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Advanced Inorganic Semiconductor Materials, 3rd Edition

Edited by
Sake Wang, Nguyen Tuan Hung and Minglei Sun

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Guest Editors

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Nguyen Tuan Hung

Minglei Sun



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About the Editors

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Sake Wang earned his Ph.D. in physics at Southeast University, China, in 2016. During this period, he was awarded the national scholarship for doctoral students. Since 2021, he has been an Associate Professor at the Jinling Institute of Technology, China. He was a Visiting Scientist at Tohoku University, Japan, from 2019 to 2021. His current interests focus on theoretical studies of spin and valley transport, as well as valley-optoelectronic devices in two-dimensional materials. He is PIs of the National Science Foundation for Young Scientists of China and the Natural Science Foundation of Jiangsu Province. He has published 1 book (first author, IOP Publishing) and 71 papers with more than 4,500 citations; he was the first author or the corresponding author in 33 of these papers. Four of his first-authored and corresponding-authored papers are in the top 1% of ESI highly cited papers. He was ranked in the World's Top 2% most-cited scientists from 2021 to 2025 by Stanford University. He also served as an Associate Editor of the *Journal of Superconductivity and Novel Magnetism* (Springer Publishing) since 2020 and as an Editorial Board Member in *Discover Physics* (Springer Publishing) since 2025, as well as having been an outstanding reviewer of five SCI journals.

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Preface

Building upon our previous edition, *Advanced Inorganic Semiconductor Materials*, 2nd Edition, the present Reprint of *Advanced Inorganic Semiconductor Materials*, 3rd Edition continues our effort to provide a coherent and forward-looking perspective on the rapidly evolving landscape of inorganic and hybrid semiconductor research. This volume brings together a carefully selected collection of original research articles and authoritative reviews that reflect both the depth and breadth of current advances in materials synthesis, defect engineering, heterostructure design, device integration, and functional applications.

The primary aim of this Reprint is to document and disseminate recent progress in inorganic semiconductor materials that underpin modern and emerging technologies, including power electronics, optoelectronics, catalysis, sensing, flexible systems, and chiral photonics. By highlighting diverse material platforms—from wide-bandgap oxides and mixed-metal nanostructures to hybrid organic–inorganic halides—this edition seeks to illustrate how fundamental materials design principles translate into practical device functionalities. Beyond reporting individual breakthroughs, the collected contributions emphasize unifying concepts such as interface engineering, defect control, multi-physics integration, and energy transduction, thereby offering readers a structured view of the field’s current challenges and opportunities.

This Reprint is intended for a broad scientific audience, including materials scientists, physicists, chemists, and device engineers, as well as graduate students and early-career researchers entering the field of semiconductor materials. We hope that the balance between fundamental insights and application-oriented studies will make this volume a useful reference for both academic research and technological development.

The success of this Special Issue would not have been possible without the dedication and creativity of the contributing authors. We feel particularly grateful to all the authors from Brazil, Bulgaria, China, Germany, Portugal, Serbia, and Spain for choosing this Special Issue as a platform to share their excellent science. Their collective efforts highlight the truly international character of contemporary semiconductor research and demonstrate how global collaboration continues to drive innovation across disciplinary and geographical boundaries.

We also sincerely acknowledge the editorial team and reviewers for their careful evaluations, constructive feedback, and continuous support throughout the preparation of this volume. Their commitment to scientific rigor and clarity has significantly enhanced the quality and impact of the published contributions.

Finally, we hope you find the articles in this Reprint as enlightening and inspiring as we did during their assembly, and that this collection stimulates new ideas, collaborations, and discoveries. We warmly invite readers and contributors alike to participate in future developments and to contribute to the next edition of the Special Issue, *Advanced Inorganic Semiconductor Materials*, 4th Edition.

Sake Wang, Nguyen Tuan Hung, and Minglei Sun

Guest Editors



Advanced Inorganic Semiconductor Materials, 3rd Edition

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1. Introduction

Building upon our previous editions [1,2], the third edition of *Advanced Inorganic Semiconductor Materials* highlights the rapidly expanding frontier of inorganic and hybrid semiconductors, covering wide-bandgap oxides, functional mixed oxides, tribocatalytic materials, thin-film heterojunctions, ultra-thin chip mechanics, chiral hybrid halides, and luminescent organic–inorganic hybrids [3]. The nine featured contributions (references [4–12]) trace innovations at every scale—from atomic-level defect engineering and heterostructure design to macroscopic mechanical stability in ultra-thin devices—demonstrating how versatile inorganic semiconductor materials have become in modern electronics, optoelectronics, catalysis, and sensing [13]. Collectively, these works were contributed by authors from Brazil, Bulgaria, China, Germany, Portugal, Serbia, and Spain, showcasing the globally collaborative nature of semiconductor research.

These papers can be categorized into four major themes:

1. Wide-bandgap and transition-metal oxide semiconductors (papers [4–9]).
2. Mechanical and device engineering for flexible inorganic electronics (paper [10]).
3. Hybrid and chiral metal halide semiconductors (papers [11,12]).
4. Cross-cutting advances in charge transport, defect engineering, and photophysical mechanisms (spanning all nine contributions).

Below, each category is discussed in detail.

2. Wide-Bandgap and Transition-Metal Oxides: Design, Doping, and Applications

2.1. W-Doped Ga₂O₃ for Conductive Oxide Devices (Paper [4])

In the first contribution, W-doped Ga₂O₃ thin films are deposited via electron beam evaporation, achieving dramatically enhanced conductivity and n-type carrier characteristics without annealing. The increased electron mobility, reduced resistivity, and formation of high-quality heterojunction diodes on both p- and p⁺-Si substrates underscore how aliovalent doping can tune wide-bandgap oxides for power electronics and rectifiers [4].

This work exemplifies a powerful strategy: dopant-induced defect engineering to shift carrier concentration and mobility in ultra-wide-bandgap oxides, which are historically limited by deep donor levels and self-trapping behavior.

2.2. Tribocatalytic ZnO for Antibiotic Degradation (Paper [5])

Kaneva and co-workers advance the field of mechanochemistry by demonstrating a tribocatalytic pathway in which ZnO particles, synthesized by sol–gel and hydrothermal routes, interact mechanically with a PTFE-sealed magnetic stir bar to produce oxidative holes capable of degrading the antibiotic Cefuroxime Axetil even in the dark [5]. Their systematic study shows how stirring speed, magnetic rod geometry, and beaker material influence charge transfer and oxidation kinetics. Rather than treating mechanical agitation as an incidental experimental detail, this work reframes ambient mechanical energy as an intentional activation source for oxidative chemistry. The mechanistic picture—friction-induced electron transfer to the PTFE surface that leaves holes in the catalyst valence band—is supported by comparative activity measurements and highlights opportunities for designing low-energy, light-free processes for water and wastewater treatment.

2.3. Laser-Induced Resistivity Reduction in LaNiO_3 Thin Films (Paper [6])

Cichetto et al. report a versatile post-growth route to tune electrical resistivity in LaNiO_3 films by localized femtosecond laser irradiation [6]. The effect—resistivity reductions ranging from roughly 38% to 52% depending on substrate and temperature regime—appears to stem from locally modified crystallinity and defect populations induced by ultrafast laser pulses. Crucially, this approach provides a maskless, spatially selective method to program electrode resistivity, enabling patterned functionality without additional deposition steps. Such a capability is valuable for non-volatile memory electrodes and other devices where local electrical tuning is required.

2.4. Broadband Photoresponse in MoVO_x Nanobelts (Paper [7])

Ma and colleagues synthesized MoVO_x nanobelts using a one-pot approach and found pronounced broadband photoresponses from visible into the NIR (405–1064 nm) with self-powered operation [7]. V doping both narrows the bandgap and introduces defect states that, together with a strong built-in interfacial field, promote efficient separation of photogenerated carriers and suppress recombination. Notably, the photodetectors retained measurable response after two years of storage, a striking indicator of device robustness. The authors also report a subtle power-dependent inversion of the photocurrent sign, illustrating how the balance between defect populations and photogenerated carriers can produce non-intuitive device responses—an important consideration when engineering mixed-oxide photonic devices.

2.5. SnS/TiO_2 Heterostructure Thin Films for Photocatalysis (Paper [8])

Ding et al. used radio-frequency magnetron sputtering to construct SnS/TiO_2 heterostructured thin films and systematically varied the SnS layer thickness to optimize performance [8]. The optimized heterostructure (approximately 244 nm SnS over 225 nm TiO_2) shows a dramatic enhancement in photoelectrochemical activity—a photocurrent nearly 14 times greater than a pure TiO_2 film of equivalent thickness—and significantly improved dye degradation performance. The improvements are attributed to a type-II band offset [14–16] that increases visible light absorption while facilitating carrier separation. This study reinforces that careful control of thickness and interface quality is as important as intrinsic material choice when designing efficient photocatalytic heterojunctions.

2.6. Oxygen-Sensing Mixed Oxides $\text{TiO}_2\text{--CeO}_2$ (Paper [9])

Stevanović and collaborators investigate the oxygen-sensing behavior of TiO_2 -modified CeO_2 created by high-energy ball milling and show that milling speed and composition strongly influence vacancy concentration, surface chemistry, and sensor per-

formance [9]. XPS provides quantitative insight into surface oxidation states and charging behavior, while electrical testing demonstrates improved sensitivity at modest temperatures relative to pure CeO₂. The work highlights how solid-state mechanochemical processing can be used to tune defect landscapes and electron transport pathways in sensor materials.

3. Mechanics and Integration of Ultra-Thin Chips (Paper [10])

Zheng et al. address a practical but often overlooked challenge: how to integrate brittle inorganic chips as ultra-thin elements within flexible assemblies without premature debonding or fracture [10]. By formulating an energy-based mechanical model that distinguishes debonding and non-debonding regimes, they derive design rules that quantitatively relate chip thickness, interface adhesion coefficient, and bending radius to debonding risk. These theoretical predictions are corroborated with experiments: thinner chips, stronger interface adhesion, and larger bending radii markedly reduce the probability of debonding and chip failure. The study thus provides a practical engineering toolkit for designers of wearable and bendable systems who must reconcile the electrical performance of inorganic semiconductors with mechanical compliance.

4. Hybrid Metal Halides: Chiral and Luminescent Systems

4.1. Chiral OIMHs (Paper [11])

Chiral OIMHs combine structural tunability with unusual chiroptical responses. Zhu and co-authors review synthetic strategies, lattice structures, and mechanisms by which molecular chirality transfers to inorganic frameworks, producing CPL and enabling circularly polarized light detection devices [11]. They discuss the interplay between organic ligand design and inorganic lattice symmetry, emphasizing both the promise of these materials for spin-selective photonics and the practical challenges—particularly stability and integration into device architectures.

4.2. Luminescent OIMHs (Paper [12])

The complementary review by Sheng et al. surveys luminescent OIMHs, focusing on synthetic versatility, photophysical mechanisms, and diverse applications from LEDs to X-ray imaging and information security [12]. The authors synthesize recent advances in exciton management and molecular-level design strategies that deliver high radiative efficiencies. They also highlight unresolved issues such as ion migration, environmental stability, and scale-up that must be addressed for broader technological impact.

Together, papers [11,12] demonstrate how hybrid halides continue to broaden the materials palette for high-performance, solution-processable optoelectronics.

5. Thematic Integration and Comparative Summary

To situate the nine contributions within broader semiconductor research, Table 1 summarizes their key materials, techniques, and application domains, while Table 2 tabulates their performance enhancements.

Table 1. Overview of materials, methods, and applications in the third edition.

Paper/Review	Material System	Key Technique(s)	Main Phenomenon/Property	Application Domain
[4]	W-doped Ga ₂ O ₃	E-beam evaporation, Hall analysis	High conductivity, n-type transport	Rectifying diodes
[5]	ZnO (sol–gel, hydrothermal)	Tribocatalysis	Dark oxidation of antibiotics	Environmental remediation
[6]	LaNiO ₃	Pulsed laser deposition + femtosecond laser	Resistivity reduction	Memory electrodes
[7]	MoVO _x	One-pot synthesis	Broadband NIR photoresponse, self-powered	Photodetectors
[8]	SnS/TiO ₂	Magnetron sputtering	Type-II charge transfer	Photocatalysis
[9]	TiO ₂ –CeO ₂	High-energy milling	Oxygen vacancy tuning	Gas sensors
[10]	Ultra-thin Si chips	Mechanical modelling	Debonding thresholds	Flexible electronics
[11]	Chiral OIMHs	Chiral synthesis	CPL, spin selectivity	Chiral optoelectronics
[12]	Luminescent OIMHs	Hybrid synthesis	Exciton engineering	LEDs, X-ray imaging

Table 2. Comparative performance enhancements.

Paper	Improvement Reported	Magnitude
[4]	Conductivity increase vs. undoped	Orders of magnitude decrease in resistivity
[5]	Cefuroxime degradation rate	Higher at 500 rpm with sol–gel ZnO
[6]	Resistivity reduction	38–52%
[7]	Photocurrent stability	Maintain signal after 2 years, NIR response to 1064 nm
[8]	Photocurrent vs TiO ₂	13.8×
[9]	Sensor resistance	Mixed oxides lower than pure CeO ₂

6. Cross-Cutting Insights

A coherent interpretation of the nine articles emerges when examined through shared physical mechanisms and engineering trade-offs rather than by material class alone. Below, we expand the short subheadings used previously into integrated, contextualized discussions that explain why these themes matter for both fundamental understanding and device engineering.

6.1. Defect Engineering as a Design Lever

Across oxides and hybrids, a clear message is that intentional control of defects—oxygen vacancies, aliovalent dopants, and local disorder—is not merely a method for compensating material imperfections but a primary knob for tuning electronic, optical, and catalytic behavior. For wide-bandgap oxides such as Ga₂O₃, W-doping introduces carriers and raises mobility; for MoVO_x, it creates mid-gap states that extend absorption into the NIR and enable zero-bias photodetection; for TiO₂–CeO₂ mixtures, vacancy manipulation directly enhances sensor response. The implication for materials synthesis is that reproducible, quantitative control of defect concentrations should be a central objective in any synthetic workflow, and complementary characterization (Hall, XPS, deep-level spectroscopy) must be used to connect observed device behavior to underlying defect landscapes.

6.2. Interface Engineering Drives Device Function

Interfaces dictate whether photogenerated carriers recombine or contribute to useful currents. The SnS/TiO₂ type-II junction is a prototypical example where careful band-offset alignment accelerates charge separation, converting absorbed photons into measurable photocurrent and catalysis. Similarly, the stability and built-in field at MoVO_x interfaces impart resilience and self-powered behavior. For memory and electrode engineering, the local modification of LaNiO₃ resistivity by femtosecond lasers underscores that the spatially resolved control of interface and near-surface properties can be as important as bulk composition. Taken together, these studies argue for an engineering viewpoint in which the interface is designed in parallel with the bulk material, not as an afterthought.

6.3. Ambient Energy Harvesting and Sustainable Transduction

The tribocatalytic ZnO study demonstrates that mechanical energy—stirring, friction, and surface contact—can directly drive oxidative chemistry. When combined with photovoltaically driven self-powered devices like MoVO_x, a broader paradigm emerges: materials can be engineered to transduce a variety of ubiquitous ambient energies (mechanical, optical, thermal) into chemical or electrical outputs. For environmental and off-grid applications, these low-power or zero-bias operation modes substantially expand the range of feasible deployments.

6.4. Stability, Manufacturability, and Multi-Physics Integration

Many promising demonstrations falter if stability or process compatibility are not addressed. The two-year persistence of the MoVO_x photodetectors and the sputtering-based fabrication of SnS/TiO₂ suggest paths toward manufacturability; however, hybrid halides still face stability and ion migration challenges that limit application. Moreover, the mechanical modeling of ultra-thin chips highlights that long-term performance requires simultaneous attention to electrical, chemical, and mechanical degrees of freedom: bending fatigue, interfacial adhesion, and temperature cycling can all impact device lifetime. Future work must merge in situ diagnostics, accelerated aging studies, and multi-physics modeling to close the gap between lab demonstrations and deployable technologies.

7. Outlook

The research published in this edition illustrates how inorganic semiconductors are rapidly evolving into multifunctional materials platforms. The following directions appear especially promising [17–21]:

1. Integration of ultrafast laser processing with oxide electronics.
2. Mechanochemical routes for catalytic activation under ambient conditions.
3. Self-powered broadband photodetectors for internet of things and autonomous sensors.
4. Chiral and hybrid halides with engineered quantum and spin interactions.
5. Mechanically compliant inorganic chips for wearable and implantable technologies.

By uniting experimental innovation, theoretical modeling, and practical device demonstration, the nine papers in this edition collectively advance the science and technology of inorganic semiconductor systems.

8. Conclusions

Advanced Inorganic Semiconductor Materials—3rd Edition showcases a diverse, global, and forward-looking collection of works that expand the capabilities of inorganic and hybrid semiconductors across optics, electronics, mechanics, catalysis, and sensing [22]. The insights gained here will undoubtedly guide the design of next-generation materials and devices that are more efficient, sustainable, multifunctional, and integrable than

ever before [23], which we hope will contribute to the next edition of this Special Issue—“Advanced Inorganic Semiconductor Materials: 4th Edition” [24].

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

Abbreviations

The following abbreviations are used in this manuscript:

CPL	circularly polarized luminescence
LED	light-emitting diode
NIR	near-infrared
OIMH	organic–inorganic metal halide
PTFE	polytetrafluoroethylene
XPS	x-ray photoelectron spectroscopy

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Article

Characterizations of Semiconductive W-Doped Ga₂O₃ Thin Films and Application in Heterojunction Diode Fabrication

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Abstract

In this study, high-conductivity W-doped Ga₂O₃ thin films were successfully fabricated by directly depositing a composition of Ga₂O₃ with 10.7 at% WO₃ (W:Ga = 12:100) using electron beam evaporation. The resulting thin films were found to be amorphous. Due to the ohmic contact behavior observed between the W-doped Ga₂O₃ film and platinum (Pt), Pt was used as the contact electrode. Current-voltage (J-V) measurements of the W-doped Ga₂O₃ thin films demonstrated that the samples exhibited significant current density even without any post-deposition annealing treatment. To further validate the excellent charge transport characteristics, Hall effect measurements were conducted. Compared to undoped Ga₂O₃ thin films, which showed non-conductive characteristics, the W-doped thin films showed an increased carrier concentration and enhanced electron mobility, along with a substantial decrease in resistivity. The measured Hall coefficient of the W-doped Ga₂O₃ thin films was negative, indicating that these thin films were n-type semiconductors. Energy-Dispersive X-ray Spectroscopy was employed to verify the elemental ratios of Ga, O, and W in the W-doped Ga₂O₃ thin films, while X-ray photoelectron spectroscopy analysis further confirmed these ratios and demonstrated their variation with the depth of the deposited thin films. Furthermore, the W-doped Ga₂O₃ thin films were deposited onto both p-type and heavily doped p⁺-type silicon (Si) substrates to fabricate heterojunction diodes. All resulting devices exhibited good rectifying behavior, highlighting the promising potential of W-doped Ga₂O₃ thin films for use in rectifying electronic components.

Keywords: W-doped Ga₂O₃ thin films; electron beam evaporation; Hall effect measurements; p-type silicon; heterojunction diodes

1. Introduction

As global energy demand continues to surge, the development of energy-efficient and high-performance electronic devices has become increasingly imperative, especially for applications in the Internet of Things, automotive electronics, and renewable energy systems, such as electric vehicles and sustainable energy infrastructure. In these sectors, the efficiency, reliability, and miniaturization of power components directly influence the overall system performance. However, conventional first-generation silicon-based power semiconductor devices are rapidly approaching their inherent physical limits in terms of breakdown voltage, thermal stability, and switching performance. As a result,

wide-bandgap compound semiconductors, most notably GaN and SiC, are being actively explored as next-generation materials for high-performance power devices. Nevertheless, the high cost and processing complexity of GaN and SiC have posed significant barriers to their large-scale adoption. Against this technological backdrop, β -phase Ga_2O_3 has emerged as a promising candidate due to its ultra-wide bandgap (~ 4.9 eV) [1] and exceptionally high critical electric breakdown field, reaching up to 8 MV/cm [2]. This breakdown field strength is significantly higher than that of GaN (3.3 MV/cm) and SiC (2.5 MV/cm), enabling β - Ga_2O_3 to maintain stable operation in high-voltage environments. Although its electron mobility is relatively modest (~ 300 cm²/V·s) [2], the high breakdown field allows for the design of shorter gate-to-drain distances, supporting the development of compact devices with rapid switching speeds.

From a materials perspective, β - Ga_2O_3 also demonstrates a remarkable Baliga Figure of Merit (BFOM) of 3214, which is roughly 10 times higher than that of SiC, 4 times higher than that of GaN, and approximately 3000 times greater than that of silicon [2]. The BFOM, a key metric for evaluating the trade-off between breakdown voltage and on-resistance in power devices, highlights the intrinsic advantages of β - Ga_2O_3 for high-power, high-efficiency applications. These superior material properties have fueled extensive interest in the use of Ga_2O_3 for next-generation high-voltage power converters and high-speed switching circuits [3,4]. However, intrinsic Ga_2O_3 suffers from a low native carrier concentration and limited electron mobility, both of which constrain its electrical transport capabilities. To address these limitations, researchers have focused on improving Ga_2O_3 thin films through impurity doping, as well as refining deposition techniques and exploring alternative substrate materials. Recent advancements include the growth of not only β -phase Ga_2O_3 but also non- β polymorphs [5,6], amorphous Ga_2O_3 thin films [7,8], and heteroepitaxial thin films deposited on non-native substrates such as a-plane, r-plane, and c-plane sapphire, silicon, and MgO [9]. These efforts aim to improve crystallinity and enhance the electrical performance of Ga_2O_3 -based devices.

Intrinsic point defects in Ga_2O_3 , such as oxygen vacancies (V_{O}) and gallium vacancies (V_{Ga}), also play critical roles in determining its electrical and optical behavior. For instance, oxygen vacancies can act as shallow donor levels that enhance n-type conductivity [10,11], while gallium interstitials may introduce deep-level traps that impede carrier mobility or even trigger unwanted self-doping effects [12,13]. Therefore, achieving controlled n-type or p-type conductivity via selective doping strategies has become a central research objective in the development of Ga_2O_3 -based semiconductor devices. In parallel, WO_3 , a direct-bandgap semiconductor with an energy gap of approximately 2.6 eV, has garnered attention for its favorable electrical properties, including its high conductivity, low threshold voltage, and excellent current-handling capabilities. The n-type behavior of WO_3 arises from oxygen vacancies and dopant-induced free electrons, which form shallow donor levels and elevate the carrier concentration, typically reaching an intrinsic carrier concentration of $\sim 10^{19}$ cm⁻³ [14]. Recent studies have demonstrated that incorporating WO_3 into Ga_2O_3 can effectively modulate its band structure and interfacial properties. This doping strategy has the potential to improve the Schottky barrier height, enhance the overall device performance, and increase selectivity and sensitivity in sensing applications [15,16].

Based on previous studies, few reports have directly achieved n-type wide-bandgap Ga_2O_3 semiconductors using such a simplified approach. The first major innovation of this work is the development of a streamlined fabrication method that allows for the direct deposition of W-doped Ga_2O_3 thin films exhibiting n-type wide-bandgap semiconductor behavior, without the need for post-deposition processing or formation of the β -phase crystal structure. In this research, tungsten is introduced at a concentration of 10.7 at% using WO_3 as the doping source. By systematically varying the doping concentration, thin films

with differing electronic properties are synthesized and evaluated as active-layer materials in power semiconductor devices. A novel and nontraditional fabrication methodology is proposed, diverging from conventional methods for β -Ga₂O₃ synthesis. Comprehensive characterization is performed to determine the thin films with optimal electrical properties. These optimized thin films are subsequently integrated into heterojunction diode structures, demonstrating their functional viability in electronic devices [17–19].

This advanced manufacturing technique represents a breakthrough by enabling Ga₂O₃ thin films to retain wide-bandgap semiconductor functionality even in the absence of the β -phase, thereby expanding the scope of Ga₂O₃ applications in high-performance electronics. Furthermore, heterojunction diodes, a critical component in the development of modern semiconductor devices, are utilized to validate the film's practical performance. The fundamental concept of a heterojunction diode involves combining two semiconductors with different band structures and material properties to form an interface with controlled electronic and optoelectronic characteristics. Unlike homojunction diodes, heterojunctions allow for the formation of band discontinuities at the interface, which can modulate carrier transport behavior, improve current injection efficiency, and enhance energy conversion, making them indispensable in advanced device architectures. In previous work, we successfully deposited In₂O₃-doped SiC thin films with n-type characteristics and integrated them onto p-type silicon substrates to form diodes exhibiting Schottky behavior [20].

Building upon this foundation, the second innovation of this study involves the deposition of the WO₃-doped Ga₂O₃ thin films onto both p-type silicon (with a carrier concentration of 10^{14} cm^{-3}) and p⁺-type silicon (with a carrier concentration of 10^{18} cm^{-3}) substrates to fabricate heterojunction diodes. Moreover, previous studies have rarely reported the direct fabrication of Zener diodes based on n-type Ga₂O₃ thin films on p⁺-type silicon substrates using this approach to form heterojunctions. We will demonstrate that the p⁺-type silicon/W-doped Ga₂O₃ thin-film devices exhibit apparent Zener diode behavior. These experimental results provide compelling evidence for the material's potential in practical device applications and reinforce the feasibility of this simplified, doping-based fabrication strategy. This research makes substantial contributions to the field of wide-bandgap semiconductors by presenting a cost-effective and scalable method for fabricating Ga₂O₃ thin films with enhanced electrical properties, even without forming the β -phase structure. By integrating WO₃ doping and exploring heterojunction architectures, the study paves the way for the development of next-generation Ga₂O₃-based power devices while supporting broader objectives in energy efficiency, miniaturization, and industrial innovation.

2. Methodology

In this study, a surface-cleaned p-type Si wafer with (100) orientation was initially employed as the substrate for depositing W-doped Ga₂O₃ thin films. The substrate preparation process began with a meticulous cleaning protocol that utilized sequential solvent treatments to eliminate surface contamination. Acetone served as the primary cleaning agent, effectively dissolving grease, organic residues, and adherent impurities from the substrate surface. This was followed by isopropanol treatment, which removed any residual acetone traces, while subsequent deionized water rinsing ensured complete solvent elimination. To maintain processing quality and prevent water stain formation, immediate nitrogen gas drying of the polished substrate was performed. The target preparation phase involved subjecting Ga₂O₃ powder to preliminary thermal treatment at 950 °C for one hour. Ga₂O₃ and 10.7 at% WO₃ powders were carefully measured to maintain the desired Ga:W ratio of 100:12 and then introduced into the ball mill apparatus, where homogeneous blending occurred. After mechanical mixing was completed, the powder blend underwent transfer

to a forming die, resulting in the creation of green compacts through powder consolidation. These compacts were then subjected to thermal sintering in a furnace at 500 °C for one hour, ultimately producing the target material required for the deposition process. The final deposition stage commenced with positioning the sintered targets within the e-beam evaporation crucible, followed by the initiation of vacuum evacuation procedures. Once the chamber pressure was established at 8×10^{-6} torr, the room temperature deposition of W-doped Ga₂O₃ thin films began, completing the fabrication sequence.

During the 15 min deposition process, deposition rate parameters were carefully controlled while the chamber pressure remained unregulated. This approach successfully produced W-doped Ga₂O₃ thin films with an approximate thickness of 200 nm. For electrode fabrication, Pt was chosen as the contact material owing to its exceptional ability to form reliable ohmic contacts with semiconductor materials. The electrode preparation process began with positioning the samples on a precision heating platform, followed by depositing Pt electrodes with 0.25 cm × 0.25 cm squares onto the film surface through thermal evaporation, thereby forming the Ohmic contact configuration illustrated in Figure 1a. The heterojunction diode fabrication required a more complex multi-step procedure. Initially, silicon substrates underwent surface preparation using buffered oxide etch (BOE) solution to completely remove SiO₂ layers from both surfaces through controlled etching. Following etching, the substrates received thorough cleaning to eliminate any residual chemical contamination. The device assembly proceeded systematically: first, the back electrode attached was deposited on the cleaned silicon substrate. Subsequently, W-doped Ga₂O₃ thin films were deposited onto the opposite substrate surface using the E-beam deposition technique.

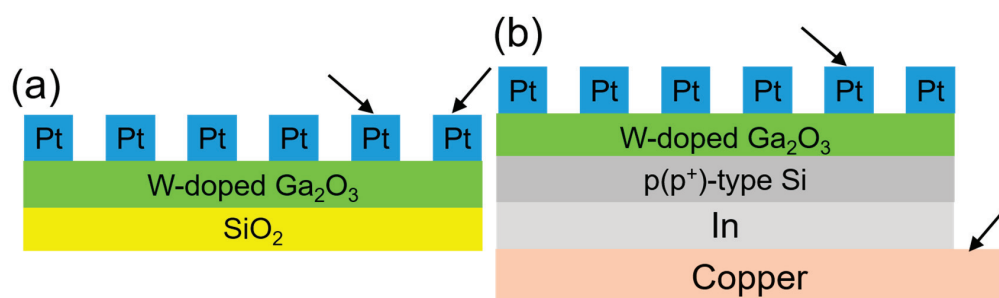


Figure 1. Schematic diagrams of (a) the structure used for I-V measurements and (b) the structure used for I-V measurements of W-doped Ga₂O₃ thin films-p-type Si heterojunction diode. Arrows indicate the measurement contact points.

The fabrication process concluded with Pt top electrode deposition, creating the complete device structure, as Figure 1b illustrates, ready for current-voltage (I-V) characterization measurements. A comprehensive set of characterization techniques was employed to evaluate the properties of the W-doped Ga₂O₃ thin films. Field emission scanning electron microscopy (FESEM) was used to observe the surface morphology and determine W-doped Ga₂O₃ thin films' thickness. When combined with Energy-Dispersive X-ray Spectroscopy (EDS), FESEM also enabled elemental quantitative analysis, confirming the successful incorporation of W into the Ga₂O₃ matrix. X-ray diffraction (XRD) was performed to identify the crystalline phases present in the films. In addition, UV-Vis spectroscopy was used to determine the optical bandgap by analyzing the transmission spectra, with measurements carried out on films deposited on transparent sapphire substrates. Elemental quantitative analysis and depth profiling was also conducted by using X-ray photoelectron spectroscopy (XPS) to analyze the distribution of these elements throughout the W-doped Ga₂O₃ thin films' thickness.

XPS measurements were performed using a PHI VersaProbe 4 (Physical Electronics, Chanhassen, MN, USA) equipped with a monochromatic Al K α X-ray source (1486.6 eV). Sample regions of interest were identified and aligned using the scanning X-ray imaging (SXI) mode, and the system's ion gun (500 eV–5 keV monatomic Ar⁺) was available for sputtering. Survey spectra were acquired at a pass energy of ~93 eV with a step size of 0.5–1 eV, while high-resolution core-level spectra were recorded at a pass energy of ~23.5 eV with a step size of 0.05–0.1 eV. Multiple scans (typically 3–10 accumulations) were accumulated to improve the signal-to-noise ratio. Electrical characterization included current–voltage (I–V) measurements using an Agilent B1500A analyzer (Keysight Technologies, Santa Rosa, CA, USA) over a voltage range of –2 V to 2 V, generating I–V response curves. Furthermore, Hall effect equipment was used to determine key electrical parameters such as the carrier mobility, carrier concentration, and resistivity of the W-doped Ga₂O₃ thin films. As for the Hall measurements, they were performed using the van der Pauw configuration with indium contacts deposited at the four corners of the thin-film samples. A Hall measurement system (Lakeshore 7707, Lake Shore Cryotronics, Inc., Westerville, OH, USA) equipped with a calibrated electromagnet was employed. The carrier concentration, mobility, and resistivity were extracted under a magnetic field of ± 0.55 T at room temperature.

3. Results and Discussion

Figure 2 examines the effect of WO₃ doping on the microstructural characteristics of W-doped Ga₂O₃ thin films. As shown in the SEM surface image in Figure 2a, the surface morphology of the thin film is clearly observed. The image reveals that the surface of the W-doped Ga₂O₃ thin film is relatively smooth, with densely packed grains and no significant variation in grain size across the film. This uniform and compact morphology suggests that the WO₃ doping process does not disrupt surface integrity but rather promotes a highly uniform film structure. According to the literature, tungsten doping is known to enhance the film's density and surface uniformity [21,22]. This improvement is primarily attributed to the lower melting point of WO₃ (~1473 °C) compared to that of Ga₂O₃ (~1900 °C). During the electron beam (E-beam) evaporation process, WO₃ vaporizes earlier than Ga₂O₃, making it more likely to serve as a nucleation facilitator during film deposition. The early vaporization of WO₃ generates a large number of nucleation sites, which contribute to the rapid and uniform formation of grains. These nucleation centers effectively suppress abnormal grain growth, resulting in a fine-grained and dense microstructure.

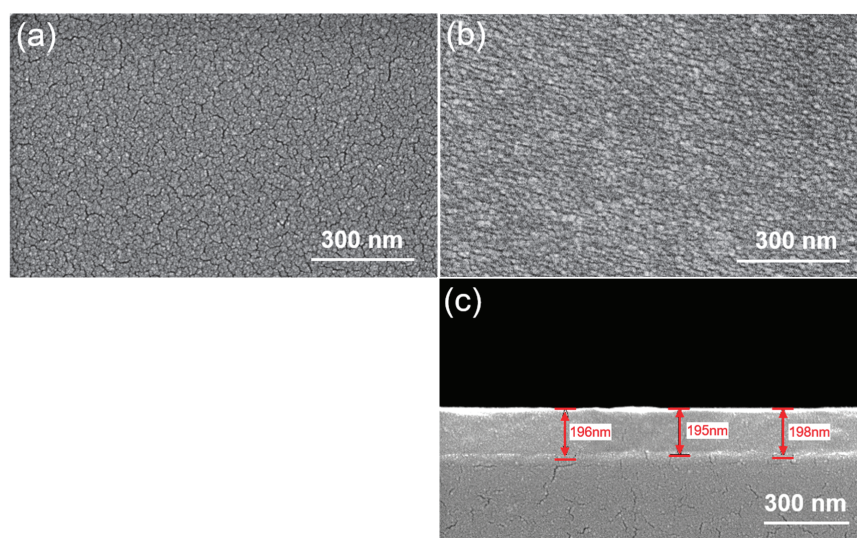


Figure 2. SEM images of (a) the as-deposited un-doped and (b) W-doped Ga₂O₃ thin films and the surface (c) cross sectional W-doped Ga₂O₃ thin films.

This phenomenon is further supported by the depth-profile elemental analysis presented later in the study, which indirectly confirms that WO_3 tends to vaporize prior to Ga_2O_3 during the deposition process. The elemental distribution data imply that the presence of WO_3 in the early stages of deposition plays a crucial role in modifying the film's nucleation dynamics and growth behavior. The formation of such a dense and uniform microstructure is particularly beneficial for applications requiring high-quality dielectric or semiconducting thin films. Furthermore, improved surface uniformity contributes to better interface characteristics when the film is integrated into device architectures. Therefore, WO_3 doping not only improves the microstructural integrity of Ga_2O_3 thin films but also has potential implications for the performance and reliability of next-generation electronic and optoelectronic devices. Figure 2a illustrates the surface morphology of the as-deposited un-doped Ga_2O_3 thin films, which appear smooth and composed of densely packed particles. Nevertheless, noticeable cracks and voids are observed across the surface. These defects are commonly attributed to the nature of E-beam deposition, which can result in non-uniform film growth and localized structural discontinuities such as cracking or porosity.

In contrast, Figure 2b reveals a markedly different morphology for the as-deposited W-doped Ga_2O_3 thin films. The surface clearly exhibits the presence of microcrystalline structures, indicating that W doping induces partial crystallization within the otherwise amorphous matrix. This microstructural evolution reveals that tungsten incorporation plays a significant role in modifying the nucleation and growth dynamics during deposition, potentially enhancing the film's structural integrity and altering its physical properties. Notably, no cracks or pores are observed on the film surface, suggesting that the film maintains good structural integrity and compactness. The absence of such defects is advantageous, as it contributes to improved mechanical stability and minimizes potential pathways for leakage currents in electronic applications. This also reflects the high quality of the deposition process and the beneficial role of WO_3 doping in promoting a uniform and defect-free microstructure. Figure 2c presents the cross-sectional view of the W-doped Ga_2O_3 thin films. From the image, the film thickness is estimated to be approximately 200 nm. The cross-sectional morphology reveals that the film exhibits excellent thickness uniformity across the entire area, indicating a highly controlled and stable deposition process. This level of uniformity not only reflects the consistency of the E-beam evaporation parameters but also demonstrates the reliability of the process in producing films with well-defined and reproducible thicknesses. Such uniformity is essential for ensuring predictable electrical and optical behavior in device applications, where film thickness plays a critical role in performance.

Figure 3a shows the EDS mapping regions selected for compositional analysis of the W-doped Ga_2O_3 thin films, including a small area (yellow rectangle) and a larger area (green rectangle). These mappings were performed to verify the uniform distribution of different elements throughout the deposited films. The corresponding EDS spectra, shown in Figure 3b, clearly identify the presence of Ga, O, and W in the as-deposited films, confirming the successful incorporation of tungsten species. Quantitatively, the average atomic ratio of Ga, O, and W in the yellow-square area scan was 34.0:62.4:3.6, which closely matches the nominal target composition of 34.6:62.4:4.0. Notably, these values indicate that the Ga:O ratio deviated from the theoretical 2:3 stoichiometry of Ga_2O_3 and that there is a relatively lower W content. Using an accelerating voltage of 10 keV for EDS analysis allows the electron beam to penetrate beyond 200 nm into the sample. As a result, the measured composition predominantly reflects the W concentration across the entire thickness of the thin film. Furthermore, this deviation can be attributed to the introduction of WO_3 , which raises the oxygen content, thereby reducing the Ga:O ratio. When performing EDS analysis

on thin film samples, the collected signal may include contributions not only from the film itself but also from the underlying layers or even the substrate. If the film thickness is insufficient, the resulting signal may be diluted by these contributions, leading to deviations in the measured elemental composition. In our case, the W-doped Ga_2O_3 thin films have a thickness of approximately 200 nm, which may not be sufficient to fully eliminate substrate influence, thereby introducing potential deviations in the quantified elemental ratios. These results collectively reinforce that WO_3 is effectively incorporated into the Ga_2O_3 matrix, demonstrating the feasibility of the doping approach and its capability to tune the film composition in a controlled manner.

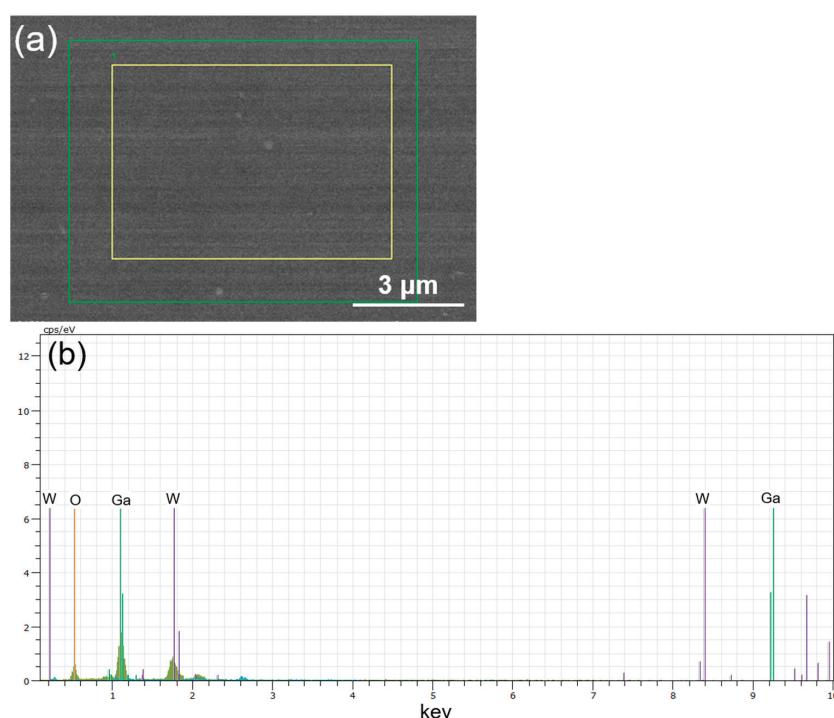


Figure 3. EDS analysis of the W-doped Ga_2O_3 thin films: (a) two analysis areas (yellow and green) and (b) EDS spectra.

The XRD spectra provide insights into the crystalline properties of both un-doped and W-doped Ga_2O_3 thin films, with the diffraction peaks serving as indicators of potential structural and phase transformations. The results displayed in Figure 4 show that both the un-doped and W-doped Ga_2O_3 thin films predominantly exhibit an amorphous phase. For the un-doped Ga_2O_3 thin films, the XRD pattern displays a smooth and broad diffraction profile, characteristic of a fully amorphous structure [23]. In contrast, the W-doped Ga_2O_3 thin films exhibit irregular fluctuations in the diffraction spectrum. This difference can be attributed to the deposition dynamics during the E-beam evaporation process. In the case of un-doped Ga_2O_3 , the evaporated material solidifies into a completely amorphous phase. However, for the W-doped Ga_2O_3 thin films, although the overall structure remains largely amorphous, the presence of WO_3 , which has a lower melting point than Ga_2O_3 , can facilitate localized liquid-phase-assisted crystallization during film formation [24,25]. This process can promote the nucleation and growth of fine microcrystalline domains embedded within the amorphous matrix. As a result, the irregular fluctuations observed in the XRD pattern of the W-doped Ga_2O_3 thin films are likely caused by these undetectable or weakly diffracting crystalline phases, which are too small or too sparsely distributed to produce well-defined diffraction peaks but still perturb the amorphous background signal.

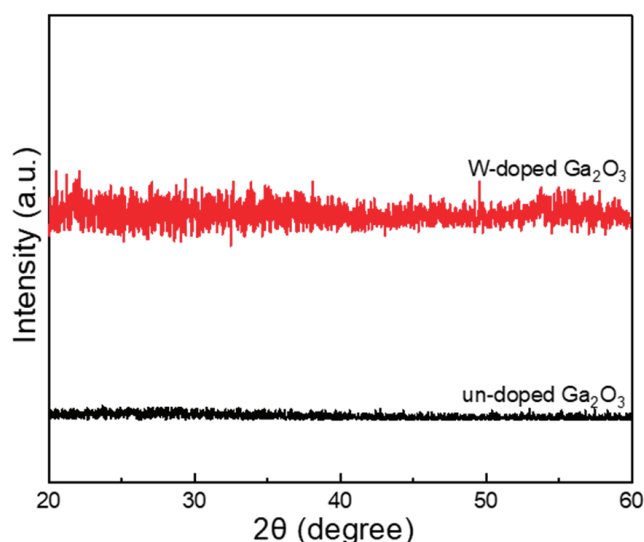


Figure 4. XRD patterns of the un-doped and W-doped Ga_2O_3 thin films.

To further investigate the elemental composition of Ga, W, and O within the thin films, quantitative XPS analysis was performed, and the depth at which the XPS data were obtained, along with the original analysis spectrum, is presented in Figure 5a. The average atomic ratios of Ga (Ga_{2p3}), O (O_{1s}), and W (W_{4f}) were determined to be 34.3:63.0:2.7. Notably, the relative concentration of W obtained from XPS was significantly lower than that measured via EDS. This discrepancy arises from the fundamental nature of XPS, because XPS is a highly surface-sensitive analytical technique. When used for elemental analysis, XPS primarily reflects the composition of the topmost surface layers of the material. This differs from depth profiling applications, where sputtering is employed to reveal subsurface information. Without sputtering, the measured elemental ratios predominantly represent the near-surface chemical composition, typically within a depth of 1–10 nm. As a result, it often fails to reflect the overall elemental distribution across the entire film thickness. This surface limitation of XPS becomes particularly relevant when considering the physical properties of the materials involved. According to previous SEM observations and known thermophysical characteristics, WO_3 has a substantially lower melting point compared to Ga_2O_3 . During the e-beam evaporation process, materials with lower melting points tend to vaporize and condense earlier than those with higher melting points. This suggests that WO_3 likely undergoes preferential vaporization and subsequently deposits earlier at the film–substrate interface. Moreover, literature reports have shown that, at elevated substrate temperatures, the sticking coefficient of oxygen atoms on the substrate surface is lower than that of tungsten atoms [14].

This variation in surface adsorption behavior further suggests that fewer W atoms remain on the outermost surface layer of the thin film, which explains the lower W concentration detected by surface XPS measurements, and the analysis results for Ga, W, O, and Si elements are shown in Figure 5b. Based on this observation, it is reasonable to infer that the actual W doping concentration may be underestimated by surface-level XPS analysis. To validate this hypothesis and obtain a more complete picture of the W distribution throughout the film thickness, XPS depth-profile analysis was performed. This method enabled the investigation of the spatial distribution of W atoms under different doping conditions, as well as assessments of film uniformity and structural consistency. Figure 5b presents the atomic concentration profiles of Ga, W, O, and Si elements as a function of sputtering depth in the W-doped Ga_2O_3 thin films. The depth-resolved data reveal a clear gradient in W concentration: in the near-surface region (0–30 nm), the W concentration is

relatively low. However, as the etching depth increases, the W concentration gradually rises, reaching its maximum near the film–substrate interface, around 200 nm. Beyond this depth, the W concentration slightly surpasses that of Ga in the same region. In contrast, the Ga concentration consistently decreases with increasing depth.

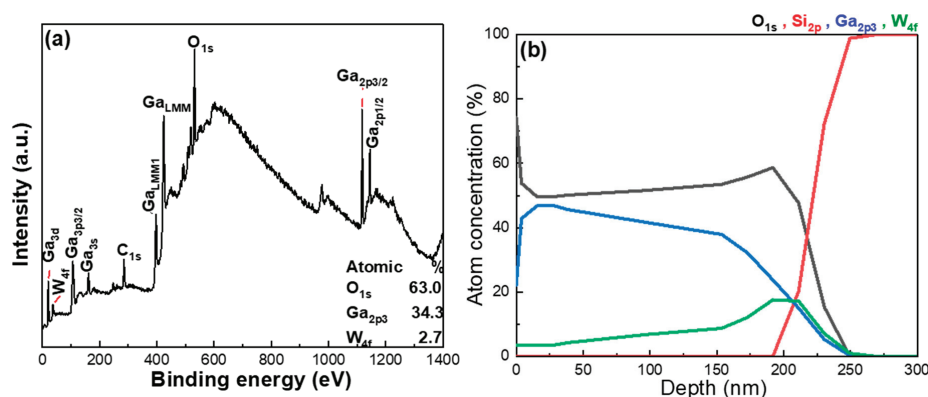


Figure 5. (a) The original analysis spectrum and (b) the depth profile analysis of Ga, W, O, and Si elements of the W-doped Ga₂O₃ thin films.

These findings strongly support the earlier hypothesis. The lower melting point of WO₃ facilitates its early vaporization during deposition, allowing it to preferentially settle near the substrate interface. This results in a vertical compositional gradient, with W atoms becoming concentrated toward the bottom of the film. Importantly, the depth-profile results corroborate the surface XPS data and together offer a coherent explanation for the initially observed discrepancy in W content. The results confirm that conventional XPS primarily reflects surface composition and is insufficient for capturing the complete dopant distribution in the bulk of the film. The combination of surface XPS and depth-profile analyses reveals that W atoms exhibit a distinct decreasing trend in W atom concentration within the W-doped Ga₂O₃ thin films. This distinct decreasing trend is a direct consequence of the deposition dynamics governed by material properties such as the melting point and surface adhesion behavior. The findings highlight a crucial aspect of the WO₃ doping strategy used in this study, namely, the tendency of W atoms to segregate toward the bottom of the film. This insight not only clarifies the limitations of surface analysis techniques but also underscores the importance of depth-resolved methods in accurately evaluating doping uniformity in thin-film systems.

Figure 6a presents the O_{1s} spectra of W-doped Ga₂O₃ thin films. In general, the O_{1s} peak can be deconvoluted into three nearly Gaussian components, denoted as O_I, O_{II}, and O_{III}. For the W-doped Ga₂O₃ thin films, the O_{1s} peak was centered at 530.9 eV, and the peaks of O_I, O_{II}, and O_{III} were located at 530.1 ± 0.1 eV (O_I), 530.9 ± 0.1 eV (O_{II}), and 531.6 ± 0.1 eV (O_{III}). Such detailed analyses of the O_{1s} spectra provide critical insights into the bonding characteristics of oxygen and their influence on the electronic and interfacial properties of the W-doped Ga₂O₃ thin films. The low binding energy peak (O_I) is attributed to lattice oxygen (O^{2−} in Ga–O), which reflects the presence of a well-ordered Ga₂O₃ crystal structure. The high binding energy peak (O_{III}) corresponds to surface-adsorbed oxygen species, such as OH[−], H₂O, and CO_x groups, which are typically associated with surface contamination or adsorption from the surrounding environment. In earlier studies, the medium binding energy peak (O_{II}) was often attributed to oxygen vacancy-associated oxygen or defect-induced nonstoichiometric Ga₂O₃ states. Oxygen vacancies (V_O) have been widely regarded as the primary source of n-type conductivity in Ga₂O₃ thin films, since they can act as shallow donors and contribute free electrons to electrical transport [26].

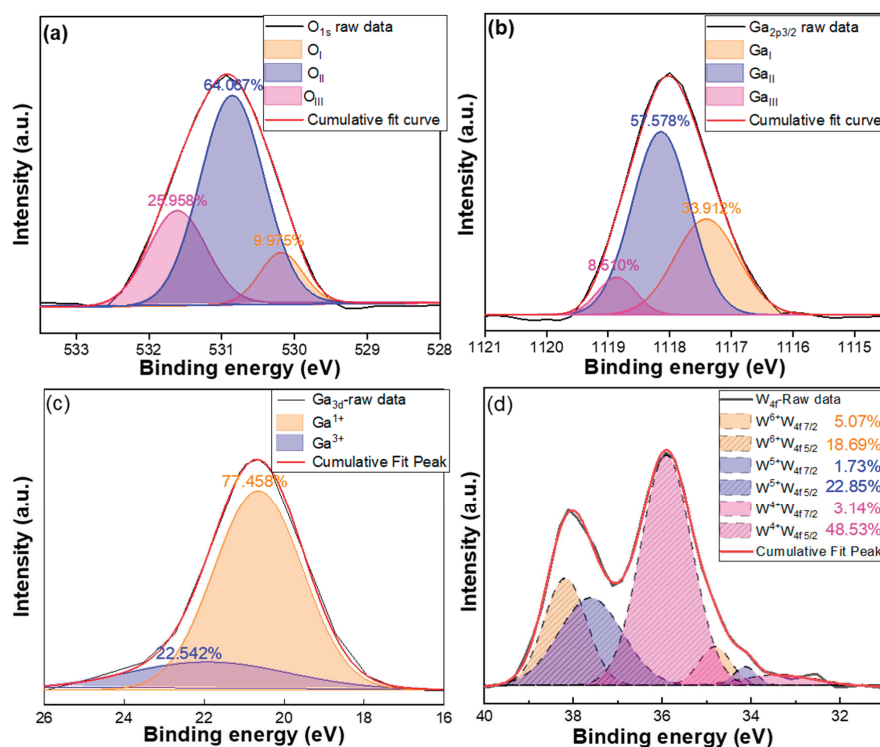


Figure 6. XPS analysis spectra and the Gaussian-resolved components of the W-doped Ga_2O_3 thin films: (a) O_{1s} spectrum, (b) $\text{Ga}_{2p_{3/2}}$ spectrum, (c) Ga_{3d} spectrum, and (d) W_{4f} spectrum.

However, H. Idriss has argued that this interpretation is incorrect and proposed that the O_{II} component most likely originates from surface hydroxyls (dissociatively adsorbed water, ~ 531.3 – 531.5 eV), molecularly adsorbed water (~ 532.5 – 533 eV), and/or adventitious oxygen-containing contaminants [27]. As emphasized by Idriss, ex situ O_{1s} signals in this energy range should not be taken as direct evidence of oxygen vacancies, since ambient exposure rapidly heals surface vacancies through water adsorption, and more reliable identification would require monitoring changes in the metal cation oxidation states or in situ/temperature-dependent measurements. Nevertheless, it should be noted that there is still no complete consensus in the literature, and many reports continue to interpret the O_{II} component within the framework of oxygen-vacancy-related states. In this study, we follow this conventional approach to discuss our results. The O_{II} component accounts for as much as 64.067% of the total O_{1s} peak area, which suggests a relatively high concentration of donor-like defect states within the thin films. Such a pronounced proportion strongly supports the view that oxygen deficiency plays a critical role in enhancing the intrinsic n-type conductivity of Ga_2O_3 thin films and further indicates that the deposition conditions employed in this work effectively promote the formation of vacancy-related states favorable for carrier generation.

For the W-doped Ga_2O_3 thin films, the $\text{Ga}_{2p_{3/2}}$ spectrum can be deconvoluted into three distinct components, as Figure 6b shows. The first component, Ga_I , appearing at 1117.4 eV, is attributed to metallic bonding states such as Ga–Ga or Ga–W. The second component, Ga_{II} , located at 1118.1 eV, corresponds to the Ga_2O_3 lattice structure and represents gallium in its typical trivalent oxidation state. The third component, Ga_{III} , observed at 1118.9 eV, is associated with Ga–O bonding environments or higher oxidation state gallium species present at the film surface or interface, such as $\text{Ga}(\text{OH})_3$ or hydrated oxides [28]. The relative intensities of these three components provide valuable insights into the chemical states of Ga, the degree of oxidation, and the surface chemistry of the W-doped Ga_2O_3 thin films. Among these, the low binding energy sub-peak Ga_I is widely regarded

as a feature associated with oxygen vacancies, which play a crucial role in determining the electronic properties of Ga_2O_3 . Since oxygen vacancies provide shallow donor states that release free electrons, Ga_1 serves as the most direct spectral signature of enhanced n-type conductivity in Ga_2O_3 . In this study, the Ga_1 component accounts for 33.912% of the total $\text{Ga}_{2p_{3/2}}$ peak area, indicating a considerable concentration of vacancy-related states. This relatively high proportion strongly suggests that the W-doped Ga_2O_3 thin films possess abundant donor-like defects, which play a decisive role in boosting electron density and electrical transport. Compared with typical reports where Ga_1 contributions are often lower, the observed value highlights the effectiveness of the deposition conditions in promoting oxygen vacancy formation and further demonstrates the potential of these films for applications in power electronics and devices requiring stable n-type conductivity.

The Ga_{3d} spectrum of the W-doped Ga_2O_3 thin films can be deconvoluted into two distinct components: a Ga^{1+} -related peak and a Ga-O bonding peak. The Ga^{1+} peak, located at the lower binding energy side, is generally attributed to oxygen vacancies or lattice defects, where Ga atoms exist in a partially reduced valence state, such as Ga_2O [29]. According to the XPS reference data, metallic Ga exhibits characteristic binding energies at $\text{Ga}_{2p_{3/2}}$ and Ga_{3d} (~18.8 eV), while Ga^{3+} does at ~20.3 eV of Ga_{3d} . Therefore, if the Ga_1 component observed in $\text{Ga}_{2p_{3/2}}$ were truly due to metallic Ga, a corresponding signal should also be present in the Ga_{3d} core level. The absence of such a peak suggests that the assignment of Ga_1 to metallic Ga may not be valid [30,31]. The pronounced Ga^{1+} component observed in the Ga_{3d} spectrum indicates a highly reduced chemical environment, which is commonly associated with donor-like defects that can strongly influence the electrical conductivity, defect density, and carrier concentration of Ga_2O_3 thin films. In contrast, the higher binding energy peak corresponds to the conventional Ga-O bonding environment, where Ga predominantly exists in the Ga^{3+} state. While oxygen vacancies have often been proposed as one of the primary contributors to the intrinsic n-type conductivity of Ga_2O_3 , it is important to note that such vacancies cannot be directly detected by XPS. Instead, the large proportion of Ga^{1+} , accounting for as much as 77.458% of the total Ga_{3d} peak area, suggests a significant presence of reduced Ga states that may be related to oxygen deficiency or other non-stoichiometric features. This substantial fraction implies that W-doping effectively promotes the formation of donor-like defect states, which are likely favorable for enhancing n-type conductivity and improving the suitability of Ga_2O_3 thin films for power electronics and next-generation semiconductor devices.

The W_{4f} spectrum of the W-doped Ga_2O_3 thin films was deconvoluted into contributions from W^{6+} , W^{5+} , and W^{4+} oxidation states. Each oxidation state was fitted as a spin-orbit doublet consisting of $\text{W}_{4f_{7/2}}$ and $\text{W}_{4f_{5/2}}$ peaks with a fixed area ratio of 4:3 and a spin-orbit splitting of ~2.1 eV, consistent with the degeneracy rule and standard XPS parameters for tungsten oxides. The highest binding energy doublet, assigned to W^{6+} , corresponds to W^{6+} -O bonding in WO_3 -like environments or substitutional W replacing Ga^{3+} in the Ga_2O_3 lattice. Such high-valence substitution acts as a shallow donor, since W^{6+} provides extra free electrons when occupying Ga^{3+} lattice sites, thereby serving as a direct contributor to n-type conductivity. The intermediate binding energy doublet, assigned to W^{5+} , is commonly associated with oxygen-deficient environments and may also donate electrons to the conduction band, thus further enhancing conductivity. The lowest binding energy doublet, corresponding to W^{4+} , reflects more strongly reduced W-O defect structures formed under highly reducing conditions, which may also contribute to donor-like behavior [32]. In this study, the W^{6+} component is clearly resolved, with the fitted $\text{W}_{4f_{7/2}}$ and $\text{W}_{4f_{5/2}}$ peaks accounting together for 23.76% of the total W_{4f} peak area. This substantial proportion of W^{6+} indicates that a significant fraction of tungsten atoms substitute for Ga^{3+} in the lattice, effectively supplying a large number of donor electrons.

These results strongly support the conclusion that W^{6+} substitution is a key mechanism driving the enhanced n-type conductivity observed in the W-doped Ga_2O_3 thin films.

In the past, various techniques have been used to calculate the optical bandgap (E_g) of different materials [1]. In this study, the E_g value was primarily determined using transmittance spectra data, analyzed via the Tauc plot method. This approach is based on the Tauc relation, which is commonly employed for estimating the optical bandgap of amorphous and crystalline semiconductors. The Tauc equation relates the absorption coefficient (α) and photon energy ($h\nu$) as follows:

$$(\alpha h\nu)^n = A (h\nu - E_g) \quad (1)$$

where A is a constant, E_g is the optical bandgap, and n depends on the nature of the electronic transition (for direct allowed transitions, $n = 2$; for indirect allowed transitions, $n = 1/2$). As shown in Figure 7a, the variation in the bandgap energies is clearly observed. The calculated E_g value for the W-doped Ga_2O_3 thin films was 4.13 eV, which is noticeably higher than that of conventional amorphous Ga_2O_3 thin films. This significant increase in E_g can be attributed to the pre-sintering of the Ga_2O_3 powder at 950 °C, which partially transformed the material into the crystalline β - Ga_2O_3 phase prior to deposition. Although the as-deposited W-doped Ga_2O_3 thin films appear amorphous in nature, the elevated temperature during deposition, induced by the E-beam evaporation process, facilitated partial crystallization, particularly the formation of microcrystalline regions within the thin film.

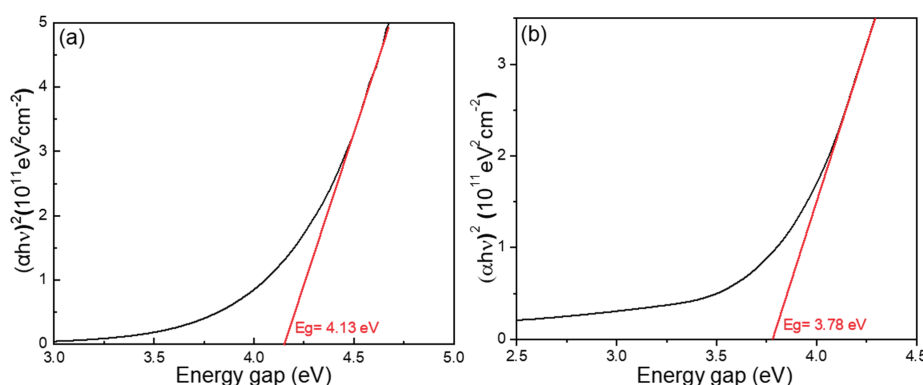


Figure 7. Tauc plots of (a) the W-doped and (b) the undoped Ga_2O_3 thin films.

The presence of microcrystalline structures in the W-doped Ga_2O_3 thin films, as shown in Figure 1b, results from the deposition process using E-beam evaporation. During this process, the high-temperature melting, subsequent vaporization, and re-deposition cycles promote localized crystallization within the otherwise amorphous film. The microcrystal formation occurs due to the presence of WO_3 , which has a relatively low melting point compared to Ga_2O_3 . During E-beam deposition, this lower melting point enhances atomic mobility, promoting local grain growth and crystallite formation even without a post-deposition annealing process. Moreover, the high thermal energy supplied by the E-beam activates residual β - Ga_2O_3 phase characteristics within the film. While the overall structure remains largely amorphous, localized regions exhibit β -phase-like behavior, contributing to the elevated E_g value. For comparison, Figure 7b shows the E_g calculation for undoped Ga_2O_3 thin films, which yielded an E_g of 3.78 eV. This value is significantly lower than the E_g of the W-doped Ga_2O_3 thin films, further supporting the conclusion that the increase in the bandgap is primarily a result of the E-beam-induced partial crystallization and the synergistic role of WO_3 in enhancing crystallinity during deposition.

To enhance the electrical conductivity of as-deposited Ga₂O₃ thin films, which are inherently insulating, this study introduced WO₃ as a dopant. As shown by the I-V measurements, the undoped Ga₂O₃ thin films exhibited negligible conductivity, making it nearly impossible to observe any meaningful I-V characteristics. Therefore, the corresponding I-V data for pure Ga₂O₃ thin films are not presented in this work. In contrast, the as-deposited W-doped Ga₂O₃ thin films demonstrated significantly improved electrical conductivity. Electrical characterization was performed using a Keysight B1500A semiconductor device analyzer, and the results are presented in Figure 8. Within the voltage range of −2 V to +2 V, the W-doped Ga₂O₃ thin films exhibited a clear conductive response, with the maximum current density reaching approximately 3×10^{-3} A/cm². This result confirms that WO₃ doping effectively enhances the electrical performance of Ga₂O₃ thin films, suggesting their potential for use in electronic device applications. Ga₂O₃ is generally known to exhibit n-type semiconducting behavior due to the presence of intrinsic defects or impurities that generate excess electrons within the bandgap. However, in practice, it is challenging for E-beam-deposited pure Ga₂O₃ thin films to display such n-type behavior; this result is caused by the limited defect formation or insufficient carrier activation under the deposition conditions.

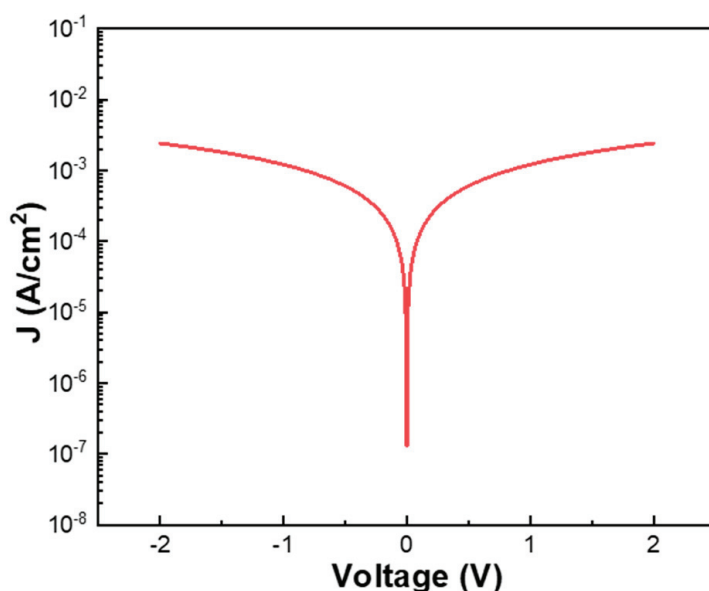


Figure 8. Current–voltage curve of the W-doped Ga₂O₃ thin films.

In the case of W-doped Ga₂O₃ thin films, the enhanced n-type semiconducting characteristics are believed to arise from multiple contributing factors. WO₃ itself is known to be an easily tunable semiconductor that can exhibit either n-type or p-type behavior depending on its stoichiometry and defect states [33]. The current–voltage characterization demonstrated that the as-deposited W-doped Ga₂O₃ thin films exhibit significantly enhanced electrical properties. To further investigate these properties, Hall effect measurements were conducted on the as-deposited W-doped Ga₂O₃ thin films. The results revealed a carrier mobility of 4.2×10^0 cm²/Vs, a carrier concentration of 2.135×10^{16} /cm³, and a resistivity of 1.01×10^2 Ω·cm. Since the Hall coefficient exhibits a negative value, it indicates that the W-doped Ga₂O₃ thin films are n-type semiconductors. In contrast, the undoped Ga₂O₃ thin films showed negligible conductivity, rendering it impossible to accurately measure mobility and carrier concentration. These findings highlight the substantial improvement in electrical performance achieved through W doping.

The conductivity characteristics (current–voltage curve) and Hall parameters are significantly influenced by various factors such as the film thickness, doping concentration, material purity, and fabrication conditions employed during deposition. In this study, the incorporation of W into the Ga_2O_3 matrix could introduce donor states and increase the free electron concentration, thereby promoting n-type conduction in the resulting thin films. These parameters collectively govern the electrical behavior of W-doped Ga_2O_3 thin films, underscoring the inherent complexity in optimizing their conductivity for practical applications. WO_3 can be readily incorporated into the Ga_2O_3 matrix during high-temperature deposition processes, primarily due to several favorable characteristics. First, WO_3 has a notably lower melting point compared to Ga_2O_3 , allowing it to exist in a molten-like state under deposition conditions, which promotes its interaction and integration with the host matrix. The enhanced conductivity of the W-doped Ga_2O_3 thin films can be attributed to the incorporation of W^{6+} ions, which increases the impurity concentration and effectively donates free carriers within the Ga_2O_3 matrix. Moreover, the high-temperature melting and deposition process inherent to E-beam evaporation facilitates the deeper and more uniform incorporation of WO_3 into the Ga_2O_3 lattice, further amplifying these effects and resulting in the observed enhancement in conductivity.

Additionally, the ionic radius of W^{6+} (~0.060 nm) is close to that of Ga^{3+} (~0.062 nm), facilitating the effective substitution of Ga atoms within the Ga_2O_3 lattice. This similarity in ionic size minimizes lattice distortion and supports the structural incorporation of tungsten ions. WO_3 is intrinsically an n-type semiconductor, and the W^{6+} dopants serve as donor ions, contributing free electrons to the system. When incorporated into Ga_2O_3 , these electrons enhance the overall carrier concentration and improve the film's electrical conductivity. Furthermore, the introduction of W^{6+} may alter the electronic band structure of Ga_2O_3 , resulting in the formation of shallow donor levels or band tailing. Such modifications facilitate charge carrier generation and transport, thereby amplifying the n-type semiconducting behavior. In this study, we successfully transformed initially insulating Ga_2O_3 thin films into conductive W-doped Ga_2O_3 thin films through controlled WO_3 doping. This transition highlights the effectiveness of our doping strategy and its significant impact on modifying the electrical properties of Ga_2O_3 thin films. The results demonstrate not only the feasibility of tuning conductivity via W incorporation but also the potential for employing such doped films in next-generation electronic and optoelectronic devices.

Figure 9 presents the I–V characteristics of heterojunction diodes formed by W-doped Ga_2O_3 thin films on p-type and p^+ -type Si substrates. Both device configurations exhibit pronounced rectifying behavior, indicating that the W-doped Ga_2O_3 thin films/p-Si structure possesses Schottky contact characteristics. The conduction mechanism is likely governed jointly by the potential barriers formed at both the metal–oxide and oxide–silicon interfaces. When the Si substrate is p-type, the forward turn-on voltage of the diode is approximately 5.5 V, with a maximum forward current density of about 0.10 mA/cm^2 at an applied bias of 20 V. In reverse bias, the conduction is weak, with a maximum reverse current density of around 0.010 mA/cm^2 at –20 V. When the substrate is changed to p^+ -type Si, the device exhibits a significantly lower forward turn-on voltage, indicating that it conducts more readily. The forward turn-on voltage decreases to approximately 2.5 V, after which the current rises sharply, reaching 1.0 mA/cm^2 at around 3 V. In reverse bias, conduction becomes more pronounced: the diode begins conducting in reverse at approximately –3.6 V, and by –3.8 V, the reverse current reaches the instrument's measurable limit of 1.0 mA/cm^2 .

The observed differences in the electrical characteristics between devices fabricated on p-type and p^+ -type Si substrates can be attributed to variations in the interfacial barrier properties. For the p-type Si substrate, a relatively higher barrier is formed at the $\text{Ga}_2\text{O}_3/\text{Si}$

interface, requiring a larger forward bias (~ 5.5 V) to initiate conduction. As a result, the forward current density increases gradually, while the reverse leakage current remains relatively low. In contrast, the heavily doped p^+ -type Si substrate reduces the interfacial barrier height due to enhanced band bending and Fermi level alignment, thereby facilitating carrier injection or tunneling across the junction. This leads to a much lower forward turn-on voltage (~ 2.5 V) and significantly higher forward current. However, the reduced barrier also makes the junction more susceptible to reverse conduction, resulting in a pronounced increase in reverse leakage current, which becomes measurable at approximately -3.6 V. These results are consistent with the Hall effect measurements, which revealed an increase in the carrier concentration and conductivity with higher doping levels, confirming that an increased dopant concentration enhances carrier transport efficiency. Notably, the I-V curve of the p^+ -type Si sample exhibits a distinct current surge in the reverse bias region, a behavior reminiscent of a Zener diode. This phenomenon can be attributed to the following:

- Barrier reduction and tunneling effect—The higher doping concentration in the p^+ -Si substrate lowers the potential barrier, concentrating the built-in electric field within the junction region. At a certain critical reverse bias, this facilitates electron tunneling (Zener tunneling) or defect-assisted conduction.
- Depletion width compression—The high hole concentration in p^+ -Si produces a strong screening effect, further narrowing the depletion region and enabling the junction to enter reverse conduction more easily.

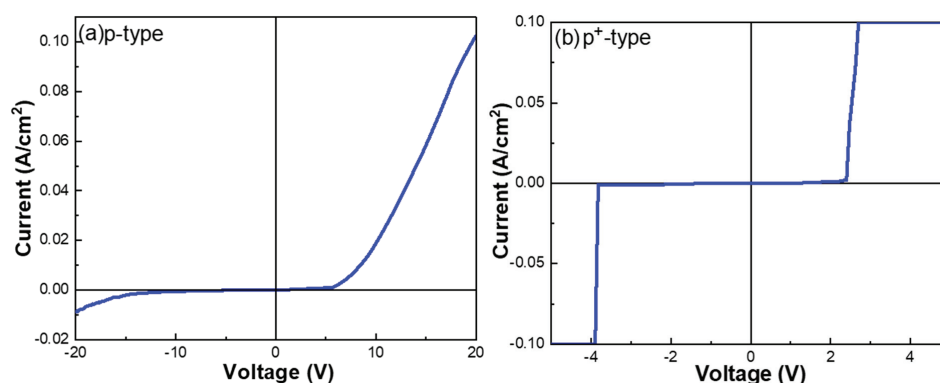


Figure 9. The I-V characteristics of heterojunction diodes formed by W-doped Ga_2O_3 thin films on (a) p-type and (b) p^+ -type Si substrates.

This reverse conduction behavior not only highlights the substantial impact of heavy doping on the band structure and junction electric field distribution but also suggests that such devices, when operated in a stable Zener region, hold potential for applications in overvoltage protection, voltage regulation circuits, and related device designs.

4. Conclusions

This study systematically investigated the structural, compositional, optical, and electrical properties of as-deposited un-doped and W-doped Ga_2O_3 thin films prepared via E-beam deposition. Surface morphology analysis revealed that un-doped Ga_2O_3 thin films exhibit smooth, densely packed particles but are interspersed with cracks and voids, defects commonly arising from the non-uniform growth inherent to E-beam processes. In contrast, W-doped Ga_2O_3 thin films displayed distinct microcrystalline features, indicating that tungsten incorporation induces partial crystallization within the otherwise amorphous matrix. EDS results confirmed that the atomic ratios of Ga, O, and W in both large-area and small-area scans closely match the nominal target composition, demonstrating high compositional fidelity in the deposition process. Complementary XPS analysis revealed a

depth-dependent W distribution: near the surface, the W concentration is relatively low, gradually increasing with depth and reaching its peak near the film–substrate interface (~ 200 nm), where it slightly exceeds the Ga content. Conversely, the Ga concentration steadily decreases with increasing depth. Optical measurements indicated a noticeable bandgap widening with W doping. The W-doped Ga_2O_3 thin films exhibited an E_g of 4.132 eV, higher than that of the un-doped Ga_2O_3 thin films (3.784 eV) and the typical values reported for amorphous Ga_2O_3 . This enhancement can be attributed to structural modification and local ordering effects induced by tungsten incorporation. The electrical characterization of the heterojunction diodes further highlighted the influence of substrate doping. For devices with p-type Si substrates, the forward turn-on voltage was ~ 5.5 V, with a maximum forward current density of ~ 0.10 mA/cm² at 20 V and minimal reverse conduction (~ 0.010 mA/cm² at -20 V). Substituting a p⁺-type Si substrate significantly improved forward conduction, reducing the turn-on voltage to ~ 2.5 V and yielding a rapid current increase to ~ 1.0 mA/cm² at ~ 3 V. In reverse bias, conduction commenced at ~ -3.6 V and quickly reached the measurement limit (~ 1.0 mA/cm²) at ~ -3.8 V. Overall, the findings demonstrate that W doping effectively tailors the microstructure, enhances the optical bandgap, and influences the carrier transport properties of Ga_2O_3 thin films. Furthermore, the choice of substrate doping type plays a crucial role in determining heterojunction diode performance, offering a viable pathway for optimizing Ga_2O_3 -based electronic and optoelectronic devices.

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Article

Tribocatalysis of Cefuroxime Axetil: Effect of Stirring Speed, Magnetic Rods, and Beaker Material Type

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Abstract

Mechanical energy is a plentiful, environmentally friendly, and sustainable energy source in the natural world. In this paper, ZnO tribocatalysts were synthesized using the hydrothermal and sol–gel methods. Under magnetic stirring, the catalyst particles and the polytetrafluoroethylene (PTFE)-sealed magnetic bar rub against each other, transferring electrons across the contact interface. While the PTFE absorbs the electrons, holes are left in the catalyst. The holes in the valence band of sol–gel catalysts exhibit strong oxidative ability, allowing for effective oxidation of organic pollutants. Tribocatalytic tests demonstrated that sol–gel ZnO could remove the antibiotic Cefuroxime Axetil (Axetine) more quickly when stirred magnetically in the dark. Sol–gel and hydrothermal ZnO was enhanced by varying the stirring speed (100, 300 and 500 rpm), the length (2, 2.5 and 3 cm) of magnetic rods, and the type of beaker material (glass and polytetrafluoroethylene). This work presents a viable pathway for transforming environmental mechanical energy into chemical energy, which could be utilized in sustainable energy and environmental remediation, in addition to creating a green tribocatalysis method for the oxidative purification of organic pollutants.

Keywords: tribocatalysis; ZnO; Cefuroxime Axetil degradation

1. Introduction

Wastewater poses a significant threat to the global environment and is a major cause of harm to human health due to its complex composition and slow degradation rate [1–3]. One promising method for degrading organic compounds in wastewater is the utilization of catalysts and widely dispersed environmental energy sources, such as solar, thermal, and mechanical energy [4–7]. A catalyst for the photocatalysis (e.g., degradation of pollutants, water splitting, CO₂ reduction) needs to meet several conditions: It must absorb light of the desired energy range (usually UV or visible), the conduction band (CB) should be more negative than the reduction potential of the target reaction (e.g., $H^+ \rightarrow H_2$). The valence band (VB) should be more positive than the oxidation potential (e.g., $OH^- \rightarrow \bullet OH$). Photoexcited electrons and holes must not recombine quickly. The material should promote separation and migration to the surface where reactions occur. It must be chemically and thermally stable under irradiation and in the reaction environment (aqueous, oxidative, etc.). Many semiconductors photocorrode. Preferably inexpensive, environmentally safe, and easy to synthesize at scale. Solar energy is a clean and renewable resource that certain photocatalysts can harness to facilitate various photocatalytic reactions, including the breakdown of organic pollutants, the reduction of CO₂, and the decomposition of water into H₂ [8–10]. However, both thermal and solar energy can be unstable, as they depend

on environmental conditions. An eco-friendly approach for treating wastewater is the photocatalytic degradation of organic pollutants, which occurs when wastewater is subjected to ultraviolet or visible light. Despite this, the practical applications of photocatalysis technology are limited due to the high rate of photoexcited carrier recombination. Also, not every photocatalyst is effective—only those meeting the electrochemical (if electron–hole recombination is too fast, efficiency will be negligible; If the band gap is too narrow, the CB/VB may not straddle the redox potentials needed for the reaction) and stability criteria are useful.

The introduction of pyroelectric catalysis offers new prospects for energy-driven breakdown of organic pollutants. Most pyroelectric catalysts require a significant rate of temperature change to effectively convert thermal energy into chemical energy. However, achieving the necessary conditions for thermal catalysis during natural diurnal processes can be challenging [11,12]. Therefore, finding a novel catalytic method is crucial for addressing current environmental pollution challenges. Both tribocatalysis and piezocatalysis harness mechanical energy to initiate a series of chemical reactions [13]. Piezocatalysis is based on the deformation of piezoelectric materials subjected to external forces [14]. The charges generated from this deformation fuel various electrochemical catalytic processes, including the breakdown of organic pollutants, water splitting, and CO₂ conversion [15–17]. Today, most piezocatalysis is performed using ultrasound, as a substantial external force is needed to deform the piezoelectric material. An innovative catalytic technique known as tribocatalysis captures weak mechanical energy from the environment to induce chemical reactions [18]. The tribocatalysis effect has garnered significant attention due to its unique advantages of reproducibility and environmental sustainability [19–21]. The triboelectric effect generates triboelectric charges when two materials come into contact with one another [22–24]. Utilizing the positive and negative triboelectric charges produced during the friction process to react with hydroxyl ions and oxygen in water, respectively, presents a promising method for reducing environmental pollution through pollutant decomposition [25,26]. The tribocatalysis effect has led to substantial advancements in environmental dye pollution to date. Thus, utilizing the frictional effect of nanomaterials for dye degradation is an effective concept. The drug degradation with nanomaterials with varying morphologies has not been evaluated in these studies. The research object for this work was chosen to be ZnO nanomaterials. Zinc oxide is widely studied because the band gap is approximately 3.2 eV, similar to that of TiO₂. It helps reduce electron–hole recombination. It is abundant, inexpensive, non-toxic (relatively green), and chemically stable. It can be synthesized into nanostructures (nanorods, nanoparticles, nanosheets) that increase surface area and reactivity. The large specific surface area is generally considered crucial for materials used in tribocatalysis.

This work examined the tribocatalysis activity of degrading cephalosporin antibiotics under dark conditions using hydrothermal and sol–gel ZnO nanomaterials with varying morphologies. By adjusting the stirring speed, and quantity of magnetic PTFE rods, as well as the types of beaker materials, the degradation efficiency can be improved. All findings demonstrate that the catalytic materials' larger specific surface area can more effectively promote charge carrier separation and transfer.

2. Results and Discussion

2.1. The Morphology, Specific Area and Structure of Zinc Oxide

On one hand, the material's specific surface area is determined by the shape of the catalyst. Conversely, it influences the force conditions during material friction. ZnO is widely used in sensors, batteries, luminescence, and catalysis. Its advantages include non-toxicity, good compatibility, chemical stability, and thermal stability. This study investigates

how specific surface area and structural morphology affect the tribocatalytic breakdown of cephalosporin antibiotics using sol–gel and hydrothermal ZnO. The morphology of two types of ZnO is examined with scanning electron microscopy (Figure 1). These micrographs clearly display differences in the surfaces of the samples. The hydrothermal ZnO, shown in Figure 1a, features irregularly shaped particles, varying in size and shape, scattered across a relatively smooth surface. The sol–gel ZnO sample has a homogeneous surface with small particles. The average particle diameter for hydrothermal ZnO is $0.9 \pm 0.2 \mu\text{m}$, according to an analysis of the SEM images; in the sol–gel ZnO case, this diameter drops to $0.5 \pm 0.1 \mu\text{m}$. The different method, respectively, the low treatment temperature, does not preserve the morphology of the samples. Test results indicate that these two materials have specific surface areas of 10.3 and $14.5 \text{ m}^2/\text{g}$, respectively. The findings demonstrate that a higher specific surface area promotes more effective tribocatalysis. This observation aligns with literature data [19,27]. The insets show minimal change in the morphology of ZnO after tribocatalysis. This is also supported by the values of the specific surface area (11.8 and $15.7 \text{ m}^2/\text{g}$). The magnetic stirring during tribocatalytic tests caused a slight increase in the ZnO surface area, indicating an increase in the number of surface sites. This is probably due to a minor change in surface morphology (insets in Figure 1a,b) resulting from the prolonged degradation of the drug.

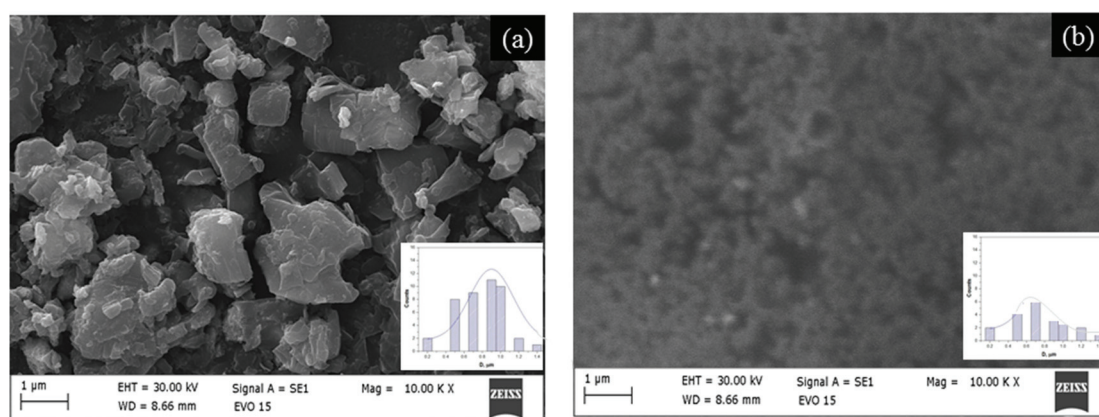


Figure 1. SEM images of hydrothermal (a) and sol–gel (b) ZnO. The insert is the particle size distribution.

ZnO samples are analyzed using energy-dispersive X-ray spectroscopy (EDS). Hydrothermal and sol–gel ZnO are the two types of tribocatalysts whose atomic percentages of elements are known. There were no additional elemental peaks discovered, confirming the ZnO tribocatalysts' purity (Figure 2).

Figure 3 displays TEM images of the hydrothermal and sol–gel ZnO distinct phases. Selected area electron diffraction patterns (SAED, Figure 3c) obtained from TEM images validate the hexagonal wurtzite structure of ZnO and are consistent with the XRD data. The interplanar distances of the crystal lattice of the two varieties of ZnO catalysts (d_{100} –0.2817 nm, d_{101} –0.2478 nm, and d_{102} –0.1807 nm) do not alter, as shown in Figure 3c.

Figure 4 shows the ZnO XRD spectra of the two morphologies. The main diffraction peaks appear at 31.85° , 34.45° , 36.3° , 47.75° , 56.8° , and 63.05° , corresponding to (100), (002), (101), (102), (110), and (103). All peaks confirm that the zinc oxide phase is hexagonal wurtzite and match the standard card, PDF #96-230-0117 [28]. The samples are of high purity and good crystallinity, as indicated by the sharp diffraction peaks and the absence of impurity peaks.



Figure 2. EDS spectra of hydrothermal (a) and sol-gel (b) ZnO.

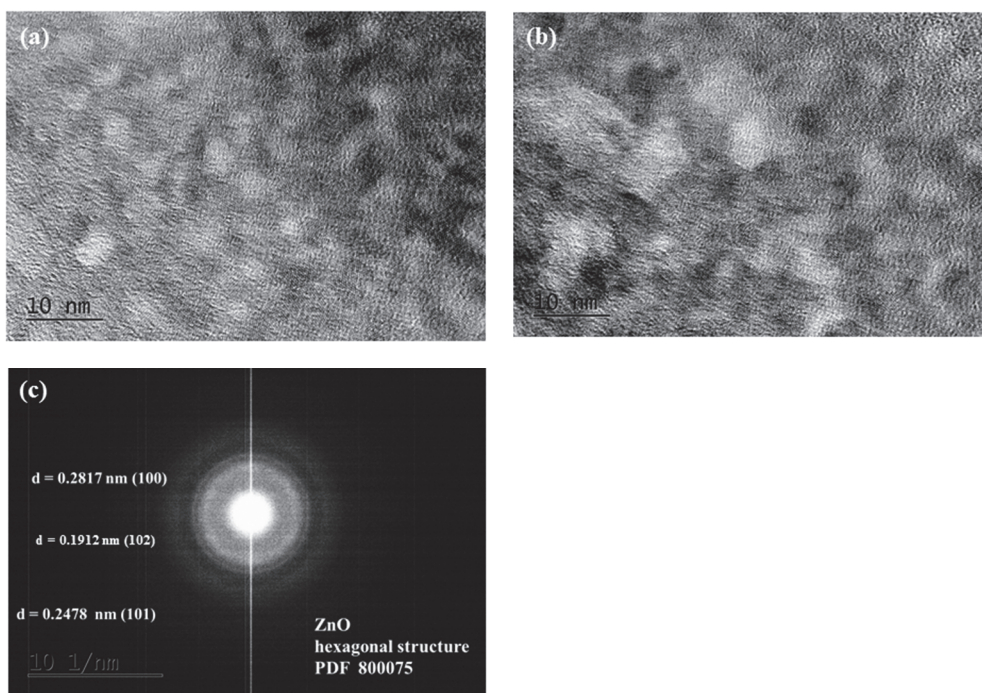


Figure 3. HRTEM image of (a) hydrothermal and (b) sol-gel ZnO; (c) SAED pattern.

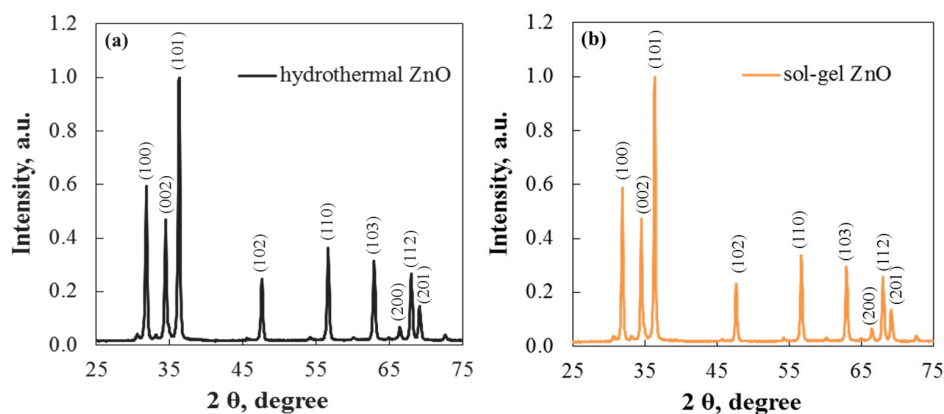


Figure 4. XRD pattern of (a) hydrothermal and (b) sol-gel ZnO.

Additionally, Table 1 shows the structural parameters that are calculated for sol-gel and hydrothermal tribocatalysts. Indicating that the crystalline lattice stayed comparatively stable, the average crystallite size decreased. The hydrothermal and sol-gel samples' structural parameters are shown in Table 1. In both samples, it is discovered that the ZnO unit cell parameters are remarkably similar. The calculations used positive values to indicate tensile strain. The sol-gel particles showed a greater magnitude of tensile strain than the pure samples, and the strain in the samples derived from sol-gel is tensile, based on the values in Table 1.

Table 1. The XRD patterns of the sol-gel and hydrothermal samples were used to calculate the structural parameters.

ZnO Tribocatalysts	Crystallite Size, nm	Parameters, Å
Hydrothermal	42.4	a, b = 3.250 c: 5.207
Sol-gel	36.9	a, b: 3.2407 c: 5.2017

2.2. Optical Properties of Hydrothermal and Sol-Gel Zinc Oxide

One method commonly used to study the optical properties of materials is UV-visible absorption spectroscopy. Tauc's equation is used to plot $(\alpha E)^2$ with respect to E and extrapolate as a straight line along the x-axis to determine the bandgap energy values. The values obtained from extrapolation for the ZnO samples' energy band gap are shown in Figure 5. The band gaps of hydrothermal (3.25 eV) and sol-gel (3.23 eV) ZnO are nearly identical. Therefore, based on these results, there is no difference in the band gap.

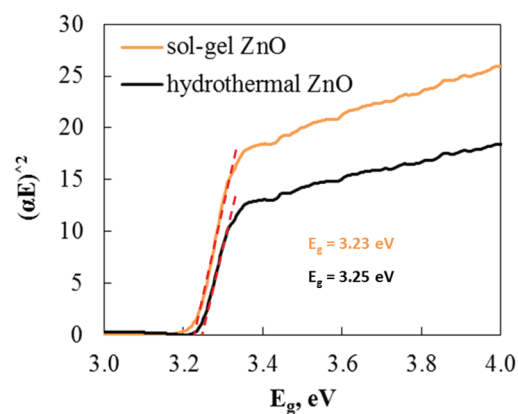


Figure 5. Energy band gap calculated from Tauc's equation of hydrothermal and sol-gel ZnO.

2.3. Tribocatalysis of Cefuroxime Axetil—Effect of Stirring Speed (100, 300 and 500 rpm)

The degradation of the Cefuroxime Axetil under dark conditions was assessed to determine the tribocatalytic efficiency of hydrothermal and sol-gel ZnO powders. Magnetic stirring with a 2.5 cm rod facilitated the tribocatalytic process, and the drug concentration was 75 mg/L in all tests. UV-vis spectroscopy was used to monitor Axetine degradation by tracking the absorption maxima at 291 nm. Sol-gel ZnO powder shows the fastest degradation rate after 24 h of friction, as demonstrated by the tribodegradation results at various stirring speeds in Figure 6. Conversely, a control experiment without a tribocatalyst exhibited very little degradation (about 4%), highlighting the catalyst's importance in the friction process. Both sample types exhibit catalytic efficiencies following the sequence 500 rpm > 300 rpm > 100 rpm. The higher efficiency of sol-gel ZnO is likely due to its surface morphology. The entire surface is uniform with small particles, which improves carrier participation in redox reactions [27]. The morphology of the hydrothermal samples, where agglomeration of particles is observed, is significantly different. As a result of agglomeration, the active surface area of the catalyst decreases, and the likelihood of recombination of the generated electron-hole pairs increases. The reaction rate constants (k), shown in Figure 6b,d, were determined using the pseudo-first-order kinetics equation $-\ln(C/C_0) = kt$, commonly used for catalytic removal [29]. Sol-gel ZnO exhibited the highest rate constant ($k = 0.087 \text{ h}^{-1}$) at 500 rpm, further supporting these results. Degradation efficiencies (D , $D(\%) = ((C_0 - C)/C_0) \times 100$, where C and C_0 are at time t and the initial concentration) for the sol-gel ZnO sample were 60.68%, 78.94%, and 88.82% at 100, 300, and 500 rpm, respectively. The tribocatalytic efficiency increases with rotation speed because higher speeds enhance contact between drug molecules and the catalyst, promoting the tribocatalytic reaction. Similarly, Wu et al. [30] observed that in the tribocatalytic degradation of Rhodamine B by Bi_2WO_6 , pollutant degradation efficiency rose with increasing rotation speed. However, excessively high speeds can cause the stirrer to rebound during stirring, splashing the catalyst onto the beaker wall and reducing catalytic efficiency. The aforementioned research demonstrates that magnets are significant in the tribocatalytic process, with friction area, frequency, and charge transfer efficiency between materials all closely linked to the formation of tribocatalytic charges. The percentages of Axetine decomposition and rate constants after the initial tribocatalytic cycle are shown in Table 2.

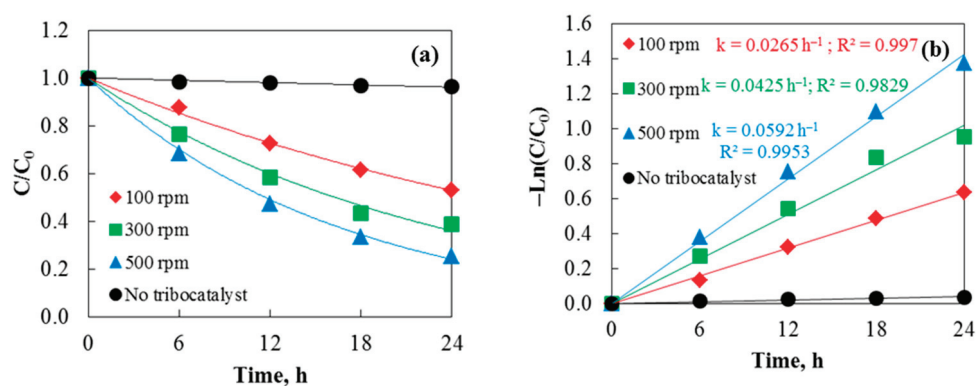


Figure 6. Cont.

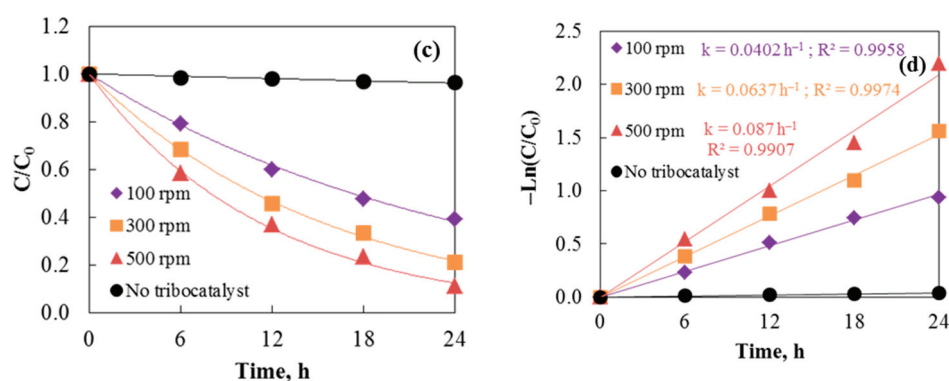


Figure 6. Tribocatalysis of Cefuroxime Axetil using hydrothermal (a,b) and sol-gel (c,d) ZnO at three different stirring speeds with 2.5 cm magnetic rod.

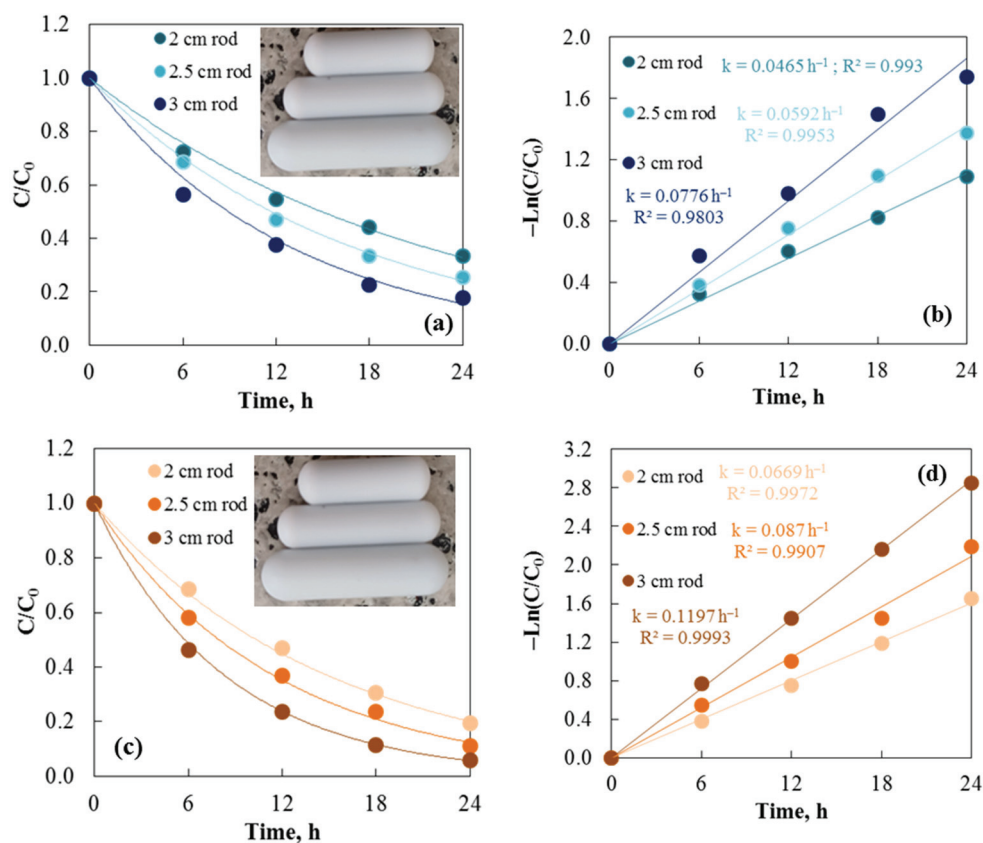
Table 2. The values of rate constants and percent of Axetine decomposition using the ZnO.

Zinc Oxide Powders	100 rpm		300 rpm		500 rpm	
	k, h ⁻¹	D, %	k, h ⁻¹	D, %	k, h ⁻¹	D, %
hydrothermal	0.0265	46.90	0.0425	61.38	0.0592	74.65
sol-gel	0.0402	60.68	0.0637	78.94	0.0807	88.82

2.4. Tribocatalysis of Cefuroxime Axetil—Effect of Length of Magnetic Rods

The number, size, shape, length, and speed at which the stirring rods are used all alter the friction efficiency between the materials, which in turn affects the tribocatalytic efficiency. Three magnetic rods of different lengths (2, 2.5, and 3 cm) are used to demonstrate the tribocatalytic efficiencies of hydrothermal and sol-gel ZnO powders for degrading Axetine in Figure 7. It illustrates how the efficiency of all catalysts increases as the rod length increases. Figure 7b,d, which display the corresponding rate constant values for both tribocatalysts, confirm the trend of higher tribocatalytic efficiency at longer lengths. The highest reaction rate was achieved with the longest rod (3 cm): $k_{\text{sol-gel}} = 0.1197 \text{ h}^{-1}$ and $k_{\text{hydrothermal}} = 0.0776 \text{ h}^{-1}$. The contact area between the rod and the catalyst increases with bar size. As a result, the catalyst's tribocatalytic efficiency improves as the rod length increases [31,32]. All of these findings have been independently verified from Wu et al. [31], who also studied the effect of stirring rods on the tribocatalytic degradation of Rhodamine B, using rod lengths of 2.0, 2.5, and 3.0 cm. The results show that the degradation rate of Rhodamine B increased as the stirring rod's length grew.

The tribocatalytic properties of ZnO powders are confirmed and contrasted in Figure 7e for the degradation of Axetine dissolved in distilled water using rods of three distinct lengths. The decomposition of the drug with a 2 cm rod is 66.47% and 80.74% using hydrothermal and sol-gel ZnO, while it increases to 74.65 and 88.82%, 82.44 and 94.21%, at 2.5 and 3 cm, respectively. High gravity is created and the catalyst-stirring rod contact surface is improved by the 3 cm stirring rod's greater mass compared to the 2.5 and 2.0 cm stirring rods [33].



(e) Tribocatalysis of Axetine

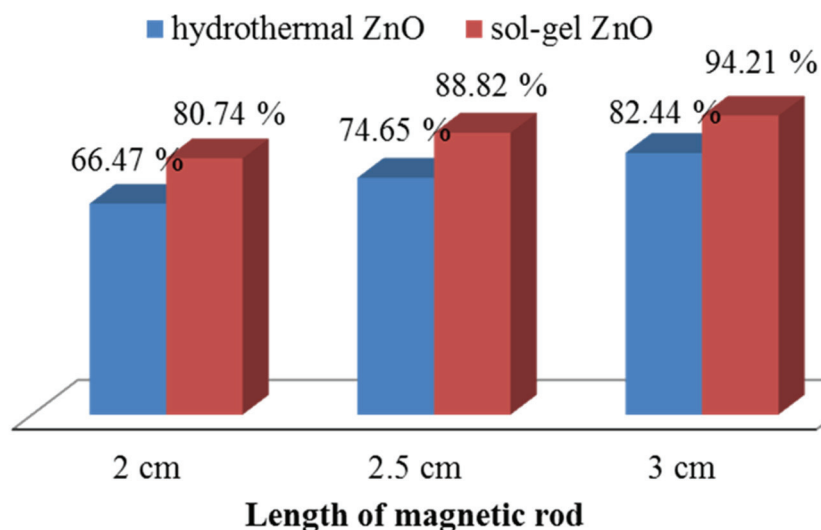


Figure 7. Tribocatalysis of Cefuroxime Axetil at 500 rpm stirring speed using hydrothermal (a,b) and sol-gel (c,d) ZnO with three different lengths of magnetic rods. Degrees of Axetine degradation versus length of magnetic rods (e).

2.5. Tribocatalysis of Cefuroxime Axetil—Effect of Type Beaker Material

The efficiency of tribocatalysis is greatly affected by electron transfer between the friction pairs. During stirring, electron transfer may occur due to friction between the catalyst and the vessel or between the stirrer and the reactor bottom. Since the vessel significantly influences the tribocatalytic efficiency, the material of the vessel is now considered during tribocatalysis. It was discovered that polytetrafluoroethylene can absorb more

electrons than glass during the friction process [34]. Consequently, the catalyst releases more electrons upon contact with the PTFE stirrer and PTFE beaker, resulting in increased tribocatalytic efficiency. To investigate the impact of beaker material on tribocatalysis using ZnO as a catalyst, two different beakers were used. Experimental results showed that the degradation rates of Axetine in the glass and PTFE beakers were 94.2% and 99.7%, respectively, after 24 h of stirring with a PTFE rod (Figure 8). The same trend was observed with hydrothermal tribocatalysts, though with less degradation of the drug. The electron affinity of different materials influences the electron transfer caused by friction [35,36]. A higher tribocatalytic efficiency occurs when the catalyst interacts with the PTFE beaker and stirring rod because PTFE can transfer more electrons during friction than glass. Additionally, a dark phase adsorption experiment was conducted with Axetine in a glass and PTFE beaker in the presence of ZnO tribocatalysts and a 3 cm magnetic rod. In all four cases, the drug concentration decreased by 6–10%. The adsorption data are shown in Figure 8c.

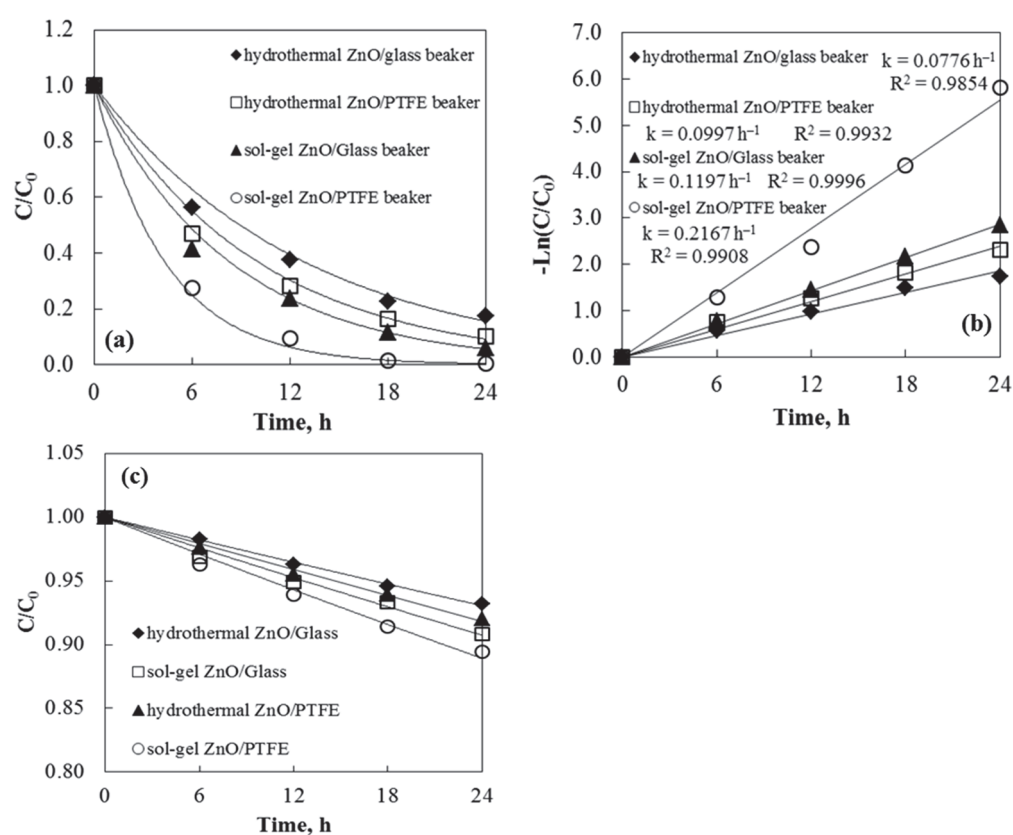


Figure 8. Tribocatalysis and beaker materials' effects: (a) degradation of Axetine at 500 rpm stirring speed; (b) kinetic fitting. Adsorption test in the presence of tribocatalyst and magnetic rod, without stirring (c).

Figure 9 shows a potential tribocatalysis principle diagram. Stirring the ZnO catalysts and applying friction results in the production of positive (q^+) and negative (q^-) charges on the surfaces of the ZnO powders and the PTFE stirring rod [37]. When ZnO is excited by friction, it produces both positive and negative charges. Like photocatalytic drug decomposition based on photogenerated carriers, Cefuroxime Axetil decomposition can also be accomplished by triboelectrically generated electric charges. Although the positive charges on the ZnO powders' surface are released into the water, creating active $\text{OH}^\bullet$ radicals, superoxide radicals ($\text{O}_2^{\bullet-}$) are created when oxygen molecules react with negative charges [37–40]. The antibiotic is further degraded by these radicals into inorganic substances like water and carbon dioxide.

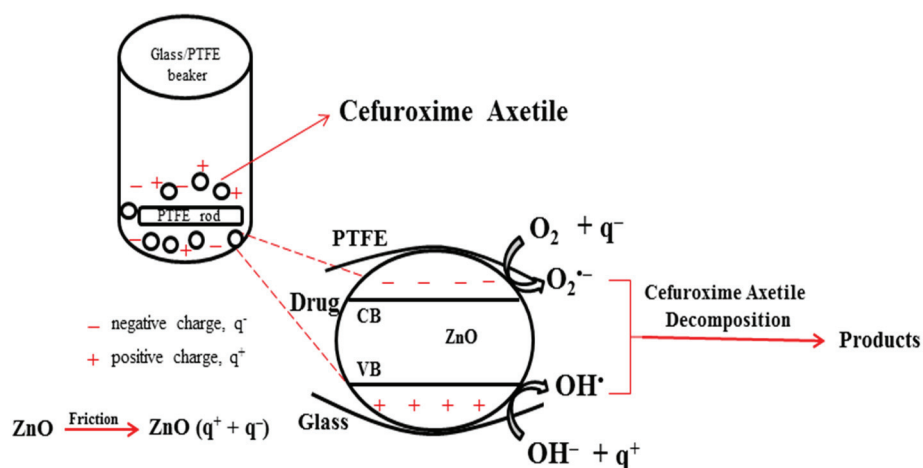


Figure 9. Diagram of a potential reaction mechanism for the tribocatalytic effect.

The role of the holes, superoxide, and hydroxyl radicals involved is demonstrated by a radical scavenger assay. Figure 10 shows the data. Axetine's degradation by holes, superoxide, and hydroxyl radicals was quantified by adding ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), ascorbic acid (AA), and isopropyl alcohol (IPA) scavengers, which capture the corresponding reactive species [38–40]. The addition of EDTA-2Na and IPA did not significantly alter the degradation efficiency of Axetine. As a result, h^+ plays a negligible part in the drug's tribodegradation over ZnO tribocatalyst [31,41,42]. But AA showed a stronger inhibition (compared to EDTA decreases by about 8–13% in glass and 13–27% in PTFE beaker), suggesting that the production of superoxide radicals contributes more to the rate of Axetine degradation. As illustrated in Figure 10, the tribocatalysis process of Axetine drug degradation was 67.11%, 94.84%, and 89.32% when AA, EDTA-2Na, and IPA were added. In contrast, a PTFE beaker containing sol-gel ZnO powder achieved 99.7% degradation without the addition of any scavengers. Superoxide radicals were crucial for drug breakdown, as shown in Figure 10, which shows that the AA scavenger caused the least amount of degradation.

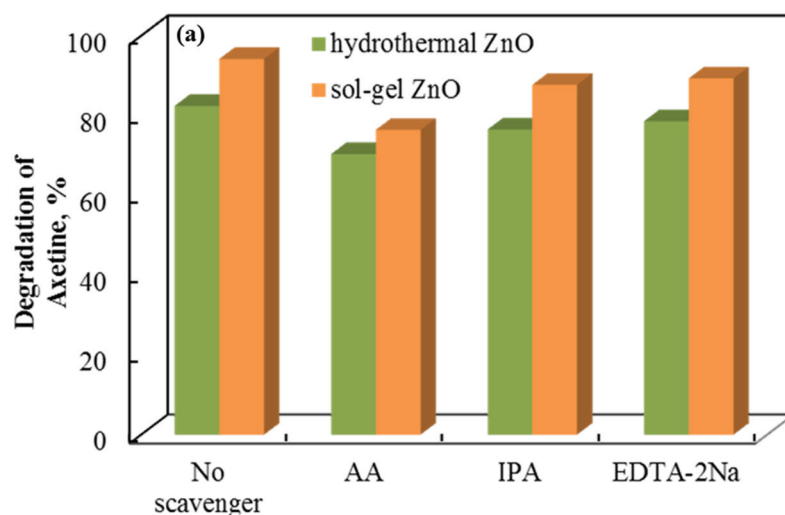


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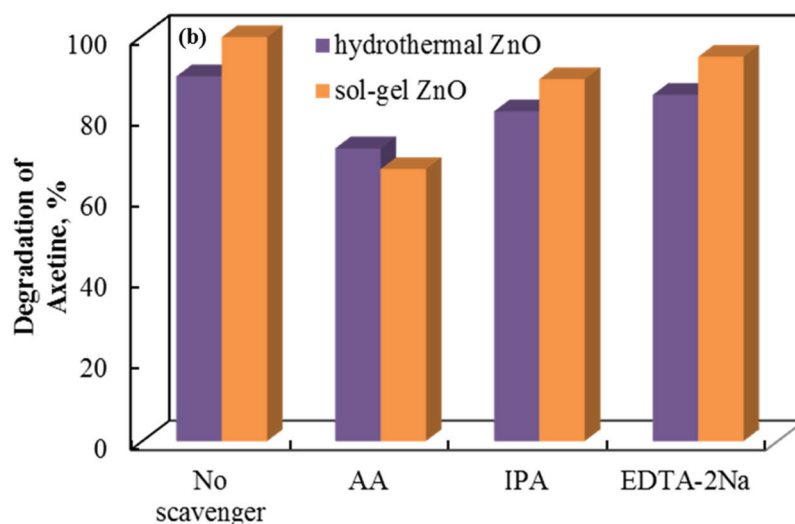


Figure 10. Radical scavenger assay for the tribocatalytic decomposition of Axetine in (a) glass and (b) PTFE beaker with ZnO.

UV-vis spectroscopy was used to monitor the absorption maximum at 291 nm, tracking the degradation of Cefuroxime Axetil at 500 rpm. Spectral changes in the degradation of cephalosporin antibiotic were reviewed to ascertain the activity of the two types of ZnO and the various beaker materials during the tribocatalytic process. Figure 11 presents the UV-vis spectra and the percent degradation of Axetine.

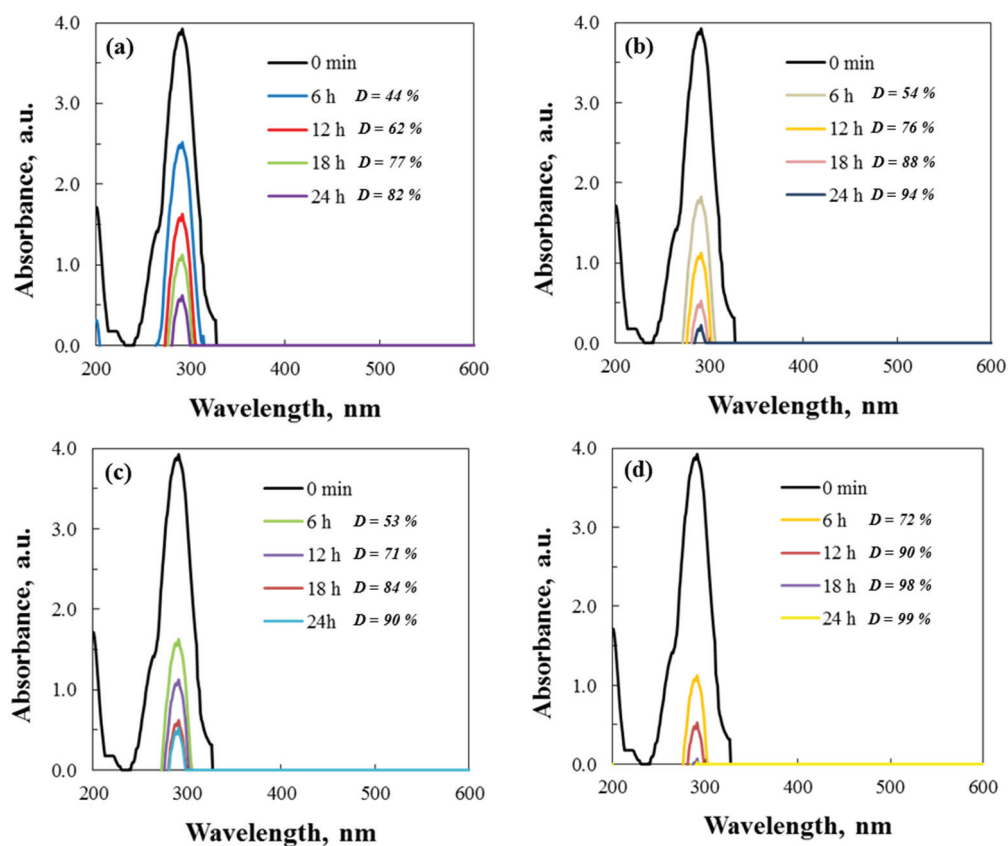


Figure 11. Spectral data for the tribodegradation of Axetine in glass ((a) hydrothermal and (b) sol-gel ZnO) and PTFE ((c) hydrothermal and (d) sol-gel ZnO) beaker.

A possible mechanism for Cefuroxime Axetil degradation, caused by a reaction with hydroxyl radicals, has been reported in the literature [43]. According to Hernández-Coronado et al. [43], who used titanium dioxide, $\text{HO}^\bullet$ radicals cleave the $\text{N}=\text{C}$ double bond in the first step, causing the central heterocyclic molecule to open up. The hydroxyl radicals attack and produce smaller molecules, such as methane, ethanoic, oxalic, propanoic, and 2,4-hexene-1,6-dioic acids. As a result of the subsequent attack, the antibiotic is degraded to carbon dioxide and water. In this article related to the tribocatalysis of Axetine, it is assumed that a similar mechanism is used to degrade the drug. Evidence for this is the straight lines observed in the UV-vis spectrum in Figure 11.

2.6. Tribocatalysis of Cefuroxime Axetil—Effect of Stability

Tribocatalysts used in environmental applications must be able to sustain consistently high tribocatalytic properties over time. Tribocatalytic tests are thus performed to assess the cycling stability of four distinct catalyst types for the degradation of Axetine at 500 rpm. The findings of an investigation into sample regeneration and repurposing are shown in Figure 12, which shows a progressive decline in catalytic quality with each cycle. After three cycles, the tribocatalytic breakdown of Axetine for the hydrothermal ZnO/Glass, sol-gel ZnO/Glass, hydrothermal ZnO/PTFE, and sol-gel ZnO/PTFE catalysts dropped by about 2%. Nonetheless, the nanostructures continued to demonstrate elevated photocatalytic activity following three experimental cycles.

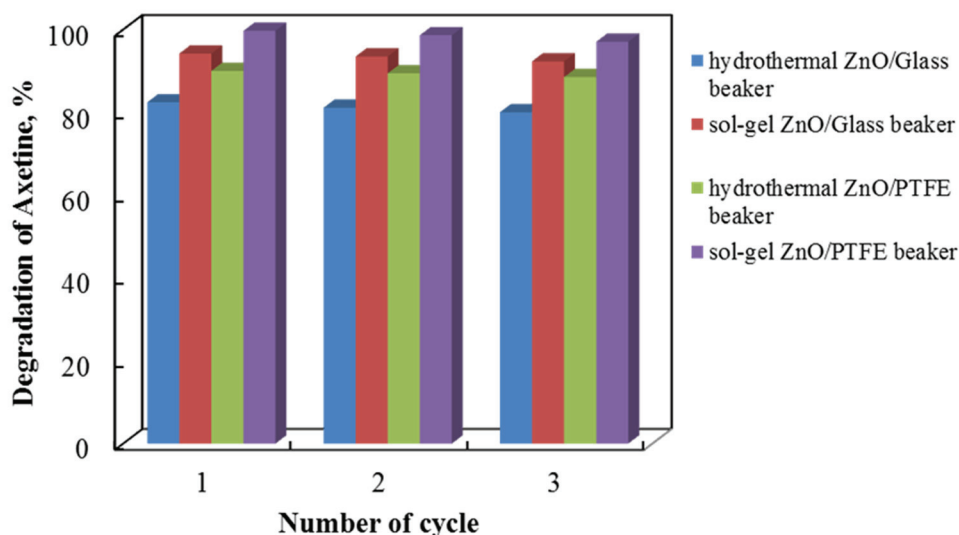


Figure 12. Tribocatalytic stability of hydrothermal and sol-gel ZnO in both types of beaker material with a 3 cm magnetic rod.

3. Materials and Methods

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$, >99.5%), 1-propanol ($\text{C}_3\text{H}_8\text{O}$, >99.0%), triethylamine ($\text{C}_6\text{H}_{15}\text{N}$, >99.5%), sodium hydroxide (NaOH , >99.0%), and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, >99.0%) were sourced from Fluka (Buchs, Switzerland). Distilled water was used in all experiments, and all other chemicals and reagents were of analytical reagent grade.

All tribocatalytic tests utilized the commercial drug Axetine ($\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_{10}\text{S}$, $\lambda_{\text{max}} = 291 \text{ nm}$, 99.0%, cephalosporin antibiotic, antipyretic medication) as a model contaminant. The widespread presence of Cefuroxime Axetil (Axetine) in the environment, particularly in aquatic environments, indicates that it is not a totally safe medication and can have harmful effects because of its widespread use and high production [44]. In addition to increasing liver enzymes, the antibiotic may also decrease platelets, which are cells that aid in blood clotting, and increase eosinophilia, a type of white blood cell [45].

The tribocatalytic tests demonstrated how Axetine breaks down in the presence of various impurities, mimicking natural water systems with distilled water.

To create the hydrothermal ZnO nanoparticles, 50 milliliters of 1-propanol were stirred while preparing $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.1 M) stock solutions. A NaOH solution made in 1-propanol (25 mL) was added to this stock solution while being constantly stirred (300 rpm), adjusting the reactants' pH values between 8 and 11. Under autogenous pressure, these solutions were maintained at various temperatures between 100 and 200 °C for six to twelve hours after being transferred to sealed stainless steel autoclaves lined with PTFE (Polytetrafluoroethylene). They were then allowed to cool down naturally to room temperature. Once the reaction was completed, the white solid products were washed with 1-propanol and dried in a laboratory oven set at 80 °C.

The sol–gel method was the second technique employed to produce ZnO particles. In a round-bottom flask equipped with a reflux condenser, 0.5 g of zinc acetate dihydrate, 0.15 mL of ethylene glycol, 20 mL of 1-propanol, and 0.35 mL of triethylamine were combined and stirred at 300 rpm for 15 min at room temperature. The resulting solution was then stirred for 60 min at 80 °C. To produce powders for the tribocatalytic degradation of Axetine, the zinc oxide particles were rinsed twice with pure 1-propanol, and dried in a lab oven at 80 °C.

To investigate the morphology and microstructure of the obtained samples, we used an imaging device a Zeiss Evo 15 microscope (Bruker Resolution 126 eV, Berlin, Germany) and energy-dispersive X-ray spectroscopy (EDS, Tokyo, Japan). At low temperatures (−196 °C), nitrogen adsorption was used to measure the specific surface areas using a Quantachrome Instruments, Anton Paar, NOVA 1200e, Boyton Beach, FL, USA). XRD (Siemens D500 with Cu K α radiation, Karlsruhe, Germany) was employed to analyze the crystallinity and phase composition of the catalysts. Scherrer's equation was applied to estimate the average crystallite sizes. PowderCell [46] was used for Rietveld analysis, and the March–Dollase texturing model [47] was utilized to investigate the presence of preferential orientation in the hydrothermal and sol–gel ZnO samples. Thermo Scientific's Evolution 300 spectrophotometer (Madison, WI, USA), equipped with a DRA-EV-300 Diffuse Reflectance Accessory, was employed to acquire UV–vis spectra. A laboratory dryer with forced convection for hydrothermal syntheses, model: SLW 53 SMART, brand: Pol-Eko, manufacturer: Pol-Eko—Kokoszyska, Poland.

Tribocatalysis was employed to degrade a 50 mL Axetine solution. Using distilled water and a magnetic stirrer, the medication was prepared in a 100 mL beaker. At a constant room temperature of 23 ± 2 °C, the tribocatalytic reaction occurred in the absence of light. Initially, the antibiotic concentration was 75 ppm. Fifty mg of hydrothermal or sol–gel ZnO catalyst was added to a reactor containing the drug solution. The suspension was magnetically stirred with a magnetic bar sealed with polytetrafluoroethylene (PTFE). The resulting mixture was soaked for 30 min without any magnetic stirring to achieve the adsorption equilibrium between the tribocatalysts and the Cefuroxime Axetil solution. The reactor was then switched on, initially spinning at a steady 300 rpm. Aliquots of the reaction solution, each containing two milliliters, were regularly collected. The tribocatalyst was then centrifuged at 6000 rpm. Aside from variations in the length of the magnetic rods, the magnetic stirring conditions (100 and 500 rpm), and the type of beaker material (glass and PTFE), this process was consistent across all other decomposition performance tests. Consequently, the catalyst releases more electrons upon contact with the PTFE stirrer and PTFE beaker, resulting in increased tribocatalytic efficiency. To obtain the UV–vis spectra of Axetine in the 200–600 nm range, Thermo Scientific's Evolution 300 spectrophotometer (Madison, WI, USA) was utilized. The reactive species that were causing the Cefuroxime Axetil to break down were investigated using a scavenger test. Ethylenediaminetetraacetic

acid disodium salt (EDTA-2Na), isopropyl alcohol (IPA) and ascorbic acid (AA) were used as scavengers to absorb holes, superoxide and hydroxyl radicals, respectively. The specific reactive species that led to the tribocatalysis-induced degradation of the organic drug (50 mL) were identified by using six milligrams of each scavenger separately.

4. Conclusions

In summary, by utilizing the friction energy from stirring, two distinct types of zinc oxide (hydrothermal and sol–gel) are used to produce strong tribocatalysis for the breakdown of Axetine. The ZnO sol–gel composite showed a higher specific surface area and more effective degradation. The tribocatalytic drug decomposition ratio reaches approximately 94.21% (in a glass beaker) and 99.70% (in a PTFE beaker) after the drug is agitated for 24 h at 500 rpm using the longest rods. According to the data, mechanical energy absorbed during friction effectively excites the electrons and holes in zinc oxide particles, leading to efficient drug breakdown. The tribocatalytic effect is a promising and eco-friendly way to use environmental mechanical energy to fight pollution. By promoting drug degradation, tribocatalysis opens up new avenues for reducing environmental contamination.

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Article

Electrical Resistivity Control for Non-Volatile-Memory Electrodes Induced by Femtosecond Laser Irradiation of LaNiO_3 Thin Films Produced by Pulsed Laser Deposition

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Abstract

In this work, we investigated how the electrical resistivity of LaNiO_3 thin films deposited on SrLaAlO_4 (100), LaAlO_3 (100), and MgO (100) single-crystal substrates by the pulsed laser deposition (PLD) technique can be controlled by femtosecond laser irradiation. Thin films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (SEM-EDS), and temperature-dependent electrical resistivity measurements. The XRD data indicated good crystallinity and preferential crystallographic orientation. The electronic transport parameters of irradiated samples showed a remarkable decrease in the electrical resistivity for all studied films, which ranged from 38% to 52% depending on the temperature region considered and the type of substrate used. The results indicate a new and innovative route to decrease the electrical resistivity values in a precise, controlled, and localized manner, which could not be performed directly by well-known growth processes, allowing for direct application in non-volatile-memory electrodes.

Keywords: pulsed laser deposition; femtosecond laser irradiation; non-volatile memories

1. Introduction

The compound LaNiO_3 (LNO) is characterized by a perovskite structure with a pseudocubic lattice parameter ($a = 0.384$ nm). Bulk LNO exhibits Pauli paramagnetism [1] and

Fermi-liquid behavior [2] at all temperatures. Band structures calculations for confined LNO films predict changes in electronic and magnetic properties [3], including the possibility of high-temperature superconductivity [4]. In recent years, LNO has drawn significant attention due to its use as a bottom electrode in non-volatile ferroelectric random-access memories (FeRAMs) and resistive random-access memories (ReRAMs), as well as fuel cells, microsensors, and capacitors [5–12].

Among these applications, LNO is particularly attractive as a bottom electrode in electronic devices. For this specific application, some distinct features are important, such as metallic behavior over a wide range of temperatures (1–1000 K), even when electrodes are only a few nanometers thick [13–16], and crack-free, oriented epitaxial growth [17,18] that improves electronic transport (e.g., carrier mobility) [13]. Moreover, when used as a bottom electrode in FeRAMs, LNO significantly mitigates ferroelectric fatigue [19].

For bottom electrodes, a key requirement is to minimize electrical resistivity across the operating temperature range. In the vast majority of studies carried out to reduce the electrical resistivity of LNO, many authors have investigated how the oxygen content can modify its electrical and structural properties [20]. In fact, the presence of oxygen vacancies can effectively control the resistivity of the material, i.e., $\text{LaNiO}_{2.75}$ shows semiconducting behavior, while an insulating phase is obtained with a further decrease in oxygen content, as in $\text{LaNiO}_{2.5}$ [21–24]. In addition, some authors have also investigated the performance of LNO films with different La/Ni ratios, as a function of the cation off-stoichiometry, and their effect on the (possible) reduction of electrical resistivity [25–27]. The electrical resistivity can be tuned according to the La/Ni ratio. For example, at $\text{La/Ni} \approx 0.83$ and $\text{La/Ni} \approx 0.75$ ratios, Zhu et al. [25] and Cole et al. [26] found a clear decrease in the electrical resistivity when compared to $\text{La/Ni} = 1$. From a structural point of view, when the La/Ni ratio is in the $0.75 < \text{La/Ni} < 0.85$ range, the decrease in La content leads to a contraction in the c-axis (with respect to stoichiometric LNO) and, consequently, to increases in the Ni-O-Ni bond angle and the Ni-O bond length [26]. These early works indicate that the resistivity of LNO can change due to the local coordination of Ni cations (i.e., oxygen surroundings), leading to different hybridization strength effects between the Ni-3d t_{2g} and O 2p states [28].

Variation in the Ni content, and consequently the La/Ni ratio, can be achieved in different ways, depending on the growth technique. In the pulsed laser deposition (PLD) technique [29], the La/Ni ratio is set by the target composition, which subsequently affects the thin-film stoichiometry. In molecular-beam epitaxy (MBE), the ratio is controlled by adjusting the elemental flux/source rates. When using the sol-gel method, La/Ni is defined by the molar ratio of the precursors [30]. In all these cases, the resulting films are typically highly stoichiometric and homogeneous, leading to uniform electrical properties. By design, these growth methods produce uniform stoichiometry and offer no practical handle to induce spatially resolved, thermally driven stoichiometric modifications.

To fulfill the modern industrial requirement of miniaturization, it is desirable to modify the electrical properties of local regions of LNO films with nano- to micrometric spatial resolution, to tune and control the local electrical resistivity. A direct application is the development of non-volatile-memory (NVM) technologies [31–33], which are fundamental for the next generation of electronic products.

To tailor material properties as outlined above, femtosecond laser irradiation has delivered remarkable results across diverse materials, proving a powerful route to induce modifications via light-matter interaction on ultrashort timescales [34–37]. These capabilities have been demonstrated across numerous materials and applications, such as surgery, microfabrication, annealing, and biomedical uses [38–44].

Laser technologies stand out for their versatility, accuracy, and precision. Owing to high-spatial-resolution femtosecond laser sources, micrometer-scale modifications can be performed in selected regions of films/substrates [45]. Another important feature is that femtosecond irradiation can induce microstructural modifications more efficiently by minimizing the damaged area around the ablated zone [46]. This is due to the short duration of the pulse in contrast to the electron-lattice relaxation time, resulting in an accurate interaction with a small or negligible heat-affected zone [47]. This is an advantage of using femtosecond in contrast to nanosecond pulsed lasers, where the thermally affected area is more significant in comparison to the ultra-short regime due to the mechanism involved in the process [48].

Based on these considerations, the report in this paper the growth of epitaxial LNO thin films on different single-crystal substrates by pulsed laser deposition (PLD), followed by localized femtosecond laser irradiation. The samples were characterized by XRD, SEM-EDS, and temperature-dependent electrical transport measurements. These techniques were applied to different selected areas of the films, some of which were non-irradiated, and others irradiated by a femtosecond laser beam. The results show a clear decrease in electrical resistivity in all irradiated regions, The results show a clear decrease in electrical resistivity in all irradiated regions, irrespective of the substrate. The temperature-dependent resistivity curves indicated that the electrical behavior of the samples remained unchanged. Therefore, the use of the route proposed in this work arises as an alternative that can be used to manipulate the electrical resistivity in a controlled and reliable way (in terms of dimension and intensity). In short, we present a fast procedure to tune the resistivity of PLD-grown LNO thin films by ultrashort femtosecond laser exposure, without any post-treatment.

In this context, the present work investigates the potential of femtosecond laser irradiation as a localized and efficient tool to modify the electrical resistivity of epitaxial LaNiO_3 thin films grown by pulsed laser deposition on different single-crystal substrates. The films were selectively irradiated and analyzed to assess structural, morphological, and electrical changes resulting from the laser–material interaction. This paper is organized as follows: Section 2 details the experimental methods for film fabrication, laser irradiation, and characterization techniques. Section 3 presents and discusses the results, including the electrical, structural, and compositional changes induced by irradiation. Finally, Section 4 summarizes the key findings and their relevance for future applications in miniaturized electronic devices and non-volatile-memory technologies.

2. Results and Discussions

To avoid the influence of possible changes in film stoichiometry or thickness on the electrical measurements, electron-transport investigations were performed on films with only half of the surface area irradiated (Group I, as will be detailed in Section 3—Materials and Methods). Measuring the irradiated region and subsequently the non-irradiated region on the same film allowed for a direct comparison of changes induced by the laser–film interaction. Figure 1a shows a schematic of the electrical contacts used on the films. Measurements were taken for both increasing and decreasing temperatures on the irradiated and non-irradiated areas. The temperature-dependent resistivity curves are presented in Figure 1b,d. The $\rho(T)$ curves show a clear decrease in the resistivity when comparing values before (green) and after (purple) irradiation, as summarized in Table 1. The resistivity of films grown on LAO and MgO substrates (see Figure 1b,c) shows a monotonic behavior as the temperature is lowered.

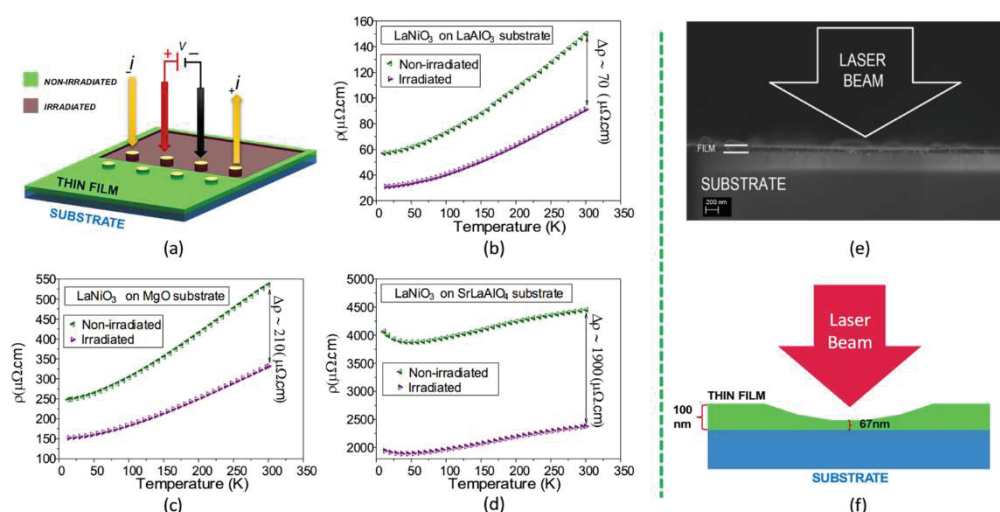


Figure 1. Panel (a) shows the experimental setup for the electrical measurements. In panels (b–d), the temperature dependence resistivity of LNO films grown on different substrates (LAO, MgO, and SLAO, respectively) are depicted. The green curves represent measurements in the non-irradiated regions, and the purple ones correspond to those performed in the irradiated regions. The approximate $\Delta\rho$ values at room temperature are also shown. In (e), an FEG-SEM image of an LNO/LAO film irradiated by the laser beam is shown. It can be seen that the thickness reduces from 100 nm in the non-irradiated region to 67 nm. Panel (f) shows a scheme for a better visualization and understanding of the image in panel (e).

Table 1. The data presented in this table is taken from Figure 1b–d. The data sets are separated into two blocks. (i) Resistivity values for the non-irradiated (Normal) and irradiated (Irrad) regions at 10 K. (ii) Resistivity values for the non-irradiated (Normal) and irradiated (Irrad) regions at 300 K.

Substrate	(i) ρ (T = 10 K) ($\mu\Omega\cdot\text{cm}$)			(ii) ρ (T = 300 K) ($\mu\Omega\cdot\text{cm}$)		
	Normal	Irrad.	Decrement (%)	Normal	Irrad.	Decrement (%)
LAO	57.03	31.10	45.5	150.11	91.03	39.4
MgO	248.08	152.51	38.5	535.51	330.66	38.3
SLAO	4039.32	1940.80	52.0	4451.10	2376.79	46.6

To complement these results, we aimed to understand how the laser scan used to irradiate the samples affects the type of electrical resistivity behavior in LNO films. Specifically, we investigated how the metal insulating transition (MIT) [49] presented in one of the films changes when irradiated by the femtosecond laser beam. Since MIT is closely tied to the structural changes of films, its evolution could be used as a probe of the femtosecond laser effect. The literature reports several approaches to understand the behavior of MIT in LNO films. Here, the curves presented in Figure 1d are not intended to establish a model, but rather to mark structural changes in our samples. The femtosecond laser irradiation resulted in a noticeable reduction in resistivity without changing the character of the mechanisms underlying the MIT effect, as can be seen in Figure 1d.

The resistivity was calculated from the measurement geometry using standard thin-film expressions, and the film thickness was determined from cross-sectional FEG-SEM. Another important factor verified during FEG-SEM characterization was a slight decrease in the film thickness due to the interaction with the femtosecond laser beam. On its own, such a contraction in the thickness would lead to an increase in the $\rho(T)$ values, as shown in our previous work [13], which contrasts with the behavior found here (the resistivity of irradiated films also decreased). Thus, we believe that the lower ρ values after irradiation

are related to the densification of the films, which in turn results in a different percolation path (showing lower resistance), for electrons.

Figure 1e,f shows a cross-sectional FEG-SEM image of an LNO/LAO film, highlighting the written (ablated) and non-written regions and the consequent narrowing of the irradiated area. SEM-EDS measurements indicate a stoichiometry change from $\text{La}/\text{Ni} = 1$ (non-irradiated region) to $\text{La}/\text{Ni} \approx 0.9$ (irradiated region), which is consistent with the observed decrease in resistivity.

Figure 2a–c shows the XRD patterns of non-irradiated and irradiated LNO films grown on LAO, MgO, and SLAO substrates, respectively. The XRD patterns of all LNO films are in good agreement with the pseudo-cubic structure (space group $\text{Pm}\bar{3}\text{m}$), according to the JCPDS 33-710 card. For the three different substrates, the LNO films exhibited only reflection peaks corresponding to the (100) orientation, indicating epitaxial growth on the oriented substrates. No impurities or secondary phases were detected in any of the samples. Due to the relatively low thickness of the LNO films, which affects the intensity of the reflection peaks compared to the respective substrates, a magnified view of the (200) peak region is shown as an inset in each XRD figure. Specifically in Figure 2c, the LNO (100) peak is also observed in the diffractogram of the non-irradiated region (blue). However, its intensity is lower, as the LNO (200) peaks were used as reference for the conclusions presented in Figure 2d,e.

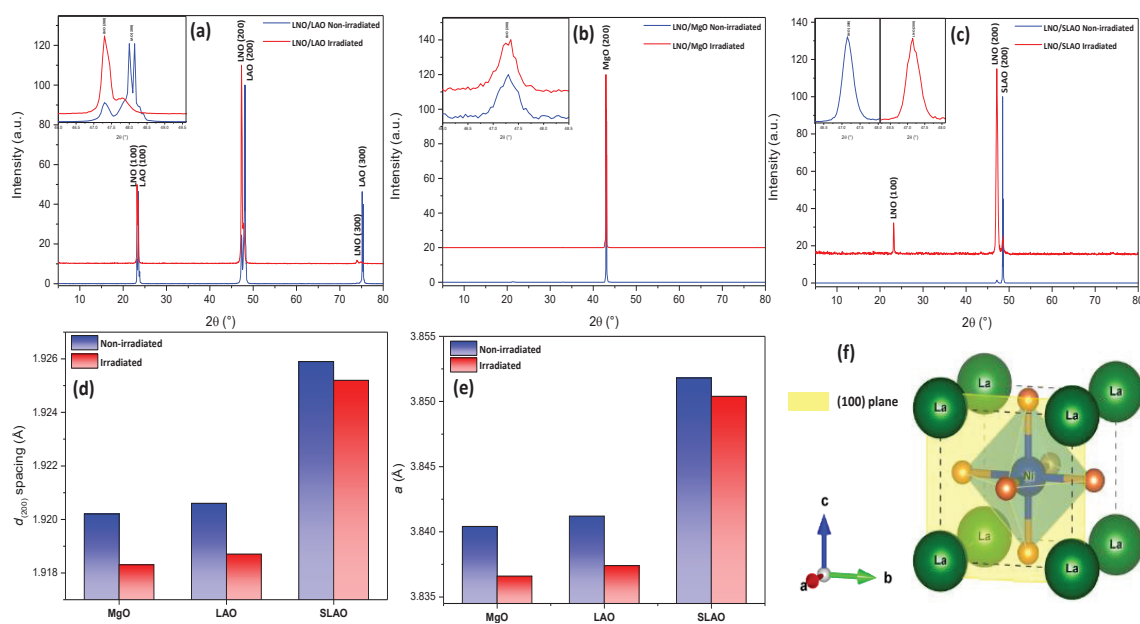


Figure 2. XRD patterns of LNO films grown on (a) LAO, (b) MgO, and (c) SLAO substrates. (d) (200) d-spacing. (e) A lattice parameter of non- and irradiated LNO films. (f) Pseudo-cubic unit cell of LaNiO_3 .

In order to understand the effects of femtosecond laser irradiation on the crystal structure of LNO, an analysis of the interplanar distance of the most intense peak (200) was performed, and the lattice parameter was calculated for all samples, as shown in Figure 2d,e, respectively. We can see a difference in the $d_{(200)}$ values for the non-irradiated samples, which arises from the strain generated by the lattice mismatch in the specific substrate/film interface, that once the LNO tends to expand or contract, its unit cell tends to grow in the oriented direction of the substrate [50,51]. It was observed that the lattice parameter of the LNO films in the three substrates slightly decreases in the irradiated samples. However, due to the relatively low fluence of the femtosecond laser, the irradiation did not cause significant structural modifications or damage to the samples. These slight changes in

the lattice parameter are directly related to changes in the coordination parameters of the composing clusters (building blocks), i.e., changes in the bond angles and lengths of the $[\text{NiO}_6]$ and $[\text{LaO}_{12}]$ [52,53]. Figure 2f shows the unit cell of the LNO structure with the visualization of the (100) plane. As can be seen, the atoms composing the interplanar distance of the (100) plane are the $[\text{NiO}_6]$ cluster. Herein, changes in the distance of this family of planes can be assigned to changes in the coordination parameters of $[\text{NiO}_6]$ clusters. Therefore, the slight compression of the $d_{(200)}$ and consequently of the lattice parameter due to the femtosecond laser irradiation can be related to distortions in the $[\text{NiO}_6]$ clusters. A decrease in the bond length and an increase in the bond angle of the $[\text{NiO}_6]$ is promoted to maintain its crystal structure, as predicted by the Jahn–Teller effect [54]. In brief, ultrashort pulses in ambient air drive a highly non-equilibrium, non-thermal interaction with a minimal heat-affected zone (HAZ). Under these conditions, preferential cation removal (surface La depletion) and slight oxygen redistribution can occur near the surface, resulting in $\text{La}/\text{Ni} < 1$ in the irradiated tracks, as measured by SEM-EDS ($\text{La}/\text{Ni} \approx 0.9$). The resulting $[\text{NiO}_6]$ octahedral distortions (shorter Ni–O bonds, larger Ni–O–Ni angles) enhance bandwidth and reduce resistivity, consistent with prior reports that cation off-stoichiometry reduces ρ in LNO.

Regarding the reduction in electrical resistivity, we confirm that it is permanent when compared to the non-irradiated areas. Durability tests were conducted, and new electrical characterizations performed six months after the initial measurements showed that the resistivity reduction effects remained unchanged, both in magnitude and in the behavior of the ρ vs. T curves. This indicates that femtosecond laser irradiation is a reliable technique in terms of the durability of the resistivity reduction effect, i.e., it is not reversible. This is a key factor for potential applications in non-volatile-memory devices.

3. Materials and Methods

To evaluate the effects of femtosecond laser irradiation on the electrical resistivity of LaNiO_3 thin films, a series of epitaxial films were fabricated and subjected to controlled post-deposition processing. The experimental procedures were designed to ensure reproducibility and enable direct comparison between irradiated and non-irradiated regions of the same sample. This section describes the fabrication of the LaNiO_3 thin films using the pulsed laser deposition (PLD) technique, followed by the laser irradiation methodology, structural and morphological characterizations, and electrical transport measurements performed to analyze the impact of laser interaction on the physical properties of the films.

3.1. Manufacturing LaNiO_3 Thin Films by PLD

LaNiO_3 thin films were grown by pulsed laser deposition (PLD) on three single-crystal substrates: SrTiO_3 (STO) (100), MgO (MgO) (100), and SrLaAlO_4 (SLAO) (100). The LNO target was prepared by the Pechini method [55,56] to ensure compositional homogeneity during the ablation process. Before each deposition, the target surface was polished with SiC abrasive paper and conditioned with 1000 laser pulses using a laser fluence of $1.5 \text{ J}/\text{cm}^2$ to stabilize the plume.

Substrates were preheated to 750°C in the evacuated process chamber ($\approx 10^{-7}$ mbar) and then cooled to the deposition temperature specified for each substrate (Table 2). After establishing a base oxygen pressure of 1.2×10^{-1} mbar, the film (thickness 90 nm, nominal growth rate $0.06 \text{ nm}/\text{s}$) was deposited using a pulsed laser beam. A focused Kr-F excimer laser ($\lambda = 248 \text{ nm}$) was used, impinging the stoichiometric LNO target at 45° with a fluence of $\sim 1.7 \text{ J}/\text{cm}^2$, for all depositions, at a 4 Hz repetition rate. Table 2 summarizes the parameters used during the deposition of thin films by PLD for the different substrates.

Table 2. Parameters employed for PLD deposition. Thin-film deposition temperature (T_{dep}), oxygen pressure during deposition (P_{dep}), and distance between target and substrate ($D_{\text{t-s}}$).

Crystal Substrate	Tdep (°C)	Pdep (mbar)	Laser Fluence (J/cm ²)	D _{t-s} (cm)
LAO	610	1.2×10^{-1}	1.68	4.5
MgO	670	1.8×10^{-1}	1.84	5
SLAO	645	1.8×10^{-1}	1.65	4

The substrates were attached to the heater using colloidal silver paste, and the distance between the substrate and the target was set to 4 and 5 cm, depending on the substrate, as reported previously [13,56,57]. It is important to note that the film thickness depends not only on the number of laser pulses but also on the chamber pressure and the target–substrate spacing. Therefore, the number of pulses used for each film was chosen from prior growth-rate calibrations performed for each substrate. Post deposition in situ annealing was carried out at the sintering temperature for 1 h at 5×10^{-2} mbar to suppress oxygen vacancies and to preserve the phase stoichiometry of the film. After the oxygenation step, the samples were cooled to room temperature.

3.2. Femtosecond Laser Irradiation of LaNiO_3 Thin Films

Samples were exposed to laser irradiation using the STELA laser (Santiago Terawatt Laser; model Alpha 10/XS, 45 TW; manufacturer: Thales Optronique SAS—Thales Laser Solutions, Élancourt, France) of the University of Santiago de Compostela (Spain), a Ti: Sapphire laser. The pulse duration was 35 fs at 800 nm central wavelength with a bandwidth of 75 nm. The maximum output energy was 1 mJ per pulse with a 1 kHz repetition rate.

The beam was focused onto the thin film with a high-precision XYZ stage (Lasing S. L) and kept normal to the surface of the thin films. A Mitutoyo M Plan APO NIR20X microscope objective was employed for this purpose, with an effective focal length of 10 mm. All irradiation processes were carried out in an air environment.

Tests were conducted to find the optimum parameters for the irradiation of the samples. First, keeping the laser power constant, lines with a length of 500 μm were drawn. The separation between the surface of the sample and the objective (see Figure 3a) was varied for each. In particular, the objective-surface distance was increased or decreased in $d = 100 \mu\text{m}$ steps from the focal point (Z_0). This procedure was performed for different laser power values.

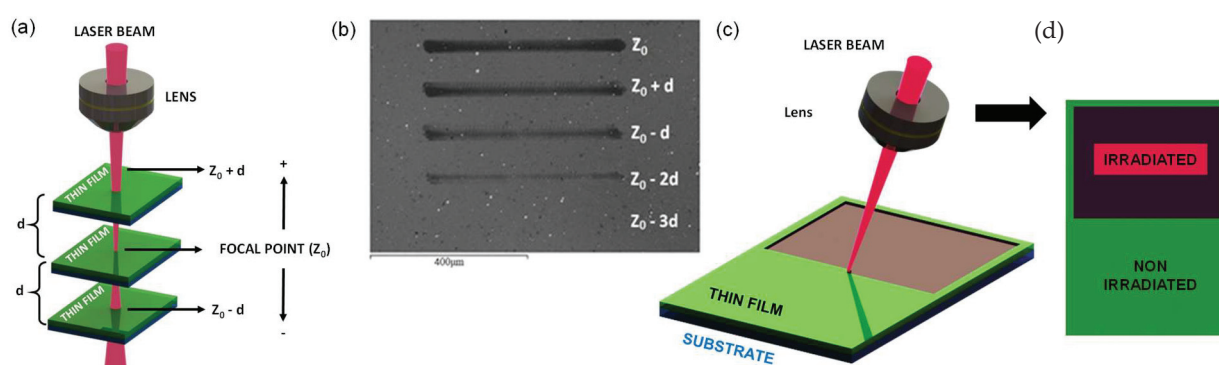


Figure 3. (a) Scheme showing the laser beam, objective, and positions relative to the focal point (Z_0) separated by a $d = 100 \mu\text{m}$ space where the tests were performed. (b) Lines irradiated at each of the different positions relative to the focal point. (c) Sketch representing the lines drawn (irradiated) by the femtosecond laser beam. (d) Indication of the irradiated and non-irradiated areas.

Using the methodology outlined above, it was possible to find an upper limit for the power value of the laser that should be used to ensure that the laser–film interaction was not intense enough to completely ablate the film and reach the substrate. Subsequently, each line was analyzed in SEM-EDS (FESEM, ZEISS MERLIN Compact; manufacturer, Carl-Zeiss-Strasse, Oberkochen, Germany) to measure the width of the ablated line (see Figure 3b). The morphology and composition of each line were also verified and compared to a non-irradiated nearby region that served as a reference for the comparison of irradiated and non-irradiated regions.

The optimum parameters found during the tests were a laser power of 2.5 mW and a scanning speed of 50.0 mm/s. For a line width $w \approx 50 \mu\text{m}$, the fluence was $0.15 \text{ J}/\text{cm}^2$. The scanning speed was selected to ensure the homogeneity of the fabricated line. After the tests, the thin films with dimensions of $0.5 \times 0.5 \text{ cm}^2$ were irradiated and separated into two groups.

For the first group (Group I), only half of the surface area was irradiated—that is, $0.25 \times 0.5 \text{ cm}^2$. Using these samples, electrical transport measurements were performed to compare the irradiated and non-irradiated areas and directly evaluate the changes generated by the interaction between the ultra-short femtosecond laser beam and the film.

For the second group (Group II), the full film area was raster-irradiated for XRD characterization. It is important to note that films from groups I and II were produced simultaneously during a single PLD deposition to prevent any kind of changes in morphology or thickness.

Lines were drawn (irradiated) side by side, separated by approximately $1 \mu\text{m}$, as indicated in Figure 3c, to cover the desired area of the film surface. During the laser raster scanning over the surface of the film, the distance between the lines was chosen to avoid any overlap between them. It is important to note that due to the low fluence used, changes in the surface of films were imperceptible to the naked eye.

The crystal structures of irradiated and non-irradiated LNO films grown on different substrates were characterized by XRD θ – 2θ scans (XRD, Rigaku D/MAX-2500; manufacturer: Rigaku, Cedar Park, TX, USA) with a Cu K- α radiation source ($\lambda = 1.5406 \text{ \AA}$). Electrical transport was measured using the conventional four-point-probe method. For these measurements, metal electrodes (Ag, 100 nm with a diameter of $500 \mu\text{m}$ and also separated by $500 \mu\text{m}$) were micro-fabricated using standard lithographic/masking techniques.

Four-point-probe transport measurements were performed from 8 to 300 K using a closed-cycle helium cryostat (Janis model CCS150; manufacturer, Lake Shore Cryotronics, Westerville, OH, USA). The samples were kept at a pressure lower than $5 \times 10^{-6} \text{ mbar}$. The resistance was measured with standard low-frequency AC lock-in (Signal Recovery model 7265; manufacturer, AMETEK Advanced Measurement Technology, Oak Ridge, TN, USA) at $f = 13 \text{ Hz}$ and DC techniques (Keithley SMU model 2400C; manufacturer, Tektronix, Beaverton, OR, USA). The excitation current was adjusted to avoid nonlinear transport from high-field effects and undesired Joule heating. Initial electrical characterization (current-voltage curves) displayed a linear shape.

4. Conclusions

The electrical behavior of LaNiO_3 thin films deposited on different substrates MgO , LaAlO_3 , and SrLaAlO_4 (100) by PLD and subsequently irradiated with a femtosecond laser was investigated. Structural and morphological characterizations indicate that epitaxial thin films have been obtained with crystallographic orientation and good surface quality without surface outgrowths or particulates on the surface of the film.

From the XRD results, we observed a slight contraction in the lattice parameters of the growth direction and the (100) planar distance for the irradiated samples. These contractions

arose from the changes in the bond lengths and angles of $[\text{NiO}_6]$ clusters due to structural rearrangement by the Jahn–Teller effect, which directly affected the electrical behavior of the sample.

The temperature-dependent resistivity curves show a substantial decrease in resistivity when samples were irradiated with ultrashort pulses from a Ti: Sapphire. The reduction values ranged from 45% to 52% at a temperature of 10 K and 38% to 46% at 300 K. In all cases, resistivity decreased independently of the type of substrate used, i.e., regardless of the substrate and film mismatch (tensile or compressive strain). SEM-EDS results of irradiated regions suggested that the subtle difference in the La/Ni ratio, with a value close to 0.9, is related to the decrease in the resistivity of the LNO films due to the oxygen around Ni atoms. In brief, ultrashort pulses in air drive a highly non-equilibrium, non-thermal interaction with minimal heat-affected zone. Under these conditions, preferential cation removal (surface La depletion) and slight oxygen redistribution can occur at the near-surface, resulting in $\text{La/Ni} < 1$ in the irradiated tracks, as measured by SEM-EDS ($\text{La/Ni} \approx 0.9$). The resulting $[\text{NiO}_6]$ octahedral distortions (shorter Ni–O, larger Ni–O–Ni angle) enhance bandwidth and lower resistivity, consistent with the literature on cation off-stoichiometry lowering ρ in LNO [26–29].

This new method for the in situ micrometric control of the electrical resistivity of LNO thin films can be prospectively employed to achieve specific changes in resistivity in micrometric regions of functional devices to fulfill the modern industrial miniaturization requirement. As mentioned in the introduction, our data, obtained using the PLD technique followed by femtosecond laser irradiation, showed greater reliability and a precise control of results when compared to other techniques such as molecular beam epitaxy and the sol–gel method. This indicates that the technique developed and presented in this work can provide better and more reliable samples for application in non-volatile-memory devices. Laser technologies allow for the micrometric control of irradiation and can be applied in a fine-tuned, fast, and permanent way, besides the reduction in the amount of energy used to make such modifications and so the energy costs. We have shown that it is possible to adjust the values of LNO electrical resistivity, thus highlighting the promising application of the manufactured LNO thin films as NVM devices. It is important to note that resistivity reduction values larger than 40% at room temperature, such as those achieved for the femtosecond-irradiated LNO thin films, represent a great advantage for the manufacture of miniaturized electronic devices in terms of energy efficiency and temperature management due to the reduced thermal-energy losses. Therefore, the results presented here use a new and innovative femtosecond laser irradiation route to decrease the electrical resistivity values in an in situ, precise, controlled, and localized manner, which could not be performed directly by well-known growth processes. These findings may pave the way for the development of highly technological integrated circuits for nanodevices and quantum computers.

The ability to locally and permanently reduce the electrical resistivity of LaNiO_3 thin films through femtosecond laser irradiation opens new avenues for engineering the performance of functional oxide materials at the microscale. This technique enables the in situ tuning of transport properties without compromising the film crystallinity, offering a non-invasive, maskless, and scalable method for the post-fabrication optimization of oxide-based electronic components.

From a technological standpoint, this approach is particularly attractive for the development of non-volatile-memory (NVM) devices and other miniaturized systems where selective resistivity control is critical. The observed resistivity reductions—exceeding 40% at room temperature—translate into lower-Joule heating and improved energy efficiency, which are essential for the advancement of high-density, thermally stable integrated circuits

and quantum electronic platforms. The methodology presented here may serve as a foundation for future device architectures requiring the precise control of electronic transport at micrometric or nanometric scales.

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Article

One-Pot Synthesis of the MoVO_x Mixed Oxide Nanobelts and Its Photoelectric Properties in the Broadband Light Spectrum Range Exhibiting Self-Powered Characteristics

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Abstract

To exploit the near-infrared (NIR) light of MoO₃, the MoVO_x mixed oxide was synthesized using a one-pot approach. The effects of different electrodes, V doping, and bias on the optoelectronic properties were investigated. The photoelectric responses to light sources with wavelengths of 405, 532, 650, 780, 808, 980, and 1064 nm were studied using both Au and carbon electrodes with 6B pencil drawings. The results demonstrate that the MoVO_x nanobelts exhibit photocurrent switching characteristics across the broadband region of the light spectrum. Even when zero bias was applied and the mixed oxide sample was stored at room temperature for over two years, a good photoelectric signal was still observed. This demonstrates that the MoVO_x nanobelts present an interface where interfacial charge transfer forms a strong built-in electric field, promoting photogenerated charge separation and transfer while suppressing photogenerated carrier recombination, and exhibiting self-powered characteristics. Interestingly, reducing the power of the typical excitation light sources resulted in a transition from positive to negative photocurrent features. This reflects the result of an imbalance between the concentration of material defects and the concentration of photogenerated electrons. The MoVO_x nanobelts not only enhance charge transport performance, but also significantly improve the exploitation of near-infrared light. Doping with V significantly improves the nanocomposites' near-infrared (NIR) photoelectric sensitivity. This study demonstrates that heavily doping aliovalent ions during the in situ preparation of nanocomposites effectively enhances their photophysical properties. It provides a straightforward approach to narrowing the band gap of wide-bandgap oxides and effectively avoiding the recombination of photogenerated carriers.

Keywords: MoVO_x nanobelts; nanocomposite aggregation states; carrier recombination suppression; broadband light spectrum range; self-powered characteristics

1. Introduction

MoO₃ is an n-type semiconductor with a band gap of approximately 3.17 eV [1]. However, there are variations in reports from different sources. The use of available light is generally limited. Extending the utilization of its spectrum with a significant red-shift remains a major challenge. MoO₃ and its modified products have been widely investigated in a

multidisciplinary field. Examples include solar cells [1,2], photodetectors [3,4], supercapacitors [5–10], various batteries [11–13], resistive switches [14], flexible electronics [15], gas sensors [16,17], electrochromic devices [18], and photocatalytic applications [19], etc. To reduce the width of the band gap or tailor the physicochemical properties of MoO₃, doping [20], heterojunction [21,22], and defect engineering [23] are widely accepted. Doping mainly includes cation doping, anion doping and doping with non-metallic elements. Cation doping exploits the electronic effect of d-orbital hybridization and the differences in ionic radii, which induce lattice stresses that modulate optical and physical properties. Studies have focused on various cation doping, including Ti-doped MoO₃ [3,18], La-doped MoO₃ [20,24], Ce-doped MoO₃ [25–27], cobalt-doped MoO₃ [28–31], Ni-doped MoO₃ [32–34], Cr-doped MoO₃ [35], Zn-doped or co-doped MoO₃ with other metal cations [19,36–40], Cu-doped MoO₃ [1,41,42], Fe-doped MoO₃ [16,43–46], Ru-doped MoO₃ [47], Er, Gd and Pr-doped MoO₃ [48], W-doped MoO₃ [49], Eu-doped MoO₃ [50,51], indium-doped MoO₃ [52], Cd-doped MoO₃ [53], Sn-doped MoO₃ [54], V-doped MoO₃ [55–58], etc.

It has been demonstrated that transition metal cation doping is dominant due to the abundance of d-electrons and empty orbitals. There are various ways to control the electronic states of materials through transition metal cation doping. Consequently, cation doping has many applications in the aforementioned fields, particularly in gas sensors and photocatalysis. This far exceeds the capabilities of anion-doped and non-metallic element-doped material systems. It also reflects the diversity of options for modifying or functionalizing oxides. Some representative areas of research are described below. Soundharaya and co-workers [1] synthesized Cu-doped α -MoO₃ nanostructures for dye-sensitized solar cells. Şakar and co-workers [3] reported self-powered UV-Vis-NIR photodetector based on Ti-doped MoO₃. Habashyani and co-workers [18] compared the electrochromic properties of undoped and Ti-doped MoO₃. Vinay Kumar and co-workers [19] conducted the photocatalytic and photoluminescence studies on Zn-doped MoO₃. Tian and co-workers [20] constructed a gas sensor based on La-doped MoO₃. Tutel and co-workers [28] reported on dual-band electrochromic devices that exhibited excellent cyclic stability using cobalt-doped MoO₃. Benameur and co-workers [30] compared the same physical properties of pure and Co-doped MoO₃. Biju Bennie and co-workers [35] studied the Cr-doped MoO₃ nanoflakes for energy storage. Pepe and co-workers [37] investigated the nonlinear absorption and photoluminescence properties of MoO₃ doped with Zn, Fe, Cu, V, and Ni, and examined the effect of these dopants on the bandgap width. Xian and co-workers [46] reported that iron-doped MoO₃ nanosheets enhance nitrogen fixation. Maurya and co-workers [47] produced hydrogen evolution in both acidic, as well as alkaline medium using Ru-doped MoO₃. Kamoun and co-workers [51] conducted a physical study of Eu-doped MoO₃. Camacho and co-workers [55] reported on V-doped MoO₃ nanosheets with superior lithium ion storage capability. Feste and co-workers [57] prepared vanadium-doped MoO₃ with a tunable work function. Nickel-doped MoO₃ showed high performance in aluminum ion batteries and enhanced hydrogen evolution [59,60], etc. Although good results have been achieved with cation doping thus far, the variety of cationic species means that they can influence the electronic properties of materials in a multitude of ways. Consequently, they are widely used to modify certain inorganic functional materials. Doping can be divided into homogeneous and heterogeneous doping. Heavy cation doping inevitably produces new defects that are inextricably linked to defect, interfacial, and lattice stress engineering. This reflects the synergy of multiple interactions. While heavy doping reduces carrier mobility due to scattering, high doping improves the absorption and utilization of light with a longer wavelength. There are potential applications in multiple disciplines. Heavy doping is also an important method of preparing nanocomposites with enhanced properties. Other methods of modulating the physical and chemical properties of metal

oxides have also been widely used in nanocomposite design. The effects of S, N, and B doping, as well as oxygen vacancies, defect engineering and interface/lattice stress engineering. Regarding the electronic structure, conductivity, plasmon properties, optoelectronic properties, photocatalysis, electrocatalysis, thermal catalysis, and photothermal catalysis have also been extensively studied [61–72]. Aliovalent cation doping generally produces oxygen vacancies, which improve charge transfer and significantly impact photophysical properties [73]. Regulating oxygen vacancies is important for the functional properties of materials.

It is well known that doping is an important way of modifying semiconductor materials. High doping can significantly narrow the bandgap. The preparation of nanocomposites mostly involves synthesizing one component in the presence of the others. High doping can be used as a means of in situ nanocomposite preparation for use in multidisciplinary fields. These ideas in the field of semiconductor materials can inspire the development of multifunctional nanocomposites with exceptional properties.

The physicochemical properties of a material primarily depend on the valence electrons of its constituent atoms, or the bonding and antibonding orbitals of its constituent molecules. Modulating the electronic behavior of materials can enhance the physicochemical properties of nanocomposites. The electronic behavior of a material is closely related to its energy band structure, as well as to its interfaces and defects. These key factors also determine the absorption and excitation of light at different wavelengths. This reflects the modulation of materials' photophysical properties by light of different wavelengths.

Nanomaterials are designed to a large extent with their size and dimensionality effects in mind. Although some techniques can characterize certain physical properties of individual nanostructures, it is generally difficult to characterize the properties of a single nanostructure because it is time-consuming. Often, nanostructures are found in aggregated states. There are many defects at grain boundaries, which hinder charge transport. Therefore, studying the photophysical properties of nanomaterials in an aggregated state poses a significant challenge.

The design of nanocomposites is primarily based on integrating multiple components, phases and dimensions. The interaction between these components is the primary consideration. Varying the preparation parameters can result in the production of multiphase and multidimensional structures. For oxides with a wide bandgap, reducing the bandgap remains extremely important, as does suppressing the recombination of photogenerated carriers, which is a major challenge. As electron–hole recombination has been a key bottleneck in multidisciplinary fields for several decades, the material itself must have a strong built-in electric field to promote charge separation and transfer. Therefore, a strong built-in electric field is an important indicator of photogenerated carrier recombination suppression. As with nanocomposites, heavy doping produces heterojunctions that form built-in electric fields due to interfacial charge transfer. To improve the utilisation of near-infrared light by MoO_3 , Ma and co-workers [74] had studied the interfacial interaction between MoO_3 and polymer-derived carbon materials to enhance NIR utilisation. In another publication, the surface S-doping of MoO_3 was performed to tailor the electronic state [75]. In this contribution, the MoVO_x mixed oxide was synthesized using a one-pot process based on the multivalent oxidation state of V and the plasmonic properties of heavily doped oxides. This extends the photocurrent extraction of near-infrared light and strengthens the self-driving properties for charge separation. The recombination of photogenerated carriers is effectively avoided. This work is presented here for multidisciplinary reference. It is also intended to facilitate interaction between light and matter.

2. Results and Discussion

The one-pot synthesis of the MoVO_x mixed oxide is very simple. Sodium molybdate dihydrate and dilute hydrochloric acid were mixed together to form molybdate. Similarly, ammonium metavanadate and dilute hydrochloric acid were mixed together to form metavanadate. The molybdate and metavanadate were then mixed in the correct proportions and heated to dehydrate them and, as a result, MoVO_x was formed.

The multivalent transitions of vanadium can affect the electronic structure of molybdenum trioxide. The V atom has both d-orbital electrons and empty orbitals. The distribution of electrons outside the nucleus of V atom is as follows: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$. Its oxidation state varies from +2 to +5, and it readily produces oxygen vacancies. It exhibits an electron donor effect. This helps passivate defects and improve the extraction of photoelectrons. At the same time, the atomic radius of the V atom is smaller than that of the Mo. Doping with heteroatoms can generate localized compressive or tensile stresses, altering the optical and photophysical properties.

The representative SEM image, XRD, and UV-Vis of the MoVO_x are shown in Figure 1.

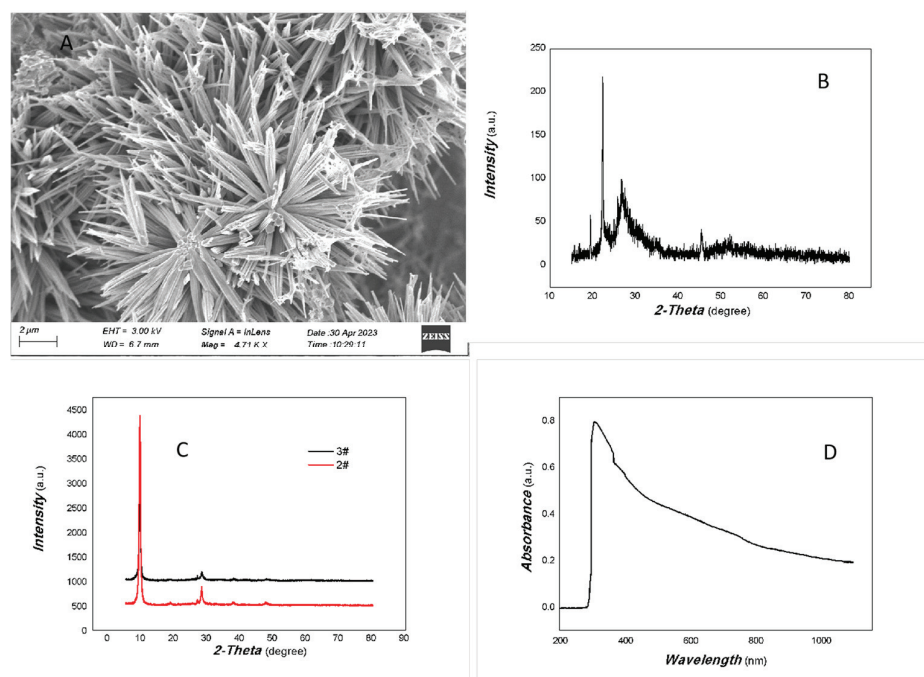


Figure 1. A representative SEM image, XRD, and UV-Vis curve of MoVO_x ((A) SEM; (B) 1#-XRD; (C) 2#,3#-XRD; (D) UV-Vis curve).

As can be seen in Figure 1A, the nanobelt has a very uniform morphology. The nanobelt is about 4–6 μm long. The width is approximately 40 nm. The uniform morphology of the MoVO_x is excellent overall.

The XRD results of MoVO_x are shown in Figure 1B,C. The UV-Vis-NIR of MoVO_x is shown in Figure 1D.

As shown in Figure 1B, the crystallinity of the MoVO_x is not very good, while the noise level is bigger. However, some diffraction peaks can still be identified, such as those at 16.87°, 19.41°, 25.84°, 34.29°, 35.46°, 45.45°, 46.62°, 52.22°, and 56.44°, which are the peaks of the (110), (200), (210), (220), (310), (410), (404), (330), and (218) planes of MoO₃ (PDF# 21-0569), respectively. The diffraction peaks at 26.85°, 27.52°, and 39.53° belong to the peaks of the (11-1), (011), and (002) planes of VO₂ (PDF# 44-0252). As the amount of V doping increased, no significant diffraction peaks of VO₂ were observed. This indicates that VO₂ is not well crystallized or intercalated in the material. Otherwise, as shown in

Figure 1C, 2θ at 9.39° is quite strong, indicating that the material growth is preferred along (100) planes of MoO_3 (PDF# 21-0569). The diffraction angle is slightly reduced compared to the standard PDF (2θ at 9.69° (100)). It indicates that the V intercalation has increased the face spacing. Therefore, the resulting nanomaterial contains some MoO_3 and VO_2 components forming the MoVO_x heterojunction.

As shown in Figure 1D, the optical absorption of the MoVO_x was covered the entire visible spectrum and part of the near-infrared (NIR) region. Since the band gap width of MoO_3 is approximately 2.8–3.85 eV, the absorption of the broad spectrum is likely due to V doping. Pepe and co-workers [37] have previously studied the nonlinear absorption and photoluminescence properties of Zn-, Fe-, Cu-, V-, and Ni-doped MoO_3 , examining the effects of these dopants on the band gap width. The results showed that doping significantly narrowed its bandgap, i.e., $\alpha\text{-MoO}_3$: 3.85 eV; Fe-doped $\alpha\text{-MoO}_3$: 3.46 eV; Cu-doped $\alpha\text{-MoO}_3$: 3.43 eV; Zn-doped $\alpha\text{-MoO}_3$: 3.34 eV; Ni-doped $\alpha\text{-MoO}_3$: 3.48 eV; V-doped $\alpha\text{-MoO}_3$: 3.67 eV. This study showed that the absorption edge of the V-doped MoO_3 was located in the NIR region. This may be due to the introduction of intermediate states by V doping. Further support for the optoelectronic signals in the NIR is required later.

In the study of the interaction between light and matter, good optical absorption is crucial for detecting photoelectric signals. The detection of optoelectronic signals depends heavily on factors such as the width of the band gap, material defects, interface contacts, electrodes, and substrate. Gold is generally easy to characterize for this purpose, as it has a high work function and a low contact barrier. We first used gold electrodes to determine the photoelectric properties over a wide spectral range. Representative results are shown in Figures 2 and 3.

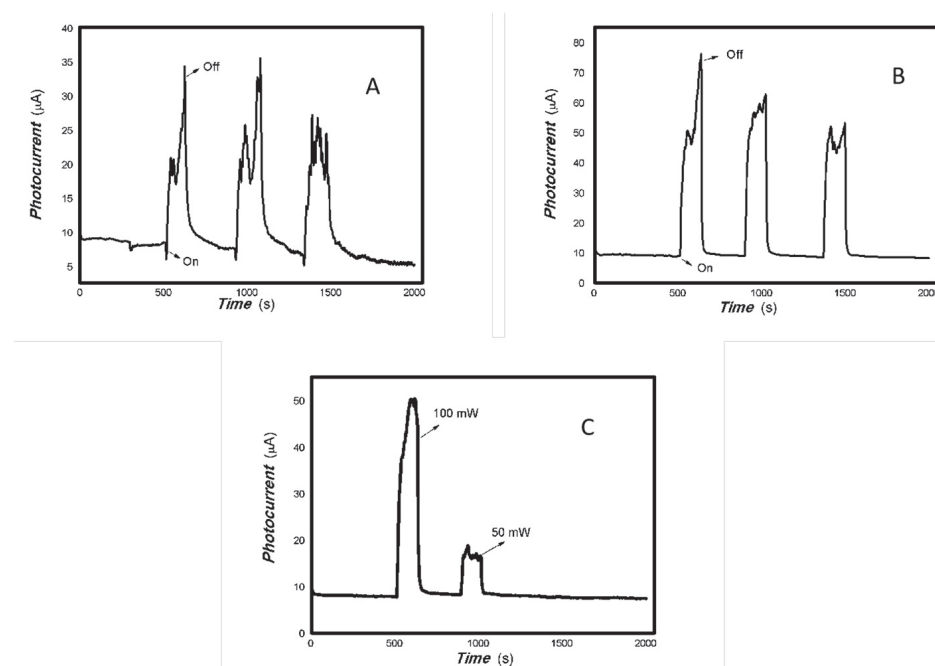


Figure 2. The optoelectronic responses of MoVO_x (1#) to the visible light ((A) 40 W visible light; (B) 100 mW 650 nm; (C) 100, 50, and 5 mW 650 nm) (using gold gap electrodes and PET film substrates, 1 V bias applied).

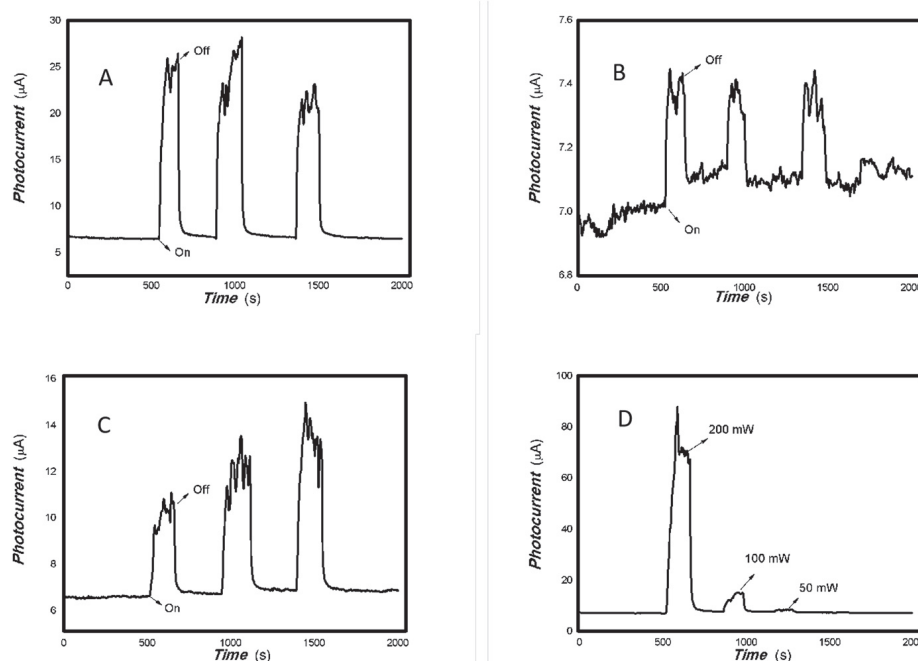


Figure 3. The optoelectronic responses of MoVO_x (1#) to 808, 980, and 1064 nm ((A) 200 mW 808 nm; (B) 20 mW 1064 nm; (C) 200 mW 980 nm; (D) 200, 100, 50, and 5 mW 980 nm) (using gold gap electrodes and PET film substrates, 1 V bias applied).

As shown in Figures 2 and 3, the resulting MoVO_x nanobelts can convert incident light signals into electrical signals. When visible light and certain wavelengths of near-infrared light hit the aggregated state of the nanobelts, the photons' energy excites electrons, causing them to transition from the ground state to the excited state, and generate electron–hole pairs. An external bias then drives these photogenerated charges to move in a directed manner, forming a photocurrent. When the light is removed, the current gradually returns to its original state. This is the result of the interaction between light and matter producing non-equilibrium carriers. This is a typical reversible transition process from balanced carriers to unbalanced carriers. This clearly demonstrates that the carrier concentration in the material can be controlled by the light field. This indicates that the resulting nanocomposite is responsive to visible and near-infrared light stimuli. The nanocomposite is expected to have potential applications in multidisciplinary fields. Experiments also revealed that MoVO_x (1#) nanobelts exhibited strong photocurrent signals in response to the light sources of 50 mW at 650 nm, 100 mW at 808 nm, 200 mW at 980 nm, and 20 mW at 1064 nm. This demonstrates that the MoVO_x nanobelts can effectively utilize the visible light and NIR. This supports the results of UV-Vis curve of MoVO_x (Figure 1D). Further confirmation was obtained that the resulting nanomaterial absorbs in the visible and near-infrared range. However, there was almost no response to the 5 mW light sources at 650 and 980 nm. This suggests that material defects trap all the photogenerated charges under low-incident power irradiation, making it difficult to extract the photocurrent signal. The representative results of the optoelectronic signals with an increasing V-doping content are shown in Figures 4 and 5.

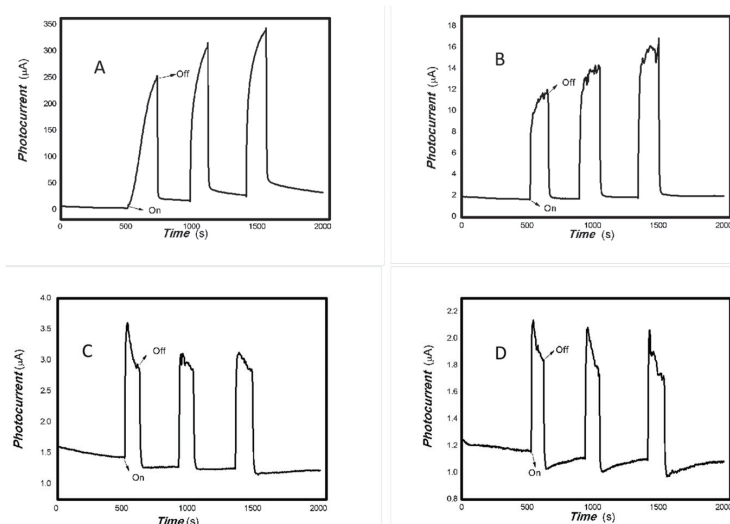


Figure 4. The optoelectronic responses of MoVO_x (2#) to 650, 808, 980, and 1064 nm ((A) 100 mW 650 nm; (B) 200 mW 808 nm; (C) 100 mW 980 nm; (D) 20 mW 1064 nm) (using gold gap electrodes and PET film substrates, 1 V bias applied).

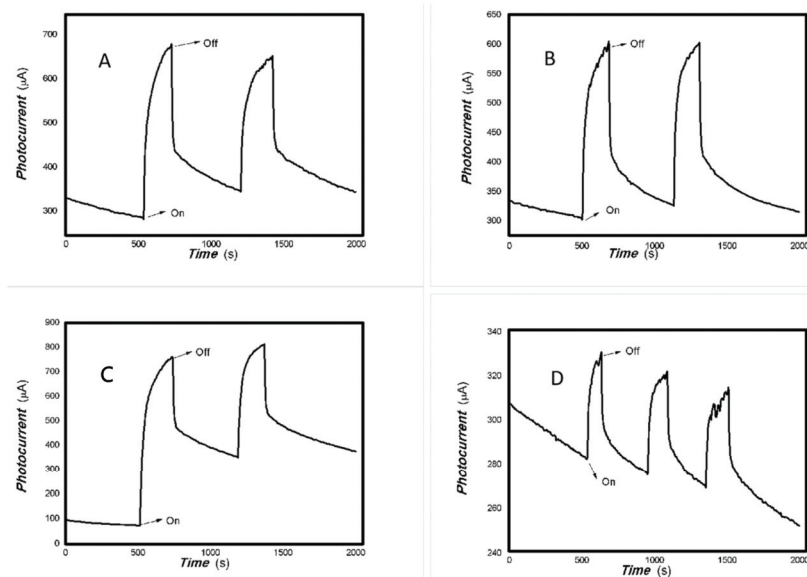


Figure 5. The optoelectronic responses of MoVO_x (3#) to 650, 808, 980, and 1064 nm ((A) 100 mW 650 nm; (B) 200 mW 808 nm; (C) 200 mW 980 nm; (D) 20 mW 1064 nm) (using gold gap electrodes and PET film substrates, 1 V bias applied).

As shown in Figures 4 and 5, increasing the amount of V doping still allows for the photoelectric signals to be measured. However, the recovery time is relatively long and the baseline current is less stable. Regarding the nanocomposite itself, the VO₂ has a low degree of crystallization (Figure 1B), with almost no noticeable effect from increased V addition (Figure 1C). Low crystallinity means an increased disorder degree in the material. High disorder leads to increased non-radiative energy consumption and a large photothermal effect. The slow response and recovery in Figures 4 and 5 also illustrate these issues. In the fields of luminescence, solar cells and photodetectors, decreasing non-radiative energy consumption requires control of the material's microstructure. This photothermal effect will also be utilized in other interdisciplinary fields. A low degree of crystallization increases the likelihood of electron–electron and electron–phonon scattering, slowing down charge transport.

The study of light matter interactions involves many photophysical properties and physical mechanisms, as well as multidisciplinary applications. Some ideas from the fields of photodetectors and solar cells provide excellent inspiration for multidisciplinary applications [76–78]. Important performance parameters, such as open-circuit voltage, short-circuit current, responsivity (R), external quantum efficiency (EQE), and detectivity (D) accurately reflect the key performance of solar cells and photodetectors. However, our research does not focus on these devices or related materials. Our focus is on interdisciplinary aspects and complementary content based on qualitative and semi-quantitative characterization. To this end, we have summarized key data from Figures 2–5 and in Table 1 for easier analysis and discussion.

Table 1. The comparative photocurrent signals of 1#, 2#, 3#-MoVO_x nanobelt aggregation states using Au gap electrodes and PET film to some representative light sources (1 V bias applied).

Excitation Light Wavelength (nm)	Sample	Response Time (s)	Recovery Time (s)	Ratio of on/off
100 mW, 650 nm	1#-MoVO _x	36.8	12.0	5.74
100 mW, 650 nm	2#-MoVO _x	48.9	24.0	19.68
100 mW, 650 nm	3#-MoVO _x	65.1	106.3	2.28
200 mW, 808 nm	1#-MoVO _x	48.8	28.3	3.85
200 mW, 808 nm	2#-MoVO _x	41.1	20.6	7.81
200 mW, 808 nm	3#-MoVO _x	57.4	143.1	1.89
200 mW, 980 nm	1#-MoVO _x	32.6	32.6	1.84
200 mW, 980 nm	2#-MoVO _x	64.8	50.2	93.28
100 mW, 980 nm	2#-MoVO _x	7.7	20.6	2.01
200 mW, 980 nm	3#-MoVO _x	106.3	138.8	9.80
20 mW, 1064 nm	1#-MoVO _x	16.3	22.0	1.05
20 mW, 1064 nm	2#-MoVO _x	4.3	12.0	1.63
20 mW, 1064 nm	3#-MoVO _x	53.1	78.0	1.14

As shown in Table 1, the switching ratio initially increases and then decreases as the V doping concentration rises for 650 nm, 808 nm, and 980 nm light sources. Meanwhile, the response and recovery speeds slow down accordingly. This trend is also generally observed for other light sources, albeit with greater fluctuations. This indicates that, as the amount of V added increases, the degree of disorder, the number of defects and the amount of non-radiative energy consumption increase, leading to more scattering opportunities and causing greater fluctuations. This includes both the photoelectric and photothermal effects. The photothermal effect is inevitable.

Based on the results shown in Figures 2–5, it can be confirmed that the synthesized MoVO_x nanobelts exhibit good optoelectronic signals in the broadband spectral range when used with gold gap electrodes. This is likely due to V-doping creating intermediate states, thereby increasing the potential for photoexcitation and electron transformation. In addition to the materials and their microstructures themselves, the electrodes and substrates also play an important role in acquiring optoelectronic signals. The acquisition of optoelectronic signals is the result of various factors combined. Untreated paper is known to contain a large number of defects, particularly O groups. These groups tend to trap photogenerated electrons, which hinders the acquisition of optoelectronic signals when using untreated paper as a substrate. Conversely, graphite electrodes with pencil drawings were among the most cost-effective in the study. These electrodes were composed of 84%

graphite and 16% clay. These carbon electrodes themselves can be regarded as composites, and their defects cannot be ignored. The use of these carbon electrodes naturally traps some of the photogenerated carriers, which can degrade the photoelectric signal. Another important factor in driving the carrier transfer is the bias applied. Applying a suitable external bias voltage drives the directional flow of carriers and prevents photogenerated carrier recombination. To suppress photogenerated carrier recombination, the material itself must have a strong built-in electric field to drive charge movement. Taking these factors into account, the MoVO_x nanobelts were chosen to investigate the effect of bias voltage on photogenerated current using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings. Representative results are shown in Figures 6–12.

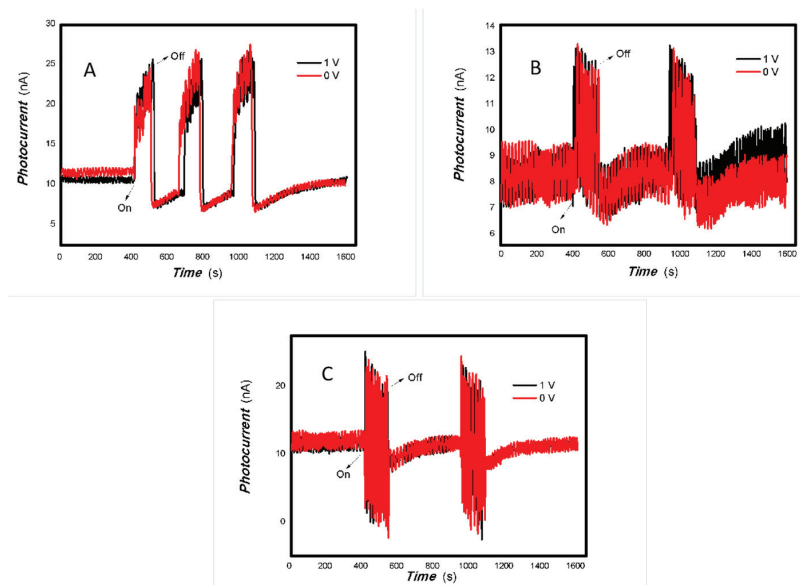


Figure 6. The effect of the bias voltage on the photogenerated current for the MoVO_x (1#) to 808, 980, and 1064 nm ((A) 200 mW 808 nm; (B) 100 mW 980 nm; (C) 20 mW 1064 nm) (Red line: 0 V bias; Black line: 1 V bias) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

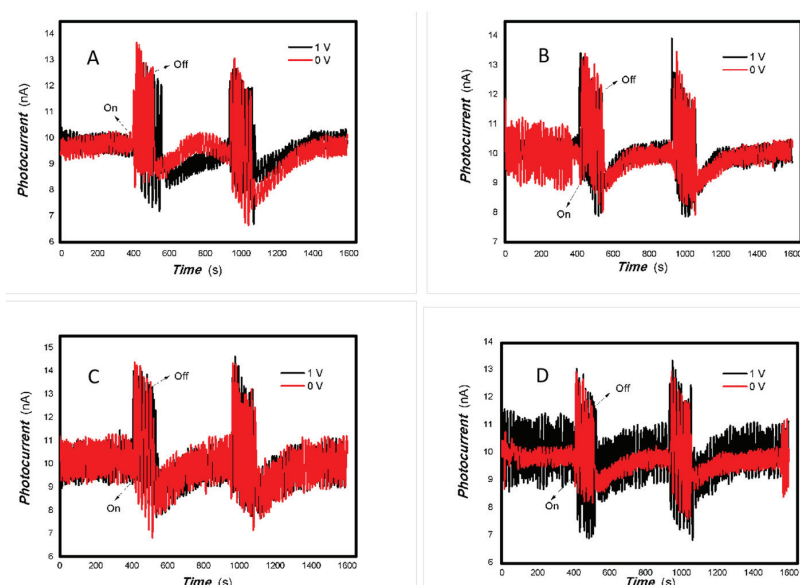


Figure 7. The effect of the bias voltage on the photogenerated current for the MoVO_x (1#) to 405, 532, 650, and 780 nm ((A) 50 mW 405 nm; (B) 50 mW 532 nm; (C) 50 mW 650 nm; (D) 50 mW 780 nm) (Red line: 0 V bias; Black line: 1 V bias) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

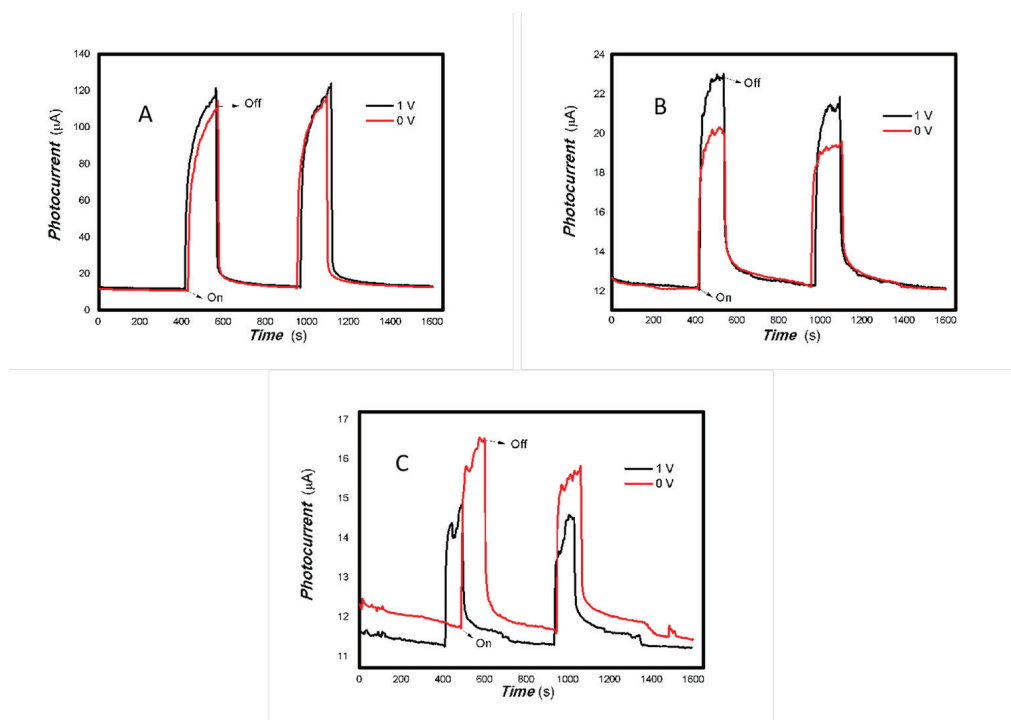


Figure 8. The effect of the bias voltage on the photogenerated current for the MoVO_x (3#) to 808, 980, and 1064 nm ((A) 200 mW 808 nm; (B) 100 mW 980 nm; (C) 20 mW 1064 nm) (Red line: 0 V bias; Black line: 1 V bias) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

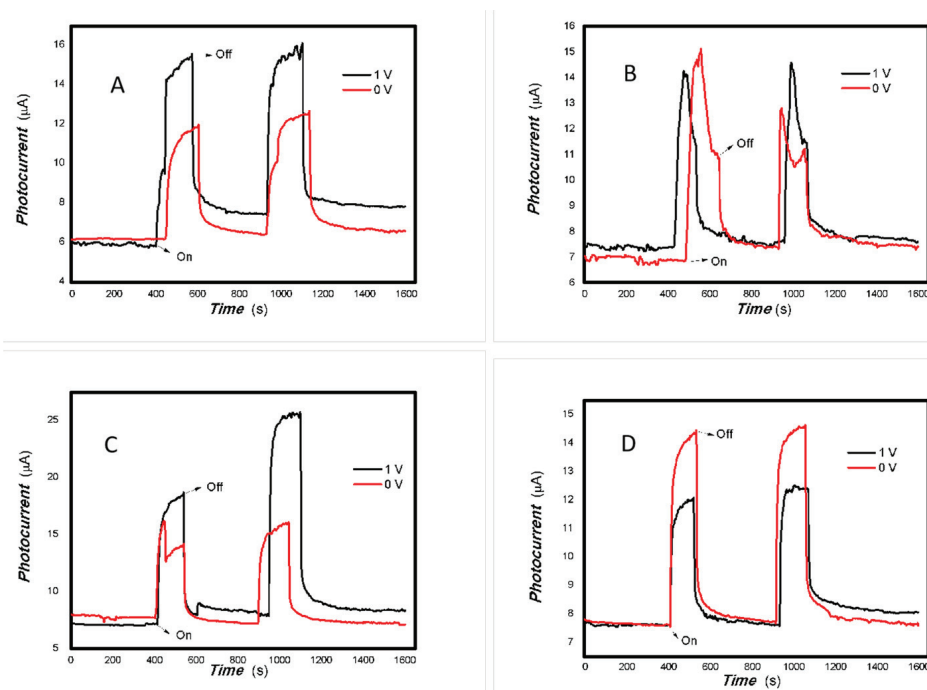


Figure 9. The effect of the bias voltage on the photogenerated current for the MoVO_x (3#) to 405, 532, 650, and 780 nm ((A) 50 mW 405 nm; (B) 50 mW 532 nm; (C) 50 mW 650 nm; (D) 50 mW 780 nm) (Red line: 0 V bias; Black line: 1 V bias) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

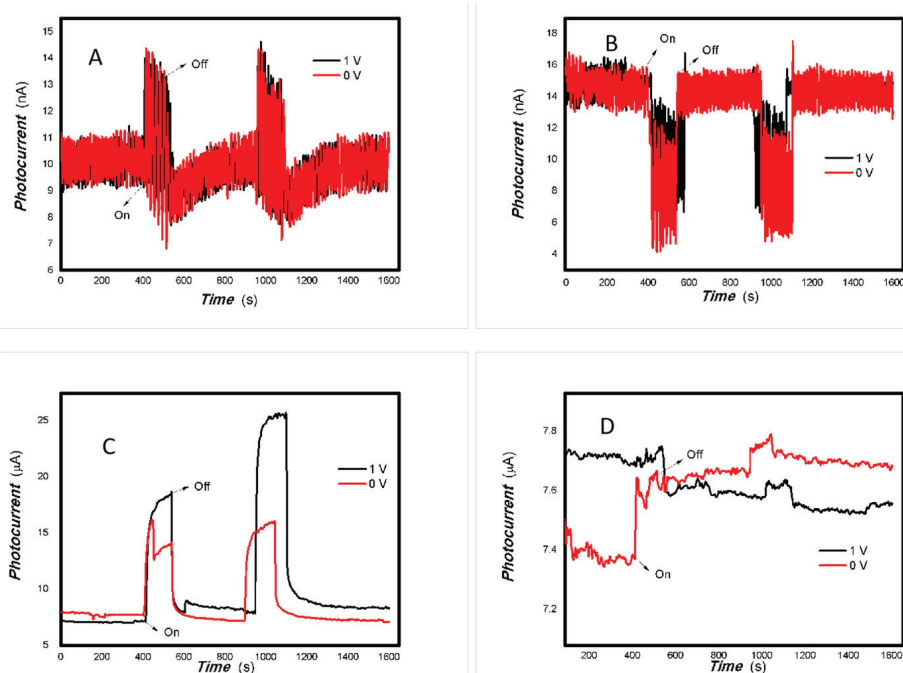


Figure 10. The effect of the bias voltage and power of typical light sources on the photogenerated current for the MoVO_x (1, 3#) to 650 nm (Red line: 0 V bias; Black line: 1 V bias) ((A) 1# to 50 mW 650; (B) 1# to 5 mW 650 nm; (C) 3# to 50 mW 650; (D) 3# to 5 mW 650 nm) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

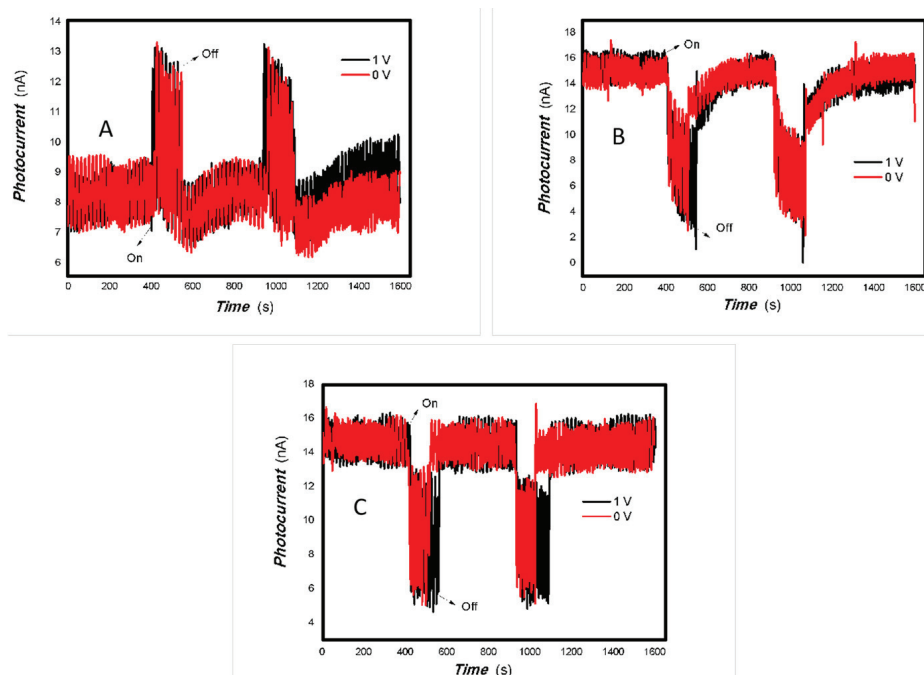


Figure 11. The effect of the bias voltage and power of typical light sources on the photogenerated current for the MoVO_x (1#) to 980 nm (Red line: 0 V bias; Black line: 1 V bias) ((A) 100 mW; (B) 50 mW; (C) 5 mW) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

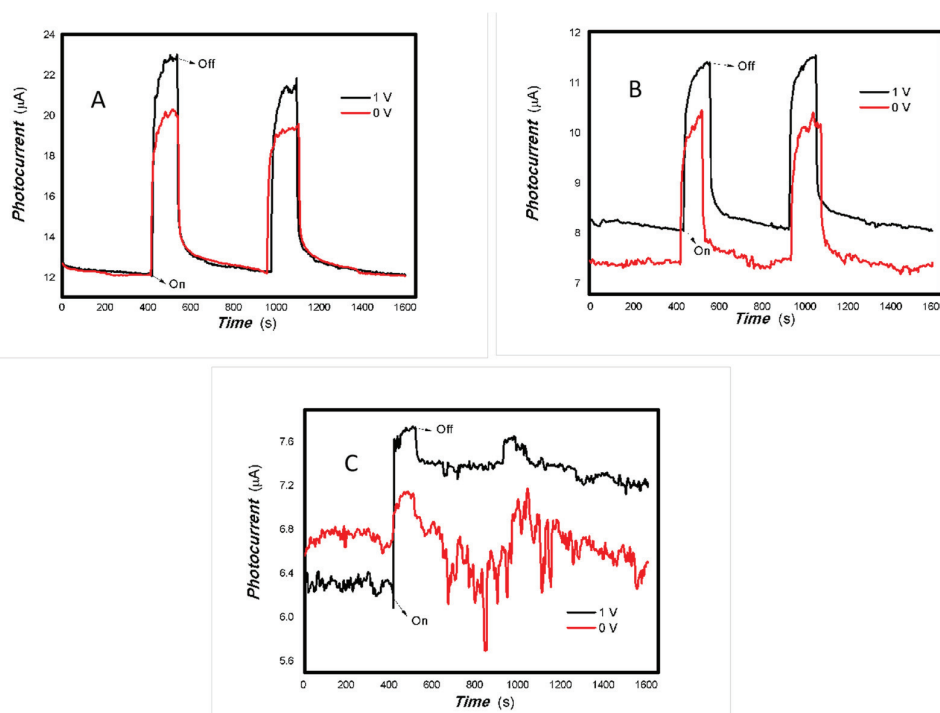


Figure 12. The effect of the bias voltage and power of typical light sources on the photogenerated current for the MoVO_x (3#) to 980 nm (Red line: 0 V bias; Black line: 1 V bias) ((A) 100 mW; (B) 50 mW; (C) 5 mW) (using A4 printing paper as substrates and the graphite electrodes with 6B pencil drawings).

As can be seen in Figures 6–12, a good photoelectric signal was still determined even when zero bias was applied and the graphite electrodes with 6B pencil drawings on A4 printing paper were used. This indicates that the MoVO_x nanobelts can produce a strong intrinsic electric field to promote photogenerated carrier transport, enabling self-powering. Self-powered devices are an important area of research due to their low energy consumption [79–82]. Similarly, self-driven nanomaterials also play a significant role in preventing the recombination of photogenerated charges. In most cases, the bias applied in this study was found to have little effect. Increasing the bias voltage increases the photogenerated current when the material is excited by light of certain wavelengths. This demonstrates that interfaces exist within the mixed oxides prepared by the one-pot method. Charge transfer between these interfaces generates a built-in electric field. The built-in electric field created by the MoVO_x nanobelts is strong enough to facilitate the transport of photogenerated charges, and inhibit their recombination. Increasing the V-doping content significantly increases the base current from nA to μA. This is mainly due to the unfilled d electrons of the V element. This suggests that V doping can enhance the conductivity of the mixed oxide. This improves the transport of photogenerated carriers. However, as shown in Figure 6, a large fluctuation in the photocurrent of the MoVO_x nanobelts was observed when a 20 mW, 1064 nm light source was used. This may be due to electron-electron and electron-phonon scattering affecting charge transport. Therefore, controlling the microstructure of materials is important in terms of suppressing the recombination of photogenerated carriers and reducing non-radiative energy consumption. The presence of an internal electric field can suppress photogenerated charge recombination, which is useful for the material itself.

Additionally, Figures 10–12 show an interesting phenomenon: a transition from positive to negative photoconductivity in the low V-doping sample as the power of typical light sources decreased. This phenomenon was not observed in the high V doping mixed oxide sample. This reflects the result of an imbalance between the concentration of mate-

rial defects and the concentration of photogenerated electrons. As the power of the light sources was reduced further, the concentration of photogenerated electrons decreased too. When the concentration of photogenerated electrons is lower than the concentration of material defects, all the photogenerated electrons are trapped by the material defects. The net increase in photocurrent is negative. This indicates negative conductivity. Heavily V-doped MoO₃ resulted in a high VO₂ content in the heterojunction. Since the valence state of V varies between +2 and +5, VO₂ contains many oxygen vacancies, which have an electron-donating effect. This electron-rich effect of VO₂ can passivate the material defects, resulting in a positive net increase in current. This response is known as defect-assisted photoconductive behavior. Additionally, highly V-doped MoO₃ exhibits plasmonic effects that contribute to the interfacial charge transfer. In our previous publication [83], we introduced the phenomenon of the transition from negative to positive photocurrent response by passivating the grain boundary defects of the nanocomposite with metal nanomaterials. Consequently, the impact of material defects and interfaces on the acquisition of optoelectronic properties was substantial. The modulation of material defects for different applications is an ongoing process.

For ease of comparison, the key data in Figures 6–9 are summarized in Table 2.

Table 2. The comparative photocurrent signals of 1#, 3#-MoVO_x nanobelt aggregation states using carbon electrodes with 6B pencil drawings and A4 paper as a substrate to some representative light sources (0 V bias applied). * Negative photoconductivity.

Excitation Light Wavelength (nm)	Sample	Response Time (s)	Recovery Time (s)	Ratio of on/off
50 mW, 405 nm	1#-MoVO _x	11.7	7.9	1.30
50 mW, 405 nm	3#-MoVO _x	39.7	55.6	2.02
50 mW, 532 nm	1#-MoVO _x	3.8	19.6	1.26
50 mW, 532 nm	3#-MoVO _x	39.7	39.7	1.62
50 mW, 650 nm	1#-MoVO _x	7.94	31.8	1.34
50 mW, 650 nm	3#-MoVO _x	28.0	43.5	1.78
5 mW, 650 nm	1#-MoVO _x	12.1	15.9	3.10 * (negative photoconductivity)
5 mW, 650 nm	3#-MoVO _x	4.2	19.6	1.01
50 mW, 780 nm	1#-MoVO _x	4.2	12.1	1.22
50 mW, 780 nm	3#-MoVO _x	31.8	51.8	1.86
200 mW, 808 nm	1#-MoVO _x	20.1	20.1	2.62
200 mW, 808 nm	3#-MoVO _x	55.6	20.1	9.66
100 mW, 980 nm	1#-MoVO _x	12.1	4.2	1.45
100 mW, 980 nm	3#-MoVO _x	36.0	79.8	1.65
5 mW, 980 nm	1#-MoVO _x	19.6	28.0	2.33 * (negative photoconductivity)
5 mW, 980 nm	3#-MoVO _x	47.6	43.9	1.06
20 mW, 1064 nm	1#-MoVO _x	3.8	4.2	1.77
20 mW, 1064 nm	3#-MoVO _x	19.6	47.6	1.37

As shown in Table 2, as the V doping concentration increases, the switching ratio increases, while the response and recovery speeds slow down accordingly. This indicates an increase in defects, which in turn exacerbates scattering and affects the response speed.

Under light irradiation of 5 mW at 650 nm (it is shown in Figure 10), and 5, 50 mW at 980 nm (it is shown in Figure 11), 1#-MoVO_x nanobelts exhibit a negative photoconductive effect. This is due to an imbalance between the defect concentration and the photogenerated carrier concentration. All photogenerated electrons are captured by defects, leading to a decrease in the photocurrent. On the other hand, it also shows that even when using carbon electrodes and paper substrates, it is still possible to obtain broad-spectrum photocurrent signals. Defects originate not only from the MoVO_x nanobelt itself, but also from the carbon electrodes with 6B pencil drawings and paper substrate. Despite the presence of so many defects, it is still significant that photogenerated carriers can still be extracted. From the perspectives of cost and multidisciplinary research, the findings are highly valuable.

Since it is still possible to achieve better photoelectric signal extraction at zero bias using graphite electrodes with 6B pencil drawings, the effect of bias on the photoelectric signal was examined again using gold electrodes due to Au's low barrier. Representative results are shown in Figures 13–26. Since the resulting oxide nanobelts have been stored at room temperature for over 2 years, these research results also reflect the photophysical stability of the nanomaterials.

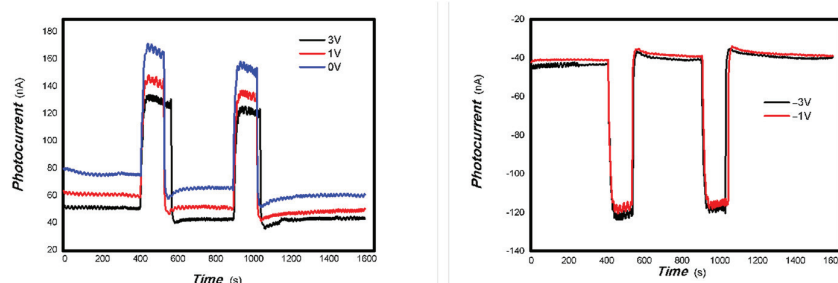


Figure 13. The effects of bias on the optoelectronic signal to 200 mW 808 nm light source for the 1#-MoVO_x (using Au gap electrodes on PET film).

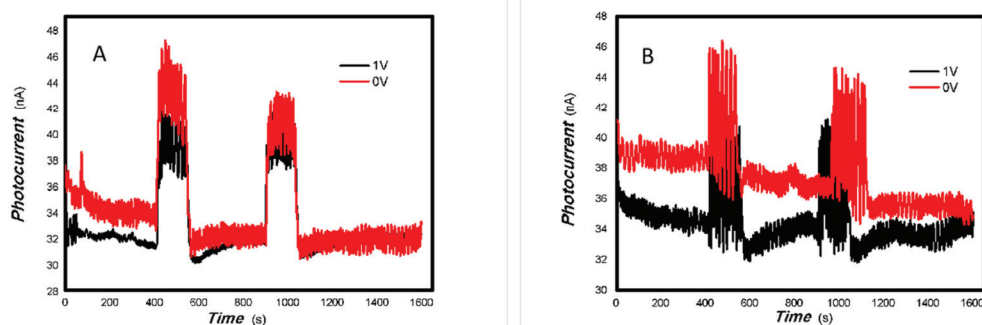


Figure 14. The effects of bias on the optoelectronic signal to the 980 and 1064 nm light sources for the 1#-MoVO_x ((A) 980 nm (100 mW); (B) 1064 nm (20 mW)) (using Au gap electrodes on PET film).

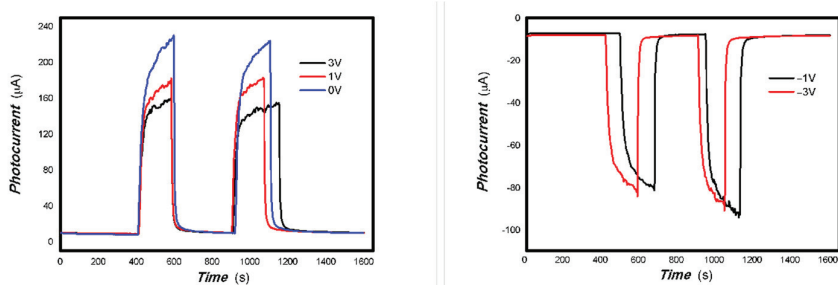


Figure 15. The effects of bias on the optoelectronic signal to 200 mW 808 nm light source for the 2#-MoVO_x (using Au gap electrodes on PET film).

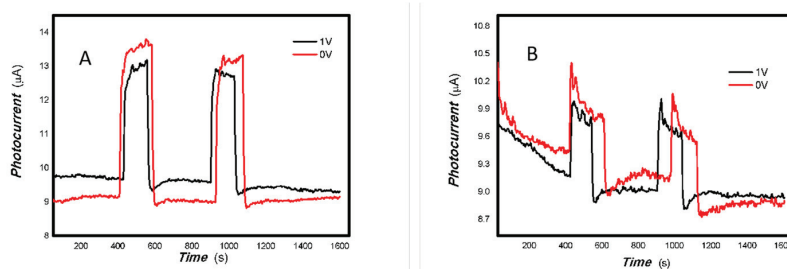


Figure 16. The effects of bias on the optoelectronic signal to the 980 and 1064 nm light sources for the 2#-MoVO_x ((A) 980 nm (100 mW); (B) 1064 nm (20 mW)) (using Au gap electrodes on PET film).

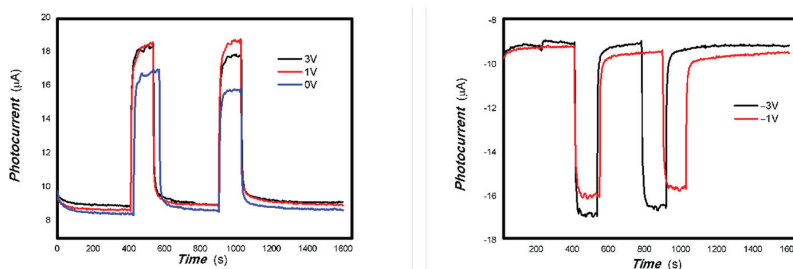


Figure 17. The effects of bias on the optoelectronic signal to the 980 nm light source for the 3#-MoVO_x (using Au gap electrodes on PET film).

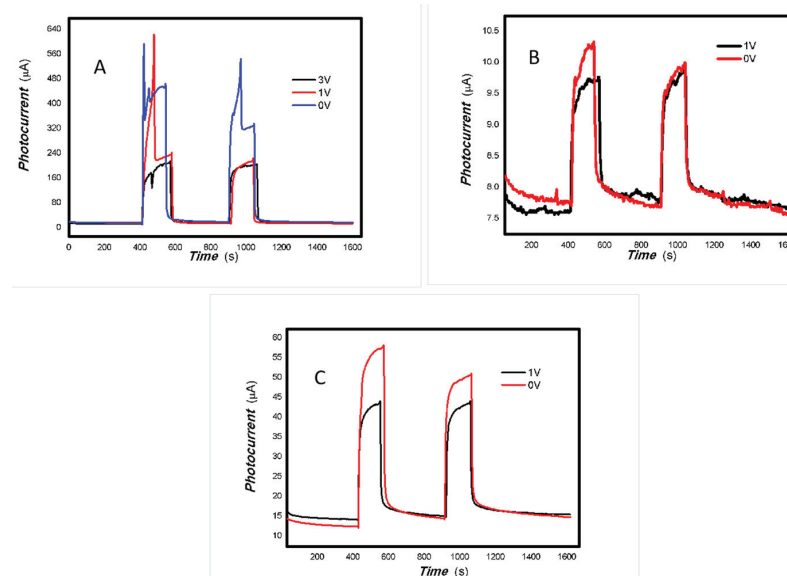


Figure 18. The effects of bias on the optoelectronic signal to the representative light sources for the 3#-MoVO_x ((A) 808 nm (200 mW); (B) 1064 nm (20 mW); (C) 650 nm (50 mW)) (using Au gap electrodes on PET film).

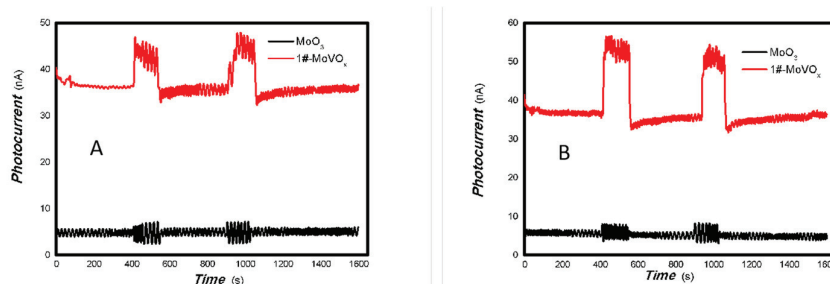


Figure 19. The effects of V doping on the optoelectronic signal of 1#-MoVO_x ((A) 405 nm (50 mW); (B) 650 nm (50 mW)) (using Au gap electrodes on PET film).

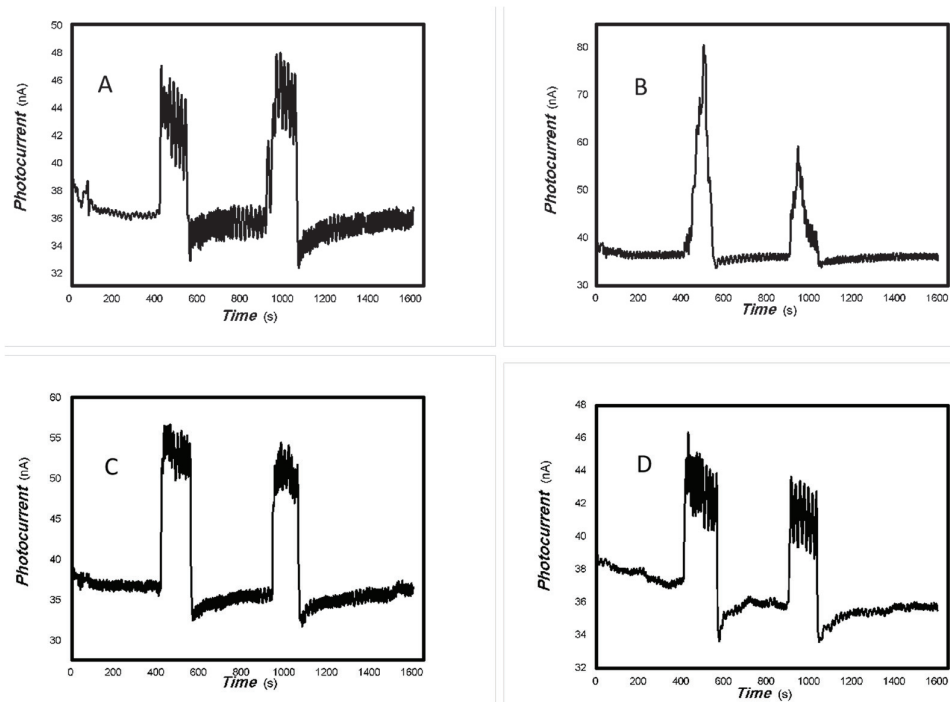


Figure 20. The comparative photocurrent signals of 1#-MoVO_x to the light source with different wavelengths ((A) 50 mW 405 nm; (B) 50 mW 532 nm; (C) 50 mW 650 nm; (D) 50 mW 780 nm) (using Au gap electrodes on PET film).

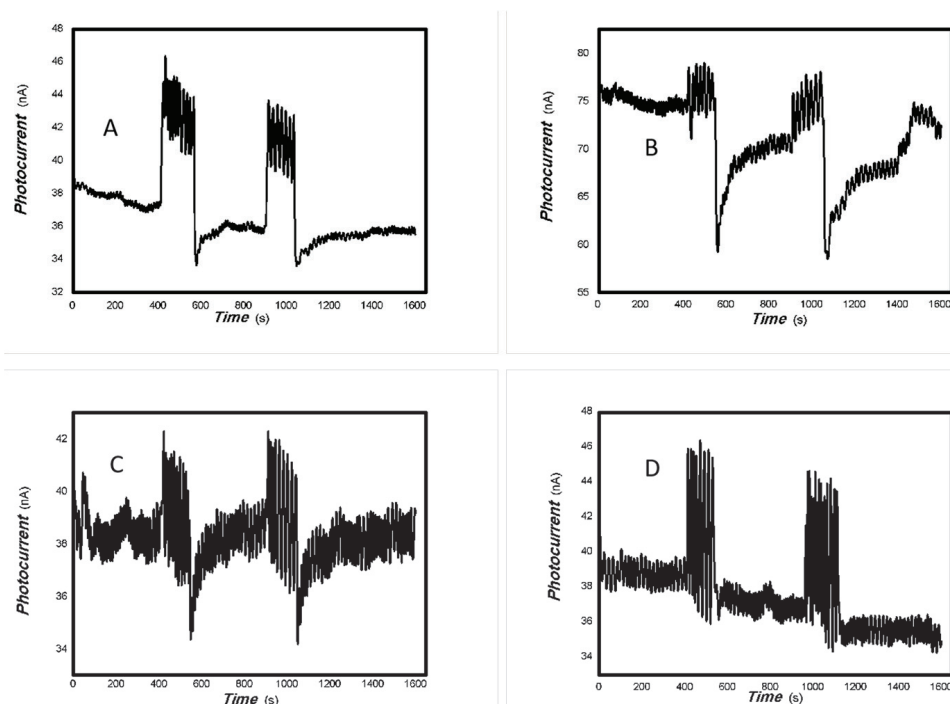


Figure 21. The comparative photocurrents signals of 1#-MoVO_x to the light source with different wavelengths ((A) 780 nm (50 mW); (B) 808 nm (50 mW); (C) 980 nm (50 mW); (D) 1064 nm (20 mW)) (using Au gap electrodes on PET film).

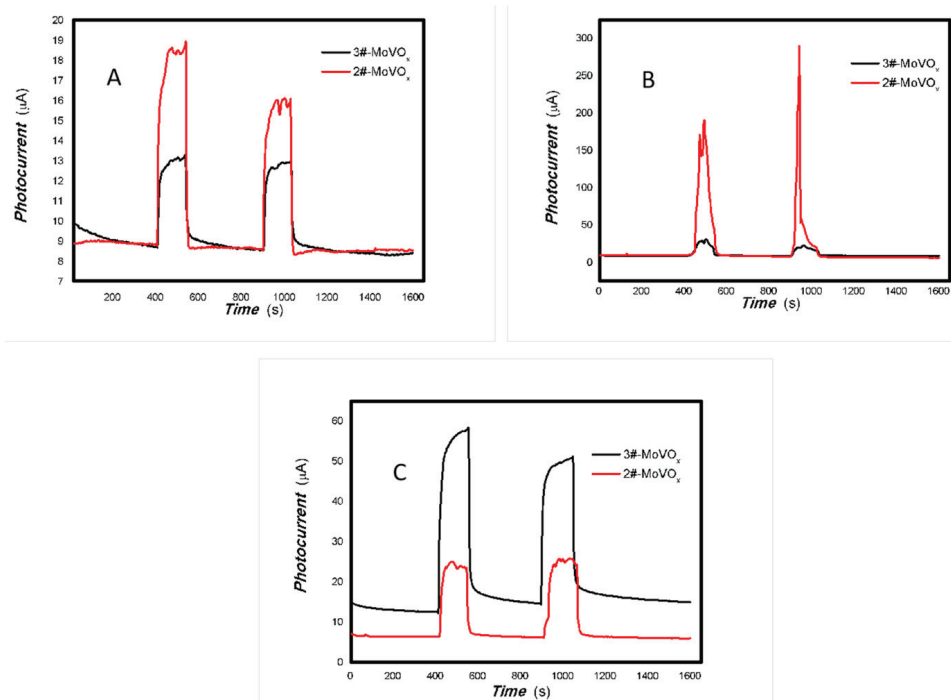


Figure 22. The comparative photocurrents signals of 2#,3#-MoVO_x to the light source with different wavelengths ((A) 405 nm (50 mW); (B) 532 nm (50 mW); (C) 650 nm (50 mW)) (using Au gap electrodes on PET film).

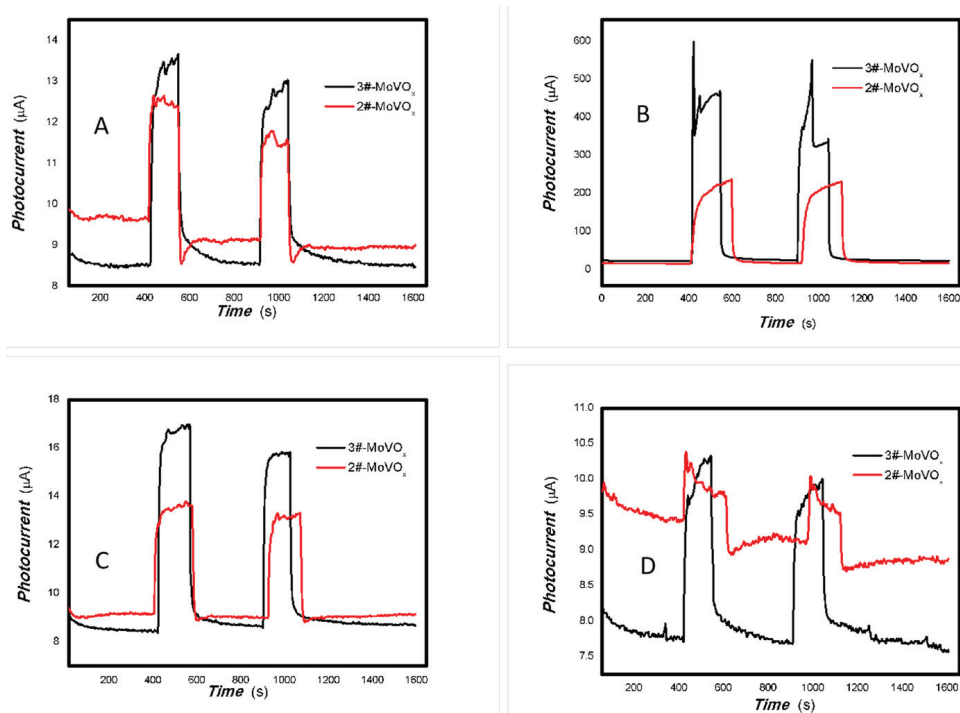


Figure 23. The comparative photocurrents signals of 2#,3#-MoVO_x to the light source with different wavelength ((A) 780 nm (50 mW); (B) 808 nm (200 mW); (C) 980 nm (100 mW); (D) 1064 nm (20 mW)) (using Au gap electrodes on PET film).

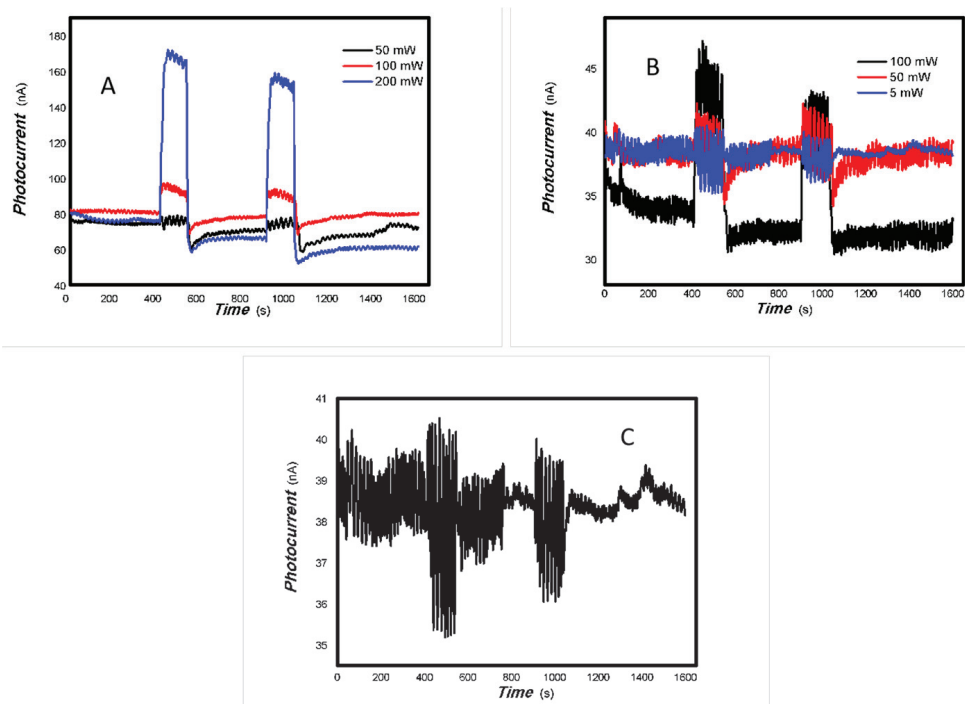


Figure 24. The dependence of the photocurrent signals of 1#-MoVO_x on the power of incident light sources ((A) 808 nm; (B) 980 nm; (C) 5 mW 980 nm) (using Au gap electrodes on PET film).

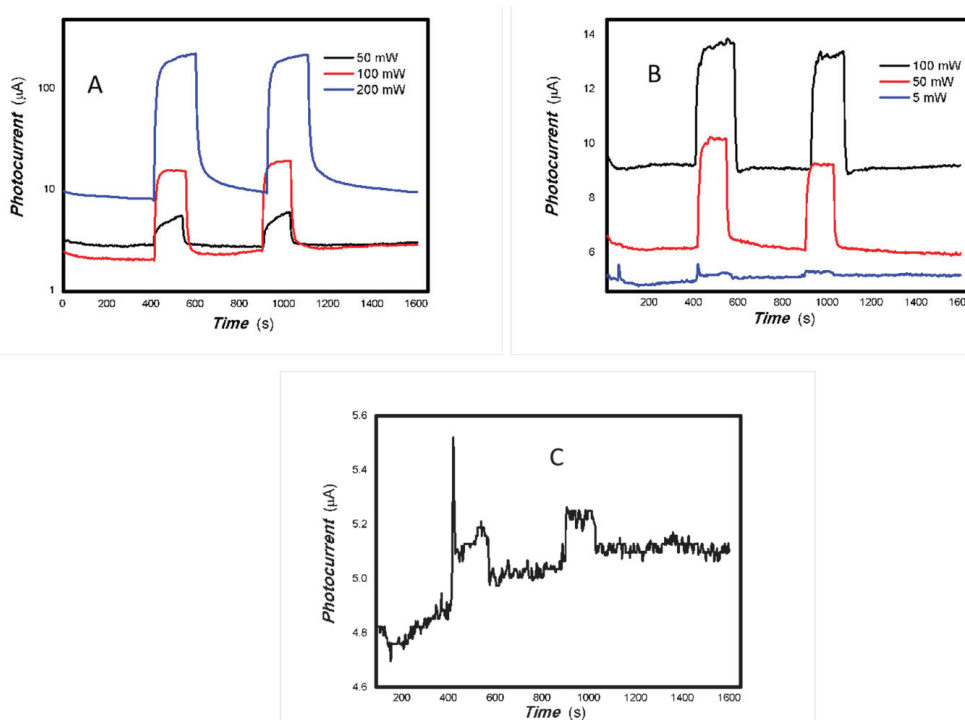


Figure 25. The dependence of the photocurrent signals of 2#-MoVO_x on the power of incident light sources ((A) 808 nm; (B) 980 nm; (C) 5 mW 980 nm) (using Au gap electrodes on PET film).

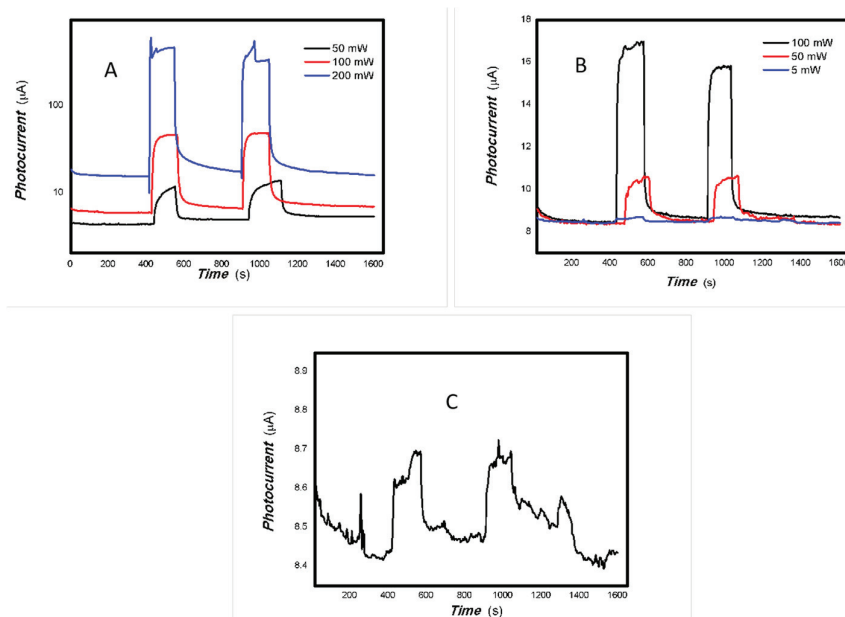


Figure 26. The dependence of the photocurrent signals of 3#-MoVO_x on the power of incident light sources ((A) 808 nm; (B) 980 nm; (C) 5 mW 980 nm) (using Au gap electrodes on PET film).

The effect of bias on the optoelectronic signal was examined by selecting several representative light sources first. These results are shown in Figures 13–18.

Figure 13 shows that the bias has a little effect on the optoelectronic signal to 200 mW 808 nm light source for the 1#-MoVO_x.

Figure 14 shows that the applying a bias voltage slightly reduces the photoelectric signal for the 1#-MoVO_x sample with 980 nm and 20 mW 1064 nm light sources. This trend of decrease is more obvious for the 2#-MoVO_x sample. These results are shown in Figures 15 and 16. This is primarily due to the built-in electric field being in the opposite direction to the applied bias voltage, which counteracts part of the driving force for charge transfer.

Figures 17 and 18 demonstrate that applying a bias voltage significantly increases the transfer of photogenerated charge. This indicates differences in the strength of the built-in electric field of various V-doped nanocomposites, reflecting the differing effects of applying different bias voltages to photogenerated electrical signals.

In order to compare the doping effect of different V, representative light sources were selected and examined. This is shown in Figure 19.

Figure 19 shows that low V doping improves both the photoelectric signal and the base current. V doping can improve the conductivity of the material. However, the 50 mW 405 and 650 nm light sources triggered large fluctuations in the base current for the MoO₃ reference sample only. This suggests that radiation from these light sources increases the likelihood of collisions between electrons and material defects, resulting in significant fluctuations in the base current.

The above experimental investigations illustrate that the prepared mixed oxides themselves have a built-in electric field that can drive the directional movement of photogenerated charges to form photocurrents. The effect of zero bias applied on different wavelengths of light is shown in Figures 20 and 21.

Figures 20 and 21 demonstrate that the 1#-MoVO_x nanobelts still exhibited excellent photocurrent extraction capabilities when exposed to light sources of 50 mW at 405, 650, 780, and 980 nm, as well as 20 mW at 1064 nm, with a bias of 0 V applied.

It was found that increasing V doping improves the electrical conductivity of the material. The baseline current changes from nA to μA. To facilitate the comparison of the effect of increasing V doping on the photoelectric signals, the photoelectric signals of the

2#, 3# nanocomposite samples were compared in the same figure. The results are shown in Figures 22 and 23.

Figures 22 and 23 demonstrate that the photoelectric signal in the near-infrared (NIR) region (780, 808, 980 and 1064 nm) increases significantly with V doping. Therefore, V doping greatly increases the red shift of the material.

For ease of comparison and analysis, some of the key data from the above figure are summarized in Table 3.

Table 3. The comparative photocurrent signals of 1#, 2#, 3#-MoVO_x nanobelt aggregation states using Au gap electrodes and PET film to some representative light sources (0 V bias applied).

Excitation Light Wavelength (nm)	Sample	Response Time (s)	Recovery Time (s)	Ratio of on/off
50 mW, 405 nm	1#-MoVO _x	10.0	10.0	1.26
50 mW, 405 nm	2#-MoVO _x	43.47	12.1	2.09
50 mW, 405 nm	3#-MoVO _x	28.0	35.9	1.49
50 mW, 532 nm	1#-MoVO _x	65.5	13.1	1.46
50 mW, 532 nm	2#-MoVO _x	19.6	47.6	18.64
50 mW, 532 nm	3#-MoVO _x	59.4	36.0	3.32
50 mW, 650 nm	1#-MoVO _x	6.6	13.4	1.51
50 mW, 650 nm	2#-MoVO _x	27.6	28.0	3.71
50 mW, 650 nm	3#-MoVO _x	23.8	31.8	4.60
50 mW, 780 nm	1#-MoVO _x	13.1	6.6	1.19
50 mW, 780 nm	2#-MoVO _x	20.1	7.9	1.30
50 mW, 780 nm	3#-MoVO _x	35.5	59.8	1.58
50 mW, 808 nm	1#-MoVO _x	3.4	13.1	1.05
50 mW, 808 nm	2#-MoVO _x	55.6	28.0	1.94
50 mW, 808 nm	3#-MoVO _x	63.5	43.9	2.68
50 mW, 980 nm	1#-MoVO _x	13.1	13.1	1.07
50 mW, 980 nm	2#-MoVO _x	23.8	28.0	1.66
50 mW, 980 nm	3#-MoVO _x	32.2	83.6	1.25
5 mW, 980 nm	1#-MoVO _x	6.6	10.0	1.04
5 mW, 980 nm	2#-MoVO _x	18.6	12.4	1.05
5 mW, 980 nm	3#-MoVO _x	19.5	19.5	1.02
20 mW, 1064 nm	1#-MoVO _x	6.6	16.2	1.18
20 mW, 1064 nm	2#-MoVO _x	7.9	11.7	1.05
20 mW, 1064 nm	3#-MoVO _x	20.1	56.0	1.32

As shown in Table 3, the general trend is that the photoconductivity ratio first increases and then decreases as the V doping concentration increases. The response and recovery times are also prolonged. There are also some fluctuations. This is primarily due to the numerous defects present in the mixed oxides. Defect-induced scattering reduces charge transport, leading to significant baseline and photocurrent fluctuations. A comparison of Tables 2 and 3 shows that the resulting material using Au electrodes and a PET film substrate did not exhibit a negative photoconductive effect. This indicates that the defects in the carbon electrode with 6B pencil drawings and paper substrate played a significant

role for the acquisition of optoelectronic signals and photoconductive behaviors. Light scattering caused by defects plays an important role in the fluctuation of photocurrent.

The representative results of their photoelectric signals dependent on the incident light power are shown in Figures 24–26.

As shown in Figures 24–26, the photoelectric signal clearly depends on the incident light power. A good photoelectric signal is still obtained with increased V doping (samples 2# and 3#) for a 5 mW, 980 nm light source. This is demonstrated in Figures 25 and 26. However, there is significant fluctuation at a low V doping amount for a 5 mW, 980 nm light source. This is shown in Figure 24. This is primarily due to the fact that mixed oxides with low V doping contain more defects that can easily capture photogenerated electrons, thereby increasing the likelihood of electron–electron and electron–defect collisions. This affects charge transport and leads to large photocurrent fluctuations. A comparison of Figures 22 and 23 shows that sample 2# has higher near-infrared (NIR) photoelectric sensitivity. The improvement in near-infrared photoconductivity is mainly due to the appropriate doping concentration of V element. According to the reference [84], the band gap of VO_2 is approximately 1.17 eV, this is the primary reason for the enhanced near-infrared photoelectric sensitivity. However, other factors, including changes in the valence state, plasma characteristics and the high proportion of amorphous material, also affect its photophysical properties and physical mechanisms. These factors work together to promote the extraction of photo-generated charges from the material and bring about different physical effects. The one-pot preparation of nanocomposites that exhibit photogenerated charge extraction properties in the near-infrared spectrum has been demonstrated to be a simple and feasible process. Suppressing photogenerated carrier recombination and improving charge extraction properties is important for applications in multidisciplinary fields [85]. As electron–hole recombination has been a key bottleneck in these fields for several decades, this study focused on a different nanocomposite system to improve the extraction of photogenerated charges across the broadband spectrum. This provides an important reference for these fields.

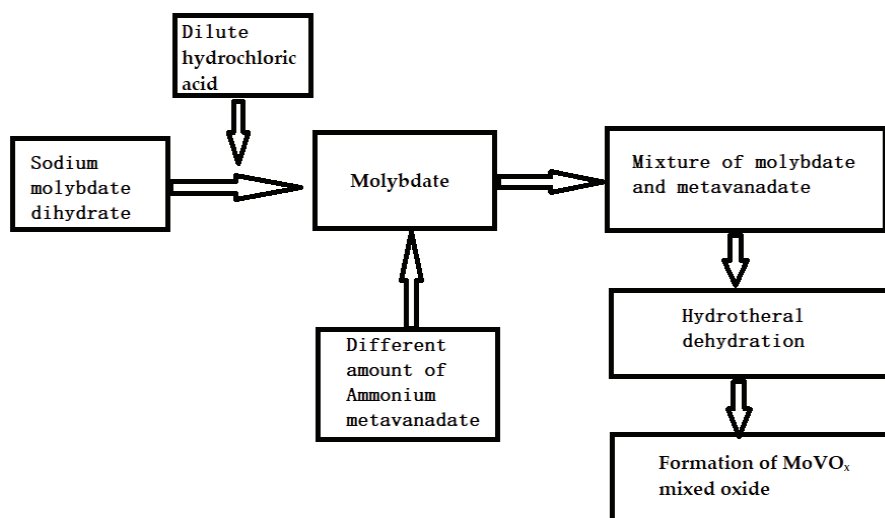
3. Materials and Methods

3.1. Raw Materials

The following materials were used in this study: sodium molybdate dihydrate (analytical reagent, AR), Tianjin Fengchuan Chemical Reagent Co. (Tianjin, China); ammonium metavanadate (NH_4VO_3) (AR), Tianjin Bodi Chemical Co (Tianjin, China); and hydrochloric acid (AR), Hongteng Weiye New Material Co., Ltd. (Yantai, China).

3.2. Synthesis of MoVO_x Mixed Oxide with One Pot

The dilute hydrochloric acid and the synthesis of MoVO_x was similar to that of MoO_3 in reference [74]. First, 1 g of sodium molybdate was added to 1#, 2#, 3# hydrothermal kettle, and then 40 mL of dilute hydrochloric acid, 20 mL of H_2O , and 0.2 g, 0.5 g, 0.8 g ammonium metavanadate were added, and stirred for about 10 min. The hydrothermal reaction was maintained at 170 °C for 6 h. The resulting products are labeled 1#, 2#, 3#- MoVO_x . The synthesis process of the MoVO_x is as follows (it is shown in Scheme 1).



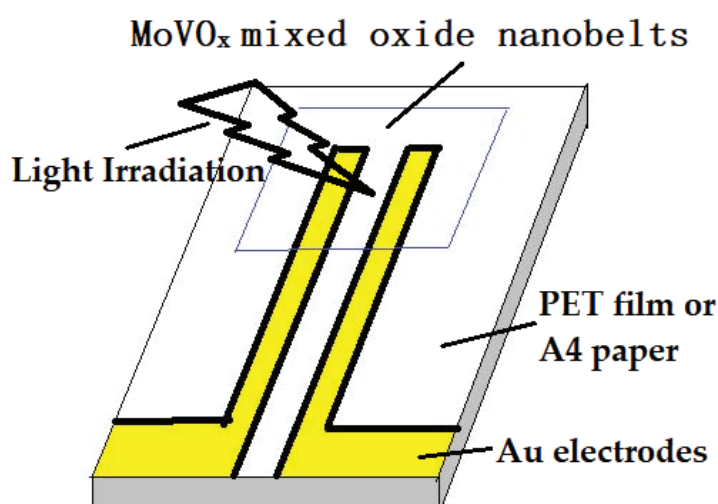
Scheme 1. The synthesis process of the MoVO_x.

3.3. Characterization with SEM, UV-Vis-NIR Spectrum, and XRD

The characterizations by scanning electron microscope (SEM), UV-VIS-NIR spectrophotometer (UV-Vis-NIR) and X-ray powder diffraction (XRD) were similar to the reference [74,75,83]. The instruments used were a ZEISS Gemini SEM300 (Oberkochen, Germany), TU-1810 spectrophotometer (Beijing Puxi General Instrument Co., Ltd., Beijing, China), and XRD-7000 from SHIMADZU (Shimadzu, Kyoto, Japan).

3.4. Measurement of the Optoelectronic Signal of MoVO_x Mixed Oxide in the Wide Spectral Range

The MoVO_x mixed oxide suspension was cast on the Au gap electrodes on a flexible polyethylene terephthalate (PET) film. For the photodetector structure of the photoconductor type, the structure of the electrodes is shown in Scheme 2. The determination of the optoelectronic response to the weak visible light (40 W) or 405, 532, 650 nm (100, 50, and 5 mW) and 780, 808, 980, and 1064 nm NIR (10, 40, 50, 100, and 200 mW) was similar to that in reference [74,75,83]. Another electrodes was used 6B pencil drawings and A4 printing paper as a substrate in this study. The bias applied was 0 and 1 V.



Scheme 2. The structure of the electrodes used in this study.

4. Conclusions

In short, the MoVO_x mixed oxide nanobelt was synthesized using the one-pot hydrothermal method. Good photoelectric signals were still measured within the broadband

light response range, even with zero bias applied, and using graphite electrodes with 6B pencil drawings and Au electrodes. This demonstrates that the MoVO_x mixed oxide presents a strong built-in electric field that promotes the photogenerated carrier transport, which can be self-powered. Doping with V significantly improved the NIR photoelectric sensitivity of the nanocomposites, and brought about different physical effects. This inexpensive, simple method can be used to obtain metal oxide nanocomposites that exhibit a photocurrent response over a wide spectral range. It is also expected to be suitable for bandgap narrowing in other wide-bandgap oxide material systems. These results are probably due to the introduction of intermediate states through V doping or intercalation. This study also provides an effective way to suppress the recombination of photogenerated carriers by controlling the microstructure of the nanocomposite and forming a strong built-in electric field.

Author Contributions: Conceptualization, methodology, investigation, writing—original draft preparation, writing—review and editing, funding acquisition, resources, X.M.; investigation, X.M., X.Z., M.G., R.H. and Y.W.; resources, G.L.; all authors analyzed the data; all authors discussed the results of the paper. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: Not applicable.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

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Article

Photoelectrochemical and Photocatalytic Properties of SnS/TiO₂ Heterostructure Thin Films Prepared by Magnetron Sputtering Method

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Abstract

Tin(II) sulfide(SnS)/titanium(IV) oxide (TiO₂) heterostructure thin films were prepared by radio-frequency magnetron sputtering to investigate the enhancement effect of the formed heterojunction on the photocatalytic performance. By adjusting the sputtering time to vary the thickness of the SnS layer, the crystallinity and light-absorption properties of the light-absorbing layer and the quality of the heterojunction interface were effectively controlled, thereby optimizing the fabrication process of the heterojunction. It was found that when the SnS layer thickness was 244 nm and the TiO₂ layer thickness was 225 nm, the heterostructure film exhibited optimal photoelectrochemical performance, generating the highest photocurrent of 3.03 $\mu\text{A}/\text{cm}^2$ under visible light, which was 13.8 times that of a pure TiO₂ film and 2.4 times that of a pure SnS film of the same thickness. Additionally, it demonstrated the highest degradation efficiency for methylene blue dye. The improved photoelectrochemical performance of the SnS/TiO₂ heterostructure film can be primarily attributed to the following: (1) the incorporation of narrow-bandgap SnS effectively broadens the light-absorption range, improving visible-light harvesting; (2) the staggered band alignment between SnS and TiO₂ forms a type-II heterojunction, significantly enhancing the charge carrier separation and transport efficiency. The present work demonstrated the feasibility of magnetron sputtering for constructing high-quality SnS/TiO₂ heterostructures, providing insights into the design and fabrication of photocatalytic heterojunctions.

Keywords: SnS; TiO₂; heterojunction; photoelectrochemical properties; magnetron sputtering

1. Introduction

Photocatalytic technology has garnered significant attention among various environmental remediation approaches due to its notable advantages of high efficiency, environmental friendliness, and mild reaction conditions. This technique utilizes solar energy to excite electrons in the photocatalyst, generating electron-hole pairs that subsequently produce highly reactive oxygen species, including hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2^{\bullet-}$). These reactive species demonstrate remarkable efficacy in degrading organic pollutants into harmless H₂O and CO₂ [1–3].

A variety of binary or ternary semiconductor materials, including oxides [4], nitrides [5], chalcogenides [6], and perovskites [7], have been employed in photocatalytic applications. In addition to single-phase semiconductors, heterojunctions formed by combining two or more semiconductor materials have attracted extensive research attention in

photocatalysis [8,9]. Currently, the most prevalent heterojunctions can be classified into three main types: type-II, Z-scheme, and S-scheme heterojunctions [10]. In type-II heterojunctions, the band structures of the two semiconductors exhibit a staggered alignment, where electrons migrate to the semiconductor with a lower conduction band potential, while holes transfer to the material with a higher valence band potential, thereby achieving effective charge separation [11].

As one of the earliest semiconductor materials employed in photocatalysis, TiO_2 possesses advantageous characteristics including non-toxicity, low cost, and excellent chemical stability [12]. With a bandgap of approximately 3.2 eV [13], TiO_2 can only absorb ultraviolet light with wavelengths shorter than 387 nm, which severely limits its solar energy utilization and practical photocatalytic efficiency [14]. Various modification strategies have been developed to enhance the photocatalytic performance of TiO_2 . The visible-light response can be extended through noble metal deposition [15,16], element doping [17–19], and sensitization with narrow-bandgap semiconductors [20–22]. Designing one-dimensional nanostructures, such as nanowires or nanotube arrays, can shorten the carrier diffusion path [2]. In addition, introducing defect states such as oxygen vacancies can increase the carrier concentration and enhance electrical conductivity [23]. Coupling TiO_2 with narrow-bandgap semiconductors represents a well-established and effective strategy that simultaneously addresses two critical aspects. The narrow-bandgap component extends optical absorption into the visible-light region, while the formed heterojunction structure enhances charge separation and transport through built-in interfacial electric fields, collectively leading to significantly improved photocatalytic efficiency [24–26].

SnS has a relatively narrow optical bandgap with remarkable tunability. Its bandgap can be categorized into an indirect bandgap (1.0–1.5 eV) and a direct bandgap (1.3–2.3 eV), with specific values influenced by synthesis methods, lattice strain, and sulfur stoichiometry [27,28]. Coupled with its high optical absorption coefficient of 10^4 to 10^5 cm^{-1} under visible light [29,30], SnS emerges as an ideal material for light-absorbing layers. Previous studies have demonstrated that SnS/TiO_2 heterostructures can effectively enhance photoelectric conversion efficiency [31,32]. Zhang et al. developed SnS/TiO_2 nanotube array (NTA) photoanodes with significantly enhanced photocatalytic degradation performance toward 2,4,6-trichlorophenol under visible-light irradiation. The construction of a type-II heterojunction by integrating SnS with TiO_2 suppressed the charge carrier recombination and improved separation efficiency. The nanostructure shortened charge diffusion pathways while increasing the specific surface area and exposing more active sites. After five consecutive degradation cycles, the SnS/TiO_2 NTAs maintain a removal efficiency of over 90% for the target pollutant, demonstrating excellent cycling stability and structural durability [33]. Successive ionic layer reaction (SILAR) remains the predominant fabrication technique, employing sequential immersion in cation and anion precursor solutions for thin film deposition [34,35]. Other established methods comprise hydrothermal synthesis [36], chemical bath deposition [37], and electrodeposition [33]. Beyond pollutant degradation, the SnS/TiO_2 heterojunction demonstrates versatile applications in solar cells [38], photocatalytic hydrogen production [39], and sensors [40]. Al Ahmed developed a solar cell using Zn_3P_2 as the hole transport layer, SnS as the light-absorbing layer, and TiO_2 as the electron transport layer, achieving 30.45% power conversion efficiency through optimized band alignment [38].

Currently, chemical methods predominantly serve as the primary approach for fabricating SnS/TiO_2 composites. Nevertheless, these solution-based processes are prone to generating impurity phases, either through excessive S^{2-} in the precursors or the oxidation of Sn^{2+} during reactions [34,41]. Such impurities not only compromise the light-absorption characteristics of SnS films due to bandgap misalignment but also introduce deep-level de-

fects that significantly impair charge carrier mobility [42]. In contrast, physical deposition methods conducted under vacuum conditions minimize the introduction of impurities and oxides, facilitating the formation of high-quality SnS/TiO₂ heterojunction interfaces.

This study employed magnetron sputtering, a widely used physical vapor deposition method, to fabricate SnS/TiO₂ heterostructure thin films. Compared to conventional solution-based approaches, this method enabled the precise control over film thickness and composition. The resulting SnS films maintained phase purity, and their integration with TiO₂ effectively extended the light-absorption range. Furthermore, the heterostructure films exhibited significantly improved charge carrier transport efficiency, contributing to enhanced photocatalytic performance relative to the individual SnS and TiO₂ components. These results confirmed magnetron sputtering as a controllable fabrication method that enables the tuning of crystallinity and interface properties, demonstrating its potential for constructing well-defined SnS/TiO₂ heterostructures for photocatalytic applications.

2. Results and Discussion

2.1. Structural Characterization

When the sputtering power was fixed at 80 W, the deposition rate typically remained stable. Consequently, the film thickness of SnS generally increased linearly with a prolonged sputtering time. The thicknesses of SnS and TiO₂ layers in different samples are shown in Table 1.

Table 1. Thicknesses of each layer in the SnS/TiO₂ thin films prepared with different sputtering time of SnS.

Sputtering Time of SnS (min)	Thicknesses of SnS (nm, ± 4)	Thicknesses of TiO ₂ (nm, ± 4)
8	102	220
12	244	225
16	359	217
20	462	231

The thickness of the TiO₂ layer was maintained at approximately 220 nm, while the thickness of SnS layer exhibited a linear dependence on the sputtering time, as shown in Figure 1a. The linear regression analysis yielded a coefficient of determination (R^2) of 0.9918, confirming an excellent linear relationship between the thickness of SnS film and deposition time. Specifically, as the sputtering duration increased from 8 to 20 min, the corresponding thickness increased from 102 to 462 nm.

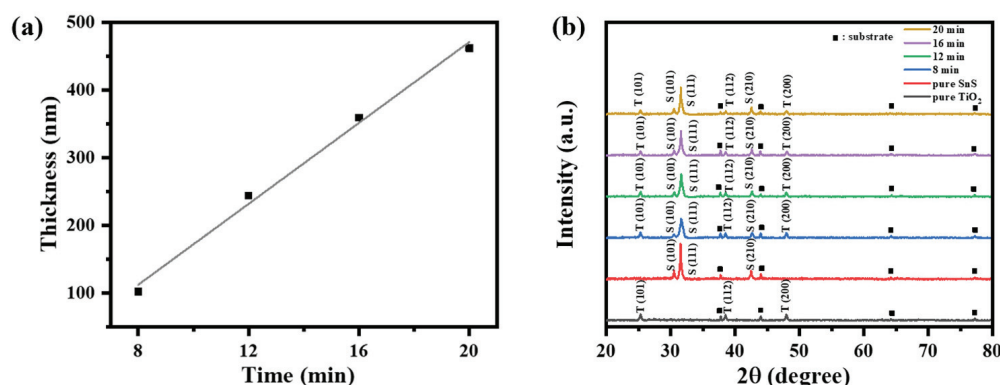


Figure 1. SnS/TiO₂ thin films prepared with different sputtering times of SnS: (a) the relationship between the thickness of the SnS layer and the sputtering time and (b) XRD patterns (T represents the diffraction peaks of TiO₂ as the anatase phase, and S represents the diffraction peaks of SnS).

The XRD patterns of the SnS/TiO₂ heterostructure, pure SnS, and pure TiO₂ thin films are shown in Figure 1b. All SnS/TiO₂ films exhibited diffraction peaks corresponding to both SnS and TiO₂ phases. As the sputtering time of the SnS layer increased, the diffraction peaks of SnS became more intense while those of TiO₂ showed a gradual decrease in intensity. The SnS layers displayed an orthorhombic structure with a polycrystalline nature that matched well with the standard diffraction pattern (JCPDS No. 39-0354), with characteristic peaks observed at approximately 30.52°, 31.60°, and 42.60°, corresponding to the (101), (111), and (210) planes of SnS, respectively. With an increasing sputtering time, the (111) and (210) diffraction peaks shifted slightly toward lower angles, and no diffraction peaks corresponding to impurity phases such as SnS₂ or Sn₂S₃ were detected. Additionally, three diffraction peaks of TiO₂ were observed and identified as the anatase phase (JCPDS No. 21-1272), including the (101) plane peak at 25.29°, the (112) plane peak at 38.51°, and the (200) plane peak at 47.97°. The relatively weak intensity of these TiO₂ diffraction peaks is likely due to the fact that the TiO₂ layer was located beneath the SnS layer and had a relatively small thickness.

The crystallite size (*D*) and microstrain (ϵ) of both SnS and TiO₂ were calculated using Scherrer's formula (Equation (1)) and the strain equation (Equation (2)), respectively [43,44]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

$$\epsilon = \frac{\beta}{4\tan\theta} \quad (2)$$

where *K* is the Scherrer constant, λ denotes the X-ray wavelength (0.15406 nm), β represents the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle.

The lattice parameters of both thin films were calculated using Bragg's law (Equation (3)) and the interplanar spacing formula (Equation (4)) [45], where λ represents the incident X-ray wavelength, d_{hkl} denotes the interplanar spacing, θ is the diffraction angle, (*h*, *k*, *l*) are the Miller indices, and (*a*, *b*, *c*) stand for the lattice constants. SnS crystallizes in the orthorhombic system, while anatase TiO₂ adopts a tetragonal structure (with *a* = *b*) [46,47]. The calculated crystallite sizes and lattice parameters are summarized in Table 2.

$$\lambda = 2d_{hkl}\sin\theta \quad (3)$$

$$\frac{1}{d_{hkl}^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2 \quad (4)$$

Table 2. Calculation of the structural parameters of the SnS/TiO₂ thin films prepared with different sputtering times of SnS.

Sputtering Time of SnS (min)	SnS					TiO ₂		
	<i>D</i> ± 0.8 (nm)	ϵ ± 0.09 (×10 ^{−3})	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>D</i> ± 0.8 (nm)	<i>a</i> (Å)	<i>c</i> (Å)
8	18.5	6.87	4.3199	10.8950	3.9765	27.0	3.7900	9.4453
12	22.6	5.44	4.3210	10.9415	3.9757	27.3	3.7928	9.4292
16	23.8	5.10	4.3219	11.1500	3.9775	27.2	3.7848	9.5549
20	24.6	4.95	4.3277	11.1054	3.9777	27.9	3.7900	9.4725
pure SnS	27.5	4.29	4.3279	11.1735	3.9771	/	/	/
pure TiO ₂	/	/	/	/	/	27.5	3.7899	9.4736

The TiO₂ thin films had a grain size of about 27 nm, with lattice parameters close to standard values (*a* = *b* = 3.7852 Å, *c* = 9.5139 Å). For the SnS films, when the sputtering

time increased from 8 to 20 min, the grain size grew from 18.5 nm to 24.6 nm, yet remained smaller than that of pure SnS films deposited directly on glass substrates. The variation in microstrain across different crystallographic planes is illustrated in Figure 2a, showing a consistent decreasing trend in microstrain for all observed planes with an increasing sputtering time. The most significant changes in both grain size and microstrain occurred when the sputtering time increased from 8 to 12 min, with subsequent prolongation showing diminished variation amplitudes. As the film thickness increased, the grains developed more completely through the growth and merging of smaller crystallites, resulting in larger grain sizes and improved crystallinity [48]. The standard lattice parameters for orthorhombic SnS are $a = 4.3291 \text{ \AA}$, $b = 11.1923 \text{ \AA}$, and $c = 3.9838 \text{ \AA}$. The deviations of lattice constants for different samples from standard values are presented in Figure 2b, as determined by the following Equation (5):

$$\delta_a = \frac{a - a_0}{a_0}; \delta_b = \frac{b - b_0}{b_0}; \delta_c = \frac{c - c_0}{c_0} \quad (5)$$

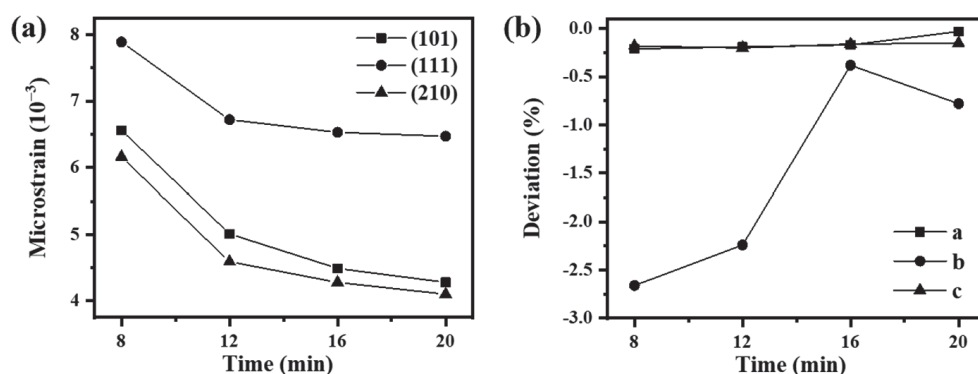


Figure 2. SnS/TiO₂ thin films prepared with different sputtering time of SnS: (a) microstrain calculated from different crystallographic planes and (b) deviation of lattice constants from standard values.

Considerable deviations occurred at the shorter sputtering time of 8–12 min, while films deposited for 16–20 min showed better agreement with standard values. This behavior may be attributed to the insufficiently smooth surface of the TiO₂ films, which imposed a localized strain on the overlying SnS films and hindered proper grain growth, causing lattice distortion. Additionally, the poor lattice matching between the SnS films and substrate contributed to the deviation of lattice parameters [49].

The morphology of the SnS/TiO₂ thin films are shown in Figure 3. Figure 3a,b presents the surface and cross-sectional views of the heterostructure film, respectively, where the SnS layer was deposited for 12 min. The SEM images clearly revealed the heterostructure. Figure 3c–f display the AFM images of various samples, showing that the film surface exhibited enhanced planarity as the SnS sputtering time increased from 8 to 20 min. As shown in Table 3, the root mean square (RMS) roughness ranged from 1.60 to 1.93 nm.

Table 3. Root mean square (RMS) of the SnS/TiO₂ thin films prepared with different sputtering times of SnS.

Sputtering Time of SnS (min)	RMS (nm)
8	1.93
12	1.74
16	1.63
20	1.60

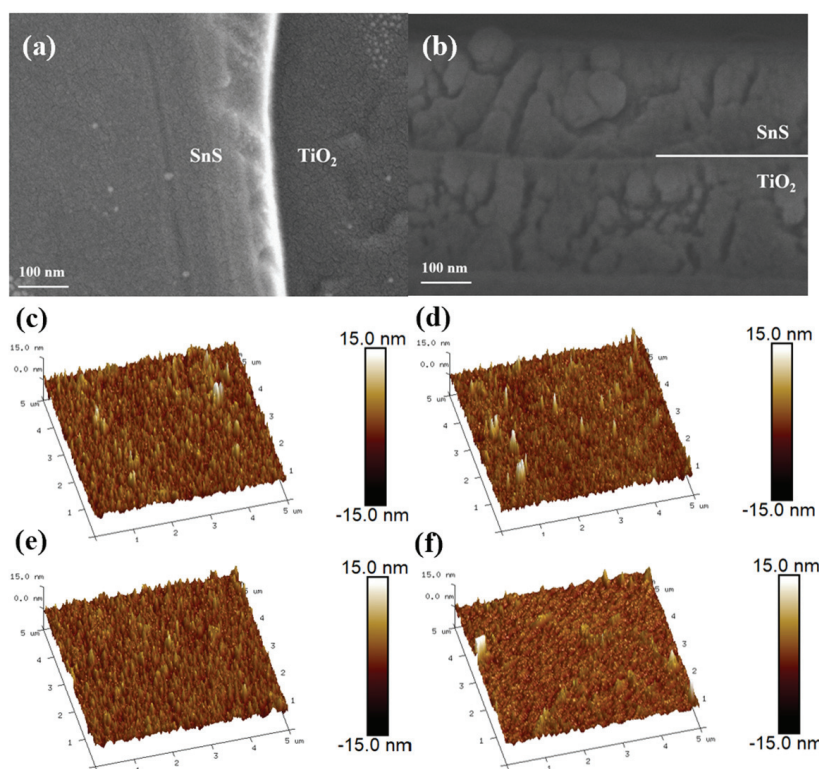


Figure 3. SEM images of the SnS/TiO₂ thin films with the SnS sputtering time of 12 min: (a) surface (b) cross-section; AFM images of the SnS/TiO₂ thin films prepared with different sputtering time of SnS: (c) 8 min; (d) 12 min; (e) 16 min; and (f) 20 min.

The elemental composition of SnS/TiO₂ films prepared with different sputtering times of SnS showed no significant variations. Therefore, representative EDS and XPS spectra from the sample with the 8 min sputtering time of SnS are presented in Figure 4. The EDS spectrum revealed the elemental distribution, with atomic percentages for different samples summarized in Table 4. As the SnS layer thickness increased, the atomic percentages of Sn and S progressively rose, while those of Ti and O correspondingly decreased. In the heterostructure films, the Ti:O ratio was approximately 1:2.12, close to the theoretical value of 1:2. The Sn:S ratio was about 1.23:1, indicating a Sn-rich and S-deficient composition in the SnS films. This deviation primarily arises from the much higher saturated vapor pressure of S compared to Sn, causing the preferential re-evaporation of S atoms from the film surface during deposition.

Table 4. Atomic percentages of the SnS/TiO₂ thin films prepared with different sputtering times of SnS.

Sputtering Time of SnS (min)	Ti (At%)	O (At%)	Sn (At%)	S (At%)
8	21.08	45.85	18.24	14.83
12	15.24	32.18	29.01	23.57
16	7.06	14.97	43.18	34.79
20	4.63	9.69	47.36	38.32

Due to the shallow probing depth of XPS, the characterization of heterostructure films was conducted in two stages: first, the pure TiO₂ film was analyzed to obtain high-resolution spectra of Ti and O elements, shown in Figure 4e,f; subsequently, after the SnS layer deposition, another measurement was performed to determine the elemental composition and chemical states of the SnS film. Figure 4b shows the XPS survey spectrum of the upper SnS layer, while Figure 4c,d presents the high-resolution spectra of Sn and S elements, respectively. In the Sn 3d spectrum, the peaks at 485.5 eV and 494.0 eV

corresponded to the Sn 3d_{5/2} and Sn 3d_{3/2} energy levels, respectively, with a binding energy difference of 8.5 eV, confirming the presence of Sn²⁺ [50]. The S 2p spectrum exhibited two peaks at 160.3 eV and 161.5 eV, attributed to the spin–orbit splitting of S^{2−} [51]. Combined with XRD results, it was demonstrated that the phase-pure nature of the magnetron-sputtered SnS layer effectively avoided detrimental effects from impurity phases on the light-absorption properties. Figure 4e,f displays the high-resolution spectra of Ti and O elements from the pure TiO₂ film. The Ti 2p spectrum showed characteristic peaks at 458.4 eV of Ti 2p_{3/2} and 464.1 eV of Ti 2p_{1/2}, with a spin–orbit splitting of 5.7 eV, consistent with Ti⁴⁺ [52]. The O 1s spectrum revealed two components: the peak at 529.8 eV originated from Ti–O bonds, while the peak at 531.7 eV was assigned to surface –OH groups [53].

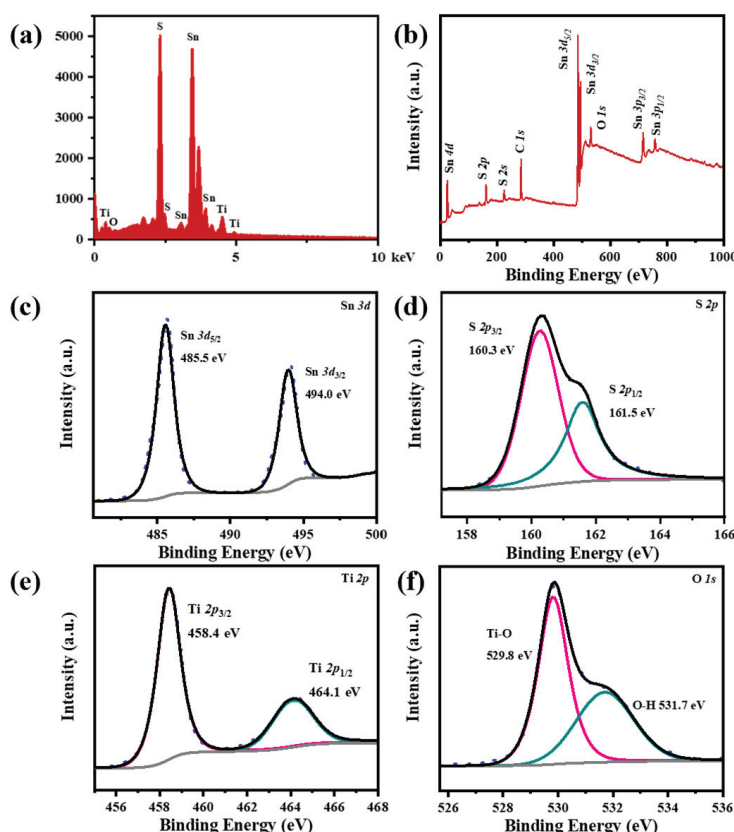


Figure 4. SnS/TiO₂ thin film prepared with 8 min sputtering time of SnS 8 min: (a) EDS spectrum; (b) XPS survey spectrum of SnS layer; (c) Sn 3d high-resolution spectrum of SnS layer; (d) S 2p high-resolution spectrum of SnS layer; (e) Ti 2p high-resolution spectrum of the pure TiO₂ film; and (f) O 1s high-resolution spectrum of the pure TiO₂ film.

Figure 5a presents the UV-Vis-NIR diffuse reflectance spectra of SnS/TiO₂ heterostructure thin films prepared with different sputtering time of SnS. The Tauc equation (Equation (6)) was employed to calculate the bandgaps of both pure SnS and TiO₂ films [54,55]:

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g) \quad (6)$$

α represents the absorption coefficient, A is a constant, and the value of n depends on the electronic transition characteristics of the semiconductor. The direct bandgap of SnS was calculated with $n = 1/2$, while TiO₂, as an indirect bandgap semiconductor, was assigned $n = 2$ [56,57]. In indirect transitions, the energy contribution from electron–phonon interactions is much smaller than the photon energy. Near the band edges, the influence of phonon energy on the absorption coefficient is relatively weak. Therefore, the phonon

energy is approximated as a perturbation to the bandgap and directly incorporated into the effective bandgap value [54,58]. The Tauc plot of the pure SnS and TiO₂ film is shown in Figure 5b,c, with the corresponding absorption spectra provided as insets. The pure SnS film, deposited with a sputtering time of 20 min and a thickness of 456 nm, exhibited a bandgap of 1.27 ± 0.03 eV, while the pure TiO₂ film with a thickness of 231 nm had a bandgap of 3.26 ± 0.03 eV. The SnS thin film with a narrow bandgap exhibited superior visible-light absorption compared to TiO₂. When composited with TiO₂ to form the heterostructure, the resulting films demonstrated a pronounced red shift in absorption edge and significantly enhanced the visible-light-absorption capacity. As the sputtering time of SnS layers increased from 8 to 12 min, the films showed substantial improvement in light absorption. However, the further extension of the deposition time yielded diminishing returns, with the 20 min sample displaying a slightly lower absorption than the 16 min counterpart. This thickness-dependent optical behavior can be attributed to several inter-related factors. Thinner films suffer from incomplete photon absorption due to a limited optical path length, while increased thickness promotes more efficient light harvesting through extended propagation paths and improved crystallinity [59]. This improvement correlates with grain growth and structural perfection, which collectively induce bandgap narrowing and broaden the spectral response. Beyond optimal thickness, the absorption efficiency approaches saturation, with potential performance degradation caused by intensified light scattering and reflection losses [60]. Notably, the most significant enhancements in both grain size and light absorption occur during the initial 8 to 12 min of thickness increase, highlighting the critical influence of SnS crystallinity in determining the optical performance of heterostructure system.

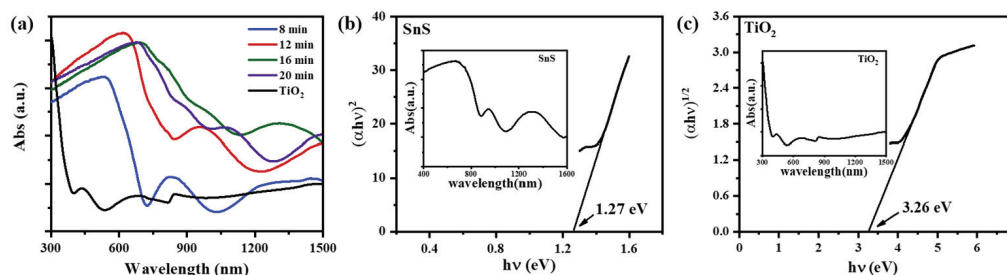


Figure 5. (a) UV-Vis-NIR absorption spectra of SnS/TiO₂ thin films prepared with different sputtering times of SnS; (b) $(\alpha h\nu)^2$ - $h\nu$ curve of the pure SnS thin film with absorption spectra as insets; and (c) $(\alpha h\nu)^{1/2}$ - $h\nu$ curve of the pure TiO₂ thin film with absorption spectra as insets.

2.2. Photoelectrochemical Characterization

Transient photocurrent tests were performed under visible-light irradiation using SnS/TiO₂ heterostructure thin films prepared with different sputtering times of SnS as photoanodes, with the results shown in Figure 6a. When the deposition time of SnS layer increased from 8 to 12 min, the photocurrent density of the heterostructure films exhibited a significant enhancement, rising from $1.98 \mu\text{A}/\text{cm}^2$ to $3.03 \mu\text{A}/\text{cm}^2$. However, the further prolongation of the sputtering time and corresponding increase in the SnS layer thickness led to a noticeable decline in photocurrent generation under visible light, with the 20 min sample showing a photocurrent density comparable to that of the 8 min sample. This phenomenon can be attributed to the improved crystalline quality and structural ordering of SnS layers with increasing thickness, which initially enhances their light-absorption capability. Nevertheless, when the film thickness exceeds an optimal range, the absorption approaches saturation while charge carrier scattering at grain boundaries and interfaces becomes more pronounced, ultimately reducing charge transport efficiency and photocurrent density [60,61]. Pure SnS and TiO₂ films of equivalent thickness to the optimized

12 min heterostructure served as controls to demonstrate the photoelectrochemical performance improvement. The current–time curves of these three configurations are presented in Figure 6b. The pure TiO_2 film demonstrated a minimal photocurrent density due to its poor visible-light absorption. While the pure SnS film generated a photocurrent density of $1.28 \mu\text{A}/\text{cm}^2$, the optimized heterostructure achieved $3.03 \mu\text{A}/\text{cm}^2$, representing a 13.8-fold enhancement over the pure TiO_2 film and a 2.4-fold improvement compared to SnS.

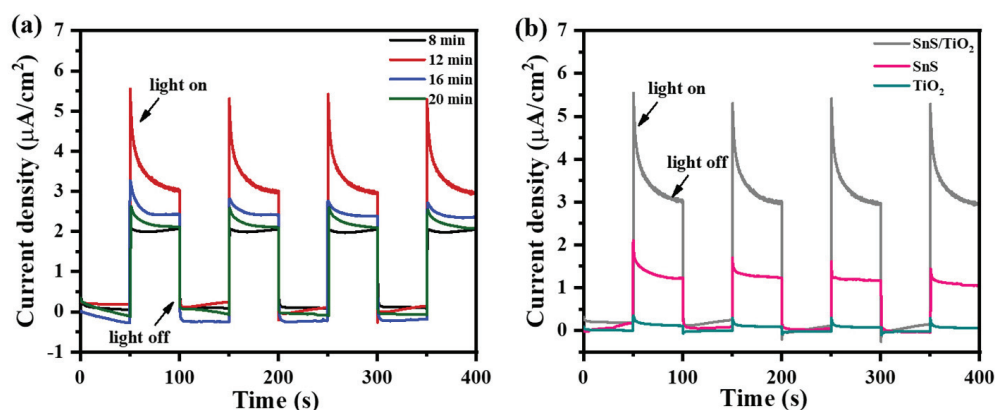


Figure 6. i-t curves under visible light: (a) The SnS/TiO_2 thin films prepared with different sputtering time of SnS and (b) samples with different structures.

To analyze the differences in photoelectrochemical performance among the various structures, electrochemical impedance spectroscopy (EIS) measurements were conducted to elucidate the charge transport and interfacial reaction mechanisms that may occur in different film architectures. Figure 7 displays the Nyquist plots of the samples, where the impedance (Z) is defined as a standard complex function comprising a real component (Z') and an imaginary component (Z'') [62]:

$$Z(\omega) = Z'(\omega) + iZ''(\omega) \quad (7)$$

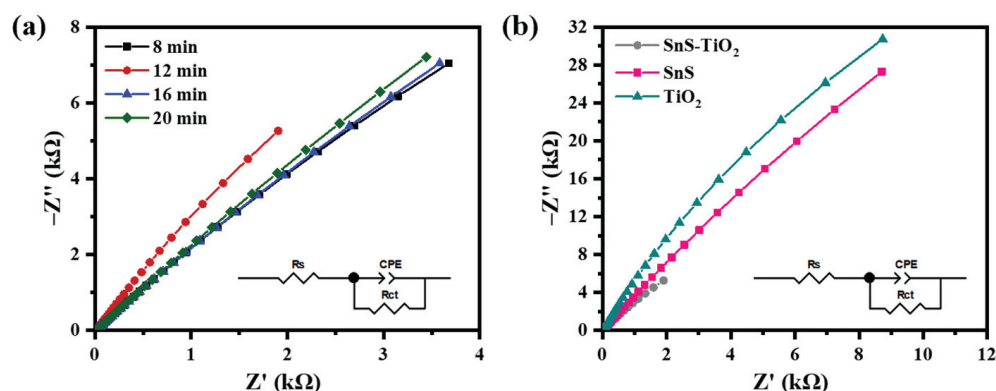


Figure 7. Electrochemical impedance spectra: (a) the SnS/TiO_2 thin films prepared with different sputtering time of SnS and (b) samples with different structures.

All EIS spectra exhibited semicircular arcs, indicating that the electrochemical processes at the semiconductor/electrolyte interface were primarily controlled by charge transfer [62]. The spectra were fitted using the equivalent circuit shown in the figure, where R_s represents the solution resistance, CPE denotes the constant phase element, and R_{ct} is the charge transfer resistance at the electrode surface. The fitted parameters are listed in Table 5. When the sputtering time of SnS increased from 8 to 12 min, the R_{ct} of the SnS/TiO_2 films decreased from 99.85 k Ω to 79.96 k Ω . However, with further increases in sputtering

time, the R_{ct} gradually rose to 168.33 k Ω , demonstrating that the interfacial charge transfer efficiency initially improved but subsequently deteriorated with an increasing SnS layer thickness. To further investigate the kinetics of the relevant electrochemical processes, the electron transfer rate constant (k^0) at the film/electrolyte interface was calculated using Equation (8) [62]:

$$k^0 = \frac{RT}{n^2 F^2 A R_{ct} C} \quad (8)$$

where R , T , and n represent the universal gas constant, reaction temperature, and number of electrons involved in the S^{2-}/S redox reaction, respectively, F denotes the Faraday constant ($\sim 96,485$ C/mol), A is the electrode surface area, and C is the concentration of the S^{2-}/S redox couple in solution.

Table 5. Fitting parameters of the electrochemical impedance spectra.

Sputtering Time of SnS (min)	R_{ct} (k Ω)	R_s (Ω)	CPE_{dl} (μF)	n	k^0 ($\times 10^{-9}$ m/s)	J_0 ($\times 10^{-8}$ A/cm 2)
8	99.85	10.55	47.70	0.74	13.11	12.65
12	79.96	15.65	14.94	0.82	16.37	15.80
16	123.32	10.52	48.49	0.73	10.61	10.24
20	168.33	14.02	31.22	0.74	7.78	7.50
SnS	523.53	25.13	26.71	0.84	2.50	2.41
TiO $_2$	289.52	13.47	16.54	0.89	4.52	4.36

The exchange current density (J_0) was additionally calculated using Equation (9) [63], with the results listed in Table 5:

$$J_0 = \frac{RT}{nFR_{ct}} \quad (9)$$

When the SnS layer was deposited for 12 min, the heterostructure film achieved maximum values for both k^0 of 1.637×10^{-8} m/s and J_0 of 1.580×10^{-7} A/cm 2 , demonstrating that an optimal SnS thickness can significantly enhance the charge transfer efficiency. However, when the sputtering time exceeded 12 min, both k^0 and J_0 decreased, likely because the increased thickness of the light-absorption layer began to adversely affect charge carrier transport pathways, thereby elevating recombination probability [64].

The pure SnS and TiO $_2$ films of equivalent thickness exhibited R_{ct} values of 523.53 k Ω and 289.52 k Ω , respectively. In contrast, the heterostructure demonstrated significantly reduced R_{ct} values, accompanied by substantially enhanced k^0 and J_0 values. To further investigate the charge transfer facilitation mechanism in the heterojunction, a Mott–Schottky (M-S) analysis was performed on both SnS and TiO $_2$ films, with the resulting curves presented in Figure 8. Equation (10) is as follows [65]:

$$\frac{1}{C_{sc}^2} = \frac{2}{e\epsilon_r\epsilon_0 N_D} \left(V - V_{fb} - \frac{k_B T}{e} \right) \quad (10)$$

where C_{sc} represents the space charge layer capacitance, ϵ_r is the relative dielectric constant of the semiconductor, ϵ_0 denotes the vacuum permittivity, e is the elementary charge, N_D stands for the donor concentration, V is the applied potential, V_{fb} indicates the flat-band potential, k_B is the Boltzmann constant, and T is the temperature. The flat-band potentials (V_{fb} vs. RHE) of the TiO $_2$ and SnS films were determined to be -0.31 V and -0.67 V, respectively, by extrapolating the linear portion of the M-S curves to the intercept with the x-axis. For n-type semiconductors, the conduction band potential (E_{CB} vs. RHE) can be approximated as the V_{fb} (vs. RHE) [66]. Combined with the bandgap values obtained from

UV-Vis-NIR spectroscopy, the valence band potentials (E_{VB} vs. RHE) were calculated using Equation (11) [67]:

$$E_{VB} = E_{CB} + E_g \quad (11)$$

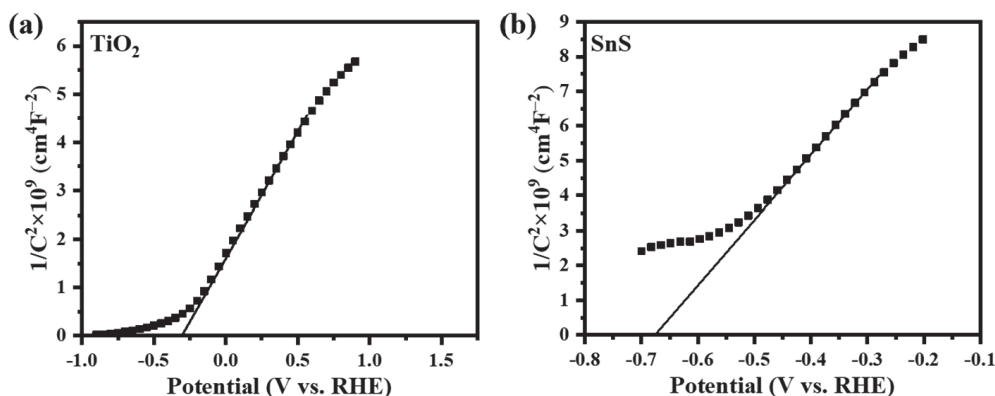


Figure 8. Mott-Schottky curves: (a) TiO₂ and (b) SnS.

The calculated (E_{VB} vs. RHE) of the TiO₂ and SnS thin films were 2.95 V and 0.60 V, respectively. Based on these results, the energy band diagrams of TiO₂ and SnS were constructed, as shown in Figure 9. Under visible-light irradiation, electrons in SnS were excited from the valence band to the conduction band. The formation of a type-II heterojunction between TiO₂ and SnS facilitated the directional charge carrier migration, where photogenerated electrons were transferred from the conduction band of SnS to TiO₂, while holes migrated toward and accumulated in the valence band of SnS [10]. This spatial separation of electrons and holes not only enhanced the charge separation efficiency but also intensified the upward band bending at the SnS/electrolyte interface [35,68]. As a result, hole injection into the electrolyte was promoted, accelerating interfacial oxidation reactions. Consequently, the charge transfer resistance (R_{ct}) at the semiconductor/electrolyte interface was significantly reduced, indicating markedly improved charge transfer kinetics.

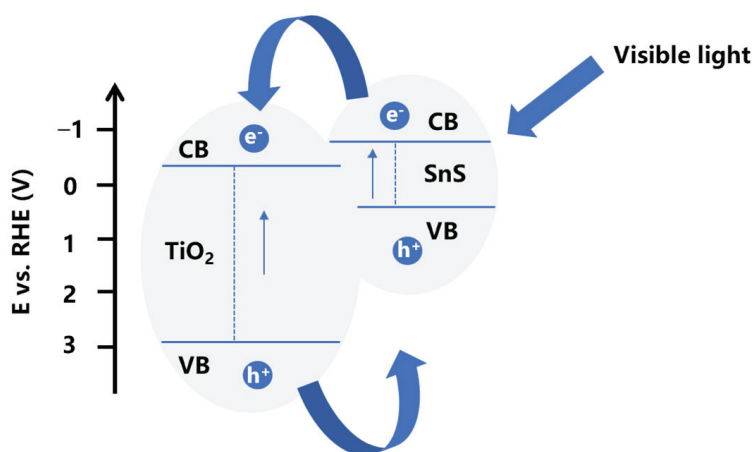


Figure 9. Schematic diagram of the carrier transport mechanism between SnS and TiO₂.

Photocatalytic degradation tests of methylene blue were conducted on the 12 min sputtered SnS/TiO₂ heterostructure film along with pure SnS and TiO₂ films of equivalent thickness. For first-order reactions, the photocatalytic rate constant can be calculated using the following equation [69,70]:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (12)$$

The photocatalytic degradation kinetics were analyzed using the first-order reaction model, where C_0 represents the initial solution concentration, C is the concentration after irradiation time t , and k denotes the reaction rate constant. Figure 10a plots the $-\ln(C/C_0)$ values versus time for all samples, with the fitted R^2 values and k rate constants summarized in Table 6. The R^2 values exceeding 0.99 confirmed that the photocatalytic degradation followed first-order kinetics for all samples. The pure SnS and TiO₂ films exhibited relatively low-rate constants, attributable to the poor visible-light absorption of TiO₂ and the rapid charge recombination of SnS, despite its strong visible-light harvesting capability. In contrast, the SnS/TiO₂ heterostructure film achieved the highest rate constant of 0.0170, demonstrating superior catalytic performance with 87% methylene blue degradation within 120 min under visible light. The reproducibility testing of SnS/TiO₂ demonstrated consistent performance across three successive cycles, as illustrated in Figure 10b. The rate constants for the second and third cycles were determined to be 0.0157 and 0.0151, respectively, while the third cycle achieved 84% degradation efficiency for methylene blue. The degradation mechanism likely involved the generation of reactive oxygen species such as hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\text{O}_2^{\cdot-}$) through redox reactions, as reported in similar photocatalytic systems [71–73]. These active species were responsible for the oxidative breakdown of the dye molecules.

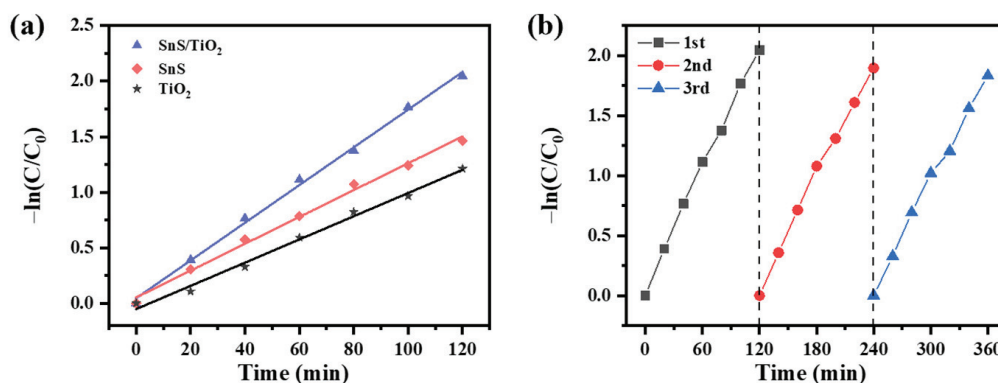


Figure 10. (a) Photocatalytic degradation curves of different samples and (b) degradation curves of the SnS/TiO₂ thin film in three cycles.

Table 6. Calculation of the photocatalytic rate constants of different samples.

Samples	k	R ²
SnS/TiO ₂	0.0170	0.9967
SnS	0.0121	0.9932
TiO ₂	0.0104	0.9910

The SnS/TiO₂ heterostructure demonstrated superior photoelectrochemical performance compared to its individual counterparts due to synergistic interactions across multiple stages [74]. Under visible-light irradiation, the narrow bandgap of SnS enabled efficient light absorption [27]. The type-II band alignment played a crucial role by facilitating charge separation, where photogenerated electrons in SnS transferred to the TiO₂ conduction band due to its more negative potential, while holes migrated to the SnS valence band, thereby effectively suppressing recombination and improving charge transport efficiency [69]. Additionally, the heterojunction interface likely contained unique active sites such as defect states that further enhanced redox reaction kinetics [75]. These combined effects achieved photocatalytic performance comparable to other TiO₂-based catalysts reported in other works such as N-doped TiO₂ [76], CdS/TiO₂ [20], and Cu₂O/TiO₂ [25] systems.

3. Materials and Methods

3.1. Preparation of SnS/TiO₂ Heterostructure Thin Films

SnS/TiO₂ heterostructure thin films were prepared using a vacuum deposition equipment (SY-500, Beijing Shengdeyu Vacuum Technology Co., Ltd., Beijing, China). Glass slides were used as substrates and sequentially cleaned by ultrasonication in acetone, absolute ethanol, and deionized water for 10 min each. TiO₂ thin films were deposited by radio-frequency magnetron sputtering using a TiO₂ target (99.99%, ZhongNuo Advanced Material Technology Co., Ltd., Beijing, China) with a sputtering power of 300 W for 30 min. During deposition, the Ar flow rate was maintained constant at 70 sccm with a working pressure of 0.55 Pa. The as-deposited TiO₂ films were then annealed in a tube furnace at 500 °C for 2 h in air. In our previous work, the preparation process of SnS thin films was optimized, including parameters such as sputtering power, annealing time, and annealing temperature. Subsequently, SnS thin films were deposited on the TiO₂ films by radio-frequency magnetron sputtering using a SnS target (99.99%, ZhongNuo Advanced Material Technology Co., Ltd., Beijing, China) with a constant sputtering power of 80 W. The sputtering time varied between 8, 12, 16, and 20 min for different samples. A final annealing process was performed in the tube furnace at 300 °C for 1 h under Ar atmosphere to complete the preparation of SnS/TiO₂ heterostructure thin films.

3.2. Characterization and Measurements

The crystal structure and phase composition of the samples were characterized by X-ray diffraction (Bruker D8 with Cu-K α radiation, Billerica, MA, USA). Scanning electron microscopy (SEM) (ZEISS Gemini 300, Jena, Germany) and atomic force microscopy (AFM) (Bruker Dimension ICON, Billerica, MA, USA) were employed to analyze the surface and cross-sectional morphology. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, Waltham, MA, USA) was used to determine the elemental composition and chemical states of the thin films. The optical absorption properties were evaluated using ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometry (Shimadzu UV-3600, Kyoto, Japan).

The photoelectrochemical performance of the samples was tested using a three-electrode system connected to an electrochemical workstation (CHI660E) at room temperature. The three-electrode system consisted of a working electrode (the thin-film samples deposited on FTO glass with an effective area of 1 cm²), a reference electrode (saturated calomel electrode, SCE), and a counter electrode (Pt disk electrode). A xenon lamp served as the light source, equipped with an optical filter to control the visible-light wavelength range between 420 and 780 nm, delivering an irradiance of 62 mW/cm² at the sample surface. The measurements were conducted in a 0.5 mol/L Na₂SO₄ aqueous electrolyte solution (pH = 7). All measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation (Equation (13)) [77], where E_{RHE} represents the potential relative to the reversible hydrogen electrode (RHE), E_{SCE} is the potential measured against the saturated calomel electrode (SCE), and E_{SCE}^{θ} denotes the standard electrode potential of SCE:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.0591\text{pH} + E_{\text{SCE}}^{\theta} \left(E_{\text{SCE}}^{\theta} = 0.2415 \text{ vs. NHE at } 25^{\circ}\text{C} \right) \quad (13)$$

For transient photocurrent tests, an open-circuit potential was applied to the working electrode while recording current–time profiles under alternating light-on and light-off conditions. Each state (illuminated/non-illuminated) was maintained for 50 s, with a total test duration of 400 s. Electrochemical impedance spectroscopy (EIS) was performed under visible-light irradiation across a frequency range of 0.1 Hz to 100,000 Hz. A Mott–Schottky

analysis was conducted in dark conditions at a fixed frequency of 1000 Hz with an AC amplitude of 10 mV.

The photocatalytic degradation performance of the thin films was evaluated using a methylene blue (MB) dye solution as the model pollutant. A film sample with a surface area of $1 \times 1 \text{ cm}^2$ was immersed in 50 mL of MB aqueous solution (4 mg/L), consistent with our previous work [78]. Prior to illumination, the reactor was placed on a magnetic stirrer and kept in dark conditions for 30 min to establish adsorption–desorption equilibrium on the catalyst surface. During the photocatalytic test, the sample was irradiated with visible light from a xenon lamp positioned at a distance of 30 cm. Aliquots of 4 mL were collected at 20 min intervals over a total irradiation period of 120 min. The concentration of MB in each collected sample was immediately determined using an ultraviolet-visible spectrophotometer (UV-2300, Shanghai Techcomp Instruments Ltd., Shanghai, China).

4. Conclusions

SnS/TiO₂ heterostructure thin films were fabricated by RF magnetron sputtering with a fixed TiO₂ thickness of 225 nm and varying SnS deposition times. The characterization confirmed phase-pure SnS layers, with optimal optoelectronic performance at a 244 nm SnS thickness. The increased SnS thickness enhanced crystallinity, grain growth, and light absorption, but excessive thickness led to absorption saturation and reduced charge transport due to carrier scattering. The 12 min SnS sputtered heterostructure thin film exhibited a maximum photocurrent density of $3.03 \mu\text{A}/\text{cm}^2$ under visible light, which was 13.8 times that of pure TiO₂ thin film and 2.4 times that of pure SnS thin film with an equivalent thickness. This enhancement arose from the following: (1) the narrow-bandgap SnS effectively extended the light absorption; (2) the type-II band alignment promoted charge separation. Photocatalytic tests showed 87% methylene blue degradation in 120 min, far outperforming pure SnS and TiO₂ films. These results demonstrated the feasibility of using a purely physical method for constructing SnS/TiO₂ heterojunctions with tunable structural parameters and controlled interface quality. Additionally, further investigations are required to examine the influence of pH values and initial pollutant concentrations on the degradation rate, as well as to explore the degradation mechanism through radical trapping experiments and byproduct analysis.

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Article

Insight into the Oxygen-Sensing Mechanisms of TiO₂–CeO₂ Mixed Oxides Treated in a High-Energy Ball Mill: An XPS Analysis

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Abstract: This study explored the oxygen-sensing mechanism of CeO₂ modified with TiO₂ via high-energy ball milling at different speeds. Different characterization techniques were employed to investigate the obtained materials. Quantitative surface analysis by X-ray photoelectron spectroscopy was conducted to elucidate their sensitivity mechanisms and assess the impact of the introduction of TiO₂. A comparable concentration of oxygen vacancies was found in the samples milled at 350 and 450 rpm. Electrical measurements conducted at temperatures lower than required for semiconductor gas sensors revealed the higher sensitivity of these two samples in comparison to pure CeO₂ at an oxygen concentration above 10%. In contrast, the samples derived from precursors milled at the highest speed exhibited the lowest sensitivity. This may be linked to a slight decrease in the vacancy concentration and the presence of a differentially charged carbon-containing phase. Eventually, the C 1s line provided significant insight into the surface characteristics of the materials. The uniform and non-uniform charging found for pure TiO₂ and CeO₂, respectively, along with the high charging of CeO₂, suggest that TiO₂ promotes the contact between the sensing layer and the overlayer. Sensor testing showed the significantly lower resistance of mixed oxides in comparison to CeO₂, which increases the utility of metal oxide-based sensors.

Keywords: mixed oxides; high-energy ball milling; oxygen sensing; materials characterization

1. Introduction

The increase in CO₂ emissions dates back to the Industrial Revolution and continues to this day [1]. The main contribution comes from human activities, primarily the burning of fossil fuels for electricity, heat, and transport. An effective way to reduce the carbon footprint is to control the internal combustion conditions of engines within the power and heating sectors. To achieve this, a reliable and fast response by the sensor used for monitoring the oxygen concentration is necessary [2]. Accurate oxygen measurement is also of great importance in a variety of industrial environments to predict hazards in real time when oxygen levels drop significantly due to oxidation or combustion [3]. Among the many types of oxygen sensors developed over time [4], semiconductor-based oxygen sensors have emerged as the most suitable for a wide range of industrial applications. Their

simplicity, cost-effectiveness, and low power consumption make them ideal for integration into distributed sensor networks intended for monitoring the combustion processes and oxygen concentrations [4,5]. Due to its exceptional oxygen storage capacity, cerium dioxide (CeO_2) is one of the most commonly used materials for oxygen-sensing applications. CeO_2 efficiently absorbs and releases oxygen in response to changes in its concentration due to the reversible and fast Ce^{4+} – Ce^{3+} redox transition. CeO_{2-x} is a non-stoichiometric form of the oxide with a certain amount of Ce^{3+} , accompanied by the creation of nearby oxygen vacancies that act as electron donors to chemisorbed oxygen [4,6–9]. CeO_2 exhibits the highest oxygen sensitivity at a temperature of approximately 600–700 °C [4]. However, its poor thermostability leads to sintering at elevated temperatures, which significantly reduces its oxygen storage [10] and long-term response stability [4,6]. At lower temperatures, electrical measurements of metal oxide-based gas sensors often encounter difficulties due to the inherently high resistance of oxides [11]. A widely studied method for enhancing the electronic, catalytic, and sensing properties of metal oxide-based sensors is the introduction of a second oxide [6,12,13]. Over the past two decades, research has identified TiO_2 as a particularly promising dopant for this purpose [14–17]. Various methods have been used for the preparation of TiO_2 – CeO_2 materials, such as hydrothermal, co-precipitation, sol–gel, microemulsion, and incipient wetness impregnation [18]. In response to the growing need for sustainable methods with minimal environmental impact, this study employed high-energy ball milling. This type of mechanochemical synthesis offers significant advantages over conventional methods, including reduced energy consumption, elimination of harmful waste, and avoidance of toxic precursors and multistep procedures. Large quantities of the powder catalysts, alloys and ceramics can be obtained under ambient conditions in a short time span, making mechanochemistry a suitable tool for industrial applications [19–29]. During the milling process, energy is released through collision, shear, and friction between the balls and the reactants, and it is adsorbed by the solid reactants, stimulating chemical reactions. The intense mechanical stress and induced bond breakage lead to structural changes that increase the surface reactivity, decrease the particle and crystallite size, possibly increasing the specific surface area, and introduce dislocations and oxygen vacancies [21,26,27]. Among the numerous parameters that influence the milling process [24], the frequency (rotational speed) and time have been identified as critical [26].

Despite extensive research, the understanding of the sensing behavior of mixed oxide sensors remains insufficient. Since the initial step in the sensing process involves the atomic-level interactions between the oxygen and the top layer of the material [4,11], describing the surface characteristics is essential for elucidating the underlying sensing mechanisms. To this end, we conducted a comprehensive XPS analysis of TiO_2 -modified CeO_2 materials (for simplicity, also referred to as TiO_2 – CeO_2) that were high-energy ball-milled at three different rotational speeds: 350, 450 and 550 rpm. Thick sensing films were subsequently fabricated from the powder precursors. The resulting samples were labeled TiCe-1, TiCe-2, and TiCe-3, corresponding to milling speeds of 350, 450, and 550 rpm, respectively.

Our study focused on several key aspects: the efficiency of creating oxygen vacancies through high-energy ball milling, the effect of TiO_2 on these defects, and the characterization of the overall surface chemistry of the resulting materials, including their dependence on the milling speed. Calculations derived via XPS were used to model the outermost surface layer. The structural and morphological properties were analyzed using the particle size distribution (PSD), X-ray diffraction (XRD), 2D profilometry, scanning electron microscopy (SEM), and Raman spectroscopy. By correlating the results of the characterization methods with the sensor response, we aimed to understand how materials' structural features govern sensing performance. Given the limited research on the sensing properties of

mechanochemically treated, TiO₂-modified CeO₂, this study also contributes to expanding the field of application of this treatment in the sensor fabrication industry.

2. Results

2.1. Particle Size Distribution (PSD) Analysis of Powders

Considering the crucial role of the particle size in affecting the functionality of semiconductor sensors [4,12], it is important to examine the granularity of the obtained ball-milled powders. Figure 1 shows the influence of different milling speeds on the particle size distribution (PSD) of TiO₂-CeO₂. The following characteristic diameters are listed in Table 1: d₁₀ (10% of particles have a diameter smaller than this value), d₅₀ (median value, sometimes taken as a measure of the average particle size), and d₉₀ (90% of particles are smaller than this value). The width of the distribution is quantified by calculating the span as (d₉₀ − d₁₀)/d₅₀ [30].

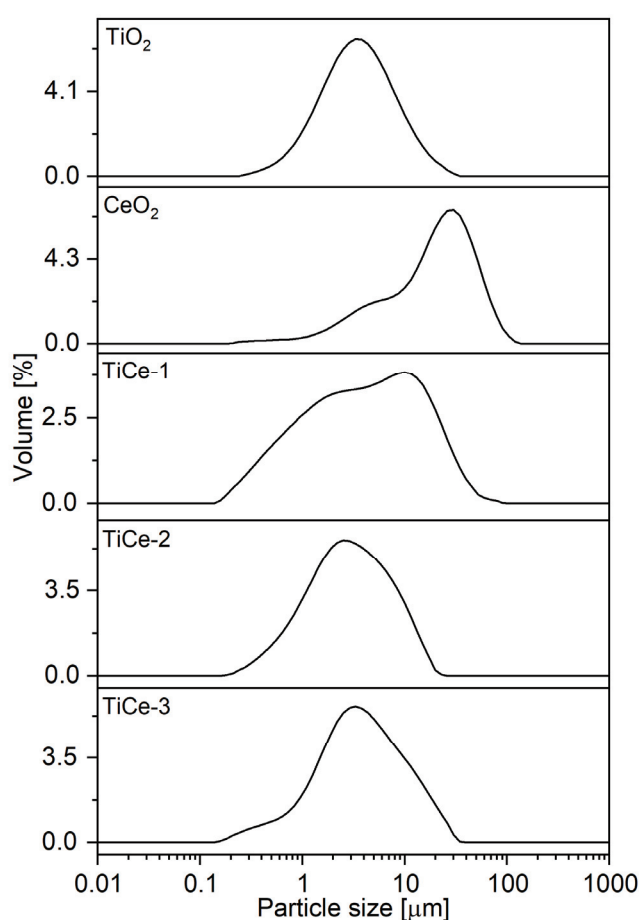


Figure 1. Volume-based particle size distribution of the pure and milled powders.

Table 1. Characteristic diameters (d₁₀, d₅₀, and d₉₀) and span values of the particle size distributions.

Sample	d ₁₀ [μm]	d ₅₀ [μm]	d ₉₀ [μm]	Span
TiO ₂	1.25	3.70	10.61	2.53
CeO ₂	3.80	22.58	55.81	2.30
TiCe-1	0.67	4.46	21.06	4.57
TiCe-2	0.75	2.64	8.53	2.94
TiCe-3	0.90	3.375	12.01	3.29

The fragmentation of agglomerates during the milling process is noticeable in the extended particle size distribution curve of the TiO_2 – CeO_2 powders [31,32]. The bimodal and extensive distribution of the TiCe-1 powder indicates the lowest particle uniformity among the measured samples. The span of the particle size distributions (2.94) and the disappearance of the bimodal shape suggest the highest uniformity of TiCe-2 among the powders. With a further increase in the rotation speed, the second peak emerges again, and the distribution curve broadens. While the d_{10} value shows a minimal variation with the milling speed, a significantly greater variation is observed in the larger particle size dimensions, particularly in the d_{50} and, most notably, in the d_{90} values. The smallest median particle size is observed for the powder TiCe-2 milled at the second speed, 450 rpm (2.604 μm). The cause of the non-linear change in the particle size is attributed to the impact coefficient and impact frequency of the milling balls, both of which are amplified with the speed [33]. This leads to higher surface energy, and eventually, to particle agglomeration as a mechanism to reduce the energy under intense forces. Notably, the d_{10} increases linearly with the milling speed, indicating the coalescence of smaller particles and supporting this interpretation of the PSD measurements.

2.2. X-Ray Powder Diffraction (XRPD)

The diffractograms of the isolated and mixed oxide powders are presented in Figure 2. Characteristic reflections of the cubic form of CeO_2 were identified in all the samples. The presence of TiO_2 was not detected, possibly due to its low weight percentage compared to CeO_2 or its small crystallite size [29]. No evidence of a chemical reaction between TiO_2 and CeO_2 was found, due to the absence of reflections corresponding to new crystal structures in the TiO_2 – CeO_2 diffractograms [34]. This observation indicates a physical mixture of the two oxide phases rather than a chemical interaction.

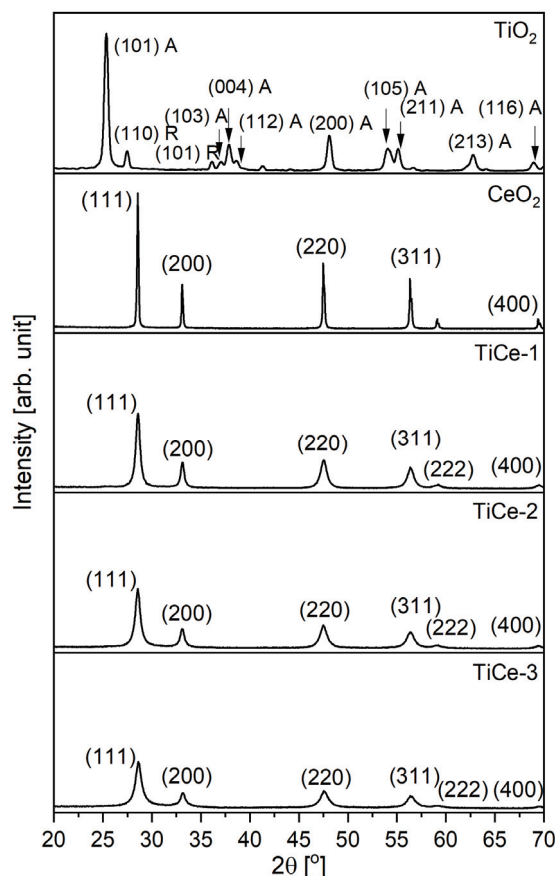


Figure 2. XRD patterns of the starting and milled powders. “A” denotes anatase, while “R” denotes rutile.

The data obtained from the analysis of the most intense CeO₂ (111) peak in the PANalytical X'pert software (version 4.9) are given in Table 2. Apart from the effect on the particle and crystal size, the synergy of the impact and frictional forces created a certain level of lattice distortion, also known as microstrain [35,36]. The localized atomic displacements induced by the ball milling or chemical dissimilarities showed up as dislocations, vacancies, and stacking faults [37,38]. The change in the particle size is thus a rather complex process influenced by both the surface-to-volume ratio and the lattice distortion [35].

Table 2. CeO₂ (111) peak position and interplanar, or d-spacing, in the pure and TiO₂-modified oxides.

Sample	Peak Position [°]	d-Spacing [Å]
CeO ₂	28.55	3.124
TiCe-1	28.54	3.125
TiCe-2	28.53	3.126
TiCe-3	28.61	3.117

The average crystallite size and microstrain were estimated using the Williamson–Hall plot. The obtained graphs are shown in the Supplementary Materials and numerical data are given in [39]. The results are presented in Figure 3. The analysis of the CeO₂ revealed a crystallite size of 78.3 nm and a microstrain of $1.3 \cdot 10^{-4}$. The gradual weakening of the diffraction peaks indicated a reduction in the degree of crystallinity with an increasing rotation speed [40].

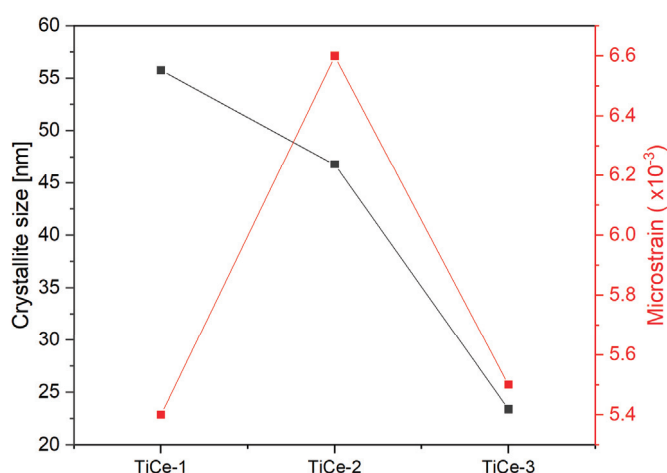


Figure 3. Average crystallite size and microstrain of the milled mixtures.

The influence of the mechanical action on the crystallite size was the most pronounced for the sample obtained at the highest milling speed (TiCe-3), whilst the largest lattice strain was found for the sample milled at the medium speed (TiCe-2), with the smallest average particles. The reduction in the lattice strain at the highest speed could be explained as follows: the effect of frictional forces and collisions during the milling led to the creation of so-called hotspots, characterized by a short-term sharp temperature surge in the ball–ball or ball–wall contact region [25,41]. As the milling speed increased, both the friction coefficient and the collision frequency amplified [41,42]. Sufficient localized heating facilitated the recovery and recrystallization processes, thereby minimizing the crystal lattice deformation and promoting grain growth [25,38,43].

The slight up-shift in the CeO₂ reflections (Table 2) observed in the TiCe-3 diffractogram indicated a modification of the d-spacing [44,45]. Namely, the shift in the XRD peaks of the mixed oxide system suggested a change in the lattice parameters due to the

incorporation of dopants into the host lattice [44]. In the $\text{TiO}_2\text{--CeO}_2$ system, the ionic radius of Ti^{4+} (0.068 nm) was significantly smaller than that of Ce^{4+} (0.093 nm) or Ce^{3+} (0.103 nm), which facilitated the substitution of cerium ions by titanium ions [46]. This resulted in the formation of a fluorite-type crystal structure with the formula $\text{Ce}_{1-x}\text{Ti}_x\text{O}_2$. Such solid solutions of TiO_2 and CeO_2 have already been well documented in the literature [46–48]. Furthermore, the incorporation of Ti^{4+} into the fluorite-like structure of other tetravalent oxides has also been documented [49]. This may account for the absence of TiO_2 peaks in the TiCe-3 diffractogram.

2.3. Two-Dimensional Profilometry of Sensing Layers

The roughness and thickness of the $\text{TiO}_2\text{--CeO}_2$ films was determined using 2D profilometric measurement. The surface roughness can affect the gas sensitivity of the film, as higher roughness may lead to an increased contact area with the gaseous species [50]. The thickness of the sensing material governs the sensor response by affecting the morphology, porosity, and finally, roughness. However, there is inconsistency among studies regarding the observed changes in the sensing properties with increasing thickness [51]. The average surface roughness is given in the form of the arithmetic average height (R_a), which is defined as the arithmetic mean of the absolute values of the vertical deviation from the mean line passing through the profile of a film. As a parameter that is more sensitive to larger deviation than the R_a , the root mean square roughness (R_q) is also used for describing the surface [52]. The values of the surface roughness parameter and thickness of the mixed oxides are shown in Table 3. Numerical data and calculation of their values are given in [39]. Considering that the effect of screen printing and the particle size on the roughness and thickness of the films is not the focus of this research, a discussion on these properties, as well as 2D profiles of a surface, can be found in the Supplementary Materials.

Table 3. Surface roughness parameters and thicknesses of the mixed oxides obtained from the 2D profilometry data.

Sample	R_a [nm]	R_q [nm]	Thickness [μm]
TiCe-1	660	820	≈ 7.7
TiCe-2	543	752	≈ 4.4
TiCe-3	562	711	≈ 4.7

2.4. Scanning Electron Spectroscopy (SEM) and Energy Dispersive Spectroscopy (EDS) of Sensing Layer

SEM inspection of the CeO_2 film surface (Figure 4) revealed a randomly organized structure of larger flake-like particles and smaller ones that appeared spherical. Many agglomerates allocated beneath the smaller grains formed a discontinuous structure with visible cracks. The surface of the mixtures appeared to be slightly different from that of the pure CeO_2 , featuring fewer agglomerates and better cross-linking of the particles (Figure 4). All the mixtures exhibited similar surface characteristics, displaying a lack of particle ordering. The morphology of both $\text{TiO}_2\text{--CeO}_2$ and CeO_2 arises from the wide range of particle size distributions present in the powders and the chosen method of preparation.

The EDS analysis was performed on a surface of $6.5 \times 5 \mu\text{m}$ and the results are summarized in Table 4 (images and graphs can be found in the Supplementary Materials). The ratio of Ti and Ce on the surface of the mixtures did not correspond to the initial ratio of the oxides (1:4). We attribute this discrepancy to random experimental errors that may have been introduced during the multiple steps of the paste preparation, to the retention of powder on the walls of the milling vessel, but mainly to the non-homogeneous distribution of the two oxides across the film depth. Moreover, given the poor sensitivity of the EDS

technique for the detection of elements with a low atomic number, it is likely that the actual presence of oxygen is underestimated, which may have affected the accuracy of the quantitative analysis.

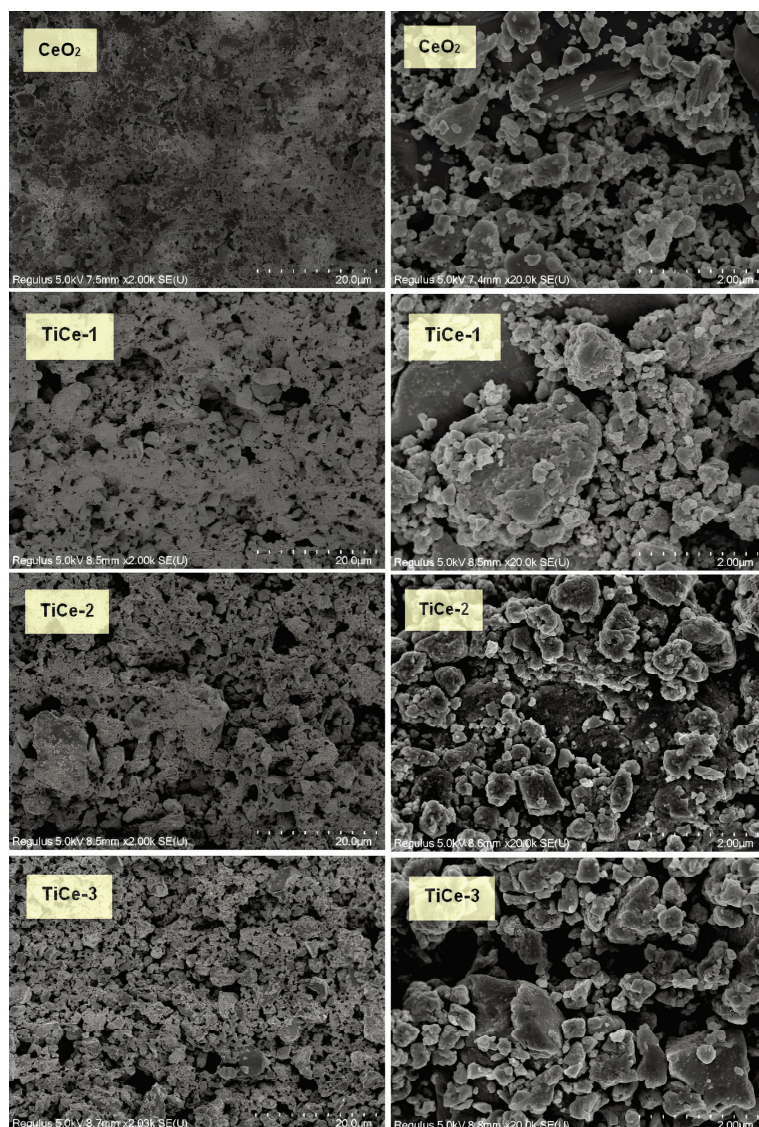


Figure 4. SEM images showing the surfaces of pure CeO_2 and TiO_2 -modified CeO_2 at magnifications of 2 k (left) and 20 k (right). All the images are taken from the center of the paste region.

Table 4. Results of the EDS elemental analysis of the TiCe-1, TiCe-2 and TiCe-3.

Sample	Weight (%)					Ti:Ce Weight Ratio Expected/Calculated
	Ti	Ce	O	C	Al	
TiCe-1	11.00	61.93	20.79	5.99	0.29	0.25/0.18
TiCe-2	11.23	64.71	17.77	5.96	0.33	0.25/0.17
TiCe-3	10.44	59.83	21.28	8.12	0.33	0.25/0.17

The significant amount of carbon detected in all the samples probably belongs to the decomposition products of the organic matter formed during the heating in argon flow during the sensor fabrication. Namely, the heat treatment of organic compounds in an oxygen-free environment, a process known as pyrolysis, yields carbon-containing products when using CeO_2 as a catalytic material [53]. The highest percentage of carbon was found

in the sample milled at the highest speed, TiCe-3. Lastly, the small amount of aluminum identified in all the mixtures suggested that the surface of the alumina substrate was not completely or uniformly covered by the sensing layer.

2.5. Raman Spectroscopy of Sensing Layers

Figure 5 shows the Raman spectra of the film of the starting oxides and mixtures. In agreement with the literature data, the starting TiO_2 shows distinctive Raman bands of anatase and rutile phases, while the CeO_2 exists in the fluorite cubic form [54,55]. The most intense TiO_2 band is assigned to the E_{1g} mode [56], while the single CeO_2 band corresponds to the F_{2g} mode [57]. No compounds between TiO_2 and CeO_2 are detected.

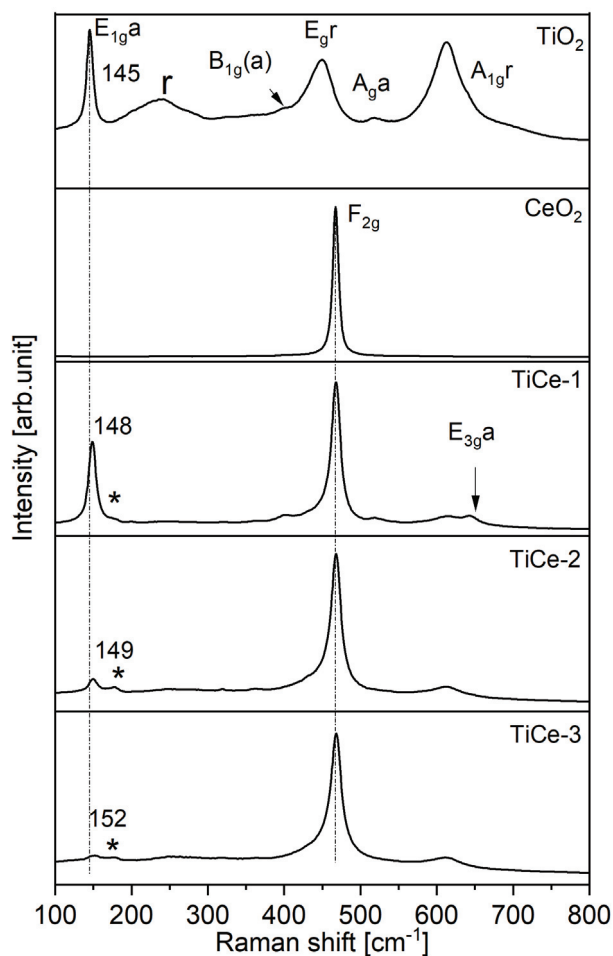


Figure 5. Raman spectra of the starting oxides and mixtures; an asterisk (*) denotes the band at 177 cm^{-1} , while “r” is ascribed to multiple phonons scattering on the rutile phase.

The feature at 642 cm^{-1} , present only in the TiCe-1 spectra, is assigned to the vibrations of a moderately distorted anatase lattice (E_{3g} mode) [56,58]. A reason for its absence in the spectra of the TiO_2 is masking by the intense rutile band A_{1g} ($A_{1g}r$ in Figure 5). The origin of the band at 177 cm^{-1} observed for all the mixed oxides (marked with an asterisk) remains unclear. According to the literature, the similar features at 181 cm^{-1} [59] and 170 cm^{-1} [60] are correlated with the TiO_2 II phase, which is irreversibly formed from anatase or rutile at high pressures. Earlier studies have documented the phase transformation from anatase to TiO_2 II through high-energy ball milling [60,61].

The relative intensities of the E_{1g} anatase to the A_{1g} rutile mode (Ia–Ir) in the mixtures differ from those in the spectrum of the pure TiO_2 (Table 5). A significant rise in the anatase–rutile intensity ratio in the spectrum of TiCe-1 implies that the presence of CeO_2 impedes

the anatase-to-rutile transformation [10,62]. The Raman spectra of TiCe-2 and TiCe-3 reveal an exactly opposite effect: the weakening of the anatase band and a decrease in the Ia:Ir ratio, which is indicative of the promotion of the anatase-to-rutile transition. The phase transformation is presumably driven by additional impact energy and heat generated upon a rise in the rotation speed [63,64]. Namely, it has been found that the Ce atom effectively stabilizes the anatase crystals, but only up to a critical temperature point [65]. Another possible explanation is that ball milling induces the amorphization of the anatase phase. Notably, at the medium rotation speed, a significant loss of anatase is observed, yet TiO₂ II remains present. As the rotation speed increases, TiO₂ II also diminishes, ultimately resulting in a predominantly rutile phase.

Table 5. Intensity ratio of the anatase-to-rutile phase.

Spectrum	Ia–Ir
TiO ₂	1.12
TiCe-1	5.49
TiCe-2	1.46
TiCe-3	1.12

The composition of the TiO₂ phase can be of great importance from the aspect of gas detection. Materials composed of CeO₂ and rutile–TiO₂ have been demonstrated to possess a higher content of Ce³⁺ compared to materials involving CeO₂ with other TiO₂ phases [66]. The broad and asymmetric nature of the bands, as observed for F_{2g} in mixed oxides' spectra, is commonly attributed to the grain size reduction, the inhomogeneous strain, and the presence of defects [67–69]. The blue shift of the anatase band, E_{1g}, observed in the spectra of the mixtures reaches about 7 cm^{−1} for the TiCe-3 sample. This may be attributed to the change in the materials' crystal cell [44,70–73], although it also can be due to the change in the background slope.

2.6. X-Ray Photoelectron Spectroscopy (XPS) of Sensing Layers

The XPS measurements of the TiO₂, CeO₂, and mixed oxides were characterized by sample charging caused by their reduced conductivity, particularly at room temperatures. The most obvious consequence of the sample charging during the XPS measurements was the shift of the photoelectron and Auger peaks to higher binding energy. However, the effects of non-uniform charging, where different regions of the analyzed sample showed different electrical potentials, required a more detailed analysis. Non-uniform (or differential) charging contributes to the broadening of all the photoelectron lines and in some cases deforms the line shapes, making it impossible to follow even modest changes in the binding energy attributed to different chemical bonds. In the most severe cases of non-uniform charging, the same photoelectron line may appear at two positions in the spectrum. This phenomenon arises from sudden changes in the electrical potential between two surface regions, potentially representing separate chemical phases with different electron (or hole) transport properties. If the actual binding energy of a particular phase is known, the measured binding energy can be used to calculate the electric potential of a sample, or of a part of the sample containing that phase. If two photoelectron lines have distinctively different binding energy shifts, they obviously originate from different sample regions and consequently cannot belong to the same chemical phase. Similar ideas have been recently used to separate the chemical phases from samples with strong non-uniform charging. Since the exact shape of a photoelectron line carries information about the spatial distribution of a certain element, lines of the same chemical phase should have the same shape [74]. By applying these considerations to the XPS analysis within this study, it

appeared that the seemingly least significant photoelectron lines in our samples, that is, the C 1s lines from adventitious carbon, carried potentially very important information about the overall surface structure of the samples. Therefore, it is in our interest to properly describe and quantify the overlayer(s) of the hydrocarbons that are inevitable contaminants in air-exposed samples.

2.6.1. TiO₂ Sample

Detailed spectra taken from the reference TiO₂ sample are shown in Figure 6a,c,d. The fitting of the Ti 2p line was performed with the spin–orbit pair of only one contribution, which corresponded to the TiO₂ phase (Figure 6a). Contributions attributed to Ti₂O₃ or TiO, which would appear at lower binding energies, were not observed. If the Ti 2p_{3/2} line originated from TiO₂, its position should be at 458.6 eV [75]. Accordingly, the atoms of the TiO₂ phase should be at the potential of 1.6 V. The dominant peak of the C 1s line (Figure 6c), corresponding to adventitious carbon, was situated at about 1.8 eV relative to its expected position [75], implying rather uniform surface charging. Three contributions were observed in the spectrum of the O 1s line (Figure 6d), which can be addressed (from right to left) as bulk metal oxide O1, always accompanied by defective/hydroxylated surface oxygen O2, and oxygen of organic compounds O3 [76]. We were applying the same peak model for the O 1s line for all the samples. As the sample was charged, all the peaks appeared to shift about 1.6 eV toward the higher binding energies (Figure 6d). C–O bonds could be also identified in the C 1s line (Figure 6c).

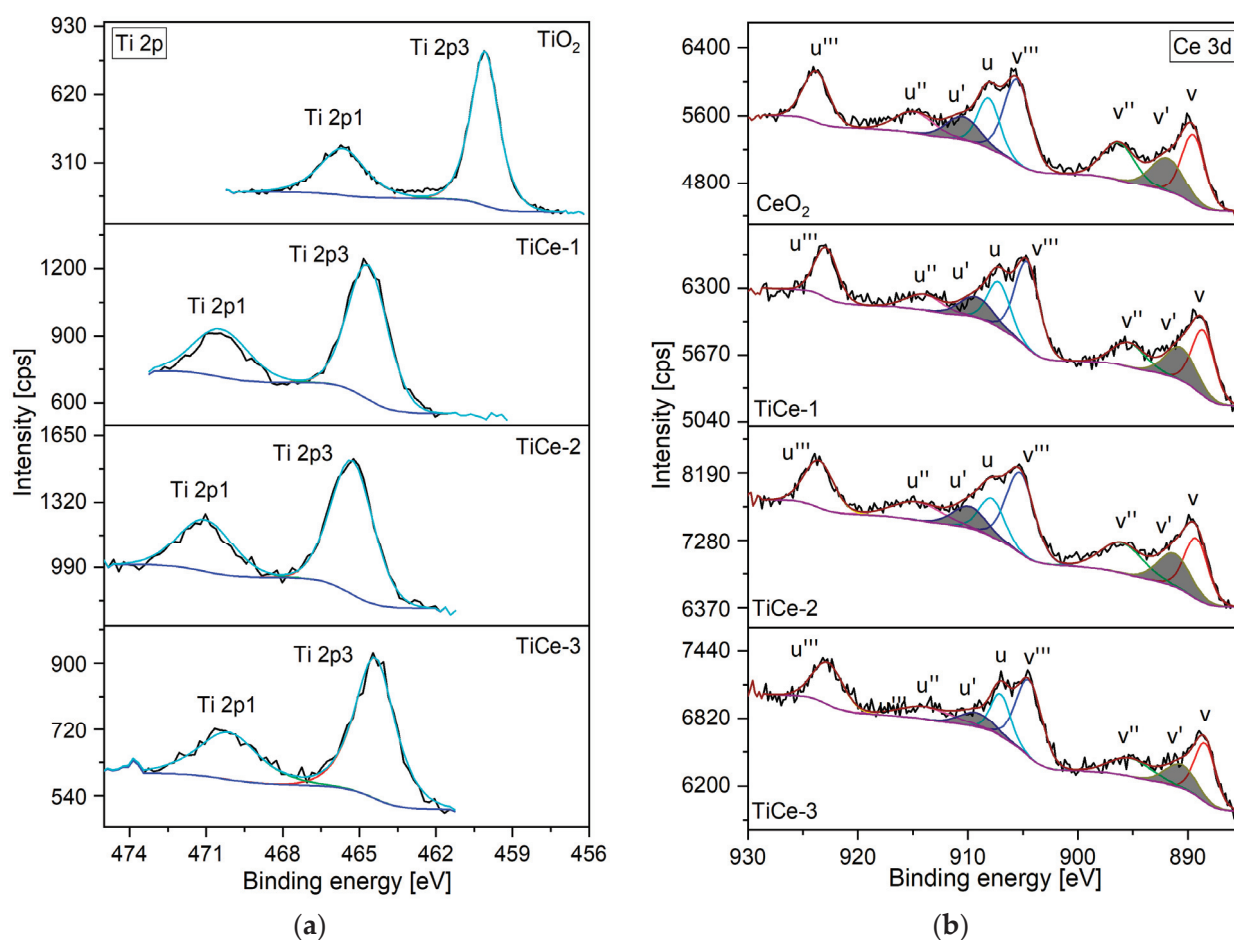


Figure 6. Cont.

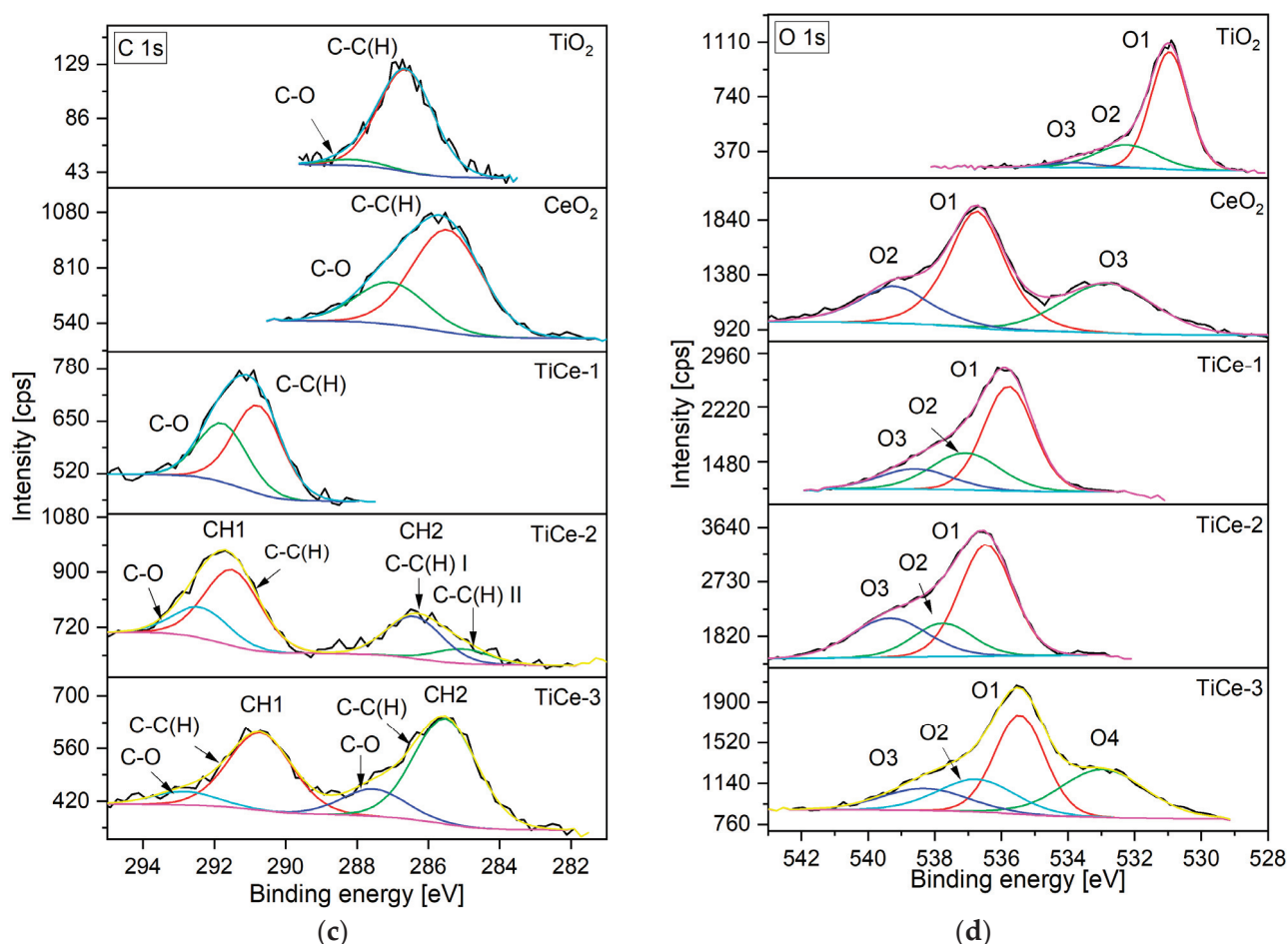


Figure 6. Detailed spectra of (a) the Ti 2p line; (b) the Ce 3d line (the shaded peaks belong to Ce^{3+} , while the set of “v” peaks is assigned to the angular momentum 5/2, and “u” to 3/2); (c) the C 1s line; and (d) the O 1s line.

2.6.2. CeO₂ Sample

The overall shape of the Ce 3d photoelectron line (Figure 6b), taken from the CeO₂ sample, was successfully reconstructed using the fitting model proposed by Burroughs et al. [77]. The small discrepancies between the fitting results and the experiment can be attributed to the background calculation and carbon contamination that preferentially screens the Ce 3d signal on the high binding energy side. The line was fitted to eight peaks, four for each value of the angular momentum ($j = 5/2, 3/2$). The sets of “v” and “u” peaks belonged to the Ce 3d_{5/2} and Ce 3d_{3/2} photoelectron line, respectively. The peak v/u was the main contribution of the CeO₂ phase, v’/u’ corresponded to the Ce³⁺ oxidation state and the rest of the peaks represented satellites attributed to the CeO₂ phase. By comparing the measured position of the main Ce 3d_{5/2} (the peak v) with that expected in the non-charged sample [78], the potential of CeO₂ was found to be about 7.2 V. The amount of Ce atoms in the +3 oxidation state evaluated from the sum of the v’ and u’ peak areas relative to the overall line intensity was determined to about 18.4%. If all the Ce³⁺ were placed at the surface, implying their sole origin from oxygen vacancies, and given that the introduction of one vacancy results in the formation of two Ce³⁺ ions [79], we may roughly estimate the upper limit of these defects to be about 9% relative to the total Ce surface concentration. The hydrocarbon layer with C–O bonds (Figure 6c) and the metallic oxide phase (Figure 6a,b) were on different potentials, which is an example of non-uniform charging, contrary to the TiO₂ sample. We presume the reason for this is the lack of ohmic contact between the

hydrocarbon layer and the Ce–oxide, which would otherwise enable equal transport and distribution of electrons through the two distinct phases.

2.6.3. TiCe-1 Sample

Both the Ce 3d_{5/2} and Ti 2p_{3/2} photoelectron lines were shifted for about 6.1 eV relative to their reference positions (882.3 eV and 458.6 eV, respectively), implying uniform charging of the two oxide phases. A hydrocarbon layer on top of this sample was found to follow the potential of the metallic oxides. By comparing with the results obtained for the single oxide samples, it appeared that the TiO₂ grains established a galvanic contact between the CeO₂ and the hydrocarbon layer.

The expected position of the O1 line in the CeO₂ phase, calculated from its relative position with respect to the Ce 3d_{5/2} line [76], was 529.5 eV, practically coinciding with that of the O1 peak of the TiO₂ phase (529.7 eV [75]). Therefore, the O 1s line was successfully fitted to three contributions, as in the case of the single oxide phase samples. The same peak fitting model was then applied for the samples TiCe-2 and TiCe-3.

2.6.4. TiCe-2 Sample

The metallic oxide phases of the TiCe-2 sample appear to be on a rather uniform electric potential of about 6.7 V during the XPS measurements (Figure 6a,b). Yet, the C 1s line shows up in the form of two distinct peaks separated for 5 eV, which indicates that TiCe-2 is non-uniformly charged (Figure 6c). The structure at the higher binding energy CH1 has a contribution of adventitious carbon and an additional one that we attribute to C–O bonds. Its position corresponds to that of the metallic oxides. The signal at the lower energies CH2 also has two peaks that we attribute to adventitious carbon from two differentially charged regions. This interpretation is supported by the fitting of the O 1s line, consisting of only three contributions being on the same potential as the oxide phases (Figure 6d). After correcting for charging (6.7 V), the O3 is found at 532.6 eV, further confirming that the CH1 structure lies at the same potential as the metallic oxides and that the region from which CH2 originates does not contain oxygen.

2.6.5. TiCe-3 Sample

Strong non-uniform charging is also observed while measuring the TiCe-3 sample, as seen from the detailed spectra of the C 1s line (Figure 6c). The potential of the structure CH1 is equal to the common potential of metal oxides, which is for this sample approximately 5.8 V. The peak of the highest intensity belongs to a differentially charged structure, CH2, with an electric potential of 0.8 V. The O 1s line is fitted to four peaks. Apart from the bulk and surface metallic oxide contributions O1 and O2, two contributions for organic oxygen have to be added: one for each of the differentially charged hydrocarbon regions CH1 (O3) and CH2 (O4). The relative position of the O1 peak with respect to the metallic photoelectron lines for TiCe-3 is O1–Ti 2p_{3/2} = 71.1 eV and Ce 3d_{5/2}–O1 = 352.9 eV, being identical, in the frame of the experimental uncertainty, with the other samples. After correcting the binding energies for the potential of the structures CH1 and CH2, the peaks O3 and O4 are both situated at 532.5 eV. Their position practically coincides with the binding energies of organic oxygen in the previous spectra. From the relative positions of the metal and O 1s photoelectron lines, it appears that the pure and mixed oxides have the same chemical bonds: Ti is present as TiO₂, while Ce is present dominantly as CeO₂, with a certain amount of Ce³⁺.

2.6.6. XPS Quantitative Analysis

Employing the same approach as for CeO₂, the Ce³⁺ percentage in TiCe-1, TiCe-2 and TiCe-3 is calculated to be 19.1%, 17.8%, and 14.9%, respectively. Considering the various

sources of uncertainty, we can say that the amount of Ce^{3+} in the mixtures and pure CeO_2 (18.4%) is constant except in the last sample, where a certain decrease in the amount of Ce^{3+} ions is evident. The binding energies of all the contributions in the Ti 2p, Ce 3d, C 1s and O 1s lines are listed in the Table 6. In contrast to the reference TiO_2 , CeO_2 , and TiCe-1, the spectra of TiCe-2 and TiCe-3 reveal two distinct hydrocarbon contributions (Figure 6c). This observation suggests a lack of electrical conductivity between the CH1 and CH2 components, with only one of these acting as the top layer of the film.

Table 6. Binding energies [eV] of the Ti 2p, Ce 3d, C 1s, and O 1s core-level peaks. Only one component of the spin–orbit splitting for Ti 2p and Ce 3d is shown.

	Ti 2p		Ce 3d			C 1s		O 1s			
	3/2	v	v'	v''	v'''	C-C(H)	C-O	O1	O2	O3	O4
TiO ₂	460.1	/	/	/	/	286.6	288.1	531.0	532.3	533.9	/
CeO ₂	/	889.5	891.9	896.3	905.5	285.5	287.0	536.7	539.2	532.8	/
TiCe-1	464.7	888.6	890.6	895.4	904.6	290.8	291.8	535.8	537.1	538.6	/
TiCe-2	465.3	889.2	891.2	896.0	905.2	291.5 (CH1) 286.4 (CH2 I) 285.0 (CH2 II)	292.4 (CH1)	536.5	537.8	539.3	/
TiCe-3	464.4	888.4	890.6	895.2	907.0	290.7 (CH1) 285.5 (CH2)	292.8 (CH1) 287.5 (CH2)	535.4	536.7	538.3	533.0

Through bond identification, we have determined that the covering layer of TiCe-1 shares the same potential as the bulk of the oxides. Consequently, we propose that the CH1 structure in the C1s spectra of TiCe-2 and TiCe-3 originates from the hydrocarbon layer atop both the TiO_2 and CeO_2 in the respective samples. This can be confirmed by calculating its thickness. The fraction of the total carbon layer covering TiO_2 is denoted as θ_{Ti} , while the part covering the CeO_2 patches is θ_{Ce} . The details of the quantitative analysis, the relevant literature sources [23,80–86], as well as the modeling of the TiO_2 -modified CeO_2 film, are given in the Supplementary Materials. The numerical data and calculation within the quantitative analysis can be found in [39]. The results derived from the analysis based on the hypothesized model are listed in Table 7. According to the data, the thickness of the carbon-containing overlayer above the mixed oxides is significantly smaller than that on the pure CeO_2 . The thinnest overlayer is found for TiCe-1 sample, which contains the highest surface coverage of TiO_2 patches (θ_{Ti}) among the mixed oxides.

Table 7. The surface coverage values (θ_{Ti} and θ_{Ce}), hydrocarbon layer thickness (d), and concentration ratio (O:Ti–O:Ce).

Sample	$\theta_{\text{Ti}}:\theta_{\text{Ce}}$ [%]	d [nm]	O:Ti–O:Ce
TiO_2		1.15	O:Ti = 1.98
CeO_2		2.73	O:Ce = 2.52
TiCe-1	43:57	1.51	O:Ce = 2.65
TiCe-2	31.7:68.3	2.42	O:Ce = 2.72
TiCe-3	34.5:65.5	2.15	O:Ce = 2.70

2.7. Results of Electrical Measurements

The measurements of the TiO_2 – CeO_2 sensor (hereinafter referred to as the TCO sensor) presented in this study were performed at 310 °C. This operating temperature was selected because it represents the minimum temperature at which the resistance of the sensor over the entire O_2 concentration range is low enough to be measured by most available

instruments, while the stability of the response is satisfactory. To investigate the sensing behavior of the obtained $\text{TiO}_2\text{-CeO}_2$ materials, we measured the current–voltage curves of the TCO sensors at the chosen working temperature, using the Keithley 2450 Source Meter Unit (SMU) (Solon, OH, USA). It was found that all the mixtures exhibited ohmic contact characteristics, as can be seen in the example given in the Supplementary Materials.

The resistance values were recorded for 15 min at each O_2 concentration. As an example, the result of the time-dependent electrical measurements for TiCe-3 is given in the Supplementary Materials. The resistance value for each O_2 percentage as well as the standard deviation were calculated from the final 200 s of exposure. The dependence of the DCR values of the sensor on the oxygen percentage is presented in Figure 7. The data plotted with a linear scale are shown in the Supplementary Materials. To evaluate the reproducibility of the sensing layer fabrication process, two mixtures were screen-printed twice and their response to O_2 was measured. Plots of the same color in Figure 7 belong to TCO sensors manufactured from identical mixtures.

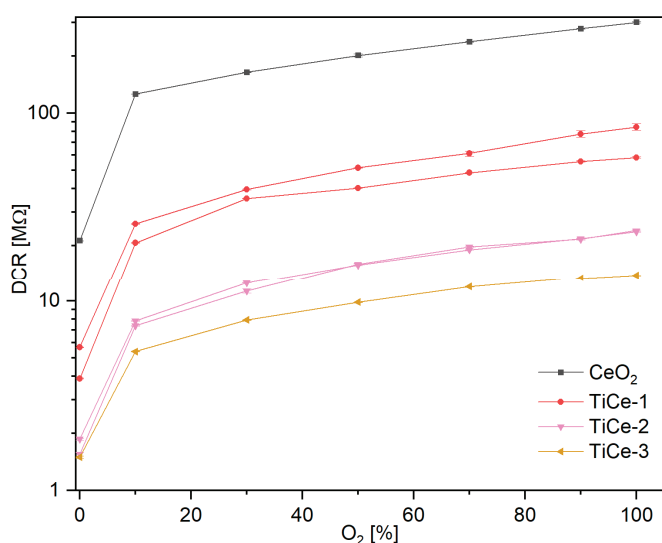


Figure 7. DC resistance of the CeO_2 and mixed oxides when exposed to different volumetric concentrations of O_2 at a temperature of 310°C : data plotted with a logarithmic scale.

Variations in parameters such as the squeegee pressure and amount of paste during the manual application of each layer may affect the repeatability of a process, which can be reflected in the performance of the final sensing material. The responses of two TiCe-1 sensors based on identical mixtures showed slight differences, although the resistance values at the same O_2 exposure tended to cluster (Figure 7). This discrepancy may also arise from random errors in the paste preparation and the wide particle size distribution of the milled powders. Indeed, the sensor responses of the two TiCe-2 samples, made from powder with a narrower span in the particle size distribution (Table 1), appeared to match. However, the small inconsistency in the sensor response did not affect the application of high-energy ball milling for fabrication of the sensing layer: each sensor will be calibrated before use.

The highest change in the sensors' resistance was in the range of low oxygen concentrations (0–10%), approaching saturation thereafter. The high resistance of the CeO_2 film, reaching several hundreds of $\text{M}\Omega$, posed a challenge for practical applications due to the difficulties in measuring the resistances of this order. Even at the low O_2 percentages, its resistance exceeded $100\text{ M}\Omega$. In contrast, the sensor based on the $\text{TiO}_2\text{-CeO}_2$ films showed significantly lower resistance over the entire O_2 concentration range, whilst preserving a similar relative change in the resistance. The resistance of the mixed oxide films decreased

with increasing milling. It was also observed that TiCe-2 and TiCe-3 showed a similarity in the DCR value at identical O₂ concentrations, while the mixture milled at the lowest speed (TiCe-1) exhibited greater resistance by about an order of magnitude. In this study, the sensitivity was calculated as the slope of the DCR-O₂ dependence curve divided by the resistance value at 0% O₂, labeled as DCR_{Ar} [87]:

$$S = \Delta \text{DCR} / \Delta \text{O}_2 \cdot 1 / \text{DCR}_{\text{Ar}} \quad (1)$$

The sensitivity, presented in Figure 8, is a function of the oxygen partial pressure due to the non-linear response of the sensors (Figure 7). The sensitivity strongly depended on the O₂ concentration, with a maximum observed in the 0–10% region, followed by a sharp decrease to a saturated value. At lower percentages of O₂ (0–10%), the best oxygen sensitivity was observed for the pure CeO₂, which was about 0.06 above that of TiCe-1. At higher partial pressures of O₂, TiCe-1 and TiCe-2 were more sensitive than CeO₂, while the TiCe-3 film (obtained by the highest rotation speed) had the lowest sensitivity throughout the whole concentration range.

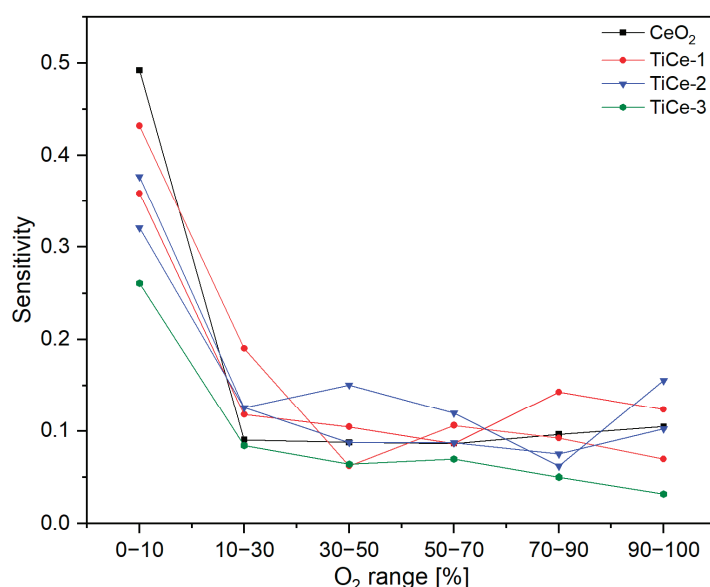


Figure 8. Change in the sensitivity with the O₂ concentration for CeO₂ and the sensors based on mixtures.

3. Discussion

At the grain surface, oxygen molecules extract electrons from the conduction band, trapping them at the surface in the form of ions, which induces upward band bending. This causes the formation of an electron-depleted region (space charge layer within the grain), which represents a potential barrier that hinders the movement of electrons between the two grains (Figure 9). Consequently, the electron mobility, as well as the number of electrons free to act as a carrier, is reduced, resulting in a decrease in the electrical conductivity of the n-type semiconductor as the oxygen partial pressure increases, following the Equation (2):

$$\sigma = A \cdot \exp(-E_A \cdot (k \cdot T)) \cdot p_{\text{O}}^{1/N} \quad (2)$$

Here, σ represents the conductivity, A is a constant, E_A is the activation energy for conductivity, k is the Boltzmann constant, T stands for the operating temperature, and p_{O} is the oxygen partial pressure. N is a value that depends on the type and number of the defects, and for the case of n-type semiconductors, it is negative [4]. The increase in the DC resistance with the rising O₂ concentration suggests that TiO₂-modified CeO₂ acts like a

single n-type oxide over the entire partial pressure range. The trend observed in Figure 8 arises from the increasing probability of vacancy filling during the exposure to higher O_2 concentrations. At sufficiently elevated O_2 levels, saturation occurs: vacancies become fully occupied, rendering further oxygen exposure inert. Consequently, the resistance stabilizes as it reaches its maximum value [4,11].

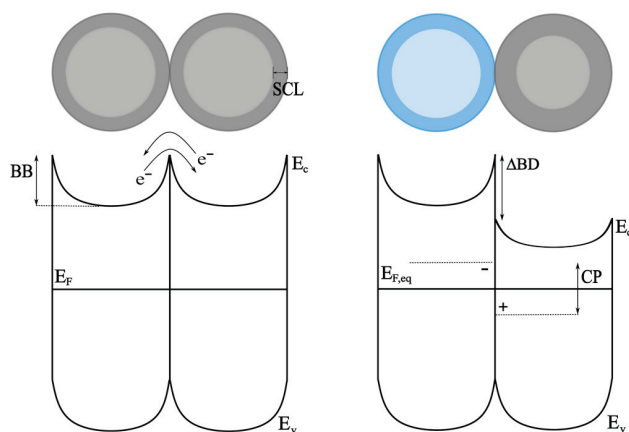


Figure 9. Schematic illustration of the homo-contact between the grains of the same semiconductor (**left**) and the hetero-contact between two types of semiconductors (**right**) in contact after reaching equilibrium; “SCL” stands for the width of the space charge layer, “BB” for the banding of the valence and conduction band, “CP” for the contact (hetero) potential and “ ΔBD ” for the band edge difference. Two different colors (blue and gray) represent different types of semiconductors.

Increasing the number of oxygen vacancies is expected to enhance the sensitivity of the detection process [4,6]. However, the X-ray photoelectron spectroscopy (XPS) analysis reveals that the relative amount of Ce^{3+} remains consistent in both the CeO_2 and the mixtures (approximately 18%), although there is a slight reduction noted for the TiCe-3 (14.9%). These findings suggest that increasing the milling speed within the tested range does not significantly affect the formation of oxygen vacancies until a certain threshold (TiCe-2), beyond which it appears to act as an inhibitor. The presence of TiO_2 also does not affect the formation of vacancies in TiO_2 – CeO_2 mixtures. According to the Ce 3d and Ti 2p detailed spectra, oxygen vacancies are generated exclusively in the CeO_2 domains. The XPS did not detect Ti^{3+} ions, indicative of the presence of oxygen vacancies at room temperature. The difference in the amount of defects will persist under elevated temperatures and oxygen-deficient conditions, due to the substantial differences in stability between the two oxides.

The effects of the so-called “poisoning” of a surface by carbon-containing species can lead to the occupation of the active sites and the reduction in the concentration of oxygen species adsorbed [88]. Two different hydrocarbon phases (CH1 and CH2) are identified on the surfaces of TiCe-2 and TiCe-3. In the case of TiCe-3, both are partially oxidized, while for the TiCe-2, they appear to be just differentially charged adventitious carbons, with no evidence of oxidation. The two carbon-containing phases are galvanically isolated, indicating the absence of physical contact between them. Otherwise, we would expect to observe some deformation of the C 1s line, rather than a complete separation into two distinct regions. Therefore, only one of these phases can be considered an overlayer. We propose that it is the one with the same potential as the oxide phases, CH1, found in all three mixtures. All the evidence suggests that CH2 is present on the samples’ surface but is physically displaced by metal oxides. It is possible that this phase resides at the boundaries between two identical or different grains. Grain boundaries, whether a homo- or hetero-interface, represent a type of microstructural defect characterized by an electronic property

that differs from that of the surrounding surface [17]. This distinctive electronic structure may cause a different charging of the CH2 phase, which could partially or completely coat the grain surface, somehow alternating the electron transport or oxygen diffusion. Since it is not observed for the TiCe-1 mixture, such carbon-containing species could have been introduced during the milling at a rotational speed above 350 rpm. Nevertheless, the common potential of the metallic lines suggests that CH2 does not inhibit the contact between TiO₂ and CeO₂.

The presence of differentially charged oxidized species is not detected in the cases of TiCe-1 and TiCe-2. Both samples demonstrate higher sensitivity than TiCe-3 across the entire range of oxygen concentrations and CeO₂ for the concentrations above 10%. TiCe-1 is also characterized by the absence of a differentially charged CH2 phase, the smallest thickness of the carbon overlayer, and the highest surface roughness. Increasing the powder precursors' milling speed up to 550 rpm reduces the sensitivity of the layer, potentially due to the introduction of oxygen-containing CH2 species, causing a small decrease in the surface roughness, but most likely due to the lowest amount of oxygen vacancies. It is also worth noting that the EDS results also show that the TiCe-3 sample contains the highest amount of carbon. This observation further supports the hypothesis that the CH2 phase is not a surface contaminant but rather is located in the sub-surface microstructure of the sample. However, the role of the CH2 phase in reducing the sensitivity of TiCe-3 remains inconclusive without XPS experiments conducted at elevated temperatures. This phase, due to the oxygen present in its structure, may potentially inhibit the binding of ambient oxygen that penetrates through defects (gaps) in the overlayer and reaches the grain boundaries. The content of the TiO₂ crystalline phases does not affect the sensitivity in the expected manner, but its incorporation in the CeO₂ layer reduces the amount of surface contamination, i.e., the thickness of the overlayer, *d* (Table 7). The average surface roughness, *R_a*, of the mixtures (Table 3) appears to decrease with the increasing thickness of the carbon-containing overlayer CH1, *d* (Table 7).

The homo-contact established at the boundary between two grains is a decisive factor in the free carrier transport in semiconductor devices. The mechanism of electron transfer from one domain to another in the presence of a potential barrier caused by the existence of a depletion region is described with the double Schottky barrier [6,17,89]. The charge carrier mobility through the barrier occurs at elevated temperatures and governs the conversion of the reaction into an electrical signal [90]. By assembling semiconductors with different physical properties or working functions into one structure, apart from the homo-contacts, hetero-contacts and band edge differences are created. The hetero-contact represents a thin double layer of physically separated positive and negative charges at the interface of the grains of dissimilar semiconductors. The formed potential reduces the mobility of electrons moving in the direction against it, without affecting the electrons coming from other directions toward the positive side of the interface. Yet, their role in shaping the sensing functions is significant only if the structure of the sensing layer is properly designed. In such cases, the response of the sensor to the target gas is doubly affected: by oxygen-binding-induced changes in the surface electron density and by the reduced mobility of electrons passing through the contact, leading to a remarkably higher sensitivity [89,91]. The surface structure of the TiO₂–CeO₂ mixtures consists of irregularly distributed grains of varying sizes forming agglomerates, as observed in the SEM images. N. Yamazoe and K. Shimano [89] proposed that mixing the grains of two semiconductor materials almost halves the resistance of the resulting structure, regardless of the presence of the target gas and the combination of materials. This chaotic arrangement allows current to flow through paths of lower resistance, primarily homo-contacts, while hetero-contacts play a minor role in electron transport [88,91]. Indeed, the main difference in the response of the TCO

compared to the pure CeO₂ sensor is precisely the markedly lower electrical resistance in the entire range of O₂ concentrations. The latter makes TCO sensors much more suitable, while the sensitivity is slightly lower only for the lowest oxygen concentrations. While the contact potential modulates the drift mobility of the electrons, the band edge difference plays an important role in establishing an exchange current under the unbiased condition [91].

As already said, the common potentials of the Ti 2p and Ce 3d lines suggest the establishment of well-defined contact between TiO₂ and CeO₂, facilitating electronic transport between these two phases. The formation of the well-defined contact is further supported by the Raman spectroscopy, which indicates a noticeable effect of CeO₂ on the phase composition of TiO₂. Given that neither ball-milled nor thermally induced chemical reactions are detected, it is likely that the interactions occurring at the interface between the two oxides are predominantly physical in nature. However, it remains uncertain whether this contact resembles the one depicted in Figure 9. The presence of a rectifying contact within a domain significantly smaller than the overall TiO₂-modified CeO₂ layer cannot be directly observed, as the I–V curves reflect the behavior of the entire sensing material. Even if rectifying properties form at the oxide–oxide interface, they do not significantly affect the sensitivity of the TiO₂–CeO₂ system, that is, not to an observable extent.

4. Materials and Methods

4.1. High-Energy Ball Milling

Three different TiO₂-modified CeO₂ powders were obtained in a high-energy ball mill (Planetari Micro Mill Pulverisette 7, Fritsch, Germany) at three different rotational speeds. TiO₂ (purity > 99%, Alfa Aesar, Kandel, Germany) and CeO₂ (99.9% purity, Johnson Matthey-Alfa, Karlsruhe, Germany) powders served as the starting materials. Milling was carried out under atmospheric conditions in an 80 cm³ silicon nitride vial with 25 silicon nitride balls (10 mm diameter), maintaining a ball to powder mass ratio of 10:1 and a total powder weight of 4.87 g. A CeO₂:TiO₂ mass ratio of 0.8:0.2 was chosen for this study. Milling lasted 160 min, with a 5 min break every 20 min, at speeds of 350, 450 and 550 rpm for each powder. Thick sensing films were made from these powders as described in the following section. The resulting samples were designated as TiCe-1, TiCe-2, and TiCe-3 based on their respective milling speeds: 350, 450 and 550 rpm.

4.2. Paste Preparation and Sensor Fabrication

CeO₂ and mixed oxide pastes were prepared according to the recipe for TiO₂ paste production for dye-sensitized solar cells established by Ito and colleagues [92]. Prior to applying each layer, the pastes were homogenized by stirring on a magnetic stirrer (MR 3001 K, Heidolph, Wood Dale, IL, USA). Six layers were screen-printed on an alumina substrate using custom-made screen equipment. Commercial substrates with interdigitated gold electrodes and a platinum heater on the back side were used (DropSense with interdigitated Gold Electrode/200 µm lines and gaps, IDEAU200-HPT-WB, Metrohm AG, Herisau, Switzerland). Following the printing of each layer, the substrate was dried on a hotplate (PZ28-2, Prazitherm, Harri Gestigkeit GmbH, Dusseldorf, Germany) at 125 °C for 6 min. The samples were then sintered in an oven under an argon flow gradually rising to 800 °C. Prior to this, the samples were briefly exposed to a flow of synthetic air at 400 °C to remove organic components from the paste. By triggering the growth of the so-called neck between the particles, the sintering improved the electromechanical bonding of the particles [93]. The thick film of CeO₂ and the mixtures showed good attachment to the alumina substrate. The resulting structures were mounted between two pairs of copper connector wires, which were custom-made in our facilities.

4.3. Characterization of Powders

To determine the effect of the milling speed on the average particle size of the TiO_2 – CeO_2 powders, particle size distribution (PSD) analysis was employed. The used instrument was the laser-diffraction-based Mastersizer 2000 (Malvern Panalytical, Malvern, UK) analyzer, covering the particle size range of 0.02–2000 μm . To perform the PSD measurements, the powders were dispersed in ethanol and subjected to ultrasonic treatment at a frequency of 40 kHz and power of 50 W. The crystal structure of the powders after undergoing mechanochemical treatment was investigated by the X-ray powder diffraction (XRPD) technique. Diffraction data were acquired in Bragg–Brentano geometry over the range of the scattering angle from 15° to 99° , with a step size of $2\theta = 0.05^\circ$ and a scan step time of 55.245 s. Measurements were performed using a PANalytical X'Pert PRO MPD diffractometer (Almelo, The Netherlands) equipped with an X'Celerator Ultrafast 1D detector based on Real Time Multiple Strip (RTMS) technology. The $\text{CuK}\alpha$ source with a wavelength of 1.542 Å was used. The peak analysis was performed with PANalytical X'pert (version 4.9) software to identify the phases and determine their position, full width at half maximum (FWHM or β), and d-spacing. The Williamson–Hall plot was constructed based on the obtained results to distinguish the contributions of the crystallite size and microstrain of the milled powders.

4.4. Characterization of Sensing Material

The roughness and thickness of the screen-printed films were determined using a Rank Taylor Hobson Ltd. profilometer (Leicester, UK), with a step setting of 0.04 mm for the thickness and 0.02 mm for the roughness measurements. The roughness and thickness were calculated as the average values of data collected from the three, i.e., five regions on the sample, and shown in Table 3. The surface profile was obtained by applying the roughness filter (0.33 Hz) of the instrument. The results of the 2D profile measurements of the films are given in the Supplementary Materials. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (Zeiss Auriga with Oxford XMax 150 EDS, Jena, Germany) were employed to investigate the morphology of the CeO_2 and TiO_2 – CeO_2 films on the substrate. The Raman spectra were acquired using a DXR Raman microscope (Thermo Fisher Scientific, Madison, WI, USA), equipped with a research optical microscope and a CCD detector. A frequency-stabilized single-mode diode laser with an excitation wavelength of 532 nm was employed. The laser power was adjusted to 2 mW and the exposure time to 5 s. The XPS measurements were performed on a XPS system with a Class 100 energy analyzer (VSW, Bushey, UK), which was part of an experimental setup Multitécnica assembled for the surface investigation [94]. The survey spectrum was recorded in a fixed transmission mode with a pass energy of 44 eV (FAT 44), an energy step of 0.5 eV and a dwell time of 0.5 s. Due to the overall low signal intensity and charging problems introducing line broadening, detailed spectra of the Ce 3d core-level were also recorded in FAT 44 mode, with an energy step of 0.2 eV and dwell times of 8 s and 12 s per scan. A non-monochromatic Mg $\text{K}\alpha$ line with photon energy of 1253.6 eV was used as an excitation source. Calibration of the energy axis was performed using a single Ag (110) crystal and polycrystalline Au previously cleaned by Ar ion sputtering. The energy was calibrated to the peak positions of the Ag 3d_{5/2} and Au 4f_{7/2} core-level spectra, with binding energies of 368.22 eV and 83.96 eV, respectively. The samples were in a high vacuum for 24 h prior to the measurements.

4.5. Sensor Response Measurements

Electrical measurements of the obtained sensing structures (Figure 10) were conducted to explore the sensing behavior of the TiO_2 -modified CeO_2 . A scheme of the setup for

measuring the sensor response in the gas flow regime developed for testing the TCO sensors is given in [29]. The sensors were exposed to varying volumetric concentrations of O₂, ranging from 0 to 100%. To achieve different O₂ concentrations, the flow rates of O₂ (5 N purity) and Ar (5 N purity) were adjusted using two mass flow controllers (MC-200SCCM-D/5M, Alicat Scientific, Tucson, AZ, USA).

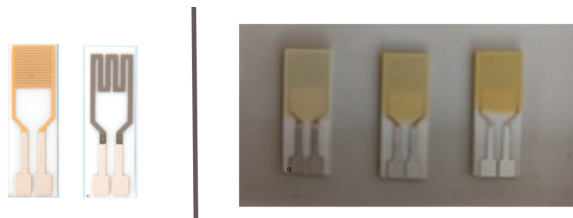


Figure 10. TCO sensor, on the (left): top side of a substrate with electrodes and underside of a substrate with heater; on the (right): final products.

The total gas mixture flow remained at 200 SCCM during all the measurements. Monitoring of the O₂ concentration was carried out by measuring the response of the reference sensor (AA428-210 (AO₂) Citicel, Honeywell City Technology, Bangalore, India) with a multimeter (34461A, Keysight, Santa Rosa, CA, USA). The TCO sensor mounted in a copper holder was placed in a closed glass flask with inlets for the gas mixture and electrical contacts, and gas outlets. The sensor was heated by connecting a back-side platinum heater to a direct current power supply (9174B, B&K Precision, Yorba Linda, CA, USA), labeled DCPS. The supply voltage level was set to 7 V, 8 V, and 9 V to obtain different operating temperatures of the TCO sensor (270 °C, 310 °C, and 350 °C). The direct current resistance (DCR) of the sensors was measured using a multimeter (34410A, Agilent, Santa Clara, CA, USA), with a range for measuring the resistance up to 1 GΩ.

5. Conclusions

The surface properties of TiO₂-modified CeO₂ layers, treated in a high-energy ball mill at three different rotational speeds, were examined to elucidate their sensing behavior when exposed to oxygen. The TiCe-1 sample prepared from precursors milled at the lowest speed (350 rpm) exhibited the highest oxygen sensitivity. Both TiCe-1 and TiCe-2 (450 rpm) outperformed pure CeO₂ in terms of the sensitivity at oxygen concentrations above 10%. All the measurements of the sensor response were conducted at operating temperatures lower than those typical for single metal oxide-based sensors. The XPS analysis revealed that incorporating TiO₂ in the CeO₂ layer helped in reducing the surface contamination, i.e., decreasing the thickness of the overlayer of adventitious carbon. At the speeds above 350 rpm, a new carbon-containing phase, CH₂, was introduced. This phase is hypothesized to be physically separated from the carbon overlayer and located near the grain boundaries, potentially modifying the electron transport properties of the TiCe-2 (450 rpm) and TiCe-3 (550 rpm) layers. The TiCe-3 sample, treated at the highest milling speed, exhibited the lowest sensitivity among the tested samples. Potential contributing factors to this are the partially oxidized structure of the CH₂ phase or a slightly reduced number of oxygen vacancies in comparison to the other samples. Furthermore, the XPS results indicated that oxygen vacancies, the primary active sites for oxygen adsorption, were exclusively formed within the CeO₂ domains. This suggests that while TiO₂ enhances electrical conductivity, its role in oxygen reactions is minimal or indirect. It is worth noting that the addition of TiO₂ also significantly lowered the resistance of the CeO₂ sensor across the entire range of O₂ concentrations, thereby simplifying the practical application of the sensor.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics13050159/s1>, Figure S1: Williamson-Hall plot for CeO₂ and mixed oxides; Table S1: Position of peaks used for the construction of Williamson-Hall plot for the CeO₂ powder; Figure S2: Thickness measurements of TiCe-1, TiCe-2, and TiCe-3 film using a 2D profilometer; Table S2: Position of peaks used for the construction of Williamson-Hall plot for the TiCe-1 powder; Figure S3: Surface roughness of TiCe-1, TiCe-2, and TiCe-3 measured on five different regions; Table S3: Position of peaks used for the construction of Williamson-Hall plot for the TiCe-2 powder; Figure S4: Elemental EDS mapping of Al K series, C K series, Ce L series, Ti K series, and O K series on the center of the TiCe-1 film; Table S4: Position of peaks used for the construction of Williamson-Hall plot for the TiCe-3 powder; Figure S5: EDS layered image taken in the center of the TiCe-1 film; Table S5: Data obtained from EDS mapping for sample TiCe-1; Figure S6: EDS map spectrum of the TiCe-1 film taken from the center; Table S6: Data obtained from EDS mapping for sample TiCe-2; Figure S7: Elemental EDS mapping of Al K series; C K series; Ce L series; Ti K series, and O K series on the center of the TiCe-2 film; Table S7: Data obtained from EDS mapping for sample TiCe-3; Figure S8: EDS layered image taken in the center of the TiCe-2 film; Figure S9: EDS map spectrum of the TiCe-2 film taken from the center; Figure S10: Elemental EDS mapping of Al K series, C K series, Ce L series, Ti K series, and O K series on the center of the TiCe-3 film; Figure S11: EDS layered image taken in the center of the TiCe-3 film; Figure S12: EDS map spectrum of the TiCe-3 film taken from the center; Figure S13: Current-voltage characteristics of a TiCe-1-based sensor at 10, 50 and 90% of O₂ at 310 °C; Figure S14: Example of resistance time tracking at different volume concentrations of O₂ for the sample TiCe-3; Figure S15: Relative change of resistance with for the sample TiCe-3; Figure S16: DC resistance of CeO₂ and mixed oxides when exposed to different volume concentrations of O₂ at a temperature of 310 °C; Figure S17: Schematic representation of the experimental setup for measuring the sensor response. References [23,80–86] are cited in Supplementary Materials.

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Article

Mechanical Modelling of Integration and Debonding Process of Ultra-Thin Inorganic Chips

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Abstract

The research on ultra-thin inorganic chips is an important field in the development of inorganic flexible electronics. By thinning the inorganic (mainly silicon-based) chip to less than 50 μm , it will gain a certain degree of flexibility. After the ultra-thin chip is integrated into the flexible substrate, it is bent repeatedly during the operation of the system. When the bending angle is excessively large, the chip and substrate will debond, or the chip will break. In this process, whether the chip can be stably adhered to the substrate depends on many factors, and debonding can only be reduced by continuously adjusting the process parameters. From an energy method perspective, this study divides the bending process of flexible silicon-based chips and flexible films into two states: debonding and non-debonding. A debonding mechanical model of flexible chips is established, and the regulatory relationship between the adhesion coefficient between the chip and film, chip geometric size, and material parameters was established. Experiments were also conducted to verify the relevant theoretical results. The theoretical results show that the risk of chip debonding decreases with a reduction in chip thickness, an increase in interface adhesion, and an increase in bending radius. Improving the interface adhesion during the bending process can effectively stabilize the adhesion of flexible chips. This paper provides a theoretical basis for the integration and bending of ultra-thin flexible chips and flexible substrates, promoting the practical assembly and application of ultra-thin chips.

Keywords: flexible electronics; ultra-thin chips; debonding; energy method

1. Introduction

Since their inception, flexible electronics have attracted countless researchers with their ever-changing electronic device morphology and rich application prospects, and they continue to develop rapidly [1,2]. From the organic devices to the inorganic devices, the research on flexible electronics has progressed from a simple concept to a flourishing field in various fields in the past 20 years. Flexible electronic devices with various forms, functions, and principles have emerged. Energy devices [3], sensors [4], display equipment [5], microsystems [6], skin-like devices [7], and other types of flexible electronic technologies have been widely used in consumer electronics, medical electronics, military fields, and biological monitoring. Compared with traditional electronic devices, flexible electronic devices can withstand external loads, such as bending and stretching, without failure; therefore, they can adapt to surfaces of different shapes [8], especially in terms of integration with the surface of human skin, which has a unique advantage [9].

There are two main research directions for flexible electronic devices: organic flexible electronics based on organic materials [10] and inorganic flexible electronics based on inorganic semiconductor materials. Organic flexible electronic devices have material flexibility and ductility but weak electrical properties, while inorganic electronic devices have good electrical properties but are fragile and easy to damage due to the characteristics of the material. Therefore, since the proposal of inorganic flexible electronic devices, improving their flexibility and ductility has been a hot topic in academic research [11]. Converting hard electronics into flexible electronics through structural and mechanical design is a major research direction in inorganic flexible electronics. The development of flexible electronic technology requires chips to be flexible and conform to the bending of flexible substrates. The chip thickness can be designed to have a certain bending and deformation capability. Unlike traditional chips, flexible chips are required to perform the set functions under large deformations, which is also the key to their application [12,13]. In recent years, the bending performance and flexibility of flexible electronic devices have been continuously improved by structural design and material optimization. Related research includes colloidal QD photodetectors [14], silicon solar cells [15,16], and sensors [17,18]. However, the better the bending performance, the greater the deformation. Currently, the reliability of flexible electronic devices, especially chip bonding reliability, is becoming increasingly demanding.

During the preparation of flexible packaging systems, the peeling of flexible chips and the bonding reliability of flexible substrates are extremely important. After the system is packaged, it often needs to withstand an external bending load, causing a certain amount of bending deformation. If the bonding reliability of the flexible chip and flexible substrate is insufficient, debonding will occur at the bonding interface. Therefore, to verify whether the interface between the chip and flexible substrate is sufficiently reliable after pasting, the system is generally bent at a fixed bending radius tens of millions of times after the chip is bonded to confirm whether the interface has sufficient strength under the bending load.

Some studies have been conducted to analyze the interface problems of flexible chips and substrates, such as the double-layer chip-substrate model [19] and three-layer chip-adhesive-substrate model [20–22]. Modeling of the adhesive layer is particularly important for analysis. There are many analytical models for the interface behavior of layered structures as well, which can be mainly divided into two categories. The first type is the model based on fracture mechanics theory [23], which uses characteristic parameters such as the J integral [24], stress intensity factor [25], and energy release rate [26]. The second type is a model based on classical strength theory [27]. Some models describe the generation of singular stress fields at the edge of layered bounded structures and at the interface crack tip [28], and some describe the debonding process based on the theoretical bilinear cohesive zone model [29]. In addition to theoretical models, experimental test methods have also been proposed [30].

However, most existing work focuses on the chip peeling process. The chip peeling process requires the use of concentrated forces, such as ejector pins, or the setting of pressure distribution to peel the chip. When analyzing this external force, the type of external force must be preset in advance. It is difficult to determine a fixed external force in the bending process of a flexible system. Therefore, if a method can be found to analyze the bending state of the chip from the perspective of the state without setting the type of external force, it will be beneficial for simplifying the analysis process. At the same time, methods based on fracture mechanics often require a preset crack path, which also has a certain impact on the analysis.

In this study, a debonding mechanical model of flexible chips was established from an energy standpoint. The bending process of flexible silicon-based chips and flexible films

was divided into two states: debonding and non-debonding. The effects of the adhesion coefficient, geometric dimensions, and material parameters on the chip debonding process were studied, the critical thickness of the flexible chip was determined, and experiments were conducted to verify the relevant theoretical results.

2. Results

2.1. Modeling

The bonding interface of the chip has a significant impact on the reliability of the flexible system. In order to better control this process, the mechanical behavior of the chip and system when bent is analyzed here. In the bending experiment, the experimental device imposes an additional bending radius R on the entire system. The bent system is shown in Figure 1, where the deformation of the flexible substrate board can be approximated to an arc. In this model, since the interface properties of the chip when it is debonded are explored, the situation when the system is bent downward is considered. When the system is bent upward, the chip has no corresponding debonding trend; therefore, this type of situation is not considered.

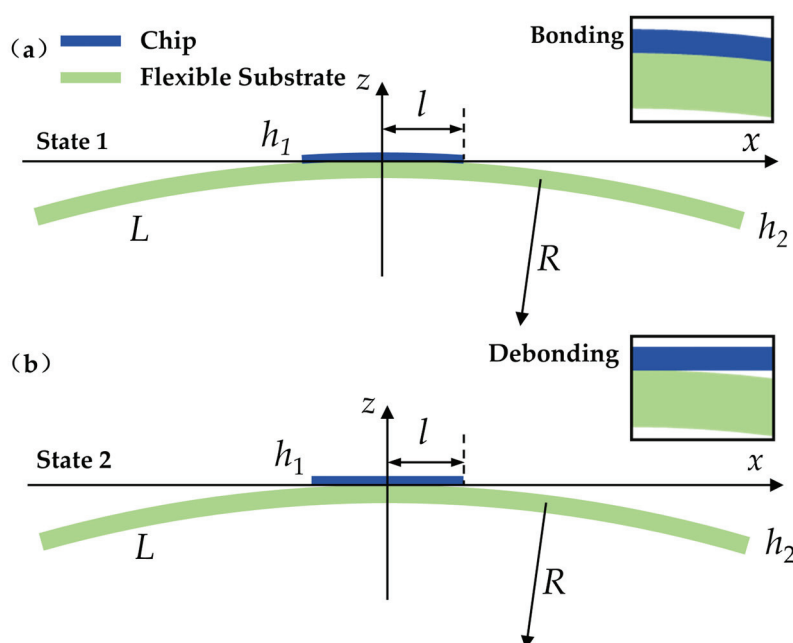


Figure 1. Schematic diagram of the flexible chip bonding test model (a) The ultra-thin chip and the flexible substrate deform together; (b) The ultra-thin chip and the flexible substrate debond.

In Figure 1, the length of the chip is $2l$, the length of the flexible substrate is $2L$, the thickness of the chip is h_1 , and the thickness of the flexible substrate is h_2 . During the bending process of the system, there are two states between the chip and flexible substrate: the first state is that the chip deforms together with the system and flexible substrate, which is defined as state 1 (Figure 1a); the second state is the interface debonding between the chip and flexible substrate. At this time, the chip does not deform, the flexible substrate deforms, and the interface energy of the interface between the chip and flexible substrate is released at the same time, which is defined as state 2 (Figure 1b). Next, using the energy principle, we compared the total energies of the system in States 1 and 2. The system always tends to a state with lower energy, which is used to obtain the standard for determining whether the chip and flexible substrate are in a debonding state.

As shown in the coordinate axis of Figure 1, for flexible substrates, the external load of the general reliability analysis is a bending load with a certain bending radius. Therefore,

it is assumed that the deformation of the flexible substrate and the chip are both arcs, and pure bending occurs within the linear elastic range. Generally speaking, the external bending radius R and the thickness of the chip h_1 meet the inequality $R \gg h_1$, so it can be approximately considered that the bending radius of the flexible substrate and the chip is R . For pure bending loads, it is easy to obtain the strain energy of the chip:

$$U_{chip} = \frac{\bar{E}_1 h_1^3}{24} \cdot \frac{2l}{R^2} = \frac{\bar{E}_1 h_1^3 l}{12R^2}, \quad (1)$$

where $\bar{E}_1 = E_1 / (1 - \nu_1^2)$ is the plane strain elastic modulus, E_1 is the elastic modulus of the chip material, and ν_1 is the Poisson's ratio of the chip material.

By summing the strain energies of the chip and flexible substrate, the total energy of the chip/flexible substrate system in the two states can be obtained as follows:

$$\begin{aligned} U_1 &= U_{chip} + U_{sub} \\ &= \frac{\bar{E}_1 h_1^3 l}{12R^2} + U_{sub} \end{aligned} \quad (2)$$

$$\begin{aligned} U_2 &= U_{inter} + U_{sub} \\ &= 2\gamma l + U_{sub} \end{aligned} \quad (3)$$

where γ is the interface energy per unit length between the chip and the flexible substrate.

By subtracting Equation (2) from Equation (3), the total energy difference between the two states is

$$\Delta U = U_2 - U_1 = 2\gamma l - \frac{\bar{E}_1 h_1^3 l}{12R^2} \quad (4)$$

In addition, when the bending radius of the system is much larger than the chip size, the small deflection theory can be applied, and the deflection expression of the chip is as follows:

$$w = -R + \sqrt{R^2 - x^2}. \quad (5)$$

The second derivative of (5) is

$$\frac{d^2 w}{dx^2} = -\frac{R^2}{(R^2 - x^2)^{\frac{3}{2}}} \quad (6)$$

Thus, the strain energy of the chip when it is deformed can be calculated as follows:

$$\begin{aligned} U'_{chip} &= \frac{\bar{E}_1 h_1^3}{12} \int_{-l}^l \frac{1}{2} \left(\frac{d^2 w}{dx^2} \right)^2 dx \\ &= \frac{\bar{E}_1 h_1^3}{12} \int_{-l}^l \frac{1}{2} \left(-\frac{R^2}{(R^2 - x^2)^{\frac{3}{2}}} \right)^2 dx \\ &= \frac{\bar{E}_1 h_1^3}{12} \frac{5R^3 l - 3Rl^3}{(R^2 - l^2)^2} + 3 \operatorname{arctanh} \left(\frac{l}{R} \right) \end{aligned} \quad (7)$$

The parameters are made dimensionless as follows:

$$\frac{l}{R} = \lambda_1 \quad (8)$$

Then, (7) can be simplified as

$$U'_{chip} = \frac{\bar{E}_1 h_1^3}{96R} \left[\frac{5\lambda_1 - 3\lambda_1^3}{(1 - \lambda_1^2)^2} + 3\operatorname{arctanh}(\lambda_1) \right] \quad (9)$$

The strain energy of the substrate can also be calculated as follows: Here we consider ΔU : when $\Delta U < 0$, $U_2 < U_1$, the chip/flexible substrate system tends to state 2, and the chip and the flexible substrate are debonded; when $\Delta U > 0$, $U_2 > U_1$, the chip/flexible $U_2 < U_1$ system tends to state 1, and the chip and the flexible substrate are deformed together. Observing (4), it can be seen that when the chip length $2l$ remains unchanged, the chip thickness h_1 , the interface energy per unit length γ , and the bending radius R will affect the value of the energy difference, thereby affecting whether the system interface debonds.

2.2. Effect of Various Parameters

First, the relationship between chip thickness h_1 and energy difference when the interface energy per unit length γ and bending radius R change is studied. The ultra-thin chip studied in this paper is mainly based on a semiconductor material, silicon. Since the thickness of the chip functional layer is much smaller than the thickness of silicon, it is believed that the mechanical properties of the chip are approximately the mechanical properties of silicon, elastic modulus $E_1 = 190$ GPa and Poisson's ratio $\nu_1 = 0.28$. The chip length is taken as $2l = 4$ mm, and the relationship between the energy difference and the chip thickness is calculated, as shown in Table 1. The results are presented in Figure 2. As shown in the figure, as the chip thickness increases, the energy difference gradually decreases, which means that the thicker the chip, the easier it is for the chip/flexible substrate system to debond, which is one of the reasons for achieving full flexibility in flexible electronics. The thicker the chip, the easier it is to detach from the flexible substrate when the system as a whole is subjected to a bending moment, and the more likely it is that the system will fail. By contrast, the thinner the chip, the easier it is to adhere to the flexible substrate. At the same time, since the absolute value of the slope of the curve increases, it can be considered that regardless of the size of the interface energy per unit length and the bending radius, as long as the system is bent, there must be a chip thickness that is sufficiently large to cause the chip and the flexible substrate to debond. Therefore, chip thickness significantly influences the interface reliability of the chip/flexible substrate system in a bent state.

Table 1. Material parameters used for calculations in this paper.

E_1	ν_1	$2l$
190 GPa	0.28	4 mm

As can be seen from Figure 2a, when the interface energy per unit length γ remains unchanged, that is, when the viscosity of the interface does not change, the larger the bending radius, the more the system energy tends to state 2, that is, the smaller the absolute value of the slope of the curve, that is, the less likely the system is to debond. Therefore, the smaller the curvature applied to the flexible system, the more likely the chip is to debond, which is consistent with the experimental results. As can be seen from Figure 2b, when the bending radius R does not change, changing the interface energy per unit length, the system energy tends to state 2, that is, the absolute value of the slope of the curve is the same, but the starting point of the curve is different. Increasing the interface energy per unit length γ helps the system maintain state 1; that is, it is more difficult for debonding to occur.

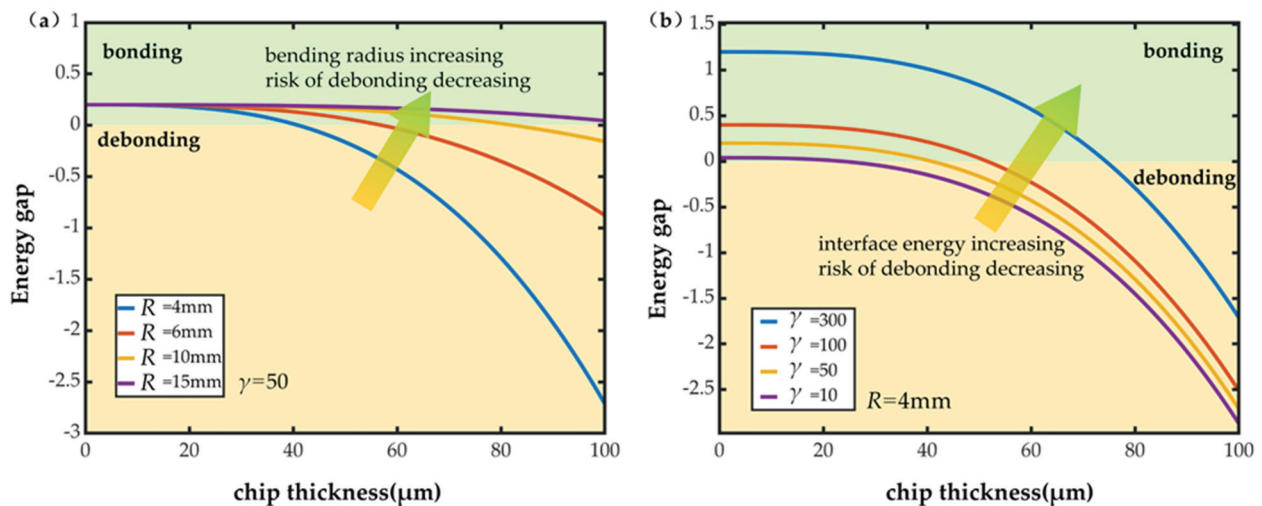


Figure 2. Relationship between chip thickness h_1 and energy difference between two states ΔU (a) under different bending radius R while γ remains constant; (b) under different unit length interface energy γ while bending radius R remains constant.

Subsequently, the relationship between the bending radius R and the energy difference ΔU when the chip thickness h_1 changes is studied. The results are presented in Figure 3. It can be observed that with an increase in the bending radius, the system energy tends to change from state 2 to state 1; that is, the system is less likely to debond. Under a certain unit length interface energy γ , for chips of certain thicknesses, as shown in the curve $h_1 = 20\text{ }\mu\text{m}$ in the figure, the bending radius is reduced to 3 mm, and the chip cannot be debonded. Therefore, according to different system application scenarios and requirements, it is very important to adapt ultra-thin flexible chips of different thicknesses for the production of flexible electronics.

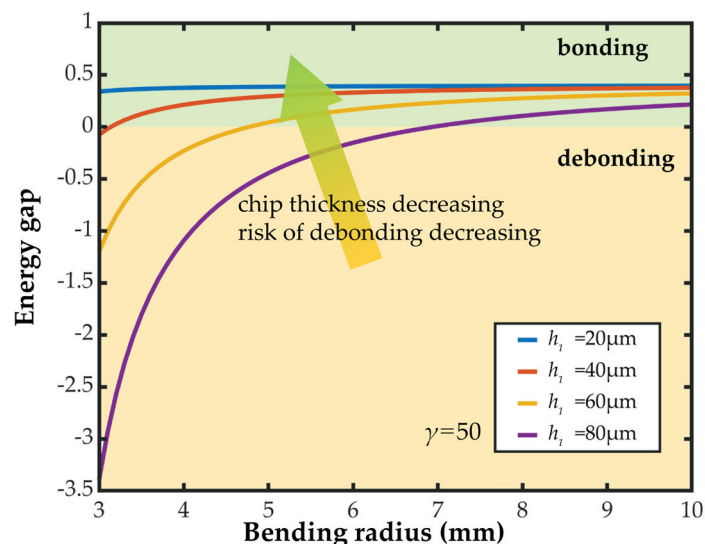


Figure 3. Relationship between the bending radius of the system and the energy difference between the two states.

3. Discussion

3.1. Critical Thickness

Further research on Figures 2 and 3 shows that there is a certain chip thickness h_1 or bending radius R that can put the system in a critical state $\Delta U = 0$. Assuming that the chip

thickness when $\Delta U = 0$ is the critical thickness for the chip not to fall off, then from (4) we can obtain:

$$h_{1cri} = \sqrt[3]{\frac{24\gamma R^2}{E_1}} \quad (10)$$

Continue to take the elastic modulus of the flexible chip $E_1 = 190$ GPa, Poisson's ratio $\nu_1 = 0.28$, and the chip length $2l = 4$ mm as the condition, and draw the relationship between the critical chip thickness h_{1cri} , the interface energy per unit length γ , and the bending radius R , as shown in Figure 4:

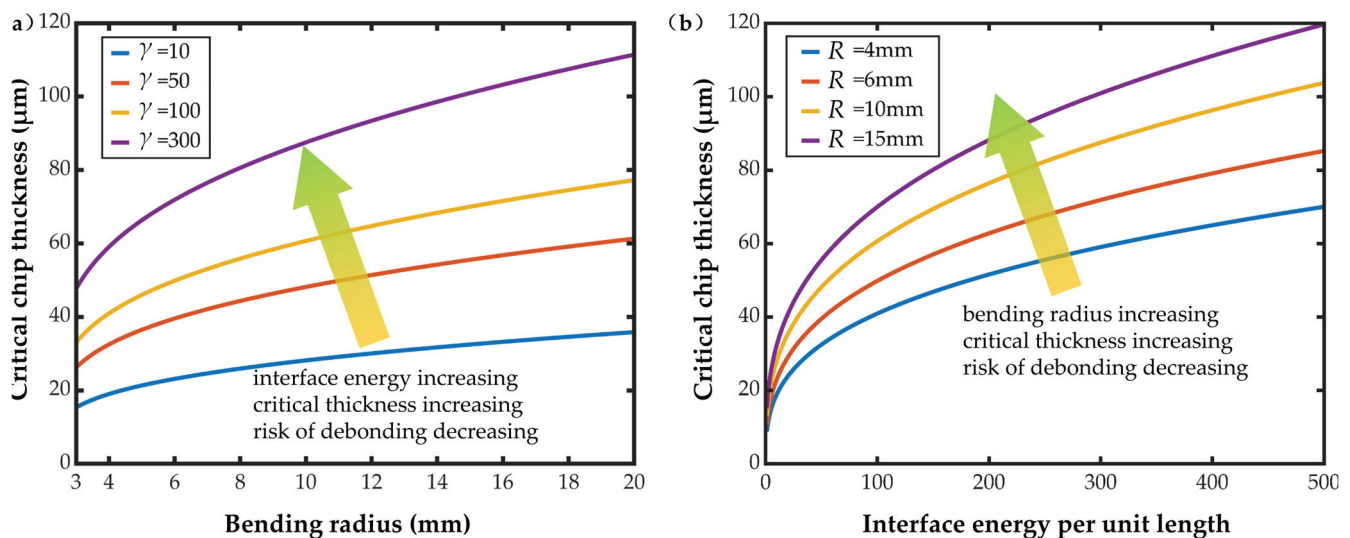


Figure 4. Relationship between critical chip thickness h_{1cri} , interface energy per unit length γ , and bending radius R (a) Relationship between critical chip thickness h_{1cri} and bending radius R at different interface energies per unit length γ ; (b) Relationship between interface energy per unit length γ and critical chip thickness h_{1cri} at different bending radius R .

Figure 4a shows the relationship between the critical chip thickness h_{1cri} and the bending radius R under different interface energies per unit length γ . It can be observed that the critical thickness of the bonded chip increases with the bending radius, but the increasing trend slows down. A larger interface energy per unit length increases the critical thickness. Figure 4b shows the relationship between the critical chip thickness h_{1cri} and the interface energy per unit length γ under different bending radii R . It can be observed that the critical thickness of the chip that can be bonded increases with an increase in the interface energy per unit length, and the increasing trend also slows down. Therefore, it can be considered that when the interface energy per unit length increases to a certain extent, its influence on the critical thickness of the chip is minimal.

3.2. Effect of Changes in Silicon Material Properties

According to relevant research [31], the material properties of silicon wafers change to a certain extent after the thickness is reduced and doped. According to research [32], the elastic modulus of doped silicon wafers decreases. When boron is doped, the elastic modulus is about 155 GPa; when phosphorus is doped, the elastic modulus is about 145 GPa; and when arsenic is doped, the elastic modulus is about 135 GPa. In addition, according to relevant research [33], the Poisson's ratio of the silicon film is reduced to about 0.24.

In this study, bulk silicon was used for the calculations. Considering the impact of changes in the silicon wafer material properties on the calculation results, a theoretical

estimate of the impact of the critical thickness of silicon wafers when the elastic modulus and Poisson's ratio change is made here, as shown in Figure 5.

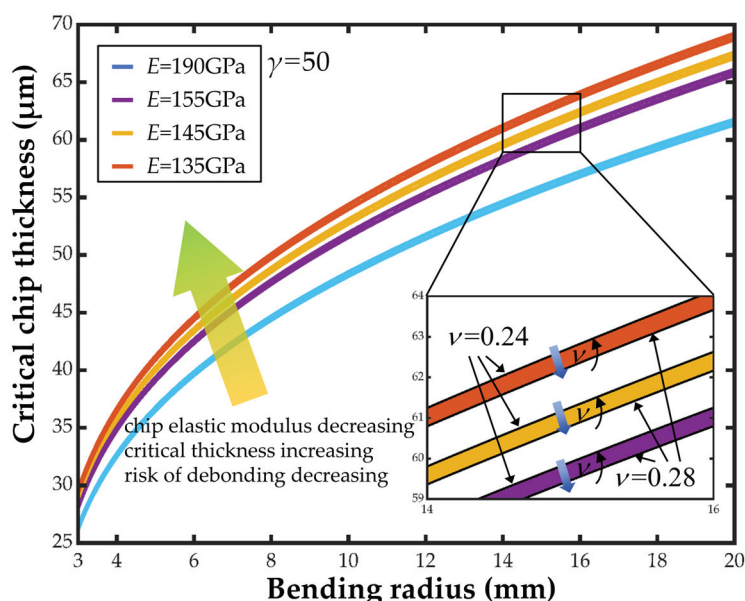


Figure 5. Effect of changes in silicon material properties on critical thickness.

As shown in Figure 5, when the elastic modulus decreases, the critical thickness of the chip continues to decrease, and at the same time, the risk of debonding of the chip-substrate system decreases. Therefore, it can be considered that when the chip thickness decreases and the chip is doped, the risk of chip debonding decreases, and the calculated critical thickness of the chip increases by about 7%~11% compared with that of bulk silicon.

On the other hand, the inset of Figure 5 (inset image) shows the change in the critical thickness of the silicon wafer when the Poisson's ratio of the silicon chip changes. Regardless of the elastic modulus, when the Poisson's ratio of the silicon wafer decreases from 0.28 to 0.24, the critical thickness increases slightly by about 0.8%, that is, it will not change. Therefore, the critical thickness of the silicon wafer is not sensitive to changes in its Poisson's ratio.

3.3. Chip Bending Experiment

The performance of ultra-thin chips in a bent state was tested based on the conclusions obtained in this study. Figure 6 shows an ultrathin chip with a thickness of 20 μm bonded to a glass rod and bent. In the state shown in Figure 6, the radius of the glass rod, that is, the bending radius of the ultra-thin chip, is continuously changed to observe whether the ultra-thin chip is debonded. The bending radius gradually decreases from 40 mm. The experiment shows that when the bending radius of the chip is greater than or equal to 5 mm, the chip can be deformed during bonding. After the bending radius decreases to 3 mm, the chip debonds. In the reliability test of flexible electronic systems, the bending radius of the system is generally set to 8 mm. It can be seen that ultra-thin chips can adapt to the corresponding packaging requirements of flexible integrated systems and have certain advantages.

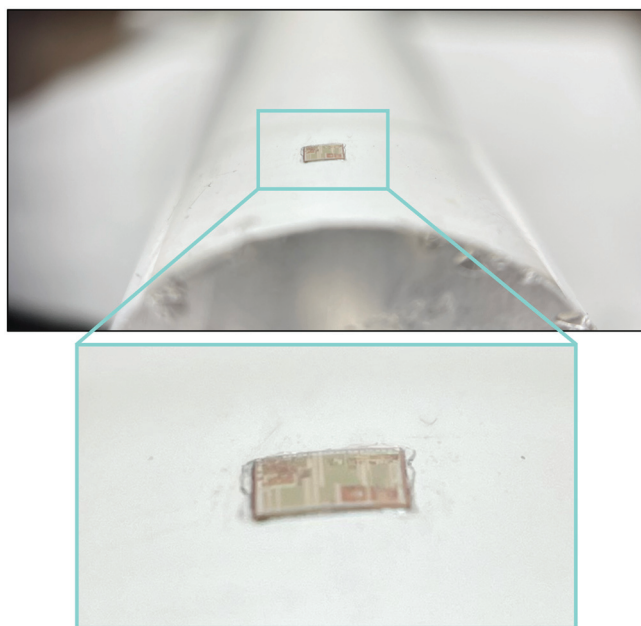


Figure 6. Schematic diagram of the bending of an ultra-thin chip attached to a glass rod.

3.4. Interfacial Adhesion-Regulating Layer

In order to develop the relevant conclusions obtained in this work, we conceived and designed a method to transfer flexible chips by regulating the interface adhesion coefficient. After the chip is thinned, a polyimide (PI) film and DAF Film (Die) (Nitto EM-715L2 (-P)) are attached to the back of the chip. The PI film is a strength support film for the flexible chip, and the DAF film is an interface adhesion-regulating film during the pickup and placement of the flexible chip. During the wafer thinning and dicing process, the DAF film can fix the flexible chip and the blue film used for thinning together. The interface between the DAF film and the flexible chip exhibited strong adhesion. Both the blue film and DAF film were sticky and could support the completion of the dicing and cutting processes. After the dicing process is completed, irradiating the blue film with ultraviolet light can weaken the adhesion between the DAF film and the blue film, thereby regulating the adhesion between the flexible chip and the blue film and completing the peeling process. After the flexible chip is peeled off from the blue film, it is transferred to a flexible circuit board to complete the placement of the flexible chip. During the mounting process, the flexible circuit board was heated to 120 °C, and a pressure greater than 0.1 MPa was applied to the flexible chip for a time greater than 2 s, so that the DAF film completed the adhesion transition and the interface between the flexible chip and the flexible circuit board became a strong adhesion interface, thereby achieving the mounting of the flexible chip, as shown in Figure 6.

Compared with the previous chip peeling process analysis, this work focuses more on the bending state after the chip is integrated with the flexible substrate. The energy method used in this work analyzes the chip debonding state from the perspective of the bending state without the need to pre-assume the specific form of the external force. At the same time, in the process of calculating the energy difference, the strain energy of the substrate is eliminated; therefore, the focus of the analysis can be placed on the chip rather than the substrate. In addition, the energy method analyzes the entire process without the need to preset the crack path, which is relatively simple and clear. Of course, the energy method also has certain problems, that is, the calibration of related parameters is difficult, which is also the focus we hope to solve in future work.

4. Materials and Methods

The analysis method used in this paper is a mechanical analysis method based on the small deflection theory and linear elasticity assumption. That is, the curvature is approximated as the second derivative of the bending deformation, and the load and deformation are considered linearly related.

In general, the pure bending strain of a silicon wafer at a specific bending radius can be expressed as $\varepsilon = \frac{h}{2R}$: where 'a' h is the thickness of the silicon wafer and R is the bending radius. In this work, the thickness of the silicon-based chip was less than 100 μm , and the minimum bending radius was 3 mm. The maximum strain calculated was 1.67%, which meets the 5% standard of the small deformation theory.

Another assumption involved in this article is the linear elastic assumption, that is, the chip deforms linearly when bent. Silicon is a hard and brittle material, and plastic deformation usually does not occur during the fracture process, but directly from elastic deformation to fracture [34]. Researchers have also conducted bending experiments on silicon-based chips [35]. The results show that the load-displacement curve of the silicon-based chips during the bending fracture process is approximately linear, and there is no obvious plastic area. Therefore, it is reliable to use the linear elastic assumption to analyze the chip-substrate bending process.

The chip used in this paper is the Bluetooth chip AC8976A8 (1.8 mm $\times$ 1.7 mm, JieLi Tech, Zhuhai, China).

This paper did not use any relevant database data. This paper did not involve animal or human experiments. GenAI was not used in this paper except for text editing.

5. Conclusions

In summary, this work established a debonding model for ultra-thin inorganic chip integration based on the energy method. The results show that as the chip thickness decreases, the bending radius and interface strength increase, and the risk of chip debonding decreases. Based on the above analysis, the critical thickness of the chip is used as an indicator to provide a criterion for determining whether the chip debonds after integration with the flexible substrate.

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Review

Chiral Hybrid Organic–Inorganic Metal Halides: Preparation, Luminescent Properties, and Applications

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Abstract

Organic–inorganic metal halides (OIMHs) have emerged as highly promising semiconductor materials owing to their outstanding optoelectronic properties. Incorporation of chiral organic molecules into the metal–halide framework enables the construction of chiral OIMHs, which exhibit unique chiroptical phenomena in addition to the intrinsic advantages of perovskite-based semiconductors. This review provides a systematic overview of recent progress in chiral OIMHs, covering synthetic approaches, crystal structures, mechanisms of chirality transfer, circularly polarized luminescence, and circularly polarized light detection. We further highlight the current challenges and outline future research directions, emphasizing the need for strategies that enhance chiroptical responses, stability, and device integration. By bridging fundamental insights with design principles, this work aims to guide the rational development of next-generation chiral functional materials for advanced optoelectronic and spintronic applications.

Keywords: chiral OIMHs; preparation; optoelectronic properties; luminescent mechanism; circularly polarized light

1. Introduction

Chirality is the geometric property of an object that cannot be superimposed on its mirror image. As a fundamental feature of biological systems and nature, chiral materials and their mirror-image counterparts (enantiomers) lack inversion symmetry and exhibit distinctive physical and chemical behaviors [1,2]. They are being actively explored for circularly polarized photodetectors, circularly polarized light-emitting diodes (CP-LEDs), bioimaging, three-dimensional (3D) displays, quantum computing and communication, non-volatile memory, and spintronic devices [3–7]. Although artificial optical elements such as metasurfaces and wave plates can reproduce certain chiroptical effects, their dependence on complex nanofabrication or bulky components elevates cost and can reduce efficiency. By contrast, intrinsically chiral materials offer a direct route to miniaturized, integrated devices with simplified processing [8–11]. Since the first report of a hydrogenated indanone derivative exhibiting circularly polarized luminescence (CPL) in 1967, the field has grown into an interdisciplinary frontier spanning molecular materials, nanotechnology, photochemistry, and optoelectronics [12].

Recently, hybrid organic–inorganic metal halides (OIMHs)—including perovskite families across different dimensionalities—have drawn intense interest for optoelectronics owing to their strong optical absorption, efficient charge transport, long carrier diffusion

lengths, and solution processability. Introducing enantiomerically pure organic molecules into the metal–halide lattice during crystallization enables low-cost, solution-grown chiral OIMHs. These materials exhibit pronounced chiroptical responses (circular dichroism, CPL) and spin-related phenomena such as strong spin–orbit coupling, Rashba splitting, and extended spin lifetimes, making them promising for spintronic applications. Billing and co-workers reported the first low-dimensional chiral OIMHs in 2003, followed by systematic structural analyses in 2006 and 2013 [13–15]; in 2017, thin-film chiral OIMHs were comprehensively characterized for their chiroptical responses, marking a key milestone. Notably, even achiral organic cations can induce symmetry breaking through stereoselective arrangements of inorganic octahedra, yielding helical, chain-like architectures. Such structural engineering allows precise modulation of optical and electronic properties via rational selection of the chiral component (Figure 1).

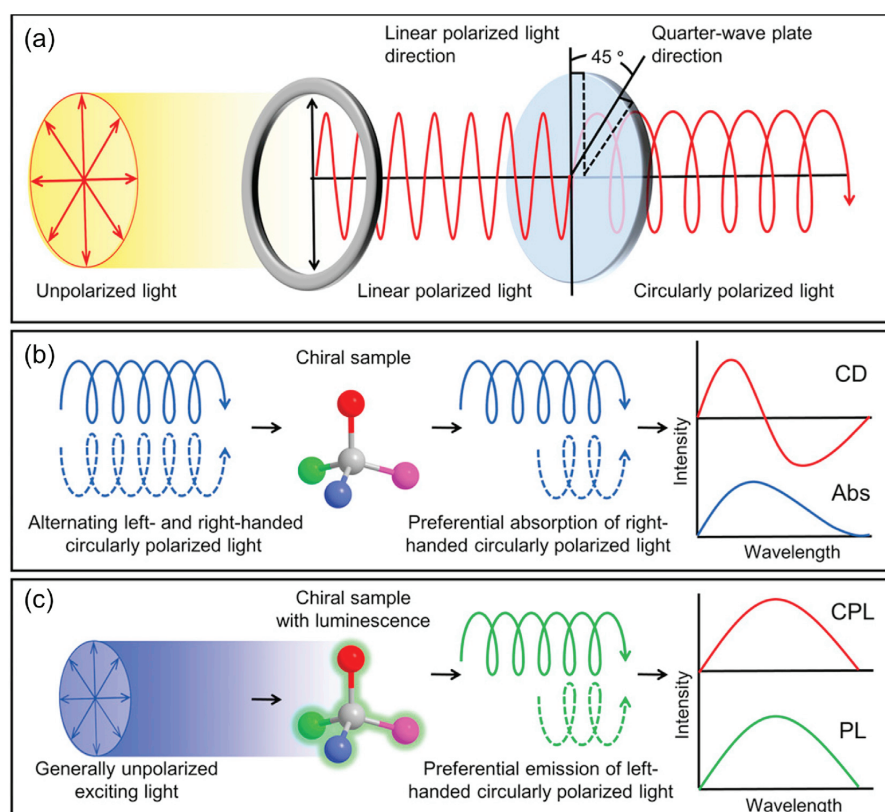


Figure 1. Fundamental properties of chiral OIMHs. (a) Relationship between unpolarized light, linearly polarized light and circularly polarized light. Schematic illustration of (b) CD and (c) CPL [16]. Reprinted with permission from Ref. [16]. Copyright 2019, Wiley.

Extensive efforts now focus on incorporating diverse chiral spacers to enhance structural asymmetry and chiroptical strength in OIMHs [13,14,17]. Remarkably, these materials display CPL and optical activity without external magnetic fields, coupling chirality directly with perovskites' superior optoelectronic features. The hybrid lattice thus unites high carrier mobility and strong absorption from the inorganic framework with the functional flexibility of chiral organic moieties, enabling phenomena including circular dichroism, CPL, nonlinear optical effects, ferroelectricity, and the chirality-induced spin selectivity (CISS) effect. Dimensional control has revealed that two-dimensional (2D) and quasi-2D chiral OIMHs often show enhanced chiroptical responses and favorable exciton transport, supporting applications in light-emitting diodes and photodetectors. In addition, chiral organic cations can induce chiral phonons in the perovskite lattice, giving rise to strong Raman optical activity and opportunities in chiral phononics. OIMHs do not have a single

emission origin. Depending on dimensionality and metal center, their PL typically falls into a few well-defined photophysical buckets (CPL is a polarization property layered on top of these same emissive states). Usually, the CPL emission arises from (i) band-edge/free excitons, (ii) self-trapped excitons in low-dimensional soft lattices, (iii) ns^2 -ion-centered ($Sb^{3+}/Bi^{3+}/Sn^{2+}$) s-p/CT states, (iv) transition-metal dopant d-d transitions (e.g., Mn^{2+}), and (v) cluster/charge-transfer states, with appropriate references [18–21].

Herein, we first introduce key concepts of chirality, including luminescence asymmetry factors and related evaluation metrics. We then summarize recent advances in chiral OIMHs, covering synthetic strategies, crystal structures, mechanisms of chirality transfer, and emerging applications in CPL emitters, circularly polarized photodetectors, and spintronic devices. Finally, we highlight major challenges and unresolved issues and outline a forward-looking perspective on designing next-generation chiral functional materials with improved stability and device performance.

2. Circular Dichroism (CD) Spectroscopy and CPL Spectroscopy

Among various spectroscopic tools for the characterization of chiral materials, the key tools for investigating the optical response of chiral materials are CD spectroscopy and CPL spectroscopy, which characterize the chiroptical properties in the ground state and excited state, respectively. CD spectroscopy is a spectral technique based on the differential absorption of left- and right-handed circularly polarized light by optically active substances. The CD phenomenon originates from the distinct absorption characteristics of chiral molecules towards left- and right-handed circularly polarized light. When plane-polarized light passes through an optically active medium, it can be decomposed into two circularly polarized beams with equal amplitude and phase but opposite rotation directions. During measurement, a xenon lamp source alternately generates circularly polarized light of both handedness. By comparing the intensity differences between incident and transmitted light through the chiral material, the CD spectrum is obtained. The Cotton effect typically appears at the characteristic absorption peaks of the material (Figure 1a). If the medium exhibits different absorption coefficients ($\Delta\epsilon$) for these circularly polarized lights, the emergent light becomes elliptically polarized, a phenomenon known as CD:

$$\Delta\epsilon = \epsilon_L - \epsilon_R \quad (1)$$

The magnitude of CD can be quantified using the absorption dissymmetry factor (g_{abs} , also called g_{CD}):

$$g_{\text{abs}} = \frac{\Delta\epsilon}{\epsilon} = 2 \times \frac{(\epsilon_L - \epsilon_R)}{\epsilon_L + \epsilon_R} \quad (2)$$

Experimentally, g_{abs} can be directly calculated from the ellipticity (θ) measured by CD spectroscopy and the absorbance (A) using the following formula:

$$g_{\text{abs}} = \frac{\theta}{32980 \times A} \quad (3)$$

where θ is directly measured by CD spectropolarimeter in millidegrees (m_{deg}), representing the change in elliptical polarization state caused by differential absorption (ΔA) of left- and right-circularly polarized light. A is typically calculated from UV-Vis spectroscopy or the transmitted light intensity in CD spectra.

CPL spectroscopy serves as a crucial characterization tool for investigating the excited-state properties of chiral luminescent materials by detecting the differential emission intensity between left- and right-handed circularly polarized light. CPL measurements typically employ unpolarized excitation sources to avoid artificial polarization effects on the genuine CPL signal [22–24]. Upon excitation, chiral emitters exhibit distinct emission

intensities for left- (I_L) and right-handed (I_R) circularly polarized components. The CPL spectrum, which reflects this emission anisotropy, always accompanies the corresponding fluorescence spectrum (Figure 1b). Notably, while chiral systems exhibiting CD signals may not necessarily demonstrate CPL activity, materials with CPL properties invariably display Cotton effects in their CD spectra [16]. The CPL spectrum quantifies the intensity difference between emitted circularly polarized components:

$$\Delta I = I_R - I_L \quad (4)$$

In practice, direct measurement of absolute intensities faces technical challenges such as detector response variations and optical path losses. Thus, the luminescence dissymmetry factor (g_{lum}), ranging from 0 (unpolarized) to ± 2 (fully polarized), is adopted to quantify CPL asymmetry:

$$g_{lum} = 2 \times \frac{I_L - I_R}{I_L + I_R} \quad (5)$$

From a quantum mechanical perspective, g_{lum} correlates with the scalar product of electric (μ) and magnetic (m) transition dipole moments:

$$g_{lum} = 4 \cos \theta \frac{|m||\mu|}{|m|^2|\mu|^2} \quad (6)$$

For systems where $|m| \ll |\mu|$ (i.e., electric-dipole-allowed transitions), Equation (6) simplifies to:

$$g_{lum} \approx 4 \cos \theta \frac{|m|}{|\mu|} \quad (7)$$

The sign of g_{lum} is determined by the relative phase between μ and m , which is positive when parallel (left-handed dominance) or negative when antiparallel (right-handed dominance). Pure electric-dipole ($|m| \rightarrow 0$) or magnetic-dipole ($|\mu| \rightarrow 0$) transitions yield $g_{lum} \approx 0$. The theoretical limit (± 2) occurs when $|\mu| = |m|$ with a phase difference of $\pm \pi/2$. In practical molecular systems, $|m|$ is typically 1–2 orders of magnitude smaller than $|\mu|$, resulting in g_{lum} values of 10^{-5} – 10^{-2} for most organic emitters.

Equation (7) reveals a critical trade-off: while a small $|\mu|$ enhances g_{lum} , achieving high quantum yield necessitates a large $|\mu|$. This inherent contradiction poses significant challenges in designing materials simultaneously exhibiting high g_{lum} and quantum yield [25].

Chiral purity denotes the relative abundance of one enantiomer over its counterpart within a chiral substance. A higher chiral purity indicates a greater proportion of chiral molecules or nanostructures with a specific configuration and a lower content of the opposing enantiomer. Achieving high chiral purity is crucial for enhancing the chiroptical properties of materials, particularly in applications involving CPL. To further amplify CPL of chiral OIMHs, two key challenges are being addressed: (1) Developing Structural Control Methods: Researchers are focusing on constructing highly uniform and ordered CPL-active materials. This involves precise engineering of the perovskite lattice to ensure consistent chirality throughout the material. (2) Designing Robust CPL Systems: Efforts are being made to design CPL systems with larger dissymmetry factors. This includes reinforcing the chiral structure to effectively amplify CPL, thereby enhancing the material's chiroptical response. CD and CPL spectroscopy are pivotal in providing insights into the structural characteristics of chiral materials. Understanding the interacting mechanisms between chiral optics and chiral substances, as well as the structural selectivity toward polarized light, is essential. This knowledge aids in elucidating the structure–property relationships

of chiral materials, offering strong support for designing novel chiral functional materials and advancing cutting-edge applications.

3. Crystal Structures of Chiral OIMHs

Current research on chiral OIMHs spans a wide range of dimensionalities at the molecular level, including three-dimensional (3D) networks, two-dimensional (2D) layers, one-dimensional (1D) chains, and zero-dimensional (0D) isolated structures [26–28]. This dimensional hierarchy reflects differences in the separation of inorganic octahedral frameworks by organic molecules, which directly impact optical and electronic properties. Low-dimensional chiral OIMHs typically exhibit more pronounced chiral characteristics due to their higher content of chiral organic ligands (Figure 2).

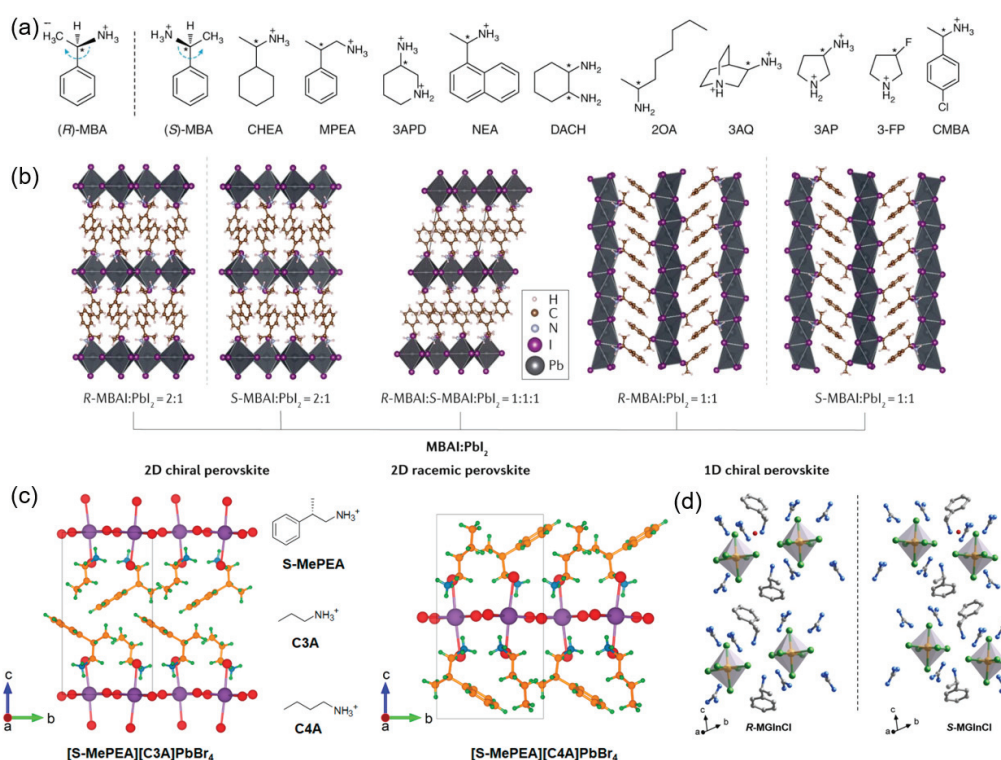


Figure 2. (a) Representative chiral ligands and chiral OIMHs. * stands for the chiral carbon atoms. (b) Single-crystal structures of 2D and 1D chiral OIMHs and of a 2D racemic achiral HOMH based on MBA:(R-MBA)₂PbI₄, (S-MBA)₂PbI₄, R-MBAPbI₃, S-MBAPbI₃ and (rac-MBA)₂PbI₄. (c) Schematic crystal structures of [S-MePEA][C3A]PbBr₄ (left) and [S-MePEA][C4A]PbBr₄ (right) viewed along the a axis [29]. (d) Schematic structures of R-MGInCl (left) and S-MGInCl (right) single crystals [30]. Reprinted with permission from Ref. [29]. Copyright 2021, American Chemical Society. Reprinted with permission from Ref. [30]. Copyright 2023, Wiley.

3.1. Three-Dimensional Chiral OIMHs

Three-dimensional chiral OIMHs, often referred to as three-dimensional perovskites, typically adopt centrosymmetric structures, inherently lacking chirality. This structural limitation prevents the manifestation of second-order nonlinear optical effects and CPL, thereby restricting their direct application in chirality-related functional devices. In contrast, low-dimensional OIMHs circumvent the restrictions imposed by the tolerance factor. By precisely tuning the composition of their organic and inorganic components, these materials enable exact control over both crystal structure and band characteristics [31].

In 3D perovskites, with the general formula ABX₃, the [MX₆] octahedra form a 3D framework through corner-sharing, with A-site cations occupying the interstitial voids. These structures typically exhibit high symmetry, such as cubic or tetragonal systems, often

belonging to centrosymmetric point groups. This symmetry constraint makes it challenging to introduce chirality through simple structural design. To achieve a stable crystal structure, the chiral organic cations must be sufficiently small. However, most chiral organic cations are relatively large, complicating the direct synthesis of 3D chiral perovskites and often resulting in poor stability [26,27]. Furthermore, chirality must be effectively transferred from the organic components (e.g., chiral amines) to the inorganic framework (e.g., $[\text{PbX}_6]^{4-}$ octahedra), but the rigidity of the 3D structure may weaken this transfer efficiency. Since most 3D perovskites lack intrinsic chirality, they rely on exogenous chiral molecules (e.g., chiral organic amines) for induction. However, such molecules are prone to racemization under high-temperature or solution-phase synthesis conditions [32,33].

Recent studies have demonstrated methods to induce chirality in 3D perovskites [34]. For instance, Yang et al. reported a universal and controlled method for synthesizing chiral 3D lead halide perovskites using organic amines or alcohols as chiral templates. Introducing these templates to PbCl_2 in *N,N*-dimethylformamide (DMF) under acidic conditions induced the crystallization of R/S [DMA]PbCl₃, showcasing a potential approach to overcome the challenges associated with 3D chiral perovskite synthesis. Long et al. theoretically demonstrated that the introduction of chiral R or S-chlorofluoromethylammonium (R-/S-CFMA) cation can transfer the chirality of organic molecules to the internal structural framework and produce 3D OIMHs [35].

Additionally, co-assembly of non-chiral OIMHs with chiral molecules has been employed to construct 3D chiral OIMHs. In such systems, chiral molecules can transfer their structural asymmetry to the metal halide lattice, thereby inducing CD and CPL signals. [36,37]. For example, Shi's group co-assembled non-chiral CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) perovskite nanocrystals with chiral lipid-based gelators featuring helical structures, achieving CPL across multiple wavelengths with a dissymmetry factor on the order of 10^{-3} . Notably, this CPL response was induced by the aggregated state, enabling reversible switching of the CPL signal via heating or cooling [37,38].

3.2. Two-Dimensional and Quasi-2D Chiral OIMHs

Two-dimensional OIMHs are characterized by planar inorganic octahedral frameworks and exhibit compositional and structural diversity, making them the most extensively studied configuration for chiral OIMHs systems [39,40]. Compared to 3D structures, 2D OIMHs demonstrate superior properties. Firstly, hydrophobic effects from long-chain organic molecules significantly improve moisture resistance and photo/thermal stability. Secondly, their photoelectronic properties can be precisely regulated by adjusting the inorganic layer number and chemical composition. In the realm of chiral 2D OIMHs, significant strides have been made in enhancing chiral purity to achieve stronger CPL signals. So far, advancements in the synthesis of chiral 2D OIMHs have led to materials exhibiting high degrees of CPL, with maximum g_{lum} reaching 17%.

In 2003, Billing et al. first reported chiral 2D OIMHs employing (S)-methylbenzylamine (S-MBA) as the chiral organic ligand (Figure 2a) [13,14]. By 2006, the 2D single-crystal structures of these materials were resolved, demonstrating corner-sharing layered frameworks $[(\text{R/S-MBA})_2\text{PbI}_4]$. After, Xiong et al. reported the 2D OIMHs ferroelectrics $(\text{R/S-CPEA})_2\text{PbI}_4$ ($\text{R/S-CPEA} = \text{R/S-1-(4-chlorophenyl)-ethylammonium}$) with outstanding ferroelectric performance and robust CD and CPL signals [27]. Meanwhile, $(\text{R/S-MBA})_2\text{CuCl}_4$ with a 2D structure in which each $[\text{CuCl}_4]^{2-}$ tetrahedron is isolated separately are reported, with a record g -factor as high as ~ 0.06 . The corresponding CD spectra hardly changed after storage under ambient conditions for over a month [41]. In 2019, Ma et al. found that chiral 2D $(\text{R-MBA})_2\text{PbI}_4$ and $(\text{S-MBA})_2\text{PbI}_4$ exhibit an average degree of circularly polarized PL of 9.6% and 10.1% at 77 K, respectively, and a maximum degree of the circularly

polarized PL of 17.6% is achieved in (S-MBA)₂PbI₄ (Figure 2b) [42]. In 2020, mixed-cation 2D chiral perovskites were developed, combining chiral aromatic amines with non-chiral spacers to modulate CD properties without complex synthesis of new chiral cations. As shown in Figure 2c, Wei's group reported a 2D chiral OIMHs composed of chiral aromatic amines and non-chiral alkylammonium spacer cations (1:1 molar ratio) [29]. These novel 2D chiral OIMHs integrate unprecedented chirality with alkyl-aryl functionality, governed by non-covalent intermolecular interactions (e.g., CH $\cdot\pi$ interactions) within their crystal structures. Unlike purely chiral cation-based analogs, the mixed-cation 2D chiral HOMH system exhibits distinct CD properties, offering a new strategy to modulate the chiral optical behavior of known chiral OIMHs without requiring complex synthesis of new chiral cations.

Two-dimensional OIMHs usually exhibit low PLQY values at room temperature. Recent work on chiral layered HOMHPs found that using chiral organic cations further decreased the PLQY, indicating strong losses from nonradiative recombination. However, Shangpu et al. found that 2D OIMHs (R/S)-3BrMBA₂PbI₄ show large PLQY values of 39% and a high degree of CPL of up to 52%. Chiral 3BrMBA molecules provide an excellent option to increase the perovskite crystal angle distortion degrees, resulting in outstanding chiral optical features, as well as structural configurations that strongly decrease the impact of nonradiative loss channels during recombination, resulting in fast radiative decay with large PLQY value [43].

2D/quasi-2D OIMHs can be represented by the general formula (RNH₃)₂A_{n-1}MX_{3n+1}, where n denotes the number of inorganic layers between adjacent organic cation layers (n = 1 for pure 2D structures, n > 1 for quasi-2D structures), and RNH₃ represents the chiral ligand embedded between inorganic layers. The pure 2D OIMHs exhibit the strongest chirality. Differently, quasi-2D crystal structures (n = 2) endow OIMHs with chirality and PL properties simultaneously. Researchers incorporated a wider range of chiral organic spacers, enabling quasi-2D structures (n > 1) that combine chirality with tunable PL properties. In quasi-2D chiral OIMHs, the absorption dissymmetry factor demonstrates a decreasing trend with increasing n value between chiral ligands [3]. Guan et al. achieved efficient blue CPL in corrugated quasi-2D R/S-(BPEA)FAPbBr₄·H₂O (BPEA = 4-bromophenylethylammonium). By incorporating the achiral FA⁺ cation alongside BPEA, they achieved an 8-fold increase in g_{lum} (~8.4 × 10⁻³). This enhancement was attributed to FA⁺ reducing lattice distortion and altering the octahedral connectivity from edge-to-edge to corner-to-corner [44]. These developments emphasized robust 2D and quasi-2D systems that maintain chiral optical activity under ambient conditions and offer tunable optoelectronic properties.

3.3. One-Dimensional Chiral OIMHs

In 1D chiral OIMHs, the inorganic metal halide units that share corner-, edge-, or face can form a chain-like inorganic frameworks surrounded by organic cations. In contrast to 2D and quasi-2D chiral OIMHs, 1D chiral OIMHs exhibit a characteristic chemical formula of RNH₃MX₃, requiring a 1:1 stoichiometric ratio between chiral organic alkylammonium cations and metal cations. The earliest reports introduced chiral organic ammonium cations into 1D halide frameworks, typically forming face-sharing [MX₆] chains or edge-sharing motifs. These studies established that 1D systems can accommodate relatively bulky chiral cations, unlike 3D OIMHs. However, research was mostly limited to crystallographic description, with little attention to optical chirality [45].

After these initial studies, broader classes of aromatic and aliphatic chiral cations (e.g., R-/S-MBA, R-/S-PEA derivatives) were employed, yielding stable 1D chiral OIMHs. Tailored ligand design, co-assembly strategies, and enhanced exciton–phonon coupling in 1D lattices enabled stronger chirality transfer than in higher-dimensional counterparts.

In 2003, Billing and Lemmerer pioneered to report the synthesis and crystal structure of 1D (S-MBA)PbBr₃ chiral OIMHs [13]. Moreover, researchers achieved robust CD and CPL signals in 1D chiral OIMHs by optimizing cation–inorganic interactions and chain distortions. It has been reported that the (R-/S-MBA)PbI₃ exhibits a 1D crystal structure consisting of extended face-sharing [PbI₆]₄ octahedral chains, which are orientated along the a-axis and separated by isolated organic cations. It has been reported that 1D (R-/S-MBA)PbI₃ thin films exhibited significantly enhanced stability and almost the same spin transport properties within one month. One-Dimensional (R/S- α -PEA)PbI₃ (where α -PEA = α -phenylethylamine) chiral OIMHs with a unique crystal configuration: highly distorted face-sharing [MX₆] octahedral chains surrounded by chiral cations, forming a distinctive stacked framework structure [46]. In addition, it is reported that (R/S-DMPZ)PbBr₄ (DMPZ = cis-2,5-dimethylpiperazine) can achieve a high g_{lum} of 2.3×10^{-2} , and moisture-stable 1D HOMH containing chiral R/S-3-aminopiperidine cations and water molecules that exhibit broadband yellowish-white CPL with a g_{lum} of 1.8×10^{-3} [47,48]. Until now, a series of 1D chiral OIMHs emitting white light have been reported, representing a significant breakthrough in chiral symmetry breaking in OIMHs. These works highlighted the anisotropy and exciton confinement effects inherent to 1D structures, giving them distinct chiroptical properties compared to 2D systems. The chain-like inorganic frameworks of 1D chiral OIMHs not only tolerate large chiral cations but also facilitate efficient chirality transfer, making them promising candidates for CPL emitters, spintronic devices, and chiral optoelectronics.

3.4. 0D Chiral OIMHs

The octahedral units in 0D OIMHs are completely isolated by surrounding organic molecules, allowing for the generation of STEs emission characterized by a large Stokes shift and broadband. 0D chiral OIMHs exhibit outstanding PLQY due to their pronounced quantum confinement effects and large Stokes shifts [49].

Additionally, 0D systems usually display enhanced environmental stability compared to 3D/2D perovskites because the isolated clusters reduce moisture sensitivity. The development of 0D chiral perovskites has progressed from early structural prototypes in the 2000s. First attempts at introducing chiral cations into isolated [MX₆] octahedra or [MX₄] tetrahedra produced 0D chiral OIMHs. These systems were structurally stable but initially received limited attention since their optical activity was weaker than 2D/1D counterparts. The focus was mainly on structural chirality rather than photophysical applications. Researchers demonstrated that chirality transfer can persist even in 0D systems, where inorganic clusters (e.g., [PbBr₆]^{4−} or [CuCl₄]^{2−}) are completely isolated. Key studies showed strong CD due to the rigid environment provided by bulky chiral cations.

With novel design strategies (e.g., chiral ammonium salts, aromatic chiral cations, and hydrogen-bonded supramolecular assemblies) introduced, robust CPL emission with g_{lum} reaching values is achieved comparable to those of 2D systems. Through the self-assembly of chiral R/S-(3-chloro-2-hydroxypropyl)trimethylammonium chloride with antimony(III) chloride, Xuan et al. synthesized 0D OIMHs (R)-C₆H₁₅C₁₂NO·SbCl₅ and (S)-C₆H₁₅C₁₂NO·SbCl₅ with CPL activity. These materials feature a 0D structure where SbCl₅ pyramidal units are isolated by chiral organic cations. Optical characterization revealed they have exceptionally high PLQY of 71.2%, originating from STEs emission. The presence of chiral organic cations endows this material with mirror-symmetric CD signals in the ground state and pronounced CPL activity in the excited state, exhibiting g_{lum} of 2.5×10^{-4} (R-form) and -1.6×10^{-4} (S-form), respectively. This work represents the first report of 0D chiral OIMHs material demonstrating CPL activity, thereby providing a novel design strategy for developing environmentally friendly CPL materials with high emission

efficiency [49]. Moreover, Liu et al. found that chiral 0D OIMHs exhibit near-unity PLQY and large g_{lum} values up to around 1×10^{-2} . Du et al. found that partial substitution of $InCl_3$ with $SbCl_3$ in $DMA_4In_{1-x}Sb_xCl_7$ (DMA=dimethylammonium) can result in strong CPL signals ($g_{lum} \sim 1.4 \times 10^{-2}$) and a high PLQY of 69.13% [50].

It is found that the choice of different chiral ligands can modify the strength of hydrogen bonding interactions in these 0D OIMHs, to maximize their g_{lum} values.

Reports highlighted large Stokes shifts, reduced reabsorption losses, and minimized non-radiative recombination, making 0D chiral OIMHs efficient CPL emitters. Combined with their solution processability, diverse chemical architectures, and distinctive optoelectronic properties, chiral 0D OIMHs show great promise in developing efficient CPL-active materials. In addition, researchers also uncovered multifunctionality: some 0D chiral OIMHs exhibited ferroelectric, nonlinear optical, or CISS-related behaviors, broadening their potential in spin-optoelectronics.

4. Synthetics Strategies for Chiral OIMHs

Considering the advanced applications of optoelectronic-active chiral materials, the construction of chiral OIMHs is of critical importance for structure analysis to meet the different demands. At present, a variety of synthetic strategies have been exploited to synthesize chiral OIMHs (Figure 3). The synthesis methods of chiral OIMHs can be primarily categorized into two approaches: in situ synthesis and ex situ synthesis methods, according to the strategies employing distinct chemical pathways to introduce and modulate chirality within the metal halide lattice.

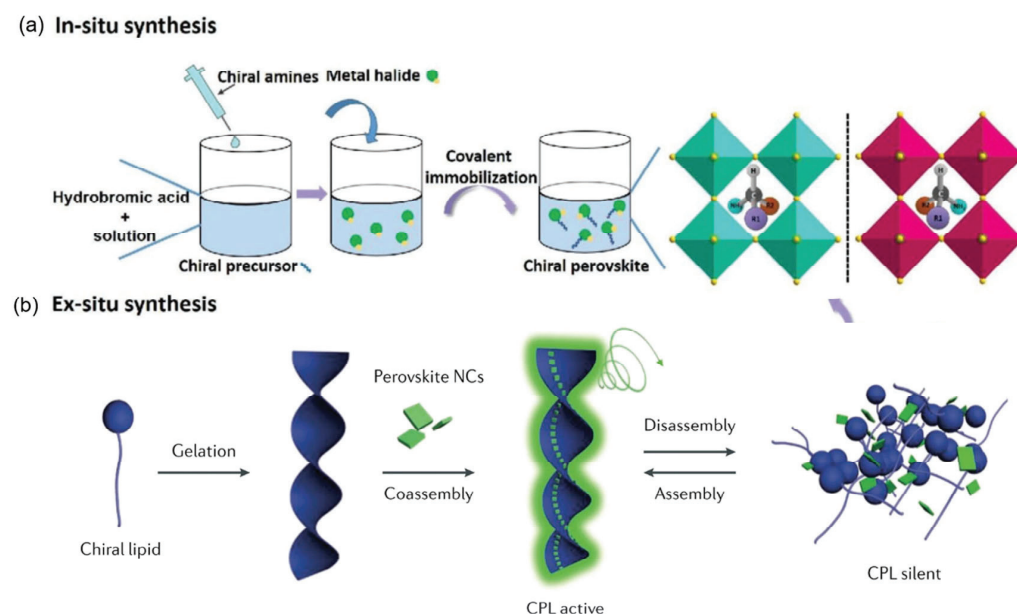


Figure 3. Schematic illustration of synthesizing chiral OIMHs via (a) in situ synthesis at room temperature [51]. (b) Illustration of the possible co-assembly induced chirality of perovskite NCs in chiral gels via ex situ synthesis strategy. Reprinted with permission from Ref. [51]. Copyright 2019, Wiley.

4.1. In Situ Synthesis

In situ synthesis is a well-established route to chiral OIMHs, as illustrated in Figure 3a. In the presence of precursor salts and chiral amine monomers, long-chain chiral ammonium cations stabilize the lattice and enhance chiroptical responses—CD and CPL. This method enables the direct growth of chiral OIMHs with tunable sizes, varied dimensionalities, helical morphologies, and tailored chiral organic components [13,14,52,53]. It reliably affords phase-pure, highly oriented films, facilitating systematic studies of chirality transfer, and

has been scaled to thin films and nanocrystals, making it directly compatible with device integration. In addition, in situ self-assembly with chiral templates, gels, or supramolecular frameworks allows fine tuning of both chirality strength and emission properties.

Common protocols include temperature-lowering crystallization, solvent-evaporation crystallization, antisolvent vapor-assisted crystallization (AVC), and aqueous syntheses, which improve film uniformity and strengthen chiral induction. For example, Dong et al. used AVC in which CHCl_3 gradually diffused into a DMF/DMSO ternary solvent, yielding a chiral HOMH of composition $(\text{MPEA})_{1.5}\text{PbBr}_{3.5}(\text{DMSO})_{0.5}$; the coordinating DMSO partially binds Pb^{2+} within edge-shared octahedra, producing a distorted, edge-shared layered architecture [54]. Chen's group employed a chiral-template inducer, (R/S)-2-amino-1-propanol, in a PbCl_2 /DMF system under acidic conditions to obtain chiral R/S-[DMA] PbCl_3 featuring helical $[\text{Pb}_2\text{Cl}_9]^{5-}$ chains. The products' optical rotation matched the template's handedness and exhibited strong CD and circularly polarized absorption. Devices based on these chiral OIMHs showed excellent CPL detection, with a photocurrent anisotropy factor up to 0.296, demonstrating a general, controllable in situ strategy for chiral OIMHs [28,38].

4.2. Ex Situ Synthesis

Ex situ approaches impart chirality after OIMHs are formed by directly modifying pre-synthesized materials with chiral organic ligands or intermediates, so that synergistic ligand–HOMH interactions generate chiral responses [55]. Chiral ligands are crucial not only for preparation and colloidal stabilization of inorganic nanocrystals in solution, but also for assembling them into ordered structures/superlattices; the transferred interfacial asymmetry induces CD and CPL. A key advantage is that ex situ modification preserves the intrinsic stability of the host perovskite while introducing chirality. Limitations arise because chirality is often surface-localized, which can lead to weaker chiroptical signals and reduced robustness under thermal or solvent stress. To address this, researchers co-assemble perovskite nanocrystals with chiral organic frameworks such as lipid-based gelators, helical polymers, or supramolecular scaffolds. For instance, Shi's group achieved CPL from CsPbX_3 nanocrystals embedded in chiral lipid gels, with tunable dissymmetry factors ($g_{\text{lum}} \approx 10^{-3}$).

Recently, ex situ strategies have expanded to post-synthetic ion exchange, layer-by-layer assembly, and chiral doping of perovskite films. Shilpa et al. used poly(lauryl methacrylate) (PLMA) as a matrix to encapsulate CsPbBr_3 nanocrystals and fabricate CsPbBr_3 –PLMA films, enabling efficient chirality transfer from ligands to OIMHs [56]. Likewise, electrospun PVA nanofibers loaded with MAPbX_3 nanocrystals produced long-axis alignment of HOMH nanocrystals along the fiber direction [57].

A widely used starting point is surface-ligand exchange on pre-synthesized CsPbX_3 nanocrystals with chiral amines, lipids, or helicenenes. For example, Shi et al. first passivated surfaces with OA/OAm to mitigate interference from highly polar chiral molecules (e.g., diamines), then introduced chiral ligands to achieve co-assembly in which configurational transfer of chiral groups induces lattice distortion and ultimately macroscopic chiral architectures (Figure 3b) [37]. In post-synthetic chiral ligand exchange, native ligands are partially or fully replaced by chiral ones, and the resulting chirality arises from surface chiral distortion, chiral packing of capping layers, and chiral field effects rather than bulk-phase reconstruction. Following this principle, He et al. replaced OAm with (1R,2R)- or (1S,2S)-diaminocyclohexane (R/S-DACH) to prepare chiral OAm-capped CsPb(I/Br)_3 nanocrystals, showing that chiroptical properties scale with capping-ligand loading and yielding well-defined chiral OIMHs [32]. In parallel, mechanical rubbing during solvent

evaporation offers a simple route to well-oriented CsPbBr₃ nanowires, increasing the degree of polarization from 0.148 to 0.5 [58–60].

Overall, ex situ modification has delivered significant gains in CPL dissymmetry (often up to $\sim 10^{-2}$) and ambient stability. Demonstrations in thin films, nanocrystal arrays, and heterostructures make this approach directly relevant to polarized emitters, detectors, and spintronic devices. Unlike in situ growth, ex situ methods flexibly integrate reversible, tunable, multifunctional chirality into pre-formed OIMHs; the remaining challenge is achieving deep, beyond-surface chirality transfer. Together with in situ routes, these strategies are paving the way toward scalable, device-compatible chiral OIMHs.

5. Properties of Chiral OIMHs

5.1. CD

CD refers to the differential absorption of left- and right-circularly polarized light by a chiral medium, is a widely used spectroscopic tool to measure the chiroptical responses (Figure 4). To date, the CD properties of chiral OIMHs have been widely reported in various forms, including solutions, thin films, powders, and single crystals. Recent studies reveal that OIMHs materials, owing to their distinctive inorganic framework structures, can efficiently couple with various chiral components to form chiral crystals exhibiting pronounced CD signals. Zhang's group proposed a ligand-exchange strategy: by modifying CsPbBr₃ nanocrystals with chiral ligands, they obtained chiral perovskite nanocrystals with tunable CD signals and a PLQY approaching 100% [61]. Ahn's group successfully synthesized chiral OIMHs single crystals (S-MBA)₂PbI₄ and (R-MBA)₂PbI₄ by incorporating S-/R-MBA molecules into layered lead iodide frameworks [58]. As shown in Figure 4a, their CD spectra demonstrate optical activity in the 350–800 nm wavelength range, primarily originating from the chirality transfer effect of organic cations. CD spectra can be employed as a powerful tool in material design techniques and growth monitoring for chiral OIMHs architectures.

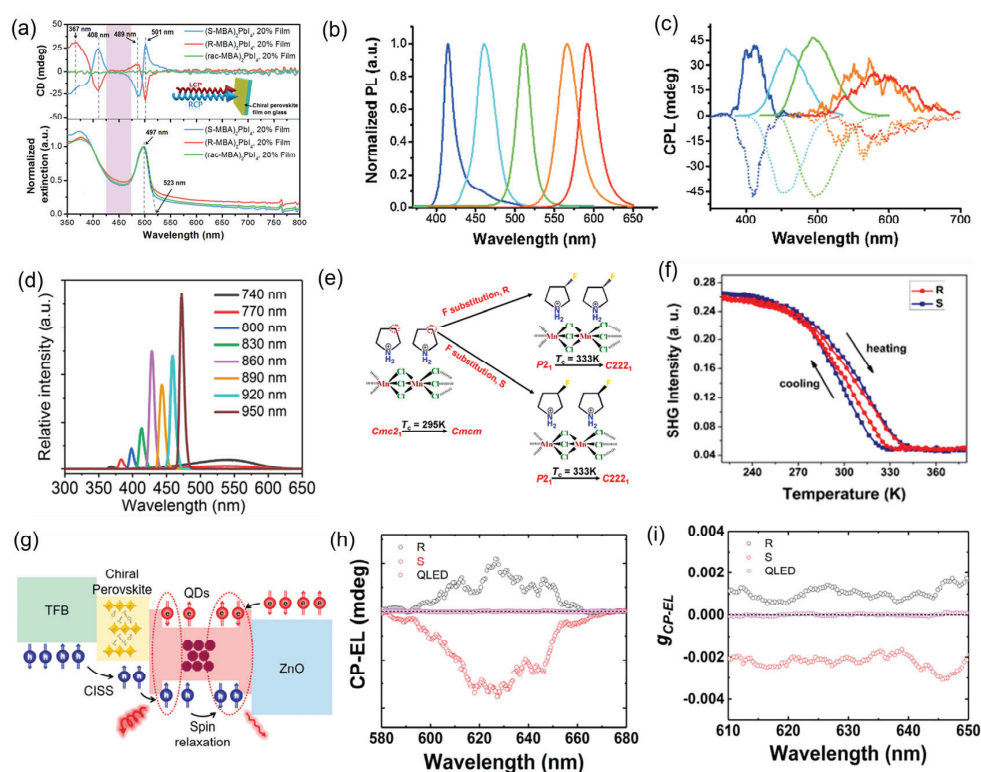


Figure 4. (a) Transmission CD spectra (up), and normalized extinction spectra of (S-MBA)₂PbI₄, (R-MBA)₂PbI₄, and (rac-MBA)₂PbI₄ films. (b) Fluorescence spectra of CsPbX₃ NCs doped DGAm. and

corresponding (c) mirror-image CPL spectra. (d) NLO spectra of a (R-MPEA)_{1.5}PbBr_{3.5}(DMSO)_{0.5} nanowire pumped at various wavelengths. (e) Design of Molecular Ferroelectrics through H/F Substitution. (f) Temperature-dependent second harmonic generation (SHG) response [28]. The schematic illustration of CP-EL emission in the spin-QLED (g), CP-EL degrees as a function of wavelength and related g_{CP-EL} , (h,i) for the devices prepared with 0.05 m of chiral precursors [62]. Reprinted with permission from Ref. [28]. Copyright 2019, American Chemical Society. Reprinted with permission from Ref. [62]. Copyright 2023, Wiley.

5.2. CPL

CPL spectroscopy explicitly measures the differential spontaneous emission of left and right circularly polarized radiations by a luminescent system and thereby served as another key technique to act as chiral probes. At present, CPL studies based on halide OIMHs are mostly focused on films and powders. Liu et al. employed amine-containing lipid N,N'-dioctadecyl-d-glutamic diamide (DGAm) as building blocks to construct chiral spaces through molecular co-assembly. This co-gel system not only achieved high PLQY but also realized CPL (Figure 4b,c). The prepared CPL-active CsPbX₃ nanocrystals exhibited broad-spectrum emission spanning blue to red wavelengths. The co-assembly CsPbX₃ with lipid molecules successfully induced chiral characteristics while achieving CPL signals with g_{lum} up to 10^{-3} [37].

Compared with films and powders, the CPL signals of chiral OIMHs single crystals have been rarely reported, mainly due to the presence of linear polarized luminescence effects and crystal defects in single-crystal structures. Therefore, preparing single-crystal chiral OIMHs with high CPL activity remains a major challenge. In addition, the CPL activity of chiral OIMHs solutions has also been reported; however, the complicated preparation steps and the large number of organic solvents required have severely limited the development and application of these materials.

5.3. Nonlinear Optical Properties

Nonlinear optics investigates the nonlinear response of media under photoexcitation conditions with optical power as the variable. Chiral OIMHs, with their tunable chemical structures and electronic bandgaps, represent highly promising nonlinear optical materials for advanced techniques [63–66]. Due to their excellent nonlinear optical coefficients, current research primarily focuses on the third-order and higher-order nonlinear optical properties of these materials. However, for applications in optical information transmission, processing, and storage, the second-order nonlinear response characteristics of optical components are equally crucial. The inherent non-centrosymmetric nature of chiral molecules can induce non-zero electric dipole moments, thereby endowing chiral OIMHs with significant second-order nonlinear responses [67].

Taking the typical chiral (*R*-or *S*-MPEA)_{1.5}PbBr_{3.5}(DMSO)_{0.5} as an example (Figure 4d), its structure consists of non-centrosymmetric chirality, DMSO intercalation, and partial edge-sharing [54]. This chiral HOMH exhibits outstanding second-order nonlinear performance. Theoretical studies suggest that due to the magnetic effects arising from molecular structural asymmetry, chiral media can alter the polarization state of incident light [68,69]. Moreover, taking advantage of fluorine substitution on the reported molecular ferroelectric, (pyrrolidinium)MnCl₃, Yong et al. present enantiomeric perovskite ferroelectrics, namely, (*R*) and (*S*)-3-(fluoropyrrolidinium)MnCl₃ [28]. The temperature-dependent second harmonic generation (SHG) signal is sensitive to the inversion symmetry breaking and the generation of ferroelectric polarization (Figure 4e,f). Thus, by modulating the chiral configuration, the magnetic dipole moment can be optimized, thereby enhancing second-order nonlinear effects. Consequently, through further optimization of chiral synthesis and structural control, chiral OIMHs hold broad application prospects in the field of nonlinear optics.

5.4. Bulk Photovoltaic Effect (BPVE) in Chiral OIMHs

BPVE refers to the property of generating a steady-state photocurrent in a material even in the absence of an external bias voltage. The introduction of chirality can break spatial inversion symmetry, leading to the formation of asymmetry. The Miyasaka research group confirmed the BPVE in chiral perovskites by measuring the current–voltage (*I*–*V*) dependence of layered perovskite *R/S*-(MPA)₂(MA)Pb₂I₇ single crystals. The results showed that, at zero bias, the sign of the photocurrent depends on the polarization direction (*P_m*) within the material. This indicates that the BPVE originates from the alignment of dipole moments induced by the chiral components. Therefore, by regulating polarity and chirality, perovskites offer new breakthroughs for BPVE materials.

5.5. Ferroelectric Properties

Ferroelectric materials have attracted significant attention due to their reversible spontaneous polarization controllable by external electric fields, which enables coupling with various electronic/optical properties [70]. Recently, chiral OIMHs have gained prominence for their unique ferroelectric characteristics [71–73]. The breaking of spatial inversion symmetry serves as a critical prerequisite for ferroelectric effects [74]. According to the Neumann-Curie principle, when chiral OIMHs crystallize in special point groups (*C*₁, *C*₂, *C*₃, *C*₄, *C*₆), they can exhibit intrinsic ferroelectric properties [75,76]. Current research on ferroelectric behavior in chiral OIMHs spans diverse structural types, including 3D chiral OIMHs, 2D lead-based chiral metal halides, and 1D manganese-based chiral metal halides [26,27]. For instance, in the fluorine-modified (pyrrolidinium) MnCl₃ system, the derived chiral materials *R(S)*-3-FP-MnCl₃ (3-FP structure demonstrate a remarkably high Curie temperature of 333 K, which is a significant improvement over the parent compound

pyrrolidinium manganese trichloride (295 K) [28,77]. This enhancement demonstrates that judicious selection of chiral organic cations can induce low-symmetry polar space groups, facilitating molecular rearrangement and establishing ferroelectric orientation ordering. The incorporation of chiral ligands not only provides tunability in composition and structure for metal halide systems but also opens new possibilities for developing novel ferroelectric functional materials in quantum communication and optical engineering applications.

5.6. Spintronics

Spintronics, combining the properties of spins with electronics, offers the opportunities for functionalizing conventional electronic devices by manipulating the degree of freedom of the electron's spin. Chiral OIMHs demonstrate unique advantages for spintronic device applications due to their pronounced tunable spin-orbit coupling and extended spin lifetimes. Chirality-induced spin selectivity (CISS) refers to the ability of chiral materials to preferentially transport spin-polarized carriers without the need for an external magnetic field. This CISS effect effectively suppresses spin-flip elastic backscattering processes [78,79]. Studies indicate that electrons moving in a chiral electrostatic field generate an effective magnetic field along the propagation direction, which stabilizes electronic states with specific spin orientations. Moreover, chiral symmetry couples electron spin with linear momentum, enabling selective transmission of spin-polarized electrons and thereby achieving spin-dependent charge transport [80].

Beard and co-workers reported a 2D (R/S-MBA)₂SnI₄, with strong octahedral distortion. Their study demonstrated that the vertical charge transport in (R/S-MBA)₂SnI₄ films exhibits pronounced spin dependence, representing a concrete manifestation of the CISS effect in chiral OIMHs. Furthermore, they showed that the spin polarization in the current-voltage characteristics reached as high as 94%. This work highlights the tremendous potential of chiral hybrid semiconductors in controlling both spin and charge degrees of freedom.

Wang et al. have demonstrated a pronounced CISS effect in low-dimensional chiral OIMHs prepared by introducing chiral amine ligands. In this study, 2D chiral OIMHs were employed as the CISS spin injection layer, combined with a CdSe/ZnS quantum dot emitting layer, to successfully fabricate a novel spin light-emitting diode device [62]. The research further revealed that the optical rotation properties and thickness modulation of the chiral OIMHs significantly influence the device's circularly polarized electroluminescence performance. Notably, the spin injection polarization efficiency of this 2D chiral OIMHs exceeds 80%, with the highest achieved dissymmetry factor reaching 1.6×10^{-2} . This work establishes a groundbreaking approach for developing high-performance spin-LEDs. Chiral OIMHs offer a feasible way to optimize and control the electronic responses, providing much possibility for various electronic applications.

6. Optoelectronic Applications of Chiral OIMHs

In recent years, chiral OIMHs have garnered extensive interdisciplinary research interest in chemistry, physics, biology, and medicine, demonstrating promising optoelectronic applications in bio-monitoring, sensing, imaging, chiral photonics, and electronics. This section focuses on the advances in applications of chiral OIMHs, systematically discussing their unique properties and potential in various cutting-edge fields.

6.1. Circularly Polarized Spin Light-Emitting Diodes (Spin-LEDs)

In traditional optoelectronic approaches, control over spin, charge, and light requires the use of both electrical and magnetic fields. In a spin-LED, charges are injected, and

circularly polarized light is emitted from spin-polarized carrier pairs. Circularly polarized spin-LED were first reported by Meijer et al. [81]. Inspired by their structure, researchers introduced chiral OIMHs into the system, developing spin-LEDs capable of electrically driven circularly polarized emission [82]. Under an electric field, electrons and holes are injected and transported into the chiral hybrid metal halide layer, where they form excitons or electron-hole pairs via Coulomb interactions. The energy of these excitons is subsequently transferred to the chiral OIMHs. Finally, the excitons in the excited state of the chiral emitter undergo radiative recombination back to the ground state. If the chiral component of the luminescent material exhibits selective asymmetry, circularly polarized emission is generated. Developing novel spin-LEDs that simultaneously achieve high device efficiency and strong CP-EL effects is significant. The breakthrough in this research direction, enabled by chiral emitters with superior device performance and pronounced CP-EL, will open new opportunities for advancing circularly polarized optoelectronic devices in quantum-based optical computing and information processing, three-dimensional (3D) displays, bioencoding, and tomography.

The performance of spin-LEDs is typically evaluated based on two key aspects: device performance and circularly polarized electroluminescence (CP-EL) characteristics. For device performance, the evaluation criteria resemble those of conventional LEDs. In terms of optical properties, the chiroptical performance of spin-LEDs is primarily characterized by the dissymmetry factor. Young et al. demonstrated spin-LEDs based on solution-processed HOMH heterostructures in which spin-polarized holes were injected into an adjacent layer of OIMHs emitters (Figure 5a). The formation of a well-defined CISS/CsPbI₃ heterostructure was confirmed by time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiling (Figure 5b). The spin polarized hole injection layer is composed of a 30 to 60 nm thick chiral 2D layered R-/S methylbenzylammonium lead iodide [(R-/S-MBA)₂PbI₄] polycrystalline bulk film. The spin-LEDs showed a turn-on voltage of 2.4 V and external quantum efficiencies (EQEs) 10.05%, 10.53%, and 11.05% for spin-LEDs based on (R-MBA)₂PbI₄, (S-MBA)₂PbI₄, and (rac-MBA)₂PbI₄ (Figure 5c), respectively. Spin-LEDs based on CISS/CsPbI₃ NC heterostructure showed distinct CP-EL spectra centered at 688 nm with average PCP-EL = $\pm 0.25\%$ at $660 \leq \lambda \leq 740$ nm (Figure 5f,g) and showed similar PCP-EL values with different CISS layer thicknesses (~30 and ~60 nm). By contrast, the (rac-MBA)₂PbI₄-based devices exhibited no CP-EL emission. The similar P_{spin} values suggested that spin-polarized injection from the CISS layer into the NC layer was high and that the spin-diffusion length in the NC layer was at least one to two NCs (Figure 5d,e). In addition, they found that the prepared spin-LEDs control the orientation and intensity of CP-EL, depending on the spin polarization of the injected carriers, and the spin-LED achieves $\pm 2.6\%$ circularly polarized electroluminescence at room temperature without applying a magnetic field or using a ferromagnetic contact with a spin-polarized current of >80% (Figure 5f,g). Ye et al. fabricated a multilayer spin-LED using core-shell structure luminescent layer comprising a 3D MAPbBr₃ core surrounded by a 2D perovskite layer with R/S-MBA, allowing spin-selective carrier injection via the shell while maintaining the optical and structural integrity of the luminescent core. The spin-LED exhibited a PLQY of 54% and a g_{lum} of 4.0×10^{-3} , increasing to 6×10^{-3} under electroluminescent operation [83]. After, Jooho Moon used R/S-NEA to substitute the R/S-MBA, achieving an enhanced PLQY of 78% and a high CP-EL efficiency of 12%.

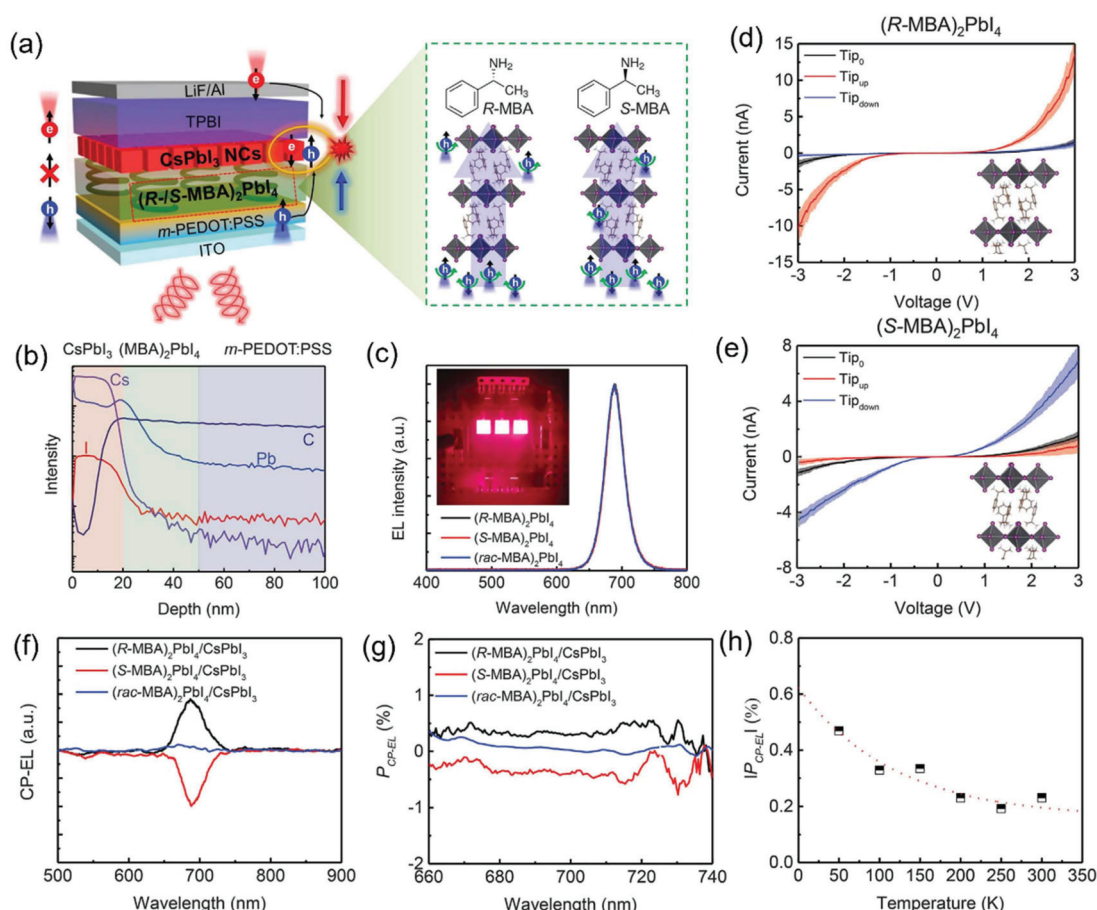


Figure 5. (a) Schematic illustration of spin-polarized charge injection and CP-EL emission in spin-LEDs. (b) TOF-SIMS depth profile of m-PEDOT:PSS/CISS layer/CsPbI₃ NC heterostructure. (c) EL spectrum

and operating device image (inset) of spin-LEDs based on CISS layer/CsPbI₃ NC heterostructure. (d,e) Current voltage curves of ITO/m-PEDOT:PSS/(R-MBA)₂PbI₄/CsPbI₃ NC films (d) and ITO/m-PEDOT:PSS/(S-MBA)₂PbI₄/CsPbI₃ NC films (e) and crystal structures of (R-/S-MBA)₂PbI₄ (insets). (f,g) The CP-EL spectra (f) and the EL polarization degree, PCP-EL (g) of spin-LEDs based on CISS layer/CsPbI₃ NCs. (h) Temperature-dependent absolute average values of |P_{CP-EL}| in spin-LEDs based on (S-MBA)₂PbI₄/CsPbI₃ NCs.

6.2. Circularly Polarized Light Detector

Conventional optical detectors require complex optical components, which severely limit device miniaturization and flexibility. Current optical-element-free detectors primarily employ chiral organic semiconductors or metallic metamaterials, yet these materials suffer from low responsivity. Chiral OIMHs, combining the circular dichroism effect of chiral ligands with the efficient charge transport properties of inorganic frameworks, offer a novel strategy for direct circularly polarized light detection. Tang et al. developed a groundbreaking circularly polarized photodetector based on chiral OIMHs (Figure 6a–c), achieving remarkable performance metrics: a responsivity of 797 mA W^{−1}, detectivity of 7.1 × 10¹¹ Jones, and environmental stability exceeding one month [46]. It has been reported that the average g_{current} of the chiral circularly polarized photodetector based on chiral (R)-3BrMBA₂PbI₄ is ~0.5% under 490 nm excitations, which is slightly larger than expected from the CD results, likely because of additional effects from spin-related carrier generation and transport [43]. These comprehensive parameters demonstrate significant competitive advantages of Chiral OIMHs in circularly polarized light detection.

6.3. Circularly Polarized Scintillator Imaging

Traditional X-ray detectors typically adopt a coupled scintillator array-photosensor design. However, the isotropic propagation of radioluminescence (RL) signals from scintillators induces optical crosstalk between adjacent pixels, substantially degrading spatial resolution and imaging quality [84–86]. Scintillator materials exhibit centrosymmetric structures, where isotropic light emission is an intrinsic property of achiral systems, making physical modulation of RL behavior fundamentally challenging. Chiral OIMHs can be encoded into a polarized scintillator pair with the capacity to regulate RL propagation, providing a new opportunity to improve X-ray imaging quality, especially at the boundary region between adjacent scintillators.

Wang et al. pioneered chiral OIMHs scintillators (*R*-3AP)PbBr₃Cl·H₂O (*R*-3APP) and (*S*-3AP)PbBr₃Cl·H₂O (*S*-3APP), establishing the first material system with circularly polarized RL (Figure 6) [87]. These scintillators demonstrate exceptional performance, including a PLQY of 27.6%, dissymmetry factor of 4×10^{-2} , and outstanding X-ray absorption coefficients. They further explored their polarized RL properties as exhibited in Figure 6d. The RL intensity of *S*-3APP and *R*-3APP displays a significant polarization dependence (Figure 6e), but the RL intensity (Figure 6f) of CsI:Tl, LYSO, Cs₂Na_{0.5}Ag_{0.5}InCl₆ bulk crystals and Cs₄PbBr₆ in polycrystalline crystals remains constant regardless of the rotation angle, consistent with isotropic propagation. The chiral *R*-3APP and *S*-3APP scintillators enable propagation control of RL through circular polarization selection, significantly enhancing signal contrast resolution (Figure 6g). X-ray imaging experiments confirm superior image quality compared to conventional scintillators, as displayed in Figure 6h. This work proposes an innovative paradigm for addressing persistent optical crosstalk that by precisely engineering the RL propagation direction, interference between adjacent pixels can be fundamentally suppressed. Therefore, the chiral scintillator concept opens new avenues for high-resolution radiation imaging technologies.

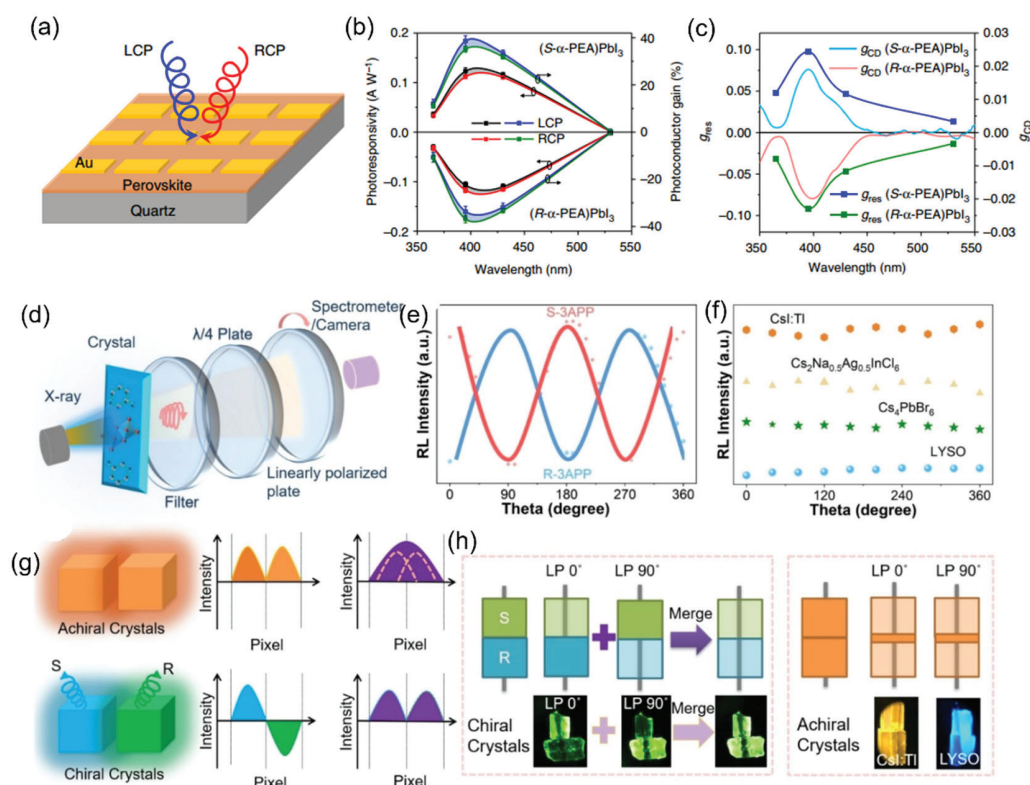


Figure 6. (a) Schematic diagram of circularly polarized photodetector. (b) The responsivity and photoconductor gain of (R- and S- α -PEA)PbI₃ device under LCP and RCP light at the wavelengths of 365, 395, 430, and 530 nm. (c) The wavelength dependent g_{res} spectra [46]. (d) Schematic illustration of a homemade polarized light collecting system under X-ray excitation. (e) The polarization-dependent RL of chiral S-3APP and R-3APP under X-ray excitation. (f) The RL of LYSO, Cs₂Na_{0.5}Ag_{0.5}InCl₆, Cs₄PbBr₆, and CsI:Tl under X-ray excitation. (g) Illustration of the minimization of optical crosstalk by polarized RL. (h) The X-ray imaging using chiral S-3APP and R-3APP achieve a high definition of image boundary quality [87]. Reprinted with permission from Ref. [46]. Copyright 2019, Springer Nature. Reprinted with permission from Ref. [87]. Copyright 2022, Wiley.

7. Conclusions

Chiral OIMHs have emerged as a novel class of functional materials, offering unprecedented opportunities for next-generation photonics and the development of advanced materials due to their unique organic-inorganic hybrid structure, intrinsic chirality, and outstanding optoelectronic properties. When it comes to practical uses, both high PLQYs and large g_{lum} values are crucial for the practical applications of CPL-active materials. Despite their remarkable advantages such as of high PLQYs over 80% or 90% in certain chiral OIMHs, several critical challenges remain to be addressed. Despite these advancements, challenges remain in the synthesis and stability of chiral OIMHs. Issues such as moisture sensitivity and scalability of fabrication processes need to be addressed to facilitate the practical application of these materials. Future research directions include the development of novel synthetic strategies, exploration of non-toxic and lead-free chiral perovskites, and integration of chiral OIMHs into functional devices for real-world applications.

Current studies predominantly rely on a narrow selection of chiral organic amines (e.g., 3-methylpiperidine, 3-hydroxypiperidine) as structure-directing agents, restricting versatility of chiral OIMHs. Thus, the development of novel chiral organic cations is urgently needed.

Improvements in g -factor and PLQY have been reported via molecular spacer design, nanoconfinement, host-guest doping, and compositional tuning. A fundamental compro-

mise exists between high g_{lum} factor and PLQY. For instance, 0D indium-based materials achieve PLQY up to 83.44% but exhibit weak g_{lum} ($\sim 10^{-3}$), whereas 3D counterparts show enhanced g_{lum} ($\sim 10^{-1}$) at the expense of reduced PLQY. simultaneously achieving large room-temperature g -factors and high PLQY remain a major challenge.

Additionally, most reported chiral OIMHs suffer from instability, and lead-based variants pose toxicity risks, significantly impeding commercial viability. It has been found that humidity has been found to disrupt the structural integrity and chiroptical activity of chiral 2D OIMHs, highlighting the need for robust materials that can maintain their chiral properties under varying environmental conditions. The development of chiral HMOHs with long-term environmental stability under moisture, heat and light is still urgently needed to avoid obstacles to practical applications.

Enhancing chiral purity in chiral OIMHs is a critical step toward achieving strong CPL signals and developing advanced chiroptical devices. Precise control over chiral structure, crystal orientation, and optoelectronic properties requires deeper mechanistic studies on chirality-property relationships. Through innovative synthesis methods and a deeper understanding of structure–property relationships, significant progress is being made in this field, paving the way for the next generation of chiral functional materials. Further advancements in material processing, device architecture, and performance optimization are essential for practical applications.

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Review

Synthesis, Photophysical Mechanisms, and Applications of Luminescent Organic–Inorganic Hybrid Metal Halides

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Abstract

Organic–inorganic hybrid metal halides (OIMHs) have attracted widespread attention due to their unique chemical properties, excellent electronic performance, and low-cost fabrication processes. These hybrid materials impose fewer size constraints on the organic components, providing an exciting platform for the molecular-level design of new materials and functionalities. In this review, we discuss the latest progress in OIMHs. Specifically, we summarize recent advances in their structures, synthetic strategies, and luminescence mechanisms, and highlight their applications in light-emitting diodes (LEDs), information encryption and anti-counterfeiting, sensors, and X-ray imaging. Finally, we discuss the challenges related to structural design, mechanistic understanding, and stability, along with perspectives on future opportunities for OIMHs.

Keywords: hybrid metal halides; preparation; optoelectronic properties; luminescent mechanism; electronic applications

1. Introduction

In recent years, organic–inorganic hybrid metal halides (OIMHs) have received extensive attention owing to their unique crystal structures and remarkable optoelectronic properties [1,2]. These materials can combine structural tunability, facile preparation, and cost advantages with a precisely adjustable optical bandgap, strong defect tolerance, and outstanding photophysical performance. As next-generation functional materials, OIMHs exhibit particularly excellent luminescence properties, including a high color rendering index (CRI), broadband tunable emission, wide color gamut coverage, and high photoluminescence quantum yields (PLQYs) [3]. Together, these advantages make OIMHs promising alternatives to conventional phosphors, with potential applications in LED lighting, X-ray imaging, and luminescent probes and sensors [4,5].

The dimensionality of OIMHs is defined by the arrangement and connectivity of inorganic polyhedra within the crystal lattice. Depending on the connectivity of metal–halide octahedra, OIMHs can adopt different dimensional structures. When the organic cations are relatively small, the inorganic octahedra extend continuously via metal–halide coordination bonds to form three-dimensional (3D) networks. In contrast, introducing bulky organic cations disrupts the octahedral network, reducing the structural dimensionality and yielding two-dimensional (2D) layered, one-dimensional (1D) chain-like, or zero-dimensional (0D) cluster-like OIMHs, collectively referred to as OIMHs (Figure 1a) [6]. Low-dimensional OIMHs exhibit higher exciton binding energies and therefore superior

emissive properties and radiative recombination characteristics [7–11]. At the same time, low-dimensional OIMHs offer enhanced stability and reduced toxicity, making them attractive replacements for 3D Pb-based OIMHs; they display excellent optical performance and have achieved notable progress across optoelectronic applications. Consequently, the rational design and synthesis of functional OIMHs are of substantial research significance for enabling diverse practical uses [12–15]. Nevertheless, challenges persist in the structural design and mechanistic understanding of low-dimensional OIMHs. Issues such as limited stability and luminescence efficiency loss remain to be addressed. Against this backdrop of opportunities and challenges, a systematic review is essential for advancing the understanding and future development of OIMHs.

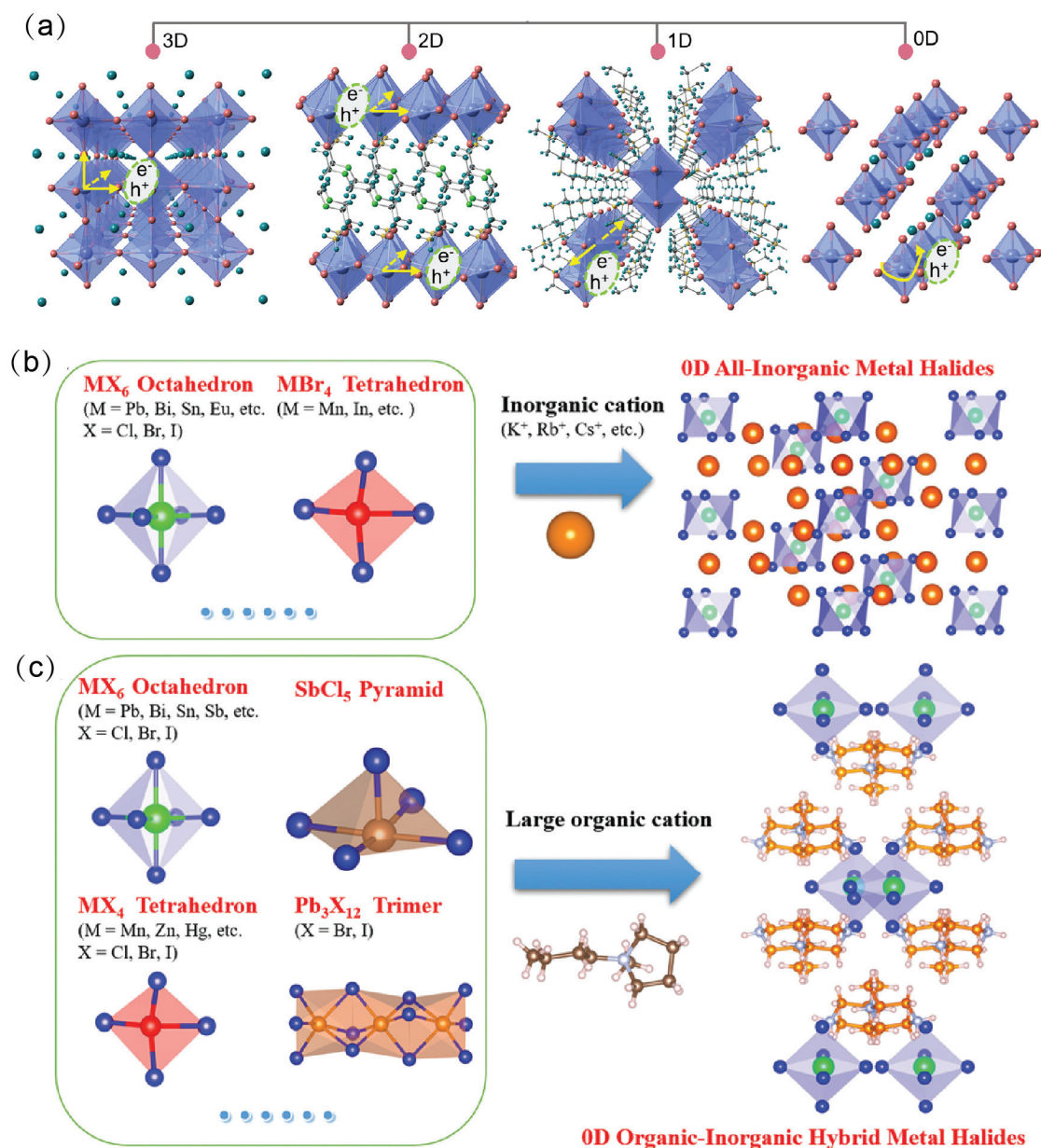


Figure 1. (a) Typical structures of OIMHs [6]. Reprinted with permission from Ref. [6]. Copyright 2024, Wiley; (b,c) 0D OIMHs with different interlayer cations [2,16]. Reprinted with permission from Ref. [2]. Copyright 2020, Wiley. Reprinted with permission from Ref. [16]. Copyright 2021, Royal Society of Chemistry.

In this article, we have summarized recent advances in OIMHs, including their structures, synthetic methods, optical properties, luminescence mechanisms, and appli-

cations. We particularly emphasize the role of structural design in guiding the formation of OIMHs and analyze the relationships between structural composition and photophysical properties. Considering their excellent optical and multifunctional luminescent features, we highlight the potential applications of OIMHs in LEDs, information encryption and anti-counterfeiting, sensors, and X-ray imaging, and provide an outlook on future research directions.

2. Structural Characteristics and Stability of Organic–Inorganic Hybrid Metal Halides

2.1. Structural Characteristics

OIMHs are composed of metal–halide anions and organic cations. In terms of composition, the selection of the metal cation plays a pivotal role in shaping the properties of OIMHs. The chemistry of the ns^2 ion (Pb^{2+} , Bi^{3+} , Sn^{2+} , Sb^{3+} , etc.) is closely related to the electronic properties and dielectric properties of ns^2 cation-based OIMHs. Moreover, the organic unit in OIMHs is typically an ammonium species or a sulfur-/phosphorus-containing cation. The structural diversity of OIMHs is governed primarily by the types of organic cations present and by the spatial packing of the inorganic polyhedral framework units [12–14,17]. During formation, multiple intermolecular forces drive the orderly assembly of the organic and inorganic parts: organic cations attract each other through van der Waals interactions and hydrogen bonding, whereas the inorganic units connect via corner-, edge-, or face-sharing coordination. Strong hydrogen bonding between the organic cations and the inorganic polyhedra further ensures a highly ordered structure, endowing OIMHs with excellent optoelectronic properties [9,10,12,15]. Figure 2 displays some typical organic cations in the reported 2D, 1D, and 0D OIMHs [18].

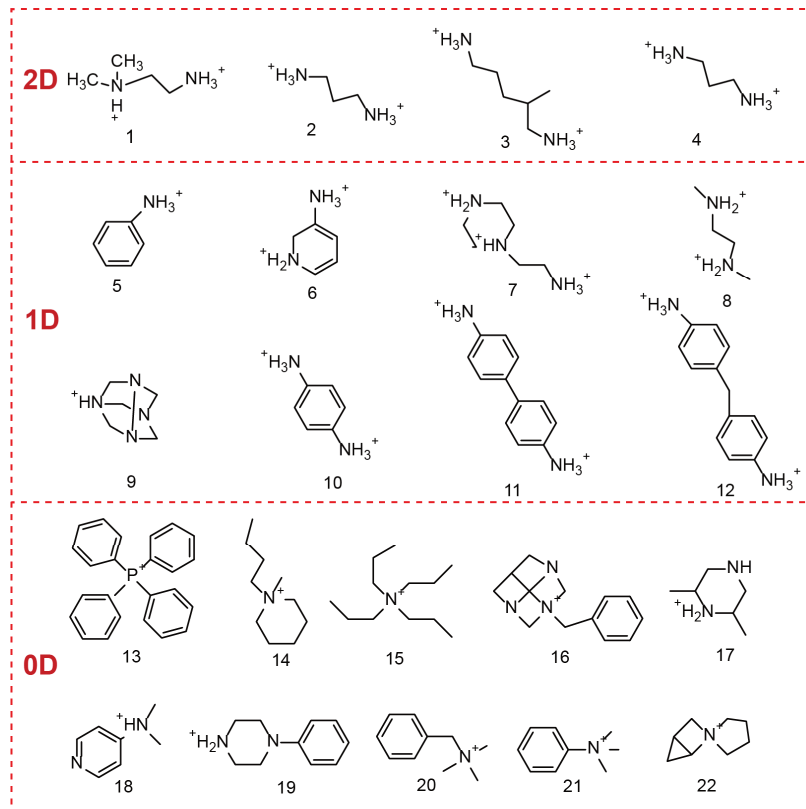


Figure 2. Organic cations used in low-dimensional OIMHs.

From a crystallographic perspective, 3D OIMHs are built from metal–halide octahedra that are corner-linked into a 3D network, with small A-site cations uniformly occupying the interstitial cavities. In the archetypal 3D OIMH structure (ABX_3), A denotes a monovalent cation such as methylammonium MA^+ , formamidinium FA^+ , or Cs^+ ; M denotes a metal cation such as Pb^{2+} , Sn^{2+} , or Ge^{2+} ; and X denotes a halide anion (Cl^- , Br^- , I^-). Owing to their high absorption coefficients, tunable optical bandgaps, low exciton binding energies, and long carrier-diffusion lengths, 3D OIMHs have shown broad application in solar photovoltaics [19]. Because 3D OIMHs generally possess small exciton binding energies (20–50 meV), their radiative recombination efficiencies and PLQYs tend to be low, which limits their performance in light-emitting devices.

Two-dimensional OIMHs comprise layered structures formed by corner-, edge-, or face-sharing polyhedra, with bulky organic cations residing between the layers to yield a characteristic “sandwich” architecture [20]. Two-dimensional OIMHs can be categorized structurally into $\langle 100 \rangle$ -oriented, $\langle 110 \rangle$ -oriented, and $\langle 111 \rangle$ -oriented structures. Linear carbon chain cations are one of the first spacer types. For example, butylammonium cation is the extensively studied spacer, and other spacers such as propylammonium, pentylammonium, and hexylammonium cations have been demonstrated for the multilayer 2D structures [21]. Also, some cyclic monoammonium and aromatic cations have been widely studied. Organic amine cations with distinct intrinsic physical and chemical properties exert three main effects on 2D OIMHs: crystal structure, optical properties, and film properties [22].

Further reducing dimensionality to 1D systems produces chain-like inorganic backbones: metal–halide octahedra extend as single or double chains via point-, edge-, or face-sharing, while large organic cations spatially isolate neighboring chains [23]. In 1D OIMHs, organic cations are usually bulky diammonium or multiammonium species, sometimes cyclic or aromatic (ethylenediammonium derivatives, quinoline, naphthalene derivatives). Diammonium/multiamine spacers are used to enhance interchain hydrogen bonding and lattice robustness.

In 0D OIMHs, sufficiently large organic cations separate individual metal-centered tetrahedra, pentahedra, octahedra, or their clusters, embedding each unit within an insulating organic matrix and producing discrete “host–guest” assemblies (Figure 1b,c) [16,24]. The individual organic cations in 0D OIMHs usually encompass only one positive charge. Moreover, their unsaturated atoms (N/P/S) are surrounded in the center site of organic cations, such as tetraphenylphosphonium (TPP^+) and triphenylsulfonium (Ph_3S^+) cations. The large-size organic cations can fully separate the inorganic anions, leading to highly localized excitons upon excitation. These localized excitons induce strong electron–phonon interactions, resulting in high PLQY. Moreover, the non-networked metal halide polyhedra or clusters in 0D OIMHs offer diverse coordination environments, providing opportunities to tune both structure and luminescence, and thus present significant potential for optoelectronic applications.

2.2. Stability

The stability of 3D, 2D, 1D, and 0D OIMHs is of paramount importance for their applications. While these materials have demonstrated exceptional optoelectronic properties—such as high PLQYs, tunable bandgaps, and strong excitonic effects—their practical application is often limited by sensitivity to environmental stressors, including moisture, oxygen, light, and heat [25]. Usually, different families of OIMHs display markedly different vulnerabilities to moisture, oxygen, light, heat, and charge stress.

Three-dimensional Pb-based OIMHs are highly sensitive to humidity and oxygen. Their dominant degradation routes involve hydration and precursor back-reaction (yielding

PbI₂, CH₃NH₂, HI), which can be accelerated by the synergistic action of illumination, trapped charges, and O₂, promoting I[−] oxidation to I₂/I₃[−], phase transitions, and vacancy growth. Sn-based OIMHs (e.g., FASnI₃) are limited primarily by spontaneous Sn²⁺ → Sn⁴⁺ oxidation, accompanied by vacancy formation and deep defect states, leading to rapid degradation in air; even when short-term operation is feasible, synthesis and film deposition are typically conducted under low-O₂/low-H₂O conditions with antioxidant additives and/or reducing atmospheres [26]. Consequently, practical devices require encapsulation, and stability is typically improved via compositional engineering, defect passivation, and encapsulation strategies.

Two-dimensional OHMHs offer enhanced resistance due to their organic spacer barriers [27]. Two-dimensional/quasi-two-dimensional systems incorporate organic spacer layers that provide hydrophobic barriers and suppress ion migration, conferring substantially better tolerance to moisture and oxygen than their 3D counterparts. One-dimensional and zero-dimensional OHMHs, with their reduced dimensional connectivity, generally show greater robustness but may suffer from limited charge mobility and exciton confinement effects. A systematic understanding of these stability–property trade-offs is crucial, as it directly informs the design of devices ranging from solar cells and light-emitting diodes to scintillators and sensors [28]. 6s² cation-based OHMHs and 0D/1D Cu-based OIMHs are comparatively more robust—particularly against moisture—yet they can still suffer photo- or thermally driven halide migration and surface-defect formation [16].

3. Common Techniques of Organic–Inorganic Hybrid Metal–Halide Crystals

Solution-based methods are widely employed for the synthesis of OIMH crystals owing to their low cost, mild reaction conditions, simple equipment requirements, and short synthesis cycles. They are particularly useful for exploratory studies of growing new OIMH crystals quickly.

3.1. Solution-Cooling Method

The solution-cooling method represents one of the most straightforward and widely employed strategies for growing OIMH crystals. In a typical process, the organic cation and the metal halide precursor are dissolved in a suitable solvent at a prescribed stoichiometric ratio and heated until the components fully react to form a homogeneous solution. As the solution is subsequently cooled, the solubility of OIMHs decreases with temperature, leading to supersaturation and the initiation of crystallization. The rate of cooling plays a decisive role: rapid cooling generally promotes the formation of numerous small crystallites, whereas controlled, slow cooling favors fewer nucleation sites and the growth of larger crystals with higher structural perfection. Consequently, by carefully adjusting the cooling gradient, OIMH crystals with improved crystallinity, reduced defect density, and enhanced optical quality can be obtained [29]. For example, by gradually cooling the reaction solution, the Ma group readily produced large quantities of 1D (C₄N₂H₁₄)SnBr₄ crystals [30].

3.2. Solvent Evaporation Method

The solvent evaporation method is another widely used route for growing OIMH crystals. Typically, the organic cation and metal–halide precursors are fully dissolved in a suitable solvent at a defined stoichiometric ratio; controlled, slow evaporation of the solvent then drives supersaturation and nucleation, followed by crystal growth. Because many OIMHs are moisture-sensitive, aprotic organic solvents are generally employed—most commonly DMF, DMSO, γ -butyrolactone (GBL), N-methyl-2-pyrrolidone (NMP), or acetonitrile—to mitigate hydrolysis and compositional drift. Compared with solution-

cooling, solvent evaporation is often more time-consuming, as mass-transport is governed by the evaporation rate; however, it is experimentally straightforward and can yield high-quality single crystals when the evaporation flux is carefully regulated (via temperature, headspace, humidity, and exposed surface area) to minimize secondary nucleation and defects. Variants such as isothermal slow evaporation and vapor-mediated evaporation further refine nucleation–growth balance and are frequently adopted for OIMHs requiring narrow crystallization windows. For example, using solvent evaporation, Xiong’s group obtained 2D $(C_7NH_{10})_2PbCl_4$ crystals measuring $5 \times 10 \times 2 \text{ mm}^3$ within a few days [31].

3.3. Solvent Diffusion Method

In this method, the reactants are dissolved in two mutually miscible solvents that differ markedly in density and solvent quality. The lower-density solvent is gently layered over the higher-density phase to form a sharp interface; under gravity-assisted, Fickian interdiffusion, smooth concentration and solvent-quality gradients develop across the interface. These gradients drive controlled supersaturation, localizing nucleation near the moving diffusion front and enabling defect-suppressed crystal growth. Solvent diffusion is especially useful when a metal–halide/solvent system exhibits weak temperature dependence of solubility or when the good solvent struggles to evaporate: a poor solvent is allowed to diffuse into the precursor solution to trigger crystallization. For example, at room temperature, the Ma group diffused diethyl ether into DMF solution containing $SbCl_3$ and Ph_4PCl to afford 0D $(Ph_4P)_2SbCl_5$ crystals [32].

3.4. Antisolvent Crystallization

Antisolvent crystallization lowers the solubility of dissolved precursors until the solution becomes supersaturated, thereby triggering nucleation and crystal growth [33]. In practice, crystal quality and grain size are governed by (i) the polarity/miscibility contrast between the good solvent and the antisolvent, (ii) crystallization temperature, and (iii) supersaturation kinetics dictated by the antisolvent addition/diffusion rate. After dissolving the metal–halide precursors in an appropriate coordinating solvent (e.g., DMF, DMSO, GBL), the controlled introduction of a poorly coordinating, volatile antisolvent (e.g., chlorobenzene, dichloromethane, ethanol, n-hexane, toluene, diethyl ether) reduces solubility and raises supersaturation according to the LaMer framework, initiating nucleation once the critical threshold is reached. To favor growth over secondary nucleation and to suppress defect-rich crystallites, the antisolvent flux must be carefully regulated—commonly by vapor-diffusion across a partially covered vessel or by metered liquid addition. The diffusion rate can be tuned by the aperture geometry and headspace path length, as well as by temperature (which simultaneously affects solvent vapor pressure, viscosity, and solubility). Although replenishing precursors is inconvenient with the antisolvent method, it enables crystallization at concentrations below the nominal solubility limit and is well suited for growing small-sized OIMH crystals [34].

3.5. Mechanochemical Method

Mechanochemical synthesis induces chemical transformation by imparting mechanical energy to solid reactants—typically under solvent-free or solvent-minimized conditions. Although the microscopic mechanism of solid-state grinding is not fully resolved, prevailing views attribute reactivity to repeated particle-size reduction, the continuous exposure of “fresh” reactive surfaces, and localized shear/pressure “hot spots,” all of which lower kinetic barriers and accelerate bond formation. For OIMHs, mechanochemistry has emerged as a fast, scalable, and solvent-lean route that offers (i) inherently lower toxicity by avoiding bulk organic solvents, (ii) precise stoichiometric control in closed systems, and (iii) straightforward implementation using a mortar and pestle or electrically powered

ball mills. Variants such as liquid-assisted grinding further widen the crystallization window by introducing microliter-scale protic/aprotic additives to modulate ion mobility and intermediate adduct formation. In many cases, the approach affords high yields with few side products and is therefore attractive for upscaling OIMH production [35]. Practical considerations include brief post-annealing or vapor-phase treatments to enhance crystallinity and phase purity when required, as well as careful control of milling parameters (ball-to-powder ratio, frequency, time) to balance nucleation and growth while minimizing defect generation [36]. However, mechanochemical methods attractive for OIMHs typically yield polycrystalline powders or microcrystals suitable for PXRD, not the millimeter-scale single crystals required for full single-crystal XRD analysis or many device-physics studies. Mechanochemical methods are not the choice when device-grade or diffraction-quality OIMH single crystals are required.

4. Photophysical Mechanisms of Organic–Inorganic Hybrid Metal Halides

OIMHs feature rich chemistries and structural diversity. In particular, in low-dimensional OIMHs, photogenerated carriers are spatially confined within isolated metal-halide polyhedra, which effectively increases the probability of radiative recombination and thus enables high PLQY, broadband emission, large Stokes shifts, and self-absorption-free STE emission [37]. Despite rapid progress, key aspects of the emission mechanisms in OIMHs remain to be clarified—for example, dopant/ion-centered emission, defect-state emission, and emission behaviors regulated by external fields such as temperature and pressure. It is therefore important to probe the exciton dynamics and intrinsic physical properties of these systems. Current evidence indicates that the PL emission arises mainly from four pathways (Figure 3): (1) band-edge exciton dynamics; (2) ion-centered (activator) emission; (3) defect-induced emission; (4) STE emission [16,38].

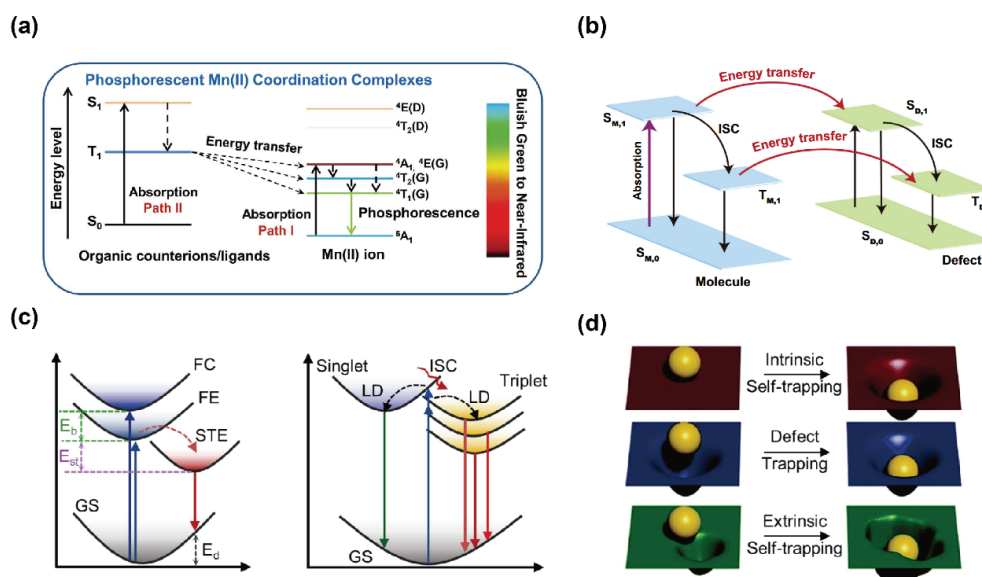


Figure 3. (a) Emission mechanism of Mn-based OIMHs [39]. Reprinted with permission from Ref. [39]. Copyright 2020, Wiley. (b) Schematic of energy transfer between singlet and triplet defect states [40]. Reprinted with permission from Ref. [40]. Copyright 2024, Springer Nature. (c) Typical STE formation process, where E_b is the exciton binding energy, E_{st} is the self-trapping energy, and E_d is the lattice deformation energy; schematic STE formation pathways in 0D OIMHs, where LD denotes lattice distortion; (d) intrinsic vs. extrinsic STE formation in 0D OIMHs [6]. Reprinted with permission from Ref. [6]. Copyright 2024, Wiley.

4.1. Band-Edge Exciton Dynamics

Band-edge exciton dynamics refer to radiative recombination of tightly bound excitons formed at the conduction- and valence-band edges. In low-dimensional OIMHs, reduced dielectric screening together with enhanced quantum confinement markedly increases the exciton binding energy, enabling stable, room-temperature excitonic emission. As a result, band-edge processes typically produce narrowband, high-purity photoluminescence with short lifetimes, a combination that is highly attractive for optoelectronic applications. Excitons are strongly governed by structural dimensionality: in 3D frameworks, photogenerated excitons experience negligible spatial confinement and behave as free excitons (FEs) with low binding energies, which readily dissociate into free carriers at room temperature. While such dissociation suppresses radiative recombination, it benefits carrier transport and thus device operation in, for example, photodetectors and solar cells [41]. By contrast, 2D and lower-dimensional lattices confine carriers within metal-halide layers or clusters, stabilizing band-edge excitons and favoring radiative decay. Representative cases include 2D (PEA)₂PbI₄, which exhibits sharp excitonic emission around ~520 nm at room temperature due to strong confinement within Pb-I layers [42], and 3D CsPbBr₃ nanocrystals, which show intense green band-edge emission (~515 nm) with PLQY approaching unity [43].

4.2. Ion Emission

Incorporation of transition-metal and rare-earth ions in OIMHs can bring emissive centers. Mn²⁺ ions with distinctive 3d⁵ configuration exhibit coordination-environment-dependent optics: it emits green light in four-coordinate, tetrahedral (weak-field) sites and red light in six-coordinate, octahedral (strong-field) sites; under certain conditions, even dynamic interconversion between these two coordination environments can be realized [44–46]. The PL emission of Mn-based OIMHs arises primarily from spin-forbidden *d*–*d* transitions of Mn²⁺. As illustrated in Figure 3a, two archetypal excitation pathways are distinguished by complex type. For neutral Mn complexes (Path II), the ligand first absorbs a photon and is promoted to a singlet excited state, and then it undergoes intersystem crossing (ISC) and transfers energy to triplet levels of Mn²⁺, culminating in the radiative transition ⁴T₁ → ⁶A₁ to yield efficient, long-lived phosphorescence. For ionic Mn-based OIMHs (Path I), UV excitation promotes the Mn²⁺ center directly from ⁶A₁ to higher-energy ⁴T₁, ⁴T₂, or ⁴A₁ states, followed by the radiative ⁴T₁ → ⁶A₁ emission [39,47].

4.3. Defect Emission

Defect luminescence can be divided into intrinsic and extrinsic types. “Intrinsic defects” arise when atoms in the lattice deviate from their ideal crystallographic sites; such defects are highly localized and, under external stimuli (e.g., illumination, temperature), can enable nonradiative recombination. Whenever electrons or holes reside on intrinsic defect levels, the resulting emission should be classified as intrinsic defect-induced luminescence, whereas “extrinsic defects” are introduced by impurity ions during doping [48].

Although defects are often deemed detrimental to emission, in some cases, the introduction of sub-bandgap states with suitable energies produces distinctive luminescence, turning defects into new radiative recombination centers [49]. The presence of defects can generate additional localized electronic levels in any material, where a fraction of electrons/holes become trapped within bandgap defect states. These carriers may lose energy through lattice thermal vibrations or, via exciton trapping and radiative transitions, give rise to defect-induced luminescence. As shown in Figure 3b, upon photoexcitation, carriers are promoted from the ground state (*S*₀) to the excited singlet state (*S*₁); a portion of the excited electrons then transfers to triplet states (*T*_n) through ISC. Because defect-related triplet states can also store energy, bidirectional energy transfer between the singlet and

triplet manifolds can occur via mixed energy transfer pathways, producing defect-state emission and, consequently, afterglow.

4.4. Self-Trapped Exciton Emission

Exciton emission in OIMHs exhibits a pronounced dependence on structural dimensionality. In 3D OIMHs, emission is typically dominated by FEs, whereas in 2D and 1D systems, both FE and self-trapped exciton (STE) emission can coexist due to partial confinement. The reduced dimensionality enhances quantum confinement effects, restricting exciton migration and simultaneously promoting self-trapping through strong electron–phonon coupling, which manifests as distinctive broadband luminescence [50,51]. When the dimensionality is reduced to 0D, extreme exciton localization suppresses FE features, and only broadband STE emission is observed at room temperature [52].

Two principal models have been proposed to explain the large-Stokes-shift broadband emission from STEs in OIMHs [6]. In conventional low-dimensional OIMHs (Figure 3c), photogenerated carriers form FEs that relax into STEs via lattice distortions induced by electron–phonon coupling. The resulting large Stokes shift reflects the combined contributions of exciton binding energy, self-trapping energy, and lattice reorganization. However, 0D OIMHs display a distinct STE formation route (Figure 1c), and excitons directly drive excited-state lattice distortions within isolated metal–halide polyhedra, producing multiple STE states without an FE intermediate. The absence of an energy barrier between FE and STE states in 0D systems creates ideal conditions for efficient self-trapping.

Experimental studies further confirm that the extent of lattice distortion in isolated polyhedra correlates directly with emission bandwidth. Strong electron–phonon coupling, described by the Huang–Rhys factor (S), broadens the spectrum according to the following [53]:

$$\text{FWHM}(T) = 2.36\sqrt{S}\hbar\omega_{\text{phonon}}\sqrt{\coth\left(\frac{\hbar\omega_{\text{phonon}}}{2k_{\text{B}}T}\right)} \quad (1)$$

where $\hbar$, ω , k_{B} , and T are the reduced Planck constant, the phonon frequency, the Boltzmann constant, and temperature, respectively. S is the Huang–Rhys factor, reflecting the strength of electron–phonon coupling. In general, larger S favors STE formation; however, excessively strong coupling enhances nonradiative recombination and leads to quenching. Thus, moderating the coupling strength is essential for efficient broadband STE emission [54].

Because STE emission originates from excited-state lattice distortions, it is sometimes described as a defect of the excited state, as shown in Figure 3d. Unlike defect-induced luminescence, which depends on intrinsic defect density, STE emission arises from a perfect ground-state lattice with only transient excited-state perturbations. Moreover, extrinsic STEs can form when dopant ions introduce local inhomogeneity. In both intrinsic and extrinsic cases, distributions of self-trapping depths promote broadband emission [8,50]. While STE-based luminescence offers unique advantages for OIMHs, limitations such as restricted spectral tunability and thermal quenching motivate exploration of alternative or hybrid emission pathways [55].

5. Applications of Organic–Inorganic Hybrid Metal Halides

OIMHs, owing to their excellent optoelectronic properties, band-structure tunability, near-unity PLQYs, and compatibility with low-cost solution processing, have found broad applications in optoelectronic devices such as LEDs [56], information encryption and anti-counterfeiting [57], luminescent probes and sensors [58], and X-ray scintillation imaging [59]. Among these, Pb-based OIMHs remain the mainstream materials because of their nearly 100% PLQY and wide bandgap tunability. Representative compounds include 3D CsPbBr_3 and 2D $(\text{R-MBA})_2\text{PbI}_4$, which have been extensively employed in

LEDs, encryption, anti-counterfeiting, and scintillation imaging. Beyond lead-based systems, Mn-based OIMHs have demonstrated significant potential in information security, anti-counterfeiting, and sensing applications due to their long-lived orange-red emission arising from Mn^{2+} d–d transitions. In parallel, Bi- and Sb-based OIMHs, benefiting from the high atomic numbers of Bi^{3+} and Sb^{3+} , exhibit strong X-ray absorption, making them attractive candidates for scintillation imaging. Their unique energy-level structures also provide opportunities for use in luminescent probes and sensors. Notably, Sb^{3+} -based 0D OIMHs, which share the $5s^2$ lone-pair electronic configuration with Sn^{2+} but avoid the oxidation instability of Sn, have emerged as particularly promising long-wavelength broadband emitters [60,61].

5.1. Light-Emitting Diodes

White LEDs have become leading replacements for traditional incandescent sources because of their high brightness, energy efficiency, and long lifetime. At present, two main technologies are used to fabricate white LEDs: (i) a UV chip that simultaneously excites three primary-color emitters to produce white light; and (ii) a down-conversion approach in which a blue chip and a color-conversion layer (typically a yellow phosphor) are co-packaged in a polymer matrix, yielding white emission by mixing the chip's blue light with the converted yellow light. However, white LEDs produced by these routes still suffer from complex processing, limited tunability, insufficient luminous efficiency, and a relatively low CRI [62]. OIMHs have emerged as promising alternatives for next-generation WLEDs. These materials offer the combined advantages of low-cost processing, high PLQYs, and fully tunable emission spectra, which collectively address many of the limitations of rare-earth phosphors [63,64].

Recent advances in Mn^{2+} -based 0D OIMHs highlight their potential for high-efficiency display and lighting applications. For example, Xia et al. discovered high-efficiency 0D OIMHs, $(\text{C}_{10}\text{H}_{16}\text{N})_2\text{MnBr}_4$, through structural design engineering, and its excellent thermal stability is also highly competitive in practical LCD applications. The as-fabricated WLED device exhibited a high luminous efficiency of 120 lm W^{-1} , together with CIE chromaticity coordinates of (0.3054, 0.3088), which fall within the white-light region [65]. In parallel, Yan's group prepared a series of 0D Sb^{3+} -based OIMHs. Driven by noncovalent interactions between inorganic cores and organic shells, the monomer Sb-2DMAP forms well-defined 1D microrods, while the dimer Sb/In-4DMAP yields 2D microplates. Leveraging the complementarity between deep-blue thermally activated delayed fluorescence (TADF) and orange room-temperature phosphorescence (RTP), they proposed that tuning the ratio of deep-blue Sb-2DMAP to orange-emitting Sb/In-4DMAP would enable white emission. As shown in Figure 4a, increasing the Sb/In-4DMAP mass fraction enhances the orange band at 627 nm, and the emission color can be continuously tuned from blue (CIE: 0.20, 0.10) to orange (CIE: 0.44, 0.37). At a 30% Sb/In-4DMAP mass ratio, deep-blue and orange emissions reach an optimal balance to produce standard white light (CIE: 0.33, 0.33), as shown in Figure 4b. This 30% mixture was then integrated with a commercial 365 nm UV chip to construct a WLED (Figure 4c). The device exhibits a well-balanced distribution of the three primaries (blue 42.6%, green 21.5%, red 35.9%), achieving standard white emission, along with a low correlated color temperature (CCT = 5270 K) and a high color rendering index (CRI = 80), fully meeting the requirements for high-quality white-light illumination.

Beyond down-conversion WLEDs, direct electroluminescence from OIMHs represents an exciting frontier. In such devices, holes injected from the p-type hole-transport layer (HTL) and electrons from the n-type electron-transport layer (ETL) recombine within the emissive interlayer to form excitons, which subsequently radiatively decay [66–68].

While significant progress has been made in monochromatic LEDs spanning the blue, green, red, and near-infrared regions, achieving stable and efficient white EL within a single device remains challenging. A notable strategy was proposed by Ma and co-workers [69], who combined narrowband sky-blue emission from 2D CsPbBr₃ nanoplatelets (NPLs) with broadband orange/red emission from 0D TPPcarzSbBr₃. The bilayer structure (40 nm/70 nm) was solution-processed, yielding stable white emission with a CCT of 6000 K. Importantly, charge-carrier mobility studies confirmed well-matched transport between the 0D and 2D components, ensuring balanced exciton recombination. The optimized device achieved CIE coordinates of (0.32, 0.35), a peak external quantum efficiency (EQE) of 4.8%, and a luminance of 1507 cd m⁻². Although the efficiency remains below theoretical limits, these results underscore the promise of 0D/2D heterostructure designs for realizing high-performance, solution-processable white EL devices (Figure 4e–g).

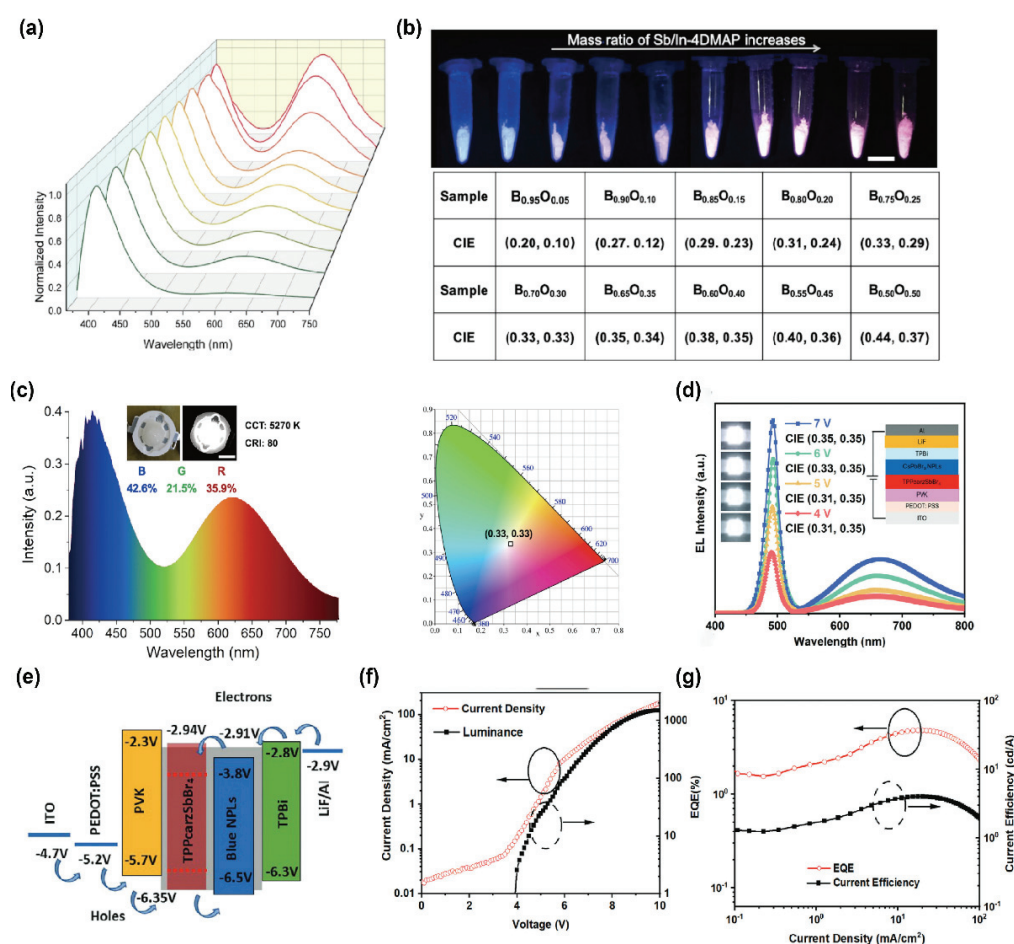


Figure 4. (a) PL spectra of Sb/In-4DMAP at mass ratios of 5–50%; (b) photographs under 365 nm excitation and corresponding CIE coordinates (“B”: Sb-2DMAP; “O”: Sb/In-4DMAP; scale bar 1 cm); (c) photographs (inset), EL spectra, and CIE coordinates of the WLED before/after operation [64]. Reprinted with permission from Ref. [64]. Copyright 20123, Wiley. (d) EL spectra and CIE coordinates of the 0D TPPcarzSbBr₄/2D CsPbBr₃ NPLs white LED at different drive voltages (inset: device photo and schematic); (e) working principle; (f) current density–voltage–luminance curves; (g) EQE–current density–current efficiency plots [69]. Reprinted with permission from Ref. [69]. Copyright 2024, Wiley.

5.2. Information Encryption and Anti-Counterfeiting

Information recording, storage, and security technologies represent a cornerstone of modern information systems, with vital applications spanning national defense, financial

protection, and daily life [70]. Among these, information encryption ensures confidentiality, integrity, and authenticity, thereby preventing tampering, forgery, and unauthorized access. Optical-materials-based encryption has gained considerable interest owing to its unique advantages: by modulating optical responses, materials can achieve efficient information encoding, covert storage, and selective decryption under specific excitation conditions. Mainstream approaches currently include laser holography, photoluminescence (PL) encoding, magnetic tagging, and pattern-based anti-counterfeiting. Notably, PL-based fluorescent encryption has emerged as particularly attractive, due to its high visibility, operational convenience, and excellent concealability, making it suitable for a wide range of application scenarios [71].

To overcome the poor stability of Sn^{2+} -based OIMHs, Xia's group developed the Sn^{4+} -based 0D compound $\text{ATPP}_2\text{SnCl}_6$ (ATPP = acetyltriphenylphosphine) and its Sb^{3+} -doped derivatives, which exhibit excitation-wavelength-dependent luminescence. Owing to the rigid Sn^{4+} lattice and Sb^{3+} dopants as emission centers, the materials display tunable emission across red, white, and green. Specifically, orange-red STE emission is observed under 302 nm excitation, intrinsic blue-green emission emerges at 450 nm, and simultaneous activation under 375 nm yields white light. For practical validation, flexible $\text{ATPP}_2\text{SnCl}_6:\text{Sb}^{3+}@\text{PDMS}$ composites were fabricated and applied in anti-counterfeiting demonstrations. Screen-printed floral and numeric patterns exhibited dynamic, wavelength-dependent color switching, enabling selective decryption under UV or filtered excitation. Furthermore, QR-code encryption systems combining doped and undoped composites achieved secure information storage: full decoding was only possible under specific excitation (390 nm) with an optical filter, while the code remained invisible under other conditions. These results highlight the stability, multicolor tunability, and excitation-dependent encryption capability of Sn^{4+} -based OIMHs, underscoring their promise for advanced luminescent security applications (Figure 5a–c).

Copper-based OIMHs offer complementary advantages, including low cost, low toxicity, and natural abundance. Kuang et al. demonstrated that the 0D $(\text{AEP})_2\text{Cu}_2\text{I}_6 \cdot 2\text{I} \cdot 2\text{H}_2\text{O}$ (AEP = N-aminoethylpiperazinium) is a promising information-storage and anti-counterfeiting luminophore. By formulating $(\text{AEP})_2\text{Cu}_2\text{I}_6 \cdot 2\text{I} \cdot 2\text{H}_2\text{O}@\text{PDMS}$ as a printable gel ink, well-defined patterns were produced via screen printing. The printed “branch” motif is invisible under ambient light yet readily revealed under UV excitation and NIR laser, enabling dual-channel authentication. As a proof of concept for document security, a monochrome “panda” image was first laser-printed on sulfuric paper; a bamboo-shaped overprint using the $(\text{AEP})_2\text{Cu}_2\text{I}_6 \cdot 2\text{I} \cdot 2\text{H}_2\text{O}@\text{PDMS}$ ink allowed selective verification under UV illumination. These results highlight the material's stimulus-responsive, covert-to-overt contrast and compatibility with scalable printing, underscoring its potential for covert tagging, multi-modal encryption, and practical anti-counterfeiting of paper-based records (Figure 5d,e) [72].

Stimuli-responsive smart luminescent materials are drawing intense interest for optical data recording and storage devices. In particular, such materials—capable of reversible luminescent responses to external stimuli such as light, electricity, magnetism, heat, and mechanical force—are becoming a research focus in optical information storage. They enable multi-mode information encoding, including fluorescence-intensity modulation, emission-wavelength shifts, and lifetime control, thereby showing great potential for high-density optical data storage, dynamic anti-counterfeiting labels, and rewritable display devices [73–75]. Li's group successfully synthesized two 0D OIMHs: a green broadband emitter $(\text{TAEA})\text{InCl}_6 \cdot \text{Cl} \cdot 4\text{H}_2\text{O}:\text{xSb}^{3+}$ (denoted as $1:\text{xSb}^{3+}$) and a yellow emitter $(\text{TETA})\text{InCl}_6 \cdot \text{Cl} \cdot \text{H}_2\text{O}:\text{xSb}^{3+}$ (denoted as $2:\text{xSb}^{3+}$). Notably, 1:0.5% Sb^{3+} exhibits a thermally driven, reversible green→orange color change with a fast response time of 20 s and a

low transition temperature of 333 K. By contrast, heat-treated 2:1% Sb^{3+} does not display cold-hot reversible luminescence over short timescales. Combining the two materials enables a heating-triggered digital encryption-decryption system. As shown in Figure 6a, a numeric template “8888” with spatially segregated regions (2:1% Sb^{3+} and 1:0.5% Sb^{3+}) was designed: under sunlight, it displays the decoy “8888”; after the first decryption with 365 nm UV, it shows the false message “2088”; following a second thermal step, regions containing 1:0.5% Sb^{3+} switch to orange emission, revealing the true message “2044.” Upon cooling to room temperature, the orange emission reverts to green, re-masking the true information and achieving cyclic encryption. Figure 6b–d further demonstrate a two-input logic gate constructed from the temperature-responsive PL-switch pair (1:0.5% Sb^{3+} and heat-treated 2:1% Sb^{3+}) [76]. Define input A as the material identity (1:0.5% Sb^{3+} = “1”; heat-treated 2:1% Sb^{3+} = “0”) and input B as the ambient-temperature signal (heated = 1; room temperature = 0); the emission color serves as the output (orange = 1; green = 0). The output becomes “1” (gate ON) only when both inputs A and B are 1. In addition, 2:1% Sb^{3+} was formulated as a writable fluorescent ink: as shown in Figure 6e, patterns written with this ink exhibit bright yellow emission under UV illumination, highlighting its practical promise for anti-counterfeiting labels.

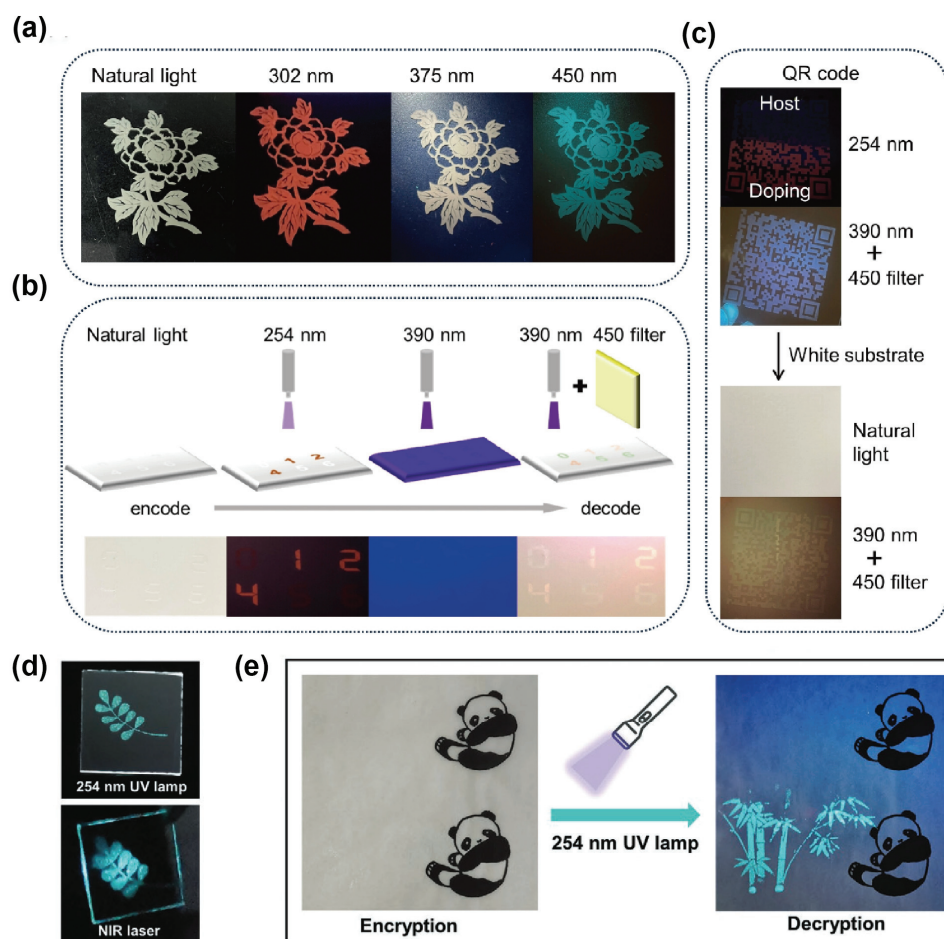


Figure 5. (a) Photographs of $\text{ATPP}_2\text{SnCl}_6\text{:Sb}^{3+}\text{@PDMS}$ floral patterns on glass under ambient and different excitation wavelengths; (b) schematic of digit encoding/decoding on a white substrate; (c) QR codes screen-printed on glass/white substrates demonstrating anti-counterfeiting [57]. Reprinted with permission from Ref. [57]. Copyright 2024, Wiley. (d) Images of $(\text{AEP})_2\text{Cu}_2\text{I}_6\cdot 2\text{I}\cdot 2\text{H}_2\text{O}$ patterns under UV and NIR; (e) encrypted (visible) vs. decrypted (UV) bamboo patterns screen-printed on real documents using $(\text{AEP})_2\text{Cu}_2\text{I}_6\cdot 2\text{I}\cdot 2\text{H}_2\text{O}\text{@PDMS}$ [72]. Reprinted with permission from Ref. [72]. Copyright 2022, Wiley.

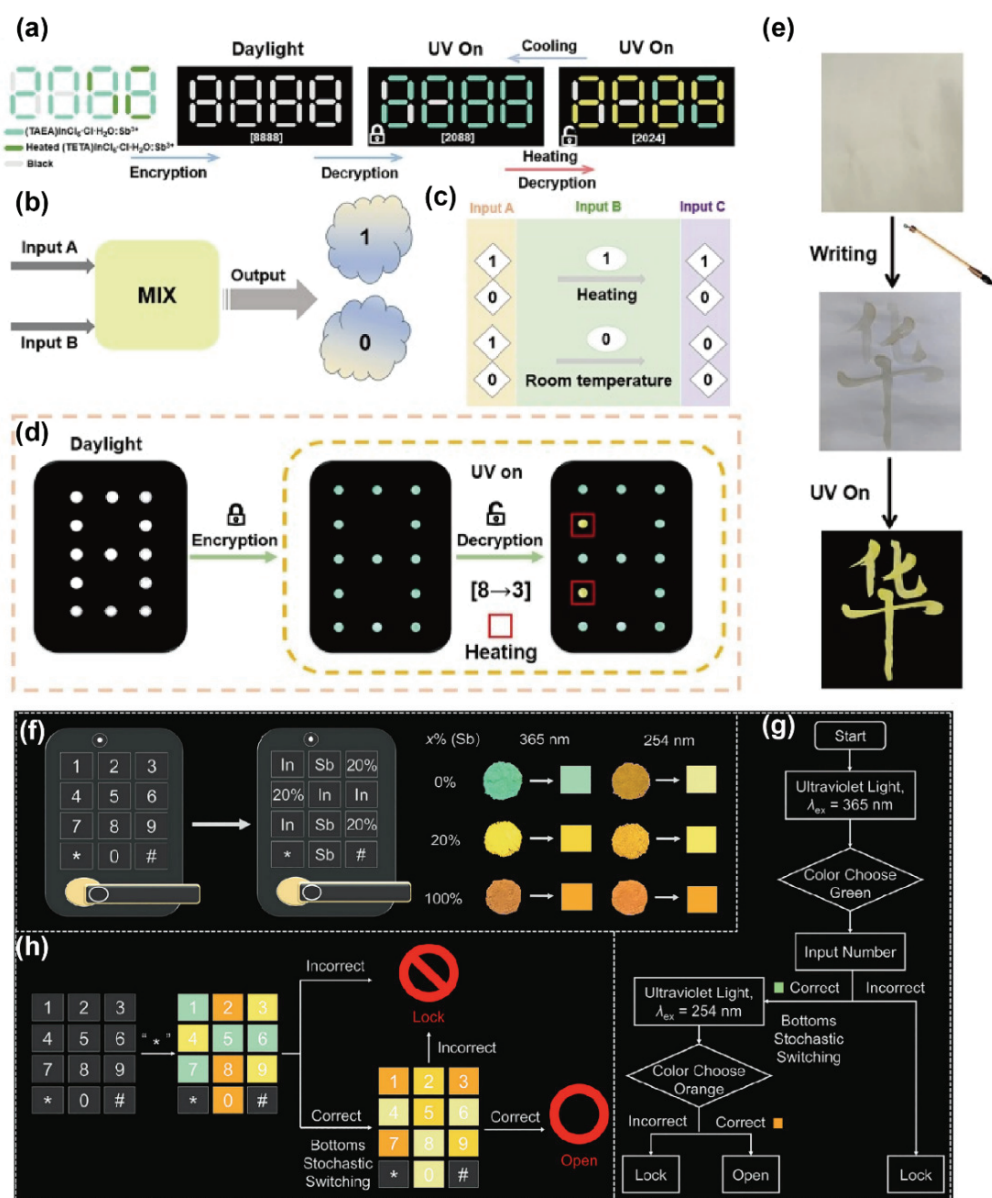


Figure 6. (a) Schematic of dual encryption-decryption using the "8888" template; (b,c) optical logic-OR gate based on 1:0.5% Sb³⁺ and 2:1% Sb³⁺; (d) experimental design of the light-controlled logic gate; (e) fluorescent ink application of 1:0.5% Sb³⁺. (f–h) Dynamic color-code keypad using B-site Sb³⁺/In³⁺ alloying [77]. Reprinted with permission from Ref. [77]. Copyright 2024, Wiley. * stands for the encryption-decryption process.

Zhang's group found that 0D (Me₂NH₂)₄MCl₆·Cl (M = Sb, In) exhibit multicolor emission under 254 nm and 365 nm excitation, enabling an anti-counterfeiting workflow for access-control applications. As shown in Figure 6f, the color distribution under 365 nm and 254 nm excitation varies with the Sb³⁺ doping level. Figure 6g,h depict the unlocking protocol: after the first press of the "*" key, excitation with 365 nm UV light reveals the green-emitting digits that constitute the correct password; an incorrect input locks the keypad. Following the first decryption, the emitters are randomly reconfigured. Pressing "*" again and switching to 254 nm excitation reveals the orange-emitting digits that form the correct password. Only by entering the correct code twice in succession will the system unlock; otherwise, it remains locked. Featuring randomness and exclusivity, this encryption scheme markedly enhances security and shows great promise for access-control anti-counterfeiting systems [77]. Compared with established security inks and tags, OIMHS

uniquely combine multi-channel optical keys with reconfigurable chemistry and low-temperature patternability, enabling high-density, hard-to-replicate encryption. While environmental stability and lead content remain concerns, 2D/0D architectures and Pb-free chemistries provide practical pathways. These attributes explain the growing interest in OIMHs for next-generation information encryption and anti-counterfeiting.

5.3. Luminescent Probes and Sensors

Owing to their distinctive optical properties, luminescent probes and sensors can transduce specific environmental inputs (e.g., temperature, pH, metal ions, gases, or solution composition) into sensitive optical signals, enabling rapid detection. Key performance metrics for such applications include response speed, selectivity, and reversibility, and certain low-dimensional OIMHs with special optical functionalities have already shown outstanding performance in this arena [58,78].

Zhang's group found that $(\text{Me}_2\text{NH}_2)_4\text{MCl}_6 \cdot \text{Cl}$ ($\text{M} = \text{Sb}, \text{In}$) exhibits composition- and temperature-dependent multicolor emission, arising from the competition between triplet STE emission ($\text{T}^n \rightarrow \text{S}_0$) in the inorganic $[\text{MCl}_6]^{3-}$ units and singlet emission ($\text{S}_1 \rightarrow \text{S}_0$) from the organic Me_2NH_2^+ cations. Under UV excitation, the crystals show distinct temperature-responsive color switching (cyan $\rightarrow$ yellow $\rightarrow$ orange, 80–305 K), with dual-band cooperative emission observed for the In-based variant. Notably, the Sb^{3+} compound enables visual temperature indication in the ultralow-temperature range (5–80 K) and was demonstrated in temperature-indicator strips integrated into a dial for extreme-environment sensing. This work highlights the potential of OIMH as multifunctional luminescent materials for spacecraft and cryogenic temperature monitoring (Figure 7a) [77].

Remote thermometry and thermographic detection based on temperature-sensitive luminophores represent an emerging sensing application of OIMHs with strong value in medicine and biology. Leveraging the pronounced temperature dependence of PL lifetimes in low-dimensional OIMHs, particularly Sn^{2+} -based 0D and 1D halides, Kovalenko's group demonstrated precise lifetime-based thermography. The mechanism relies on STEs: photoexcited carriers relax into STE states, and thermally assisted detrapping accelerates nonradiative pathways, shortening PL lifetimes with increasing temperature. Representative compounds provide distinct sensing windows from -100 to 110°C , with steep lifetime responses (up to $20 \text{ ns} \cdot ^\circ\text{C}^{-1}$) and excellent reproducibility. To overcome the limitations of single-channel time-resolved detection, these OIMHs were further integrated with time-of-flight fluorescence-lifetime imaging (ToF-FLI), enabling phase-resolved lifetime mapping. Compared with conventional infrared thermography, ToF-FLI based on Sn-halide OIMHs delivers markedly improved lateral resolution, high precision, and fast response, highlighting the potential of low-dimensional OIMHs for low-cost, high-performance thermographic imaging (Figure 7) [79].

5.4. X-Ray Scintillation Imaging

Compared with direct X-ray detectors that convert X-ray photons directly into electrical signals, scintillator-based indirect detectors first convert high-energy X-ray photons into lower-energy photons and then transduce them into electrical signals. Owing to their fast response and low cost, indirect detectors are attracting considerable attention in medical diagnostics and security screening [80–82]. Scintillators play a pivotal role in multiple fields such as medical imaging, radioactive contaminant detection, non-destructive testing, high-energy physics, and homeland security. To obtain high-quality scintillators with high light yield, fast decay, large absorption coefficients, and high energy resolution, extensive research has been conducted.

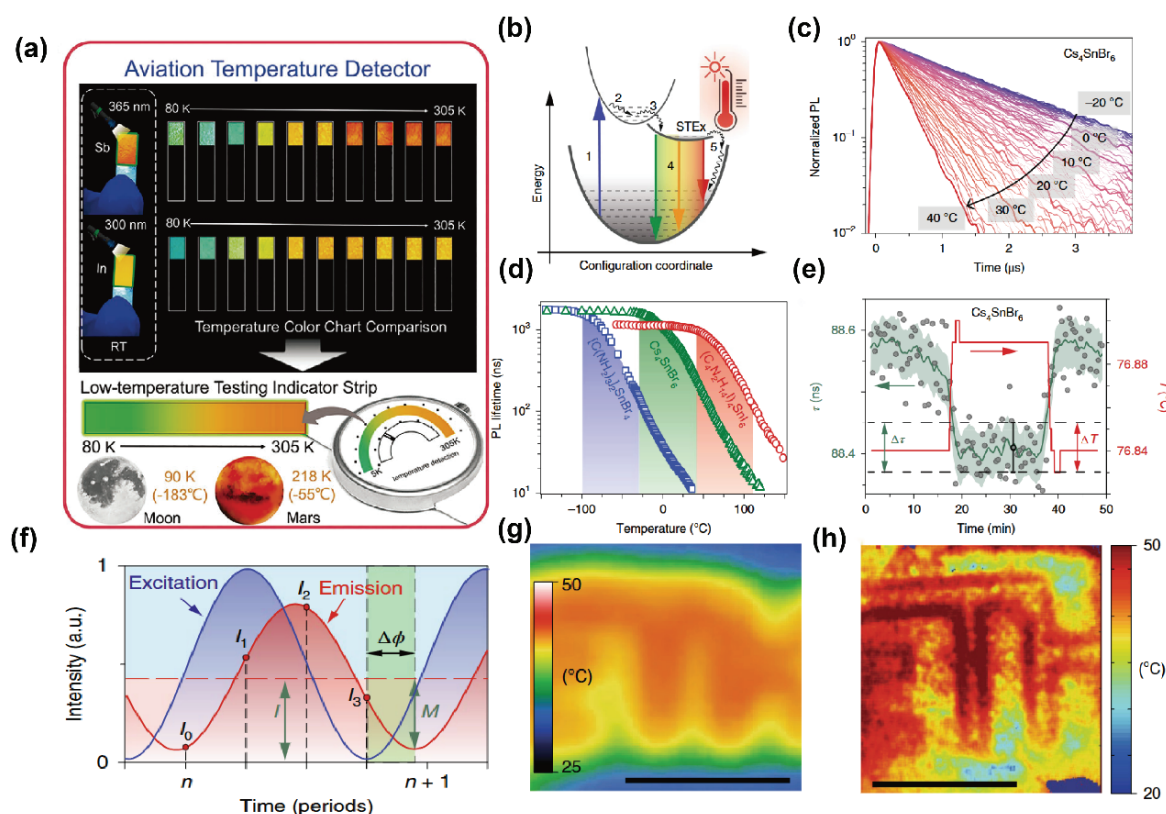


Figure 7. (a) Multicolor emission of $(\text{Me}_2\text{NH}_2)_4\text{MCl}_6 \cdot \text{Cl}$ ($\text{M} = \text{Sb}, \text{In}$) under 365/300 nm excitation and aerospace thermometry concept [77]; reprinted with permission from Ref. [77]. Copyright 2024, Wiley. (b) STE-related processes; (c) temperature evolution of TRPL traces for Cs_4SnBr_6 (355 nm excitation); (d) temperature-dependent PL lifetimes for $[\text{C}(\text{NH}_2)_3]_2\text{SnBr}_4$, Cs_4SnBr_6 , and $(\text{C}_4\text{N}_2\text{H}_{14})_4\text{SnI}_6$; (e) response to 0.05 °C steps (lifetime SD 0.04 ns; temperature SD 0.013 °C); (f) phase-domain reconstruction; (g) LWIR thermograph; (h) ToF-FLI thermograph under identical heating [79]. Reprinted with permission from Ref. [79]. Copyright 2021, Wiley.

In recent years, OIMH scintillators have become a focal point. Relative to conventional scintillators (which often require high-temperature synthesis, have inferior mechanical properties, and offer limited tunability in the visible range), OIMHs are easier to prepare and feature tunable emission wavelengths. In particular, low-dimensional OIMHs—by virtue of strongly localized emissive centers, large Stokes shifts (enabling efficient optical coupling), and strong X-ray absorption from heavy elements—are regarded as ideal candidates for achieving high scintillation efficiency [4,59]. Wang's group introduced two kinds of 1D chiral OIMHs, namely $(\text{R/S-3AP})\text{PbBr}_3\text{Cl} \cdot \text{H}_2\text{O}$, which exhibit circularly polarized RL and a light yield of about 19,000 photons/MeV. Furthermore, they demonstrated that circularly polarized RL offers a novel strategy to mitigate optical crosstalk in X-ray imaging [83]. In 2021, Zhao's group presented the Mn-doped $\text{STA}_2\text{PbBr}_4$ film as a fast neutron scintillator with a high hydrogen density of $9.51 \times 10^{28} \text{ m}^{-3}$ and a PLQY of 58.58%. This film served as a scintillator screen for fast neutron radiography, demonstrating a spatial resolution of 0.5 lp mm^{-1} [84].

Other Pb-free OIMHs are also reported to show great potential in X/ γ -ray detection. In 2020, Ma's group demonstrated high-performance, eco-friendly X-ray scintillators utilizing a 0D $(\text{C}_{38}\text{H}_{34}\text{P}_2)\text{MnBr}_4$. Remarkably, high-quality $(\text{C}_{38}\text{H}_{34}\text{P}_2)\text{MnBr}_4$ SCs with sizes exceeding 1 inch exhibited exceptional thermal stability and emitted bright green light peaking at 517 nm. The scintillator showcased a high PLQY of $\approx 95\%$, a high light yield of 80,000 photons/MeV, and a low detection limit of 72.8 nGy s^{-1} . The scintillator powder can be combined with polymer for flexible X-ray imaging. However, there is still

incompatibility between the powder and the polymer material for the scintillation screen, impacting spatial resolution. To create large-area screens, in 2023, Jin's group presented a scalable fabrication method for transparent films of $\text{HTP}_2\text{MnBr}_4$ through low-temperature melt-quenching. Impressively, the largest film achieved dimensions of 30×30 cm, making it well suited for flat panel detector applications [85]. Huang's group reported that $(\text{C}_{12}\text{H}_{24}\text{O}_6)_2\text{Na}_2(\text{H}_2\text{O})_3\text{Cu}_4\text{I}_6$ (CDSCI) flexible scintillator films exhibit low optical scattering and high transparency, enabling clear imaging of line-pair charts. They also show excellent mechanical compliance, maintaining optical performance under elongations up to 125%. In X-ray imaging, the films convert transmitted intensity into visible emission with high fidelity, resolving fine internal structures such as a capsule with oil and a shrimp with heterogeneous tissue density. At a dose rate of 2.9 mGy s^{-1} , the films achieve a spatial resolution of 20 lp mm^{-1} , approaching the theoretical limit of 24.8 lp mm^{-1} determined by MTF analysis. Moreover, their ultrashort emission lifetime supports dynamic real-time imaging, capturing rapid capsule motion without motion blur even at 50° s^{-1} . These results highlight the potential of CDSCI flexible scintillators to combine processability, high spatial resolution, and dynamic imaging capability, offering a promising pathway for next-generation medical diagnostics and industrial X-ray inspection (Figure 8) [70].

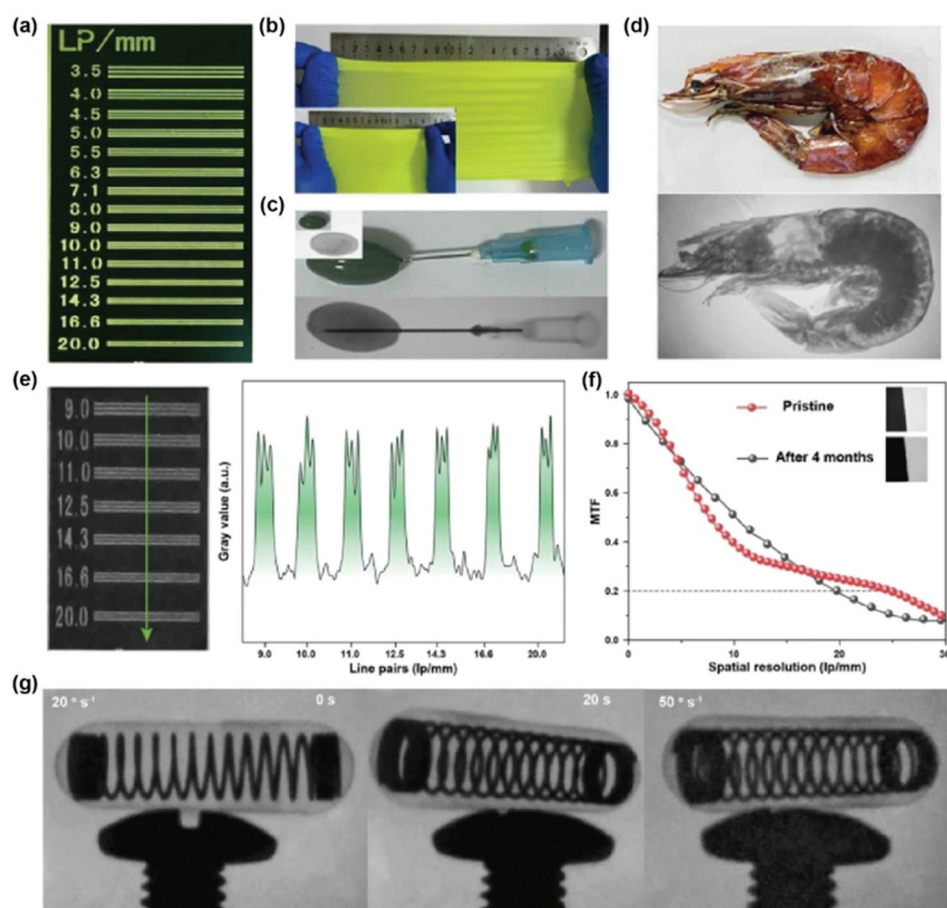


Figure 8. Flexible CDSCI scintillator films for X-ray imaging: (a) line-pair chart; (b) photographs at different stretch ratios; (c,d) X-ray images and photographs of an oil-filled capsule (top) and shrimp (bottom); (e) X-ray image and grayscale profile of the line-pair chart; (f) MTF via slanted-edge; (g) real-time dynamic imaging of a rotating spring capsule [86]. Reprinted with permission from Ref. [86]. Copyright 2024, Springer Nature.

Shen and colleagues developed a 0D $\text{C}_{38}\text{H}_{36}\text{P}_2\text{Sb}_2\text{Cl}_8$, which exhibits a wide bandgap, large Stokes shift, high PLQY, and strong X-ray absorption. They fabricated large-area, ultra-

flexible scintillator films with excellent mechanical compliance, capable of being stretched, rolled, or folded into complex shapes while maintaining bright yellow fluorescence and stable emission under 365 nm illumination. When applied to X-ray imaging, these films outperform conventional planar scintillators by conformally attaching to curved surfaces, thereby eliminating blur and data loss and enabling clear visualization of fine structural details. Durability studies showed that even after repeated stretching cycles at 150% strain, the films retained high-resolution imaging capability. In addition, their hydrophobic nature (contact angle 118.2°) ensures water resistance and stability; after prolonged immersion, imaging resolution was essentially unchanged. Together, these results highlight the unique advantages of $\text{C}_{38}\text{H}_{36}\text{P}_2\text{Sb}_2\text{Cl}_8$ flexible scintillator films for nonplanar and underwater X-ray imaging, pointing to strong potential in advanced non-destructive testing applications (Figure 9) [87].

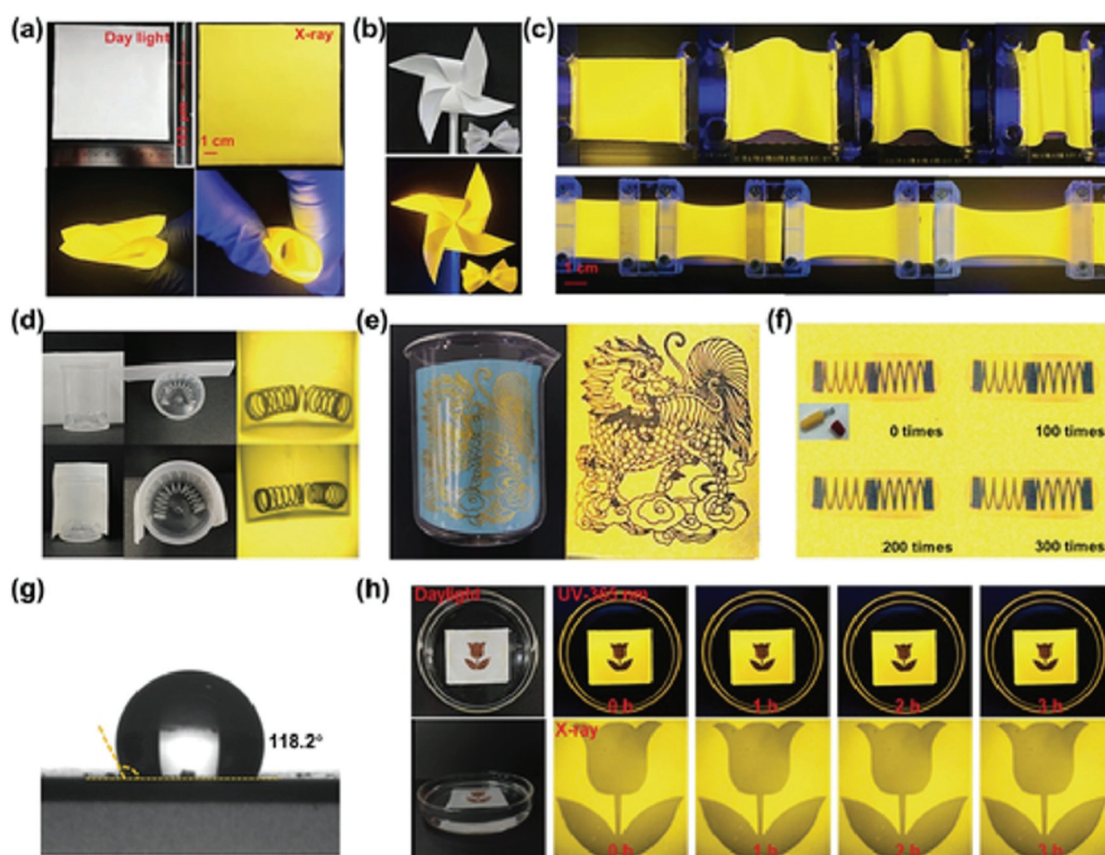


Figure 9. Curved-surface and underwater X-ray imaging using large-area ultraflexible $\text{C}_{38}\text{H}_{36}\text{P}_2\text{Sb}_2\text{Cl}_8$ scintillator films [87]. Reprinted with permission from Ref. [87]. Copyright 2024, Wiley. (a) Scintillator screen under daylight, X-ray, folding, and curling. (b) Scintillator film patterned as a windmill and bow, under daylight and UV light. (c) Scintillator screen under UV light during bending and stretching. (d) X-ray images of a curved spring via planar vs. curved scintillator screens. (e) Angled X-ray imaging of a curved object. (f) Scintillator screen X-ray images after 0, 100, 200, and 300 stretching cycles at 150% strain. (g) Scintillator screen water contact angle. (h) Scintillator screen in water over time, under UV and X-ray.

6. Conclusions

In this work, we summarize the common synthetic approaches of organic–inorganic hybrid metal halides, along with the recent advances in structures, PL mechanisms, and applications. In particular, their emission mechanisms are governed by multiple factors, including dimensionality, organic–inorganic hybrid nature, and local structural distortions.

Although progress has been made, several challenges remain: the absence of a unified model, the coexistence of multiple emission pathways that are difficult to disentangle, and—on the design/synthesis side—a lack of in-depth mechanistic studies and systematic, reliable theoretical guidance. Unlike the many design rules established for assembling 3D and 2D structures by tuning the organic/inorganic components and synthesis conditions, rational strategies for constructing low-dimensional hybrids are not yet well developed.

Despite the excellent performance reported to date—for example, PLQYs approaching unity and promising prospects in X-ray detection, white-light LED lighting, and information anti-counterfeiting/encryption—expanding application scenarios are imposing stricter requirements, particularly for X-ray instrumentation in specialized contexts such as precision non-destructive testing under extreme conditions, thermally driven pathological diagnosis, and device thermal-failure analysis. These use cases often demand stable operation at elevated temperatures, posing a severe challenge to the radioluminescence stability of scintillators. Moreover, the intrinsic chemical fragility of low-dimensional hybrids—e.g., thermolysis of organic constituents and the high volatility of halide ions—renders them susceptible to oxidative degradation in humid and oxygen-containing environments, severely limiting long-term deployment.

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