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Evaluation of Recent Studies on Morphology Modulation of Seawater Electrocatalysts on Seawater Splitting

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Abstract

Electrocatalytic water splitting is an advanced way to obtain energy to produce green, renewable hydrogen (H_2). However, its widespread application is hampered by the scarcity of freshwater resources. With its abundant reserves, seawater desalination offers a potentially viable alternative for large-scale H_2 production. However, the complexity of seawater poses additional challenges for electrocatalytic processes. This evaluation assesses the processes and difficulties of splitting seawater through electrocatalysis to produce H_2 and emphasizes recent progress in enhancing the efficiency of electrocatalysts in seawater. It also offers suggestions for future research paths to advance this technology.

Review Article

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1. Introduction

The acceleration of the industrialization process in parallel with the increase in population worldwide has increased the demand for non-renewable resources, such as fossil fuels, thus triggering both environmental crises and energy crises (Liu et al., 2022; Orak and Yüksel, 2022). Many researchers have proposed to replace fossil fuels with clean and sustainable energy sources (solar, geothermal, hydrogen and tidal etc.) to reliably sustain life on Earth and at the same time tackle climate change and the energy crisis (Lund and Boyd, 2016; Onat et al., 2021; Sansaniwal et al., 2018).Hydrogen is considered one of the most desirable energy carriers in the 21st century due to its non-polluting nature, high energy density, and sustainable nature (Zhao et al., 2024). Traditional methods like methane reforming and coal gasification are not enough to tackle the issues of energy shortage and pollution (Orak and Yüksel, 2021). On the other hand, water electrolysis provides a solution for environmentally friendly hydrogen production (Ishaq et al., 2022; Bakır et al., 2024). However, the use of freshwater as a source increases the expense of the process and severely limits the widespread application of electrocatalytic water splitting. In contrast, seawater, which makes up 97 of the world's total water reserves, offers a much more abundant resource (Zhang et al., 2020). Electrolysis of seawater can prevent the depletion of freshwater resources and facilitate electrolysis in areas where freshwater is scarce. Seawater, with its high ionic conductivity of 33.9 mS/cm at 25°C, is comparable to a 0.5 M NaCl solution. This means that no extra acids or bases are required to adjust its conductivity, thereby lowering the overall cost of the electrolysis process (Li et al., 2022).

The primary challenge to improve the efficiency of hydrogen production is to develop an energy-efficient and environmentally friendly electrocatalyst. A catalyst of this nature should significantly reduce the energy barrier for the hydrogen evolution reaction (HER) at low overpotential, thereby facilitating efficient seawater electrolysis (Liu et al., 2024a). However, the electrocatalytic seawater desalination process faces challenges such as chlorine release, formation of insoluble precipitates, local acidity changes. These factors significantly complicate the efficiency and sustainability of electrocatalytic seawater separation. Therefore, developing methods and materials that can overcome these challenges is critical for the efficient production of hydrogen from seawater. In order to find solutions to these challenges, several studies have been carried out in recent years to investigate structures with different morphological properties.

This study initially analyzes the mechanism and summarizes the challenges associated with seawater-derived hydrogen production, along with recent advances in this field. It is also highlighted the importance of morphology modulation to improve the performance of the electrocatalyst and seawater electrolyzer. Finally, the perspectives for the future growth prospects of seawater electrolysis are estimated.

2. Electrocatalysts for the her in seawater

The structural stability of electrocatalysts is the main criterion for corrosion resistance. Therefore, developing both durable and active catalysts is one of the leading parameters in optimizing the energy efficiency of seawater electrolyzers (Wang et al., 2022). Currently used HER catalysts prefer platinum, a highly precious metal known as a transition metal, due to its reliability, performance, and durability (Chen et al., 2023). However, due to the high demand limiting the amount of Pt and the high cost, it is important to search and develop materials that are abundant in nature and cost-effective. The interest in noble and non-noble composite structures to reduce the reliance on precious metals such as Pt has developed an alternative approach in recent years (Chen et al., 2024; Liu et al., 2024b; Saquib et al., 2024). These studies were prepared using both natural, alkaline solution with NaCl, and alkaline solution with seawater as the electrolyte condition and proposed various strategies to overcome unfavorable conditions for HER electrocatalysts. In general, catalysts based on phosphides, alloys, sulfides, nitrides, carbon, complex metal hydrides and transition metal carbides are expressed as a group of catalysts with improved HER performance and durability in alkaline seawater (AS), while nitrogen-doped transition metals are suggested to be more suitable as catalysts for direct seawater separation (Yu et al., 2019; Altuntas et al., 2021; Onat et al., 2021).

2.1. Mechanism of HER

In the electrochemical splitting of water to generate oxygen and hydrogen, an external electrical energy source is necessary to initiate the process. In acidic solutions, the participating ions are H^+, whereas in alkaline solutions, they are OH^- (Anantharaj and Aravindan, 2020). Consequently, the pathways for the two half-reactions are expressed differently:

In acidic conditions:

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Anode: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

In alkaline conditions:

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Anode: $2OH^- \rightarrow H_2O + 2e^- + 1/2O_2$

In neutral seawater, the mechanism for HER aligns with that of AS HER. However, compared to acidic conditions where the reaction is facilitated by abundant H^+ ions, neutral and alkaline electrolytes pose a challenge due to lower H^+ concentrations. This necessitates additional energy for water cleavage, resulting in higher energy barriers and slower reaction kinetics.

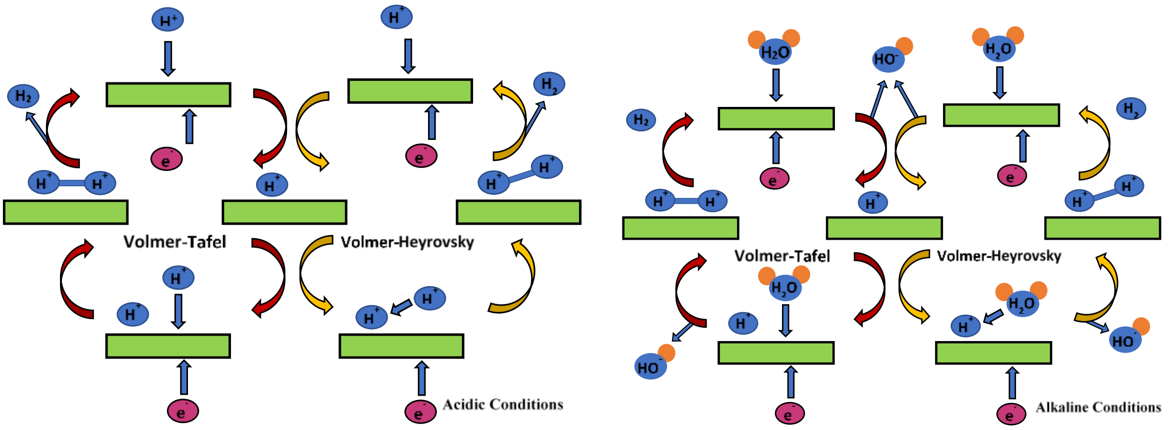

Figure 1. The HER mechanism on the catalyst surface in acidic conditions (top) and alkaline conditions (bottom) is illustrated as follows.

Typically, HER involves two steps:

Volmer process: A proton adsorbs onto the catalyst surface and couples with an electron from the external circuit, forming an adsorbed hydrogen atom (H*) intermediate.

Tafel reaction: Two H* combine, or the Heyrovsky reaction: H* combines with an electron and a proton.

The nature of the adsorbed protons varies with the electrolyte and is crucial for the HER mechanism. Under acidic conditions, protons are H^+, while under alkaline or neutral conditions, water molecules act as the proton source.

a. In acidic conditions

Protons (H^+) from the electrolyte adsorb onto the catalyst surface. An electron from the external circuit couples with the adsorbed proton, forming an adsorbed hydrogen atom (Volmer step; $H^+ + e^- \rightarrow H^*$). Two adsorbed hydrogen atoms (H*) combine to form a hydrogen molecule (H_2), releasing from the catalyst surface (Tafel step; $2H^* \rightarrow H_2$ or Heyrovsky step; $H^+ + H^* + e^- \rightarrow H_2$).

b. In alkaline conditions

Water molecules (H_2O) from the electrolyte adsorb onto the catalyst surface. An electron from the external circuit couples with an adsorbed water molecule, breaking the O-H bond and forming an adsorbed hydroxide ion (OH*) (Volmer step; $H_2O + e^- \rightarrow OH^- + H^*$). Another water molecule adsorbs onto the catalyst surface, and its proton (H^+) interacts with the adsorbed hydroxide ion (OH*) to form an adsorbed water molecule and release a hydroxide ion (OH^-) back into the electrolyte (Heyrovsky step; $H_2O + H^* + e^- \rightarrow H_2 + OH^-$). Two adsorbed hydrogen atoms (H*) combine to form a hydrogen molecule (H_2), releasing from the catalyst surface (Tafel step; $2H^* \rightarrow H_2$).

In assessing the electrocatalytic activity of HER, the adsorbed hydrogen atom (H*) on the electrocatalysts plays a key role. The free energy of adsorbed hydrogen (ΔG_{H^*}) serves as a crucial evaluation index. Additionally, the energy required for water (H_2O) dissociation is of importance, particularly in environments like alkaline or neutral seawater where free protons are limited.

ΔG_{H^*} value close to zero, along with low energy for water dissociation, synergistically boosts the kinetics of HER. These conditions facilitate the rapid generation of hydrogen gas by reducing the energy barriers associated with both the adsorption of hydrogen atoms and the dissociation of water molecules (Carneiro-Neto et al., 2016; Cheng and Niu, 2007; Skúlason et al., 2010)

2.2. Challenges realized in HER mechanism of seawater splitting

In contrast to fresh water, the abundance of various substances such as chloride, magnesium, calcium, Cu^{2+} and Pd^{2+}, etc., ions (Table B) in seawater complicates the process of using electrocatalysis for the HER. These substances cause corrosion and precipitation reactions as well as the accumulation of inactive metals that interfere with the main reaction of the HER. As a result, the efficiency of the HER process is reduced and the stability and activity of the electrocatalysts are compromised (Zhang et al., 2022).

3. The design strategies of seawater hydrogen catalysts

The sluggish kinetics of dissociation of neutral seawater and the presence of impurity ions can impede the electrolysis treatment's effectiveness. To overcome these challenges and make seawater electrolysis a viable method for hydrogen production, the development of low-cost catalysts with high activity, selectivity and overall stability is crucial. Highly active and stable catalysts can accelerate the rate of the desired electrochemical reactions while minimizing side reactions and corrosion. Moreover, ensuring selectivity is essential to prevent the formation of unwanted by-products that could decrease the overall efficiency of the process.

Cost-effectiveness is also a significant factor, especially for large-scale industrial applications. Utilizing inexpensive materials and scalable synthesis methods can help reduce the overall cost of catalyst production and make seawater electrolysis economically competitive with other hydrogen production methods.

By focusing on the development of such catalysts, researchers aim to overcome the limitations associated with neutral seawater splitting and pave the way for the widespread adoption of this sustainable and abundant resource for hydrogen generation. Various modification strategies can enhance the intrinsic activity of electrocatalysts for seawater separation.

3.1. Morphology modulation

A larger specific surface area increases the efficiency of the catalyst by providing more active sites for electrochemical reactions to take place. Furthermore, a morphology that exposes a greater number of reactive sites can facilitate faster reaction kinetics and promote desirable electrocatalytic activity (Zhang et al., 2022). In the field of electrochemistry, researchers often seek to design and engineer catalysts with precisely tailored morphologies to optimize their performance for seawater electrolysis. Techniques such as nanomaterial synthesis, surface engineering, and nanostructuring are widely used to control the morphology of catalysts at the nanoscale in order to achieve desired electrocatalytic properties. The development of nano-electrocatalysts with different morphologies has been an important research area in recent years, especially for applications such as seawater splitting, which holds promise for sustainable hydrogen production. Various nanostructures, including nanoparticles, quantum dots, nanosheets, nanorods and nanowires, offer unique advantages in terms of surface areas, exposed active sites and electron transport properties, all of which can significantly affect their electrocatalytic activity (Li et al., 2022).

3.1.1. Nanosheets

The use of nanosheet structures in HERs is an important area of research to improve the efficiency of these reactions, optimize energy storage and conversion processes, and provide innovative solutions for future energy needs.

For example, Jin et al., studied the design and synthesis of atoms thin nitrogen-rich nanosheets such as Mo_5N_6 using a Ni-induced mode of growth. The single crystal electrocatalyst with a large amount of metal-nitrogen interacting surface shows outstanding activity in HER over a wide pH range (0-14). In addition, 2D Mo_5N_6 nanosheets display high HER efficiency and high stability in natural seawater compared to other transition metal nitrates and especially platinum. They found that by integrating synchrotron-based spectroscopy and electron density state calculations, the enhanced properties of these nitrogen-rich Mo_5N_6 nanosheets are due to the platinum- similar to platinum electronic structure and the highly valent state of Mo atoms (Jin et al. 2018).

Liu et al., prepared an efficient interface electrocatalyst for high-performance HER in seawater using N/S co-doped carbon nanosheets with modified rhodium (Rh) nanoparticles. These graphene-type nanosheets, derived by guanine sulfate pyrolysis, are remarkable for their thin structure and have a large target surface area of 437.1 m^{-2} g, which allows for a uniform distribution of Rh nanoparticles. X-ray photoelectron spectroscopy results show that the addition of sulfide to graphene-like nanosheets can improve the interactivity between Rh nanoparticles and carbon backing. This encourages the deflection of electrons off Rh and their transfer to the Rh-carbon interaction, creating a new interface catalyst. Taking advantage of electron enrichment, this Rh-derived bulk interfacial catalyst demonstrates outstanding HER activities very similar to those of 20% commercial Pt/C over the entire pH range, moreover, even when the Rh loading is only 0.5 wt%. Electrocatalyst demonstrates high activity, capable of providing a current density of -15 mA/cm^2 for 10 hours with high stability, even in a seawater environment (pH=8.32). This work constitutes an essential step in the development of innovative interface electrocatalysts to enable high-performance and stable hydrogen production (Liu et al., 2019).

Wu et al., report a unique Ru nanocrystal-bonded amorphous crystalline $Ni(Fe)P_2$ nanosheet bifunctional catalyst ($Ru-Ni(Fe)P_2/NF$), which results from the partial substitution of Fe in $Ni(Fe)P_2$ to Ni atoms. In this study, the electrocatalytic mechanism was investigated by means of DFT (density functional theory) calculations. By virtue of the combination of the high electric conductivity of the crystal phases, the desaturated coordination of the amorphous phases and the pairing of Ru species, the Ru $Ni(Fe)P_2/NF$ catalyst requires only overpotentials of 375/295 and 520/361 mV for the oxygen evolution reaction (OER)/HER in alkaline water/seawater. It achieves a high current density of 1 A cm^{-2}, outperforming commercial Pt/C/NF and RuO_2/NF catalysts. Moreover, it maintains stability under high average current density conditions for 50 hours in both alkaline and seawater environments (Wu et al., 2023).

In the present study by Shen et al., CoMoNx and Fe-doped CoMoNx nanosheet arrays were grown in place on Ni foam with abundant through holes, abundant multi-level interfaces and $Co_{5.47}N/MoN@NF$ (A) and Fe-$Co_{5.47}N/MoN@NF$ (B) surfaces. The morphologies and structures of $Co_{1.2}MoO_{4.2}@NF$ and $Co_{5.47}N/MoN@NF$ nanosheets were investigated by SEM and TEM. $Co_{1.2}MoO_{4.2}$ nanosheets with a thickness of ≈100 nm were observed to grow on Ni foam in a uniform and compacted manner. It is remarkable that the structure of the nanosheet arrays remains unchanged even after nitridation at a high temperature of 500 °C. Requiring low overpotentials of 213 and 296 mV for the HER and OER under alkaline media, respectively, these arrays can reach current densities of 800 mA cm^{-2}. Both have low Tafel slopes and non-decreasing stability over 80 hours. Furthermore, the electrolyzer with combined A and B needs voltages as low as 1.735 V to achieve 500 $mAcm^{-2}$ in alkaline water. In particular, in AS they exhibit outstanding electrocatalytic properties. Both experimental studies and theoretical calculations confirm that Fe addition reduces the energetic energy barrier from OH* to O* to O* by-products during the OER treatment after catalyst reconfiguration and exhibits the lowest theoretical overpotential from MoN to the unmetallic N site. This outstanding remarkable level of catalytic performance is assigned to the optimal internal electron local configuration and the nanostructure (Shen et al., 2024).

3.1.2. Nanorods

The work of Zhang et al., reveals the importance of building Cu_2S nanorod arrays here as a foundation for enhancing the HER of surface nickel catalysts. The study shows that the arrangement of Cu_2S nanorods seems to have a pivotal role in enhancing the HER efficiency of the catalyst. These nanorod arrays probably provide a high surface area and specific morphology favorable to efficient hydrogen evolution. The combination of Cu_2S nanorods and nickel plating ($Cu_2S@Ni$) on copper foam substrate proved to be particularly effective for HER. This configuration shows a favorable HER activity, outperforming other counterparts such as $Cu_2O@Ni$ and pure Ni catalysts. Their in-depth analysis shows that the enhanced HER activity of $Cu_2S@Ni$ can be ascribed to the interplay between nickel and sulfur (Ni-S) from the underlying Cu_2S nanorods. This interaction probably enhances its catalytic performance by optimizing hydrogen adsorption energy on the catalyst surface. Furthermore, the $Cu_2S@Ni$ nano-array electrode exhibits remarkable stability during HER, indicating its suitability for long-term operation. This stability makes it a promising candidate for applications such as AS electrolysis where durability is important. Overall, this research underlines the importance of nanostructuring and synergistic interactions between different materials to optimize catalyst performance in electrochemical processes such as HER with potential implications for renewable energy technologies (Zhang et al. 2021).

Wang et al., have developed a complex nanostructure, $S\text{-}NiMoO_4@NiFe\text{-}LDH$ (X)/NF, consisting of sulfur-modified nickel molybdate nanorods coated with an amorphous and crystalline NiFe layered double hydroxide (NiFe-LDH) layer, all supported on a porous nickel foam. They achieved this by a combination of hydrothermal and electrodeposition techniques. This nanostructure shows remarkable catalytic activity in two important reactions OER and HER, which are crucial in processes such as seawater electrolysis. It benefits from high intrinsic activity, numerous active sites, and rapid electron transfer. Both in laboratory-simulated AS and in real seawater electrolytes, the X/NF catalyst shows outstanding performance. The catalyst requires relatively low overpotentials to reach a current density of 100 mA cm^{-2}: 273-315 mV for OER and 170-220 mV for HER in salt-added freshwater and pure seawater, respectively. When used as both anode and cathode in an electrolyser, the X/NF catalyst shows excellent seawater splitting activity, requiring voltages as low as 1.68 and 1.73 V to achieve a current density of 100 mA cm^{-2} in simulated AS and real AS, respectively.

More importantly, it shows resistance to chlorine and provides satisfactory durability. Compared with the commonly used IrO_2||Pt/C pair and other reported bifunctional catalysts, this electrolyser outperforms them, revealing significant potential for practical seawater electrolysis applications. The electrocatalytic results of the study show that the NiFe-LDH layer primarily facilitates OER, while the underlying S-$NiMoO_4$ nanorods are responsible for HER activity, especially under simulated AS conditions (Wang et al., 2022).

Zhang et al., have successfully developed Mo-NiS@NiTe (Y) core–shell nanorods supported on nickel foam (Y/NF). They reported that these nanorod arrays, which are both hydrophilic and self-supporting, act as catalysts for the HER without the need for additional binding materials and facilitate rapid electron transfer from the NiTe core, nickel foam substrate to the NiS shell. In addition, it was also emphasised that the incorporation of the heteroatom Mo at the interface between NiTe and NiS synergistically changes the electronic structure of the NiS shell. This modification enhanced the adsorption and dissociation of water molecules, resulting in improved reaction kinetics. Thanks to these improvements, Y/NF was reported to exhibit outstanding performance in HER with exceptional stability in the long term. In 1.0 M KOH solution and AS, only 34 and 57 mV overpotentials were required to achieve a current density of 10 mA cm^{-2}, respectively, and almost 100% Faraday efficiency for hydrogen production was achieved, maintaining excellent stability over long cycles. In particular, YTe(-)||RuO_2(+) pairs outperformed Pt/C(-)||RuO_2(+) pairs and exhibited remarkable stability, demonstrating their potential as highly efficient catalysts for practical applications. They have specifically stated that core NiTe nanorods act as scaffolds connecting active NiS and substrate NF, effectively reducing system impedance and improving stability (Zhang et al., 2023).

In their work, Hemmati et al., introduce a bifunctional catalyst obtained through morphological engineering, resulting in hierarchical NiO microspheres assembled into nanorod arrays (NRAHM-NiO). This unique three-dimensional structure resembles a sea urchin that combines oxide and hydroxide materials, specifically designed for efficient seawater separation while preventing chloride oxidation. It is explained that the NRAHM-NiO catalyst has many advantageous features. These are listed as abundant intrinsic electroactive sites, excellent charge transfer capabilities, efficient gas bubble release, corrosion resistance and a hydrophilic surface. These features contribute to the outstanding performance of both HER and OER, which is essential for general seawater separation. At room temperature, the NRAHM-NiO catalyst exhibited low cell voltages of 1.66 V and 2.01 V to reach current densities of 100 mA cm^{-2} and 500 mA cm^{-2}, respectively. The catalytic activity was reported to exceed the benchmark systems such as Pt/C(-)||Pt/C(+) and Pt/C(-)||IrO_2(+). Even more importantly, the NRAHM-NiO apparatus showed specific stability and selectivity towards OER in seawater, resulting in 99% faradaic efficiency without generating any chlorine by-products. The experimental findings were supported by DFT calculations. Furthermore, when operated with a single solar cell, the integrated photolysis system achieved a solar-to-hydrogen (STH) efficiency of 9.9%, demonstrating its potential as a sustainable method for hydrogen production (Hemmati et al. 2023).

3.1.3. Nanoparticles

Hydrogen production from seawater is an emerging field as nanoparticles can dramatically improve the efficiency and feasibility of the process as they exhibit properties such as enhanced catalytic activity, efficient light absorption, selective catalysis and enhanced catalytic activity (Ece et al., 2021). Huang et al.'s, study discusses the synthesis and performance evaluation of carbon nanoparticles doped with nitrogen (N) and phosphorus (P), which are also decorated with small amounts of platinum (Pt) nanoparticles. The synthesis process entailed pyrolyzing aminophenol resin spheres, followed by microwave irradiation with a platinum compound, and subsequent phosphorization. Scanning electron microscope (SEM) images indicated that Pt-decorated carbon nanoparticles (Pt/NPC) consist of carbon particles of approximately 200 nm in size, decorated with Pt particles of approximately 10.9 nm in diameter. In terms of catalytic performance, the catalyst exhibited low overpotentials for hydrogen production in both acidic and alkaline conditions, with overpotentials of 33 mV and 25 mV, respectively, at a current density of 10 mA/cm^2, while a high of 99% for chlorine production at an overpotential of 100 mV. They reported that the catalyst demonstrated activity comparable to commercial Pt/C catalysts with high selectivity. In seawater electrolysis, it exhibited low overpotentials for hydrogen and chlorine evolution, measuring 116 mV and 190 mV respectively, at a current density of 50 mA cm^{-2}. The synergy from doping carbon with nitrogen (N) and phosphorus (P), combined with the incorporation of highly crystallized platinum (Pt) nanoparticles through phosphorization, created additional active sites and altered the electronic properties of the Pt particles. Specifically, the interaction between the Pt nanoparticles and the negatively charged P-doped carbon caused a downshift in the d-band center of the Pt particles, enhancing their catalytic activity. DFT calculations supported the experimental findings, showing that the electronic state of the doped carbon was influenced by the differences in electronegativity among the C, N, and P dopants. This modulation led to a reduced bandgap, facilitating charge transfer during the catalytic reaction. Overall, the study demonstrates that decorating carbon materials with low-content metal particles, using various heteroatom doping strategies, can enhance catalytic activity, particularly for hydrogen and chlorine generation from both freshwater and seawater sources (Huang et al., 2022).

Cheshideh et al., a novel electrode, termed s-Ni/TiO_2/Ti, have developed by grafting Ni nanoparticles onto titanium dioxide (TiO_2) nanotubes and subjecting them to surface reconstruction. The process involved electrochemical grafting of Ni nanoparticles onto TiO_2 nanotubes under various circumstances, followed by thermal treatment to enhance electrical conductivity and provide better template adherence. The surface reconstruction resulted in the formation of heterojunction intermediates, such as $Ni(OH)_2$ and NiOOH, on the surface of the nickel nanoparticles. This modification facilitated the facile HER in both alkaline and chloride solutions. The s-Ni/TiO_2/Ti electrode demonstrated excellent performance in HER, requiring an extremely low overpotential of 126 mV in 1.0 M KOH solution. This overpotential was even lower than that of platinum-based catalysts (Pt/C), which are commonly regarded as benchmark materials for HER. Moreover, the electrode demonstrated a comparably low overpotential of 127 mV for the (HER) in a solution comprising 1.0 M KOH and 0.5 M NaCl, indicating its effectiveness in corrosive environments such as seawater. The electrode's long-term stability over 100 hours of operation suggests that it is highly active and cost-effective (Cheshideh et al., 2023).

Study of Yang et al., describes a new approach to enhancing the performance of Pt nanoalloys in HER by precisely controlling the composition of the material. Specifically, the strategy involves surface-controllable anchoring of Cu on nanostructured PtNi, resulting in a material termed Cu/PtNi. The nanostructured Cu/PtNi material is designed to have distinct functionalities contributed by its constituent elements. The presence of oxophilic Ni promotes rapid water dissociation, while Pt facilitates efficient hydrogen adsorption and production. Furthermore, copper (Cu) was introduced to induce a favorable Gibbs free energy for efficient hydrogen adsorption and thus promote hydrogen desorption. The Cu/PtNi electrocatalyst exhibits excellent performance in the (HER), which is demonstrated by a low overpotential of 23 mV at a current density of 10 mA cm^{-2} in AS. This activity level is five times higher than the mass activity of commercial Pt/C catalysts, which require a higher overpotential of 70 mV. DFT calculations support these experimental findings by confirming that key processes involved in the HER pathway, such as water dissociation, hydrogen adsorption, and hydrogen desorption, are facilitated by the multifunctional metal sites of Pt, Ni, and Cu in the AS environment. In summary, the Cu/PtNi electrocatalyst represents a promising advancement in HER performance, leveraging the synergistic effects of multiple metal components to achieve superior catalytic activity in challenging conditions such as AS (Yang et al., 2023).

Wang et al., developed an efficiently catalytic material, named Ru_1+NPs/N-C, containing a combination of monatomic Ru-N_4 sites and Ru nanoparticles supported on nitrogen-doped carbon. Mentioned material is synthesized via the coordination-pyrolysis strategy involving melamine formaldehyde resin. This innovative approach likely offers significant advantages in terms of catalytic performance and stability, potentially finding applications in various fields such as energy conversion, environmental remediation, or chemical synthesis. The Ru_{1+NPs}/N-C catalyst exhibits remarkable HER performance on several metrics including overpotential, Tafel slopes, mass activity, turnover frequency and stability in both acidic and alkaline media. Particularly noteworthy is its comparative performance with the 20% Pt/C catalyst in natural and simulated seawater, showing similar hydrogen production capacity and higher faradic efficiency. The catalyst's efficiency arises from synergistic interactions between the Ru-N_4 site and Ru nanoparticles, which alter the electronic structure and enhance HER kinetics. The efficiency of the catalyst is due to the synergistic interactions between the Ru-N_4 site and Ru nanoparticles, modifying the electronic structure to improve HER kinetics. This synergy enables the efficient decomposition of water to adsorbed hydrogen and facilitates the coupling of adsorbed hydrogen to molecular hydrogen (H_2) and subsequent desorption. These findings provide valuable insights for designing highly efficient electrocatalysts for large-scale seawater electrolysis, which is critical for sustainable hydrogen production (Wang et al., 2022).

3.1.4. Nanowires

Solar-driven water and seawater separation systems show promise for sustainably producing hydrogen fuel, but their intermittent nature poses challenges for practical implementation. To address this, Xu et al. developed a novel approach: integrating an energy storage module between photovoltaic cells and an electrolyser. This setup enables continuous operation of a self-powered electrolyser, overcoming the limitations of sunlight variability. Their work focuses on self-supporting $Pd_{0.2}Ni_{58}Fe_{30}O_{11.8}$ nanowires, a trifunctional electrocatalyst that serves both Zn-air batteries and general seawater separation. These nanowires have a unique 3D network structure with hierarchical connectivity that enhances surface charge and mass transfer. The self-supporting nanowires exhibit extremely low overpotentials (77 mV for hydrogen evolution and 233 mV for oxygen evolution) enabling high current densities of 100 mA cm^{-2}. This performance places them at the forefront of industrialisation prospects. More importantly, the researchers successfully set up a solar-powered 24-hour integrated water exchange system, maintaining a constant output voltage of 1.88 V and constant current density. This achievement heralds exciting possibilities for completely sustainable and renewable energy practices and marks an important step towards the realization of solar-powered continuous water separation systems (Xu et al., 2023).

Dong et al., introduced n^+-p Si photocathodes powered by Pt nanoclusters attached to GaN nanowires. The integration of nanowires is critical for several reasons. Firstly, GaN nanowires provide a scaffold for anchoring Pt nanoclusters, ensuring their stability and efficient interaction with water molecules. Second, the nanowire structure offers a large surface area, increasing the number of active sites for the catalytic reaction. Experimental results demonstrate the remarkable performance of these Pt/GaN/Si photocathodes. They reach impressive current densities of -10 mA/cm² at relatively low overpotentials (0.15 and 0.39 V vs. RHE) in seawater and phosphate-buffered seawater, respectively. They also exhibit high applied bias photon-current efficiencies of 1.7% and 7.9% in these conditions. These findings underline the efficiency and stability of nanowire-enhanced photocathodes for hydrogen production in different seawater environments. Furthermore, under concentrated sunlight (9 suns), the Pt/GaN/Si photocathodes show a record high photocurrent density of ~169 mA/cm². This emphasizes their potential for solar hydrogen production. More importantly, the Pt/GaN/Si assembly can continuously produce hydrogen even without light by simply changing the electrical contact, demonstrating its robustness and versatility. In summary, the integration of Pt nanoclusters on GaN nanowires within the Si photocathode structure significantly improves the catalytic reactions for seawater HER. This innovative design not only improves the performance but also offers energy saving advantages, making it a promising candidate for efficient and sustainable hydrogen production via seawater splitting (Dong et al., 2023).

Although seawater electrolysis holds great promise for hydrogen production, it is plagued by challenges such as severe chloride ion (Cl^-) corrosion due to high Cl^- concentrations and competition from the chlorine evolution reaction (CER). To combat these problems, Yang et al. designed a core-shell structure on a nickel foam substrate, named S-$Fe(OH)_3$/NiSe/NF, containing a sulfur-modified amorphous $Fe(OH)_3$ layer on top of intersecting NiSe nanowires. Hence the nanowire structure enables the electrode to have a large number of active sites, this innovative electrode exhibits exceptional catalytic prowess for both HER and OER in simulated and natural AS electrolytes. The overpotentials for OER in simulated and natural AS electrolytes at a current density of 100 mA cm^{-2} are 234 and 232 mV, respectively. In contrast, the figures for HER are 331 and 341 mV, respectively. Furthermore, when used as both anode and cathode, the electrolyser containing S-$Fe(OH)_3$/NiSe/NF exhibits excellent performance in simulated and natural seawater electrolytes, having voltages of 1.85 and 1.87 V at 100 mA cm^{-2}, respectively. This achievement underlines the significant potential of this electrolyser for practical seawater electrolysis and offers a promising way to overcome the difficulties encountered with conventional electrolysis techniques in marine environments (Yang et al., 2024).

To develop abundant, efficient and stable electrocatalysts in soil for hydrogen production without platinum group metals (PGMs) is a desirable but challenging goal. Mass production of high-purity of hydrogen fuel through seawater electrolysis represents a transformative technology for sustainable alternatives. Poudel and coworkers reported a heterostructure consisting of molybdenum selenide-nickel selenide (Mo3Se4-NiSe) core-shell nanowire arrays built on nickel foam by a one-step in situ hydrothermal process. These nanowires are fabricated on nickel foam using a single-step in situ hydrothermal process. This specific architecture is crucial as it enhances the intrinsic activity and electrical conductivity of the catalyst, facilitating efficient charge transfer essential for the HER. Experimental results demonstrate the outstanding performance of Mo_3Se_4-NiSe nanowire electrodes in both alkaline and natural seawater conditions. In alkaline and natural seawater electrolytes, they respectively require significantly low overpotentials of 84.4 and 166 mV to reach a current density of 10 mA cm-2. This indicates the effectiveness of the nanowire-based catalysts in promoting the HER process. Furthermore, theoretical calculations support the experimental findings by revealing that the interface between Mo_3Se_4 and NiSe in the nanowires yields an ample amount of active sites for the HER pathway. These active sites play an essential role in tailoring the binding energies of the adsorbed species and lowering the energy barrier for the reaction. Therefore, nanowire-based catalysts represent a promising approach to design advanced electrocatalysts for hydrogen production without platinum group metals (PGMs), suitable for both alkaline and seawater electrolysis. This addresses the urgent demand for sustainable energy solutions (Poudel et al., 2024).

3.1.5. Quantum dots

The use of quantum dots in seawater desalination is a promising innovative approach for sustainable energy production. Seawater desalination involves using renewable resources such as sunlight and seawater to produce hydrogen fuel through a process called water electrolysis. Quantum dots, nanoscale semiconductor particles, can be tailored to efficiently absorb specific wavelengths of light, making them ideal candidates for improving the efficiency of solar-powered seawater desalination (Horoz and Sahin, 2017; Jin et al., 2021). Below are some of the studies investigating the effect of the quantum dot structure used in hydrogen production from seawater.

Chen et al. demonstrated the efficiency of three-dimensional (3D) MoS_2 quantum dot (MoS_2QD) aerogel as a cathode electrocatalyst to improve HER in various environments, including acid, neutral and alkaline (e.g. real seawater) conditions. Through investigating the impact of exfoliated MoS_2 sizes on HER performance, they found that biofunctionalized exfoliated MoS_2 quantum dots (MoS_2QD) demonstrated significantly higher cathodic density, lower energy input, and a reduced Tafel slope compared to larger exfoliated MoS_2 supported by chlorophyll. This underscores the important role of MoS_2 aerogel size in accelerating HER performance. More importantly, the quantum dot structure of MoS_2QD contributes to its superior performance by facilitating efficient charge separation and catalytic activity. In addition, the electrocatalytic activity of MoS_2QD-aerogel surpasses that of Pt under neutral conditions. Remarkably, in actual seawater, the MoS_2QD-aerogel sample maintains stable HER performance even after 150 consecutive cycles, whereas the HER activity of Pt declines significantly after only 50 cycles. These findings represent a pioneering demonstration of how the 3D MoS_2 configuration in MoS_2 aerogel, especially in combination with quantum dots, can effectively facilitate hydrogen production for clean energy applications (Chen et al., 2019).

Fan et al., have developed a globally abundant layered double hydroxide (LDH) electrocatalyst that exhibits exceptional stability during seawater electrolysis, even under ultra-high current densities. An important aspect of their work involves the addition of carbonate ions to the interlayers of the LDH structure and the fixation of graphene quantum dots (GQDs) to the surface. Quantum dots play a crucial role in this innovation. The surface anchoring of GQDs to the LDH electrocatalyst provides several benefits. Firstly, quantum dots and carbonate ions effectively inhibit the unfavorable adsorption of chloride ions, which can hinder the performance and stability of the electrocatalyst during seawater electrolysis. Secondly, the presence of quantum dots contributes to the enhancement of the electrocatalyst's resistance to chloride ion corrosion, improving its durability and longevity. Experimental findings demonstrate the remarkable performance of the LDH electrocatalyst modified with graphene quantum dots. The electrocatalyst maintains stable electrolysis of seawater for more than 2,800 hours under an ultra-high current density of about 1.25 A/cm². This longevity is attributed to the protective effects of quantum dots against chloride ion corrosion. The researchers have integrated the modified LDH electrocatalyst into a photovoltaic-electrolysis device, utilizing it as a catalyst for both oxygen and hydrogen evolution. This device achieved a record solar-to-hydrogen efficiency of 18.1% for overall seawater separation, highlighting the effectiveness of the quantum dot-modified electrocatalyst in harnessing solar energy for sustainable hydrogen production. Furthermore, the device shows good stability for 200 h under high operating current exceeding 440 mA. In summary, surface attachment of graphene quantum dots on the LDH electrocatalyst significantly improves its stability, performance and resistance to chloride ion corrosion during seawater electrolysis. This innovative approach represents an important step in green hydrogen production and the realisation of a sustainable energy future (Fan et al., 2024).

In particular, great efforts have been made to focus on a large specific surface area in the design of seawater-based catalysts. However, often not enough consideration has been given to the change in morphology even after long-term stability has been achieved. Changing morphology can affect the specific surface area, which can lead to a reduction of active sites. Therefore, in addition to stability tests, morphology needs to be scrutinized.

4. Conclusion

Seawater contains abundant reserves that can enable the production of large amounts of H_2. But because seawater has a complex composition, the efficiency of electrolysis for hydrogen production is reduced. In this review, one of the strategies highlighted for improving seawater splitting efficiency is morphology control, categorized into nanosheets, nanorods, nanoparticles, nanowires, and quantum dots. Although some successes have been achieved, seawater partitioning research is not yet fully mature and faces some challenges. Future work should focus on the following research areas.

The reactivity and long-term stability of electrocatalysts are affected by the complex constituents of seawater and still face major challenges. However, designing high-performance and durable catalysts through morphology editing is recognized as an effective strategy to overcome these challenges. By proper morphology arrangement, the activity and stability of electrocatalysts in seawater can be enhanced. The design of seawater electrolyzers faces significant challenges due to the presence of complex seawater components. Several physical and chemical factors such as ions, bacteria, microorganisms and solid sediments complicate the design process. Therefore, for seawater electrolyzers to work efficiently, it is often necessary to pre-treat seawater, which requires additional effort and resources. Moreover, existing research is often limited to the laboratory level, making it difficult to develop suitable solutions to support H_2 production on an industrial scale. In this context, it is important to design and scale-up new and efficient catalysts and electrolyzers. To better understand the mechanism of seawater separation reactions, advanced characterization technologies are required. The integration of methods such as spectroscopy and chromatography, as well as theoretical computing and research methods, can accelerate progress in this field. This could contribute to making seawater electrolyzers more efficient and sustainable. Although seawater-based electrocatalysts and electrolyzers are not yet fully grown, it is believed that after further research and optimization, more efficient and safer systems can be designed in the future. We anticipate that this review will advance applications in seawater splitting by emphasizing advancements in electrocatalysts and electrolyzers. In this way, we believe that seawater splitting can play an important role in renewable energy production in the future.

References

Altuntas, I., Kocak, M.N., Yolcu, G., Budak, H.F., Kasapoğlu, A.E., Horoz, S., Gür, E., Demir, I., 2021. Influence of the PALE growth temperature on quality of MOVPE grown AlN/Si (111). *Materials Science in Semiconductor Processing*, 127.

Anantharaj, S., Aravindan, V., 2020. Developments and Perspectives in 3d Transition-Metal-Based Electrocatalysts for Neutral and Near-Neutral Water Electrolysis. In *Advanced Energy Materials*, 10(1).

Bakır, R., Orak, C., Yüksel, A., 2024. Optimizing hydrogen evolution prediction: A unified approach using random forests, lightGBM, and Bagging Regressor ensemble model. *International Journal of Hydrogen Energy*, 67: 101–110.

Carneiro-Neto, E.B., Lopes, M.C., Pereira, E.C., 2016. Simulation of interfacial pH changes during hydrogen evolution reaction. *Journal of Electroanalytical Chemistry*, 765: 92–99.

Cheng, Y.F., Niu, L., 2007. Mechanism for hydrogen evolution reaction on pipeline steel in near-neutral pH solution. *Electrochemistry Communications*, 9(4): 558–562.

Chen, H., Luo, X., Huang, S., Yu, F., Li, D., Chen, Y., 2023. Phosphorus-doped activated carbon as a platinum-based catalyst support for electrocatalytic hydrogen evolution reaction. *Journal of Electroanalytical Chemistry*, 948.

Chen, I.W.P., Hsiao, C.H., Huang, J.Y., Peng, Y.H., Chang, C.Y., 2019. Highly Efficient Hydrogen Evolution from Seawater by Biofunctionalized Exfoliated MoS 2 Quantum Dot Aerogel Electrocatalysts That Is Superior to Pt. *ACS Applied Materials and Interfaces*, 11(15): 14159–14165.

Chen, X., Zhao, J.Y., Zhang, W.S., Wang, X. M., 2024. Cactus-like NC/CoxP electrode enables efficient and stable hydrogen evolution for saline water splitting. *Xinxing Tan Cailiao/New Carbon Materials*, 39(1): 152–163.

Cheshideh, H., Chen, H.Y., Liao, K.W., Wang, K.C., Chen, GC., Huang, H.C., Wang, C.H., 2023. Reactive surface intermediates over Ni-grafted TiO2 nanotube arrays towards hydrogen evolution reaction in alkaline and chloride media. *International Journal of Hydrogen Energy*, 48(81): 31479–31490.

Dong, W.J., Xiao, Y., Yang, K.R., Ye, Z., Zhou, P., Navid, I.A., Batista, V.S., Mi, Z., 2023. Pt nanoclusters on GaN nanowires for solar-asssisted seawater hydrogen evolution. *Nature Communications*, 14(1).

Ece, M.Ş., Ekinci, A., Kutluay, S., Şahin, Ö., Horoz, S., 2021. Facile synthesis and comprehensive characterization of Ni-decorated amine groups-immobilized Fe3O4@SiO2 magnetic nanoparticles having enhanced solar cell efficiency. *Journal of Materials Science: Materials in Electronics*, 32(13): 18192–18204.

Fan, R., Liu, C., Li, Z., Huang, H., Feng, J., Li, Z., Zou, Z., 2024. Ultrastable electrocatalytic seawater splitting at ampere-level current density. *Nature Sustainability*, 7(2): 158–167.

Hemmati, K., Kumar, A., Jadhav, A.R., Moradlou, O., Moshfegh, A.Z., Lee, H., 2023. Nanorod Array-Based Hierarchical NiO Microspheres as a Bifunctional Electrocatalyst for a Selective and Corrosion-Resistance Seawater Photo/Electrolysis System. *ACS Catalysis*, 13(8): 5516–5528.

Horoz, S., Sahin, O., 2017. Investigations of structural, optical, and photovoltaic properties of Fe-alloyed ZnS quantum dots. *Journal of Materials Science: Materials in Electronics*, 28(13): 9559–9565.

Huang, Y., Seo, K.D., Jannath, K.A., Park, D.S., Shim, Y.B., 2022. Heteroatoms doped carbon decorated with tiny amount Pt nanoparticles as a bifunctional catalyst for hydrogen and chlorine generation from seawater. *Carbon*, 196: 621–632.

Ishaq, H., Dincer, I., Crawford, C., 2022. A review on hydrogen production and utilization: Challenges and opportunities. *International Journal of Hydrogen Energy*, 47(62): 26238–26264.

Jin, L., Zhao, H., Wang, Z.M., Rosei, F., 2021. Quantum Dots-Based Photoelectrochemical Hydrogen Evolution from Water Splitting. *Advanced Energy Materials*, 11(12).

Li, J., Sun, J., Li, Z., Meng, X., 2022. Recent advances in electrocatalysts for seawater splitting in hydrogen evolution reaction. *International Journal of Hydrogen Energy*, 47(69): 29685–29697.

Liu, J., Duan, S., Shi, H., Wang, T., Yang, X., Huang, Y., Wu, G., Li, Q., 2022. Rationally Designing Efficient Electrocatalysts for Direct Seawater Splitting: Challenges, Achievements, and Promises. *Angewandte Chemie - International Edition*, 61(45).

Liu, J., Song, X., Gao, S., Chen, F., Lang, X., Zhang, T., Lv, Z., Ma, G., 2024a. Collaborative coupling catalytic interface enabling efficient hydrogen evolution in universal-pH electrolytes and seawater. *International Journal of Hydrogen Energy*, 49: 1625–1632.

Liu, J., Song, X., Gao, S., Chen, F., Lang, X., Zhang, T., Lv, Z., Ma, G., 2024b. Collaborative coupling catalytic interface enabling efficient hydrogen evolution in universal-pH electrolytes and seawater. *International Journal of Hydrogen Energy*, 49: 1625–1632.

Liu, Y., Hu, X., Huang, B., Xie, Z., 2019. Surface Engineering of Rh Catalysts with N/S-Codoped Carbon Nanosheets toward High-Performance Hydrogen Evolution from Seawater. *ACS Sustainable Chemistry and Engineering*, 7(23): 18835–18843.

Lund, J.W., Boyd, T.L., 2016. Direct utilization of geothermal energy 2015 worldwide review. *Geothermics*, 60: 66–93.

Onat, E., Şahin, Ö., İzgi, M.S., Horoz, S., 2021. An efficient synergistic Co@CQDs catalyst for hydrogen production from the hydrolysis of NH3BH3. *Journal of Materials Science: Materials in Electronics*, 32(23): 27251–27259.

Orak, C., Yüksel, A., 2021. Photocatalytic Hydrogen Energy Evolution from Sugar Beet Wastewater. *ChemistrySelect*, 6(43): 12266–12275.

Orak, C., Yüksel, A., 2022. Comparison of photocatalytic performances of solar-driven hybrid catalysts for hydrogen energy evolution from 1,8–Diazabicyclo[5.4.0]undec-7-ene (DBU) solution. *International Journal of Hydrogen Energy*, 47(14): 8841–8857.

Poudel, M.B., Logeshwaran, N., Prabhakaran, S., Kim, A.R., Kim, D.H., Yoo, D.J., 2024. Low-Cost Hydrogen Production from Alkaline/Seawater over a Single-Step Synthesis of Mo3Se4-NiSe Core–Shell Nanowire Arrays. *Advanced Materials*, 36(5).

Sansaniwal, S.K., Sharma, V., Mathur, J., 2018. Energy and exergy analyses of various typical solar energy applications: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 82: 1576–1601.

Saquib, M., Arora, P., Bhosale, A.C., 2024. Nickel molybdenum selenide on carbon cloth as an efficient bifunctional electrocatalyst for alkaline seawater splitting. *Fuel*, 365.

Shen, X., Li, H., Ma, T., Jiao, Q., Zhao, Y., Li, H., Feng, C., 2024. Construction of heterojunction-rich metal nitrides porous nanosheets electrocatalyst for alkaline water/seawater splitting at large current density. *Small*.

Skúlason, E., Tripkovic, V., Björketun, M.E., Gudmundsdóttir, S., Karlberg, G., Rossmeisl, J., Bligaard, T., Jónsson, H., Nørskov, J.K., 2010. Modeling the electrochemical hydrogen oxidation and evolution reactions on the basis of density functional theory calculations. *Journal of Physical Chemistry C*, 114(42): 18182–18197.

Wang, H., Chen, L., Tan, L., Liu, X., Wen, Y., Hou, W., Zhan, T., 2022. Electrodeposition of NiFe-layered double hydroxide layer on sulfur-modified nickel molybdate nanorods for highly efficient seawater splitting. *Journal of Colloid and Interface Science*, 613: 349–358.

Wang, S., Wang, M., Liu, Z., Liu, S., Chen, Y., Li, M., Zhang, H., Wu, Q., Guo, J., Feng, X., Chen, Z., Pan, Y., 2022. Synergetic Function of the Single-Atom Ru-N4Site and Ru Nanoparticles for Hydrogen Production in a Wide pH Range and Seawater Electrolysis. *ACS Applied Materials and Interfaces*, 14(13): 15250–15258.

Wang, X., Zhou, X., Li, C., Yao, H., Zhang, C., Zhou, J., Xu, R., Chu, L., Wang, H., Gu, M., Jiang, H., Huang, M., 2022. Asymmetric Co-N3P1 Trifunctional Catalyst with Tailored Electronic Structures Enabling Boosted Activities and Corrosion Resistance in an Uninterrupted Seawater Splitting System. *Advanced Materials*, 34(34).

Wu, D., Liu, B., Li, R., Chen, D., Zeng, W., Zhao, H., Yao, Y., Qin, R., Yu, J., Chen, L., Zhang, J., Li, B., Mu, S., 2023. Fe-Regulated Amorphous-Crystal Ni(Fe)P2 Nanosheets Coupled with Ru Powerfully Drive Seawater Splitting at Large Current Density. *Small*, 19(36).

Xu, G.R., Zhang, N., Sun, Q., Zhang, W., Wu, Z., Wang, L., 2023. Self-supportive Pd0.2Ni58Fe30O11.8 nanowires for solar-driven self-powered water/seawater splitting with large current density. *Chemical Engineering Journal*, 476.

Yang, C., Jiang, X., Li, Y., Zeng, J., Liang, H.P., 2024. Construction of S-modified Amorphous Fe(OH)3 on NiSe Nanowires as Bifunctional Electrocatalysts for Efficient Seawater Splitting. *ACS Applied Nano Materials*, 7(4): 3960–3967.

Yang, X., Xiao, Y.X., Chen, J. B., Yu, F., Tian, G., Pu, F.F., Zhang, S., de Torresi, S.I.C., Symes, M.D., Janiak, C., Yang, X.Y., 2023. Surface controllable anchoring of Cu onto nanostructured PtNi for efficient electrochemical hydrogen evolution from seawater. *Science China Materials*, 66(10): 3887–3894.

Yu, L., Zhu, Q., Song, S., McElhenny, B., Wang, D., Wu, C., Qin, Z., Bao, J., Yu, Y., Chen, S., Ren, Z., 2019. Non-noble metal-nitride based electrocatalysts for high-performance alkaline seawater electrolysis. *Nature Communications*, 10(1).

Zhang, B., Xu, W., Liu, S., Chen, X., Ma, T., Wang, G., Lu, Z., Sun, J., 2021. Enhanced interface interaction in Cu2S@Ni core-shell nanorod arrays as hydrogen evolution reaction electrode for alkaline seawater electrolysis. *Journal of Power Sources*, 506.

Zhang, H., Luo, Y., Chu, P. K., Liu, Q., Liu, X., Zhang, S., Luo, J., Wang, X., Hu, G., 2022. Recent advances in non-noble metal-based bifunctional electrocatalysts for overall seawater splitting. *Journal of Alloys and Compounds*, 922.

Zhang, J., Hu, W., Cao, S., Piao, L., 2020. Recent progress for hydrogen production by photocatalytic natural or simulated seawater splitting. *Nano Research*, 13(9): 2313–2322.

Zhang, K., Yang, E., Zheng, Y., Yu, D., Chen, J., Lou, Y., 2023. Robust and hydrophilic Mo-NiS@NiTe core-shell heterostructure nanorod arrays for efficient hydrogen evolution reaction in alkaline freshwater and seawater. *Applied Surface Science*, 637.

Zhao, Z., Zhao, H., Du, X., Zhang, X., 2024. Controllable preparation of Cu2S@Ni3S2 grown on nickel foam as efficient seawater splitting electrocatalyst. *International Journal of Hydrogen Energy*, 49: 1528–1537.