High-Entropy Alloy Nanocatalysts for Efficient Water Splitting

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Abstract. High-entropy alloy (HEA) nanocatalysts have garnered increasing attention as a cutting-edge solution to the challenges of sustainable hydrogen production via water splitting, offering significant improvements over traditional catalysts. These advanced nanocatalysts, composed of five or more principal elements, exhibit exceptional catalytic activity, superior thermal and electrochemical stability, and notably reduced overpotential for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). This review delves into the synthesis methodologies of HEA nanocatalysts, including their structural and electrochemical characterization, while highlighting their superior performance in water electrolysis for green hydrogen production. We also evaluate the scalability, cost-effectiveness, and environmental impact of these nanocatalysts, comparing them to conventional systems. Furthermore, the review discusses the key challenges and emerging research directions, such as optimizing elemental composition and surface properties to enhance catalytic efficiency and address commercialization barriers. Through this comprehensive analysis, we aim to provide insights into the future potential of HEA nanocatalysts in promoting sustainable energy solutions.

Keywords: high-entropy alloy; hydrogen evolution reaction; oxygen evolution reaction; water splitting; hydrogen production.

1. Introduction

With global warming and environmental degradation becoming pressing issues, the term “low carbon” has gained significant traction worldwide. This concept emphasizes the need to reduce carbon emissions and transition to energy sources that have minimal environmental impact. As the global demand for clean energy surges, the search for sustainable alternatives has become a critical focus. Hydrogen, the most abundant substance in the universe, has emerged as a promising candidate for meeting the growing need for renewable energy due to its high energy density, versatility, and zero-emission potential [1]. When used as a fuel, hydrogen can produce energy with water as its only byproduct, making it an ideal solution for a low-carbon lifestyle. However, despite its numerous advantages, the full-scale adoption of hydrogen energy is hindered by the inefficiencies and high costs associated with its production, particularly through water hydrolysis. One of the primary challenges in harnessing hydrogen’s potential is the reliance on hydrolysis technologies that require expensive catalysts, such as platinum, which have limited availability. Platinum and other precious metals are typically used in water electrolysis because of their excellent catalytic properties, but their high cost and scarcity make large-scale production of hydrogen economically unfeasible. This limitation necessitates the development of alternative catalyst materials that are not only cost-effective but also scalable to meet global energy demands.

In this context, high-entropy alloy (HEA) nanomaterials have recently emerged as a promising solution in the field of catalysis. High-entropy alloys are composed of five or more principal elements, creating a complex matrix with unique structural properties. This multi-element composition imparts HEA nanomaterials with several advantages over traditional catalysts, such as low overpotential, high thermal stability, and fast reaction kinetics. These properties make HEAs highly effective in promoting the hydrogen evolution reaction (HER) during water electrolysis, thereby enhancing the overall efficiency of hydrogen production. Moreover, HEA nanomaterials exhibit excellent resistance to corrosion and degradation, which ensures long-term stability and durability under operational conditions. Compared to conventional industrial catalysts characterized by high costs, high energy consumption, and low efficiency, HEA nanocatalysts offer tunable properties and improved catalytic performance. The versatility in their composition allows for precise control over their catalytic activity, making them ideal for a wide range of hydrolysis applications. For instance, by varying the elemental ratios and combinations, researchers can optimize the electronic structure and surface characteristics of HEA catalysts to achieve superior performance in specific reactions.

This review aims to delve into the mechanisms, applications, and future directions of HEA nanocatalysts for sustainable hydrogen production. By examining recent advances in this field, this paper seeks to elucidate how HEA nanocatalysts can overcome current limitations in water electrolysis and pave the way for efficient and cost-effective hydrogen production. This review will also highlight potential innovations and strategies to further improve the catalytic properties of HEA materials, ultimately contributing to the development of sustainable energy solutions. As the world continues to transition toward a low-carbon future, HEA nanomaterials hold great promise for revolutionizing hydrogen production and supporting the widespread adoption of clean energy technologies.

2. Fundamental Mechanisms of Water Splitting

Hydropyrolysis is the chemical decomposition of water into oxygen and hydrogen, also known as the HER and oxygen evolution reaction (OER). Each of these reactions has different mechanistic pathways and catalytic requirements, so efficient catalysts for HER and OER must be developed to optimize the overall hydrolysis process. HEA nanocatalysts with unique multi-element structures have emerged as promising materials for improving the efficiency and durability of these reactions.

2.1. HER

The HER is a cathodic half-reaction of water decomposition in which protons are reduced to form hydrogen gas. The reaction typically occurs through a multi-step mechanism involving proton adsorption onto the catalyst surface followed by electron transfer and subsequent desorption of hydrogen molecules. One of the main challenges in hydrogen precipitation reactions is overcoming the reaction overpotential, i.e., the excess energy required to drive the reaction beyond its thermodynamic equilibrium potential. Catalysts play a crucial role in reducing this overpotential by providing active sites that promote efficient proton adsorption and electron transfer.

Conventional HER catalysts, such as platinum-based materials, are known for their high catalytic activity and low overpotential due to their optimal hydrogen binding energy. However, their high cost and limited availability restrict their widespread use. This has driven research toward developing alternative catalysts, such as transition metal-based materials and HEA nanocatalysts. HEAs, composed of multiple metal elements, exhibit unique physicochemical properties that make them promising candidates for HER. The high configurational entropy in HEAs leads to stable solid-solution phases, resulting in enhanced catalytic performance and durability under a variety of reaction conditions [1]. For example, HEAs such as CoNiCuRuPd have shown superior stability and low overpotential during HER due to their synergistic multi-element interactions, which enhance hydrogen bonding and electron transfer [1].

Additionally, single-atom catalysts, such as Pt anchored on Ni nanoparticles, have been reported to achieve ultrahigh mass activity for HER. This is attributed to the dual-active-site catalytic mechanism, where coordinated Ni atoms trigger water dissociation, and the split hydrogen atoms migrate toward the central Pt sites for hydrogen release [2]. These findings highlight the potential of HEA and alloy-based catalysts to achieve high efficiency and durability, making them competitive alternatives to traditional platinum-based catalysts in HER applications.

2.2. OER

The OER is a complex anodic reaction that involves multiple proton and electron transfer steps, making it a kinetically sluggish process that typically requires a high overpotential. The challenge in developing efficient OER catalysts lies in reducing this overpotential while maintaining high stability under the harsh acidic or alkaline conditions typically used in water-splitting systems. Current state-of-the-art OER catalysts, such as Iridium (Ir)-based binary and ternary alloys, show excellent activity in acidic solutions but are limited by high cost and low abundance.

To address this, researchers have developed nanoporous high-entropy alloys (np-HEAs) with reduced Ir content, which maintain or even enhance catalytic activity and durability. For example, an AlNiCoIrMo np-HEA with only 20 at% Ir demonstrated record-high OER activity due to its tunable electronic properties and increased structural stability [3]. The ability to incorporate multiple elements into a single phase allows for fine-tuning of the catalyst's surface properties, making np-HEAs a promising platform for optimizing OER performance with lower noble metal content.

2.3. Role of HEA Nanocatalysts in HER and OER

HEA nanocatalysts have emerged as highly effective materials for both HER and OER due to their unique multi-element structures, which provide numerous active sites and synergistic effects that enhance catalytic performance. The high configurational entropy in HEAs leads to stable solid-solution phases, which contribute to their excellent structural and chemical stability during water-splitting reactions. Moreover, the ability to finely tune the elemental composition of HEAs enables researchers to optimize the binding energy of reaction intermediates, improving the catalytic efficiency for both HER and OER.

For HER, HEA nanocatalysts can reduce overpotential by modulating the electronic properties of the active sites, leading to efficient proton adsorption and hydrogen desorption. For OER, HEA nanocatalysts facilitate the formation of favorable oxygen-containing intermediates, thereby lowering the energy barrier for oxygen production. Additionally, the enhanced corrosion resistance of HEAs ensures long-term durability under both acidic and alkaline conditions, making them versatile catalysts for a wide range of electrochemical environments.

Overall, the multi-element nature of HEA nanocatalysts offers a transformative approach to overcoming the limitations of traditional catalysts in water splitting. Their tunable properties, stability, and enhanced catalytic performance make them a compelling candidate for next-generation water-splitting technologies, paving the way for efficient and sustainable hydrogen production.

3. Synthesis and Characterization of HEA Nanocatalysts

3.1. HEA Synthesis Methods

HEA nanocatalysts were synthesized using various techniques to achieve precise control over their composition, morphology and particle size. Common synthesis methods include:

Carbon Thermal Shock (CTS) method: the CTS method has attracted much attention due to its ability to generate finely controlled poly alloyed nanoparticles (NPs). The CTS method employs rapid heating and cooling of precursor-containing samples on conductive carbon carriers to produce HEA nanoparticles with a narrow and uniformly dispersed size distribution. The CTS method has been used to synthesize HEA nanoparticles from Pt, Pt, and Pb. The method has been successfully used to alloy various elements such as Pt, Pd, Ni, Co, Fe, Au, Cu and Sn into single-phase solid solutions [4].

Solvothermal Synthesis: The solvothermal method allows for the synthesis of HEA nanocatalysts by tuning reaction parameters like temperature, reaction time, and solvent properties. This approach is effective in producing bimetallic and multi-metallic HEA nanoparticles with well-defined phases and stability under high temperatures. Phases and stability under high temperatures [4]. The choice of the metal precursor has a great influence on the synthesis process, with different pre-nucleation structures leading to different reaction pathways. The interaction of the metal with the coordination compounds affects the co-precipitation process, which is crucial for the formation of alloys.

Mechanical Alloying: Mechanical ball milling is used to alloy multiple metal powders under high-energy collisions to form HEA nanoparticles. Conventional mechanical ball milling is limited by the need for longer grinding times and the tendency to contamination. A unique method was developed by casting and cryogenic milling, which resulted in the formation of nanostructured HEAs with a narrow distribution of 6 nm, as it reduced the milling time and suppressed contamination from the atmosphere and milling tools. In addition, cryogenic ball milling utilizes liquid nitrogen and very low temperatures to accelerate the fracture process, which contributes to the formation of nanostructures and early grain refinement [4].

3.2. Structural and Compositional Characterization

Structural and compositional characterization of HEA nanocatalysts is essential to understand their catalytic behavior. Techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are commonly used to analyze crystal structure, particle size and elemental distribution. Atomic-scale characterization, including high-angle annular dark field (HAADF) imaging and energy dispersive X-ray spectroscopy (EDS), provides detailed information on the distribution of constituent elements and phase purity of HEA nanocatalysts. Together, these techniques provide a comprehensive understanding of the physical and chemical properties of HEA, which is essential for optimizing its performance in catalytic applications.

4. Applications of HEA Nanocatalysts in Water Splitting

High entropy alloy nanocatalysts have attracted a great deal of attention in the field of water decomposition due to their unique properties, including high catalytic activity, stability and tunable electronic structure. These properties make HEA ideal for improving the efficiency of HER and OER processes and for facilitating the decomposition of more challenging waters such as seawater. In addition, HEA has the potential to be integrated into future energy storage and conversion systems, such as hydrogen fuel cells, thus contributing to the development of sustainable energy technologies.

4.1. Structural and Compositional Characterization

HEA nanocatalysts are being used as cathode and anode materials for HERs due to their synergistic catalytic activity and stability under harsh electrochemical conditions. The use of HEA as HER cathodes offers several advantages over conventional metal catalysts, including enhanced reaction kinetics and excellent corrosion resistance. The unique composition and microstructure of HEA, as well as the high entropy effect of polymetallic, effectively reduces the reaction energy barriers to the catalytic process and the amount of precious metals used, which improves the activity of the catalysts and reduces the cost at the same time. These advantages stem from the multi-elemental composition of HEA, which allows one to tailor its electronic structure and adsorption properties for optimal hydrogen adsorption/desorption behavior. For example, HEAs such as CoFeNiMo and PdPtRuRhIr exhibit high activity and low HER overpotentials due to the strong binding energy of hydrogen intermediates on the alloy surface.

Similarly, HEA nanocatalysts are effective anode materials for OER. The multi-elemental nature of HEA facilitates the generation of various oxidation states during the OER process, leading to improved charge transfer and catalytic performance. A theoretical strategy for optimizing IrPdPtRhRu HEA for ORR was first developed by applying regression modeling by Batchelor and co-workers. Löffle et al. further demonstrated that CrMnFeCoNiNb and CrMnFeCoNiMo HEA can be considered promising candidates for ORR [5]. In addition, the high conformational entropy of HEA improves the resistance to oxidation and structural degradation, which are key factors for the long-term stability of OER catalysts. It has been shown that HEAs such as (NiFeCrCoMn)Ox and (CoNiFeCuZn)Ox can achieve low overpotentials and high stability, making them suitable candidates for anodic OER applications.

4.2. Seawater Decomposition

The use of HEA nanocatalysts in seawater decomposition provides a viable solution for the production of hydrogen from abundant natural resources. Seawater contains various impurities, including chloride ions, which cause electrode corrosion and the formation of undesirable by-products (e.g., chlorine gas) during water electrolysis by constructing FeO nanostructures with different sizes and highly regular structures on the surface of Pt(111) and investigating the kinetics of its deep oxidation. Bao's team found that FeO nanoparticles with diameters of less than 3 nm exhibit better antioxidant capabilities [6]. The HEA nanocatalysts proved to be highly resistant to corrosion and impurities, which could alleviate these problems. The tunable surface chemistry of HEA enables selective catalysis, which inhibits competing reactions such as chlorine release and improves the overall efficiency of seawater decomposition.

For example, HEAs such as FeCoNiCuZn have shown promising results in seawater electrolysis, where they exhibit high catalytic activity toward HER and OER while providing excellent resistance to chloride-induced degradation. This stability in harsh environments makes HEAs suitable for practical seawater decomposition applications, paving the way for large-scale hydrogen production in marine environments.

4.3. Integration into Energy Storage and Conversion Systems

The incorporation of HEA nanocatalysts into energy storage and conversion systems, such as hydrogen fuel cells, represents a transformative approach to achieving sustainable energy solutions. HEAs can serve as efficient electrocatalysts in proton-exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs) due to their high activity and durability under operational conditions. The ability to design HEAs with specific compositions allows for the optimization of catalytic properties, such as oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) activities, which are critical for fuel cell performance.

Moreover, HEA nanocatalysts can be integrated into hybrid systems that couple water splitting with energy storage devices, such as batteries and supercapacitors. In these configurations, HEAs can facilitate the conversion of electrical energy into chemical energy in the form of hydrogen, which can then be stored and reconverted to electricity as needed. This integration offers a pathway to overcome the intermittency issues associated with renewable energy sources like wind and solar, thus providing a more reliable and efficient energy supply chain.

Overall, the application of HEA nanocatalysts in water splitting and their integration into energy storage and conversion systems highlight their potential to revolutionize the field of sustainable energy. As research continues to explore the full capabilities of HEAs, these materials are poised to play a pivotal role in the development of next-generation energy technologies.

5. Challenges and Future Development

Despite the significant progress and promising results of HEA nanocatalysts in water-splitting applications, several challenges remain that must be addressed to facilitate their widespread adoption. Key areas of focus include the scalability and cost of HEA production, the optimization of their catalytic performance, and the environmental and sustainability considerations associated with their use in large-scale hydrogen production. Continued research and innovation in these areas will be essential for realizing the full potential of HEA nanocatalysts in sustainable energy technologies.

5.1. Scalability and Cost

One of the primary challenges in the development of HEA nanocatalysts is the scalability of their production for industrial applications. The synthesis of HEAs often involves complex processes such as high-temperature arc melting, mechanical alloying, or chemical reduction methods, which can be energy-intensive and costly. Additionally, the multi-element nature of HEAs requires the precise control of element ratios and homogeneity, which complicates large-scale fabrication. These factors contribute to the high cost of HEA nanocatalyst production, limiting their feasibility for widespread commercial use.

To address these challenges, researchers are exploring alternative synthesis routes that are more cost-effective and scalable, such as solution-based methods and electrodeposition techniques. These approaches aim to reduce the production cost while maintaining the desired structural and compositional properties of HEAs. Moreover, advancements in 3D printing and additive manufacturing technologies hold promise for producing HEA nanocatalysts with customized morphologies and structures at larger scales. By improving the scalability and reducing the cost of HEA production, it will become possible to integrate these advanced materials into industrial water-splitting systems and other energy applications.

5.2. Optimization of Catalytic Performance

The optimization of the catalytic performance of HEA nanocatalysts remains a critical area of ongoing research. While HEAs offer a unique platform for tailoring catalytic properties through compositional and structural adjustments, achieving maximum catalytic efficiency requires an in-depth understanding of the relationship between composition, morphology, and catalytic activity. The high configurational entropy of HEAs can lead to complex interactions between elements, which influence the adsorption energies of reaction intermediates and the overall catalytic mechanism.

Efforts to optimize HEA nanocatalysts focus on fine-tuning their composition to create active sites with high intrinsic activity and selecting appropriate support materials to enhance conductivity and stability. For instance, doping HEAs with transition metals or rare-earth elements has been explored to modulate their electronic structures and improve their performance in HER and OER. Additionally, controlling the size, shape, and surface area of HEA nanocatalysts is essential for increasing the number of active sites and enhancing reaction kinetics. Advanced characterization techniques, such as in situ spectroscopy and microscopy, are being used to gain insights into the atomic-level structure and behavior of HEA nanocatalysts during electrochemical reactions, thereby guiding the rational design of these materials.

5.3. Sustainability Considerations

The application of HEA nanocatalysts in large-scale hydrogen production presents both opportunities and challenges in terms of environmental impact and sustainability. While HEAs have the potential to enable more efficient and durable catalytic processes, the sourcing and use of multiple metal elements in their composition raise concerns regarding resource availability and environmental footprint. For example, the mining and refining of certain elements used in HEAs, such as platinum, cobalt, and rare-earth metals, can have significant environmental consequences, including habitat destruction and greenhouse gas emissions.

To mitigate these issues, researchers are exploring the use of earth-abundant and non-toxic elements in the formulation of HEA nanocatalysts. Developing HEAs based on sustainable materials, such as iron, nickel, and manganese, can reduce the environmental impact associated with their production and use. Additionally, efforts are being made to increase the recyclability and reusability of HEA nanocatalysts, which would minimize waste and contribute to the circular economy. As HEAs become integrated into hydrogen production and other energy systems, it will be crucial to consider their life cycle impacts and ensure that their deployment aligns with global sustainability goals, such as reducing carbon emissions and promoting the use of clean energy technologies.

In conclusion, while HEA nanocatalysts hold great promise for water splitting and energy applications, overcoming challenges related to scalability, cost, and environmental impact will be key to their future development. Continued research and collaboration across disciplines will be essential to optimize HEA properties and establish sustainable production methods, paving the way for their role in the next generation of energy technologies.

6. Conclusions

HEA nanocatalysts have emerged as a transformative class of materials for water splitting, offering several advantages over traditional catalysts. The multi-element composition of HEAs imparts a range of beneficial properties, such as high catalytic activity, stability, and tunable electronic structures, making them highly effective for both HER and OER. HEA nanocatalysts are uniquely capable of reducing overpotentials, enhancing reaction kinetics, and providing excellent corrosion resistance under harsh conditions, such as seawater electrolysis. These properties make HEAs promising candidates for efficient and durable hydrogen production, paving the way for their integration into advanced energy systems like hydrogen fuel cells and hybrid energy storage devices.

Despite these notable advantages, several challenges must be addressed to enable the widespread adoption of HEA nanocatalysts. The high cost and complexity of synthesizing HEAs at a large scale remain significant barriers. Current production methods, such as high-temperature arc melting and mechanical alloying, are energy-intensive and may not be economically viable for industrial applications. To tackle these issues, future research should focus on developing scalable and cost-effective synthesis methods, such as solution-based or additive manufacturing techniques. Additionally, optimizing the composition and morphology of HEA nanocatalysts to achieve maximum catalytic efficiency while minimizing the use of scarce or costly elements is a critical area of ongoing investigation.

From a sustainability perspective, the environmental impact of HEA production and its long-term stability must be carefully considered. Exploring the use of earth-abundant and environmentally friendly elements in HEA formulations, as well as improving their recyclability and reusability, will be essential to ensure that HEAs contribute to global sustainability goals.

Looking ahead, HEA nanocatalysts have the potential to play a pivotal role in achieving scalable, sustainable hydrogen production. With continued research and innovation, HEAs can address the limitations of current water-splitting technologies, contributing significantly to the transition toward a low-carbon future and the widespread adoption of clean energy technologies.

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