

Special Issue Reprint

Electroanalysis of Biochemistry and Material Chemistry

Edited by
Guangjin Wang

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Electroanalysis of Biochemistry and Material Chemistry

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Guest Editor

Guangjin Wang



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About the Editor

Guangjin Wang

Guangjin Wang has been a Full Professor at the School of Materials and Energy, Foshan University, China, since 2019. He received his B.Eng. degree in Inorganic Nonmetallic Materials and Engineering from the School of Materials Science and Engineering, Jingdezhen Ceramics Institute, in 2009, and his Ph.D. in New Energy Materials from the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, in 2014. From 2012 to 2014, he was a visiting student at the Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences. From 2014 to 2019, he joined the School of Chemistry and Materials Science, Hubei Engineering University, where he served as a Lecturer and then Associate Professor. In 2018, he went to the Center for Functional Nanomaterials, Brookhaven National Laboratory, as a visiting scholar. His research focuses on the design and fabrication of electrocatalysts for a range of electrochemical reactions, including oxygen reduction/evolution, hydrogen oxidation/evolution, carbon dioxide reduction, and biomass conversion reactions. His work also involves exploring the reaction mechanisms of these electrochemical reactions via first-principles calculation methods. Recently, his research interest has extended to the detection of contaminants in seawater (uranyl ions) and food (heavy metal ions and pesticide residues) matrices by means of electrochemical sensing technology.

Electroanalysis of Biochemistry and Material Chemistry

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1. Introduction

Electrochemistry, which is an interdisciplinary science, has been applied in many fields [1]. Electrochemical technologies such as electrodeposition, electroreduction and electrospinning are a popular choice for the preparation of a wide range of materials, due to their advantages of mild reaction conditions, controllable processes, adjustable parameters and eco-friendliness [2,3]. Electroanalysis methods based on the detection of electrical signals, which offer the advantages of fast response and high sensitivity, have been applied to evaluate the electrochemical stability and electrocatalytic activity of various materials [4,5]. For the preparation and electroanalysis of high-performance materials, different kinds of electrochemical devices, such as fuel cells, supercapacitors and Li-ion batteries, have been developed [6–8]. In addition, through the combination of electrochemistry with other disciplines, such as optics and computer science, the fields of photoelectrochemistry and computational electrochemistry have emerged. Photoelectrochemical technologies have been leveraged to provide solutions to environmental pollution [9], and computational electrochemical methods have been employed to explore the mechanisms involved in electrochemical reactions and to design novel electrochemical materials [10]. This Special Issue of *Molecules*, “Electroanalysis of Biochemistry and Material Chemistry”, aims to collate the latest research in electrochemistry and its related fields. Herein, a brief overview of the papers published in this Special Issue is provided, summarizing their respective findings.

2. An Overview of the Published Articles

Wang et al. (contribution 1) fabricated biomimetic, three-dimensional, sponge-filled, nanofibrous nerve guidance conduits, preparing a polymeric (L-lactide-co-glycolide) membrane using electrospinning technology and synthesizing a collagen matrix using a freeze-drying method. The porosity, pore size and tensile strength of the polymeric membrane, as well as the crosslinking degree, porosity and pore structure of the collagen matrix, were studied, and the in vitro biocompatibility of the polymeric membrane and collagen matrix was evaluated. The results showed that the composite biomimetic nerve guidance conduits have broad application prospects for the repair of defects in long nerves. Liu et al. (contribution 2) synthesized gallium-doped hydroxyapatite nanoparticles using a chemical precipitation method, and discussed the effect of gallium ions on their crystal growth and morphology.

Zhao et al. (contribution 3) deposited an FeCrMoSi amorphous coating onto a 304 stainless steel substrate using an atmospheric plasma spraying process. The physico-chemical properties and corrosion resistance of the amorphous coating were characterized. The results showed that boosting the surface roughness of the substrate improved the adhesion force between the amorphous coating and the substrate. The introduction of the Mo element significantly increased the hardness of the amorphous coating. The formation

of an amorphous phase was conducive to decreasing the surface energy of the amorphous coating and enhancing its hydrophobicity. Because of these outstanding physicochemical properties, the coating exhibited excellent corrosion resistance and considerable interfacial contact resistance under the simulated operating conditions of a proton exchange membrane fuel cell. In addition, Zhao et al. (contribution 4) also reported that the commercial alloy Hastelloy χ displayed good mechanical properties, on account of its single γ -phase with a typical face-centered cubic structure. To explore the possibility of using Hastelloy χ as the bipolar plate in proton exchange membrane fuel cells, water contact angle measurement and electrochemical characterization techniques were employed to analyze its hydrophobicity and corrosion resistance. It was found that the water contact angle of Hastelloy χ was 79.5° , and that the charge transfer resistance of Hastelloy χ was $47.58 \Omega \text{ cm}^{-2}$. More importantly, the interfacial contact resistance of Hastelloy χ was $7.4 \text{ m}\Omega \text{ cm}^{-2}$, which was almost one-twentieth that of 304 stainless steel ($144.8 \text{ m}\Omega \text{ cm}^{-2}$) under the same testing conditions.

Li et al. (contribution 5) prepared NiTi alloys using a suction casting method. The mechanical properties, corrosion resistance and interfacial contact resistance of the alloys were characterized. The hardness of the alloys was 289.7 HV, much higher than that of pure metals. Due to their higher open-circuit potential and lower corrosion current densities, the alloys exhibited higher corrosion resistance than that of pure Ni and Ti under the simulated operating conditions of a proton exchange membrane fuel cell. Moreover, the interfacial contact resistance of the alloys was $16.8 \text{ m}\Omega \text{ cm}^{-2}$, which was attributed to the high concentration of metallic Ni in the alloys. These newly-fabricated alloys show promise as novel materials for the development of bipolar plates in proton exchange membrane fuel cells.

Zhao et al. (contribution 6) investigated the electrochemical performance of $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathodes under high carbon dioxide concentrations by using electrochemical impedance spectroscopy at different operating temperatures. They found that the introduction of carbon dioxide caused an obvious decrease in the electroconductivity of the cathodes, because carbon dioxide molecules were adsorbed and occupied the active sites on the surface of the cathodes, and thus limited the exchange rate of oxygen molecules. Fortunately, the blocking effect caused by the adsorbed carbon dioxide on the surface of the cathodes was reversible. For this reason, it was concluded that the cathodes exhibited excellent corrosion resistance under high carbon dioxide concentrations and different operating temperatures.

Fu et al. (contribution 7) summarized several modification methods to improve the electrocatalytic activity and electrochemical stability of perovskite oxides during oxygen reduction/evolution reactions under alkaline conditions, and proposed a combined method of experimental investigation and theoretical calculation to investigate the oxygen reduction/evolution mechanism of oxides and design high-performance oxides for oxygen reduction/evolution reactions.

Chen et al. (contribution 8) proposed a revised grand canonical potential kinetics method on the basis of the conventional density functional theory calculation model, deriving a calculation method which they then used to investigate the impact of surface charges on the kinetics and thermodynamics mechanism of the hydrogen evolution reaction on the surface of platinum. According to the calculation results, the optimal adsorption energy of hydrogen atoms on the surface of platinum is about -0.2 eV , which is attributed to the accumulation of electrons on the surface of platinum.

Zhong et al. (Contribution 9) assembled a flexible composite electrolyte, using $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ particles prepared using conventional solid-phase synthesis methods as filler, and investigated its Li^+ conduction performance in all-solid-state batteries. The

electrochemical analysis results showed that the flexible composite electrolyte exhibited high Li^+ conduction and excellent electrochemical stability. The discharge capacity of the all-solid-state batteries was found to be 140 mA h g^{-1} at an overpotential of 0.15 V.

Chen et al. (contribution 10), using a chemical deposition method, deposited Ag-doped CdS nanoparticles onto S-doped graphitic carbon nitride to construct a Z-scheme heterostructure. The results showed that the synergistic effect of the doping of Ag atoms and the formation of the Z-scheme heterostructure was conducive to accelerating the transportation and separation of the photogenerated carriers, and thus to improving their photocatalytic performance for the degradation of Rhodamine B and methyl orange. Long et al. (contribution 11) used a combination of the sol-gel method and the spin coating process to prepare TiO_2 films with different thicknesses. According to the results of photoelectrochemical measurements, the films with a thickness of $1.09 \mu\text{m}$ displayed the lowest photoelectrochemical reaction energy barrier and the fastest kinetics, due to these films exhibiting the highest short-circuit current density and open-circuit potential. In addition, the optimal photoelectrochemical parameters for the photoelectrocatalytic degradation of methyl orange on the surface of the TiO_2 films were investigated. Under the optimized parameters, the degradation rate of methyl orange on the surface of the best film samples reached 88.6%, which was attributed to the interaction between reactive oxygen species and methyl orange.

Yang et al. (contribution 12) reviewed the use of photoelectrocatalytic water splitting for hydrogen production, covering a range of topics, from reaction mechanisms to semiconductor materials. They also proposed four effective methods to improve the yield of photoelectrocatalytic hydrogen production: morphological control, metallic/nonmetallic heteroatom doping, heterostructures and surface treatment.

3. Conclusions

This Special Issue highlights the latest research on the applications of electrochemical, photoelectrochemical and computational electrochemical technologies in the fields of biomimetic biology, material synthesis, computational materials and environmental chemistry. The studies included in this Special Issue employed electrochemical preparation methods to synthesize high-performance molecular polymers for use as biomedical materials. Several electroanalysis methods, such as linear potential scanning, cyclic voltammetry and electrochemical impedance spectroscopy, were applied to reveal the relationship between the corrosion resistance of alloys/oxides and their geometric structure and surface components, and to explore the performance of various oxides in electrocatalytic oxygen reduction/evolution. Electrochemical computational methods were used to uncover the mechanisms underlying the electrocatalytic activity of noble metals in hydrogen evolution reactions. Photoelectrochemical technologies were utilized to investigate the electrochemical performance of oxides/heterojunctions in organic dye degradation, and to analyze the mechanism involved in water splitting on semiconductor materials. The findings presented in this Special Issue provide a useful reference for researchers working in the fields of electrochemistry, photoelectrochemistry and computational electrochemistry.

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List of Contributions:

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Article

Electrospun Nanofibrous Conduit Filled with a Collagen-Based Matrix (ColM) for Nerve Regeneration

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Abstract: Traumatic nerve defects result in dysfunctions of sensory and motor nerves and are usually accompanied by pain. Nerve guidance conduits (NGCs) are widely applied to bridge large-gap nerve defects. However, few NGCs can truly replace autologous nerve grafts to achieve comprehensive neural regeneration and function recovery. Herein, a three-dimensional (3D) sponge-filled nanofibrous NGC (sf@NGC) resembling the structure of native peripheral nerves was developed. The conduit was fabricated by electrospinning a poly(L-lactide-co-glycolide) (PLGA) membrane, whereas the intraluminal filler was obtained by freeze-drying a collagen-based matrix (ColM) resembling the extracellular matrix. The effects of the electrospinning process and of the composition of ColM on the physicochemical performance of sf@NGC were investigated in detail. Furthermore, the biocompatibility of the PLGA sheath and ColM were evaluated. The continuous and homogeneous PLGA nanofiber membrane had high porosity and tensile strength. ColM was shown to exhibit an ECM-like architecture characterized by a multistage pore structure and a high porosity level of over 70%. The PLGA sheath and ColM were shown to possess stagewise degradability and good biocompatibility. In conclusion, sf@NGC may have a favorable potential for the treatment of nerve reconstruction.

Keywords: biodegradability; electrospinning process; nanofibrous; porosity; Schwann cells

1. Introduction

Peripheral nerve injury (PNI) is a clinically common degenerative disease with complex pathogenic mechanisms, which disrupts the signal transmission from the central nervous system to the limbs and body organs [1]. Once PNI occurs, patients may suffer from impaired sensation and reduced motor and autonomous function. Although PNI is usually accompanied by an active regeneration process, complete nerve regeneration and functional recovery have always been among the toughest clinical issues in neurosurgery, especially for long-segment defects [2]. Peripheral nerve regeneration consists of four main phases: establishment of a particular microenvironment and a channel suitable for axonal regrowth; axon sprouting and extension; regeneration of nerve fibers correctly in contact with the target organs; and myelination and maturation of the regenerated nerve [3]. It is a highly sophisticated pathophysiological process that involves various changes at different

stages, concerning molecules, cells, and organs [4]. The therapeutic effect of treatments for nerve defect repair is closely associated with the extent of the injury and the strategy of nerve repair.

The current gold standard for repairing a long nerve segment is the implantation of an autograft to bridge the gap between two injured nerve stumps. However, nerve autografting also faces difficult challenges such as the scarce availability of donors, potential complications at the implantation donor site, compatibility issues between the donor and the recipient, as well as incomplete recovery [5,6]. As a result, the development of advanced nerve guidance conduits (NGCs) to replace autologous nerve transplantation has become an effective strategy. To date, it is established that an ideal NGC should provide adequate physical support, guide axon regeneration, avoid scar tissue infiltration and allow the diffusion of neurotrophic factors [7,8]. That is, specific microarchitectures and bioactive components should be considered when design and fabricating NGCs.

Over the past thirty years, substantial progress was achieved in developing autograft-like conduits utilizing different technologies, structures with a wide variety of geometrical arrangements, as well as various functionalized materials [9–11]. Notably, the electrospinning technique is widely utilized for nanofiber fabrication due to its ability to generate a hierarchical structure that mimics the extracellular matrix (ECM), featured with high specific surface area and porosity. According to a previous study, NGCs possessing precisely controlled nanofiber structures have the capability to offer contact guidance for the attachment and migration of Schwann cells (SCs), thereby facilitating the process of nerve regeneration [12]. Hollow conduits authorized by the U.S. Food and Drug Administration (FDA) are first-generation conduits used in clinical practice and include NeuroTube, Neurolac, NeuraGen, NeuroMatrix, etc. [3,8]. Nevertheless, these NGCs exhibit comparable efficacy to that of autologous transplantation only in repairing short-gap injuries (<2 cm) [13]. This is ascribed to wrong target innervation and axonal dispersion in the simple hollow conduits. Thus, various fillers like hydrogels, sponges, and filaments have been introduced in hollow tubes to resemble the endoneurial microarchitecture of native peripheral nerves. These inner fillers play a vital role in creating a desirable microenvironment for nerve regeneration, further directing axonal sprouting and extension [14,15].

In searching for effective approaches to successfully bridge nerve gaps, a range of natural and synthetic materials have been proposed. Collagen, a structural protein of the ECM, is present within the endoneurium and basal lamina and harbors cell binding motifs that aid in the promotion of axon outgrowth [16]. It has been extensively employed in the fabrication of NGCs to significantly improve the nerve regeneration process [17–20]. The observation of the reinnervation of a 10 mm sciatic nerve defect in rats revealed that a collagen–glycosaminoglycan conduit promoted a notable augmentation in axon number 6 weeks after implantation [21]. In fact, the application of pure collagen is hindered to a certain extent by undesirable features such as poor mechanical strength and fast degradation. Biodegradable aliphatic polyesters such as PLGA (a copolymer of glycolic acid (GA) and lactic acid (LA)) and its homologues have already been adapted for fabricating NGCs. A cylindrical nerve conduit made of PLGA (GA/LA = 10:90) exhibited favorable flexibility, biodegradability, permeability, and ease of suturing transected nerve stumps. When a PLGA NGC was surgically inserted into a 12 mm gap in the sciatic nerve of rats, a fibrin matrix filled the conduit, allowing for successful nerve regeneration [22]. PLGA exhibits desirable mechanical properties and processability, but hydrophobicity and lack of bioactive motifs limit its application. Evidence suggests that combining natural and synthetic polymers as well as using advanced fabrication techniques will allow obtaining favorable nerve grafts mimicking the microarchitecture of native nerves [23,24]. On the basis of the research results obtained so far, we fabricated a hybrid NGC consisting of a PLGA hollow tube and a collagen-based intraluminal filler, which is expected to promote the process of nerve regeneration thanks to the complementary functions of its components.

In this work, a hierarchical and biomimetic NGC (sf@NGC) composed of a nanofiber external tube and an inner filler was prepared by electrospinning and freeze-drying. The

primary aim of this study was to develop sf@NGC utilizing a PLGA tube and a ColM intraluminal filler and evaluate its potential in nerve reconstruction therapy. We hypothesized that the unique properties of the PLGA sheath and ColM could enhance nerve regeneration and functional recovery. Specifically, ColM with an ECM-like topography was inserted into the PLGA nano-fibrous tube to construct a novel nerve-guiding conduit. Compared to other intraluminal fillers, ColM, with its randomly oriented fibers within the PLGA tube, offers both structural and biological support. This characteristic of ColM promotes cell alignment and guides axonal growth, facilitating nerve regeneration across the injured site. Additionally, the structural support offered by the PLGA tube would help prevent the collapse or compression of surrounding tissues, ensuring the integrity of the nerve pathway. This hybrid NGC with an ECM-like microstructure is believed to provide sufficient mechanical support and contact guidance for axons regrowth, further creating a desirable microenvironment for nerve regeneration.

2. Results and Discussion

2.1. Confirmation of the Successful Preparation of ColM

In order to imitate the natural architecture of peripheral nerves, 3D ColM samples consisting of collagen and OBC were prepared to be used as intraluminal fillers for NGCs. In our previous study, OBC emerged as a promising candidate for peripheral nerve repair due to its prominent mechanical properties, biocompatibility, and ECM-like structure [25]. It is worth to note that dialdehyde cellulose was reported to be an attractive crosslinker for modifying collagen due to its biocompatibility and eco-acceptability [26]. The combination of collagen with OBC is a facile strategy to enhance the inadequate mechanical strength and decrease the biodegradation rate of collagen. The reaction scheme for fabricating ColM is presented in Figure 1A. Amino groups like lysine, hydroxylysine, and arginine in collagen can bind the aldehyde groups of OBC through the Schiff base reaction.

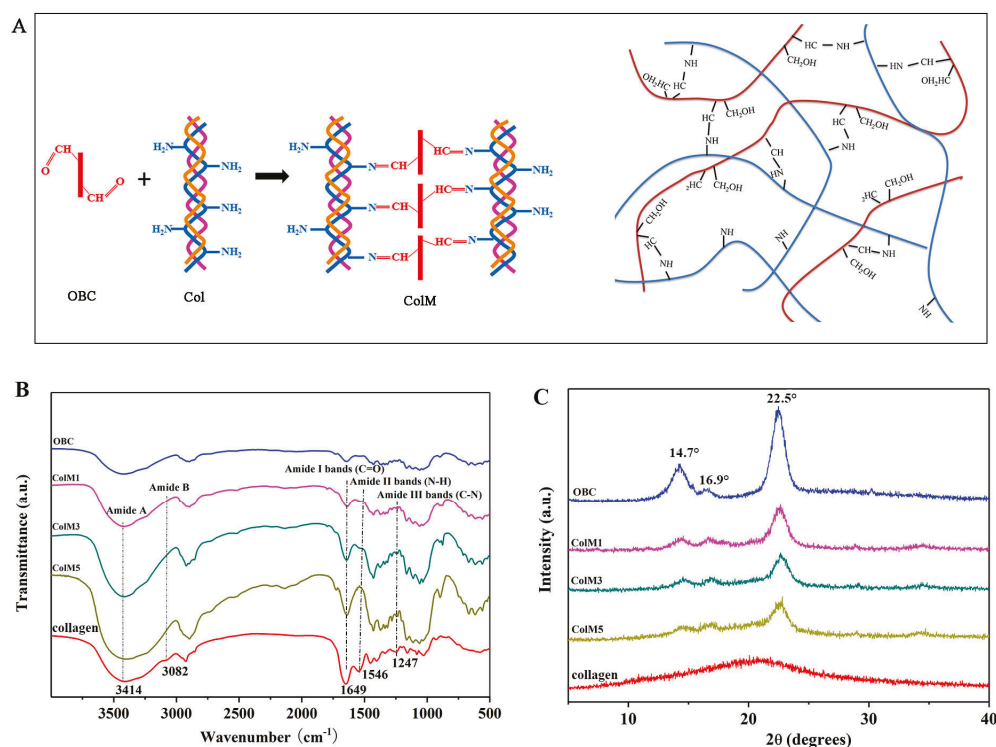


Figure 1. (A) Schematic formation mechanism of ColM by the crosslinking of Col and OBC, (B) FTIR spectra, and (C) XRD diffraction patterns of OBC, Col, and the series of ColM samples. Collagen is composed of three polypeptide chains that are intertwined with each other in a triple helix conformation. The three different colors represent the three polypeptide chains.

FTIR. The FTIR spectra of Col, OBC, and the ColM fillers are presented in Figure 1B. The prominent absorption bands centered at 1740 cm^{-1} and 880 cm^{-1} were ascribed to the C=O stretching vibration and the formation of hemiacetal bonds in OBC [25]. In the spectra of the ColM samples, the characteristic peaks of OBC had nearly disappeared. Instead, three distinctive peaks occurred at 1649 cm^{-1} , 1546 cm^{-1} , and 1247 cm^{-1} , which corresponded to amide I, amide II, and amide III, respectively [27]. The disappeared absorption bands and the new absorption peaks at 1649 cm^{-1} demonstrated the crosslinking reaction between Col and OBC.

XRD. The typical XRD patterns of Col, OBC, and the ColM samples are reported in Figure 1C. Two distinct diffraction peaks appeared at 14.7° and 22.5° on the XRD pattern of OBC, which were ascribed to the crystalline fraction of cellulose [28], while a weak peak centered at 16.9° corresponded to the amorphous fraction of cellulose. In contrast, a broad peak present in the XRD pattern of pure collagen, indicated that collagen was amorphous. After crosslinking collagen with OBC, the ColM samples exhibited characteristic peaks corresponding to OBC. However, the intensities of the peaks corresponding to the crystalline fraction declined as the collagen ratio increased from 10% to 90%. The hindered crystallization of OBC was ascribed to the Schiff base reaction between amino groups in collagen and aldehyde groups in OBC. By combining these results with those of the FTIR analysis showing newly developed amide absorption peaks, these findings further validated the successful preparation of ColM.

Thermal stability. Typical thermogravimetric (TGA) and differential thermogravimetric (DTG) curves of pure collagen and the series of ColM fillers are reported in Figure 2A,B. Two stages of weight loss were found in the TGA curves of all samples. The first weight loss measured from 50°C to 120°C was related to the breakage of hydrogen bonds as well as to the loss of small amounts of moisture. The subsequent reduction in weight occurred from 250°C to 400°C and corresponded to the thermal decomposition of each sample. Pure collagen showed a decomposition onset temperature (T_{on}) of approximately 250°C and a maximum decomposition temperature (T_{max}) of 301°C , whereas the T_{on} and T_{max} of ColM were significantly higher, reaching over 290°C and 350°C , respectively. In addition, the thermal stability of the ColM samples was improved as the crosslinking degree between collagen and OBC increased. The enhanced thermal stability of ColM can be attributed to the formation of Schiff base links between the aldehyde groups in OBC and the amino groups in the collagen molecule. The significant differences between the TGA curve of the ColM5 sample and those of the other ColM samples could indeed be due to the higher collagen-to-OBC weight ratio in ColM5. The 9:1 collagen-to-OBC ratio in ColM, indicating a greater amount of collagen in the composition of ColM5, could affect the thermal stability and degradation behavior of the sample, thus resulting in a different TGA curve. Collagen and OBC have different thermal properties; so, a high proportion of collagen could make the ColM5 sample behave differently under the same conditions compared to samples with lower collagen-to-OBC ratios.

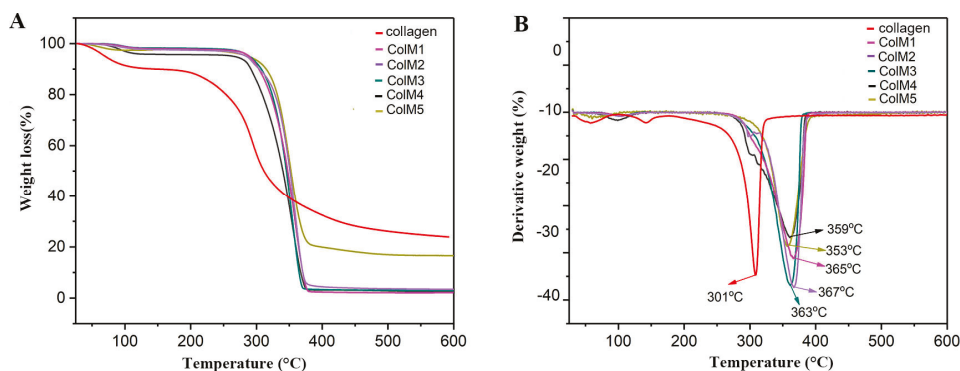


Figure 2. TGA (A) and DTG (B) thermograms of collagen and the series of ColM fillers with different proportions of collagen and OBC.

Solubility analysis. The solubility of implantable NGCs is crucial for the successful guiding of nerve regrowth and functional recovery. Therefore, the stability of the blended matrix was evaluated by investigating the weight loss of the ColM fillers in different buffer solutions. Figure 3 presents the mass loss of an un-crosslinked collagen/BC composite and various crosslinked ColM fillers after 28 days of incubation. All the ColM fillers exhibited good stability when exposed to neutral and alkaline environments. However, under acidic conditions, a noticeable mass loss was observed for the un-crosslinked collagen/BC composite and the ColM fillers with a lower degree of crosslinking (ColM1, ColM4, and ColM5). In contrast, the ColM2 and ColM3 fillers, possessing a higher crosslinking degree (Table S1, Supporting Information), displayed stability, with a mass loss below 10%. Therefore, a higher crosslinking degree provided the ColM fillers with increased stability and resistance to mass loss even in acidic environments. In fact, the microenvironment at the nerve injury site is typically acidic due to inadequate blood supply and presents inflammatory reactions caused by the metabolic byproducts of dead cells [29]. By maintaining stability in an acidic environment, ColM2 and ColM3 could support the attachment, growth, and migration of nerve cells, further facilitating the regeneration of an injured nerve.

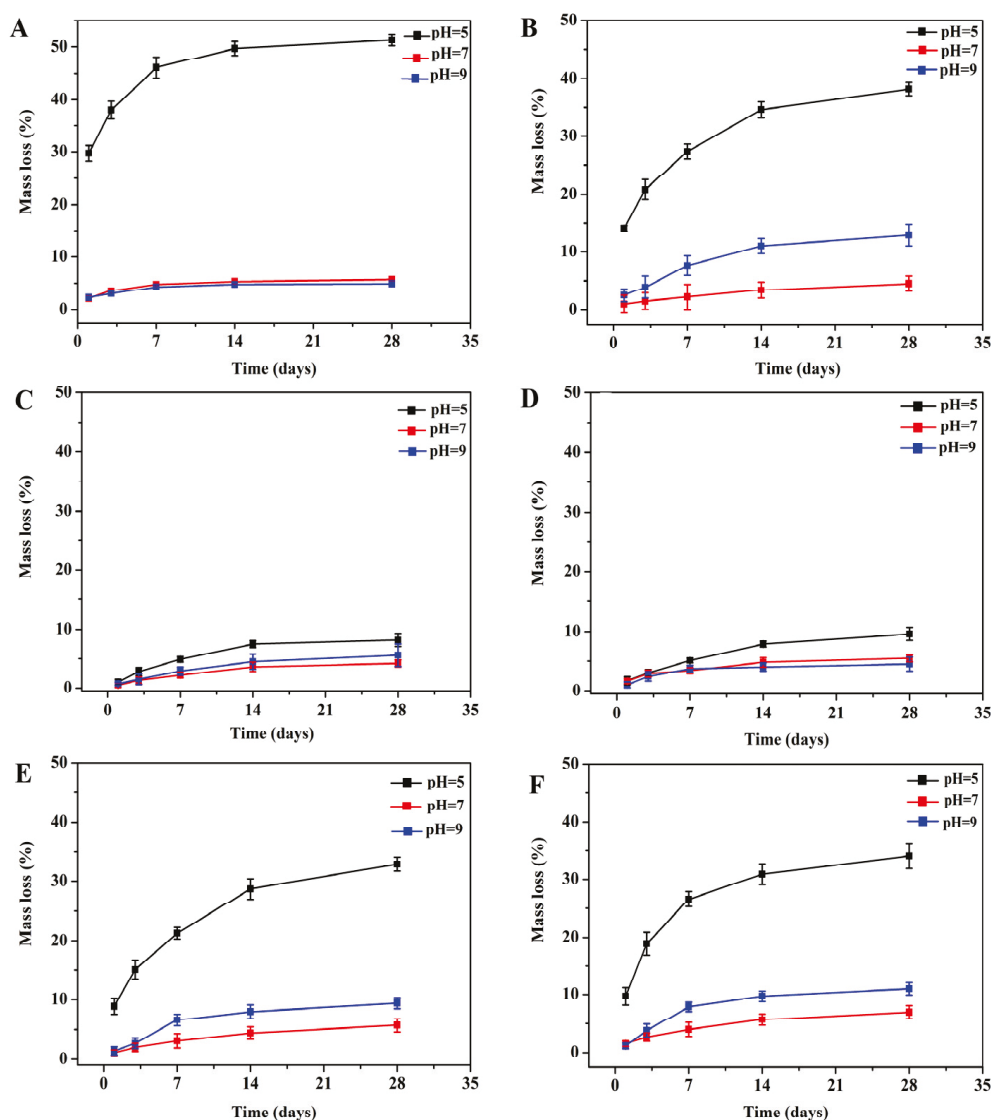


Figure 3. Mass loss of the ColM fillers incubated in three buffer solutions with different pH values. (A) collagen/BC composite, (B) ColM1, (C) ColM2, (D) ColM3, (E) ColM4, and (F) ColM5.

2.2. Optimization of the Parameters of the Electrospinning Process

Electrospinning enables the easy production of micro/nanofibers that replicate the intricate structure of the native extracellular matrix (ECM). These fibers possess a high specific surface area, desirable pore interconnectivity, and customizable topography. Such characteristics are advantageous for promoting cell adhesion, proliferation, growth, and efficient nutrient delivery [30]. Numerous studies documented the use of scaffolds or matrices fabricated by electrospinning as viable options for tissue substitutes and drug delivery systems [30–32]. Electrospinning is an electrohydrodynamic process that involves charging a polymer solution or molten droplets to create a jet at the spinneret, which is subsequently followed by uniaxial stretching and elongation to generate fibers. Generally, an electrospinning set up involves a high-voltage power supply, a syringe pump, a needle spinneret, and a conductive collector [33,34]. It is known that the processing parameters have a great influence on the surface morphology and diameter of electrospun fibers. In this work, electrospinning was employed to fabricate a PLGA nanofiber membrane varying parameters such as solution concentration, spinning voltage, and liquid flow rate. A comprehensive investigation was conducted to examine the impact of these different parameters on the morphology and diameter of the obtained nanofibers. The average diameter (AD) value of the nanofibers was determined by analyzing SEM images with Image J (Image J 1.46r, National Institute of Health, Bethesda, MD, USA). In total, 100 fibers were randomly selected to measure their average diameter in each experimental condition.

PLGA concentration. To explore the impact of the initial PLGA concentration on the morphology of the nanofibers, solutions with PLGA concentrations varying from 8 to 20 wt% were prepared specifically for the electrospinning process. As shown in Figure 4A, at the low PLGA concentration of 8 wt%, only a limited number of nanofibers were observed, accompanied with a large number of beads. In this case, the low viscosity of the solution resulted in weak interactions among the polymer molecules, leading to the direct deposition or spraying of the liquid droplets onto the collector under the electric field, rather than to the stretching and elongation of the charged jet to form fibers. When the PLGA concentration was increased to 10 wt%, the resulting nanofibers exhibited a discontinuous and non-uniform structure, and fewer beads were observed. As the PLGA concentration increased to 15 wt%, bead-free, uniform, and consistent nanofibers were obtained. The gradual increase in the concentration of the PLGA solution promoted the formation of a Taylor cone, as well as the stretching, thinning, and solidification of the charged jet. Consequently, suitable nanofibers were collected. As the PLGA concentration was further raised to 20 wt%, the nanofibers exhibited aggregation and had a larger diameter. Moreover, the high viscosity of the solution resulted in the spinneret being prone to blockage, ultimately leading to a failure in the jetting process. An increase in the nanofiber AD from 65 ± 12 to 747 ± 117 nm was observed as the PLGA solution concentration increased from 8 wt% to 20 wt%. Taking into account these findings, the concentration of the PLGA solution was optimized to 15 wt%.

Spinning voltage. The spinning voltage directly determines the electrostatic force exerted on the liquid droplets, that is, the surface charge density of the jet. Fiber formation through spraying and elongation of the polymer jet occurs when the accumulated charge on the droplet's surface surpasses the surface tension. In order to investigate the impact of applied voltage on fiber morphology, different spinning voltages ranging from 8 to 20 kV were applied for electrospinning, during which the PLGA concentration and liquid flow rate were kept constant at 15 wt% and 0.8 mL/h, respectively. As shown in Figure 4B, the AD of the nanofibers decreased from 594 ± 183 to 160 ± 32 nm, and the distribution range of the diameters became narrower with increasing spinning voltage. It is evident that higher voltage facilitated the formation of thinner fibers. However, as the voltage raised to 20 kV, a fluctuation of the jet was observed as a consequence of the intermittent flow of the PLGA solution, which was caused by the droplets being sprayed at a higher rate than the solution feeding rate. According to the findings of Yin et al. [35], a highly charged liquid jet is more prone to split into smaller jets, generating excrescent spots on the collector. This, in

turn, hinders the achievement of fibers with a continuous, uniform, and smooth surface structure. It was reported that the highest voltage that can produce a continuous jet stream is named the quasi-stable point, at which a balance is achieved between the jet flow rate and the solution feeding rate [36]. Obviously, only with an appropriate increase in applied voltage, a continuous and uniform nanofiber will be generated from the spinneret. Thus, 15 kV was selected as the proper voltage for the electrospinning of PLGA.

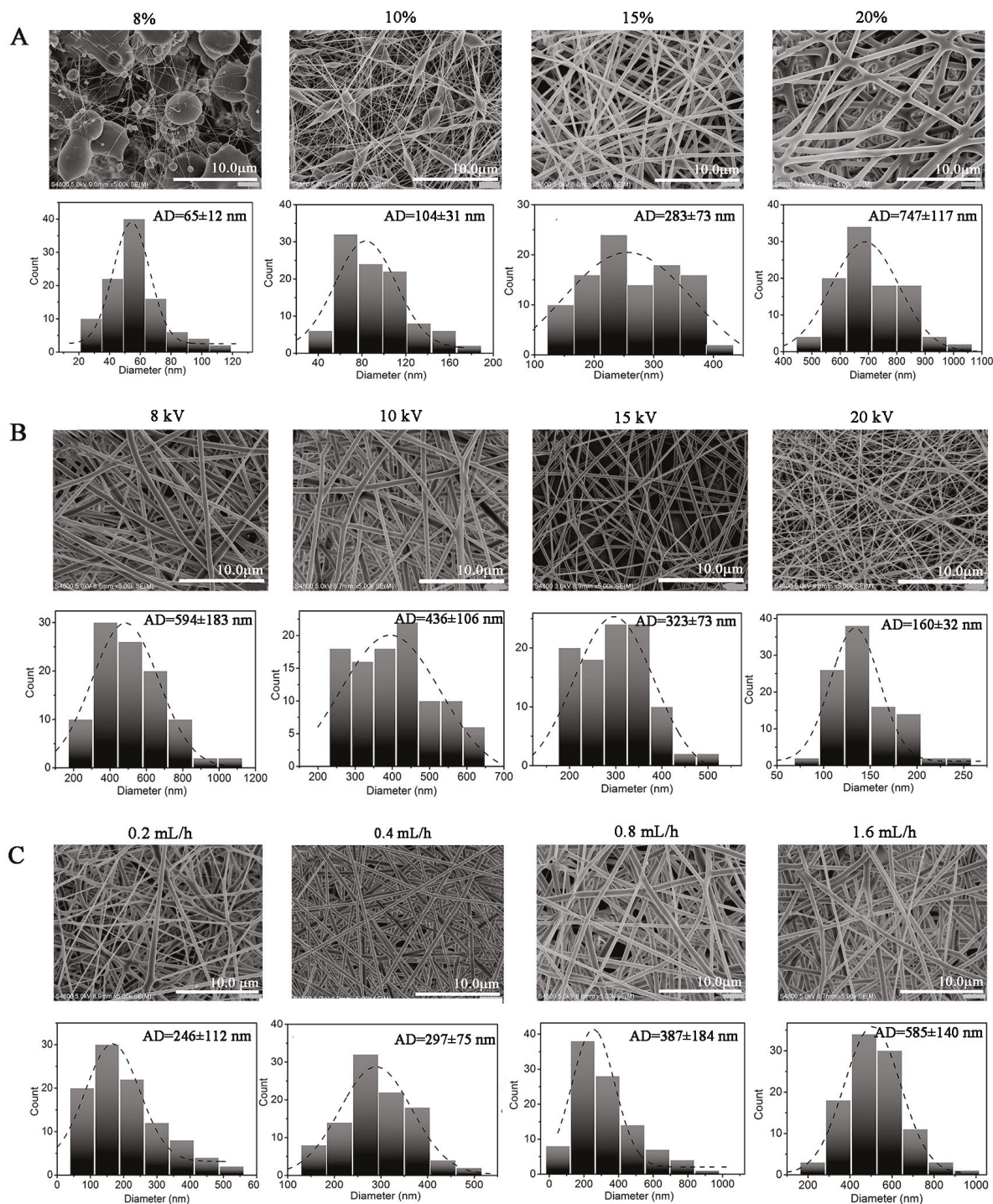


Figure 4. The SEM micrographs and the diameter distribution diagrams of electrospun PLGA fibers with different (A) concentrations of PLGA solution, (B) spinning voltages, and (C) liquid flow rate. The working distance between the spinneret needle and the collector was fixed at 15 cm during the experiments. Data are presented as means ± SD ($n = 3$).

Liquid flow rate. The liquid flow rate is also considered one of the vital parameters regulating the trajectory of the jet and the stability of the Taylor cone, further affecting the diameter and distribution of the fibers. The flow rate of the PLGA solution was varied from 0.2 to 1.6 mL/h to evaluate its impact on the morphology of the fibers. This investigation was carried out while maintaining a constant PLGA concentration of 15 wt% and a spinning voltage of 15 kV. A lower flow rate is generally advantageous for ensuring sufficient solvent evaporation, jet solidification, and proper deposition of the fibers. At a flow rate of 0.2 mL/h, only a small quantity of PLGA solution was expelled from the needle spinneret, and the liquid jet displayed intermittent breaks. By increasing the flow rate, the quantity of the ejected solution gradually increased, resulting in the formation of a stable jet and facilitating the production of continuous fibers. As shown in Figure 4C, the AD of the nanofibers increased from 246 ± 112 to 585 ± 150 nm with the increase in the flow rate from 0.2 to 1.6 mL/h. It is believed that larger droplets formed at higher flow rates. Consequently, the fibers were prone to merge together due to deficient stretching and elongation of the jet, as well as to an insufficient time for the residual solvent to dry. Therefore, the liquid flow rate was optimized at 0.4 mL/h to achieve continuous, uniform PLGA nanofibers with a smooth surface.

2.3. Characterization of the Electrospun PLGA Tube

Mechanical properties. Desirable physicochemical features like adequate mechanical properties and appropriate biodegradability and permeability can be achieved in NGCs by adjusting their chemical composition and structure. The mechanical properties of NGCs are significantly influenced by factors such as structure, wall thickness, and porosity. In order to optimize the performance of the external conduit of sf@NGC, PLGA tubes with varying wall thicknesses of 50 μm (PLGA 50), 100 μm (PLGA 100), 150 μm (PLGA 150), 200 μm (PLGA 200), and 300 μm (PLGA 300) were prepared by adjusting the duration of the electrospinning process. As illustrated in Figure 5A, PLGA 50 was prone to break, with a quite small deformation. As the PLGA wall thickness increased from 100 to 300 μm , the tensile strength (TS) increased from 1.2 MPa to 4.7 MPa, while the elongation at break improved from 9.6% to 27.9% (see Figure 5B). NGCs need to exhibit adequate mechanical strength to ensure their structural integrity during surgical suturing, while also withstanding mechanical compression stresses from surrounding tissues until nerve regeneration is achieved. A study reported that the TS of the rat fresh sciatic nerve was 2.7 MPa [37]. Interestingly, both PLGA 200 and PLGA 300 exhibited comparable TS (3.1 MPa and 4.7 MPa, respectively) to that of the natural sciatic nerve.

In vitro degradation. A suitable degradation rate is crucial for implantable scaffolds; otherwise, complications may arise after long-term implantation. In general, the neurogenesis process takes approximately 2–3 months to complete. Studies on the therapeutic assessment of NGCs for long-gap nerve injuries may even last 3–48 months. FDA-approved commercial neural scaffolds such as Neuroflex and NeuroGen achieve a complete degradation after implantation for 8 and 48 months, respectively [38]. Figure 5C illustrates the in vitro degradation curves of PLGA tubes with different wall thickness. As expected, a significant mass loss was observed in all PLGA tubes after incubating them in PBS at 37 °C for 12 weeks. Among them, the PLGA 50 tube showed the highest mass loss, with a value of 35.2%. An excessively rapid degradation rate sacrifices the mechanical properties of NGCs, which is unfavorable for supporting nerve regrowth and extension. The degradation of PLGA primarily occurs due to the detachment of small molecules at the ends of molecular chains or side chains. As the wall thickness of the PLGA tubes increased from 100 μm to 300 μm , the mass loss rate gradually slowed down. PLGA 200 presented a relatively moderate mass loss. After 12 weeks of evaluation, the mass loss rate of PLGA 300 was only 12.1%. However, this slow degradation rate could inadvertently hinder nerve regeneration by limiting the space available for new nerve growth.

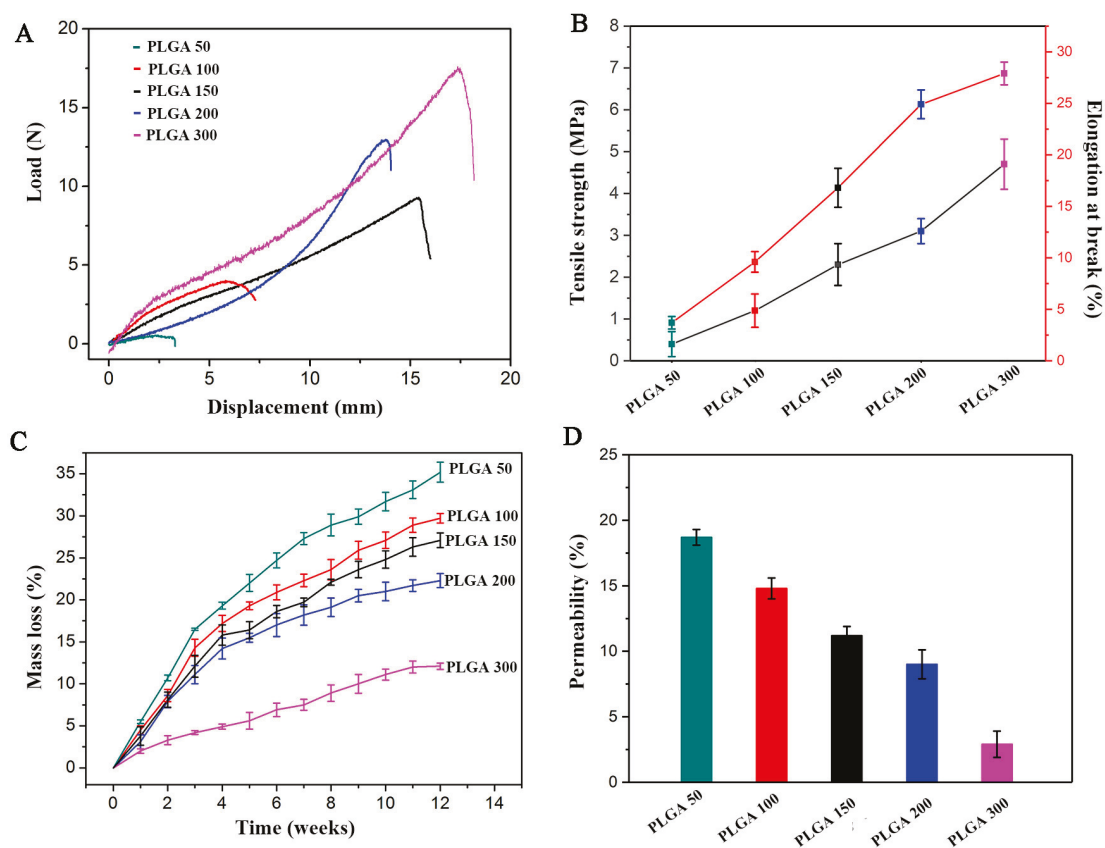


Figure 5. Mechanical, degradable, and permeable characterization of nanofibrous PLGA tubes. (A) Representative load–displacement curves, (B) tensile strength and elongation at break curves, (C) mass loss curves, and (D) permeability of a glucose solution in PLGA tubes with varying wall thickness. Data are presented as means $\pm$ SD ($n = 3$).

Permeability and porosity. Wall permeability is one of the vital characteristics of NGCs, as it enables the smooth transportation of nutrients and oxygen to cells. Studies indicated that the permeability of NGCs is affected by factors such as their thickness, degree of porosity, and pore size. Table 1 and Figure 5D show the porous characteristics and permeability of nanofibrous PLGA tubes with varying wall thickness. The PLGA 200 tube exhibited a porosity of $64.5 \pm 2.3\%$ and an average pore size of $11.8 \pm 1.7 \mu\text{m}$. There were no significant differences in porosity, average pore size, and pore size distribution between PLGA tubes with different thickness. It appeared that a pore size over $30 \mu\text{m}$ could result in the invasion of fibroblasts and in the loss of nutrients. This could be avoided with a pore size within the range of $10\text{--}20 \mu\text{m}$ [39].

Table 1. The porous properties of electrospun PLGA tubes with different thickness.

Samples	Porosity (%)	Average Pore Size (μm)	Pore Size Distribution (μm)
PLGA 50	58.2 ± 2.2	12.3 ± 1.3	4–18
PLGA 100	59.0 ± 1.0	10.5 ± 2.1	6–16
PLGA 150	62.8 ± 1.8	12.2 ± 1.6	2–25
PLGA 200	64.5 ± 2.3	11.8 ± 1.7	6–20
PLGA 300	64.8 ± 1.5	12.5 ± 2.4	5–22

To evaluate the impact of wall thickness on the permeability of PLGA tubes, the diffusion rate of the glucose solution was further examined. Following a 24 h incubation in PBS at 37°C , PLGA 50 exhibited the highest permeability at 18.7%. At the same time, the

permeability to the glucose solution decreased progressively from 14.8% to 11.2%, 9.6%, and then 2.9% for PLGA 100, PLGA 150, PLGA 200, and PLGA 300, respectively (Figure 5D). The decrease in permeability was attributed to the layer-by-layer stacking of the nanofibers, which impeded the diffusion of glucose. Therefore, considering the results of the analyses of the mechanical, degradation, and permeable properties, the optimal wall thickness for the PLGA tubes was determined to be 200 μm .

2.4. Morphology and Structure of sf@NGC

An ideal NGC should have certain physicochemical properties and be biocompatible; these features closely depend on the materials selected for NGC fabrication and on the structural design. Although hollow tubes contribute to promoting the nerve repair process, challenges such as nerve mismatch and incomplete functional recovery still persist. Introducing a specially structured matrix into hollow tubes to enhance axonal growth and extension is a promising strategy to achieve improved reinnervation. The natural ECM consists of randomly arranged fibers and plays a vital role in providing structural and biological support to tissues. Inspired by the natural architecture of peripheral nerves, we designed a biomimetic sf@NGC consisting of a tubular sheath and 3D sponge fillers.

The sf@NGC construct was produced by rolling the electrospun PLGA membrane into a tubular shape and subsequently inserting ColM into its inner lumen. Figure 6 shows a digital photograph and SEM images of sf@NGC. The data on the pore structure of ColM are summarized in Table 2. As shown in Figure 6B, the PLGA tube with an optimized wall thickness of 200 μm and a length of 15 mm was loaded with ColM2 fillers. The PLGA tube exhibited an external homogeneous and smooth nanofibrous composition, characterized by a porosity and a pore size of approximately $64.5 \pm 2.3\%$ and $11.8 \pm 1.7 \mu\text{m}$, respectively. The microscopic morphology of the ColM fillers is shown in Figure 6D–F. The ColM fillers possessed an ECM-like architecture with a 3D interconnected porous structure interwoven with high-aspect-ratio fibers. This biomimetic structure would facilitate the transport and exchange of nutrients and metabolites in the process of tissue regeneration. The porosity of the different ColM fillers was approximately 70%, while the average pore size slightly decreased with the increase in the proportion of collagen in the hybrid matrix. It was found that the ColM fillers presented 70% of medium pores (20–100 μm), 20% of large pores (>100 μm), and 10% of small pores (<20 μm). This multistage pore structure would be favorable for cell adhesion, proliferation, and migration, as well as support nutrient delivery and metabolite efflux [8].

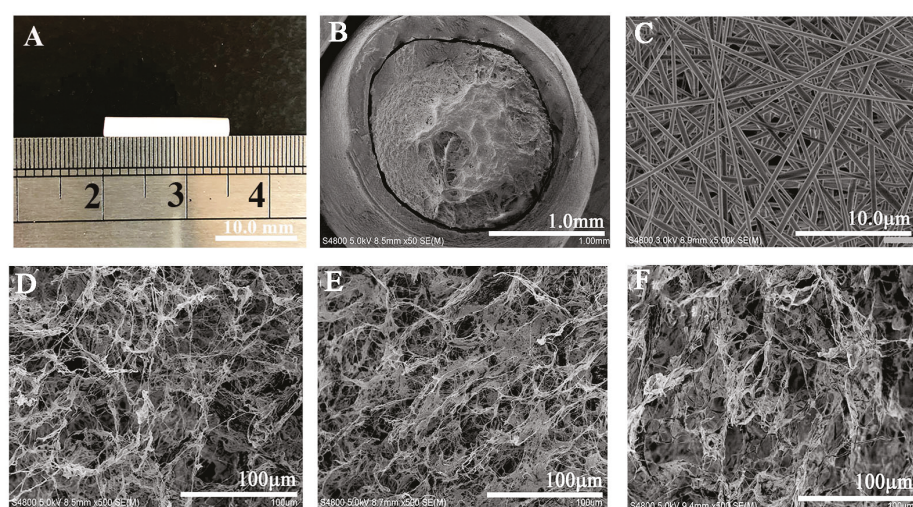


Figure 6. Photograph (A) and SEM characterization of sf@NGC. Transverse section of (B) sf@NGC showing a tight combination of the PLGA tube with ColM, (C) PLGA tube with uniform and smooth nanofibers, (D–F) ColM fillers with varying component proportions ((D), ColM1, (E), ColM3, and (F), ColM5).

Table 2. Characteristics of the pore structure of the ColM fillers quantified using mercury porosimetry.

Codes	Porosity (%)	Average Pore Size (μm)	Distribution of Pore (μm)				
			>100	100–20	20–10	10–5	<5
ColM1	72.3	60.2	23.3	72.4	3.4	0.2	0.7
ColM2	71.6	58.0	21.1	70.8	6.7	0.9	0.5
ColM3	70.1	57.4	19.4	70.5	8.8	0.6	0.7
ColM4	72.9	56.1	20.4	69.7	8.6	0.7	0.6
ColM5	71.8	55.0	18.8	71.7	7.2	1.0	1.3

2.5. Assessment of Biocompatibility In Vitro

SCs were used to assess the biological properties of the PLGA tube and ColM fillers in vitro using an extraction method. Figure 7 shows the results of morphological, cell viability, and living cell ratio analyses of SCs cultured in different conditioned media for different times. A Hoechst 33342 and PI staining kit was employed to determine the viability of SCs. Normal/apoptotic cells were dyed blue, and dead cells were dyed red. After 2 days of culture, comparable cell morphology and survival ratios were observed in the different conditioned media. Over 90% of SCs were found to be alive with abundant pseudopods. In contrast, a large number of dead SCs were discovered in the DMSO sample (Figure 7A,C). The viability of SCs cultured in different conditioned extracts was further determined by the MTT assay. Compared to the control group, no significant differences in OD were observed for SCs in PLGA, ColM2, and ColM3 conditioned media; significant differences were found for the DMSO group. These results showed that both PLGA and ColM fillers had no negative effects on cell viability and proliferation.

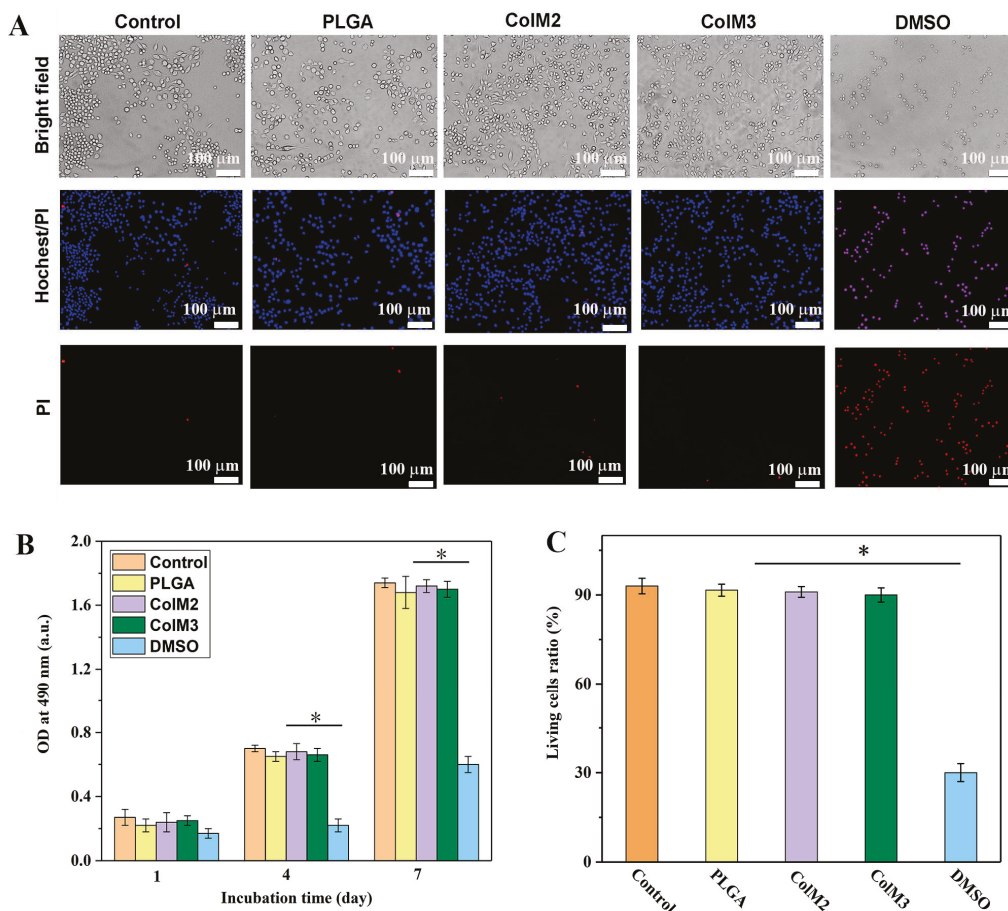


Figure 7. Assessment of the biocompatibility of the PLGA tube and ColM fillers in vitro using SCs. (A) Representative morphology of SCs cultured in media with extracts of the different samples for 2 days

(SCs were stained with Hoechst 33342 and PI fluorescent dyes), (B) cell viability assessment in different samples by the MTT assay, (C) statistical results of the survival rate of SCs cultured in different extracts for 2 days. Data are presented as means $\pm$ SD ($n = 6$, * $p < 0.05$).

In the current study, we successfully developed a hybrid sf@NGC for nerve reconstruction therapy. The conduit was fabricated by electrospinning PLGA membranes to create a tube, while the internal filler was obtained by freeze-drying ColM, resulting in a structure that resembled the extracellular matrix. This development represents a significant step forward in the field of nerve reconstruction therapy. The study thoroughly investigated the impact of the electrospinning process and the composition of ColM on the physicochemical properties of sf@NGC. In addition, the biocompatibility of the PLGA sheath and ColM was assessed. The staged degradability and good biocompatibility of PLGA and ColM, along with the high porosity and tensile strength of the PLGA nanofiber membrane and the ECM-like structure of ColM, could potentially enhance nerve regeneration and functional recovery. While our study represents a progress in the field, further in vivo experiments are necessary to validate the effectiveness of sf@NGC in repairing long-gap nerve defects. This study provides a promising strategy for the treatment of peripheral nerve injuries, which are common but challenging clinical problems. sf@NGC could potentially improve the outcomes of nerve reconstruction surgery and reduce the associated morbidity. We believe that with constant research and development, sf@NGC could become a viable option for nerve reconstruction therapy in the near future.

3. Materials and Methods

3.1. Raw Materials

The copolymer poly(L-lactide-co-glycolide) (PLGA) ($M_w = 100$ kDa, LA/GA = 75/25) was offered by Jinan Daigang Biological Co., Ltd. (Jinan, China). Type I collagen was purchased from Sigma-Aldrich (St. Louis, MO, USA). Bacterial cellulose (BC) was obtained from Hainan Yida Food (Haikou, China). Dimethylacetamide, dichloromethane, and phosphate-buffered saline (PBS) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Fetal bovine serum (FBS), trypsin, and penicillin–streptomycin were purchased from HyClone (Logan, UT, USA). SCs were collected and cultured in our laboratory.

3.2. Preparation of the 3D Collagen-Based Matrix (ColM)

Firstly, oxidized bacterial cellulose (OBC) was prepared by periodate oxidation of BC, as previously described [25]. Secondly, a well-dispersed OBC solution at a concentration of 0.1 mg/mL was prepared by ultrasonic emulsification. Thirdly, a 10 mg/mL collagen solution was mixed with the OBC solution at various mass ratios (1:9, 3:7, 5:5, 7:3, 9:1) and magnetically stirred for 24 h at 25 °C. Finally, the resulting mixtures were poured into cylindrical molds and then freeze-dried at -20 °C for 48 h to obtain the ColM. The crosslinking degree of the collagen and OBC mixtures is reported in Table S1.

3.3. Fabrication of the PLGA Tube and Optimization of the Parameters of the Electrospinning Process

PLGA particles were completely dissolved in a solvent mixture containing dimethylacetamide and dichloromethane (in a ratio of 1:3 v/v) at different concentrations, namely, 8 wt%, 10 wt%, 15 wt%, 20 wt%. The PLGA solutions were loaded into a syringe equipped with a needle (0.21 mm). Electrospinning was performed at various voltages (8–20 kV) and flow rates of the liquid (0.2–1.6 mL/h). The working distance between the needle and the collector was maintained constant at 15 cm during the experiments. The as-prepared PLGA nanofibrous membrane was dried overnight at room temperature to remove the residual solvent and then wrapped around a mold to obtain a tubular sheath. The thickness of the PLGA tube was measured using a hand-held digital thickness gauge at five randomly selected locations, and the average value was recorded.

3.4. Assembly of the Nanofibrous Sponge-Filled NGC (sf@NGC)

The ColM was gently inserted within the PLGA hollow tube to obtain sf@NGC. The fabrication process of sf@NGC is showed in detail in Figure S1. Afterwards, the as-prepared sf@NGC was sterilized for further use.

3.5. Characterization

3.5.1. Fourier Transform Infrared (FTIR) Spectroscopy

The ColM samples were mixed with potassium bromide and compressed into pellets. FTIR spectroscopic measurements of the freeze-dried ColM samples were recorded on a Nicolet Avatar 360 spectrometer, performing 32 scans at a resolution of 1 cm^{-1} .

3.5.2. X-ray Diffraction (XRD) Analysis

The XRD patterns of the lyophilized ColM samples were determined by a D/MAX-RB RU-200B diffractometer using a Cu K α radiation source. Scanning was operated at 40 kV and 40 mA with $2\theta = 5\text{--}40^\circ$. The scanning rate and accumulation time were $2^\circ/\text{min}$ and 15 s for per step, respectively.

3.5.3. Thermal Properties

The thermal properties of pure collagen and the series of ColM samples were determined using a TGA Q500 calorimeter (TA Instrument, New Castle, DE, USA). Each sample prepared at same weight was scanned at a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen flow of $25\text{ mL}/\text{min}$. The thermogram curves were recorded between 25°C to 600°C for each sample.

3.5.4. Soluble Stability of the ColM Fillers

The ColM samples were incubated in three kinds of buffer solutions with pH values of 5 (acetate), 7 (PBS), and 9 (borate) at 37°C . After incubating for 3, 7, 14, and 28 days, the samples were removed and thoroughly washed with distilled water, followed by freeze-drying to determine the mass loss. Each sample was weighed at least three times, and the average weight was recorded.

3.5.5. Morphology Observation and Porosity Analysis

The microstructures of the PLGA nanofibrous tube and ColM fillers were examined by SEM (Hitachi S4800, Hitachi, Santa Clara, CA, USA). Before SEM observation, a thin layer of gold was applied to each sample as a coating. The porosity of the PLGA nanofibrous conduit and ColM fillers was measured by an automatic mercury porosimeter (AutoPore IV 9500, West Conshohocken, PA, USA) as previously described [25].

3.5.6. Permeability Analysis

The electrospun PLGA tube was firstly incubated in a saline solution for 24 h. Then, $50\text{ }\mu\text{L}$ of a glucose solution was injected into the tube, which was sealed completely, followed by incubation in PBS at 37°C for 24 h. The concentration of glucose in PBS after diffusion was measured by the GO kit, obtaining the percentage of glucose solution diffused through the wall into the outer PBS solution. As the concentration of the solution inside and outside the membrane was equal, the permeability of the fiber membrane was 100%.

3.5.7. Mechanical Property Analysis

The tensile strength of the PLGA nanofibrous membrane was acquired by a tension testing machine (Instron 5967, Instron, Norwood, MA, USA) equipped with a loaded cell of 100 N at 25°C . Rectangular samples were uniformly prepared with length and width of about 50 and 10 mm. Before testing, the top and bottom of the samples were secured in place with fixtures mounted on the testing machine to prevent them from slipping or moving. A 30 mm long gauge was used during each tensile experiment.

3.5.8. In Vitro Degradation Test

The biodegradability of the PLGA nanofibrous tube was determined by incubating the samples in PBS for various times at 37 °C. At preselected time intervals, the samples were removed and extensively rinsed with distilled water, followed by freeze-drying and weighing. The weight loss ratio was acquired by Equation (1):

$$\text{Weight loss ratio(\%)} = \frac{M_0 - M_t}{M_0} \times 100\% \quad (1)$$

where M_0 and M_t are the initial and post-degradation masses of the samples, respectively.

3.6. Biocompatibility Evaluation

SCs were cultured in complete DMEM containing 10% FBS and 1% penicillin/streptomycin at 37 °C in a 5% CO₂ environment. The in vitro biocompatibility of the PLGA nanofibrous tube and ColM fillers was examined using an extraction method in accordance with the ISO 10993-5 standardized testing procedure [40]. Briefly, the samples were sterilized by immersion in ethanol 75% for 24 h followed by rinsing with PBS and then air-dried by irradiation under a UV lamp for 1 h. The sterilized samples were incubated in culture medium containing 10% FBS at 37 °C for 24 h, and extracts were acquired by filtering out the degraded particles. After 2 days of cultivation, SCs were dyed with Hoechst 33342 and PI using a double-fluorescence staining kit for 15 min and thoroughly washed with PBS. Then, the stained SCs were observed using a fluorescence microscope (IX71, Olympus, Tokyo, Japan). The living cell ratio was calculated by counting the number of alive and dead cells in the Hoechst 33342/PI staining acquired images using Image J 1.46r, National Institute of Health, USA ($n = 50$).

The viability of the cells was studied by a modified MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] assay. Specifically, SCs were seeded at a density of 1×10^3 cells per well in 96-well culture plates and left adhere. After cellular adhesion, the culture medium was substituted with 100 µL of the extracts, and the cells were incubated at 37 °C in 5% CO₂ for 1, 3, and 7 days. Subsequently, the extracts were removed, and the cells were incubated in 25 µL of MTT at 37 °C for 4 h. The reaction solution in each well was then substituted with 100 µL of DMSO to obtain the dissolution of blue formazan. Afterwards, the optical density (OD) at the wavelength of 490 nm was examined using a Bio-Tek (Winooski, VT, USA) Synergy HT microplate reader ($n = 6$).

3.7. Statistical Analysis

All data are expressed as means $\pm$ standard deviation (SD) of at least triplicate measurements. Statistical comparisons were evaluated using SPSS Statistics 24.0 software. Before conducting the statistical analysis, the data were tested for equal variances and normality. Values exhibiting unequal variances were subjected to log transformation and subsequently reassessed for equal variances. Differences between the groups were assessed for significance using one-way analysis of variance (ANOVA) followed by Tukey's post hoc test. Differences were considered significant at $p < 0.05$.

4. Conclusions

In summary, the development of a biomimetic sf@NGC construct that mimics the architecture of native peripheral nerves was successfully achieved. sf@NGC consists of a PLGA tube and a ColM intraluminal filler. First, ColM was successfully developed through Schiff base linkage between amino groups in collagen and aldehyde groups in OBC, resulting in enhanced stability compared to pure collagen. Among all ColM specimens, ColM2 and ColM3 with crosslinking degrees of 6.8% and 5.7% showed optimal stability in acid environment. The ColM fillers exhibited a high porosity of 70% and an ECM-like architecture with an interconnected multistage pore structure. Second, homogenous and uniform PLGA nanofibers were obtained by optimizing solution concentration, spinning voltage, and liquid flow rate at 15 wt%, 15 kV, and 0.4 mL/h, respectively. The PLGA

200 tube exhibited considerable properties with a porosity of $64.5 \pm 2.3\%$, a pore size of $11.8 \pm 1.7 \mu\text{m}$, and a tensile strength of 3.1 MPa. Third, studies conducted in vitro verified the biocompatibility of both the PLGA tube and ColM. This was demonstrated by the similar morphology and comparably high survival rates of SCs grown in the various conditioned media and control SCs and by the lack of significant differences in the OD value between treated SCs and control SCs. Overall, the combination of a PLGA nanofibrous conduit and ECM-like ColM fillers mimics the architecture of natural nerves and provides a supportive environment for cell growth, migration, and tissue regeneration. This research presents a novel approach for the treatment of large-gap nerve defects, aiming to achieve comprehensive innervation.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules28227675/s1>, Figure S1: Schematic illustration of the fabrication of sf@NGC; Table S1: Sample codes and crosslinking degree of the ColM fillers. Reference [41] is cited in the Supplementary Materials.

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Article

Gallium-Doped Hydroxyapatite: Shape Transformation and Osteogenesis Activity

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Abstract: In this study, we employed a chemical precipitation method to successfully synthesize nanoparticles of gallium-doped hydroxyapatite (Ga-HAp). The microstructure of Ga-HAp was precisely tailored by modulating the concentration of gallium ions. Our findings unequivocally demonstrate that gallium ions exert a pronounced inhibitory influence on the growth of HAp crystals, and this inhibitory potency exhibits a direct correlation with the concentration of gallium. Furthermore, gallium ions facilitate the metamorphosis of HAp nanoparticles, transitioning them from nanoneedles to nanosheets. It is worth noting, however, that gallium ions exhibit a limited capacity to substitute for calcium ions within the crystal lattice of HAp, with the maximum substitution rate capped at 4.85%. Additionally, gallium plays a pivotal role in constraining the release of ions from HAp, and this behavior remains consistent across samples with varying Ga doping concentrations. Our in vitro experiments confirm that Ga-doped HAp amplifies both the proliferation and osteogenic differentiation of bone marrow mesenchymal stem cells.

Keywords: gallium; hydroxyapatite; osteogenesis

1. Introduction

Natural bone tissue possesses a hierarchical structure characterized by the precise arrangement of inorganic minerals and an organic matrix. This intricate configuration imparts robust mechanical properties to bone tissue, ensuring the protection of human tissues and enabling essential mobility functions [1]. Although bone tissue exhibits innate self-repair capabilities, surgical implantation of bone or bone-like tissue becomes imperative when bone defects exceed a critical size, thereby promoting effective bone tissue regeneration [2,3].

Biomimetic ceramics, particularly hydroxyapatite (HAp), are widely employed for bone regeneration due to their chemical composition resembling that of natural bone minerals [4–6]. This similarity grants HAp exceptional biocompatibility, bioactivity, and osteogenic potential, which has garnered significant interest. However, pure-phase HAp faces challenges in bone repair, including a slow degradation rate and limited osteoinductive activity [7]. Furthermore, it struggles to address the demands of repairing bone defects arising from pathological conditions such as infections, tumors, and osteoporosis [8]. While achieving these functionalities through drug loading is conceivable, challenges remain in terms of restricted drug loading capacity, intricate control of drug release behavior, and achieving sustained drug release [9,10].

In bone tissue, a diverse array of trace elements, including Mg, Zn, Sr, Fe, Mn, Ga, and even rare earth elements, play pivotal roles in the intricate process of bone regeneration. Typically, calcium ions within the hydroxyapatite structure readily undergo substitution

with other metal ions, resulting in the creation of numerous defects. Consequently, this leads to a reduction in crystallinity coupled with an increase in solubility, ultimately culminating in the substantial release of bioactive ions in localized regions, thereby amplifying the material's osteogenic and angiogenic activity. Extensive research is thus devoted to enhancing the bone repair performance of hydroxyapatite through ion doping [11,12].

Gallium (Ga), a metallic element discovered by chemist Paul in 1875, is positioned in the third main group of the periodic table. Its pronounced affinity for tissue growth and remodeling, including bone and tumor tissues, has been elucidated through extensive research [13]. Within the realm of bone tissue, Ga's potential for anti-resorptive effects has garnered significant attention [14]. Clinical applications of Ga can be categorized into two types: firstly, the suppression of bone resorption and associated pain caused by multiple myeloma and bone metastasis [15]; secondly, the addressing of hypercalcemia induced by malignant tumors [16]. Furthermore, Ga finds application in treating osteitis deformans (Paget's disease of bone) [17]. In vitro studies have revealed that Ga can effectively inhibit osteoclast differentiation and bone resorptive activity without affecting osteoblasts, thus mitigating the risk of bone fractures. Deeper investigations have demonstrated that Ga achieves the suppression of osteoclast differentiation by inhibiting NFATc1 expression [18]. Osteoporosis, characterized by diminished bone density and degradation of bone microstructure, resulting in reduced bone toughness and heightened fracture susceptibility, represents a systemic ailment. Bisphosphonates have demonstrated commendable effectiveness in elevating bone density, curbing bone loss, and diminishing fracture risk within clinical practice. However, their requirement for long-term, regular medication administration poses considerations [19,20].

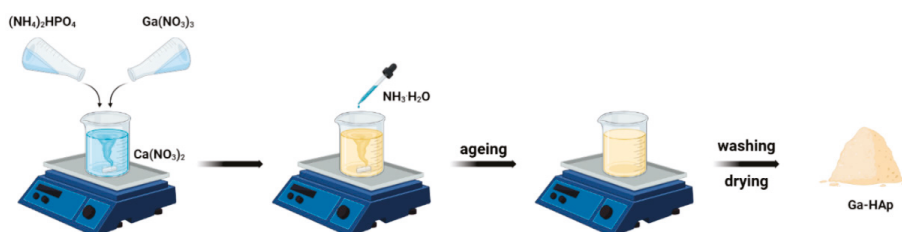
Moreover, numerous studies have highlighted Ga's capacity to impede the nucleation and growth of HAp crystals [21]. Surprisingly, scant attention has been paid in the literature to the impact of Ga on the microscopic morphology of HAp nanoparticles, despite the profound connection between particle topology and the osteogenic differentiation behavior of mesenchymal stem cells. Furthermore, Ga, being a trivalent metal ion, engenders ongoing debate regarding its potential for high-dose, stable doping within HAp crystals in mild synthesis systems.

Given Ga's promising osteogenic activity and its affinity with HAp crystals, we successfully synthesized Ga-doped HAp nanoparticles via the chemical precipitation method. Our study comprehensively investigated the influence of Ga incorporation on the crystal structure, morphology, and phase composition of HAp crystals. Furthermore, we assessed the potential effects of Ga-doped HAp powder and bulk materials on the proliferation and osteogenic differentiation behavior of bone marrow mesenchymal stem cells.

2. Results and Discussion

In this study, Ga-doped hydroxyapatite (Scheme 1) was synthesized using the chemical precipitation method (Scheme 1). In the context of synthesizing HAp, the incorporation of additional ions not only exerts an influence on the crystallinity and lattice structure of HAp, but also plays a role in modulating the aggregation behavior of nanocrystals [12,22]. Consequently, distinctive micro–nano morphologies emerge in the final product. In the present investigation, the introduction of Ga into the HAp synthesis process was pursued. Examination of SEM images unveiled the fact that Ga integration could effectively mitigate the inherent self-aggregation tendencies of nanocrystals (Figure 1). Moreover, research studies have indicated that Ga has the capacity to hinder the growth of HAp crystals, resulting in the formation of smaller particles [23,24]. However, it is important to note that this particular conclusion cannot be directly inferred from Figure 1. It is noteworthy that while the extent of Ga doping is proportional to the concentration of Ga in the reaction solution, the ultimate quantity of Ga incorporated into the crystal lattice of HAp remains relatively modest. In the case of 10 Ga-HAp, the Ga doping level stands at a mere 0.76% (in atomic percentage). Even in 50 Ga-HAp, the doping level only reaches 4.85%. This

observation points to the challenge Ga encounters in effectively integrating into the crystal lattice of HAp.



Scheme 1. Schematic of Ga-doped hydroxyapatite synthesis.

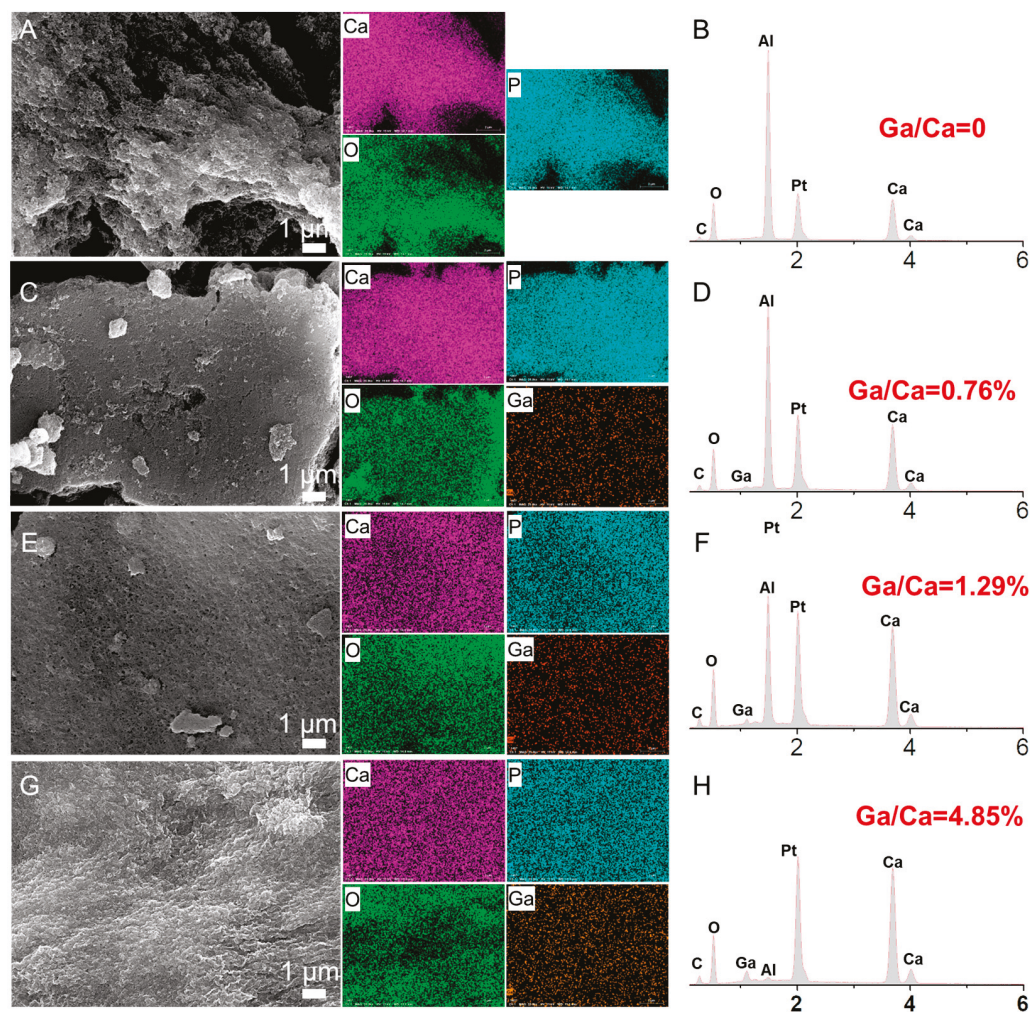


Figure 1. SEM images, EDS mapping and spectra of Ga-HAp with different Ga concentrations. (A,B) HAp, (C,D) 10 Ga-HAp, (E,F) 25 Ga-HAp, (G,H) 50 Ga-HAp.

To further validate the SEM results, we conducted detailed examinations of the product morphology using TEM (Figure 2). From the TEM results, it can be observed that when Ga was not present in the reaction system, the product primarily consisted of nanorod-shaped particles with a length of approximately 100 nm (Figure 2A,B). Additionally, scattered nanosheet-like particles were also observed within the field of view. The surface of these nanosheet structures exhibited an ordered stacking arrangement of nanorod-shaped particles in the two-dimensional direction. At a Ga doping concentration of 10%, the length of the nanorod-shaped particles shortened, and their quantity decreased relatively, indicating that the introduction of Ga inhibited the growth of nanorod-shaped particles along their

long axis (Figure 2C,D). When the Ga doping level reached 25%, the product consisted mainly of nanosheet-like structures, although isolated nanorod-shaped particles could still be observed (Figure 2E,F). With a further increase in Ga doping to 50%, the product consisted predominantly of nanosheet-like particles (Figure 2G,H). However, it is worth noting that while the size and quantity of nanorod-shaped particles changed significantly with increasing Ga content, the size of nanosheet-like particles remained relatively unchanged. In a word, Ga incorporation was found to inhibit the growth of nanorod-shaped units, particularly along their long axis, while having minimal impact on the assembly of nanorod-shaped particles in the two-dimensional direction. This ultimately resulted in a shift from nanorod-shaped particles being the predominant form to nanosheet-like structures becoming predominant as the Ga content increased.

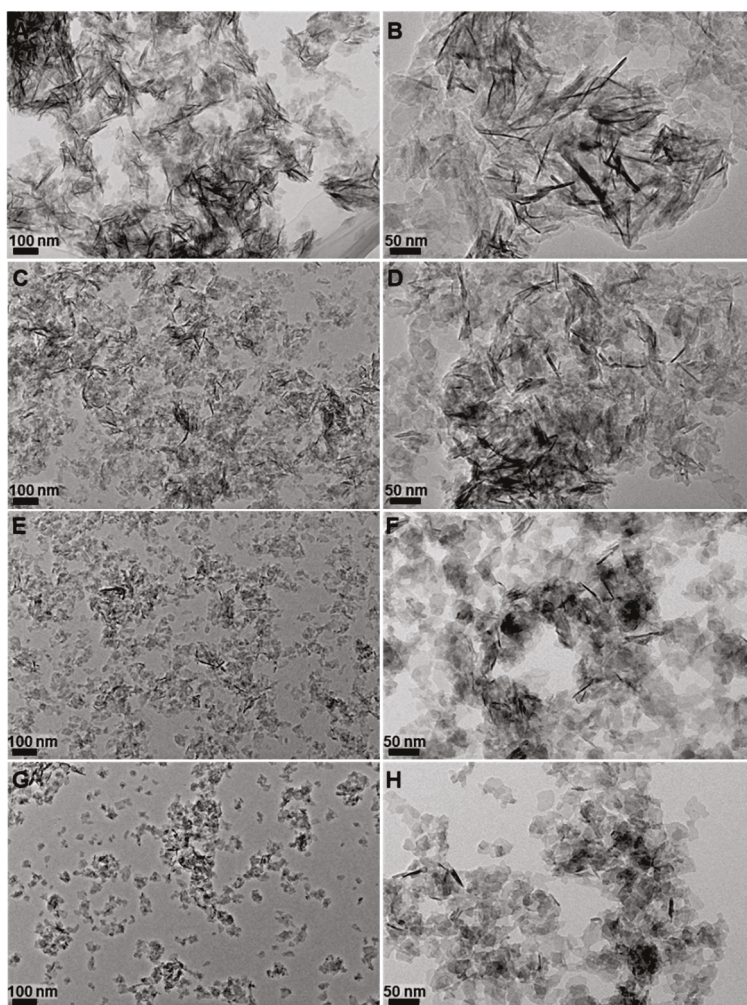


Figure 2. TEM images of Ga-HAp with different Ga concentrations. (A,B) HAp, (C,D) Ga/Ca = 1/9, (E,F) Ga/Ca = 1/4, (G,H) Ga/Ca = 1/1.

We conducted XRD analysis to investigate the crystal phase of the product (Figure 3). The results revealed that no other crystal phases were present in the product apart from the HAp crystal phase, indicating that the introduction of Ga did not lead to the formation of other crystal phases. Additionally, it is noteworthy that previous research has reported Ga's ability to inhibit the nucleation and growth of HAp crystals [25]. Therefore, relative to the HAp control samples, the introduction of Ga should result in a reduction in crystallinity, manifesting as broadening of XRD peaks. The crystalline peak at around 25° corresponds to the (002) crystal plane diffraction of HAp. It can be observed from the XRD pattern that with the introduction of Ga, the relative intensity of the (002) crystal plane diffraction

peak decreased. Hence, we can deduce that Ga can inhibit the preferential growth of HAp along the c-axis direction. Furthermore, as the amount of introduced Ga increased, the (002) crystal plane exhibited a shift towards higher angles. This observation suggests that the incorporation of Ga induces a contraction in the unit cell volume of hydroxyapatite. This phenomenon can be attributed to the smaller ionic radius of Ga (0.062 nm) in comparison to Ca (0.099 nm). Notably, this outcome corroborates findings reported in other studies [26]. Combining these results with the TEM analysis, it is apparent that during the synthesis process, HAp tends to spontaneously grow along the c-axis, leading to the formation of rod-shaped nanocrystals, with the long axis of the nanorods aligned along the c-axis. However, the introduction of Ga suppresses the growth of nanorods along their long axis, thereby inhibiting their c-axis-oriented growth tendency. As the Ga content increases, this inhibitory effect becomes more pronounced [23]. Furthermore, the results of the FTIR analysis indicate that the introduction of Ga does not lead to significant changes in the chemical composition of the product (Figure 4). Simultaneously, the results reveal distinct carbonate absorption peaks in the infrared absorption spectrum. These carbonate ions might originate from the hydration of carbon dioxide in the air during the synthesis process, leading to the formation of carbonate ions. These carbonate ions then enter the HAp lattice, resulting in the formation of carbonated hydroxyapatite. This phenomenon has been extensively reported in the literature [27,28].

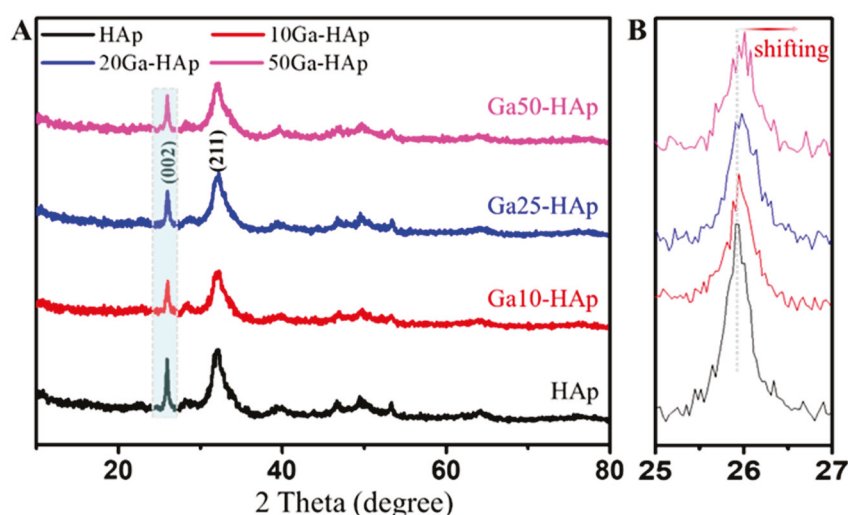


Figure 3. (A) XRD patterns of Ga-doping HAp with different Ga concentrations; (B) enlargement of the diffraction peak of the (002) lattice plane of the samples.

The Ca and Ga ion-release profiles of the products before and after Ga^{3+} doping are shown in Figure 5. The results indicate that the doping of Ga ions significantly reduces the release level of Ca ions in pure HAp. After 14 days of release, the Ca ion release from pure-phase HAp particles is approximately 700 μg , while after Ga^{3+} doping, the Ca ion release from the product decreases to around 400 μg , indicating that Ga ion doping can significantly inhibit the dissolution of HAp crystals. This observation aligns with findings reported in other literature [29], supporting the clinical use of Ga to treat conditions such as hypercalcemia caused by bone cancer [30]. Upon ingestion of soluble gallium salts by the body, Ga deposits within bone mineral tissue, inhibiting mineral dissolution behavior and consequently lowering the blood Ca^{2+} levels [31]. It is noteworthy that, with increasing Ga doping levels, there are no significant differences observed in the release levels of either Ca^{2+} or Ga^{3+} among the three groups of doped samples. This could be attributed to the overall higher levels of Ga doping, resulting in similar dissolution behaviors in the doped samples.

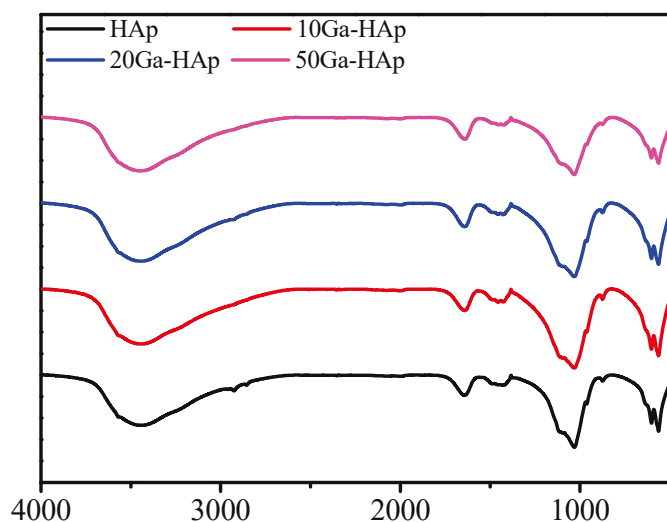


Figure 4. FT-IR spectra of Ga-doping samples with different Ga concentrations.

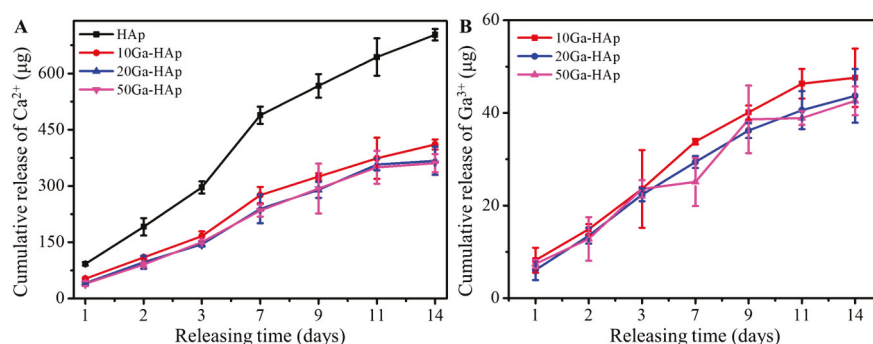


Figure 5. (A) Cumulative releasing profile of Ca^{2+} from the as-prepared powders; (B) Cumulative releasing profile of Ga^{3+} from the as-prepared powders.

Research has revealed the potential cytotoxicity of micro–nanoparticles [32,33]. To validate the biocompatibility of Ga-doped HAp particles, we investigated cell proliferation after co-culturing the powder with cells (Figure 6A). The results demonstrate that pure-phase HAp exhibits an inhibitory effect on cell proliferation, while this inhibitory effect diminishes upon Ga doping of HAp. This phenomenon might be attributed to the potential of high concentrations of Ca^{2+} released by low-crystallinity HAp to inhibit cell proliferation. Ga doping, however, lowers the release levels of Ca^{2+} , thereby reducing the inhibitory effect of the powder on cell proliferation.

Subsequently, we further examined cell proliferation behavior on the surface of bulk materials (Figure 6B). The results demonstrate that both HAp and Ga-doped HAp exhibit excellent biocompatibility. After 1 day of cultivation, cells on the material surface maintain good activity. As the cultivation period extends to 5 days, Ga-doped samples are more conducive to cell proliferation compared to the undoped samples. However, no significant differences are observed among the 10 Ga-HAp, 20 Ga-HAp, and 50 Ga-HAp groups. Studies have indicated that under in vitro culture conditions, a certain concentration of Ca^{2+} can promote osteoblast proliferation, while high concentrations of Ca^{2+} can exhibit inhibitory effects on cell proliferation [34]. The lower calcium ion release rate of the Ga-doped materials compared to undoped HAp might be the direct reason for the enhanced cell proliferation behavior, as evident from the ion release results [35]. Furthermore, due to the similar ion release behaviors among the three Ga-doped groups, no significant differences are detected among them.

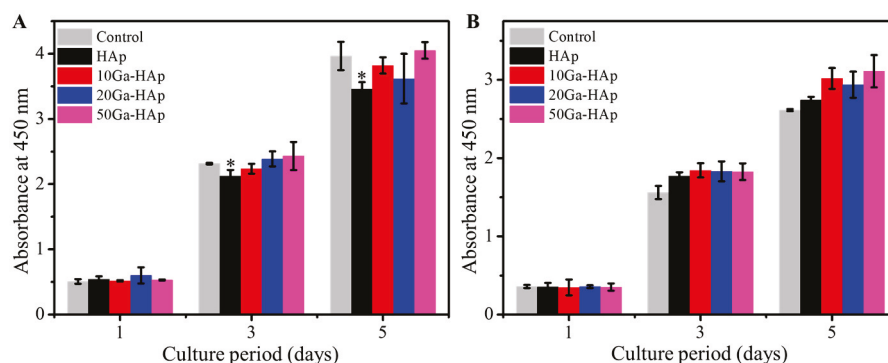


Figure 6. (A) Proliferation of mBMSCs with the HAp and Ga-doped-HAp powders; (B) Proliferation of mBMSCs with the HAp and Ga-doped-HAp bulks. Polystyrene discs with a diameter of 1 cm were used as a control group, and * represents that a significant difference exists as compared with the control group.

As the ion release behavior and biocompatibility of the three groups of Ga-doped HAp samples were comparable, we selected 10 Ga-HAp for further investigation of its osteogenic activity, with GaOOH used as the control group (Figure 7). HAp significantly upregulates the expression of the ALP gene, and this enhancing effect is well maintained, even after extending the cultivation time to 14 days. However, when Ga is introduced into the material, the promotion of ALP gene expression by 10 Ga-HAp is less pronounced. Similarly, HAp promotes the expression of the ColI gene in osteoblasts, but the modified materials exhibit a certain degree of attenuation in upregulating cell osteogenic differentiation compared to pure HAp. Notably, at 14 days of induction culture, there is a significant difference between the 10 Ga-HAp group and the control group, but the difference compared to the HAp is not as apparent. The expression peak of the OC gene during osteogenic differentiation corresponds to the mature stage of cells, where a large number of calcium nodules appear in the culture environment, facilitating new bone formation. The results indicate that pure-phase HAp is most effective in upregulating OC gene expression, and after 14 days of culture, both the HAp and 10 Ga-HAp groups can promote OC gene expression.

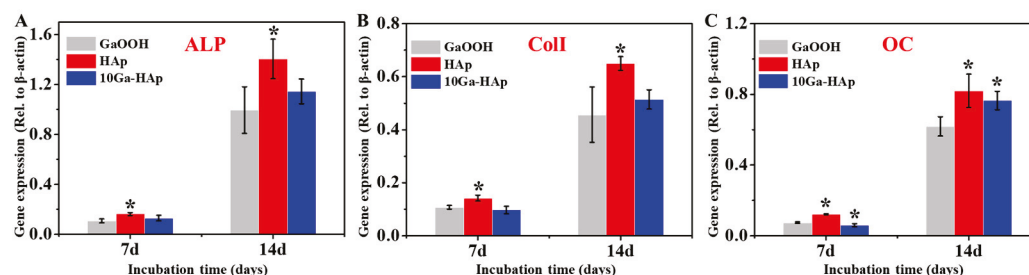


Figure 7. Relative expression level of ALP (A), ColI (B), and OC (C) as cultured on the surface of the bulk materials for 7d and 14d. GaOOH discs with a diameter of 1cm were used as a control group. * represents that a significant difference exists as compared with the control group.

Ca^{2+} is ubiquitous in living organisms and is closely associated with various cellular processes such as fertilization, mitosis, neurotransmission, muscle contraction and relaxation, gene transcription, and cell death. Generally, the intracellular calcium ion concentration is around 100 nM, but it can increase to 500–1000 nM under external stimuli [36]. Additionally, different calcium ion concentrations have a significant impact on osteoblast behavior. Shinichi et al. [35], using type II collagen loaded with varying concentrations of Ca^{2+} as a model, studied the effects of different Ca^{2+} concentrations on osteoblasts. They found that calcium ion concentrations of 2–4 mM were conducive to maintaining cell viability and promoting cell proliferation, while an environment with 6–8 mM Ca^{2+} favored osteoblast differentiation. However, when calcium ion concentration exceeded 10 mM, it

led to some cytotoxicity. Another study by Ekolou-Kalonji et al. [37] revealed that when calcium ion concentration was between 2 and 5 mM, there were no significant changes in cell proliferation behavior, but differentiation rates decreased with higher calcium ion concentrations. Further increasing calcium ion concentration to 7–10 mM resulted in a decrease in both osteoblast proliferation and differentiation behavior.

In this study, both HAp and Ga-HAp continuously released Ca^{2+} during cell culture, participating in various cellular processes. The introduction of Ga led to a decrease in the rate of ion dissolution from the material, consequently resulting in a relatively lower calcium ion concentration in the culture medium compared to the HAp group. This might explain the differences in the promotion of osteogenic gene expression levels between the two materials. The consistent expression of the OC gene in the later stages of culture suggests that as the culture time extends the expression of the OC gene becomes less sensitive to changes in Ca^{2+} concentration within a certain range.

3. Materials and Methods

3.1. Preparation of Ga-Doped HAp

A total of 10 mL of 0.1 mol/L $\text{Ga}(\text{NO}_3)_3$ solution and 90 mL of 0.1 mol/L $\text{Ca}(\text{NO}_3)_2$ solution were mixed, and the mixture was continuously stirred for 30 min. Subsequently, 60 mL of 0.1 mol/L $(\text{NH}_4)_2\text{HPO}_4$ solution was added dropwise to the above mixture, while maintaining high-speed stirring during the reaction. After 30 min of reaction, the pH of the solution was adjusted to 10 using ammonia solution. Following 24 h of stirring at room temperature, the precipitate particles were washed three times with deionized water, separated by centrifugation, and then transferred to a 50 °C oven for 24 h of drying, resulting in Ga-doped HAp. According to the molar ratio of $\text{Ga}/(\text{Ga}+\text{Ca})$, the sample was labeled as 10 Ga-HAp. Additionally, we obtained HAp, 20 Ga-HAp, and 50 Ga-HAp samples by varying the content of Ga and utilizing the synthesis method described above.

3.2. Material Characterization

The phase composition of the inorganic powders was analyzed using an X-ray diffraction spectrometer (XRD; X'Pert PRO, PANalytical Co., Amsterdam, The Netherlands) with a working voltage of 40 kV and current of 40 mA. The scanning range was 10° to 80°, and the scanning speed was 2°/min. Scanning electron microscopy (SEM, Carl Zeiss Sigma NTS GmbH, Oberkochen, Germany) and transmission electron microscopy (TEM; FEI, Tecnai G220, Oregon, OR, USA) were employed to observe the microstructure and morphology of the products. The chemical composition of the products was analyzed using Fourier-transform infrared spectroscopy (FTIR; Nicolet IS 10, ThermoFisher Scientific, Waltham, MA, USA), with a spectral scanning range of 4000 to 400 cm^{-1} .

3.3. Cumulative Release Profile of Ca and Ga Ions from the Powders

We weighed 40 mg of powder and placed it in 20 mL of PBS solution. Subsequently, we centrifuged it at specific time points, collected 5 mL of the supernatant, and replaced with an equal volume of fresh PBS solution to mix in the release system. We measured the concentration of calcium ions (Ca^{2+}) and gallium ions (Ga^{3+}) in the collected samples using inductively coupled plasma mass spectrometry (ICP-MS, NexION 350X, PerkinElmer, Shelton, CT, USA).

3.4. Cell Culture

Mouse bone marrow mesenchymal stem cells (BMSCs, CRL-12424, ATCC) were utilized to investigate the cytocompatibility and osteogenic activity of the powder particles and bulk materials. The cells were cultured in DMEM medium containing 10% fetal bovine serum, 100 IU/mL penicillin, and 0.1 mg/mL streptomycin. The culture environment was maintained at 5% carbon dioxide and 37 °C with humidity. The culture medium was changed every two days during cell cultivation. When the cell confluence reached 80–90%,

the cells were detached using 0.25% trypsin-EDTA solution and centrifuged at $125\times g$ to separate the cells. The cells used in this experiment were from the 5th passage.

3.5. Biocompatibility Evaluation of the Powder and Bulk Materials

Cells were seeded into 24-well plates at a density of 1×10^4 cells per well, with 1 mL of culture medium added to each well, and then incubated overnight. Sterile powder was dispersed in the cell culture medium at concentrations of 200 $\mu\text{g/mL}$. After co-culturing the cells with the powders for 1, 3, and 5 days, the cell numbers were determined using the CCK-8 assay kit to assess cell proliferation status in the co-culture system.

Simultaneously, we assessed the biocompatibility of the bulk material products. A quantity of 0.2 g of powder was poured into a mold, and the mold was subjected to pressure at 4 MPa for 5 min. After pressure release, the circular samples (1 cm in diameter) were removed from the mold, soaked in 75% ethanol overnight, and then washed three times with PBS for further use. Additionally, polystyrene discs with a diameter of 1 cm were used as a control group. Before the bulk materials were transferred to a 24-well plate, the well was treated with agarose, and then 20 μL of cell suspension containing 5×10^3 cells was dropped onto the surface of the bulk materials. After incubating for 2 h, 1 mL of culture medium was added. The CCK-8 assay kit was used to measure cell proliferation on the co-cultured bulk materials for 1, 3, and 5 days.

3.6. In Vitro Effects of Ga-Doped HAp Powders and Bulk on Osteoblastogenesis

A total of 2×10^4 cells were seeded onto the surface of the bulk materials, and GaOOH, prepared using the coprecipitation method, was used as the control group. After 1 day of incubation in growth medium, the osteogenic induction medium (RASMIX-90021, Cyagen Biosciences, Inc., Santa Clara, CA, USA) was substituted for the growth medium. This was replaced with fresh medium every 2 days. After co-culturing for 14 days, the expression levels of osteogenic-related genes such as type I collagen (ColI), alkaline phosphatase (ALP), and osteocalcin (OC) were detected using real-time polymerase chain reaction (RT-PCR) technology.

3.7. Statistical Analysis

In this study, experimental data were presented as the mean $\pm$ standard deviation (mean $\pm$ SD). One-way analysis of variance (ANOVA) and Tukey's multiple comparison test were performed using SPSS software to analyze the data. Statistical significance was confirmed when the p -value was less than 0.05.

4. Conclusions

In conclusion, this study successfully synthesized highly concentrated Ga-doped HAp material. The introduction of Ga directly influenced the growth behavior of HAp crystals, inhibiting their oriented growth along certain directions. With increasing Ga doping content, the morphology of the particles transitioned from nanoneedles to nanosheets. Additionally, Ga incorporation significantly reduced the dissolution rate of HAp crystals, thereby enhancing the material's biocompatibility and promoting the proliferation of mBM-SCs. In comparison to pure HAp, Ga-doped HAp exhibited a weakened osteoinductive potential. Furthermore, the study results indicated that GaOOH could also serve as a potential osteogenic material. This research provides valuable insights for the development of novel Ga-doped ceramic materials for bone repair applications.

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Article

High Hardness, Excellent Hydrophobicity, and Favorable Corrosion Resistance of Plasma-Sprayed FeCrMoSi Amorphous Coatings on 304 Stainless Steel

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Abstract: The FeCrMoSi amorphous coatings were fabricated on the surface of a 304 stainless steel (SS) base material using atmospheric plasma spraying. A comprehensive investigation was carried out to evaluate the structure, morphology, adhesion to base material, hardness, hydrophobicity, interfacial contact resistance, and corrosion resistance of the coatings. The results show a remarkable hardness of 1180.1 HV, a strong bond strength of up to 64.3 N/mm², and excellent hydrophobicity with a water contact angle reaching 141.2°. Additionally, in an acidic environment with fluoride ions (0.5 M H₂SO₄ + 2 ppm HF, 80 °C), the FeCrMoSi amorphous coating demonstrated superior corrosion resistance compared with 304 SS while maintaining similar electroconductibility. Detailed analysis of the structural characteristics and corrosion resistance of FeCrMoSi amorphous coatings provided valuable insights into their mechanics. These promising results signify a bright future for FeCrMoSi amorphous coatings in various industrial sectors, including transportation, petroleum, and electric power industries.

Keywords: FeCrMoSi amorphous coating; corrosion resistance; hardness; hydrophobicity; bonding strength

1. Introduction

304 Stainless Steel (SS) is widely used in the manufacture of equipment and machine parts that require superior all-round performance [1,2]. One of its most notable properties is excellent corrosion resistance. This is due to the high Cr content, which forms a stable Cr oxide layer on the surface of the 304 SS [3,4]. This not only provides effective protection against water, oxygen, and many chemicals but also makes it the material of choice in wet, acidic, alkaline, and corrosive environments [5]. It also has appropriate strength and temperature resistance. This allows it to be used in a wide range of applications including construction, manufacturing, chemical, and high temperature applications [6]. Despite its superior corrosion resistance and durability, the Cr oxide layer of 304 SS may not be sufficient to provide adequate protection in some extreme corrosive environments [7,8]. Therefore, it is necessary to apply anticorrosion coatings to the surface of 304 SS to increase its corrosion resistance [9]. Corrosion-resistant coatings play a crucial role in safeguarding base materials from corrosion or retarding the rate of corrosion. For different corrosive environments, a wide array of such coatings have been developed. For example, Meghwal et al. found that AlCoCrFeNi high-entropy alloy coating exhibited better corrosion resistance than that of 316 L SS in seawater [10]. Similarly, Duran et al. discovered that poly(N-vinyl carbazole) films can provide anodic protection and reduce the corrosion rate

of 304 SS by six times in sulfuric acid solution [11]. Additionally, Sun et al. deposited Cr–Al coating on 304 SS and found it to have good corrosion resistance under static lead–bismuth eutectic [12].

Amorphous alloy coatings are highly popular and cost-effective choices for corrosion resistance coatings. They can be easily prepared by thermal spraying techniques. In this process, raw material powder is heated to a molten or semi-molten state, then accelerated using a high-speed flame to coat the surface of the base material. In most cases, thermal spray coatings demonstrate remarkable protection to the base material by providing favorable resistance to corrosion, wear, and oxidation. Currently, thermal spraying technologies include flame spraying [13], arc spraying [14], plasma spraying [15,16], supersonic flame spraying [17], and explosive spraying [18]. Among these technologies, plasma spraying, which has been widely applied to protect metal base materials in industrial production by improving their corrosion resistance, wear resistance, and microhardness, is frequently used [19]. For example, Zhao et al. used atmospheric plasma spraying (APS) to deposit a Mo-based amorphous nanocrystalline coating on the surface of ordinary carbon steel base material. They found that the hardness and the abrasiveness of the carbon steel with the coating were significantly increased compared with the base material [20]. The fabrication of amorphous coatings by APS cannot only achieve large area construction, simple operation, and low cost but also does not lose the intrinsic excellent properties of amorphous raw materials. Therefore, APS is a simple and efficient way to fabricate amorphous coatings.

Fe-based amorphous coatings have also emerged as a cost-effective solution, offering high hardness and excellent wear resistance [21,22]. For instance, Hamid et al. deposited Fe-based amorphous coatings using high-velocity oxygen fuel (HVOF) spraying, showcasing remarkable ability to resist friction and wear performance [23]. Meanwhile, Cao et al. fabricated a crack-free Fe-based amorphous coating on a 304 SS base material using laser processing technology. Their findings suggested that the amorphous phase of the coating and its optimized microstructure significantly increased the hardness with a favorable effect on the coefficient of friction and wear rate [24]. Qiao et al. fabricated a superhydrophobic Fe-based amorphous coating using APS on a Q235 steel base material and demonstrated that the coating had an ultra-high microhardness and good antiwear properties [25]. These previous studies confirmed that Fe-based amorphous coating could be simply fabricated to provide good protection to the base material. However, the corrosion resistance and corresponding mechanism of Fe-based amorphous coatings to a harsh acidic environment remain unclear to date.

This study focuses on the fabrication of FeCrMoSi amorphous coatings through APS on a 304 SS base material. A comprehensive investigation was conducted, covering the structure, morphology, hydrophobicity, bonding strength to the base material, and corrosion resistance in a mixed sulfuric acid and hydrofluoric solution at 80 °C, as well as the interface contact resistance of the coatings.

2. Results and Discussion

2.1. Structure and Morphology

The phase structure of FeCrMoSi alloy raw materials powder and as-fabricated FeCrMoSi amorphous coatings were examined using X-ray diffraction (XRD); the XRD patterns are presented in Figure 1a. The XRD pattern of the raw materials exhibited a single broadened and diffused diffraction peak at approximately 43°. This indicates that the FeCrMoSi alloy raw materials are in a completely amorphous state. Similarly, each XRD pattern of the coatings also exhibited a broadened and diffused diffraction peak around 43°, consistent with that of the raw materials, further confirming that the coatings are predominantly in an amorphous state. However, in each XRD pattern of the FeCrMoSi amorphous coatings, a small sharp peak at about 35°, which could be attributed to Fe₃O₄, was observed [25,26]. This finding suggests the occurrence of a certain oxidation reaction during the fabrication of the coatings by APS. In addition, the bright field transmission electron microscopy (TEM) images of FeCrMoSi amorphous coatings show a typical amorphous morphology

(Figure 1b) and the corresponding selected area electron diffraction (SAED) pattern only shows a typical diffuse ring. Consequently, both XRD patterns and TEM observation demonstrated that FeCrMoSi amorphous coatings with high amorphous phase content may contain a very small amount of crystalline structure.

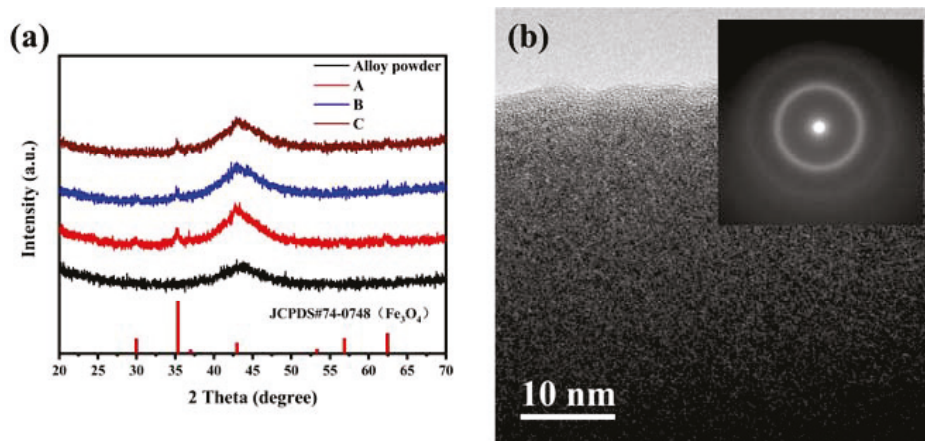


Figure 1. (a) XRD patterns of FeCrMoSi alloy powder raw materials and as-fabricated FeCrMoSi amorphous coatings; (b) TEM image and the corresponding SAED pattern (in set).

The surface morphology of the coatings and the interface between the coatings and the base material were observed using scanning electron microscopy (SEM); the images are depicted in Figure 2. Each coating (Figure 2a–c) exhibited partially molten particles and micropores. The number of partially molten particles on the surface gradually decreased with the increase in applied current during APS. Among the coatings, coating C displayed the highest degree of melting under a current of 600 A. The high-temperature molten FeCrMoSi alloy particles experienced rapid impact on the surface of the 304 SS base material during APS. Some particles were fully deformed, forming a typical layered structure and resulting in a certain smooth surface, meanwhile others remained spherical after APS, leading to incomplete packing between molten flat particles and the appearance of a small number of pores. Additionally, the cold shrinkage of molten flat particles during solidification may have contributed to the formation of some pores [24]. Figure 2d–f show the cross-sectional morphologies of the coatings. With increasing current, the presence of pores in the coatings reduced. However, even at the maximum current, some pores persisted between the coatings and the 304 SS base material. These pores can be found to be oxygen-rich by X-ray energy dispersive spectroscopy (EDS) mapping (Figure 2g,h). These phenomena may be attributed to slight oxidation in air [27], considering that the raw materials needed to be heated to their melting temperature during APS. Subsequently, the chemical composition of the FeCrMoSi amorphous coatings was examined using EDS and the results are summarized in Table 1. The chemical composition of the as-fabricated coatings generally reflects that of the FeCrMoSi alloy powder raw materials, with slight oxidation observed. The elemental distribution of coating C and the base material was measured by EDS line scanning and the results are shown in Figure 2i. It is seen that the coating mainly contains the elements Fe, Cr, and Mo and the distribution of these three elements is uniform. Comparing to 304 SS base materials, the Cr content in the coating is slightly lower than that of 304 SS. The Fe content in the coating is largely lower than that of 304 SS. Meanwhile, 304 SS base material does not contain Mo element. Previous studies have shown that adding Mo to an alloy can form a protective film on the surface, which can effectively prevent further corrosion inside the alloy [28]. Furthermore, the migration or diffusion of the alloying elements from the base material to the coating and vice versa may occur during the coating process. However, the current EDS line scanning does not detect this phenomenon, which can be further studied in the future.

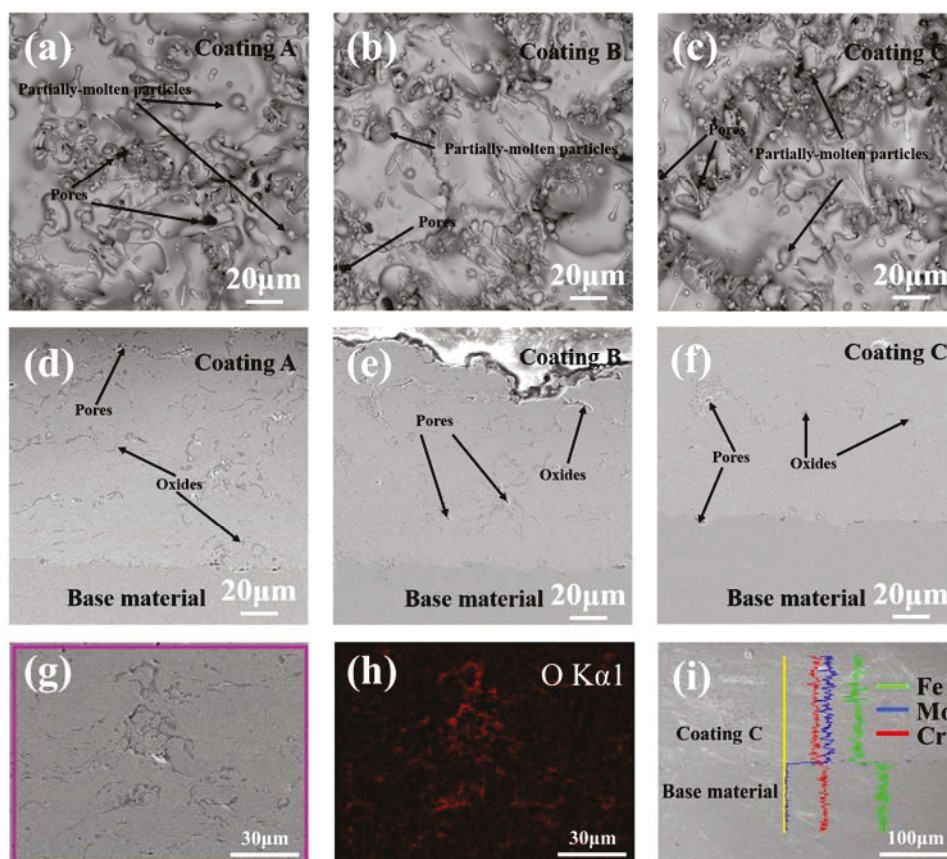


Figure 2. SEM images of FeCrMoSi amorphous coatings: surface morphologies of coatings (a) A, (b) B, and (c) C; cross-section morphologies of coatings (d) A, (e) B, and (f) C; (g) surface area of coating C used for EDS mapping and (h) corresponding EDS mapping of O element; (i) EDS line scanning result from coating to base material.

Table 1. Chemical composition of FeCrMoSi amorphous coatings (at. %).

Coatings	Mo	Cr	Si	O	Fe
A	17.17	16.26	0.76	8.12	Bal.
B	15.56	15.35	1.56	7.35	Bal.
C	13.38	14.58	1.21	5.21	Bal.

2.2. Bonding Strength

The bonding strengths between the coatings and the 304 SS base material were measured using the tensile test and the results are summarized in Table 2. Coatings A, B, and C exhibited bonding strengths of 64.3, 61.6, and 53.1 N/mm², respectively. For comparison, Zhang et al. prepared Fe-based amorphous coatings on WE43 magnesium alloy using HVOF spraying, with bonding strength reaching 56 MPa [29]. In another study, Zhang et al. prepared laminar coatings comprising multi-amorphous Fe₄₈Mo₁₄C₁₅Y₂C₁₅B₆ layers and a crystalline NiCrAl layer using the HVOF technique and the bonding strength of those coatings was only 40 MPa [30]. In our work, the bonding strength of the coatings reached up to 64.3 N/mm², indicating a strong bonding state between the coating and the base material. SEM images of the fracture surface of the coating and the base material after the bonding strength test revealed some flat FeCrMoSi alloy particles still attached to the base material, demonstrating a robust binding force between them (Figure 3). Prior to spraying, the base materials were sandblasted to increase the surface roughness, thus enhancing the bonding strength between the coatings and the base material. Notably, FeCrMoSi amorphous alloy particles experienced rapid heating in atmospheric plasma, resulting in

inevitable oxidation [31]. Subsequently, these molten particles were sequentially sprayed onto the base material's surface, forming laminar patches with oxygenated interfaces on the 304 SS base material (Figure 2). Based on the above observations and tests, the bonding and failure mechanism of the as-prepared FeCrMoSi amorphous coatings can be analyzed as follows: During the initial APS, the sprayed FeCrMoSi alloy particles combine with the base material and leave cavities between the particles, resulting in a porous structure on the coating surfaces. As atomic diffusion is sufficiently active, the particles undergo plastic deformation, leading to an improved engagement between the coatings and the base material. When the coating is subjected to tensile force, cracks continue to extend along the defective areas due to the presence of some oxides and pores. Consequently, when the extended cracks contact each other, the fracture occurs in the weakest region inside the coating.

Table 2. Bonding strength between the coatings and 304 SS.

Coatings	A	B	C
N/mm ²	64.3	61.6	53.1

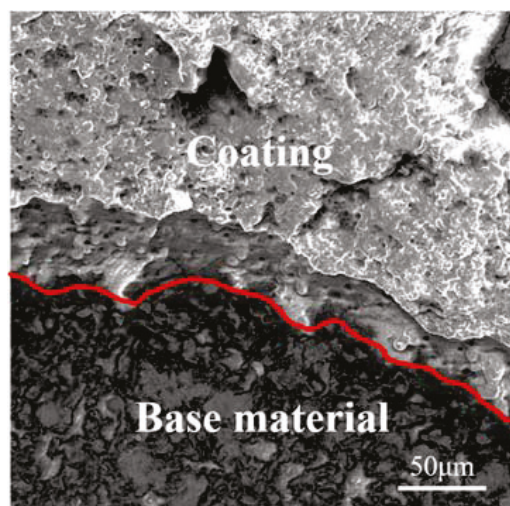


Figure 3. SEM image of the fracture surface of the coating and base material after bonding strength test.

2.3. Hardness

The Vickers hardness values of the coatings and the 304 SS base material are summarized in Table 3. Evidently, each FeCrMoSi amorphous coating exhibits a hardness approximately five times greater than that of the 304 SS base material. This significant increase in hardness could be attributed to the presence of Mo element in the coatings, which has been known to substantially enhance material hardness [32]. The remarkable hardness of the coatings bodes well for their wear resistance, offering effective protection to the base material [22–24].

Table 3. Vickers hardness of the coatings and 304 SS.

Coatings	Hardness (HV)
A	1180.1 ± 2.3
B	1063.6 ± 1.2
C	1057.4 ± 2.4
304 SS	209.3 ± 1.3

2.4. Hydrophobicity

Hydrophobicity was characterized by measuring the water contact angle (WCA) of the FeCrMoSi amorphous coatings and the 304 SS base material, as depicted in Figure 4. Remarkably, the FeCrMoSi amorphous coatings exhibited excellent hydrophobicity, with WCAs ranging from 136.6° to 141.2° . In contrast, the WCA of the 304 SS was only 77.5° . The hydrophobicity of the FeCrMoSi amorphous coatings surpassed that of the NiCrBSi coating, which recorded a WCA of 128° [33], and even exceeded the chromium-doped titanium nitride film, with a WCA of only 115.86° [34].

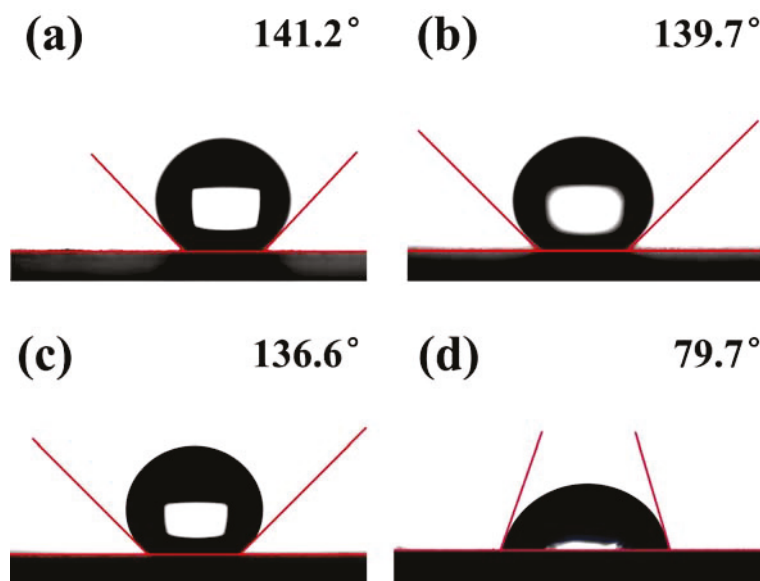


Figure 4. WCA of (a–c) FeCrMoSi amorphous coatings and (d) 304 SS.

The hydrophobicity of a coating is closely related to its surface morphology [35] and the direct attraction of water droplets to the surface materials, which is minimized due to the lower surface energy. Generally, greater surface roughness results in improved hydrophobicity [36]. Models used to describe hydrophobic states can be divided into two types. The first is called the Wenzel state, wherein water droplets completely penetrate the roughness [37]. The second is the Cassie–Baxter state, which assumes that only the upper region of the rough surface is in contact with water and an air pocket exists between them [38]. For the FeCrMoSi amorphous coatings in this study, the hydrophobicity of the FeCrMoSi amorphous coatings suggests that the water droplets cannot fully penetrate any part of the coating surface and can only form an “air wall” at the groove, which traps the air in the groove, creating a slight “air cushion” effect [39]. This effect supports the water droplets, thereby increasing the hydrophobicity of the coating (Figure 5). According to SEM observations, numerous small humps are present on the surface of the coatings (Figure 3), which likely result from the partial melting and simultaneous splashing of the molten or semi-molten alloy particles during APS [40].

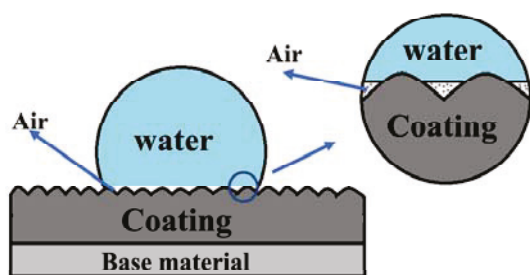


Figure 5. Schematic illustration for the hydrophobic mechanism of FeCrMoSi amorphous coatings.

2.5. Corrosion Resistance

The potentiodynamic polarization curves of the FeCrMoSi amorphous coatings and the 304 SS base material in a hydrogen-passing sulfuric acid and hydrofluoric mixed solution (0.5 M H₂SO₄ + 2 ppm HF, 80 °C) are presented in Figure 6, with the corresponding electrochemical parameters summarized in Table 4. The results demonstrate an active–passive transition for the 304 SS base material. As the potential increases, the anodic polarization curve of 304 SS forms a stable passivation region at 0.09–1 V. However, as the anode polarization potential further increases, the anode current density rises rapidly, indicating that the passivation film begins to break down, losing its passivation ability in the 1–1.2 V range. In contrast, the FeCrMoSi amorphous coatings exhibit superior corrosion resistance compared to 304 SS, evidenced by their lower corrosion current density (I_{corr}) and higher corrosion potential value (E_{corr}). The E_{corr} of the FeCrMoSi amorphous coatings is approximately 90 mV greater than that of the 304 SS. Particularly noteworthy is the fact that the I_{corr} of the FeCrMoSi amorphous coatings is lower than that of the 304 SS base material by one to two orders of magnitude. According to the potentiodynamic polarization curves (Figure 6), the FeCrMoSi amorphous coatings form a passivation film at lower current densities, remaining stable at higher potentials. Coatings A and B exhibit a slow activation process before passivation. Once the E_{corr} reaches approximately 0.15 V, the I_{corr} increases rapidly until reaching the equilibrium state of active dissolution and passivation. However, the I_{corr} of coating C increases rapidly before passivation, and passivation begins near 0.25 V. This active reaction is primarily attributed to the dispersed distribution of particles, oxides, and pores in the coating. Such structural defects often become sites of initial corrosion, leading to a swift increase in the early I_{corr} of anodic polarization until the appearance of a passivation state.

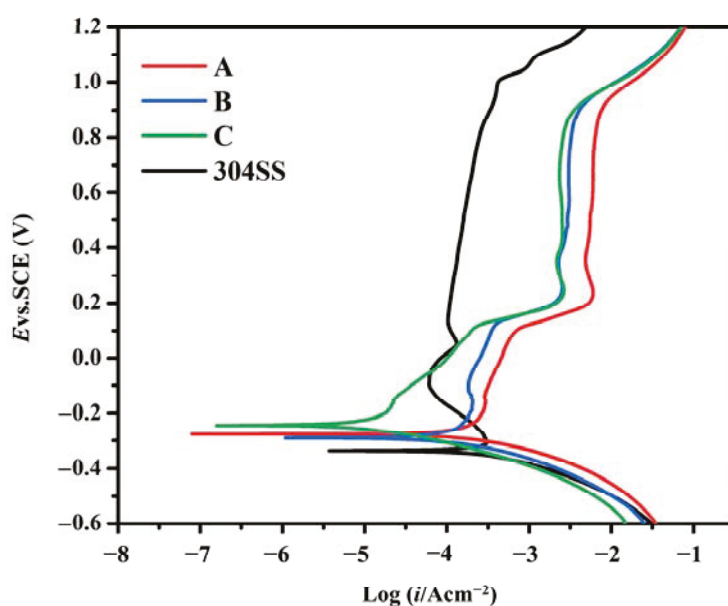


Figure 6. Potentiodynamic polarization curves of FeCrMoSi amorphous coatings and 304 SS.

Table 4. Electrochemical parameters of FeCrMoSi amorphous coatings and 304 SS.

Coatings	E_{corr}/V	$I_{\text{corr}}/\text{A}\cdot\text{cm}^{-2}$
A	−0.28	$2.8 \times 10^{-4} \pm 3.1 \times 10^{-9}$
B	−0.29	$3.3 \times 10^{-4} \pm 1.4 \times 10^{-8}$
C	−0.24	$1.5 \times 10^{-5} \pm 1.7 \times 10^{-11}$
304 SS	−0.34	$4.1 \times 10^{-4} \pm 1.2 \times 10^{-8}$

The surface morphologies of a typical FeCrMoSi amorphous coating C and the 304 SS base material before and after the corrosion resistance test were observed using SEM, as depicted in Figure 7. Clearly, the 304 SS suffered severe corrosion damage, with the surface covered in corrosion products and corrosion pits (Figure 7a). In contrast, the overall morphology of the FeCrMoSi amorphous coating did not change significantly, with only a small number of corrosion pits observed on the surface (Figure 7b). These SEM observations further confirm that the FeCrMoSi amorphous coating exhibits superior corrosion resistance compared with 304 SS.

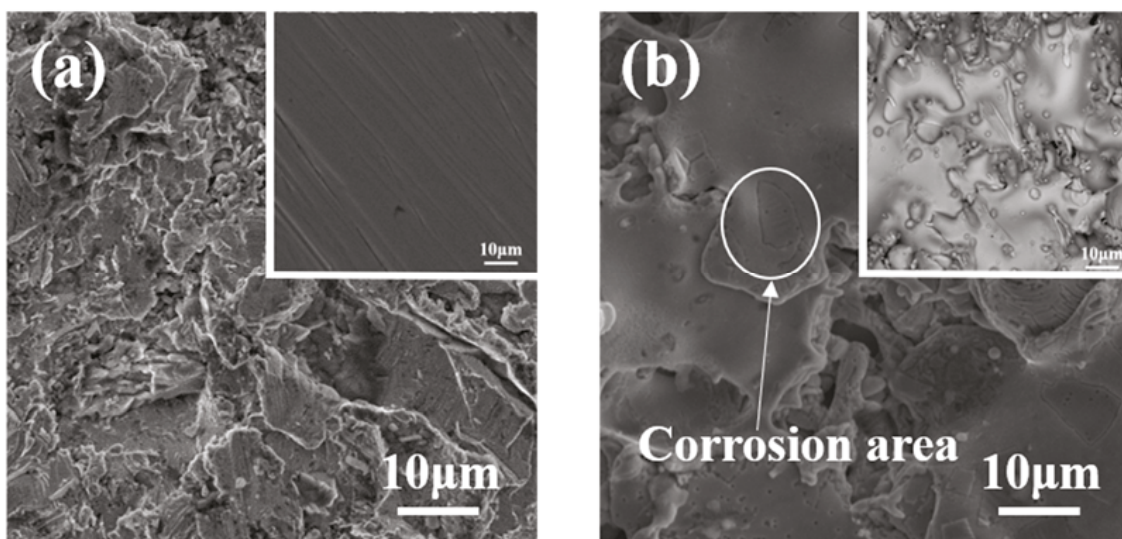


Figure 7. SEM images of (a) 304 SS and (b) coating C after corrosion resistance test. Insets are corresponding SEM images before corrosion resistance test.

The chemical state and composition of the corrosion products of the typical FeCrMoSi amorphous coating C before and after the corrosion resistance test were investigated using X-ray photoelectron spectroscopy (XPS). The original XPS data were initially calibrated with carbon 1 s (284.6 eV). Subsequently, XPS data analysis was carried out using the XPS Peak 4.1 program and a Shirley function was employed to subtract the background. The Fe 2p, Cr 2p, and Mo 3d core-level spectra were fitted with Lorentzian–Gaussian curves [41]. For the Fe 2p_{1/2}, Fe 2p_{3/2}, Cr 2p_{1/2}, and Cr 2p_{3/2} core-level spectra, a 1:2 ratio was applied in the curve fitting of all the Fe 2p and Cr 2p XPS spectra. Similarly, the Mo 3d_{3/2} and Mo 3d_{5/2} signal areas had a 2:3 ratio which was applied in the curve fitting of all the Mo 3d XPS spectra.

The XPS survey spectrum (Figure 8) clearly indicates that in addition to adventitious carbon, some main elements include Fe, Mo, Cr, Si, and O. The XPS core-level spectra of Fe before the corrosion resistance test can be identified to be composed of Fe 2p_{1/2} and Fe 2p_{3/2} peaks of Fe⁰, Fe²⁺, and Fe³⁺ states [42], as depicted in Figure 9a. The presence of Fe²⁺ and Fe³⁺ indicates that a small amount of Fe has been oxidized during APS. This reaction corresponds to the appearance of Fe₃O₄ in the XRD patterns (Figure 1), which is composed of FeO and Fe₂O₃ [43]. The XPS core-level spectra of Mo before the corrosion resistance test can be identified to be composed of Mo 3d_{3/2} and Mo 3d_{5/2} peaks of Mo⁰ and Mo⁶⁺ states [44,45], as displayed in Figure 9b. The presence of Mo⁶⁺ indicates that a small amount of Mo has been oxidized during APS. The XPS core-level spectra of Cr before the corrosion resistance test can be identified to be composed of Cr 2p_{1/2} and Cr 2p_{3/2} peaks of Cr⁰, Cr³⁺, and Cr⁶⁺ states [46], as presented in Figure 9c. The presence of Cr³⁺ indicates that a small amount of Cr has been oxidized during APS.

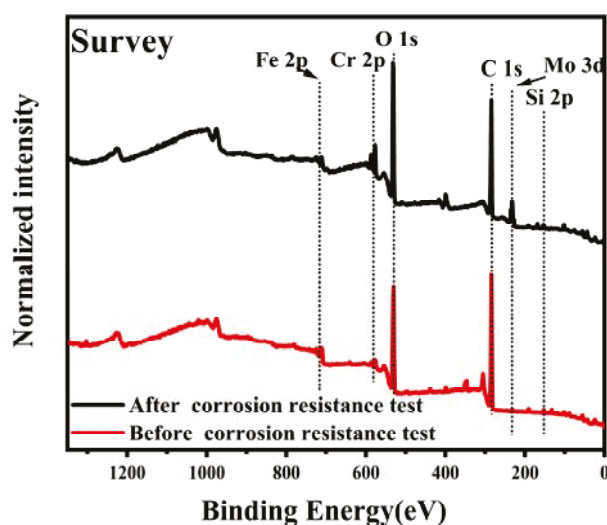


Figure 8. XPS survey spectrum of coating C before and after corrosion resistance test.

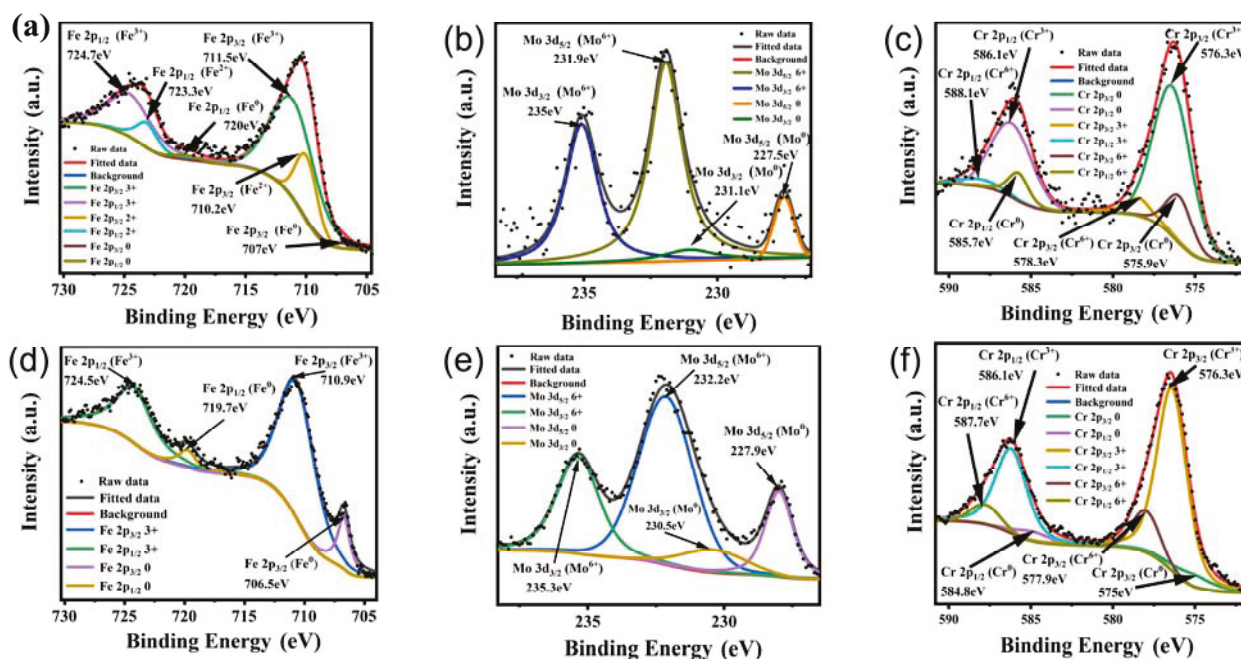


Figure 9. XPS core-level spectra of (a) Fe 2p, (b) Mo 3d, and (c) Cr 2p before and (d) Fe 2p, (e) Mo 3d, and (f) Cr 2p after corrosion resistance test of coating C.

The XPS core-level spectra of Fe after the corrosion resistance test reveal the presence of Fe 2p_{1/2} and Fe 2p_{3/2} peaks corresponding to Fe⁰ and Fe³⁺ states, as marked in Figure 9d. In comparison to the XPS core-level spectra of Fe before the corrosion resistance test (Figure 9a), Fe²⁺ ions were not found, indicating that Fe²⁺ is more soluble in the acidic solution (0.5 M H₂SO₄ + 2 ppm HF, 80 °C). Similarly, the XPS core-level spectra of Mo after the corrosion resistance test exhibit Mo 3d_{3/2} and Mo 3d_{5/2} peaks corresponding to Mo⁰ and Mo⁶⁺ states, as marked in Figure 9e. Likewise, the XPS core-level spectra of Cr after the corrosion resistance test show Cr 2p_{1/2} and Cr 2p_{3/2} peaks corresponding to Cr³⁺ states only, as marked in Figure 9f. These spectra are consistent with those before the corrosion resistance test, indicating that the Mo and Cr elements can withstand the corrosion of this specific acidic solution (0.5 M H₂SO₄ + 2 ppm HF, 80 °C).

Based on the above analysis, the passivation film on the surface of the coating is believed to be composed of oxides of Cr, Fe, and Mo, with the main compounds being Fe₃O₄, Cr₂O₃, and MoO₃. These oxides significantly improve the stability of the passivation

film and enhance the protective effect of the chromium oxide film [47]. Xia et al. have proposed that hexavalent chromium dissolves in water and increases the corrosion current density, but it possesses a self-healing ability and can promote the formation of dense chromium oxide [48]. The presence of Cr ions is crucial for the corrosion resistance of FeCrMoSi amorphous alloy coatings as they can form chromium hydroxide passivation films. Additionally, Cr reacts with H_2O to form Cr_2O_3 , which further enhances its corrosion resistance [49]. This also explains the significant reduction in the intensity of Cr^0 after corrosion. Moreover, Tian et al. have suggested that MoO_3 can accumulate on the surface and hinder the diffusion of corrosion ions into the interior (Figure 10), effectively preventing pitting corrosion [43]. Thus, FeCrMoSi amorphous coatings demonstrate better corrosion resistance than 304 SS due to their higher Cr and Mo contents. Furthermore, the chemical composition of the corroded surface of coating C (Table 5) shows that the O content has doubled compared to that of the as-fabricated coating, indicating a substantial production of oxides on the surface of the coating during the corrosion resistance test.

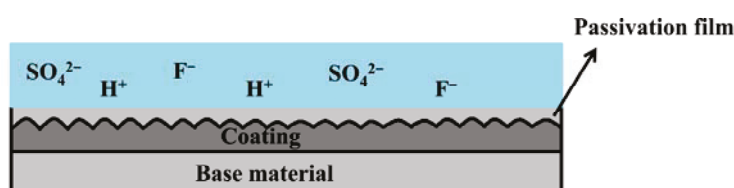


Figure 10. Schematic illustration for the corrosive ions and the passivation film.

Table 5. Chemical composition of coating C after corrosion resistance test.

Elements	Mo	Cr	Si	O	Fe
at. %	12.25	11.12	1.12	15.51	Bal.

2.6. Interfacial Contact Resistance (ICR)

The electrical conductivity of FeCrMoSi amorphous coatings and 304 SS under different compaction forces was measured using ICR and the results are presented in Figure 11. The ICR decreases with increasing compaction forces, attributed to the increase in effective contact area [45]. Specifically, the ICR values at 140 N/cm^2 are summarized in Table 6. Coating A exhibits a high ICR with increasing compressive force, indicating low electrical conductivity of the coating. The ICR of coating C is lower than that of coating A. However, the ICR of coating B is significantly lower than that of the 304 SS ($123.5\text{ m}\Omega\cdot\text{cm}^2$) [44].

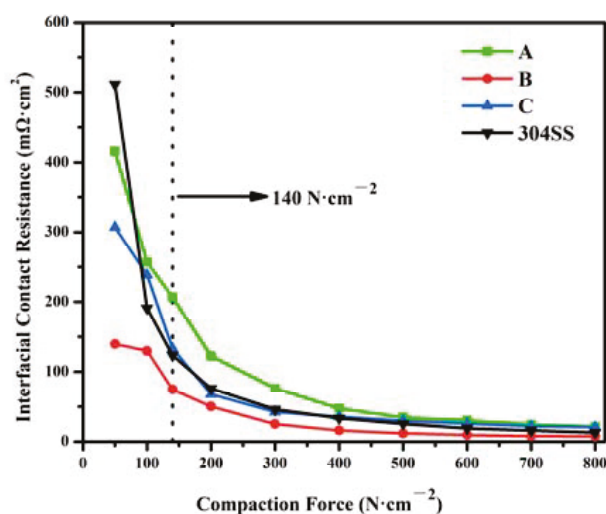


Figure 11. ICR of FeCrMoSi amorphous coatings and 304 SS under 50–800 N/cm^2 compaction forces.

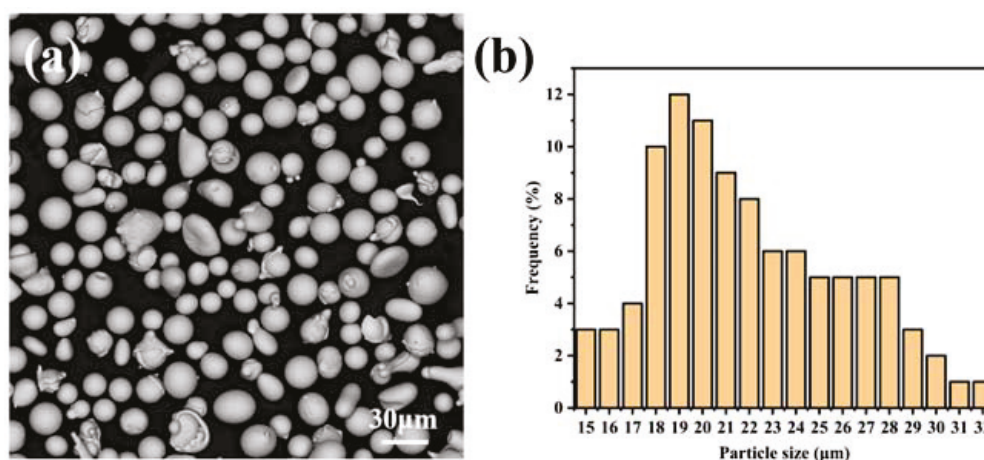
Table 6. ICR of FeCrMoSi amorphous coatings and 304 SS at 140 N/cm².

Coatings	ICR (mΩ·cm ²)
A	206.5 ± 1.2
B	74.7 ± 0.7
C	133.3 ± 1.5
304 SS	123.5 ± 3.5

Although the electrical conductivity of FeCrMoSi amorphous coatings is much better than that of 304 SS, the ICR still failed to meet the 2025 U.S. Department of Energy (DOE) target (<10 mΩ·cm²) for bipolar plate of hydrogen fuel cell [50]. Further improvement for decreasing the ICR of FeCrMoSi amorphous coatings may be conducted in the future.

3. Materials and Methods

The feedstocks of FeCrMoSi alloy powder raw materials (Figure 12a) were procured from Sunny Metal Technology Company, Republic of Korea. The majority of the powders are spherical, with diameters ranging from 15–32 µm (Figure 12b). An EDS was employed to analyze the chemical composition of the FeCrMoSi amorphous alloy powders, revealing Fe, Mo, Cr, and Si as the main elements, as shown in Table 7. The base material utilized for this study was 304 SS, with dimensions of 40 × 40 × 2 mm³. Prior to APS, the 304 SS base material underwent sandblasting to remove the oxide layer and achieve a rough surface. The FeCrMoSi amorphous coatings were fabricated using a UniCoatPro APS system (Oerlikon, Pfäffikon, Switzerland) with a F4MB gun and the spraying parameters are detailed in Table 8. The coatings produced using low, intermediate, and high spraying currents were labeled as coatings A, B, and C, respectively.

**Figure 12.** Morphology of FeCrMoSi amorphous alloy powder: (a) SEM image; (b) particle size.**Table 7.** Chemical composition of FeCrMoSi alloy powder raw materials.

Elements	Mo	Cr	Si	Fe
at. %	18.05	19.51	3.16	Bal.

Table 8. Spraying parameters of FeCrMoSi amorphous coatings.

Coatings	Current (A)	Ar (L/min)	H ₂ (L/min)	Feed Rate (g/min)
A	400	45	13	24
B	520	45	5	24
C	600	45	5	24

The surface morphology and chemical composition of the coatings, along with the interface morphology between the coatings and the base materials, were observed and measured using a TM3030 SEM (Hitachi, Tokyo, Japan) equipped with an Swift 3000 EDS (Oxford Instruments, Oxford, UK). The phases of the coatings were examined using a Ultima IV XRD (Rigaku, Tokyo, Japan) at 40 kV and 30 mA, with a scanning speed of 5°/min. Meanwhile, a cross-sectional TEM sample was prepared using a twin-jet electropolisher, as shown in Figure 13. The coating on the surface of the 304 SS base material can be clearly identified, as marked with the arrow. The coating thickness was measured to be about 136 μm . Bright field TEM and selected area electron diffraction images were collected on a Talos F200X S/TEM (Thermo Scientific, Waltham, MA, USA) at an accelerating voltage of 200 kV. WCA was measured using a JC2000D1B video-based optical instrument (Zhongchen, Shanghai, China) with 5 μL deionized water droplets. Each sample was measured 10 times and the average value was recorded. The bonding strength between the coatings and the base material was determined using a Roell Z250 electronic universal testing machine (Zwick, Ulm, Germany) through a pairwise tensile method. The specimens were cylindrical with a diameter of 25.4 mm, tested following ASTM C633-01 Standard Test Method for Adhesion or Cohesion Strength of Thermal Spray Coatings. The Vickers hardness of the coatings and the base material was measured using an HXS-1000 microhardness tester (Shangguang, Shanghai, China) with a load of 100 gf and a holding time of 15 s, following ASTM E384-22 Standard Test Method for Microindentation Hardness of Materials. To minimize measuring errors, 10 indentations were conducted for each sample.

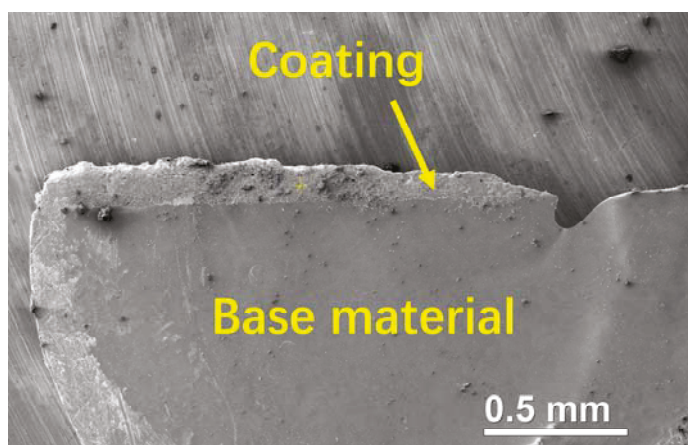


Figure 13. SEM image of the cross-sectional TEM sample.

The ICR test [51] entailed positioning carbonized paper and copper plates on both sides of the sample, subjecting it to varying compressive forces via a M350-CT (Testometric, Rochdale, UK) universal testing machine, while recording the resistance with a ZY9858 digital micro-ohmmeter (Zhengyang, Shanghai, China). Each sample underwent three measurements and the average value was recorded.

The corrosion resistance testing was carried out using a three-electrode system comprising a platinum sheet as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the specimen as the working electrode. A CS150M electrochemical workstation (CorrTest, Wuhan, China) was employed with 1 cm^2 of the sample surface area exposed to the electrolyte. The electrolyte consisted of 0.5 M H_2SO_4 + 2 ppm HF. Initially, the samples were immersed in the electrolyte for 1 h while open circuit potential tests were performed. Subsequently, potentiodynamic polarization tests were conducted in the range of -0.6 V to $+1.2$ V at a scanning speed of 0.2 mV/s. Corrosion potentials and corrosion current densities were obtained through Tafel extrapolation, implemented in the electrochemical analysis software, with Tafel fitting performed in the potential range of ± 200 mV around the open circuit potential. The corrosion resistance tests were conducted

at 80 °C with H₂ bubbles at a gas flow rate of 20 mL/min. After the corrosion resistance test, the surface morphology of each sample was observed again using SEM and the chemical composition of the coatings was re-examined using EDS.

X-ray photoelectron spectroscopy (XPS) was utilized to analyze the chemical composition and chemical state of FeCrMoSi amorphous coatings both before and after the corrosion resistance test. The ESCALAB 250Xi spectrometer (Thermo Scientific, Waltham, MA, USA) was employed for this purpose, maintaining a base pressure below 1.0×10^{-7} Pa through a combination of a mechanical pump and a turbo molecular pump. The excitation source was a nonmonochromatic dual anode X-ray source emitting Al K α photons with an energy of 1486.6 eV, operating at 14.6 kV. During acquisition, the survey spectrum was scanned with a step of 1 eV, followed by sequential acquisition of the O 1s, Fe 2p, Mo 3d, and Cr 2p core-level spectra with a scan step of 0.05 eV. The analyzed area formed a circle with a diameter of 400 μ m. To compensate for the charge up effect, a charge neutralizer was employed.

4. Conclusions

This paper presents the fabrication and characterization of FeCrMoSi amorphous coatings using atmospheric plasma spraying technology. The coatings were subjected to XRD, SEM, hydrophobicity test, bonding strength test, hardness test, corrosion resistance test, and electroconductibility test. The results reveal that the chemical composition of the plasma-sprayed coatings undergoes only slight changes with variations in current and hydrogen during the fabrication process. Notably, the FeCrMoSi amorphous coatings demonstrate a higher passivation film breakdown potential (~1 V) and exhibit less corrosion damage, indicating superior corrosion resistance compared to 304 SS. Furthermore, the coatings exhibit an impressive hardness of up to 1180.1 HV, which is five times greater than that of the 304 SS, showcasing excellent wear resistance. Additionally, the coatings display excellent hydrophobicity with a water contact angle reaching 141.2°. These unique properties suggest that FeCrMoSi amorphous coatings have the potential to serve as exceptional protective materials in harsh corrosive environments containing H⁺, F[−], SO₄^{2−}, and H₂, particularly in marine, hydraulic, and fuel cell applications.

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Article

Investigation of the Performance of Hastelloy X as Potential Bipolar Plate Materials in Proton Exchange Membrane Fuel Cells

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Abstract: The phase, mechanical properties, corrosion resistance, hydrophobicity, and interfacial contact resistance of Hastelloy X were investigated to evaluate its performance in proton exchange membrane fuel cells (PEMFCs). For comparison, the corresponding performance of 304 stainless steel (304SS) was also tested. Hastelloy X exhibited a single-phase face-centered cubic structure with a yield strength of 445.5 MPa and a hardness of 262.7 HV. Both Hastelloy X and 304SS exhibited poor hydrophobicity because the water contact angles were all below 80°. In a simulated PEMFC working environment (0.5 M H₂SO₄ + 2 ppm HF, 80 °C, H₂), Hastelloy X exhibited better corrosion resistance than 304SS. At 140 N·cm⁻², the interfacial contact resistance of Hastelloy X can reach as low as 7.4 mΩ·cm². Considering its overall performance, Hastelloy X has better potential application than 304SS as bipolar plate material in PEMFCs.

Keywords: corrosion resistance; tensile strength; interfacial contact resistance; hardness; hydrophobicity

1. Introduction

Hastelloy X is a typical solid-solution strengthened nickel-based high-temperature alloy with excellent oxidation resistance and high-temperature strength [1]. Hastelloy X was found to exhibit relatively good corrosion resistance in sodium borate buffer solution [2]. And the ultimate tensile strength of Hastelloy X at 750 °C still stayed as high as 310 MPa [3]. Due to its desirable corrosion resistance and oxidation resistance, it has been widely used in high-temperature components, including gas turbine engines and gas-cooled reactors [4,5]. Another notable feature of Hastelloy X is its good fatigue resistance [6], which maintains its strength and toughness under cyclic loading conditions, making it highly durable and reducing the risk of material damage and fatigue fractures during operation [7].

Proton exchange membrane fuel cells (PEMFCs) are regarded as significant devices for addressing environmental and energy issues in the future [8]. They can directly convert chemical energy into electricity and offer advantages such as high conversion efficiency and zero emissions, making them subject to extensive research [9]. In PEMFCs, bipolar plates play crucial roles in carrying the current from the cell and preventing leakage of reactants and coolants [10,11]. They account for 45% of the stack cost and 80% of the weight [12]. Consequently, to better meet the requirements of fuel cells, an increasing number of researchers have proposed the use of metallic materials as bipolar plates.

Traditional graphite bipolar plates, despite their excellent conductivity and chemical stability, are limited in their development prospects in the field due to drawbacks such as

brittleness and high cost [13]. In contrast, metal bipolar plates are considered the optimal alternative to graphite bipolar plates due to their superior mechanical durability and high conductivity [14]. Nickel-based high-temperature alloys form a dense metal oxide layer on the surface, which not only prevents oxygen from permeating into the alloy matrix but also inhibits metal dissolution, thus exhibiting outstanding oxidation resistance and corrosion resistance [15]. Furthermore, through the solid-solution strengthening mechanism, these alloys maintain high strength at elevated temperatures, demonstrating excellent high-temperature mechanical properties [16]. The 304 stainless steel (304SS) has excellent corrosion resistance as it forms oxide film on the surface [17]. When 304SS is exposed to solutions containing halide ions, especially fluoride ions, the protective film on the surface may partially break down, exposing the underlying metal, and then lead to local corrosion, including pitting and intergranular corrosion.

Currently, there is relatively limited research on the application of Hastelloy X in bipolar plates of PEMFCs. Therefore, this study aims to thoroughly investigate the electrochemical performance of Hastelloy X in a simulated PEMFC working environment and also assess its mechanical properties. For comparison, 304SS is also evaluated.

2. Results and Discussion

2.1. Phase

The phase of the two alloys was examined by XRD, and the results are shown in Figure 1. The XRD pattern of Hastelloy X only has three clear characteristic peaks between 2θ of 40° and 80° , which demonstrates a typical face-centered cubic (FCC) polycrystalline diffraction pattern, indicating a single γ -phase [18]. According to the standard PDF card [19], 304SS exhibits austenitic and martensitic phases. This is similar to the results found by Djamel et al. [20]. At the same time, we calculated the lattice constant a by using the Bragg equation ($2d_{hkl}\sin\theta = n\lambda$) and the formula for the FCC crystal plane spacing $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$. The obtained results are shown in Table 1.

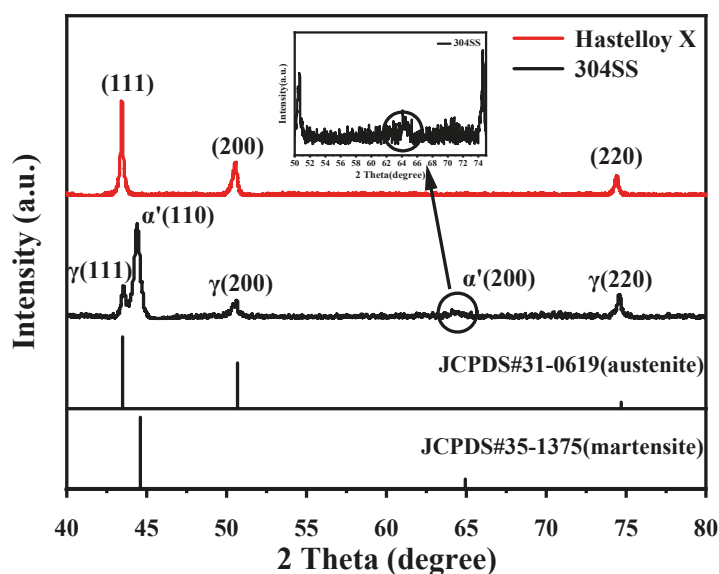


Figure 1. XRD patterns of Hastelloy X and 304SS.

Table 1. X-ray diffraction angles of peaks and lattice constant of the alloys.

Alloys	θ_{111} ($^\circ$)	θ_{200} ($^\circ$)	θ_{220} ($^\circ$)	a (nm)
Hastelloy X	21.77	25.35	37.27	0.3603
304SS	21.74	25.34	37.34	0.3464

2.2. Corrosion Resistance

Figure 2a shows the curve of the open circuit potential (E_{ocp}) of Hastelloy X in a 0.5 M H_2SO_4 + 2 ppm HF at 80 °C. The shift of the open circuit potential towards a negative potential is probably due to the dissolution of the passivation layer. The E_{ocp} of Hastelloy X gradually decreases over time and then stabilizes at approximately -0.23 V after 500 s of immersion. In contrast, the potential of 304SS shifts towards a positive potential over time. In order to assess the corrosion resistance of Hastelloy X in a simulated PEMFC working environment, a potentiodynamic polarization method was used. Figure 2b shows the electrochemical polarization curves, and the corresponding corrosion parameters are also summarized in Table 2. It can be seen from Figure 2b that Hastelloy X undergoes a transition from cathodic polarization, activation, activation to passivation, and finally the formation of a passivation film, and then the passivation film dissolves. In the cathodic polarization region (-0.6 , -0.23) V, the current density decreases with increasing potential. When the scanning potential exceeds -0.23 V, the current density increases with increasing potential and then decreases with increasing potential after exceeding $+0.05$ V, finally stabilizing at $2.84 \times 10^{-4} \text{ A}\cdot\text{cm}^{-2}$. As the anodic polarization potential continues to increase, the anodic current density increases rapidly, indicating that in the range of ($+0.84$, $+1.20$) V, the passivation film begins to break and loses its passivation capability completely. In contrast, 304SS exhibits a much higher corrosion current, demonstrating its poor corrosion resistance in a simulated PEMFC working environment. Figure 2c shows potentiostatic polarization curves in a simulated PEMFC working environment for further assessing the corrosion resistance and stability of Hastelloy X and 304SS. As can be seen from the graph, the current density drops rapidly in the initial phase after voltage application and stabilizes after 30 s, indicating that Hastelloy X has good stability in a simulated PEMFC working environment. In order to further improve its electrochemical properties, proper surface modification techniques can be used to improve corrosion resistance [11].

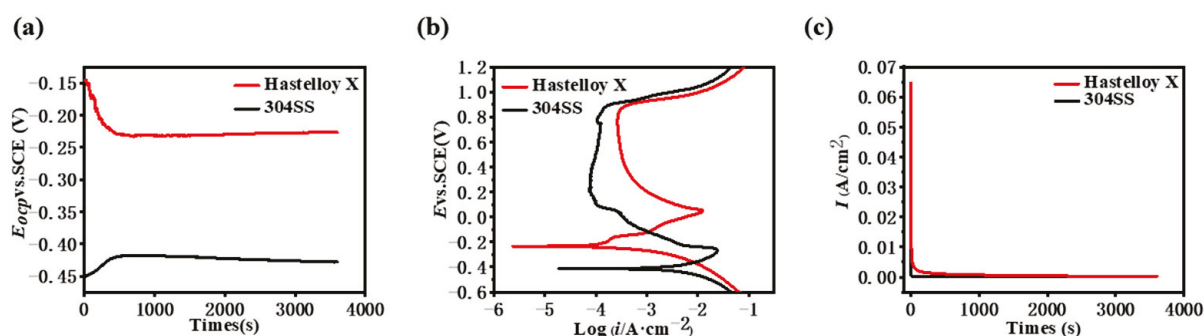


Figure 2. Corrosion resistance test results of Hastelloy X and 304SS (a) Open circuit potential curves; (b) potentiodynamic polarization curves; (c) potentiostatic polarization curves.

Table 2. Electrochemical parameters of the alloys.

Alloys	E_{ocp} (V)	E_{corr} (V)	I_{corr} ($\text{A}\cdot\text{cm}^{-2}$)
Hastelloy X	-0.23	-0.23	$(1.01 \pm 0.01) \times 10^{-4}$
304SS	-0.45	-0.34	$(7.36 \pm 0.03) \times 10^{-3}$

The surface morphology of Hastelloy X and 304SS before and after electrochemical testing was observed using SEM, and the images are shown in Figure 3. Before electrochemical testing, the surfaces of both alloys showed machined filamentary morphology (Figure 3a,b). After the testing, pitting appeared on the surfaces of Hastelloy X and 304SS (Figure 3c,d). As shown in Tables 3 and 4, the atomic ratio of Cr to Mo decreased in both samples, and oxygen atoms were present, probably due to the formation of Cr and Mo oxides during the corrosion process. For 304SS, the presence of Cr oxide in its surface passivation film is

attributed to the selective dissolution of Fe during the passivation process, resulting in the enrichment of Cr within the passivation film [21].

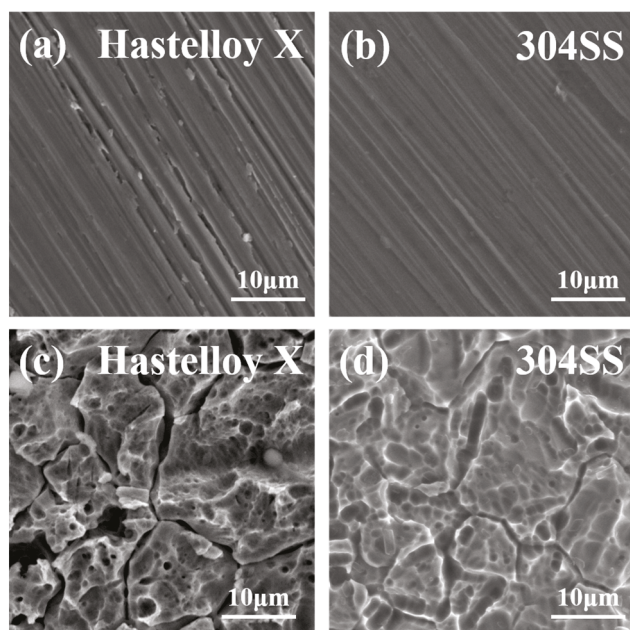


Figure 3. SEM images of the surface of Hastelloy X and 304SS (a,b) before and (c,d) after electrochemical testing.

Table 3. Chemical composition of Hastelloy X (at. %).

	Ni	Fe	Cr	Mo	Co	Al	O
Before electrochemical testing	49.28	20.10	23.36	5.09	1.96	0.2	/
After electrochemical testing	52.04	16.84	15.79	3.92	1.97	0.03	9.40

Table 4. Chemical composition of 304SS (at. %).

	Ni	Fe	Cr	Si	O
Before electrochemical testing	7.23	72.62	18.96	0.64	/
After electrochemical testing	5.95	61.41	16.47	0.62	15.55

Electrochemical impedance spectroscopy (EIS) is another powerful technique to evaluate corrosion protection performance. Compared to 304SS, Hastelloy X showed a positive shift in impedance arc radius in both the high and medium frequency ranges (Figure 4), indicating that Hastelloy X is more resistant to corrosion. The equivalent circuit model as shown in Figure 5 was proposed to fit the EIS data based on the above analysis. R_s , $CPE1$, R_f , $CPE2$, and R_{ct} are the solution resistance, oxide film protection capacitance, oxide film protection resistance, double layer capacitance, and charge transfer resistance, respectively. Notably, since the capacitor loop in Nyquist plots were not perfect semicircles, a constant phase element is employed to replace the ideal capacitor.

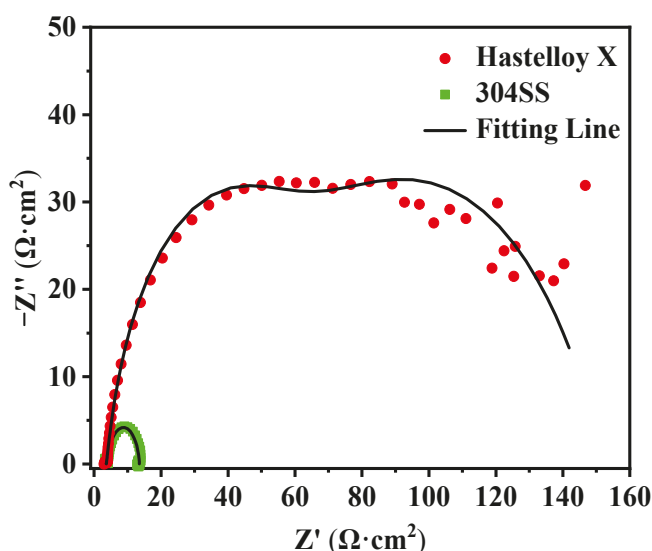


Figure 4. Nyquist plot of the alloys after corrosion.

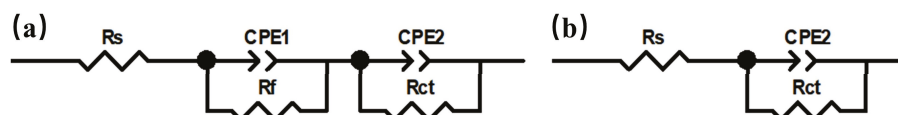


Figure 5. Equivalent circuits for fitting the impedance diagram of (a) Hastelloy X and (b) 304SS.

The fitting impedance parameters are summarized in Table 5. The results show that Hastelloy X has higher R_{ct} value, which demonstrates better corrosion resistance than that of 304SS. Furthermore, it is well known that CPE is an important indicator of the corrosion area of metals, and the smaller the CPE value, the smaller the area of corrosion indicated. From Table 5, an elevated order of CPE2 can be implied: Hastelloy X ($1.4 \times 10^{-3} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$) < 304SS ($1.1 \times 10^{-2} \Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$), suggesting the smallest corrosion area for Hastelloy X.

Table 5. EIS analyzed results of the alloys.

Alloys	$\text{CPE1}/\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$	n1	$R_f/\Omega \cdot \text{cm}^2$	$\text{CPE2}/\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^n$	n2	$R_{ct}/\Omega \cdot \text{cm}^2$
Hastelloy X	$(1.9 \pm 0.1) \times 10^{-3}$	0.651 ± 0.002	100.7 ± 5.2	$(1.4 \pm 0.1) \times 10^{-3}$	0.920 ± 0.012	47.58 ± 0.43
304SS	/	/	/	$(1.1 \pm 0.2) \times 10^{-2}$	0.915 ± 0.023	9.57 ± 0.50

2.3. Mechanical Properties

The tensile stress–strain curves of Hastelloy X and 304SS are shown in Figure 6a, and the corresponding mechanical properties are summarized in Table 6. The tensile data of Hastelloy X are similar to the results obtained by Ghiaasiaan et al. [22]. The yield strength of Hastelloy X is 445 MPa, which is higher than that of 304SS (127 MPa), indicating that Hastelloy X has a higher resistance to stress. The ultimate tensile strength of Hastelloy X is 823.9 MPa, surpassing the 616.3 MPa of 304SS, demonstrating its ability to withstand higher tensile forces. The uniform elongation is an indicator of the plastic deformation capacity of a material. The uniform elongation for Hastelloy X is 56.5%, slightly lower than the 61.4% of 304SS. Higher uniform elongation usually indicates better ductility. The elastic modulus, which represents the material's response to stress, is 203.8 GPa for Hastelloy X, which is lower than that of 304SS (273.7 GPa), indicating that Hastelloy X is more flexible. Hardness is an indicator of a material's resistance to localized plastic deformation and surface damage. The hardness of Hastelloy X is 262.7 HV, which is slightly higher than that of 304SS (215.3 HV). Higher hardness usually suggests better wear resistance [23]. The

higher hardness of Hastelloy X may be due to it being a solid-solution strengthened high-temperature alloy without reinforcing precipitates like the gamma phase. Consequently, Hastelloy X obviously outperforms 304SS in yield strength, ultimate tensile strength, and hardness, indicating that Hastelloy X has excellent mechanical properties. Due to the use of 304SS produced by different manufacturers, the mechanical properties of 304SS differ slightly from those of previous reports [24].

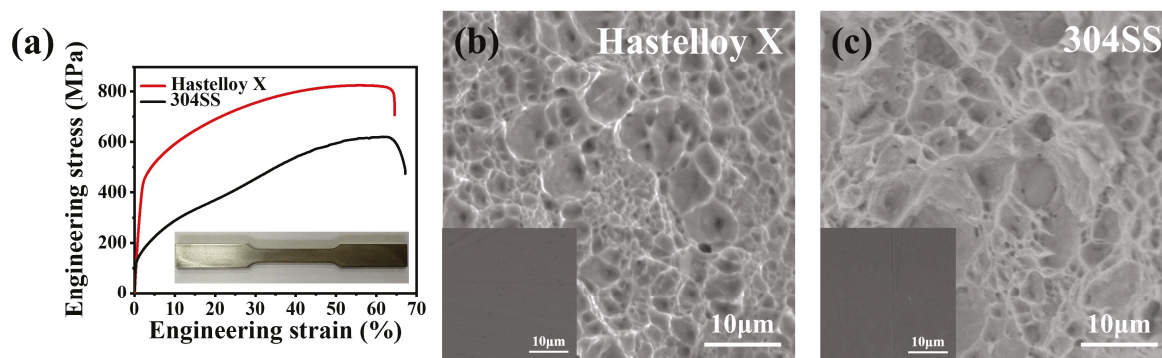


Figure 6. Mechanical testing results of Hastelloy X and 304SS. (a) Tensile stress–strain curves of alloys; SEM images of the fracture surface of (b) Hastelloy X and (c) 304SS (left bottom inset in panels (b,c) is the SEM image of the corresponding alloy before tensile testing).

Table 6. Mechanical properties of Hastelloy X and 304SS.

Alloys	Yield Strength 0.2% Offset (MPa)	Ultimate Tensile Strength (MPa)	Uniform Elongation (%)	Elastic Modulus (GPa)	Hardness (HV)
Hastelloy X	445.5 ± 2.3	823.9 ± 5.1	56.5 ± 1.3	203.8 ± 5.7	262.7 ± 1.2
304SS	127.3 ± 4.6	616.3 ± 4.3	61.4 ± 2.5	273.7 ± 3.8	215.3 ± 6.5

The fracture morphologies of Hastelloy X and 304SS after tensile testing were observed using SEM to analyze their fracture mechanism. Both of the fracture surfaces of Hastelloy X and 304SS exhibit numerous dimples and continuous fiber networks, as shown in Figure 6b,c, indicating typical ductile fracture and implying good ductility. This observation is consistent with the uniform elongation values of 56.5% and 61.4% for Hastelloy X and 304SS, respectively. Particularly, the dimple size of 304SS is larger than that of Hastelloy X, indicating that 304SS undergoes greater plastic deformation before fracture. This characteristic aligns with the higher elongation capability of 304SS.

2.4. Hydrophobicity

For bipolar plates, water management is crucial to improving the performance of PEMFCs. It helps to prevent flooding in the channels and gas diffusion layer, thereby avoiding deterioration of mass transport and the occurrence of corrosion. Therefore, hydrophobic bipolar plates with high water contact angles are preferable to PEMFCs. Water contact angle (WCA) testing was employed to evaluate the hydrophobicity of the two alloys, and the measurement results are shown in Figure 7. Hastelloy X exhibits a WCA value of 79.5°, which is larger than that of 304SS (76.2°). Meanwhile, the hydrophobicity of Hastelloy X was significantly better than in our previous studies on Hastelloy C-276 and Hastelloy B [25]. However, both of the WCA values of Hastelloy X and 304SS are less than 80°, indicating poor hydrophobicity.

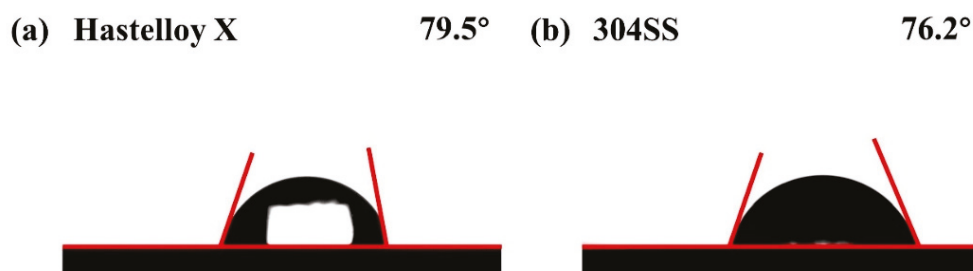


Figure 7. Water contact angle of (a) Hastelloy X and (b) 304SS.

2.5. Interfacial Contact Resistance (ICR)

ICR is a critical parameter that significantly impacts the performance of bipolar plates. Maintaining a low ICR is crucial for the materials utilized in these plates, as a high ICR can lead to a reduced lifespan of PEMFCs. Figure 8 illustrates the correlation between compaction force and ICR values for Hastelloy X and 304SS. Compared to Hastelloy X, 304SS demonstrates higher ICR values. The ICR values of 304SS [26] decrease with increasing compaction force and stabilize at higher compaction forces. This phenomenon can be attributed to the fact that, under high load conditions, the actual contact area between the interfaces expands, resulting in improved conductivity. Table 7 provides the ICR values of the two alloys at a compaction force of $140 \text{ N}\cdot\text{cm}^{-2}$ [27]. The ICR of 304SS is higher than that of Hastelloy X, with a value of $144.8 \text{ m}\Omega\cdot\text{cm}^2$. This elevated ICR in 304SS can be attributed to the presence of surface oxide layers composed of iron, nickel, and chromium oxides. On the other hand, Hastelloy X demonstrates excellent conductivity, with an ICR of $7.4 \text{ m}\Omega\cdot\text{cm}^2$ at $140 \text{ N}\cdot\text{cm}^{-2}$, which satisfies the 2025 Department of Energy (DOE) target of less than $10 \text{ m}\Omega\cdot\text{cm}^2$ [28]. The very low ICR of Hastelloy X can be attributed to the addition of Cr^{3+} to oxides of Ni or Co [29], which largely increases the conductivity of the passivation film on the surface of Hastelloy X.

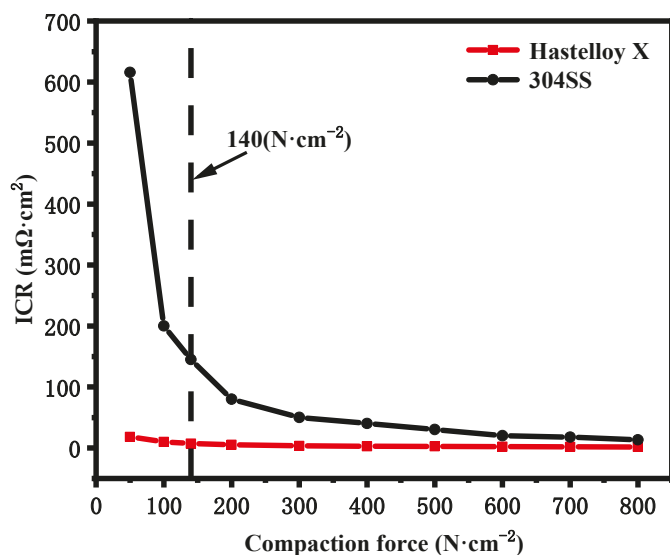


Figure 8. ICR of the alloys at different levels of compaction force.

Table 7. ICR of the alloys at $140 \text{ N}\cdot\text{cm}^{-2}$.

Alloys	ICR ($\text{m}\Omega\cdot\text{cm}^2$)
Hastelloy X	7.4 ± 0.3
304SS	144.8 ± 5.4

3. Materials and Methods

Commercially available Hastelloy X was used. The samples were prepared according to the standard test method for tensile testing of metallic materials [30]. The samples were respectively cut into dog bone shapes (Figure 9), square shapes with dimensions of $20\text{ mm} \times 20\text{ mm} \times 2\text{ mm}$ and $50\text{ mm} \times 50\text{ mm} \times 2\text{ mm}$, using wire cutting. The samples used for electrochemical performance testing were circular discs with a diameter of 15 mm and a thickness of 2 mm. All samples were polished using SiC paper before testing.

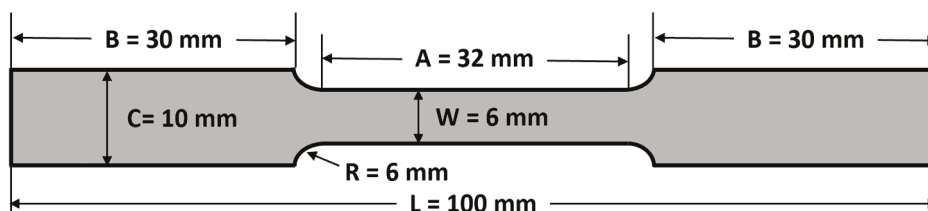


Figure 9. Geometry of tensile samples.

The surface morphology of the samples before and after corrosion was observed using a Hitachi SU-1500 scanning electron microscope (SEM, Tokyo, Japan), and composition analysis was conducted using an energy-dispersive X-ray spectrometer (Horiba, Tokyo, Japan, EMAX x-act model). The scanning area of each SEM image was $63.84\text{ }\mu\text{m} \times 47.88\text{ }\mu\text{m}$. To investigate the phase composition of Hastelloy X, we utilized a TD-3500 X-ray diffractometer (XRD) produced by Tongda Corporation (Dandong, China). The X-ray source employed the characteristic $K\alpha$ line ($\lambda = 0.15406\text{ nm}$) of a Cu target. The scanning angle range was set from 40° to 80° with a step size of 0.02° and a scanning speed of $1^\circ/\text{min}$.

Electrochemical testing was conducted using the CorrTest CS150M electrochemical workstation (Wuhan, China). Platinum foil was used as the counter electrode, a saturated calomel electrode (SCE) served as the reference electrode, and the sample acted as the working electrode. Each sample was immersed into a simulated PEMFC working environment ($0.5\text{ M H}_2\text{SO}_4 + 2\text{ ppm HF}$, 80°C , 20 mL/min H_2) for one hour to reduce experimental errors. Open circuit potential (OCP) testing was then performed until the entire system stabilized. The potentiodynamic potential polarization was scanned from -0.6 V to $+1.2\text{ V}$ at a scan rate of 0.2 mV/s to evaluate the corrosion resistance of the alloys with a 60 min potentiostatic polarization test. The corrosion potential and corrosion current density were obtained using the Tafel extrapolation method. The frequency range for EIS testing was set at $10^5\text{--}10^{-2}\text{ Hz}$, and a perturbation voltage of 20 mV was utilized. To ensure reliability, all tests were replicated three times.

Tensile testing was conducted using an MTS Landmark testing machine at a rate of 1 mm/min . A video extensometer with a gauge length of 25 mm was used to record displacement. The samples were tested three times to evaluate the variation in tensile performance, and the fracture surface was observed using SEM. Hardness testing was performed using an HXS-1000tac microhardness tester (Zhongkekaihua Technology Development Co., Ltd., Lanzhou, China) with a load of 200 N and a dwell time of 15 s , following the test method [31] for microindentation hardness of materials. To reduce measurement errors, the hardness tester was calibrated with a standard hardness block ($238\text{ HV}_{0.2}$), and 10 measurements were taken from each sample.

The hydrophobicity of the samples was tested using a JC2000D1B water contact angle measurement instrument (YIMA, Hong Kong, China). To minimize errors, the contact angle value was determined as the average of 10 measurements.

The ICR was determined following the method proposed by Jin et al. [32]. Carbon paper was placed on both sides of the sample and placed between two copper plates with gold coating. The Testometric M350-CT universal testing machine (The Testometric Co. Ltd., Rochdale, UK) provided compressive force and recorded data, while the resistance between the copper electrodes was measured using the ZY9858 digital micro-ohmmeter (Shanghai

Instrumentation Co., Shanghai, China). The sample resistance was tested three times to reduce errors.

4. Conclusions

We conducted a comprehensive study on the performances of Hastelloy X and 304SS as potential bipolar plate materials of PEMFCs. Hastelloy X exhibited excellent mechanical performance due to its single-phase FCC structure. However, significant differences were observed in their corrosion resistance and ICR. In a simulated PEMFC working environment, Hastelloy X demonstrated better corrosion resistance compared to 304SS, although it still fell short of meeting the 2025 DOE target. Fortunately, under a compaction force of $140 \text{ N} \cdot \text{cm}^{-2}$, Hastelloy X achieved an ICR as low as $7.4 \text{ m}\Omega \cdot \text{cm}^2$, which can meet the 2025 DOE target. Therefore, Hastelloy X shows excellent mechanical properties and conductivity, making it a potential candidate material for PEMFC metal bipolar plates.

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Article

Corrosion and Interfacial Contact Resistance of NiTi Alloy as a Promising Bipolar Plate for PEMFC

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Abstract: Titanium (Ti) is generally considered as an ideal bipolar plate (BPP) material because of its excellent corrosion resistance, good machinability and lightweight nature. However, the easy-passivation property, which leads to increased interfacial contact resistance (ICR) and subsequently decreased cell performance, limits its large-scale commercial application in proton exchange membrane fuel cells (PEMFCs). In this paper, we proposed a NiTi alloy prepared by suction casting as a promising bipolar plate for PEMFCs. This NiTi alloy exhibits significantly decreased ICR values ($16.8 \text{ m}\Omega \text{ cm}^2$ at 1.4 MPa) compared with pure Ti ($88.6 \text{ m}\Omega \text{ cm}^2$ at 1.4 MPa), along with enhanced corrosion resistance compared with pure nickel (Ni). The superior corrosion resistance of NiTi alloy is accredited to the nobler open circuit potential and corrosion potential, coupled with low corrosion current densities and passive current densities. The improved ICR can be interpreted by the existence of high-proportioned metallic Ni in the passive film, which contributes to the reduced capacitance characteristic of the passive film (compared with Ti) and enhances charge conduction. This work provides a feasible option to ameliorate BPP material that may have desirable corrosion resistance and ICR.

Keywords: NiTi alloy; corrosion resistance; interfacial contact resistance; bipolar plates; PEMFC

1. Introduction

To alleviate the increasingly severe energy shortage and environmental issues caused by the continuous consumption of non-renewable fossil fuels, the development of clean and efficient energy sources has attracted significant attention [1,2]. Among these sources, hydrogen is considered an ideal environmentally friendly alternative to conventional fuels due to its high calorific value and negligible environmental pollution [3,4]. The efficient utilization of hydrogen energy necessitates the advancement of innovative technologies, with the proton exchange membrane fuel cell (PEMFC) being one of the most advanced and efficient energy generation methods for converting chemical energy (hydrogen and oxygen gases) into electricity [5,6]. However, the widespread usage of PEMFCs is still hindered by its high-cost components [7]. The membrane electrode assembly (MEA), gas diffusion layer (GDL) and bipolar plates (BPPs) are the main components of PEMFC [8–10]. Among these, the bipolar plates are considered as highly critical components, because they

account for 80% of the total weight and 40% of the total cost of PEMFCs [11,12]. These plates serve to collect current, as well as separate and distribute reactants and oxidant gases. The acidic working environment of the PEMFC can lead to corrosion damage to BPPs, which in turn reduces the output power and service life of the fuel cell [13]. Therefore, exploring advanced strategies or new materials to develop BPPs with enhanced anti-corrosive performance, high mechanical strength and superior electrical conductivity is highly anticipated [14].

Recently, several materials have shown promise as competitive options for BPPs. Graphite and its composites have the advantages of excellent electrical conductivity and chemical stability, but the poor manufacturability, durability and permeability limit their commercial application [15,16]. Unlike the brittle nature of graphite and its composites, metallic BPPs (such as those made from Ni, aluminum, titanium and stainless steel, etc.) can satisfy the requirements for mechanical properties, gas permeability and manufacturing costs [17]. Among these materials, titanium and its alloys stand out due to their high specific strength and exceptional corrosion resistance in harsh environments [5]. However, titanium and its alloys face challenges related to the increased interfacial contact resistance, attributed to the nonconductive passive film formed on the surface in the service process. Although the passive film can enhance the corrosion resistance, there still exists non-negligible issues in impairing electrical conductivity, leading to power waste and degenerate electric output in PEMFCs [18,19].

In this work, we introduce a NiTi alloy with superior corrosion resistance and favorable ICR, which makes it a promising material for BPPs to be used in PEMFCs. Compared with commercial Ti plate, the NiTi alloy has a fairly improved ICR value of $16.8 \text{ m}\Omega \text{ cm}^2$ at 1.4 MPa. Additionally, the NiTi alloy shows much better corrosion resistance compared with commercial Ni plates. Furthermore, the surface states of NiTi alloy in simulated PEMFC environments have been investigated to analyze its remarkable performance.

2. Results and Discussion

The microscopic morphology, elemental distribution and phase constituents of the NiTi alloy sample prepared by suction casting are shown in Figure 1. The scanning electron microscopy (SEM) image reveals a homogeneous microstructure with minimal defects (Figure 1a), owing to the rapid solidification process employed during suction casting. The darker regions observed mainly at grain boundaries are identified to contain NiTi_2 precipitates [20]. According to energy dispersive spectroscopy (EDS) mapping results (Figure 1b,c) from the indicated region in Figure 1a, Ni and Ti elements distribute homogeneously within the grain interior, but show depletion and enrichment at grain boundaries, respectively, because of the presence of NiTi_2 . Analysis of the X-ray diffraction (XRD) pattern (Figure 1d) indicates that the diffraction peak positions of the as prepared NiTi alloy agree well with those of the standard austenitic B2 phase (JCPDS No. 96-901-4020) [21], confirming the consistency in phase structure. However, the shift of the highest diffraction peak from (110) to (200) suggests the presence of strong texture that formed during rapid solidification. Notably, the texture also results in the absence of detectable NiTi_2 phase in XRD analysis. These characteristics of the NiTi alloy sample prepared by suction casting are quite different from that of the NiTi alloy prepared by conventional melting, which exhibits the existence of as-cast dendrites and a lack of strong texture (as shown in Figure S1, Supplementary Materials).

Evolution of open circuit potential (E_{OCP}) with the immersion time and the potentiodynamic polarization results are employed to investigate the corrosion resistance of NiTi alloy, pure Ti and pure Ni in $0.5 \text{ mol/L H}_2\text{SO}_4 + 2 \text{ ppm HF}$ solutions. As shown in the $E_{\text{OCP}}-t$ curves in Figure 2a, the E_{OCP} of pure Ti electrode decreases at the initial stage of immersion and then reaches a stationary value, while the E_{OCP} of NiTi alloy and Ni increases gradually and then tends to be stable. The two different tendencies at the initial stage of immersion may be caused by the naturally formed passive films on the surface, which is an intrinsic character that would be destroyed in the solution that contains halide ions (specifically F^-

ions in this work) [22]. The E_{OCP} stabilizes after a long immersion for all samples, meaning that the dissolution and growth of the passive films reach a dynamic equilibrium. When compared with pure Ti and pure Ni, the NiTi alloy displays a more positive E_{OCP} value, signifying the higher inertness property and expected superior corrosion resistance [23].

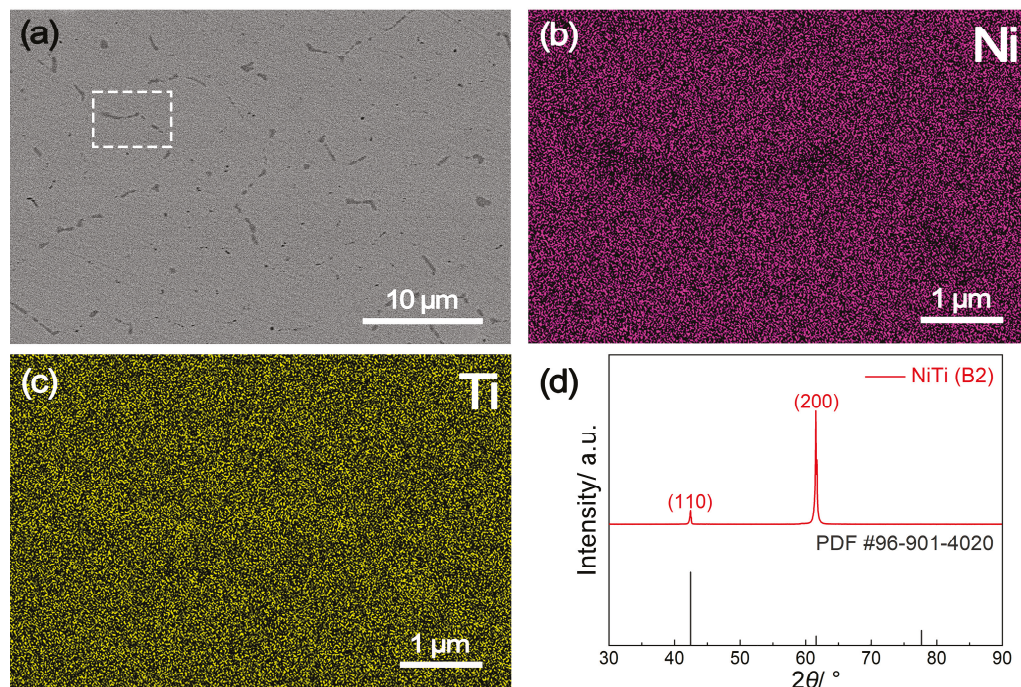


Figure 1. The (a) scanning electron microscopy (SEM) image and (b,c) corresponding elemental mapping results of the indicated region (white square in subfigure (a)) of the NiTi alloy prepared by suction casting, along with (d) the X-ray diffraction (XRD) pattern.

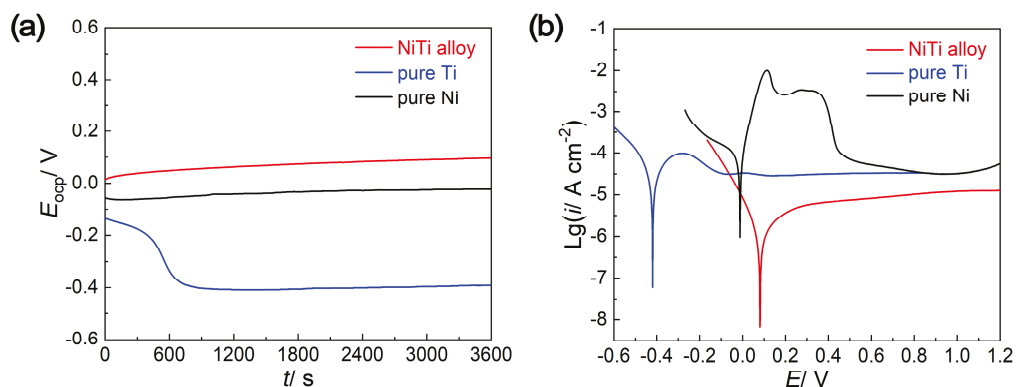


Figure 2. The (a) open circuit potential versus time ($E_{\text{OCP}}-t$) curves and (b) potentiodynamic polarization curves of NiTi alloy, pure Ti and pure Ni.

The potentiodynamic polarization curves are exhibited in Figure 2b, and the corresponding electrochemical parameters are listed in Table 1. Clearly, the corrosion potential (E_{corr}) of NiTi alloy is much nobler than that of pure Ti and pure Ni, and the current density (i_{corr}) of NiTi alloy is an order of magnitude lower than that of pure Ti and pure Ni. In addition, typical passivation behavior can be observed in the anodic branches of potentiodynamic polarization curves for all samples, with the contribution of passive elements Ti and Ni [24]. However, both the anodic branches of pure Ti and pure Ni possess the active–passive dissolution process, which is generally considered to be the oxidation process of the unstable transition oxides (sub-oxides) [25]. In contrast, the anodic branch of NiTi alloy changes directly into the passive region without an active–passive transition,

indicating the superior passive property that the protective film can be formed almost spontaneously at the E_{corr} [26]. Furthermore, the NiTi alloy has a lower passive current density (i_{pass}) than that of pure Ti and pure Ni, which can also reveal a better passive property. By comparing the electrochemical parameters related to general corrosion (E_{ocp} , E_{corr} , i_{corr}) and the passivation characteristics of the anodic process (i_{pass}), it can confirm the superior electrochemical stability of NiTi alloy in the acidic solution containing F^- ions.

Table 1. Electrochemical parameters extracted from the open circuit potential versus time ($E_{\text{OCP}}-t$) curves and the potentiodynamic polarization curves.

Samples	E_{OCP} (V)	E_{corr} (V)	i_{corr} ($\mu\text{A cm}^{-2}$)
NiTi	0.095	0.082	1.13
Pure Ti	−0.023	−0.419	28.80
Pure Ni	−0.397	−0.011	79.28

The critical properties for BPPs, including durability, interfacial contact resistance (ICR) and hardness, are displayed in Figure 3. Potentiostatic polarization tests at a simulated cathodic working potential (+0.85 V vs. SHE) were carried out to assess the durability requirements in a PEMFC environment (Figure 3a). At the initial stage, the current densities (i_{cathode}) for all samples decrease rapidly to lower values, because of the formation of passive films at this working potential, which lies within the passive regions for all samples (Figure 2b) [21–25]. Afterwards, pure Ni shows a relatively unstable and higher current density, signifying more electrochemical reactions and dissolution of metal ions from the Ni electrode [27]. For the NiTi alloy plate, its current density is slightly higher than the DOE standard of less than $1 \mu\text{A cm}^{-2}$, measuring at $1.28 \mu\text{A cm}^{-2}$. This indicates the good durability of the NiTi alloy, proving it to be a potential material for BPPs. The current density of the pure Ti plate is slightly lower than that of the NiTi alloy plate, confirming its preeminent corrosion resistance, due to the rapid oxidation on its surface to form TiO_2 in the simulated cathode environment. However, the passive film formed on the surface of the Ti plate could result in an increased ICR value and the degradation of the cell's performance [24].

The ICR between the BPPs and the GDL, one of the most significant resistances occurring at all interfaces within the PEMFC stack, is another critical factor affecting fuel cell performance. Figure 3b,c show the ICR values of the NiTi alloy, pure Ti and pure Ni after 8 h potentiostatic polarization at a cathode potential of 0.85 V vs. SHE in a 0.5 M H_2SO_4 and 2 ppm HF solution, under varying compaction forces and a pressure of 1.4 MPa. As shown in Figure 3b, the ICR values for all samples decrease rapidly at low compaction force, and then decrease slightly after reaching the pressure of 1.4 MPa (a typical compaction force for a single cell), revealing that the higher pressure ensures sufficient contact areas between BPPs and GDL [27]. Under each pressure, the ICR values are in the order of pure Ni < NiTi alloy < pure Ti. The ICR of the NiTi alloy ($16.8 \text{ m}\Omega \text{ cm}^2$) especially, is rather lower than that of pure Ti ($88.6 \text{ m}\Omega \text{ cm}^2$) under the pressure of 1.4 MPa, and is close to that of pure Ni ($7.6 \text{ m}\Omega \text{ cm}^2$) (Figure 3c). The ICR of NiTi alloy is only slightly higher than the US DOE 2020 requirement ($10 \text{ m}\Omega \text{ cm}^2$ under a compaction force of 1.4 MPa), but can be comparable with many surface treatment coatings (e.g., Cr electroplating coatings, double cathode glow discharge ZrCN nanocrystalline coatings, plasma-nitrided layers, etc.) [23,28]. Compared with these surface coatings, the NiTi alloy offers a significant advantage because of its simplified fabricating process and lower fabrication cost.

In addition, the hardness of the NiTi alloy (289.7 HV) is higher than that of pure Ti and pure Ni (218.1 and 122.8 HV, respectively) (Figure 3d), which contributes to enhancing the mechanical strength of the BPPs. Therefore, the NiTi alloy prepared by suction casting, as presented in this study, showcases a significant potential as BPP materials in PEMFCs, due to its considerable corrosion resistance (compared with pure Ni), lower ICR (compared with pure Ti) and superior mechanical strength.

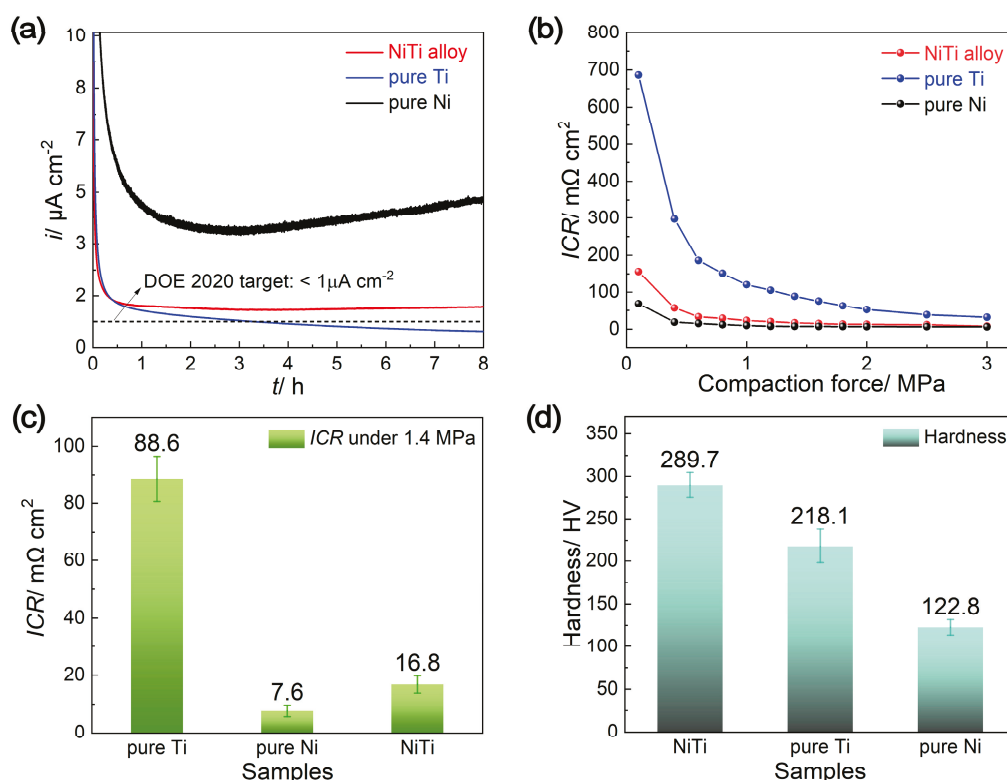


Figure 3. The (a) potentiostatic polarization curves, interfacial contact resistance (ICR) values: under (b) different compaction force and (c) the pressure of 1.4 MPa, along with (d) the hardness of NiTi alloy, pure Ti and pure Ni.

To thoroughly understand the remarkable performance of NiTi alloy in terms of corrosion resistance and ICR, the surface states of NiTi alloy, pure Ti and pure Ni were analyzed by X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). According to the deconvoluted XPS spectra for Ni 2p and Ti 2p (Figure 4a,b), Ni(OH)_2 (855.6 eV), NiO (853.7 eV) and metallic Ni (852.6 eV) are present on the surfaces of both the NiTi alloy and pure Ni, while TiO_2 (458.5 eV) and metallic Ti (454.1 eV) are found on the surfaces of both the NiTi alloy and pure Ti [29]. Meanwhile, the O 1s spectra consist of O^{2-} (530.0 eV) and OH^- (531.6 eV) peaks (Figure 4c) [30]. The OH^- species can originate from hydrated metal oxides or adsorbed H_2O [26]. The estimated ratios of different chemical states on the surfaces of NiTi alloy, pure Ti and pure Ni are listed in Table 2. When compared with pure Ti, the NiTi alloy has a relatively higher proportion of metallic components (76.34% metallic Ni, 12.28% metallic Ti), which is related to the metallic-type electrical conduction mechanism and contributes to high electrical conductivity and low ICR [29,31]. However, the presence of nonconductive TiO_2 species on the surface of the NiTi alloy leads to its ICR being slightly higher than that of pure Ni (Figure 3c). The ratio of $\text{O}^{2-}/\text{OH}^-$ also reflects the surface condition of the metals, representing the oxide content in the passive film [32]. Apparently, the pure Ti has the highest $\text{O}^{2-}/\text{OH}^-$ ratio (2.94), indicating good corrosion resistance but poor electrical conductivity due to the dense passive film. Conversely, pure Ni exhibits the opposite effect, with an $\text{O}^{2-}/\text{OH}^-$ ratio of 0.10. Consequently, the NiTi alloy possesses a moderate $\text{O}^{2-}/\text{OH}^-$ ratio (0.64), achieving a good balance between anti-corrosion and electrical conductivity performance. Moreover, an appropriate passive film on the surface of NiTi alloy can also prevent Ni ions from leaching [33,34].

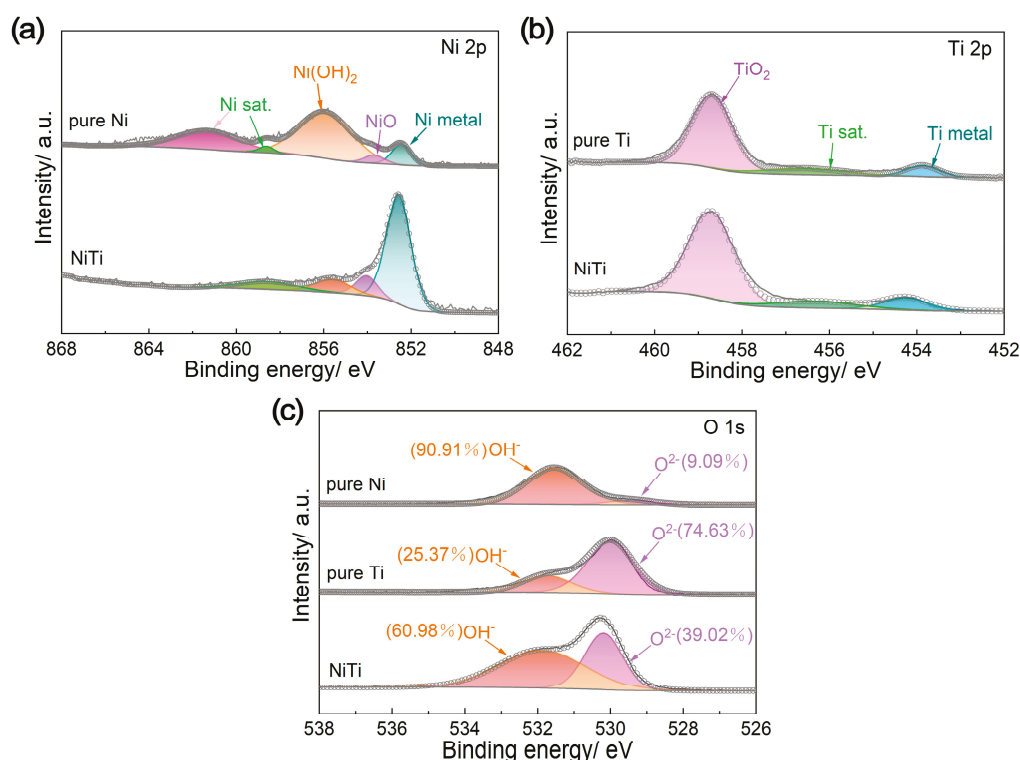


Figure 4. X-ray photoelectron spectroscopy (XPS) analysis results of different materials (NiTi alloy, pure Ti and pure Ni): (a) Ni 2p, (b) Ti 2p and (c) O 1s.

Table 2. The estimated ratios of different chemical states on the surface of electrodes.

Samples	Ni 2p (%)		Ti 2p (%)		O^{2-}/OH^{-}
	NiO + Ni(OH) ₂	Metallic Ni	TiO ₂	Metallic Ti	
NiTi	23.66	76.34	87.72	12.28	0.64
Pure Ti	/	/	88.5	11.5	2.94
Pure Ni	86.99	13.01	/	/	0.1

The EIS results are displayed in Figure 5, and have been fitted to an equivalent circuit (EEC, shown in Figure S2, Supplementary Materials), where R_s represents the solution resistance, R_1 and R_2 represent the charge transfer resistance and passive film resistance, respectively, and CPE_1 and CPE_2 represent the contrast phase elements corresponding to the double-layer capacitance and passive film. The fitting results are shown in Table 3, with chi-square (χ^2) values in the range of 10^{-4} – 10^{-3} , indicating that the EEC reasonably reflects the actual electrochemical process occurring on the surface of the tested samples in the simulated PEMFC environment. From the Bode-phase angle plots (Figure 5c,d), it can be observed that the $\log|Z|$ and $\log|f|$ of the NiTi alloy and pure Ti exhibit linear relationships over a wide frequency range, with slopes close to -1 . However, Ni only shows a linear relationship within a narrow frequency band in the mid-frequency region (f : 10^3 – 10^1 Hz), signifying that the corrosion resistance of the NiTi alloy and pure Ti is significantly better than that of Ni [22]. Additionally, both the NiTi alloy and pure Ti display a platform in the mid-to-low-frequency range, with their maximum phase angles approaching 90° , suggesting obvious capacitive characteristics related to the protective passive films [19,23]. In contrast, pure Ni displays a time constant in the mid-frequency region, which is characteristic of metallic material in electrolytes [26,35]. In addition, the capacitive characteristics of pure Ti are stronger than those of the NiTi alloy, which can be concluded from the fact that (1) the Z'' parts in the Nyquist plots of pure Ti are larger than those of the NiTi alloy (Figure 5a,b) and (2) $Y_{0-\text{pure Ti}} > Y_{0-\text{NiTi alloy}}$ (Table 3). Here, the

thickness of passive film (δ) can be compared by $1/Y_0$ [36]. These results can effectively account for the ICR order: pure Ni < NiTi alloy < pure Ti.

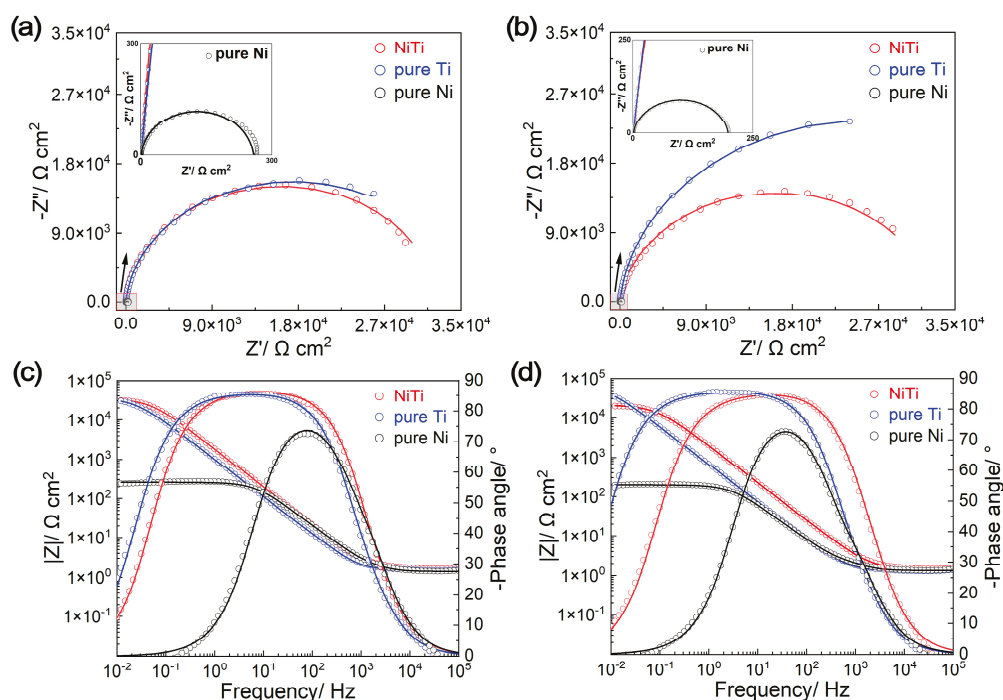


Figure 5. Electrochemical impedance spectroscopy (EIS) analysis of NiTi alloy, pure Ti and pure Ni before ((a) Nyquist plots, (c) Bode-phase plots) and after ((b) Nyquist plots, (d) Bode-phase plots) potentiostatic polarization.

Table 3. Electrochemical parameters obtained from the equivalent circuits simulation (the EIS data fitting results before and after potentiostatic polarization).

Before potentiostatic polarization	Elements	CPE_1-Y_0 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	R_1 ($\Omega \text{ cm}^2$)	CPE_2-Y_0 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	R_2 ($\Omega \text{ cm}^2$)	$\Sigma\chi^2$
	NiTi	7.19×10^{-5}	4.27	4.14×10^{-5}	3.25×10^4	1.08×-10^3
	Pure Ti	8.49×10^{-5}	2.71	9.06×10^{-5}	3.42×10^4	1.02×-10^3
	Pure Ni	5.34×10^{-5}	8.54	2.31×10^{-5}	219.20	2.16×-10^3
After potentiostatic polarization	Elements	CPE_1-Y_0 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	R_1 ($\Omega \text{ cm}^2$)	CPE_2-Y_0 ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$)	R_2 ($\Omega \text{ cm}^2$)	$\Sigma\chi^2$
	NiTi	4.59×10^{-5}	5.64	4.54×10^{-5}	4.14×10^4	1.56×-10^3
	Pure Ti	2.65×10^{-4}	6.97	1.35×10^{-4}	8.15×10^4	1.57×-10^3
	Pure Ni	1.04×10^{-4}	2.87	1.18×10^{-4}	184.95	1.97×-10^3

The SEM images and EDS results of the NiTi alloy, along with pure Ni and pure Ti as comparative samples, following potentiostatic polarization measurements are illustrated in Figure 6. As evident in Figure 6a, pure Ni suffered from severe intergranular corrosion under the cathode operating condition of the PEMFC, leading to the unstable cathodic current densities during the potentiostatic polarization over time (Figure 3). In contrast, pure Ti reveals almost no evidence of corrosion (Figure 6b), which benefits from the passivation process in the meantime. Similarly, there is no sign of corrosion on the NiTi alloy either (Figure 6c). Additionally, the EDS mapping results of the indicated region in Figure 6a differ little from those obtained before potentiostatic polarization. While the grain boundaries of the NiTi alloy display depletion of Ni and enrichment of Ti, the elemental distribution within the grain interior remain uniform (Figure 6d,e). It is noteworthy that the semi-quantitative analysis of NiTi alloy did not detect the presence of oxygen (Figure 6f),

implying the formation of a relatively thinner passive film on the NiTi alloy surface. These results can thoroughly confirm the high corrosion resistance of NiTi alloy, which is similar to pure Ti.

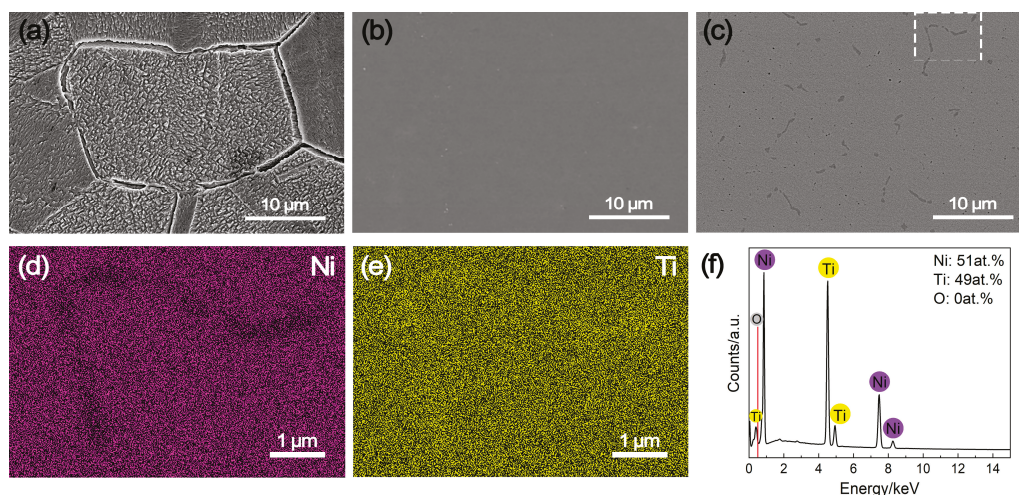


Figure 6. SEM images of (a) pure Ni, (b) pure Ti and (c) NiTi alloy after potentiostatic polarization measurements, along with (d,e) elemental mapping results and (f) semi-quantitative result of the indicated region (white square in subfigure (c)).

3. Materials and Methods

Electrolytic Ni (purity > 99.9%) and sponge Ti (purity > 99.7%) with an atomic ratio of 51:49 were utilized to fabricate melting cast NiTi alloy in a non-consumable vacuum arc melting furnace (WK-I, Physcience Opto-electronics Co., Ltd., Beijing, China). Then, the rectangular NiTi plates measuring 20 mm × 10 mm × 1 mm were obtained by suctioning the molten alloy into a water-cooled copper mold. Meanwhile, pure Ti and pure Ni with the same dimensions were also used in this study for comparative analysis. Thereafter, all samples were grinded and polished, as well as cleaned with deionized water and anhydrous ethanol.

The OCP, potentiodynamic polarization, potentiostatic polarization and EIS measurements were conducted to investigate the electrochemical performance of NiTi alloy in the electrolytic cell solution (0.5 mol/L H₂SO₄ + 2 ppm HF), which is usually used to simulate the working environment of the fuel cell. All tests were performed using a CHI660E electrochemical workstation (Chenhua, Shanghai, China), employing a three-electrode electrochemical cell, consisting of the NiTi alloy serving as the working electrode, a Pt sheet as the counter electrode, and a saturated Hg/Hg₂SO₄ electrode as the reference electrode. In this paper, all experiments were repeated at least three times to ensure accuracy. Furthermore, the obtained potentials (V vs. Hg/Hg₂SO₄) were converted to potentials versus a standard hydrogen electrode (SHE) according to the relationship: V vs. SHE = V vs. Hg/Hg₂SO₄ + 0.658.

Initially, the OCP versus time relationship was recorded for 3600 s to obtain a stable surface condition. The potentiodynamic polarization was measured in the range of −0.6 V vs. SHE to 1.0 V vs. SHE with a scan rate of 1 mV/s. The potentiostatic polarization was conducted at a potential of 0.85 V vs. SHE for 8 h. The EIS measurement was tested at the OCP frequency range spanning from 100 kHz to 10 mHz, applying a perturbation magnitude of 10 mV.

The microstructure and corresponding elemental distribution were characterized by SEM (Apreo S Hivac, Thermo Fisher, Waltham, MA, USA) equipped with EDS (Ultim Live 100X, Oxford, Abingdon, England). The crystal structure was analyzed by XRD (SmartLab SE, Rigaku, Tokyo, Japan) with Cu K α radiation at a scanning step 0.02° and a scanning speed of 10°/min. The composition and chemical state of the passivation film formed on

the sample surface were analyzed using XPS (AXIS SUPRA+, Shimadzu, Kyoto, Japan). The hardness was tested using a small load Vickers hardness tester (HV-1000B, Huayin, Wuhan, China) with a loading force of 500 g and a holding time of 20 s. Each sample underwent 10 measurements and the average value was taken.

The ICR values were measured by a sandwich configuration proposed by Wang et al. [27], as shown in the schematic diagram in Figure 7, and calculated using following equation:

$$ICR = S(R_{\text{total}} - R_{\text{GDL}})/2$$

where S is the contact area between the sample and the carbon paper. R_{total} signifies the measured total resistance, whereas R_{GDL} denotes the resistance attributed to the GDL within carbon paper. The operating load spanned from 0.1 to 3.0 MPa, containing the range used to record the ICR values under different compaction forces.

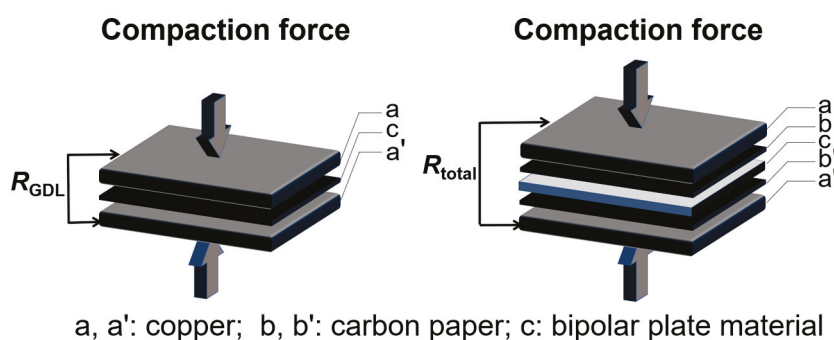


Figure 7. The schematic diagram for testing the R_{GDL} and R_{total} values.

4. Conclusions

A NiTi alloy bipolar plate material was prepared by suction casting and its corrosion resistance, ICR and hardness were investigated in the simulated PEMFC environments. The NiTi alloy has a fairly low ICR value of $16.8 \text{ m}\Omega \text{ cm}^2$ at 1.4 MPa, which is a considerable improvement over the pure Ti plate ($88.6 \text{ m}\Omega \text{ cm}^2$ at 1.4 MPa) and slightly higher than the US DOE 2020 target. Additionally, the NiTi alloy shows superior corrosion resistance in electrochemical measurements and remains corrosion-free after potentiostatic polarization in a simulated cathodic environment for 8 h. In addition, the NiTi alloy has a higher hardness (289.7 HV) compared with pure Ti (218.1 HV) and pure Ni (122.8 HV). Overall, this work showcases the significant potential of the NiTi alloy prepared by suction casting as a BBP material in PEMFCs. In the near future, further investigation is warranted on the long-term use of NiTi alloy for BPPs, including factors such as pH value, fluoride ion concentration, Ni ion leaching and cell efficiency.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/molecules29153696/s1>, Figure S1: The (a) scanning electron microscopy (SEM) image and (b) X-ray diffraction (XRD) pattern of the NiTi alloy prepared by conventional melting; Figure S2: Equivalent electrical circuit used for modeling experimental electrochemical impedance spectroscopy (EIS) data.

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Communication

Mechanistic Study on the Corrosion of (La,Sr)(Co,Fe)O_{3-δ} Cathodes Induced by CO₂

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Abstract: Solid Oxide Fuel Cell (SOFC) cathodes operating in ambient atmospheric conditions inevitably encounter CO₂ contamination, leading to sustained performance deterioration. In this investigation, we examined the impact of CO₂ on three variants of (La,Sr)(Co,Fe)O_{3-δ} cathodes and employed the distribution of relaxation times method to distinguish distinct electrochemical processes based on impedance spectra analysis. We meticulously analyzed and discussed the corrosion resistance of these (La,Sr)(Co,Fe)O_{3-δ} cathodes under high CO₂ concentrations, relying on the experimental data. Electrochemical impedance spectroscopy results revealed that La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF–6428), La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF–4628), and La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-δ} (LSCFN–46271) cathodes exhibited persistent degradation when exposed to CO₂ at temperatures of 650 °C or 800 °C during the durability-testing period. An increase in electrode polarization resistance was observed upon CO₂ introduction to the electrode, but electrode performance recovered upon returning to a pure air environment. Furthermore, X-ray diffraction and scanning electron microscopy analyses confirmed that CO₂ did not cause permanent damage to the (La,Sr)(Co,Fe)O_{3-δ} cathodes. These findings indicate that the (La,Sr)(Co,Fe)O_{3-δ} cathodes exhibit excellent resistance to CO₂-induced corrosion.

Keywords: CO₂ corrosion; (La,Sr)(Co,Fe)O_{3-δ} cathodes; stability study; degradation mechanisms

1. Introduction

Solid oxide fuel cells (SOFCs) stand as the most efficient devices devised to date for the direct conversion of chemical fuels into electrical power [1–3]. Nevertheless, despite several decades of development, long-term stability remains a formidable obstacle impeding the widespread commercialization of SOFC technology [4]. Among the crucial components of the SOFC, the cathode assumes a pivotal role, with its overpotential often accounting for a substantial portion of energy loss. Ensuring the chemical and morphological stability of electrode materials under the demanding operational conditions of SOFCs remains of paramount significance [5–7].

In both research and practical applications, ambient air is typically directed straight to the cathodes. This air carries contaminants, such as CO₂, which are challenging to eliminate and contribute to cathode corrosion and degradation [8]. Consequently, an in-depth investigation into the effects of CO₂ on the performance and durability of SOFC cathodes becomes imperative.

CO₂ readily engages in reactions with alkaline-earth elements present in cathode materials, leading to the formation of carbonates [9,10]. Consequently, the Ba-based Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) cathode, recognized for its superior performance, demonstrates limited resilience to CO₂ due to the presence of Ba and Sr as A-site alkaline-earth elements [11,12]. Yi, Wang, and Yang reported that the introduction of partial Co substitution with Fe or Nb, yielding cathodes such as BaCo_{0.4}Fe_{0.4}Nb_{0.2}O_{3-δ}, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Nb_{0.1}O_{3-δ},

and $\text{Ba}_{0.9}\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$, substantially enhances corrosion resistance against CO_2 [13–15]. Investigations into the effects of CO_2 on La-based cathodes, such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, and $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$, have also been systematically conducted [16,17]. Notably, the absence of Ba in La-based cathodes results in improved tolerance to CO_2 . It is worth noting that the CO_2 corrosion mechanism varies among different cathodes due to the diversity in cathode chemical composition and crystal structure [18].

$(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathodes have garnered considerable attention due to their exceptional catalytic activity, mixed electronic–ionic conductivity, and compatibility with other cell components, both chemically and mechanically. Within the diverse spectrum of $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathode compositions, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF–6428) stands out as a favored choice among IT-SOFC developers [19–21]. The impact of atmospheric CO_2 on surface segregation and phase formation in LSCF–6428 was investigated [22,23]. The findings revealed that the presence of atmospheric CO_2 accelerated the kinetics of Sr surface segregation, primarily due to the heightened thermodynamic driving force for SrCO_3 formation. Nevertheless, the crystal structure and performance of both $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Nb}_{0.2}\text{O}_{3-\delta}$ materials remained largely unaffected under a CO_2 atmosphere, demonstrating their robust CO_2 tolerance [17,24].

Previous research has demonstrated that to further enhance the performance of LSCF–6428, the partial substitution of La by Sr at the A-site and the addition of a small amount of Nb to the B-site can improve its electrical conductivity and chemical stability [25–28]. Consequently, the resultant $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.7}\text{Nb}_{0.1}\text{O}_{3-\delta}$ cathodes contain a higher proportion of Sr element. Therefore, it becomes imperative to investigate CO_2 corrosion on these two cathode variants and compare them with the state-of-the-art LSCF–6428 cathode.

In this study, we delve into the mechanisms of CO_2 -induced corrosion affecting $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, and $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.7}\text{Nb}_{0.1}\text{O}_{3-\delta}$ cathodes.

2. Results and Discussion

2.1. Impedance and DRT Analysis of Three Electrode Configurations under Various Oxygen Partial Pressures

To determine the frequency range associated with various electrochemical processes of oxygen electrode reactions, impedance spectra Nyquist plots and Bode plots were obtained for LSCF–6428, LSCF–4628, and LSCFN–46271 symmetric electrodes at 800 °C (see additional data in Supplementary Materials). These electrodes were exposed to four different oxygen partial pressure atmospheres, as depicted in Figure 1: 5% O_2 –95% N_2 , 20% O_2 –80% N_2 , 50% O_2 –50% N_2 , and 100% O_2 . From the Nyquist plots, it can be observed that the polarization impedance of the symmetric electrodes increases with decreasing oxygen partial pressure. The same conclusion can be drawn from the modulus curves of impedance in the Bode plots. Additionally, the Bode plots illustrate changes in the phase angle within specific frequency domains, showing that significant variations occur primarily below 400 Hz.

As illustrated in Figure 2, the distribution of relaxation time (DRT) was calculated based on the EIS data recorded at 800 °C. The electrode processes were arbitrarily divided into three distinct peaks, denoted as P1, P2, and P3, signifying the occurrence of three limiting sub-processes. P1 manifested when the O_2 concentration dropped below 5%, with its appearance closely tied to oxygen concentration. Typically, the frequency range of 0–10 Hz is attributed to gas diffusion within and around the cathodes. The area beneath the P2 peaks displayed variability with oxygen partial pressure, and previous studies indicate its association with chemical reactions [29–31]. P2 was predominantly identified as a process linked to the chemical surface exchange of O_2 , featuring a frequency range of approximately 10–400 Hz. At higher frequencies, the DRT curves exhibited overlap, indicating that this region remained unaffected by fluctuations in O_2 concentration. Consequently, P3 pertains to the electrode–electrolyte interface process and corresponds to charge transfer reactions at the triple phase boundary, encompassing a frequency range of 400–10,000 Hz. Notably,

in Figure 2, P2 is characterized by the tallest peaks, suggesting that the surface exchange kinetics of oxygen at the cathode are likely the rate-determining reaction.

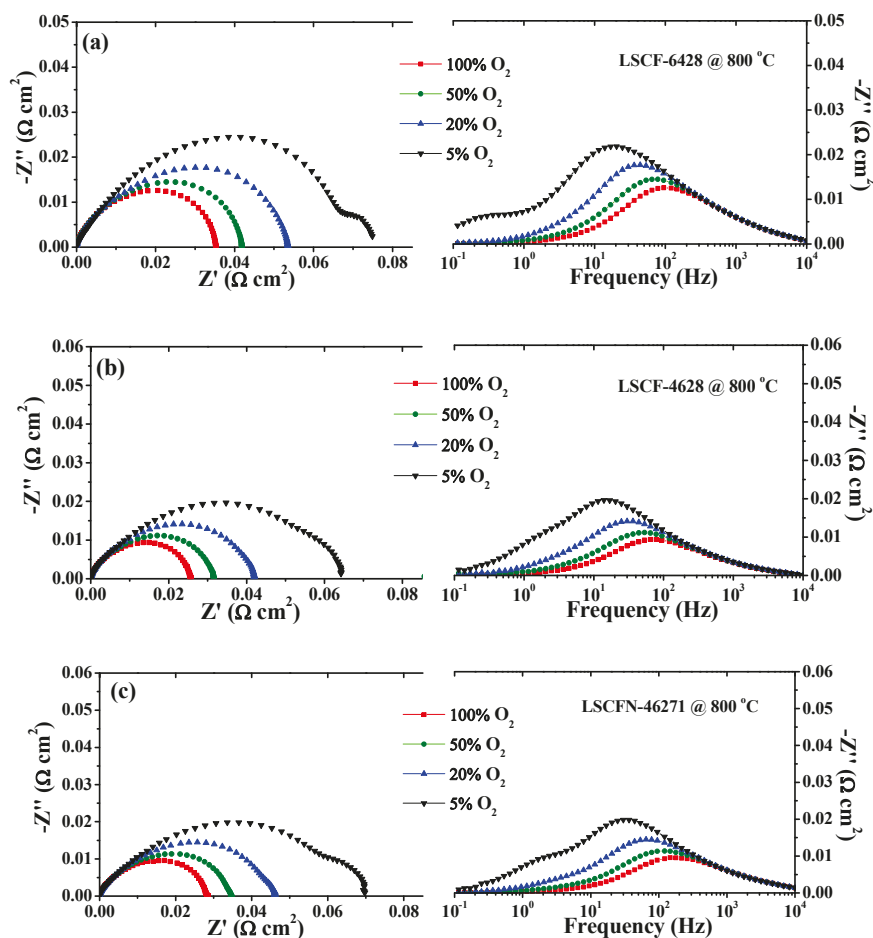


Figure 1. Nyquist plots and Bode plots for (a) LSCF-6428, (b) LSCF-4628, and (c) LSCFN-46271 electrodes measured at 800 °C under different oxygen partial pressures in $\text{O}_2 + \text{N}_2$ mixtures.

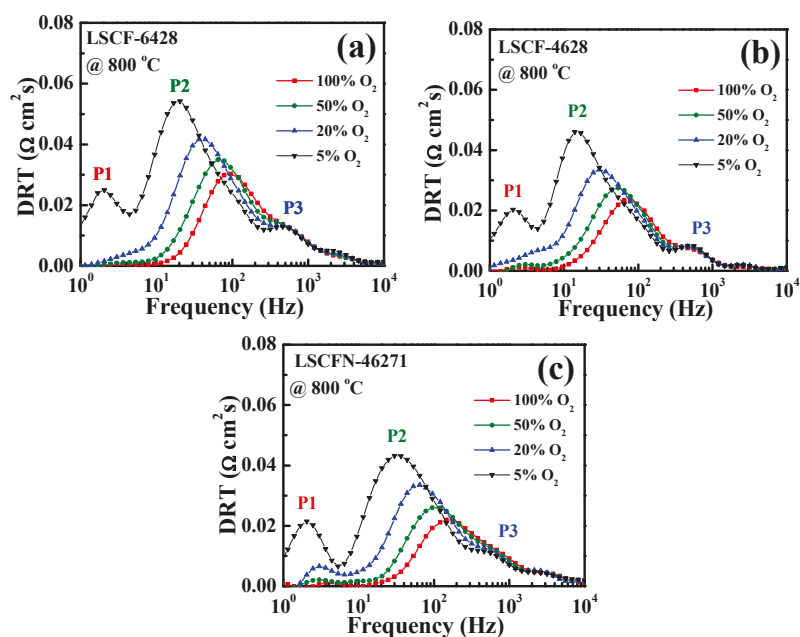


Figure 2. DRT plots for (a) LSCF-6428, (b) LSCF-4628, and (c) LSCFN-46271 electrodes measured at 800 °C under different oxygen partial pressures in $\text{O}_2 + \text{N}_2$ mixtures.

2.2. The Influence of CO₂

The LSCF–6428, LSCF–4628, and LSCFN–46271 electrodes underwent testing at temperatures of 650 °C and 800 °C under various gas atmospheres, each featuring different CO₂ concentrations. Figure 2 illustrates that augmenting the CO₂ content in the air led to an increase in the electrode polarization resistance (Rp).

From these findings, it becomes evident that the performance alteration of (La,Sr)(Co,Fe)O_{3-δ} cathodes appears to be more responsive to CO₂ at the lower temperature of 650 °C than at 800 °C. Specifically, for LSCF–6428 at 650 °C, Rp values of 0.510 Ω cm² (air), 0.534 Ω cm² (20% CO₂-air), and 0.556 Ω cm² (50% CO₂-air) were recorded. In comparison, LSCF–4628 and LSCFN–46271 exhibited Rp values of 0.390 Ω cm², 0.414 Ω cm², and 0.443 Ω cm² and 0.400 Ω cm², 0.415 Ω cm², and 0.430 Ω cm², respectively, under the same gas atmospheres. Notably, the Rp increased with rising CO₂ content in the air. Under identical atmospheric conditions, LSCF–6428 exhibited the highest Rp, while the difference between LSCF–4628 and LSCFN–46271 was relatively minor.

However, at 800 °C, Rp did not exhibit a clear trend under the three atmospheres. For instance, the initial impedances of the LSCF–6428, LSCF–4628, and LSCFN–46271 electrodes were approximately 0.050 Ω cm², 0.039 Ω cm², and 0.043 Ω cm², respectively. Comparative analysis revealed that the Rp values of LSCF–4628 and LSCFN–46271 were lower than those of LSCF–6428.

Given the significant influence of CO₂ content on EIS at 650 °C, DRT analysis was applied to these results. Figure 3b,d,f display the primary response frequencies. With increasing CO₂ content, the P2 peaks shifted towards lower frequencies, and their area also expanded. As depicted in Figure 1, the P2 peak correlates with the surface exchange of O₂. Consequently, it can be inferred that CO₂ predominantly impacts the oxygen surface exchange reaction [32]. The observed degradation is likely attributed to the competition between CO₂ and O₂ for available oxygen vacancies, leading to a competitive mechanism that affects cathode performance.

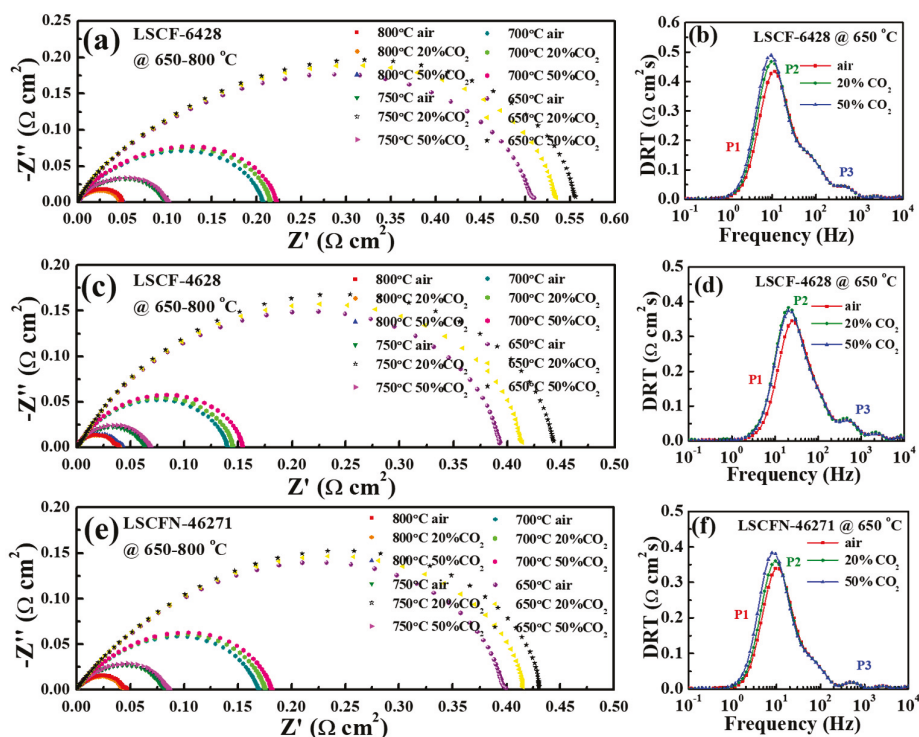


Figure 3. Polarization impedance spectra of LSCF–6428 (a), LSCF–4628 (c), and LSCFN–46271 (e) at 600–800 °C and different CO₂ concentrations, and DRT plots of LSCF–6428 (b), LSCF–4628 (d), and LSCFN–46271 (f) at 650 °C.

2.3. Electrode Durability

The endurance of (La,Sr)(Co,Fe)O_{3-δ} cathodes when exposed to CO₂ was further scrutinized at 800 °C under a 50% CO₂-air atmosphere for durations of up to 60 h. Figure 4a,c,e depict the EIS and Bode spectra for LSCF–6428, LSCF–4628, and LSCFN–46271, respectively. Over time, the R_p values for all three electrodes exhibited an upward trend. Specifically, LSCF–6428 increased from ~0.064 Ω cm² at 1 h to 0.085 Ω cm² at 60 h. Similarly, LSCF–4628 and LSCFN–46271 increased from ~0.053 Ω cm² to 0.084 Ω cm² and ~0.057 Ω cm² to 0.073 Ω cm², respectively. The evolution of R_p values over time is illustrated in Figure 4g, indicated by solid symbols. Across the three (La,Sr)(Co,Fe)O_{3-δ} cathodes, the trends were remarkably similar, with all three R_p values showing a relatively rapid increase during the initial 10 h, followed by a more gradual rise. Notably, LSCF–4628 exhibited the most pronounced degradation rate.

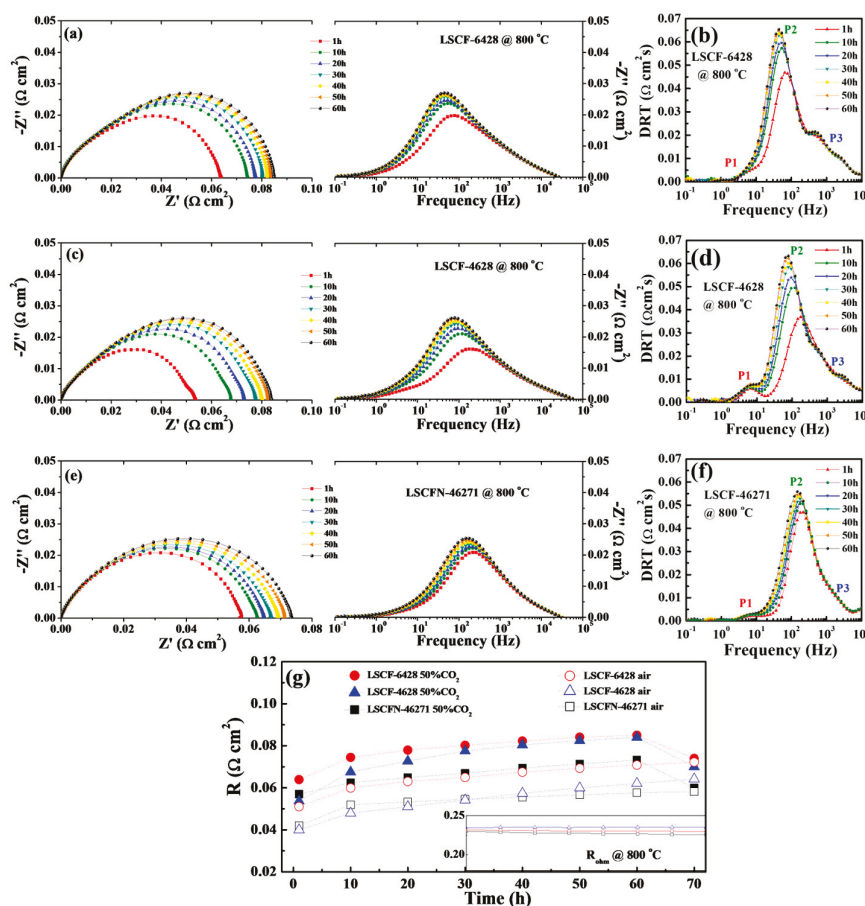


Figure 4. LSCF–6428 (a), LSCF–4628 (c), and LSCFN–46271 (e) impedance Nyquist and Bode tests in a 50% CO₂-50% air atmosphere at 800 °C, and DRT plots for LSCF–6428 (b), LSCF–4628 (d), and LSCFN–46271 (f), (g) shows the polarization impedance numerical changes corresponding to a 70 h stability test for the 3 electrodes (inset displays ohmic impedance values).

The DRT analysis of the EIS results is illustrated in Figure 4b,d,f. The electrochemical processes associated with P1 and P3 remained relatively stable throughout the test duration. However, P2, corresponding to the oxygen adsorption and release process, shifted to lower frequencies over time, accompanied by an increase in peak area. Consequently, a plausible inference is that adsorbed CO₂ partially covered the catalytically active sites of (La,Sr)(Co,Fe)O_{3-δ} for the oxygen reduction reaction, thus hindering the diffusion of O₂.

To assess the magnitude of the CO₂ effect, a baseline test was conducted. The three (La,Sr)(Co,Fe)O_{3-δ} cathodes were subjected to testing at 800 °C under 100% air for 70 h (i.e., not exposed to CO₂). The results are presented in Figure 4g, indicated by hollow symbols.

In the absence of CO_2 , the degradation rates of Rp were considerably lower than those observed under the 50% CO_2 -air mixed gas atmosphere. According to previous studies, the performance degradation of $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathodes over time might be attributed to Sr migration and segregation on the electrode surfaces at high temperatures [33].

For cathodes subjected to a CO_2 -rich environment, at the 60 h mark, the gas flow was reverted to atmospheric air for a duration of 10 h to assess the possibility of reversing the increase in Rp upon CO_2 removal. EIS measurements demonstrated that the Rp values decreased and closely approximated those of the electrodes that had not been exposed to CO_2 . In other words, the electrode performance experienced a substantial recovery. This observation suggests that exposure to CO_2 likely did not result in any permanent damage to the $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathodes.

In the figure within Figure 4g, the impedance change over time of the three symmetrical electrodes is represented by the impedance evolution. It can be observed from the figure that the ohmic impedance remained almost constant during the 70 h stability test, and its influence can be neglected.

The corrosion stability of the $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ cathodes at 650°C was also investigated, and the results are presented in Figure 5. The test commenced with the use of ambient air, after which the gas flow was transitioned from 100% air to a 50% CO_2 -air mixture, maintained for a duration of 60 h, before reverting to 100% air conditions. In the case of LSCF-6428, the Rp increased from $0.510\ \Omega\ \text{cm}^2$ to $0.611\ \Omega\ \text{cm}^2$ within the initial 10 h. Nevertheless, in comparison with EIS conducted at 800°C , the impedance value did not exhibit significant alterations after 50 h. This observation suggests that LSCF-6428 demonstrated a higher degree of stability at lower temperatures. Upon replenishing the tube furnace with 100% air for 10 h, the EIS readings dropped back to approximately $0.520\ \Omega\ \text{cm}^2$. Similar trends were observed for cathodes LSCF-4628 and LSCFN-46271. To better illustrate the changes in impedance values, the impedance variations during the process are presented in Table 1. It becomes evident that the degradation patterns of the LSCF cathodes at 650°C resembled those at 800°C . Importantly, the exposure to CO_2 did not lead to permanent damage to the electrodes, as the electrode performance could be readily restored upon CO_2 removal.

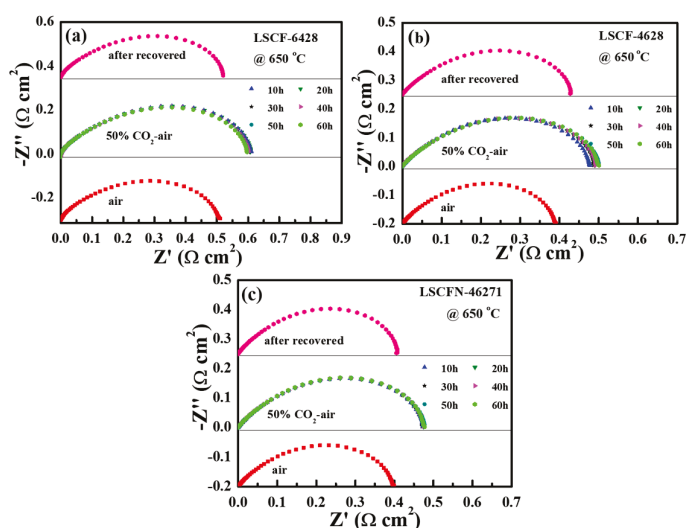


Figure 5. EIS stability test of LSCF-6428 (a), LSCF-4628 (b), and LSCFN-46271 (c) in a 50% CO_2 -air environment at 650°C .

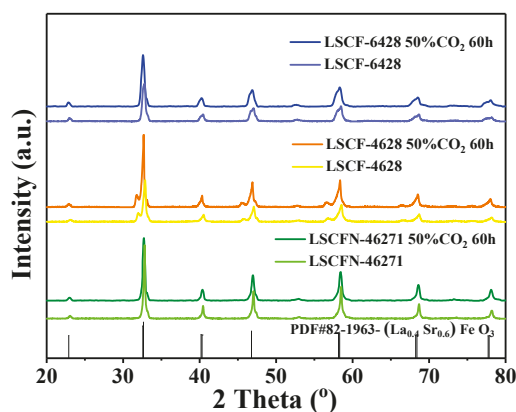
This CO_2 -induced performance degradation is most likely attributable to the competition between CO_2 and O_2 molecules vying for active sites on the electrode surface during oxygen exchange reactions [34,35].

Table 1. Polarization impedance values during the transition between air and 50% CO₂-air.

Electrode	Air/ Ω cm ²	50% CO ₂ -Air 10 h/ Ω cm ²	50% CO ₂ -Air 30 h/ Ω cm ²	50% CO ₂ -Air 60 h/ Ω cm ²	After Recovered/ Ω cm ²
LSCF-6428	0.510	0.611	0.601	0.597	0.520
LSCF-4628	0.392	0.478	0.488	0.501	0.427
LSCFN-46271	0.400	0.475	0.472	0.478	0.406

2.4. XRD Analysis

XRD patterns of the (La,Sr)(Co,Fe)O_{3-δ} cathodes, both before and after annealing in a 50% CO₂-air environment at 800 °C, are illustrated in Figure 6. Through a comparative analysis with the reference spectra obtained without heat treatment and the standard PDF cards (PDF#82-1963), it can be unequivocally concluded that all three (La,Sr)(Co,Fe)O_{3-δ} cathodes retained their singular-phase perovskite structure with a cubic lattice. No evidence of any additional impurity phases was detected, or if present, their content was below the detection limit of the XRD analysis. These findings serve as strong indicators that all three cathodes remained stable when exposed to a CO₂-containing atmosphere and did not undergo any reactive interactions with CO₂ during the testing period.

**Figure 6.** XRD patterns of the three cathodes before and after testing at 800 °C in 50% CO₂-air for 60 h.

2.5. SEM Analysis

The morphological evaluation of the (La,Sr)(Co,Fe)O_{3-δ} cathodes, both prior to and after the CO₂ stability testing, is depicted in Figure 7. SEM images of the LSCF electrode surfaces before the testing phase are displayed in Figure 7a,c,e, corresponding to LSCF-6428, LSCF-4628, and LSCFN-46271, respectively. These electrodes were characterized by fine particle structures with a high degree of porosity, ensuring efficient gas diffusion. Notably, the surface morphologies of all three cathodes exhibited striking similarities.

Figure 7b,d,f present SEM images of the LSCF electrode surfaces after being subjected to 60 h exposure to 50% CO₂-air at 800 °C. A comparison of these two sets of images clearly indicates that there was virtually no discernible alteration in electrode porosity or particle size following the 60 h CO₂ exposure period. The combined results from XRD and SEM provide compelling evidence that the LSCF-6428, LSCF-4628, and LSCFN-46271 cathodes remained stable when exposed to high-temperature, high-CO₂ atmospheres. Importantly, they did not undergo any reactive interactions with CO₂ throughout the testing process, and their surfaces remained smooth and devoid of impurities at the conclusion of the test.

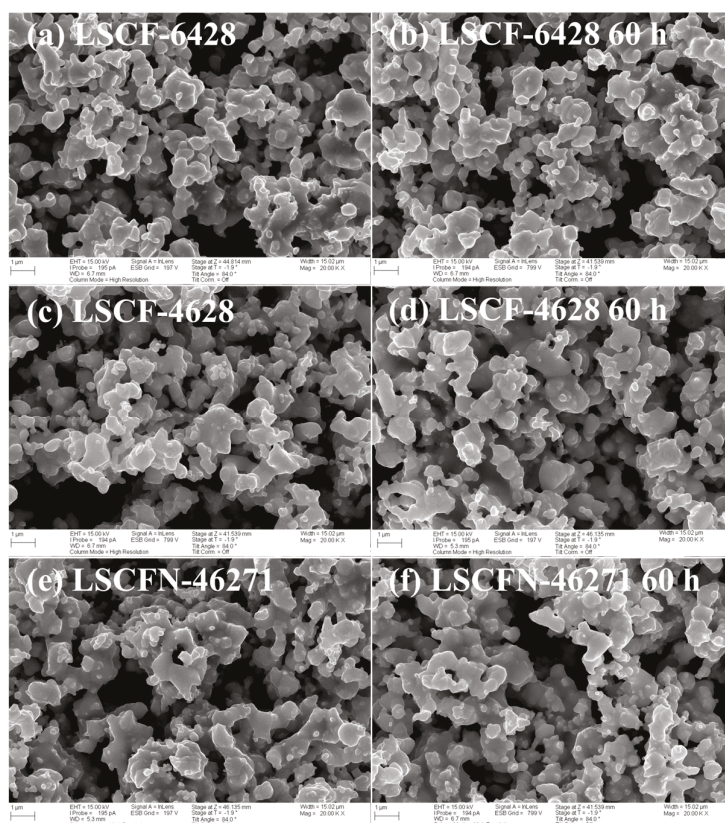


Figure 7. SEM micrographs on the surfaces of (a,b) LSCF–6428, (c,d) LSCF–4628, and (e,f) LSCFN–46271 before and after 60 h corrosion in 50% CO₂-air at 800 °C.

3. Experimental Section

3.1. Material Synthesis and Electrode Fabrication

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF–6428), La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF–4628), and La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-δ} (LSCFN–46271) cathode powders were synthesized using the solid-phase synthesis method. Details regarding the material selection, preparation procedures, and the formulation of the electrode ink can be found in our prior publication [20]. As the electrolyte, a gadolinia-doped ceria (GDC) substrate with a thickness of 150 µm was employed, sourced from Kerafol Keramische Folien GmbH, Germany. Subsequently, the GDC substrate was precisely laser-cut into square pieces measuring 9 mm × 9 mm.

For the measurement of electrochemical impedance spectroscopy (EIS), symmetric (La,Sr)(Co,Fe)O_{3-δ} electrodes were meticulously fabricated. (La,Sr)(Co,Fe)O_{3-δ} powder was admixed with a slurry composed of pine oil alcohol and ethyl cellulose. LSCF–6428, LSCF–4628, and LSCFN–46271 electrode inks were screen-printed on both sides of the GDC substrates, followed by sintering in air at 1100 °C for 2 h. The thickness of (La,Sr)(Co,Fe)O_{3-δ} and GDC was about 30 µm and 150 µm. This process yielded three distinct types of symmetric electrodes: LSCF–6428 || GDC || LSCF–6428, LSCF–4628 || GDC || LSCF–4628, and LSCFN–46271 || GDC || LSCFN–46271. The active area of the electrodes was 0.81 cm².

3.2. Material Characterization

Initially, the symmetric electrodes underwent testing under varying oxygen partial pressures within N₂ + O₂ mixtures at 800 °C, followed by exposure to air containing different levels of CO₂ at temperatures ranging from 650 °C to 800 °C. To assess changes resulting from these tests, the phase compositions of the electrodes were examined using a Bruker D8 Advance X-ray diffractometer (XRD). Additionally, the microstructure of the

sample surfaces was characterized through the utilization of a ZEISS Merlin scanning electron microscope (SEM).

The electrochemical impedance spectroscopy (EIS) responses of the symmetric electrodes subjected to various atmospheres were investigated using a Solartron 1260 instrument employing a signal amplitude of 10 mV across a frequency range of 10^{-1} – 10^6 Hz, and the bias potential was set to 0. The symmetric electrodes were placed inside a controlled-atmosphere furnace, with a collector layer consisting of gold paste and silver wires serving as conductive leads. During the measurement, various gases were introduced to the symmetric electrodes at a flow rate of 6 L/h.

Figure 8 illustrates the EIS data for LSCF–6428 at 1 h, as shown in Figure 4a, along with the corresponding EIS fitting diagram. The equivalent circuit model for the symmetric electrode consists of an inductor (L), a resistance element (Rs), and three R-CPE components. L and Rs primarily represent the inductance of the conductor and the overall ohmic impedance. R_{HF} , R_{MF} , and R_{LF} correspond to the high-frequency, mid-frequency, and low-frequency polarization resistances, respectively. The total cell Rp is the sum of these three components. The fitting results of this equivalent circuit in the figure closely match the experimental data [36]. Using impedance spectra to calculate the area-specific resistance (ASR) is a method used to evaluate the electrochemical performance of symmetric electrodes. The ohmic resistance is adjusted to zero, and due to the symmetrical unit structure, the calculated values are divided equally to obtain the ASR value for a single electrode [37].

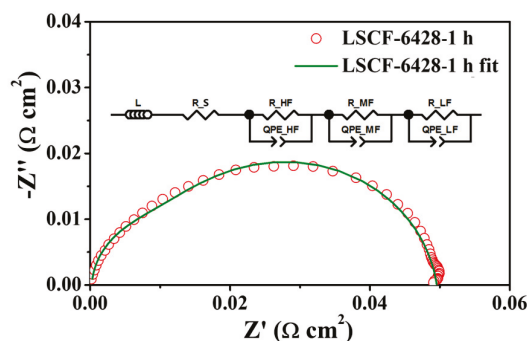


Figure 8. EIS at 800 °C in air for LSCF–6428, fitting results, and fitted equivalent circuit diagram.

DRT analysis entails fitting complex impedance data to a relaxation time distribution. The fundamental concept behind this technique is to disentangle the impedance spectrum into a sequence of relaxation processes. The Kramers–Kronig transformation establishes a mathematical integral relationship between the real and imaginary components of impedance. The general mathematical expression for this transformation is expressed as follows:

$$\text{DRT}(\tau) = -2/\pi \int [Z'(\omega) - Z'_{\infty}]/\omega f(\tau/\omega) d\omega,$$

$\text{DRT}(\tau)$ signifies the distribution of relaxation times as a function of τ , which represents the relaxation time. $Z'(\omega)$ denotes the real component of impedance with respect to angular frequency (ω). Z'_{∞} corresponds to the high-frequency limit of the real impedance. $f(\tau/\omega)$ is a weighting function employed in the analysis. The identification of characteristic peaks within the DRT spectrum was conducted through a comprehensive analysis. Variations in the DRT peaks, as an integral part of the relaxation time spectrum, were associated with distinct electrochemical processes. Impedance data analysis was carried out using the rapid and versatile data analysis/visualization (Ravdav) software version 0.9.7 [38].

4. Conclusions

In this research, we conducted a comprehensive investigation into the performance and stability of three distinct (La,Sr)(Co,Fe)O_{3-δ} cathodes when exposed to CO₂-enriched air environments. Utilizing DRT analysis, we successfully identified three distinct electrochem-

ical processes along with their corresponding frequency ranges. Under CO₂-containing atmospheres at temperatures ranging from 650 °C to 800 °C, EIS measurements revealed a consistent increase in impedance across all three cathodes as CO₂ concentrations increased. This phenomenon was attributed to the adsorption of CO₂ molecules onto the active oxygen sites present on the electrode surfaces, leading to a reduced oxygen exchange rate and, consequently, an increase in Rp.

Crucially, XRD and SEM analyses confirmed the absence of any adverse reactions or corrosion of the electrodes induced by CO₂ exposure. No secondary phases were detected, demonstrating the resilience of the cathode materials to CO₂-induced corrosion or degradation. This suggests that (La,Sr)(Co,Fe)O_{3-δ} cathodes do not undergo chemical reactions with CO₂ and maintain their structural integrity during exposure to CO₂-enriched atmospheres.

Furthermore, when the gas supply was reverted to 100% air, the recorded EIS spectra indicated a remarkable recovery in electrode performance. This recovery can be attributed to the removal of CO₂ from the electrode surface, allowing the active oxygen sites to become available for oxygen exchange reactions once again. In essence, our findings reveal that the performance deterioration observed in (La,Sr)(Co,Fe)O_{3-δ} electrodes when exposed to CO₂ is entirely reversible upon CO₂ removal, highlighting the excellent corrosion resistance exhibited by these cathodes in the face of CO₂ exposure.

Among the three different cathode compositions examined in this study, it is noteworthy that LSCF-6428 and LSCFN-46271 displayed superior durability compared to LSCF-4628. Both LSCF-6428 and LSCFN-46271 emerge as promising cathode materials for SOFCs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28227490/s1>.

Author Contributions: N.X.: writing—original draft; conceptualization; experimentalize; S.Z.: investigation; experimentalize; Q.Z.: writing—review and editing; H.W.: formal analysis; L.Z.: resources; writing—review and editing; Z.X.: resources; writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement: Not applicable.

Data Availability Statement: This study did not involve the creation of new data, and it did not include original data that can be shared. Data sharing is constrained by privacy and ethical considerations. Therefore, we are unable to provide additional data support. We acknowledge the importance of data sharing in scientific research and encourage future studies to actively seek data sharing when possible. If there are any data requests or inquiries, please feel free to contact us, and we will make every effort to provide further information about the research.

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

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Review

Research Progress of Perovskite-Based Bifunctional Oxygen Electrocatalyst in Alkaline Conditions

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Abstract: In light of the depletion of conventional energy sources, it is imperative to conduct research and development on sustainable alternative energy sources. Currently, electrochemical energy storage and conversion technologies such as fuel cells and metal-air batteries rely heavily on precious metal catalysts like Pt/C and IrO₂, which hinders their sustainable commercial development. Therefore, researchers have devoted significant attention to non-precious metal-based catalysts that exhibit high efficiency, low cost, and environmental friendliness. Among them, perovskite oxides possess low-cost and abundant reserves, as well as flexible oxidation valence states and a multi-defect surface. Due to their advantageous structural characteristics and easily adjustable physicochemical properties, extensive research has been conducted on perovskite-based oxides. However, these materials also exhibit drawbacks such as poor intrinsic activity, limited specific surface area, and relatively low apparent catalytic activity compared to precious metal catalysts. To address these limitations, current research is focused on enhancing the physicochemical properties of perovskite-based oxides. The catalytic activity and stability of perovskite-based oxides in Oxygen Reduction Reaction/Oxygen Evolution Reaction (ORR/OER) can be enhanced using crystallographic structure tuning, cationic regulation, anionic regulation, and nano-processing. Furthermore, extensive research has been conducted on the composite processing of perovskite oxides with other materials, which has demonstrated enhanced catalytic performance. Based on these different ORR/OER modification strategies, the future challenges of perovskite-based bifunctional oxygen electrocatalysts are discussed alongside their development prospects.

Keywords: perovskite oxide; bifunctional electrocatalyst; oxygen reduction reaction; oxygen evolution reaction; modification strategy

1. Introduction

With the rapid advancement of science and technology, there has been a notable enhancement in people's living standards. However, this progress has also resulted in excessive consumption of conventional fossil fuels and low energy conversion efficiency, leading to substantial emissions of carbon dioxide and sulfur dioxide. Consequently, these emissions have given rise to critical issues such as greenhouse effects, acid rain, and global warming. Numerous researchers have dedicated their efforts to investigating electrochemical energy storage and conversion devices, such as fuel cells [1–3] and metal-air batteries [4–7], in response to the exhaustion of resources and environmental deterioration. However, the kinetics of electrochemical systems in the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) during operation are sluggish, necessitating significant overpotentials to drive their kinetic processes. Until now, the excellent catalytic activities of precious metal (oxide) electrocatalysts, such as platinum-based materials for ORR and Iridium-based and Ruthenium-based materials for OER, are significantly

constrained by the scarce resources, high cost, low bifunctional activity, and poor durability [8–10]. In order to address these challenges, researchers have devoted considerable efforts to reducing the loading of precious metals in catalysts by employing alloys or carbon supports [11]. However, reducing the loading of precious metals often leads to a simultaneous decline in catalytic activity, posing a significant obstacle for practical applications. At the same time, methodologies for catalyst morphologies, structural characteristics, physical and chemical properties, and screening pathways also need to be considered to design the optimal bifunctional electrocatalysts [12]. Therefore, it is crucial to develop highly efficient and durable bifunctional electrocatalysts that are not dependent on precious metals, addressing the urgent need for sustainable and cost-effective alternatives in the large-scale implementation of renewable energy technologies.

Schuhmann et al. proposed a measure of bifunctional properties, referred to as the bifunctional index (BI), which quantifies the difference in potential required to achieve an OER current density of 10 mA/cm^2 and an ORR current density of -1 mA/cm^2 [13,14]. An ideal bifunctional catalyst holds great promise as a crucial component in the next generation of sustainable energy storage devices and shows potential application as a bifunctional catalyst for both ORR and OER [15–19]. In recent years, ABO_3 -based perovskite oxides have attracted significant attention as promising alternatives to high-efficiency bifunctional oxygen electrocatalysts owing to their unique compositional variability, special physicochemical properties, low cost, and environmentally friendliness [20–23]. Normally, the A-site is occupied by large-radius rare earth or alkali metal ions (such as La, Ca, Sr, Ba), which exhibit higher electronegativity and are 12-fold coordinated with oxygen ions. Meanwhile, the B-site is occupied by transition metal ions (like Co, Fe, Mn, Ni, etc.) located at the octahedral center of a cubic compact stack with a 6-fold oxygen coordination. In particular, partial substitution at the A and/or B sites in perovskite oxides can lead to alterations in the valence states of A- and B-site cations, as well as the formation of oxygen vacancies.

This crystal structure of perovskite oxides offers an opportunity to flexibly modulate their electronic and catalytic properties while exhibiting remarkable stability in alkaline environments [24–28]. However, the electron conductivity of perovskite bifunctional oxygen electrocatalysts at room temperature is insufficient, hindering efficient electron transport that is crucial for ORR/OER reactions and limiting their practical applicability [29,30]. Various strategies have been investigated to address this issue and enhance the catalytic performance and stability of perovskite bifunctional oxygen electrocatalysts, including crystallographic structure tuning, cationic regulation, anionic regulation, nano-processing, and composite processing (Figure 1).

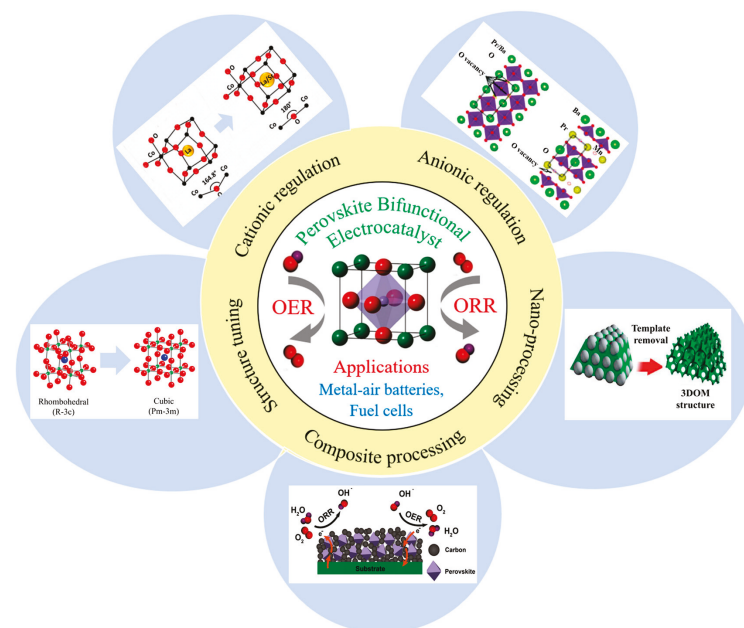


Figure 1. Modification strategy of perovskite bifunctional electrocatalyst for ORR/OER.

2. Crystallographic Structure Tuning

Crystallographic structure tuning has been demonstrated as an effective strategy for enhancing the electrocatalytic performance of perovskite oxides [31–33]. Currently, the crystal structure and surface properties of perovskite electrocatalysts can be modified by adjusting the firing temperature of the crystals, thereby effectively improving the catalytic performance in ORR and OER [34–37]. For instance, tuning the B-O bond property using variation of the annealing temperature, thereby enhancing the catalytic performance of perovskite oxides. Zhou et al. proposed that the rhombohedral structure of LaNiO_3 perovskite crystal transitions to the cubic structure as the annealing temperature is increased from 400 °C to 600 °C (Figure 2a) [38]. This phase transition directly reflects the influence of annealing temperature on the crystal structure. The length of the O-Ni bond increases with increasing annealing temperature, accompanied by an increase in the Ni-O-Ni bond angle, which results in an improvement in the electrocatalytic activity of LaNiO_3 . Jung et al. eliminated the inhomogeneous spinel surface that originally existed between the amorphous outer layer and the inner cubic phase layer of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$ ($x = 0.2/0.8$) by heat-treating at 950 °C in an argon atmosphere (Figure 2b), resulting in a significant improvement that enables the material to achieve the ORR limiting current density of 6.4 mA/cm^2 at 0.1 V versus RHE, slightly surpassing that of commercial Pt/C catalysts [39].

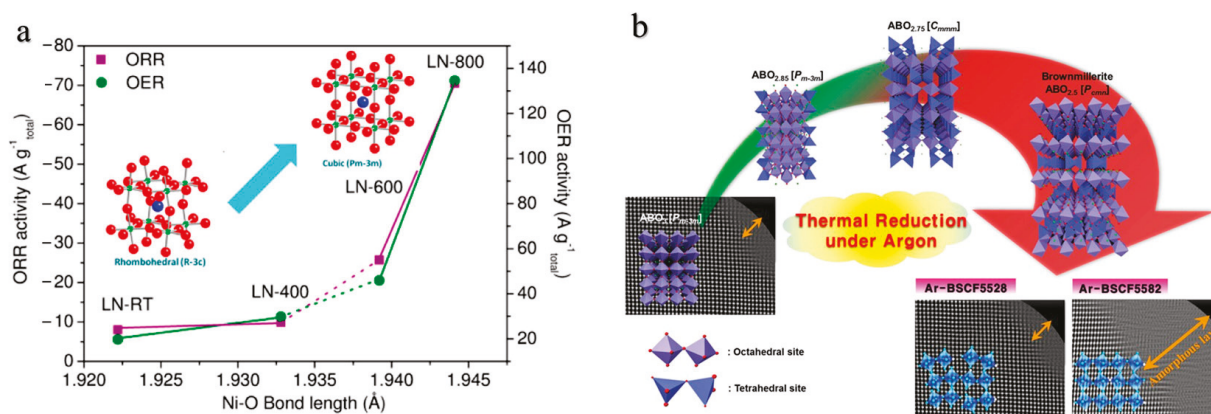


Figure 2. (a) Correlation of the ORR/OER activity of $\text{LaNiO}_{3-\delta}$ perovskites with their crystallographic structure [38]. (b) Schematic diagrams of the surface structural changes according to heat treatment at 950 °C for 24 h in argon atmosphere for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ [39].

Tuning the crystallographic structure in perovskite-based oxides is considered an important factor that affects their electrocatalytic performance [40–42]. Adjusting the preparation method of perovskite oxides can induce modifications in their crystal structure, morphology, surface properties, and internal defects, thereby influencing the catalytic performance of the electrocatalyst. Currently, several methods have been established for tuning the crystallographic structure of perovskite oxides, including the conventional solid-state method [43], electrospinning technique [44], hydrothermal and solvothermal methods [45], sol-gel method [46], and polymer-assisted method [47]. In addition, Gonell synthesized pure pseudocubic perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (pc-LSMO) nanocrystals via the molten salt method, which exhibited high mass-normalized ORR activity of 21.4 $\text{A}/\text{g}_{\text{oxide}}$ at 0.8 V/RHE in alkaline conditions [48]. The author proposed that the improvement in catalytic performance of pc-LSMO can be attributed to its relatively large surface area, high crystallinity, and electron mobility. Kim et al. employed a glycine-nitrate combustion method to synthesize three distinct perovskite oxide crystals, among which the triple perovskite oxide $\text{Nd}_{1.5}\text{Ba}_{1.5}\text{CoFeMnO}_{9-d}$ (NBCFM) exhibited superior ORR/OER activity characterized by higher current density and lower overpotential owing to its tetragonal crystal structure [49].

3. Cationic Regulation

Cationic regulation is a widely employed modification technique for perovskite materials, as reported in previous studies [50–52]. The selection of an appropriate introduced cation requires consideration of several factors, such as the cationic radius, the valence state of the cation, and the interaction between the introduced cation and the perovskite parent. Firstly, it is important for the cationic radius to be close to that of the perovskite parent since this contributes to both the integrity and stability of the lattice. An excessively large or small cationic radius has the potential to disrupt the crystal structure of the perovskite parent. Secondly, the valence state of the cation must also match that of the perovskite parent in order to ensure effective replacement and maintain electrical neutrality within the crystal structure. Additionally, accurate control over the ratio of the introduced cation to that of the perovskite parent is imperative to ensure the desired modification effect. However, excessive introduction may result in detrimental consequences such as crystal structure destruction or instability [53,54]. Various approaches have been reported in many research studies, including A-site cation regulation, B-site cation regulation, A-site and B-site cation regulation, and cation vacancies.

3.1. A-Site Cation Regulation

The A-site cations of perovskite oxides generally do not directly participate in the oxygen electrode reaction process for ORR/OER; however, they indirectly enhance the catalytic reaction [55–57]. The substitution at the A-site has been shown in numerous reports to result in a significant enhancement of catalytic activity [58–60]. Partial substitution of A-site cation ions, such as La, Sr, Ca, and Ba, can introduce novel lattice defects that significantly enhance the catalytic activity and stability of perovskite electrocatalysts. Hu et al. [61] demonstrated that the catalytic activity of LaMnO_3 perovskite oxide-graphene composites could be effectively modulated by incorporating Ca ions without altering the structure of the perovskite. Kumar et al. [62] successfully incorporated Gd ions into the A-site of the double-layer perovskite oxide ($\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_6$), resulting in superior catalytic activity in both ORR and OER, characterized by a high catalytic current density and low overpotential. Cheng et al. [63] found that partial substitution of Sr ions for La in LaCoO_3 facilitates a preferential arrangement of Co-O-Co bonds, resulting in a transition from a rhombohedral phase to a cubic phase (Figure 3a). Additionally, this substitution leads to an increase in the valence state of Co ions (Figure 3b). The density functional theory calculations indicate that the rearrangement of Co-O-Co bonds and the enhanced valence state of Co ions facilitate an improved overlap between the occupied O 2p valence band and unoccupied Co 3d conduction band, thereby enhancing both Ex situ conductivity of $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_3$ and intrinsic activity for OER.

3.2. B-Site Cation Regulation

Numerous studies have demonstrated that the B-site cations in perovskite oxides exhibit direct involvement in the catalytic reactions of ORR and OER [64–67]. Therefore, partial substitution of B-site cations is a promising strategy for enhancing the catalytic activity of perovskite-based oxide [68–71]. Ni-doped perovskite oxide $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ (LSMN) was synthesized using the sol-gel method, as reported by Yuan [72] et al. In comparison to undoped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, LSMN exhibits a higher concentration of oxygen vacancies and demonstrates enhanced bifunctional catalytic activity (Figure 3c,d). In particular, the overall overpotential of LSMN in ORR and OER is significantly low, approaching that of commercial Pt/C.

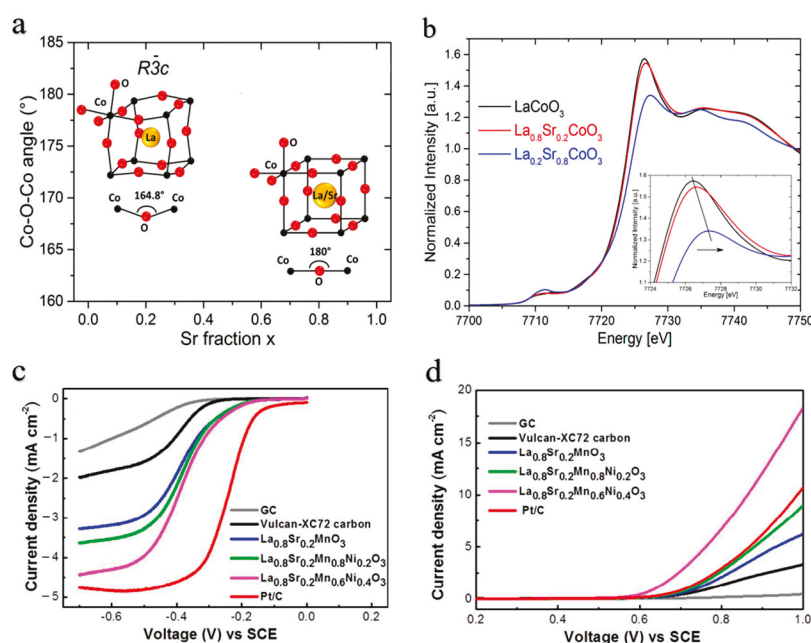


Figure 3. (a) Evolution of the pseudocubic ($x \leq 0.4$) and cubic ($x \geq 0.6$) Co–O–Co angle as a function of the Sr fraction [63]. (b) Co–K-edge XANES spectra of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0, 0.2, 0.8$) at room temperature; the inset shows the main peak region [63]. (c) ORR (negative scan) and (d) OER (positive scan) polarization profiles of Glassy carbon (GC), VC, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$, Pt/C at 1600 rpm [72].

Wang et al. utilized the metal cation Ta^{5+} to dope SrCoO_3 with a cubic perovskite structure, resulting in the formation of $\text{SrCo}_{1-x}\text{Ta}_x\text{O}_{3-\delta}$ ($x = 0.05/0.1$) [73]. This doping strategy effectively compensated for the deficiency of lattice oxygen during high-temperature synthesis and significantly enhanced the phase stability of the material. Duan [74] et al. synthesized a Fe-doped LaCoO_3 electrocatalyst and optimized the electronic structure of LaCoFeO_3 catalysts by adjusting the amount of Fe doping. The results demonstrate that the catalytic activity towards OER of $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ electrocatalyst is significantly enhanced by a doping amount of 0.1 Fe. Furthermore, the authors employed density functional theory simulations and calculations to elucidate the underlying reasons for this improved catalytic activity. It has been discovered that a 10% Fe doping leads to an increase in the strength of covalent bonds between Co 3d and O 2p orbitals, thereby effectively reducing OER overpotential and promoting enhanced OER activity. Sun et al. utilized the metal ions Mn–Ni pairs as dual dopants at B-site cations in lanthanide perovskite-based oxides $\text{LaMn}_x\text{Ni}_y\text{Co}_z\text{O}_3$ ($x + y + z = 1$) to enhance the bifunctional ORR and OER activities [75]. The findings demonstrate that the enhanced bifunctional performance of the optimized $\text{LaMn}_x\text{Ni}_y\text{Co}_z\text{O}_3$ ($x:y:z = 1:2:3$) catalyst can be attributed to a reduction in the number of e_g orbital electron and the modulation of the O 2p-band closer to the Fermi level.

3.3. A-Site and B-Site Cation Regulation

The co-regulation of A-site and B-site cations represents a unique approach to enhancing the electrocatalytic performance of perovskite oxide catalysts for ORR and OER. This strategy involves the substitution of cationic components in the A and B sites of the perovskite crystal structure, thereby altering its properties and catalytic behavior [76–78]. Li et al. [79] incorporated Bi^{2+} and Fe^{3+} ions into the A and B sites of SrCoO_3 , respectively, exploiting the disparity in ionic radii between Bi^{2+} , Fe^{3+} , and the original A/B sites. The synthesized $\text{Bi}_{0.15}\text{Sr}_{0.85}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ powder possesses a surface area of $5.81 \text{ m}^2 \text{ g}^{-1}$ and exhibited excellent ORR and OER activity, low overpotential and favorable chemical kinetics. The specific co-doping strategy induced alterations in surface properties and valence states, leading to enhanced electrocatalytic performance. Shao et al. developed a

triple-conducting nanocomposite material, $\text{BaCe}_{0.16}\text{Y}_{0.04}\text{Fe}_{0.8}\text{O}_{3-\delta}$, using a sol-gel method. This material in cathode exhibited remarkable properties for intermediate-temperature proton ceramic fuel cells (IT-PCFCs). It's important to note that this composition involved co-doping with Ce and Y at the B-site of $\text{BaFeO}_{3-\delta}$. This co-doping strategy was employed to stabilize the phase structure and introduce proton conductivity simultaneously. The optimized nanocomposite material in the cathode demonstrated excellent activity and stability for the ORR [80].

Yuan et al. [81] synthesized a bifunctional catalyst, Fe-doped mangan-based perovskite $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.7}\text{Fe}_{0.3}\text{O}_3$ with A-site defect, using the traditional CA-EDTA method. Compared to the pristine $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ catalyst, this modified catalyst demonstrated superior ORR and OER activity under alkaline conditions owing to increased surface oxygen vacancies as well as adjustments in Mn and Fe valence states within the perovskite structure, thereby enhancing catalytic performance. Wei et al. [82] prepared a novel $\text{La}_{1.7}\text{Sr}_{0.3}\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_{4+\delta}$ with a layered perovskite structure that was synthesized using the sol-gel method. In comparison with undoped $\text{La}_2\text{NiO}_{4+\delta}$, $\text{La}_{1.7}\text{Sr}_{0.3}\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_{4+\delta}$ exhibits significantly enhanced catalytic activity for both ORR and OER, characterized by higher limiting current density, larger positive onset potential, improved half-wave potential, as well as enhanced stability.

3.4. Cation Vacancies

The introduction of cation vacancy defects is also regarded as an effective strategy for enhancing the catalytic activity of perovskite oxides [83–86]. Cation vacancies primarily occur at the A-site in perovskite oxides. By precisely adjusting the cation stoichiometry at the A-site, it is possible to effectively modulate the valence state of ions at the B-site, thereby exposing a greater number of active sites. This adjustment reduces the energy barrier for oxygen migration, enhances oxygen vacancy formation, alters the electronic structure, and ultimately enhances the bifunctional catalytic activity of the perovskite oxides [87,88]. Cheng et al. [89] introduced appropriate A-site cation defects into $\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ to optimize the occupancy of e_g orbitals in B-site transition metals and enhance the generation of oxygen vacancies, thereby improving the bifunctional catalytic performance of perovskite under alkaline conditions, specifically in terms of OER activity.

Zhu [90] et al. introduced A-site cation defects into LaFeO_3 perovskite oxides to improve their catalytic activity for ORR/OER in alkaline environments. This phenomenon can be attributed to the perturbation of transition metal valence states caused by the introduction of A-site defects. In perovskite-based oxides, A-site defects not only modify the valence states of B-site elements but also influence particle size, surface oxygen vacancies, and the number of active sites available for ORR and OER. Yuan [91] et al. synthesized A-site cation-deficient $(\text{La}_{0.8}\text{Sr}_{0.2})_{1-x}\text{MnO}_3$ ($x = 0.02, 0.05$) via the sol-gel method, which demonstrated superior bifunctional catalytic activity in alkaline electrolytes compared to $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$. The observed outcomes were ascribed to the presence of cation deficiency, which led to a reduction in particle size, an increase in oxygen vacancies, and the attainment of an appropriate Mn valence state. Consequently, these factors facilitate the transport of oxygen ions and improve ORR/OER performance.

4. Anionic Regulation

The incorporation of anionic defect engineering, such as oxygen vacancies or anion doping, has been previously demonstrated to positively influence the bifunctional electrocatalytic activity and stability towards ORR/OER in perovskite oxides [92–96]. The presence of anionic defects can enhance the capability of electron trapping, fine-tune energy band structures, and optimize catalytic reaction pathways in perovskite oxides. Oxygen vacancies are intricately linked to the electronic structure and valence state of B-site transition metals within the perovskite framework, with a substantial abundance of oxygen vacancies serving as active sites for adsorption and reaction processes. These introduced vacancies interact with adsorbed intermediates during catalytic reactions, facilitating efficient charge

transfer. Chen et al. synthesized a new type of oxygen-deficient BaTiO_{3-x} perovskite electrocatalyst with a unique hexahedral crystal structure via the sol-gel method followed by reductive heat treatment at 1300 °C in vacuum [97]. They proposed that the presence of oxygen vacancies in h-BaTiO_{3-x} crystal structures facilitates the adsorption of reactants and enhances charge transfer. The results indicated that the oxygen-deficient $\text{BaTiO}_{2.76}$ electrocatalyst exhibited excellent bifunctional catalytic activity, particularly surpassing the performance of the IrO_2 catalyst in terms of OER activity at relatively low potential (<1.6 V).

Heat treatment under moderately reducing conditions enables the controlled incorporation of varying concentrations of oxygen vacancies in perovskite oxides while preserving their original crystal structure. Wang [98] et al. successfully transformed $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ (PBM), a perovskite oxide, into layered $\text{PrBaMn}_2\text{O}_{5+\delta}$ (H-PBM) by annealing PBM in H_2 at 800 °C for 15 h. This method allowed for the generation of a high concentration of oxygen vacancies in the layered H-PBM material without altering its chemical composition. Remarkably, H-PBM exhibited exceptional catalytic activity towards both ORR and OER, as evidenced by significant enhancements in onset potential and catalytic limiting current density (Figure 4b,c).

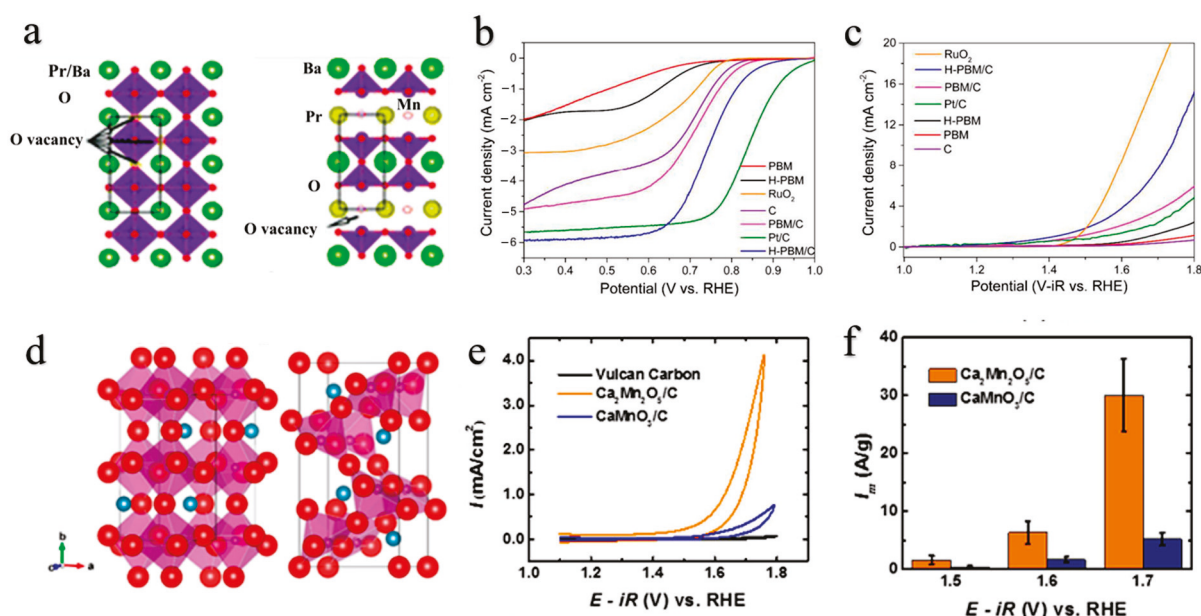


Figure 4. (a) Unit cell structures of $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ (PBM, left) and $\text{PrBaMn}_2\text{O}_{5+\delta}$ (H-PBM, right); Oxygen vacancies are represented by arrows. (b) ORR and (c) OER polarization curves of PBM, H-PBM, RuO_2 , C, PBM/C, Pt/C, and H-PBM/C [98]. (d) Unit cell structures of CaMnO_3 (left) and $\text{Ca}_2\text{Mn}_2\text{O}_5$ (right); (e) OER performance of $\text{Ca}_2\text{Mn}_2\text{O}_5/\text{C}$, CaMnO_3/C , and Vulcan carbon XC-72; (f) mass activities at various applied potentials [99].

A single phase of $\text{Ca}_2\text{Mn}_2\text{O}_5$ was synthesized by Kim [99] et al. at 350 °C and 5% H_2/Ar , resulting in the formation of oxygen-deficient perovskite oxide $\text{Ca}_2\text{Mn}_2\text{O}_5$ with intrinsic molecular-level pores at the oxygen-deficient sites (Figure 4d), facilitating favorable ion transport for OER [100–102].

Introducing non-metallic ions such as N, P, and S is an effective method to optimize the electron configuration, alter the valence state of ions, and enhance the activity of perovskite electrocatalysts [103–106]. Peng et al. [107] prepared sulfur-doped perovskite CaMnO_3 (CMO/S) nanotubes using an electrospinning technique followed by calcination and sulfurization treatment (Figure 5a). These catalysts exhibit enhanced bifunctional oxygen electrocatalytic activity and stability in alkaline solutions compared to the pristine CaMnO_3 (Figure 5b,c). The authors proposed that these results were attributed to sulfur doping, which can substitute oxygen atoms to enhance intrinsic electrical conductivity and

introduce abundant oxygen vacancies to provide adequate catalytically active sites. The sulfur-doped perovskite oxides LaCoO_3 (S-LCO), synthesized by Ran et al., exhibited significantly enhanced bifunctional oxygen electrocatalytic activities, which can be attributed to the introduction of S-dopants and oxygen defects [108]. First-principles calculations and experiments were employed to demonstrate that the S-dopant enhances the lattice distortion while simultaneously regulating the electronic filling of Co^{3+} e_g states.

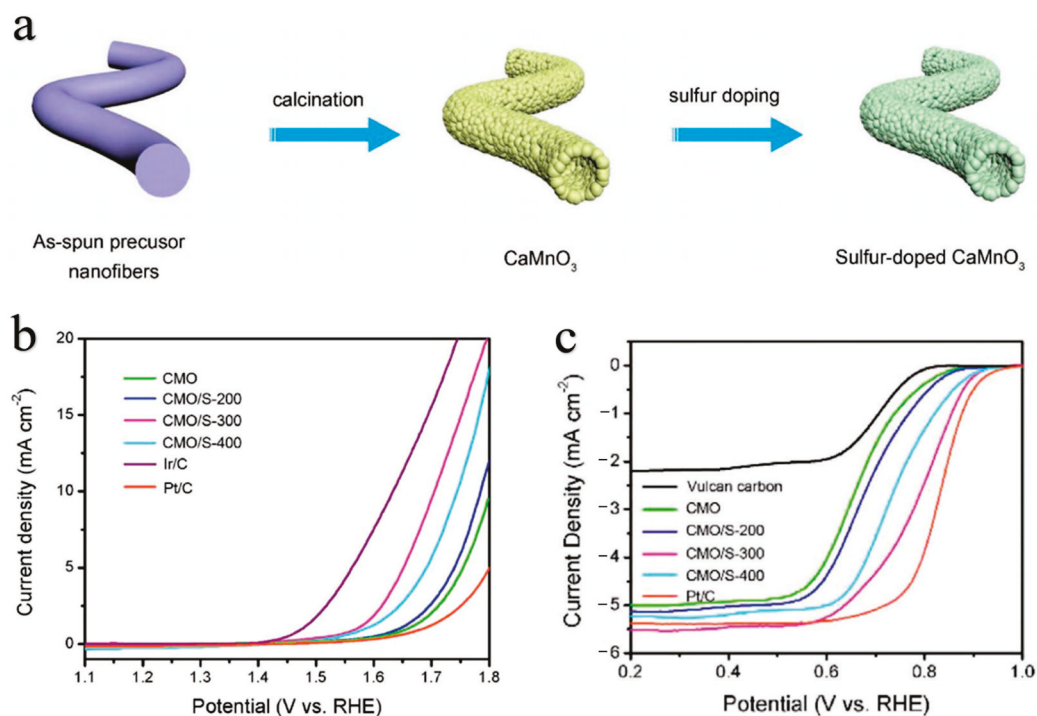


Figure 5. (a) Scheme of the formation of CMO/S. (b) OER polarization curves of CMO, CMO/S-200, CMO/S-300, CMO/S-400, Pt/C, and Ir/C measured in N_2 -saturated 0.1 M KOH solution at a scan rate of 5.0 mV s^{-1} . (c) ORR polarization curves of Vulcan XC-72, CMO, CMO/S-200, CMO/S-300, CMO/S-400, and Pt/C in O_2 -saturated 0.1 M KOH solution at a scan rate of 5 mV s^{-1} and rotation rate of 1600 rpm [107].

5. Nano-Processing

Nano-processing has been demonstrated as an effective strategy for enhancing the bifunctional catalytic activity of perovskite-based oxide electrocatalysts, owing to their high specific surface area and well-defined pore structure. These characteristics facilitate efficient electron and oxygen transfer processes while also providing stability to specific oxygen-containing intermediates [109–112]. However, the conventional synthesis methods for preparing perovskite oxides, such as solid-phase synthesis and sol-gel method, often suffer from drawbacks, including large particle size and unclear morphological characteristics. The challenge lies in the precise design of particle size, morphology, composition, surface properties, and porosity of nanostructured materials to achieve nanoporous perovskite electrocatalysts.

At present, the main synthetic approaches employed for the preparation of perovskite nanomaterials include soft template [113], hard template [114], colloid crystal template [115], electrospinning [116], and hydrothermal methods [117]. These approaches effectively yield perovskite nanomaterials with reduced particle size, thereby increasing their surface area and exposing a greater number of active sites, consequently enhancing their bifunctional catalytic activity [118].

The hollow structure of porous perovskite oxide nanotubes $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ (PNT-LSM) was fabricated by Xu et al. using the electrospinning technique, followed by calcination at 650°C for 3 h (Figure 6a–c) [119]. This unique structure of the perovskite

electrocatalyst facilitates an increased specific surface area and exposes a greater number of active sites, thereby enhancing bifunctional catalytic activity. Liu et al. [120] have developed a mesoporous/macroporous nanotube-structured perovskite oxide, $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ (HPN-LSC) via electrospinning, serving as a bifunctional electrocatalyst for both ORR and OER in Li-oxygen batteries. This electrocatalyst structure enhances both electron conduction and the specific surface area, providing more space for product precipitation or storage (Figure 6d,e).

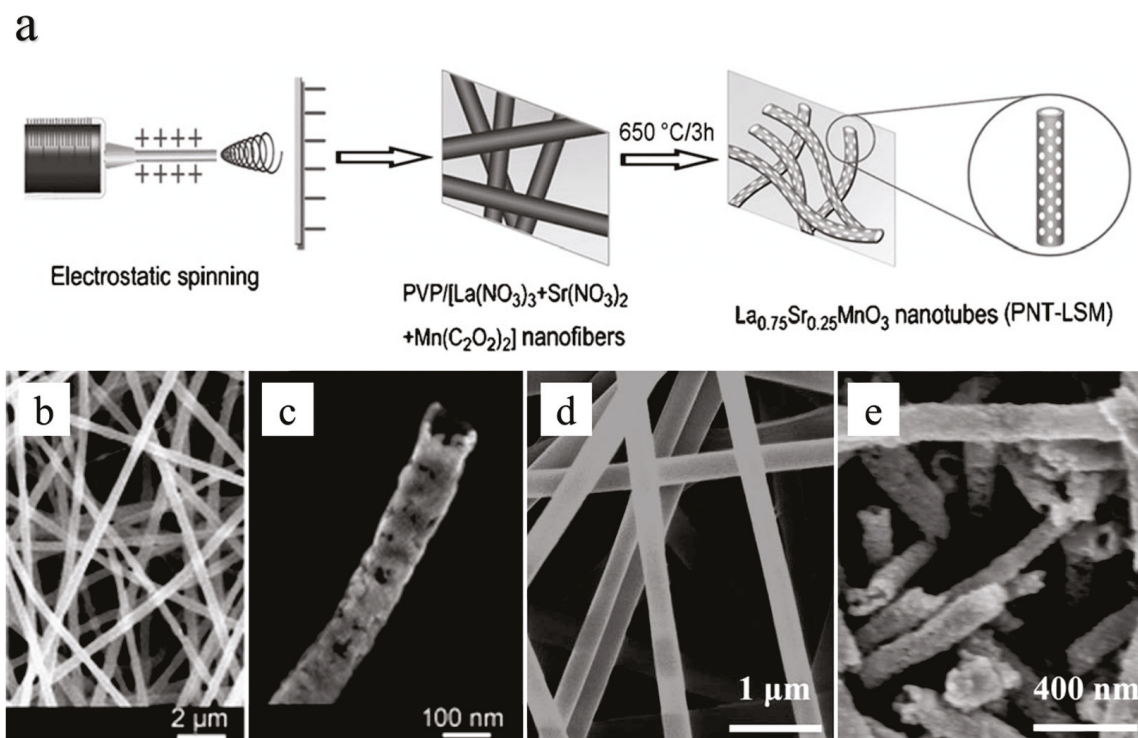


Figure 6. (a) the synthesis strategy of the PNT-LSM catalyst [119]. (b) As-electrospun composite fibers and (c) PNT-LSM after calcination at 650 °C for 3 h [119]. (d) As-obtained electrospun composite nanofibers and (e) HPN-LSC after thermal treatment at 750 °C for 3 h in air [120].

The nanoscale perovskite oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) was synthesized via the sol-gel method by Cheng et al. [121], and its potential as a cathode catalyst for non-aqueous lithium-air batteries was investigated. The results indicate that the LSCF nanoparticles, with an average particle size of 60 nm, are beneficial for both ORR and OER processes, resulting in a significant reduction in charge–discharge overpotential. Mesoporous nanofibers (PBSCF-NF) were successfully synthesized by Bu et al. [122] and exhibited excellent electrochemical performance in a 6 mol/L KOH electrolyte. At a current density of 300 mA/cm², PBSCF-NF demonstrated a higher power density of 127 mW/cm² compared to the pristine air electrode (109 mW/cm²). This enhancement can be attributed to the increased number of catalytic sites and enhanced reactant–catalyst contact facilitated by the nanostructures. Jung et al. synthesized $\text{La}_x(\text{Ba}_{0.5}\text{Sr}_{0.5})_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) nanoparticles with a size of approximately 50 nm by precisely controlling the lanthanum concentration and calcination temperature to manipulate oxide defect chemistry and particle growth mechanisms [123]. The resulting electrocatalyst demonstrated a more than twenty-fold increase in gravimetric activity (A/g) compared to IrO_2 during half-cell testing using 0.1 M KOH electrolyte while also surpassing the charge/discharge performance of Pt/C (20 wt%) in zinc-air full-cell testing employing 6 M KOH electrolyte.

6. Composite Processing

In general, composite electrocatalysts derived from the combination of perovskite oxides with carbon materials, transition metals, noble metals, etc., exhibit significantly

enhanced catalytic activity compared to pristine perovskite electrocatalysts [124–126]. This composite processing facilitates the modification of both the electronic structure and active sites of catalysts, thereby serving as an effective strategy for enhancing the electrocatalytic activity of perovskite oxides.

6.1. Dual Components Integrated Electrocatalyst

To tackle the significant challenge of poor electrical conductivity in perovskite oxides, the researchers propose a strategic approach for fabricating perovskite/carbon-based dual components integrated electrocatalysts using composite processing [127–131]. The bifunctional activity of perovskite/carbon-based dual components integrated electrocatalysts has been consistently demonstrated to surpass that of single-component perovskite or carbon materials in numerous reports. For instance, Park et al. have developed a bifunctional composite electrocatalyst composed of porous perovskite oxide $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF-PR) nanorods and nitrogen-doped reduced graphene oxide (NRGO) [132]. In this study, LSCF-PR is embedded between NRGO sheets to form an efficient composite morphology of LSCF-PR/NRGO, which exhibits excellent catalytic performance for both ORR and OER in alkaline media.

In addition, the utilization of in situ grown perovskite/carbon-based dual components integrated electrocatalyst represents an effective strategy to further enhance catalytic performance. Following this concept, Wu et al. first synthesized cobalt-free oxide $\text{SrFe}_{0.85}\text{Ni}_{0.05}\text{Ti}_{0.1}\text{O}_{3-\delta}$ using chemical vapor deposition, and subsequently, modified carbon nanotubes were formed in situ on its surface [133]. The resulting perovskite/carbon-based dual components integrated electrocatalyst exhibit superior catalytic activity in alkaline media compared to single-component parent perovskite $\text{SrFe}_{0.85}\text{Ni}_{0.05}\text{Ti}_{0.1}\text{O}_{3-\delta}$ or carbon nanotubes alone, due to the potential synergy between the perovskite/carbon nanotube phases that facilitate rapid charge transfer rates, increased surface areas, and exposed active sites. Furthermore, numerous perovskite/carbon-based dual components integrated electrocatalysts have been extensively documented in the literature. For example, perovskite $\text{La}(\text{Co}_{0.55}\text{Mn}_{0.45})_{0.99}\text{O}_{3-\delta}$ nanorods integrated with N-doped reduced graphene oxide composites [134] and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) combined with g- C_3N_4 -Vulcan Carbon composites [135] have also been investigated.

To date, a range of carbon-supported perovskite oxides have been synthesized, exhibiting enhanced ORR and OER activity compared to pure perovskite oxides or carbon alone. Numerous studies attribute this phenomenon to the synergistic effect resulting from the interfacial interaction between these two components, leading to superior performance than that of each individual component [136,137]. To elucidate the synergistic effect of perovskite/carbon-based dual components integrated electrocatalyst, Shao et al. [138] classified it into three aspects: the ligand effect (Figure 7a), the formation of interfacial heterostructure (Figure 7b) and the spillover effect (Figure 7c). Ligand effects pertain to the modification of electronic structure by ligand molecules in a material, thereby facilitating electron transfer. For instance, Fabbri's group observed this phenomenon in the BSCF perovskite/acetylene black (AB) carbon composite, where AB was found to modulate the Co oxidation state of BSCF, reduce it, enhance its inherent conductivity, and improve its oxide adsorption capacity [139]. Consequently, the composite catalyst exhibited heightened ORR/OER activity. The formation of interfacial heterostructures, such as covalent bonds or new phases at the interface, serves as the underlying mechanism for synergistic improvements in both ORR and OER performance. The well-dispersed perovskite-based LaMnO_3 nanoparticles were synthesized by Liu et al. via physical mixing of carbon and LaMnO_3 nanoparticles, followed by loading onto modified carbon black and subsequent sintering at various temperatures [140]. Among these catalysts, the carbon- LaMnO_3 hybrid with a mass ratio of 2:3 exhibited superior electrocatalytic activity for ORR. This remarkable enhancement in ORR electrocatalytic activity can be attributed to the formation of C-O-M (M = La, Mn) covalent bonds between metal oxide nanoparticles and the carbon support, which effectively enhances ORR kinetics. The spillover effect involves the diffusion and

transport of reactants at the perovskite/carbon interface. Perovskite materials adsorb and catalyze reactants while carbon materials facilitate their diffusion to a wider area, increasing coverage on catalyst surfaces and enhancing reaction rates. These aforementioned effects synergistically enhance the overall catalytic activity of the composite catalyst, thereby significantly improving its efficiency in facilitating both ORR and OER [138].

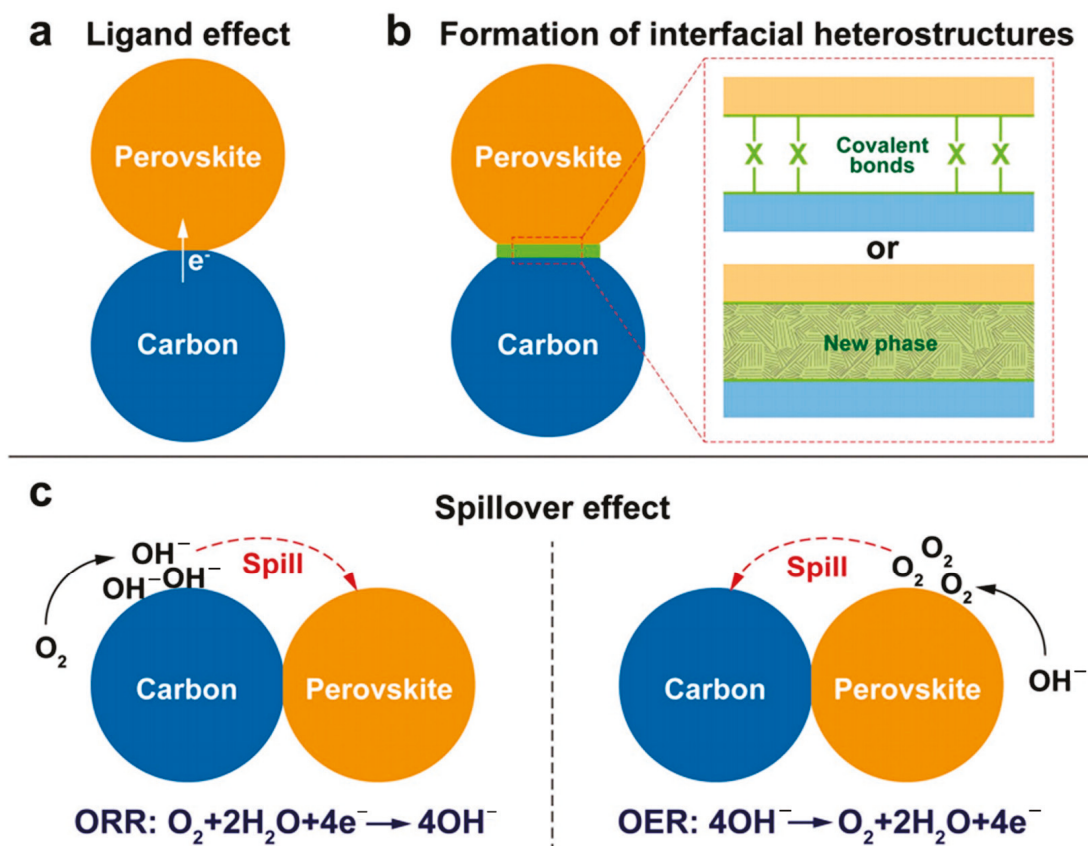


Figure 7. Schematic illustration of possible origins of the synergistic effect between the perovskite and carbon. (a) Ligand effect. (b) Formation of interfacial heterostructures. (c) Spillover effect [138].

6.2. Multiple Components Integrated Electrocatalyst

Multiple components integrated electrocatalysts consist of at least three components, wherein the electrocatalytic activity for ORR and OER originates from distinct active sites. The composite nature of these catalysts provides opportunities to independently design and construct specific ORR and OER active sites, thereby benefiting from a wider range of available active sites, more versatile regulation strategies, and potentially additional assistance in fine-tuning the ORR/OER activities. Consequently, composite electrocatalysts generally exhibit superior performances compared to their single-component counterparts. In addition to interacting with carbon-based materials, perovskites can also be combined with transition metal compounds or precious metals to load onto carbon-based materials, thereby enhancing the catalytic activity of composites for ORR/OER.

Perovskite/carbon/transition metal integrated electrocatalysts have attracted significant attention as bifunctional catalysts for ORR and OER [141–145]. Hua et al. reported that a three components-integrated catalyst consisting of $\text{La}_{0.45}\text{Sr}_{0.45}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ perovskite and Fe_3C and Carbon exhibited excellent catalytic activity for both ORR and OER under alkaline conditions [146]. A bifunctional electrocatalyst composed of perovskite oxides LaCoO_3 and transition metal oxide MnO_2 and Vulcan XC-72 was developed by Benhangi et al. in saturated 6 M KOH, the synergistic effect between these materials is evident as the bifunctional activity of $\text{MnO}_2/\text{LaCoO}_3/\text{Vulcan XC-72}$ surpasses that of MnO_2 or LaCoO_3 alone [147].

Furthermore, the researchers synthesized composite materials of perovskite oxides with precious metals such as Pt/C or IrO₂. Platinum is widely recognized as an exceptional electrocatalyst for ORR, despite its drawbacks, including high cost and limited durability. By integrating perovskite oxides with precious metals to load onto carbon-based materials, it becomes possible to design a bifunctional electrocatalyst that exhibits superior performance [148–150]. The potential of Perovskite/carbon/precious metals integrated electrocatalyst has been demonstrated in relevant literature [151,152]. The precious metal Pt and Sr(Co_{0.8}Fe_{0.2})_{0.95}P_{0.05}O_{3-δ} (SCFP) and C-12 were physically mixed via ball milling by Wang et al. [153], resulting in the synthesis of a bifunctional ORR/OER electrocatalyst with exceptional performance. This apparent enhancement in catalytic activity can be attributed to accelerated electron transfer, an abundance of surface oxygen vacancies, increased active sites, and reduced energy barriers due to the spillover effect between Pt and SCFP. Zhu [154] et al. employed a facile ultrasonic mixing technique to combine the Pt/C catalyst with the perovskite oxide Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) at an optimal ratio, resulting in a composite that exhibits excellent ORR activity. This integration of Pt/C and BSCF enhances the electron transfer mechanism of BSCF and facilitates synergistic catalysis between the two catalysts, thereby significantly boosting the bifunctional oxygen catalytic performance of BSCF.

In addition to the aforementioned methods of compounding perovskite materials, it is also feasible to effectively compound perovskite materials with other substances such as metal-organic frameworks (MOF), perovskites [155], and spinels [156], thereby enhancing their bifunctional oxygen catalytic activity.

The potentials of various perovskite-based bifunctional electrocatalysts with different modification strategies are presented in Table 1, at a current density of 10 mA/cm² for ORR and −1 mA/cm² for OER, along with the corresponding potential difference (ΔE). In a way, a smaller potential difference (ΔE) indicates superior bifunctional catalytic activity. These data revealed that the activity of perovskite-based bifunctional electrocatalysts can be significantly influenced by cationic regulation, composite processing, and nano-processing. Specifically, the regulation of B-site cations tends to have a more pronounced effect on the catalytic activity of perovskite bifunctional electrocatalysts. Taking the LaMn_xNi_yCo_zO₃ (x:y:z = 1:2:3) electrocatalyst as an example, its potential difference (ΔE) was calculated as 0.76 V (1.60–0.84 V), which is lower than the other samples listed in Table 1. This remarkable performance is attributed to the dual Mn-Ni dopant at the B-site, which allows precise tuning of the catalyst's electronic structure. Consequently, this electrocatalyst not only exhibits outstanding activity for both ORR and OER but also serves as a model for further investigations into structure–activity relationships.

Table 1. Assessment of perovskite-based bifunctional catalysts in 0.1 M KOH for the above reported.

Catalyst	Modification Strategy	ORR Potential (V) @ −1 mA cm ^{−2}	OER Potential (V) @ 10 mA cm ^{−2}	ΔE (V)	Reference
LaNiO _{3-δ}	Crystallographic Structure Tuning	−0.25 vs. Ag/AgCl	0.73 vs. Ag/AgCl	0.98	[38]
La _{0.8} Sr _{0.2} Co _{0.4} Mn _{0.6} O ₃	B-site regulation	0.81 vs. RHE	1.72 vs. RHE	0.91	[52]
La _{0.75} Sr _{0.25} Mn _{0.5} Fe _{0.5} O ₃	nano-processing and B-site regulation	0.74 vs. RHE	1.66 vs. RHE	0.92	[69]
LaMn _x Ni _y Co _z O ₃ (x:y:z = 1:2:3)	B-site regulation	0.84 vs. RHE	1.60 vs. RHE	0.76	[75]
(La _{0.8} Sr _{0.2}) _{0.95} Mn _{0.5} Fe _{0.5} O ₃	A-site deficiency and B-site regulation	0.12 vs. Ag/AgCl	0.89 vs. Ag/AgCl	0.77	[91]
Vacancy-induced LaMnO ₃	anionic regulation	0.94 vs. RHE	1.84 vs. RHE	0.90	[96]
nsLaNiO ₃ /NC	nano-processing	0.74 vs. RHE	1.62 vs. RHE	0.88	[110]
Ni ₃ S ₂ /PrBa _{0.5} Sr _{0.5} Co ₂ O _{5+δ}	composite processing	0.81 vs. RHE	1.63 vs. RHE	0.82	[124]
La(Co _{0.55} Mn _{0.45}) _{0.99} O _{3-δ} /NrGO	composite processing	0.84 vs. RHE	1.72 vs. RHE	0.88	[134]
10%g-C ₃ N ₄ -LaNiO ₃	composite processing	−0.32 vs. SCE	0.76 vs. SCE	1.08	[136]

7. Conclusions and Perspectives

In this paper, we provided an overview of the recent progress in bifunctional perovskite-based electrocatalysts for both oxygen reduction and oxygen evolution reactions under alkaline conditions. We present and analyze various modification strategies for manipulating perovskite-based oxides to enhance their bifunctional catalytic activity and stability, including crystallographic structure tuning, cationic regulation, anionic regulation, nano-processing, and composite processing. Among these strategies, the regulation of B-site cations has demonstrated the most significant influence on enhancing the catalytic activity of perovskite-based bifunctional electrocatalysts. Further, cationic regulation, composite processing, and nano-processing have also exhibited a greater impact on improving their catalytic activity. Despite this, related studies are still in the experimental stage, and there are still numerous challenges that remain for large-scale commercial applications. The practical applications often necessitate the comprehensive utilization of multiple modification strategies to attain superior performance owing to the multifactorial nature that influences the catalytic activity of perovskite-based oxides. Therefore, the integration of these strategies in the development of perovskite-based oxides has the potential to significantly enhance their electrocatalytic performance. Furthermore, it is imperative to conduct additional experimental investigations and theoretical calculations in order to comprehensively explore the bifunctional catalytic mechanism of perovskite oxides and to design more efficient nanostructured perovskite-based electrocatalysts. With the advancement of research, widespread applications of bifunctional perovskite-based electrocatalysts can be anticipated in the foreseeable future.

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Article

Surface Charge Effects for the Hydrogen Evolution Reaction on Pt(111) Using a Modified Grand-Canonical Potential Kinetics Method

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Abstract: Surface charges of catalysts have important influences on the thermodynamics and kinetics of electrochemical reactions. Herein, we develop a modified version of the grand-canonical potential kinetics (GCP-K) method based on density functional theory (DFT) calculations to explore the effect of surface charges on reaction thermodynamics and kinetics. Using the hydrogen evolution reaction (HER) on the Pt(111) surface as an example, we show how to track the change of surface charge in a reaction and how to analyze its influence on the kinetics. Grand-canonical calculations demonstrate that the optimum hydrogen adsorption energy on Pt under the standard hydrogen electrode condition (SHE) is around -0.2 eV, rather than 0 eV established under the canonical ensemble, due to the high density of surface negative charges. By separating the surface charges that can freely exchange with the external electron reservoir, we obtain a Tafel barrier that is in good agreement with the experimental result. During the Tafel reaction, the net electron inflow into the catalyst leads to a stabilization of canonical energy and a destabilization of the charge-dependent grand-canonical component. This study provides a practical method for obtaining accurate grand-canonical reaction energetics and analyzing the surface charge induced changes.

Keywords: Pt(111); hydrogen adsorption energy; hydrogen evolution reaction; charge effect; modified grand-canonical potential kinetics method

1. Introduction

Hydrogen electrocatalysis reactions, including the hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR), have been the cornerstone of the hydrogen economy and carbon neutralization [1–3]. Among all of the HER catalysts, platinum (Pt) has the best HER/HOR performance and thus has been the only one option available for commercial applications [4–6]. Although there have been extensive studies on the reaction thermodynamics and kinetics on Pt [6–10], using both experimental and computational methods, nearly all of the existing theoretical calculations are based on the electronic canonical ensemble (CE), which assumes a charge neutral reaction condition and ignores the electrochemical surface charges. Under electrochemical conditions, however, electrons flow into or out from a catalyst so that the electronic chemical potential keeps in balance with the external voltage [11]. This induces a dynamical change of the surface charge as the reaction is proceeding, which may generate substantial impacts on the reaction thermodynamics and kinetics. This effect cannot be captured under the electronic CE.

The surface charge effect has been attracting increasing attention in recent years. Han and coworkers found that both the reaction energy and barrier of the HER on S vacancies of MoS₂ decrease when the negative charges on the catalyst surface increase [12]. However,

their calculations are based on the electronic CE, which impedes an accurate description of the charge dependence. Liu et al. used the grand-canonical DFT package JDFTx to study the HER reaction thermodynamics of a series of catalysts, and found that the grand-canonical hydrogen adsorption energies are dramatically different from the canonical counterparts due to the impact of surface charges [11]. Meanwhile, Goddard et al. proposed a grand-canonical potential kinetics (GCP-K) model, which uses a quadratic GCP constructed from a set of canonical calculations to locate the grand-canonical geometry R and surface charge n of a catalyst during an electrochemical reaction [13]. This model provides a theoretical fundamental to explore practical approaches to address the effect of surface charge on reaction kinetics. However, it fails to quantitatively predict the grand-canonical reaction barrier and Tafel slope because it uses the total charge of an electrochemical double layer (EDL) system to represent the catalyst surface charge. Though different schemes have also been developed to implement the grand-canonical ensemble in the DFT framework [14,15], it remains a challenge to accurately predict reaction kinetics properties, hitherto. Recently, Chen and coworkers developed a grand-canonical iteration method based on DFT calculations to accurately locate the transition state and, meanwhile, to track the continuous change of surface charge in a reaction [16]. This method enables a direct optimization of grand-canonical energy with respect to n and R for both stable states and transition states without knowing the accurate analytical expression of the GCP. It can also separate the stabilization and the destabilization effects induced by surface charge variation, facilitating the analysis of the reaction mechanism beyond the traditional Butler–Volmer picture.

In this study, we propose a modified version of the GCP-K method, which is capable of obtaining reaction barriers that are in good agreement with the experimental results. This method separates the surface charge on the catalyst side from the total charge of an EDL system, making it possible to obtain accurate results of reaction energetics. Using the Pt(111) system as an example, we show that surface charges have substantial influences on both the reaction thermodynamics and kinetics. Hydrogen adsorption on Pt(111) under the SHE condition is much stronger than what we have assumed due to the high density of surface negative charges. We also demonstrate that surface charges can change the reaction barrier even for the Tafel reaction by affecting the charge-dependent grand-canonical energy term. This study provides a practical method for obtaining accurate grand-canonical reaction energetics and analyzing the surface charge induced changes.

2. Results and Discussions

2.1. Structure Models

A bare Pt(111) surface was simulated using a rectangular slab model consisting of four layers of Pt atoms, as shown in Figure 1a,b. The atoms at the bottom two layers were fixed at their bulk positions, whereas the top two layers were allowed to relax. There are eight on-top sites available for hydrogen adsorption. A thick vacuum region of 20 Å was used to separate the neighboring structural images. To model the Pt(111)/H₂O interface, 10 water molecules were added onto the surface to construct an EDL. Hydrogen atoms were added into or removed from the solution to obtain different proton concentrations. Different water networks could be obtained by sampling the conformational space using *ab-initio* molecular dynamics simulations (AIMD). According to a previous Pourbaix diagram calculation [17], the Pt(111) surface has a 100% hydrogen coverage and the proton concentration is 0% within the Helmholtz layer under the standard hydrogen electrode (SHE) condition. Therefore, we constructed a series of EDL structures with this characteristic, but with different water networks. Then, we selected the lowest energy structure around the equilibrium potential as the thermodynamically stable interfacial structure in acidic environment to study the reaction thermodynamics and kinetics. In fact, the surface charge effect exists for all electrochemical conditions, including both acidic and basic cases. The magnitude of this effect is not determined explicitly by the pH of solution. Instead, it relies on the change of surface charge during a reaction in terms of Equation (8). For simulating the basic

condition, a separate Pourbaix diagram for the interface including alkali metal ions in solution should be established carefully, which is computationally expensive and beyond the range of this work.

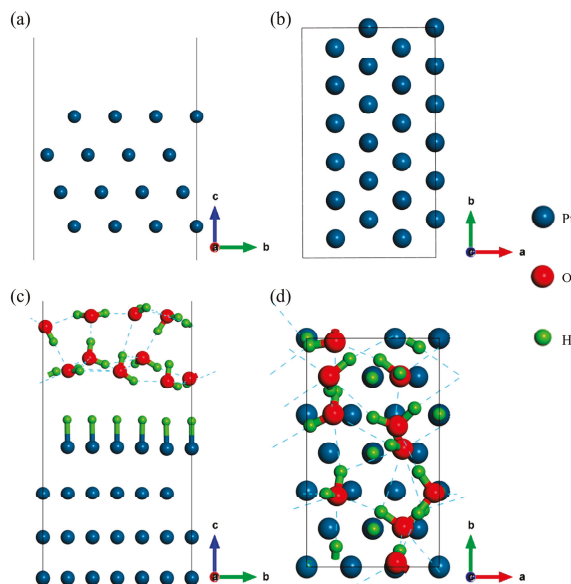


Figure 1. Structural models of the Pt(111) surface and the Pt(111)/H₂O interface. (a) Side, and (b) top views of Pt(111); (c) side, and (d) top views of the Pt(111)/H₂O interface under the SHE condition. The vectors a, b, and c represent the x, y, and z direction in the Cartesian space, respectively.

2.2. Hydrogen Adsorption Energies

H adsorption energy ΔG_H has long been used as an effective descriptor to evaluate the HER activity [18]. Quite a lot of canonical DFT calculations have indicated that H adsorption on the Pt surface is thermodynamically neutral, i.e., $\Delta G_{H,CE} \approx 0$ eV, under the SHE condition, which accounts for the state-of-the-art HER activity that was experimentally observed. In Figure 2a, we plot the calculated ΔG_H as a function of H coverage by both canonical and grand-canonical ensembles. For the latter case, the potential U is fixed at 0 V, and the variation of the total electron number n_{total} with H coverage is plotted in Figure 2b.

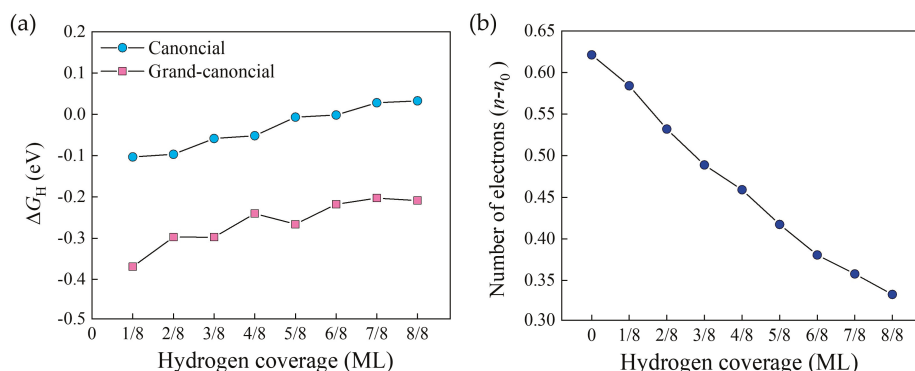


Figure 2. (a) H adsorption energy ΔG_H as a function of H Coverage on the Pt(111) Surface under the SHE potential. Both canonical and grand-canonical results are shown. (b) Net electron number $n_{total} = n - n_0$ as a function of H Coverage. n is the total number of electrons in the system and n_0 is the electron number at the electroneutral state. ML means one monolayer of adsorbed H atoms.

As expected, the canonical $\Delta G_{H,CE}$ is close to zero for the whole range of H coverage, consistent with previous calculations [8,18]. For the high coverage region around one, which is the case of the SHE condition in acidic environment [8,17], $\Delta G_{H,CE}$ is slightly

positive, indicating that H desorption should be easy. For both ensembles, ΔG_H increases as H coverage increases. Interestingly, $\Delta G_{H,GCE}$ is much more negative than $\Delta G_{H,CE}$, indicating that hydrogen adsorption on Pt is much stronger than what we have assumed if the potential is kept fixed during calculation. It is of note that the volcano plot established in the literature based on canonical DFT calculations locates the optimum ΔG_H to 0 eV [18,19]. Our calculation challenges this traditional belief and suggests that the optimum ΔG_H should be moved to a more negative position of ca. -0.2 eV. The reason for this change could be ascribed to the surface charge effect, as revealed in Figure 2b. For the low coverage region, the surface features a high density of negative charges (a large n_{total}), and as H coverage increases, n_{total} decreases gradually. This high density of negative charges induces an enhanced adsorption of H atoms on the Pt surface. This effect is totally ignored in canonical ensemble calculations.

Although this result is difficult to be experimentally validated, it can be rationalized in an indirect manner. The 100% H-covered Pt(111) surface has ca. 0.33 electrons under the grand-canonical ensemble (Figure 2b). Using the method of our previous work [20], we calculate the proton affinities for the electroneutral and the negatively charged surfaces with 100% H coverage, which are 0.559 and 0.573 eV, respectively. The larger proton affinity for the latter demonstrates that hydrogen adsorption is indeed enhanced when the surface is negatively charged.

2.3. Reaction Kinetics

Using the EDL structure established in Figure 1c, which is suggested by a previous Pourbaix diagram calculation [17], we can move to calculate the reaction kinetics using both the canonical and the modified grand-canonical method. In acidic environment, H atoms adsorb on the Pt surface underpotentially [8,21]. Therefore, one only needs to consider H desorption pathways. Because previous studies have demonstrated that the Tafel route is superior to the Heyrovsky route [8,22], we take the Tafel route as an example to study the surface charge effect.

As shown in Figure 3, the Tafel reaction takes place when two adsorbed H atoms on the surface combine together to form an H_2 molecule. The canonical free energy barrier is calculated to be 0.66 eV, with all of the correction terms summarized in Table S1. The experimental exchange current density j_0 of Pt is $3.162 \text{ mA}\cdot\text{cm}^{-2}$ [23]. According to the relationship between Turnover Frequency (TOF) and j_0 ,

$$\text{TOF} = \frac{j_0}{2qN} \quad (1)$$

one can derive the reaction rate on a single active site $\text{TOF} = 20.20 \text{ s}^{-1}\cdot\text{site}^{-1}$. Based on the transition state equation,

$$k(U) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger(U)}{k_B T}\right) \quad (2)$$

TOF can be transformed to the reaction barrier $\Delta G^\ddagger = 0.69$ eV. Obviously, the canonical Tafel barrier is in good agreement with the experimental result.

We then evaluate the grand-canonical barrier using the modified GCP-K method introduced in Section 3.4. For the initial state (IS) and final state (FS) of the reaction, the calculation takes two steps. First, we use VASP to relax the EDL structures with different electron numbers n and JDFTx to obtain the corresponding canonical JSSE $F(n)$. Then, we use a grand-canonical potential $G(n, U = 0 \text{ V}) = F(n) - n \times \mu_{e,\text{SHE}}$ to perform a quadratic fitting for the $F(n) \sim n$ relationship at $U = 0 \text{ V}$ [13]. For an electrode potential U other than 0 V, one can perform a quadratic fitting for the grand-canonical potential $G(n, U_{\text{SHE}}) = F(n) - n \times (\mu_{e,\text{SHE}} - eU_{\text{SHE}})$ at the potential U to obtain the corresponding barrier. The results are shown in Figure 4a,c. The minimums of the curves determine the net electron numbers $n_{total} = n - n_0$, grand-canonical energies $G_{IS/FS,GCE}$ and geometry

structures for the IS and FS. Calculation of the grand-canonical transition state (TS) follows a similar method. The difference is that the CI-NEB method is used in the first step as the optimizer to locate the TS structures with different n . The result of the quadratic fitting is exhibited in Figure 4b.

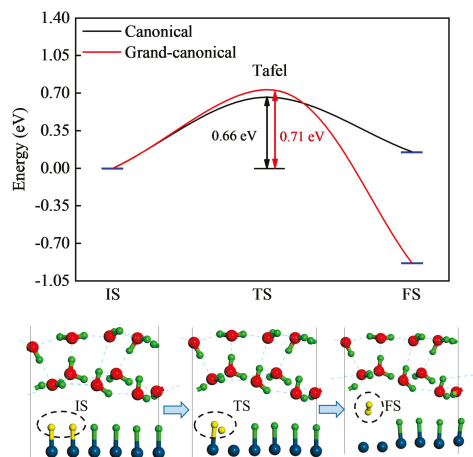


Figure 3. Tafel pathway for hydrogen desorption in acid. Both canonical and grand-canonical results are shown. Yellow balls in each interfacial structure represents the hydrogen atoms taking part in the reaction.

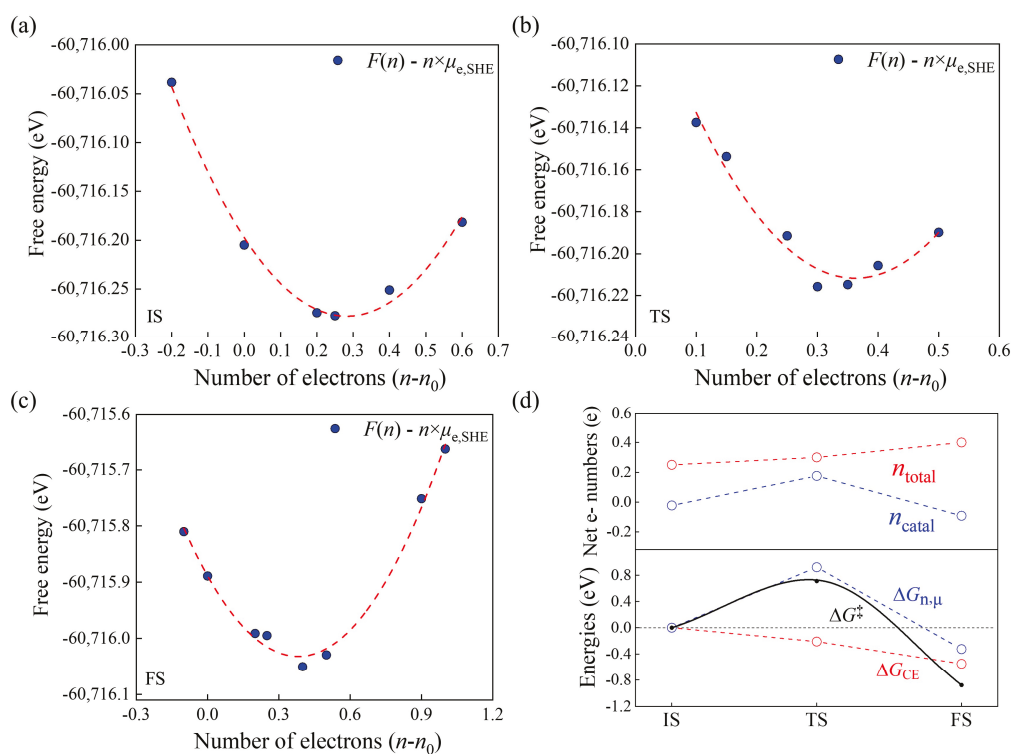


Figure 4. Net electron number $n_{\text{total}} = n - n_0$ as a function of grand-canonical free energy in IS (a); TS (b) and FS (c) of Tafel. n is the total number of electrons in the system and n_0 is the electron number at the electroneutral state. The red curve is the polynomial fitting curve. (d) Net electron numbers and energies for the Tafel reactions. Upper panel: Net electron number of the EDL system (n_{total}) and that on the catalyst side (n_{catal}) along the reaction routes. Lower panel: Relative changes in reaction free energy $\Delta G^\ddagger$, canonical energy ΔG_{CE} and the grand-canonical part $\Delta G_{n,\mu} = -\Delta n_{\text{catal}} \times \mu_{\text{e,SHE}}$ along the routes of Tafel reactions.

From the minimums in Figure 4a–c, we derive $G_{\text{IS,GCE}} = -60,716.28$ eV, $G_{\text{TS,GCE}} = -60,716.22$ eV and $G_{\text{FS,GCE}} = -60,716.05$ eV. One can also obtain $n_{\text{IS,total}} = 0.25$, $n_{\text{TS,total}} = 0.30$ and $n_{\text{FS,total}} = 0.40$. If we use Equation (7), i.e., the original GCP-K method, to calculate reaction barrier, then $\Delta G^\ddagger = 0.06$ eV is obtained, which is obviously too small compared to the experimental barrier of 0.69 eV [23]. This is because Equation (7) includes the contribution of n_{total} , and thus overestimates the surface charge and $\Delta G^\ddagger$.

We now use Equation (8) to evaluate the reaction barrier. First of all, one needs to determine n_{catal} for the three states. By Bader charge analysis, we obtain the total electron number n for all of the water molecules at the IS and TS of the Tafel reaction, as shown in Table 1. From the IS to the TS, the catalyst obtains 0.05 electrons (n_{total} , Figure 4d). The four water molecules highlighted by “*” in Table 1 also obtain electrons, which means that they behave the same way as the catalyst in exchanging electrons with the external electron reservoir. Therefore, they should be treated as the catalyst side when calculating n_{catal} . The reason why one should do this is that electrons from the external circuit may tunnel through the interface and electrify some adjacent water molecules in the Helmholtz layer. We obtain $n_{\text{IS,catal}} = -0.02$, $n_{\text{TS,catal}} = 0.18$ and $n_{\text{FS,catal}} = -0.09$, which means that $\Delta n_{\text{catal}} = 0.20$ when moving from the IS to the TS. Using this value in Equation (8), we then derive the grand-canonical barrier $\Delta G^\ddagger = 0.71$ eV (Figure 3), which is in good agreement with the experimental value of 0.69 eV. In terms of Equation (2), one can estimate that the corresponding reaction rate is $6.10 \text{ s}^{-1} \cdot \text{site}^{-1}$. In fact, a similar enhanced agreement has also been reported for S vacancies on MoS_2 when Equation (8) is used [16]. This suggests that accurate calculation of the surface charges that can freely exchange with the external electron reservoir is important for the prediction of grand-canonical barriers, even for the Tafel reaction, in which no interfacial charge transfer occurs. Compared to the canonical result of 0.66 eV, the slightly larger value of the grand-canonical one originates from the surface charge effect.

Table 1. Net electron numbers n_{total} for different parts of the interfacial structure (Figure S1) at the grand-canonical initial states and transition states of the Tafel reaction. Δn_{total} indicates the change of electron number $n_{\text{TS,total}} - n_{\text{IS,total}}$ when moving from the initial state to the transition state. The H_2O molecules denoted by “*” are selected as a part of the catalyst.

Species	$n_{\text{IS,total}}$	$n_{\text{TS,total}}$	Δn_{total}
H_2O -1	7.94	7.90	−0.04
H_2O -2	7.95	7.95	−0.004
H_2O -3	8.04	7.98	−0.06
H_2O -4 *	7.95	8.01	+0.06
H_2O -5	8.04	8.03	−0.01
H_2O -6	8.05	8.01	−0.04
H_2O -7	8.00	7.97	−2.04
H_2O -8 *	8.03	8.04	+0.01
H_2O -9 *	7.96	7.99	+0.03
H_2O -10 *	8.00	8.05	+0.05
Catalyst	390.04	390.08	+0.05
Total	470.0002	470.0001	−2.0001

According to Equation (8), a grand-canonical barrier or reaction energy contains the canonical energy contribution ΔG_{CE} and the charge-dependent grand-canonical portion $\Delta G_{n,\mu} = -\Delta n_{\text{catal}} \times \mu_{\text{e,RHE}}$. To analyze how surface charge affects the reaction energetics along the reaction route, we plot these two energy terms, together with n_{total} and n_{catal} , in Figure 4d. When moving from the IS to the TS, n_{total} increases by only 0.05 e, but n_{catal} increases by 0.20 e, implying that electrons keep flowing into the catalyst before the saddle point. The former causes a minor decrease of G_{CE} by 0.21 eV, but the latter induces a significant increase of $G_{n,\mu}$ by 0.92 eV. The total effect is that a barrier of 0.71 eV is generated. Obviously, $\Delta G_{n,\mu}$ destabilizes the system while ΔG_{CE} serves a stabilizing factor. Along the whole route, n_{catal} remains smaller than n_{total} , which indicates that n_{catal} is a part of

n_{total} and the former should be used for calculation of reaction energetics. Compared to the canonical case, the grand-canonical FS is more exothermic. This arises from the electron outflow from the catalyst after the saddle point (i.e., n_{catal} decreases), which moves $\Delta G_{n,\mu}$ to the negative side. Meanwhile, n_{total} keeps increasing, which means that both ΔG_{CE} and $\Delta G_{n,\mu}$ become the stabilization factor.

3. Methods

3.1. DFT Computational Details

Canonical DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP), which uses the Projector Augmented Wave (PAW) method to address electron–nuclei interactions [24–26]. The optB86b exchange–correlation function was employed to describe van der Waals (vdW) interactions [27–29]. A cutoff energy of 450 eV and a Monkhorst–Pack k-grid of $5 \times 3 \times 1$ were used to obtain energies. Forces on atoms were relaxed with a criterion of 0.03 eV/Å. Reaction transition states were determined using the Climbing Image Nudged Elastic Band (CI-NEB) method [30–34]. Work function drifting along the reaction path was corrected by the charge extrapolation scheme [35]. Zero-point energy changes between two states were included to obtain the free energy difference [36].

Grand-canonical total energy calculations utilized the JDFTx-1.7.0 package with the CANDLE solvent model [24,37]. This package was developed to calculate the joint slab–solution energy (JSSE) for a slab system under a specified voltage [11]. Compared to the canonical results, computational parameters, such as exchange–correlation functions, cutoff energy and convergence criteria, remain the same as those used in VASP.

3.2. Canonical Calculation of Hydrogen Adsorption Energy

In a canonical DFT calculation, a catalyst is typically treated as an electrically neutral system. We can calculate the hydrogen adsorption energy by using the following the traditional method [18],

$$\Delta G_{m\text{H}} = \Delta E_{m\text{H}} + \Delta E_{\text{ZPE}} - T\Delta S \quad (3)$$

$$\Delta E_{m\text{H}} = E_{m\text{H}} - E_{(m-1)\text{H}} - \frac{1}{2}E_{\text{H}_2} \quad (4)$$

where $\Delta G_{m\text{H}}$ is the change in free energy for the adsorption of the m -th H atom. $E_{m\text{H}}$ and $E_{(m-1)\text{H}}$ are the total energies for catalysts with m and $m - 1$ H atoms, respectively. E_{H_2} is the total energy of an H_2 molecule. ΔE_{ZPE} is the change in zero-point energy between the adsorbed H atom and the gaseous H_2 . $\Delta S = 0.5S_{\text{H}_2}$ is the entropy change between the adsorbed state and the gaseous state.

3.3. Grand-Canonical Calculation of Hydrogen Adsorption Energy

Under electrochemical conditions, however, a catalyst works under a constant external potential (μ_e), which is established by the electron exchange between the catalyst and the external electron reservoir. This means that the catalyst surface charge may change during an electrocatalytic reaction. Therefore, the hydrogen adsorption energy under a given potential could be calculated using the following formula [38]:

$$\begin{aligned} \Delta G_{\text{H}} &= G_{\text{sol}}(\text{H}^{*\text{Q}2}) - G_{\text{sol}}(^*\text{Q}1) - G(\text{H}^+(\text{sol})) - (Q1 - Q2 + 1)\mu_e \\ &= G_{\text{sol}}(\text{H}^{*\text{Q}2}) - G_{\text{sol}}(^*\text{Q}1) - \frac{G(\text{H}_2(\text{g}))}{2} + |e|U - (Q1 - Q2)\mu_e \end{aligned} \quad (5)$$

Here, $G_{\text{sol}}(\text{H}^{*\text{Q}2})$ and $G_{\text{sol}}(^*\text{Q}1)$ are the canonical free energies of the catalyst with and without hydrogen adsorption, respectively. $G(\text{H}^+(\text{sol}))$ represents the energy of a proton in the solution, $(Q1 - Q2 + 1)\mu_e$ implicates the surface charge change upon hydrogen adsorption and μ_e is the electron chemical potential, i.e., the Fermi level E_{F} . U is the applied

voltage. $Q1$ and $Q2$ are the net surface charges before and after H adsorption, respectively. They should satisfy the following constraint:

$$E_F(^*Q1) = E_F(H^*Q2) = \mu_e \quad (6)$$

3.4. Modified GCP-K Method

A grand-canonical potential kinetics (GCP-K) model has been developed in a recent study [13]. This model optimizes the grand-canonical energy (G_{GCE}) with respect to the net electron number n_{total} and geometry coordinate R under a given voltage using a quadratic GCP. Specifically speaking, it uses VASP to relax structures for different n_{total} and JDFTx with the CANDLE solvation model to obtain the corresponding canonical JSSEs. By fitting the JSSE vs. n_{total} curve using a quadratic GCP and locating the minimum, one can determine n_{total} , R and G_{GCE} for the system under a specified potential. Then, the reaction barrier (or reaction energy) could be derived from

$$\Delta G^\ddagger = G_{TS/FS,GCE} - G_{IS,GCE} \quad (7)$$

which contains the contribution of n_{total} . Essentially, n_{total} is the result of the electron flow between the catalyst and the external electron reservoir, which establishes the electron chemical potential balance. For an EDL system, however, n_{total} represents the total number of electrons distributing not only on the surface, but also on the electrolyte. Only the part residing on the catalyst side (n_{catal}) can freely exchange with the electron reservoir. Therefore, Equation (7) may overestimate the energy change due to the use of n_{total} . This is the reason why the GCP-K method fails to reproduce the experimental reaction barrier [16].

Herein, we propose a modified version of the GCP-K method, which can accurately separate n_{catal} from n_{total} and thus give a more reasonable prediction for reaction kinetics. n_{catal} represents the net surface charge that can exchange directly with the external electron reservoir. Under electrochemical conditions, electrons from the external circuit may tunnel through the interface. Therefore, calculation of n_{catal} should take into account the water molecules that changes their charges by the same sign as the catalyst does during a reaction. For instance, if the catalyst gains electrons in a reaction, the water molecules that synchronously gain electrons should be treated as the part of the catalyst side. n_{catal} can be calculated from the Bader analysis and should be a part of n_{total} , which will be discussed in the following Section 2.3. Using n_{catal} , one can rewrite Equation (7) as

$$\Delta G^\ddagger = (G_{TS/FS,CE} - G_{IS,CE}) - \mu_{e,RHE}(n_{TS/FS,catal} - n_{IS,catal}) \quad (8)$$

The subscript CE denotes the canonical JSSE. $\mu_{e,RHE}$ is the electron chemical potential at a given potential vs. the reversible hydrogen electrode (RHE). For the SHE condition, $\mu_{e,SHE} = -4.66$ eV within the CANDLE solvation model. This formula includes the contribution of n_{catal} and, therefore, may give a more reasonable evaluation of reaction energetics. When $n_{catal} = n_{total}$, Equation (8) becomes Equation (7). In fact, for surfaces without water layers, Equations (7) and (8) give the same result.

Equation (8) divides a grand-canonical barrier (reaction energy) into a charge-dependent grand-canonical portion $\Delta G_{n,\mu} = -\Delta n_{catal} \times \mu_{e,RHE}$, and a canonical energy component ΔG_{CE} , facilitating an analysis of the charge-dependent reaction mechanism. The former only correlates with n_{catal} at a given potential, whereas the latter is dependent on n_{total} (usually a higher n_{total} may lead to a lower G_{CE}) [16]. When electrons flow into the catalyst during a reaction, the second term stabilizes the system whereas the first term destabilizes it. Instead, if there is a net electron outflow during the reaction, the two effects are reversed [16].

4. Conclusions

In conclusion, we have developed a modified version of the GCP-K method based on DFT calculations to quantitatively predict reaction kinetics for electrochemical reactions.

This method can separate the surface charges that freely exchange with the external electron reservoir and, therefore, can accurately predict reaction barriers. Using Pt(111) as an example, we studied the hydrogen adsorption thermodynamics and the Tafel reaction kinetics. We find that the equilibrium hydrogen adsorption energy under the SHE condition should be around -0.2 eV, rather than 0 eV, if one consider the high density of surface negative charges. Even for the Tafel reaction, in which no charges transfer across the interface, surface charges may lead to a remarkable difference in prediction of reaction barrier. We demonstrate that the net electron inflow into the catalyst during the Tafel reaction leads to a stabilization of canonical energy and a destabilization of the charge-dependent grand-canonical component, inducing a slightly higher barrier (by 0.05 eV). This study provides an effective and practical grand-canonical method to predict reaction kinetics and to analyze the surface charge effect. It is noteworthy that this law is universal for all electrocatalysts because Equation (8) has been derived without specification of the types of materials and reactions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29081813/s1>, Table S1. Corrections from zero-point energy (ΔZPE) and charge extrapolation (ΔCE) for canonical barriers and reaction energies. Figure S1. Structural models of Pt (111)/H₂O (a) Top and (b) side views of the grand-canonical initial state structure of the Tafel reaction in acid.

Author Contributions: X.C. conceived, designed and organized the work. S.K., M.O., W.C. and Y.A. performed all of the calculations. X.C. and S.K. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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Article

Li⁺ Conduction in a Polymer/Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ Solid Electrolyte and Li-Metal/Electrolyte Interface

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Abstract: The solid oxide electrolyte Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP) with a NASICON structure has a high bulk ionic conductivity of 10^{−4} S cm^{−1} at room temperature and good stability in the air because of the strong P⁵⁺-O^{2−} covalence bonding. However, the Ge⁴⁺ ions in LAGP are quickly reduced to Ge³⁺ on contact with the metallic lithium anode, and the LAGP ceramic has insufficient physical contact with the electrodes in all-solid-state batteries, which limits the large-scale application of the LAGP electrolyte in all-solid-state Li-metal batteries. Here, we prepared flexible PEO/LiTFSI/LAGP composite electrolytes, and the introduction of LAGP as a ceramic filler in polymer electrolytes increases the total ionic conductivity and the electrochemical stability of the composite electrolyte. Moreover, the flexible polymer shows good contact with the electrodes, resulting in a small interfacial resistance and stable cycling of all-solid-state Li-metal batteries. The influence of the external pressure and temperature on Li⁺ transfer across the Li/electrolyte interface is also investigated.

Keywords: composite solid electrolyte; polymer membrane; Li-ion conduction; interfacial transfer; NASICON

1. Introduction

Nowadays, the heavily used conventional vehicles have consumed large amounts of fossil fuels and caused severe environmental issues globally. To alleviate this problem, the governments of many countries continuously introduce incentive policies for the rapid development of pure electric vehicles (EVs) [1,2]. To date, the limited driving range of EVs, which causes range anxiety, still requires resolution. Therefore, the mass and volume energy density of the batteries keeps increasing to meet the demand of the application [3]. Lithium metal is considered the most promising anode for rechargeable Li-ion batteries due to its low density (0.59 g cm^{−3}), high theoretical specific capacity (3860 mAh g^{−1}), and its having the lowest working potential (−3.04 V vs. the standard hydrogen electrode) [4–6]. However, the metallic lithium anode reacts with the ether/ester based on an organic electrolyte and forms an uneven solid electrolyte interphase, resulting in the irregular deposition of lithium during charging and fast lithium dendrite formation. The continuous growth of lithium dendrites leads to capacity decay and severe safety problems (e.g., fire, explosion, etc.), and the consumption of organic electrolytes reduces the coulombic efficiency and cycling life of the rechargeable Li-metal batteries [7–9]. Therefore, it is practical to solve these problems by replacing the conventional organic liquid electrolyte with a fast Li⁺-conducting solid electrolyte having high mechanical strength [10–12].

During the past decade, research on solid electrolytes has been focused on different compositions and structures, including sulfide [13–16], oxide [17–20], halide [21–23], and composite electrolytes [24–26]. Sulfide and halide electrolytes have high room-temperature ionic conductivities above $10^{-3} \text{ S cm}^{-1}$, but these solid electrolytes are moisture sensitive, and their ionic conductivities will significantly reduce in moist air. Oxide electrolytes have relatively high ionic conductivities from 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ at room temperature, and most oxide electrolytes are stable in air, which will reduce the handling cost of oxide electrolytes during cell preparation. Oxide electrolytes with garnet, NASICON, and perovskite structures have fast Li-ion transport channels and high Li-ion conductivity. Among them, the NASICON oxide with the general formula $\text{LiM}_2(\text{PO}_4)_3$ ($\text{M} = \text{Ti}$ and Ge , etc.) shows a high ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ at room temperature and good chemical stability in moist air because $\text{P}^{5+}\text{-O}^{2-}$ has a strong covalent bonding [27–30]; large-scale commercial production of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) has been achieved. However, applying LATP/LAGP electrolytes in all-solid-state Li-metal batteries still faces significant challenges. The poor solid–solid physical contact between LATP/LAGP ceramic and the metallic lithium anode leads to the large interfacial resistance of the battery, and the uneven local current distribution at the interface causes the formation and growth of lithium dendrites. Moreover, the $\text{Ti}^{4+}/\text{Ge}^{4+}$ ions of the LATP/LAGP electrolytes will be reduced on contact with lithium metal, which hinders the application of these electrolytes in rechargeable Li-metal batteries [31,32]. Therefore, it is urgent to develop solid organic/NASICON polymer electrolytes to solve the problems of NASICON electrolytes.

Unlike rigid inorganic electrolytes, solid polymer electrolytes are flexible and have good contact with electrodes in all-solid-state Li-metal batteries. Moreover, the preparation process and the thickness of solid polymer electrolytes could be well controlled based on the technique of conventional Li-ion batteries; a thin and robust polymer electrolyte with a low density also enables the batteries with a high energy density. Polyethylene oxide (PEO), as a high Li^+ -conducting polymer electrolyte, has been widely investigated [33]; the dissolved lithium salts provide Li^+ conduction through the motion of the polymer chain [34,35]. However, PEO polymer has a mixed amorphous and crystalline phase at room temperature [33,35]. Only the amorphous component can move freely to conduct Li^+ , and the crystalline PEO phase blocks the Li^+ transport and reduces the ionic conductivity of the PEO electrolyte.

Different strategies, including adding plasticizers/ceramic fillers and preparing crosslinked/block polymers, have been investigated to inhibit PEO crystallization and increase the concentration of the amorphous phase [36–40]. Among them, adding fillers to the polymer electrolyte is simple and effective in improving the Li^+ conductivity and mechanical strength of the polymer electrolytes. Although different ceramic fillers, such as Li-ion conductors like garnet electrolytes and Li-ion insulators like Al_2O_3 , have been investigated in polymer electrolytes, the ionic conductivity of polymer electrolytes is still not high enough for their application [37,41]. Moreover, the influence of external pressure and temperature on Li^+ transport at the Li/polymer electrolyte interface is not well studied. Suitable pressure during cell testing helps solve the volume change problem, however, the cell could be short-circuited at a large pressure, and the cell will have high internal resistance at a small working pressure. Here, we introduce NASICON LAGP particles with high ionic conductivity to prepare PEO/LiTFSI/LAGP composite solid electrolytes. The results showed that adding LAGP particles increased the content of the PEO amorphous phase and effectively improved the ionic conductivity of the composite electrolyte. Moreover, the coating of LAGP particles with PEO prevented the reduction in LAGP by the metallic lithium anode. The PEO/LAGP composite solid electrolyte has a high ionic conductivity of $8 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and an increased electrochemical window of 4.5 V, which is much better than the PEO/LiTFSI electrolytes. The all-solid-state Li-metal battery with PEO/LiTFSI/LAGP electrolyte realized stable cycling at room temperature.

The interfacial resistance of PEO/LAGP solid-state electrolytes and lithium metal can be significantly reduced with external pressure and high-temperature treatment.

2. Results and Discussion

The XRD pattern of the LAGP pellet prepared using the solid-state reaction is shown in Figure 1a; all of the XRD peaks of the samples after high-temperature sintering agreed well with the standard NASICON $\text{LiGe}_2(\text{PO}_4)_3$ (PDF#01-080-1923), confirming the high purity of the LAGP electrolyte. The SEM results of the LAGP powders in Figure 1b showed the LAGP particles have smooth surfaces and uniform size distribution (1–2 μm). In order to test the Li^+ conductivity of the LAGP solid electrolyte, the Li^+ -blocking Ag electrode was evenly coated on both sides of the LAGP pellet, and Figure 1c shows the impedance spectrum of the LAGP pellet. The curve could be fitted with the equivalent circuit ($R_b // CPE / R_{gb} // CPE$); R_b , R_{gb} , and CPE are the bulk resistance, grain-boundary resistance, and constant phase components, respectively. The impedance spectrum has an incomplete depressed semicircle in the high-frequency region, corresponding to Li^+ conduction at the grain boundary, and the bulk resistance is the intercept between the zero point and the starting point of the curve. The tail of the curve at the low-frequency region is caused by the Li^+ -blocking Ag electrode. The bulk and total ionic conductivity of the LAGP pellet are 4×10^{-4} and $2 \times 10^{-4} \text{ S cm}^{-1}$, respectively. The CV experiment of LAGP in Figure 1d was conducted to confirm the electrochemical stability of LAGP solid electrolytes; the LAGP solid electrolyte was electrochemically stable within a voltage window of 1–6 V, and the two peaks at 0.5 and -0.5 V were mainly from the plating and stripping of lithium, respectively. However, the larger current density during the anodic process is possibly related to the reduction in Ge^{4+} and P^{5+} ions at low voltages. Therefore, preparing composite electrolytes by coating the surface of LAGP powders with PEO could help increase the stability of LAGP against lithium metal.

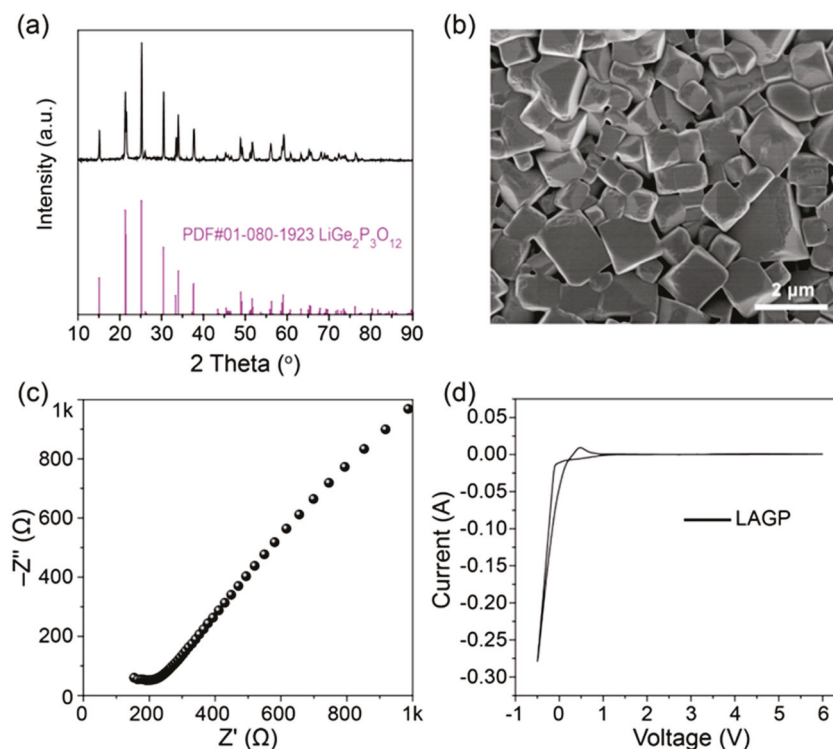


Figure 1. (a) XRD; (b) SEM; (c) impedance spectrum; and (d) CV curve of NASICON LAGP electrolyte after high-temperature sintering.

The XRD pattern of the PEO/LiTFSI/LAGP composite solid electrolyte is shown in Figure 2. Due to the low concentration of LAGP in the polymer electrolyte, no diffraction

peaks of LAGP were observed in the composite electrolytes. The diffraction peaks at 19 and 23 degrees in the composite electrolyte were from the crystalline PEO phase, and the broad hump from 20 to 25 degrees was from the amorphous PEO, confirming the coexistence of crystallization and the amorphous phase of PEO in the composite electrolyte. The crystalline PEO was significantly reduced compared to the PEO electrolyte without ceramic fillers. Figure 2b shows SEM images of the surface of the PEO/LiTFSI/LAGP composite electrolyte. The composite electrolyte has a relatively smooth surface and few closed pores; moreover, the LAGP particles are evenly dispersed in polymer electrolytes. The cross-section of the composite solid electrolyte (Figure 2c) shows that the membrane is dense and uniform with a thickness of 50 μm , and no pores are observed. Due to the brittleness of inorganic solid electrolytes, the thickness of inorganic solid electrolyte membranes like LAGP pellets in all-solid-state batteries is usually above 200 μm . In contrast, the smaller thickness of the PEO/LAGP composite solid electrolyte helps to realize a higher energy density of all-solid-state Li-metal batteries.

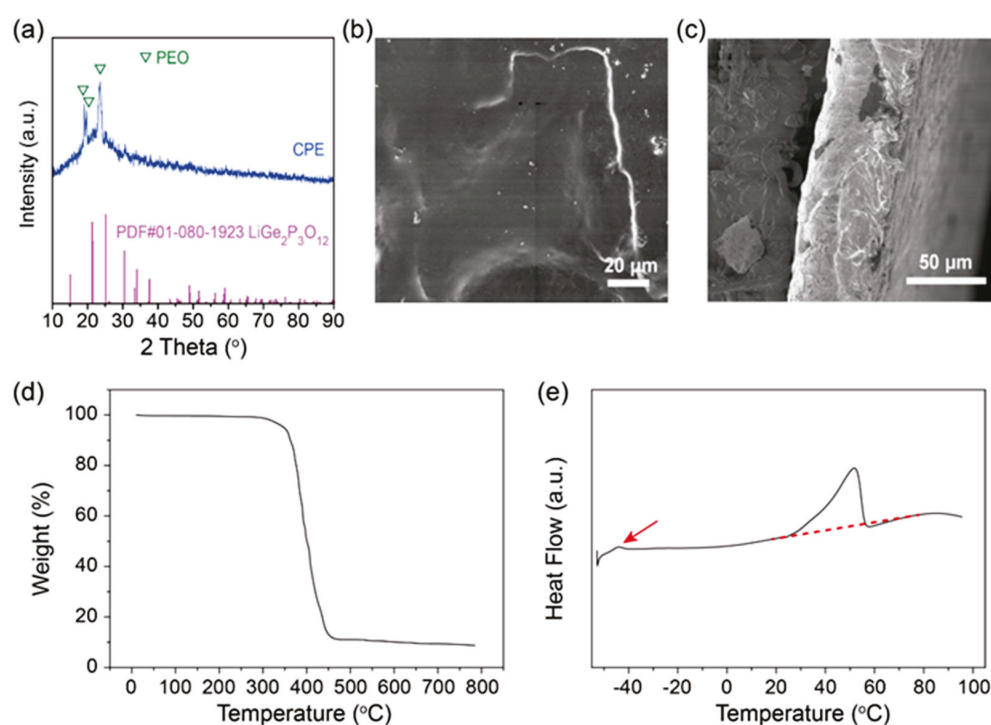


Figure 2. (a) XRD; (b) surface image; (c) cross-section image; (d) TGA; and (e) DSC curve of the PEO/LiTFSI/LAGP composite solid electrolyte.

The residual solvent and adsorbed water in the composite solid electrolyte will affect the performance of the polymer electrolyte. A TGA experiment was employed to determine the thermal stability of the PEO/LiTFSI/LAGP solid electrolyte and whether there was residual solvent in the composite electrolyte; the result of the composite electrolyte is shown in Figure 2d, and there was almost no weight loss at temperatures below 300 °C. The thermal decomposition of PEO and lithium salts occurred from 300 to 450 °C. Moreover, there was almost no solvent and water absorption in the polymer electrolytes. The DSC curve of the PEO/LAGP composite electrolyte (Figure 2e) showed the membrane had a glass phase transition temperature of $-42.3\text{ }^{\circ}\text{C}$ and a melting temperature of $50\text{ }^{\circ}\text{C}$, indicating higher amorphous phase content of the composite electrolyte at room temperature, which agrees well with its higher Li^+ conductivity.

The impedance spectrum and fitting curve of the PEO/LiTFSI/LAGP composite solid electrolyte at room temperature are shown in Figure 3a. According to the fitting results, the Li^+ conductivity of the composite solid electrolyte was $8 \times 10^{-5}\text{ S cm}^{-1}$ at $25\text{ }^{\circ}\text{C}$, which is one order of magnitude higher than that of the PEO/LiTFSI electrolyte; the addition

of LAGP as a filler to PEO/LiTFSI can effectively improve the Li^+ -ion conductivity of polymer electrolytes.

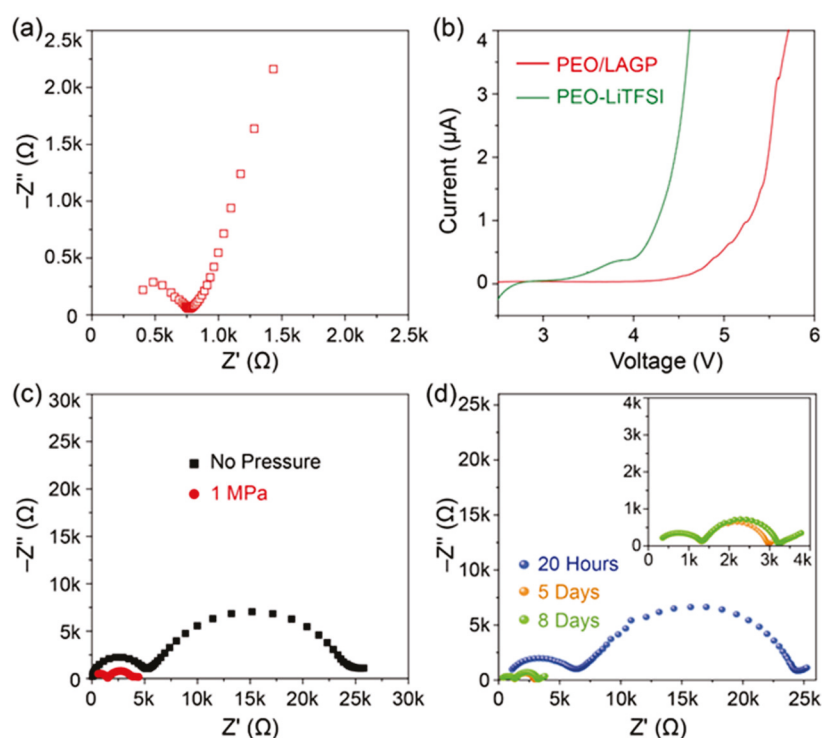


Figure 3. (a) The impedance spectra; (b) the LSV curve of the composite electrolytes of the membranes; (c) the impedance spectra of the symmetric Li/composite electrolyte/Li cell before and after applying an external pressure; and (d) heat treatment.

The electrochemical stability of the composite electrolyte is an important indicator to determine the applied voltage range of the solid electrolyte in all-solid-state batteries. The LSV curves of the PEO/LiTFSI and PEO/LiTFSI/LAGP composite solid electrolytes are shown in Figure 3b. The PEO/LiTFSI electrolyte showed an increased oxidation current at 3.5 V; the narrow voltage window of the PEO/LiTFSI electrolytes limits their application in batteries with a high-voltage cathode. When the LAGP filler was added to the PEO/LiTFSI electrolyte, the electrochemical stability of the PEO/LAGP composite solid electrolyte was significantly improved, and the oxidation current of the cell began to increase at voltages above 4.5 V (Figure 3b). The increased stability may be related to the ceramic/PEO interaction, which is confirmed by several previous reports [41,42]. The cell had a small current less than 1 μA at 5.0 V vs. Li^+/Li . The large electrochemical window of the PEO/LiTFSI/LAGP electrolytes enables their application in batteries with high-voltage cathodes like $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, which helps increase the energy density of the batteries.

In order to study the influence of applied external pressure on the interfacial resistance of the PEO/LAGP composite solid electrolyte and lithium metal, different external pressure was applied to the symmetric Li/Li cell, and the impedance spectra of the cells were measured, as shown in Figure 3c. The impedance spectra of the cell has a semicircle in the high-frequency and low-frequency regions, respectively; the low-frequency part represents the interfacial resistance, which can be attributed to the phase boundary resistance between organic polymers and ionic ceramics fillers or Li^+ transport resistance through the Li anode/composite electrolyte interface [43,44]. The symmetric cell had a total impedance of 25,000 Ω with no external pressure. When 1 MPa pressure was applied to the Li/Li symmetric cell, the total impedance of the cell was reduced to 4000 Ω , which is only 1/6 of the total resistance of a cell without pressure; applying a certain pressure can greatly reduce the internal resistance. The resistance of the solid composite electrolyte and the Li/electrolyte interface of the cell with no pressure and 1 MPa pressure was obtained by

fitting the impedance spectra. The resistance of the PEO/LAGP composite solid electrolyte decreased from 5031 to 1497 Ω at 1 MPa. The composite solid electrolyte has good characteristics of flexibility and ductility, and the external pressure could reduce the thickness of the electrolyte and increase the Li/electrolyte contact and Li^+ transport at the interface. In addition, intimate interfacial contact between the phase boundary can be stimulated with appropriate external pressure, resulting in a decrease in interfacial resistance [45,46]. The interfacial resistance between the PEO/LAGP composite solid electrolyte and lithium metal was 1194 Ω at 1 MPa, which is only 1/8 of the cell with no pressure (9684 Ω). The cell short-circuited when the pressure applied to the Li/Li symmetric was further increased to 2 MPa. Due to excessive pressure, the flexible PEO/LAGP composite solid electrolyte becomes very thin, and the bumps or edges on the lithium metal sheet may puncture the electrolyte and cause a short circuit. Therefore, applying 1 MPa pressure to the Li/CPE/Li symmetric cell can effectively reduce the interfacial resistance.

The effect of heat treatment on the interfacial resistance between the composite electrolyte and lithium metal is rarely reported. In order to study the influence of temperature on the interface between the PEO/LAGP composite solid electrolyte and lithium metal, the assembled Li/Li symmetrical cell with the composite electrolyte was kept at 60 $^{\circ}\text{C}$ for different times. After the treatment, the total resistance of the symmetric cell was significantly reduced (Figure 3d). The impedance data of the symmetric Li/Li cell at room temperature were fitted to obtain the resistance of the solid electrolyte and the Li/electrolyte interface. After being held at 60 $^{\circ}\text{C}$ for 20 h, the resistances of the electrolyte and interface at room temperature were 7123 and 8493 Ω , respectively. After being held at 60 $^{\circ}\text{C}$ for 5 days, the resistance (1235 Ω) of the composite solid electrolyte at 25 $^{\circ}\text{C}$ was only 1/5 of that before the heat treatment, and the interfacial resistance was reduced to 876 Ω . The composite solid electrolyte had an interfacial resistance of 934 Ω after being held at 60 $^{\circ}\text{C}$ for 8 days. The heat treatment helps reduce the resistance of the electrolyte because high temperature will increase the amorphous phase of the polymer. The reduction in the Li/electrolyte interface could be related to better contact between polymer electrolytes and Li-metal at high temperatures. Moreover, the high temperature could help increase the wetting ability of the solid polymer electrolytes by the Li-metal anode.

The Li/Li symmetrical cell was held at 60 $^{\circ}\text{C}$ for 5 days and was cycled at a constant current (0.05 mA cm^{-2}) at 25 $^{\circ}\text{C}$. Figure 4a shows the voltage curve of the symmetric cell, and the cell had a stable polarization of 0.18 V and a long cycling life of more than 300 h. There was no voltage increase and no short-circuit of the symmetric cell, indicating that the cell had a stable electrolyte and Li/electrolyte interface. The testing temperature of all-solid-state Li-metal batteries in most reported results was from 40 to 60 $^{\circ}\text{C}$, which limits their application at room temperature. Because the heat treatment (60 $^{\circ}\text{C}$ for 5 days) helped reduce the interfacial resistance, we assembled all-solid-state Li/LFP cells, and the cell was heated at 60 $^{\circ}\text{C}$ for 5 days and kept at 25 $^{\circ}\text{C}$ for 24 h. Figure 4b showed the charge/discharge curve of the all-solid-state Li/LFP cell from 2.5 to 3.6 V at 0.1 C and 40 $^{\circ}\text{C}$, and the LFP cathode in the cell had a discharge capacity of 140 mAh g^{-1} at room temperature with an overpotential of 0.15 V. The cycling performance of the cell in Figure 4c showed more than 100 cycles at room temperature with a capacity retention of 85% and a relatively high coulombic efficiency of 99%. The stable cycling of the symmetric Li/Li cell and the Li/LFP cell confirmed the composite electrolyte could suppress lithium dendrite formation during cycling. Suitable external pressure and heating treatment could reduce the required working temperature for polymer-based solid batteries.

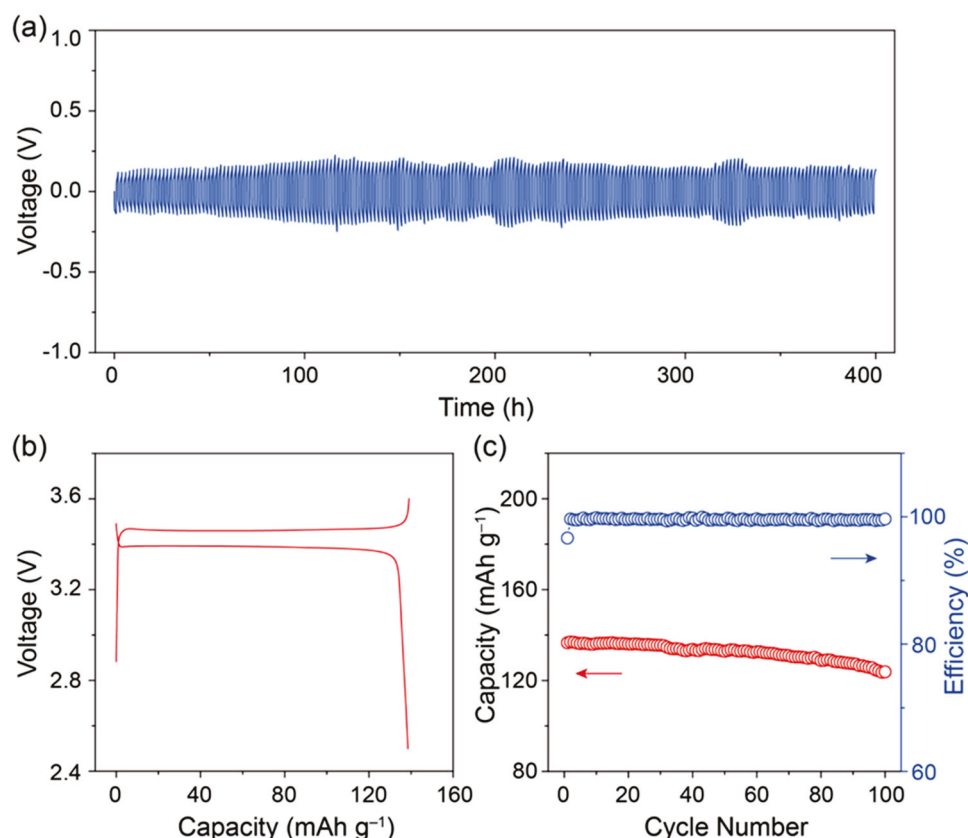


Figure 4. (a) The cycling performance of the symmetric Li/Li cell with the composite electrolyte; (b) the voltage/capacity curve, and (c) the cycling performance of the all-solid-state Li/LFP cell with the composite electrolyte at 25 °C.

3. Materials and Methods

NASICON $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) powders were prepared using a conventional solid-state reaction. Li_2CO_3 , $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, $\text{Al}(\text{OH})_3$, and GeO_2 were ball-milled with a planetary ball-milling machine for 2 h; the materials were mixed and heated at 600 °C in the air in the box furnace for 6 h. The obtained powders were ball-milled for 3 h, pressed into pellets, and sintered at 900 °C in the air for 24 h. The LAGP powders were prepared by grinding the LAGP pellet with a high-energy ball-milling machine (Pulverisette7 premiumline, Idar-Oberstein, Germany). PEO (molecular weight 600,000) and LiTFSI were dissolved in anhydrous acetonitrile solvent, and the molar ratio of [EO] to Li^+ was 10:1. After stirring the solution at 60 °C for 12 h, LAGP powder (10 wt%) was added to the acetonitrile solution and stirred for 24 h. The obtained solution was poured into a polytetrafluoron (PTFE) plate and dried under a vacuum at 40 °C for 24 h to obtain the PEO/LAGP composite solid electrolyte (CPE). The blank sample of PEO/LiTFSI polymer without LAGP filler was prepared using the same process.

The phase composition and microstructure of LAGP and PEO/LiTFSI/LAGP composite electrolytes were analyzed with a Rigaku MiniFlex 600 X-ray diffraction (XRD, Tokyo, Japan, Rigaku Corp.) apparatus and a FEI Quanta 650 scanning electron microscope (SEM, Eindhoven, North Brabant, The Netherlands), respectively. Ag and stainless steel were used as the blocking electrodes for LAGP and the composite polymer electrolytes, respectively, to confirm their ionic conductivity. The AC impedance spectra of the solid electrolytes were collected with the AutoLab workstation; the applied amplitude and frequency ranges were 10 mV and 1 MHz to 0.1 Hz, respectively. The cyclic voltammetry (CV) and the linear sweep voltammetry (LSV) curves of the LAGP and the composite electrolyte were collected with a scanning rate of 1 mV s^{-1} ; Li/LAGP/Au and Li/composite electrolyte/stainless

steel cells were assembled for the CV and LSV measurement, respectively. The TG curves of the PEO/LiTFSI/LAGP composite electrolytes were measured with a Mettler thermogravimetric analyzer at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 20 to $800\text{ }^{\circ}\text{C}$. The glass phase transition temperature and melting process of the composite electrolytes were determined using a Mettler-Toledo differential scanning calorimeter.

The performance of the PEO/LiTFSI/LAGP composite electrolyte in all-solid-state Li-metal batteries was tested in Li/LiFePO₄ and symmetric Li/Li batteries. LiFePO₄ composite electrode is prepared by mixing LiFePO₄, carbon, PEO, and LiTFSI salt (mass ratio: 70:10:13:7) in anhydrous acetonitrile solvent; the obtained slurry was coated on a carbon-coated Al current collector and vacuum dried at $60\text{ }^{\circ}\text{C}$ for 24 h. The loading of LiFePO₄ was 4 mg cm^{-2} . The Li/Li symmetric and Li/LiFePO₄ batteries were tested in the landing testing system; the testing voltage range of the Li/LiFePO₄ cell was from 2.5 to 3.6 V.

4. Conclusions

A PEO/LiTFSI composite solid electrolyte with Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP) as the ceramic filler was prepared, and the composite electrolyte has a high Li-ion conductivity of $8 \times 10^{-5}\text{ S cm}^{-1}$ at room temperature and good electrochemical stability above 4.5 V vs. Li⁺/Li. The influence of external pressure and temperature on the interfacial resistance of the Li/composite electrolyte was investigated in the symmetric Li/Li cell, and the optimized pressure and heat treatment were 1 MPa and $60\text{ }^{\circ}\text{C}$ for 5 days, respectively, which reduced the interfacial resistance to 1/8 and 1/10 of that measured at room temperature. The symmetric Li/Li cell had a long cycling life of 320 h at room temperature, indicating the good capability of the composite electrolyte to suppress dendrite formation and growth. Moreover, the all-solid-state Li/LFP battery had a high discharge capacity of 140 mAh g^{-1} and relatively stable cycling at $40\text{ }^{\circ}\text{C}$.

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Article

Preparation of S-C₃N₄/AgCdS Z-Scheme Heterojunction Photocatalyst and Its Effectively Improved Photocatalytic Performance

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Abstract: In this study, S-doped graphitic carbon nitride (S-C₃N₄) was prepared using the high-temperature polymerization method, and then S-C₃N₄/AgCdS heterojunction photocatalyst was obtained using the chemical deposition method through loading Ag-doped CdS nanoparticles (AgCdS NPs) on the surface of S-C₃N₄. Experimental results show that the AgCdS NPs were evenly dispersed on the surface of S-C₃N₄, indicating that a good heterojunction structure was formed. Compared to S-C₃N₄, CdS, AgCdS and S-C₃N₄/CdS, the photocatalytic performance of S-C₃N₄/AgCdS has been significantly improved, and exhibits excellent photocatalytic degradation performance of Rhodamine B and methyl orange. The doping of Ag in collaboration with the construction of a Z-scheme heterojunction system promoted the effective separation and transport of the photogenerated carriers in S-C₃N₄/AgCdS, significantly accelerated its photocatalytic reaction process, and thus improved its photocatalytic performance.

Keywords: semiconductor photocatalysis; Z-scheme heterojunction; S-doped graphitic carbon nitride; Ag-doped CdS nanoparticles; photocatalytic degradation

1. Introduction

Solar energy is inexhaustible and it is one of the most abundant energy sources that people can obtain on Earth [1]. In order to alleviate global energy shortages and mitigate environmental pollution, photocatalytic technology that is in line with the sustainable development of human society has emerged [2–4]. At present, the degradation of organic pollutants in water or air under artificial or natural light irradiation has been widely studied [5]. Although photocatalytic technology has become a hot topic in recent years, it must be acknowledged that the recombination speed of the electron–hole pair generated by single component photocatalysts is very fast, and only 10% of the separated charges can successfully reach the surface of the photocatalyst to undergo chemical reactions [6]. This is an extremely low utilization of solar light energy, that is, the light conversion efficiency in the light reaction is very low. In order to improve and overcome these problems, reasonable modification of photocatalysts has become necessary. Morphological control, elemental doping, and the construction of heterojunction systems are effective ways to improve photocatalytic performance [7–9], playing a very important role in alleviating current environmental pollution and energy crisis issues.

Graphitic carbon nitride (g-C₃N₄) and CdS are two hot materials in the field of photocatalysis [10,11]. g-C₃N₄ has a two-dimensional graphite-like phase structure, which

can provide a large number of active sites in the photocatalytic reaction process and is conducive to the rapid progress of the photocatalytic process [12]. Narrow-band gap CdS material (2.4 eV) can effectively absorb and utilize visible light, and it has a fast electron transmission rate and good photocatalytic performance [13]. However, the recombination of the photoinduced charge carriers generated by individual photocatalysts of g-C₃N₄ or CdS is fast, which hinders their effective reactions in the photocatalytic process and limits their further application in the field of photocatalysis. By establishing an effective heterojunction system, the recombination of photoinduced charge carriers can be effectively suppressed. Under the action of heterojunction electric fields, the photogenerated charge carriers can be effectively separated, and their photocatalytic performance can be significantly improved. Xu et al. [14] found that the CdS/g-C₃N₄ composite photocatalyst can significantly shorten the migration distance of the photogenerated carriers to the interface, realize the rapid separation of photogenerated electron–hole pairs, and reduce the recombination of photogenerated carriers. The degradation rate of azo-dye methyl orange (MO) by composite CdS/g-C₃N₄ is 93.8%, and its photocatalytic activity is much better than that of CdS and g-C₃N₄ alone. Xu Y et al. [15] prepared CdS/g-C₃N₄ for photocatalytic degradation of Rhodamine B (RhB), and found that $\cdot\text{O}_2^-$ was the major oxidation species for photocatalytic degradation. They proved that the photocatalytic activity of CdS/g-C₃N₄ was significantly enhanced compared with that of single-component photocatalysts. Li et al. [16] successfully prepared g-C₃N₄/CdS composites with a Z-scheme structure, and found that the Z-scheme heterojunction structure could inhibit the photoinduced self-corrosion of CdS, and verified that its photocatalytic activity on erythromycin (Ery) and tetracycline (TC) was significantly enhanced compared to that of pure g-C₃N₄ and pure CdS. Therefore, the rational design of an effective heterojunction photocatalytic system is of great significance for improving the photocatalytic performance of materials.

Doping is another effective way to improve the performance of the photocatalyst. Doping is the process of introducing foreign elements into the parent photocatalyst without generating new crystalline forms, phases, or lattice structures, and its purpose is to adjust the energy band structure of the photocatalyst by a very small amount, so as to make more efficient use of visible light and improve the separation efficiency of photogenerated electron–hole pairs [17]. Since Liu et al. [18] verified that sulfur-doped carbon nitride (S-C₃N₄) has efficient photocatalytic performance in 2010, a large number of subsequent corresponding studies has been carried out based on S-C₃N₄ [19,20], and photocatalysts with excellent performance have been obtained. At the same time, many doped photocatalysts, such as doped TiO₂ [21], doped ZnO [22], doped CdS [23], doped WO₃ [24], etc., have been widely considered because of their good photocatalytic performance. Establishing an effective heterojunction system with doped photocatalysts is bound to further enhance the photocatalytic performance of the photocatalysts.

Based on this, we first prepared S-C₃N₄, and then constructed effective S-C₃N₄/AgCdS heterojunction by further loading Ag-doped cadmium sulfide nanoparticles (AgCdS NPs) onto the surface of S-C₃N₄ through chemical deposition. The photocatalytic performance of the prepared photocatalysts is studied in the present paper. The S-C₃N₄/AgCdS photocatalyst possesses excellent photocatalytic performance in the degradation of RhB and MO due to the synergistic effect of Ag doping and the constructed Z-scheme heterojunction. Compared to type-II heterojunction systems, Z-scheme heterojunctions have stronger redox capabilities to promote rapid removal of pollutants. This work utilized doped photocatalysts to establish an effective heterojunction system and significantly improved its photocatalytic performance. In the process of establishing heterojunctions, various modification methods of photocatalysts such as doping, morphology control, and heterojunction establishment were fully utilized. This provides a good reference for designing effective photocatalytic systems.

2. Results

The XRD patterns of the prepared photocatalysts are shown in Figure 1a. The diffraction peaks of CdS are observed at 26.5° , 43.8° , and 51.9° , which correspond to the (111), (220), and (311) crystal faces of the face-centered cubic structure CdS, respectively, and are consistent with the standard card JCPDS 65-2887 [25]. Figure 1b shows the XRD patterns near the characteristic diffraction peak at 2θ of 26.5° . The locally magnified spectra near 26.5° show a slight left shift in the characteristic diffraction peak of AgCdS compared to that of the (111) crystal plane of CdS, indicating the successful doping of Ag into the CdS lattice structure. For S-C₃N₄, the strongest diffraction peak at 27.7° is assigned to the (002) diffraction plane reflected by the interlayer stacking of aromatic structure [26–28]. This matches well with the standard card JCPDS 87-1526 [29]. For the XRD patterns of S-C₃N₄/CdS, the diffraction peaks are consistent with those of S-C₃N₄ and CdS, respectively. Similarly, for the XRD patterns of the S-C₃N₄/AgCdS photocatalyst, the characteristic diffraction peaks of S-C₃N₄ and AgCdS can be clearly observed. The XRD results in Figure 1 indicate that the S-C₃N₄/CdS and S-C₃N₄/AgCdS photocatalysts are successfully prepared.

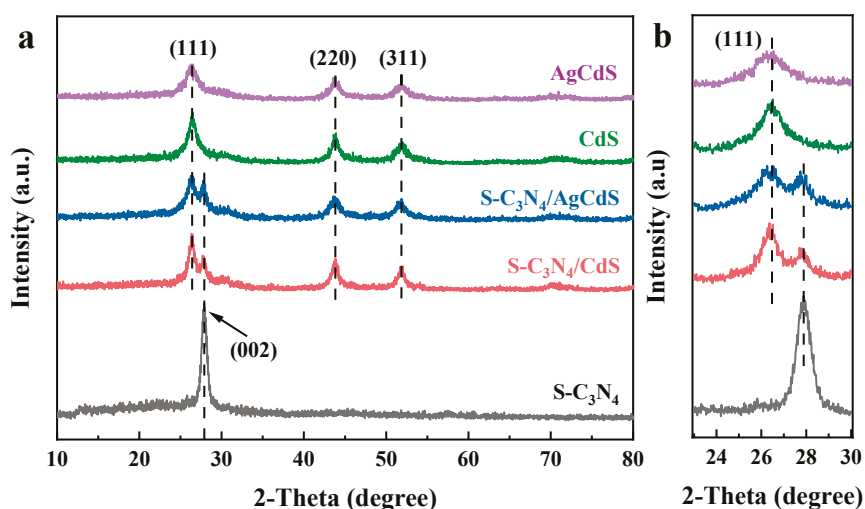


Figure 1. The XRD patterns (a,b) of the prepared photocatalysts.

Figure 2 shows the microstructure and elemental mapping of the prepared photocatalysts. Figure 2a shows the SEM image of S-C₃N₄, and the layered stacking structure can be clearly observed. The CdS NPs shown in Figure 2b exhibit a spherical cluster structure, which may have transformed into clusters assembled by nanoparticles due to water-bath heating and aggregation. Figure 2c shows the SEM image of the prepared AgCdS nanoparticles, which exhibit the same morphology and structure as CdS nanoparticles shown in Figure 2b. Combined with the XRD results shown in Figure 1 and the SEM results shown in Figure 2b,c, Ag doping does not change the crystal and morphology of CdS. Figure 2d,e are the SEM images of S-C₃N₄/CdS and S-C₃N₄/AgCdS, respectively, and the lamellar structure of S-C₃N₄ can still be observed. In addition, the nanoparticle structure can be observed on the lamellar surface of S-C₃N₄, which is attributed to the deposition of CdS and AgCdS nanoparticles. By further enlarging the SEM image of S-C₃N₄/AgCdS, as shown in Figure 2f, it can be clearly observed that nanoparticles are uniformly deposited on the surface of S-C₃N₄ nanosheets. Figure 2g,h are the TEM images of the S-C₃N₄/AgCdS photocatalyst, where the deposition of nanoparticles onto nanosheets can be observed. By further observing the HRTEM images (Figure 2h), the S-C₃N₄ edges (the red dashed line area) of sheet-like structures and lattice stripes of AgCdS nanoparticles can be observed. The lattice fringes with spacing of 0.17, 0.21, and 0.33 nm correspond to the (311), (220), and (111) crystal faces of AgCdS. Figure 2i shows the scanning elemental distribution of S-C₃N₄/AgCdS, in which the presence of C, N, Ag, Cd, and S elements can be observed. Each element is evenly dispersed in the scanning area and fully matches with the mor-

phology and structure obtained, indicating that AgCdS are uniformly distributed on the surface of S-C₃N₄. The results shown in Figures 1 and 2 demonstrate that, for the prepared S-C₃N₄/AgCdS photocatalyst, AgCdS nanoparticles are uniformly deposited on the surface of S-C₃N₄ nanosheets and form a good heterojunction structure.

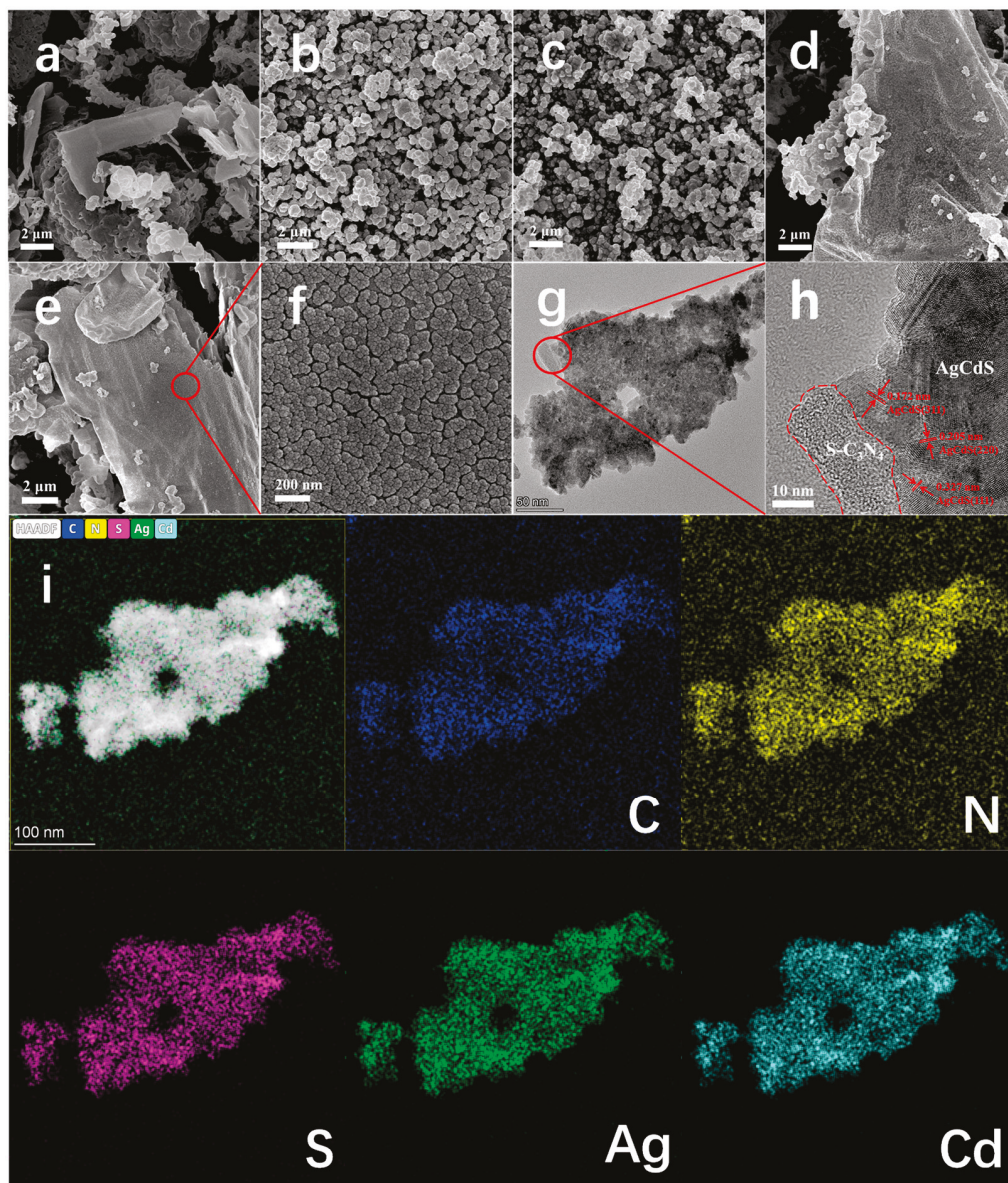


Figure 2. The SEM images of the prepared S-C₃N₄ (a), CdS (b), purAgCdS (c), and S-C₃N₄/CdS (d); the SEM images (e,f), TEM images (g,h) and elemental mapping (i) of the prepared S-C₃N₄/AgCdS.

XPS was used to further explore the elemental state and valence bond binding information of the prepared S-C₃N₄/AgCdS photocatalyst, and the corresponding results are shown in Figure 3. The elements of C, Ag, S, Cd, and O can be clearly observed in the total survey spectrum shown in Figure 3a, where the characteristic binding energy peak of O element comes from the surface adsorbed oxygen of S-C₃N₄/AgCdS. Figure 3b–f shows the Cd 3d, Ag 3d, C 1s, S 2p, and N 1s core-level XPS high-resolution spectra, respectively. According to Figure 3b, the characteristic binding energy peaks at 405.18 eV and 411.92 eV correspond to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively, which are derived from Cd²⁺ in AgCdS [30]. In Figure 3c, the binding energy peaks at 368.22 eV and 374.23 eV are attributed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively, which belong to Ag⁺ in AgCdS [31]. The binding energy peaks at 284.78 eV and 288.34 eV in the C 1s core-level spectrum shown

in Figure 3d and corresponds to C-C and C-N-C, respectively; the binding energy peak of 286.59 eV comes from the sp^3 coordinated carbon species with defects in $g\text{-C}_3\text{N}_4$ [32,33]. Figure 3e shows the S 2p core-level XPS spectrum, where the characteristic binding energy peaks at 161.53 eV and 162.73 eV are assigned to attributed to S^{2-} in CdS [34]. In Figure 3f, the characteristic binding energy peaks at 398.87 eV, 399.37 eV, and 401.01 eV and corresponds to sp^2 nitrogen, sp^3 tertiary nitrogen $\text{N}(\text{C})_3$, and amino (C-N-H) in the triazine ring ($\text{C-N}=\text{C}$), respectively [35,36].

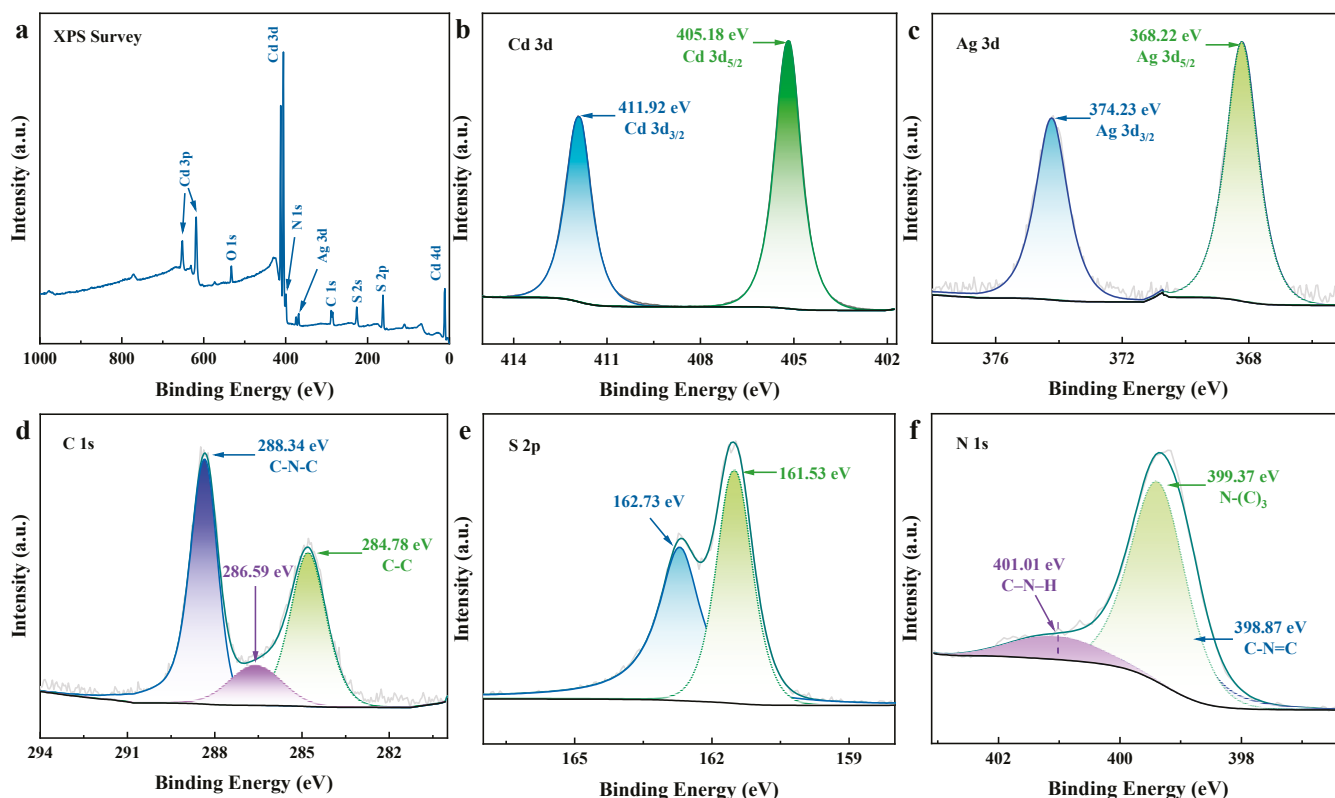


Figure 3. The XPS spectra of the prepared S-C₃N₄/AgCdS photocatalyst. Total survey spectra (a), and Cd3d (b), Ag3d (c), C1s (d), S2p (e) and N1s (f) XPS core level spectra.

The optical absorption performance of the prepared photocatalysts was further analyzed by testing the UV–visible absorption spectra, and the results are shown in Figure 4. The absorption threshold of pure S-C₃N₄ is around 440 nm, while that of pure CdS is around 510 nm. After doping with Ag, the light absorption threshold of AgCdS in the visible light region was slightly expanded, and its optical absorption performance was enhanced in the visible light region of 520–650 nm. The UV–visible absorption spectrum of S-C₃N₄/CdS clearly shows two absorption thresholds, which correlate to the characteristic light absorption performance of S-C₃N₄ and CdS, respectively. It is undeniable that composite materials of S-C₃N₄/CdS and S-C₃N₄/AgCdS exhibited better light absorption performance than S-C₃N₄, which is mainly attributed to the strong optical absorption performance of CdS and AgCdS. However, S-C₃N₄/CdS and S-C₃N₄/AgCdS also exhibited weaker optical absorption performance than CdS and AgCdS, which is mainly attributed to the decrease in CdS and AgCdS mass fractions. S-C₃N₄/AgCdS exhibited a wider light absorption performance than S-C₃N₄/CdS, indicating its higher light absorption and utilization. All prepared photocatalysts exhibited good visible light absorption performance. This will help the absorbance and utilization of visible light to achieve excellent photocatalytic performance.

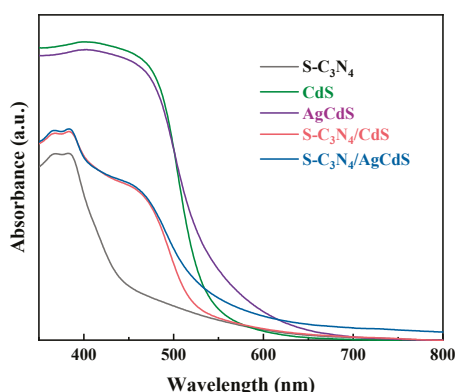


Figure 4. The UV–visible absorption spectra of the prepared photocatalysts.

Figure 5 shows the test results of the photocatalytic degradation performance of the prepared photocatalyst on RhB under visible-light irradiation. As shown in Figure 5a, the prepared photocatalyst exhibited excellent RhB photocatalytic degradation performance. It achieved the removal of over 90% of RhB even under 60 min of light illumination. Among them, $S-C_3N_4/AgCdS$ achieved the removal of 99% of RhB under 40 min of light illumination, demonstrating the best photocatalytic RhB degradation performance. To analyze the degree of complete degradation of RhB by the prepared photocatalysts, Figure 5b–f shows the absorption spectra of the degradation solution during the RhB degradation by the prepared photocatalysts. It can be clearly observed that pure CdS and AgCdS exhibit significant shifts in characteristic peaks, indicating that they have not achieved complete degradation of RhB. During the photocatalytic RhB degradation process, $S-C_3N_4$, $S-C_3N_4/CdS$, and $S-C_3N_4/AgCdS$ show slight shifts in the characteristic absorption peaks. However, the intensities of all characteristic absorption peaks decrease throughout the entire RhB degradation process, indicating that the complete degradation of RhB can be achieved.

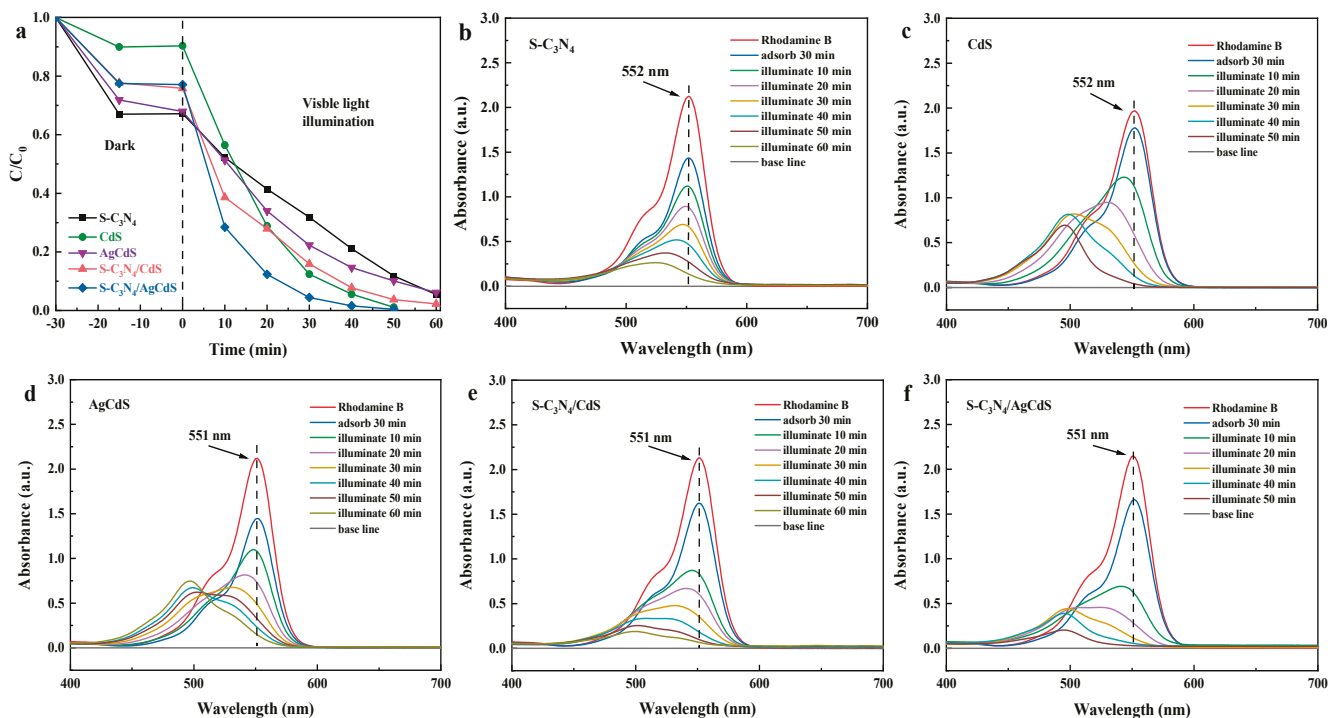


Figure 5. The RhB dye degradation curves (a) of the prepared photocatalysts, and the absorption spectra of the degradation solution during the RhB degradation process using different photocatalysts (b–f).

Figure 6 shows the photocatalytic MO degradation performance of the prepared photocatalysts under visible-light irradiation. As shown in Figure 6a, S-C₃N₄ and CdS exhibited weak photocatalytic MO degradation performance. AgCdS showed good photocatalytic MO degradation performance in the first 20 min, however, its photocatalytic MO degradation performance weakened after more than 20 min of degradation. Both S-C₃N₄/CdS and S-C₃N₄/AgCdS exhibited stable and sustained photocatalytic MO degradation performance. S-C₃N₄/AgCdS exhibited the best photocatalytic MO degradation performance, achieving a removal of over 95% of MO under 40 min of visible-light irradiation. Figure 6b–f show the absorption spectra of the degradation solution during the MO degradation by different photocatalysts. No other characteristic peaks were observed during the degradation of MO by the prepared photocatalysts, indicating the complete degradation of MO. Based on the results shown in Figures 5 and 6, both S-C₃N₄/CdS and S-C₃N₄/AgCdS exhibit good photocatalytic RhB and MO degradation performance, while the S-C₃N₄/AgCdS photocatalyst exhibits the best photocatalytic RhB and MO degradation performance.

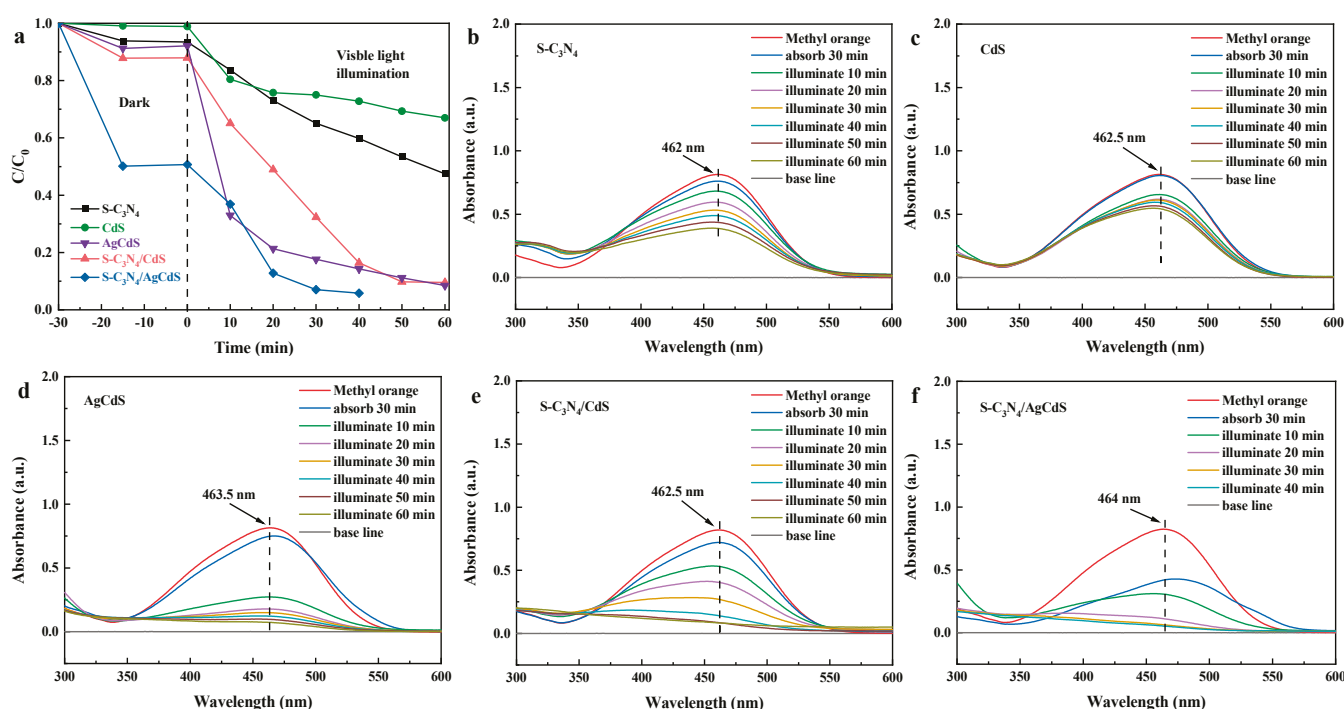


Figure 6. The MO dye degradation curves (a) of the prepared photocatalysts, and the absorption spectra of the degradation solution during the MO degradation process using different photocatalysts (b–f).

In order to investigate the electron migration ability and the charge carrier recombination rate of S-C₃N₄/CdS and S-C₃N₄/AgCdS photocatalysts, the EIS spectra and the PL spectra of these two photocatalysts were tested both in the dark and under light illumination, respectively. The corresponding results are shown in Figure 7. Figure 7a shows the EIS spectra of S-C₃N₄/CdS and S-C₃N₄/AgCdS in the dark and under light illumination, respectively. The smaller the arc radius, the better the electron transfer performance [37]. Under visible-light irradiation, both S-C₃N₄/CdS and S-C₃N₄/AgCdS exhibited higher electron transfer performance. This is attributed to the formation of more excited photo-generated carriers that flow directionally under the action of heterojunction electric fields, accelerating the separation of photogenerated carriers. S-C₃N₄/AgCdS exhibited faster photogenerated carrier migration performance under both in the dark and under light illumination, which is beneficial for the rapid migration of photogenerated carriers to the catalyst surface during the photocatalytic degradation reaction process and thus improves the separation efficiency of the photogenerated charge carriers. Figure 7b shows the PL

spectra of S-C₃N₄/CdS and S-C₃N₄/AgCdS. The weak peak appearing around 440 nm and the typical strong peak appearing around 520 nm are attributed to the characteristic light diffraction peak characteristics of S-C₃N₄ and CdS in S-C₃N₄/CdS, respectively. The typical peak of S-C₃N₄/AgCdS appearing around 520 nm shows a slight right shift, which is attributed to the doping of Ag in CdS. S-C₃N₄/CdS exhibited strong fluorescence intensity in the range of 400–700 nm, which can be attributed to the rapid recombination of the photogenerated carriers. In contrast, the PL intensity of S-C₃N₄/AgCdS was significantly lower than that of S-C₃N₄/CdS, indicating that the recombination rate of the photoinduced electrons and holes generated by S-C₃N₄/AgCdS was significantly suppressed. This will definitely achieve effective separation of photogenerated carriers, accelerate the photocatalytic degradation reaction process, and thus possess excellent photocatalytic performance.

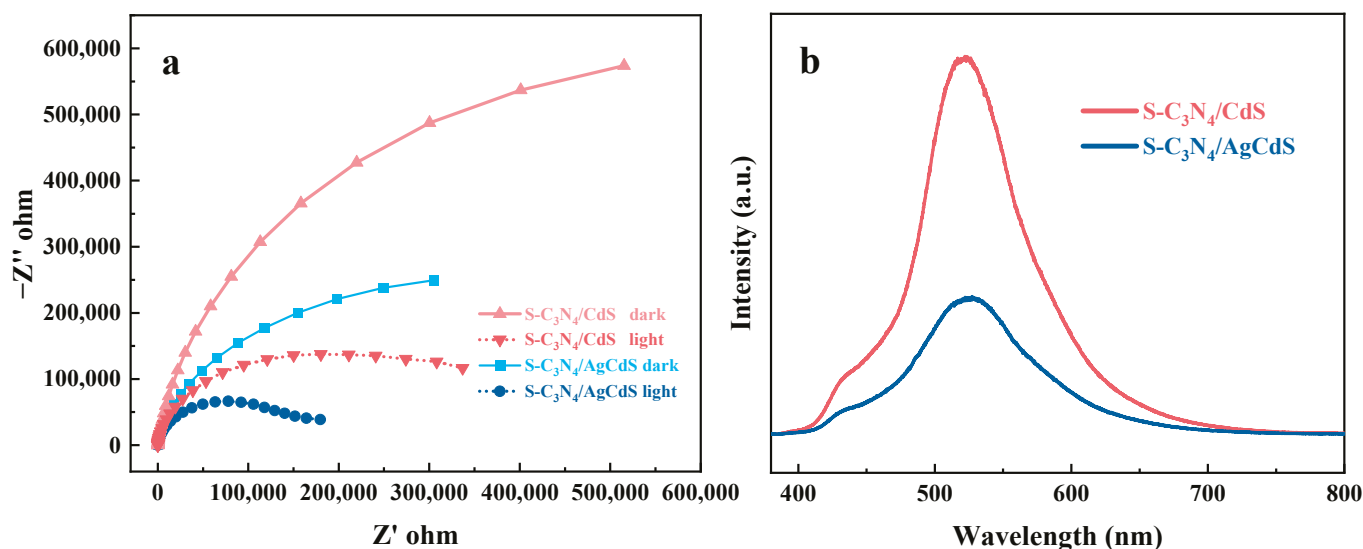


Figure 7. The EIS spectra of the prepared S-C₃N₄/CdS and S-C₃N₄/AgCdS measured in the dark and under light illumination (a), and the PL spectra of the prepared S-C₃N₄/CdS and S-C₃N₄/AgCdS (b).

The semiconductor types, flat band potentials, and bandgap widths of S-C₃N₄, CdS and AgCdS were further explored and the results are shown in Figure 8. Figure 8a–c show the Mott–Schottky curves of the prepared photocatalysts. The tangent slopes of the Mott–Schottky curves of S-C₃N₄, CdS, and AgCdS are all positive, indicating that the prepared catalysts are n-type semiconductors. The flat band potential of an n-type semiconductor can be approximately equal to its conduction band (CB) potential [38]. Therefore, the flat band potentials of S-C₃N₄, CdS, and AgCdS are roughly determined by the intersection of tangent lines at different frequencies on the horizontal axis. Therefore, the values of the CB potentials of S-C₃N₄, CdS, and AgCdS are approximately equal to -1.10 V, -0.45 V, and -0.37 V (vs. Ag/AgCl), respectively. Figure 8d–f show the relations of $(\alpha h\nu)^2$ with E_g , from which the bandgap widths of S-C₃N₄, CdS, and AgCdS can be obtained as 2.84 eV, 2.39 eV, and 2.37 eV, respectively. Based on the equation of $E_{CB} = E_{VB} - E_g$ [39], the valence band (VB) potential values of S-C₃N₄, CdS, and AgCdS are calculated to be 1.74 V, 1.94 V, and 2.00 V (vs. Ag/AgCl), respectively.

Figure 9 illustrates the energy band structures of CdS, AgCdS, and S-C₃N₄, as well as the photocatalytic degradation reaction mechanism of S-C₃N₄/AgCdS. As shown in Figure 9a, the VB potential of AgCdS is more positive than that of CdS, which makes the oxidation capability of the photoinduced holes generated by AgCdS stronger than that of the photoinduced holes generated by CdS. Many research results have confirmed that the heterojunction system formed by g-C₃N₄/CdS usually follows the photocatalytic reaction mechanism of Z-scheme [40–44]. Compared to CdS, the CB potential of AgCdS is more positive and closer to the valence band of S-C₃N₄, making it easier to follow the Z-scheme

reaction mechanism in the photocatalytic degradation reaction process. Figure 9b schematically presents the photocatalytic reaction mechanism of the S-C₃N₄/AgCdS heterojunction photocatalyst. Under visible-light irradiation, the photoinduced electrons generated by the CB of AgCdS quickly recombine with the photoinduced holes on the VB of S-C₃N₄, leaving the photogenerated holes with stronger oxidizing capability in the VB of AgCdS. The photoinduced electrons generated in the CB of S-C₃N₄ quickly transfer to the surface of the photocatalyst to participate in the photocatalytic reaction, ultimately achieving the rapid degradation of organic pollutants of RhB and MO.

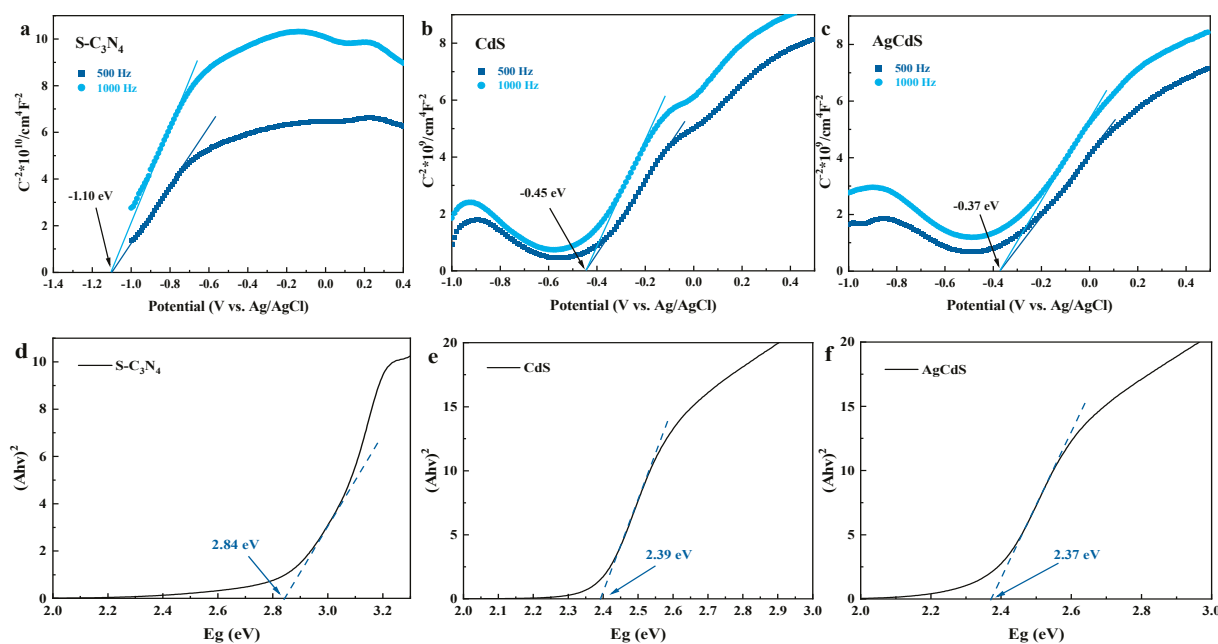


Figure 8. The Mott-Schottky curves (a–c) and the relations of $(\alpha h\nu)^2$ with E_g (d–f) of the prepared S-C₃N₄, CdS, and AgCdS.

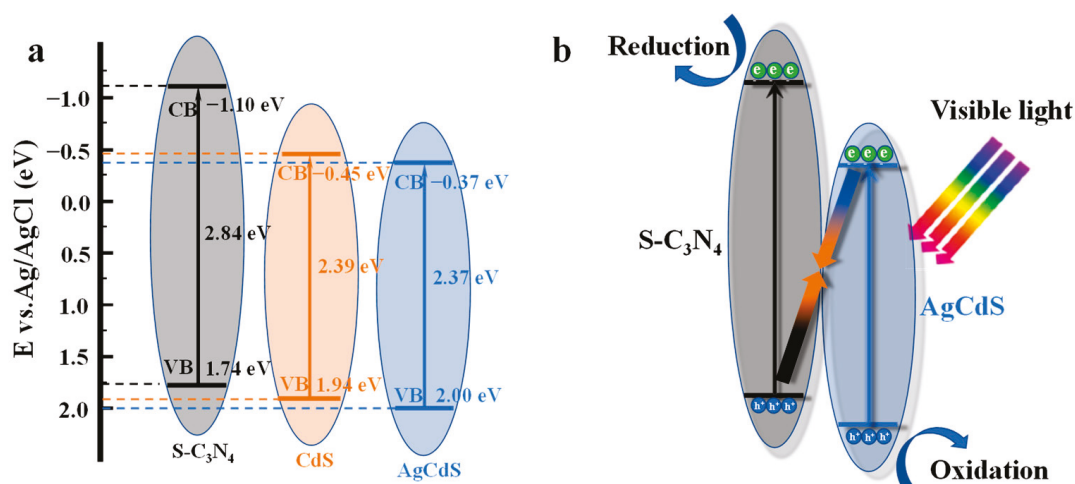


Figure 9. (a) Energy band structures of CdS, AgCdS, and S-C₃N₄ and (b) the proposed photocatalytic reaction mechanism of S-C₃N₄/AgCdS.

3. Materials and Methods

All reagents used in this experiment were from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), and were not further processed.

3.1. Preparation of S-C₃N₄ Photocatalyst

S-C₃N₄ was prepared in a tube furnace via high-temperature thermal polymerization. Firstly, 3 g of trithiocyanic acid was evenly spread in the porcelain ark. It was then placed in the center of the tube furnace, and was maintained at 600 °C in an air atmosphere for 2 h. The heating and cooling rate of the tube furnace was 5 °C·min^{−1}. The S-C₃N₄ photocatalyst was obtained.

3.2. Preparation of CdS and AgCdS Photocatalysts

Pure CdS was prepared through a simple water-bath reaction. 30 mmol of Cd(NO₃)₂·4H₂O and 30 mmol of thioacetamide (TAA) were added to 60 mL of deionized water. After adding the stirrer, magnetic stirring was performed to dissolve Cd(NO₃)₂·4H₂O and TAA into deionized water. The solution was then placed in a water bath at 60 °C for 30 min. The precipitate was collected, washed with deionized water and alcohol three times to remove excess ions, and finally placed in a blast drying oven at 60 °C for 24 h to obtain pure CdS.

3.3. Preparation of S-C₃N₄/CdS and S-C₃N₄/AgCdS Photocatalysts

30 mmol of Cd(NO₃)₂·4H₂O and 30 mmol of TAA were added to 60 mL of deionized water. After adding the stirrer, magnetic stirring was performed to dissolve Cd(NO₃)₂·4H₂O and TAA into deionized water. A total of 0.2 g of pure S-C₃N₄ powder was subsequently added into the solution and it was ultrasonically dispersed for 3 min. This solution was then heated in a water bath at 60 °C for 30 min. The precipitate was collected, washed with deionized water and alcohol three times to remove excess ions, and finally dried at 60 °C for 24 h to obtain S-C₃N₄/CdS photocatalyst.

The S-C₃N₄/AgCdS photocatalyst was prepared by adding 30 mmol of Cd(NO₃)₂·4H₂O, 0.15 mmol of AgNO₃ and 30 mmol of TAA to 60 mL of deionized water, and repeating the above operation steps to obtain the S-C₃N₄/AgCdS photocatalyst.

3.4. Characterizations

X-ray diffraction (XRD; TD-3500; Dandong Tongda Technology Co., Ltd. (Dandong, Chian)) was used to identify the crystal structure of the prepared samples. The microstructure of the prepared photocatalyst was observed using a scanning electron microscope (FE-SEM, Ultra 55, Zeiss, Jena, Germany). High-resolution transmission electron microscopy (HRTEM; TecnaiG2F20, FEMompany, Hillsborough, OR, USA) was used to observe the surface microstructure and interface binding information of S-C₃N₄/AgCdS. X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition and bonding information of composite material S-C₃N₄/AgCdS. The optical absorption characteristics of the prepared photocatalysts were measured using a UV–visible near-infrared spectrophotometer (UV vis DRS; UV 3600Plus, Shimadzu, Kyoto, Japan). A fluorescence spectrometer (PL; FluoroMax-4, HORIBA Jobin Yvon, Palaiseau, France) was applied to study the photoluminescence spectra of the prepared photocatalysts.

3.5. Photocatalytic Degradation Performance Measurements

50 mg of photocatalyst and 100 mL of RhB solution with the concentration of 10 mg·L^{−1} or 100 mL of MO solution with the concentration of 10 mg·L^{−1} were used in the photocatalytic degradation experiments. To keep the photocatalyst particles in the adsorption equilibrium state, the mixed solution needed to be stirred continuously in the dark for 30 min. During the photocatalytic degradation process, a 300-W xenon lamp was used as the light source and a UV cut-off filter ($\lambda > 420$ nm) was used to generate visible light. The continuous transport of the condensed water was maintained during the entire photocatalytic degradation process to keep the temperature of the solution at 25 °C. After turning on the xenon lamp for illumination, the absorbance and UV–visible absorption spectra of the degradation solution were measured every 10 min using a UV–visible spectrophotometer.

3.6. The Preparation and Photoelectrochemical Performance Measurement of the Photoelectrodes

Before preparation of the photoelectrodes, the FTO conductive glass was cleaned, and the specific cleaning steps were as follows. The FTO conductive glass was cut to $20 \times 10 \text{ mm}^2$, was completely immersed in the mixed solution with the volume ratio of deionized water, isopropanol, and anhydrous ethanol of 1:1:1 for a 30 min ultrasonic treatment. Finally, the FTO conductive glass was rinsed with deionized water, and dried for 6 h. An amount of 2 mg of prepared photocatalyst, 10 μL of naphthol, 10 μL of isopropyl alcohol and 150 μL of deionized water were put into an agate mortar, and were carefully ground for 20 min to obtain a uniform dispersion solution. Subsequently, this solution was evenly applied on the conductive surface of the cleaned FTO conductive glass with the coating area controlled at $10 \times 10 \text{ mm}^2$. The photoelectrode could then be obtained after natural drying.

The electrochemical performance of the prepared photocatalysts was tested using a Coaster electrochemical workstation. A conventional three-electrode system was used for the tests: a Pt electrode acted as the counter electrode, an Ag/AgCl electrode was used as the reference electrode, and the prepared photoelectrode acted as the working electrode. An amount of 0.1 M Na_2SO_4 solution was used as the electrolyte during the tests. The frequency range of the EIS test was 10–0.01 Hz, with an AC amplitude of $10 \text{ mV}\cdot\text{s}^{-1}$. The measurement was performed both in the dark and under light illumination. For the measurement of the Mott–Schottky curves, the scanning potential range was from -1.0 V to 0.5 V , and the frequency was tested at 500 Hz and at 1000 Hz.

4. Conclusions

In the present paper, $\text{S-C}_3\text{N}_4/\text{AgCdS}$ Z-scheme heterojunction photocatalyst was successfully prepared. The AgCdS nanoparticles were uniformly loaded onto the surface of $\text{S-C}_3\text{N}_4$ nanosheets and a good heterojunction structure was formed in the prepared $\text{S-C}_3\text{N}_4/\text{AgCdS}$ photocatalyst. The prepared $\text{S-C}_3\text{N}_4/\text{AgCdS}$ Z-scheme heterojunction photocatalyst exhibits excellent photocatalytic RhB and MO degradation performance. Through further investigations performed in this work, $\text{S-C}_3\text{N}_4/\text{AgCdS}$ more likely follows the photogenerated carriers transport mode of the Z-scheme heterojunction system compared to $\text{S-C}_3\text{N}_4/\text{CdS}$. The Ag doping combined with the Z-scheme heterojunction system enables $\text{S-C}_3\text{N}_4/\text{AgCdS}$ to possess a faster photogenerated carrier transport rate and much better separation efficiency of the photogenerated carriers; therefore, the photocatalytic degradation performance of the prepared $\text{S-C}_3\text{N}_4/\text{AgCdS}$ photocatalyst is significantly improved.

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Data Availability Statement: Data are contained within the article.

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

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Article

Photoelectrocatalytic Processes of TiO₂ Film: The Dominating Factors for the Degradation of Methyl Orange and the Understanding of Mechanism

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Abstract: Various thicknesses of TiO₂ films were prepared by the sol–gel method and spin-coating process. These prepared TiO₂ films exhibit thickness-dependent photoelectrochemical performance. The 1.09-μm-thick TiO₂ film with 20 spin-coating layers (TiO₂-20) exhibits the highest short circuit current of 0.21 mAcm^{−2} and open circuit voltage of 0.58 V among all samples and exhibits a low PEC reaction energy barrier and fast kinetic process. Photoelectrocatalytic (PEC) degradation of methyl orange (MO) by TiO₂ films was carried out under UV light. The roles of bias, film thickness, pH value, and ion properties were systematically studied because they are the four most important factors dominating the PEC performance of TiO₂ films. The optimized values of bias, film thickness, and pH are 1.0 V, 1.09 μm, and 12, respectively, which were obtained according to the data of the PEC degradation of MO. The effect of ion properties on the PEC efficiency of TiO₂-20 was also analyzed by using halide as targeted ions. The “activated” halide ions significantly promoted the PEC efficiency and the order was determined as Br > Cl > F. The PEC efficiency increased with increasing Cl content, up until the optimized value of 30 × 10^{−3} M. Finally, a complete degradation of MO by TiO₂-20 was achieved in 1.5 h, with total optimization of the four factors: 1.0 V bias, 1.09-μm-thick, pH 12, and 30 × 10^{−3} M Cl ion content. The roles of reactive oxygen species and electric charge of photoelectrodes were also explored based on photoelectrochemical characterizations and membrane-separated reactors. Hydrogen peroxide, superoxide radical, and hydroxyl radical were found responsible for the decolorization of MO.

Keywords: TiO₂; photoelectrochemical performance; photoelectrocatalytic performance; methyl orange; reactive oxygen species

1. Introduction

Energy and environmental crises have become serious threats to human society in the world today. Industrialization and population growth are major factors that result in environmental pollution and energy shortages [1]. Organic materials including dyes dumped into the water by organic industries are hazardous to aquatic life. The production of synthetic dyes has increased rapidly to meet the demands of the textile, food, printing, ink, tannery, paper, pharmaceutical, and cosmetic industries. However, the chemicals used in the production of these dyes are toxic and carcinogenic [2]. Therefore, it is obligatory for the scientific community to explore ways for overcoming the issues related to industrial effluents loaded with dye contaminants [3].

Photoelectrocatalysis (PECs) has attracted considerable interest since the discovery of the Honda–Fujishima effect [4] in 1972, especially following the serial stories reported by Carey et al. [5,6] that degradation-resistant organics such as polychlorinated biphenyl can

be decomposed by TiO_2 photoelectrode. In 1989, Tanaka, K. et al. [7] proved that reactive oxygen species (ROSs) such as hydroxyl radicals ($\bullet\text{OH}$) play a key role in photocatalysis, achieving great progress in photocatalytic (PC) mechanism. Furthermore, ROSs can be more effectively produced in photoelectrocatalytic (PEC) processes in a voltage bias photoelectrode, contributing significantly to the PEC synergy effect and enhanced PEC efficiency [8,9]. PECs combines the advantages of both PC and electrocatalytic technologies. Palanisamy's group [10] demonstrated that the PEC process effectively eliminated 76.2% of amoxicillin within 120 min at 0.8 V, outperforming the removal rates attained by the PC (52.6%) and electrocatalytic (32.3%) processes. PECs can both make use of the solar energy and regulate the photocatalytic process by using photoelectrodes with an appropriate external bias. Moreover, the PEC process is convenient for recycling photoelectrodes, avoiding the dilemma encountered in the photocatalytic process. PECs have been regarded as a technique revolution owing to the combination of photocatalysis, electrocatalysis, and solar energy utilization [11].

Various factors affecting PEC performance have been widely reported for TiO_2 photoelectrodes. Zhao's group [12] observed that anatase TiO_2 with a {001} crystal plane exposed shows prominent PEC activity. Wang and co-authors [13] demonstrated that the PEC efficiency increases when the UV light intensity ranges from $700 \mu\text{Wcm}^{-2}$ to 2.5 mWcm^{-2} . Iltaf Shah et al. [2] revealed that a basic alkaline medium is more suitable for a higher degradation rate of ethyl violet dye than acidic and neutral media. Lu Li and his teammates [14] announced that the PEC kinetics constant (K') was a 6.0-fold increase compared to the PC system. They observed that the PEC degradation efficiency of o-chlorophenol was 96.6% in 180 min under optimum conditions (bias: 0.5 V, solution pH: 6.3). Yan et al. [15] claimed that the PEC efficiency is approximately proportional to the thickness of the TiO_2 film; however, excessive thickness causes deterioration of the PEC efficiency. Anderson's team [16] reported the effect of bias, pH, inorganic ions on the PEC efficiency. Particularly, halide ions can be "activated" by a photoelectrode with sufficient bias and transformed into an "active halide" with highly catalytic oxidation activity, greatly improving the PEC efficiency of decomposing seawater to produce hydrogen [17]. To conclude, extensive investigations have been carried out on one or several of the factors affecting the PEC efficiency of TiO_2 , including the crystal phase, light source and light intensity, film thickness, bias, ion properties, and pH value [11]. However, a systematic study on the factors dominating the PEC efficiency and related mechanisms is still absent so far.

Numerous metal oxides such as TiO_2 , SnO_2 , ZnO , WO_3 , and Cu_2O have been used as photoelectrodes in PECs [18]. TiO_2 is considered one of the most important photoelectrodes due to its high activity, stability, and low cost [19]. Various forms of nanostructured TiO_2 film have been used in various applications such as detectors, memories, high-efficiency hydrolysis, diodes, transistors, sensors, etc. [20,21]. With regard to the feasibility of the application of TiO_2 photoelectrodes, film thickness, bias, ion properties, and pH value are the four most important factors. Therefore, in this study, we initiate a systematic study on the four factors dominating the PEC efficiency. The roles of ROSs and the electric charge of electrodes were also investigated to explore the related PEC mechanisms based on photoelectrochemical characterizations combined with membrane-separated reactors. This study might be beneficial to PEC research fields involved in the appropriate choice and optimization of experimental conditions and parameters.

2. Results

2.1. Structure, Morphology, and Optimal Properties of TiO_2 Films

Figure 1a shows the X ray diffraction (XRD) pattern of TiO_2 -20. All the diffraction peaks in the pattern are well-indexed to TiO_2 and F-doped tin oxide (FTO). The peaks located at $2\theta = 25.3^\circ$, 37.8° , 39.2° , 48.1° , 55.1° , 56.2° , and 69.1° are attributed to anatase types of TiO_2 . No other diffraction peak arises from possible impurities, indicating that a pure-phase TiO_2 film is produced. The variation curves of thickness and absorbance of the

films are given as the number of layers in Figure 1b. It is obvious that both the thickness and absorbance of the films increase with increasing layers of coatings.

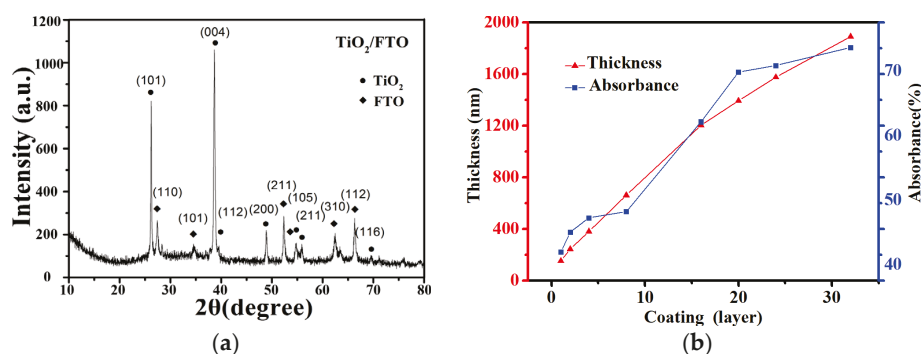


Figure 1. (a) XRD pattern of TiO₂-20, (b) the variation curves of film thickness and absorbance as the layers of coatings increase.

Figure 2a–c shows the scanning electron microscopy (SEM) images of TiO₂-1, TiO₂-4, and TiO₂-20. TiO₂-1 has a uniform, smooth, and dense surface (Figure 2c). We observed that the surface morphologies of TiO₂-2 and -3 are similar to that of TiO₂-1. Cracks began to appear in TiO₂-4 and then gradually widened as the layers increased. SEM images of TiO₂-4 and -20 in Figure 2b,c are given, respectively, as representative examples. The inset in Figure 2a is the high-magnification SEM image of TiO₂-1. The surface morphology in the red box in Figure 2b,c is similar to that of the inset. The results indicate that all TiO₂ films are composed of nanoparticles with a size of 20–30 nm. The microstructure of the TiO₂ films was further investigated with transmission electron microscopy (TEM). Figure 2d shows the representative TEM images of TiO₂-20. Grain crystal particles of TiO₂-20 shown in the TEM image can be clearly observed, which also indicate that TiO₂-20 is composed of 20–30 nm size nanoparticles.

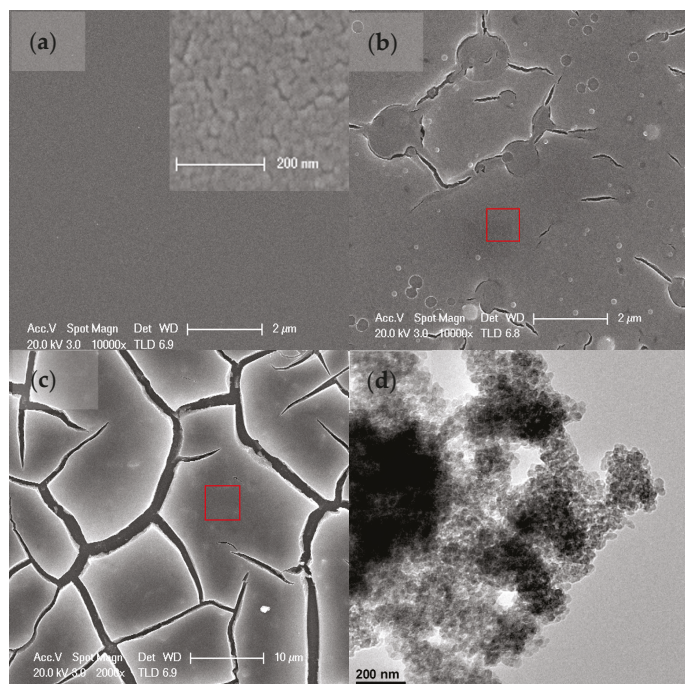


Figure 2. (a) SEM images of TiO₂-1, (b) TiO₂-4, (c) TiO₂-20, and (d) TEM of TiO₂-20. Inset is the close-ups of TiO₂-1. Red boxes in Figure 2b,c designate two continuous small areas in surface of TiO₂-4 and TiO₂-20.

2.2. Photoelectrochemical Properties of TiO₂ Photoelectrodes

Before the measurement of PEC regulation of MO by TiO₂ photoelectrodes, the cyclic voltammetry (CV) technique was used to examine the charge transfer between the FTO and the electrolyte. Figure 3a shows that the onset potentials for the anodic and cathodic dark current are essentially independent of the film thickness and scan rate. Representative samples of TiO₂-1, -8, -20, and -32 displayed nearly perfect blocking characteristics, indicating that all the films are pinhole free [22]. The result is also supported by the SEM data showing that the surface of the FTO substrate is completely covered by a very thin and compact TiO₂ coating. Moreover, even if there are cracks in some of the TiO₂ samples such as TiO₂-20, the inner coatings contacting the FTO substrates are still uniform and dense enough to separate FTO substrates from electrolytes, blocking charge transfer between them. In this case, charge transfer can only proceed between the TiO₂ photoelectrode and the electrolyte in the PEC reaction. The position of the flat-band potential was obtained by taking the x intercept of the Mott–Schottky plots of the TiO₂ films (Figure 3b), which gave all the samples a considerably negative flat-band potential, for example, -0.51 V for TiO₂-20. The positive slope of the plots again proved the n-type nature of the TiO₂ films. The application of a potential over the flat-band potential can suppress the charge carrier recombination. Thus, a zero or positive bias over the flat-band potential on the TiO₂ film electrodes may improve the PEC efficiency.

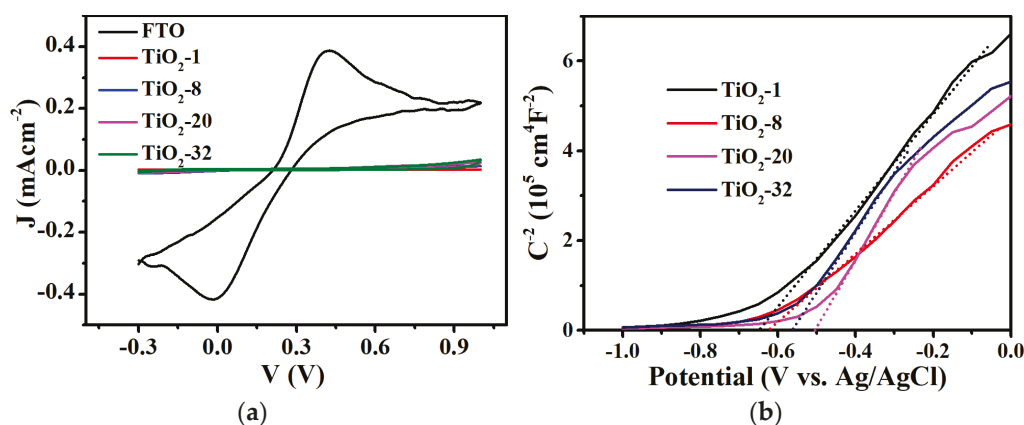


Figure 3. (a) CV of FTO, TiO₂-1, -8, -20, and -32. The measurement was carried out by a three-electrode system with TiO₂ film as working electrode, Pt plate as counter electrode, and Ag/AgCl electrode as reference electrode, respectively, and a scan rate of 20 mV s^{-1} . The electrolyte solution was $0.5 \times 10^{-3} \text{ M K}_4\text{Fe(CN)}_6 + 0.5 \times 10^{-3} \text{ M K}_3\text{Fe(CN)}_6$ in aqueous 0.5 M KCl . (b) Mott–Schottky plots of TiO₂ films; measured at 10 kHz , sweep rate 100 mVs^{-1} . The electrolyte solution was $0.5 \times 10^{-3} \text{ M Na}_2\text{SO}_4$.

Figure 4a,b shows the variation in the short circuit current (I_{SC}) and open circuit voltage (V_{OC}) as the layers of TiO₂ coatings. The data of I_{SC} , V_{OC} , and film thickness were abstracted from Figure S3. The behavior of the anode photocurrent and shift to negative potential under irradiation in Figure S3 indicate an n-type semiconductor behavior. The I_{SC} and V_{OC} increased at first and then decreased as the film thickness increased. TiO₂-20 achieved the highest I_{SC} of 0.21 mA cm^{-2} and V_{OC} of 0.58 V . The thickness-dependent photoelectrochemical properties of the TiO₂ films were also observed by M. L. Hitchman [23] and M. Rodríguez-Pérez [24] in polycrystalline anatase. EIS is particularly useful for explaining the interface charge transport and recombination [25]. Figure 4c shows Nyquist plots of the TiO₂-1, -8, -16, -20, -24, -32. The zoom of the high-frequency range in Figure 4d indicates that the semicircle part of TiO₂-20 has a minimum diameter among all the TiO₂ films. In the same frequency, a small impedance semicircle indicates a large capacitance value at the corresponding time constant and a low Faraday current impedance, signifying a fast kinetic process [26]. Thus, TiO₂-20 was chosen and used for the follow-up PEC experiment owing to its fast kinetic process and low PEC reaction energy barrier.

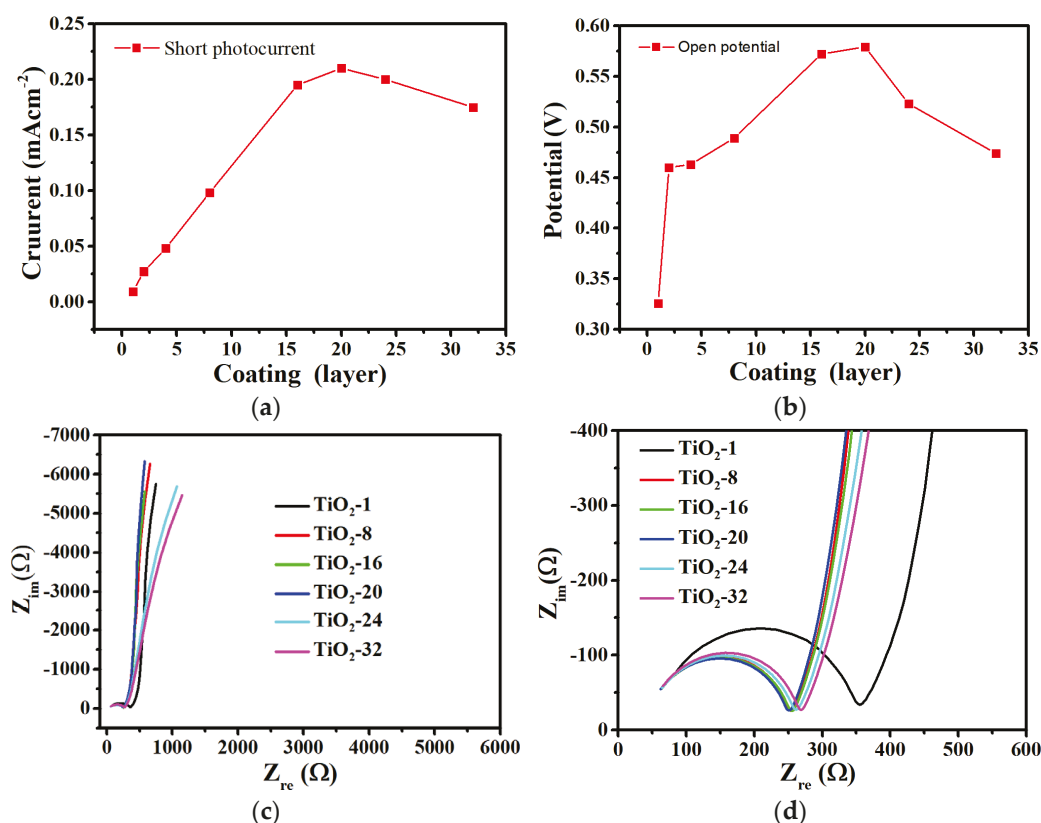
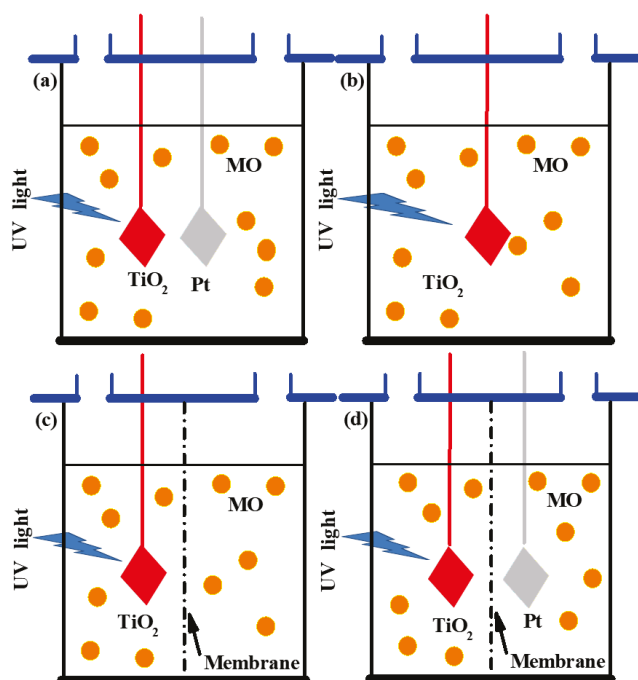


Figure 4. Patterns of variation in (a) short circuit current and (b) open circuit voltage as the layers of coatings of TiO₂ films. (c) Complete range Nyquist plot and (d) zoom at high-frequency region. Measuring condition: a 20 mV of AC signal was applied for a frequency range from 100 mHz to 400 kHz under UV-LED irradiation at a direct current bias of 0 V. The electrolyte solution was 0.5×10^{-3} M Na₂SO₄.

2.3. PEC Degradation of MO by TiO₂ Photoelectrodes

We carried out the PEC degradation of MO using the PEC reactor as shown in Scheme 1a. Figure 5a shows the variation in the degradation rate of pristine MO using the TiO₂-20 photoelectrode, with the potential bias ranging from 0 V to 1.2 V. Generally, in the PEC process, the degradation rate increased with an increasing bias, up until the optimized value of 1.0 V. Song et al. [27] and Zanoni et al. [28] reported similar results, in which at the optimal potential bias (for a given light intensity and film thickness), the electrons and holes were so well separated that enhancing the potential bias led to no significant improvement in the PEC activity. The PEC degradation of MO was further carried out using different thicknesses of TiO₂ photoelectrodes. As expected, TiO₂-20 achieved the highest degradation rate of 88.6% in 6 h among the representative samples at a bias of 1.0 V (Figure S4). This result is in accordance with the data of photoelectrochemical characterizations. Therefore, PEC regulation of MO by TiO₂-20 with a 1.0 V bias was chosen and used for the tests of different pH, halide ion, and concentrations of Cl, respectively.



Scheme 1. Schematic diagrams of experimental reactors with about 100 mL of volume glass container for PEC and PC regulation of MO. (a) PEC, (b) PC, (c) PEMS, and (d) PECMS reactors.

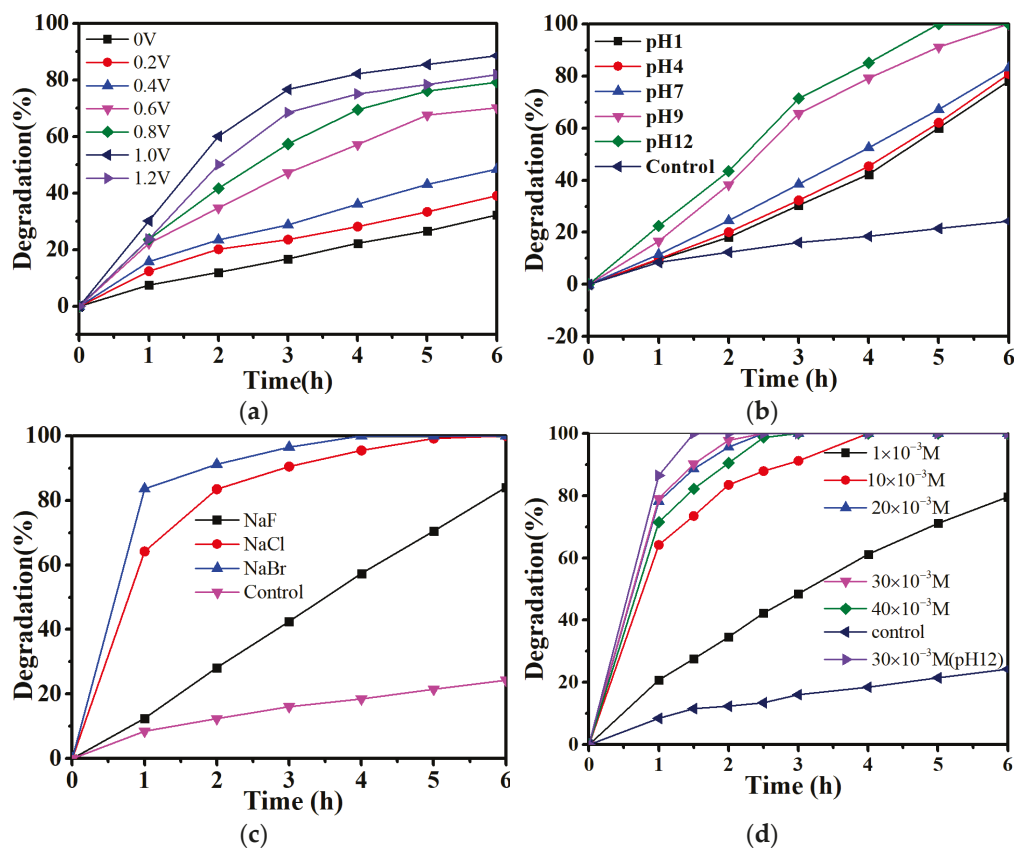


Figure 5. (a) PEC regulation of original MO by TiO₂-20 at different bias. PEC regulation of MO by TiO₂-20 with 1.0 V bias at different (b) pH, (c) halide ions, and (d) concentrations of Cl⁻. The PEC reactor is depicted as Scheme 1a.

Figure 5b shows the degradation rates of MO by TiO₂-20 with 1.0 V bias at different pH levels of 1, 4, 7, 9, and 12. The pH value of the solution was adjusted by dropwise adding H₂SO₄ and NaOH. The pH value of original MO solution in the control experiment was 5.8. One can see that the increasing pH value contributes to an enhanced degradation rate. Moreover, the degradation rates of all pH-adjusted MO solutions are higher than that of the pristine one. The reason is that the high conductivity of the MO solution increases the mass transfer and improves the PEC efficiency due to the addition of electrolytes H₂SO₄ and/or NaOH [29].

The influence of different electrolytes on the PEC degradation of organics has extensively been investigated in NaCl, NaNO₃ and Na₂SO₄, NaBr, and NaClO₄ [15,29,30]. The effects depend on the types and concentrations of negatively charged ions [11]. Halide ions can be transformed into “active halide” with highly catalytic oxidation activity, substantially improving the PEC efficiency and producing organic halides of industrial and medicinal importance [17]. Thus, in this study, we focused on the effect of halide ions on the PEC efficiency of TiO₂-20. Iodine ion (I[−]) was not included here because of its highly chemical reduction [31]. Figure 5c shows the degradation of MO by halide ions F, Cl, and Br. The order of the PEC efficiency was determined as Br > Cl > F. The halide ions can be activated to form highly oxidizing free radicals, significantly improving the PEC efficiency [30]. Considering that the Cl ion is very important and spreads over the water on earth, we carried out PEC experiments on the degradation of MO with different concentrations of Cl ion. Figure 5d shows that the addition of Cl greatly increased the photocurrent and PEC efficiency. The degradation rate rapidly increased as the Cl content increased from 0 to 10 × 10^{−3} M. However, the increase in the degradation rate slowed down as the concentration of Cl ranged from 10 × 10^{−3} M to 30 × 10^{−3} M. Moreover, excessive Cl content caused a decrease in degradation rate. The results indicate that the content of “active” Cl reached nearly its maximum, meaning that increasing the content of Cl cannot produce more “active” Cl but suppresses the PEC efficiency. In all, the PEC efficiency can be substantially improved by optimizing factors dominating the PEC performance of TiO₂ films. A complete degradation of MO by TiO₂-20 was achieved in 1.5 h in the PEC process with total optimization of the four factors: a thickness of 1.09 μm, a bias of 1.0 V, a content of 30 × 10^{−3} M Cl ion, and pH 12. The PEC degradation efficiency of MO by TiO₂-20 is pretty high and typical examples of comparative literature values are included in Table 1.

Table 1. Typical examples for pollutant degradation using PEC systems. (NPs = nanoparticles, NTs = Nanotubes).

Photoelectrode	Target Pollutant	Degradation Rate (%)	Degradation Time (min)	Ref.
TiO ₂ NPs	MO	100	90	Our work
TiO ₂ NPs	amoxicillin	76.2	120	[10]
TiO ₂ NTs	triclosan	78.7	30	[32]
Ti/TiO ₂ NTs	Chlortetracycline	74.2	120	[33]
Y-TiO ₂	MO	82.8	360	[34]
Double-faced TiO ₂	tetracycline	96.4	60	[35]
Au/TiO ₂	MO	54	300	[36]

2.4. The Contrast of PEC and PC Degradation of MO

The contrast of the PEC and PC efficiency of TiO₂-20 was carried out using PCMS and PECMS reactors, as shown in Scheme 1c,d. Figure 6a shows that the degradation rate of MO by TiO₂-20 in the PCMS reactor is 41.5% in 6 h in the PC process, while that with a 1.0 bias in the PCMS reactor is 100% in 5 h in the PEC process. Figure 6b shows that the TiO₂-20 in the PC reactor earned 26.3% degradation of MO, while the same TiO₂-20 with 0 V bias using the PEC reactor gained an enhanced degradation rate of 32.3%. It is expected that the application of a potential (0 V) over the flat-band potential (−0.51 V for TiO₂-20) can suppress the charge carrier recombination and improve the PEC efficiency according to

data of photoelectrochemical characterizations. These results indicate that the PEC process under electrochemical control achieves a much higher degradation rate than the PC one.

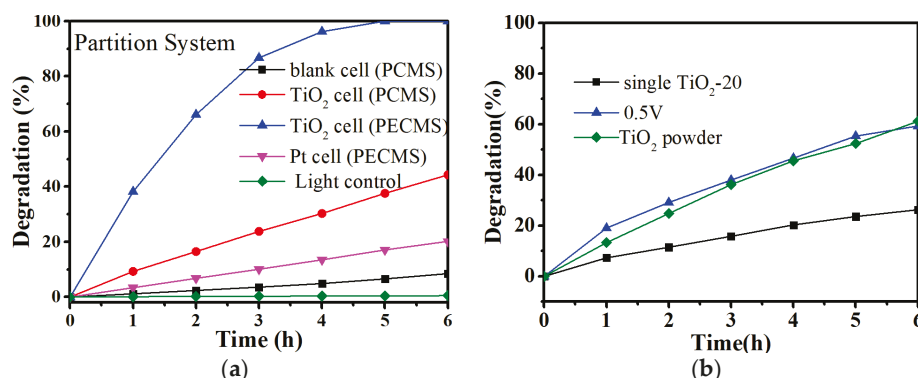
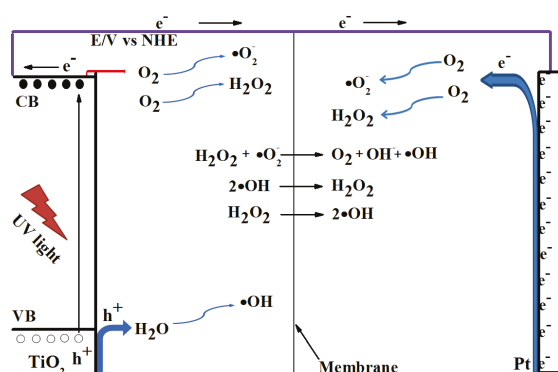


Figure 6. (a) The PC and PEC degradation of MO by TiO₂-20 using PCMS (Scheme 1c) and PECMS (Scheme 1d) reactors, respectively. (b) The PC degradation of MO by TiO₂ film and powder using PC reactor shown in Scheme 1b.

A comparison of the PEC efficiency of TiO₂-20 in a PEC reactor with the PC efficiency of TiO₂ powder in a PC reactor was also carried out. The film mass of TiO₂-20 was determined as 3.81 mg by measuring the difference of mass between FTO and TiO₂-20-coated FTO. Figure 6b shows that the single TiO₂-20 film can decolor 26.3% of MO, while TiO₂ powder (3.81 mg) can decompose 44.3% of MO in 6 h. The reason is that the TiO₂ powder is highly dispersed and has much larger contact area with MO solution than that of the single TiO₂-20 film. However, the TiO₂ film photoelectrode is very easy to be recycled and reused compared to the TiO₂ powder catalyst. Moreover, the TiO₂ film photoelectrode is convenient for the PEC process. Particularly, the PEC efficiency can be improved by electrochemical regulation; for example, TiO₂-20 with a bias of 0.5 V can achieve an equivalent degradation rate of MO as a 3.81 mg TiO₂ powder (Figure 6b).

2.5. The Roles of ROSs and Electric Charge of Electrodes

The general principle of PECs is well-documented in the pioneering work and follow-up studies [4,37–42]. Scheme 2 shows the energy level diagram of the TiO₂ film and the events possibly occurring during the PEC process. Under UV irradiation, the electrons (e[−]) in TiO₂ are excited to the conduction band, which creates holes (h⁺) in the valence band. The excited holes can oxidize water into oxygen and interact with O₂ and H₂O to form an assortment of ROSs, (i.e., •OH, H₂O₂). The excited electrons are collected and removed by an external circuit to the counter electrode, where they are frequently captured by oxygen to form ROSs (i.e., •O₂[−], H₂O₂). Here, we carried out PC and PEC tests to explore the origin of ROSs with a partition system (see Scheme 1c,d) under different conditions.



Scheme 2. Energy level diagram of TiO₂ film and the events possibly occurring during the PEC process.

Figure 7a shows that the $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ yield increased with increased irradiation time in both TiO_2 and Pt cells of the PECMS reactor (Scheme 1d). The species of $\bullet\text{OH}$ in the TiO_2 of the PECMS reactor were probably produced by a hole-induced oxidation process [43]:

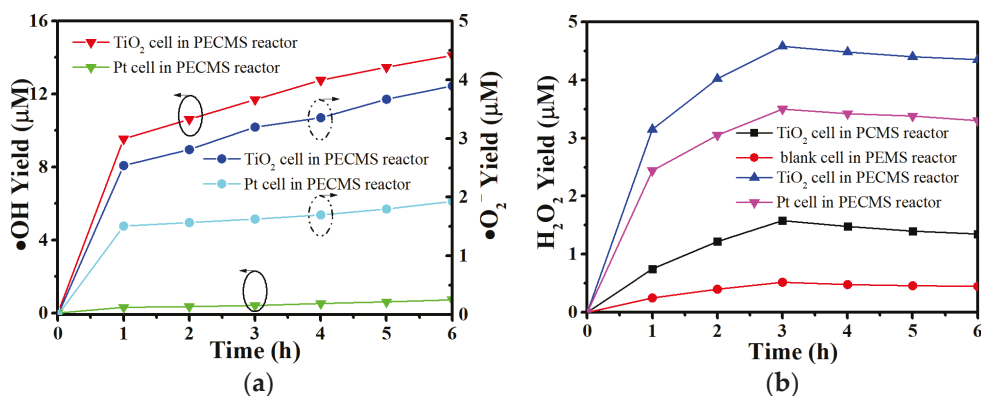


Figure 7. (a) $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and (b) H_2O_2 yield in TiO_2 and Pt cell of PECMS reactor under UV irradiation.

The $\bullet\text{OH}$ yield in the Pt cell of the PECMS reactor should originate from the Pt electrode because $\bullet\text{OH}$ in TiO_2 cell has a very short lifetime and cannot pass through the membrane to the Pt cell. It is well known that electrons can react with O_2 to produce $\bullet\text{O}_2^-$, and then H_2O_2 and $\bullet\text{OH}$ through a reductive process (Formulas (2)–(6)) [44,45]. The very low $\bullet\text{OH}$ yield suggests that a low level of kinetics evolution of $\bullet\text{OH}$ proceeds in the Pt cell of a PECMS reactor.



Figure 7b shows that all of the H_2O_2 yields increased at first and became stable with prolonged irradiation time due to the decomposition of H_2O_2 in parallel with its production. The equilibrium concentration of H_2O_2 in the TiO_2 and blank cells of the PEMS reactor was estimated to be 1.48 and 4.8 μM , respectively. It is no doubt that no PC process happened in the blank cell of the PEMS reactor so the supply of H_2O_2 in the blank cell attributed to the diffusion of H_2O_2 , which was produced in the PC process of the TiO_2 cell in the PEMS reactor and had a long life span and could pass through the membrane [46].

The equilibrium concentration for H_2O_2 in the TiO_2 and Pt cells of the PECMS reactor significantly increased up to 4.58 and 3.5 μM , respectively. Although H_2O_2 can be derived from $\bullet\text{OH}$ according to Formulas (3) and (5), the formation kinetics reaction of H_2O_2 is very slow due to its second-order reaction. In this case, the much higher H_2O_2 yield in the TiO_2 cell compared to the Pt cell of the PECMS reactor suggests that H_2O_2 can be probably produced from other sources. We believe that the supply of H_2O_2 in the TiO_2 cell of the PECMS reactor originates from the back electrons (see the red arrow in Scheme 2) of TiO_2 [47], which were transferred to the solution and underwent a reductive process as Formulas (2)–(5). The related mechanism and detailed descriptions on back electrons will be published elsewhere.

Note that an 8.5% degradation of MO was observed in 6 h in the blank cell of the PCMS and little degradation of MO under light control indicates that UV light cannot

decompose MO in our experimental conditions (Figure 6a). In addition, ROSs including $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ were produced in the TiO_2 cell of the PCMS, but they cannot pass through the semi-membrane because of their short lifetime. In this case, only H_2O_2 is responsible for the 8.5% degradation of MO in the blank cell of the PCEMS. It is reported that $\bullet\text{O}_2^-$ with highly catalytic oxidation activity can also decompose MO [48]. So, H_2O_2 , $\bullet\text{O}_2^-$, and $\bullet\text{OH}$ were responsible for the decolorization of MO. The much higher yields of H_2O_2 , $\bullet\text{O}_2^-$, and $\bullet\text{OH}$ in the TiO_2 cell than those in the Pt cell of the PCEMS reactor suggest that the TiO_2 photoelectrode plays a major role in the PEC process.

3. Materials and Methods

3.1. Materials

Tetrabutyl titanate (99% purity), sodium sulfate (99.0% purity), absolute ethanol (99.9% purity), sodium fluoride, sodium chloride, sodium bromide, MO, sulfuric acid, sodium hydroxyl, and nitric acid were purchased from Sinopharm Group (Shanghai, China). 2,3-bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide (XTT) (>98% purity), Terephthalic acid (TA) (98% purity), and horseradish peroxidase (POD) (activity: 250–330 units/mg solid) were received from Sigma-Aldrich (Shanghai, China). FTO glass was obtained from Youxuan Technology Corp. (Liaoning, China). All were used as obtained. The solutions used in this work were prepared with deionized water further purified with a Millipore Milli-Q (Millipore, Bedford, MA, USA) purification system (resistivity 18.6 M Ω).

3.2. The Preparation of TiO_2 Film Photoelectrodes and TiO_2 Powder

In this step, 15 mL ethanol containing 0.3 mL water was added dropwise into the mixture of 5 mL tetrabutyl titanate, 30 mL ethanol, and 0.3 mL nitric acid, stirring vigorously. Then, the whole mixture was continuously stirred for 2 h. A colorless and transparent TiO_2 gel was obtained by keeping the whole mixture sealed for one day. On an FTO glass substrate ($1.5 \times 2.5 \text{ cm}^2$), a thin film of sol was spin-coated at 2000 rpm for 30 s, followed by annealing in air with different ramping rates to the final 500 °C. FTO substrates with 1, 2, 4, 8, 16, 20, 24, 32 layers of coatings were achieved by repeating the spin-coating process and were denoted as TiO_2 -1, -2, -4, -8, -16, -20, -24, and -32, respectively. TiO_2 electrodes with $1 \times 1 \text{ cm}^2$ of surface exposed were prepared by sealing them with epoxy resin. TiO_2 -20 was chosen for XRD measurement. TiO_2 powder was collected by scraping the films off several TiO_2 -20 samples.

3.3. Characterization of TiO_2 Films

XRD measurements were carried out on a PW 1840 powder X-ray diffractometer, using Cu K α (1.54 Å) as the incident radiation. SEM images were obtained on a field-emission scanning electron microscopy (JSM-6700F, JEOL, Tokyo, Japan) at 30 kV. TEM were carried out with JEOL JEM100CXII. The absorption spectra were measured by a UV–vis spectrophotometer (CARY5000, Varian, Australia). The thickness of films was determined by a step profiler (Dektak XT, Bruker, Germany). Photoelectrochemical measurements and characterizations were conducted by a three-electrode system with a TiO_2 film electrode as working electrode, Pt plate electrode as counter electrode, and Ag/AgCl electrode as reference electrode, respectively, on a CHI660D station (Chenhua, Shanghai, China). The electrolytes were either $0.5 \times 10^{-3} \text{ M K}_4\text{Fe}(\text{CN})_6 + 0.5 \times 10^{-3} \text{ M K}_3\text{Fe}(\text{CN})_6$ or air-saturated $1.0 \times 10^{-3} \text{ M Na}_2\text{SO}_4$ solution. The light source was a UV-LED whose spectrum was given in Figure S1. The light intensity was measured by a light meter (LI-COR, Lincoln, NE, USA), and the light intensity for the experiments was fixed at 100 mW/cm 2 .

3.4. Detection of $\bullet\text{OH}$, $\bullet\text{O}_2^-$ and H_2O_2

The production of $\bullet\text{OH}$ was detected by a photoluminescence (PL) method by using terephthalic acid (TA) as a probe molecule [49]. The experimental procedure was similar to the measurement of PEC and PC activity except that the MO aqueous solution was replaced by the $5 \times 10^{-4} \text{ M TA}$ aqueous solution with a concentration of $2 \times 10^{-3} \text{ M NaOH}$. The

superoxide radical ($\bullet\text{O}_2^-$) was measured by XTT [50,51], which can be reduced by $\bullet\text{O}_2^-$ to form XTT-formazan. The formazan has an absorption spectrum (measured by UV/Vis spectrophotometer (Blue Star A, Fort Lauderdale, FL, USA) with a peak at 470 nm) can be used to quantify the relative amount of superoxide. H_2O_2 was analyzed photometrically by the Peroxidase (POD)-catalyzed oxidation product of DPD [52,53], which was measured by UV/Vis spectrophotometer (CARY5000, Varian, Australia) at 551 nm.

3.5. PC and PEC Experiments of TiO_2 Photoelectrodes

Scheme 1 shows four kinds of reactors: (a) PEC reactor, in which TiO_2 film, Pt were used as working electrode, counter electrode, respectively; (b) PC reactor, in which TiO_2 film was dipped in solution; (c) membrane-separated (MS) reactor, and (d) PEC membrane-separated (PECMS) reactors which are the same as (a), (b), respectively, except that the reactors are separated into two compartments by a semipermeable membrane. The photographs of experimental set-up of PEC, PC reactors and MS, PECMS reactors are given in Figure S2. The pore size of the semipermeable membrane was 5 nm, whereas that of MO was about 6–8 nm in size so that MO cannot pass through the membrane. PEC degradation of MO was conducted with the TiO_2 film as working electrode, Pt wire electrode as counter electrode, respectively, on a DXW-12V100A DC Voltage Regulator (Suzhou, China). At different time intervals, aliquots of the sample were collected. The MO concentration was analyzed by recording variations in the absorption band maximum at 465 nm (defined as A_t) in the UV-vis spectra of MO by using a UV-vis spectrophotometer. MO concentration of the reaction solution was defined as A_0 . The degradation efficiency of MO was calculated according to the equation: degradation rate (%) = $(A_0 - A_t)/A_0 \times 100\%$. The liquid phase degradation of MO was used for the evaluation of the PC activity of the TiO_2 powder.

4. Conclusions

The effects of bias, film thickness, pH value, and ion properties on the PEC performance of TiO_2 films were systematically studied under UV irradiation. At an optimized bias of 1.0 V, the TiO_2 -20 photoelectrode can degrade 84.5% of MO in 6 h, which outperforms the other TiO_2 film samples. We observed that a high pH value contributed to enhanced degradation of MO. The “activated” halide ions can significantly promote PEC efficiency and the order of PEC efficiency was determined as $\text{Br} > \text{Cl} > \text{F}$. The degradation rate increased with an increasing Cl content in an MO solution, up until the optimized value of 30×10^{-3} M. However, excessive Cl content causes a decrease in degradation rate. The PEC efficiency can be significantly improved and a complete degradation of MO was achieved in 1.5 h using TiO_2 -20 with 1.0 V bias and 30×10^{-3} M Cl ion content at Ph 12. The roles of ROSs and electric charge of electrodes were investigated to explore the related PEC mechanisms and H_2O_2 , $\bullet\text{O}_2^-$, and $\bullet\text{OH}$ were found responsible for the decolorization of MO.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules28247967/s1>, Figures S1–S4. Figure S1: The light spectrum of the UV lamp used in irradiation experiments. The peak is located at 365 nm. Figure S2: The photographs of experimental set-up of (a) PC, PEC reactors and (b) MS, PECMS reactors. Figure S3: The short circuit photocurrent (a), open circuit potential (b) and (c) absorbance of TiO_2 -1, -2, -4, -8, -16, -20, -24 and -32. (d) variation of film thickness as the layers of coatings. Figure S4: PEC degradation of MO by TiO_2 -1, -8, -16, -20 and 32 photoelectrodes at 1.0 V bias under UV irradiation.

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Review

Progress in Promising Semiconductor Materials for Efficient Photoelectrocatalytic Hydrogen Production

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Abstract: Photoelectrocatalytic (PEC) water decomposition provides a promising method for converting solar energy into green hydrogen energy. Indeed, significant advances and improvements have been made in various fundamental aspects for cutting-edge applications, such as water splitting and hydrogen production. However, the fairly low PEC efficiency of water decomposition by a semiconductor photoelectrode and photocorrosion seriously restrict the practical application of photoelectrochemistry. In this review, the mechanisms of PEC water decomposition are first introduced to provide a solid understanding of the PEC process and ensure that this review is accessible to a wide range of readers. Afterwards, notable achievements to date are outlined, and unique approaches involving promising semiconductor materials for efficient PEC hydrogen production, including metal oxide, sulfide, and graphite-phase carbon nitride, are described. Finally, four strategies which can effectively improve the hydrogen production rate—morphological control, doping, heterojunction, and surface modification—are discussed.

Keywords: photoelectrocatalysis; hydrogen energy; semiconductor; photoelectrode

1. Introduction

Hydrogen is known as the 21st century's most promising clean energy due to its status as an efficient energy carrier with a high energy combustion value (142.5 kJ/g), and the end product of its use is water [1,2]. To some extent, the development and utilization of hydrogen energy in relation to renewable energy sources has alleviated the fossil energy crisis [3,4]. Solar energy is inexhaustible but inconveniently used due to its dispersion. In this case, converting solar energy into hydrogen energy is a very promising energy solution because it can be more easily stored and effectively used [5,6].

Photoelectrocatalytic (PEC) hydrogen evolution using semiconductor photoelectrodes under irradiation has been widely studied as one of the effective ways to convert solar energy into hydrogen energy [7,8]. TiO₂ has been one of the most important and frequently studied PEC photoelectrodes since the discovery of the Fujishima–Honda effect [9]. After decades of development, PEC photoelectrodes have sufficiently expanded to a variety of TiO₂-based and other new photoelectrode materials; the influence of these photoelectrodes on PEC hydrogen production has been widely studied, and the related mechanisms have been exhaustively discussed [10–12].

The purpose of this review is to consider the progress on photoelectrocatalysis (PECs) for hydrogen generation from water using high-performance photoelectrode materials. In particular, this work considers the key material properties of photoelectrodes and the trends in research focused on the development of photoelectrodes that may bring PEC technology to commercial maturity. We focus on the preparation and modification of semiconductor

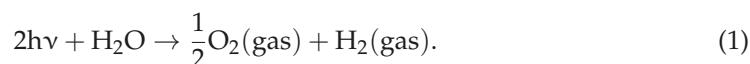
photoelectrode materials that have been widely investigated by researchers. Various high-performance photoelectrode materials, including metal oxide, sulfide, and graphitic carbon nitride semiconductors, are discussed. Numerous considerations are limited solely to oxide materials, which appear to exhibit superior properties as photoelectrodes in comparison to other types of materials.

2. The PEC Process of Water Decomposition

2.1. Mechanisms

PECs combines the advantages of both photocatalytic and electrocatalytic technologies. PECs can both make use of solar energy and regulate the photocatalytic process by using photoelectrodes with an appropriate external bias. Moreover, photoelectrodes are convenient for recycling in PEC processes, avoiding the dilemma encountered in the photocatalytic process.

When a semiconductor (e.g., photoanode) is irradiated, electrons and holes can be formed in the conduction band and the valence band, respectively. An electric field at the electrode/electrolyte interface is required in order to avoid the recombination of these charge carriers. The electrons generated in the photoanode are transferred over the external circuit to the cathode, resulting in a reduction reaction (for example, hydrogen ions are reduced into gaseous hydrogen). The light-induced holes lead to the splitting of water molecules into gaseous oxygen and hydrogen ions. The overall reaction for the PEC process may be expressed in the following form:



Reaction (1) takes place through a high energy barrier with a Gibbs free energy value of 237.2 kJ/mol, and the electrochemical decomposition of water is possible when the electromotive force of the cell is equal to or larger than 1.23 eV [13].

Concerning the mechanisms of the reactions, the principle of PEC water decomposition is highly related to the energy band structure of the photoelectrode semiconductor. Figure 1 shows a schematic diagram of a typical semiconductor energy band structure, illustrating the various band levels of established electrodes and comparing them with the potentials corresponding to H_2/H^+ and $\text{H}_2\text{O}/\text{O}_2$ redox couples. The bandgap of the photoelectrode semiconductor should be greater than 1.23 eV for the overall reaction for PEC water decomposition. Meanwhile, the conduction band of the semiconductor should be more negative than the electrode potential of H_2/H^+ , while the valence band position should be more positive than the electrode potential of $\text{H}_2\text{O}/\text{O}_2$ for the complete decomposition of water. Moreover, the water decomposition voltage is frequently higher than the theoretical value of 1.23 V [14] due to the existence of overpotential in practical PEC systems. It is well known that most semiconductors can satisfy only one of these conditions [15]. Figure 1 shows the band structures of some semiconductors.

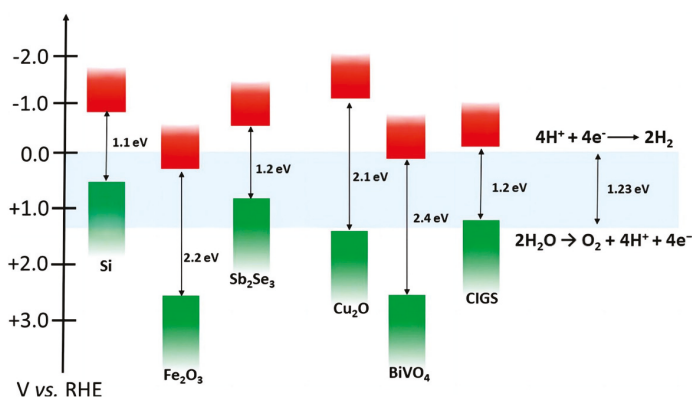


Figure 1. Band structures of typical semiconductors [16]. Reproduced with permission from Yang, W., *Chemical Society Reviews*, published by Royal Society of Chemistry, 2019.

In addition, the hydrogen half-reaction involves the transfer of only two electrons, whereas the half-reaction of oxygen production requires the transfer of four electrons and the formation of O-O bonds. Therefore, the generation of hydrogen is thermodynamically favorable, and the oxygenation reaction is the bottleneck of the whole reaction process if one takes into account the slowest process that determines the overall rate [17].

2.2. PEC Cell

Generally, the PEC cell is composed of a photoelectrode, counter electrode, reference electrode, and electrolyte solution. The photoelectrode, used as the working electrode, is mainly composed of a conductive substrate and a semiconductor film material. N- and p-type semiconductors are generally used as photoanodes for PEC oxygen production and photocathodes for PEC hydrogen evolution, respectively.

Materials with good charge collection performance and low reaction overpotential, such as platinum counter electrodes, are usually selected to fulfil the role of the counter electrode.

The electrolyte solution is responsible for mass transfer in the PEC cell. Therefore, the electrolyte solution should have a high conductivity. Salt substances such as Na_2SO_4 and K_2SO_4 are commonly used in neutral electrolyte solution, while acidic and alkaline solutions, as well as buffer solution, are employed for specific experimental conditions.

PEC cells can be divided into PEC photoanode cells, PEC photocathode cells, and PEC tandem cells, depending on the way that the semiconductor photoelectrodes are arranged. The PEC photoanode cell generally takes a n-type semiconductor as the working electrode and a platinum electrode as the counter electrode. The PEC photocathode cell often uses a p-type semiconductor as the working electrode and a platinum electrode as the counter electrode. The configuration of the PEC tandem cell is depicted in Figure 2, where a n-type and a p-type semiconductor are used as a photoanode and photocathode, respectively. The first two kinds of cells, using a single semiconductor as a working electrode, frequently require an external bias to promote the decomposition of water [16]. Fortunately, in a PEC tandem cell, the combination of a photoanode and photocathode is highly possible to ensure the complete photosplitting of water under sunlight without bias. As shown in Figure 2, photoanode and photocathode materials with different light absorption ranges can broaden the spectral range in the PEC tandem cell. The configuration of the PEC tandem cell is helpful for increasing photocurrent density and improving the efficiency of solar water splitting [18,19].

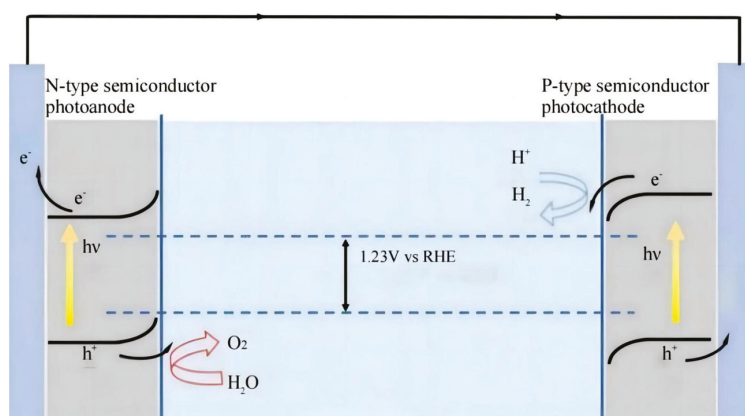


Figure 2. Diagram of a PEC tandem cell [20]. Reproduced with permission from Grätzel, M., *Nature*, published by Springer Nature, 2001.

3. Semiconductor Materials for PECs

In 1972, Fujishima Akira et al. [9] first reported the successful PEC decomposition of water on the surface of TiO_2 single-crystal electrodes under UV irradiation. Subsequently, researchers around the world observed a similar phenomenon of PEC hydrogen production

on other semiconductor materials, such as BiVO_4 [21,22], Cu_2O [23,24], Fe_2O_3 [25,26], WO_3 [27,28], and ZnO [29,30]. After decades of development, PEC hydrogen evolution using semiconductor photoelectrodes has made great progress.

3.1. Metal Oxide Materials

Currently, metal oxide semiconductors are considered for their advantages in terms of photochemical stability, their low cost, and their suitability for large-scale preparation [31–33]. TiO_2 has been widely studied due to its excellent photocatalytic activity, stability, safety, non-toxicity, rich content, and ease of preparation. However, TiO_2 with a wide bandgap of 3.2 eV can only be activated by UV light with a wavelength below 387 nm. Thus, many efforts have been taken to improve the PEC efficiency of TiO_2 . For example, the visible light activity of TiO_2 can be enhanced by modification. In particular, in the late 1980s, researchers devoted their efforts to developing second-generation TiO_2 that could absorb both UV (290–400 nm) and visible (400–700 nm) light and thereby enhance the overall efficiency. N-type BiVO_4 [34] and p-type Cu_2O [35] are widely regarded as promising semiconductor materials for efficient PEC hydrogen production due to their bandgap widths and suitable band structures.

3.1.1. TiO_2

TiO_2 , possessing excellent photoelectric performance and high photochemical stability, has always been a very promising PEC material. However, as mentioned above, TiO_2 can only absorb UV light, and the photogenerated charges are easy to recombine, resulting in a low PEC efficiency. Fortunately, the PEC efficiency of TiO_2 can be effectively improved by doping and constructing composite structures.

(1) Doping

Gong [36] and co-workers reported a tungsten-doped TiO_2 nanotube arrays (W- TiO_2 NTs) photoelectrode with an exclusive anatase phase utilizing a facile and novel anodization process on a Ti sheet. The results showed that W atoms were successfully incorporated into the TiO_2 lattice in the form of W^{6+} ions, which did not influence the morphologies of the TiO_2 NTs samples. The samples were evaluated by XPS to analyze the chemical states of W in W- TiO_2 NTs. The peaks of $\text{C}1s$, $\text{O}1s$, $\text{Ti}3p$, $\text{Ti}2p$, and $\text{W}4f$ were observed, as shown in Figure 3A. Figure 3B clearly shows that the peak of $\text{Ti}3p$ shifted from 35.9 to 36.9 eV because of the presence of W in the TiO_2 lattice. Thus, the W^{6+} ions were loaded into the bulk TiO_2 lattice by displacing Ti^{4+} ions and forming W-O-Ti bonds. As shown in Figure 4, the highest photocurrent density and hydrogen production rate were observed for the 15 mM W- TiO_2 NTs annealed at 400 °C. Under illumination, the photocurrent density quickly reached a constant value of 0.3 mA/cm², which indicates that the transfer of the photogenerated charge is quite rapid. The photocurrent pattern is highly reproducible for several on-off light cycles. The photogenerated electrons are rapidly transported from the TiO_2 nanotube arrays to the counter electrode to produce the photocurrent [37].

The PEC performance of TiO_2 can also be improved by metal element doping to increase its conductivity. A simple saturated aqueous solution method was used to synthesize a novel rutile Nb- TiO_2 /g- C_3N_4 photoanode, whose photocurrent was 1.39 times larger than that of its pristine counterparts under UV light [38]. In addition, the unoccupied conduction band of TiO_2 comprises $\text{Ti}3d$, $4s$, $4p$ orbitals, whereas the occupied valence band (VB) comprises $\text{O}2p$ orbitals. $\text{Ti}3d$ orbitals dominate in the lower position of the conduction band [39,40]. An impurity level can be induced by doping with other metal ions (cations) in place of Ti. The resultant intermediate energy level promotes visible light absorption by acting as either an electron donor or acceptor. By doping Fe into TiO_2 , the absorption peak of the sample can gradually shift to red with the increase in the amount of Fe^{3+} loading, as shown in Figure 5A. The red shift of the absorption edge in Fe/ TiO_2 might be attributed to the excitation of $3d$ electrons of Fe^{3+} ions to the TiO_2 conduction band (charge transfer transition) [41]. Figure 5B shows that the hydrogen evolution rate reached the maximum in the 1.0 wt% Fe/ TiO_2 photocatalyst. Meanwhile, the H_2 evolution rate decreased in the 2.0 wt%

Fe/TiO₂ photocatalyst, which might be due to the role of excess Fe³⁺ as a recombination site. Compared with the W-TiO₂ NTs mentioned above, the hydrogen production rate was reduced because more energetic ultraviolet light below 400 nm is shielded. However, its response to visible light makes Fe/TiO₂ more widely used.

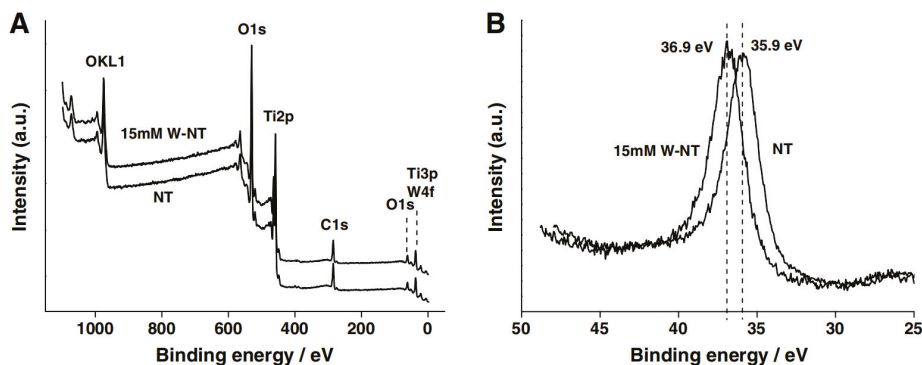


Figure 3. XPS spectra of (A) global range and (B) high-resolution spectra of Ti3p orbit of TiO₂ NTs and 15 mM W-TiO₂ NTs, respectively [36]. Reproduced with permission from Gong, J., *Catalysis Communications*, published by Elsevier, 2013.

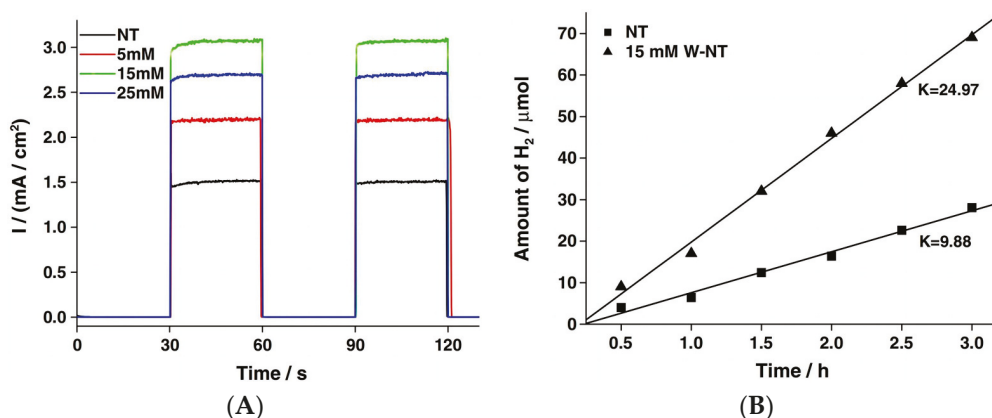


Figure 4. (A) The transient photocurrent responses of W-TiO₂ NTs. (B) Amount of H₂ evolution in the photocatalytic processes of TiO₂ NTs and 15 mM W-TiO₂ NTs, respectively [36]. Reproduced with permission from Gong, J., *Catalysis Communications*, published by Elsevier, 2013.

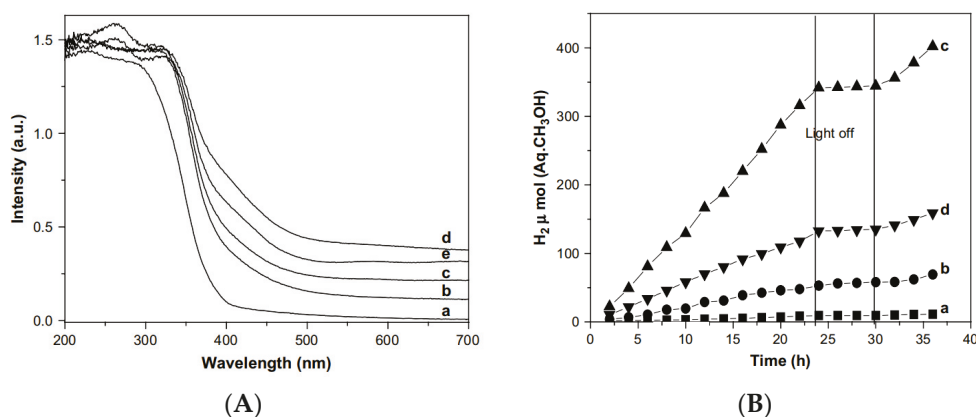


Figure 5. (A) UV-vis DRS spectra of (a) TiO₂, (b) 0.1 wt% Fe/TiO₂, (c) 0.5 wt% Fe/TiO₂, (d) 1.0 wt% Fe/TiO₂, and (e) 2.0 wt% Fe/TiO₂. (B) Hydrogen evolution in photocatalytic water splitting in 20% methanol aqueous solution under visible light irradiation: (a) 0.1 wt% Fe/TiO₂, (b) 0.5 wt% Fe/TiO₂, (c) 1.0 wt% Fe/TiO₂, and (d) 2.0 wt% Fe/TiO₂ [41]. Reproduced with permission from Khan, M. A., *International Journal of Hydrogen Energy*, published by Elsevier, 2008.

(2) TiO₂-based composites

Liu [42] and co-workers reported a TiO₂ NTs/Bi₂MoO₆ type-II heterojunction (a detailed description of type-II heterojunctions is available in Section 3.3) photocatalyst prepared using a simple solvothermal method. Bi₂MoO₆ nanoparticles (NPs) with nanosheet microstructures were successfully loaded on the surface of TiO₂ NTs through the adjustment of reaction intervals. With increasing reaction time, the amount of Bi₂MoO₆ deposition increased gradually. The absorption edges of the samples with reaction times of 14, 18, 22, and 26 h were located at 380, 414, 495, and 452 nm, respectively (Figure 6a). Furthermore, the band gaps of the samples could be estimated using transformational Tauc plots, and their band gaps were calculated to be 3.2, 2.9, 2.4, and 2.7 eV (Figure 6b). Reductions in band gap values were beneficial to solar energy absorption and photoelectric performance. Because the CB and VB position of Bi₂MoO₆ are more negative than TiO₂, a type-II heterojunction can be formed at the interface of TiO₂ NTs/Bi₂MoO₆. As shown in Figure 7, the electrons in the VB of the composite material are motivated by photon energy and jump to the CB. Then, electrons in the Bi₂MoO₆ CB transfer to that of TiO₂, and the holes in the TiO₂ VB transfer to the Bi₂MoO₆ VB via the assistance of the internal electric field of the type-II heterojunction. This structure greatly suppresses the recombination of photogenerated electron–hole pairs.

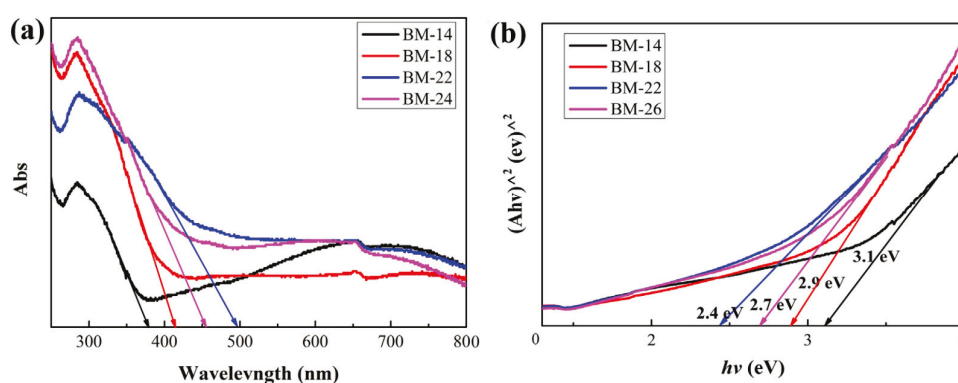


Figure 6. UV-Vis absorption (a) and a Kubelka–Munk plot (b) of a TiO₂ NTs/Bi₂MoO₆ heterojunction photocatalyst [42]. Reproduced with permission from Liu, Z., *Journal of Colloid and Interface Science*, published by Elsevier, 2019.

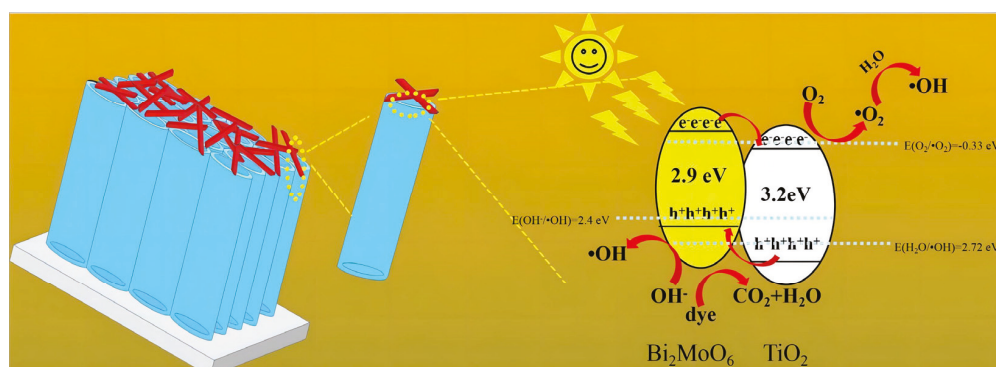


Figure 7. Schematic diagram of the degradation of dyes by a TiO₂ NTs/Bi₂MoO₆ heterojunction photocatalyst under solar irradiation [42]. Reproduced with permission from Liu, Z., *Journal of Colloid and Interface Science*, published by Elsevier, 2019.

Adamopoulos [43] and co-workers reported a photoanode which was made by depositing, on FTO electrodes, either a nanoparticulate WO₃ film alone or a bilayer film made of nanoparticulate WO₃ at the bottom, covered with a nanoparticulate TiO₂ film on the top. Due to the scattering of light by the top TiO₂ layer, the photocurrent increased by enhancing the light absorption by WO₃, as shown in Figure 8.

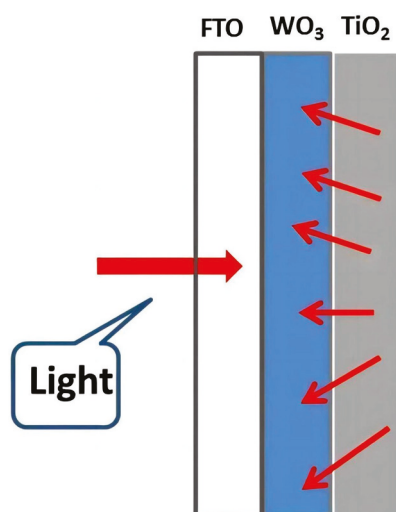


Figure 8. Graphical representation of the direction of photons in the presently used setup [43]. Reproduced with permission from Adamopoulos, P.M., *Catalysts*, published by MDPI, 2019.

Our research group and a few others developed several TiO_2 -based composite systems for energy storage, such as TiO_2/WO_3 [44,45], $\text{TiO}_2/\text{MoO}_3$ [46], and $\text{TiO}_2/\text{Ni}(\text{OH})_2$ [47]. The energy can be stored either in reduced WO_3 , MoO_3 , or in oxidized $\text{Ni}(\text{OH})_2$ under UV-light irradiation. In 2008, Yasomanee et al. [48] reported that a $\text{TiO}_2/\text{Cu}_2\text{O}$ film photoelectrode led to the continuous generation of H_2 from water splitting in the dark after UV-vis light irradiation stopped. The following year, we demonstrated that Ti^{3+} in a $\text{TiO}_2/\text{Cu}_2\text{O}$ bilayer film has energy storage ability under visible light irradiation. We observed that H_2 evolution was still noticeable after the irradiation stopped until the third hour. We believe that the electrons trapped in Ti^{3+} ions as stored energy lead to the evolution of H_2 from H_2O in the dark [49]. As shown in Figure 9, the photoelectrons of Cu_2O were captured by Ti^{4+} ions in TiO_2 , resulting in the reduction of Ti^{4+} ions to Ti^{3+} ions. The electrons trapped in Ti^{3+} ions would have been released if suitable electron acceptors existed. Two years later, we [50] also found that the $\text{TiO}_2/\text{Cu}_2\text{O}$ composite is capable of both organic degradation and photocatalytic H_2 evolution under visible light. Different from the two TiO_2 composites mentioned above, the TiO_2 layer here also plays a protective role for the Cu_2O layer. It is well known that Cu_2O is highly susceptible to photocorrosion. The existence of the TiO_2 protective layer improves the stability of the photocatalyst.

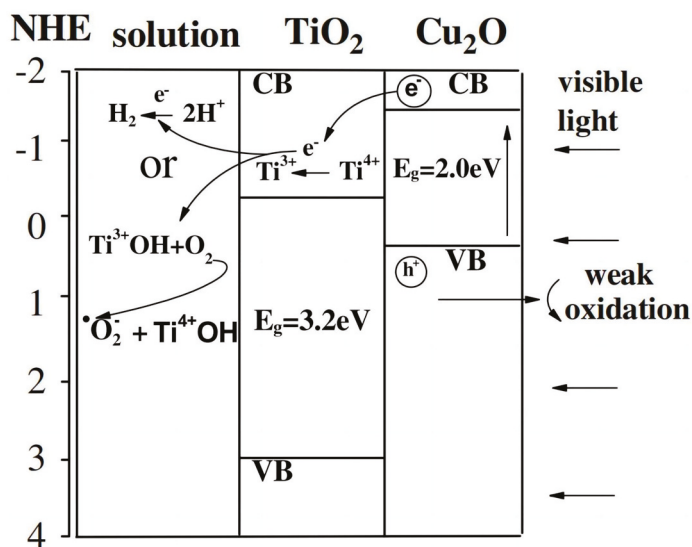


Figure 9. Electron migration diagram of a $\text{Cu}_2\text{O}/\text{TiO}_2$ composite [50]. Reproduced with permission from Xiong, L., *Journal of Physics and Chemistry of Solids*, published by Elsevier, 2011.

3.1.2. BiVO₄

BiVO₄ is considered as one of the most promising materials in the field of PEC water decomposition thanks to its visible light response, good stability, safety, and non-toxicity. In 1998, Kudo et al. [51] first reported that BiVO₄ powder can be used as a photocatalyst to decompose water under visible light. Five years later, Sayama et al. [52] first demonstrated that a BiVO₄-based photoanode successfully decomposed water into hydrogen and oxygen gas.

(1) Doping

At present, BiVO₄ photoanodes are mainly prepared by coating and electrodeposition. Firstly, a precursor solution containing Bi, V, or other impurity elements are prepared for the deposition of BiVO₄ films; secondly, the precursor solution is coated on the conductive substrate (FTO or ITO) by spin-coating, dip-coating, spraying, or scraping technology; finally, BiVO₄ film photoanodes can be obtained by post-annealing [53,54]. The preparation process is convenient for regulating the composition of the film, contributing to a suitable way to study the effect of doping on a BiVO₄ film. Luo et al. [55] examined the PEC performance of BiVO₄ photoanodes doped with 11 different kinds of elements through the above process. They found that the PEC performances of the BiVO₄ photoanodes significantly improved after they were doped with W or Mo. Abdi et al. [56] found that the charge separation efficiency values of the BiVO₄ photoelectrodes significantly improved as the content of W in the precursor ranged from 0% to 1%.

Kim [57] and co-workers used dimethyl sulfoxide with low hydrophilicity to dissolve acetylacetonate to phenoxy vanadium as a vanadium source solution before coating it on the surface of BiOI thin film electrodes. The problem regarding the poor infiltration of ammonia solution and the BiOI film was solved by this step. Crucially, Kim et al. subjected nanoporous BiVO₄ to a mild annealing treatment under N₂ flow, which resulted in nitrogen being incorporated into the oxygen sites. The bandgap of the sample was reduced, while the carrier mobility was increased.

(2) BiVO₄-based composites

In addition to doping, the separation of photogenerated electron–hole pairs can be promoted by constructing BiVO₄ heterojunctions to improve PEC performance. Liang et al. [58] reported on highly efficient and reproducible BiVO₄ photoanodes prepared by a new spray pyrolysis method. As shown in Figure 10, the collection and transfer of carrier charge was substantially improved due to the blocking effect induced on holes, attributable to SnO₂ being introduced as a thin interfacial layer between the FTO and BiVO₄. The strategy of using a thin SnO₂ layer as a hole mirror can benefit other photoanode materials to avoid the recombination of defect states at the FTO/BiVO₄ interface. This provides an effective method for enhancing the hydrogen production efficiency of FTO-based photoelectrode materials.

Li et al. [59] synthesized a Bi₂S₃/BiVO₄ photoelectrode with a heterojunction structure through a two-step conversion process. As shown in Figure 11a, it is obvious that the hybrid Bi₂S₃/BiVO₄ nanostructure exhibited a higher photocurrent density than the bare BiVO₄. Compared with Figure 4A, the photocurrent density curve has a sharp decrease at the beginning of each cycle. This phenomenon is caused by the recombination of partial photogenerated charges in the composite, which is very common in composites with heterojunction structures [42,43]. Meanwhile, the results showed that Bi₂S₃/BiVO₄ has a higher carrier concentration relative to the bare BiVO₄. In addition, the flat band potential had a negative shift for the hybrid Bi₂S₃/BiVO₄ compared with the bare BiVO₄, which was ascribed to the more negative position of the conduction band for Bi₂S₃ than that of BiVO₄ (Figure 11b). The negative flat band potential shift contributed to the separation of the photogenerated charge. Because the energy band positions of Bi₂S₃ were both more negative than that of BiVO₄, the photoelectrons in the conduction band of Bi₂S₃ transferred to the conduction band of BiVO₄, and the photogenerated holes transferred from BiVO₄

to Bi_2S_3 in the same way (Figure 12). The photocharge recombination can be effectively suppressed, which improves the photocurrent density.

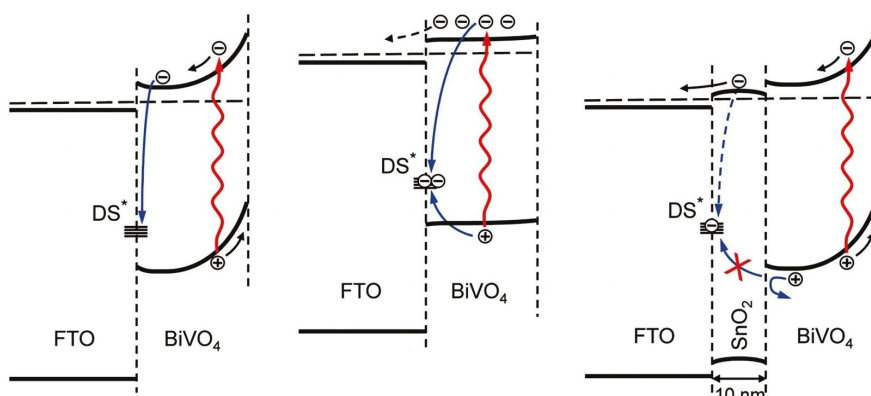


Figure 10. Schematic diagrams illustrating the recombination at the defect state present at the FTO/BiVO₄ interface and the hole mirror effect of the SnO₂ layer, respectively [58]. Reproduced with permission from Liang, Y., *The Journal of Physical Chemistry C*, published by American Chemical Society, 2011.

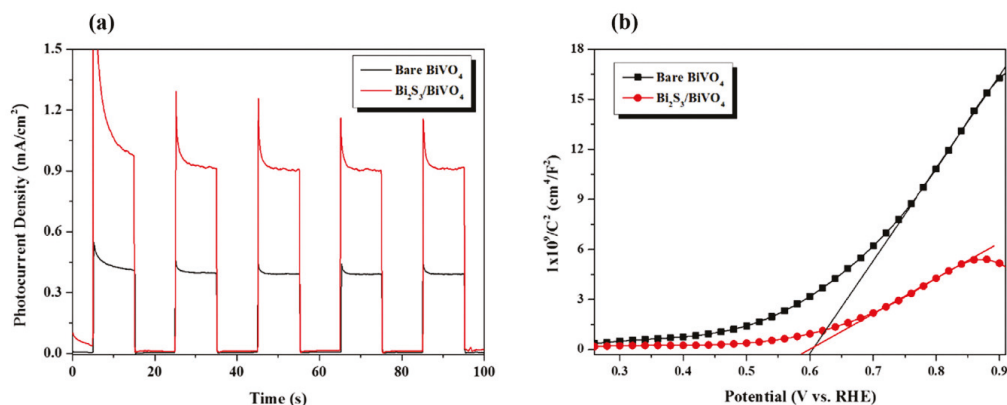


Figure 11. (a) Photocurrent density and (b) Mott-Schottky plots of the as-prepared photoelectrodes measured in a 0.2 M Na₂SO₃ solution [59]. Reproduced with permission from Li, F., *Chemical Engineering Science*, published by Elsevier, 2020.

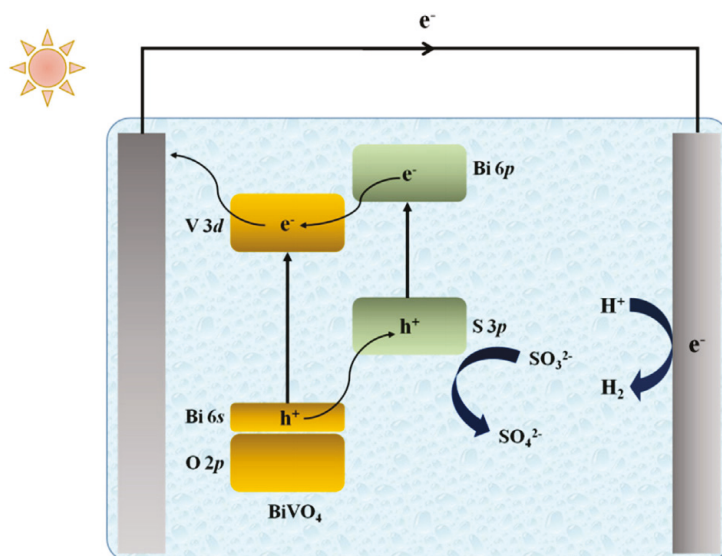


Figure 12. Energy band structure of a hybrid Bi₂S₃/BiVO₄ photoelectrode and its electron transfer pathway in photoelectrocatalytic hydrogen production under solar light irradiation [59]. Reproduced with permission from Li, F., *Chemical Engineering Science*, published by Elsevier, 2020.

3.1.3. Cu_2O

Cu_2O has attracted considerable interest in the field of PECs since Kondo et al. [60] first reported that Cu_2O can photocatalytically carry out complete water decomposition in 1998. Cu_2O has a narrow band gap of about 2.1 eV and a high absorption coefficient. It shows red, orange, and other different colors due to its different synthesis methods and particle sizes. Cu_2O has various advantages, such as its appropriate band gap, excellent photoelectric performance, simple preparation, and low cost. However, Cu_2O photocathodes are extremely prone to photocorrosion due to their oxidation–reduction potentials located in the band gap of Cu_2O [61,62]. At present, a large number of studies in the literature are devoted to the stability of Cu_2O as a photocathode in the process of PECs. Siripala et al. [63] first proposed that the stability of a Cu_2O photocathode can be substantially improved if a TiO_2 protective layer with a thickness of about 100 nm is deposited on the surface of Cu_2O by the electron beam method.

Wu et al. [64] reported a $\text{MoS}_2/\text{Cu}_2\text{O}$ nanohybrid prepared by a simple wet chemical method. This heterojunction structure effectively promoted the separation of photogenerated electron–hole pairs, resulting in a significant increase in the photocurrent of the nanohybrid. Peerakiatkhajohn et al. [65] originally introduced a Al_2O_3 thin-film layer between Au@TiO_2 and Cu_2O . On the one hand, strong inherent electric fields at the interfaces, produced by the introduction of an extremely thin Al_2O_3 film, suppress the recombination of photogenerated electron–hole pairs. On the other hand, humic acid served as an electron donor to clear holes and suppressed electron hole recombination by capturing the remaining holes. In the presence of humic acid, the hydrogen production efficiency of the PEC device was significantly improved. A bifunctional PEC system with the function of simultaneous hydrogen production and humic degradation was achieved through using the multi-layer $\text{Au@TiO}_2/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ photoelectrodes, as shown in Figure 13.

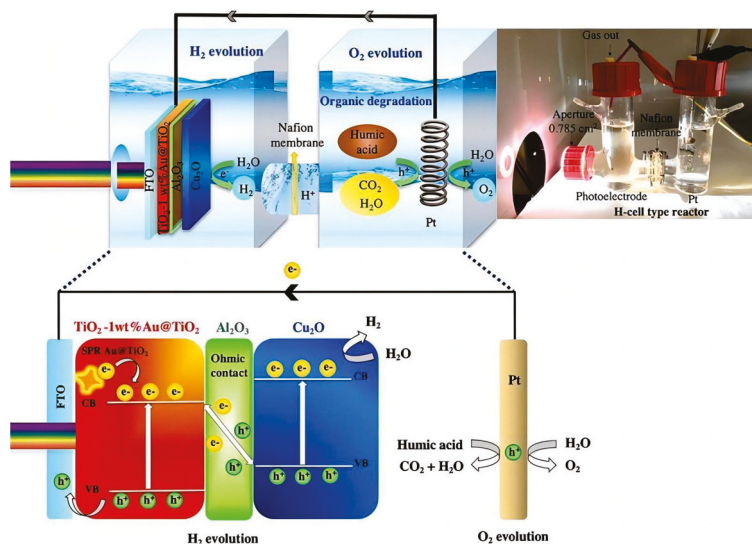


Figure 13. A schematic visualization of a bifunctional PEC system (hydrogen generation and humic acid degradation) with a direct Z-scheme mechanism of $\text{TiO}_2\text{-1 wt\% Au@TiO}_2/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ photoelectrodes in a H-cell type reactor [65]. Reproduced with permission from Peerakiatkhajohn, P., *Journal of Hazardous Materials*, published by Elsevier, 2021.

3.2. Sulfide Materials

Metal sulfides such as cadmium sulfide (CdS), cadmium zinc sulfide solid solution ($\text{Zn}_x\text{Cd}_{1-x}\text{S}$), and indium zinc sulfide (ZnIn_2S_4) have been extensively studied for their wide range of sources, simple preparation methods, appropriate band structures, and good PEC activity. Solid-phase synthesis is one of the important methods for preparing sulfides. Bao et al. [66] prepared CdS nanocrystals via the pyrolysis of a cadmium thiourea complex at high temperature in a N_2 atmosphere. However, the crystal produced by this method

had a large crystalline grain size and small specific surface area, which is not conducive to the PEC reaction.

With the development of colloidal chemistry, people have gradually developed a variety of liquid-phase synthesis methods to prepare sulfide materials with high PEC performance. In early studies, CdS was often prepared by a chemical precipitation method, and the precursor was usually cadmium brine solution. H_2S , Na_2S , thiourea, and other sulfur-containing organic or inorganic compounds are used as precipitants [67]. The microwave hydrothermal method is also an important synthesis method for preparing high-quality sulfides. The electromagnetic field in the microwave reactor changes direction at a frequency of tens of thousands of hertz, causing the dipolar vibration of reactant molecules. The entire reaction system is heated rapidly and evenly, which greatly improves the reaction rate [68].

3.2.1. Doping

For sulfide semiconductors, doping is also an effective way to adjust their band structures for improving PEC performance. Tian et al. [69], Zhang et al. [70], and Barpuzary et al. [71], respectively, incorporated Cu, Co, and Mn elements into CdS, which introduces shallow energy levels into its band gap, improving the PEC performance of doped CdS due to the enhancement in carrier separation efficiency and visible light absorption. As shown in Figure 14, compared with the XPS spectrum of the CdS, the two peaks corresponding to $\text{Cd}3d_{5/2}$ (404.1 eV) and $\text{Cd}3d_{3/2}$ (411.7 eV) had a slight shift towards to a higher binding energy. The introduction of Cu^{2+} changed the crystal structure of CdS due to the introduction of lattice defects. Similarly, the absorption edge of the UV/Vis spectrum shifted to red because of the Cu defect states formed in the forbidden gap (Figure 15). The 7% Cu-CdS exhibited the best hydrogen production ability, with a rate of $1115 \mu\text{mol h}^{-1} \text{g}^{-1}$, which is almost 5.3 times higher than that of undoped CdS of $212 \mu\text{mol h}^{-1} \text{g}^{-1}$ (Figure 16A). Furthermore, a Cu-CdS/ MoS_2 composite can reach a hydrogen production rate of $10.18 \text{ mmol h}^{-1} \text{g}^{-1}$, which is about 48 times higher than that of pure CdS (Figure 16B). MoS_2 can provide a lot of active sites at the edge of its sheets, leading to improved hydrogen production. The photoelectric performances of photoelectrodes with composite structures are often better than those based on pure doping.

In addition to doping, the energy band structure of sulfides can also be modified by forming solid solutions with different precursors of sulfides. The energy band structure of solid solutions can be precisely controlled by changing the composition of different precursors. For example, the band gaps of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ [72] and $\text{Cu}_x\text{Ag}_{1-x}\text{InS}_2$ [73] can be precisely tuned by adjusting the composition of Zn/Cd and Cu/Ag, respectively. In this case, both of the tuned sulfides can respond to visible light, allowing for the efficient utilization of solar energy. Moreover, such solid solutions show better PEC performances than doped sulfides.

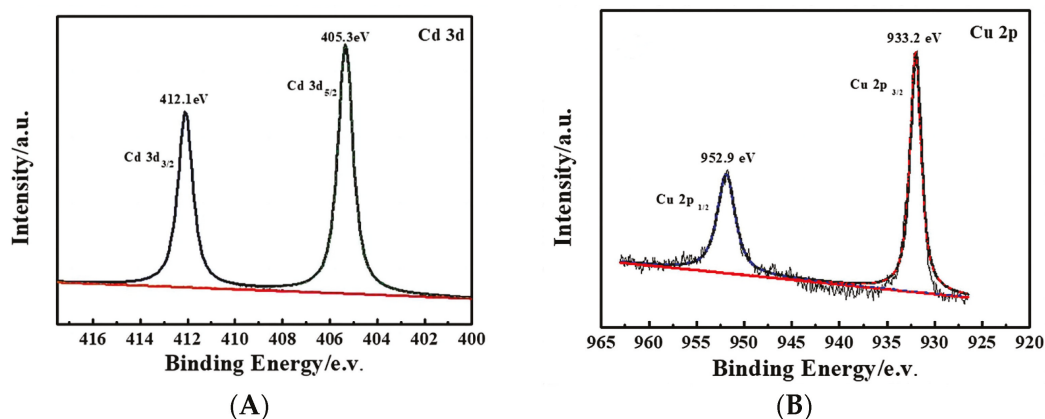


Figure 14. XPS spectra of (A) Cd3d and (B) Cu2p [69]. Reproduced with permission from Tian, H., *ChemElectroChem*, published by John Wiley and Sons, 2018.

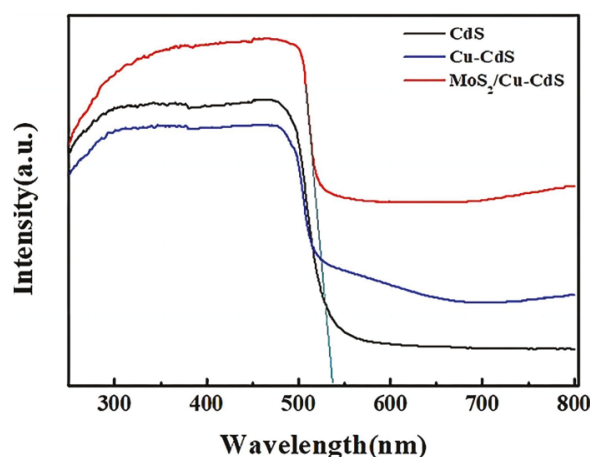


Figure 15. UV/Vis absorption spectra of CdS, Cu-CdS, and MoS₂/Cu-CdS [69]. Reproduced with permission from Tian, H., *ChemElectroChem*, published by John Wiley and Sons, 2018.

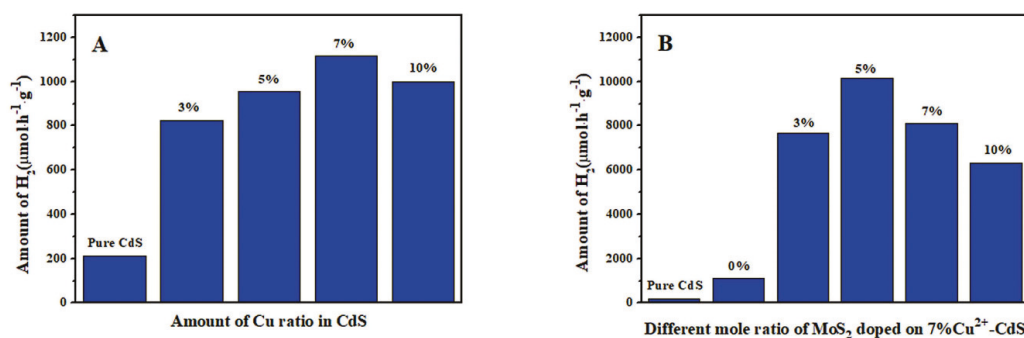


Figure 16. Comparison of the photoelectrocatalytic H₂ evolution rate of (A) Cu-CdS and (B) Cu-CdS/MoS₂ [69]. Reproduced with permission from Tian, H., *ChemElectroChem*, published by John Wiley and Sons, 2018.

3.2.2. Sulfide-Based Composites

Like sulfides, sulfide-based composites have also attracted considerable attention [74]. Gao et al. [75] prepared ZnIn₂S₄ nanosheets on flexible graphite felt by using a hydrothermal method. They found that a photoelectrode with a 5 mm-thick graphite felt and ZnIn₂S₄ coating exhibited the best PEC properties compared to other photoelectrodes. Guo et al. [73] designed a series of Cu_xAg_{1-x}InS₂/ZnS colloidal quantum dots (CQDs) by the defect passivation of a ZnS shell and the incorporation of Cu ions to engineer its band structure. ZnS shell-assisted defect passivation suppressed charge carrier recombination because of the formation of the core/shell heterojunction interface, enhancing the performance of PEC devices with better charge separation and stability. Furthermore, Cu ion doping in AgInS₂ CQDs results in a shift in the energy band of the quantum dots, which greatly promote the interface's charge separation and transfer (Figure 17).

Mollavali [76] reported the composite structures of a variety of sulfides on Co-doped/modified TiO₂. TiO₂ nanostructures were first sensitized by nitrogen and carbon with a one-step low-cost anodic oxidation process, and then NiS/CdS/ZnS NPs were deposited on the surfaces of TiO₂ nanostructures by successive ionic layer adsorption and using a successive ionic layer adsorption and reaction (SILAR) method at room temperature (Figure 18). These vertically aligned C, N-co-doped TiO₂ nanotube arrays (TNAs) electrode provide a large surface area for the deposition of NPs, and they are also well-defined channels for efficient charge transport (Figure 19a). The NiS nanoparticles have small aggregation rather than large aggregation on the top of the TNAs (Figure 19b). Although some aggregates of the nanoparticles can be observed in the final photoanode due to the dense particle loading, the nanotubes remain predominantly open after all deposition steps,

which is an important factor to maximize light absorbance and photoactivity, as well as electrolyte transport (Figure 19c,d). The optical properties of a C, N-TiO₂/NiS/CdS/ZnS photoanode were enhanced due to a reduction in the recombination of electrons and holes, improving the surface carrier transfer rate and photogenerated carrier separation.

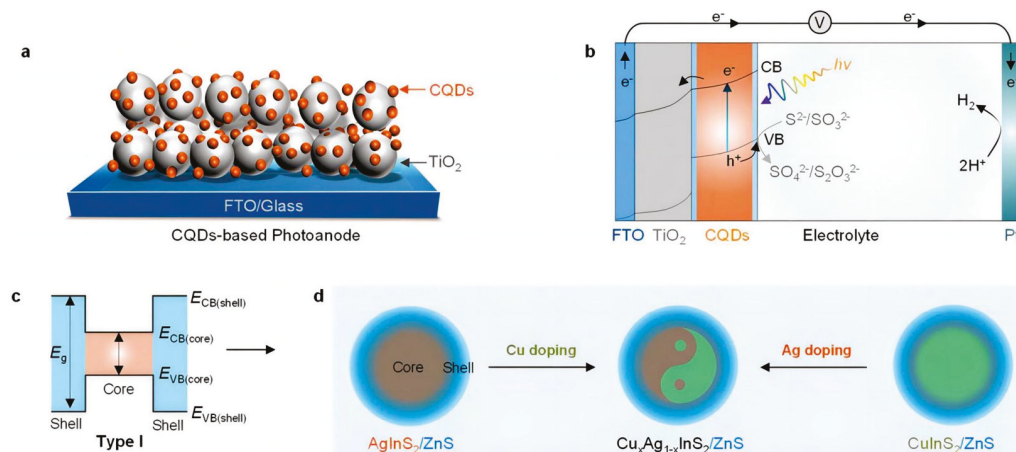


Figure 17. Manipulating the catalytic activity of photoanodes by modulating the structure of CQDs: (a) Schematic diagram for a CQD-based photoanode with a structure comprising glass | FTO | TiO₂ | CQDs. (b) Figure and predictable band alignment of a CQD-based photoanode photoelectrochemical cells. (c) The band structure of type-I CQDs. (d) Schematic illustration for band structure engineering and defect passivation of Cu-doped AgInS₂/ZnS CQDs [73] (a detailed description of type-I heterojunctions is available in Section 3.3). Reproduced with permission from Guo, H., *ACS Omega*, published by American Chemical Society, 2022.

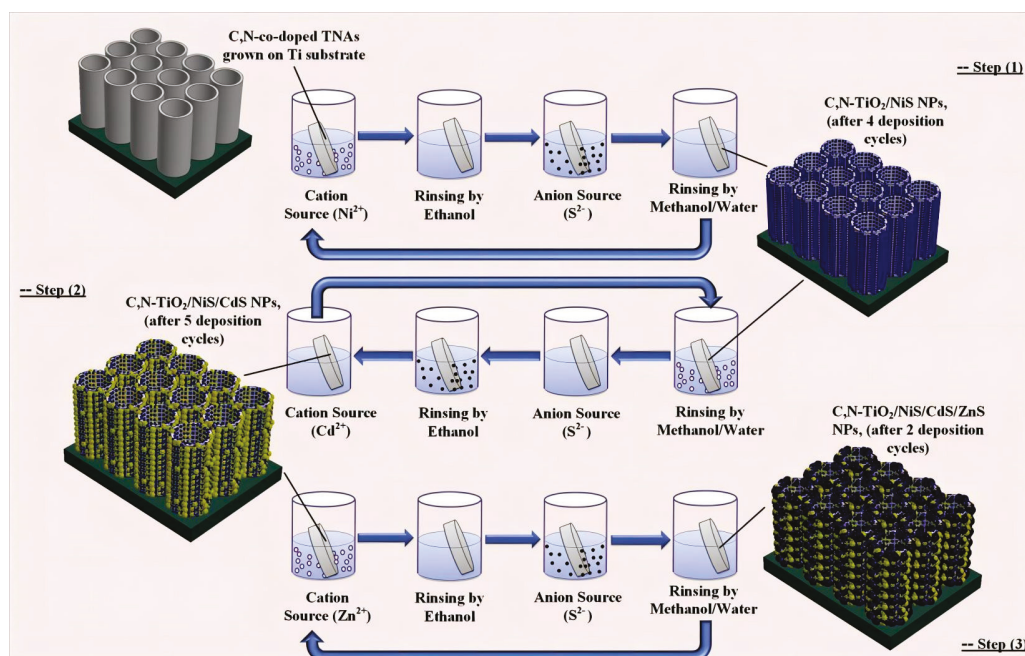


Figure 18. Schematic diagram illustrating the SILAR process for depositing NiS, CdS, and ZnS NPs on a C, N-co-doped TNA substrate [76]. Reproduced with permission from Mollavali, M., *International Journal of Hydrogen Energy*, published by Elsevier, 2018.

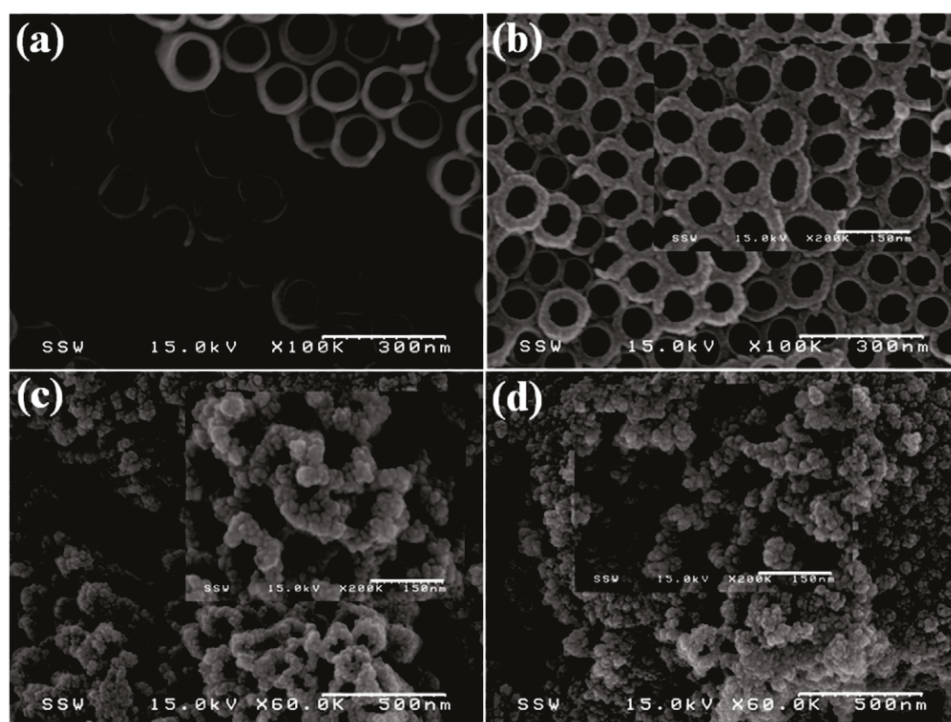


Figure 19. Top-view FE-SEM images for (a) C, N-co-doped TNAs; (b) C, N-TiO₂/NiS; (c) C, N-TiO₂/NiS/CdS; and (d) C, N-TiO₂/NiS/CdS/ZnS electrodes [76]. Reproduced with permission from Mollavali, M., *International Journal of Hydrogen Energy*, published by Elsevier, 2018.

3.3. Graphite-Phase Carbon Nitride (g-C₃N₄)

In 2009, Wang [77] first reported that g-C₃N₄ can photocatalytically decompose water into hydrogen and oxygen with a sacrificial agent under visible light. The band gap of g-C₃N₄ is 2.7 eV. Its minimum conduction band and maximum valence band are −1.1 eV and +1.6 eV, respectively, which makes it possible to decompose water completely under visible light. It can be made by calcining common raw materials such as melamine, cyanuric chloride, and urea at high temperature. The C/N ratio of g-C₃N₄ varies depending on the calcination temperature [78].

3.3.1. Doping

Wang et al. [79] found that fluorine doping into g-C₃N₄ can form a C-F bond, narrowing its band gap and increasing its optical absorption range. Wu et al. [80] reported that phosphorus (P)-doped g-C₃N₄ synthesized by a simple sintering method exhibited 1.4 μA/cm² of photocurrent at 1.2 V versus Ag/AgCl under near-IR light (>800 nm) irradiation. The introduction of P into g-C₃N₄ reduced its bandgap from 2.75 eV to 1.37 eV, in favor of a superior infrared light response. Meanwhile, the doping of P also improved the separation and transfer of photogenerated charges. In addition to non-metal doping, metal doping has also been extensively used to improve the PEC performance of g-C₃N₄. Rouby et al. [81] reported on the synthesis of an elongated g-C₃N₄ nanostructure which was fabricated by the direct pyrolysis of a supramolecular melamine precursor. The as-prepared material was used to host specific amounts of bismuth, a doping element used to adjust the band gap of the hosting matrix. XRD measurements confirmed the absence of bismuth oxide in the photoanode (Figure 20). The bandgap width was reduced due to the introduction of Bi in g-C₃N₄ (Figure 21). The 2.5% Bi-doped g-C₃N₄ photoelectrode was twice as efficient as pure g-C₃N₄ in terms of PEC water decomposition. The schematic diagram shown in Figure 22 shows the energy band structure of a typical element-doped and molecularly modified g-C₃N₄ sample.

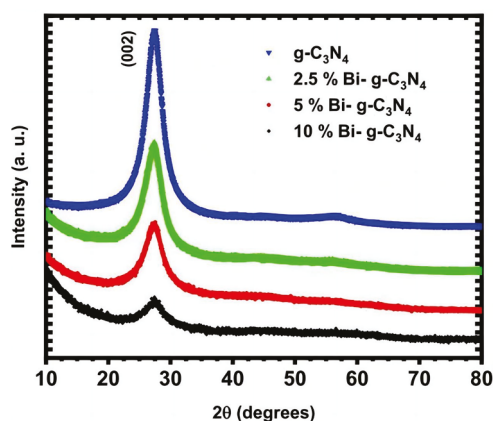


Figure 20. XRD patterns of $g\text{-C}_3\text{N}_4$ and a series of Bi-doped $g\text{-C}_3\text{N}_4$ samples [81]. Reproduced with permission from El Rouby, *Solar Energy*, published by Elsevier, 2020.

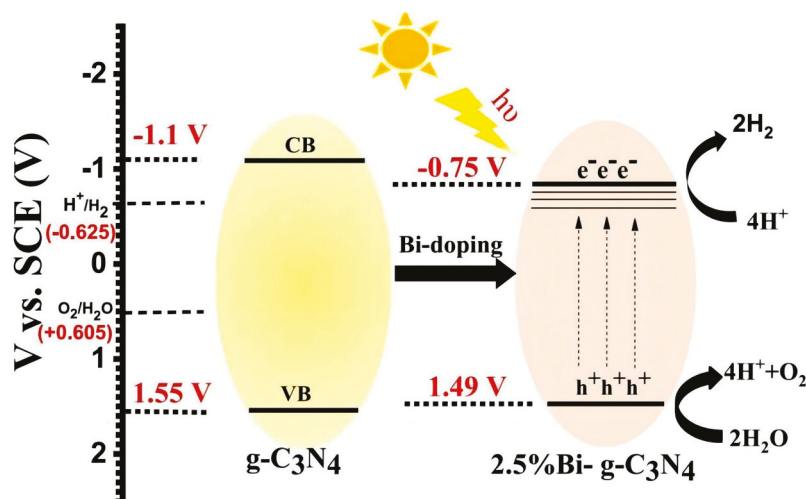


Figure 21. Schematic illustrations for the valence bands and the conduction bands of neat $g\text{-C}_3\text{N}_4$ and 2.5% Bi- $g\text{-C}_3\text{N}_4$ [81]. Reproduced with permission from El Rouby, *Solar Energy*, published by Elsevier, 2020.

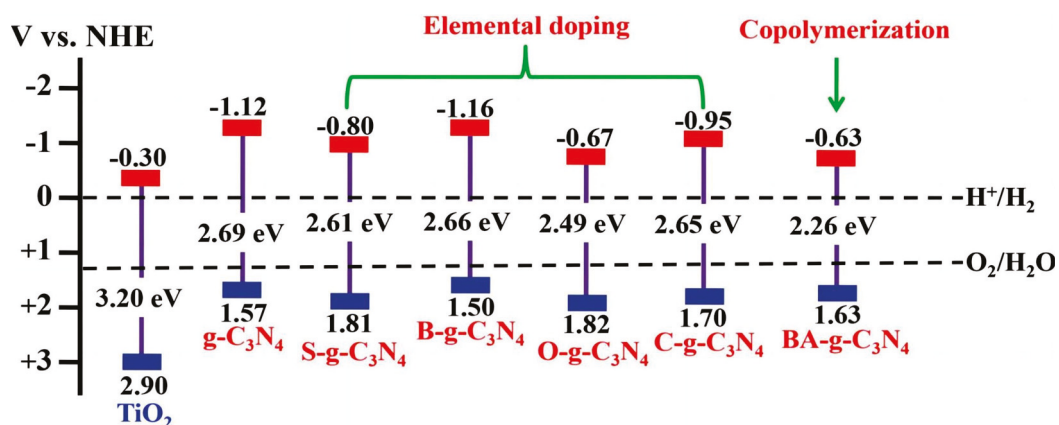


Figure 22. Schematic illustration of the band structures of typical $g\text{-C}_3\text{N}_4$ samples in comparison to TiO_2 samples: $g\text{-C}_3\text{N}_4$, S- $g\text{-C}_3\text{N}_4$, B- $g\text{-C}_3\text{N}_4$, O- $g\text{-C}_3\text{N}_4$, C- $g\text{-C}_3\text{N}_4$, and BA- $g\text{-C}_3\text{N}_4$ [82]. Reproduced with permission from Cao, S., *Advanced Materials*, published by John Wiley and Sons, 2015.

3.3.2. g-C₃N₄ Composites

Semiconductor heterojunctions can effectively promote the separation of photogenerated electron–hole pairs, thus enhancing the PEC activity of semiconductor materials. As a kind of flexible material, g-C₃N₄ is beneficial for closely compounding with other semiconductors. Available materials include metal oxides (ZnO [83,84], TiO₂ [85,86], WO₃ [87], BiIO [88], Al₂O₃ [89]), sulfides (CdS [90], MoS₂ [91]), graphene [92], activated carbon [93], and noble metal Au [94]. Velusamy et al. [88] prepared a noble metal-free nano-heterostructure of neodymium (Nd)-doped graphitic carbon nitride (g-C₃N₄) and bismuth oxyiodide (BiOI) by using a two-step thermal poly-condensation and hydrothermal method. The doping of Nd reduced the bandgap width of the photoelectrode, thereby increasing its response range to visible light. At the same time, the construction of heterojunctions can improve the transfer and suppress the recombination of photogenerated charges. The combination of the two methods improves the optical and electrical properties of the photoelectrode, leading to an enhancement in PEC performance (Figure 23).

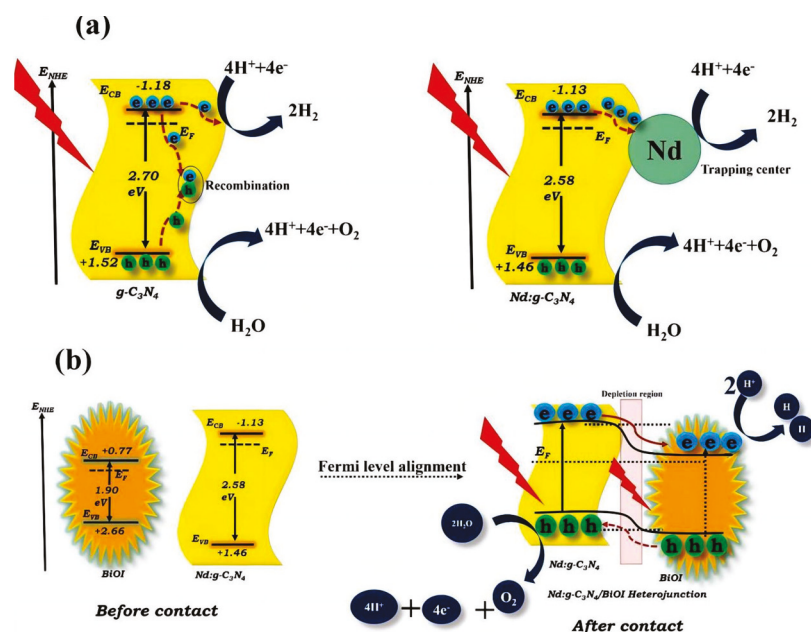


Figure 23. Schematic diagram of the PEC mechanism of (a) undoped and Nd-doped g-C₃N₄ samples and (b) a Nd-doped g-C₃N₄/BiOI heterostructure [88]. Reproduced with permission from Velusamy, P., *Applied Surface Science*, published by Elsevier, 2021.

4. Strategies to Improve the Efficiency of PEC Hydrogen Evolution

Based on the present understanding of the principle of PECs, we discussed the promising semiconductor materials and related experimental methods and means currently used in the PEC decomposition of water. PEC hydrogen evolution involves diversiform chemical and physical processes such as the preparation of a photoelectrode material, photon absorption, semiconductor excitation, and the separation and migration of electron–hole pairs. Considering these important chemical and physical processes involved in PECs, this section summarizes strategies that might be useful for improving the efficiency of PEC hydrogen production.

4.1. Morphological Control

The morphological properties of semiconductor photoelectrode materials, such as the thickness of film electrodes and the surface microstructure, have a very important influence on PEC efficiency. For example, the morphology of single-crystalline TiO₂ NTs is beneficial for directional charge transport due to their nanotube confinement effect [95]. In one study, after size-controllable g-C₃N₄ quantum dots (QDs) were synthesized in situ and grafted

onto TiO₂ NTs, the unique morphology and structure efficiently inhibited self-gathering and the leaching of g-C₃N₄ QDs, leading to excellent PEC performance [95]. The reactions of oxidation and reduction occur only when the carrier charges migrate from the inside to the surface of the semiconductor photoelectrode or counter electrode. Thus, a considerable part of the carrier charges is likely to recombine before they reach the electrode surface due to the low carrier mobility or excessive thickness of the photoelectrode film. In this case, the thinner the photoelectrode film is, the faster the carrier charges can be transferred to the surface of the photoelectrode. However, excessive reduction of the thickness of the photoelectrode film will weaken the light absorption [96,97]. Therefore, a balance regarding the light harvest and fast transfer of the carrier charges should be achieved by optimizing the thickness of the photoelectrode film [98].

It is well known that crystal surfaces play an important role in the PEC activity of photoelectrodes. Compared with a stable anatase (101) crystal surface, a metastable (001) crystal surface has more unsaturated coordination surface dangling bonds. Yang [99] was the first to successfully synthesize anatase TiO₂ micro crystals with an exposure ratio of (001) crystal plane up to 47% through the regulation of hydrofluoric acid (HF). This groundbreaking work led to an upsurge in the study of anatase (001) facet synthesis and related PEC properties. However, HF is highly corrosive. Thus, various fluorides have been used as additives to study the effect of stabilizing (001) crystal facets, including ammonium fluoride, ammonium hydrogen fluoride, sodium fluoride, or fluorine-containing surfactants [100]. BiVO₄ film photoelectrodes composed of nanoplates with highly reactive exposed facets (001) also exhibit a photocurrent density more than five times higher than that of nanorods grown along the (100) direction. Similarly, WO₃ nanomultilayers with highly exposed (002) facets (60%) exhibited much better PEC performances than WO₃ nanorods with less exposed (002) facets (20%) [31].

4.2. Doping

Doping can create defect energy levels in the bandgap of a semiconductor, thus changing its energy band structure. On one hand, the defect energy levels usually offer a narrow sub-bandgap in the semiconductor, contributing to increasing the light absorption; on the other hand, the defect energy levels can form a charge capture center and thus increase the carrier life. In addition, doping can also regulate the electrical properties of semiconductors, such as carrier concentration and carrier mobility, enhance the conductivity and carrier mobility of semiconductors, and improve the efficiency of charge separation and transfer [101–103]. Therefore an optimal amount of doping should be determined for photoelectrode materials to achieve optimal PEC performance [104].

4.3. Heterojunctions

A heterojunction is the interfacial contact region of two different semiconductors; heterojunctions are mainly divided into types I, II, and III. As shown in Figure 24a, in a type-I heterojunction, both the conduction band (CB) and the valence band (VB) of semiconductor A are included in the bandgap of semiconductor B. The photogenerated electrons transfer from CB(B) to CB(A), while the photogenerated holes transfer from VB(B) to VB(A). All photogenerated charges are accumulated in semiconductor A, probably resulting in the recombination problem of charge carriers. In a type-II heterojunction (Figure 24b), both the CB and the VB of semiconductor B are more negative than those of semiconductor A, meanwhile, the VB of semiconductor B is located in the bandgap of semiconductor A. In this case, the photogenerated electrons and holes are likely to accumulate in the CB (A) and VB(B), respectively, improving the efficiency of the separation of carrier charges, thus enhancing the PEC decomposition of water. Numerous composite photoelectrodes mentioned above employ this type-II heterojunction structure. For example, the PEC performance of TiO₂ can be significantly improved when coupled with Cu₂O [105] and ZnO [106] to form type-II heterojunctions. In a type-III heterojunction (Figure 24c), the

whole band position of semiconductor B is further offset to that of semiconductor A. Such arrangements of band positions are also called broken-gap situations.

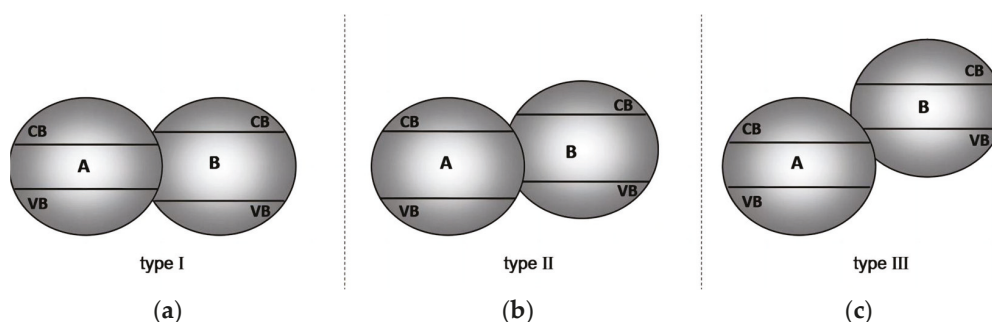


Figure 24. Different types of semiconductor heterojunctions. (a) Type-I heterojunction, (b) type-II heterojunction, (c) type-III heterojunction [107]. Reproduced with permission from Marschall, R., *Advanced Functional Materials*, published by John Wiley and Sons, 2013.

For type-II heterojunctions, despite the fact that they can effectively separate the charge, their oxidation–reduction abilities have not yet been maximized in this system. In contrast, Z-scheme heterojunctions can achieve strong oxidation–reduction abilities. As shown in Figure 25 [108], in Z-scheme heterojunctions, the photogenerated electrons in semiconductor II are inclined to combine with the photogenerated holes in semiconductor I. In this case, the photogenerated electrons and holes are likely to accumulate in the CB of semiconductor I and VB of semiconductor II, respectively. The structures of Z-scheme heterojunctions can both enhance the separation of charge carriers and retain the strong reduction and oxidation ability, thus improving the PEC performance of the photoelectrode.

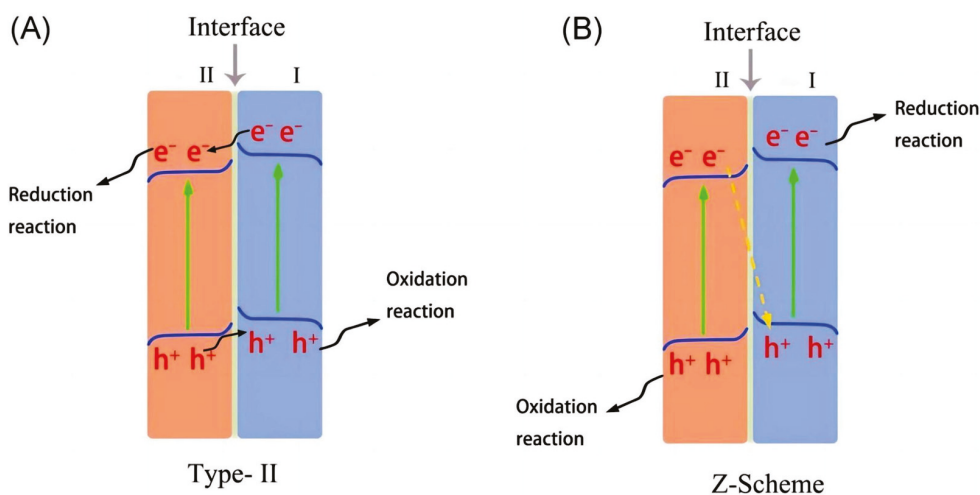


Figure 25. Schematic illustration of charge carrier transfer for (A) type-II and (B) Z-scheme heterojunctions [108]. Reproduced with permission from Li, J., *Carbon Energy*, published by John Wiley and Sons, 2022.

4.4. Surface Modification

Metals, especially noble metals (such as Pt) with large work functions (i.e., low Fermi levels) can effectively collect electrons and enjoy a low activation energy and overpotential for the hydrogen production reaction. Therefore, noble metals are often considered as suitable cocatalysts for PEC hydrogen production. Pop et al. [109] reported a “PEC Leaf” photoelectrode consisting of nano titanium dioxide particles as photocatalysts and a commercial carbon paste enriched with a small quantity of Pt NPs (0.0134 mg/cm²) as electrocatalysts. As shown in Figure 26, Pt can effectively enrich photogenerated electrons from the photoelectrode, greatly improving hydrogen production efficiency with the help

of a sacrificial agent. It is worth noting that the loading amount of Pt directly affects the PEC performance of the sample, and the excessive loading of Pt will lead to a decrease in the PEC performance of the sample [110]. In addition, the hydrogen production performance of photoelectrodes can also be affected by the particle size and shape of the noble metal cocatalyst [111].

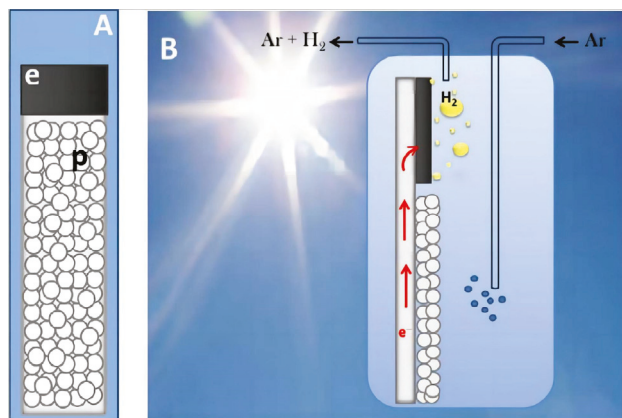


Figure 26. Illustration of a “PEC Leaf” (A) showing the area covered by the nanoparticulate photocatalyst (p), the area covered by the electrocatalyst (e), and a reactor producing hydrogen by employing a photocatalytic leaf (B) [109]. Reproduced with permission from Pop, L., *Applied Surface Science*, published by Elsevier, 2015.

However, the high cost of noble metals limits their use on a large scale. So, some transition metals and oxides have been used as low-cost substitutes, such as NiO [112] and CuO [113]. Kim et al. [114] reported a ternary hybrid solar desalination process coupled with PEC water treatment and H₂ production in a low-cost device with an oxide photoelectrode and transition sulfate cathode. The desalination of brackish water in the desalination cell is initiated via photoinduced charge generation with a thermochemically reduced TiO₂ nanorod array photoanode. As shown in Figure 27, a three-cell device was designed to achieve hydrogen production and seawater desalination. The Ni-Mo-S composite catalyst greatly promoted the generation of hydrogen at the cathode, thereby improving the seawater desalination rate of the entire device.

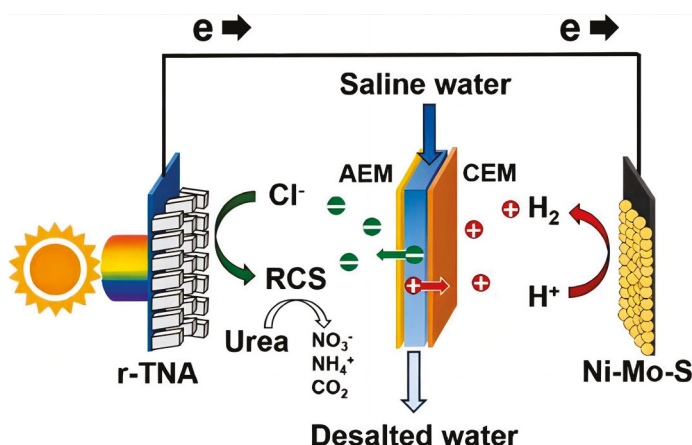


Figure 27. Illustration of a sunlight-driven ternary hybrid desalination device. The device consists of a thermochemically reduced TiO₂ nanorod array (r-TNA) photoelectrode in the anode cell, saline water in the (middle) desalination cell, and a Ni-Mo-S (Ni₂S₃/MoS₂) electrocatalyst in the cathode cell. The anode and desalination cells were separated by an anion exchange membrane (AEM), whereas the desalination cell and cathode cell were separated by a cation exchange membrane (CEM) [114]. Reproduced with permission from Kim, S., *Applied Catalysis B: Environmental*, published by Elsevier, 2021.

5. Concluding Remarks

An overview of promising semiconductor materials for efficient PEC hydrogen production has been given. The general characteristics, preparation methods, and applications of metal oxides, sulfide materials, and g-C₃N₄, as well as their modifications and composites, have been covered, as summarized in Table 1. The benefits and drawbacks of the photoelectrode materials and their corresponding remedial schemes have also been discussed. An efficient PEC photoelectrode should possess an appropriate energy band structure, wide wavelength light absorption, effective carrier separation and transport, and high stability. Doping and modification are effective approaches for improving the PEC performance of hydrogen evolution and stability of photoelectrode materials. Particularly, constructing type-II and Z-scheme heterojunctions using multiple materials is also a good way to effectively promote the separation and transport of carrier charges. We hope a comprehensive understanding of the relationship between the structures and properties of semiconductor materials will benefit the precise control of semiconductor materials as photoelectrodes and thus promote the development of PEC hydrogen production.

Table 1. A summary of promising photoelectrocatalysts with improved photoelectric performance for the hydrogen production.

Photoelectrocatalyst	Modification Strategy	Rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Incident Light (nm)	Ref.
BiVO ₄ /FTO	morphological control	150	UV-Vis	[22]
ZnO/Ag	surface modification	10	UV-Vis	[29]
W-TiO ₂ NTs	doping	24.97	UV-Vis	[36]
TiO ₂ nanotube arrays	morphological control	97	UV-Vis	[37]
Nb-TiO ₂ /g-C ₃ N ₄	doping/heterojunction	43.26	>400	[38]
Fe ³⁺ -TiO ₂	doping	12.5	>400	[41]
TiO ₂ /WO ₃ /FTO	heterojunction	210	UV-Vis	[43]
ITO/Cu ₂ O/TiO ₂	heterojunction	12.15	UV-Vis	[48]
TiO ₂ /Cu ₂ O	protective layer/Ti ³⁺	0.068	>420	[50]
N-BiVO ₄	doping	3.7	UV-Vis	[57]
Bi ₂ S ₃ /BiVO ₄	heterojunction	33.4	UV-Vis	[59]
MoS ₂ /Cu ₂ O	heterojunction	12.3	UV-Vis	[64]
TiO ₂ -1 wt% Au@TiO ₂ /Al ₂ O ₃ /Cu ₂ O	heterojunction/surface modification	147	UV-Vis	[65]
MoS ₂ /Cu-CdS	doping/heterojunction	1115	UV-Vis	[69]
CdS/ZnO	heterojunction	1008	>400	[71]
Cd _{0.5} Zn _{0.5} S	morphological control	14,440	>420	[72]
Pt/C-ZnIn ₂ S ₄	morphological control/surface modification	1032.2	>400	[74]
FTO/P-g-C ₃ N ₄	doping	1.27	>800	[80]
Nd-doped g-C ₃ N ₄ /BiOI	doping/heterojunction	288	>420	[88]
g-C ₃ N ₄ /reduction graphene oxide/nickel foam	heterojunction/morphological control	6000	>420	[92]
Pt-TiO ₂ /C	morphological control/surface modification	300	UV-enhanced light	[109]
Ni-Mo-S/reduced titania nanorods	surface modification	40	UV-Vis	[114]

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