface. A pair of diametrically magnetized permanent magnet cylinders, equipped with electromechanical rotation control and ferrite flux homogenizers [38], is used to apply a magnetic field $B_{||}$ up to ± 222 mT. The NV centers in the diamond sensor are continuously excited over an area of $\sim 30 \times 30 \mu m^2$ (top surface of the sensor) through the coverslip using a 532 nm green laser (Sprout-G-10W, Lighthouse Photonics Inc., San Jose, CA, USA) with a power of ~ 200 mW. The laser light is focused through a $100\times$ microscope objective with a numerical aperture of 1.25 ($100\times/1.25$ Oil, $\infty/0.17$, ZEISS, Jena, Germany). The emitted red fluorescence is collected by the same objective and spectrally separated using a

dichroic mirror (DMLP567R, Thorlabs, Newton, NJ, USA) and a long-pass filter (Thorlabs FEL0600). The fluorescence is then delivered via a tube lens (Thorlabs TTL200) to either an sCMOS sensor of an Andor Neo 5.5 camera or an avalanche photodiode detector (Thorlabs APD410A). The photodiode detector is connected to a digital oscilloscope (Yokogawa DL6154, Yokogawa, Tokyo, Japan) for faster tuning and alignment (trimming) of the NV axis along the magnetic field B_0 . The same QDM setup can also be used to obtain optical images by collecting white light delivered through the same objective and reflected from the sensor surface and the magnetic vaterite microspheres on it.

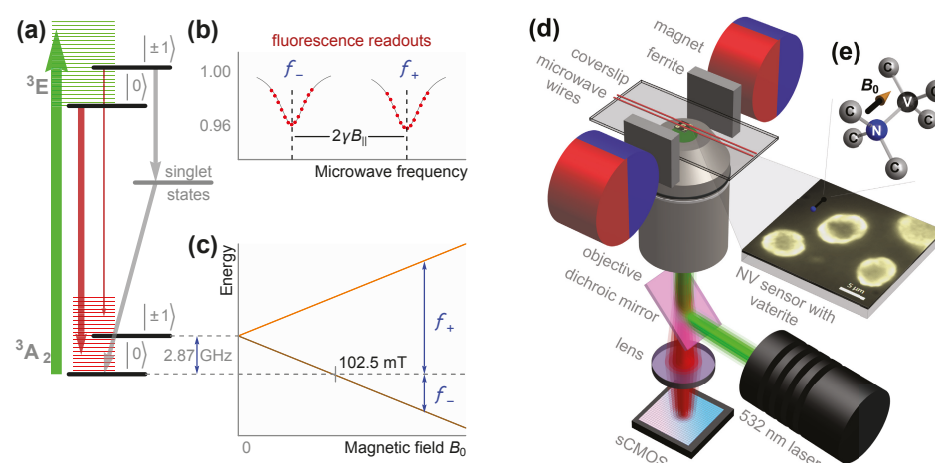


Figure 2. Quantum diamond microscope (QDM) for magnetic imaging using NV centers. (a) Energy level diagram of the NV center in diamond, showing optical excitation (green arrow), spin-dependent fluorescence (red), and nonradiative decay via singlet states (gray). (b) Optically detected magnetic resonance (ODMR) spectrum, where fluorescence readout reveals resonance dips at frequencies f_+ and f_- split by the magnetic field. (c) Zeeman splitting of the NV center ground state as a function of the applied magnetic field (B_0). (d) Schematic of the QDM, including magnets, microwave wires, an optical detection system, and an NV sensor with vaterite microspheres. (e) Atomic structure of the NV center and an optical image of the NV sensor detecting vaterite microspheres.

The MW sweeps are triggered by a pulse from the Andor Neo 5.5 sCMOS camera, Andor Technology Ltd., Belfast, UK, which records twelve 400×400 pixel frames per sweep. Twenty series of frames are accumulated and processed using a LabVIEW 2022 virtual interface, NI Corporation, Austin, TX, USA, where they are converted into a single magnetic image of B_{str} —the additional magnetic field component along the NV axis due to the sample—over an area of $26 \times 26 \mu\text{m}$ using a weighted average method [37]. The magnetic images are accumulated over ~ 5 min to reduce noise, while fast inline processing minimizes the impact of ODMR drift during accumulation. The saved magnetic images are further analyzed using Wolfram Mathematica, Champaign, IL, USA. The finite-element analysis was carried out in COMSOL Multiphysics 6.2, COMSOL Inc., Burlington, MA, USA using the Static Magnetic Fields interface. Stray magnetic fields from uniformly magnetized spherical shells were integrated over a 200 nm thick layer positioned tangent to the shell surface, with a geometry that mimicked the NV sensing layer in diamond.

3. Results and Discussion

3.1. Magnetic Imaging of Individual Particles

In three samples of vaterite microspheres containing Fe_3O_4 MNPs (diameters of 5 nm, 10 nm, and 20 nm), we identified >35 individual vaterite particles using reflective optical imaging under white light illumination. All microspheres exhibit nearly spherical shapes with diameters of several micrometers, while the depth of field of the microscope objective

is approximately one micrometer. To assess particle size, we adjusted the image plane to the center of the microspheres, maximizing the apparent size of the particle. This approach yields a sharp image of the surface along the sphere's great circle, while the rest of the sphere's surface appears blurred and dark. Two representative vaterite microspheres are shown in Figure 3, left panels. Throughout the subsequent text, we designate them as Microsphere A (Figure 3a) and Microsphere B (Figure 3b).

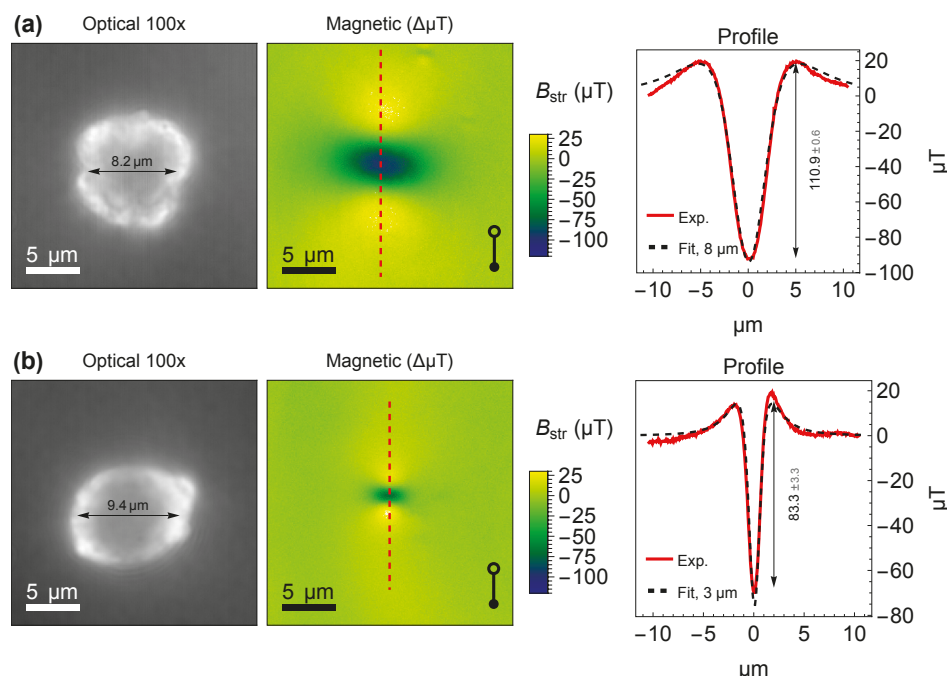


Figure 3. Optical and magnetic imaging of vaterite microspheres with quantum diamond microscopy. (a) Optical (left) and magnetic (middle) images of a vaterite microsphere uniformly functionalized with 20 nm Fe_3O_4 magnetic nanoparticles. The corresponding magnetic field profile (right) along the red dashed line reveals a symmetric dipole-like signal with a PP amplitude of $110.9 \pm 0.6 \mu\text{T}$. (b) Optical and magnetic images of a vaterite microsphere exhibiting non-uniform magnetization, functionalized with 10 nm Fe_3O_4 MNPs. The magnetic profile shows a weaker and more localized field distribution with a PP amplitude of $83.3 \pm 3.3 \mu\text{T}$. Black dashed lines are simulated profiles for uniformly magnetized spheres with diameters of 8 and 3 μm , correspondingly.

For magnetic imaging, we refocused the system onto the diamond surface containing the NV centers. Magnetic images of the corresponding microspheres are presented in the middle panels of Figure 3. The dumbbell legend, featuring open and closed circles, indicates the alignment of the NV centers relative to the image plane, and thus the direction of the applied magnetic field (B_{app}), and the measured component of the stray field (B_{str}). Despite the microspheres' size of several micrometers, the shapes of the magnetic signals closely resemble those of the point spread function of a magnetic dipole, with magnetization aligned along the measured component of the magnetic field. This magnetic pattern shows two faint yellow maxima of field strength and a prominent blue minimum between them, set against a green zero-field background.

We further reduced the dimensionality by deriving magnetic profiles (Figure 3, right panels) along a dashed red line connecting the two maxima within the 2D magnetic images. These measured magnetic profiles (red solid lines) were compared with simulated profiles (black dashed lines) generated via finite-element analysis, modeling uniformly magnetized spherical shells of varying diameters. A shell thickness of 100 nm was assumed, based on EDS mapping (see Figure 1d). The simulations reveal that the width of the dip in the profile depends on the diameter of the magnetized shell, enabling us to determine the

diameter of each measured microsphere by fitting the measured and simulated profiles. For example, Microsphere A, with a diameter of 8.2 μm , is accurately represented by an 8 μm magnetized shell. We found that this “magnetization diameter” does not always correspond to the actual diameters of the microspheres in the studied samples. For instance, Microsphere B has a diameter of 9.4 μm , yet its magnetic signal matches that of a 3 μm spherical shell, as evidenced by the fit in Figure 3b. We hypothesize that Microsphere B exhibits reduced porosity across most of its surface, with MNPs penetrating only one side, compactly occupying a volume equivalent to that of a 3 μm sphere. The EDS map in Figure 1c reveals a similar uneven deep penetration of MNPs, particularly in the lower-left region of the microparticle. Note that the magnetic pattern approach can confirm whether a sphere is uniformly magnetized along all angles in spherical coordinates, but it is insensitive to the radial distribution of MNPs. Specifically, a vaterite sphere with a surface uniformly functionalized with MNPs produces the same magnetic signal width as an identical sphere with the MNPs uniformly distributed throughout its volume.

The magnetic profiles are utilized to assess the PP amplitude, as illustrated in the right panels of Figure 3. This amplitude serves as a direct measure of the magnetic contrast, which is of interest for the biomedical applications of such composite particles. Furthermore, the PP amplitude of the simulated profiles is unequivocally correlated with the volume magnetization, serving as a fitting parameter. By fitting the measured magnetic profile, we can estimate the number (N) of MNPs captured by the vaterite microsphere and contributing to the magnetic signal. Using the volume V_{np} of the Fe_3O_4 MNPs and their magnetization M_{np} from specifications, along with the volume V_{ms} and magnetization M_{ms} of the microspheres derived from the fit, we calculate the number of captured MNPs as $N = (V_{\text{ms}} \cdot M_{\text{ms}}) / (V_{\text{np}} \cdot M_{\text{np}})$. For Microsphere A, with a diameter of 8 μm , the magnetization $M_{\text{ms}} = 1226 \text{ A/m}$. It contains 20 nm Fe_3O_4 MNPs with a magnetization $M_{\text{np}} = 3.89\text{--}4.14 \times 10^6 \text{ A/m}$. This yields $N = 1388 \pm 123$ MNPs captured by Microsphere A. Similarly, for Microsphere B, with a magnetization $M_{\text{ms}} = 2365 \text{ A/m}$ and a 3 μm ‘magnetization diameter,’ the number of 10 nm Fe_3O_4 MNPs with $M_{\text{np}} = 3.63\text{--}4.14 \times 10^6 \text{ A/m}$ is $N = 3086 \pm 286$. Thus, this estimate confirms the capacity of a single vaterite microsphere to concentrate and retain thousands of MNPs.

Furthermore, the magnetic image in Figure 3a exhibits distinctive magnetic signals in the top-right corner, originating from two small MNPs. These are likely individual Fe_3O_4 MNPs that have detached from the vaterite microsphere. Their magnetic signals are relatively strong due to their proximity to the NV layer. The sharp magnetic signal from a single 20 nm Fe_3O_4 MNP is averaged over an optical resolution area of approximately $0.5 \times 0.5 \mu\text{m}^2$.

In addition, we performed a measurement of the full hysteresis curve for another 5.5 μm vaterite microsphere, as shown in Figure 4, along with a fit to the Langevin function. This measurement confirms the superparamagnetic response of the microsphere embedded with 10 nm Fe_3O_4 MNPs, with the peak-to-peak amplitude of the stray magnetic field projected onto the (110) NV plane saturating at approximately 8.8 μT . It serves as a demonstration of the capability of QDM to perform quantitative magnetic field imaging across a broad dynamic range. Despite the ground-state spin level anti-crossing at 102.5 mT, which shifts the ODMR frequencies outside the device bandwidth, both regions of interest (near $B_0 = 0$ and in the saturation regime) remain readily accessible using QDM.

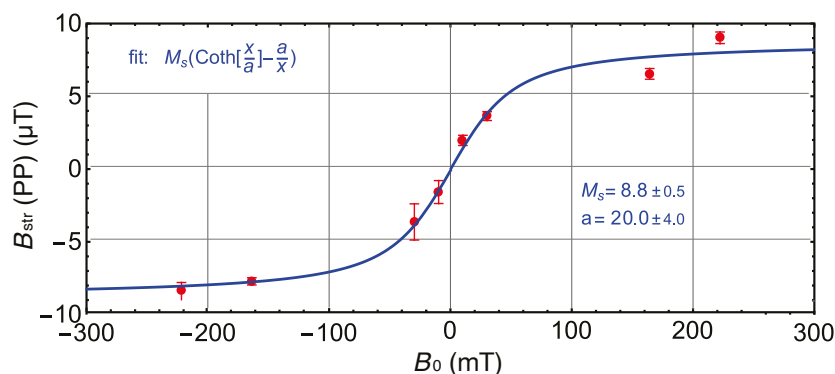


Figure 4. B_{str} projected onto the (110) NV plane as a function of the applied magnetic field. The plot shows the peak-to-peak amplitudes of the stray magnetic field of a 5.5 μm vaterite microsphere containing embedded 10 nm Fe_3O_4 MNPs. The data exhibit saturation behavior, reaching approximately 8.8 μT . The solid line represents a fit to the Langevin function, indicating the superparamagnetic response of the embedded MNPs. Error bars represent the fitting uncertainty.

3.2. Batch Analysis

Finally, we applied the analysis described in Figure 3 to >35 individual vaterite microspheres to investigate the magnetization uniformity of the prepared samples. The vaterite microspheres exhibited diameters ranging from 5 μm to 10 μm , with an average of $\sim 7 \mu\text{m}$. Figure 5a presents the PP amplitudes of the stray magnetic field as a function of microsphere diameter. These PP amplitudes range from 3.4 to 81 μT , excluding several outliers not displayed on the plot. Figure 5b illustrates the PP amplitudes averaged across the samples. Samples containing 5 nm and 10 nm superparamagnetic Fe_3O_4 MNPs exhibit significantly higher mean stray field amplitudes ($41 \pm 1 \mu\text{T}$) compared to those with 20 nm MNPs ($12 \pm 1 \mu\text{T}$). This reduction in magnetic field amplitude may result from the mutual cancellation of ferromagnetic domains or may be attributed to the larger diameter of the 20 nm Fe_3O_4 MNPs, which could limit their ability to penetrate the vaterite pores. The last hypothesis is supported by the observation that Microsphere B, as shown in Figure 3, contains over 3000 nanoparticles with a diameter of 10 nm within a 3 μm ‘magnetization diameter’, whereas Microsphere A contains more than 1300 nanoparticles with a diameter of 20 nm, despite having a volume approximately 19 times larger.

These data are presented as probability density distributions of microsphere diameters (Figure 5c) and PP amplitudes (Figure 5d). Although the vaterite microspheres of the sample with 20 nm Fe_3O_4 MNPs exhibit a size distribution similar to that of the sample with 10 nm Fe_3O_4 MNPs, their PP amplitudes are markedly distinct from those of samples with 5–10 nm MNPs. This step-like change in stray field amplitude more strongly supports a phase transition from superparamagnetism to ferrimagnetism than a gradual decrease in MNP penetration into the vaterite matrix. This size-dependent transition is consistent with earlier reports showing that iron oxide nanoparticles exhibit superparamagnetic behavior below 10–15 nm and ferrimagnetic behavior at larger sizes [10].

We now evaluate the potential of these MNP-loaded microspheres as T_2 contrast agents in magnetic resonance imaging (MRI). A 40 μT signal, measured at a distance of several micrometers from a microsphere containing approximately 4000 MNPs, indicates a significant local effect. While this field is not substantial for a single particle, its scalability suggests promising applications. For comparison, standard Fe_3O_4 -based contrast agents, such as Feridex, generate fields of 10–100 μT at distances of a few nanometers. A local field of 40 μT can substantially shorten T_2 relaxation times by inducing magnetic field gradients across a region spanning several micrometers. The T_2 -shortening effect scales with the square of the magnetic field (ΔB^2) and diminishes inversely with the sixth power of the distance ($1/r^6$). For a single 20 nm particle, this field decays rapidly; however, aggregation

or higher concentrations amplify the effect. At a concentration of approximately 0.1 mM, corresponding to hundreds of such microspheres per milliliter of tissue, the T_2 relaxation time could be reduced by 20–50%, which is sufficient to produce a noticeable contrast in MRI. The vaterite loading process relies on diffusion into the mesoporous vaterite host and can be further enhanced using cold infusion methods [40] if higher concentrations are required. An alternative strategy to increase the magnetic loading is freeze-induced infusion, which has been shown to enhance nanoparticle uptake into calcium carbonate carriers by up to fivefold [41]. While not employed in the present study, this method may be used in future work to further improve magnetic contrast for both NV magnetometry and biomedical applications.

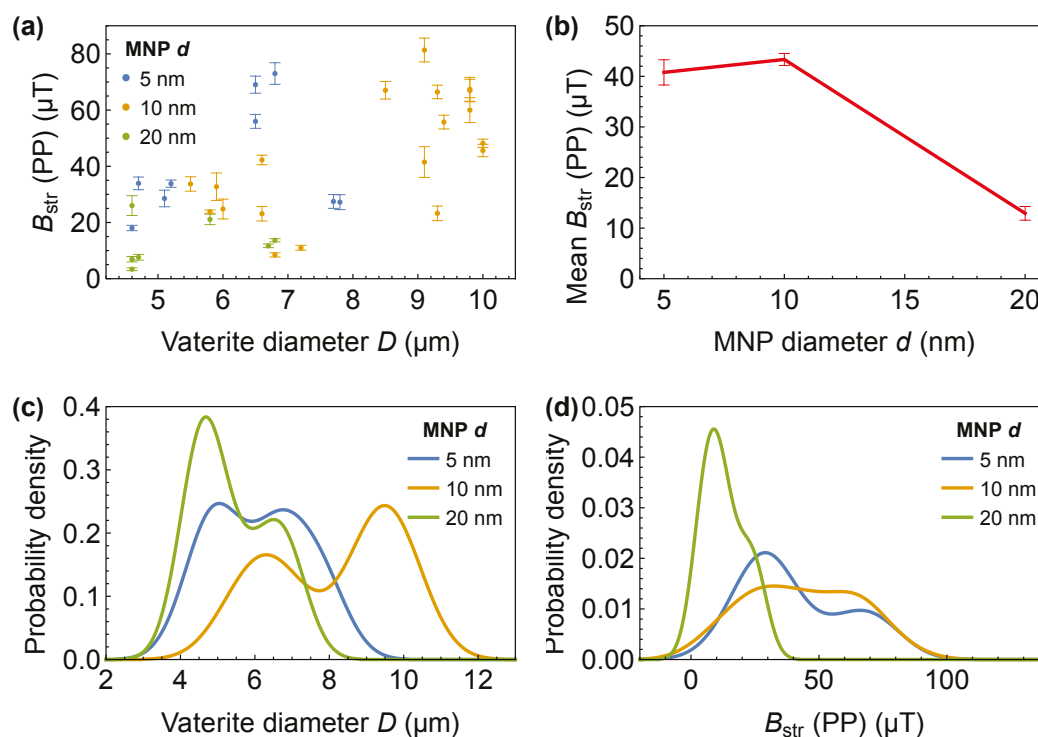


Figure 5. Stray magnetic fields of vaterite microspheres with embedded Fe_3O_4 MNPs. (a) Stray field measured below vaterite microspheres as a function of their diameter, for different Fe_3O_4 MNP sizes (5 nm, 10 nm, and 20 nm). PP denotes the peak-to-peak amplitude of the stray magnetic field, with error bars representing the fitting uncertainty. (b) Mean stray field as a function of Fe_3O_4 MNP diameter, showing a decrease for larger Fe_3O_4 size. Error bars indicate the standard deviation of the measured values. (c) Probability density distribution of vaterite microsphere diameters for different Fe_3O_4 MNP sizes. (d) Probability density distribution of stray field values, illustrating the dependence of magnetic signal strength on Fe_3O_4 MNP size.

4. Conclusions

We loaded vaterite microspheres with Fe_3O_4 MNPs and characterized the accumulated stray magnetic fields from individual vaterite microspheres using a widefield optical microscopy technique. The observed magnetic patterns align with theoretical models assuming uniform 100-thick shell magnetization of the vaterite microspheres. The PP amplitudes of the magnetic signals suggest that each vaterite microsphere contains thousands of embedded MNPs. Additionally, we identified a phase transition from superparamagnetic to ferromagnetic behavior between 10 nm and 20 nm MNPs, manifested as a significant reduction in total magnetization. While this paper does not address these aspects, future studies will investigate the impact of varying vaterite microsphere sizes, shapes, and the controlled incorporation of magnetic materials. These efforts are expected to enhance the

efficiency and precision of drug loading and release, thereby facilitating more effective drug delivery.

Our method offers new insights into the magnetic behavior of MNPs by enabling the observation of magnetism in individual micro- and nanoparticles. A primary limitation is the optical resolution, which prevents the resolution of individual MNPs in samples with a density exceeding one particle per $0.5 \times 0.5 \mu\text{m}^2$ area. However, at low densities, even a single MNP can be detected owing to the high sensitivity of quantum diamond imaging. The NV microscope employed in this study can generate magnetic images of features as small as $1.4 \mu\text{T}$ within less than five minutes, utilizing parallel ODMR detection across a 400×400 pixel array.

Compared to other magnetic characterization techniques, QDM provides a unique combination of wide-field, quantitative, and non-invasive magnetometry under ambient conditions. While magnetic force microscopy achieves higher spatial resolution ($\sim 10\text{--}50 \text{ nm}$) and micro-SQUIDs offer superior sensitivity (down to nT or single Bohr magnetons), both techniques require sequential scanning or cryogenic conditions and are less suited for real-time imaging of large particle ensembles. In contrast, QDM achieves $\sim 1 \mu\text{T}$ sensitivity at $\sim 300 \text{ nm}$ resolution with minimal sample disturbance, making it particularly well-suited for biological and heterogeneous materials where ensemble-averaging methods fall short. Further refinements may enable sensitivity in the nanotesla range, broadening QDM's applicability in materials and biomedical research.

Author Contributions: M.A. and T.A. synthesized the magnetic nanoparticles and vaterite microspheres, conducted particle characterization, and verified the MNP load estimation. (SEM, TEM) under the supervision of H.B. and N.B.-G. I.F. developed the quantum diamond microscope and created software for the analysis and simulation of vaterite microspheres. M.J. performed the final sample preparation, conducted magnetic imaging, and analyzed the resulting data. M.J. drafted the manuscript with support from I.F., incorporating contributions and feedback from all authors. I.F., J.A., T.S., and P.G. designed the experiments and provided overall project supervision. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

NV	nitrogen-vacancy center
MNP	magnetic nanoparticles
QDM	quantum diamond microscope
ODMR	optically detected magnetic resonance
SQUID	superconducting quantum interference device
TEM	transmission electron microscopy
EDS	energy-dispersive spectroscopy
PP	peak-to-peak

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Article

Microwave Dielectric Permittivity of Nanostructured RMn_2O_5 Manganate, $\text{R}_2\text{Ti}_2\text{O}_7$ Titanate, and LiCoPO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ Orthophosphate Composites

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Abstract

The complex dielectric permittivity has been studied with the waves of millimeter wavelength for rare earth manganate and titanate and LiCoPO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ orthophosphate composites. The measurements are carried out at frequencies of 26 to 38 GHz via measurements of transmission and reflection coefficients through a plate. A special method on how to extract the real and imaginary parts of dielectric permittivity is applied. Discussion is conducted on a nonmonotonic type of the frequency dependences for both real and imaginary parts of permittivity, and it has been shown that relaxation is non-Debye. The Cole–Cole, Havriliak–Negami, and Kohlrausch–Williams–Watts models cannot also explain the nonmonotonic frequency dependence of the real part of dielectric permittivity. Investigation of the structure and phase composition of nanocomposites has been carried out.

Keywords: nanocomposites; artificial opal; manganates; titanates; orthophosphates; microwaves; transmission and reflection coefficients; complex permittivity; dielectric relaxation

1. Introduction

The frequency dependences of the dielectric permittivity of nanostructures and nanocomposites have specific features conditioned by the space limitation of the components of heterogeneous media [1]. As noted in [2], a multi-channel propagation and scattering of phonons and photons is possible in nano-objects that influence the frequency dependences of permittivity. In recent years, an essential interest has attracted investigation of the magnetoelectric effect in multiferroics. This effect is studied specifically in rare earth manganates with the general formula RMn_2O_5 , where R is a trivalent rare earth ion [3–5], and in the orthophosphates LiNiPO_4 and LiCoPO_4 [6]. In these systems, a complicated magnetic ordering of the antiferromagnetic type is realized at low temperatures, which can transform into an incommensurate noncollinear type of magnetic structure as temperature increases. The crystal and magnetic structures of several manganates have been investigated in [7] using magnetometry and neutron scattering. The crystal structures of RMn_2O_5 are orthorhombic at room temperature with the Pbam space group. The magnetic and dielectric properties of five rare earth manganates have been studied in [8]. The magnetic and dielectric phase transitions were demonstrated to occur simultaneously. As a rule, a ferroelectric polarization exists if the spin configuration for Mn^{4+} and Mn^{3+} ions is in the commensurate magnetic phase. The electric polarization in erbium and terbium manganates is studied in [9], and a special attention is drawn to the fact that the electric

polarization presents, induced by local polar phase separation domains. In relaxors, standing ferroelectric phonons develop in nanoregions at the frequency when a wavelength equals the polar nanoregion size [10]. High values of the real part of dielectric permittivity have been found for manganates with $R = \text{Tb}$, Dy , and Er in the paraelectric phase at temperatures above 78 K at frequencies of 100 Hz to 1 MHz [11]. A correlation between the high dielectric permittivity and the size of R ions has been proposed. The influence of doping by yttrium on the complex dielectric permittivity of gadolinium manganate is studied in [12].

The magnetic structure of orthophosphates is investigated in a magnetic field up to 56 T by neutron diffraction and magnetometry [6]. The conditions that allow the magnetoelectric phase in LiNiPO_4 to exist have been established. These orthophosphate compounds have an orthorhombic crystalline structure (space group $Pnma$) and commensurate antiferromagnetic ground states. A detailed study of the LiNiPO_4 structure by scanning electron transmission microscopy and X-ray diffraction pointed that a considerable proportion of antisite defects presents in this compound, which may have a pronounced effect on the electrochemical and magnetoelectric properties [13]. The dielectric permittivity of LiNiPO_4 is examined in [14]. Investigation of dielectric permittivity, performed over the frequency range 10 Hz to 1 MHz at temperatures of 150 to 300 °C, convinced that the relaxation is of non-Debye type. The dielectric permittivity and alternating current conductivity of the LiNiPO_4 compound were investigated by impedance spectroscopy [15]. The presence of two thermally activated peaks is established from the temperature dependence of impedance. Raman and far-infrared spectra of LiNiPO_4 were measured and discussed in [16]. It has been established that the value of losses is linked with the distortion of the $[\text{NiO}_6]$ octahedra. A low dielectric constant $\epsilon' = 5.18$ at a frequency $f = 17.2$ GHz is found in ceramics sintered at 825 °C. The LiNiPO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ compounds are synthesized by the solid-state reaction method [17]. It is shown that the electrical conductivity of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ is higher than that of pure LiNiPO_4 . Zinc-doped LiCoPO_4 was prepared by the solid-state reaction method [18]. It has been obtained from the temperature dependence of conductivity that both pure and Zn^{2+} -doped samples obey the Arrhenius law.

The scenario of dielectric relaxation and the specific features of relaxors are discussed in the review [19]. The high-temperature dielectric properties of BiMn_2O_5 manganate are examined in [20], where it has been shown that BiMn_2O_5 ceramic demonstrates relaxor behavior. Using the impedance spectroscopy method, it was found that Dy-substituted YMn_2O_5 manganate exhibits a non-Debye type of relaxation [21]. The relaxation of dynamically correlated clusters is discussed theoretically in [22]. The Havriliak–Negami and Kohlrausch–Williams–Watts approaches are regarded as more suitable for the micro/mesoscopic relaxing systems. The non-Debye dielectric relaxation is inherent in complex heterogeneous media [23].

As a rule, the high real parts of the dielectric permittivity of rare earth manganates and orthophosphates up to tens of thousands are realized at low frequencies [9,14,21]. A drastic decrease in the real part occurs in GdMn_2O_5 and YMn_2O_5 at 2–3 kHz [12,21]. In ErMn_2O_5 , TbMn_2O_5 DyMn_2O_5 manganates, it sharply decreases at frequencies of 10–100 kHz [11]. In relaxor bismuth manganite, a gradual monotonic decrease in the real part occurs starting from kilohertz to megahertz [20].

The dielectric permittivity of BaZrO_3 – BaTiO_3 solid solutions is studied in a wide frequency range [24]. The high values of the real part of dielectric permittivity are about 200, remaining up to $\sim 10^{11}$ Hz. A peak of losses at 100–200 GHz corresponds to a Debye-type relaxation. Additionally, another peak of losses presents in the GHz range. Its frequency dependence satisfies to the Cole–Cole model, and the relaxation time is related to thermally activated processes. In $\text{Ba}_2\text{LaTi}_2\text{Nb}_3\text{O}_{15}$ and $\text{Ba}_2\text{La}_{0.5}\text{Nd}_{0.5}\text{Ti}_2\text{Nb}_3\text{O}_{15}$ niobates,

the relaxation takes place mostly at frequencies of MHz and GHz ranges and continues up to ~500 GHz [25]. The real part of permittivity at frequencies of less than 1 kHz is about 800, and it decreases monotonically if the frequency rises. The millimeter-wave dielectric permittivity of nanocomposite rare earth titanates is studied in [26]. The tendency is established that the real part of the dielectric constant of the rare earth nanocomposite titanate increases with the increase in quantum number S of rare earth ion R^{3+} . The microwave dielectric permittivity of LiNiPO_4 ceramic for LTCC applications is explored in [27]. The relaxation time was demonstrated to vary by TiO_2 addition. The centimeter-wavelength dielectric permittivity of flower-like NiO structures was studied in [28]. These structures reveal enhanced microwave absorption properties. A new high-performance cobalt-free $\text{BaCe}_{0.16}\text{Y}_{0.04}\text{Fe}_{0.8}\text{O}_{3-\delta}$ nanocomposite was synthesized and studied [29].

As presented above, a short review of the dielectric properties of rare earth manganates and orthophosphates shows that these properties are valuable in order to understand magnetoelectric behavior. Most of the studies concern polycrystalline or ceramic samples, while nanocomposite samples are less examined. The structure and microwave dielectric properties of nanocomposite manganates with R^{3+} : Er, Tb, Yb, and La; titanates $\text{R}_2\text{Ti}_2\text{O}_7$ with R^{3+} : Gd, Tb, Yb, Er, and Sm; and orthophosphates LiCoPO_4 and $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ at frequencies of 26 to 38 GHz are studied in this paper. All nanocomposites have been obtained by impregnation of particles in artificial opal matrices. Greatest attention is paid to which type of the frequency dependence of dielectric permittivity is realized, monotonic or nonmonotonic.

2. Preparation and Characterization of Nanocomposite Samples

Artificial opal matrices with a submicron SiO_2 sphere diameter close to 260 nm were chosen as a matrix for nanocomposite samples. The opal matrices were prepared in JSC “Central Research Institute of Technology” Technomash. The nanocomposites were obtained by the impregnation method with subsequent thermal treatment [30]. The matrix was saturated by a water precursor solution. Drying and thermal treatment were performed later. In order to obtain the rare earth manganates, annealing at 900 °C was needed. To increase the filling of the inter-spherical voids, the impregnation and thermal treatment procedures were repeated 4–6 times. The structure of the samples was investigated with the scanning electron microscope Tescan MIRA LMS (Tescan, Brno, Czech Republic). An image of the structure of the sample with TbMn_2O_5 is shown in Figure 1a. The particles of the embedded substance (they are light in Figure 1a) had either irregular or close to spherical shape. The size of most particles did not exceed 60 nm.

The elemental composition was performed with an EDAX instrument. For the sample with TbMn_2O_5 particles, this analysis determined the following elements: Tb, Mn, O, and Si. The elemental composition of this sample is presented in Table 1. An X-ray diffraction image for the sample with TbMn_2O_5 particles is shown in Figure 2a. XRD refinement was conducted to identify the detailed structural information and the phase content [31]. The X-ray data for the sample are given in Table 2. The X-ray diffraction data obtained with DRON-3M and XRD-6000 with $\text{CuK}\alpha$ irradiation show that, besides SiO_2 (hexagonal syngony, space group P3_221), the following crystalline phases are present in the composite: TbMn_2O_5 (orthorhombic syngony, Pbam , 50-0294), in accordance with the ICDD PDF-2 database, and also small amount of Mn_2O_3 (cubic syngony, Ia-3 , 89-4836).

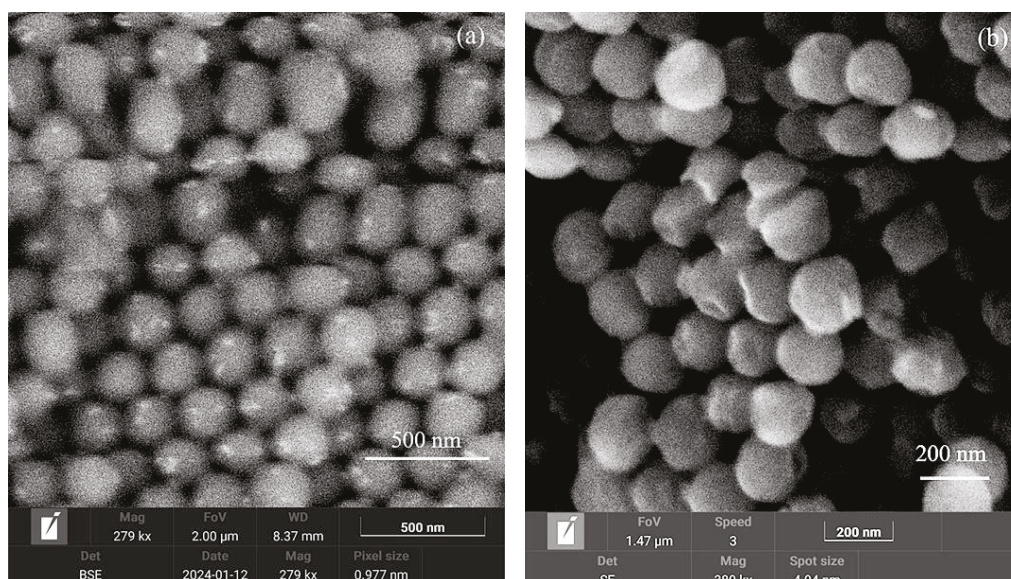


Figure 1. Structure of the nanocomposite with TbMn_2O_5 particles (a) and of the nanocomposite with LiCoPO_4 particles (b) obtained with the scanning electron microscope Tescan MIRA LMS.

Table 1. The elemental composition of sample with TbMn_2O_5 particles.

Element	Type of Line	Wt.%	At.%
O	K	51.46	66.97
Si	K	42.76	31.70
Mn	L	2.31	0.88
Tb	M	3.47	0.45

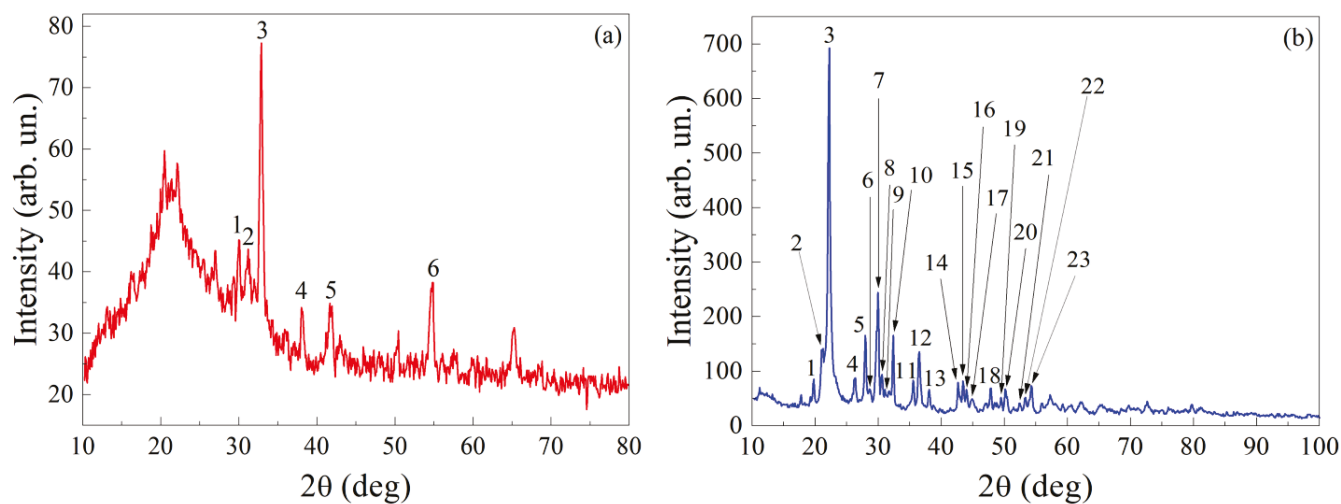


Figure 2. The X-ray diffraction images for samples with TbMn_2O_5 (a) and LiCoPO_4 (b) particles.

Table 2. The X-ray data for sample with TbMn₂O₅ nanoparticles.

Peak's Number	Experimental Data			Data from ICDD PDF-2					
	Intensity, arb. un.	Intensity, %	Bragg Angle 2 θ , deg.	Peak Semiwidth, deg.	Interplane Space, Å	Mn ₂ O ₃ —Cubic Syngony, Space Group Ia-3 (89-4836)		TbMn ₂ O ₅ —Orthorhombic Syngony, Space Group Pbam (50-0294)	
						d, Å	I, %	d, Å	I, %
1	17.93	23	29.820	0.396	2.9934			3.0400	121
2	17.30	22	30.967	0.396	2.8851			2.8580	211
3	77.25	100	32.688	0.396	2.7370	2.7152	100	2.7430	220
4	6.28	8	37.827	0.253	2.3761	2.3515	13.7	2.3740	131
5	10.48	14	41.745	0.417	2.1617			2.1540	311
6	15.51	20	54.716	0.341	1.6760	1.6627	39.9	1.6740	420
7	12.00	16	65.155	0.289	1.4304	1.4180	17.6	1.4140	060

The crystalline structure of LiMPO_4 orthophosphates belongs to the olivine type of structure, and it is described by the crystallographic space group $Pnma$ [32]. The element cell of orthophosphates contains four Co^{++} or/and Ni^{++} ions. The crystalline structure has a rhombic symmetry. In order to obtain composites, a sample of an opal matrix is placed in Li_3PO_4 and $\text{Ni}_3(\text{PO}_4)_2$ or $\text{Co}_3(\text{PO}_4)_2$ solution, where it is kept for certain number of minutes so that the inter-spherical voids are filled with the solution. After drying, annealing at 900°C is performed. This procedure is repeated 4–6 times for more infilling of voids by orthophosphate. The method for preparing composite multiferroics in the opal matrices is described in [33].

The structure of the nanocomposite samples with orthophosphate particles has been studied with the scanning electron microscope Tescan MIRA LMS. The results for the sample with LiCoPO_4 particles are shown in Figure 1b. The embedded substance is found in the inter-spherical voids. Therefore, the maximal size of the particles is less than 60 nm. The shape of the particles is either irregular or close to spherical. The elemental composition obtained with EDAX is presented in Table 3. X-ray structure analysis is carried out in CuK_α irradiation. The X-ray diffraction image for samples with LiCoPO_4 particles is shown in Figure 2b. The X-ray data for the sample with LiCoPO_4 nanoparticles are presented in Table 4. Silicon dioxide (SiO_2) is mostly in X-ray amorphous state and partially in the crystalline one. The crystalline phase of SiO_2 corresponds to cristobalite (tetragonal syngony, $P4_12_12$) and tridymite (hexagonal syngony, $P6_3/mmc$). The introduced substance LiCoPO_4 or $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ is related to orthorhombic syngony, $Pnma$. Estimations give sizes of 37–50 nm for the regions of coherent X-ray scattering.

Table 3. The elemental composition of a sample with LiCoPO_4 particles.

Element	Type of Line	Wt. %	At. %
O	K	56.33	69.83
Si	K	41.28	29.15
P	K	0.69	0.45
Co	K	1.70	0.57

A characterization of the samples of rare earth titanates is presented in [34]. A list of the samples used in this paper is presented in Table 5. The chemical composition of particles in nanocomposites is shown, as well as the number of impregnations applied during preparation. The values of the real ϵ' and imaginary ϵ'' parts of the dielectric permittivity of the samples averaged over the frequency range 26 to 38 GHz are presented in Table 5.

As a whole, all samples under study have the elemental and phase composition close to the nominal one. The nanoparticles of the embedded substance are located in the inter-spherical voids of an opal matrix. The concentration of the embedded substance is below the percolation threshold. Particles are either irregular in shape or close to spherical.

Table 4. The X-ray data for the sample with LiCoPO₄ nanoparticles.

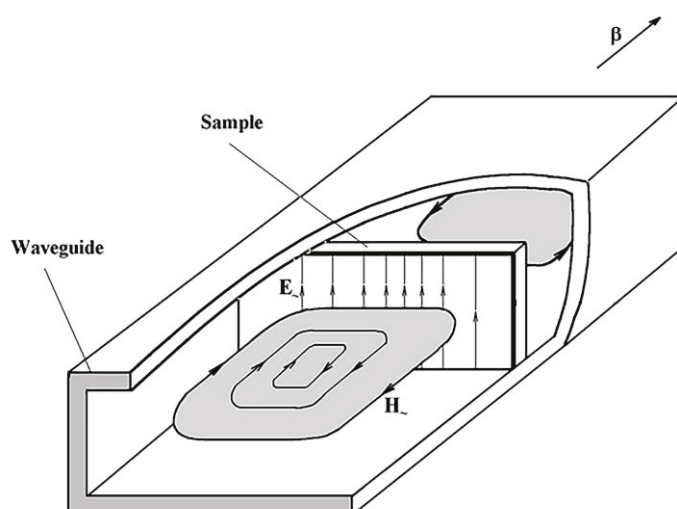
Experimental Data						Data from ICDD PDF-2									
Peak's Number	Intensity, arb. un.	Intensity, %	Bragg Angle 2θ, deg.	Peak Semiwidth, deg.	Interplane Space, Å	SiO ₂ (Cristobalite)— Tetragonal Syngony, Space Group P4 ₁ 2 ₁ 2 (89-3434)			LiCoPO ₄ — Orthorhombic Syngony, Space Group Pnma (85-0002)			SiO ₂ (Quartz)— Hexagonal Syngony, Space Group P3 ₂ 21 (86-1565)			
						d, Å	hkl	I, %	d, Å	hkl	I, %	d, Å	hkl	I, %	
1	34.99	5	19.523	0.328	4.5427										
2	105.34	15	20.908	0.328	4.2448				4.2610	101	67.5				
3	692.02	100	21.984	0.328	4.0394	4.0281	101	100				4.0722	100	22.1	
4	35.17	5	26.172	0.271	3.4017				3.4583	111	81.1				
5	81.98	12	27.823	0.220	3.2035										
6	14.53	2	28.528	0.220	3.1259										
7	105.78	15	29.732	0.157	3.0020				2.9821	211	10.3				
8	25.48	4	30.343	0.157	2.9430				2.9599	020	64.0				
9	10.94	2	30.847	0.157	2.8960										
10	60.06	9	32.143	0.157	2.7821	2.8340	102	11.4	2.7527	301	24.5				
11	35.20	5	35.237	0.316	2.5446				2.5600	220	2.4				
12	97.48	14	36.186	0.316	2.4800				2.4960	311	100				
13	27.59	4	37.776	0.316	2.3792	2.4793	200	13.5	2.3419	002	17.5	2.3511	110	12.0	
14	40.96	6	42.391	0.225	2.1303	2.1114	211	2.6				2.1461	111	5.3	
15	39.12	6	43.172	0.225	2.0935				2.1305	112	16.7				
16	22.70	3	43.733	0.225	2.0680										
17	20.00	3	44.618	0.225	2.0290	2.0140	202	1.9	2.0157	321	4.4	2.0361	200	7.8	
18	35.55	5	47.539	0.374	1.9109	1.9246	113	4.8	1.9319	420	2.2	1.8986	021	1.5	
19	18.82	3	49.189	0.374	1.8506	1.8660	212	4.8							
20	38.70	6	49.957	0.374	1.8239				1.8380	230	12.1				
21	12.33	2	52.210	0.243	1.7504										
22	22.29	3	53.130	0.243	1.7222				1.7291			1.7522	112	8.6	
23	50.37	7	54.088	0.243	1.6940	1.6871	203	2.3							

Table 5. Designation and mean values of dielectric permittivity of composites.

No. of Sample	Chemical Composition of Samples	Number of Impregnations	$\langle \epsilon' \rangle$	$\langle \epsilon'' \rangle$
1	LiCoPO ₄	6	2.94	0.13
2	LiCo _{0.5} Ni _{0.5} PO ₄	5	3.45	0.21
3	LiCoPO ₄	5	2.59	0.13
4	Gd ₂ Ti ₂ O ₇	5	3.17	0.16
5	Tb ₂ Ti ₂ O ₇	5	2.73	0.07
6	Yb ₂ Ti ₂ O ₇ + TiO ₂	5	2.52	0.07
7	Er ₂ Ti ₂ O ₇	5	2.39	0.12
8	Sm ₂ Ti ₂ O ₇	5	2.52	0.16
9	Er ₂ TiO ₅	5	2.74	0.023
10	YMn ₂ O ₅	10	2.36	0.13
11	LaMn ₂ O ₅	5	2.81	0.12
12	YbMn ₂ O ₅	6	2.85	0.2
13	ErMn ₂ O ₅	6	2.72	0.06

3. Measurement of Microwave Dielectric Permittivity

The microwave measurements are carried out using the wave transmission/reflection method at room temperature [35]. The measurements are performed in the frequency range 26 to 38 GHz. The scheme of the sample disposition in a waveguide is shown in Figure 3. The power transmission T and reflection R coefficient modules and their frequency dependences are measured.

**Figure 3.** Scheme of microwave fields during the measurements of transmission and reflection coefficients.

The view of the frequency dependence of transmission and reflection coefficients is determined by the following factors: (1) the relation between the sample thickness d and the wavelength λ , (2) the value of the absorption coefficient, and (3) the dispersion of TE₁₀ mode in the rectangular waveguide. The frequency dependences of transmission and reflection coefficients are used in order to restore the effective dielectric permittivity $\epsilon = \epsilon' - i\epsilon''$ of a nanocomposite medium [35]. Let us denote the impedance for the part of the waveguide with the sample as Z_2 and the impedance outside the sample as Z_1 . The complex propagation constant in the sample is indicated as $\beta_2 = \beta'_2 + i\beta''_2$. The thickness of

the sample equals d , and the greater side of the waveguide is a . The complex transmission T and reflection R coefficients can be calculated via the formulas [36,37]

$$T = \frac{1}{\cos \beta_2 d + \frac{i}{2}(\zeta + \zeta^{-1}) \sin \beta_2 d} \quad (1)$$

$$R = \frac{\frac{i}{2}(\zeta - \zeta^{-1}) \sin \beta_2 d}{\cos \beta_2 d + \frac{i}{2}(\zeta + \zeta^{-1}) \sin \beta_2 d} \quad (2)$$

where $\zeta = Z_2/Z_1$ is the ratio of the impedances. The propagation constant is calculated as $\beta_2 = \sqrt{(\frac{\omega}{c})^2 \varepsilon \mu - (\frac{\pi}{a})^2}$, where ε and μ are the effective dielectric permittivity and magnetic permeability of the composite media. We believe that $\mu \approx 1$ at our frequencies ~ 30 GHz. Let us designate the experimentally measured transmission coefficient module as $|T_*|$ and the difference between the theoretical transmission coefficient from (1) and the experimental transmission coefficient at a given frequency $\omega = 2\pi f$ as $\Delta_T = \Delta_T(\omega, \varepsilon) = |T| - |T_*|$. In the same way, we can introduce $\Delta_R = \Delta_R(\omega, \varepsilon) = |R| - |R_*|$ for the reflection coefficient. The value of the complex permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ is an unknown quantity. Using the least square method, we search for the minimal value of the total approximation error

$$(\Delta(\varepsilon'_*, \varepsilon''_*))^2 = \min_{\varepsilon'=\varepsilon'_*, \varepsilon''=\varepsilon''_*} \min_{\varepsilon''} \left[(\Delta_R(\omega, \varepsilon', \varepsilon''))^2 + (\Delta_T(\omega, \varepsilon', \varepsilon''))^2 \right] \quad (3)$$

The value $\varepsilon_* = \varepsilon'_* - i\varepsilon''_*$ obtained as a result is considered an estimate of the dielectric permittivity. The minimization of the error (3) can be performed both in the entire frequency range, in which measurements were performed, and in narrower intervals within it, which can be called windows. By moving such a window over the frequency range, it is possible to determine the frequency dependences of the complex permittivity, rather than its single value, as when estimating over the entire range. Thus, the use of a frequency window makes it possible to identify the dispersion of permittivity of the material under study. The minimal width of the window is selected in such a way that it contains at least one period of oscillation of the frequency dependences of the reflection and transmission coefficients, which can appear due to the partial mismatch of the waveguide measuring line to the load at its output. Averaging the data within the frequency window makes it possible to reduce the influence of these oscillations on the result of the permittivity estimation.

The part of the power dissipated inside the sample is designated as dissipation D . The absorbed and scattered power contributes to the dissipation and the power of non-propagating modes transformed from the fundamental waveguide mode TE_{10} . The dissipation can be calculated from the transmission and reflection coefficients as

$$D = 1 - |T|^2 - |R|^2 \quad (4)$$

4. Dielectric Permittivity of Manganate Composites

Let us consider the results of the frequency dependences' measurement of transmission and reflection coefficients for manganate composite samples. These dependences for a nanocomposite sample with $ErMn_2O_5$ particles are shown in Figure 4. It is obvious that the calculated dependence is close to the measured one, and small differences are conditioned by a slight mismatch of the microwave tract. The application of the method described in the above section allows us to restore the frequency dependence of the real and imaginary parts of the complex dielectric permittivity. The results for samples with YMn_2O_5 , $ErMn_2O_5$, $YbMn_2O_5$, and $LaMn_2O_5$ particles are shown in Figure 5. The designation of the manganate samples is given in Table 5. Within the range concerned, the real part of permittivity ε' of sample 10 with YMn_2O_5 particles varies nonmonotonically with the increase in frequency,

and it has a maximum close to 33 GHz. The dependences for other samples increase in the frequency range 26 to 38 GHz, but they evidently have maxima at higher frequencies because ϵ' must tend toward 1 if the frequency rises infinitely. The imaginary part ϵ'' for samples 11, 12, and 13 is a nonmonotonic function; moreover, for these samples, it has a maximum at frequencies of 30–32 GHz. In the high-frequency region of the range, namely, at frequencies of more than 35 GHz, the ϵ'' function increases again. The inequality $\epsilon'' \ll \epsilon'$ is valid for all samples in the whole frequency range 26–38 GHz. For comparison, the dielectric permittivity of an empty opal matrix is about 2.4–2.5. In principle, a low value of ϵ'' is not surprising for multiferroics; see [38], for example.

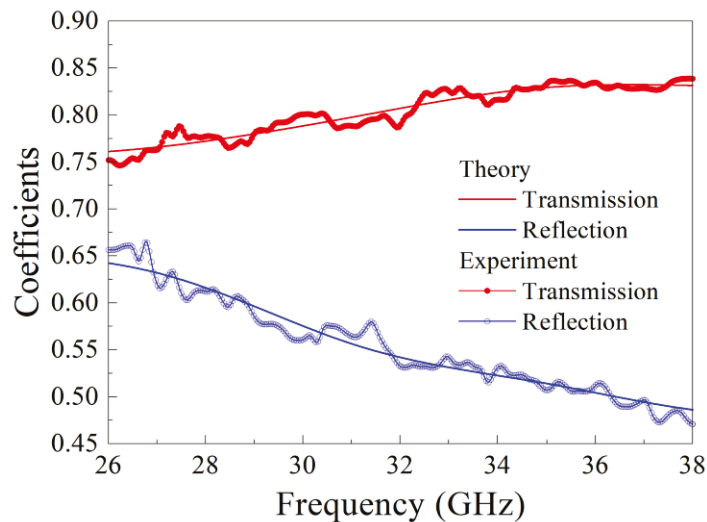


Figure 4. Frequency dependences of transmission and reflection coefficients of electromagnetic waves for a nanocomposite sample with ErMn_2O_5 particles: experimental dependences are bold lines, and calculated dependences are thin solid lines.

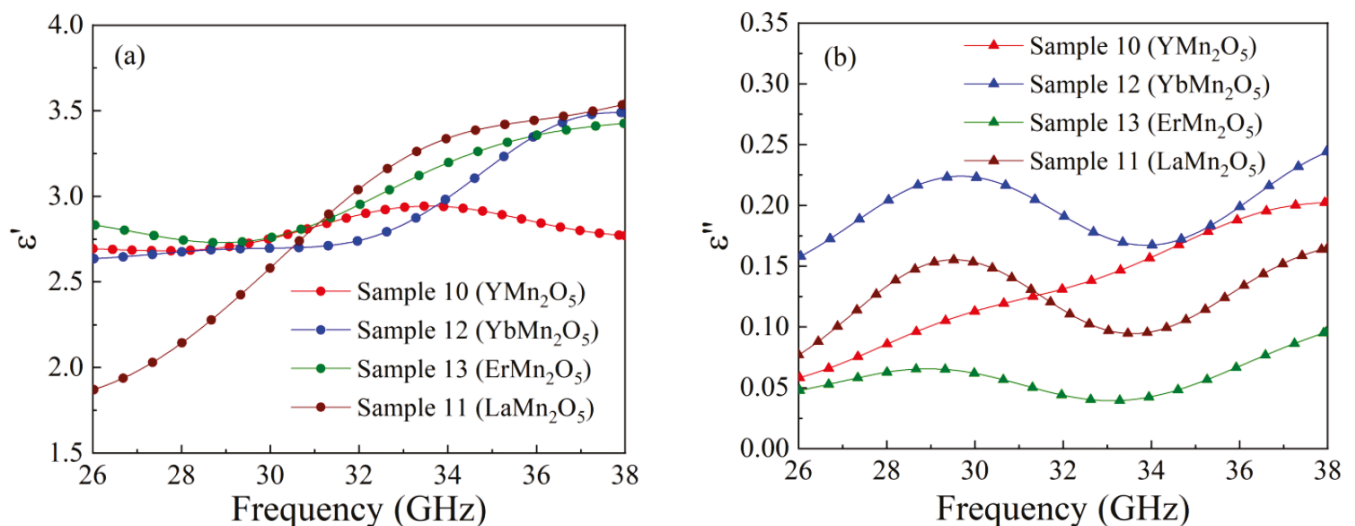


Figure 5. Frequency dependences of real (a) and imaginary (b) parts of the dielectric permittivity of the composite with manganate particles.

5. Dielectric Permittivity of Rare Earth Titanate Composites

The frequency dependences of transmission and reflection coefficients for sample 4 with $\text{Gd}_2\text{Ti}_2\text{O}_7$ particles are shown in Figure 6. The bold lines indicate the measured dependences, whereas the thin lines are related to the calculated ones via Formulas (1) and (2). The frequency dependences of the real and imaginary parts of the dielectric

permittivity of the nanocomposites with rare earth titanate particles are shown in Figure 7, and the averaged ones over the frequency range values are placed in Table 5. The frequency dependences of ϵ' for samples 4–6 are nonmonotonic within the discussed range. For samples 5, 7, and 8 at frequencies above 35 GHz, an increase in ϵ' is seen if the frequency rises. Probably, the maximum takes place at higher frequencies. For the imaginary part of the dielectric permittivity, the maximum is found close to 29–30 GHz for samples 4–7. Therefore, the nonmonotonic frequency dependence for both the real and imaginary parts of the dielectric permittivity is observed for almost all samples of rare earth titanates under study.

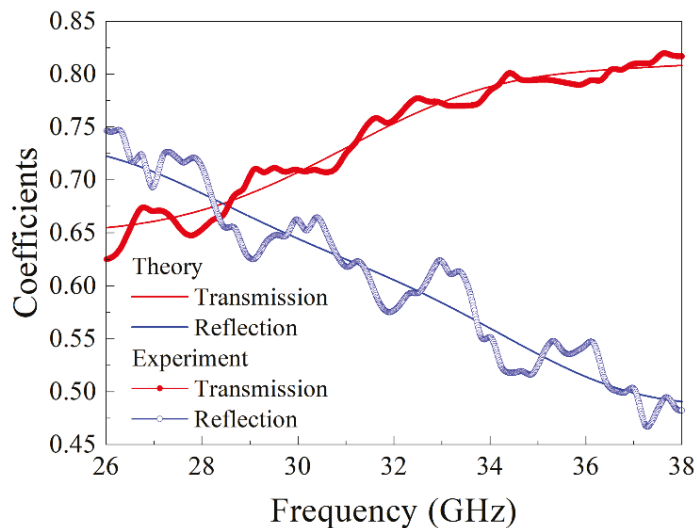


Figure 6. Frequency dependences of transmission and reflection coefficients of electromagnetic waves for a nanocomposite sample with $\text{Gd}_2\text{Ti}_2\text{O}_7$ particles: experimental dependences are bold lines, and calculated dependences are thin solid lines.

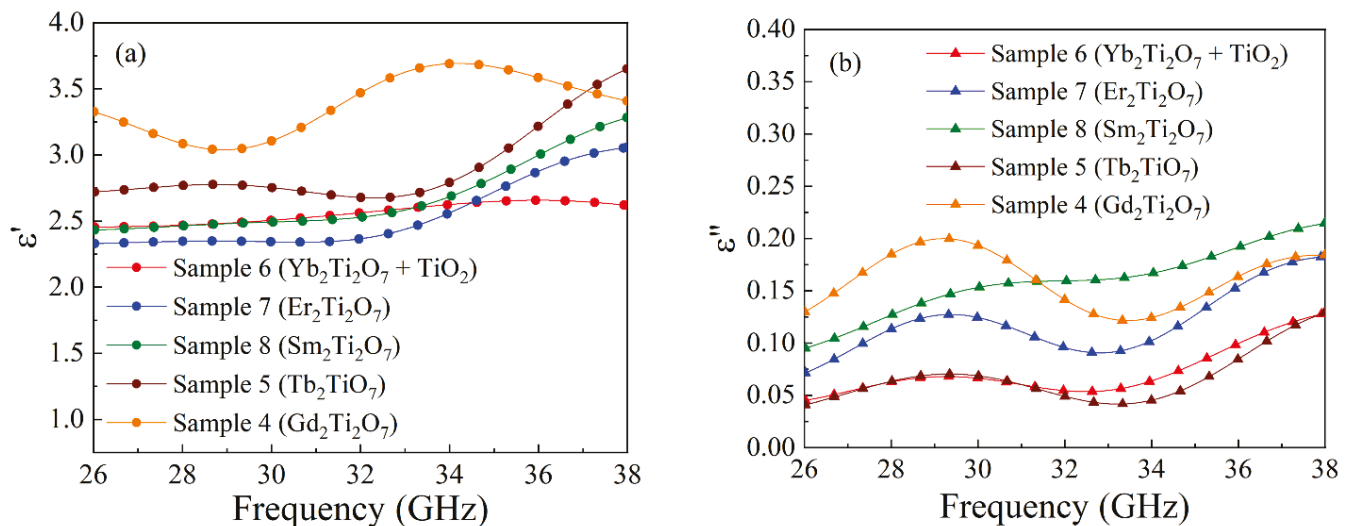


Figure 7. Frequency dependences of real (a) and imaginary (b) parts of the dielectric permittivity of the composite with rare earth titanates.

6. Dielectric Permittivity of Orthophosphate Composites

Let us now discuss the results of measurements of transmission and reflection coefficients for the samples with orthophosphate particles. The measurements are carried out with three samples: with LiCoPO_4 particles and different impregnations and with the sample of a composite with $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{PO}_4$ particles. Frequency dependences of transmis-

sion and reflection coefficients of electromagnetic waves for nanocomposite sample 1 with LiCoPO_4 particles and 6 impregnations are shown in Figure 8.

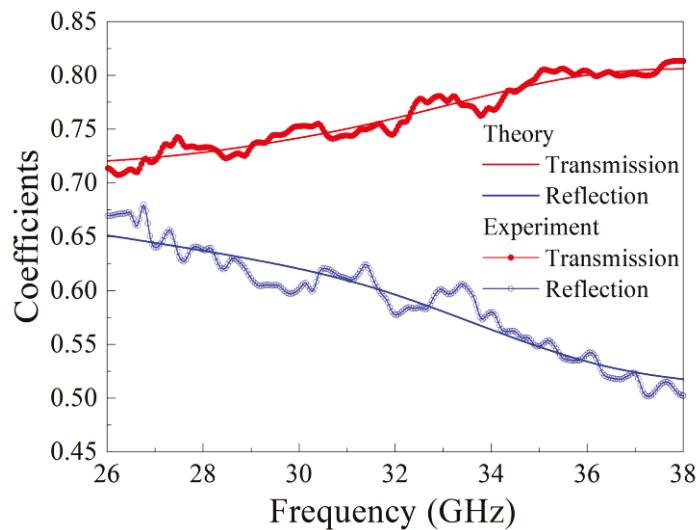


Figure 8. Frequency dependences of transmission and reflection coefficients of electromagnetic waves for nanocomposite sample 1 with LiCoPO_4 particles: experimental dependences are bold lines, and calculated dependences are thin solid lines.

Small differences between the calculated and measured values of the coefficients are caused by the minor mismatch of the tract. Frequency dependences of the real and imaginary parts of dielectric permittivity are shown in Figure 9. The ϵ' dependence is a nonmonotonic function for samples 1 and 2, and ϵ'' has a maximum for all samples. The inequality $\epsilon'' \ll \epsilon'$ is realized for all samples in the whole frequency range 26–38 GHz. The mean values of the real and imaginary parts of dielectric permittivity averaged over the range 26–38 GHz are presented in Table 5.

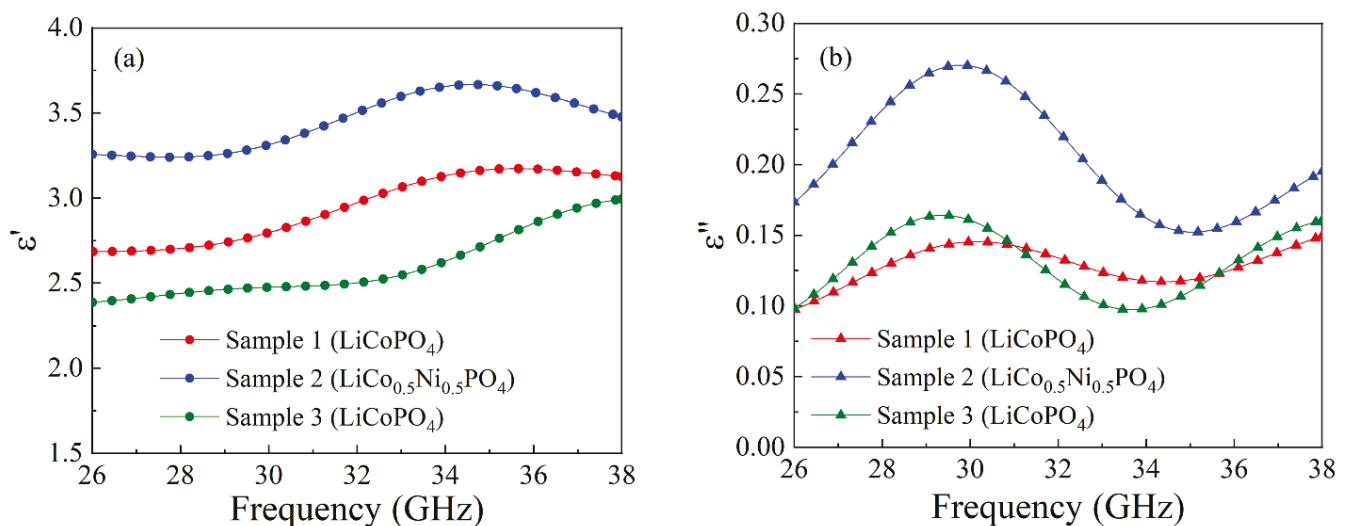


Figure 9. Frequency dependences of real (a) and imaginary (b) parts of the dielectric permittivity of the composite with orthophosphate particles.

7. Discussion

From the electromagnetic wave theory in condensed matter is known that the dielectric permittivity possesses dispersion, and its frequency dependence is expressed in terms of the frequencies of the transverse and longitudinal phonons, as follows [1]:

$$\varepsilon(\omega) = \varepsilon^\infty + \frac{\varepsilon^0 - \varepsilon^\infty}{1 - \omega^2/\omega_{TO}^2} = \varepsilon^\infty \frac{\omega_{LO}^2 - \omega^2}{\omega_{TO}^2 - \omega^2} \quad (5)$$

where ε^0 and ε^∞ are the isothermal and adiabatic dielectric permittivity, respectively; ω_{LO} is the frequency of longitudinal phonons; $\varepsilon(\omega_{LO}) = 0$, ω_{TO} is the frequency of transversal phonons; and $\varepsilon(\omega_{TO}) = 0$. We deal with the frequencies $\omega \ll \omega_{LO}, \omega_{TO}$. That is why we will analyze the diverse simple models and try to approximate the dependences shown in Figures 5, 7 and 9. The simplest and generally used is the Debye model [39], as follows:

$$\varepsilon(\omega) = \varepsilon^\infty + \frac{\varepsilon^0 - \varepsilon^\infty}{1 + i\omega\tau} \quad (6)$$

where τ is the relaxation time. It is adopted in this model that relaxation is described by one oscillator. In the Cole–Cole model, the following expression is proposed [40]:

$$\varepsilon(\omega) = \varepsilon^\infty + \frac{\varepsilon^0 - \varepsilon^\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (7)$$

where α is a coefficient, $\alpha \in [0, 1)$. The Davidson–Cole model is close the this one [41]; it looks like

$$\varepsilon(\omega) = \varepsilon^\infty + \frac{\varepsilon^0 - \varepsilon^\infty}{(1 + i\omega\tau)^\beta} \quad (8)$$

where β is a constant, $\beta \in (0, 1]$. The Havriliak–Negami model [42] contains two parameters, α and β , as follows:

$$\varepsilon(\omega) = \varepsilon^\infty + \frac{\varepsilon^0 - \varepsilon^\infty}{\left(1 + (i\omega\tau)^{1-\alpha}\right)^\beta} \quad (9)$$

where $\alpha \in [0, 1)$, $\beta \in (0, 1]$. The real and imaginary parts of dielectric permittivity corresponding to (9) can be written in the explicit form (see [43]), as follows:

$$\varepsilon'(\omega) = \varepsilon^\infty + (\varepsilon^0 - \varepsilon^\infty) r^{-\frac{\beta}{2}} \cos(\beta\theta) \quad (10)$$

$$\varepsilon''(\omega) = (\varepsilon^0 - \varepsilon^\infty) r^{-\frac{\beta}{2}} \sin(\beta\theta) \quad (11)$$

where

$$r = \left[1 + (\omega\tau)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right)\right]^2 + \left[(\omega\tau)^{1-\alpha} \cos\left(\frac{\alpha\pi}{2}\right)\right]^2 \quad (12)$$

and

$$\theta = \text{atan} \left[\frac{(\omega\tau)^{1-\alpha} \cos\left(\frac{\alpha\pi}{2}\right)}{1 + (\omega\tau)^{1-\alpha} \sin\left(\frac{\alpha\pi}{2}\right)} \right] \quad (13)$$

Models (6)–(9) can be generalized for the case of several discrete relaxation times. The sum of several terms is necessary to write corresponding to every relaxation time. For example, Formula (6) for K relaxation times takes the form

$$\varepsilon(\omega) = \varepsilon^\infty + \sum_{k=1}^K \frac{\Delta\varepsilon_k}{1 + i\omega\tau_k} \quad (14)$$

where $\Delta\varepsilon_k = \varepsilon_k^0 - \varepsilon_k^\infty$, $\varepsilon^\infty = \varepsilon_K^\infty$, and $\varepsilon^0 = \varepsilon_1^0$. Where $\varepsilon^0 = \varepsilon(\omega = 0)$ and $\varepsilon^\infty = \lim_{\omega \rightarrow \infty} \varepsilon(\omega)$. Let us notice that the following expressions result from (14):

$$\varepsilon'(\omega) = \varepsilon^\infty + \sum_{k=1}^K \frac{\Delta\varepsilon_k}{1 + (\omega\tau_k)^2} \quad (15)$$

$$\varepsilon''(\omega) = \sum_{k=1}^K \frac{\omega\tau_k\Delta\varepsilon_k}{1 + (\omega\tau_k)^2} \quad (16)$$

It is possible to generalize the Formulas (15) and (16) for the case when the continuous function of the relaxation times distribution $\xi(\tau)$ is discussed against of the discrete relaxation times. Therefore, the integral relations are following from (15) and (16)

$$\varepsilon'(\omega) = \varepsilon^\infty + \int_0^\infty \frac{\xi(\tau)d\tau}{1 + (\omega\tau)^2} \quad (17)$$

$$\varepsilon''(\omega) = \int_0^\infty \frac{\omega\tau\xi(\tau)d\tau}{1 + (\omega\tau)^2} \quad (18)$$

which correspond to the Fröhlich model [44]. In the case of the discrete set of relaxation times, when $\xi(\tau) = \sum_{k=1}^K \Delta\varepsilon_k\delta(\tau - \tau_k)$, where $\delta(x)$ is the Dirac delta function, Formulas (17) and (18) go into relations (15) and (16).

One more possibility is to explain the frequency dispersion of permittivity if a stretched exponential decay is realized in the composites under study [45]. The function $\Phi(t)$ is introduced in order to describe the time dependence of the electric polarization if the electric field is switched on instantaneously, as follows:

$$P(t) = P(t \rightarrow \infty)\Phi(t) \quad (19)$$

The dielectric permittivity can be calculated from the time derivative of $\Phi(t)$, as follows:

$$\varepsilon'(\omega) - 1 = (\varepsilon'(\omega \rightarrow 0) - 1) \int_0^\infty \left(-\frac{d\Phi}{dt} \right) \cos \omega t dt \quad (20)$$

$$\varepsilon''(\omega) = (\varepsilon'(\omega \rightarrow 0) - 1) \int_0^\infty \left(-\frac{d\Phi}{dt} \right) \sin \omega t dt \quad (21)$$

The function $\Phi(t)$ in the Debye model has the following form:

$$\Phi(t) = \exp\left(-\frac{t}{\tau}\right)$$

and our calculations show that an exponential decay of this sort does not satisfy our experimental data. In the case of stretched exponential decay, $\Phi(t)$ is chosen in the form of the Kohlrausch–Williams–Watts function, as follows:

$$\Phi(t) = \exp\left(-\frac{t}{\tau}\right)^\gamma \quad (22)$$

where $\gamma > 0$. Under the choice of (22), the real and imaginary parts of dielectric permittivity can be calculated via the Formulas (20) and (21) [19]. In the case of stretched exponential

decay, the ϵ' function decreases more slowly than in the Debye model, and it is possible to diminish ϵ'' to some extent within a definite frequency range.

All examined models (6)–(9), (20), and (21) result in a conclusion that the frequency dependences of the real part of dielectric permittivity are represented by the monotonically decreasing functions. In the case of two or more relaxation times, this dependence can look like a stepwise function also decreasing monotonically; see Formulas (14)–(16). For the composite materials, dielectric permittivity should be considered an effective permittivity. This effective permittivity can be calculated by mixing formulas from the permittivities of components [46]. It is possible to make sure that the Maxwell Garnett and Bruggeman formulas for the effective permittivity also led to a monotonic frequency dependence of ϵ' . Therefore, within the discussed models, we face an irreconcilable contradiction with the experimental fact that the frequency dependence of a real part of dielectric permittivity is a nonmonotonic function for a number of nanocomposite samples of rare earth manganates and titanates, as well as lithium orthophosphates.

As an example, we now consider the results of the approximations of the frequency dependence of the real part of permittivity for sample 12 using the Debye, Cole–Cole, Havriliak–Negami, and Kohlrausch–Williams–Watts models, which are shown in Figure 10.

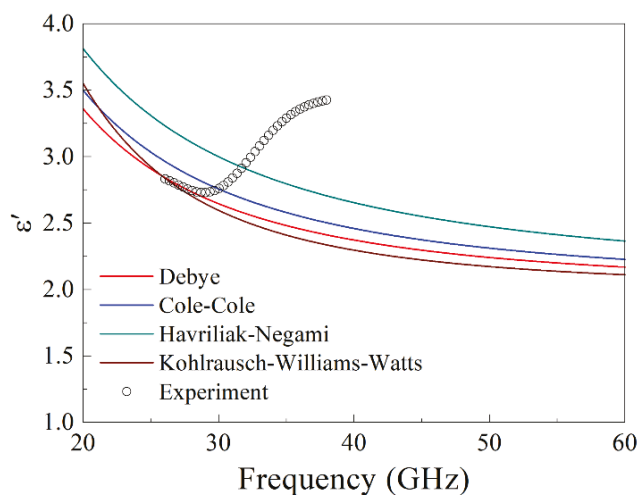


Figure 10. Approximations of the frequency dependence of ϵ' for sample 12 with YbMn_2O_5 particles, which are made using different relaxation models.

The experimental dependence being considered here was derived from the results of microwave measurements of transmission and reflection coefficients; see Figure 5. The calculations were performed using Formulas (6), (7), (9) and (20)–(22) for the following parameter values: $\epsilon^0 = 11.75$, $\epsilon^\infty = 1$, $\tau = 2.2 \cdot 10^{-11}$ s, $\alpha = 0.02$, $\beta = 0.95$, $\gamma = 1.3$. The choice of this set provides an approximation of the “regular” part of the experimental curve where the permeability decreases with increasing frequency.

Let us discuss why the imaginary part of the dielectric permittivity ϵ'' is essentially less than the real one, i.e., $\epsilon'' \ll \epsilon'$. Of course, we deal now with the frequency range of 26 to 38 GHz. Following the data from Table 5, ϵ'' is only 2–4% from ϵ' for the samples with ErMn_2O_5 , $\text{Tb}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_2\text{O}_7 + \text{TiO}_2$, and Er_2TiO_5 particles.

A possibility to explain the very low values of ϵ'' lies in the analytic properties of the $\epsilon''(\omega)$ function. For the media with spatial dispersion, this function is not a single-valued function of the complex frequency $\omega = \omega' - i\omega''$, and the singularities of a function can present in the upper half plane. Then the Kramers–Kronig dispersion relations in their typical view fail, and the relation between $\epsilon'(\omega)$ and $\epsilon''(\omega)$ can vary. For example, an essential difference between the Debye model and the Kramers–Kronig dispersion

relations as regards the decrease in ε'' has been observed in optics near the exciton state [47]. Further investigations are required in order to make the type of relaxation clear. Under our conditions, the inequality $q'l \ll 1$ is valid and the spatial dispersion is considered to be weak [48]. Here, q' is the real part of the wavenumber, and l is a length characteristic for the space scale of the nanocomposite structure. This is either the size of a separate particle ~ 60 nm or the period of the matrix structure ~ 260 nm. These spatial scales are too small in order to destroy the inequality. As known, the long-range crystalline ordering within the regions ≤ 1 mm in length is present in opal artificial crystals [49]. In principle, this extensive spatial scale could be a reason for the spatial dispersion taken into account. Therefore, the relation between the real and imaginary parts of dielectric permittivity can vary.

8. Conclusions

The frequency dependences of the transmission and reflection coefficients have been measured, and the complex dielectric permittivity for several nanocomposite rare earth manganates and titanates and Co-Ni lithium orthophosphates has been defined. These objects are chosen for study because they are multiferroics and possess a magnetoelectric effect. The composites are obtained by the impregnation of particles of multiferroics into artificial opal matrices. The dispersion of complex dielectric permittivity is studied at frequencies of 26 to 38 GHz. It has been established that the imaginary part of dielectric permittivity is much less than the real part in this frequency range. A comparison of the frequency dependences of the real and imaginary parts of permittivity with those prescribed by the Debye, Cole–Cole, Havriliak–Negami, and Kohlrausch–Williams–Watts models is performed, and it is demonstrated that all these models fail to satisfactorily describe the dispersion of the dielectric permittivity. In particular, these models cannot explain a nonmonotonic frequency dispersion of the real part of the dielectric permittivity observed for a number of nanocomposite samples of rare earth manganates and titanates and lithium orthophosphates.

Author Contributions: Conceptualization, A.B.R.; methodology, A.B.R. and D.V.P.; software, D.V.P.; validation, A.B.R., D.V.P. and M.S.S.; formal analysis, D.V.P.; investigation, A.B.R., E.A.K. and M.S.S.; writing—original draft preparation, A.B.R.; writing—review and editing, A.B.R. and D.V.P. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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Article

Evaluating the Output Performance of the Semiconductor Bridge Through Principal Component Analysis

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Abstract: The complex burst characteristic parameters of SCB were subjected to dimensionality reduction using principal component analysis (PCA), enabling accurate evaluation of the output performance of SCB. The accuracy and reliability of the PCA method were also validated. A 100 μ F tantalum capacitor was utilized to excite the SCB, while a digital oscilloscope recorded the characteristic parameters of the SCB explosion. The experimental results demonstrate that the critical burst time of SCB decreases with the rising voltage, and the critical burst energy decreases first and then increases with the rising voltage. The total burst time and total burst energy of SCB all decrease first and then increase with the rise of voltage. The PCA results indicate that as the voltage increases, the score of SCB output capacity initially decreases and then increases, reaching its lowest point at 17 V. The SCB was utilized to ignite lead styphnate (LTNR) under varying circuit conditions; the characteristic parameters obtained were analyzed using PCA to derive comprehensive scores. The same dataset was then input into the PCA model for pure SCB to calculate corresponding comprehensive scores. The consistency between the two sets of scores validated the accuracy and reliability of PCA in assessing SCB output capability.

Keywords: semiconductor bridge; electric explosion parameter; output capacity; principal component analysis

1. Introduction

As the initiating element and energy transfer system of weapon systems, initiating explosive devices have been extensively utilized in various applications such as weapon launching, ammunition propulsion, and attitude control of micro-nano satellites. Semiconductor bridges (SCBs) [1–4], representing a novel category of pyrotechnic devices, have garnered significant attention in both military and civilian sectors due to their distinctive operating principles and broad application potential [5]. Compared with traditional bridge wire pyrotechnics, SCB pyrotechnics offer enhanced safety and reliability, compact size, rapid response, and superior control over energy output [6,7].

In the explosion process of SCB, the initial event in the bridge area involves the conversion of electrical energy into thermal energy [8–10]. As the temperature increases, the bridge material vaporizes and transitions into a plasma state, which enables the SCB to ignite the charge through high-temperature plasma [11–13]. Consequently, two coupled energy

conversion modes are involved in the ignition process. These modes operate synergistically on the ignition agent, complicating the evaluation of SCB's output capacity. The SCB explosion process encompasses multiple characteristic parameters, such as critical burst time, critical burst energy, total burst duration, and total burst energy [14–16]. These parameters exhibit interdependencies, which add layers of complexity to the analysis. Analyzing a single parameter in isolation often leads to fragmented insights and underutilization of available data. Reducing the number of indices without careful consideration can result in a significant loss of valuable information and potentially erroneous conclusions.

In various research and application domains, it is often necessary to observe data sets containing multiple variables [17,18], collect extensive amounts of data, and analyze them to identify patterns. Multivariate big data sets provide rich information for research and applications but also significantly increase the workload associated with data collection [19–21]. Therefore, it is crucial to develop a method that reduces the number of indicators to be analyzed while minimizing the loss of information contained in the original indicators, thereby facilitating comprehensive analysis of the collected data. Given the inherent correlations among variables, transforming closely related variables into fewer new variables can be beneficial. These new variables should be uncorrelated, allowing fewer comprehensive indicators to represent the diverse types of information contained in each variable. Principal component analysis (PCA) is one such dimensionality reduction algorithm [22–25].

PCA aims to explain most of the variance in the original data using fewer variables. It transforms many highly correlated variables into mutually independent or uncorrelated variables. Typically, a few new variables, known as principal components, which are fewer than the original variables and can explain most of the variation in the data, are selected to serve as comprehensive indicators for interpreting the data [26–28].

For the complex explosion process of SCB, PCA can effectively retain most of the original information from the SCB explosion process, thereby enabling a more precise evaluation of the output capacity of SCB. In this paper, a 100 μF tantalum capacitor is utilized to excite the SCB with a voltage gradient ranging from 10 V to 34 V. A digital oscilloscope captures the characteristic parameters of the SCB during the burst process, and these parameters are subsequently summarized and analyzed. To comprehensively evaluate the output capacity of the SCB, PCA is employed to analyze the collected characteristic parameters. Finally, the SCB is used to ignite lead styphnate, thereby validating the accuracy and reliability of PCA in assessing the SCB's output capacity.

2. Experiment

2.1. Materials

The structure of the SCB features a “double V” shape. Figure 1a illustrates the schematic diagram of the SCB, which is encapsulated with a ceramic plug. The pad material of the SCB is Ti/Au, while the material in the double V bridge region is phosphorus-doped polysilicon with a doping concentration of $7 \times 10^{19} \text{ cm}^{-3}$. Figure 1b shows the physical appearance of the SCB. The central bridge region exhibits a V-shaped angle of 150° , with dimensions of $120 \mu\text{m} \times 415 \mu\text{m} \times 2.5 \mu\text{m}$, and the resistance of the SCB is 1Ω .

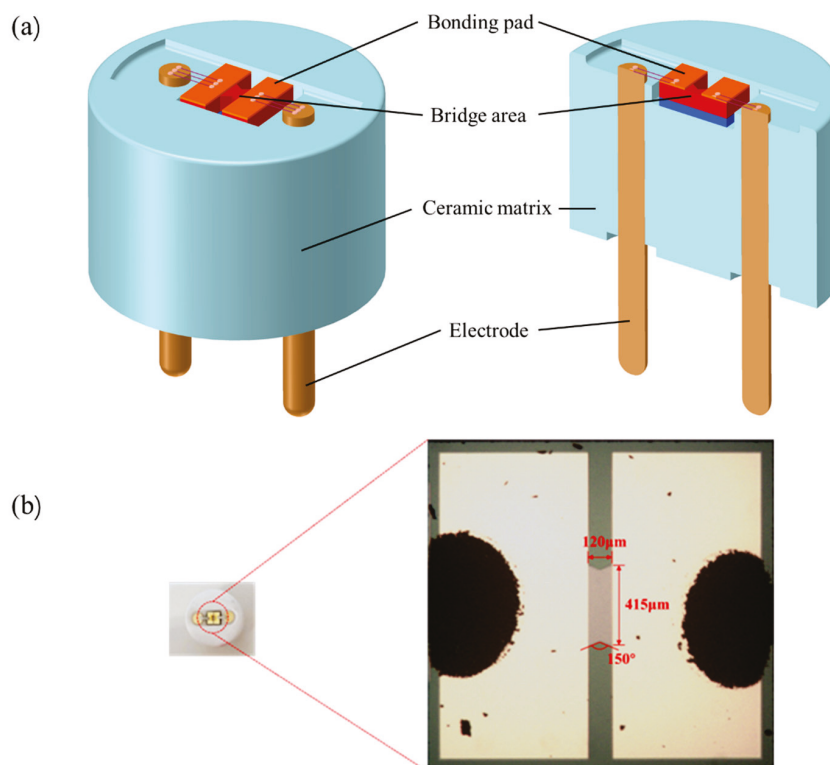


Figure 1. Structure diagram of SCB: (a) the schematic diagram of SCB; (b) the physical diagram of SCB and dimensional specifications of the bridge region.

2.2. The Firing Test System

The schematic diagram of the experimental setup for detonating SCB using capacitor discharge is illustrated in Figure 2. A tantalum capacitor with a capacitance of 100 μF was employed. The experiment was conducted at voltages ranging from 10 V to 34 V in increments of 1 V up to 24 V, followed by 26 V, 28 V, 30 V, and 34 V, with two parallel experiments performed at each voltage level. During the experiment, the SCB was connected to the circuit. Switch S2 was closed to charge the capacitor to the desired test voltage, after which switch S1 was closed to initiate the discharge of the SCB. Simultaneously, an oscilloscope (44Xs, Teledyne LeCroy Inc., Los Angeles, CA, USA) recorded the current and voltage waveforms across the SCB.

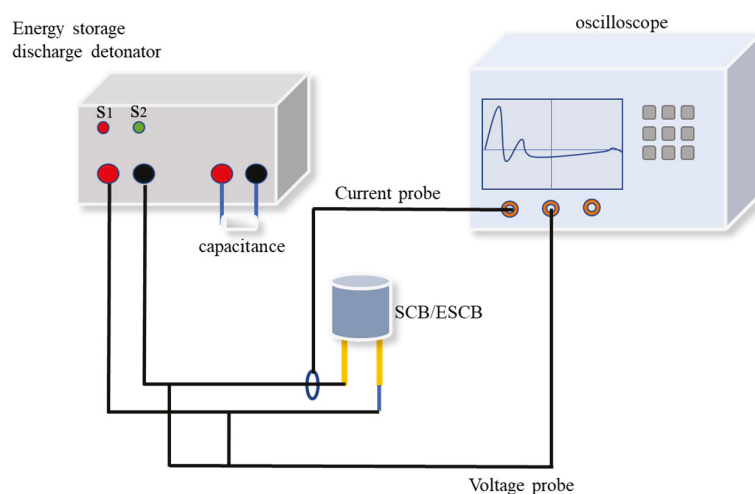


Figure 2. Schematic representation of the SCB electrical initiation device.

2.3. Evaluating the Output Capacity of SCB by Principal Component Analysis

By calculating the covariance matrix of the data matrix, we obtain the eigenvalues and eigenvectors of this matrix. We then select the matrix composed of the eigenvectors corresponding to the k largest eigenvalues (which represent the largest variances). This transformation projects the data matrix into a new space, achieving dimensionality reduction while preserving the most significant features.

The specific process is as follows [29,30]: Let $x_1, x_2, \dots, x_p$ denote p feature quantities in the SCB burst process, and $c_1, c_2, \dots, c_p$ denote the weights assigned to each feature quantity. The weighted sum is defined as $s = c_1x_1 + c_2x_2 + \dots + c_px_p$. The goal is to choose appropriate weights that can effectively differentiate the influence of each feature on SCB. Each voltage corresponds to a composite score denoted as $s_1, s_2, \dots, s_n$, where n is the number of voltages. If these scores are widely dispersed, it indicates good differentiation. Therefore, we aim to find weights that maximize the dispersion of $s_1, s_2, \dots, s_n$. Statistically, let $X_1, X_2, \dots, X_p$ be random variables representing sample observations. We seek $c_1, c_2, \dots, c_p$ such that the variance of $c_1X_1 + c_2X_2 + \dots + c_pX_p$ is maximized. Since variance measures the degree of variation in the data, maximizing it ensures that we capture the largest variability among the p variables. To avoid trivial solutions, we impose the constraint that the sum of squared weights equals one. Under this constraint, the optimal solution is a unit vector in p -dimensional space, representing a “direction” known as the principal component direction. One principal component may not suffice to represent the original p variables; thus, we also seek the second, third, and fourth principal components, ensuring that subsequent components do not contain information already captured by previous ones.

3. Result and Discussion

3.1. Analysis of Characteristic Parameters of the SCB Outburst Process

As illustrated in Figure 3, among the five key time points, t_0 marks the initiation of SCB energization, t_1 signifies the onset of material melting in the bridge region, t_2 denotes the start of SCB vaporization, t_3 represents the moment when SCB generates plasma and begins to explode. If the voltage is insufficient at this stage, plasma formation does not occur, leading to loop disconnection due to bridge vaporization, causing the current to drop to zero. t_4 indicates the completion of the SCB action, with the current returning to zero. The period from t_0 to t_3 is termed the critical burst time (t_d), during which the energy consumed by SCB is referred to as the critical burst energy (E_d). The interval from t_0 to t_4 is defined as the total burst time (t_s), and the energy expended by SCB during this phase is designated as the total burst energy (E_s). The formulas for calculating E_d and E_s are presented below.

$$E_d = \int_{t_0}^{t_3} UI dt \quad (1)$$

$$E_s = \int_{t_0}^{t_4} UI dt \quad (2)$$

Figure 4 shows the characteristic parameters during the SCB explosion process. At an excitation voltage of 10 V, the bridge area temperature does not reach the melting point, resulting in a prolonged heating period. The critical burst time initially decreases with the increase in voltage. Once the voltage is sufficient to cause the SCB to fully burst, the critical burst time exhibits a slight increase and subsequently remains constant. As the voltage continues to increase, the total burst time initially decreases and subsequently increases. This phenomenon can be attributed to the fact that before reaching the critical voltage, the increased voltage is insufficient to generate plasma in the bridge area but accelerates the melting or vaporization of the bridge material, leading to circuit interruption. Consequently,

the total burst time decreases. However, beyond the critical voltage, the extended duration of plasma formation causes the total explosion time to increase.

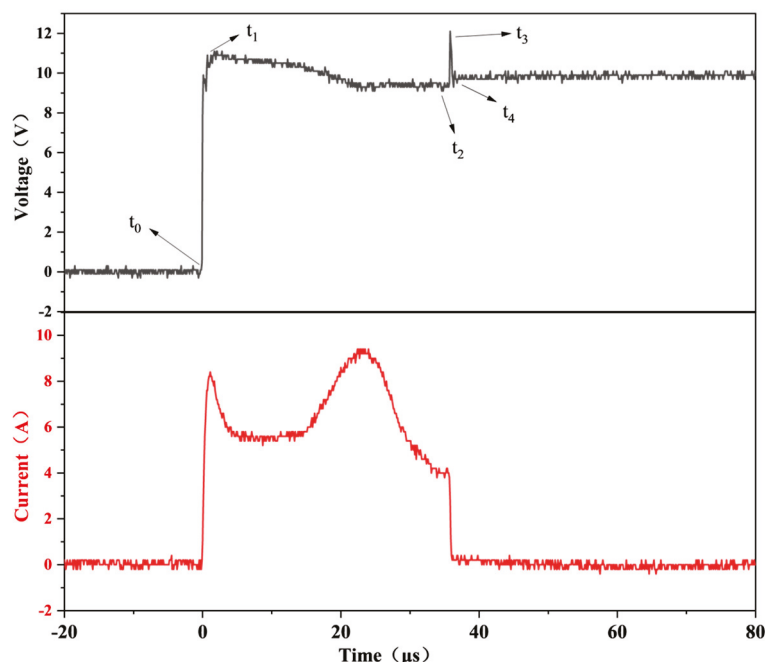


Figure 3. Typical electrical explosion curves and their characteristic points in SCB.

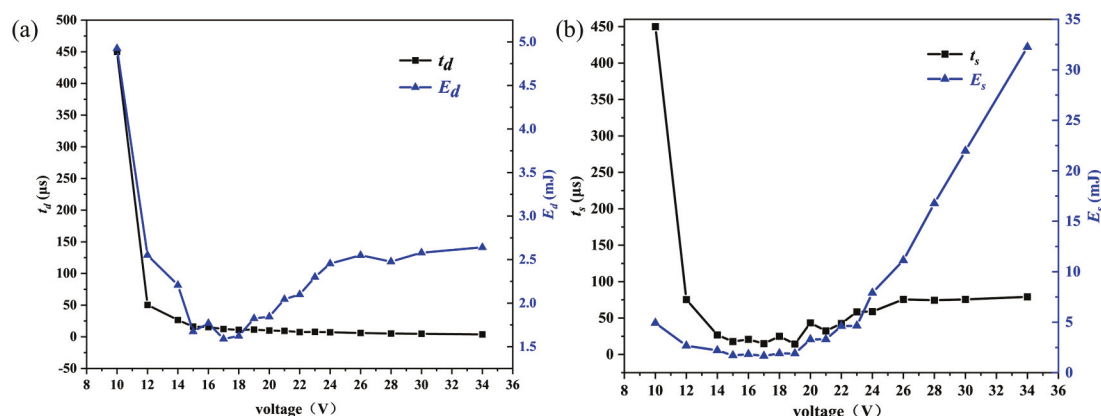


Figure 4. The variation of characteristic parameters of SCB with the increase of voltage during electrical explosion: (a) critical burst time and critical burst energy; (b) total burst time and total burst energy.

With the increase in voltage, the energy required for explosion initially decreases and then increases slightly. At 10 V, the bridge area remains in a channel state without melting, causing most of the capacitor's stored energy to act on the SCB, thereby requiring a relatively large amount of energy for explosion. Before reaching the critical voltage, increased voltage accelerates the fusion or vaporization of the bridge area, leading to circuit disconnection and preventing the capacitor's energy from being fully utilized by the SCB, thus reducing the energy required for explosion. After surpassing the critical voltage, the energy required for explosion increases slightly; once the voltage is sufficient for complete electrical explosion, the required energy stabilizes. Similarly, with increasing voltage, the total burst energy first decreases and then increases. At 10 V, the unmelted bridge area ensures that most of the capacitor's energy is applied to the SCB. Before the critical voltage, higher voltages cause circuit disconnection, decreasing the total burst energy. After the

critical voltage, plasma generated by the SCB's electrical explosion conducts electricity, closing the circuit and allowing the capacitor's energy to be released to the SCB again, resulting in an increase in total burst energy with voltage.

3.2. Evaluation of SCB Output Capacity by PCA

3.2.1. Principal Component Extraction

To more accurately assess the output capacity of SCB, additional characteristic parameters from the SCB explosion process were identified. Specifically, three new parameters—maximum voltage, maximum current, and electric explosion energy—were incorporated in Table 1. Electric explosion energy refers to the energy involved in the gasification and plasma generation processes of SCB, and its calculation formula is as follows:

$$E_P = E_s - E_d \quad (3)$$

Table 1. The change of maximum voltage, maximum current and electric explosion energy.

Voltage (V)	Maximum Voltage (V)	Electric Explosion Energy (mJ)	Maximum Current (A)
10	8.9	0	6.9
12	12.0	0.12	8.7
14	15.2	0.003	10.6
15	15.7	0.035	10.9
16	17.1	0.053	11.6
17	17.5	0.06	11.7
18	18.2	0.29	12.6
19	19.5	0.08	13.5
20	19.9	1.45	14.5
21	21.1	1.26	18.9
22	22.7	2.51	22.7
23	23.3	2.35	29.5
24	24.8	5.45	35.2
26	25.6	8.58	39.1
28	28.0	14.30	42.6
30	31.8	19.40	43.4
34	32.6	29.61	45.6

Since at 10 V voltage, the SCB only converts electrothermal energy without involving the electrical explosion process, the data under 10 V have been excluded from the analysis. Principal component analysis was conducted on seven characteristic quantities: peak current, peak voltage, critical burst time, critical burst energy, total burst time, total burst energy, and electric burst energy. The data are normalized using z-score normalization [30]. Specifically, the mean and standard deviation of the variable are calculated. Each observation of the variable is then standardized by subtracting the mean and dividing by the standard deviation; the calculation formula is as follows:

$$X_s = \frac{x - \bar{x}}{\sigma} \quad (4)$$

The principal components of the SCB feature parameters were computed to extract the eigenvalues and variance contribution rates, as presented in Figure 5.

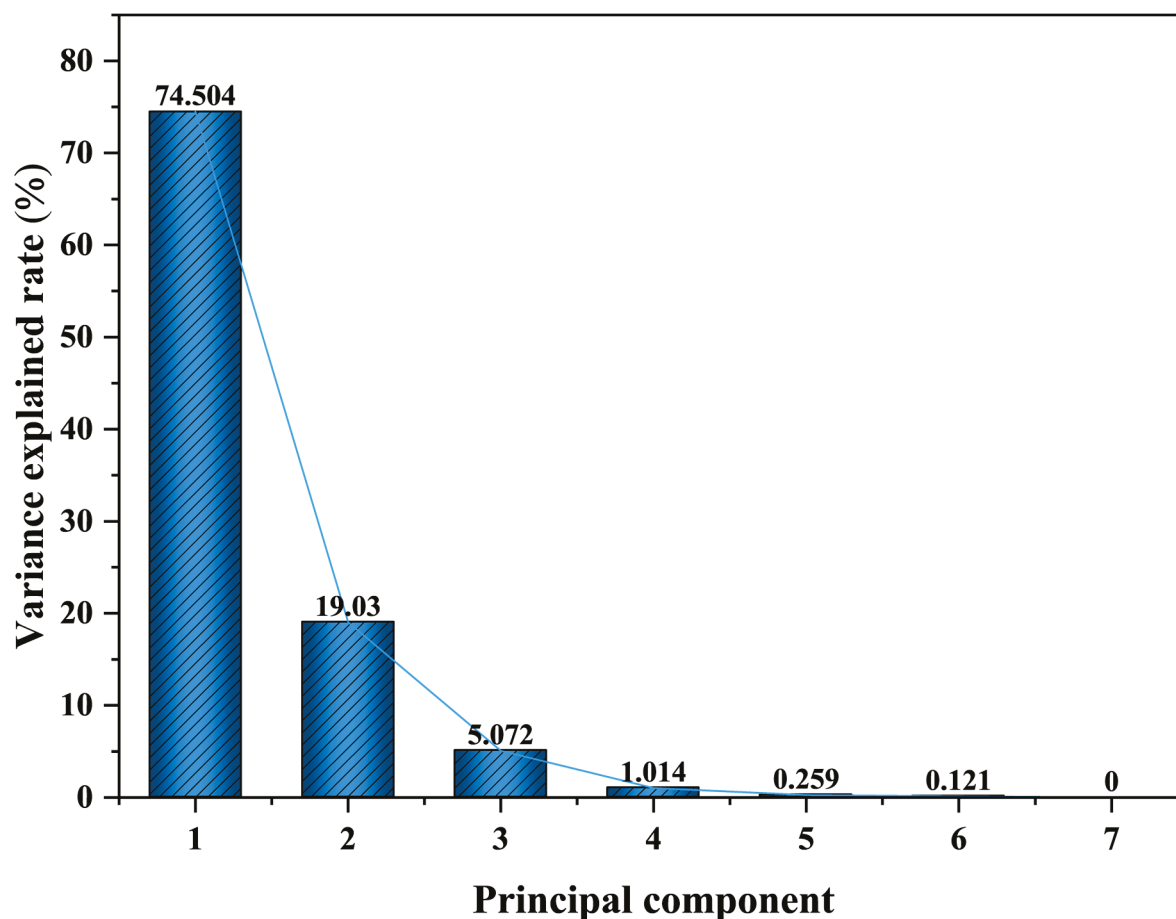


Figure 5. Lithotripsy: Explained variance ratio for each principal component.

Table 2 presents the extracted eigenvalues of principal components and their corresponding variance explanation rates. To visually assess the variance explanation rates of the principal components, a scree plot is constructed for the principal components. As can be seen from Figure 5, Principal Component 1 (PC1) accounts for 74.5% of the original information, while Principal Component 2 (PC2) accounts for 19.03%. PC1 and PC2 can already explain about 93.5% of the original information, which indicates that PC1 and PC2 collectively retain the majority of the original information, so PC1 and PC2 are chosen to replace the original information.

Table 2. Characteristic roots of principal components and variance explanation rate.

Principal Component	Principal Component Extraction		
	Characteristic Root	Variance Explanation Rate/%	Cumulative Interpretation Rate/%
1	5.215	74.504	74.504
2	1.332	19.030	93.534
3	0.355	5.072	98.606
4	0.071	1.014	99.620
5	0.018	0.259	99.879
6	0.008	0.121	100.000
7	0.000	0.000	100.000

3.2.2. Correlation Analysis

The load coefficient signifies the correlation coefficient between PC1 and PC2 with the original standardized data. A load factor exceeding 0.5 indicates a strong association,

where positive values denote a positive correlation and negative values indicate a negative correlation. As shown in Table 3, PC1 exhibits a strong positive correlation with critical electrical burst energy, total explosion time, total explosion energy, electric burst energy, critical explosion voltage, and peak current, while it shows a strong negative correlation with explosion delay time. Meanwhile, PC2 demonstrates a strong positive correlation with explosion delay time and critical electrical burst energy, a slight positive correlation with total explosion time, and slight negative correlations with other factors.

Table 3. The load coefficient of the principal component.

Characteristic Parameter	PC1		PC2	
	Characteristic Root	Load Coefficient	Characteristic Root	Load Coefficient
Critical burst time		−0.508		0.837
Critical burst energy		0.8		0.544
Total burst time		0.832		0.484
Total burst energy	5.215	0.947	1.332	−0.007
Electric explosion energy		0.941		−0.031
maximum voltage		0.947		−0.301
maximum current		0.973		−0.095

3.2.3. Principal Component Composite Score [24,29]

To determine the comprehensive score for each voltage level, we begin by calculating the individual component scores.

$$S_c = C_{lc} \times S_d \quad (5)$$

In the Formula (5), S_c represents the score of the principal component, C_{lc} represents the linear combination coefficient, and S_d represents standardized data.

The linear combination coefficient (C_{lc}) is obtained by dividing the loading coefficient by the square root of the corresponding eigenvalue.

$$C_{lc} = l_c / \sqrt{r} \quad (6)$$

where l_c represents the load coefficient and r represents the characteristic root of the corresponding principal component.

The following principal component score calculation formula is obtained:

$$S_{c1} = -0.222t_d + 0.350E_d + 0.364t_s + 0.415E_s + 0.412E_p + 0.414V_m + 0.426C_m \quad (7)$$

$$S_{c2} = 0.725t_d + 0.471E_d + 0.420t_s - 0.006E_s - 0.027E_p - 0.261V_m - 0.482C_m \quad (8)$$

where S_{c1} and S_{c2} denote the scores of PC1 and PC2, respectively, while V_m and C_m represent the peak voltage and current.

After obtaining the principal component scores, the comprehensive score is calculated by multiplying each principal component score by its corresponding variance contribution rate. The weighted sum of these products is then divided by the cumulative variance contribution rate.

$$S = (74.504S_{c1} + 19.030S_{c2}) / 93.534 \quad (9)$$

where S represents the comprehensive score, a higher comprehensive score indicates superior output capacity of SCB. As illustrated in Figure 6, the comprehensive score exhibits a trend of initially decreasing and subsequently increasing as the voltage rises from 10 V to 34 V, with minor fluctuations observed in the critical voltage region. The score

reaches its lowest point at 17 V, indicating that this voltage corresponds to the weakest output capacity of the SCB.

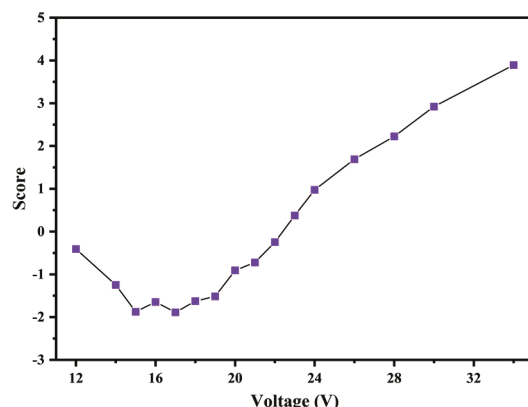


Figure 6. The comprehensive score of SCB output capacity under different voltages.

3.3. Verification of PCA Evaluation Method

To verify the accuracy of the PCA method in evaluating the output capacity of SCB, the test system as shown in Figure 2 was utilized to trigger LTNR under various conditions, including different voltages, capacitors, and line resistances. The characteristic burst parameters of SCB were collected under these conditions. Due to the presence of the agent, only critical burst time, critical burst energy, maximum voltage, and maximum current could be measured (Table 4). The four characteristic parameters were derived through PCA, and the composite scores under various testing conditions were subsequently obtained.

Table 4. Electrical explosion parameters of SCB under different circuit conditions.

Capacitance (μF)	Resistance (Ω)	Voltage (V)	Critical Burst Time (μs)	Maximum Voltage (V)	Maximum Current (A)	Critical Burst Energy (mJ)
47	0.2	21	14.0	37.7	11.66	1.94
			13.3	34.6	11.66	1.81
			12.5	42.4	8	1.69
	0.5	23	13.9	35.6	8.3	1.71
		25	12	33.6	12.6	1.82
			11.6	31.2	13.3	1.8
			12.2	29.5	12.7	1.85
		27	10.2	37.2	18.6	1.93
			10.7	52.1	16.6	1.98
			9.5	35	14.3	1.74
94	0.5	21	19.3	32.1	8.67	2.12
			17.3	43.4	6.0	1.85
			15.2	40.2	7.34	1.65
		23	14.1	37.4	12	1.85
			14.7	48	9.3	1.95
141	0.5	21	16.7	37.9	8.33	1.81
			17.0	35.2	7.0	1.83
			16.2	39.4	7.3	1.79
		30	7.7	53.5	22.3	1.93
			7.5	54.9	23.3	1.92
			8.2	44.3	23.0	2.2

To align with the characteristic parameters of the SCB that excited LTNR, three analytical factors (total burst time, total burst energy, and electric explosion energy) were excluded from Section 3.2. Consequently, a revised comprehensive score calculation model for SCB (non-igniting LTNR) was established. The SCB characteristic parameters of ignition LTNR were incorporated into the model for computation.

By comparing the two data plots, it is evident from Figure 7 that both exhibit a similar change trend with minimal discrepancy between them. By modifying the circuit conditions, it is evident that the PCA model of SCB alone aligns well with the PCA model of SCB igniting LTNR, irrespective of alterations in capacitance, resistance, or voltage. This suggests that the PCA model demonstrates higher accuracy in predicting the SCB output ability score.

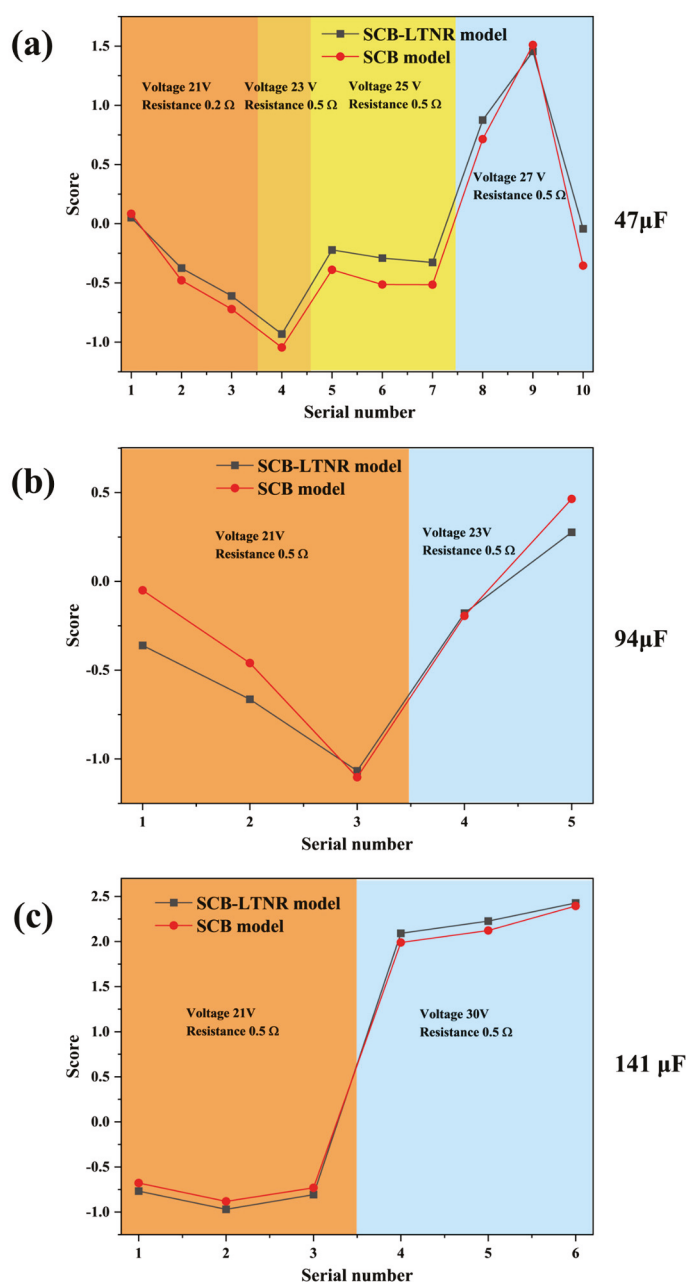


Figure 7. Comparison of the scores of the two models under different circuit conditions: (a) 47 μ F; (b) 94 μ F; (c) 141 μ F.

4. Conclusions

In this paper, a 100 μF tantalum capacitor is employed to stimulate the SCB under a steep voltage gradient. The changes in the SCB's characteristic parameters are recorded using a digital oscilloscope, and the trends of critical burst time, critical burst energy, total burst time, and total burst energy are summarized and analyzed. Principal component analysis (PCA) is utilized to comprehensively evaluate the explosion characteristics of the SCB, thereby assessing its output capacity. The PCA model of the SCB is compared with that of LTNR triggered by the SCB, verifying the accuracy and reliability of the SCB output capacity evaluation through PCA. The main conclusions derived from this study are as follows:

The critical burst time decreases as voltage increases and remains relatively constant once the voltage reaches the level required for a complete electrical burst. Prior to reaching the critical voltage, the critical burst energy decreases with increasing voltage; however, after surpassing the critical voltage, it exhibits a slight increase with further voltage increments. Once the SCB achieves complete detonation, the critical burst energy remains largely unchanged.

The total burst time and total burst energy both decrease with increasing voltage before the critical voltage is reached, but they increase with voltage increments after the critical voltage is surpassed.

The output capacity of SCB was assessed by synthesizing the characteristic parameters of the SCB explosion process using principal component analysis. The output capacity initially decreased and subsequently increased as the voltage was raised.

The PCA model of SCB is compared with that of LTNR-fired SCB under various circuit conditions. The close agreement between the two models validates the accuracy and reliability of using PCA to assess the output capacity of SCB. PCA can effectively leverage most of the information from the SCB outbreak process to evaluate the output capacity of SCB. However, as a statistical method, PCA benefits greatly from larger datasets for more robust analysis. The limitation of this work is the insufficient number of experiments, although collecting thousands of experimental data points would require collaboration among multiple working groups. The accuracy of the PCA method should be further validated using additional energetic materials.

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Article

Synergistic Regulation of Combustion Behavior and Safety Characteristics of Graphene Modified Core–Shell Al@AP Composites

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Abstract: Improving the energy release and safety of composite solid propellants is a key focus in energetic materials research. Graphene, with its excellent thermal conductivity and lubrication properties, is a promising additive. In this study, Al@AP core-shell particles doped with graphene were prepared via an in-situ deposition method. The structure, thermal decomposition, combustion, and safety performance of the graphene-doped Al@AP samples were investigated. Results showed that AP effectively coated aluminium to form a typical core-shell structure, with graphene uniformly loaded into the framework. Graphene contents of 1.0 and 4.0 wt.% reduced AP's thermal decomposition temperature by 0.97 and 16.68 °C, respectively. Closed-bomb and laser ignition tests revealed that pressure rise rates and combustion intensity increased with graphene content up to 1.0 wt.% but declined beyond that. Peak pressure reached 114.65 kPa at 1.0 wt.% graphene, and the maximum pressure increase rate was 13.29 kPa ms^{−1} at 2.0 wt.%. Additionally, graphene significantly improved safety by reducing sensitivity to impact and friction. The enhanced performance is attributed to graphene's large surface area and excellent thermal and electrical conductivity that promote AP decomposition and combustion, combined with its lubricating effect that enhances safety, though excessive graphene may hinder these benefits. This study provides balanced design criteria for graphene-doped Al@AP as solid propellants.

Keywords: al@ammonium perchlorate; graphene; thermal decomposition characteristics; combustion performance; safety performance

1. Introduction

Solid propellants provide propulsion energy for aerospace systems, and their rapid energy release and safety performance are actively researched [1]. Typical composite solid propellants are composed of oxidisers (for example, ammonium perchlorate (AP) and ammonium nitrate), fuels (aluminium powder), and polymer binders [2,3]. The oxidiser constitutes the largest proportion (typically >60%), indicating its significant effect on the performance of solid propellants [4]. Al@ammonium perchlorate (Al@AP, AP = [NH₄ClO₄]) remains the primary oxidiser in solid propellants because of its high density, oxygen content, heat release, gas production, excellent stability, and low cost [5,6]. Owing to its high energy

density, high combustion heat value, and low cost, Al powder is a major fuel in solid propellants, which significantly increases the combustion temperature and theoretical specific impulse [7–10]. The large proportions of AP and Al powder in typical solid propellant formulations significantly influence the combustion and safety performance of propellants, while core-shell structures exhibit improved ignition performance [11]. Furthermore, recent studies have shown that coating Al with AP to form a core-shell structure is effective for enhancing combustion performance. Therefore, investigating the combustion process and safety performance of Al@AP core-shell composites is crucial.

The burn rates of solid propellants are often regulated by adding catalysts [12–14]. Common catalysts used to increase the burn rate include metal oxides, nano-catalysts, and ferrocene derivatives [15–17]; however, the addition of catalysts may significantly increase the impact and/or friction sensitivity of a solid propellant, which can pose safety issues during production, storage, and use [18].

Over the past decade, two-dimensional materials such as graphene have been used extensively in various fields. Graphene is a novel nanocarbon material with a two-dimensional honeycomb crystal structure that exhibits superior physical, chemical, and mechanical properties compared to traditional carbonaceous materials [19]. Graphene can act as an effective catalyst in chemical reactions because of its excellent thermal and electrical conductivities and exceptionally large specific surface area, thereby facilitating the thermal decomposition of energetic materials [20]. Consequently, graphene-based materials are widely used in the field of energetic materials [21]. In addition, the excellent lubrication properties of graphene significantly enhance the safety performance of energetic materials. Although graphene-based materials have been investigated in the field of energetic materials, the mechanism by which pure graphene affects the thermal decomposition, ignition, and combustion and safety performance of the AP oxidiser remains unclear; understanding this mechanism is critical for the application of functional graphene materials in solid propellants. Previous studies have revealed an opposing relationship between reducing the decomposition temperature of energetic materials and improving safety performance [22,23]; however, methods to balance the burn rate and safety characteristics of energetic materials remain scarce.

In this study, Al@AP samples were prepared using an in-situ deposition method and uniformly doped with graphene. The morphology and composition of the samples were analysed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The effect of graphene content on the thermal decomposition characteristics and combustion performance of the samples was subsequently investigated using thermogravimetric analysis-differential scanning calorimetry-Fourier-transform infrared spectroscopy (TG-DSC-FTIR), laser ignition, and closed-bomb testing. The safety performance of the samples was examined using the BAM method for sensitivity testing. Finally, the mechanism by which graphene affects the combustion characteristics and safety performance of the samples was analysed. These findings provide valuable insights into the application of graphene-based materials in solid propellants.

2. Materials and Methods

2.1. Preparation of Samples

The details of the materials used in this study are listed in Table 1. The preparative process of the Al@AP composite particles is shown in Figure 1a. The specified masses of AP and Al listed in Table 2 were weighed and placed in a vial, to which a 5 mL mixture of DMF and methanol (1:4 *v/v*) was added. Next, the mixture was dispersed and dried using ultrasonic agitation in a water bath at 50 °C to obtain an Al@AP core-shell material. The process of preparing the graphene-doped Al@AP samples is illustrated in Figure 1b.

The prepared Al@AP and various masses of graphene were placed in a vial, followed by the addition of 5 mL of ethyl acetate. The mixture was then dispersed using ultrasonic agitation in a water bath at 50 °C for 2 h. Subsequently, the samples were dried in an oven at 50 °C and ground using an agate mortar.

Table 1. Physicochemical specifications of raw materials.

Material	Specification	Manufacturer
AP	Class II	Liming Chemical Co., Ltd., Luoyang, China
Al	50 nm	Zhongke Detong Technology Co., Ltd., Beijing, China
Graphene	Less than three layers	Kegong Metallurgical Materials Co., Ltd., Xingtai, China
<i>N,N</i> -Dimethylformamide (DMF)	ACS	J&K Scientific, Beijing, China
Methanol	HPLC	Beijing Tongguang Fine Chemicals Company, Beijing, China
Ethyl acetate	AR	Beijing Tongguang Fine Chemicals Company, Beijing, China

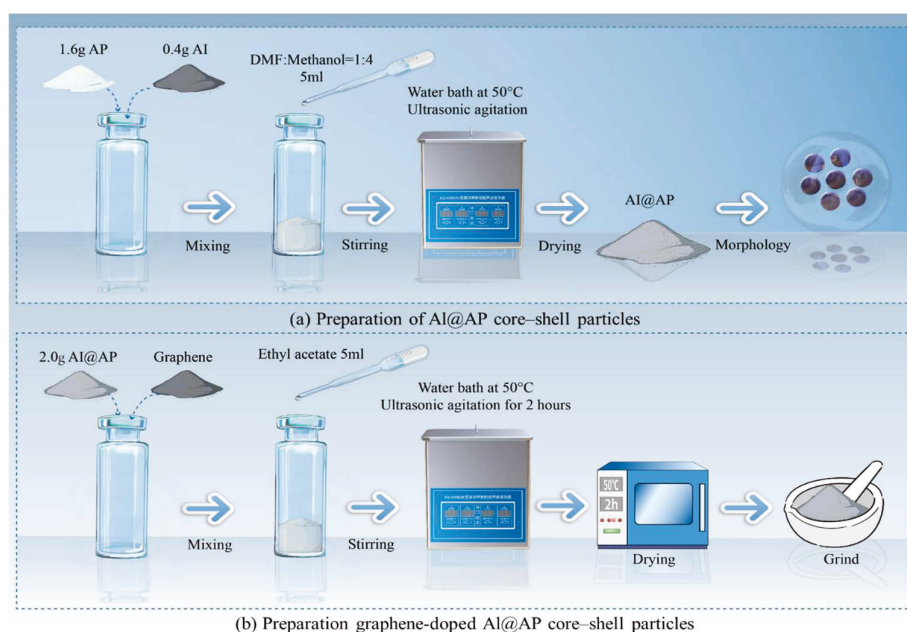


Figure 1. Hierarchical fabrication process of graphene-doped Al@AP core-shell composites.

Table 2. Formulation matrix of graphene-modified Al@AP energetic composites.

No.	AP (g)	Al (g)	Graphene (g)
G-1	1.6	0.4	0
G-2	1.6	0.4	0.01
G-3	1.6	0.4	0.02
G-4	1.6	0.4	0.04
G-5	1.6	0.4	0.08

2.2. Morphological and Structural Characterisation

Transmission electron microscopy (TEM; JEM-F200, Japan) was used to analyse the coating state of the Al@AP core-shell structure. SEM (Hitachi SU8600, Japan) was used to examine the microstructures of the graphene-doped Al@AP samples. XRD was employed to investigate the phase composition of the samples in the scanning range of $2\theta = 5\text{--}90^\circ$.

2.3. Thermal Decomposition Characterisation

Thermogravimetric analysis was conducted using a simultaneous thermal analyser-infrared mass spectrometer (Netzsch-STA449F3, Germany; FTIR Nicolet iS20, America; Netzsch-QMS 403, Germany, accessed from www.eceshi.com). Approximately 1.0 mg of sample was heated within the range of 40–800 °C under ambient conditions at a heating rate of 10 °C min^{−1}. High-purity Ar gas (flow rate = 240 mL min^{−1}) was used for purging.

2.4. Laser Ignition Test for Characterising the Combustion Characteristics

The combustion characteristics of the samples were analysed using a CO₂ laser ignition system with an output power of 10 W and a duration of 200 ms. A high-speed photography camera (Revealer X113; Hefei Agile Device Co., Ltd., China) with a frame rate of 8000 frames per second and an exposure time of 30 µs was used to analyse the ignition properties, combustion processes and flame morphology of the samples. The experimental setup in which the combustion process was recorded in synchronised triggering mode is displayed in Figure 2.

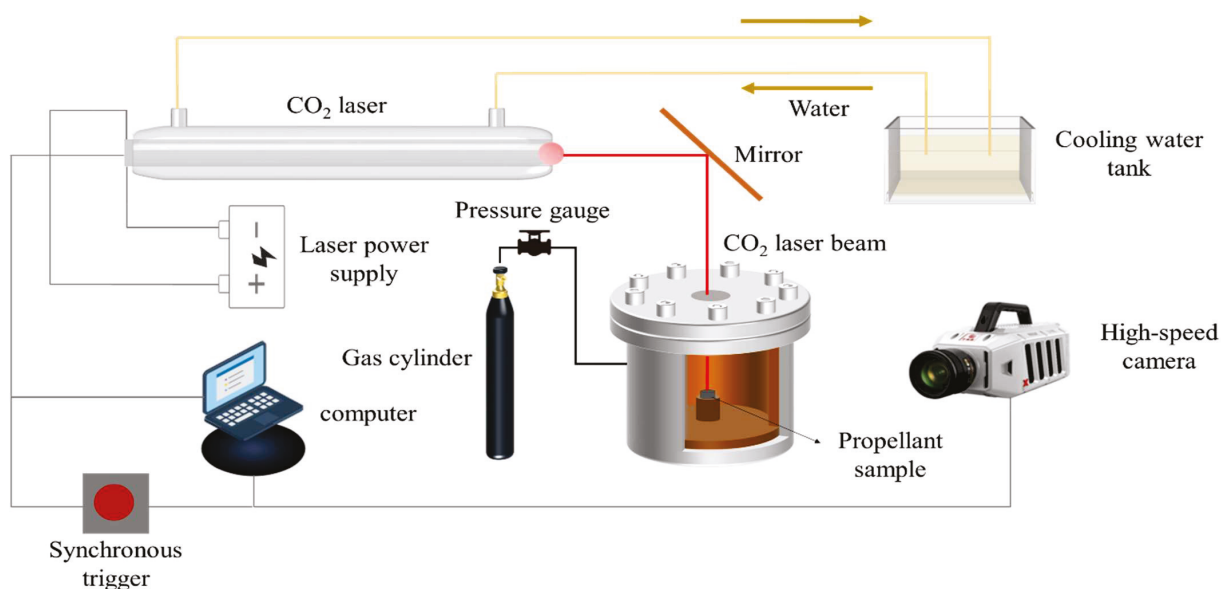


Figure 2. Schematic of the CO₂ laser ignition combustion test system.

2.5. Closed-Bomb Testing

A schematic of the experimental test device used for obtaining the combustion pressure-time curves is shown in Figure 3. During the experiment, 30 ± 0.1 mg samples were weighed and placed into a 50 mL closed-bomb vessel with an electric ignition controller.

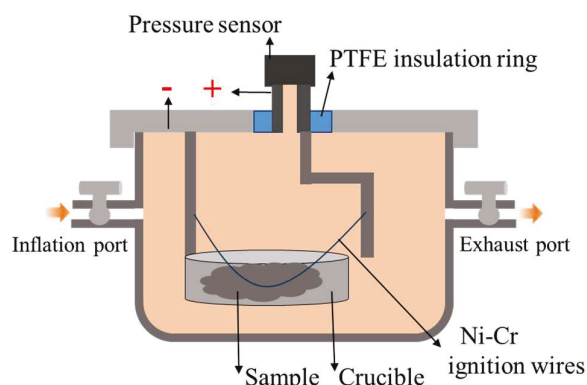


Figure 3. Schematic of the closed-bomb test device.

2.6. Impact and Friction Sensitivity Testing

Safety is critical for energetic materials. The impact (BFH-12, IDEA SCIENCE Group) and friction sensitivities (FSA-12, IDEA SCIENCE Group) were tested using the standard BAM method.

3. Results and Discussion

3.1. Surface Morphology and Structural Analysis

SEM was used to examine the microstructure of the samples and analyse the distribution and morphology of their components. As shown in Figure 4, sample G-1 exhibited a uniform distribution of Al@AP on the graphene surface. Some particles exhibited aggregation because of the recrystallisation of AP; however, no large aggregates were observed. The TEM image indicated approximately 5-nm-thick AP layers were present on the surface of the Al particles, which is suggestive of an effective coating and typical core-shell structure. Owing to the addition of graphene at a low concentration and considering the large specific surface area of graphene in G-2, the Al@AP particles were distributed on the surface of graphene with graphene wrapped around them. In G-3, more graphene was embedded in the Al@AP particles due to a higher graphene content. However, in G-4, with a graphene content of 2 wt.%, graphene was wrapped around numerous Al@AP particles. Finally, all the Al@AP particles were distributed on the graphene sheets in G-5. Overall, the distribution of Al@AP varied with increasing graphene content. Initially, the Al@AP particles were partially coated with graphene; however, the Al@AP particles tended to envelope with increasing graphene content. This transition may influence the combustion behaviour of Al@AP particles.

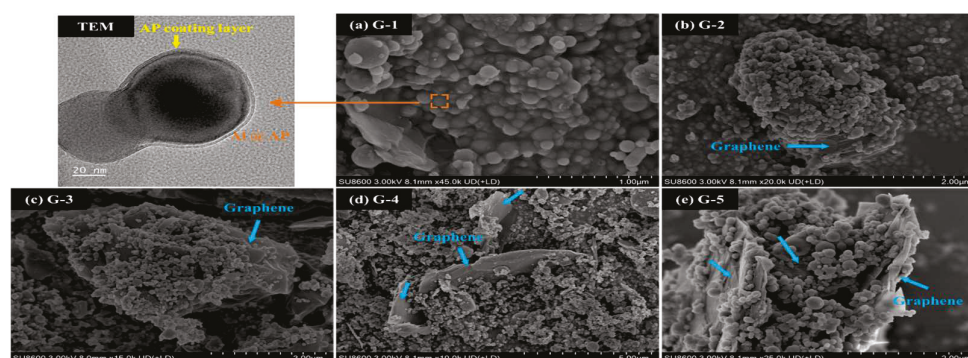


Figure 4. Microstructural evolution of graphene-doped Al@AP composites with varied doping concentrations.

The XRD patterns of the Al@AP samples with varying graphene contents are shown in Figure 5. The diffraction peak at $2\theta = 26.49^\circ$ is attributed to the (002) plane of graphene. The peaks at $2\theta = 38.50^\circ, 44.72^\circ, 65.10^\circ, 78.22^\circ$, and 82.45° were assigned to the diffraction peaks of face-centred cubic Al, and represent the (111), (200), (220), (311), and (222) crystallographic planes, respectively. The peaks at $2\theta = 19.32^\circ, 24.58^\circ, 30.72^\circ, 34.39^\circ$, and 63.95° were assigned to the diffraction peaks of AP. The XRD patterns showed sharp diffraction peaks for all samples, indicating their high crystallinity and the absence of amorphous phases. The samples prepared using the in-situ deposition method exhibited clear diffraction peaks, suggesting that this method promoted AP crystallisation without significantly altering the crystalline structure of the raw materials. In addition, the crystalline peaks of each component were distinctly identifiable in the diffraction patterns, providing an indication of the effective loading of graphene into the Al@AP framework.

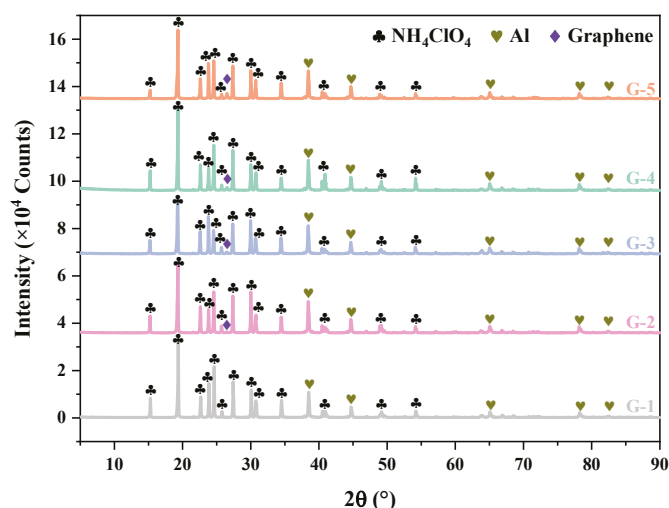


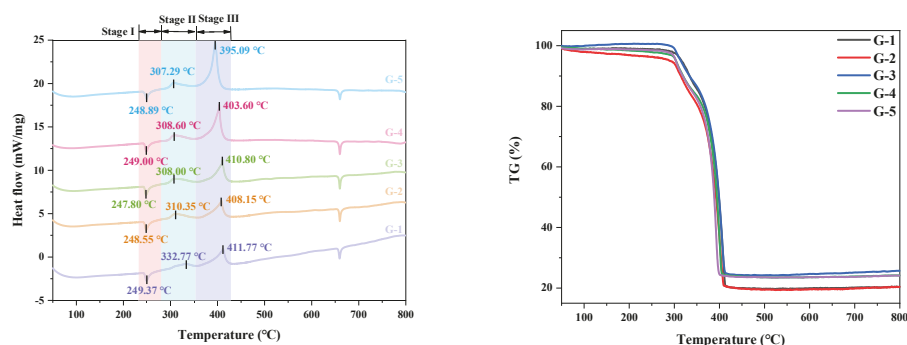
Figure 5. XRD patterns of graphene-doped Al@AP composites with varied doping concentrations.

3.2. Analysis of the Thermal Decomposition Characteristics

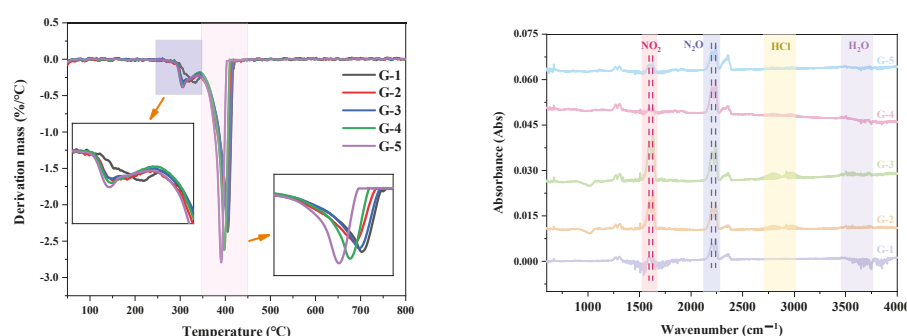
The TG-DSC-FTIR traces of the Al@AP samples with varying graphene contents are shown in Figure 6. The results show that graphene significantly influences the thermal reaction characteristics of the Al@AP samples. The DSC traces shown in Figure 6a revealed that G-1 (Al@AP) gives rise to four characteristic peaks. The first stage at 249.37 °C represents an endothermic phase transition owing to the transition from an orthorhombic to a cubic crystalline structure [24]. The second stage shows an exothermic process at 332.77 °C, which corresponds to the low-temperature decomposition (LTD) of AP, involving solid-gas reactions, dissociation, and sublimation processes. The third stage corresponds to the high-temperature decomposition (HTD) of AP, in which gas-phase reactions are the controlling steps. AP fully decomposes into volatile products such as NO, O₂, Cl₂, and H₂O, with an HTD of 411.77 °C. Compared with pure Al@AP, the addition of graphene does not affect the crystalline transition process of AP; however, it decreases both the LTD and HTD temperatures. When 0.5, 1.0, 2.0, and 4.0 wt.% graphene was added, the LTD temperature decreased to 310.35, 308.00, 308.60, and 307.29 °C, respectively, exhibiting reductions of 22.42, 24.77, 24.17, and 25.48 °C, respectively. The HTD temperatures of G-2 to G-5 were 408.15, 410.80, 403.60, and 395.09 °C, respectively, exhibiting reductions of 3.62, 0.97, 8.17, and 16.68 °C, respectively. These results are consistent with those of previous studies, in which graphene addition decreased the HTD temperature of AP [25,26]. A decrease in the HTD temperature implies an increase in the combustion rate of the samples [27]. Therefore, graphene effectively promotes the thermal decomposition of AP, and the effect is enhanced with increasing graphene content. This enhancement is attributed to the excellent electrical and thermal conductivities of graphene, which facilitate electron and heat transfer during AP decomposition.

The TG and DTG traces of the samples are shown in Figure 6b,c, respectively. The decomposition process of the pure Al@AP sample (G-1) occurred in two stages; thermogravimetric analysis indicated a mass loss of 14.92% after the first decomposition stage. Both the initial weight loss temperature and peak temperatures of the two DTG stages decreased with increasing graphene content, suggesting that graphene promoted the thermal decomposition of Al@AP, with a more pronounced effect observed at higher graphene loadings. This phenomenon can be attributed to the large specific surface area of graphene, which facilitates the adsorption of Al@AP particles to graphene. The efficient electronic transfer ability of graphene leads to the adsorption of NH₃ and HClO₄, generated during AP thermal decomposition, onto the graphene surface, thereby delaying their entry into

the gas phase and their participation in oxidation reactions. This results in a decrease in the decomposition temperature of AP.



(a) DSC curves of graphene-doped Al@AP composites with varied doping concentrations. (b) TG curves of graphene-doped Al@AP composites with varied doping concentrations.

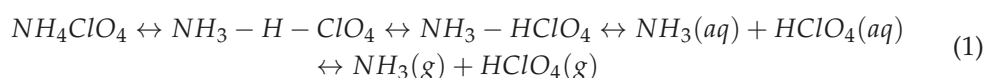


(c) DTG curves of graphene-doped Al@AP composites with varied doping concentrations. (d) FTIR curves of graphene-doped Al@AP composites with varied doping concentrations.

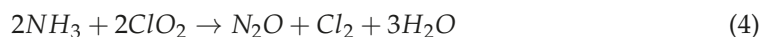
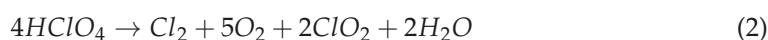
Figure 6. (a) DSC, (b) TG, (c) DTG, and (d) FTIR curves for samples G-1 to G-5.

The FTIR spectra of the gas-phase products at the peak weight loss temperatures for samples G-1 to G-5 indicate the presence of N_2O (2238 and 2201 cm^{-1}), NO_2 (1630 and 1598 cm^{-1}), H_2O (3500–4000 cm^{-1}), and HCl (2700–3012 cm^{-1} ; Figure 6d, and indicates that the main gaseous products formed during the thermal decomposition of AP were N_2O and NO_2 . For G-1, the absorption intensity of N_2O was higher than that of NO_2 . With increasing graphene content in G-2 and G-3, the absorption intensity of NO_2 was greater than that of N_2O . A further increase in the graphene content resulted in the absorption intensity of N_2O exceeding that of NO_2 (see G-4 and G-5). The variations in the N_2O and NO_2 intensities suggest a competitive relationship in their formation during the thermal decomposition of AP. Therefore, the addition of graphene significantly influences the catalytic activity of AP and its thermal decomposition, and to varying degrees, based on the amount of graphene added.

The initial step in the thermal decomposition of AP (Equation (1)) involves proton transfer, in which NH_4ClO_4 dissociates to form adsorbed NH_3 and $HClO_4$. Next, during the LTD process, reactions occur between NH_3 molecules adsorbed onto the particle surface; NH_3 remains adsorbed on the particle surface without oxidation by $HClO_4$ decomposition products at lower temperatures, resulting in eventual complete AP surface coverage by NH_3 , thus concluding LTD [28,29].



The HTD of AP involves gas-phase reactions, in which the adsorbed NH_3 and $HClO_4$ undergo desorption into the gas phase. In the gas phase, $HClO_4$ further decomposes to generate oxidised products that then oxidise NH_3 to provide the final products, such as HCl , H_2O , N_2O , NH_3 , and NO_2 [30].



According to the generally accepted theory for AP thermal decomposition, NH_3 reacts with ClO_2 to form N_2O , which is further oxidised to NO_2 . In G-2 and G-3, higher NO_2 content is indicative of more complete AP decomposition, suggesting that graphene facilitates more thorough AP decomposition. In contrast, G-4 and G-5 yielded more N_2O , indicative of incomplete decomposition caused by residual O_2 . The SEM images revealed that moderate graphene doping increases the contact area between graphene and Al@AP, facilitating NH_4ClO_4 dissociation, providing abundant active sites for AP decomposition and reducing decomposition temperatures. However, excessive graphene encapsulation around the Al@AP particles in G-4 and G-5 formed closed spaces that inhibit AP decomposition, resulting in incomplete decomposition. Such variations in thermal decomposition inevitably affect the combustion characteristics of the samples.

3.3. Analysis of Closed Combustion Pressure

The pressure-time curves of Al@AP with different graphene loadings are shown in Figure 7, and Table 3 lists the calculated parameters. The peak pressure and rate of pressure increase of the samples increased when the graphene content was increased from 0 (G-1) to 1.0 wt.% (G-3); the peak pressure increased by 2.27 and 6.30 kPa upon the addition of 0.5 and 1.0 wt.% graphene, respectively, and the rate of pressure increase correspondingly increased by 6.23 and 7.83 kPa ms^{−1}, respectively. However, both parameters for the samples containing 2.0 (G-4) and 4.0 wt.% graphene (G-5) were lower than those of G-3.

Table 3. Peak pressures and rates of pressure increase for graphene-doped Al@AP composites with varied doping concentrations.

Sample	Pressure (kPa)	$\Delta P/\Delta t$ (kPa ms ^{−1})
G-1	108.35	5.46
G-2	110.62	11.69
G-3	114.65	13.29
G-4	85.27	12.10
G-5	71.79	6.54

SEM images of G-2 and G-3 indicated that graphene was embedded into the Al@AP particles. The high thermal conductivity of graphene facilitated rapid internal heat transfer, produced from the high-temperature gases produced during combustion, along the graphene surface, thereby rapidly heating the sample in proximity to graphene and forming a heating zone; immediate ignition then occurred when the heated sample reached the ignition temperature. As a result, the maximum pressure and pressure increase rates for G-2 and G-3 were higher than those of G-1. In G-4 and G-5, as mentioned previously, graphene was wrapped around the Al@AP particles. Although the samples near graphene were heated rapidly, the larger specific surface area resulting from a higher graphene content

inhibited combustion. Consequently, the maximum pressure and rates of pressure increase for G-4 and G-5 were lower than those of G-3.

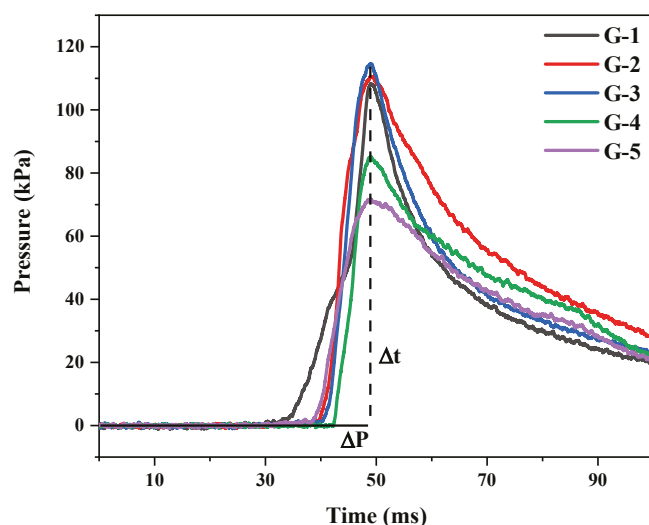


Figure 7. Pressure-time curves of graphene-doped Al@AP composites with varied doping concentrations.

3.4. Analysis of Combustion Characteristics

The ignition and combustion characteristics of the samples were assessed using a laser ignition test. As shown in Figure 8a, the flame intensity gradually increased when G-1 ignited, reaching its peak at 83.88 ms. Subsequently, the flame intensity diminished until reaching a steady state, after which combustion proceeded steadily until the sample was fully consumed. This phenomenon was consistent among all samples and occurred because upon ignition, the flame rapidly spread across the surface of the sample, which increased the combustion area and, in turn, increased flame intensity. Sample surface coverage by the flame was nearly complete as combustion continued, eventually transitioning into laminar burning, in which the flame stabilised until the sample was fully burned.

In addition, the combustion intensity of the samples increased, and the combustion duration decreased with increasing graphene content. This can be attributed to the following: (1) Carbon materials have high emissivity, which increases radiation intensity, and (2) graphene promotes the ignition and combustion of Al in the propellant, increasing the radiation intensity. At the same laser energy input and weight, a lower combustion duration indicated that a higher graphene content resulted in faster propellant combustion. This finding is consistent with the DSC results, which showed that graphene significantly reduced the thermal decomposition temperature of AP. A decrease in AP thermal decomposition temperature decreases the ignition delay and increases the combustion rate of the propellant [31].

Al@AP particle agglomeration was also observed during combustion in G-2 to G-5, where the bright particles represent ignited Al@AP. For G-2 and G-3, typical spherical agglomerates and distinct core-shell structures were observed during combustion. This represented ‘Graphene@(Al@AP)’ combustion, in which graphene-doped Al@AP agglomerates were ejected into the air by combustion gases, where they subsequently burned with graphene, acting as a heat transfer medium. Combined with the FTIR results, it can be inferred that AP combustion was complete at this stage, resulting in a bright flame intensity. For G-4 and G-5, the concentration of typical spherical agglomerated particles decreased with increasing graphene content due to the formation of ‘(Al@AP)@graphene’ agglomerates. Here, graphene enclosed the Al@AP particles into a confined environment where they were unable to burn completely, thereby leading to reduced flame intensity.

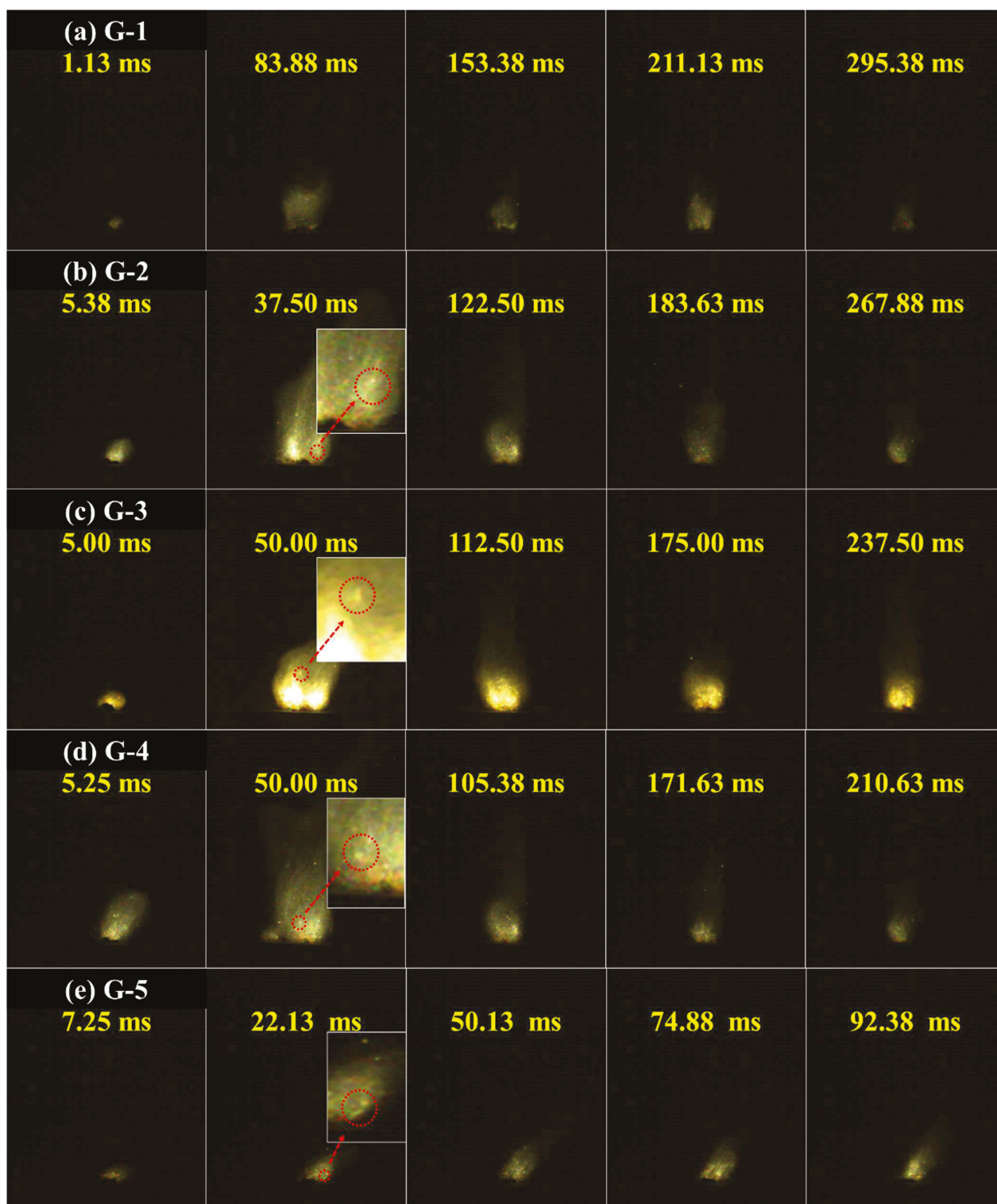


Figure 8. Ignition and combustion images of graphene-doped Al@AP composites with varied doping concentrations.

3.5. Impact and Friction Sensitivities

As shown in Figure 9, the BAM impact and friction sensitivities of G-1 are 2.5 J and 84 N, respectively, which increased to 10.0 J and >240 N when the graphene content was increased to 4.0 wt.%. This improvement is attributed to the excellent lubricating properties of graphene. The layered structure of graphene features weak interlayer bonding forces, resulting in planes that can easily slide over one another. The sliding motion reduces

frictional heat generation between energetic materials when external mechanical stimuli are applied, decreasing the formation of hot spots and enhancing the impact and friction performance. Thus, the addition of graphene resulted in a significant improvement in safety performance, indicating that graphene serves as a multifunctional and versatile additive by not only enhancing the combustion performance of Al@AP but also improving its safety characteristics.

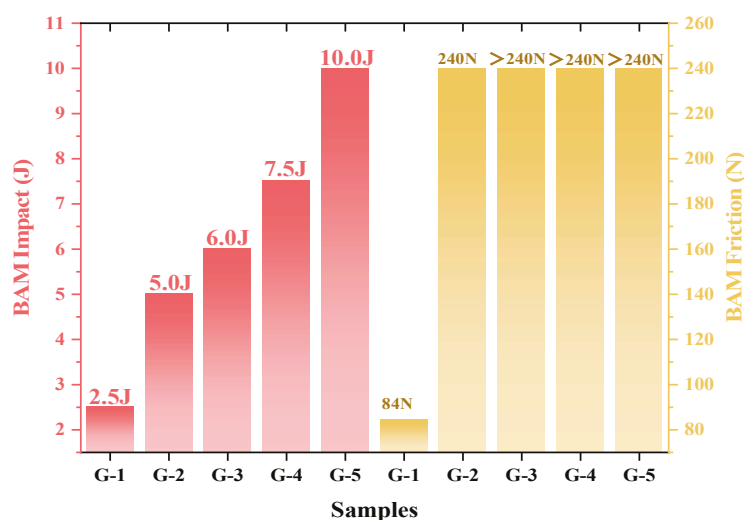


Figure 9. Results of standard BAM impact and friction sensitivity analyses for graphene-doped Al@AP composites with varied doping concentrations.

3.6. Comprehensive Effect of Graphene on Al@AP Performance

The experimental results indicate that graphene effectively altered the thermal decomposition, ignition, and combustion characteristics of Al@AP, enhancing its safety performance; the corresponding data is summarised in Table 4, and the comprehensive impact of graphene content on the combustion performance of Al@AP particles is shown in Figure 10. The sample structure was best described as ‘Graphene@Al@AP’ when the graphene content was 0.5 wt.% and 1.0 wt.%. Here, the large specific surface area of graphene facilitates electron and heat transfer, increasing the number of reaction sites for AP decomposition and facilitating chemical reactions. In addition, graphene improves the ability to capture and transfer electrons during AP decomposition, accelerating the electron transfer process and promoting the complete decomposition of AP. Furthermore, graphene promotes Al oxidation, improving combustion efficiency and intensity. However, the sample structure was best described as ‘(Al@AP)@Graphene’ when the graphene content was 2.0 and 3.0 wt.%. The large specific surface area of graphene no longer played a promotional role; instead, it enclosed the Al@AP particles, creating a confined environment that inhibited AP decomposition. The mechanism by which graphene influences combustion characteristics can be attributed to its large specific surface area and high thermal conductivity.

Table 4. Representative data for sample thermal decomposition, pressure, and safety performance.

Sample	T_{LTD} (°C)	T_{HTD} (°C)	Pressure (kPa)	BAM Impact/Friction
G-1	332.77	411.77	108.35	2.5 J/84 N
G-2	310.35	408.15	110.62	5.0 J/240 N
G-3	308.00	410.80	114.65	6.0 J/>240 N
G-4	308.60	403.60	85.27	7.5 J/>240 N
G-5	307.29	395.09	71.79	10.0 J/>240 N

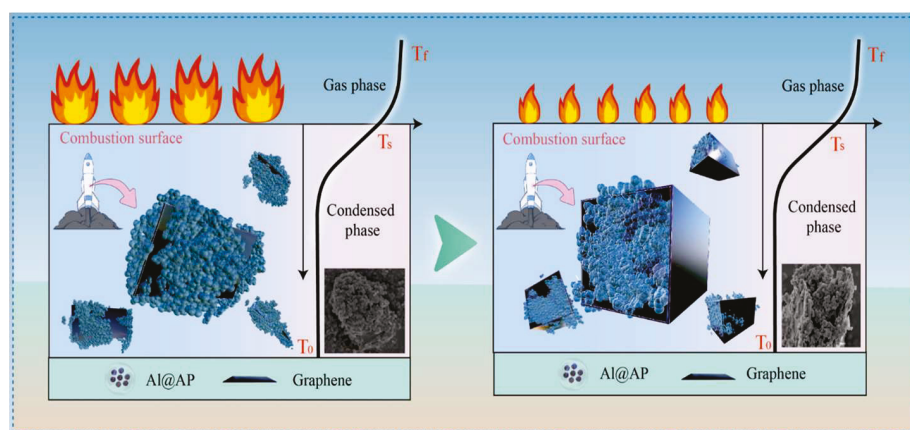


Figure 10. Proposed mechanisms describing the effect of graphene on Al@AP performance.

As shown in Figure 10, the impact and friction sensitivities of the samples increased with increasing graphene content. The mechanism through which graphene enhances safety performance can be attributed to its excellent lubricating properties. However, despite the continuous improvement in safety performance with the addition of graphene, combustion characteristics could not be optimised simultaneously. In this study, both the combustion and safety performance of the samples were maximised when the graphene content was 1.0 wt.%, thereby achieving a balanced enhancement.

4. Conclusions

Al@AP core-shell particles were prepared using an in-situ deposition method with graphene doping to adjust energy release and enhance safety performance. The high electrical and thermal conductivities of graphene, combined with its large specific surface area, facilitated charge transfer during both the low and high-temperature decomposition processes of AP, ultimately decreasing the decomposition temperature. In this study, the addition of 1.0 wt.% graphene effectively increased the rate of pressure increase and combustion characteristics of the Al@AP particles. The lubricating effect of graphene contributed to the excellent safety performance of the samples.

This study provides insight into the relationship between energy release and safety performance in energetic materials, guiding the application of graphene in solid propellants. In future studies, a binder should be added during the formation of solid propellants to investigate the influence of graphene content on their combustion characteristics and safety performance.

Author Contributions: J.S.: Conceptualization, Writing—original draft. J.L. (Jiahao Liang): Investigation, Writing—original draft, Writing—review & editing. Y.L.: Data curation. X.S.: Formal Analysis. H.Z.: Methodology. X.G.: Funding acquisition. S.Y.: Resources. J.L. (Junwei Li): Project administration. J.N.: Funding acquisition, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data is contained within the article.

Conflicts of Interest: Author Xiaole Sun was employed by the company Chongqing Hongyu Precision Industry Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AP	ammonium perchlorate
DMF	Dimethylformamide
LTD	low-temperature decomposition
HTD	high-temperature decomposition
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TG-DSC-FTIR	Thermogravimetric analysis-differential scanning calorimetry-Fourier transform infrared spectroscopy
XRD	X-ray diffraction

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Article

High-Power-Density Miniaturized VLF Antenna with Nanocrystalline Core for Enhanced Field Strength

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Abstract

In order to break through the difficulties with a very-low-frequency (VLF) miniaturized antenna with small power capacity and low radiation efficiency, this paper proposes a high-radiation-field-strength magnetic loop antenna based on a nanocrystalline alloy magnetic core. A high-permeability nanocrystalline toroidal core ($\mu_r = 50,000$, $B_s = 1.2$ T) is used to optimize the thickness-to-diameter ratio ($t = 0.08$) and increase the effective permeability to 11,000. The Leeds wires, characterized by their substantial carrying capacity, are manufactured through a toroidal winding process. This method results in a 68% reduction in leakage compared to traditional radial winding techniques and enhances magnetic induction strength by a factor of 1.5. Additionally, this approach effectively minimizes losses, thereby facilitating support for kilowatt-level power inputs. A cascaded LC resonant network (resonant capacitance 2.3 μF) and ferrite balun transformer (power capacity 3.37 kW) realize a 20-times amplification of the input current. A series connection of a high-voltage isolation capacitor blocks DC bias noise, guaranteeing the stable transmission of 1200 W power, which is 6 times higher than the power capacity of traditional ring antenna. At 7.8 kHz frequency, the magnetic field strength at 120 m reaches 47.32 dB $\mu\text{A}/\text{m}$, and, if 0.16 pT is used as the threshold, the communication distance can reach 1446 m, which is significantly better than the traditional solution. This design marks the first instance of achieving kilowatt-class VLF effective radiation in a compact 51 cm-diameter magnetic loop antenna, offering a highly efficient solution for applications such as mine communication and geological exploration.

Keywords: very low frequency; nanocrystalline alloys; high power capacity; enhanced radiation

1. Introduction

Very-low-frequency (VLF, frequency range 3–30 kHz) radio waves play a crucial role in long-distance underwater navigation and communication due to their stable propagation characteristics and low attenuation rates [1–4]. However, traditional VLF transmitter antennas [5] (e.g., T-shaped antennas, umbrella antennas, etc.) are limited in their applications because of the wavelength limitation, large physical dimensions (which usually reach several square kilometers), and the need to lay a large-area ground network. Therefore, the construction of miniaturized VLF antennas has become a current research hotspot. Research and experiments have been conducted for some feasible solutions to promote the miniaturization of VLF antennas, such as mechanical antennas and magnetic resonant coupled antennas. Ning et al. proposed a dual-driven magnetoelectric antenna based on mechanical antennas, which achieved an effective distance of 170 m for communication

through a pair of magnetoelectric heterostructures by utilizing the electrostatic effect [6]. Yang et al. designed and developed a magneto-mechanical transmission antenna of a simple, compact structure with low-power-consumption magneto-mechanical transmission antenna for ELF underwater communication up to 210 m [7]. Kurs et al. experimentally verified the feasibility of high-magnetic-field radiation by a double coil in a magnetic resonant coupling state [8]. On this basis, Zeng et al. proposed a magnetic resonant coupled metamaterial (MRCM) antenna with a dimensional near-field, adjustable frequency, and direction, which can realize effective communication up to 180 m in an open field [9]. However, the communication distance achieved by the above antenna is insufficient for many practical application scenarios.

In addition to the above antennas, magnetic loop antennas have attracted much attention owing to their small size, compact closed structure, and low ground coupling characteristics, providing a novel solution for miniaturized VLF antennas. Nanocrystalline materials can achieve high flux concentrations and greater reductions in energy loss owing to their excellent electromagnetic properties. Therefore, they are highly suitable for use in high-flux electromagnetic devices and can be integrated into electromagnetic devices to significantly reduce core losses and improve efficiency. However, they are mainly utilized in fields such as those involving transformers and motors. For example, Wu et al. [10] produced an isolation transformer based on nanocrystalline alloy materials for the impedance matching of a ring antenna, which effectively improved the radiation intensity of the ring antenna. The ring diameters of the small and large two-ring antennas were configured according to the actual application scenarios, where, for the ring diameter of the 0.3 m ring antenna, transmission distance was approximately 140 m (0.45 pT), and, for the ring diameter of the 2 m ring antenna, the effective communication distance was up to 340 m (0.8 pT). However, both can only withstand a 200 W input power. When used for mine communications and other site-restricted scenarios, the ring diameter of 2 is too large, whereas, for the 0.3 m ring antenna, the 140 m communication distance is relatively limited.

This study presents a very-low-frequency (VLF) antenna designed with a core composed of a nanocrystalline alloy material, characterized by its high-power input capacity, minimal loss, and compact structure. The antenna is made of high-carrying Leeds wire wound in a nanocrystalline alloy core and realizes high-power bearing through a large magnetic ring balun transformer and LC resonant network, which effectively improves the radiation performance of the VLF antenna. In addition, a high-voltage isolation capacitor was connected in series between the balun transformer and power amplifier to ensure a high power input to the antenna while blocking the DC bias and low-frequency noise. We analyzed the radiation enhancement mechanism of the proposed antenna using an equivalent circuit model and electromagnetic simulation. The field strength of the antenna at 120 m and 7.8 kHz was measured in an outdoor environment, which was up to 47.32 dB μ A/m. The magnetic flux density is increased by 1800 times compared with that of the traditional loop antenna, and the maximum communication distance of the antenna can be expected to be up to 240 m. If 0.16 pT is used as the communication threshold, the maximum communication distance of the antenna is expected to be up to 1446 m, which provides a potential solution for miniaturized low-frequency communication scenarios such as mine communication and geological exploration with reliable performance.

2. Basic Theory of Magnetic Loop Antenna

2.1. Radiation Performance Analysis

Figure 1a,b shows the theoretical model and simulated impedance of a typical multi-turn coiled magnetic loop antenna, respectively. The expression for the near-field radiated field of an N-turn coiled loop antenna can be derived from Maxwell's equations as

$$\begin{aligned} H_r &\approx \frac{n\mu_r IA}{2\pi r^3} \cos\theta \\ H_\theta &\approx -\frac{n\mu_r IA}{4\pi r^3} \sin\theta \end{aligned} \quad (1)$$

where H_r denotes the radial magnetic field component, H_θ the tangential magnetic field component, n the number of turns of the coil, μ_r the relative permeability of the core, I the output current, A the cross-sectional area of the magnetic ring, r the distance from the observation point to the field source, and θ the pole angle (angle from the coil axis).

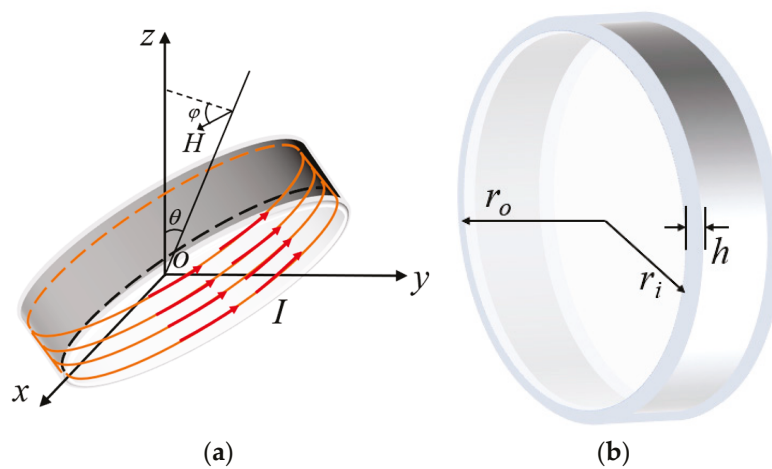


Figure 1. (a) Theoretical model of ring antenna, (b) toroidal core model.

Magnetic permeability reflects the response of a medium to a magnetic field. For an ideal magnetic circuit of infinite length and complete closure, the internal magnetic field of the magnetized material is $B = \mu_0 \mu_r H$. For actual cores, constrained by finite dimensions and geometries, an effective permeability factor m exists. The magnetic permeability of a magnetized material is the value of its internal magnetic field of the magnetized material.

For a toroidal nanocrystalline alloy core, the magnetic induction can be expressed by the following equation:

$$\begin{aligned} B &= \frac{n I m \mu_r}{l_m} \\ l_m &= \pi(r_i + r_o) \end{aligned} \quad (2)$$

l_m is the average magnetic circuit length of the toroidal magnetism; r_i and r_o are the inner and outer diameters of the core, respectively. At the desired operating frequency, a high radiated field strength can be achieved by selecting a suitable number of turns and diameter ratio. We have analyzed the effect of coil turns and core geometry on the radiation performance of the magnetic loop antenna using numerical analysis and a method of moments pair. The output current in Equation (2) can be changed by solving the output current using Ohm's law under the input voltage V .

$$\begin{aligned} B &= n V m \mu_r / (R_{tot}^2 + X_L^2) l_m \\ R_{tot} &= R_{dc} + R_c \end{aligned} \quad (3)$$

where R_{tot} is the loss resistance, X_L is the reactance, R_{dc} is the DC resistance, and R_c is the core eddy current loss.

$$\begin{cases} X_L = 2\pi fL \\ L = m\mu_r\mu_0 N^2 A / l_m \\ R_c = 2\pi f\mu_0 m\mu_r \tan\delta N^2 A / \pi r_o \\ R_{dc} = \rho_l N \pi r_o / S \end{cases} \quad (4)$$

ρ_l is the Leeds wire resistivity, S is the Leeds wire cross-sectional area, and $\tan\delta$ denotes the core loss angle tangent. Bringing Equations (3) and (4) into (2) yields

$$B = \frac{m\mu_r V}{2\pi s \sqrt{s^2 f^2 m^2 \mu_r^2 n^2 A^2 + (r_o + r_i)^2 \rho^2 r_o^2}} \quad (5)$$

In order to further investigate the effect of core geometry on the magnetic field strength of the magnetic loop antenna, the distribution of magnetic induction strength within 200 m of the magnetic loop antenna at a typical frequency (3 kHz) with different outer diameters r_o and different thickness-to-diameter ratio $t = h/r_o = (r_o - r_i)/r_o$ is analyzed by Feko electromagnetic simulation software based on the method of moments. In the simulation setup, the input voltage is set to 60 V, the diameter of the excitation line is 6 mm, the conductivity is taken as 1.68×10^6 , the relative permeability of nanocrystalline alloy is taken as 5×10^4 , the conductivity is taken as $1 \times 10^7/18$, and the X axis direction is the circumferential direction of the magnetic ring.

From Figure 2, it can be seen that, under the same thickness-to-diameter ratio, increasing the outer diameter can enhance the magnetic field strength, the circumferential magnetic field increases significantly, and the longitudinal magnetic field increases slightly or is flat. For medium ring radius ($r_o = 0.25\sim 0.35$ m), the magnetic field strength is affected by the thickness-to-diameter ratio, and the overall trend increases with the increase in thickness-to-diameter ratio; for small ring radius ($r_o \leq 0.15$ m), the magnetic field strength is determined by the ring diameter and thickness-to-diameter ratio. According to the antenna cost and different application scenarios, a different ring diameter and thickness-to-diameter ratio can be selected.

The thickness-to-diameter ratio affects the effective permeability factor m , which affects the magnetic induction strength of the magnetic loop antenna. From the data in Figure 2, we know that the magnetic field strength of the medium-ring antenna is proportional to the thickness-to-diameter ratio. In order to analyze the relationship between the effective permeability factor and the thickness-to-diameter ratio, we used Matlab 2024a numerical software to call the data from Figure 2 and then to analyze the data, as shown in Table 1.

In addition, we also analyze the effect of different coil turns on the magnetic induction intensity when the ring diameter is certain, as can be seen in Figure 3. Due to the existence of nanocrystalline alloys saturated magnetic flux, there are different cutoff frequencies for different coil turns: the more coil turns, the lower the cutoff frequency and the more gentle the change in magnetic induction intensity with the frequency. However, fewer coil turns in the high-frequency band still does not produce low magnetic induction intensity. Therefore, we can choose the appropriate number of turns according to the different operating frequencies and application scenarios.

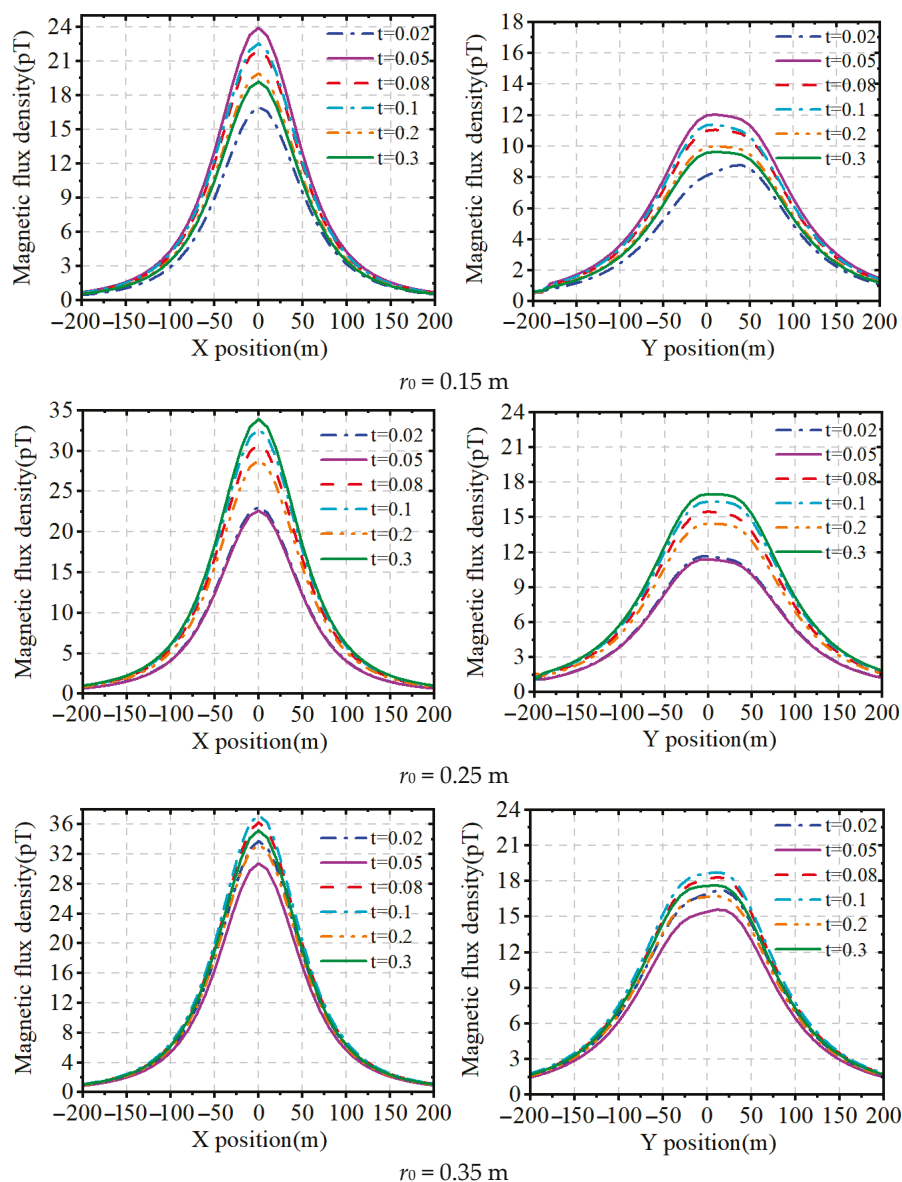


Figure 2. Magnetic induction distribution of magnetic loop antenna with different thickness-to-diameter ratios.

Table 1. Effective permeability factors of magnetic rings with different thickness-to-diameter ratios.

Thickness-to-Diameter Ratio	Effective Permeability Factor m	Effective Permeability μ_{eff}
0.02	0.1654	8270
0.05	0.16208	8104
0.08	0.22	11,000
0.1	0.2332	11,660
0.12	0.33218	16,609
0.15	0.29936	14,968
0.18	0.29856	14,928
0.2	0.20508	10,254
0.23	0.30824	15,412
0.25	0.34852	17,291
0.28	0.33508	16,754
0.3	0.37804	18,902

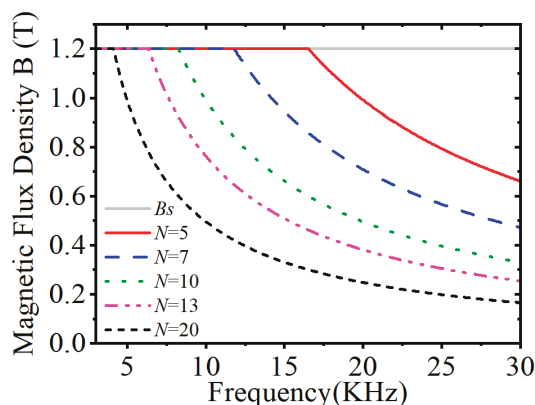


Figure 3. Magnetic induction for different coils.

2.2. Nanocrystalline Core Ring Antenna

2.2.1. Nanocrystalline Material Properties

From Equation (5), it can be seen that the magnetic induction strength of the magnetic loop antenna is directly proportional to the relative permeability of the core, and there are large differences in the performance of different cores due to their processing and material composition. The permeability, coercivity, saturation magnetization strength, and resistivity of different core materials are given in Table 2. From Table 2, it can be found that silicon steel has a high magnetic flux density, although the high coercivity leads to high hysteresis loss, limiting its potential application in VLF band scenarios. Ferrite has low saturation magnetic density and high hysteresis loss, which is not suitable for high-flux-density scenarios such as magnetic loop antennas. Amorphous alloys are excellent in permeability and coercivity, and their high-temperature stability and losses are slightly lower than those of nanocrystalline alloys. Nanocrystalline materials have low coercivity, high permeability, high saturation magnetic induction, and high temperature stability for efficient magnetization and effective permeability processes, which can be effectively used for VLF communications.

Table 2. Material properties of different core materials.

Material	Permeability	B_s	Coercion	Resistivity	T_c
silicon steel	2000~5000	1.5~2.0 T	10~50 A/m	$4 \times 10^{-5} \Omega \cdot m$	730 °C
amorphous alloy	20,000~30,000	1.2~1.6 T	1~10 A/m	$1 \times 10^{-6} \Omega \cdot m$	415 °C
nanocrystalline alloys	30,000~50,000	1.0~1.4 T	0.5~5 A/m	$1 \times 10^{-7} \Omega \cdot m$	560 °C
ferrite	2000~10,000	0.3~0.5 T	100~500 A/m	$1 \times 10^{-3} \Omega \cdot m$	180 °C

As can be seen from Figure 4, the iron loss of different materials increases with the rise in frequency. The micro-crystalline alloy not only has lower iron loss in the frequency range of 3~30 kHz, but also maintains a high magnetic flux density. Its magnetic flux is slightly lower than that of silicon steel, but significantly higher than that of ferrite. And the effective magnetic flux of about 0.6 T is still maintained at 7.8 kHz, which indicates that the nanocrystalline alloys can still maintain high magnetic properties at high frequencies, with strong demagnetization resistance and broadband stability.

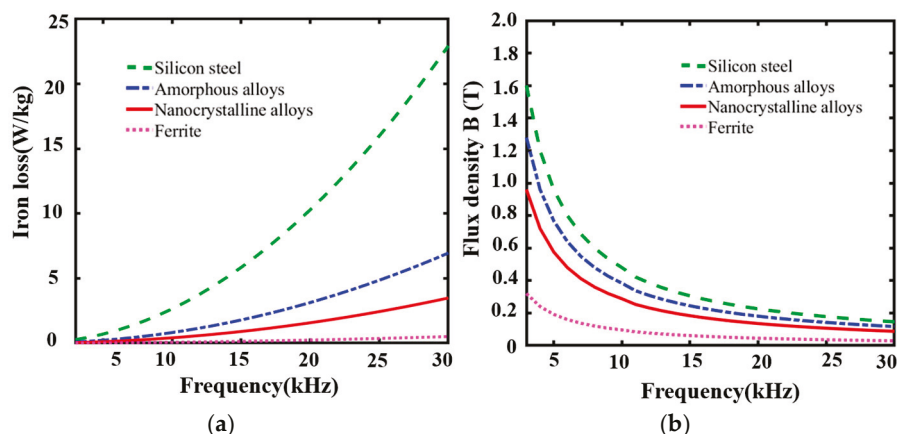


Figure 4. (a) Iron loss of different core materials; (b) Magnetic flux of different core materials.

The nanocrystalline alloy effectively suppresses the high-frequency eddy current loss through grain refinement and disordered structure design (as shown in Figure 5b), which results in excellent performance in the frequency range of more than 3–20 kHz. And the low coercivity, high permeability, and high-saturation magnetic induction strength make it suitable for high-flux-density application scenarios.

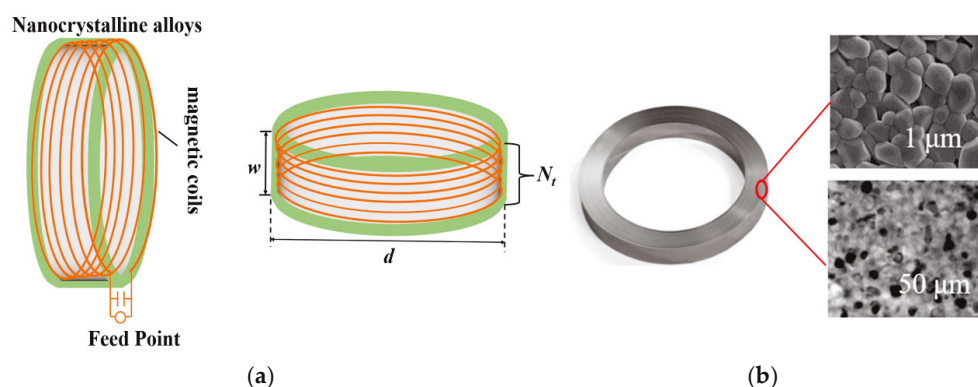


Figure 5. (a) Geometrical model of a multi-turn coil loop antenna. (b) Nanocrystalline alloy.

2.2.2. Ring Antenna Design Based on Nanocrystalline Materials

We have designed a magnetic loop antenna with 10 turns of coil, 0.51 m ring diameter, and 0.08 thickness-to-diameter ratio. Figure 3 shows the geometry of the proposed antenna, which consists of two parts: a ring-shaped nanocrystalline alloy core (Fe-Si-B-Nb-Cu) and a Leeds wire (wire diameter 6 mm); the detailed parameters of the antenna and the nanogold alloy material are shown in Table 3.

Table 3. Detailed parameters of a multi-turn coil loop antenna.

Sign	Clarification	Value
Ring antenna (with core)		
w	Antenna width	50 mm
d	Antenna ring diameter	510 mm
w_t	Antenna weight	2.5 kg
N_t	Number of turns	10
a	Leeds wire diameter	6 mm

Table 3. Cont.

Sign	Clarification	Value
Nanocrystalline Alloy Cores		
μ_r	Relative permeability	50,000
ρ_m	density	7.2 g/cm ³
$c\rho$	Resistivity	1.8 $\mu\Omega$ /m
B_s	Saturation magnetic field density	1.2 T
$\tan\delta$	Loss angle tangent (math.)	0.01

2.3. Matching Design

According to Equation (5), it can be seen that the radius and the number of turns of the ring cannot be increased infinitely due to the limitation of volume and weight; therefore, increasing the transmit current is an effective means to enhance the magnetic induction strength of the magnetic ring antenna. In order to maximize the current transmission, an equivalent circuit is constructed to demonstrate the radiation enhancement performance of the proposed high-power VLF magnetic ring antenna based on an LC resonant network with a high-power balun transformer, as shown in Figure 6. In the figure, R_r is the radiation resistance and C_A is the isolation capacitor used to block DC bias and low-frequency noise. The equivalent variable inductance of the magnetic loop antenna can be obtained from Equation (4).

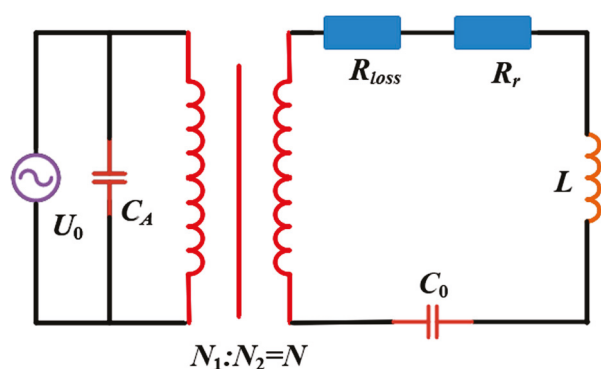


Figure 6. Equivalent circuit diagram of the ring antenna.

In order to increase the output current, a resonant capacitor C_0 is inserted in series so that the magnetic loop antenna resonates in series to obtain a high current output; the value of the series capacitance can be calculated from $\sqrt{LC_0} = 1/2\pi f$. The value of the series capacitance can be calculated; Figure 7a gives the resonant response of the loop antenna at 7.8 kHz frequency when the input voltage is 60 V and the input current is 0.86 A. It can be found that the antenna current appears to have an obvious peak of 16.8 A around 7.8 kHz, which is amplified by about 20 times compared with the input current. This implies that the LC resonant network based on the magnetic coupling resonance characteristic can greatly improve the radiation performance of the antenna.

When solving the ring antenna reactance, because the nanocrystalline alloy core is wound layer by layer, there is an air gap between adjacent layers. Its relative effective magnetic flux rate cannot be taken as 50,000; it is more appropriate to take 11,000 after the correction of the subsequent test data and after checking the effective permeability of the ring magnetic core under different diameter ratios in Table 1. Table 4 shows the comparison between the simulation results and theoretical calculations in the tuned state. The two impedance calculations are more consistent, the real part is basically the same, while the simulation of the imaginary part is large because of the consideration of the

turn-to-turn capacitance between the neighboring coils, taking into account the nonlinear change in the magnetic core permeability with frequency. However, the core permeability is regarded as a fixed value in the theoretical calculation, and the value is taken as 11,000.

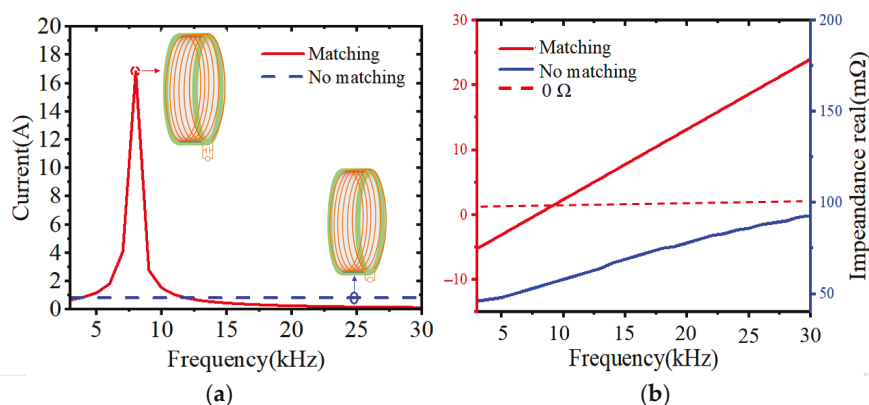


Figure 7. (a) Resonant response at 7.8 kHz. (b) Impedance characteristics at 7.8 kHz.

Table 4. Theoretical and simulated values of ring antenna reactance values.

Methodologies	Frequency	Turns	Ring Diameter	Leeds Wire Diameter	Ring Impedance	Tuning Capacitor
Theory	3 kHz	10	0.51 m	6 mm	$0.16 + j16.58\Omega$	$3.2 \mu\text{F}$
	7.8 kHz	10	0.51 m	6 mm	$0.44 + j43.12\Omega$	$0.47 \mu\text{F}$
	13 kHz	10	0.51 m	6 mm	$0.71 + j71.88\Omega$	$0.17 \mu\text{F}$
	18 kHz	10	0.51 m	6 mm	$0.99 + j99.52\Omega$	$0.08 \mu\text{F}$
	23 kHz	10	0.51 m	6 mm	$1.27 + j127.17\Omega$	$0.05 \mu\text{F}$
	28 kHz	10	0.51 m	6 mm	$1.54 + j154.81\Omega$	$0.04 \mu\text{F}$
Simulation	3 kHz	10	0.51 m	6 mm	$0.16 + j3.3\Omega$	$16 \mu\text{F}$
	7.8 kHz	10	0.51 m	6 mm	$0.48 + j8.7\Omega$	$2.3 \mu\text{F}$
	13 kHz	10	0.51 m	6 mm	$0.75 + j14.1\Omega$	$0.9 \mu\text{F}$
	18 kHz	10	0.51 m	6 mm	$1.1 + j19.5\Omega$	$0.45 \mu\text{F}$
	23 kHz	10	0.51 m	6 mm	$1.4 + j24.9\Omega$	$0.27 \mu\text{F}$
	28 kHz	10	0.51 m	6 mm	$1.7 + j30.3\Omega$	$0.18 \mu\text{F}$

To further increase the output current, the loss resistance needs to be reduced. The loss resistance of the antenna is mainly composed of the eddy current loss of the core and the DC resistance of the Leeds line.

From Equation (4), it can be seen that increasing the effective permeability of the magnetic ring antenna can reduce the eddy current loss of the magnetic core. And μ_{eff} is related to the inductance of the ring antenna itself. In the case of a certain core, different winding methods and numbers of turns of the coil will affect the antenna inductance. Figure 7 gives the inductance as well as the magnetic induction strength of the loop antenna with different winding methods under 60 V output voltage.

From Figure 8a,b, it can be found that the inductance and flux rate density of both winding methods show a gradual decrease with increasing frequency. The toroidally wound coil exhibits higher inductance in the frequency range of 3 kHz to 30 kHz of 0.8 mH at 3 kHz, with a smoother inductance decay rate. Radial winding results in a 66–69% decrease in inductance due to magnetic leakage and a 1.5-fold increase in magnetic induction. This is due to the fact that the effective cross-sectional area of the magnetic circuit is increased because the Leeds wires are evenly distributed along the circumference of the core in the circumferential direction of the winding. The spacing of adjacent coils is consistent, which reduces the skin effect and proximity effect between the coils and

improves the effective permeability of the core, thus obtaining a higher inductance value. For the choice of the number of turns of the coil, analyzing the magnetic induction intensity of different coils in Figure 3, it can be seen that, the greater the number of turns of the coil, the lower the frequency of the core to reach saturation flux. For the electromagnetic wave, the lower the frequency, the stronger the ability to penetrate the medium, making it more suitable for mine communication, geological exploration, and other scenarios. However, the excessive number of turns brings the problem of weight increase and the problem of difficulty in matching the reactance. Comparing the data in Figure 3 and Table 4, it can be seen that the cutoff frequency of the 10-turn coil is around 7.8 kHz, and the tuning capacitance is only 2.3 μF , so we chose 10 turns for the number of coil turns.

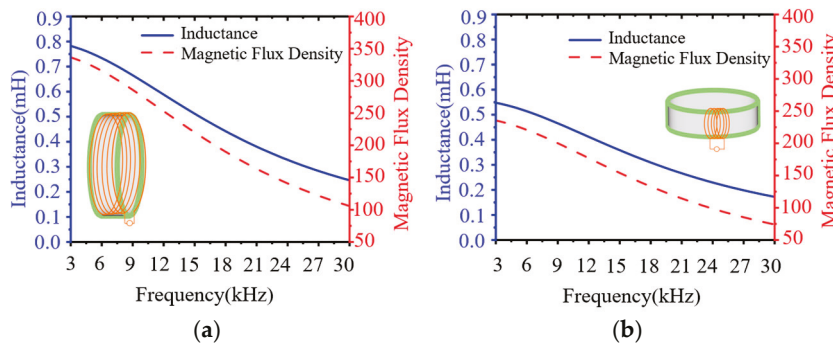


Figure 8. (a) Circumferential winding. (b) Radial winding.

High output current usually means high power capacity. In order to improve the power withstanding of the magnetic core, the ring antenna core is made of nanocrystalline alloy material, and a magnetic ring with an outer diameter of 51 cm, an inner diameter of 49 cm, and a thickness of 2 cm is fabricated. Ten turns are wound circumferentially using a Leeds wire (with a current carrying capacity of 40 A) that utilizes a wire diameter of 6 mm. A value of 7.8 kHz is selected as the resonant frequency, and, from the simulation results in Figure 7a, it can be seen that, under the condition of 60 V output voltage, the output current of the ring antenna is 16.8 A. At this time, the output power is 1008 W.

The actual size of the VLF magnetic loop antenna is much smaller than the electrical length of its corresponding frequency, so the real part of the antenna is very small—only $10^{-1} \Omega$. The RF output port of the power amplifier is 50 Ω . If the signal is transmitted directly through the 50 Ω coaxial cable without impedance matching between the two, this will lead to impedance mismatch and increased reverse power. Under high power input, this can even damage the instrument. Therefore, it is necessary to use the Barron impedance converter for impedance matching to amplify the real part of the antenna to 50 Ω by a factor of N^2 , where N is the turns ratio of the primary coil to the secondary coil. According to the simulation results in Figure 9, the closer the antenna output impedance is to 50 Ω , the smaller the reflection coefficient and the lower the mismatch power loss the magnetic loop antenna exhibits under the conditions of fixed input power (1200 W) and consistent resonant frequency (7.8 kHz).

In addition, to ensure that the Barron impedance converter can withstand 1200 W input power, an impedance converter with an outer diameter of 30 cm, an inner diameter of 25 cm, and a thickness of 3 cm is fabricated using ferrite material. And the power capacity of the transformer made with a copper conductor of 6 mm wire diameter can be expressed by the following equation [11]:

$$P_{\max} = KB_s f A A_w J A_w = (r_o - r_i) \cdot H \quad (6)$$

where P_{max} is the maximum power capacity, K is the topological constant related to the core geometry and winding method, A_w is the core window area, J is the wire current density, and H is the core thickness. For the circumferential winding of the ring core, K value is generally 0.3~0.5; using Formula (8) for calculations, we take the K value of 0.3 to obtain the maximum power of the ring in order to withstand the power of 3370 W.

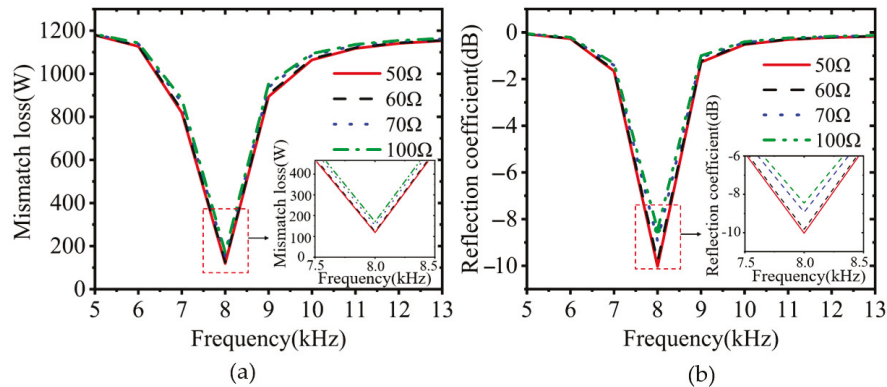


Figure 9. Simulation of (a) reflection coefficient and (b) mismatch loss power.

3. Experimental Verification

In order to evaluate the transmit performance of the ring antenna, this test was conducted with a homemade VLF ring antenna with a ring diameter of 0.5 m as the subject, and the near-field test based on the magnetic ring antenna was carried out, as shown in Figure 10.

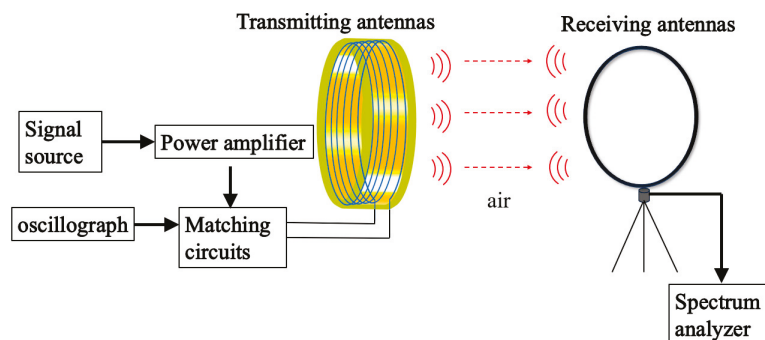


Figure 10. Schematic of VLF ring antenna magnetic field strength test.

In Figure 10, the VLF signaling system consists of a signal source (HDG2032B, Qingdao Hantai, Qingdao, China) connected in series to a power amplifier (DH17834A, Beijing Dahua, Beijing, China), which then outputs a 3.6 V excitation signal through a matched capacitor to drive a transmitter loop antenna with an operating frequency of 7.8 kHz. Before the signal source outputs the signal, the reactance value of this antenna at 7.8 kHz is measured to be $0.88 + j7.48$ by using an RLC meter (VICICR4091A, Uli De, Shenzhen, China), and the actual measured resistance value is 0.4 ohms larger than the simulated value, which may be due to the machining error in the actual process. The required tuning capacitance of the loop antenna at 7.8 kHz output is found to be $3 \mu\text{F}$ by the LC series resonance theorem. The matched capacitor was connected to an oscilloscope (MSOX3024T, KEYSIGHT, Xi'an, China) for monitoring the output current of the transmitting loop antenna, and the receiving loop antenna (HFH2-Z2E, ROHDE&SCHWARZ, Xi'an, China) was set up 120 m away from the transmitting loop antenna; the field strength level values were recorded using a spectrometer (ROHDE&SCHWARZ, ROHDE&SCHWARZ, Xi'an, China).

The test process utilizes the power amplifier to set different output voltages and rotate the orientation of the receiving loop antenna to observe the field strength value on the spectrometer until the field strength value reaches the maximum value to stop rotating and record the VLF transmitter antenna at 70 m. The induced field strength of the VLF antenna at 70 m is recorded. The magnetic field strength of the magnetic loop antenna at 70 m is shown in Figure 11. The magnetic field strength of the magnetic loop antenna at 70 m under different output voltages is given in Figure 12. The test environment is relatively noisy, and the ambient noise floor is 19 dB μ A/m. From Figure 12a, it can be seen that the antenna is at an output frequency of 7.8 kHz, and the input voltage is 60 V, at which time the output current is 23 A and the output power reaches 1380 W. The field strength value at 70 m still has 66 dB μ A/m, with strong sensing ability.

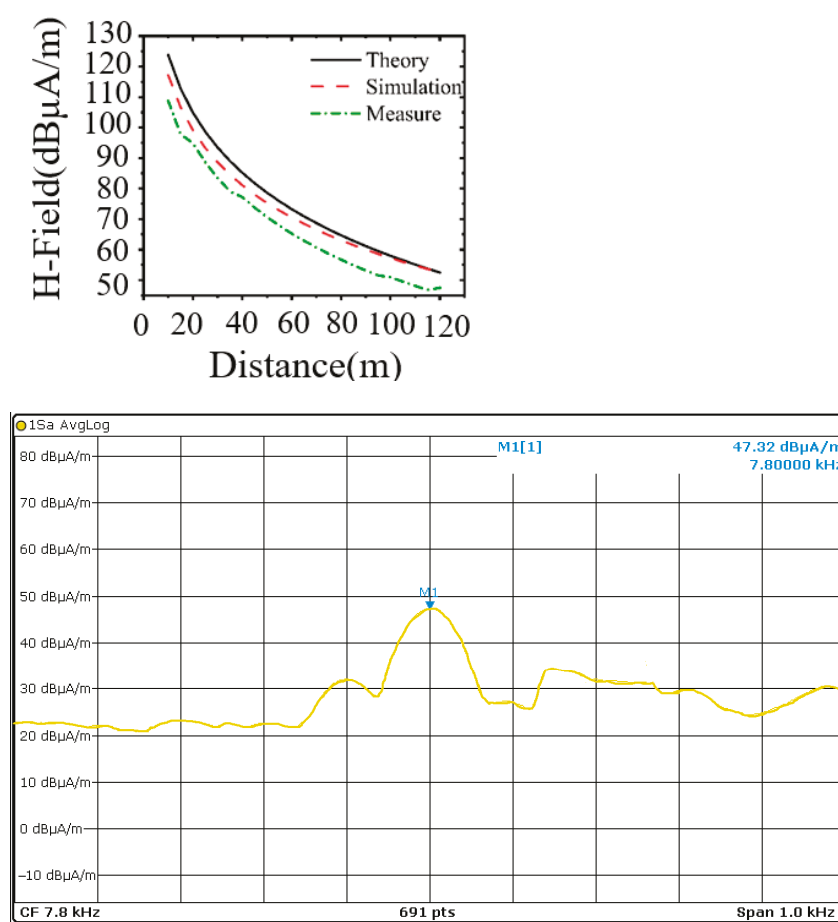


Figure 11. Magnetic field strength at 120 m for VLF loop antenna with 7.8 kHz frequency.

In order to evaluate the antenna sensing capability and to determine the maximum attenuation distance of its field strength as it propagates in air, the values of the induced field strength of the receiving loop antenna relative to the magnetic loop antenna were measured at different locations under 1200 W output power. Due to the site constraints, we only carried out the test at a range of 120 m. A comparison of the theoretical, simulated, and measured results of the induced field strength over distance in the range of 10 to 120 m when the VLF loop antenna operates at 7.8 kHz is shown in Figure 11. The theoretically calculated and simulated values are basically the same, but they are slightly higher than the simulated values in the low-frequency band because the simulation calculations take into account the ground loss. The measured values are about 4–5 dB μ A/m smaller compared with the simulated data, which is attributed to the nonlinear change in the core impedance at high voltage not considered in the theoretical model. The VLF electromagnetic wave

generated by this antenna decays rapidly in the near field, and the magnetic field strength of the loop antenna at 120 m is 47.32 dB μ A/m. It is also known from Equation (1) that the magnetic field strength decays proportionally to the third power of the distance. If 0.16 pT is used as the threshold, the calculated communication distance can reach 1446 m, thus effectively realizing the miniaturized VLF transmitter antenna.

A comparison of the proposed magnetic loop antenna with other existing reported advanced and miniaturized loop antennas is shown in Table 5. Most of the miniaturized loop antennas reported so far are based on the electrostrictive effect of piezoelectric materials or the physical motion (translation, rotation) of permanent magnet materials to realize the miniaturization of the antenna. It has been reported that the communication distance of a DDME antenna [6] can reach 170 m (1.2 pT), which is already a high level. However, the limited input power is the main factor limiting the further improvement of the radiation capability of this type of antenna. In contrast, the nanocrystalline material antenna proposed in this paper achieves significant long-distance communication over 120 m at 7.8 kHz. The radiation intensity of this antenna at a distance of 120 m is 47.32 dB μ A/m, which is at the higher level of currently reported miniaturized loop antennas.

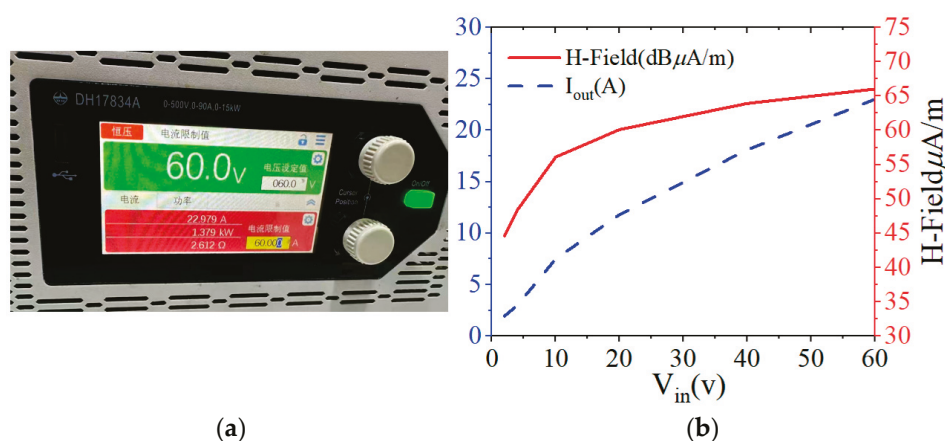


Figure 12. VLF ring antenna magnetic field strength test. (a) The voltage and current of the antenna during actual measurement. (b) The measured curves of current and magnetic field strength varying with frequency.

Table 5. Performance comparison of different antennas.

Type of Program	Sizes	Freq	Power	Magnetic Flux/ Transmission Distance	References
Magnet-based Mechanical antenna	-	1.6 kHz	20 W	5 m (50 pT)	[12]
Loop antenna	30 cm	15 kHz	200 W	135 m	[10]
Relay waveguide system	22 cm	125 kHz	-	40 m	[13]
Relay waveguide system	12 cm	1 kHz	20 W	25 m	[14]
Metamaterial antenna	18 cm	41.4 kHz	200 W	180 m (0.16 pT)	[9]
Nanomaterials antenna	51 cm	7.8 kHz	1200 W	1446 m (0.16 pT)	This work

4. Summary

In this paper, a VLF magnetic loop antenna consisting of a multi-turn coil and a toroidal nanocrystalline alloy core structure with high power input, low loss, directionally adjustable characteristics, and compact structure is proposed. A quantitative correlation model between the core thickness-to-diameter ratio ($t = 0.02$) and the effective permeability factor ($m = 0.22$) is established for the first time, and the effective permeability is increased to 11,000. The neighbor effect is suppressed by using the toroidal winding process, which

improves the magnetic induction strength by 1.5 times and reduces the loss, laying the foundation of high-frequency and high-power radiation. The antenna with 7.8 kHz as the working frequency is fabricated, and, under the condition of 1200 W input power, the measured magnetic field strength at 120 m reaches 47.32 dB μ A/m, which is consistent with the theoretical and simulation results and proves its strong radiating capability.

Compared with the traditional ring antenna, power capacity increased by 6 times, and the magnetic flux density improvement is significant, increasing by 1800 times. The theoretical model predicts that the antenna's maximum communication distance can be up to 1446 m (with 0.16 pT as the threshold), which provides a portable solution for the scenarios of mine tunneling and geological exploration. The cascaded LC resonance and balun transformer architecture provides a universal technology path for VLF magnetic loop antennas. It further expands the application scenarios of VLF miniaturized antennas.

Author Contributions: W.A.: investigation, methodology, data curation, formal analysis, writing—original draft. H.W.: investigation, resources, supervision, writing—review and editing. L.Z.: writing—review and editing. H.X.: investigation, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Article

Multimode Switching Broadband Terahertz Metamaterial Absorbing Micro-Devices Based on Graphene and Vanadium Oxide

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Abstract: In this paper, we propose a multi-mode switchable ultra-wideband terahertz absorber based on patterned graphene and VO₂ by designing a graphene pattern composed of a large rectangle rotated 45° in the center and four identical small rectangles in the periphery, as well as a VO₂ layer pattern composed of four identical rectangular boxes and small rectangles embedded in the dielectric layer. VO₂ can regulate conductivity via temperature, the Fermi level of graphene depends on the external voltage, and the graphene layer and VO₂ layer produce resonance responses at different frequencies, resulting in high absorption. The proposed absorption microdevices have three modes: Mode 1 (2.52–4.52 THz), Mode 2 (3.91–9.66 THz), and Mode 3 (2.14–10 THz), which are low-band absorption, high-band absorption, and ultra-wideband absorption. At 2.96 THz in Mode 1, the absorption rate reaches 99.98%; at 8.04 THz in Mode 2, the absorption rate reaches 99.76%; at 5.04 THz in Mode 3, the absorption rate reaches 99.85%; and at 8.4 THz, the absorption rate reaches 99.76%. We explain the absorption mechanism by analyzing the electric field distribution and local plasma resonance, and reveal the high-performance absorption mechanism by using the relative impedance theory. In addition, absorption microdevices have the advantages of polarization insensitivity, incident angle insensitivity, multi-mode switching, ultra-wideband absorption, large manufacturing tolerance, etc., and have potential research and application value in electromagnetic stealth devices, filters and optical switches.

Keywords: terahertz wideband absorbing micro-devices; metamaterial; multimode switching; graphene; VO₂

1. Introduction

Terahertz technology covers a broad spectrum of application prospects in many fields such as communication, the military, and medicine, and the utilization of metamaterials is important for the future development of terahertz technology [1–3].

Metamaterials are a class of artificially designed and manufactured composite materials that do not exist in nature through the design of their internal structures [4–6]. These electromagnetic properties make metamaterials potentially useful in radar and sensing

technologies, etc. [7–9]. Since the end of the 20th century, with progress in nanotechnology and the development of computer simulation tools, the study of metamaterials has gradually emerged and quickly become a hot field of interdisciplinary research. Many achievements have been made so far. For example, the metamaterial structure designed by Rafał Kowerdziej et al. can be effectively tuned at terahertz frequencies, with a transmittance variation of up to 19% [10]. The terahertz metamaterial absorber designed by Yadgar I. Abdulkarim et al. has a strong absorption rate of over 97% at the two absorption peaks of 0.49 THz and 0.69 THz [11]. The use of metamaterials has gradually developed from microwave to infrared and visible light, and high-performance terahertz devices based on metamaterials have also attracted wide attention [12,13]. Many efforts have been made to achieve THz absorber tunability, including the use of dynamically tunable materials such as graphene and the phase-change material VO₂ [14]. Multispectral terahertz absorbers are crucial for emerging applications such as dynamic electromagnetic stealth, multi-sensing, and optical switching [15]. Among these, the adaptive frequency response is indispensable. Unlike fixed-band devices, multi-mode switchable absorbers can adapt to various terahertz environments in real time, solving the limitations of single-function metamaterials [16,17].

Graphene is a structurally stable material; since it was successfully separated for the first time in 2004, it has quickly become a research hotspot in materials science, physics, chemistry, and other fields, and it has a good response in the terahertz frequency range [18–20]. For graphene absorbers, doping or changing the external voltage can regulate the conductivity. These characteristics have led to graphene materials being widely studied for terahertz devices in recent years [21–23]. VO₂ is a transition metal oxide with unique properties, and it is widely applied in the fields of photonics, intelligent regulation and control, and absorbers. The absorber designed by S. Hadi Badri et al., using VO₂ materials, was able to switch the absorption mechanism from narrowband to wideband; in the narrowband absorption mode, the absorption rate reached 99%, and in the wideband absorption mode, the absorption bandwidth reached 4.88 THz [24]. In addition, other works have revealed the realization of tunable terahertz polarization manipulation devices by combining the phase-change material VO₂ with a heterogeneous surface design [25]. Phase-change materials have already become a popular research subject [26]. At room temperature, VO₂ materials have insulating properties, and at a temperature of about 68 °C, they show the properties of a metallic state. Due to this unique property, VO₂ materials have important research significance in tunable, metamaterial, high-performance devices. In recent years, people have gradually turned their attention to the design of a color absorber that combines two adjustable materials. Many studies have explored the development of an absorber combining graphene and VO₂ materials that can achieve a variety of different properties. A variety of modes can be achieved during switched absorption, such as wide and narrowband switching absorption, frequency band number conversion, and multiband absorption [27–29]. The absorber designed by Zhang et al. can achieve narrowband–wideband mode switching absorption by adjusting the relaxation time of graphene [30]. Gong et al. designed an absorber that can realize tunable switching between two different frequency bands, 0.75–1.15 THz and 2.5–4.5 THz, where regulating the VO₂ conductivity and the Fermi energy of graphene can both affect its absorption [31]. Tian et al. proposed three-mode switching based on vanadium oxide and a graphene absorber; this enabled the three-mode switching of 2.7–6.2 THz absorption in the low-frequency band, and 5.8–7.6 THz absorption in the high-frequency band and during multi-frequency absorption [32]. Wang et al. designed a switchable absorber, achieving two modes of quadruple narrowband absorption and wideband absorption [33]. However, limitations on the bandwidth of the absorber remain a problem, so it is necessary to propose a terahertz metamaterial absorber with ultra-wideband switching.

In our work, by adjusting the Fermi energy of the graphene material and the conductivity of the VO₂ material, the absorber is able to switch between three absorption modes; the three modes are: Mode 1 (2.52–4.52 THz), which has an average absorption of 97.67%; Mode 2 (3.91–9.66 THz), which has an average absorption of 95.16%; and Mode 3 (2.14–10 THz), which has an average absorption of 96.07%. All three modes are absorbed over 90% within the absorption range. In addition, we also use impedance matching theory to explain the absorption mechanism, and the absorption of incident light at different incident angles and the absorption of TE wave and TM wave of the absorber are investigated. After calculation and analysis, we found that the structure has little dependence on the low incidence angle, is not affected by the polarization state, and has the features of low angle incidence and being polarization-insensitive. In addition, we also discuss the structural period size and height size, as well as the absorption of the graphene layer pattern size and VO₂ layer pattern size with different values within a certain range. Finally, we explore the electric field distribution in different modes, and further reveal the absorption mechanism.

2. Structural Design and Simulation

The periodic structure of the proposed MMA is shown in Figure 1a, and the unit structure is shown in Figure 1b. The structure consists of five layers, namely, the gold substrate, SiO₂ layer, VO₂ embedded silica layer, SiO₂ layer, and graphene layer. After constructing the basic model structure diagram, we used CST simulation software 2020 to simulate the model and adopted the FDID algorithm for simulation and calculations [34,35]. Firstly, periodic boundary conditions are applied on the X-axis and Y-axis, while the Z-axis remains open. Electromagnetic waves propagate along the negative Z-axis direction, and the grid size is set as an adaptive grid [36,37]. Based on this design, we can complete the simulation and calculation of the entire periodic array with only one device unit, as shown in Figure 1b. This greatly reduces the calculation time required, speeds up the research process, and maintains the calculation accuracy at the same time.

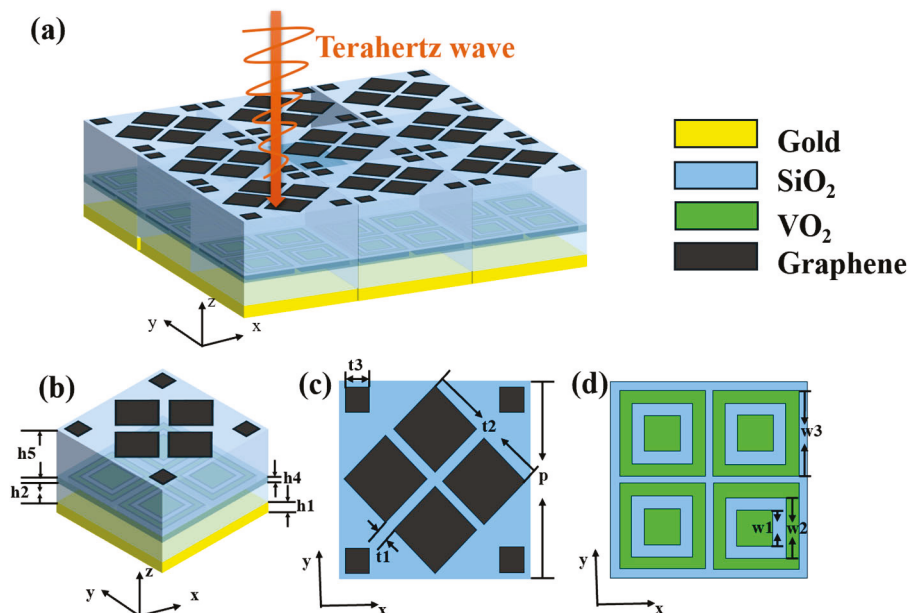


Figure 1. Periodic structure of the proposed MMA (a), dimensional parameters of the unit structure (b), dimensions of the graphene layer (c), dimensions of the VO₂ layer (d).

The thickness of the gold substrate is $h1 = 1 \mu\text{m}$; this thickness is deep enough to make it fully reflective. The thickness of VO₂ is $h4 = 0.15 \mu\text{m}$, the thickness of single-layer graphene is 1 nm, the relative dielectric constant of the dielectric layer material is 2.13,

and its thicknesses are $h_2 = 5.5 \mu\text{m}$ and $h_5 = 8.5 \mu\text{m}$, respectively. Figure 1c describes the parameters of the graphene layer and Figure 1d describes the parameters of the VO_2 layer. The middle part of the graphene layer shape is four identical squares rotated 45° in a diamond shape, and the outside is four identical small squares. The embedded VO_2 layer is a combination of four identical square boxes and a small square placed in the middle. The graphene layer structure model can be fabricated by chemical vapor deposition and graphene transfer techniques, and VO_2 film can be prepared by magnetron sputtering; by layer-by-layer deposition, the proposed composite structure can be fabricated [38,39]. The parameters were $t_1 = 1.5 \mu\text{m}$, $w_1 = 3 \mu\text{m}$, $t_2 = 12 \mu\text{m}$, $w_2 = 5 \mu\text{m}$, $t_3 = 4 \mu\text{m}$, $w_3 = 8 \mu\text{m}$, and $p = 17.5 \mu\text{m}$. By adjusting the Fermi energy of the graphene and the conductivity of the VO_2 , the relevant parameters of the three switchable absorption modes of the structure are as shown in Table 1.

Table 1. Parameters related to different modes of proposed MMA.

Mode	E_f (eV)	σ_{VO_2} (S/m)	f_l – f_h (THz)	Bandwidth (THz)	A_{ave}
I	0.8	475	2.52–4.52	2.00 THz	97.67%
II	0.2	200,000	3.91–9.66	5.75 THz	95.16%
III	0.7	200,000	2.14–10.00	7.86 THz	96.07%

The Formula (1) Kubo formula, which can describe the conductivity of graphene [40]; the conductivity can be described by the interband contribution in Formula (2) and the in-band contribution in Formula (3) [41,42]. In the formula, ω , E_f , τ , T , k_B , $\hbar$, and e , respectively, represent the frequency of the electromagnetic wave, the Fermi level, carrier relaxation time, temperature, Boltzmann constant, Planck constant, and the basic charge of the electron.

$$\sigma_g = \sigma_{\text{intra}} + \sigma_{\text{inter}} \quad (1)$$

$$\sigma_{\text{intra}} = \frac{2k_B T e^2}{\pi \hbar^2} \ln \left(2 \cosh \frac{E_f}{2k_B T} \right) \frac{i}{\omega + i\tau^{-1}} \quad (2)$$

$$\sigma_{\text{inter}} = \frac{e^2}{4\hbar} \left[H\left(\frac{\omega}{2}\right) + i \frac{4\omega}{\pi} \int_0^\infty \frac{H(\Omega) - H\left(\frac{\omega}{2}\right)}{\omega^2 - 4\Omega^2} d\Omega \right] \quad (3)$$

Because we work in the terahertz band, $E_f \gg \frac{\hbar\omega}{2}$, and because of the Pauli blocking effect, the band transition's contribution to graphene's conductivity is negligible, so its conductivity formula can be simplified to Formula (4) [43]:

$$\sigma_{\text{gra}} = \frac{e^2 E_f}{\pi \hbar^2} \frac{i}{\left(\omega + \frac{i}{\tau}\right)} \quad (4)$$

It is expressed in Formula (4) that the conductivity of graphene depends on the Fermi energy level, relaxation time, and incident light frequency. In this structure, the electrical conductivity of graphene is mainly regulated by the voltage. Existing experimental studies have shown that in the temperature-change environment required for the switching of graphene between the insulating phase and the metallic phase of VO_2 , the electrical conductivity of graphene does not show significant changes, which is attributed to the counterbalancing effect of phonon scattering and carrier mobility [44,45]. Therefore, within this range, the influence of temperature changes on the electrical conductivity of graphene can be ignored. We can adjust its surface conductivity by doping or changing the external voltage, and we set the relaxation time to 0.1 ps. Electric gate control is a common method

for regulating the Fermi level of graphene [46]. Besides this, there are also other alternative methods, such as optical illumination or strong terahertz field excitation, which have been experimentally proven [47,48]. Among these, optical illumination is achieved by irradiating a light source with a photon energy greater than the band gap of the graphene, which can avoid the problem of electrode contamination. As shown in Formula (5), photogenerated carriers are injected into graphene, changing the carrier concentration n , and thereby regulating the Fermi level E_f . V_F is the Fermi velocity and n represents the carrier concentration. The regulation of a strong terahertz field is due to the fact that when a strong terahertz field is incident, the carriers in graphene are driven by the Lorentz force, generating nonlinear drift currents, and thereby achieving dynamic conductivity modulation.

$$E_f = \hbar v_F \sqrt{\pi n} \quad (5)$$

The permittivity of VO₂ can be described by the Drude model and expressed as Formula (6) [31]:

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2(\sigma)}{\omega(\omega + i\gamma)} \quad (6)$$

In the formula, the dielectric constant $\varepsilon_\infty = 12$, damped frequency $\gamma = 5.75 \times 10^{13}$ rad/s, and plasma frequency $\omega_p(\sigma)$ can be represented as $\omega_p^2(\sigma) = \frac{\sigma}{\sigma_0} \omega_p^2(\sigma_0)$, $\omega_p(\sigma_0) = 1.45 \times 10^{15}$ rad/s, and $\sigma_0 = 3 \times 10^5$ S/m, $\sigma = 3 \times 10^5$ S/m. When $\sigma = 2 \times 10^2$ S/m, VO₂ is considered an insulating state with a corresponding temperature of 300 K, and when $\sigma = 2 \times 10^5$ S/m, VO₂ is considered a metallic state with a corresponding temperature of 340 K.

3. Results and Discussion

As shown in Figure 2a, in Mode 1, we found that in the bandwidth of 2.52–4.52 THz, the absorption of the absorber could reach 90%, with an average absorption rate of 97.67%, and that the perfect absorption was achieved at the frequency point of 2.96 THz, with an absorption efficiency of 99.98%. For the convenience of subsequent discussion, we defined this frequency point as M1. In Mode 2, where the absorber graphene has a Fermi level of 0.2 eV, a conductivity of 200,000 S/m for VO₂, and absorbs more than 90% within the frequency band of 3.91–9.66 THz, the average absorption is 95.16%. At the frequency point 8.04 THz, the absorption reaches 99.76%, which we define as M2. At a Fermi energy of 0.7 eV for graphene and a conductivity of 200,000 S/m for VO₂, the absorber is in absorption Mode 3. Figure 2b describes the absorption rate in this mode. Through the coupling effect, the absorber can realize ultra-wideband absorption of more than 90% in 2.14–10.00 THz; the general absorption efficiency is 96.07% and the general absorption efficiency is 99.85% at the frequency of 5.06 THz, achieving almost perfect absorption. The absorption rate is 99.76% at the frequency of 8.4 THz and 91.83% at the frequency of 3.49 THz. We define 3.49 THz, 5.06 THz, and 8.4 THz as M3, M4, and M5, respectively. The absorption bandwidth in Mode 3 is already higher than that of most broadband absorbers. We have made a detailed comparison and analysis between the absorber proposed and other similar structural models, as shown in Table 2 [49–54]. It can be observed that the advantages of the structure designed by us are that it can achieve a higher absorption bandwidth with fewer structural layers and can switch between multiple absorption modes.

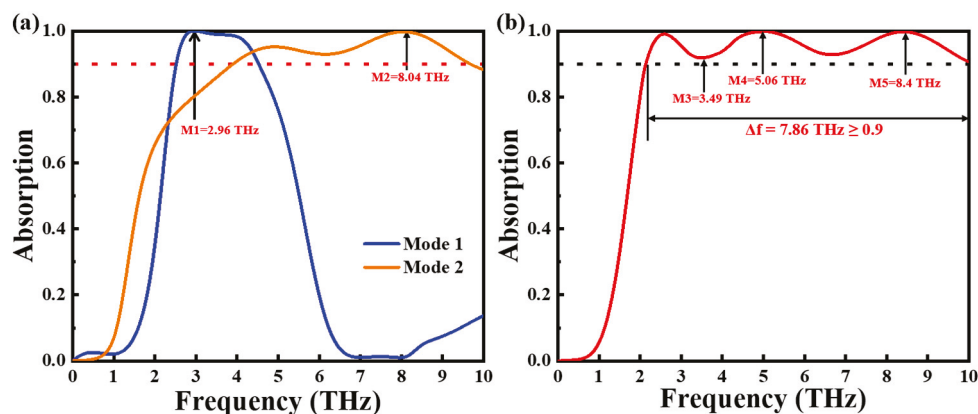


Figure 2. Absorption of Modes 1 and 2 (a), absorption of Mode 3 (b).

Table 2. The model is compared with other similar structural models.

References	Absorption Bandwidth (THz) (≥ 0.9)	Ultra-Wideband (Bandwidth > 7 THz)	Multimodal Tunability
[49]	Multiband (one peak): 0.745–0.775 broadband: 2.3–5.63	No	Yes
[50]	Multiband (one peak): 2.3 ultra-wideband: 2.85–10	Yes	Yes
[51]	Dual-band absorption: 2.55–4.35 broadband absorption: 7.6–10.85	No	Yes
[52]	Quadruple broadband: 3.58–10 1.90–5.29 5.24–6.19 5.72–8.32 7.33–10.00	Yes	Yes
[53]	2.99–6.16	No	No
[54]	3.7–8.0	No	No
Proposed	triple-band: 2.52–4.52 3.91–9.66 2.14–10.00	Yes	Yes

For the purpose of examining the absorption features of the structure in greater detail, we introduce the impedance matching principle. The relative impedance is expressed by Formula (7) [55]:

$$Z = \pm \sqrt{\frac{(1 + S_{11})^2 - S_{21}^2}{(1 - S_{11})^2 - S_{21}^2}} \quad (7)$$

S_{11} is the reflection coefficient and S_{21} is the scattering coefficient; the reflectivity can be expressed as $R(\omega) = |S_{11}|^2$ and the transmittance can be expressed as $T(\omega) = |S_{21}|^2$. We use the formula $A(\omega) = 1 - R(\omega) - T(\omega)$ to express the absorption rate, according to the impedance matching theory. When the impedance of the incident electromagnetic wave matches the characteristic impedance of the material, the energy of the electromagnetic wave will enter the material, reducing the reflection and increasing the absorption; at this

time, the real part of the complex impedance is almost equal to 1, while its imaginary part is roughly maintained at 0, and electromagnetic waves can be maximized into the material and absorbed [56–59]. Figure 3a–c shows the impedance in three modes; we found that in the range of 2.52–4.52 THz under Mode 1, 3.91–9.66 THz under Mode 2, and 2.14–10.00 THz under Mode 3, the real part of the relative impedance approaches 1, while the imaginary part approaches 0. The complex impedance satisfies the impedance matching theory, resulting in high absorption; this theoretically reveals the absorption mechanism of our absorber. In addition, at the frequency points M1 of Mode 1, M2 of Mode 2, and M4 and M5 of Mode 3, the impedance is $1.0000829-0.000118267i$, $0.99764128-0.000525042i$, $1.0013537-0.000541371i$, and $0.99863559-0.00197135i$, which is consistent with the impedance matching theory. This also reveals an absorption rate of more than 99.7% for these points.

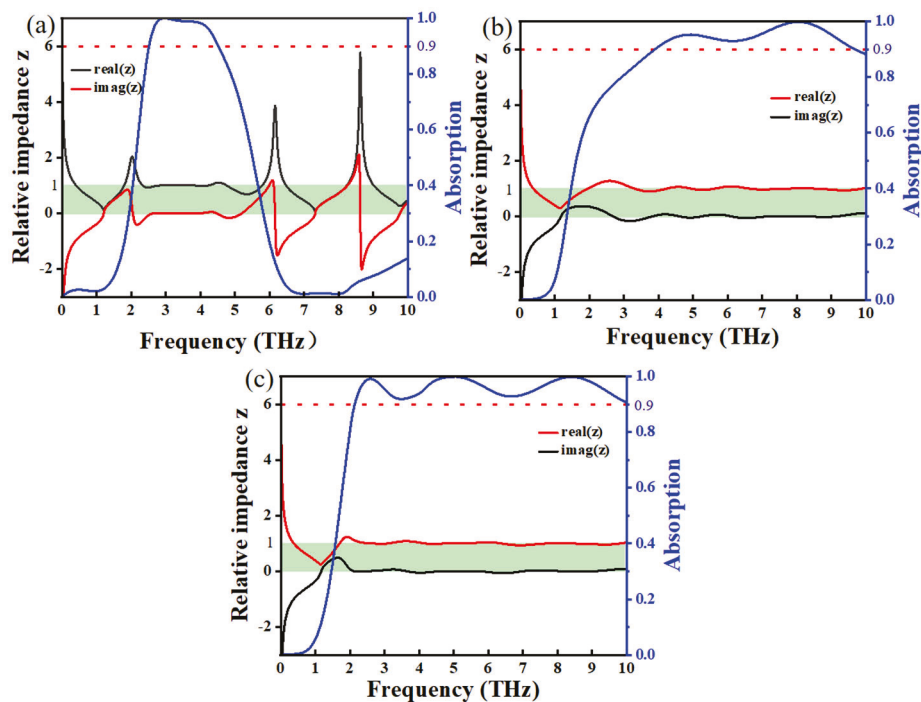


Figure 3. Relative impedance and absorption of Modes 1 (a), 2 (b), and 3 (c).

Then, we explored the absorption of the absorber Mode 1 and Mode 3 at different Fermi levels, respectively. The Fermi energy of graphene is expressed by Formula (8), where V_g , ϵ_0 , ϵ_r , and d represent the bias voltage, dielectric constant in a vacuum, relative dielectric constant of the medium, and dielectric layer thickness [60]:

$$E_f \approx h\nu_f \sqrt{\frac{\pi\epsilon_r\epsilon_0 V_g}{ed}} \quad (8)$$

Figure 4a describes the absorption at Mode 1; in this mode, VO_2 is in an insulated state, where the Fermi level changes within the range of 0.6 eV to 1.0 eV. It can be found that at 0.6 eV, the absorption bandwidth is 2.47–3.79 THz (1.32 THz), and at 0.8 eV, it is 2.52–4.52 THz (2 THz), and that the absorption bandwidth gradually increases. When the Fermi level continues to increase to 1.0 eV, the absorption bandwidth shows little variation, but the average absorption rate decreases. The average absorption rate was 97.67% at 0.8 eV and 96.67% at 1.0 eV. Figure 4b describes the absorption of the Fermi level of the absorber over the frequency range of 0.5–0.9 eV in Mode 3. The average absorption rate rises initially and then falls; the average absorption rate of 0.5 eV was 93.68%, and that of 0.7 eV and 0.9 eV was 96.07% and 95.33%. When the absorption is greater than or less than 0.7 eV, the absorption shows a small oscillation. At 0.7 eV, absorption is relatively flat; therefore, it can

be seen as the effect of the two-absorption coupling. In summary, regardless of whether VO₂ is in a metallic state or an insulated state, the regulation of the Fermi level of the graphene layer can be used to regulate the absorption.

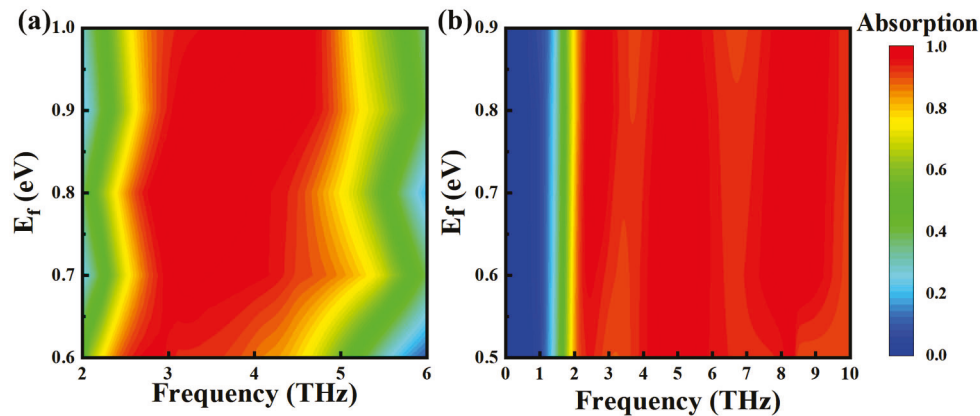


Figure 4. Absorption rate of Mode 1 at different Fermi energies (a), Mode 3 at different Fermi energies (b).

We explored the absorption for various polarization states and different incidence angles in the ultra-wideband absorption Mode 3. Figure 5a describes the absorption under a TE wave and TM wave, and it is apparent that the absorption rate is not affected by the polarization state of the incident wave. This is because the graphene layer in our absorber model, as well as the VO₂ layer pattern, are centrosymmetric. This property enables the absorber to provide consistent performance in different polarization states, which also allows the model to be applied to a wider range of practices [61–63]. Similarly, we can see that Figure 5b describes that the absorption rate of incident waves varies between 0 and 50°. The average absorption rate at 0°, 10°, 20°, 30°, and 40° is 96.07%, 95.96%, 95.65%, 94.96%, and 93.38%. Furthermore, the average absorption rate can reach over 90%, which also shows that the structure displays the features of low angle incidence and insensitivity, further expanding the use of the structure in practical applications.

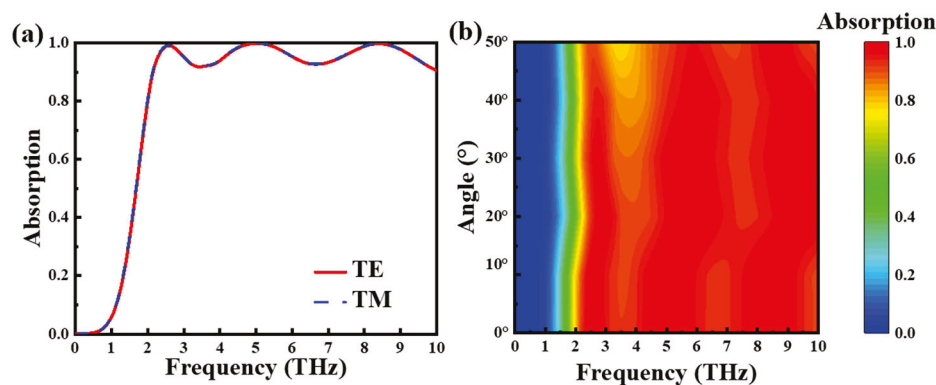


Figure 5. Absorption curves of Mode 3 at TE and TM modes (a), and Mode 3 at 0–50° incidence angles (b).

Next, we discuss the absorption of Mode 1 in various sizes of period p and embedded VO₂ layer thicknesses h_4 , as well as that of Mode 3 in various sizes period p , dielectric layer thicknesses h_2 , h_4 and embedded VO₂ layer thicknesses. As shown in Figure 6a, absorption Mode 1 is affected by the thickness of the embedded VO₂ layer, and the average absorption rate is 96.07% when $h_4 = 0.15 \mu\text{m}$. With increases or decreases in h_4 , the average absorption rate will decrease, but all rates are above 90%. When h_4 was 0.1 μm , 0.2 μm , and 0.3 μm , the average absorption rates were 95.9%, 94.96%, and 92.15%. As shown by Figure 6b, as period

p increased, there was a slight change in the absorption bandwidth. When $p = 17.5 \mu\text{m}$, the absorption range was 7.86 THz, while when $p = 19.5 \mu\text{m}$, the absorption range was 7.63 THz. Through the analysis of the above parameter period p and the absorption of vanadium oxide layer thickness variation, we can conclude that the structure allows a large manufacturing tolerance, which makes it more feasible for application.

We continue to look at Figure 7a,b, and it can be seen that the thickness of the VO_2 layer has a very small influence on the absorption of Mode 3, while the influence of period p is large. Along with the growth of period p , the average absorption rate gradually decreases. From Figure 7c, we can find that the average absorption rate of h_5 is the highest when the dielectric layer thickness is h_5 , and that the absorption bandwidth narrows when h_5 becomes larger or smaller. In addition, when $h_5 = 7.5 \mu\text{m}$, the absorption rate is less than 90% at 3.28–3.89 THz; the absorption rate of this section clearly decreased. Furthermore, when $h_5 = 9.5 \mu\text{m}$, the absorption bandwidth was 2.1–9.3 THz (7.2 THz); the decrease in the absorption bandwidth was obvious. Therefore, it is concluded that the structure is insensitive to the thickness accuracy of the dielectric layer embedded in the VO_2 layer, and the optimal values of the parameters p , h_4 , and h_5 are $18.5 \mu\text{m}$, $0.15 \mu\text{m}$, and $8.5 \mu\text{m}$, respectively.

Figure 8a–c describes the absorption of graphene layer parameters t_1 , t_2 , and t_3 at different sizes in Mode 3. We found that the absorption effect of each parameter changed very little within the explored variation range, and that the average absorption rate could always remain above 90%. When the distance t_1 between the four squares in the middle of the graphene layer increases, the average absorption of t_1 at $1.0 \mu\text{m}$ and $2 \mu\text{m}$ is 95.74% and 96.35%, respectively. When the graphene layer parameter t_2 is $11.2 \mu\text{m}$ and $12 \mu\text{m}$, the absorption is 96.5% and 96.07%. Similarly, the small square size of the four corners of the graphene layer has little effect on absorption; the average absorption of t_3 in $3.0 \mu\text{m}$, $4.0 \mu\text{m}$, and $5.0 \mu\text{m}$ was 95.82%, 96.07%, and 96%, respectively. The above parameters were in different sizes, and the absorption rate showed almost no change. This is because graphene-supported plasmon patterns typically concentrate at the edges or defects of a pattern, creating a strong local field enhancement effect. Even if the pattern size changes, the plasmon resonance effect remains significant as long as key areas remain similar. This further shows that the structure allows a large manufacturing tolerance, which is conducive to practical applications [64–66].

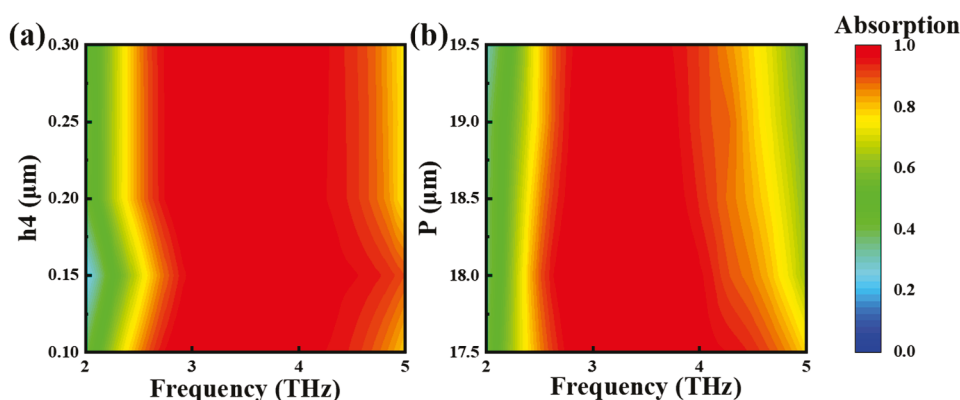


Figure 6. Absorption of Mode 1 at different thicknesses of the VO_2 layer (a), absorption of Mode 1 at different sizes of period p (b).

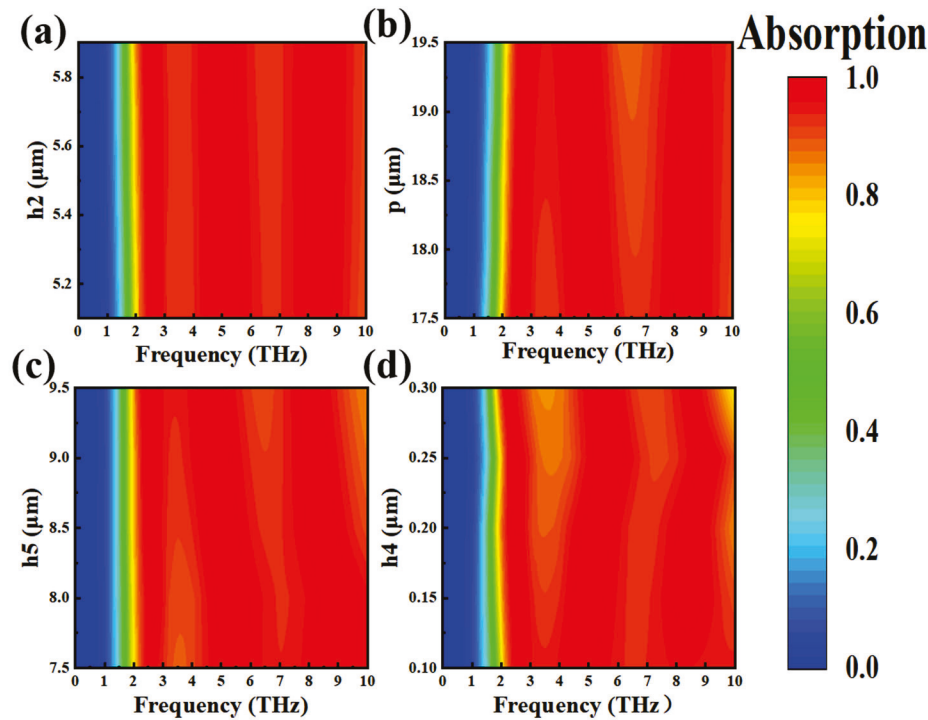


Figure 7. Absorption rate of Mode 3 at different dielectric layer thicknesses h_2 (a), Periodic p (b), h_5 (c), and VO_2 layer thicknesses h_4 (d).

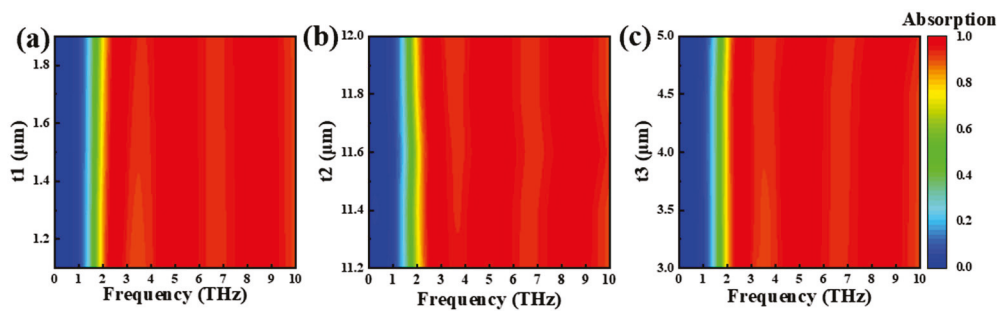


Figure 8. Mode 3 absorption rate at different sizes of graphene layer parameters t_1 (a), t_2 (b), t_3 (c).

Figure 9a describes the impact of changes in the VO_2 layer parameter w_1 on the absorption performance within a certain range. It is found that when w_1 increases from $2.6\ \mu\text{m}$ to $3.0\ \mu\text{m}$, the average absorption rate exhibits a downward trend: at $2.6\ \mu\text{m}$ and $3.0\ \mu\text{m}$, the average absorption rate is 95.36% and 96.07%, respectively; at $2.6\ \mu\text{m}$, the absorption is less than 90% and is about 89% at 6.71–7.41 THz. Increases in w_1 result in a reduction in the absorption bandwidth, and the absorption bandwidth reaches 7.19 THz when the VO_2 layer width (w_1) is $3.4\ \mu\text{m}$, but overall, the absorbers show good absorption. Similarly, Figure 9b depicts the absorption of w_2 at different values. Our analysis calculated that the average absorption rate was highest when $w_2 = 5\ \mu\text{m}$. Figure 9c shows that the parameter w_3 exerts a strong effect on the absorber. When the size of w_3 increases, the average absorption rate increases significantly and the absorption bandwidth decreases; therefore, the structure is insensitive to the parameters w_1 and w_2 of the VO_2 layer, while the optimal size of w_3 is $8.0\ \mu\text{m}$.

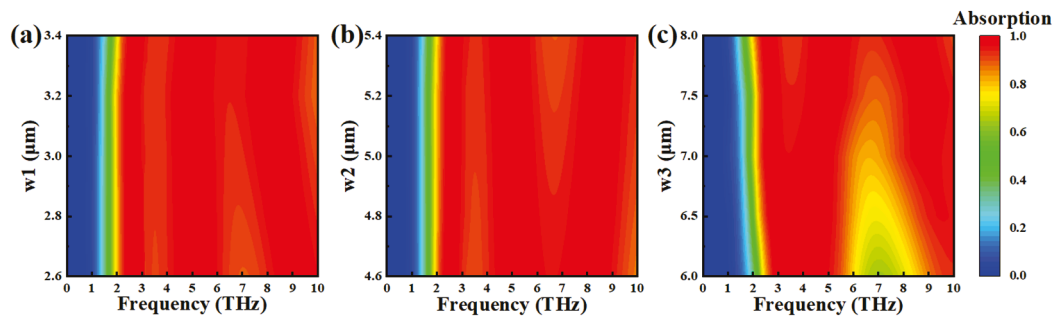


Figure 9. The absorptivity of Mode 3 under VO₂ layer parameters w_1 (a), w_2 (b), w_3 (c) at different sizes.

Then, to further elaborate on the absorption properties, we investigate the distribution of the electric field at the special frequency points M1–M4, as shown in Figure 10a,c. At the M1 frequency point of Mode 1, it is obvious that the electric field is mainly distributed in the middle four squares of the graphene layer, because the surface plasmon resonance [67–69] shows a strong intensity in this region. The electric field distribution in this region is highly concentrated, resulting in the absorption efficiency of the electromagnetic wave energy reaching a peak, while the VO₂ layer has almost no electric field, which is because the VO₂ in this mode is in an insulating state, and VO₂ is a thin insulating material sandwiched between two layers of silicon oxide [70]. It forms a relatively uniform dielectric environment with the surrounding silicon oxide layer, which means that the electric field does not change or concentrate significantly in this region. In contrast, the top layer of graphene has extremely high electron mobility and excellent electrical conductivity, which can effectively constrain the electric field near its surface, thus enhancing the concentration of the electric field in this region [71–73]. This indicates that Mode 1 is mainly derived from the graphene layer. However, in Mode 2, as demonstrated by Figure 10b,d, the electric field primarily resides on the square frame of the VO₂ layer, as opposed to the graphene layer where the electric field is relatively reduced, which indicates that Mode 2 is mainly from the VO₂ layer, because the conductivity increases significantly when VO₂ becomes a metallic state, at which point it can strongly reflect and absorb incoming electromagnetic waves. When the Fermi level of graphene is low, its internal free carrier concentration is reduced, thereby reducing its response to electromagnetic waves. The structure supports a specific resonance mode, where the VO₂ layer plays a key role in the electromagnetic coupling effect, forming a strong local field enhancement effect [74–76].

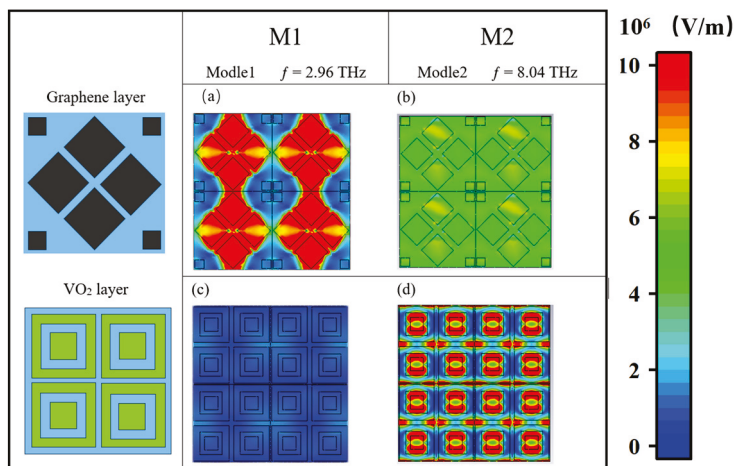


Figure 10. Electric field distribution at Mode 1 point M1 (a,c), M2 (b,d).

Finally, we also discussed the arrangement of the electric field of the three special resonance points in Mode 3, as shown in Figure 11a,d. The intense electric field at M3 is mainly distributed in the four square blocks in the middle of the graphene layer, but the strength is not as strong as that at M2, and the low-intensity electric field is dispersed at the boundary of the adjacent unit structure of the VO₂ layer. The graphene layer contributed more to the absorption at this point. As can be seen from Figure 11b,e, the electric field distribution at point M4 shows that the strong electric field is distributed in both the graphene layer and the VO₂ layer. In the graphene layer, it is distributed at the four small squares, and in the VO₂ layer, it is distributed at the junction of the box and the adjacent unit structure, indicating that both the graphene and the VO₂ contribute greatly to the high absorption there. Looking at the electric field distribution at point M5 in Figure 11c,f, we can clearly see that the strong electric field there is distributed at the junction between the box of the VO₂ layer and the adjacent unit structure, which is almost the same as the distribution of the VO₂ at the M4 point; while the electric field distribution of the graphene layer is weak, the VO₂ layer makes a greater contribution to the absorption at this point. In summary, the whole multi-layer structure acts as a resonator system, and the coupling effect between the layers of materials is generated between them; then, broadband absorption is formed.

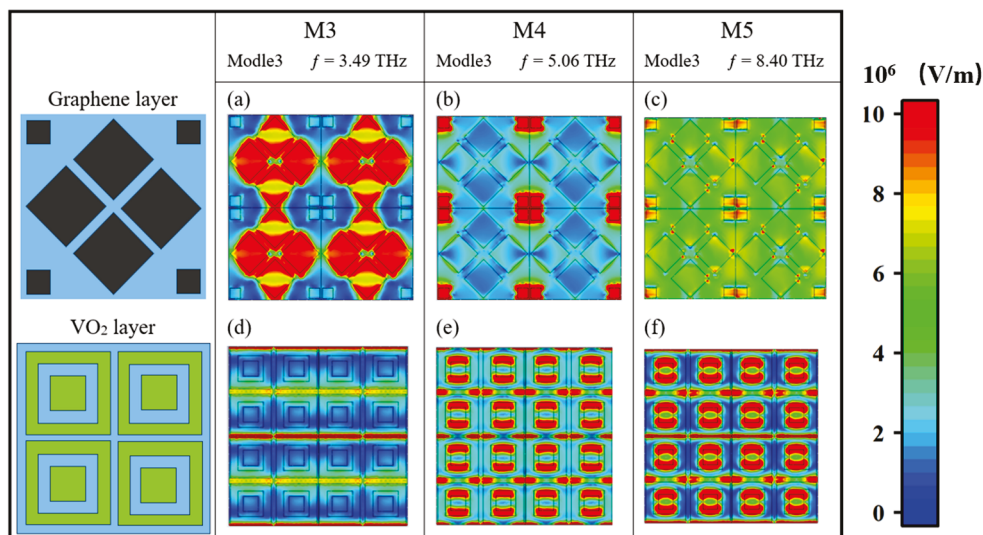


Figure 11. Electric field distribution at Mode 3 point M3 (a,d), M4 (b,e), M5 (c,f).

4. Conclusions

To sum up, we propose an absorber with three tunable modes: Mode 1 (low band absorption mode), Mode 2 (high band absorption mode), and Mode 3 (broadband absorption mode). When the absorber is in Mode 1, the absorber has greater than 90% absorption across the range of 2.52–4.52 THz. When the absorber is in Mode 2, the absorber has greater than 90% absorption across the range of 3.91–9.66 THz. When the absorber is in Mode 3, the absorption at 2.14–10 THz reaches more than 90%. The absorption mechanism was revealed by using the relative impedance theory, and the absorption of incident waves under various polarization states and different incident angles was investigated, which showed that the structure was a polarization-insensitive and low-angle-insensitive structure. The absorption of each parameter in different sizes was also investigated, and the optimal size was obtained after calculation and analysis. Finally, the electric field distribution of special frequency points in different modes was calculated and drawn. The absorption mechanism of the structure was further revealed by the theory of the electromagnetic coupling effect. Overall, this type of metamaterial device has significant application significance in fields

such as terahertz communication filtering, electromagnetic stealth, and radar detection. However, it may also encounter some practical issues, such as the need to break through bottlenecks in material regulation compatibility, manufacturing processes, and dynamic response speed. Future research should focus on new regulation mechanisms, process innovation, and intelligent design to promote the practical and integrated development of terahertz metamaterial devices.

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Article

Enhancing Silicon Anode Performance in Lithium-Ion Batteries Through Hybrid Artificial SEI Layer and Prelithiation

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Abstract: Prelithiation has been widely accepted as one of the most promising strategies to compensate for the loss of active substance and to improve the initial Coulombic efficiency in silicon-based anodes for advanced high-energy-density batteries. But because of their unstable solid electrolyte interface (SEI) layer and low initial Coulombic efficiency, they expand in volume during prelithiation and react with moisture, which makes commercialization a difficult process. Herein, we have developed a strategy using lithium bis(fluorosulfonyl)imide (LiFSI) treatment to eliminate redundant lithium and generate LiF-based inorganic compounds on the surface of the prelithiated electrode. Such method not only reduces the reactivity of the prelithiated anode but also enhances the ionic conductivity of the SEI. The rich LiF surface works as an artificial SEI, and according to electrochemical evaluation, the initial Coulombic efficiency of the prelithiated silicon anode treated with LiFSI can reach 92.9%. This technique not only increases the battery's energy density but also its cycle stability, resulting in superior capacity retention and a longer cycling life.

Keywords: prelithiation; artificial SEI layer; interfacial engineering; coulombic efficiency; silicon anode

1. Introduction

High-energy-density batteries are becoming more and more in demand as a result of the quick expansion of portable electronics and renewable energy sources. Of all the anode materials, silicon (Si) has garnered the most interest because of its superior theoretical capacity. Si has an approximate theoretical capacity of 4200 mAh/g, more than ten times that of conventional graphite anodes [1]. Although silicon anodes offer a vast amount of energy potential, there are a number of important problems that limit their use in real-world applications. Silicon has substantial volume expansion (>400%) during the lithiation and delithiation phases of the cycling process [2]. This can cause mechanical fragmentation and the loss of electrical contact, which in turn can lead to capacity deterioration. Furthermore, the electrolyte becomes unstable at the anode's working potential, reducing to create a SEI on the anode surface. The SEI is a complex mixture of organic and inorganic lithium compounds. The issue is made worse by the unstable SEI layer that results from electrolyte breakdown [3,4]. This layer keeps consuming lithium ions while destroying the electrode–electrolyte contact. The new Si surface is vulnerable to parasitic reactions and loss of active

lithium because the brittle inorganic materials, LiO and LiF, which comprise the majority of the old SEI layer, break under repetitive strain during cycling [5].

Researchers have suggested a number of optimization techniques to overcome these constraints, and prelithiation technology has proven to be a successful one [6]. Prelithiation reduces irreversible capacity loss and supplies extra active lithium to make up for lithium used during SEI rupture by adding lithium ions during the early stages of battery development. By precisely controlling lithium insertion and guaranteeing appropriate anode conditions during the first charge–discharge cycle, an ideal prelithiation technique can greatly improve energy efficiency, cycling stability, and battery longevity [7].

Multiple prelithiation techniques have been devised, such as cathode prelithiation through additives, chemical or electrochemical prelithiation pathways, and the use of lithium foil or powder for anode prelithiation [8]. Nevertheless, practical implementation of these strategies faces challenges, such as inadequate control over lithium insertion uniformity and quantity, resulting in residual lithium [9]. The recurrent SEI fracture brought on by silicon–carbon anode volume growth is not resolved by residual lithium, even if it might improve the initial active lithium supply. The SEI layer becomes more unstable with extended cycling and storage, showing increased thickening, inorganic component enrichment, and organic constituent depletion. Capacity loss and increased internal resistance are caused by these structural alterations [10,11]. The inclusion of functional additives, electrolyte solvent modification, and nanomaterial incorporation have all been used in attempts to increase SEI stability, but the results have not been ideal [12]. For instance, ether-based electrolytes (e.g., DME/DOL) can compact SEI layers and reduce the pore diameter but fail to fundamentally address these issues. In contrast, fluorinated electrolyte additives demonstrate superior efficacy in modulating SEI composition and structure, minimizing interfacial side reactions on silicon oxide anodes, and thereby improving cycling stability and rate capability. Common additives, such as fluoroethylene carbonate (FEC) and lithium bis(fluorosulfonyl)imide (LiFSI), significantly reduce SEI porosity, forming denser SEI layers [13]. Yang et al. [14] revealed that diethyl fluoromalonate, leveraging its favorable decomposition kinetics, rapidly generates a LiF-rich passivation layer at the silicon oxide interface during early SEI formation. This effectively suppresses parasitic reactions and yields an adaptive SEI layer capable of accommodating volume changes while maintaining stability over extended cycling. In addition, Wang et al. [15] proposed an innovative approach to engineer lithium bis(fluorosulfonyl)imide (LiFSI)—a material featuring fluorosulfonyl ($-\text{SO}_2\text{F}$) groups and lithium imide salt structures—onto lithium metal anode surfaces via a chemical bonding strategy. The Li-F/Li-S-bonded interfacial layer, formed through in situ reactions between sulfonyl groups in LiFSI and metallic lithium, effectively suppresses lithium dendrite growth and enhances the mechanical stability of the SEI. The study further demonstrated that the LiFSI concentration critically modulates SEI layer thickness and modulus, significantly improving cell performance [16].

This study proposes an LiFSI-based prelithiation optimization strategy to address residual lithium and insufficient SEI stability in silicon–carbon anodes during cycling. A schematic diagram of the LiFSI-based modification technique is displayed in Figure 1. LiFSI and its decomposition product, fluorosulfonyl ($-\text{SO}_2\text{F}$) groups, exhibit enhanced electrostatic affinity for Li^+ , effectively consuming residual lithium and accelerating SEI formation. Concurrently, LiFSI functional groups bind to silicon and graphite surfaces, forming a stable electrode network that significantly reinforces SEI mechanical integrity. The experimental findings show that the LiFSI-treated prelithiated silicon–carbon anode has a high initial Coulombic efficiency. It rose from 83.4% (the conventional prelithiation) to 92.9%. These findings not only validate LiFSI's pivotal role in constructing high-stability SEI

layers but also advance novel methodologies for anode prelithiation, offering substantial theoretical and practical implications for next-generation LIB development.

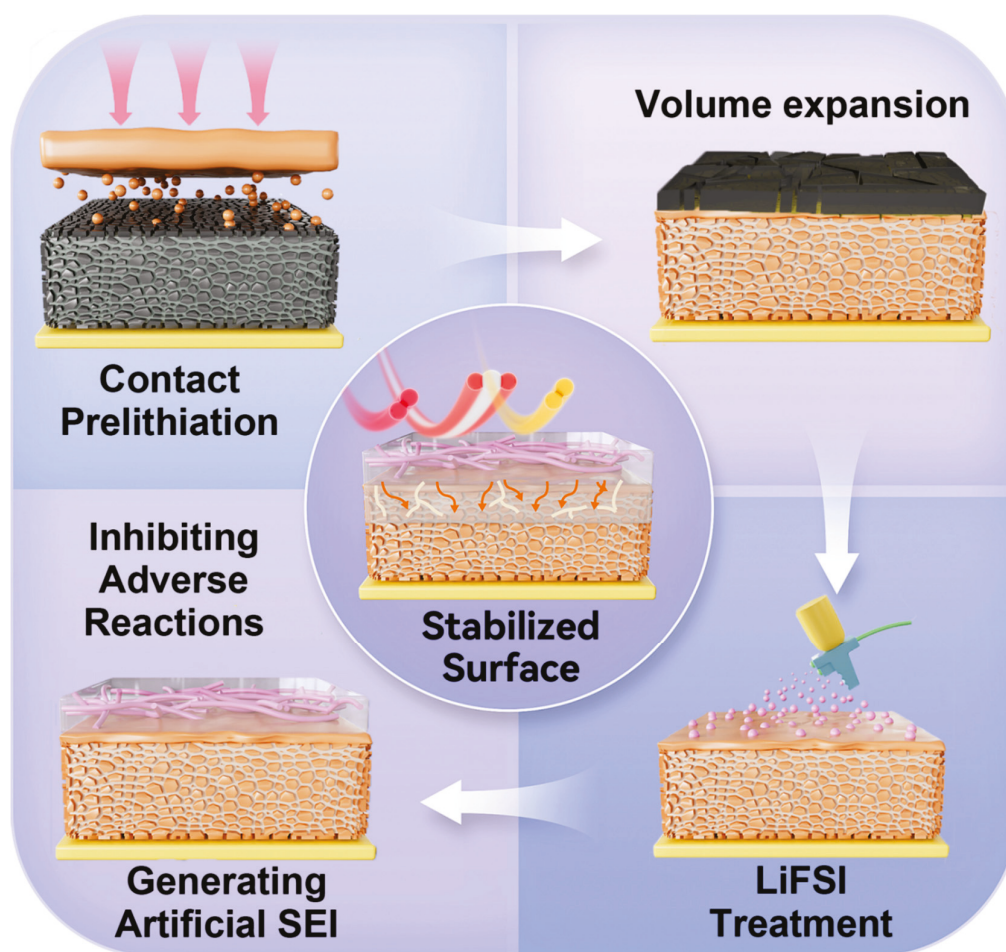


Figure 1. Schematic showing the LiFSI treatment process.

2. Experiment

2.1. Sample Preparation

To create a negative electrode slurry, we combined and stirred the conductive agent Super P carbon black (SP, 3 wt%), the binder carboxymethyl cellulose sodium (CMC, 1.5 wt%), styrene butadiene rubber (SBR, 2.5 wt%), and silicon-based active material (93 wt%). To create a negative electrode sheet, we evenly covered the slurry with 10 μm -thick copper foil and vacuum-dried it for 6 h at 100 $^{\circ}\text{C}$. Via roller pressing, a commercial lithium strip that is 3 μm -thick was joined with the manufactured electrode sheet. To guarantee adequate lithium absorption and produce a Pre-Li sample, the composite electrode sheet was vacuum-sealed and allowed to stand at room temperature for a full day. Commercial LiFSI (purity 99.8%) was mixed with DMC at a mass ratio of 1:4, and the mixture was ultrasonicated for 10 min to achieve uniform dispersion of LiFSI in the solution, obtaining a 20 wt% LiFSI reagent. Finally, the reagent containing 20% LiFSI was evenly applied to the surface of the Pre-Li sample and kept in a vacuum oven at 80 $^{\circ}\text{C}$ for 6 h to ensure complete evaporation of the solvent, obtaining the sample.

2.2. Material Characterization

The prelithiated electrodes treated with LiFSI were characterized by X-ray diffraction (XRD; Bruker D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany) between 10 $^{\circ}$ and

90°. A scanning electron microscope (SEM; HITACHI SU8010, Hitachi High-Technologies Corporation, Tokyo, Japan) was used to examine the elemental distribution and shape of various electrode materials. We utilized X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha, Thermo Fisher Scientific Inc., Waltham, MA, USA) to document the functional group distribution. The surface of the prelithiated electrode after LiFSI treatment was further characterized by TOF-SIMS (TOF-SIMS; PHI nano TOF II, ULVAC-PHI Inc., Chigasaki, Japan), giving a 50 nm-depth-profile conducted at a speed of 0.2 nm/s to obtain the distribution information of elements with depth.

The treated anode sheets were combined with lithium cobalt oxide cathode sheets (capacity: 166 mAh/g) using commercial electrolytes, and the results were tested by laminating soft-pack complete cells to confirm the samples' effect on electrical performance. The battery's initial efficiency data and charge–discharge voltage curves were acquired on the Neware apparatus at a rate of 0.04 C (charging cut-off voltage 4.5 V and discharging cut-off rate 0.01 C). Additionally, at 25 °C, the battery's long-cycle capacity retention rate was acquired at a charge–discharge rate of 0.5 C. The battery's performance was compared at 0.5 C, 1.0 C, 1.5 C, and 2.0 C (charging cut-off voltage 4.5 V and discharging cut-off rate 0.025 C). On the electrochemical workstation (CS310X-8, Corrtest Instruments Corp., Ltd., Wuhan, China), within the voltage range of 2.7–4.7 V, the cyclic voltammetry curves of the cells were obtained in the positive sweep mode at a scan rate of 0.1 mV/s.

3. Results and Discussion

To investigate the impact of LiFSI treatment on the surface structure and morphology, SEM and back SEM were used to view images of raw, prelithiated, and LiFSI-treated silicon anodes (with sizes of approximately 10 μm , 20 μm , and 50 μm , respectively), as illustrated in Figure 2.

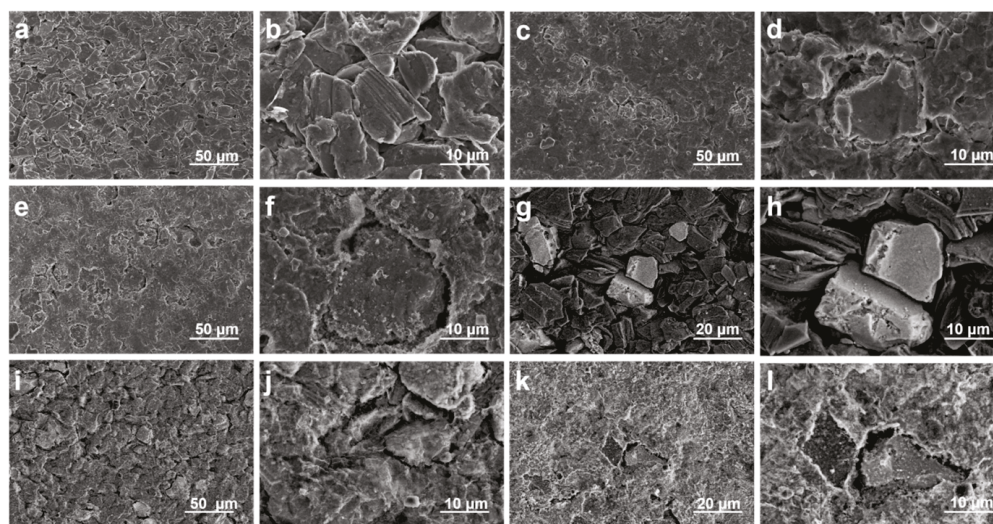


Figure 2. After adding lithium, the SEM displayed the original sample (a,b), the sample without surface treatment (c,d), and the sample with surface treatment (e,f). Following lithium supplementation, the backscatter SEM displayed the original (g,h) sample, the (i,j) sample without surface treatment, and the (k,l) sample with surface treatment.

Due to the high solubility of LiFSI in polar electrolytes and the interfacial activity of its fluorosulfonyl groups ($-\text{SO}_2\text{F}$), we proposed uniform deposition of LiFSI onto prelithiated silicon-based surfaces to ensure homogeneous contact with the anode material. The hydrophilic sulfonic acid groups ($-\text{SO}_2\text{F}$) in LiFSI act as electrolyte additives, enhancing ionic conductivity and interfacial stability.

In order to verify the promoting effect of LiFSI on the formation of stable SEI film on the negative electrode surface, we tested the SEM images of the negative electrode surface under full charge after two and a half cycles of charging and discharging at a small rate of 0.04 C. It can be found that SEI film was almost invisible on the surface of the original silicon–carbon–negative electrode, and the expanded silicon–carbon particles caused large-scale cracks on the surface (Figure 2a,b). By EDS testing, it was found that the original electrode surface contained less of the F element required to construct the SEI film (Figure S1). However, the coverage of SEI film on the surface of the pre-lithium silicon–carbon anode only increased (Figure 2c,d). EDS tests showed a slight increase in the fluorine intensity on the electrode surface (Figure S2). This is due to the fact that pre-lithium can provide more active lithium, which can accelerate the formation of the SEI film [17]. However, it did not change the structure of the SEI film, and the mechanical strength of the SEI film was not improved. Therefore, the expanded silicon–carbon particles made the negative electrode surface show large-scale cracks. At the same time, we noticed that the intensity of the S element on the surface of the pre-lithium electrode increased significantly. This is because the surface of the electrode is residual by pre-lithium, and in the preparation of the SEM test stage, the electrode will inevitably contact the air, resulting in oxidation [18]. The surface of the pre-lithium +6 M LiFSI electrode saw obvious SEI film covering the electrode surface, and the surface cracks caused by volume expansion were effectively covered (Figure 2e,f). EDS images also showed that the F element on the electrode surface was significantly increased (Figure S3). This suggests that LiFSI promoted the formation of SEI films with high stability and ionic conductivity. That is, (1) LiFSI will decompose preferentially and participate in the construction of inorganic-rich SEI components. (2) The sulfonimide groups of LiFSI will coordinate with Li^+ ions to form a stable ionic transport network. At the same time, the decomposition products of LiFSI also exhibit self-healing properties, which can mitigate the SEI film rupture caused by volume expansion.

The surface alterations brought about by the LiFSI treatment were further supported by backscattered SEM images of the same samples, which are shown in Figure 3. The untreated prelithiated anode's backscattered SEM images (Figure 2i,j) displayed contrast changes, pointing to regions of varying composition or oxidation states that were most likely the consequence of side reactions and moisture exposure. The LiFSI treatment anode, on the other hand, had a more uniform structure with less compositional variation (Figure 2k,l), indicating that the passivating layer was successfully formed. Reducing parasitic reactions and preserving the stability of the electrode–electrolyte contact depends on this homogeneity.

It is evident from the comparison of SEM and backscattered SEM pictures that the artificial SEI layer, which was created by the LiFSI spraying method, greatly enhanced the integrity and surface morphology of the prelithiated silicon anode. The LiFSI treatment is essential for increasing the overall electrochemical performance, especially for cycle stability and early Coulombic efficiency, because it efficiently suppresses side reactions and stabilizes the electrode surface.

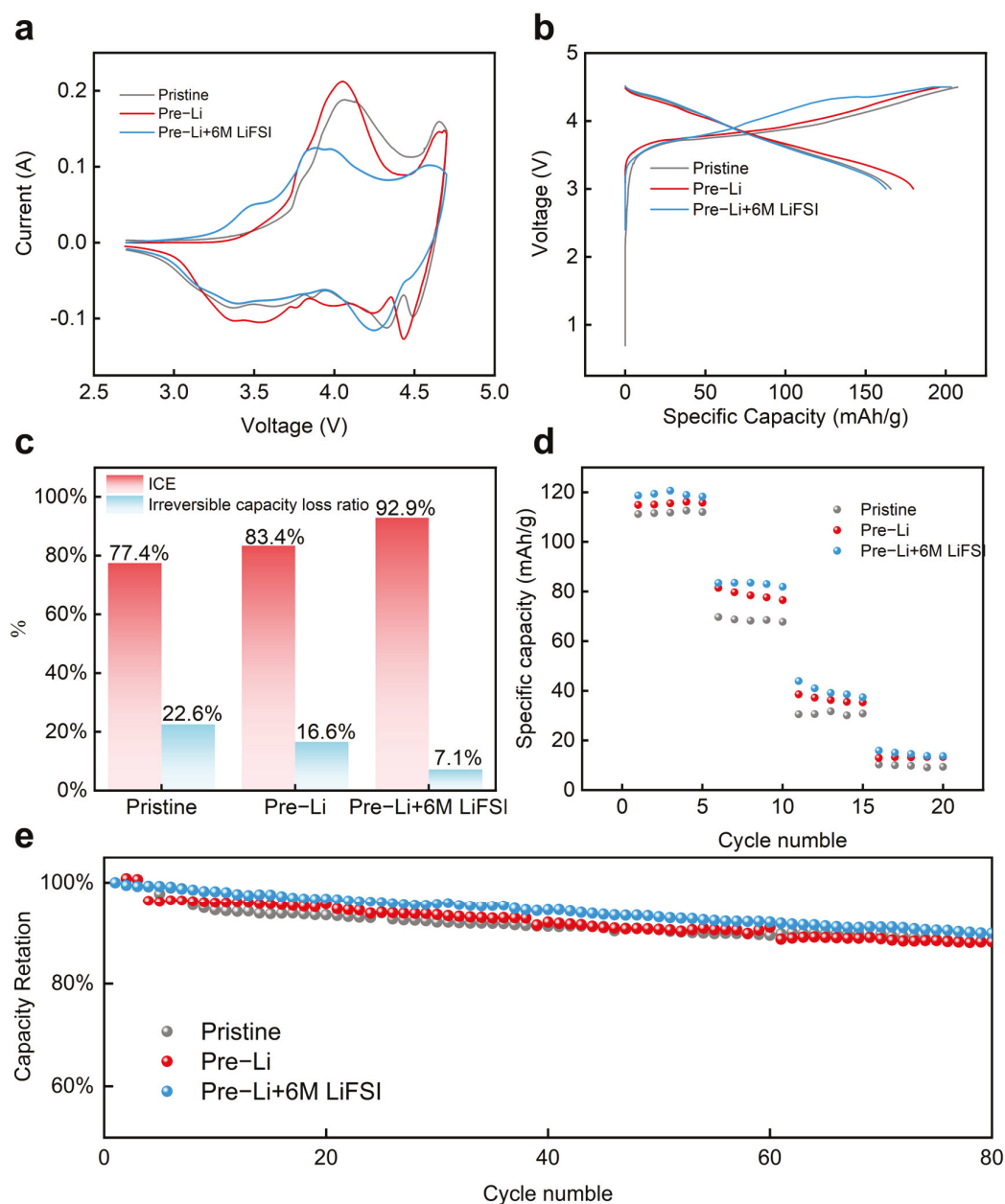


Figure 3. The electrochemical performance of variously treated samples. (a) CV, (b) voltage profile, (c) Coulombic efficiency and irreversible capacity, and (d) rate capability from 0.5 C to 2 C. (e) Cycling performance of different electrodes.

Electrochemical performance was examined using single-layer LCO || Si-C/Gr pouch cells (format: 80 mm × 64.2 mm × 0.85 mm, 0.38 Ah). The cyclic voltammetry curves in Figure 3a exhibited distinct differences in peak shapes and positions between prelithiated electrodes and LiFSI-passivated prelithiated electrodes, indicating that these treatments altered the surface characteristics and internal structure of electrode materials to influence lithium-ion intercalation and deintercalation processes. The prelithiated electrode demonstrated enhanced redox peak intensities attributed to the residual lithium metal enabling more lithium ions to participate in reversible reactions, while its broader current response range reflected elevated electrochemical activity linked to accelerated SEI film formation that improved the lithium-ion transport efficiency. LiFSI-treated electrodes exhibited significantly reduced anode peak intensity at 4 eV and disappearance of parasitic peaks at 4.45 eV, resulting from sulfonyl fluoride groups consuming residual lithium while rapidly

forming protective SEI layers to minimize electrode–electrolyte contact and suppress side reactions. The narrowed current response range in LiFSI-passivated electrodes implied enriched inorganic components, like LiF and Li₂S, in SEI layers that optimized lithium-ion transport paths and reaction kinetics [19]. Figure 3b demonstrates flatter voltage plateaus in prelithiated electrodes, indicating reduced voltage polarization beneficial for energy density enhancement, whereas the LiFSI-passivated counterparts displayed complex voltage variations in high-capacity regions with lower polarization and higher energy efficiency, corroborating the SEI modification effects observed in CV curves. The initial Coulombic efficiency increased from 77.4% for pristine anodes to 83.4% for prelithiated and 92.9% for LiFSI-passivated electrodes, with irreversible capacity losses decreasing from 22.6% to 16.6% and 7.1%, respectively, confirming LiFSI's optimization of SEI formation stability (Figure 3c) [20]. Rate capability tests (Figure 3d) showed LiFSI-treated electrodes delivering superior capacities of 118.7, 83.5, 43.9, and 15.9 mAh g^{−1} at 0.5 C to 2 C rates due to enhanced SEI ionic conductivity and structural integrity [21]. After 80 cycles (Figure 3e), LiFSI-passivated electrodes maintained 89.81% capacity retention, outperforming pristine and prelithiated samples at 88.11% and 88.25%, with prelithiated electrodes initially exceeding 100% capacity retention from residual lithium supplementation but gradually degrading due to SEI fracture–regeneration cycles caused by electrode expansion, leading to lithium loss and impedance from thickened SEI layers [22]. These findings collectively validated that LiFSI passivation reinforced SEI stability and lithium compensation mechanisms, establishing high-performance silicon-based anodes with optimized interface dynamics.

In order to explore the structural changes of the material and further demonstrate the role of LiFSI, phase analysis was performed on different electrodes. The XRD pattern in Figure 4a reveals the phase evolution of the electrodes before and after prelithiation with surface treatment. The intensity of peak C significantly decreased after prelithiation, indicating structural modifications. The emergence of new lithium–silicon phases further confirmed successful lithiation [23]. Additionally, the further reduction in peak C intensity after LiFSI treatment suggested increased amorphization, which helped mitigate volume expansion and improve electrode stability. The mechanism of SEI film formation accelerated by LiFSI was further revealed by XPS experiments. As shown in Figure 4d, it can be found from the full spectrum of XRD that only the pre-lithium electrode had a weak F peak, while the pre-lithium +6M LiFSI electrode had an obvious F peak, indicating the promoting effect of LiFSI on the formation of SEI film. The F1s XPS spectrum in Figure 4b reveals the chemical composition of the SEI layer after prelithiation +6M LiFSI surface treatment. The XPS spectrum of F1s confirmed the existence of LiF after LiFSI treatment, with a peak at 684.93 eV of LiF and a peak at higher binding energies of 688.96 eV, possibly coming from residual LiFSI after surface treatment [24]. Figure 4c displays the S2p XPS spectrum of a prelithiated and LiFSI-treated Si-based anode, revealing three characteristic binding energy peaks at 171.73 eV, 170.4 eV, and 169.31 eV, corresponding to distinct sulfur chemical states.

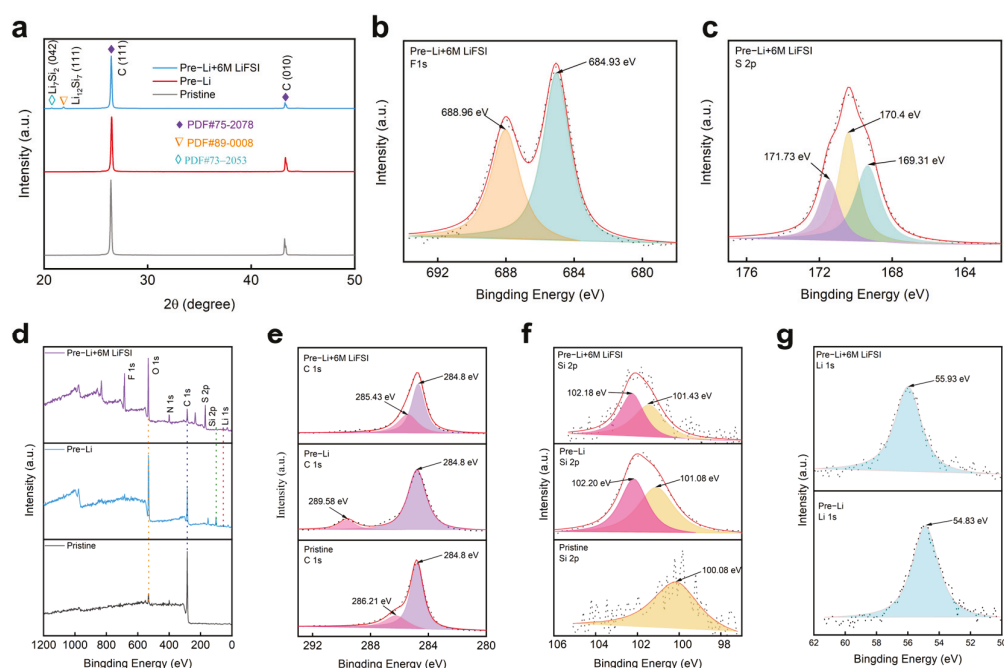


Figure 4. (a) XRD patterns of pristine material, prelithiated samples with/without surface treatment, (b) F1s XPS spectrum of LiFSI treatment after lithium compensation, (c) S2p XPS spectrum of LiFSI-coated sample after lithium compensation, (d) XPS survey spectra of three samples, (e) C1s spectra, (f) Si2p spectra, and (g) Li1s spectra comparison between surface-treated and untreated samples after lithium compensation.

The high-energy peak at 171.73 eV was attributed to S^{6+} species (e.g., sulfonate groups, $-SO_3^-$, or sulfate, SO_4^{2-}), indicating oxidative decomposition of LiFSI during interfacial reactions. The dominant peak at 170.4 eV corresponded to S^{4+} in the sulfonyl group ($-SO_2F$) of intact LiFSI residues, which enhanced the ionic conductivity of the SEI layer. The low-energy peak at 169.31 eV originated from reduced sulfur species (e.g., Li_2S_x or S^{2-}), formed through lithium-mediated reduction. This multivalent sulfur evolution demonstrated LiFSI-derived gradient SEI formation, balancing ionic transport and mechanical stress buffering [25]. Figure 4e shows the XPS C1s spectrum of the three types of electrodes. Carbon peaks at 284.8 eV and 286.21 eV appeared in the spectrum of the pristine electrode, suggesting that carbon mainly formed in the C-C bonds, and carbonyl species [15,16]. The carbonyl species converted to carboxylic species (289.58 eV) after prelithiation. Additionally, the peak of carboxylic species shifted to a lower binding energy of 288.8 eV after surface stabilization by LiFSI, suggesting that the carbon species was reduced in chemical reaction with LiFSI [26]. Figure 4f shows the Si2p spectrum of the three types of electrodes. Apparently, there was SiO_x or $LiSiO_x$ species formed after prelithiation, showing Si2p peaks at 102.2 eV, indicating high reactivity of the surface of the prelithiated electrode and its reaction with atmosphere. The peaks of SiO_x or $LiSiO_x$ shifted to a lower binding energy of 102.18 eV after surface stabilization, suggesting reduced surface reactivity after LiFSI treatment [27]. Finally, in Figure 4g, the Li1s spectrum shows two peaks at 55.93 eV and 54.83 eV, associated with lithium compounds such as $Li_xSO_yF_z$ and LiF. The upper spectrum represents the prelithiated electrode with LiFSI treatment, while the lower spectrum corresponds to the prelithiated electrode without surface treatment. The negligible shift and similar intensity between the two spectra suggested that LiFSI treatment did not significantly alter the total lithium content in the SEI but instead influenced its composition and distribution. This implies that the primary role of LiFSI was to optimize the SEI structure, leading to improved passivation, reduced side reactions, and enhanced cycling stability [28]. The SEI of the surface treatment electrode was analyzed using TOF-SIMS. Figure 5b shows the

depth profile of the electrode in the first 50 nm, revealing SEI characteristics. It was seen that LiF located at the very first 10 nm, constituting an important component of the SEI of the prelithiated anode after surface treatment by LiFSI. Additionally, there was Li_2CN species whose amount increased with the increasing depth, possibly coming from the reaction between the prelithiated electrode and LiFSI. Moreover, Li_3SiO_3 existed as a main substance in the first 50 nm SEI, likely from the prelithiation reaction and the following oxidation, consistent with the results of XPS. Finally, it was seen that Li_2O existed as an important component in the SEI of the LiFSI-treated electrode. Figure 5a presents the SEI compositions in the format of 3D cubes. It is clearly seen that LiF aggregated at the surface of the LiFSI-treated prelithiated electrode. In addition, Li_3SiO_3 distributed homogeneously, likely following the curvature of silicon–carbon composites. According to the negative-ion TOF-SIMS image shown in Figure S9, sulfonyl fluoride groups formed a high concentration of LiSO_3 on the electrode surface, which verified the XPS characterization results. In summary, the SEI layer formed by LiFSI passivation treatment was characterized by inorganic compounds, such as LiF, Li_2O , LiSO_3 , and LiSiO_3 , thereby promoting the formation of a highly stable SEI film.

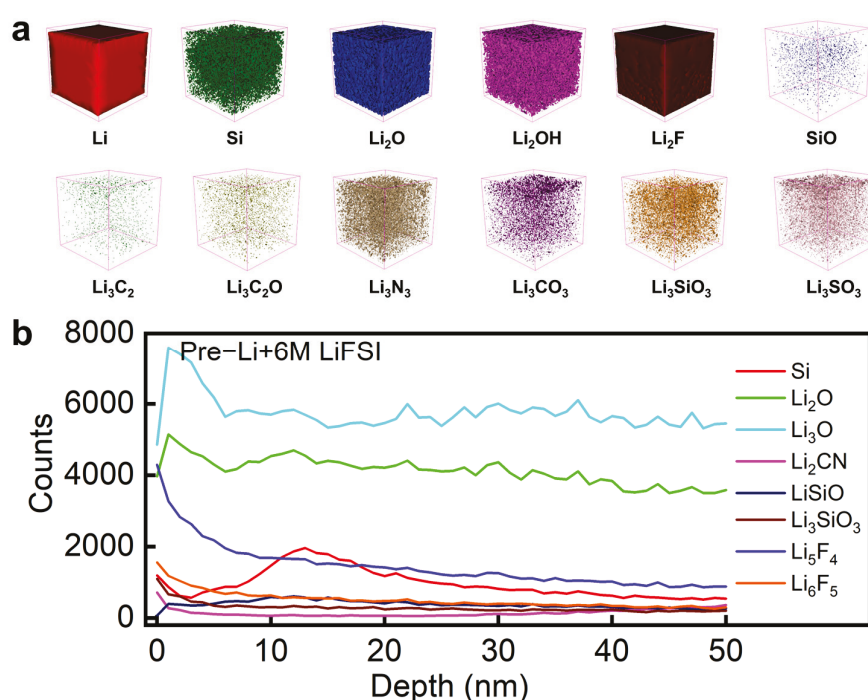


Figure 5. (a) Positive ions: 3D image and (b) depth profile of the prelithiated electrode after surface treatment, showing distribution of surface species.

4. Discussion

It was revealed that prelithiation effectively enhanced the initial Coulombic efficiency and reaction kinetics. Moreover, reversible capacities, rate capabilities, and cycling stability improved when the interface of the prelithiated electrode was stabilized by LiFSI-based modifications. LiFSI treatment reacted with redundant lithium of the prelithiated electrode, contributing to a modified SEI, which was rich in LiF variants and effectively suppressed silicon's volume expansion during cycling. Such artificial SEI had an organic core and an inorganic shell, which restricted the formation of insulating products during the prelithiation process while accommodating structural stress from silicon expansion, making the prelithiated electrode much more tolerant to humidity [29]. Also, it significantly enhanced the practical feasibility of employing contact prelithiation technologies.

Without surface treatment, the reactive prelithiated electrode would be oxidized quickly. The insulating oxidation products would passivate the electrode surface, resulting in a broken ion/electron transport pathway. For the electrode with LiFSI-induced surface stabilization, electron and ion transport pathways were retained, which amplified kinetics and maintained structural integrity against volume changes. LiFSI treatment further ensured the reaction stability of the Si-anode, limited irreversible reactions, mitigated particle pulverization caused by repeated expansion/contraction, and avoided inhomogenization during the reaction. However, it is noted that the protection effect became weaker in a harsh environment, possibly due to the fact that the established SEI was not strong enough. To guarantee long-term cycling stability against severe volume fluctuations, more effective measures are needed to tune the uniformity of surface treatment, parameters of the treatment, like temperature and time, the pretreatment process of the prelithiated electrode before contacting and reacting with LiFSI, and the post-treatment of the LiFSI-modified electrode before contacting with electrolytes.

5. Conclusions

In conclusion, we have developed a facile method to stabilize the reactive surface of the prelithiated Si-based anode by LiFSI. The LiFSI reacted with redundant lithium on the Si/C-Gr electrode and converted it into LiF-based species that protected the surface of the prelithiated anode. The LiF-based passivation species worked as an artificial SEI and avoided the volume expansion of prelithiated electrodes. It also potentially restricted the further extensive reaction between the prelithiated electrode and electrolyte, modifying the SEI of the prelithiated Si-based anode. The prelithiated silicon negative electrode treated with ASEI demonstrated a Coulombic efficiency (ICE) of up to 92.9% in the first cycle, which was much greater than the untreated sample, according to electrochemical measurements. Additionally, enhanced capacity retention and rate capabilities were identified, suggesting that kinetics was improved, possibly due to the retained electron/ion transport pathways. This further implied more uniform redox reactions because of the less-insulating components that existed in the initial SEI structure. We believe this facile method is of great significance to the realization of the contact prelithiated Si-anode and high-energy density batteries. More importantly, it reduces the manufacturing cost of the contact prelithiated Si-anode and contributes to a feasible technology in commercialization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano15090690/s1>, Figure S1. EDS images of different elements tested at full charge after two and a half cycles of the original sample at a small rate of 0.04C. (a) full spectrum, (b) carbon, (c) silicon, (d) oxygen, (e) nitrogen, (f) fluorine; Figure S2. EDS images of different elements tested in a fully charged state after two and a half cycles at a small rate of 0.04C for a sample without surface treatment after lithium supplementation. (a) full spectrum, (b) carbon, (c) silicon, (d) oxygen, (e) nitrogen, (f) fluorine; Figure S3. EDS images of different elements tested in a fully charged state after two and a half cycles at a small rate of 0.04C for surface treated samples after lithium supplementation. (a) full spectrum, (b) carbon, (c) silicon, (d) oxygen, (e) nitrogen, (f) fluorine; Figure S4. TOF-SIMS Spectra-Pre-Li+6M LiFSI; Figure S5. TOF-SIMS Positive Ions Mapping-C3; Figure S6. TOF-SIMS Positive Ions Profiles-C3; Figure S7. TOF-SIMS Negative Ions Mapping-C3; Figure S8. TOF-SIMS Negative Ions Profiles-C3; Figure S9. TOF-SIMS Negative Ions 3D Images-C3; Negative ions depth profile of the prelithiated electrode after surface treatment showing distribution of surface species; Figure S10. Negative ions depth profile of the prelithiated electrode after surface treatment showing distribution of surface species.

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Article

Controllable Hydrothermal Synthesis of 1D β -Ga₂O₃ for Solar-Blind Ultraviolet Photodetection

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Abstract: Gallium oxide (Ga₂O₃), an ultrawide bandgap semiconductor, is an ideal material for solar-blind photodetectors, but challenges such as low responsivity and response speed persist. In this paper, one-dimensional (1D) Ga₂O₃ nanorods were designed to achieve high photodetection performance due to their effective light absorption and light field confinement. Through modulating source concentration, pH value, temperature, and reaction time, 1D β -Ga₂O₃ nanorods were controllably fabricated using a cost-effective hydrothermal method, followed by post-annealing. The nanorods had a diameter of ~500 nm, length from 0.5 to 3 μ m, and structure from nanorods to spindles, indicating that different β -Ga₂O₃ nanorods can be utilized controllably through tuning reaction parameters. The 1D β -Ga₂O₃ nanorods with a high length-to-diameter ratio were chosen to construct metal-semiconductor-metal type photodetectors. These devices exhibited a high responsivity of 8.0×10^{-4} A/W and detectivity of 4.58×10^9 Jones under 254 nm light irradiation. The findings highlighted the potential of 1D Ga₂O₃ nanostructures for high-performance solar-blind ultraviolet photodetectors, paving the way for future integrable deep ultraviolet optoelectronic devices.

Keywords: hydrothermal; controllable synthesis; 1D β -Ga₂O₃ nanorods; solar-blind ultraviolet; photodetector

1. Introduction

Gallium Oxide (Ga₂O₃) has an ultrawide bandgap (larger than 4.6 eV), as well as high chemical and thermal stability. Hence, it has been applied in deep ultraviolet optoelectronic devices [1–4], particularly solar-blind ultraviolet photodetectors (SBPDs) [5–7]. Despite advancements in plane-structured Ga₂O₃ photodetectors, the limited light-sensitive area in them often leads to reduced light absorption efficiency, thereby affecting overall device performance. However, one-dimensional (1D) structural Ga₂O₃ offers distinct advantages, including high aspect ratio, enhanced light field confinement, and short electron transport paths. These properties contribute to improving optical absorption and energy harvesting, making 1D Ga₂O₃-based micro/nano structures promising for SBPD applications [8–10].

Until now, various methods have been undertaken to grow Ga₂O₃ nanostructures, such as chemical vapor deposition (CVD), chemical bath deposition, etc. For example, Fang et al. [11] utilized Ga₂O₃ microwires synthesized by the CVD method to construct

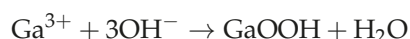
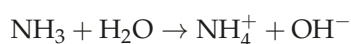
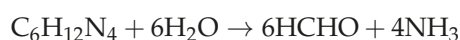
a high-performance, self-powered, solar-blind violet external photodetector, and Wang et al. [8] further enhanced its current response by the piezoelectric effect. Moreover, in recent years, Shan et al. [12] fabricated the Sn-doped Ga₂O₃ microwires and realized high performance solar-blind ultraviolet photodetector. Li et al. [13] synthesized Ga₂O₃ nanobelts via a vapor-solid growth mechanism, and fabricated a high-sensitivity ultraviolet photodetector. However, the controllable synthesis and morphology tuning are difficult to achieve. Hydrothermal synthesis, on the other hand, offers a simple, cost-effective, and controllable route for fabricating micro/nanomaterials.

In this work, a straightforward hydrothermal method was employed to synthesize 1D Ga₂O₃ nanorods with a high length-to-diameter ratio and desirable morphology. By flexible controlling of the chemical reaction parameters, such as source concentration, pH value, temperature, and reaction time, the morphology characteristics of precursor GaOOH were manipulated efficaciously and studied systematically. Then, further high-temperature annealing treatment was employed to convert GaOOH into β-Ga₂O₃ nanorods with porous surface structure, which can effectively improve photodetector (PD) performance. Moreover, metal-semiconductor-metal (MSM) type photodetectors were then fabricated using the 1D β-Ga₂O₃ nanorods, which had great performance. The results illustrated the potential of 1D porous β-Ga₂O₃ nanomaterials in high-performance, solar-blind, ultraviolet photodetectors and deep ultraviolet optoelectronic applications.

2. Experiment

2.1. Materials Growth and Device Construction

The hydrothermal method has the advantages of simple operation, low cost, and high yield [14–17]. By adjusting reaction parameters and optimizing the growth process, the flexible control over the morphology and structure of samples can be achieved. In recent years, the hydrothermal method has been utilized to prepare Ga₂O₃ nanomaterials [18–20]. In this work, the first step was uniformly dissolving Ga(NO₃)₃·xH₂O (99.9% metals basis, Aladdin™) and C₆H₁₂N₄ (99.5% calc. to the dried substance, Aladdin™) in deionized water under magnetic stirring. Next, the clear solution was obtained and conveyed to a closed reaction chamber. Then, the chemical reaction occurred under the temperature range of 100–150 °C for different times to obtain the precursor sample of GaOOH nanorods. The hydrothermal synthesis process of GaOOH nanorods included two stages of crystallization and growth of the hydrolyzed products of Ga³⁺. Therefore, the hydrolysis process of Ga³⁺ can be expressed in the following way [21]:



More importantly, in the hydrothermal reaction process, all of the experimental parameters have non-negligible influences on the sample morphology characteristics, including the source concentration, pH value, temperature, and growth time [22–24]. Consequently, it is significant to optimize the hydrothermal reaction and thermal annealing processes to modulate the morphological characteristics of the expected 1D β-Ga₂O₃ nanorod arrays.

Next, the precursor samples further needed to be treated at high temperature (850 °C) after cooling naturally, washing by deionized water and ethanol, as well as drying. The high-temperature annealing treatment could transform the precursor to β-Ga₂O₃, and improve the crystallinity simultaneously. The entire synthesis process of 1D β-Ga₂O₃

nanorods is presented in Figure 1. The thermal decomposition process can be expressed by the following formula [23].

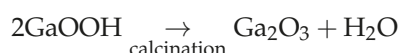


Figure 1. Schematic diagram of the synthesis process of the 1D porous β -Ga₂O₃ nanorods.

That is to say, the precursor GaOOH will transfer to the Ga₂O₃ by removing the formed water molecules under a high temperature. After obtaining the 1D porous β -Ga₂O₃ nanorods, the samples were homogeneously dispersed with anhydrous ethanol, and then slowly dripped and spun-coated onto the prepared Au interdigital electrodes with a width of 100 μm and space of 50 μm . Finally, the PD devices were obtained after drying.

2.2. Characterization Methods

The morphology of the nanorods was analyzed by field emission scanning electron microscopy (FESEM, Carl Zeiss Ultra Plus) equipped with an Energy dispersive spectroscopy (EDS) (Oxford X-Max 50). Their corresponding crystal properties were characterized with X-ray diffractometer (XRD) (Rigaku SmartLab) and Raman spectroscopy (Horiba France Sas XploRA). To obtain the bandgap of samples, the absorbance spectra were measured by an ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu, UV-2600). In addition, the X-ray photoelectron (XPS, Thermo Scientific Nexsa) was employed to study the relevant chemical composition and valence states. The photoelectric properties of the photodetector were tested by a semiconductor parameter system (Keithley 4200), integrated with a light-emitting diode (LED) with a central wavelength of 254 nm as a light source.

3. Results and Discussion

3.1. Controllable Growth Process of GaOOH

In order to study the precursor GaOOH growth process, the different reaction parameters in the hydrothermal method should be modulated, including the Ga ion source concentration, solution pH value, reaction temperature, and growth time. After that, the samples' morphology and crystal characteristics should be compared and analyzed in detail. Firstly, with the same temperature (100 °C) and reaction time (100 min), the effect of Ga(NO₃)₃·xH₂O concentration on the morphology and dimensions of GaOOH nanorods is studied by using various concentrations: 30 mmol/L, 50 mmol/L, 100 mmol/L, 110 mmol/L, 130 mmol/L, and 150 mmol/L. As presented in Figure 2, the scanning electron microscopy (SEM) images show noteworthy changes in both the length and morphology of the nanorods with increasing concentration. The GaOOH nanorods exhibit increased length with rising Ga ion concentration up to the 100 mmol/L, and the diameter of the nanorods increases slightly. In this process, the growth speed of the nanorods' length accelerates with the increase of Ga ion source concentration. Further increasing the Ga ion concentration, the GaOOH nanorods show spindle-like morphologies emerged with a progressively rougher surface. This illustrates that the excess Ga ion source inhibits the nanorod growth and changes the crystal growth orientation.

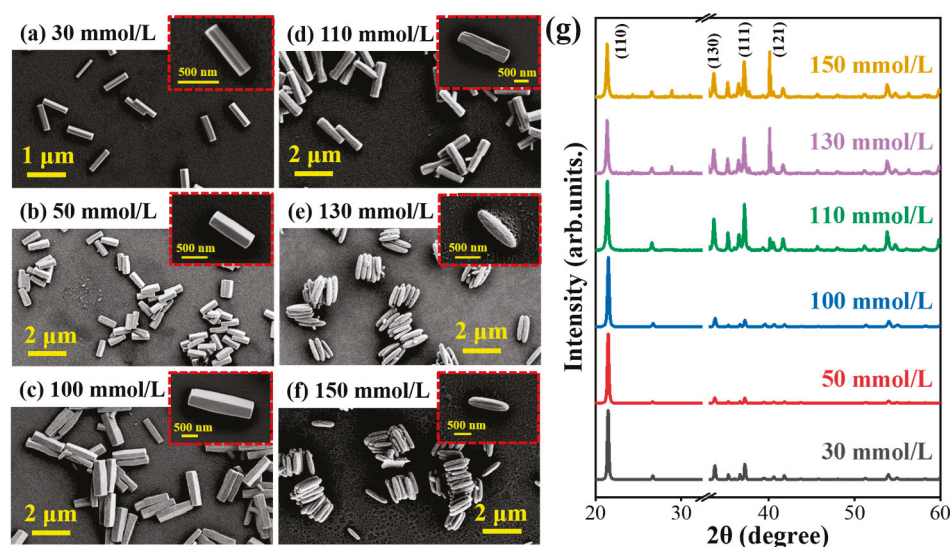


Figure 2. The influence of reaction source concentration on the produced GaOOH morphology: (a–f) SEM images and (g) XRD spectra of the samples fabricated with different Ga ion concentrations.

In addition, the X-ray diffraction (XRD) patterns of the various samples are presented in Figure 2g to analyze the crystal characteristics of the GaOOH nanorods. When the reaction source concentration is lower than the 100 mmol/L, all the samples exhibit the similar crystal diffraction characteristics with several typical diffraction peaks. The diffraction peaks are related to the orthorhombic phase of GaOOH as identified by the reference code (JCPDS no.06-0180). In detail, the main three peaks located at 21.48° , 33.74° , and 37.22° are corresponding to the crystal plane (110), (130), and (111) of GaOOH, respectively. They are in concordance with the results obtained from the SEM images, indicating that GaOOH can manifest a rod-like morphology at relatively low concentrations. From the spectra, it is observed that the diffraction peak intensity ratio of the (110) and (130) crystal plane rises with the increase of the reaction source concentration up to 100 mmol/L. Additionally, a preferential orientation along the crystal plane (110) is clearly observed, identified as the polar plane of the GaOOH nanorods. This preferential orientation defines the synthesized 1D GaOOH nanorods. However, the ratio reduces continuously when the Ga ion source concentration exceeds 100 mmol/L. Moreover, a new strong diffraction peak corresponding to the (121) crystal plane also emerges in the XRD spectra shown in Figure 2g, indicating that the preferential growth orientation along the polar plane (110) is clearly weakened. Furthermore, the concurrent reduction in diffraction peak intensity corresponding to the (110) crystallographic plane accompanied by enhanced intensities from the (130), (111), and (121) planes, the changes both in the structure and surface are simultaneously obvious. The change of the crystal characteristics leads to a gradual transformation of the 1D rhombic nanorods to the irregular spindle-like shape. Notably, when the Ga ion concentration increases from 130 mmol/L to 150 mmol/L, the spindle-shaped nanorods exhibit only minor differences in both morphology and crystal characteristics, as illustrated in Figure 2. Hence, the Ga ion source concentration in the reaction solution has a crucial influence on the 1D GaOOH nanorod crystal growth, such as the polar surface growth rate, which can modulate the morphology. When the Ga ion source concentration is below the optimal value, the nanorods' growth speed has a positive correlation with the source concentration. If the source concentration is higher than the optimal value, a different structure will be obtained, which results from the changed crystal growth speed of the different crystal plane. It is essential to select an appropriate Ga ion concentration for the synthesis of 1D GaOOH nanorods.

Further, the solution pH value should be compared to study its influence on GaOOH nanorod morphology characteristics. Aiming to tune the pH value to 3.1, 5.3, and 9.5, the sodium hydroxide (NaOH) solution is added to the original mixed solution (pH 2.0) of the hydrothermal reaction process, as described above. The different samples are obtained by varying the solution pH values while keeping the other reaction parameters the same, including a temperature of 100 °C, time of 100 min, and Ga ion source concentration of the 100 mmol/L. As shown in Figure 3a–d, it is obvious that the nanorod length decreases gradually with an increase in the reaction solution pH. Moreover, the nanorods show the shortest length and splitting surface when the pH is up to 9.5. In addition, the corresponding XRD results shown in Figure 3e reveal that the diffraction peak intensity ratio between (110) and (111) reduces gradually with increases in solution pH values. Hence, the preferential growth speed along (110) becomes weaker. In the acidic environment with the low relative activity of hydroxyl (OH^-) ions, the nanorods maintain preferential growth along the (110) crystal plane. On the contrary, under alkaline conditions, the growth rate along the polar plane (110) is inhibited. Notably, when the pH value increases beyond 11, there is barely any product in the reaction vessel. This suggests that excessive OH^- ions hinder the formation of GaOOH nanorods, as they decompose under strongly alkaline conditions ($\text{GaOOH} + \text{OH}^- + \text{H}_2\text{O} \rightarrow [\text{Ga}(\text{OH})_4]^-$). The different affinities of crystal facets to OH^- ions are attributed to their anisotropic density of unsaturated bonds, leading to varying specific surface free energy densities [25–27]. Facets with higher densities of unsaturated bonds tend to absorb more ligands, promoting relatively faster growth speed. As a result, the mobility of ligands on distinct crystal facets primarily drives the morphological evolution of the nanorods under different pH conditions. The results demonstrate that the reaction pH condition can effectively modulate both the growth speed and the morphology of GaOOH nanorods.

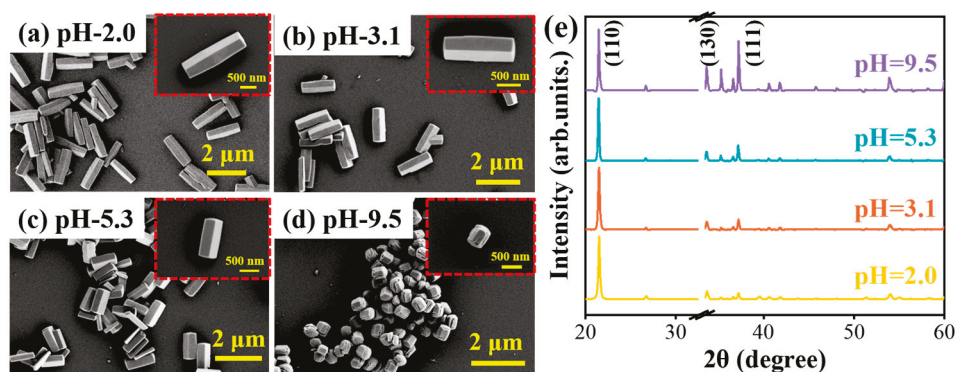


Figure 3. The influence of solution pH on the produced GaOOH morphology: (a–d) SEM images and (e) XRD spectra of the samples fabricated in different solution pH values.

In addition, the reaction temperature is another crucial issue for the crystal growth process. To investigate the influence of reaction temperature on the precursor GaOOH nanorods, samples are synthesized at different temperatures while maintaining a constant reaction time of 100 min and Ga ion source concentration of the 100 mmol/L. From the SEM images in Figure 4a–c, the GaOOH nanorods keep the same structure, but exhibit an increased length with reaction temperatures increasing. Additionally, the XRD spectra in Figure 4d illustrate that all the samples present the same crystal structure and X-ray diffraction peaks. However, an increased reaction temperature leads to a higher peak intensity ratio between (110) and (130), indicating a faster growth rate along the polar plane (110). This result is consistent with the morphology changing that the nanorod length becomes longer, as demonstrated by the SEM images in the inset of Figure 4a–c.

Consequently, the higher reaction temperature facilitates the synthesis of longer 1D GaOOH nanorods by improving the crystal growth rate of the polar plane (110).

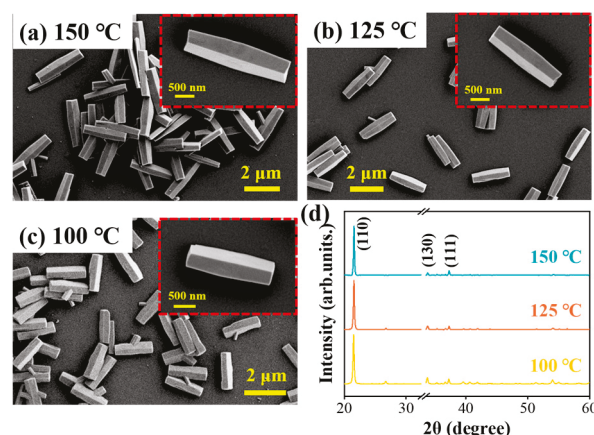


Figure 4. The influence of reaction temperature on the produced GaOOH morphology: (a–c) SEM images and (d) XRD spectra of the samples fabricated in different growth temperatures.

Finally, the reaction time is the last parameter in the hydrothermal synthesis process of precursor GaOOH nanorods. To study the influence of growth time on the morphological characteristics of GaOOH nanorods, a series of samples are synthesized at varying reaction times while keeping other experiment parameters constant: reaction temperatures (100 °C), reaction source concentration (100 mmol/L), and solution pH value (2.0). The morphological and structural evolutions of the GaOOH nanorods at different stages are compared and analyzed. As shown in Figure 5a–d, the SEM images indicate that the obvious nanorod-like structures are embedded within the thin film in the early stage (50 min). According to the Energy Dispersive X-Ray Spectroscopy (EDX) measurements, the elements distribution mapping presented in Figure 5a confirms that both the thin film and nanorods are composed of Ga and O elements. Hence, the GaOOH nanorods start to form in this stage. As growth time increases, the nanorods become longer with more complete structure, while the thin film gradually disappears. After reaction times longer than 50 min, all the GaOOH nanorods grown by different times show a rhombic cross section, with diameters in the range of hundreds of nanometers and lengths extending to several micrometers. Consequently, the composite intermediate substance forms during the initial stage, from which the nanorods emerge and develop during the reaction process. As shown by the snapshots in Figure 5, the reaction solution emphasized with red circles transitions from clear to turbid in the transparent reaction flask, followed by the stratification and subsequent downward aggregation of white precipitates. The quantity of the samples increases with the reaction time increase. However, beyond 100 min, it starts to decline slightly by 150 min, but the structure of the products remains unchanged, as exemplified in the SEM image displayed in Figure 5c. This decrease in yield at extended reaction times is attributed to the common counter-dissolution process inherent to hydrothermal synthesis [28,29]. Further, the XRD spectra are measured and presented in Figure 5e. Based on the similar structure and dimensions, the samples display consistent XRD peak locations and intensities, which illustrate the similar crystal characteristics corresponding to 1D GaOOH nanorods. Additionally, these similar characteristics of samples from different reaction times indicate that GaOOH transforms into nanorods after the reaction time exceeds 50 min, and their properties remain if the reaction time is extended. Hence, the reaction time has barely any influence on the morphological characteristics of GaOOH nanorods, while it has obvious influence on the quantity of the products.

Above all, the hydrothermal method is proven to be an efficient and brief technology for the simple and controllable synthesis of 1D Ga_2O_3 nanostructure arrays. Through modulating the key parameters in the reaction process such as reaction time, temperature, source concentration, and solution pH, the morphology of nanostructures can be precisely tuned. These findings provide a solid foundation for further exploration in low dimensional optoelectronic devices. However, a systematic study of the subsequent thermal annealing process is necessary to obtain the different phased Ga_2O_3 nanorods derived from the precursor GaOOH nanorods.

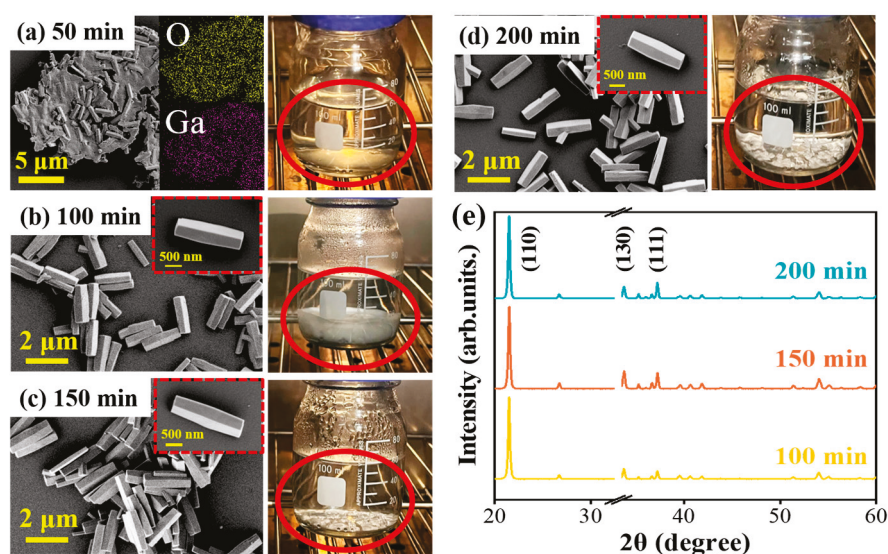


Figure 5. The influence of reaction time on the produced GaOOH morphology: (a–d) SEM images, elements distribution mappings, and snapshots of the samples in different times (50–200 min), and (e) XRD spectra of various samples. The red circles on the snapshots displays the precursor products in the reaction vessel.

3.2. Thermal Annealing GaOOH for $\beta\text{-Ga}_2\text{O}_3$

To investigate the effect of annealing temperature on the changes in nanorod crystal characteristics, XRD measurements were conducted in situ based on the sample (reaction temperature of 100 °C, Ga ion concentration of 100 mmol/L, and reaction time of 100 min). During the experiment, the samples were measured after annealing for 5 min at each temperature, and the results are presented in Figure 6. This approach enabled real-time observation of the transformation of crystal characteristics in GaOOH as the temperature increased. As shown in Figure 6a, the XRD patterns of the samples, annealed at temperatures ranging from 25 °C to 400 °C, present the diffraction peaks corresponding to the orthorhombic structure of GaOOH crystals, confirming that the nanorods remain in the original GaOOH phase within this temperature range. The nanorods maintain the same crystal characteristics, especially for the main diffraction peak (110), which corresponds to the polar plane of GaOOH . Moreover, the GaOOH nanorods always maintain the monocrystal characteristics in this temperature range. However, when the annealing temperature increases to 450 °C, the diffraction peak intensity ratio between the main peak of the crystal plane (110) at 21.49° and the other peaks obviously decreases. Furthermore, there are several new diffraction peaks appearing in the XRD spectrum, as displayed in Figure 6b, which is supposed to indicate a possible phase transformation of the nanorods.

As the annealing temperature reaches 550 °C, the disappeared diffraction peaks of GaOOH illustrate that the crystal phase transformation from GaOOH has been completed, and a new crystal phase has formed. Within the temperature range of 550–750 °C, the nanorods keep the same crystal phase, corresponding to the $\alpha\text{-Ga}_2\text{O}_3$ (JCPDS no.06-0503).

The main peaks appearing in the XRD are indexed as (104) at 33.72° and (110) at 35.98° , which show the higher-order diffraction peaks of the hexagonal structure of $\alpha\text{-Ga}_2\text{O}_3$. Similarly, the crystal structure begins to transform to the monoclinic structure at 770°C , as can be seen in Figure 6c. With the continuous increase in annealing temperature, the samples show the typical $\beta\text{-Ga}_2\text{O}_3$ crystal characteristics (JCPDS no.41-1103). The absence of any foreign phases confirms that the $\alpha\text{-Ga}_2\text{O}_3$ was fully transformed into the monoclinic $\beta\text{-Ga}_2\text{O}_3$ phase following calcination at 850°C . In addition, the relative intensities of (401), (002), (111), and (311) peaks, which are located at 30.49° , 31.82° , 35.28° , and 38.40° , increase in higher annealing temperature, indicating that the crystal orientation of these $\beta\text{-Ga}_2\text{O}_3$ crystals have better crystallinity as the annealing temperature increases. The XRD spectra in Figure 6d clearly illustrate that effective crystal phase transformation of the Ga_2O_3 nanorods can be achieved thorough annealing at specific temperatures. The transformation from GaOOH to $\alpha\text{-Ga}_2\text{O}_3$ is completed at 550°C , and this phase persists from 550°C to 750°C . By 850°C , the transformation to $\beta\text{-Ga}_2\text{O}_3$ is complete with no foreign phases. Consequently, by selecting an appropriate thermal annealing temperature, a different phase of Ga_2O_3 nanorods can be obtained. Therefore, for achieving $\beta\text{-Ga}_2\text{O}_3$ nanorods, the temperature of 850°C is chosen as thermal annealing temperature in subsequent experiments. Additionally, the size of the crystal plane in Figure 6d can be calculated with the Debye–Scherrer formula: $D = \frac{K\lambda}{\beta \cos \theta}$ [30–32], where λ is the X-ray wavelength of $1.54184 \text{ \AA}$, θ is the diffraction angle, β is the FWHM of the diffraction peak, and K is a constant of 0.89. Firstly, the very sharp diffraction peak (110) at 25°C illustrates the single crystal property for the GaOOH nanorods, where the Debye–Scherrer formula is not suitable for calculating the crystal size. After annealing treatment, the nanorods were transformed to polycrystal. Per the calculations, the crystal size of the $\alpha\text{-Ga}_2\text{O}_3$ nanorods is 15.75 nm according to the diffraction peak (104), and the crystal size of $\beta\text{-Ga}_2\text{O}_3$ is 13.43 nm based on the peak (401). Moreover, the lattice parameters of GaOOH , $\alpha\text{-Ga}_2\text{O}_3$, and $\beta\text{-Ga}_2\text{O}_3$ are calculated using XRD spectra information, which is indicated in Table 1. All lattice parameters in the table are consistent with the reference codes (GaOOH [JCPDS no.06-0180], $\alpha\text{-Ga}_2\text{O}_3$ [JCPDS no.06-0503], and $\beta\text{-Ga}_2\text{O}_3$ [JCPDS no.41-1103]). Hence, the annealing treatment under different temperatures causes a similar polycrystal structure even with different phased Ga_2O_3 .

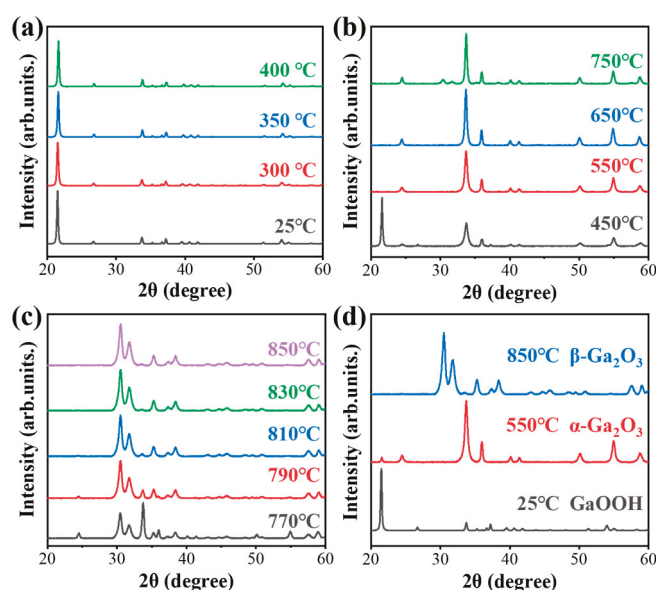


Figure 6. Thermal annealing in situ process: (a–c) XRD spectra of the same samples at different temperatures and (d) a comparison of different phases.

Furthermore, the influence of the rising temperature rate on the nanorods is investigated with the thermal annealing temperature at 850 °C. As shown in Figure 7a–f, the SEM images reveal that the nanorods maintain nearly the same porous morphological characteristics after thermal annealing treatment. Moreover, the porous surface shows similar sizes and distributions even under the different rising temperature rates. The formation of this porous structure occurs via a dehydration reaction during the calcination process: $2\text{GaOOH} \xrightarrow{\text{calcination}} \text{Ga}_2\text{O}_3 + \text{H}_2\text{O}$. However, it is important that 1D porous nanorods can enhance the light confinement ability, which is beneficial for further improving the photoelectronic response. In addition, the measured XRD peaks of the resulting $\beta\text{-Ga}_2\text{O}_3$ align well with the same monoclinic crystal structure (JCPDS no.41-1103), as displayed in Figure 7g. The dominant crystal plane diffraction peaks of (401), (002), and (111) are observed at 30.49°, 31.75°, and 35.28°, respectively. The locations and relative intensity ratio of these main peaks are almost identical, illustrating that the rising temperature rate has minimal impact on the morphological and crystal characteristics.

Table 1. The lattice parameters of Ga_2O_3 nanorods in different phases.

	Structure	a (Å)	b (Å)	c (Å)	$\beta(^{\circ})$
GaOOH	orthorhombic	4.58	9.75	2.98	-
$\alpha\text{-Ga}_2\text{O}_3$	hexagonal	4.99	-	13.49	-
$\beta\text{-Ga}_2\text{O}_3$	monoclinic	12.23	3.04	5.80	103.7

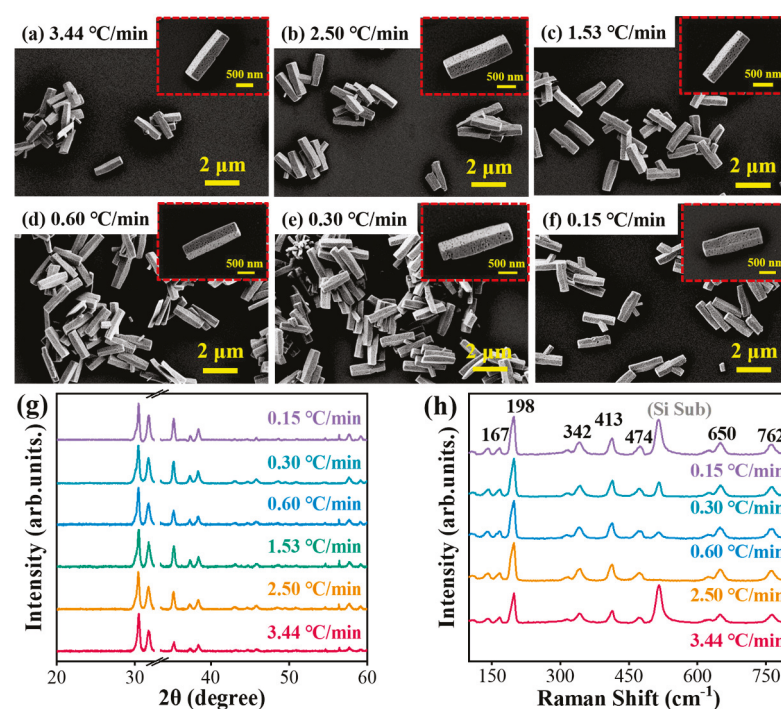


Figure 7. Thermal annealing speed influence on $\beta\text{-Ga}_2\text{O}_3$ nanorod: (a–f) SEM images and (g) XRD and (h) Raman spectra of the samples annealed at 850 °C with different rising temperature speeds.

Further characterization is conducted using Raman and X-ray photoelectron spectroscopy (XPS) measurements. The Raman spectra in Figure 7h show peaks respectively at 141 cm^{-1} , 167 cm^{-1} , and 198 cm^{-1} , which correspond to low-frequency vibration modes and transitions within tetrahedron–octahedron chains [33]. The peaks located in the range of 300–500 cm^{-1} are related to the octahedral face of $\beta\text{-Ga}_2\text{O}_3$ (Ga_2O_6), while those between 600 cm^{-1} and 800 cm^{-1} correspond to the stretching vibrations of the tetrahedral face of $\beta\text{-Ga}_2\text{O}_3$ (GaO_4) [34]. These characteristic peaks indicate that the nanorods exhibit a

monoclinic crystal structure with C_{2h} group symmetry and high crystalline quality [35,36]. In addition, the XPS results provide valuable insight into the chemical composition and electronic binding states of the β -Ga₂O₃ nanorods. The high-resolution XPS spectra for Ga 3d and O 1s are depicted in Figure 8a,b. The O 1s peak in Figure 8a is deconvoluted into two peaks, including the first peak at 531.00 eV from the lattice oxygen in Ga₂O₃, and the peak at 532.35 eV from oxygen-deficient regions or chemical-adsorbed oxygen [37]. The high-resolution XPS spectrum of Ga 3d presented in Figure 8b is deconvoluted into three overlapping peaks at 19.14 eV, 20.57 eV, and 23.60 eV, which are attributed to the Ga-O bond [38]. These peaks are corresponding to the O²⁻ ions of the Ga-O bond and the O²⁻ in the oxygen-deficient regions, respectively. The detection of Ga and O elements on the surface, along with their corresponding binding energies, confirms that the powder calcined at 850 °C successfully crystallized into Ga₂O₃ with Ga and O atoms present with a stoichiometric ratio of 2:3. Moreover, Figure 8c,d presents the normalized optical absorption spectra of the β -Ga₂O₃ nanorods annealed at different rising temperature rates, which display a minimal difference. Furthermore, the bandgap of the β -Ga₂O₃ nanorods is about 4.7 eV. The ultra-wide bandgap of the β -Ga₂O₃ nanorods illustrates the main photoresponse in the solar-blind ultraviolet range.

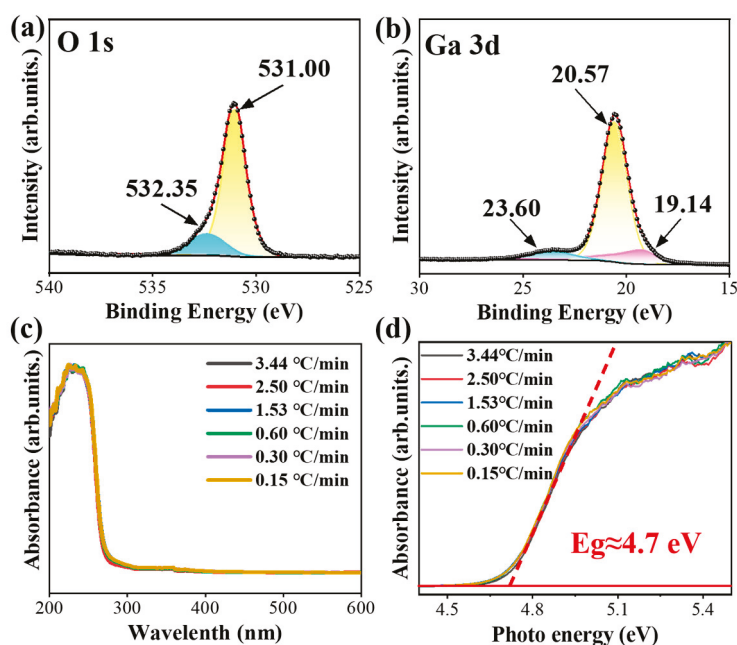


Figure 8. Thermal annealing speed influence on β -Ga₂O₃ nanorods: (a,b) high-resolution XPS spectra of O 1s and Ga 3d, and (c,d) normalized absorption spectra of the samples annealed at 850 °C with different rising temperature speeds.

3.3. Solar-Blind UV Photodetection

Based on the large length-to-diameter ratio and porous structure, the 1D β -Ga₂O₃ nanorods exhibit strong light absorption efficiency and optical confinement capabilities, which can improve the light absorption efficiency effectively to achieve high PD performance. To study the solar-blind ultraviolet photodetector performance based on the 1D β -Ga₂O₃ nanorods, the 1D porous nano-structural β -Ga₂O₃ (fabricated by 150 °C, 100 min, and 100 mmol/L Ga source concentration, and annealed for 2 h at 850 °C) is used to construct the MSM type device. The device presented in the inset of Figure 9a is created by spin-coating the nanorod samples onto the electrode substrate, followed by drying. Firstly, the I-V characteristics curves in Figure 9a illustrate that the photocurrent (I_{light}) increases with increasing light power density. Under a 20 V bias, the dark current (I_{dark}) is as low as 4.76×10^{-12} A, while I_{light} reaches 2.58×10^{-6} A under the 254 nm light with an intensity

of 7.2 mW/cm^2 , resulting in a high photo-to-dark current ratio (PDCR) of 10^6 . Furthermore, the periodic current-time (I-T) curves of the photodetector under different light power densities, depicted in Figure 9b, demonstrate that the current increases rapidly when the light is turned on and stabilizes, with the photocurrent gradually rising as the light intensity increases. Figure 9c presents the rise and decay time conducted on the photodetector at 20 V bias. The rise and fall times are defined as the times required for the photocurrent to increase from 10% to 90% or from 90% to 10% of the maximum value, and the measured typical rise and fall times of the device are 0.65s and 0.77s, respectively.

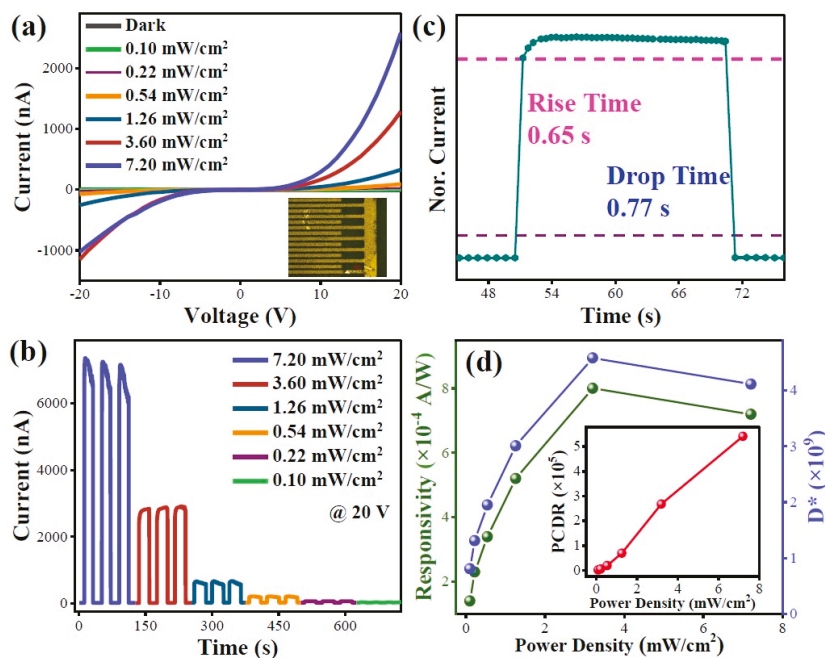


Figure 9. Photodetector parameters of 1D β - Ga_2O_3 nanorods: (a) I-V characteristics in the dark and under different power light irradiation, (b) I-T plots under different light power, (c) single periodic I-T plots irradiated under 3.6 mW/cm^2 , and (d) the relationship of PDCR, responsivity, and detectivity with light power density.

According to the equation, $R = \frac{I_{\text{photo}} - I_{\text{dark}}}{P \cdot A}$ and $D^* = R / \sqrt{2qI_{\text{dark}}A}$, the responsivity (R) and detectivity (D^*) of the device can be calculated, where P is the optical power density, A is light spot area, and q is the elementary charge. The calculated results are summarized in Figure 9d. As the light intensity increases, R and D^* of the device initially rise when the light power density is below 3.6 mW/cm^2 . At this intensity, R and D^* reach their peak values of $8.0 \times 10^{-4} \text{ A/W}$ and $4.58 \times 10^9 \text{ Jones}$, respectively. However, further increasing the light power intensity to 7.2 mW/cm^2 results in a decline in R and D^* . This reduction is attributed to the depletion of distinct available states at high light power densities, as noted in previous studies [39,40]. These results highlight the high responsiveness and efficiency of the 1D porous β - Ga_2O_3 nanorods in detecting transient light signals. This exceptional performance underscores their potential as promising candidates for solar-blind ultraviolet photodetectors, which are crucial for a range of advanced optoelectronic applications.

4. Conclusions

In summary, the 1D porous Ga_2O_3 nanorods were synthesized using a straightforward and controllable hydrothermal method. By tuning reaction parameters in the growth process, such as the source concentration, pH value, temperature, and reaction time, the structure and morphology of the nanorods were flexibly modulated. The reaction temperature and source concentration in the low range had a positive correlation with the

growth speed along the polar crystal planes of GaOOH nanorods. On the contrary, the excess Ga ion source and high pH conditions inhibited the growth process along the polar plane, changing the structure and morphology of GaOOH nanorods. Further, the thermal annealing treatment was optimized to obtain the expected 1D β -Ga₂O₃ nanorods. Based on the large length–diameter ratio, great light field confinement ability, and high field absorption efficiency, the MSM type photodetectors constructed with 1D β -Ga₂O₃ nanoarrays presented good deep ultraviolet photodetection performance. The responsivity of the photodetector reached 8.0×10^{-4} A/W, and the detectivity was as high as 4.58×10^9 Jones. Although it was necessary to improve the photodetector performance for further optoelectronic devices and other applications, the results demonstrated excellent optical field absorption and confinement, and potential applications in micro/nano solar-blind photodetectors, which was significant for minimized and integrable optoelectronic devices in the deep ultraviolet range.

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Conflicts of Interest: The authors declare no conflicts of interest.

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Article

Photocatalytic Degradation of Ciprofloxacin by GO/ZnO/Ag Composite Materials

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Abstract: This study synthesized graphene oxide (GO)/zinc oxide (ZnO)/silver (Ag) composite materials and investigated their photocatalytic degradation performance for ciprofloxacin (CIP) under visible light irradiation. GO/ZnO/Ag composites with different ratios were prepared via an impregnation and chemical reduction method and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). The results demonstrated that under optimal conditions (20 mg/L CIP concentration, 15 mg catalyst dosage, GO/ZnO-3%/Ag-doping ratio, and pH 5), the GO/ZnO/Ag composite exhibited the highest photocatalytic activity, achieving a maximum degradation rate of 82.13%. This catalyst effectively degraded ciprofloxacin under light irradiation, showing promising potential for water purification applications.

Keywords: silver; zinc oxide; graphene oxide; photocatalytic degradation; ciprofloxacin; ultraviolet rays

1. Introduction

Water resources are the basic resources for maintaining the sound operation of ecological systems and influencing the sustainable development of society and economy. China's per capita water resources amount to only 2200 cubic meters, accounting for only one-fourth of the world's average level, making it a country with scarce water resources. With the development of the industrialization process, the problem of water resource pollution has become increasingly serious, and the contradiction between the supply and demand of water resources in China has become more acute. Therefore, solving the problem of water pollution and improving the water ecological environment are of particular importance for enhancing the utilization rate of water resources [1]. In recent years, due to the widespread use of antibiotics, mixtures of antibiotics and their metabolites have been continuously released into the water environment through different pathways, and antibiotics in the equivalent range of ng/L–μg/L have been detected in sewage, surface water, and groundwater on a global scale. Research data indicate that the presence of antibiotics in the water environment can disrupt the ecological balance, promote the spread of antibiotic resistance genes, pose risks to water quality, and cause harm to human health through the bioaccumulation effect [2]. The types of antibiotics detected in water bodies mainly include sulfonamides, tetracyclines, fluoroquinolones, macrolides, etc. Fluoroquinolone antibiotics are one of the broad-spectrum antibacterial drugs with the widest application range and the best application effect, targeting the deoxyribonucleic acid of bacteria and having

inhibitory and inactivating effects on various bacteria. Among them, ciprofloxacin, as a second-generation fluoroquinolone antibiotic, is widely used in the treatment of various bacterial infections due to its excellent tissue permeability, good bioavailability, and fewer side effects, resulting in the detection of ciprofloxacin in various aquatic environments [3,4]. Since traditional physicochemical and biological treatment methods cannot completely remove ciprofloxacin at low concentrations, seeking a green, efficient, and simple method to remove trace amounts of ciprofloxacin from water has become a research hotspot both at home and abroad [5].

In the photocatalytic process, the photocatalyst generates electron-hole pairs under illumination conditions. The electrons and holes react with oxygen and water adsorbed on the catalyst surface, respectively, to generate reactive oxygen species with strong oxidizing ability, such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$). These reactive oxygen species can oxidize and decompose organic pollutants into harmless substances such as carbon dioxide, water, and inorganic ions [6]. However, wide-bandgap semiconductors only absorb ultraviolet light and have low utilization rates of visible light. The high efficiency of the photogenerated electron-hole ($e-h^+$) pair complex hinders the rapid development and practical application of wide-bandgap semiconductors. Therefore, the development of efficient photocatalytic degradation materials is very important [7].

Among many photocatalysts, zinc oxide (ZnO) has the advantages of good photocatalytic activity, stability, non-toxicity, and low cost, which is beneficial for industrial applications [8]. ZnO has been fabricated into nanoparticles, nanosheets, nanowires, nanorods, and nanobelts. Among them, one-dimensional (1-D) nanostructures have uniform shapes and efficient separation and transport of photogenerated electrons. Moreover, it is a wide-bandgap semiconductor material with a bandgap of 3.37 eV. It can generate electron-hole pairs under ultraviolet light irradiation and thus exhibit photocatalytic activity. However, pure ZnO also has some shortcomings, such as easy recombination of photogenerated electron-hole pairs and low utilization rate of visible light, which limit its practical application [9]. To improve the photocatalytic performance of ZnO, various methods have been adopted to modify it, such as doping metal ions, combining with other semiconductors, and loading noble metals [10]. One of them is the application of carbon-based materials because they can enhance the charge transfer at the interface between metal oxides and carbon materials. Carbon nanotubes, graphite, graphene, and graphene oxide (GO), when combined with ZnO, have been shown to enhance the photocatalytic efficiency of ZnO. Ahmad et al. reported the synthesis of GO/ZnO/Ag nanocomposites via the solvothermal method [11]. However, the synthesis of graphene is often challenging due to its high impurity content. Despite this, graphene oxide (GO) presents several advantageous properties that make it a highly attractive material. These include its superior mechanical strength, excellent electrical conductivity (which arises from its sp^2 hybridized carbon orbitals), unique chemical characteristics such as the potential for zero bandgap behavior, an exceptionally high specific surface area, excellent transparency to charge carriers (owing to its single-atom-thick structure), and outstanding thermal conductivity. These remarkable properties render GO a highly promising candidate for various applications, including its integration with ZnO to improve photocatalytic performance [12]. Due to its large specific surface area and two-dimensional planar conjugated structure, graphene oxide (GO) serves as an ideal scaffold for the effective anchoring of various substances. For instance, the incorporation of GO with photocatalysts such as TiO_2 or WO_3 has been extensively studied [13]. GO-based photocatalysts can prevent the agglomeration of nanoparticles immobilized on the graphene sheets, thereby increasing the available reaction sites for photocatalytic degradation. This structural feature not only enhances the adsorption capacity but also facilitates the degradation of organic pollutants. As an example, Nasrollahzadeh et al. synthesized

graphene oxide/ZnO nanocomposites and employed them as heterogeneous catalysts for the synthesis of a variety of tetrazoles [14–17]. Additionally, GO-based photocatalysts for organic contaminant removal in aqueous systems offer advantages in terms of ease of separation, which facilitates catalyst recovery and reuse, thus supporting their potential for large-scale industrial applications [18–22].

The excellent electrical conductivity of graphene oxide (GO) facilitates the transfer of photogenerated electrons and effectively suppresses the recombination of electron–hole pairs, thereby enhancing photocatalytic efficiency [23]. Additionally, the functional groups on GO can form chemical bonds with ZnO, which improves the stability of the composite material. Although the concurrent growth of ZnO and reduction in GO may lead to an uneven distribution of ZnO on the GO surface, this remains a viable approach, especially when other materials are introduced to mitigate such issues [24]. Various dopants, such as metals and metal oxides, have been employed to enhance photocatalytic activity by narrowing the bandgap of ZnO [25]. Noble metals, such as silver (Ag), exhibit surface plasmon resonance (SPR) effects. When Ag nanoparticles are integrated into the ZnO surface, the SPR effect under visible light irradiation amplifies the light absorption capabilities of ZnO, thereby improving the generation efficiency of photogenerated carriers [26,27]. Furthermore, Ag can function as an electron trap, promoting the transfer of photogenerated electrons while inhibiting the recombination of electron–hole pairs, which further augments the photocatalytic performance of ZnO [28–30]. Consequently, the synthesis of GO/ZnO/Ag composite materials, which combines the unique advantages of Ag, ZnO, and GO, holds significant potential for enhancing the photocatalytic activity of the composite system.

This paper aims to develop a highly efficient and stable photocatalytic material—GO/ZnO/Ag composite material for treating organic pollutants such as ciprofloxacin. Through research on aspects such as the preparation, characterization, and photocatalytic performance of the composite material, the photocatalytic mechanism will be thoroughly explored, providing a theoretical basis and technical support for the application of photocatalytic technology in the field of environmental governance [31]. Furthermore, through the synergistic effects of the nanocomposite material, ciprofloxacin can be efficiently degraded and transformed into non-toxic byproducts, thereby minimizing potential harm to aquatic ecosystems. This process reduces the persistence and accumulation of pollutants in water bodies, contributing to the protection of water resources and overall ecological health. Such an approach aligns with the principles of sustainable development, facilitating the creation of a cleaner and healthier environment. The motivation behind this research holds significant implications for advancing environmental protection efforts and effectively harnessing light energy to address the growing issue of antibiotic pollution in aquatic systems.

2. Materials and Methods

2.1. Chemicals and Reagents

Silver nitrate, sodium nitrate, zinc acetate, sodium hydroxide, graphite powder, potassium permanganate, concentrated sulfuric acid, hydrogen peroxide, cetyltrimethylammonium bromide (CTAB), ammonia water, N,N-dimethylformamide (DMF), sodium citrate, ethanol, methylene blue, and hydrochloric acid were all analytically pure and purchased from Aladdin Chemical Reagent. Deionized water was used in the experiment.

2.2. Synthesis of Graphene Oxide (GO)

A 100 mL three-necked flask was charged with 23 mL of concentrated sulfuric acid, which was sealed and placed in a refrigerator for 30 min. Meanwhile, 0.5 g of graphite powder and 0.25 g of sodium nitrate were added to the flask and stirred in an ice bath at a temperature of 4–7 °C for 30 min, resulting in the formation of a black suspension. Gradu-

ally, 3 g of potassium permanganate was introduced to the mixture, and the temperature was raised to 35 °C, maintaining stirring for 2 h. At this stage, the solution turned dark green. Subsequently, 50 mL of deionized water was added dropwise, and the temperature was increased to 95 °C, followed by stirring for an additional hour, resulting in a brown-yellow solution. Then, 100 mL of deionized water was added to the reaction mixture, and stirring was continued at room temperature for 1 h. Following this, 15 mL of 30% hydrogen peroxide was carefully introduced, causing the solution to boil vigorously and produce abundant bubbles. The color transitioned from an earthy brown to a bright golden hue, and the mixture was stirred at room temperature for 2 h. Afterward, the reaction mixture was allowed to stand and precipitate. The supernatant was decanted, and the precipitate was centrifuged and filtered. The solid was washed three times with 5% hydrochloric acid, followed by several washes with deionized water. Finally, the product was dried in a vacuum oven at 60 °C for 6 h to yield graphene oxide (GO).

2.3. Synthesis of GO/ZnO Composite Materials

A precise amount of 3.0 g of zinc acetate was weighed and added to a beaker. To this, 50 mL of deionized water, 2.0 mL of hydrogen peroxide (H₂O₂), and 0.4 g of cetyltrimethylammonium bromide (CTAB) were sequentially added, with thorough stirring. Next, 4.0 mL of ammonia solution (NH₃·H₂O) was added dropwise under vigorous stirring, and the reaction was allowed to proceed for 9 h. Following this, the reaction mixture was allowed to stand to facilitate precipitation, after which the supernatant was decanted. The precipitate was then subjected to centrifugation and filtration. The resulting product was dried in a vacuum oven at 80 °C for 4 h and subsequently calcined in a muffle furnace at 475 °C for 3 h to obtain zinc oxide (ZnO). For the synthesis of the composites, 0.0005 g, 0.0010 g, and 0.0030 g of ZnO were dispersed in 40 mL of deionized water under ultrasonic agitation, labeled as solutions 1, 2, and 3, respectively. An amount of 0.1 g of graphene oxide (GO) was added to these solutions and ultrasonically dispersed for 30 min. The resulting mixtures were transferred to a water bath at 25 °C and stirred magnetically for 4 h to ensure a complete reaction, yielding a suspension. The suspension was then subjected to centrifugation, followed by washing with ethanol. The final products, GO/ZnO-0.5%, GO/ZnO-1%, and GO/ZnO-3%, were obtained after further drying.

2.4. Synthesis of GO/ZnO/Ag Composite Materials

Under magnetic stirring, 15.7 mg of silver nitrate was dissolved in 100 mL of deionized water to prepare the solution. To this, 2 mL of a 1% sodium citrate solution was added as a reducing agent. The resulting mixture was then heated to boiling and maintained for 30 min. After the reaction, the solution was cooled to room temperature. The mixture was then transferred to a centrifuge tube. An amount of 50 mL of anhydrous ethanol was added to the tube, and the mixture was centrifuged at 5000 rpm for 10 min. The supernatant was discarded, and the remaining nanoparticles were resuspended in fresh ethanol. This washing step was repeated 3 times to ensure the removal of residual citrate and other soluble impurities. After the final wash, the nanoparticles were collected by centrifugation, and the ethanol was removed. The purified nanoparticles were then dried under vacuum at 60 °C for 12 h to remove any residual solvent.

For the synthesis of the GO/ZnO/Ag composite materials, the process involved using the GO/ZnO composite as a medium for silver nanoparticle deposition. Initially, the GO/ZnO-0.5%, GO/ZnO-1%, and GO/ZnO-3% composites were dispersed in 40 mL of deionized water under ultrasonic agitation, and labeled as Solution 1, Solution 2, and Solution 3, respectively. Once uniform dispersion was achieved, 0.1 mg of silver nanoparticles was added to each solution, which was then ultrasonically dispersed for 30 min.

The resulting mixture was transferred to a water bath at 25 °C and continuously stirred magnetically for 4 h to ensure the formation of a stable suspension.

Subsequently, the suspension was transferred to a polytetrafluoroethylene (PTFE) autoclave and heated at 180 °C for 4 h. After cooling to room temperature, the crude product was filtered, and the final product was washed several times with deionized water and absolute ethanol. The product was then dried under vacuum at 60 °C for 12 h to yield the GO/ZnO-0.5%/Ag, GO/ZnO-1%/Ag, and GO/ZnO-3%/Ag composites.

2.5. Sample Characterization

Structural and compositional characterization of the samples was carried out using a suite of advanced analytical techniques. X-ray diffraction (XRD) analysis was carried out using a Rigaku 3DMAX-IIIC diffractometer (Rigaku Corporation, Tokyo, Japan) and Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) to determine the crystal structure and phase composition. Diffraction patterns were acquired in the 2θ range of 10–70° with a scanning rate of 2°/min and a step size of 0.02°. Fourier-transform infrared spectroscopy (FT-IR) measurements were performed on a Nicolet NEXUS-670 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a deuterated sulfated glycine sulfate (DTGS) detector to determine the presence of functional groups and chemical bonds in the sample. Spectra were recorded over a range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and a cumulative total of 32 scans per measurement. Morphological characterization was performed using a field emission scanning electron microscope (FE-SEM, Shimadzu JSM-7800F, Shimadzu Corporation, Kyoto, Japan) with an accelerating voltage of 5–15 kV. Prior to imaging, the samples were sputter-coated with a thin layer of gold to enhance electrical conductivity. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, Norristown, PA, USA) and a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) to determine the elemental compositions, chemical states, and bonding configurations. The analysis was performed under ultra-high vacuum conditions (base pressure $< 5 \times 10^{-9}$ mbar). The binding energy scale was calibrated against the C 1s peak at 284.6 eV to compensate for any charging effects and to eliminate potential interference from incidental carbon contamination. High-resolution spectra with a pass energy of 20 eV and a step size of 0.1 eV were used for detailed chemical state analysis. The acquired data were processed using appropriate software packages, including MDI Jade 6.5 for XRD analysis, OMNIC for FTIR spectroscopy, ImageJ for SEM/TEM image analysis, and Avantage for XPS data processing. The combination of these complementary characterization techniques provides a comprehensive understanding of the structural, morphological, and chemical properties of the materials under study.

2.6. Catalytic Degradation

In order to study the degradation performance of the synthesized composite photocatalyst, CIP aqueous solution was used as the simulated pollutant, and a xenon lamp was used as the visible light source. Take 50 mL of CIP solution and a certain amount of catalyst, stir well, and let stand in the dark environment for 30 min under the stirred state. Then, turn on the light source and keep stirring. An amount of 5 mL supernatant was taken at intervals and the absorbance of the system at the maximum absorption wavelength of 278 nm was measured by ultraviolet spectrophotometer [17]. The wavelength range was 200–800 nm. The solution was placed in a 1 cm colorimetric dish with deionized water as the blank. The degradation rate of organic carbon in the system is shown in the following Equation (1).

$$D = (A_0 - A_t) / A_0 \times 100\% \quad (1)$$

where D is the degradation rate (%), A_0 is the initial absorbance value of CIP, and A_t is the absorbance value after t time of CIP degradation.

3. Results and Discussion

3.1. Surface Morphology Analysis (SEM)

The morphology of the GO/ZnO, GO/ZnO-0.5%/Ag, GO/ZnO-1%/Ag, and GO/ZnO-3%/Ag nanocomposites was analyzed using scanning electron microscopy (SEM), as illustrated in Figure 1. Panels Figure 1a,b reveal the growth of ZnO, showing the aggregation of graphene sheets along with the formation of spherical ZnO nanoparticles. SEM images further demonstrate that both ZnO and Ag are uniformly distributed and well integrated onto the GO surface, as depicted in panels Figure 1c–h. Notably, the GO/ZnO-3%/Ag composite exhibits the largest surface area and the most intimate interaction with the graphene sheets, which significantly enhances its photocatalytic activity.

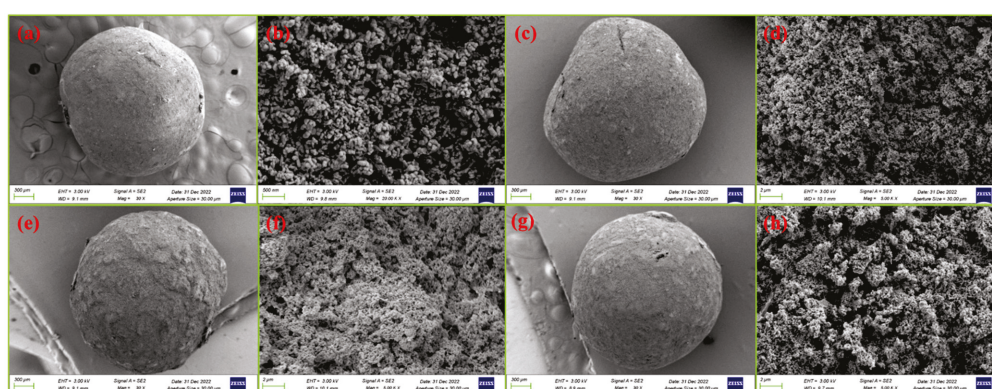


Figure 1. SEM image of (a,b) GO/ZnO, (c,d) GO/ZnO-0.5%/Ag, (e,f) GO/ZnO-1%/Ag, (g,h) GO/ZnO-3%/Ag nanocomposites.

3.2. X-Ray Photoelectron Spectroscopy (XPS) Analysis

Based on the X-ray photoelectron spectroscopy (XPS) data shown in Figure 2, combined with high-resolution spectroscopic analyses, the elemental compositions and chemical states of the prepared composites were thoroughly investigated.

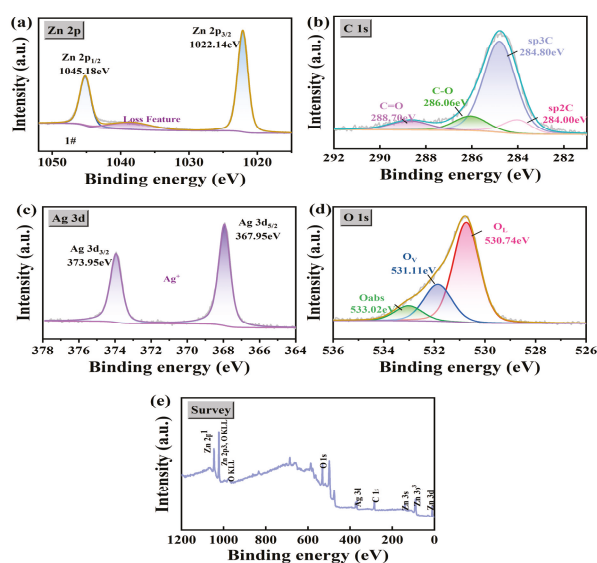


Figure 2. Survey (e) and high-resolution X-ray photoelectron spectra of GO/ZnO-3%/Ag: (a) Zn2p, (b) C 1s, (c) Ag 3d, and (d) O 1s.

In Figure 2b, the C 1s spectrum shows four distinct peaks representing different carbon bonding environments. Among them, the peak at 284.00 eV is attributed to sp^2 hybridized carbon (sp^2C), which is a component in graphene oxide (GO), while the higher binding energy peak at 284.80 eV corresponds to sp^3 hybridized carbon (sp^3C), suggesting that the complexes contain a variety of carbon species. The 286.06 eV and 288.70 eV peaks are associated with the C-O and C=O bonds, respectively, indicating the presence of oxidized functional groups on GO, which is typical for GO-based materials [32].

For the sp^2C component in Figure 2b, an asymmetric peak shape is presented on the side of the higher binding energy, and this asymmetry can be described by the Doniach–Sunjic function. This function can effectively capture the asymmetric properties of the peaks caused by spin–orbit coupling and core cavity effects. In the analysis process, the spectra were first processed with background subtraction. The Shirley background removal method was used to eliminate the interference of non-featured signals in the spectrogram to ensure the accurate extraction of the target peaks. After background subtraction, the spectra were fitted with a Gaussian–Lorentzian hybrid function, where the asymmetric part of the sp^2C was fitted by the Doniach–Sunjic function, and the remaining peaks were fitted by the standard Gaussian or Gaussian–Lorentzian hybrid function, in order to obtain the binding energy positions of the carbon for each chemical state and to gain an in-depth understanding of the distribution of the different carbon species in the composites [33].

The Zn 2p spectrum in Figure 2a shows two characteristic peaks located at 1022.14 eV (Zn 2p_{3/2}) and 1045.18 eV (Zn 2p_{1/2}). These peaks are consistent with the binding energy of Zn^{2+} , indicating that the zinc in the composite is mainly present in the oxidation state of Zn^{2+} . In addition, the loss features at higher binding energies are typical of XPS spectra and are usually attributed to the inelastic scattering of photoelectrons.

The Ag 3d spectrum in Figure 2c shows two distinct peaks located at 367.95 eV and 373.95 eV, corresponding to the Ag 3d_{5/2} and Ag 3d_{3/2} electronic lines, respectively. These peaks indicate that silver is mainly present in the composites as Ag^+ , confirming the +1 oxidation state of silver.

The O 1s spectrum in Figure 2d, on the other hand, can be decomposed into three main peaks: the peak at 530.74 eV is attributed to lattice oxygen (OL) in metal oxides, the peak at 531.11 eV is correlated with oxygen vacancies (OV), indicating the presence of oxygen defects in the material, and the peak at 533.02 eV is attributed to surface-adsorbed oxygen (Oabs), which is usually derived from surface-adsorbed hydroxyl or water molecules.

The full spectrum in Figure 2e shows the elemental composition of the composites, confirming the presence of Zn, Ag, O, and C and showing characteristic peaks corresponding to Zn 2p, O 1s, Ag 3d, and C 1s. No other impurities or undesired phases were detected, indicating the high purity of the synthesized composites.

3.3. X-Ray Diffraction (XRD) Analysis

In order to check the phase, crystal structure, and purity of the synthesized nanomaterials, X-ray diffraction (XRD) analysis was carried out. The XRD patterns of GO/ZnO and GO/ZnO/Ag nanocomposites are shown in Figure 3. The diffraction peaks of the GO/ZnO composites clearly correspond to the hexagonal sphalerite structure of ZnO. Specifically, the observed peaks at 2θ values of 31.2° , 34.1° , and 35.9° are attributed to the (100), (002), and (101) crystal planes, respectively, in accordance with the JCPDS card no. 36-1451. In particular, the significant intensity of the (101) peak indicates the anisotropic growth of the ZnO crystals and suggests the preferred direction of growth of the microcrystals.

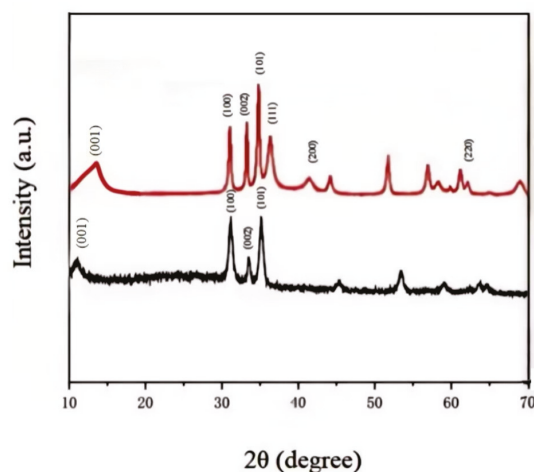


Figure 3. X-ray diffraction (XRD) analysis of GO/ZnO and GO/ZnO-3%/Ag nanocomposites.

For GO/ZnO/Ag nanocomposites, significant differences are observed when compared to the XRD patterns of GO/ZnO composites. In particular, three additional peaks appeared at 2θ values of 38.1° , 44.3° , and 64.4° , attributed to the (111), (200), and (220) crystal planes, respectively. These peaks are consistent with the crystallographic facets of silver, in accordance with JCPDS card number 04-0783, confirming the successful doping of silver into the composite structure.

3.4. FT-IR Analysis

The Fourier-transform infrared (FT-IR) spectra of the GO/ZnO and GO/ZnO/Ag nanocomposites are presented in Figure 4. The characteristic peaks corresponding to the stretching vibrations of oxygen–carbon bonds in graphene oxide are observed at 1108 cm^{-1} , 1222 cm^{-1} , and 1731 cm^{-1} . Additionally, a peak at 1568 cm^{-1} is attributed to C–C bond vibrations, as well as the bending vibrations of epoxy groups and hydroxyl deformation (O–H). A broad absorption band observed at 3454 cm^{-1} corresponds to the hydroxyl (–OH) stretching vibrations of water molecules adsorbed on the surface, while the carboxyl (–COOH) group also contributes to this broad feature [34].

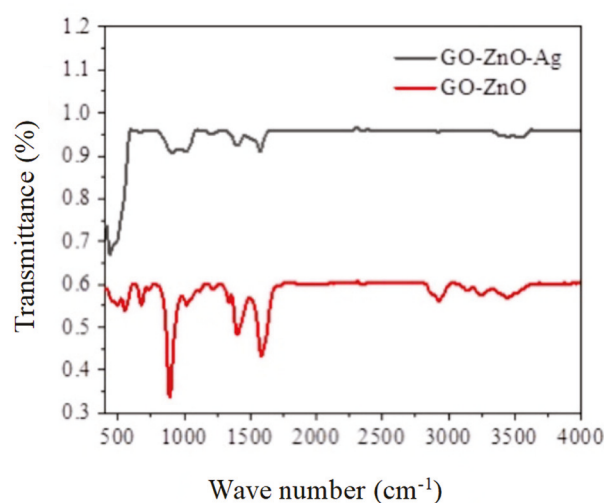


Figure 4. Fourier-transform infrared spectroscopy (FT-IR) spectra of GO/ZnO and GO/ZnO-3%/Ag nanocomposites.

Furthermore, the peak at 450 cm^{-1} is assigned to the Zn–O bond, confirming the formation of ZnO. In the GO/ZnO/Ag nanocomposite, a peak at 1629 cm^{-1} is observed,

corresponding to the C-C bond vibration region. Additionally, a peak at 1021 cm^{-1} may be linked to the symmetric and asymmetric stretching vibrations of GO, providing further evidence of the successful incorporation of graphene oxide into the composite material.

3.5. Photocatalytic Activity Measurement

The GO/ZnO/Ag nanocomposite was synthesized using a photocatalytic method and tested for its catalytic degradation of ciprofloxacin under direct sunlight, as depicted in Figure 5a. The photocatalytic activity of the GO/ZnO/Ag nanocomposite was evaluated by monitoring the intensity of the characteristic absorption peak of ciprofloxacin at 278 nm , which allowed for the assessment of degradation efficiency in aqueous solution under sunlight irradiation. The photocatalytic performance is influenced by the material's ability to absorb light and its electron-hole pair recombination rate. Efficient generation of hydroxyl radicals ($\cdot\text{OH}$) is crucial for effective degradation, which requires an appropriate bandgap energy to match the energy of incident photons. By enhancing charge carrier recombination rates and promoting effective electron transfer, the GO/ZnO/Ag nanocomposite demonstrates significantly improved photocatalytic activity.

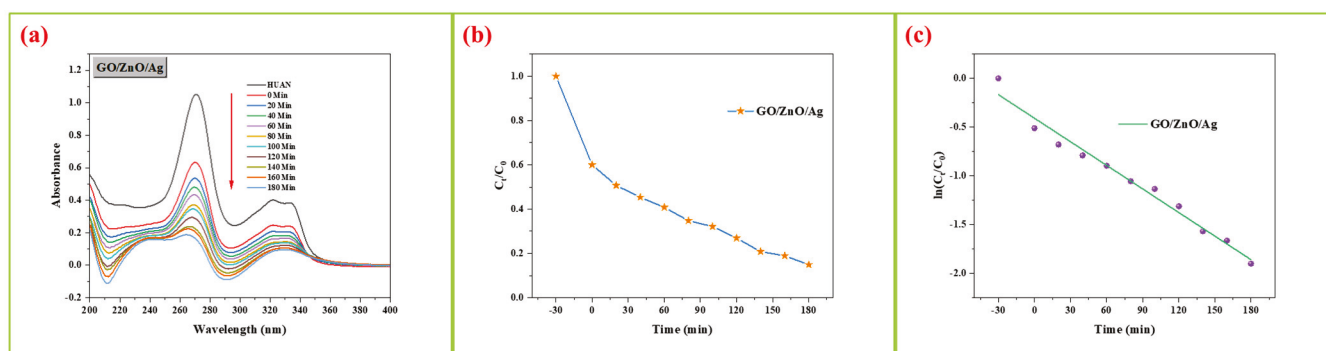


Figure 5. The UV–visible spectra of photocatalytic activity for (a) GO/ZnO/Ag nanocomposite; (b) UV–visible photocatalytic degradation of CIP; (c) UV–visible photocatalytic degradation of CIP kinetics rate constant with GO/ZnO/Ag nanocomposite.

During the degradation process, the absorption spectrum of ciprofloxacin evolves, and a strong interaction between ZnO/GO and Ag is observed, leading to the formation of C-O bonds. This bonding reduces the reactivity of the surface oxygen atoms in the composite, enhancing its photostability. The degradation study shows that as the irradiation time increases, the concentration of ciprofloxacin decreases, accompanied by a reduction in the absorption intensity in the UV–visible region. Under direct sunlight, the GO/ZnO/Ag nanocomposite achieved an 82.13% degradation rate of ciprofloxacin, as shown in Figure 5a, demonstrating its high photocatalytic efficiency.

The photocatalytic degradation process of ciprofloxacin using the GO/ZnO/Ag nanocomposite is illustrated in Figure 5b. Typically, semiconductor-based photocatalysis involves the excitation of electrons, leading to the formation of electron-hole pairs, which subsequently participate in chemical reactions. The photogenerated holes migrate to the surface of the particles, where they react with the surrounding medium and ciprofloxacin molecules, producing CO_2 and H_2O as by-products.

The kinetics of ciprofloxacin degradation were studied under optimal experimental conditions, including a ciprofloxacin concentration of 20 mg/L , a catalyst dosage of 15 mg , and an adsorption-desorption equilibrium time of 180 min . The degradation follows pseudo-first-order kinetics, as indicated by the linear relationship between $\ln(C/C_0)$ and time, where C represents the ciprofloxacin concentration, and C_0 is the initial concentration. The apparent first-order rate constant (k_{app}) was determined from the equation

$\ln(C_0/C) = k_{app}t$, yielding a value of $k_{app} = 0.00807 \text{ min}^{-1}$ for the GO/ZnO/Ag nanocomposite, as shown in Figure 5c. This result underscores the effective catalytic performance of the nanocomposite in the photocatalytic degradation of ciprofloxacin.

The photocatalytic degradation mechanism of GO/ZnO/Ag composites involves multiple synergistic effects, as shown in Figure 6. First, ZnO, under UV light irradiation, generates electron–hole pairs (e^-/h^+), and its wide bandgap allows efficient absorption of UV light, thereby driving photocatalytic reactions. The generated electrons can rapidly transfer to Ag nanoparticles, while the holes participate in the oxidation of water molecules, producing highly oxidative hydroxyl radicals ($\bullet\text{OH}$). Ag, acting as an “electron sink”, not only enhances the local electric field through surface plasmon resonance (SPR) effects but also effectively prevents the recombination of electrons and holes, thus improving the overall photocatalytic efficiency. Graphene oxide (GO) serves as an excellent electron conduction platform, facilitating the efficient transfer of electrons within the composite material. Moreover, its large surface area aids in the adsorption of pollutants. The synergistic interactions between these three components significantly enhance the generation and transfer efficiency of electrons and active species during the photocatalytic degradation process, thereby boosting the degradation of organic pollutants. Therefore, the superior photocatalytic performance of the GO/ZnO/Ag composite material is primarily attributed to the synergistic enhancement effects of ZnO, Ag, and GO.

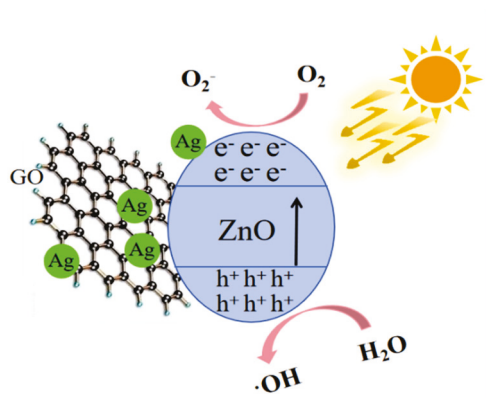


Figure 6. Photocatalytic mechanism diagram.

4. Conclusions

In conclusion, the GO/ZnO/Ag composite materials exhibit excellent photocatalytic activity for the degradation of ciprofloxacin (CIP), with a maximum degradation rate of 82.13% under optimal conditions (20 mg/L CIP concentration, 15 mg catalyst dosage, GO/ZnO-3%/Ag-doping ratio, and pH 5). However, further studies are needed to improve the long-term stability and recyclability of the composite materials. Future research could focus on enhancing the stability of these composites under prolonged exposure to light, evaluating their photocatalytic activity for other environmental pollutants, and exploring scalable synthesis methods. Additionally, a deeper understanding of the photocatalytic degradation mechanism is essential to optimize the performance of the materials.

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