A study on highly active bifunctional OER/HER electrocatalysts with ampere-level current densities

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Chapter 1: General Introduction

1-1. Hydrogen energy

The extensive use of fossil fuels has led to the depletion of fossil resources and environmental pollution. There is an increasing effort to develop renewable and green energy sources as alternatives to fossil fuels.¹ Wind, solar, and tidal energy can be converted into electricity and stored in batteries for later use. Hydrogen is a renewable fuel source that can be produced steadily through electrolysis (Figure 1-1) or chemical reactions.² Fuel cell vehicles powered by hydrogen play a crucial role in the global transition to sustainable transportation solutions as they have the potential to enable zeroemission transport. The use of hydrogen as an energy carrier has garnered significant attention due to its potential to address environmental concerns. With a high energy value of 142 MJ per kilogram, hydrogen produces environmentally friendly water as a byproduct and possesses recyclable properties. These attributes position hydrogen as a promising candidate to contribute to a sustainable energy future. At present, industrial hydrogen production primarily relies on natural gas steam reforming and coal gasification. However, these methods typically require high temperature and pressure, resulting in excessive carbon dioxide (CO₂) emissions. On the contrary, using electricity generated from renewable sources to facilitate electrochemical water splitting is a more environmentally friendly approach to producing green hydrogen. This process only produces oxygen (O₂) as a byproduct and results in zero carbon emissions. Despite these advantages, electrocatalytic hydrogen production only accounts for 4% of total hydrogen production due to its low energy conversion efficiency, high electricity costs, and limited economic appeal.³



Figure 1-1. Schematic diagram for green hydrogen cycling. Ref. [2]; Copyright 2024; American Chemical Society.

1-2. Mechanism of electrocatalytic water splitting

In order to produce large quantities of high-purity hydrogen to meet the needs of various energy fields and achieve the environmental goal of zero emissions. Typically, electrocatalytic water splitting is usually considered one of the most efficient methods for producing high-purity hydrogen gas. This process involves two half-cell reactions: the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. The theoretical thermodynamic potential for this process is 1.23 V, which corresponds to a minimum energy input of $\Delta G = 237.1 \text{ kJ mol}^{-1}$ under standard conditions. However, the catalytic performance of the electrocatalyst at the anode for oxygen generation and the cathode for hydrogen generation often significantly impacts the efficiency of electrocatalytic water splitting. If the activity of the electrocatalyst is low, a substantial potential difference will be needed to initiate the water-splitting reaction. As a result, the low activity of the electrocatalyst will result in higher energy consumption, significantly reducing the efficiency of converting electricity into hydrogen energy. This contradicts the zero-emission requirement of green energy. Therefore, considerable effort has been focused on developing efficient electrocatalysts for water splitting. To assess the performance of the catalyst, it is important to consider key parameters such as

overpotential, current density, and stability (Figure 1-2).⁴

Overpotential (η) is a crucial parameter in the analysis of electrocatalysts, defined as the potential difference between the potential at a specific current density and the thermodynamic potential of the reaction. According to the Nernst equation, the Nernst potential of a reaction is referenced to the normal hydrogen electrode (NHE), with the value being zero for hydrogen evolution. However, in reality, an overpotential is required to overcome kinetic barriers caused by factors such as low catalyst energy efficiency and high activation energy. This excess potential is needed to start the reaction, resulting in the potential required to reach the corresponding current density often not being zero.

The current density is a crucial parameter for evaluating catalyst performance since it directly affects the rate of electrocatalytic oxygen and hydrogen evolution. A high current density can accelerate the production of oxygen and hydrogen in an electrolyzer, improving the efficiency of industrial hydrogen production. However, recent research has shown that many electrocatalysts exhibit a current density of less than 500 mA cm⁻². Especially in industrial applications aiming for high efficiency, it is crucial to utilize a high current density to achieve rapid hydrogen production. Current densities exceeding 500 mA cm⁻² are often necessary.⁵

The durability of an electrocatalyst is crucial for its practical application in catalytic water splitting and should be verified through long-term stability testing. Generally, stability can be examined using several main methods: (1) repeated cyclic voltammetry (CV), (2) linear sweep voltammetry (LSV), and (3) galvanostatic and potentiostatic tests. The first two techniques involve measuring the polarization curve of the catalyst after a certain number of cycles (e.g., 1000 runs, 10,000 runs, etc.). If the overpotential remains similar to the initial polarization curve after multiple potential cycles, it confirms the required stability of the electrocatalyst. With regard to stability testing, galvanostatic and potentiostatic methods are considered the best ways, as they can intuitively determine whether the catalytic performance of the reaction catalyzed by long-term operation at various current densities is decayed. They are measured by a fixed current density or a

fixed overpotential method during the test. For instance, the hydrogen evolution reaction was tested at a current density of 100 mA cm⁻² for over 100 hours without any significant decay in overpotential.



Figure 1-2. Schematic illustration of the water splitting electrolyzer and related reaction kinetics. Ref. [4]; Copyright 2019; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1-3. Electrocatalysts for HER

Hydrogen is produced through electrocatalytic water splitting, driving researchers to seek electrocatalysts with low overpotential to reduce energy consumption effectively. In principle, the HER is a two-electron transfer process, and its pathway is always different depending on whether the medium is an acidic or alkaline electrolyte. In addition, in different media, the reaction pathways include two possible pathways: the Volmer–Heyrovsky pathway and the Volmer–Tafel pathway.

In acidic electrolytes, the first step of the HER involves the adsorption of protons on the surface of the electrocatalyst. These protons then gain electrons, resulting in the generation of hydrogen radicals. Subsequently, the reaction pathway branches into two processes: the Volmer–Tafel pathway, which directly combines two hydrogen radicals to produce H_2 , and the Volmer–Heyrovsky pathway, wherein another hydrogen ion gains electrons to form additional hydrogen radicals. These additional radicals then combine with existing hydrogen radicals to ultimately generate H_2 (Figure 1-3 (a)).

In contrast to the HER in acidic solution, HER in alkaline electrolyte is more challenging. This is because it requires more energy to break down water molecules and obtain hydrogen atoms to form hydrogen radicals. In alkaline electrolyte, the initial step of HER is the Volmer reaction, where water adsorbed on the surface of electrocatalyst gains electrons, decomposing water into hydrogen radicals and hydroxyl ions. Subsequently, the reaction path divides into two processes, similar to acidic conditions. One is the Tafel pathway, directly combining two hydrogen radicals to generate H_2 . The other is the Heyrovsky pathway, where another water molecule splits by gaining electrons to form additional hydrogen radicals. These radicals then combine with existing hydrogen radicals to produce H_2 (Figure 1-3 (b)).

Regardless of the different pathways for HER in acidic and alkaline solutions, the adsorption energy of hydrogen radicals (H*) on the catalyst surface is crucial, since both pathways involve the adsorption of H*. Usually, the HER suffers from sluggish kinetics owing to the low adsorption/desorption rates of reactants, intermediates, and products to/from the surface of the catalyst. In electrocatalytic HER processes, the adsorption and desorption balance of hydrogen radicals on the catalyst surface determines the progress of the hydrogen evolution reaction, and the free energy approaches zero can just balance the adsorption and desorption of hydrogen radicals on the catalyst surface and the H* combines easily to form hydrogen, so this is an optimal state. Otherwise, when the catalyst has a large negative free energy, it will cause the catalyst surface to have a strong adsorption capacity for hydrogen radicals, resulting in the fact that even if the hydrogen ions form hydrogen radicals to be unable to couple with each other to form hydrogen

molecules. Nevertheless, when the catalyst has a large Gibbs free energy, hydrogen ions are not easily adsorbed on the surface of the catalyst, thus directly blocking the reaction.



Figure 1-3. Schematic illustration of HER (a) in acid and (b) alkaline media, where * represents the catalytic reaction site on the catalysts.

Generally, Platinum, as the state-of-the-art catalyst for HER, is usually employed for water splitting due to its very low overpotential and fast kinetics. Nevertheless, its high price and uneven distribution of reserves impede its further large-scale use, which prompted the search for cheaper and efficient catalysts. Additionally, for water electrolysis in alkaline conditions, even platinum, also shows a magnitude lower activity compared with the acidic medium. Therefore, considerable efforts have been dedicated to developing affordable, highly efficient catalysts for hydrogen production in both acidic and alkaline environments. One promising approach is the preparation of Pt-based nanocatalysts, which involves reducing the size of Pt active sites to enhance catalyst activity and decrease the amount of Pt used, making it a cost-effective option for electrocatalyst preparation. Wang L. et al reported that anchoring platinum-clusters onto two-dimensional fullerene nanosheets exhibits 12 times higher intrinsic activity for alkaline HER than the state-of-the-art platinum/carbon black catalyst (Figure 1-4 (a)).⁶ Li F. et al also reported that Pt/C60 catalysts with high-loading, high-dispersion single-atomic platinum anchored on C₆₀ are achieved through a room-temperature synthetic strategy, which exhibits high HER catalytic performance with a low overpotential (η_{10}) of 25 mV at 10 mA cm⁻² (Figure 1-4 (b)).⁷ As mentioned above, established Pt-based catalysts always focus on decreasing platinum size and loading it onto a suitable substrate to achieve a highly active catalyst at a low price. Additionally, compared with the highpriced platinum raw material, ruthenium with a relatively low price has attracted great attention, which is a most promising alternative to substitute Pt for electrocatalytic HER due to its strong affinity of *H and *OH intermediates. Xu Q. et al developed an ordered microporous structure of N-doped nanoporous carbon with ultrafine Ru nanoclusters for efficient HER via the thermal pyrolysis of ordered microporous single crystals of ZIF-8 accommodating Ru (III) ions (Figure 1-4 (c)).8



Figure 1-4. (a) Synthesis illustration, morphology characterization and HER performance of Pt/C_{60} catalysts with high-loading, high-dispersion single-atomic platinum anchored on C₆₀. Ref. [6]; Copyright 2023; Springer nature publishing group. (b) Synthesis illustration, morphology characterization and HER performance of PtC_{60} . Ref. [7]; Copyright 2023; Springer nature publishing group. (c) Synthesis illustration, morphology characterization and HER performance of N-doped nanoporous carbon anchored with the ultrafine Ru nanoclusters. Ref. [8]; Copyright 2023; Wiley-VCH GmbH.

1-4. Electrocatalysts for OER

In water splitting, the oxygen evolution at the anode often becomes the main obstacle limiting efficient water splitting due to the sluggish reaction kinetics caused by its fourelectron transfer characteristics ($4OH^- \rightarrow 2H_2O + O_2 + 4e^-$). Because of this, the OER at the anode has become a bottleneck for the industrialization of water-splitting electrolyzers due to its high thermodynamic cost (237 kJ mol⁻¹), which leads to a large amount of overpotential and energy loss in the water splitting process.

The OER mechanism involves three intermediate steps (HO*, O*, HOO*), and the entire oxygen evolution reaction is a four-electron transfer process. Therefore, the complex reaction pathway leads to depressed reaction kinetics. In an acidic electrolyte, the H₂O molecule first adsorbs onto the active site of the catalyst and loses an electron, forming an adsorbed hydroxyl radical (HO*). The HO* then loses an electron and forms H⁺, creating O*. Next, the oxygen atom reacts with another water molecule to produce a hydroperoxyl radical (HOO*). Finally, the HOO* is oxidized to generate O₂ through an electron transfer process (Figure 1-5 (a)). In alkaline media, hydroxide ions (OH⁻) adsorb on the active sites of the catalyst and then lose an electron to form a free radical HO*. Subsequently, HO* combines with an OH⁻ to generate a free radical O* and an H₂O molecule. The free radical O* then reacts with another OH⁻ to form HOO*. Finally, HOO* combines with an OH⁻ to form O₂ and H₂O. Nevertheless, whether in acidic or alkaline conditions, in the entire reaction, the adsorption of HO- from the solution to produce HO* on the catalyst surface and the generation of adsorbed HOO* are two key processes of OER (Figure 1-5 (b)).



Figure 1-5. Schematic illustration of OER in (a) alkaline and (b) acid media, where * represents the catalytic reaction site on the catalysts.

In the recent study, RuO₂ and IrO₂ are known for their good catalytic activities for OER, but they are often limited by their unevenly distributed reserves and high cost. Additionally, the OER performance of RuO₂ and IrO₂ does not always satisfy the requirements for efficient oxygen evolution and long-term stable operation at high current density. Therefore, it is essential to minimize the use of precious metals and improve the activity and stability of the catalysts to reduce the production cost. In order to achieve efficient electrocatalytic oxygen release, significant effort has been dedicated to tuning the electron density of RuO₂ by heteroatom doping to regulate its adsorption energy for intermediates. *Wu Z. et al* reported the development of Rh doping in RuO₂ lattice on graphene (Rh-RuO₂/G) for efficient OER using an ion-exchange adsorption strategy. They utilized graphene oxide (GO) as the confined oxygenation template, which resulted in oxygen vacancy sites (O_V) for compensating the effective negative charge of doped low-valent cations. The presence of numerous O_V is crucial for enhancing the activity.

This is due to the fact that the center of the O 2p band is close to the Fermi level. This proximity facilitates charge transfer and leads to a reduction in the energy barrier for the reaction (Figure 1-6 (a)).⁹ Besides, *Zhang T. et al.* also describe an electrochemical lithium intercalation method to enhance both the activity and stability of RuO₂ for the acidic oxygen generation. In this method, lithium intercalates into the interstices of the RuO₂ lattice, donates electrons, and distorts the local structure. As a result, the valence state of Ru is reduced, leading to the formation of a stable Li-O-Ru local structure. This reduces the Ru-O covalency, which in turn prevents the dissolution of Ru, resulting in significantly improved durability. Additionally, the lattice strain causes surface structural distortion in Li_xRuO₂, activating the dangling O atom near the Ru active site as a proton acceptor. This stabilizes the OOH* and greatly enhances the activity (Figure 1-6 (b)).¹⁰

To construct highly active ruthenium-based OER electrocatalysts, previous research has demonstrated that forming alloy catalysts by combining ruthenium with other metals is an effective approach. Alloy catalysts can regulate the adsorption capability of intermediates, leading to enhanced catalytic activity. *Lee J. et al.* described the development of atomically thin amorphous RuM (M=Co, Fe, or Ni) bimetallenes as efficient electrocatalysts for OER, surpassing the performance of RuO₂ benchmark catalysts (Figure 1-6 (c)).¹¹

Besides, it is important to establish non-precious metal-based OER catalysts to reduce preparation costs. Transition metal oxides are considered an excellent choice for highperformance catalysts, due to their abundant raw materials and potential for oxygen evolution. *Ma J. et al* report a cobalt oxide incorporated with iridium single atoms (Ir-Co₃O₄) by a mechanochemical approach. During OER processes, the Ir atoms are partially oxidized to active Ir>4+, meanwhile Ir and Co atoms with their bridged electrophilic O ligands acting as active sites. Theoretical calculations further disclose the isolated Ir atoms can effectively boost the electronic conductivity and optimize the energy barrier. As a result, Ir-Co₃O₄ exhibits significantly higher mass activity and turnover frequency than those of benchmark IrO₂ in acidic conditions. The research highlights the concept of constructing single noble metal atoms incorporated cost-effective metal oxides catalysts for practical applications (Figure 1-6 (d)).¹²



Figure 1-6. (a) Synthesis illustration, morphology characterization and OER performance of Rh-RuO₂/G nanosheets. Ref. [9]; Copyright 2023; Springer nature publishing group. (b) Synthesis illustration, morphology characterization and OER performance of Li_xRuO₂. Ref. [10]; Copyright 2022; Springer nature publishing group. (c) Synthesis illustration, morphology characterization and OER performance of Ru-Co bimetallenes. Ref. [11]; Copyright 2023; Wiley-VCH GmbH. (d) Model, structural characterizations and OER performance of Ir-Co₃O₄. Ref. [12]; Copyright 2022; Springer nature publishing group.

1-5. Bifunctional OER/HER electrocatalysts

Water splitting involves two half-reactions: HER at 0 V and OER at 1.23 V, with a total thermodynamic potential of 1.23 V. In practical industrial applications, the water-splitting electrolyzers operating at ambient conditions, offer promising and flexible feasibility for water splitting to produce hydrogen. However, considering the sluggish

kinetics of both OER and HER, in order to improve the energy conversion efficiency for hydrogen generation, electrocatalytic water splitting is usually conducted in either acidic or alkaline solution to reduce solution resistance, and advanced electrocatalysts like Ptbased materials for HER and Ru/Ir-based oxides for OER are used to accelerate the reaction kinetics.

Generally, OER with four-electron transfer needs higher overpotentials than twoelectron HER even catalyzed by commercial RuO2 and IrO2 benchmarks, accountable for the main electricity consumption. Alkaline conditions are favorable to OER, and acidic electrolytes are conducive to HER. Consequently, most of the early research focuses on developing high-performance OER or HER electrocatalysts in acidic or alkaline electrolytes, respectively. However, this difference in electrolytes for OER and HER is not suitable for practical water electrolysis, wherein the same electrolyte at both cathode and anode is preferred. Although recent studies have developed alkaline HER electrocatalysts or acidic OER electrocatalysts to couple with counter electrodes for overall water splitting. However, the preparation of monofunctional (OER or HER) electrocatalysts requires different precursors, equipment, and/or procedures for separate synthesis, electrode assembly, and device fabrication, thus increasing the overall cost. Furthermore, in view of the harsh conditions during water splitting electrolysis (e.g., extreme pH, high potential, and long-term service), the reconstruction of electrocatalysts (e.g., leaching) is inevitable, which would result in severe cross-contamination between the two electrodes with different components. It is anticipated that this crosscontamination issue can be resolved by using the same materials for both OER and HER electrocatalysts.¹² In this regard, developing highly active, stable, and cost-effective bifunctional electrocatalysts with both high OER and HER activities in the same electrolyte are particularly desirable for practical applications, as it would simplify the electrocatalysts synthesis, electrodes fabrication and thus reduce the overall cost (Figure 1-7). Additionally, using the same composites for bifunctional electrocatalysts would help alleviate the issue of cross-contamination resulting from electrocatalyst reconstruction

during long-term operation.



Figure 1-7. Schematic diagram of (a) monofunctional and (b) bifunctional electrocatalysts for OER/HER.

In the pursuit of developing bifunctional OER/HER catalysts, many previous reports have been about integrating two active sites into one catalyst to achieve bifunctional catalysis, such as different components acting as reaction sites for hydrogen and oxygen evolution, respectively (Figure 1-8 (a)). Wang L. et al. proposed an approach using density functional theory (DFT) pre-analysis to manipulate electron redistribution in Ni₂P. This was achieved through cation doping and vacancy engineering. The needle-like Fe-doped Ni_2P with a P vacancy (Fe-Ni₂P_v) was successfully synthesized on nickel foam, exhibiting superior bifunctional catalytic activity for the OER and HER in alkaline seawater condition. Moreover, the DFT calculation predicts that the Ni atom on the surface of (Fe)NiOOH/Fe-Ni₂P_v is the active site for OER, and the Fe atom on the Fe-Ni₂P_v surface is the most active site for HER. (Figure 1-9 (a)).¹³ However, the preparation process of bifunctional OER/HER catalyst with dual active sites is complicated because it is not easy to control the component content during preparation, as it involves two different active sites within one catalyst. In contrast, achieving efficient OER/HER simultaneously at one single active site within the catalyst is more efficient, and it also alleviates the difficulty of controlling the component content during the preparation process. Moreover,

considering the influence of catalyst substrates on active sites, selecting a suitable substrate to establish metal-support interaction is crucial for obtaining efficient and corrosion-resistant water-splitting catalysts (Figure 1-8 (b)). *Yuan C. et al.* discovered that the interaction mechanism between Ru nanoparticles and titanium oxides (Ti₄O₇) (Ru/Ti₄O₇) takes advantage of the unique band structure, high conductivity and chemical stability. This interaction leads to an ingenious metal-support interaction through interfacial Ti–O–Ru units, which stabilize Ru species during OER and trigger hydrogen spillover to accelerate HER kinetics (Figure 1-9 (b)).¹⁴



Figure 1-8. Schematic diagram of bifunctional OER/HER catalysts with (a) two active sites and (b) one active site.



Figure 1-9. (a) Schematic diagram of the synthesis and OER/HER performance of Fe- Ni_2P_v . Ref. [13]; Copyright 2023; Wiley-VCH GmbH. (b) Synthesis description,

characterization and electrocatalytic performance diagram of Ru/Ti₄O₇. Ref. [14]; Copyright 2024; Springer nature publishing group.

1.6. Electrocatalysis at ampere-level current densities

While significant progress has been made in developing catalysts with high catalytic performance, it is crucial that a water splitting electrocatalyst intended for practical use be highly active and stable at large current densities (at least 500 mA cm⁻²) over an extended period. Most reported electrocatalysts perform well only at low current densities (typically below 200 mA cm⁻²) and have limited stability. The development of a highly active catalyst to enhance the OER/HER performance at large current densities and the understanding of the corresponding mechanism is of great significance but has been rarely explored. Wang A. et al. discovered that it creates three different hetero interfaces by attaching ultrafine Ru nanoparticles to various MoO_x nanotube (NT) substrates, such as MoO₂, MoO₂/MoO₃, and MoO₃. Specifically, MoO₂@Ru NT exhibits excellent HER activity with high current densities of 1000 mA cm⁻². Both experimental observations and theoretical calculations indicate that a moderate electron transfer from Ru to MoO2 enhances the water dissociation kinetics and optimizes the hydrogen adsorption/desorption, thereby accelerating the HER kinetics (Figure 1-10 (a)).¹⁵ Mu S. et al. found that by manipulating the dynamic microstructure of bimetallic phosphide NiCoP-120, they were able to create a unique multiscale hierarchical structure. This structure ranges from 3D-nickel foam substrates to 2D-nanosheets and down to 1Dnanoneedles. This structure allows for efficient use of active sites and rapid gas release, resulting in excellent electrocatalytic performance and stability essential for industrial applications (Figure 1-10 (b)).¹⁶



Figure 1-10. (a) Synthesis illustration, morphology characterization and HER performance of MoO₂@Ru nanotube. Ref. [15]; Copyright 2023; Wiley-VCH GmbH. (b) Schematic diagram of the synthesis and OER/HER performance of NiCoP-120. Ref. [16]; Copyright 2023; Wiley-VCH GmbH.

1-7. Motivation and objectives

To date, although many excellent monofunctional OER or HER electrocatalysts have been developed, the optimal operating conditions in the electrolyte are not always the same for different catalysts, so many researchers have devoted themselves to developing electrocatalysts with bifunctional OER/HER. In addition, bifunctional catalysts have the advantage of reducing the cost of synthesis and manufacturing. Actually, despite the considerable effort that has been devoted to developing highly active electrocatalysts for OER and HER, the current density of most reported catalysts is often limited to less than 500 mA cm⁻². Besides, their stability tests are often limited to measurements at low current densities (usually 10 mA cm⁻² or 100 mA cm⁻²), which often cannot meet the requirements of actual high current density operation and are still far from the stringent requirements of actual application. Therefore, to overcome the above challenges, developing electrolytic water catalysts with bifunctional OER/HER for industrial applications is very challenging. In addition to improving the intrinsic catalytic activity through electronic structure modulation, it is more important to design a reasonable structure to reduce the adhesion between substantial bubbles rapidly generated at large-current-density and catalyst surfaces. This ensures the full utilization of active sites and rapid mass transfer/diffusion of reactants, avoiding the shedding and activity decrease of catalysts caused by gas bombardment.

Understanding the intrinsic catalytic mechanism and real active sites of these catalysts will benefit the rational design and application of high-efficiency catalysts. Based on the above discussion, previously advanced oxygen and hydrogen evolution catalysts usually have active sites at the nanoscale, such as nanosheets, nanoclusters or nanoparticles, to expose more active sites for electrocatalysis. Besides, the catalytic activity of active sites is significantly influenced by the metallic crystal structures they are composed of, as well as the chemical environment surrounding the active crystals and the exposed crystal faces. Exposing highly active crystal faces is conducive to achieving rapid oxygen and hydrogen evolution reactions at low overpotentials because they have more optimal adsorption sites for the adsorption and desorption of reaction intermediates. The chemical environment of the active sites, such as the stable catalyst substrate used to support the active sites, has a strong interaction with the active sites and can regulate the adsorption capacity of reaction intermediates by regulating the electron cloud density, thereby improving the catalytic performance.

The aim of this thesis is to develop novel electrocatalysts based on ruthenium, platinum, and cobalt oxide (Co_3O_4) for OER and HER at ampere-level currents with ultralow overpotentials. The selection of these transition metals is based on specific criteria. Ruthenium is relatively cost-effective and has moderate binding with reactive OER/HER intermediates, as well as decent corrosion resistance. Platinum has a favorable hydrogen adsorption energy for HER. Cobalt is advantageous due to its low cost, high abundance, variety of oxidation states, 3 unfilled d-orbitals, and moderate absorption/desorption of reactants (Figure 1-11).^{2, 17, 18} In this thesis, the electrocatalysts

are achieved through optimizing crystal facets, modifying catalyst surfaces, and bonding active sites with substrates (Figure 1-12). This thesis systematically studies the characterization, performance and catalytic mechanism of the catalysts.

In chapter 1, the mechanism of electrocatalytic water splitting was systematically described, the current status of catalyst research, the challenges faced, and explain the significance and objectives of this research. In Chapter 2, the background of the ruthenium-based catalyst for electrocatalysis is presented first. The practical applications of bifunctional ruthenium-based OER/HER electrocatalysts with two active sites of Ru nanoparticles covered with RuO₂ skins are limited. One reason is the presence of multiple equally distributed facets, some of which are inactive. In contrast, ruthenium nanorods with a high aspect ratio have multiple unequally distributed facets containing the dominance of active faces for efficient electrocatalysis. However, the synthesis of ruthenium nanorods has not been achieved due to difficulties in controlling the growth. Additionally, it is known that the adsorption capacity of intermediates can be impacted by the surface of the catalyst. Inspired by these backgrounds, the surface-modified (SM) ruthenium nanorods having a dominant active facet of hcp (100) through chemisorbed oxygen and OH groups (SMRu-NRs@NF) are rationally synthesized through the surfactant coordination method. The SMRu-NRs@NF exhibits excellent hydrogen evolution in acid and alkaline solutions with an ultra-low overpotential of 215 mV and 185 mV, reaching 1000 mA cm⁻², respectively. Moreover, it has also shown brilliant oxygen evolution electrocatalysis in the alkaline solution with a low potential of 1.58 V to reach 1000 mA cm⁻². It also exhibits high durability over 143 h for the evolution of oxygen and hydrogen at 1000 mA cm⁻². Density functional theory (DFT) studies confirmed that surface modification of ruthenium nanorod with chemisorbed oxygen and OH groups can optimize the reaction energy barriers of hydrogen and oxygen intermediates. The surface-modified ruthenium nanorods strategy paves a path to develop the practical water-splitting electrocatalyst.

In Chapter 3, the background of the platinum-based catalyst for electrocatalysis is

presented initially. Platinum nanoparticles loaded on nitrogen-doped carbon nanotube exhibit brilliant HER in an alkaline solution, but its bifunctional OER/HER has not been reported due to the lack of strong Pt-C bond. In this part, platinum nanoparticles bonded in carbon nanotube (Pt-NPs-bonded@CNT) with strong Pt-C bonds are designed towards ultra-low overpotential water splitting ability in alkaline solution. During the synthesis process, the carbon nanotubes are employed as the substrate, and surface oxygencontaining groups of carbon nanotubes are modified by strong acid treatment, causing defects on the surface to capture platinum atoms, thereby promoting the embedding of platinum nanoparticles on the surface of carbon nanotubes. As a result, the Pt-NPsbonded@CNT exhibits excellent hydrogen evolution in acid and alkaline solutions with an ultra-low overpotential of 0.19 V and 0.23 V to reach 1000 mA cm⁻², respectively. Besides, it shows superior oxygen evolution electrocatalysis in the alkaline solution with a low overpotential of 1.69 V at 1000 mA cm⁻². Furthermore, it also exhibits high stability over 110 h against the evolution of oxygen and hydrogen under 1000 mA cm⁻². The exceptional performance arises from the strong interaction between platinum and highly conductive carbon nanotube substrates via the Pt-C bond. Additionally, the platinum nanoparticles bound to carbon nanotubes can offer more stable active sites. This strategy paves the way for the high performance of bifunctional electrocatalytic reaction with extraordinary stability originating from the optimized electron density of metal active sites due to strong metal-substrate interaction.

In Chapter 4, I first review the current research status of Co_3O_4 -based electrocatalysts for OER. Co_3O_4 is an attractive catalyst for OER because of its low cost and potential OER activity. However, the OER performance of previously reported Co_3O_4 nanoparticles is insufficient for ampere-level current. The reason is the lack of covalent bonds between Co_3O_4 nanoparticles and the substrate, which leads to a high electron transfer energy barrier. In this chapter, the Co_3O_4 nanoparticles supported on the layered titanium dioxide (TiO₂) surface (Co_3O_4 @layered-TiO₂) by Co-O-Ti covalent bond are carefully constructed through the MXene precursor method. TiO₂ was selected as the substrate for loading active sites due to its exceptional chemical stability and durability. As a result, the Co₃O₄@layered-TiO₂ exhibits brilliant OER performance with ultra-low potential (1.52 V to reach 100 mA cm⁻²), ampere-level current density (1.66 V to reach 1000 mA cm⁻²) and long-term durability (110 h at 500 mA cm⁻²). DFT studies have confirmed that the Co-O-Ti covalent bond can adjust the d band center to optimize reaction energy barriers. This result illuminates a new strategy for constructing highly active materials on the metal oxide substrate for efficient electrocatalysis.

In chapter 5, the thesis is summarized and a prospect for the future of electrocatalytic water splitting is provided.



Figure 1-11. Advantages of selecting these transition metals.



Figure 1-12. Content illustration of chapter 2, chapter 3 and chapter 4.

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Chapter 2: Surface-Modified Ruthenium Nanorods for Ampere-Level Bifunctional OER/HER Electrocatalyst

2.1. Introduction

Electrocatalytic water splitting based on OER and HER is a critical technology to solve the problem of fossil energy substitution.¹⁻⁴ However, the optimal operating conditions in the electrolyte are not always the same for different catalysts, so many researchers have devoted themselves to developing electrocatalysts with bifunctional OER/HER.⁵⁻⁷ In addition, bifunctional catalysts have the advantage of reducing the cost of synthesis and manufacturing.⁸⁻¹¹ Among various metals, ruthenium is considered a promising candidate for simultaneous bifunctional OER/HER due to its strong affinity for OER and HER intermediates.¹²⁻¹⁴ However, ruthenium consistently exhibits monofunctional HER catalytic performance in the reported articles, while their OER ability is poor due to the strong adsorption of intermediates. In contrast, ruthenium oxide exhibits monofunctional OER catalytic activity, whereas its HER ability is absent due to weak adsorption of intermediates. To construct bifunctional OER/HER electrocatalysts, it was previously reported that combining two active sites of Ru nanoclusters with sub-nanometer RuO₂ skin for bifunctional OER/HER, which can simultaneously inherit the high HER activity of Ru and the superior OER activity of RuO₂ skins.¹⁵ However, two drawbacks exist: the operating current density has not reached industrial levels, and the manufacturing process is complex, involving two different active sites in one catalyst. Therefore, it is very important to realize the easy synthesis of ampere-level bifunctional OER/HER ruthenium-based electrocatalysts with a single active site for industrial-scale catalysis.

To realize industrial-level bifunctional OER/HER, factors affecting catalytic activity, such as crystal facets and catalyst surface, must be considered. Firstly, since different crystal facets have different adsorption energies for intermediates due to various surface work functions, the exposed crystal faces of the catalyst significantly impact the catalytic activity. The catalytic activity of ruthenium nanoparticles is limited due to the equally

distributed multiple crystallographic facets.¹⁶⁻¹⁸ In previous work, a hexagonal-closedpacked (hcp)-Ru nanocrystal coated with a thin layer of N-doped carbon was fabricated for HER through the thermal annealing of polydopamine-coated Ru nanoparticles.¹⁹ However, its catalytic performance could not satisfy ampere-level current density. In contrast, the ruthenium nanorod structure with a high aspect ratio, having unequally distributed facets, is promising for efficient electrocatalysts due to the dominance of highly active crystal faces.^{20, 21} Wan et al. reported that oleic acid capped NaYF₄ have a nanorod structure through solvothermal reaction, with the nanorod arranged along the (100) crystal plane.²² Furthermore, there have been reports of metal nanorods such as gold nanorods and Au/Cu metal alloy nanorods, boosted by surfactant coordination to promote nucleation.^{23, 24} Notwithstanding the extensive research dedicated to creating nanometersized metallic nanorods, achieving ruthenium nanorod structures for efficient electrocatalysis remains a challenge that has not yet been overcome. Secondly, the chemical environment on the catalyst surface significantly influences the adsorption of intermediates by altering the electronic structure of the catalyst, thus playing a crucial role in reducing overpotential for efficient electrocatalysis.²⁵ Previous work shows that stably adsorbed OH group at the Mo site of intermetallic IrMo electrocatalyst supported on carbon nanotubes (IrMo/CNT) can stabilize the water dissociation product, resulting in excellent HER performance in alkaline solution.²⁶ It has been proven that the adsorption of hydroxyl groups on the surface of the catalyst can improve its catalytic activity. Based on the above discussion, achieving efficient ampere-level bifunctional electrocatalysts through a single active site by establishing highly active facet-dominated ruthenium nanorods with rational surface modification remains unexplored.

In this work, a strategy involving the surface modification of ruthenium nanorods is proposed. The surface-modified ruthenium nanorods, with a length of less than 10 nm and facets dominated by (100) and (002), are covered by chemisorbed oxygen and OH groups. These nanorods were grown on the surface of nickel foam (SMRu-NRs@NF) using a surfactant coordination method. In the synthesis process, the coordination of ruthenium ions and terephthalic acid might boost the formation of ruthenium nanorods (Figure 2-1). As a result, the SMRu-NRs@NF exhibits excellent bifunctional OER/HER performance with ultra-low overpotential. Furthermore, it also exhibits ultra-durable water splitting capability under practical conditions. The density functional theory (DFT) simulations demonstrate that the ruthenium nanorod modified by chemisorbed oxygen and OH groups exhibit the optimal adsorption and desorption of hydrogen radicals and water. In addition, it can reduce the energy barrier for OER process.



Figure 2-1. Schematic illustration of the synthesis process of ruthenium nanorods modified by chemisorbed oxygen and OH groups (SMRu-NRs@NF) towards OER/HER.

2.2. Experimental

2.2.1. Preparation of SMRu-NRs@NF

Nickel foam treatment: A piece of nickel foam was sonicated in a 4.0 M HCl solution for 10 minutes, then washed three times with deionized water to remove residual hydrochloric acid. The Ni foam was dried in the air after being sonicated in acetone and ethanol for 10 minutes. Preparation of SMRu-NRs@NF: RuCl₃ · xH₂O (1.5 mmol, 311.145 mg) and terephthalic acid (4.0 mmol, 11.825 g) as a surfactant were dissolved in a mixed solvent containing deionized water (26 mL), ethanol (2 mL) and dimethylformamide (DMF) (2 mL) by ultrasonication. A piece of per-cleaned Ni foam in the mixture solution was heated at 180 °C for 24 h in a Teflon-lined stainless-steel autoclave. The product (SMRu-NRs@NF) was dried in a vacuum oven at 60 °C for 12 hours followed by washing with ethanol and deionized water. For the synthesis of surface modified ruthenium nanoparticles on the nickel foam (SMRu-NPs@NF), benzoic acid was used as surfactant, except other conditions are unchanged from the conditions of ruthenium nanorods.

2.2.2. Materials Characterization

The macroscopic morphology of the sample was investigated by scanning electron microscopy (JEOL, JSM-5900LV). Micromorphology measurements such as selective area electron diffraction (SAED) and energy dispersive X-ray (EDX) were investigated by transmission electron microscopy (TEM) (JEOL, JEM2010). X-ray diffraction (XRD) spectra were obtained using a D/Max-III X-ray spectrometer (Panalytical, Philips X'Pert Pro) with Cu K α radiation in the 2 θ range of 5° to 80°. X-ray photoelectron spectroscopy (XPS) was used to examine electron energy dispersive spectroscopy (Thermo Fisher Scientific, Escalab 250Xi).

2.2.3. Electrochemical Measurement

The electrochemical performance tests of all catalysts were performed on an electrochemical workstation (Solartron, SI1287) using a three-electrodes system. The electrolyte used in all tests under alkaline and acid conditions was 1.0 M KOH and 0.5 M H₂SO₄ solution, respectively. During the HER and OER tests, a graphite electrode served as the counter electrode. An Ag/AgCl electrode was used as the reference electrode in acidic solutions, while an Hg/HgO electrode was used in alkaline solutions. The SMRu-NRs@NF electrode obtained by hydrothermal reaction is directly used as the working electrode, and the area of the electrode immersed in the electrolyte is 0.5×0.5 cm². The reference electrode was obtained by uniformly dropping 5 mg of Pt-C (Pt: 20 wt%) catalyst dispersion (500 µL water, 450 µL isopropyl alcohol and 50 µL Nafion solution (5%)) on the surface of the nickel foam electrode. Polarization curves were measured by linear sweep voltammetry (LSV) at a sweep rate of 5 mV s⁻¹. All obtained LSV curves were corrected with 90% iR compensation. The stability of the measurement electrodes was assessed using a potentiostat, and the electrolyte was renewed daily. The electrochemical impedance spectroscopy (EIS) test involved applying a voltage of five millivolts amplitude in the frequency range from 10000 to 0.1 Hz. The potential relative to a reversible hydrogen electrode (RHE) under alkaline conditions was calculated as $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times pH$. The formula $E_{RHE} = E_{Ag/AgCl} + 0.198 + 0.0591 \times pH$. pH is used to convert the test potential into a potential of RHE under acidic conditions. The Tafel slope (b) is determined by the equation $\eta = b \times \log |j| + a$, where η represents the potential and *j* is the current density. The electrochemical double layer capacitance (C_{dl}) is determined through cyclic voltammetry (CV) measurements at various scan rates, using a voltage range of -0.7 V to -0.9 V versus $E_{Hg/HgO}$.

2.2.4. Calculation Methods

The DFT calculations were performed by the CASTEP simulation package software (BIOVIA, Materials Studio). The interactions between ion cores and valence electrons

were described by the projector augmented wave (PAW) method. The exchangecorrelation interaction was set as generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functional.²⁷⁻²⁹ The energy cutoff for plane wave expansion was set to 500 eV for geometry optimization and energy calculations of the lattice cells. The Gaussian smearing method and a width of 0.05 eV are applied to the partial occupancies of the Kohn-Sham orbitals. Besides, convergence values of geometry optimization and energy change were set as 10^{-5} eV and 0.03 eV Å⁻¹, respectively. The convergence accuracy of the electronic step is 10^{-7} eV. The surface model was constructed based on the single crystal of hcp Ru by constructing a $3 \times 3 \times 2$ supercell and then cleaving its (100) crystal plane for surface modification. The surface of the hcp Ru (100) crystal face was modified with two appropriate modifications to correspond to the characterized results, the internal atoms are constrained, namely four pairs of lattice oxygen and hydroxyl groups attached to the surface. A vacuum of 20 Å thickness is added in the Z direction to avoid spurious interactions between periodic lattices. By optimizing the structure of the model, the final enthalpy is obtained, and the adsorption energy is calculated. Finally, the adsorption energies (E_{ads}) were calculated as $\Delta E_{ads} = E_{ad/sub} - E_{ad}$ $-E_{sub}$, where $E_{ad/sub}$, E_{ad} , and E_{sub} are the final enthalpy of the optimized adsorbate with substrate system, adsorbate, and substrate, respectively.³⁰ Calculate free energy (ΔG) using the following equation:

 $\Delta G = \Delta E_{ads} + ZPE - T\Delta S$

Where ZPE and $T \Delta S$ are zero-point energy and entropic contributions, respectively.

2.3. Results and Discussion

2.3.1. Structural Characterizations of Surface Modified Ruthenium Nanorods

Lattice defective oxygen and -OH groups modified ruthenium nanorods were conducted by a self-assembly strategy with hydrothermal through in-situ grown ruthenium nanorod crystals on the surface of Ni foam (SMRu-NRs@NF). During the synthesis process, terephthalic acid not only serves as a reducing agent but also promotes the formation of lattice defective oxygen and -OH groups modified ruthenium nanorods. Besides, the Ni foam serves as a substrate and promotes the reduction of Ru³⁺ during the hydrothermal process. After hydrothermal treatment with RuCl₃, terephthalic acid and Ni foam in a mixed solvent, ruthenium nanorod crystals are formed. The SEM images of SMRu-NRs@NF are shown in Figure 2-2, and it can be observed that highly dense ruthenium nanoparticles formed by ruthenium nanorods gathered together are formed on the surface of the nickel foam.



Figure 2-2. Different resolution SEM images of SMRu-NRs@NF.

To further confirm the component of ruthenium nanoparticles, in Figure 2-3 (a), the TEM image displays the crystalline morphology of ruthenium mostly is ruthenium nanorods shape and the compound of the ruthenium crystal was confirmed by SAED image (Figure 2-3 (b)). Additionally, the nanoparticles that appeared in SEM are formed by aggregate ruthenium nanorods together and then attach on the Ni foam surface, which

is confirmed by the same SAED images of nanorods and nanospheres (Figure 2-3 (c) and (d)).



Figure 2-3. (a) and (c). TEM images of SMRu-NRs@NF. (b) and (d). SAED patterns of SMRu-NRs@NF.

Furthermore, the SMRu-NPs@NF was prepared by a similar method except for a change of terephthalic acid to benzoic acid during hydrothermal. The SEM image can be observed that a large amount of amorphous structures are attached to the Ni foam (Figure 2-4).



Figure 2-4. Different resolution SEM images of SMRu-NPs@NF.

The crystal structure of the product through hydrothermal treatment with RuCl₃, terephthalic acid as surfactant, and Ni foam in a mixed solvent (ethanol, water and DMF) was investigated. The TEM image displays the crystalline morphology as sub-10 nm nanorods (6.8 nm in the longitudinal direction and 1.3 nm in the transverse direction.) (Figure 2-5 (a)). In addition, the nanoporous structure around the nanorods can provide an abundant active area so that the electrolyte can better penetrate the surface of the nanorods, leading to improved catalytic ability. High-resolution TEM image (HR-TEM) revealed that the lattice of ruthenium nanorod with a typical interplanar spacing of 0.214 nm is assigned to the (002) lattice plane of ruthenium crystal (Figure 2-5 (b)).³¹ The nanobeam electron diffraction pattern of the nanorod exhibits the (101), (100) and (002) diffraction spots of ruthenium, confirming hexagonal close-packed (hcp) ruthenium nanorods (Figure 2-5 (c)). The EDX elemental mapping images clearly show that Ru and Ni elements are uniformly distributed in the ruthenium nanorods (Figure 2-5 (g)). The reason for Ni contamination in the ruthenium nanorod is that the nickel foam serves as a reducing agent to convert Ru³⁺ ions to Ru during the hydrothermal process.¹³ Interestingly, compared with previously only reported ruthenium nanoparticles, this is the first report of ruthenium nanorods that have not yet been successfully prepared.²⁰⁻²² The XRD spectrum of ruthenium nanorods was matched well with ruthenium crystal (JCPDS No. 06-0663 (Ru)) (Figure 2-6 (a)). It exhibits no impurity peak such as ruthenium oxide, indicating the formation of high purity ruthenium. The XRD broad peak can be
deconvoluted into peaks at 38.4°, 42.1° and 44.0°, corresponding to the (100), (002) and (101) planes, respectively (Figure 2-6 (b)). This result is consistent with those of the nanobeam electron diffraction pattern (Figure 2-5 (c)). Besides, there are three sharp peaks appearing in HO-Ov-Ru NRs@NF, which correspond to the diffraction peaks of the nickel foam substrate (JCPDS No. 04-0850 (Ni)) (Figure 2-7). On the contrary, when benzoic acid is used as the surfactant, numerous aggregated nanoparticles are visible in the TEM image (Figure 2-5 (d)). Furthermore, the HR-TEM image revealed that nanoparticles exhibit poor crystallinity (Figure 2-5 (e)). The SAED pattern confirms the ruthenium nanoparticles and the blurred diffraction rings consists of (100), (002) and (101) facets (Figure 2-5 (f)). The EDX elemental mapping images show uniform distribution of Ru and Ni elements in the ruthenium nanoparticles (Figure 2-8). The XRD spectrum of ruthenium nanoparticles matched well with ruthenium crystal (JCPDS No. 06-0663 (Ru)) (Figure 2-9).



Figure 2-5. Surface structures. (a, b) TEM and HR-TEM images of ruthenium nanorods. (c) The nanobeam electron diffraction pattern of ruthenium nanorods. (d, e) TEM and HR-TEM of ruthenium nanoparticles. (f) The SAED pattern of ruthenium nanoparticles. (g) EDX mapping of ruthenium nanorods.



Figure 2-6. (a) XRD spectrum of ruthenium nanorods. The diffraction peak corresponds to the peak of ruthenium (Ru: 06-0663). (b) Deconvoluted XRD peaks.



Figure 2-7. XRD survey spectra of SMRu-NRs and SMRu-NRs@NF. The three sharp peaks in SMRu-NRs@NF correspond to the diffraction peaks of the nickel foam substrate (Ni: 04-0850).



Figure 2.8. EDX mapping images of Ru nanoparticles.



Figure 2.9. (a) XRD spectrum of ruthenium nanoparticles. The diffraction peak corresponds to the peak of ruthenium (Ru: 06-0663). (b) Deconvoluted XRD peaks.

The formation mechanism of ruthenium nanorods is speculated to be the coordination interaction between surfactant and ruthenium ions (Figure 2-10). Stevens *et al.* reported that the growth of gold nanorods (Au NRs) can be controlled by aromatic molecules of 4-aminophenyl phosphate (APP) with two hydrophilic groups interacting with Au ions. In the growth process, the APP molecules act to promote reduction and also as capping molecules. Adsorption of APP to bind the sides of rods inhibits the deposition of Au atoms on the sides of rods, resulting in anisotropic growth of Au NRs.^{32, 33} Similar to the growth mechanism of Au NRs, terephthalic acid has two hydrophilic carboxyl groups to

coordinate ruthenium ions. The terephthalic acid is bound to the sides of the nanorods, it might inhibit the deposition of ruthenium atoms on the sides to promote the anisotropic growth of ruthenium to form ruthenium nanorods. In contrast, benzoic acid is used as a surfactant to form ruthenium nanoparticles due to its single hydrophilic carboxyl group for coordinating ruthenium ions. The ruthenium ions might be surrounded by benzoic acid ligands, thereby promoting the formation of ruthenium nanoparticles.



Figure 2-10. Illustration of surfactants effect on production of ruthenium nanorods and nanoparticles.

The surface modified ruthenium nanorods were investigated by XPS (Figure 2-11 and 2-12). It shows that Ru, O, C and Ni elements exist in SMRu-NRs@NF with various chemical states (Figure 2-11(a)). Ru 3p spectrum displays one fitted peak appearing at 461.7 eV due to the presence of the metal state of ruthenium (Figure 2-12(a)).³⁴ In addition, the peak located at 464.2 eV is ascribed to the presence of the surface oxidation state of ruthenium.³¹ The Ru 3p spectrum confirms that the metallic state dominates in ruthenium nanorods. The spectrum of O 1s can be fitted to three peaks of O2, O3 and O4 appear at 531.2 eV, 532.2 eV and 533.5 eV, respectively (Figure 2-12(b)).³⁵ The peaks O2 is attributed to the presence of hydroxyl groups similar to those reported for metal hydroxides.^{36, 37} The peak O3 is assigned to the chemisorbed oxygen generated from the

partial surface oxidation of ruthenium nanorods. The peak of O4 corresponds to traces of moisture absorbed on the SMRu-NRs@NF. The absence of peak O1 at 529.8 eV confirmed no ruthenium oxide in SMRu-NRs@NF.³⁸ Through TEM, XRD, and XPS results, we concluded that the surface-modified ruthenium nanorods with chemisorbed oxygen and OH groups grown on the nickel foam. Additionally, the XPS spectrum (Ru 3p) of SMRu-NPs@NF reveals the dominant metallic state in ruthenium nanoparticles (Figure 2-12(c)). The O 1s spectrum indicates that the surface has been modified by chemisorbed oxygen and OH groups, similar to SMRu-NRs@NF (Figure 2-12(d)). The surface modification is achieved on the surfaces of ruthenium nanorods and nanoparticles during the nucleation process due to coordination between carboxyl groups of surfactants and ruthenium ions.



Figure 2-11. (a) XPS survey spectrum. (b) Ru 3d and C 1s spectrum of SMRu-NRs@NF.(c) Ni 2p spectrum of SMRu-NRs@NF.



Figure 2-12. Surface analysis. (a, b) High resolution of XPS spectra of Ru 3p_{3/2} and O 1s of SMRu-NRs@NF. (c, d) High resolution of XPS spectra of Ru 3p_{3/2} and O 1s of SMRu-NPs@NF.

2.3.2. Electrocatalytic Performance of HER in Acid

The HER performance of SMRu-NRs@NF electrode under acidic condition was systematically investigated by LSV (Figure 2-13 (a)). Compared to Pt-C and SMRu-NPs@NF, the SMRu-NRs@NF exhibits the best HER performance to reach ampere-level current density with a small overpotential. It is worth noting that the SMRu-NRs@NF requires an overpotential of 60 mV (η_{100}) and 130 mV (η_{500}) to reach current density of 100 mA cm⁻² and 500 mA cm⁻², and even only needs 215 mV (η_{1000}) to reach 1000 mA cm⁻². It significantly outperforms the Pt-C of an overpotential of 84 mV (η_{100}), 236 mV

 (η_{500}) and 352 mV (η_{1000}) . Due to the low crystallinity of ruthenium nanoparticles, the HER performance of SMRu-NPs@NF is worse than that of SMRu-NRs@NF, exhibiting overpotentials of 88 mV (η_{100}), 167 mV (η_{500}) and 264 mV (η_{1000}), respectively. The substrate of Ni foam shows a negligible performance for HER (Figure 2-17 (a)). Fluctuation in high current is caused by the rapid formation of bubbles of oxygen or hydrogen, which reduces the contact area between the electrode and the electrolyte. The Tafel slopes are illustrated based on the corresponding LSV curves (Figure 2-13 (b)). The SMRu-NRs@NF exhibits the smallest Tafel slope value of 20.7 mV dec⁻¹, which is much smaller than the 37.6 mV dec⁻¹ of SMRu-NPs@NF and 56.9 mV dec⁻¹ of Pt-C. These results prove the HER process dominated by the Volmer-Tafel route rather than the Volmer-Heyrovsky route, which is conducive to the rapid combination of hydrogen radicals to form hydrogen gas.³⁹⁻⁴¹ The galvanostatic HER measurement on ampere-level current density was explored whether it satisfies the ampere-level currents required in the industry. The SMRu-NRs@NF can achieve long-term stability of HER at 1000 mA cm⁻² for 114 h without obvious decay (Figure 2-13 (c)). The durability testing of SMRu-NRs@NF maintains excellent catalytic performance with almost unchanged LSV curves (Figure 2-18).

2.3.3. Electrocatalytic Performance of HER in Alkaline

In general, most of catalysts reported so far exhibits poor HER performance under alkaline conditions than under acidic conditions due to a lack of protons. However, the SMRu-NRs@NF performed better HER performance in 1.0 M KOH than in 0.5 M H₂SO₄ (Figure 2-13 (d)). The SMRu-NRs@NF shows a better HER performance than Pt-C and SMRu-NPs@NF. The overpotentials measured at 100 mA cm⁻² are 48, 160 and 65 mV for SMRu-NRs@NF, SMRu-NPs@NF and Pt-C, respectively. Even at ampere-level current density, SMRu-NRs@NF shows an overpotential of 185 mV (η_{1000}), which is significantly better than 419 mV (η_{1000}) of SMRu-NPs@NF and 311 mV (η_{1000}) of Pt-C.

The Ni foam exhibits a negligible performance for HER in alkaline solution (Figure 2-17 (b)). These results obtained at various current densities are competitive with previously reported ruthenium based alkaline HER catalysts (Figure 2-13 (e) and Table 2-1). The Tafel slope of SMRu-NRs@NF shows 45.7 mV dec⁻¹, which enables rapid HER ability (Figure 2-19). In contrast, the SMRu-NPs@NF and Pt-C show a Tafel slope of 57.1 and 62.2 mV dec⁻¹, respectively. Furthermore, the current at 1000 mA cm⁻² of SMRu-NRs@NF maintained stable operation for 160 hours with negligible attenuation (Figure 2-13 (f)). The LSV curves after 70 hours and 160 hours of durability testing at 1000 mA cm⁻² are shown in Figure 2-20.



Figure 2-13. HER electrochemical performance. (a, b) HER LSV curves and Tafel slope graph of SMRu-NRs@NF, SMRu-NPs@NF and Pt-C in 0.5 M H₂SO₄. (c) Galvanostatic measurement of HER of SMRu-NRs@NF at 1000 mA cm⁻² in 0.5 M H₂SO₄. (d) HER LSV curves of SMRu-NRs@NF, SMRu-NPs@NF and Pt-C in 1.0 M KOH. (e) HER overpotential comparison plot of the SMRu-NRs@NF with previously reported ruthenium-based catalysts in 1.0 M KOH. (f) Galvanostatic measurement HER of SMRu-NRs@NF at 1000 mA cm⁻² in 1.0 M KOH.



Figure 2-14. Electrochemical impedance spectroscopy (EIS) spectrum of SMRu-NRs@NF in 0.5 M H₂SO₄. Insert shows equivalent circuit.



Figure 2-15. EIS spectrum of Pt-C in 1.0 M H₂SO₄. Insert shows equivalent circuit.



Figure 2-16. Overpotential comparison plot of SMRu-NRs@NF, SMRu-NPs@NF and Pt-C in 0.5 M H₂SO₄.



Figure 2-17. The HER LSV curves of Ni foam in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH.(c) OER LSV curve of Ni foam in 1.0 M KOH.

 Table 2-1. Previously reported literature of splendid Ru-based catalysts hydrogen

 evolution catalysts in alkaline solution.

Reference		Catalyst
1	Adv. Funct. Mater. 2023, 33, 2303073	Mo-RuCoOx
2	Nat. Commun. 2021, 12, 4018	Ru-Mo ₂ C@CNT
3	Adv. Energy Mater: 2023, 13, 2301119	Ru-Co bimetallenes



Figure 2-18. The LSV curves of SMRu-NRs@NF electrode (a) after 42 hours and (b) 114 hours at 1000 mA cm⁻² durability testing in 0.5 M H_2SO_4 .



Figure 2-19. Tafel slopes of HER of SMRu-NRs@NF, SMRu-NPs@NF and Pt-C on Ni film in 1.0 M KOH.



Figure 2-20. The LSV curves of SMRu-NRs@NF electrode (a) after 70 hours and (b) 160 hours at 1000 mA cm⁻² durability testing in 1.0 M KOH.



Figure 2-21. EIS spectrum of SMRu-NRs@NF in 1.0 M KOH. Insert shows equivalent circuit.

Furthermore, stability of SMRu-NRs@NF after atthe current at 1000 mA cm⁻² operation for 160 hours is confirmed by XRD, SEM and XPS. The XRD pattern after the galvanostatic measurement under ampere-level clearly shows the intensity and position of the diffraction peaks unchanged, indicating that the ruthenium nanorods on the surface

of the nickel foam did not undergo any degradation or phase change during the galvanostatic test process (Figure 2-22). Besides, after stable test, the nanoparticles attached uniformly on the surface of the nickel foam can be observed, which further confirms that SMRu-NRs@NF exhibits good chemical/mechanical stability and the active sites do not detach from the Ni foam surface during galvanostatic measurements at ampere-level current (Figure 2-23). After an ampere-level current test, the XPS spectrum (Ru 3p and O 1s) of SMRu-NRs@NF indicates that the main valence state of ruthenium is still metallic. The XPS indicates that there was no degradation of samples after the HER test (Figure 2-24).



Figure 2-22. XRD patterns of SMRu-NRs@NF after test at 1000 mA cm⁻² for 160 h in 1.0 M KOH.



Figure 2-23. SEM image of SMRu-NRs@NF after test at 1000 mA cm⁻² for 160 h in 1.0 M KOH.



Figure 2-24. High resolution of XPS spectra of (a) Ru $3p_{3/2}$ and (b) O 1s of SMRu-NRs@NF after test at 1000 mA cm⁻² for 160 h in 1.0 M KOH.

2.3.4. Electrocatalytic Performance of OER and Water Splitting in Alkaline

The OER performance of the SMRu-NRs@NF was investigated in an alkaline medium (1.0 M KOH), with a carbon rod used as the counter electrode. The LSV curves

show that the SMRu-NRs@NF has the best OER capability with the potential of 1.39 and 1.58 V at 100 and 1000 mA cm⁻², respectively (Figure 2-25 (a)). This performance is significantly better than that of SMRu-NPs@NF and RuO₂. The low potential for OER obtained at various current densities is better than previously reported ruthenium based alkaline OER catalysts (Figure 2-26 and Table 2-2). The SMRu-NRs@NF exhibits a lower Tafel slope of 123.0 mV dec⁻¹ compared to 151.6 mV dec⁻¹ for SMRu-NPs@NF (Figure 2-25 (b)). Besides, OER stability under an ampere-level current exhibits no obvious attenuation of the potential after 143 hours (Figure 2-25 (c)). Almost no change in the LSV curves after the 50 h and 143 h confirms the ultra-high stability of the electrode during high-current operation (Figure 2-27). Moreover, the water splitting ability of SMRu-NRs@NF in 1.0 M KOH was tested (Figure 2-25 (d)). Apparently, the SMRu-NRs@NF||SMRu-NRs@NF maintains an almost constant voltage of 2.0 V running for 127 h under a current density of 1000 mA cm⁻². The breakpoints occur because the electrolyte was replaced after a certain period to avoid solution evaporation during the long period (Figure 2-25 (c) and (d)).



Figure 2-25. OER and water splitting performance. (a) OER LSV curves of SMRu-NRs@NF, SMRu-NPs@NF and RuO₂ in 1.0 M KOH. (b) Tafel slope of OER of SMRu-NRs@NF and SMRu-NPs@NF in 1.0 M KOH. (c) Galvanostatic measurement of OER of SMRu-NRs@NF at 1000 mA cm⁻² in 1.0 M KOH. (d) Galvanostatic measurement of full water splitting of SMRu-NRs@NF||SMRu-NRs@NF at 1000 mA cm⁻² in 1.0 M KOH.



Figure 2-26. Overpotential comparison plot of OER of SMRu-NRs@NF with previous reported ruthenium-based catalysts in 1.0 M KOH.



Figure 2-27. The LSV curves of SMRu-NRs@NF electrode (a) after 50 hours and (b) 143 hours at 1000 mA cm⁻² durability testing in 1.0 M KOH.

Reference		Catalyst
1	Appl. Catalysis B-Environ. Energy 2024, 343, 123559	Ru-RuO ₂ /Mn ₃ O ₄ /CP
2	Int. j. hydrogen energy 2020, 45, 9575- 9582	RuO ₂ /Co ₃ O ₄
3	J. Power Sources 2021, 514, 230600	Ru _{0.7} Co _{0.3}
4	J. Alloy. Compd. 2024, 976, 173076	P-Ru-CoFe LDH
5	J. Energy Chem. 2023, 87, 286-294	Co-Ru/NCN
6	Angew. Chem. Int. Ed. 2021, 60, 18821- 18829	a/c-RuO ₂
7	ACS Appl. Mater. Interfaces 2020, 12, 51437-51447	CoRu-O
8	Adv. Funct. Mater. 2023, 33, 2303073	Mo-RuCoO _x
9	Nat. Commun. 2019, 10, 1711	Ru/CoFe-LDHs
10	ACS Catal. 2023, 13, 2462–2471	Ru/Co ₃ O _{4-x}
11	Nat. Commun. 2023, 14, 7644	Ru/TiO _x
12	Adv. Energy Mater. 2023, 13, 2301119	RuCo
13	Adv. Mater. 2023, 13, 2206351	Ru@V-RuO ₂ /C HMS
14	Nat. Commun. 2023, 14, 3607	RuMoNi

 Table 2-2. Previously reported literature of splendid Ru-based catalysts oxygen evolution

 catalysts in alkaline solution.

To further demonstrate the potential of SMRu-NRs@NF for industrial applications, the stability of water splitting for SMRu-NRs@NF was also tested at 30 wt% KOH under 60 °C. It was able to maintain a voltage of 1.6 V for 420 min at a current density of 500 mA cm⁻² (Figure 2-28). This result directly confirms that SMRu-NRs@NF can be used as a catalyst with excellent full water splitting ability under alkaline solution, showing great potential for industrial-level water splitting.



Figure 2-28. (a) HER LSV curve of SMRu-NRs@NF in 30 wt% KOH solution under 60 °C. (b) OER LSV curve of SMRu-NRs@NF in 30 wt% KOH solution under 60 °C. (c) Galvanostatic measurement of full water splitting of SMRu-NRs@NF||SMRu-NRs@NF at 500 mA cm⁻² in 30 wt% KOH solution under 60 °C.

2.3.5. Electrochemically Active Surface Areas

The intrinsic catalytic activity is analyzed by electrochemical active surface areas (ECSA) of different catalysts, which are estimated by a series of CV tests with various scan rates (Figure 2-29). The ECSA has a significant impact on catalyst activity because it reflects the active area of the catalyst participating in the reaction, it can be determined by: ECSA = C_{dl}/C_s , where C_{dl} is double-layer capacitance and C_s is the specific capacitance of the sample.⁴²⁻⁴⁴ In this work, $C_s = 0.04$ mF cm⁻² was used as the value for

the general specific capacitance based on commonly reported value.¹³ As a result, the C_{dl} becomes an index of the electrochemically active area of the material, as shown in Figure 2-30 (a), the C_{dl} is obtained by fitting ΔJ (Half of the oxidation and reduction current density) values with different scan speeds of 10, 20, 30, 40, 50 and 60 mV s⁻¹. The C_{dl} of the SMRu-NRs@NF electrode exhibits a significantly higher C_{dl} value of 63.1 mF cm⁻² than SMRu-NPs@NF of 39.6 mF cm⁻² and Pt-C of 41.2 mF cm⁻², which further explains that the SMRu-NRs@NF has a high ECSA for high catalytic efficiency. The ECSA of SMRu-NRs@NF is estimated to be 1577.5 cm², which is significantly larger than the 990 cm² of SMRu-NPs@NF and the 1030 cm² of Pt-C. The normalization of polarization curves by ECSA further indicates that SMRu-NRs@NF and Pt-C (Figure 2-30 (b), (c) and (d)).



Figure 2-29. CV curves of (a) SMRu-NRs@NF, (b) SMRu-NPs@NF and (c) Pt-C on Ni Foam at different scan rates in alkaline media.



Figure 2-30. (a) The plots of the current density versus the scan rate of SMRu-NRs@NF, SMRu-NPs@NF and Pt-C. (b) HER LSV curves of SMRu-NRs@NF and Pt-C on Ni Foam normalized by ECSA in 0.5 M H₂SO₄. (c) HER LSV curves of SMRu-NRs@NF and Pt-C on Ni Foam normalized by ECSA in 1.0 M KOH. (d) OER LSV curves of SMRu-NRs@NF normalized by ECSA in 1.0 M KOH.

2.3.6. Studies on Mechanism of Catalytic Activities

To investigate the origin of the remarkable HER and OER performance of SMRu-NRs@NF, DFT simulations were carried out to understand the role of the surface modified ruthenium nanorods. The model of the hcp Ru (100) facet with chemisorbed oxygen and OH groups (HO-O-hcp Ru (100)) is constructed (Figure 2-31). The differential charge density of HO-O-hcp Ru (100) exhibits the charge redistribution behavior of the ruthenium atoms interacting with chemisorbed oxygen and OH groups (Figure 2-32 (a)). To understand the origin of the excellent HER performance of SMRu-NRs@NF under acidic conditions, the Gibbs free energy of $*H(\Delta G_{*H})$ adsorption during the reaction process was systematically investigated (Figure 2-32 (b)). Generally, the adsorption and desorption balance of hydrogen-free radicals on the catalyst surface determines the HER activity.^{45,46} The HO-O-hcp Ru (100) is estimated to be 0.01 eV, which is close to the thermal-neutral optimal value and lower than HO-O-hcp Ru (101) and HO-O-hcp Ru (001). In contrast, ΔG_{*H} on the unmodified hcp Ru (100), (101) and (001) surface are -0.33, -0.38 and -0.39 eV, respectively. Besides, the HO-O-hcp Ru (100) facet shows the lowest adsorption energy of H₂O (ΔG_{H2O}) of 0.14 eV, in contrast to HO-O-hcp Ru (101) and HO-O-hcp Ru (001). Also, its absolute value is significantly smaller than ΔG_{H2O} (-0.59 eV) of the hcp Ru (100) facet (Figure 2-32 (c)).⁴⁷ These results indicate that the ruthenium surface modification can optimize the adsorption of critical steps of the HER under alkaline conditions to accelerate the reaction. Moreover, the efficient OER performance under alkaline conditions was also revealed by Gibbs free energy calculation with the reaction condonation of *OH, *O and *OOH step on the HO-O-hcp Ru (100) facet (Figure 2-32 (d) and Figure 2-33). As a result, the rate-determining step (RDS) energy barriers of HO-O-hcp Ru (100), HO-O-hcp Ru (101) and HO-O-hcp Ru (001) are 1.38, 1.86 and 1.71 eV, respectively. The RDS of HO-O-hcp Ru (101) has a low free energy barrier of 1.38 eV, which is beneficial to accelerate the OER processes.⁴⁸⁻⁵⁰



Figure 2-31. DFT structure optimization model of HO-O-hcp Ru (100) facet slab.



Figure 2-32. Studies of catalytic activities. (a) The side views of charge density difference analysis of hcp Ru (100) facet with modified by chemisorbed oxygen and OH groups. Yellow indicates positive charges and blue indicates negative charges. (b, c) Calculation of H atom adsorption energy (ΔG_{H^*}) and the adsorption energy of H₂O (ΔG_{H2O}) on the Ru (100), Ru (101) and Ru (001) facet with modified by chemisorbed oxygen and OH groups. (d) Calculation of Gibbs free energy (ΔG) of each step of OER on Ru (100), Ru (101) and Ru (001) facet with modified by chemisorbed oxygen and OH groups.



Figure 2-33. Schematic illustration of the OER mechanism, reaction pathways of *OH, *O, and *OOH on the HO-O-hcp Ru (100) surface.

The electronic structures of the catalyst were calculated by the density of state (DOS), where the calculation parameters were same with the geometric optimization mentioned above. The d band center (ε_d) for d orbital projected density of state (PDOS) of Ru can be calculated by following:

$$\mu = \frac{\sum_{a}^{b} \varepsilon N(\varepsilon) d\varepsilon}{\sum_{a}^{b} N(\varepsilon) d\varepsilon}$$

where ε was the energy level and N(ε) is the number of orbitals at the energy level ε . The parameters a and b were defined as the top or bottom limitation of the energy level for a certain orbital. The d band center (ε_d) of d-band theory often dominates the progress of electrochemical reactions because it is directly related to the intensity of interaction with reaction intermediates. The ε_d position of HO-O-hcp Ru (100) shifts upward to -1.45 eV form -1.60 eV of hcp Ru (100) (Figure 2-34 (a)). The upshift of the ε_d might enhance the binding of ruthenium metal and intermediates of OER/HER.⁵¹⁻⁵⁴ When the d-band center approaches the Fermi level, it can often be expected that the catalyst will exhibit strong adsorption ability for reaction intermediates. Otherwise, a weaker intermediate interaction will occur when the d-band center shifts away from the Fermi level. Furthermore, compared to ruthenium, the phenomenon that the d-band center of HO-O-Ru moves upward relative to the Fermi level also corresponds to the differential charge density analysis results of the electron redistribution of HO-O-hcp Ru. Additionally, the electron localization function (ELF) (Figure 2-34 (b)) shows electron redistribution after surface modification.



Figure 2-34. (a) The PDOS plots and d band center of hcp Ru (100) facet and hcp Ru (100) facet with modify by hydroxyl and partial oxidation. (b) Electron localization function (ELF) plot of the HO-O-hcp Ru (100) slab.

2.4. Conclusions

The sub-10 nm nanosized ruthenium nanorods modified with chemisorbed oxygen and OH groups were successfully grown in situ on nickel foam. The nanometer-sized rod crystal with a high aspect ratio can expose a highly active facet of (100) for HER and OER reactions. As a result, SMRu-NRs@NF serves as an excellent HER catalyst that can reach 1000 mA cm⁻² at ultralow overpotentials of 215 mV and 185 mV in acidic and alkaline solutions. Besides, it shows superior OER performance in alkaline solution with low potentials of 1.39 and 1.49 V at 100 and 1000 mA cm⁻², respectively. Moreover, SMRu-NRs@NF exhibits superior stability at an ampere level of 1000 mA cm⁻². It can operate stably for 114 hours in acidic solutions and 160 hours in alkaline solutions without potential attenuation during HER. Additionally, it can achieve stable operation for over 143 hours in an alkaline solution for OER. Furthermore, the SMRu-NRs@NF||SMRu-NRs@NF cell can even operate stably at an almost constant voltage of 2.0 V running for 127 h under a current density of 1000 mA cm⁻². The DFT calculation shows that the SMRu-NRs@NF exhibited the best adsorption and desorption balance for hydrogen radicals and water. Besides, it also exhibits a low free energy barrier for the rate-determining step towards OER. The low reaction energy barrier obtained from these mechanism studies well explains its excellent OER/HER performance under both acidic and alkaline conditions. This study provides an in-depth insight into controlling catalytic performance by constructing the high aspect ratio nanorod crystal with a dominant active facet and modifying the catalyst surface.

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Chapter 3: Platinum Nanoparticles Bonded with Carbon Nanotube for High-Performance Ampere-Level All-Water Splitting

3.1. Introduction

Hydrogen fuel has become the most important fuel in the world today, besides fossil fuels, due to its high energy density and product cleanliness.¹⁻³ However, a large amount of energy is consumed in the process of industrial hydrogen production as the result of the constant need for high overpotential for water splitting, especially in an alkaline medium, the low proton concentration has become a serious obstacle for HER.^{4,5} In fact, developing water electrolysis catalysts for industrial applications is very challenging because they always face the bottleneck of long-term stability and low overpotential when operating at ampere-level current. The anion exchange membrane (AEM) based water electrolyzer also relies on efficient oxygen under alkaline conditions has become a thorny issue.⁶⁻⁸ Platinum is a milestone catalyst that has achieved hydrogen evolution under acidic conditions, but it is also hindered by magnitude low reaction kinetics in alkaline solution compared with acidic medium due to the key water dissociation step (H₂O + e⁻ \rightarrow *H + OH⁻).^{9,10}

Given the hydrogen evolution capability under acidic conditions, developing Pt-based electrocatalysts with low cost, fast kinetics, and long-term stability in alkaline solution has become an important strategy worth exploring. In previous studies, many efforts have been devoted to designing Pt-based catalysts to enhance their hydrogen evolution ability.¹¹⁻¹³ A common understanding for devising the strategy is that the improvement of catalytic performance mainly includes two key aspects: (1) Increase the specific surface area of the catalyst to expose more active sites, such as nanoparticles, nanocluster, nanoplates, and metal-organic framework, thereby making the electrode have more active sites to combine intermediates for improving the catalytic performance.¹⁴⁻¹⁸ (2) Construct Pt-based composite materials by confining active sites into other electrochemically active

materials or converting platinum metal to platinum compounds, such as oxide, telluride, and alloys.¹⁹⁻²²

The splendid oxygen evolution performance of platinum-based materials has rarely been studied, and achieving platinum-based catalysts with efficient bifunctional hydrogen and oxygen evolution ability is an important research field because the oxygen evolution reaction is also a pivotal part of the anion exchange membrane water electrolyzer.²³ In order to construct an efficient platinum-based catalyst for water splitting, choosing a suitable substrate to load active platinum with a stable structure to serve strong metal-support interaction is an important point.²⁴⁻²⁷ Carbon nanotube (CNT), as a stable high conductivity substrate, is most promising for anchoring active sites on the surface towards high-activity catalysts, such as nanoparticles, nanoplates, and nanowires.^{16, 28-30} Wang et al. reported that successfully synthesized Pt nanoparticles loaded on nitrogen-doped carbon nanotube with pyridinic-N and pyrrolic-N decorated, and it has shown amperelevel hydrogen evolution ability, but did not exhibit OER performance due to the lack of strong Pt-C bonds.³¹ Meanwhile, previous research is limited to achieving significant bifunctional hydrogen and oxygen evolution based on platinum and CNT through strong chemical bond interaction to reduce electron transfer energy barriers.

Inspired by the above discussion, herein, we designed platinum nanoparticles bonded in carbon nanotube (Pt-NPs-bonded@CNT) with Pt-C bonds towards ultra-low overpotential water splitting ability in alkaline solution (Figure 3-1). During the synthesis process, the carbon nanotubes are employed as the substrate, and surface oxygen-containing groups of carbon nanotubes are modified by strong acid treatment, causing defects on the surface to capture platinum atoms, thereby promoting the embedding of platinum nanoparticles on the surface of carbon nanotubes. Benefit from the strong interaction between platinum and high conductivity carbon nanotube substrates through the Pt-C bond also the platinum nanoparticles bonded in carbon nanotube can provide more stable active sites, the Pt-NPs-bonded@CNT shows splendid electrocatalytic performance. Therefore, it exhibits excellent hydrogen evolution ability, and when the

current density reaches 1000 mA cm⁻², it only requires an ultra-low overpotential of 0.19 V in acidic solution and 0.23 V in alkaline solution. Besides, it shows superior oxygen evolution electrocatalysis in alkaline solution with low overpotential of 1.69 V at 1000 mA cm⁻², respectively. Besides, it also exhibits high stability over 120 h against hydrogen evolution at 1000 mA cm⁻² in both acid and alkaline conditions, as well as long-term stability for 110 h against oxygen evolution in alkaline solution. In contrast, platinum nanoparticles attached on the surface of carbon nanotube (Pt-NPs-attached@CNT) without Pt-C bonds are established by without acid treatment and show inferior performance for HER and no bifunctional OER performance.



Figure 3-1. Schematic illustration of Pt-NPs-bonded@CNT towards bifunctional catalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

3.2. Experimental

3.2.1. Materials preparation

Preparation of Pt-NPs-embed@CNT. Acid treatment carbon nanotubes: First, 200 mg of carbon nanotubes were hydrothermally treated in 30 mL of 5 M nitric acid at 160 °C for 6 h. After that, the acid-treatment carbon nanotubes were collected by filtration and

washed four times with deionized water to remove residual nitric acid. Then, the acidtreatment carbon nanotubes were vacuum-dried for 12 hours for further use.

Prepared Pt-NPs-bonded@CNT. The platinum loading on acid treatment carbon nanotubes through a wet chemical reaction. H₂PtCl₆ \cdot 6H₂O (0.02 mmol, 10.358 mg) and acid treatment carbon nanotubes (40 mg) were dispersed in 40 mL deionized water and then kept at 90 °C for 24 hours with stirring. After that, the dispersion solution was at 90 °C for 12 hours to evaporate water to get the precursor powder of Pt-NPs-bonded@CNT. Obtained precursor of Pt-NPs-bonded@CNT was annealing at 900 °C for 2 hours with an argon atmosphere and cooling naturally.

Prepared The Pt-NPs-attached@CNT. The Pt-NPs-attached@CNT was prepared by same procedure except that the carbon nanotubes were not treated with acid.

3.2.2. Materials Characterization

The sample's morphology was observed by scanning electron microscopy (SEM, JEOL, JSM-5900LV) and high-resolution transmission electron microscopy (TEM, JEOL JEM-2100F). The elemental mapping images were tested by a TEM (JEOL JEM-2100F). The SEAD was carried out by AC-TEM (FEI Titan G2 60-300). XRD spectra were conducted by a D/Max-III X-ray spectrometer (PANalytical/Philips X'Pert Pro) when 20 values range from 5° to 80° with Cu K α radiation. XPS was investigated using electron energy disperse spectroscopy (ThermofIsher ScientifIc Escalab 250Xi).

3.2.3. Electrochemical Measurement

The electrochemical performance tests of all catalysts were performed on an electrochemical workstation using a three-electrode system. The electrolyte used in all tests under alkaline and acid conditions was 1.0 M KOH and 0.5 M H₂SO₄ solution, respectively. When testing the hydrogen evolution reaction, a graphite electrode was used
as the counter electrode, besides, an Ag/AgCl electrode and Hg/HgO electrode were used as reference electrodes in acid and alkaline solution, respectively. When testing the oxygen evolution reaction under alkaline conditions, a platinum plate electrode was used as the counter electrode. The Pt-NPs-bonded@CNT electrode was obtained by drop-dry mothed. Briefly, the 5 mg of Pt-NPs-bonded@CNT catalyst was first dispersed in a mixed solution of 50 µL of Nafion dispersion, 450 µL isopropyl alcohol and 500 µL water. Afterward, drop 40 µL of Pt-NPs-bonded@CNT dispersion evenly on the surface of the carbon paper electrode, and then use it to test the electrochemical performance after natural drying for two hours. The Pt-C electrode was prepared using the same method. Polarization curves were measured by linear sweep voltammetry (LSV) at a sweep rate of 5 mV s⁻¹. All obtained LSV curves were corrected with 100% iR compensation. All stability measurements are performed using potentiostat testing at 1000 mA cm⁻² for over 100 hours. Electrochemical impedance spectroscopy (EIS) was tested in the frequency range from 10000 to 0.1 Hz with an amplitude voltage of 5 mV.

The conversion of the test potential into a potential relative to a reversible hydrogen electrode (RHE) under acidic conditions can be calculated using the Nernst equation:

 $E_{RHE} = E_{Ag/AgCl} + 0.198 + 0.0591 \times \text{pH}.$

Under alkaline conditions, due to changes in the reference electrode, the Nernst equation that converts the potential of the reversible hydrogen electrode is:

 $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times \text{pH}.$

The Tafel slope (*b*) is obtained by linear fitting a plot derived from the logarithm of current density (*j*) versus overpotential (η) through follow equation:

$$\eta = b \times \log |j| + a$$

The electrochemical double layer capacitance (C_{dl}) is obtained by cyclic voltammetry (CV) measurement at various scan rates with a voltage of -0.7 ~ -0.9 V versus $E_{Hg/HgO}$.

3.3. Results and Discussion

3.3.1. Structural Characterizations

Pt-NPs-bonded@CNT with platinum nanoparticles bonded in carbon nanotubes was prepared through in-situ grown platinum nanoparticles on the surface of carbon nanotubes with defects, as illustrated in Figure 3-2. Firstly, defects, which means holes, oxidative functional groups such as hydroxyl and carboxyl groups, were formed on carbon nanotubes surface after hydrothermal acidification treatment. After that, the defective carbon nanotubes and platinum source were dispersed in deionized water, the platinum ions captured by the defect sites during medium temperature and then evaporation water to get precursor of Pt-NPs-bonded@CNT. Finally, annealing Pt-NPs-bonded@CNT precursor at high temperature to get the final product.



Figure 3-2. Schematic illustration of synthesis process of Pt-NPs-bonded@CNT.

The chemical state of the surface elements of Pt-CNT with acid treatment was determined by X-ray photoelectron spectroscopy (XPS) as presented in Figure 3-3. The chemical valence of platinum is detected by the spectrum of Pt 4f, as displayed in Figure 3-3 (b), there are two peaks located at 75.6 eV and 72.5 eV, which is attributed to the $4f_{5/2}$ orbital of Pt²⁺ and $4f_{7/2}$ orbital of Pt²⁺, respectively ³¹. Meanwhile, the peaks appeared at 74.8 eV and 71.5 eV are ascribed to Pt metallic states. Four peaks appeared at 284.3 eV, 284.8 eV, 286.3 eV and 289.6 eV in the high-resolution XPS spectrum of C 1s, which is attributed to Pt-C, C-C/C=C, C-O and O=C-O bond in carbon nanotubes, respectively (Figure 3-3 (c)).^{32,33} The existence of C-O and O=C-O bonds found in carbon nanotubes

verified that the surface modification is successful and oxygen-containing groups are formed on the surface of carbon nanotubes. Besides, the spectrum of O 1s is also used to check the platinum chemical state indirectly. There are only O2 and O4 peaks located at 531.2 eV and 533.5 eV, which are related to hydroxyl groups and adsorbed water (Figure 3-3 (d)).³⁴ However, the O1 peak associated with metal oxides and the O3 peak belonging to lattice defective oxygen on the metal surface are all absent, which can illustrate there are no platinum oxides existing in Pt-NPs-bonded@CNT.³⁵ This result demonstrates that divalent platinum is formed by the formation of chemical bonds between platinum and carbon (Pt-C) in the carbon nanotubes. The metallic state of platinum is related to the platinum nanoparticles bonded in the carbon nanotubes. In contrast, for Pt-CNT without acid treatment, the chemical valence of platinum in the Pt 4f spectrum is mainly Pt metallic state. In addition, the Pt-C peak at 284.3 eV in the C 1s spectrum has disappeared, suggesting the absence of Pt-C bonds between platinum nanoparticles and CNTs (Figure 3-4). These results indicate that CNT with acid treatment produces platinum nanoparticles bonded with CNT (Pt-NPs-bonded@CNT), whereas CNT without acid treatment produces no bond between platinum nanoparticles and the CNT (Pt-NPs-attached@CNT).



Figure 3-3. (a) XPS survey spectra of Pt-NPs-bonded@CNT. (b, c and d) Pt 4f, C 1s and O 1s high resolution of XPS spectra of Pt-NPs-bonded@CNT.



Figure 3-4. (a) XPS survey spectra of Pt-NPs-attached@CNT. (b, c and d) Pt 4f, O 1s and C 1s high resolution of XPS spectra of Pt-NPs-attached@CNT.

The crystal structure of the Pt-NPs-bonded@CNT is revealed by an X-ray diffraction (XRD) pattern, as presented in Figure 3-5. These diffraction peaks can be well matched with metal platinum (JCPDS No. 04-0802 (Pt)), and no impurity peak such as platinum oxide appears, indicating the high pure phases of platinum nanoparticles are formed. Nevertheless, all peaks of platinum are upshift compared to the standard of platinum. This result is caused by a slight shrinkage in the interplanar spacing of the platinum nanoparticle lattice, which is consistent with the HR-TEM result of the slightly shrunk Pt (111) facet and Bragg equation of XRD calculation results (0.05 Å). Besides, the diffraction peak position (JCPDS No. 41-1487 (CNT)) of the XRD pattern of the carbon nanotube after acid treatment is not changed compared to the pristine carbon nanotube, however, the intensity of the diffraction peak becomes weaker, which is due to defects

created on the surface of the carbon nanotube.³⁶ It is worth noting that the peak of Pt-NPs-bonded@CNT at 42.2° belongs to the (100) peak of CNT because the peak is matched well with the (100) peak of JCPDS No. 41-1487 (CNT). Besides, there is no shift in the position of the platinum peak of Pt-NPs-attached@CNT, which further confirms that the platinum nanoparticles are attached to the surface of CNT without any stress causing slight deformation of the platinum crystal lattice. As a result, we conclude that the pure platinum nanoparticles bonded on the surface of the carbon nanotube, and the presence of platinum oxides is ruled out.

Figure 3-5. XRD patterns of Pt-NPs-bonded@CNT (red), Pt-NPs-attached@CNT (blue), acid treat-CNT (black) and CNT (green). The XRD standard card data for Pt (JCPDS No. 04-0802) and CNT (JCPDS No. 41-1487) are marked in red and black.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements are carried out to authenticate the morphological information of the Pt-NPs-bonded@CNT. As shown in Figure 3-6 (a), the SEM image shows a smooth carbon nanotube shape after loading platinum particles on the acid-treated carbon nanotube surface. TEM and HAADF-STEM images demonstrated the platinum nanoparticles are

bonded on the surface of the carbon nanotube and the platinum nanoparticles are only a few nanometers in diameter, which is beneficial to expose more active sites for absorbed intermediates to enhance electrocatalytic performance (Figure 3-6 (b) and Figure 3-7). Furthermore, the HR-TEM image more clearly displays the platinum nanoparticles bonded on the surface of the carbon nanotube and covered by an amorphous carbon nanolayer (inset of Figure 3-6 (c)). Figure 3-6 (c) revealed that the platinum nanoparticles have a single interplanar spacing of 2.22 Å of the Pt (111) facet, which is the slightly shrunk typical interplanar spacing of the 2.27 Å of the standard Pt (111) crystal face.³⁷ This result is also consistent with Fourier transform of platinum lattice and selective electron area diffraction (SAED) pattern (Figure 3-8). Moreover, the energy-dispersive X-ray spectroscopy (EDS) elemental mapping confirmed that the bright spots on the carbon nanotube were platinum nanoparticles (Figure 3-6 (d)). The mass loading of Pt nanoparticles in the nanocomposites is 0.7 wt%, which is within the appropriate value range for high catalytic performance in the relevant literature.³⁸ Additionally, C and O elements are uniformly distributed in the Pt-NPs-bonded@CNT, and the O elements have very little content.

Figure 3-6. (a) SEM image of Pt-NPs-bonded@CNT. (b, c) TEM and HR-TEM images of Pt-NPs-bonded@CNT. (d) EDS mapping images of Pt-NPs-bonded@CNT.

Figure 3-7. (a) TEM image and (b) HAADF-STEM image of Pt-NPs-bonded@CNT.

Figure 3-8. (a) Fourier transform of platinum lattice of Pt-NPs-bonded@CNT. (b) SAED pattern of Pt-NPs-bonded@CNT, the green arrow corresponds to the diffraction spot of CNT and the red arrow corresponds to the diffraction spot of Pt.

In contrast, Pt-NPs-attached@CNT was prepared by same procedure without acid treatment of carbon nanotube, the SEM image shows a smooth carbon nanotube shape after loading platinum particles (Figure 3-9). The TEM image of Pt-NPs-attached@CNT

shows that platinum nanoparticles are supposed to be only attached on the surface of carbon nanotubes, and the platinum nanoparticles exhibit an amorphous structure (Figure 3-10). The elemental mapping image also verified the distribution information of platinum nanoparticles, as well as the C and O elements in Pt-NPs-attached@CNT.

Figure 3-9. SEM image of Pt-NPs-attached@CNT.

Figure 3-10. (a,b) HR-TEM images of Pt-NPs-attached@CNT. (c) EDS mappings images of Pt-NPs-attached@CNT.

3.3.2. Electrocatalysis Performance of HER in 0.5 M H₂SO₄

The hydrogen evolution ability of Pt-NPs-bonded@CNT electrode under acidic conditions was systematically tested, presented by the linear sweep voltammetry (LSV) curves in Figure 3-11 (a). Compared to Pt-C, Pt-NPs-attached@CNT and carbon paper, the Pt-NPs-bonded@CNT electrode exhibits the best HER performance and reaches ampere-level current density with a small overpotential. It is worth noting that the Pt-NPs-bonded@CNT electrode only requires an overpotential of 27 mV and 114 mV to reach 100 mA cm⁻² and 500 mA cm⁻², and even only needs 193 mV to achieve an amperelevel current density of 1000 mA cm⁻², which is significantly outperforming the benchmark electrocatalyst of Pt-C with an overpotential of 73 mV (η_{100}), 181 mV (η_{500}) and 234 mV (η_{1000}). In addition, its HER performance also exceeds that of Pt-NPsattached@CNT without acid treatment, which is 200 mV (η_{100}), 275 mV (η_{500}) and 324 mV (η_{1000}). The substrate of carbon paper shows negligible ability for hydrogen evolution. The resulting low overpotential of Pt-NPs-bonded@CNT is attributed to the platinum nanoparticle bonded in the carbon nanotube with Pt-C bond, resulting in efficiently reduced electron transfer energy barrier and highly dispersed platinum nanoparticles can provide more adsorption active sites for hydrogen radicals. Electrochemical impedance spectroscopy (EIS) of Pt-NPs-bonded@CNT, Pt-NPs-attached@CNT and Pt-C reveals the electron transfer energy barrier corresponding to charge transfer properties, as displayed in Figure 3-11 (b). In Nyquist plots, the Nyquist semicircle diameter represents the charge transfer resistance (R_{ct}). It can be found the Pt-NPs-bonded@CNT exhibit the lowest charge transfer resistance (R_{ct}) compared with Pt-NPs-attached@CNT and Pt-C, which means that the Pt-NPs-bonded@CNT has faster electron transfer properties, thereby accelerating water splitting.^{39, 40} Tafel slope is usually used as an indicator of hydrogen evolution ability. In Figure 3-11 (c), the Tafel slopes are illustrated based on the corresponding LSV curves shown in Figure 3-11 (a). The Pt-NPs-bonded@CNT demonstrates a small Tafel slope value of 25.1 mV dec⁻¹, similar to the 22.0 mV dec⁻¹ of Pt-NPs-attached@CNT, which is much smaller than the 51.8 mV dec⁻¹ of Pt-C. The results prove that the HER process is dominated by the Volmer-Tafel route rather than the Volmer-Heyrovsky route, which is conducive to the rapid combination of hydrogen radicals to form hydrogen gas.⁴¹ More importantly, a galvanostatic measurement of ampere-level current density catalytic hydrogen evolution stability was applied to demonstrate that the electrode can meet the requirements for electrocatalytic hydrogen evolution even at ampere-level currents required in industry. As a result, the Pt-NPs-bonded@CNT electrode can achieve long-term stability of hydrogen evolution at 1000 mA cm⁻² for 125 h without obvious attenuation, which proves that the platinum nanoparticles bonded in carbon nanotube maintain excellent durability even after the high current density hydrogen evolution testing (Figure 3-11 (d)).

Figure 3-11. HER electrochemical performance measurements in acid. (a) HER LSV curves of Pt-NPs-bonded@CNT, Pt-C, Pt-NPs-attached@CNT and carbon paper in 0.5

M H₂SO₄. (b) EIS of Pt-NPs-bonded@CNT, Pt-C and Pt-NPs-attached@CNT in 0.5 M H₂SO₄. (c) Tafel slope compared graph of Pt-NPs-bonded@CNT, Pt-C and Pt-NPs-attached@CNT. (d) Galvanostatic hydrogen evolution measurement of Pt-NPs-bonded@CNT at 1000 mA cm⁻² in 0.5 M H₂SO₄.

3.3.3. Electrocatalysis Performance of HER in 1.0 M KOH

Compared with the hydrogen evolution reaction under acidic conditions, the catalyst usually exhibits poor hydrogen evolution performance under alkaline conditions due to a lack of protons. Surprisingly, the Pt-NPs-bonded@CNT also performed outstanding hydrogen evolution performance in 1.0 M KOH, as presented in Figure 3-12 (a). The Pt-NPs-bonded@CNT electrode shows an obviously brilliant HER performance than Pt-C and Pt-NPs-attached@CNT. The measured overpotential corresponding to 100 mA cm⁻² is 78, 195 and 307 mV for Pt-NPs-bonded@CNT, Pt-C and Pt-NPs-attached@CNT, respectively. Even at ampere-level current density, it only requires an overpotential of 232 mV, which is significantly better than 524 mV of Pt-C and 588 mV of Pt-NPsattached@CNT. The superb low overpotential results obtained at various current densities are better than most previously reported literature of splendid CNT-based catalysts, including platinum-modified carbon nanotube catalysts (Figure 3-12 (b) and Table 3-1). The Tafel slope also shows the Pt-NPs-bonded@CNT has a much smaller value of 28.6 mV dec⁻¹ compared with 44.8 mV dec⁻¹ of Pt-C and 90.0 mV dec⁻¹ of Pt-NPsattached@CNT, which corresponds to rapid water splitting ability in alkaline solution (Figure 3-12 (c)). Furthermore, an ampere-level current of 1000 mA cm⁻² was applied to evaluate the durability of the electrode, which maintained stable operation for 128 hours with negligible attenuation (Figure 3-12 (d)). These results indicate that Pt-NPsbonded@CNT with a strong Pt-C bond achieves an excellent hydrogen evolution capability even under alkaline conditions and outstanding stability even at industrial-level current densities.

Figure 3-12. HER electrochemical performance measurements in alkaline. (a) HER LSV curves of Pt-NPs-bonded@CNT, Pt-NPs-attached@CNT, Pt-C and carbon paper in 1.0 M KOH. (b) Comparison of overpotential graph of Pt-NPs-bonded@CNT with excellent CNT-based materials at 50 mA cm⁻² and 100 mA cm⁻². (c) Tafel slope compared graph of Pt-NPs-bonded@CNT, Pt-C and Pt-NPs-attached@CNT. (d) Galvanostatic hydrogen evolution measurement of Pt-NPs-bonded@CNT at 1000 mA cm⁻² in 1.0 M KOH.

Reference		Catalyst
1	our work	Pt-N-CNT
2	Carbon 2021, 175, 176e186	Ni/Ni ₃ C-CNT
3	Electrochim. Acta 2021, 386, 138406	Ni nanoparticles-CNT
4	J. Colloid Interf. Sci. 2022, 616 210–220	Co ₂ P/Ni ₂ P/CNT
5	J. Energy Chem. 2020, 51, 280–284	Pt-CNT
6	ACS Sustainable Chem. Eng. 2020, 8, 9136–9144	Ru@Co/N-CNTs
7	ACS Sustainable Chem. Eng. 2020, 8, 12248–12259	W ₂ C@CNT
8	Adv. Energy Mater. 2022, 12, 2200110	Pt/8-NCNT
9	Adv. Mater. 2020, 32, 2006034	DSIrNi@CNTS
10	Adv. Mater. 2022, 34, 2106973	Pt nanocrystals (Dr- Pt)-CNT
11	Angew. Chem. Int. Ed. 2020, 59, 4154 – 4160	CoP/CNT
12	Angew. Chem. 2021, 133, 19216–19221	Pt–Co Nano-alloys CNT
13	Nano Res. 2020, 13, 975–982	Ni nanoparticle- encapsulated N-doped CNT
14	Nat. Commun. 2021, 12, 4018	Ru-Mo ₂ C@CNT
15	Nat. Commun. 2022, 13, 5497	IrMo NPs/CNT
16	Chem.Mater. 2017, 29, 4738-4744	1T-MoS ₂ /SWNT
17	Angew. Chem. Int. Ed. 2020, 59, 4154 – 4160	B-CoP/CNT
18	Adv. Mater. 2019, 31, 1900178	FeNi-P/NCN
19	Nat. Commun. 2022,13, 3338	Mo ₂ C/MoC/CNT

 Table 3-1. Previously reported literature of splendid CNT-based catalysts hydrogen

 evolution catalysts in alkaline.

3.3.4. Electrocatalysis Performance of OER in 1.0 M KOH

Platinum-based catalysts are rarely used for prominent oxygen evolution, even though they are a critical part of anion exchange membrane water electrolyzers. Unlike traditional platinum-based materials, which are only used for efficient hydrogen evolution, the PtNPs-bonded@CNT also exhibits excellent oxygen evolution performance in alkaline solutions. As illustrated in Figure 3-13 (a), the LSV curve shows that the Pt-NPsbonded@CNT electrode has the best oxygen evolution capability with the lowest overpotential of 1.54 V and 1.69 V at 100 mA cm⁻² and 1000 mA cm⁻², and its performance is significantly better than that of commercial RuO₂. The oxygen evolution capabilities of Pt-NPs-attached@CNT and carbon paper can be ignored because the platinum nanoparticles attached on the surface of carbon paper without strong interaction between platinum active sites and carbon nanotube substrates. On the contrary, the excellent OER performance of Pt-NPs-bonded@CNT can be ascribed to the strong Pt-C bond regulating the activity of platinum nanoparticles through the strong interaction of metal-substrate and afford stabilizing nanoparticles bonded in carbon nanotubes. The superb low overpotential for oxygen evolution results obtained at various current densities are better than most previously reported literature of splendid CNT-based electrocatalysts (Figure 3-13 (b) and Table 3-2). Moreover, the low overpotential corresponds to rapid water splitting ability also just according to the low Tafel slope value of 66.0 mV dec⁻¹ of Pt-NPs-bonded@CNT, and the RuO₂ shows Tafel slope value of 115 mV dec⁻¹ (Figure 3-13 (c)).^{42,43} In order to further demonstrate the potential for practical applications, its oxygen evolution stability under ampere-level current has also been systematically tested. There is no obvious attenuation of the overpotential after 110 hours of stable operation, which also confirms the platinum nanoparticles bonded in carbon nanotube remain remarkably stable during oxygen evolution at ampere-scale current density (Figure 3-13 (d)). Compared with Pt-NPs-bonded@CNT annealed at 900 °C, the OER/HER performance of Pt-NPs-bonded@CNT annealed at 600 °C is poor (Figure 3-14).

Figure 3-13. OER Electrochemical performance measurements in alkaline. (a) OER LSV curves of Pt-NPs-bonded@CNT, RuO₂, Pt-NPs-attached@CNT and carbon paper in 1.0 M KOH. (b) Comparison of overpotential graph of Pt-NPs-bonded@CNT with excellent CNT-based materials at 50 mA cm⁻² and 100 mA cm⁻². (c) Tafel slope compared graph of Pt-NPs-bonded@CNT and RuO₂ of OER in 1.0 M KOH. (d) Galvanostatic oxygen evolution measurement of Pt-NPs-bonded@CNT at 1000 mA cm⁻² in 1.0 M KOH.

Figure 3-14. HER LSV curves of Pt-NPs-bonded@CNT-600 °C at (a) acid and (b) alkaline solution. (c) OER LSV curves of Pt-NPs-bonded@CNT-600 °C at alkaline solution.

Reference		Catalyst
1	our work	Pt-N-CNT
2	Electrochim. Acta 2020, 331, 135362	CoPSeCoSe ₂ /CNTs
3	Electrochim. Acta 2023, 439, 141593	ZIF-67@CNT
4	Int. j. hydrogen energy. 2020, 45, 6629– 6635	CoFeCoFe ₂ O ₄ /N-CNTs
5	J. Power Sources 2020, 467, 228354	CNT@NiCo LDH-OV
6	Appl. Catalysis B-Environ. Energy 2021, 294, 120263	CuNi@Ni(ON)/CNTs-Gr
7	Chem. Eng. J. 2021, 422, 129982	CoO-CoSe2@N-CNTs/rGO
8	Chem. Eng. J. 2022, 427, 132041	NCNTs/Ni
9	Energy Storage Mater. 2021, 39, 11–20	FC-Ni ₃ N/NCNT
10	Adv. Sci. 2023, 10, 2206107	P-CoPc@CNT
11	ACS Appl. Mater. Interfaces 2023, 15, 32365–32375	Fe ₁₂ Ni ₂₃ Cr ₁₀ Co ₃₀ Mn ₂₅ /CNT
12	Int. j. hydrogen energy. 2022, 47, 12903–12913	(Fe-(NiP ₂ /Ni ₂ P)@CNT
13	Adv. Mater. 2024, 2310918	FeCoNiMnCr/CNT
14	ACS Appl. Mater. Interfaces 2020, 12, 42634–42643	CNT/NiFe
15	ACS Catal. 2020, 10, 4647-4658	N-Co-Mo-GF/CNT
16	Nano Res. 2020, 13, 437–446	Ni/NiFe ₂ O ₄ -CNTs
17	Nano Res. 2021, 14, 4534–4540	Fe ₂ O ₃ -CNT
18	Small 2023, 19, 2207196	N-NiMoO4/Ni/CNTs
19	ACS Appl. Mater. Interfaces 2020, 12, 12783–12792	FeP/Fe ₃ O ₄ /CNTs
20	Adv. Energy Mater. 2023, 2300152	NC@Vo·-RuO ₂ /CNTs
21	J. Solid State Chem. 2020, 289, 121498	NiFe/CNTs
22	J. Energy Chem. 2021, 60, 111–120	P-NiSe2@N-CNTs/NC
23	Chem. Eng. J. 2021, 413, 127531	NCNT-Ni NP@NF
24	Nano Energy 2019, 61, 576–583	Ru-RuO ₂ /CNT

 Table 3-2. Previously reported literature of splendid CNT-based catalysts oxygen

 evolution catalysts in alkaline.

3.3.5. Electrochemical Performance Measurements Normalized by ECSA

In order to identify the inherently high catalytic activity of Pt-NPs-bonded@CNT, the electrochemically active surface areas (ECSAs) of different catalysts were analyzed and

estimated through a series of cyclic voltammetry (CV) tests.⁴⁴ The electrochemical active surface area affects the catalyst activity because it reflects the active area of the catalyst participating in the reaction. It can be determined by: $ECSA = C_{dl}/C_s$, where C_{dl} is doublelayer capacitance and C_s is the specific capacitance of the sample.⁴⁵ In this work, $C_s =$ 0.04 mF cm⁻² was used as the value for the general specific capacitance based on commonly reported values.⁴⁶ The CV curves of Pt-NPs-bonded@CNT, Pt-C and Pt-NPsattached@CNT under different scan speeds are shown in Figure 3-15. As a result, the Cdl becomes an index of the electrochemically active area of the material, as shown in Figure 3-16 (a), the C_{dl} is obtained by fitting ΔJ (Half of the oxidation and reduction current density) values with different scan speeds of 10, 20, 30, 40, 50 and 60 mV s⁻¹. Consequently, the C_{dl} of Pt-NPs-bonded@CNT electrode exhibits a significantly higher ECSA value of 7.9 mF cm⁻² than Pt-NPs-attached@CNT of 5.2 mF cm², and the ECSA of Pt-C is 14.8 mF cm⁻². Carefully calculated, the electrochemically active surface area of Pt-NPs-bonded@CNT is 197.5 cm², which is significantly larger than the 130 cm² of Pt-NPs-attached@CNT, the electrochemically active surface area of Pt-C is 370 cm². The normalization of polarization curves by ECSA further indicates that Pt-NPsbonded@CNT possesses high intrinsic catalytic activity toward HER and OER compared with Pt-NPs-attached@CNT and Pt-C, as revealed in Figure 3-16 (b), (c) and (d). This result further demonstrated that platinum nanoparticles anchored on carbon nanotubes with Pt-C bonds possess excellent instinct electrocatalytic activity of hydrogen evolution in acid and alkaline conditions, as well as oxygen evolution ability in alkaline solutions.

Figure 3-15. (a) Cyclic voltammogram (CV) curves of Pt-NPs-bonded@CNT in 1.0 MKOH. (b) Cyclic voltammogram (CV) curves of Pt-NPs-attached@CNT in 1.0 M KOH.(c) Cyclic voltammogram (CV) curves of Pt-C in 1.0 M KOH.

Figure 3-16. Electrochemical performance measurements of Pt-NPs-bonded@CNT after normalized by ECSA. (a) The relationship between current density and scan rate corresponding to cyclic voltammetry curves at different scan rates. (b) HER LSV curves normalized by ECSA in 0.5 M H₂SO₄. (c) HER LSV curves normalized by ECSA in 1.0 M KOH. (d) OER LSV curves normalized by ECSA in 1.0 M KOH.

3.4. Conclusions

Platinum nanoparticles bonded in carbon nanotube (Pt-NPs-bonded@CNT) with strong Pt-C bonds are successfully established towards ultra-low overpotential water splitting ability in alkaline solution with an ampere-level current density. Benefit from the strong Pt-C bond between Pt nanoparticles and highly conductive carbon nanotubes, which can reduce the electron transfer energy barrier and accelerate electron transmission. In addition, the platinum nanoparticles bonded in carbon nanotubes can provide more stable active sites. As a result, the Pt-NPs-bonded@CNT electrocatalyst displays distinguished ampere-level electrocatalytic all-water splitting ability in alkaline solution. It exhibits excellent hydrogen evolution in acid and alkaline solutions with ultra-low overpotentials of 0.19 V and 0.23V at 1000 mA cm⁻², respectively. Besides, it shows superior ampere-level oxygen evolution electrocatalysis in alkaline solution with low overpotentials of 1.69 V at 1000 mA cm⁻², respectively. Moreover, it exhibits high stability over 120 h against hydrogen evolution at 1000 mA cm⁻² in both acid and alkaline conditions and long-term stability for 110 h against oxygen evolution in an alkaline solution. It also provides a new strategy for synthesizing new efficient catalysts, otherwise structural optimization for industrial catalytic hydrogen and oxygen evolution.

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Chapter 4: Ampere-level oxygen evolution reaction driven by Co₃O₄ nanoparticles supported on the layered TiO₂

4.1. Introduction

Hydrogen is the most promising future clean energy, and electrochemical water splitting using electrolyzers is a crucial way to produce hydrogen gas efficiently.¹⁻⁵ Regarding the evolution reaction of hydrogen gas, the slow kinetics of oxygen evolution reaction (OER) limits the water splitting ability, which makes electrolysis through a thermodynamically energy-unfavored process.⁶⁻⁸ The intrinsic dilemma in the OER process is that after the intermediate (OH) is deprotonated to form O*, an O-O bond needs to be formed in the next step, which limits the reaction kinetics.⁹⁻¹¹ The slow kinetics of OER originating from the high reaction energy barrier causes massive energy consumption during the water-splitting process. Therefore, lowering the reaction energy barrier to achieve fast reaction kinetics is required to realize efficient OER.¹²

In contrast with noble metal oxides, cobalt oxide (Co_3O_4), as first-row 3d transition metal oxides with high abundance and low cost, have attracted widespread attention as an alternative catalysts for OER.¹³⁻¹⁶ Yang *et al.* reported that Co_3O_4 nanoparticles binding to the exfoliated few-layer 2D Ti₃C₂ MXene nanosheets through electrostatic force exhibit the overpotential of 300 mV at a current density of 10 mA cm⁻² in basic solutions.¹⁷ However, due to the interfacial electrostatic interaction between Co_3O_4 nanoparticles and Ti₃C₂ MXene, its OER performance suffers from the ampere-level current. In order to obtain an electrocatalyst that meets the requirements of ampere-level current, it is essential to enhance the activity of the catalyst by reducing the overpotential. It is effective to regulate the electronic properties of the active sites to reduce overpotential. One way to achieve ampere-level OER performance is to alter the electronic properties of active sites by covalently bonding them to a substrate.¹⁸⁻²⁴ Wang *et al.* reported that the WO₃ as the substrate to bind Ir nanoparticles through the Ir-O-W bond exhibits excellent catalytic ability for hydrogen evolution.²¹ This result demonstrates that the formation of metal-oxygen covalent bonds is crucial for enhancing catalytic activity by tuning the free energy barrier for intermediates. Titanium dioxide (TiO₂) is widely used as the substrate for loading active sites due to its exceptional chemical stability and durability.^{25,26}

In this work, TiO₂ with a two-dimensional (2D) layered structure as the substrate to support the Co₃O₄ nanoparticles with a Co-O-Ti covalent bond was constructed towards efficient OER (Figure 4-1). In here, the MXene precursor method is adopted, that is, loading cobalt ions onto the surface of layered Ti₃C₂ MXene (obtained by etching Ti₃AlC₂), then converting them into cobalt oxide and titanium dioxide by annealing at low temperatures in the air. During the annealing process, the cobalt precursor (Co²⁺) on the surface of the layered Ti₃C₂ MXene is converted into Co₃O₄, while the Ti₃C₂ MXene is oxidized into TiO₂ to form a Co-O-Ti covalent bond. As a result, the Ti₃C₂ MXene-derived Co₃O₄@layered-TiO₂ composites exhibit brilliant OER performance with ultralow potential, ampere-level current density and long-term durability. Density functional theory (DFT) studies have confirmed that the Co-O-Ti covalent bond between the Co₃O₄ and TiO₂ can adjust the d-band center to optimize the reaction energy barrier for reaction intermediates.

Figure. 4-1. Schematic illustration of synthesis process of Co₃O₄@layered-TiO₂ towards OER.

4.2. Experimental

4.2.1. Preparation of layered Ti₃C₂ MXene

The Ti₃C₂ MXene was prepared by selectively etching Ti₃AlC₂ with stirring. First, 3.0 g of Ti₃AlC₂ powder was added to 60 mL of 40% hydrofluoric acid solutions to remove the Al layer by maintaining it at 60 °C for 48 hours. Afterward, the strongly acidic Ti₃C₂ MXene dispersion was centrifuged several times to obtain a neutral Ti₃C₂ MXene dispersion. Finally, the layered Ti₃C₂ was obtained by filtration and vacuum drying.

4.2.2. Preparation of Co₃O₄@layered-TiO₂

Firstly, 40 mg Ti₃C₂ MXene, 145 mg Co (NO₃)₂·6H₂O (0.50 mmol) and 76 mg (0.50 mmol) trans-1,4-cyclohexanedicarboxylic acid was ultrasonically dispersed in 30 mL of N, N'-dimethylformamide (DMF) for 30 min. Then, the obtained dispersion solution was transferred to a 50 mL autoclave reactor to be maintained at 160 °C for 16 hours in the oven. After cooling to room temperature, the black precipitate was dried overnight in a vacuum oven at 60 °C, followed by washing with ethanol and deionized water. Finally, Co₃O₄@layered-TiO₂ was obtained by annealing the above sample at 300 °C for 2 h with a heating rate of 2 °C min⁻¹ in the atmosphere. The Co₃O₄ was prepared using the same method, but without the addition of Ti₃C₂ MXene. The layered-TiO₂ was obtained by directed anneal Ti₃C₂ MXene in a tube furnace at a heating rate of 2 °C min⁻¹ at 300 °C for 2 h in an air gas atmosphere.

4.2.3. Materials characterization

The morphology of the sample was observed using scanning electron microscopy (SEM) (JEOL, JSM-6500F) and high-resolution transmission electron microscopy (TEM) (JEOL, JEM-2100). Elemental mapping images were obtained using TEM (JEOL, JEM2100). The selective area electron diffraction (SAED) was performed by AC-TEM (FEI Titan, G2 60-300). The X-ray diffraction (XRD) spectra were obtained using a D/Max-III X-ray spectrometer (Panalytical, Philips X'Pert Pro) with Cu K α radiation in the 2 θ range of 5° to 80°. The X-ray photoelectron spectroscopy (XPS) was examined by using electron energy dispersive spectroscopy (JEOL, JPS-9010TRX).

4.2.4. Electrochemical measurement

The electrochemical performance tests of all catalysts were conducted using an electrochemical workstation (Solartron, SI1287) in an electrolytic cell with a threeelectrode system. The alkaline electrolyte is 1.0 M KOH solution, the platinum plate electrode was used as the counter electrode, and a Hg/HgO electrode was used as the reference electrode. The Co₃O₄@layered-TiO₂ electrode obtained by drop-dry mothed, 5 mg of Co₃O₄@layered-TiO₂ catalyst was first dispersed in a mixed solution of 500 µL water, 450 µL isopropyl alcohol and 50 µL Nafion dispersion. Afterward, drop 40 µL of Co_3O_4 @layered-TiO₂ catalyst dispersion evenly on the carbon paper electrode with an area of 0.5×0.5 cm², then use it to test the electrochemical performance after drying. The potential relative to a reversible hydrogen electrode (RHE) under alkaline conditions was calculated by $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times \text{pH}$. Polarization curves were measured by linear sweep voltammetry (LSV) at a sweep rate of 5 mV s⁻¹. The stability measurements were performed using galvanostatic testing at a current density of 500 mA cm⁻². Electrochemical impedance spectroscopy (EIS) was tested from the 10000 to 0.1 Hz frequency range with an amplitude of 5 mV. The Tafel slope was obtained by $\eta = b \times$ $\log |j| + a$, where η , b and j are the potential, Tafel slope and the measured current density, respectively. The electrochemical double layer capacitance (C_{dl}) was obtained by cyclic voltammetry (CV) measurements at a voltage of 0.25 ~ 0.35 V versus Hg/HgO.

4.2.5. Calculation methods

All the DFT calculations were performed using the CASTEP simulation package in the Materials Studio software (BIOVIA, Materials Studio). The projector-augmented wave (PAW) method is used to describe the interactions between ion cores and valence electrons. The Perdew-Burke-Ernzerhof (PBE) functional and the generalized gradient approximation (GGA) were performed to describe exchange-correlation interaction calculation. The energy cutoff was set to 500 eV for geometry optimization and energy calculations of the lattice cells. The convergence accuracy of the electronic step is 10^{-7} eV. The model was constructed by putting the Co₃O₄ crystal on the TiO₂ crystal. A vacuum of 20 Å thickness is added in the Z direction to avoid spurious interactions between periodic lattices. After optimizing the structural model, the Co atom was chosen as the adsorption site to calculate the adsorption energy. The final enthalpy was obtained by optimizing the structure of the model. Finally, the adsorption energy (*E*_{ads}) was calculated by $\Delta E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$, where $E_{ad/sub}$, E_{ad} , and E_{sub} are the final enthalpy of the optimized adsorbate with substrate system, adsorbate, and substrate, respectively. The free energy (ΔG) was calculated by $\Delta G = \Delta E_{ads} + ZPE - T\Delta S$, where *ZPE* is the zeropoint energy and $T\Delta S$ is the entropic contribution. The d band center (ε_d) for d orbital projected density of state (PDOS) of Ru can be calculated by following:

$$\mu = \frac{\sum_{a}^{b} \varepsilon N(\varepsilon) d\varepsilon}{\sum_{a}^{b} N(\varepsilon) d\varepsilon}$$

where ε was the energy level and $N(\varepsilon)$ is the number of orbitals at the energy level ε . The parameters *a* and *b* were defined as the top or bottom limitation of the energy level for a certain orbital.

4.3. Results and Discussion

4.3.1. Structural characterizations

The XRD spectra were performed to identify the crystalline structure of the Ti_3AlC_2 , Ti_3C_2 MXene, $Co^{2+}@Ti_3C_2$ MXene and $Co_3O_4@layered-TiO_2$ (Figure 4-2 (a)). After HF etching, the peak located at 38.8° related to Al of Ti_3AlC_2 disappeared, and a new (002) peak of layered Ti_3C_2 MXene appeared at 8.8°, indicating that the Al layer of the Ti₃AlC₂ was successfully removed.^{27,28} Compared with previous work reported that Co²⁺ through solvothermal treatment in ethanol to get Co₃O₄ anchored on the surface of Ti₃C₂ MXene nanosheets, in this case, after hydrothermal reaction, the precursor of Co^{2+} grown on the surface of layered Ti₃C₂ MXene was not cobalt oxide.¹⁷ This is because the coordination of cobalt ions with trans-1,4-cyclohexanedicarboxylic acid in DMF solution can inhibit the oxidation of cobalt ions to the formation of Co₃O₄. The obtained precursor of Co^{2+} on Ti_3C_2 MXene facilitates the formation of covalent metal-oxygen bonds between metal oxides (cobalt oxide and titanium oxide) during the subsequent simultaneous oxidation process. The (002) peak of Ti₃C₂ MXene related to interlayer space was downshifted to 8.3°, which indicates that the interlayer spacing was expanded after the precursor of Co^{2+} growth. Besides, the other peaks of Ti_3C_2 MXene became weak and even vanished, which is attributed to a large amount of amorphous precursor of Co^{2+} covered on the surface of layered Ti_3C_2 MXene. The diffraction peaks at 19.0°, 31.27°, 36.85°, 59.35° and 65.23° can be well assigned to (111), (220), (311), (511) and (440) lattice planes of Co₃O₄ (JCPDS No. 42-1467), respectively. In addition, the diffraction peaks at 25.28°, 36.94°, 37.8°, 38.57°, 48.04°, 53.89° and 55.06° can be well indexed to (101), (103), (004), (112), (200), (105) and (211) lattice planes of TiO₂ (JCPDS No. 21-1272), respectively.^{29,30} No other impure diffraction peaks of metallic cobalt oxide were detected, indicating that pure phases of TiO₂ and Co₃O₄ were formed in the Co_3O_4 @layered-TiO₂. Besides, the weak diffraction peak at 8.3° corresponds to the (002) crystal plane of Ti₃C₂ MXene disappeared, which is ascribed to the oxidation of Ti₃C₂ MXene into TiO₂ during annealing. The successful preparation of layered-TiO₂ and Co₃O₄ was confirmed by XRD spectra. (Figure 4-3).

XPS further determined the chemical state of the surface elements of the $Co_3O_4@$ layered-TiO₂. The XPS survey spectra intuitively shows that Co, O and Ti elements exist in the $Co_3O_4@$ layered-TiO₂. The intensity of the C element becomes negligible, which confirms that Ti₃C₂ MXene was completely converted into TiO₂ during

the annealing treatment (Figure 4-4). In the Co 2p spectrum, the two peaks at 779.8 and 794.9 eV are attributed to the $2p_{3/2}$ and $2p_{1/2}$ peaks of Co³⁺ in Co₃O₄, respectively (Figure 4-2 (b)). Besides, the two peaks at 781.2 and 796.4 eV are attributed to the $2p_{3/2}$ and $2p_{1/2}$ peaks of Co²⁺ in Co₃O₄, respectively.³¹ In the Ti 2p spectrum, the two peaks are located at 459.2 and 465.0 eV, which correspond to $2p_{3/2}$ and $2p_{1/2}$ of Ti⁴⁺ of TiO₂, respectively (Figure 4-2 (c)).^{32,33} In the O 1s spectrum, the strong peak at 529.8 eV is attributed to the O1 peak of the metal oxide, further demonstrating the existence of TiO₂ and Co₃O₄ in the Co₃O₄@layered-TiO₂ (Figure 4-2 (d)).¹³ The O2 peak at 531.2 eV is ascribed to the hydroxyl group attached to the surface of the Co₃O₄@layered-TiO₂.³⁴ In addition, based on previously reported oxygen atoms bound to metal atoms, the peak at 530.2 eV is attributed to the Co-O-Ti covalent bond between Co₃O₄ and the TiO₂ substrate.^{24,33} Since the cobalt precursor (Co²⁺) on the surface of the layered Ti₃C₂ MXene was converted into Co₃O₄. Simultaneously, the Ti₃C₂ MXene was oxidized into TiO₂, and the oxidation process promotes the formation of Co-O-Ti bonds.

Figure 4-2. (a) XRD patterns of Ti_3AlC_2 (black), Ti_3C_2 (blue), $Co^{2+}@Ti_3C_2$ (green) and $Co_3O_4@$ layered-TiO₂ (red). The XRD standard card data for TiO₂ (JCPDS No. 21-1272) and Co_3O_4 (JCPDS No. 42-1467) are marked in purple and red. High-resolution XPS spectra of (b) Co 2p, (c) Ti 2p and (d) O 1s of $Co_3O_4@$ layered-TiO₂.

Figure 4-3. XPD patterns of (a) layered-TiO₂ and (b) Co₃O₄.

Figure 4-4. XPS survey spectrum of Co₃O₄@layered-TiO₂.

The SEM image of Ti₃AlC₂ exhibits a tightly stacked bulk structure (Figure 4-5 (a)). After removing the Al layer by HF etching, the Ti₃C₂ MXene with a layered structure was successfully prepared (Figure 4-5 (b)). Through hydrothermal treatment of Ti₃C₂ MXene, Co^{2+} and trans-1,4-cyclohexanedicarboxylic acid, the interlayers of Ti₃C₂ MXene were filled by the precursor of Co^{2+} (Figure 4-5 (c)). Finally, the precursor of Co^{2+} was successfully translated to Co₃O₄ nanoparticles by annealing in air. The Co₃O₄ nanoparticles are uniform growth on the surface of layered TiO₂ (Figure 4-5 (d)). Besides, the Co₃O₄@layered-TiO₂ maintains the layered structure of Ti₃C₂ MXene. Additionally, layered-TiO₂ obtained by direct oxidation of Ti₃C₂ MXene also exhibits a layered structure (Figure 4-6 (a)). Co₃O₄ prepared without MXene as a substrate exhibits a disordered filamentous structure (Figure 4-6 (b)). The crystal structure of Co₃O₄@layered-TiO₂ was further analyzed by TEM measurement. There is a large number of Co₃O₄ nanoparticles uniformly anchored on the surface of layered TiO₂ can be observed, which is consistent with SEM results (Figure 4-5 (e)). The average size of Co₃O₄ nanoparticles was determined to be 20.68 nm by statistical analysis of particle size distribution (Figure 4-7). In the HR-TEM image, the lattice of Co_3O_4 can be carefully recognized by a typical lattice distance of 0.46 nm corresponding to the (111) face of Co_3O_4 (Figure 4-5 (f) and 4-8).^{35,36} In addition, the SAED pattern also confirmed that Co_3O_4 and TiO₂ exist in Co_3O_4 @layered-TiO₂ (Figure 4-9). Consequently, the in-situ formation of Co_3O_4 nanoparticles attached to the surface of the layered TiO₂ substrate was successfully identified. The elemental mapping images reveal that Ti, Co and O elements were uniformly distributed in the Co_3O_4 @layered-TiO₂ (Figure 4-5 (g)). Furthermore, the EDX image indicates that Co is the primary element on the surface of Co_3O_4 @layered-TiO₂ (Figure 4-10).

Figure 4-5. SEM images of (a) Ti_3AlC_2 , (b) Ti_3C_2 MXene, (c) $Co^{2+}@Ti_3C_2$ MXene and (d) $Co_3O_4@layered-TiO_2$. (e, f) TEM and HR-TEM of $Co_3O_4@layered-TiO_2$. (g) HAADF-STEM and elemental mapping images (Ti, Co and O) of $Co_3O_4@layered-TiO_2$ from left to right.


Figure 4-6. SEM image of (a) layered-TiO₂ and (b) Co₃O₄.



Figure 4-7. Statistical analysis of particle size distribution of Co_3O_4 nanoparticles on TiO_2 substrate.



Figure 4-8. HR-TEM image of Co₃O₄@layered-TiO₂.



Figure 4-9. (a) HR-TEM image of Co_3O_4 @layered-TiO₂. (b) SEAD image of Co_3O_4 in Co_3O_4 @layered-TiO₂.



Figure 4-10. EDX image of Co₃O₄@layered-TiO₂.

4.3.2. Electrocatalytic performance of OER

The OER performance of Co_3O_4 (a) layered-TiO₂ was investigated in a typical threeelectrode system with 1.0 M KOH as electrolyte. The Co₃O₄@layered-TiO₂ dispersion droplets on the surface of carbon paper serve as the working electrode. Besides, the Pt plate and the Hg/HgO electrode were used as counter and reference electrodes, respectively. For comparison, the Co₃O₄, layered-TiO₂ and commercial RuO₂ catalyst was used as the contrast electrocatalyst, as presented by the LSV curves (Figure 4-11 (a)). Based on the EIS spectrum, LSV curves were corrected with 100% iR compensation (Figure 4-12). Compared to Co₃O₄, layered-TiO₂, RuO₂ and carbon paper, the Co₃O₄@layered-TiO₂ electrode exhibits the best OER performance, which can reach ampere-level current density with a small potential. It is worth noting that the Co₃O₄@layered-TiO₂ electrode only requires a potential of 1.52 V and 1.60 V to reach a current density of 100 mA cm⁻² and 500 mA cm⁻², respectively. In addition, it only needs 1.66 V to reach an ampere-level current density of 1000 mA cm⁻². Besides, carbon paper shows negligible performance for OER. Furthermore, the performance of Co₃O₄@layered-TiO₂ obtained after annealing at 300 °C is superior to that of Co₃O₄@layered-TiO₂ annealed at 250 °C and 350 °C (Figure 4-13). The results obtained at various current densities exhibit a superb low overpotential, which surpasses most of the previously reported literature on Co₃O₄-based catalysts (Figure 4-11 (b) and Table 4-1). Furthermore, the Co₃O₄@layered-TiO₂ exhibits the smallest Tafel slope value of 69.9 mV dec⁻¹, which is much smaller than the 94.3 mV dec⁻¹ of Co₃O₄ and 103.8 mV dec⁻¹ of RuO₂ (Figure 4-11 (c)). The results prove that the Co₃O₄@layered-TiO₂ has ultrafast kinetics for OER due to the Co₃O₄ nanoparticles supported on the TiO₂ substrate with Co-O-Ti covalent bond.³⁷ More importantly, achieving OER at high current density has always been a thorny problem. Therefore, galvanostatic measurement of half amperelevel current density was applied to demonstrate that the electrode meets industry requirements for catalytic OER stability. As a result, the Co₃O₄@layered-TiO₂ electrode can achieve long-term stability of OER at 500 mA cm⁻² up to 110 h, which proves that the Co₃O₄@layered-TiO₂ has superb stability for OER (Figure 4-11 (d)). In addition, the morphology image of Co₃O₄@layered-TiO₂ after 110 hours of durability testing remains almost unchanged, proving that the electrode maintains excellent stability even after the high current density stability test (Figure 4-14).



Figure 4-11. (a) OER LSV curves of Co_3O_4 @layered-TiO₂, Co_3O_4 , layered-TiO₂, RuO₂ and carbon paper in 1.0 M KOH. (b) Overpotential compared graph of Co_3O_4 @layered-TiO₂ with Co_3O_4 -based materials at 50 mA cm⁻² and 100 mA cm⁻². (c) Tafel slope compared graph of Co_3O_4 @layered-TiO₂, Co_3O_4 and RuO_2 . (d) Galvanostatic measurement of Co_3O_4 @layered-TiO₂ at 500 mA cm⁻² for 110 h in 1.0 M KOH.



Figure 4-12. EIS spectrum of Co₃O₄@layered-TiO₂. Insert shows equivalent circuit.



Figure 4-13. LSV curves of Co₃O₄@layered-TiO₂ under different annealing temperatures (250, 300 and 350 °C).

Reference		Catalyst
1	our work	TiO ₂ -Co ₃ O ₄
2	J. Alloys Compd. 2021, 853, 156946	Co ₃ O ₄ -MoS ₂ thin films
3	Adv. Energy Sustainability Res. 2023,	Co ₃ O ₄ /CeO ₂ heterojunction
	4, 2300123	nanonetworks
4	ACS Appl. Energy Mater. 2020, 3,	n-Co ₃ O ₄
	5439-5447	
5	Carbon Energy 2023, 5, 279	Mo-Co ₃ O ₄ @CC
6	ACS Catal. 2022, 12, 13482-13491	Ir _{0.33} @Co ₃ O4
7	Angew. Chem. Int. Ed. 2020, 59,	CoO/Co ₃ O ₄
	6929 - 6935	
8	Adv. Mater. 2018, 30, 1801211	Co ₃ O ₄ /Co-Fe oxide
9	Adv. Energy Mater. 2021, 11,	NiMoO ₄ @Co ₃ O ₄
	2101324	
10	ACS Catal. 2018, 8, 2236-2241	P _{8.6} -Co ₃ O ₄ /NF
11	ACS Catal. 2023, 13, 2462-2471	Ru/Co ₃ O _{4-x}
12	Adv. Mater. 2020, 32, 2002235	Fe-Co ₃ O ₄
13	Adv. Energy Mater. 2018, 8, 1701694	O-Co ₃ O ₄
14	Adv. Energy Mater. 2023, 13,	Ir/Ni-Co ₃ O ₄
	2302537	

Table 4-1. Previously reported literature of splendid Co₃O₄-based oxygen evolutioncatalysts.



Figure 4-14. SEM image of Co₃O₄@layered-TiO₂ after galvanostatic measurement.

The intrinsic catalytic activity was analyzed using electrochemically active surface areas (ECSAs) of different catalysts, estimated by a series of CV tests with various scan rates. The ECSA can be determined by ECSA = C_{dl}/C_s , where C_{dl} and C_s are double-layer capacitance and the specific capacitance of the electrode, respectively.³⁸⁻⁴² In this work, $C_s = 0.04 \text{ mF cm}^{-2}$ was used as the value for the general specific capacitance based on the reported value.³³ The CV curves of Co₃O₄@layered-TiO₂, Co₃O₄ and RuO₂ under different scan speeds were tested (Figure 4-15). The C_{dl} was obtained by fitting ΔJ (Half of the oxidation and reduction current density) values with different scan speeds of 10, 20, 30, 40, 50 and 60 mV s⁻¹ (Figure 4-16 (a)). As a result, the C_{dl} of the Co₃O₄@layered-TiO₂ electrode exhibits an ECSA value of 11.9 mF cm⁻². The ECSA of Co₃O₄@layered-TiO₂ still possesses the highest intrinsic catalytic activity toward OER compared with Co₃O₄ and RuO₂ (Figure 4-16 (b)). This result further proves that the Co₃O₄ nanoparticles attached on the

TiO₂ surface with Co-O-Ti covalent bond possess the optimal intrinsic electrocatalytic activity for OER in alkaline conditions.



Figure 4-15. (a) CV curves of Co_3O_4 @layered-TiO₂ in 1.0 M KOH. (b) CV curves of RuO₂ in 1.0 M KOH. (c) CV curves of Co_3O_4 in 1.0 M KOH.



Figure 4-16. (a) The plots of the current density versus the scan rate of 10, 20, 30, 40, 50 and 60 mV s⁻¹. (b) OER LSV curves of Co_3O_4 @layered-TiO₂, Co_3O_4 and RuO_2 normalized by ECSA in 1.0 M KOH.

4.3.3. Studies on mechanism of catalytic activities

To investigate the origin of the remarkable OER performance of Co₃O₄@layered-TiO₂, DFT simulations were carried out to confirm that the Co₃O₄ nanoparticles attached on the surface of TiO₂ with Co-O-Ti covalent bond have high catalytic activity. The constructed model of Co₃O₄ on TiO₂ (Co₃O₄-TiO₂) with a Co-O-Ti bond was utilized for adsorbing reaction intermediates (Figure 4-17). The charge density difference of Co₃O₄-TiO₂ indicates that the attached Co₃O₄ on the TiO₂ can effectively regulate the charge redistribution, where the Co₃O₄ and TiO₂ tend to lose electrons, and the delocalized electrons accumulate around adjacent Co-O-Ti bonds. (Figure 4-18 (a), (b) and (c)).⁴³ The d-band center (ε_d) often dominates the progress of electrochemical reactions because it is directly related to the adsorption strength of the catalyst to reaction intermediates. According to the projected density of states (pDOS), it has been observed that attaching Co₃O₄ on the TiO₂ surface tends to alter the ε_d (Figure 4-18 (d)). In here, the ε_d value of TiO₂-Co₃O₄ is closer to the Fermi level (-0.71 eV) than ε_d of TiO₂ and Co₃O₄, which is advantageous in regulating the adsorbed intermediates on the catalyst surface.^{25,44,45} Additionally, in TiO₂-Co₃O₄, the total density of states (TDOS) at the Fermi level is increased, confirming that attaching Co₃O₄ to TiO₂ can enhance the conductivity of Co₃O₄ and TiO₂. The performance of OER was determined by calculating Gibbs free energy of reaction condonation of *OH, *O, and *OOH steps (Figure 4-18 (e)). The structural model has been optimized after adsorbing OH, O, and OOH on the Co site of TiO₂-Co₃O₄ (Figure 4-19). As a result, the rate-determining step (RDS) energy barriers of Co₃O₄, TiO₂ and Co₃O₄-TiO₂ are 2.05, 2.28 and 1.78 eV, respectively. The RDS of Co₃O₄-TiO₂ (*O + OH⁻ \rightarrow *OOH + e⁻) has a low free energy barrier of 1.78 eV, which is beneficial to accelerate the OER processes (Figure 4-18 (f)). This result demonstrates that the attachment of Co₃O₄ on the TiO₂ surface with the Co-O-Ti covalent bond is beneficial for reducing the energy barrier for OER, thus boosting OER performance at ampere-level current density.



Figure 4-17. Optimized structural model of TiO₂-Co₃O₄.



Figure 4-18. The side views of charge density difference of (a) Co_3O_4 -TiO₂, (b) Co_3O_4 and (c) TiO₂. Green indicates positive charges and yellow indicates negative charges. (d) Calculated DOS and d-band center (ε_d) of Co_3O_4 -TiO₂, Co_3O_4 and TiO₂. (e) Schematic illustration of the OER mechanisms. (f) Calculation of Gibbs free energy (ΔG) of each step of OER and rate-determining step energy barriers of Co_3O_4 -TiO₂, Co_3O_4 and TiO₂.



Figure 4-19. (a) The side Optimized the structural model after adsorbing OH on the Co

site of TiO_2 -Co₃O₄. (b) Optimized the structural model after adsorbing O on the Co site of TiO_2 -Co₃O₄. (c) Optimized the structural model after adsorbing OOH on the Co site of TiO_2 -Co₃O₄.

4.4. Conclusions

The Co₃O₄ nanoparticles supported on the TiO₂ surface with a Co-O-Ti covalent bond were constructed. When the cobalt precursor (Co²⁺) on the surface of the layered Ti₃C₂ MXene was converted into Co₃O₄, the Ti₃C₂ MXene was also oxidized into TiO₂, which promotes the formation of Co-O-Ti bonds. As a result, the Co₃O₄@layered-TiO₂ exhibits brilliant OER with ultra-low potential, ampere-level current density and long-term durability. When the current density reaches 100 mA cm⁻² and 1000 mA cm⁻², the required potential is only 1.52 V and 1.66 V, respectively. Additionally, it can achieve long-term stability up to 110 h at 500 mA cm⁻². DFT studies have demonstrated that the Co-O-Ti covalent bond between the Co₃O₄ and TiO₂ can adjust the d-band center, which is beneficial for reducing the energy barrier for intermediates of OER. This result illuminates a new strategy of using metal oxide substrate to support active materials for highly efficient electrocatalysis.

4.5. References

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Chapter 5: Conclusions

This thesis is mainly devoted to the synthesis of highly active electrocatalysts for high current density HER and OER. They belong to three different systems, namely Rubased catalysts, Pt-based catalysts and cobalt oxide-based catalysts. This electrocatalyst is achieved through optimizing crystal facets, modifying catalyst surfaces, and bonding active sites with substrates. The results of the research could be concluded as follows:

In Chapter 2, ruthenium nanorods were synthesized in this thesis for the first time and proposed a new strategy for surface modification. Compared with many previously reported ruthenium nanoparticles, which have multiple equally distributed facets and lack the optimization of catalyst surfaces, resulting in unsatisfactory ampere-level current density for electrocatalysts. In this part, Ru nanorods dominated by (100) faces were innovatively constructed, with the surface modified by chemisorbed oxygen and OH groups, to achieve excellent bifunctional OER/HER performance. These nanorods were grown on the surface of nickel foam using a surfactant coordination method. In the synthesis process, terephthalic acid has two hydrophilic carboxyl groups to coordinate ruthenium ions to boost the formation of ruthenium nanorods. In contrast, benzoic acid is used as a surfactant to form ruthenium nanoparticles due to its single hydrophilic carboxyl group for coordinating ruthenium ions. As a result, the SMRu-NRs@NF exhibits excellent hydrogen evolution in acid and alkaline solutions with an ultra-low overpotential of 215 mV and 185 mV reaching 1000 mA cm⁻², respectively. Moreover, it has also shown brilliant oxygen evolution electrocatalysis in alkaline solution with a low potential of 1.58 V to reach 1000 mA cm⁻². It also exhibits high durability over 143 h for the evolution of oxygen and hydrogen at 1000 mA cm⁻². Furthermore, the DFT simulation results demonstrate that the ruthenium nanorod modified by chemisorbed oxygen and OH groups exhibit the optimal adsorption and desorption of hydrogen radicals and water. In addition, it can reduce the energy barrier for the formation of *OOH, thereby accelerating the OER process.

In Chapter 3, this work demonstrated, for the first time, that platinum nanoparticles bonded to carbon nanotubes with strong interaction via Pt-C bonds exhibit bifunctional OER/HER performance with an ampere-level current density, which significantly exceeds the performance of previously reported Pt-based catalysts, which only showed HER performance. This is because the Pt active sites have weak interactions with the substrate. During the synthesis process, we treated carbon nanotubes with a strong acid solution to form defects on their surface for capturing platinum atoms, thereby promoting the embedding of platinum nanoparticles into the surface of carbon nanotubes. Benefit from the strong interaction between platinum and high conductivity carbon nanotube substrates through the Pt-C bond also the platinum nanoparticles bonded in carbon nanotube can provide more stable active sites, as a result, the Pt-NPs-bonded@CNT exhibits excellent hydrogen evolution in acid and alkaline solution with an ultra-low overpotential of 0.19 V and 0.23 V to reach 1000 mA cm⁻², respectively. Besides, it shows superior oxygen evolution electrocatalysis in alkaline solution with low overpotential of 1.69 V at 1000 mA cm⁻². Furthermore, it also exhibits high stability over 110 h against the evolution of oxygen and hydrogen under 1000 mA cm⁻².

In Chapter 4, a two-dimensional (2D) layered structure of TiO_2 was used as a substrate to support Co₃O₄ nanoparticles with a Co-O-Ti covalent bond, aiming to enhance the efficiency of the OER. Notably, its OER performance is significantly better than that of previously reported individual Co₃O₄ nanoparticles or Co₃O₄ nanoparticles supported on substrates due to their lack of strong interactions. In this part, the MXene precursor method is adopted, where cobalt ions were loaded onto the surface of layered Ti₃C₂ MXene (obtained by etching Ti₃AlC₂). Subsequently, the cobalt precursor (Co²⁺) on the surface of the layered Ti₃C₂ MXene was converted into Co₃O₄. Simultaneously, the Ti₃C₂ MXene was oxidized into TiO₂, forming a Co-O-Ti covalent bond through annealing at low temperatures in air. As a result, the Co₃O₄@layered-TiO₂ exhibits brilliant OER performance with ultra-low potential (1.52 V to reach 100 mA cm⁻²), ampere-level current density (1.66 V to reach 1000 mA cm⁻²) and long-term durability

(110 h at 500 mA cm⁻²). We also performed a DFT study to confirm that the Co_3O_4 nanoparticles, loaded onto the layered TiO₂ surface via Co-O-Ti covalent bonds, can optimize the reaction energy barrier by adjusting the d-band center.

In this thesis, the SMRu-NRs@NF and Pt-NPs-bonded@CNT were constructed for efficient bifunctional OER/HER electrocatalysts. Compared with the Pt-NPs-bonded@CNT catalyst, the SMRu-NRs@NF seem more promising for practical application due to its lower preparation cost and easier synthesis processes. Additionally, the SMRu-NRs@NF catalyst can be directly used for electrocatalysis without the need for further treatment, such as loading it on a conductivity substrate, because the ruthenium nanorods are already stably grown on the surface of the nickel foam. Co₃O₄@layered-TiO₂ demonstrates excellent OER performance and can be combined with outstanding hydrogen evolution catalysts to reduce the practical application potential of water electrolysis.

The combination of experimental results and theoretical calculations enables a deeper understanding of how to design advanced electrocatalysts, including controlling highly active crystal faces, rational modification of the catalyst surface, and covalently bonding active sites to the substrate. The design concept of advanced electrocatalyst is not limited to the OER/HER field but also has broad application prospects in other fields, such as electrocatalytic carbon dioxide reduction, oxygen reduction and nitrogen reduction. We also hope that, in the future, more catalysts with high activity and low cost can be developed using earth-abundant materials as our inspiration.

List of publications

1. Surface-Modified Ruthenium Nanorods for Ampere-Level Bifunctional OER/HER Electrocatalyst.

Hong Tang, Takahiro Kojima, Kenji Kazumi, Kazuhiro Fukami, and Hiroshi Sakaguchi*. ACS Applied Materials & Interfaces, 2024, 16, 35053–35062. https://doi.org/10.1021/acsami.4c05286 (Chapter 2)

2. Platinum Nanoparticles Bonded with Carbon Nanotubes for High-Performance Ampere-Level All-Water Splitting.

Hong Tang, Takahiro Kojima, Kenji Kazumi, Kazuhiro Fukami, and Hiroshi Sakaguchi*. ACS Omega 2024, 9 (19), 21378–21387. https://doi.org/10.1021/acsomega.4c01662

(Chapter 3)

3. Ampere-level oxygen evolution reaction driven by Co_3O_4 nanoparticles supported on the layered TiO₂.

Hong Tang, Wu Wei, Takahiro Kojima, Kenji Kazumi, Kazuhiro Fukami, and Hiroshi Sakaguchi*.

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(Chapter 4)

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