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Review

Carbon nanomaterials for efficient oxygen and hydrogen evolution reactions in water splitting: A review

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Abstract: Water splitting has gained significant attention as a means to produce clean and sustainable hydrogen fuel through the electrochemical or photoelectrochemical decomposition of water. Efficient and cost-effective water splitting requires the development of highly active and stable catalysts for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Carbon nanomaterials, including carbon nanotubes, graphene, and carbon nanofibers, etc., have emerged as promising candidates for catalyzing these reactions due to their unique properties, such as high surface area, excellent electrical conductivity, and chemical stability. This review article provides an overview of recent advancements in the utilization of carbon nanomaterials as catalysts or catalyst supports for the OER and HER in water splitting. It discusses various strategies employed to enhance the catalytic activity and stability of carbon nanomaterials, such as surface functionalization, hybridization with other active materials, and optimization of nanostructure and morphology. The influence of carbon nanomaterial properties, such as defect density, doping, and surface chemistry, on electrochemical performance is also explored. Furthermore, the article highlights the challenges and opportunities in the field, including scalability, long-term stability, and integration of carbon nanomaterials into practical water splitting devices. Overall, carbon nanomaterials show great potential for advancing the field of water splitting and enabling the realization of efficient and sustainable hydrogen production.

Keywords: oxygen evolution reaction (OER); hydrogen evolution reaction (HER); carbon nanomaterials; surface functionalization; optimization of nanostructure and morphology

1. Introduction

Water splitting, the process of converting water into oxygen and hydrogen gases, has emerged as a promising avenue for sustainable energy production and storage. It offers a pathway to generate clean and renewable hydrogen fuel, which can be used as a versatile energy carrier. The efficient catalysis of the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) remains a critical challenge in water splitting technologies [1,2]. Catalysts used in the oxygen evolution reaction frequently experience stability problems when exposed to harsh oxidative environments, resulting in degradation and a decrease in catalytic performance over time. The oxygen evolution reaction generally necessitates a high overpotential to achieve a substantial reaction rate, diminishing overall efficiency. Many of the best catalysts for OER and HER use noble metals such as platinum, iridium, and ruthenium, which are rare and costly. This restricts their widespread use and highlights the need for affordable and abundant alternatives. Achieving high efficiency and selectivity in both OER and HER is difficult because of competing side reactions and the necessity for precise control over the reaction environment and catalyst properties [3–5]. To address this challenge, researchers have turned their attention to carbon nanomaterials, which exhibit unique structural and electronic properties that make them attractive candidates for efficient catalysis in water splitting. Carbon nanomaterials, such as carbon nanotubes, graphene, and carbon nanofibers, possess exceptional characteristics, including high surface area, excellent electrical conductivity, and chemical stability [6,7]. The high surface area of carbon nanomaterials provides a large number of active sites for catalytic reactions, facilitating the adsorption and activation of reactant molecules. This leads to increased reaction kinetics and improved catalytic efficiency. Furthermore, the excellent electrical conductivity of carbon nanomaterials enables efficient charge transfer during electrochemical reactions, reducing energy losses and enhancing overall catalytic activity [8–10].

The chemical stability of carbon nanomaterials is another advantageous attribute for water splitting. Their robust nature allows them to withstand harsh reaction conditions, such as high temperatures and corrosive environments, ensuring long-term durability and catalytic performance [11,12]. In recent years, extensive research efforts have been dedicated to exploring the catalytic properties and performance of carbon nanomaterials in water splitting. Various strategies have been employed to optimize their catalytic activity, including surface functionalization, heteroatom doping, and incorporation of other active materials. These approaches aim to enhance the catalytic efficiency, selectivity, and stability of carbon-based catalysts for both the OER and HER [13,14].

This review aims to provide an overview of the recent advancements in the utilization of carbon nanomaterials for efficient OER and HER in water splitting. It will discuss the fundamental mechanisms underlying their catalytic activity, highlight the strategies employed to enhance their performance, and address the challenges associated with their implementation in practical water splitting systems. Additionally, future research directions and opportunities for the development of carbon nanomaterial-based catalysts will be explored.

2. Importance of water splitting for sustainable energy production

Water splitting is of paramount importance for sustainable energy production because it can harness and utilize hydrogen as a clean and renewable energy source.

2.1. Hydrogen fuel

Water splitting enables the production of hydrogen gas (H_2), which can be used as a fuel in various applications. Hydrogen is a versatile energy carrier that can be used in fuel cells to generate electricity or directly combusted. Unlike fossil fuels, hydrogen combustion or utilization in fuel cells produces only water as a byproduct, making it a clean and environmentally friendly energy option [15].

2.2. Renewable energy storage

One of the significant challenges with renewable energy sources like solar and wind is their intermittent nature. Water splitting offers a way to store excess renewable energy by converting it into hydrogen [16]. The generated hydrogen can be stored and used later when energy demand exceeds supply, providing a reliable and controllable energy storage option. This helps to balance the intermittent nature of renewables and ensures a consistent energy supply.

2.3. Decarbonization

Hydrogen produced through water splitting can play a vital role in decarbonizing various sectors of the economy. When hydrogen is produced using renewable electricity, the entire process becomes carbon-neutral or even carbon-free [17]. By substituting hydrogen for fossil fuels in transportation, heating, and industrial processes, we can significantly reduce greenhouse gas emissions and mitigate climate change.

2.4. Industrial applications

Water splitting and the production of hydrogen can revolutionize various industrial processes. Hydrogen can be used as a feedstock for producing chemicals, such as ammonia and methanol, replacing fossil fuel-based methods [18]. This enables the decarbonization of industries and promotes a more sustainable and environmentally friendly manufacturing sector.

2.5. Transportation

Water splitting enables the production of hydrogen fuel for transportation applications. Hydrogen fuel cells can power vehicles, including cars, buses, trucks, and trains [19]. Hydrogen fuel cell vehicles emit only water vapor, offering a zero-emission alternative to conventional fossil fuel-powered vehicles [20]. By transitioning to hydrogen-powered transportation, we can significantly reduce air pollution and dependence on fossil fuels.

2.6. Grid flexibility

Water splitting and hydrogen production contribute to grid flexibility and stability. By utilizing excess renewable energy to produce hydrogen, we can effectively store energy and balance the electricity grid. Hydrogen can be converted back to electricity during peak demand periods, ensuring a stable power supply and enhancing the resilience of the grid [21].

3. Potential of carbon nanomaterials as catalysts or catalyst supports

Carbon nanomaterials, such as carbon nanotubes (CNTs), graphene, and carbon nanofibers, show significant potential as catalysts or catalyst supports for water-splitting reactions. Here are some key reasons for their attractiveness in this field:

3.1. High surface area

Carbon nanomaterials possess a large surface area per unit mass or volume. This high surface area provides abundant active sites for catalytic reactions, allowing for efficient utilization of the catalyst and enhancing reaction rates [22,23].

3.2. Chemical stability

Carbon nanomaterials exhibit excellent chemical stability, which is crucial for withstanding the harsh conditions of water-splitting reactions. They are resistant to corrosion and degradation, ensuring long-term catalytic activity and durability [24,25].

3.3. Electrical conductivity

Several carbon nanomaterials, such as CNTs and graphene, exhibit excellent electrical conductivity. This property enables efficient charge transfer during electrochemical reactions, minimizing energy losses and improving overall catalytic performance [26,27].

3.4. Tailorable properties

Carbon nanomaterials offer versatility in terms of their structural and surface properties. Their morphology, surface chemistry, and functionalization can be tailored to optimize catalytic activity, selectivity, and stability for specific water-splitting reactions [28,29].

3.5. Catalyst support

Carbon nanomaterials can serve as excellent supports for other catalyst materials, such as metal nanoparticles or metal oxides. The high surface area and unique structural features of carbon nanomaterials facilitate the dispersion and stabilization of active catalyst particles, enhancing their catalytic performance [30,31]. **Figure 1** demonstrates the use of graphene sheets as catalyst supports.

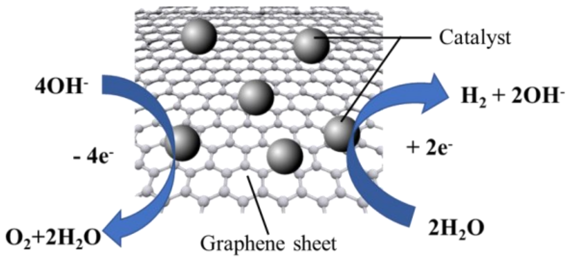

Figure 1. Graphene as catalyst support.

3.6. Abundance and low cost

Carbon is an abundant and relatively low-cost element. Carbon nanomaterials can be synthesized from various carbon sources, making them economically favorable for large-scale production and implementation in water splitting technologies [32,33].

3.7. Synergistic effects

Carbon nanomaterials can exhibit synergistic effects when combined with other catalyst materials. For example, the integration of carbon nanomaterials with transition metal-based catalysts can lead to enhanced catalytic activity and stability through synergistic interactions and improved electron transfer pathways [34,35].

While carbon nanomaterials hold great potential, challenges still exist. These include further enhancing catalytic activity, improving mass transport limitations, minimizing side reactions, and addressing potential issues such as catalyst poisoning or surface fouling. Continued research and development efforts are focused on optimizing carbon nanomaterials and harnessing their full potential as catalysts or catalyst supports for water splitting, contributing to the advancement of sustainable energy production.

4. Carbon nanomaterials for OER and HER

Carbon nanomaterials have shown great potential as catalysts for both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), which are essential processes in water splitting for hydrogen production and in various energy conversion and storage technologies. **Figure 2** depicts a range of carbon nanomaterials. Here's an overview of the potential of carbon nanomaterials for HER and OER:

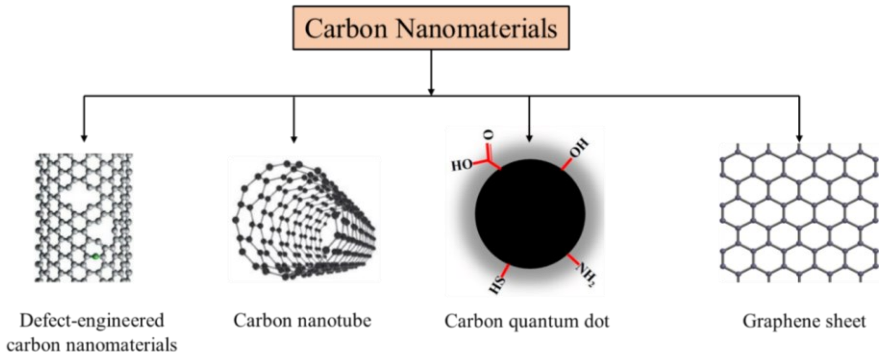

Figure 2. Various types of carbon nanomaterials.

4.1. Carbon nanotubes (CNTs)

CNTs possess high electrical conductivity, a large surface area, and unique tubular structures, making them attractive catalysts for both HER and OER. Their conductivity facilitates efficient charge transfer during the electrochemical reactions, while their high surface area provides abundant active sites. Functionalization of CNTs with metal nanoparticles or heteroatoms can further enhance their catalytic activity for both HER and OER [36–39].

4.2. Graphene

Graphene, a two-dimensional carbon material, exhibits excellent electrical conductivity and a large surface area, making it a promising catalyst for HER and OER. Pristine graphene itself has limited intrinsic activity. Strategies such as functionalization, doping, or hybridization with other materials have been explored to enhance its catalytic performance for both reactions [40,41].

4.3. Carbon nitride (C_3N_4)

Carbon nitride-based materials, such as graphitic carbon nitride (g-C_3N_4), have emerged as metal-free catalysts for both HER and OER. The structure of graphitic carbon nitride is demonstrated in **Figure 3**. These materials are abundant, low-cost, and environmentally friendly. Their unique electronic structure enables efficient charge transfer and catalytic activity during both reactions. Further modifications and optimization are required to improve their intrinsic activity and stability [42,43]. Modifications may include tailoring the shape and surface characteristics of g-C_3N_4, doping with other elements, or forming composites with other materials. These changes are intended to improve light absorption characteristics, expand the number of active sites accessible for catalytic reactions, and strengthen the material's overall resilience to operating conditions [44,45].

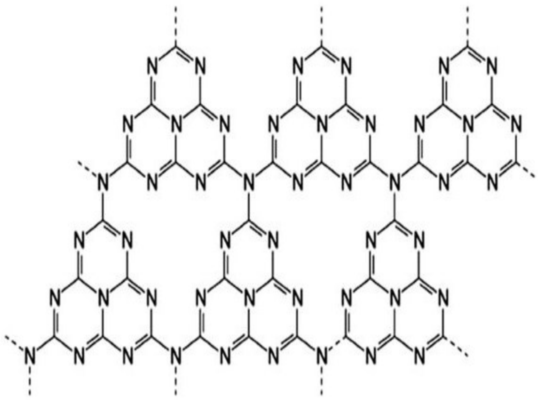

Figure 3. Structure of graphitic carbon nitride (g-C_3N_4).

4.4. Carbon quantum dots (CQDs)

Carbon quantum dots, small carbon nanoparticles, have shown promise as catalysts for both HER and OER. Their unique quantum confinement effects and tunable surface properties enable efficient charge transfer and catalytic activity. Surface functionalization or doping of CQDs with heteroatoms or metal species can further enhance their performance for both reactions [46–48].

4.5. Defect-engineered carbon materials

Introducing defects or heteroatoms into carbon nanomaterials can significantly influence their electronic structure and surface reactivity, enhancing their catalytic activity for both HER and OER. Defect engineering provides additional active sites and improves charge transfer kinetics. Tailoring the defect density and distribution can optimize the performance of carbon nanomaterials for both reactions [49,50].

While carbon nanomaterials hold promise for HER and OER catalysis, challenges remain in enhancing their intrinsic activity, stability, and mass transport properties. Additionally, understanding the underlying mechanisms and optimizing the catalyst design are ongoing research areas. Nonetheless, carbon nanomaterials offer exciting opportunities to advance HER and OER catalysis and enable efficient and sustainable energy conversion and storage technologies [51].

5. Carbon nanomaterial hybridization with other materials for enhanced catalysis

Hybridization of carbon nanomaterials with other materials has been extensively explored to enhance water splitting catalysis, particularly in the context of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Here are some examples of carbon nanomaterials hybridized with other materials for enhanced water splitting catalysis.

5.1. Carbon nanotubes (CNTs) and metal nanoparticles

CNTs can be hybridized with metal nanoparticles, such as platinum (Pt), palladium (Pd), or nickel (Ni), to form composite catalysts. Metal nanoparticles may be applied to the surface of carbon nanotubes (CNTs) to create a composite material, as seen in **Figure 4**. The metal nanoparticles provide high catalytic activity, while the CNTs act as conductive supports, facilitating electron transfer during the reactions. The hybridization enhances the overall catalytic performance and stability [52,53].

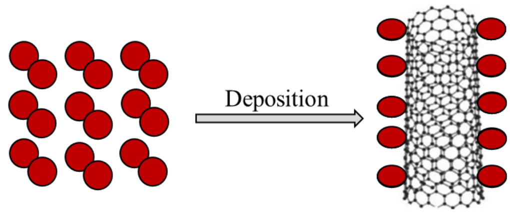

Figure 4. Deposition of metal nanoparticles on carbon nanotube.

5.2. Graphene and metal oxides

Graphene can be combined with metal oxides, such as titanium dioxide (TiO_2), iron oxide (Fe_2O_3), or cobalt oxide (Co_3O_4), to form composite catalysts. The metal oxides provide high catalytic activity, while graphene offers excellent electrical conductivity and large surface area. The hybrid structure promotes efficient charge transfer and provides additional active sites, enhancing the water splitting catalysis [54–56].

5.3. Carbon nitride (C_3N_4) and transition metal compounds

Carbon nitride-based materials, such as graphitic carbon nitride (g-C_3N_4), can be hybridized with transition metal compounds, including metal oxides or sulfides, to form composite catalysts. The transition metal compounds provide catalytic activity, while carbon nitride offers a stable and conductive support. The hybridization promotes synergistic effects, leading to enhanced water splitting catalysis [57–60].

5.4. Carbon quantum dots (CQDs) and semiconductor nanomaterials

Carbon quantum dots can be combined with semiconductor nanomaterials, such as metal chalcogenides (e.g., MoS_2, WS_2) or metal oxides (e.g., ZnO, WO_3), to form hybrid catalysts. The semiconductor nanomaterials provide light absorption and charge separation capabilities, while carbon quantum dots contribute to improved charge transfer and catalytic activity. The hybridization enables efficient utilization of solar energy for water splitting [61–65].

5.5. Carbon-based heterostructures

Carbon nanomaterials, such as CNTs or graphene, can be integrated with other functional materials, such as metal nanoparticles, metal oxides, or semiconductor nanomaterials, to form complex heterostructures. The combination of different materials in the heterostructures allows for synergistic effects, enhanced catalytic activity, and improved charge transfer kinetics [66–68].

Hybridization strategies enable the integration of the unique properties of carbon nanomaterials with those of other materials, leading to enhanced water splitting catalysis. The resulting hybrid catalysts can exhibit improved activity, stability, and efficiency, which are crucial for advancing water splitting technologies for sustainable hydrogen production and energy storage.

6. Challenges and future perspectives

Carbon nanomaterials have shown great potential for water splitting applications, but there are several challenges that need to be addressed for their effective implementation. Additionally, there are several future perspectives that can drive further advancements in this field. Here are the challenges and future perspectives of carbon nanomaterials in water splitting:

6.1. Challenges

Catalyzing the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) is crucial for efficient water splitting and sustainable energy production. Several challenges exist in developing effective catalysts for these reactions. Both OER and HER are kinetically sluggish processes, meaning that the reaction rates are relatively slow. This limits the overall efficiency and scalability of water splitting systems [69,70]. Catalysts need to accelerate the reaction rates and improve the kinetics to enhance the performance of the reactions. These reactions typically require a significant overpotential, which is the additional energy input needed to drive the reactions. High overpotentials result in increased energy losses and reduced overall efficiency [71–73]. Developing catalysts that can minimize the overpotential required for these reactions is a major challenge. Catalysts for OER and HER must be stable and durable under the harsh conditions of water splitting, including high temperatures, corrosive electrolytes, and repeated cycling. Many catalyst materials suffer from degradation, corrosion, particle detachment, or surface restructuring over time, leading to reduced activity and performance. An illustration of carbon corrosion and particle detachment is shown in **Figure 5**. Developing catalysts with high stability and durability is crucial for long-term and practical applications. The widespread adoption of water splitting technologies depends on the availability and affordability of catalyst materials. Some catalysts, such as those based on precious metals like platinum [74,75] and iridium [76,77], are expensive and scarce, limiting their large-scale deployment.

Developing catalysts based on Earth-abundant elements or low-cost materials is important for making water splitting economically viable.

Efficient water splitting systems require the integration of OER and HER catalysts with other components, such as electrodes, membranes, and electrolytes. Achieving optimal compatibility and synergy among these components is challenging. Catalyst designs that can facilitate effective coupling with other system components are crucial for maximizing overall performance. Achieving high selectivity for either OER or HER is desirable to minimize energy losses and maximize overall water splitting efficiency. Catalysts may exhibit side reactions or undesired reactions, leading to reduced selectivity. Developing catalysts that can selectively promote either OER or HER without significant crossover or side reactions is a challenge. For practical implementation, catalysts need to be scalable, meaning they should be easily synthesized, fabricated, and deployed at a large scale. Some catalyst materials may face limitations in terms of scalability due to complex synthesis methods or high-cost fabrication techniques. Developing scalable catalyst synthesis and manufacturing processes is important for commercialization.

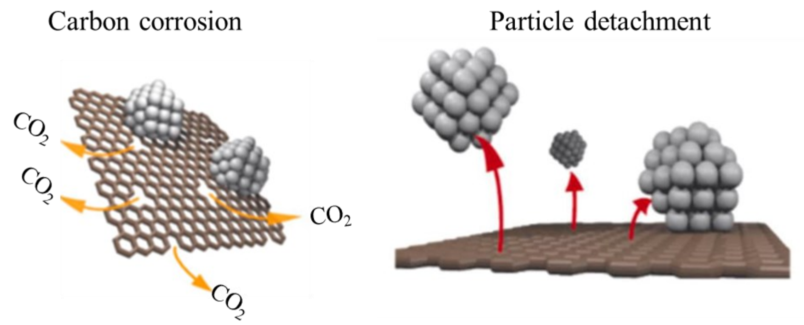

Figure 5. The reduction of catalyst activity through carbon corrosion and particle detachment.

Thus, addressing these challenges requires a multidisciplinary approach involving materials science, electrochemistry, catalysis, and engineering. Researchers are actively exploring new catalyst materials, nanostructured architectures, surface modifications, and advanced characterization techniques to overcome these hurdles and develop efficient and stable catalysts for OER and HER in water splitting systems. The key points are presented in the forthcoming paragraphs.

6.1.1. Limited catalytic activity

Carbon nanomaterials, such as carbon nanotubes and graphene, often exhibit limited intrinsic catalytic activity for water splitting reactions. Enhancing their catalytic performance is crucial for achieving efficient water splitting. Future research should focus on developing strategies to improve the catalytic activity of carbon nanomaterials through doping, functionalization, and structural modifications.

6.1.2. Stability and durability

Carbon nanomaterials can suffer from degradation and oxidation under harsh water splitting conditions, leading to reduced stability and durability. Improving the stability and durability of carbon nanomaterials is essential for long-term performance.

Future research should investigate protective coatings, surface modifications, and composite structures to enhance the stability and durability of carbon nanomaterials.

6.1.3. Mass transport limitations

Carbon nanomaterials often possess high surface area but limited porosity, which can hinder the mass transport of reactants to the catalytic sites. Improving mass transport is crucial for efficient water splitting. Future research should focus on optimizing the porous structure and surface morphology of carbon nanomaterials to enhance reactant diffusion and accessibility to active sites.

6.1.4. Cost and scalability

The cost-effective synthesis and large-scale production of carbon nanomaterials remain a challenge. Many carbon nanomaterials are still produced through complex and expensive methods. Future research should explore scalable synthesis routes and cost-effective fabrication techniques to enable the widespread implementation of carbon nanomaterials in water splitting technologies.

Integration with Other Components: Carbon nanomaterials often need to be integrated with other components, such as electrodes and membranes, in water splitting systems. Achieving effective integration and compatibility between carbon nanomaterials and other components is crucial for overall system performance. Future research should focus on developing suitable interfaces and interfacial engineering strategies to enable efficient integration of carbon nanomaterials with other functional components.

6.2. Future perspectives

6.2.1. Advanced catalyst design

Future research should focus on the rational design of carbon nanomaterial-based catalysts. This includes tailoring the morphology, structure, and composition of carbon nanomaterials to optimize their catalytic activity. Additionally, exploring novel carbon nanomaterials and hybrid systems can lead to breakthroughs in water splitting catalysis.

6.2.2. Synergistic hybrid materials

The combination of carbon nanomaterials with other functional materials, such as metal nanoparticles or metal oxides, can create synergistic effects and enhance water splitting performance. Future research should explore the development of hybrid materials that leverage the unique properties of carbon nanomaterials and other materials to achieve improved catalytic activity and stability.

6.2.3. Electrocatalysis and photocatalysis

Carbon nanomaterials can be employed in both electrocatalytic and photocatalytic water splitting systems. Future research should investigate the fundamental mechanisms and optimize the parameters for efficient electrocatalysis and photocatalysis using carbon nanomaterials. This includes exploring new carbon nanomaterial-based electrode architectures and tuning their band structures for enhanced performance.

6.2.4. Integration with renewable energy sources

Carbon nanomaterials can be integrated with renewable energy sources, such as solar energy or wind energy, to achieve sustainable and clean water splitting. Future research should explore the synergistic integration of carbon nanomaterials with renewable energy systems to develop efficient and environmentally friendly water splitting technologies.

6.2.5. Environmental impact assessment

As with any nanomaterial, it is essential to consider the potential environmental impact of carbon nanomaterials. Future research should focus on comprehensive environmental impact assessments to ensure the safe and sustainable implementation of carbon nanomaterials in water splitting technologies.

Addressing these challenges and exploring the future perspectives will drive the advancement of carbon nanomaterials in water splitting, enabling the development of efficient and sustainable hydrogen production systems. Continued research, collaboration, and innovation are crucial for realizing the full potential of carbon nanomaterials in this field.

7. Conclusion

In conclusion, carbon nanomaterials have emerged as promising catalysts for efficient oxygen and hydrogen evolution reactions in water splitting. They offer several advantages, including high surface area, tunable properties, and chemical stability. There are still challenges that need to be addressed to fully exploit their potential. Enhancing the catalytic activity and stability of carbon nanomaterials is a key focus for future research. Strategies such as doping, functionalization, and structural modifications can be employed to improve their intrinsic activity and durability. Additionally, optimizing the porous structure and surface morphology of carbon nanomaterials can enhance mass transport and reaction kinetics. The scalability and cost-effectiveness of carbon nanomaterials also require attention. Developing scalable synthesis methods and cost-effective fabrication techniques is essential for their large-scale production and practical implementation in water splitting technologies. Future perspectives include advanced catalyst design, exploring synergistic hybrid materials, and leveraging carbon nanomaterials in electrocatalytic and photocatalytic systems. The integration of carbon nanomaterials with renewable energy sources holds promise for sustainable water splitting. Additionally, comprehensive environmental impact assessments are crucial to ensuring the safe and responsible use of carbon nanomaterials. Overall, with continued research, innovation, and interdisciplinary collaborations, carbon nanomaterials have the potential to play a significant role in achieving efficient and sustainable water splitting, contributing to the development of clean energy systems, and addressing global energy challenges.

Conflict of interest: The authors declare no conflict of interest.

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