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Advances in Modification Strategies and Electrolytic Water Splitting Performance of Transition Metal Phosphide Catalysts

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Abstract. Hydrogen production from electrolytic water splitting is regarded as a core route toward sustainable hydrogen supply, although the industrialization of this technology has long been constrained by the high cost of noble metal catalysts. Transition metal phosphides (TMPs) stand out as a low-cost alternative for water electrolysis, owing to their noble-metal-like electronic structures and good stability in both acidic and alkaline media. In this review, the reaction mechanisms of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) are first introduced, followed by a summary of the mainstream preparation methods for TMPs, namely liquid-phase synthesis, pyrolysis reduction, ball milling, electrodeposition, and gas–solid reaction. Four major modification strategies—interface engineering, vacancy defects, structural regulation, and elemental doping—are then discussed in detail, with emphasis on how each approach modulates the electronic structure, increases the number of active sites, and optimizes the adsorption energy of reaction intermediates. The HER, OER, and overall water splitting performances of differently modified TMPs are also compared. Despite these advances, existing TMP catalysts still face problems such as insufficient stability at high current densities and difficulty in large-scale preparation. Looking ahead, high-entropy phosphides and multi-element co-doping are considered promising directions for developing high-efficiency bifunctional electrocatalysts for water electrolysis.

Keywords: transition metal phosphides, water electrolysis, electrocatalysis, modification, hydrogen and oxygen evolution

1. Introduction

Hydrogen energy is widely considered one of the most promising clean energy carriers, thanks to its zero-pollution nature and high calorific value, and it has therefore drawn considerable research interest. Renewable energy sources such as solar power can be stored in the form of hydrogen through hydrogen storage technologies, which helps improve the reliability and stability of the whole energy system. Depending on the production principle and the raw materials used, hydrogen can be produced by fossil fuel reforming, biological hydrogen production, or water electrolysis. Among the three routes, electrolytic water splitting decomposes water into hydrogen and oxygen

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with electricity; it produces no emissions during the process and enables green hydrogen with a purity exceeding 99% to be obtained rapidly in a single step [1]. The operation is also simple and flexible. Because of the reaction energy barriers involved, the actual voltage applied in water electrolysis must exceed the theoretical value to drive the reactions forward. To raise the energy conversion efficiency, high-performance electrocatalysts are therefore needed as electrode materials to accelerate the reaction kinetics of the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER).

2. Fundamentals of water electrolysis

Electrolytic hydrogen production can be carried out in various types of electrolyzers. When an external voltage is applied, electrons are gained at the cathode, where the hydrogen evolution reaction takes place, while electrons are lost at the anode, where the oxygen evolution reaction occurs. The overall reaction is expressed as:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (1)$$

As shown in Figure 1, the theoretical voltage required for water electrolysis is 1.23 V under standard conditions (T = 298 K, P = 1 atm), which corresponds to an energy consumption of ΔG = 237.1 kJ·mol^{-1} [2]. In practice, however, factors such as electrode polarization, wire resistance, and solution resistance mean that an additional electrode potential has to be applied to drive the water splitting reaction.

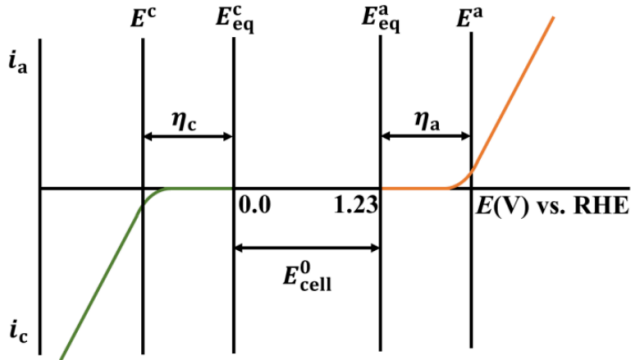


Figure 1. Schematic diagram of the theoretical potential and overpotentials in water electrolysis (ηc: cathodic overpotential, ηa: anodic overpotential)

2.1. Cathodic hydrogen evolution mechanism

Taking place first is the Volmer reaction, in which hydrogen is chemically adsorbed onto the active sites of the catalyst surface to form adsorbed hydrogen atoms. Under acidic conditions, H^+ ions migrate from the solution to the electrode surface and capture electrons at the active sites to form H. In neutral and alkaline media, by contrast, water molecules must be dissociated first, an additional energy barrier that releases a hydroxyl ion and leaves H* on the catalyst surface. The second step is the formation of H_2 molecules and their release from the catalyst surface. Two pathways are possible in any electrolyte, depending on the H* coverage. When the H* coverage is low, the H* produced in the first step combines with free H^+ or water molecules in the electrolyte, captures an electron, and yields H_2 through an electrochemical desorption process, which is known as the Heyrovsky reaction. When the H* coverage is high, on the other hand, two adjacent H* species on the catalyst surface

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combine directly with each other to form H_2 via a chemical desorption process, referred to as the Tafel reaction [3].

2.2. Anodic oxygen evolution mechanism

The OER proceeds through multiple reaction intermediates and follows a more intricate mechanism, which makes its kinetics considerably slower than those of the HER. In electrolytes, the OER mechanism is generally divided into the AEM and the LOM, as illustrated in Figure 2. For the AEM, the widely accepted pathway takes O, OH, and OOH* as the key intermediates [4]. In detail, OH^- or H_2O molecules are first adsorbed onto the active sites and oxidized through a single-electron step to form OH*, whether in alkaline or acidic media. The OH* then deprotonates to give O, which couples with another OH^- or H_2O via a single-electron oxidation reaction, losing electrons to produce the OOH intermediate. Finally, OOH* undergoes proton-coupled electron transfer, releasing O_2 and regenerating the active sites.

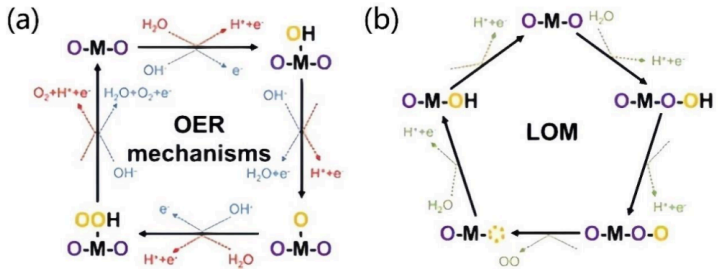


Figure 2. Schematic illustration of OER mechanisms: (a) AEM pathway (red and blue lines correspond to acidic and alkaline conditions, respectively); (b) LOM pathway [4]

3. Transition metal phosphides for electrocatalytic water splitting

TMPs have attracted growing research interest because of their unique physicochemical properties and impressive electrochemical performance. Conceptually, a TMP can be regarded as an alloy formed by incorporating atomic P into a metal lattice, which gives the material a noble-metal-like electronic structure. The strong P—M covalent bonds also ensure long-term stability in both acidic and alkaline electrolytes, which makes TMPs highly promising electrocatalytic materials for water splitting. The effect of the metal-to-phosphorus ratio in Ni_xP_γ nanoparticles on OER catalytic activity was also systematically examined by Poureshghi.

3.1. Electrocatalytic hydrogen evolution reaction

As high-activity, low-cost HER catalysts, TMPs have been the subject of extensive study. Zhao et al. fabricated a honeycomb-like porous bimetallic phosphide composite (MoP/MoNiP@NPC-800) following the procedure illustrated in Figure 3. The catalyst showed outstanding HER activity in both 1.0 M KOH and 0.5 M H_2SO_4 solutions, with overpotentials (η_{10}) as low as 50.4 mV and 72.6 mV, respectively, and remained stable for about 120 h at a current density of 50 $mA \cdot cm^{-2}$ [5]. In another work, Zheng et al. reported a nitrogen-doped carbon-coated cobalt-molybdenum phosphide nanoparticle (CoP-MoP/NC). Thanks to the synergistic effect of the bimetallic components and nitrogen incorporation, CoP-MoP/NC exposed abundant active sites and possessed optimized charge transfer kinetics, achieving efficient HER catalysis under acidic conditions with a low overpotential of 105.2 mV (η_{10}) and a small Tafel slope of 79.7 $mV \cdot dec^{-1}$ [6]. Even so, the electrocatalytic activity

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of TMPs still falls short of that of noble metal-based counterparts, so further enhancement of intrinsic activity is needed. Many researchers have responded by introducing small amounts of noble metals into TMPs, hoping to boost the intrinsic HER activity without losing cost competitiveness. Kang et al., for instance, doped Ru into Fe_2P single crystals and obtained Ru-Fe_2P with accelerated HER kinetics and superior catalytic activity (Figure 3d–f).

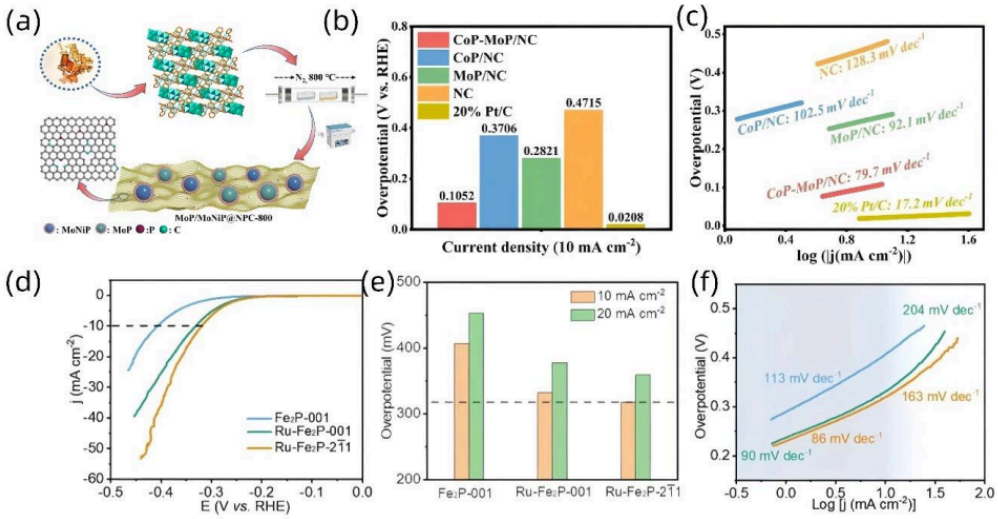


Figure 3. (a) Schematic illustration of the pyrolysis preparation process for the MoP/MoNiP@NPC-800 catalyst [7]; (b) overpotential comparison and (c) corresponding Tafel plots of different samples; (d) LSV curves, (e) overpotential comparison, and (f) Tafel plots of Fe_2P and Ru-Fe_2P [6]

3.2. Electrocatalytic oxygen evolution reaction

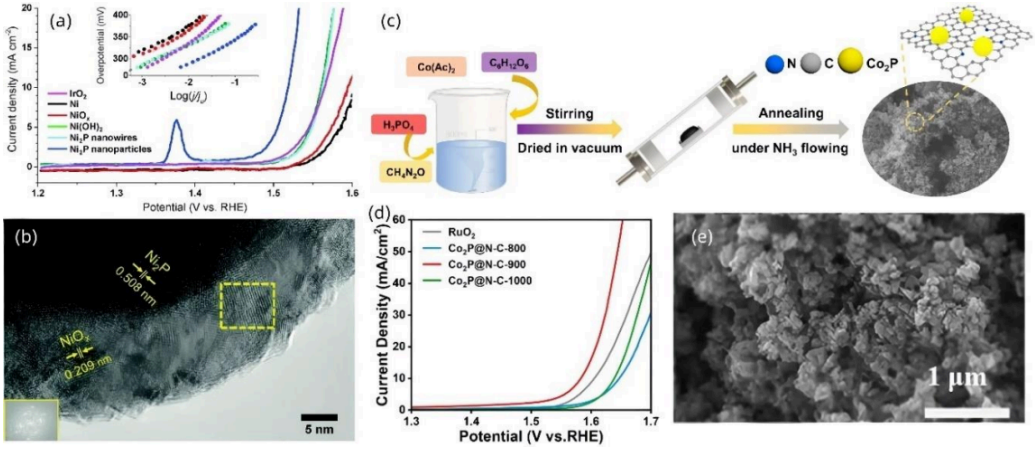


Figure 4. (a) LSV and corresponding Tafel plots of the material in alkaline solution; (b) HRTEM image [7]; (c) schematic illustration of the synthesis process for Co_2P@N-C; (d) LSV curve comparison between the as-synthesized materials and RuO_2 [7]; (e) SEM image of the FeP/CoP heterostructure material

Transition-metal phosphides (TMPs) are well-established high-efficiency electrocatalysts toward the OER. In 2015, Hu and coworkers first applied Ni_2P to alkaline OER catalysis: the catalyst delivered 10 $mA \cdot cm^{-2}$ at an overpotential of merely 290 mV in 1.0 M KOH. HRTEM characterization showed that nanoparticles of 2–3 nm were formed on Ni_2P during OER operation,

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and these in-situ constructed Ni_2P/NiO_x core-shell architectures are responsible for the superior catalytic activity. After this pioneering work, a variety of TMP materials have been explored as low-cost OER candidates. Wang's team, for example, prepared Co_2P, which reached 10 $mA \cdot cm^{-2}$ at an overpotential of 352 mV in 1.0 M KOH, surpassing commercial RuO_2 and numerous non-precious-metal electrocatalysts (Figure 4) [7].

3.3. Electrocatalytic overall water splitting

Using two different catalysts to drive the HER and OER separately raises both the cost and the system complexity of water electrolysis. Bifunctional catalysts that can catalyze both reactions efficiently are therefore of great significance for the advancement of hydrogen production from water splitting, and TMPs hold considerable promise in this respect. Sun et al., for example, used green and inexpensive adenosine triphosphate as the phosphorus source to prepare a series of nanoscale TMP catalysts encapsulated in nitrogen-phosphorus co-doped carbon; all of these catalysts exhibited excellent HER and OER activities.

4. Synthesis methods of transition metal phosphides

A number of synthetic approaches have been developed to prepare TMP electrocatalysts with desirable structures and catalytic properties. Each method has its own advantages and disadvantages, and the same TMP material can exhibit distinct morphologies and electrochemical behaviors depending on the synthetic route. This section introduces several commonly used methods, including liquid-phase reaction, pyrolysis reduction, ball milling, electrodeposition, and gas–solid reaction.

4.1. Liquid-phase reaction method

The liquid-phase reaction method is widely used in both laboratory and industrial settings. Organophosphines typically serve as the phosphorus source here, reacting with transition metal ions at elevated temperatures. The reaction is carried out in high-boiling-point organic solvents; during the process, the C—P bonds in the phosphorus source are cleaved, and the released P atoms subsequently coordinate with metal atoms (M) to form TMPs. Han et al. prepared Cu_3P nanoparticles with well-defined shapes and sizes using trioctylphosphine as the phosphorus source and examined how the amount of oleylamine solvent affects the phosphidation outcome. They observed that a higher oleylamine content resulted in a lower degree of phosphidation in the resulting nanoparticles (Figure 4) [8]. Nevertheless, this method suffers from limited controllability, and the products often have complex compositions, which hinders the use of theoretical calculations to study its catalytic mechanisms.

As a variant of the liquid-phase reaction approach, the hydrothermal method uses water as the reaction solvent under relatively high temperature and pressure. Compared with conventional liquid-phase synthesis, it is better suited to solvent-sensitive synthesis conditions. The equipment required is simple and the cost is low, and parameters such as reaction temperature and duration can be adjusted to obtain high nucleation rates and a favorable particle size distribution.

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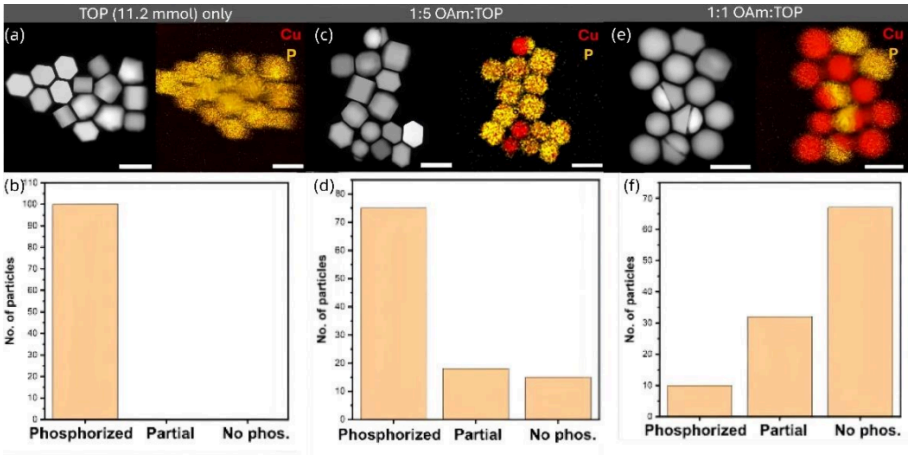


Figure 5. STEM-EDS characterization and phosphidation state distribution of Cu_3P particles with different oleylamine contents: (a–b) 0 mL oleylamine; (c–d) 1 mL oleylamine; (e–f) 5 mL oleylamine. Scale bars: 50 nm [8]

4.2. Pyrolysis reduction method

The pyrolysis reduction method is one of the earliest synthetic approaches, developed to make use of phosphorus-containing phosphate groups. In a typical process, a certain amount of metal salts and phosphates is first dissolved in water, and the solution is then evaporated to obtain a mixed powder. This powder is pyrolyzed under a reducing atmosphere (e.g., H_2) at elevated temperatures of 500–1000 °C; during pyrolysis, the P—O bonds of the phosphate groups are broken, allowing cross-linking with the metal precursors to form TMPs. Following this method, Xing et al. prepared a tightly interconnected network of MoP nanoparticles with a high specific surface area, which exhibited high activity as an HER catalyst in acidic media.

4.3. Ball milling method

The ball milling method relies on mechanical stirring to induce chemical reactions or to alter the structure and properties of materials, providing a simple and environmentally friendly alternative to high-temperature synthesis or solution chemistry. It can significantly refine grain sizes, and materials of different dimensions can be obtained by adjusting parameters such as milling media size, feed ratio, rotational speed, and milling time, which gives this method unique advantages and broad application potential. Cheng et al., for example, used a two-step high-energy ball milling (HEBM) process to gradually composite metal phosphide nanoparticles with MXene and graphene.

4.4. Electrodeposition method

Electrodeposition is a safe and inexpensive route for fabricating nanomaterials efficiently under an electric field, with hypophosphite usually serving as the phosphorus source. In a two- or three-electrode system, $H_2PO_2^-$ undergoes redox reactions with metal ions from the soluble metal salt solution on the electrode surface, forming TMP deposits on conductive substrates such as carbon cloth, copper mesh, and nickel foam. Zeng et al. deposited hydrangea-like bimetallic nickel-cobalt phosphide onto carbon nanotube arrays by potentiostatic electrodeposition; by adjusting the Ni/Co molar ratio in the solution and the deposition time, they obtained a material with optimal OER catalytic activity .

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4.5. Gas–solid reaction method

The gas–solid reaction method is an easily accessible phosphidation approach. Hypophosphites such as NaH_2PO_2 and $NH_4H_2PO_2$ are typically used as the phosphorus source, while metal oxides, metal hydroxides, or metal–organic frameworks serve as the solid metal sources. The two precursors are placed together in an inert atmosphere (commonly N_2 or Ar) and subjected to heat treatment to accomplish phosphidation. Upon heating at 250–350 °C, the hypophosphites decompose to generate reducing PH_3 gas in situ, which then reacts chemically with the metal precursors to yield TMPs.

5. Modification strategies for transition metal phosphides

TMPs have made notable progress as water-splitting electrocatalysts, yet their performance still falls short of industrial requirements and further optimization is needed. Studies have shown that the morphology, structure, and chemical composition of a catalyst play crucial roles in determining its water electrolysis performance. To enhance catalytic activity, researchers have therefore proposed various modification strategies, including interface engineering, vacancy engineering, structural regulation, and elemental doping. These strategies improve TMP performance mainly in four ways: increasing the number of active sites, enhancing the intrinsic activity of the catalyst, improving electrical conductivity, and boosting catalyst stability.

5.1. Interface engineering

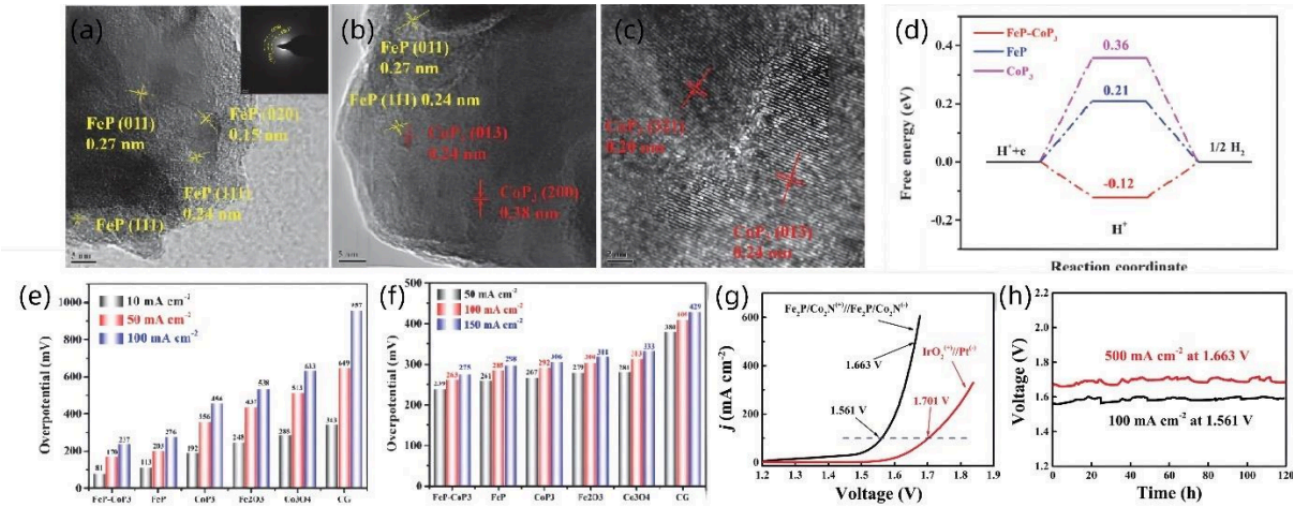


Figure 6. (a–c) HRTEM images of FeP–CoP_3; (d) calculated free energies of HER intermediates for the materials; (e) OER overpotentials of the materials; (f) HER overpotentials of the materials; (g) polarization curves of overall water splitting in 1 M KOH for Fe_2P/Co_2N(+/−) and IrO_2(+)//Pt(−) coupled electrodes; (h) stability test of the water electrolyzer at constant current density for over 120 h [9]

Interface engineering provides a powerful means of modulating the electronic structure, usually by introducing multiple heteroatoms into monometallic compounds or by combining several metal compounds to integrate different phases. The charge redistribution at the heterointerface regions influences the adsorption/desorption energy of intermediates as well as the transfer of electrons and adsorbates during electrocatalysis, thus modifying the physicochemical properties and tuning the catalytic performance of the material. An et al., for instance, synthesized ZIF-67 in situ on MIL-

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88(Fe) and then carried out low-temperature phosphidation to integrate FeP and CoP_3, effectively constructing a heterostructure between the two and modulating the electronic structure of FeP–CoP_3 [9]. HRTEM clearly evidenced the formation of the FeP–CoP_3 heterojunction, revealing a well-defined boundary between the two nanoparticle phases. Subsequent DFT calculations showed that FeP–CoP_3 possessed the lowest $|\Delta G_{H^*}|$ energy (0.12 eV) among the samples tested, approaching the ideal value. In a related study, Li et al. developed Co_2P/Ni_2P heterostructured porous nanosheets through a two-step thermal phosphidation process. Owing to the strong interfacial interaction between Co_2P and Ni_2P and the high porosity and abundant active sites of the interconnected nanoparticles, this electrocatalyst exhibited exceptional HER activity across the full pH range.

5.2. Vacancy engineering

Vacancies are defects commonly present in most nanomaterials as a result of imperfect atomic arrangements. When introduced into TMPs, they can disrupt the original charge distribution, modulate the electronic and band structures, increase the number of active sites, enhance electrical conductivity, and optimize charge transport, all of which accelerates electrocatalytic kinetics and improves catalytic performance. Yuan et al., for example, constructed phosphorus vacancy-rich CoP nanorods through a straightforward $NaBH_4$ reduction strategy. During the OER process, these phosphorus vacancies (P_v) combine with oxygen to form phosphate, which promotes the reconstruction of active $CoO_x(OH)_\gamma$ species and thus enhances the OER activity. In another study, Min synthesized Fe-doped Ni_2P nanoparticles with abundant P_v. Compared with Fe–Ni_2P (315 mV), Fe–Ni_2P–V_p exhibited superior OER catalytic activity, requiring a low overpotential of only 289 mV to drive a current density of 10 mA·cm^{-2}, lower than that of the state-of-the-art RuO_2 catalyst (334 mV).

DFT simulations, as illustrated in Figures, verify that Mo vacancies strengthen Mo–P orbital hybridization and induce electron accumulation on neighboring P atoms. As a result, abundant P sites with near-zero hydrogen-adsorption free energy are exposed and act as the dominant active centers for HER.

5.3. Structural regulation

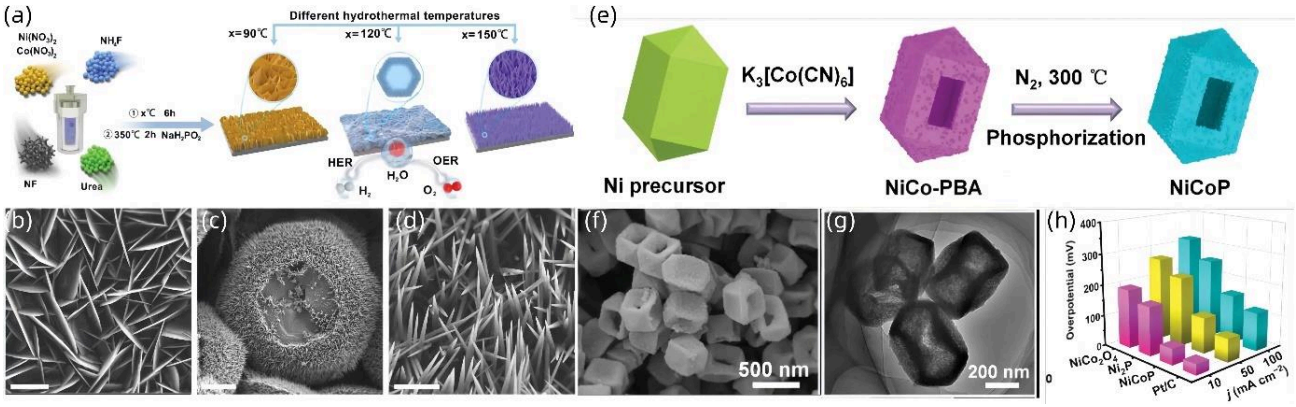


Figure 7. (a) Schematic illustration of the synthesis process for NiCoP; SEM images of samples obtained under different conditions: (b) NiCoP-90, (c) NiCoP-120, (d) NiCoP-150; (e) synthesis scheme, (f) SEM image, and (g) TEM image of NiCoP nanoprisms; (h) overpotential comparison of several materials

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Constructing specific nanostructures—nanoparticles, nanosheets, nanowires, nanoarrays, and nanoflowers among them—is the most commonly adopted design strategy for boosting the performance of water-splitting electrocatalysts. Compared with their bulk counterparts, materials with well-defined nanostructures can achieve larger specific surface areas, expose more active sites, and optimize mass transfer and charge transport. As illustrated in Figures, Ding et al. elaborately designed hollow NiCoP nanoprisms as electrocatalysts for water splitting, which benefit from the unique hollow architecture, abundant micro/mesoporous channels, and optimized electronic structure.

5.4. Elemental doping

A comparison of the HER performance of various element-doped TMPs shows that Ni, Co, Fe, Mn, Mo, and Al are the primary metal dopants in heteroatom-doped materials. When incorporated into the host lattice, these elements tend to substitute lattice atoms of similar radius and electronegativity, inducing localized lattice distortion and redistribution of electron density; the result is precise modification of the electronic structure at the atomic level and enhanced intrinsic activity. Zhao et al., for example, developed a new process combining ultrasonic cavitation and phase transformation to synthesize a novel quasi-monolayer NiCoP structure. With the introduction of Ni atoms, the electronic structure was reconfigured between $Ni\delta^+/Co\delta^+$ and $P\delta^-$, giving the material better performance than CoP. Co-doping generally outperforms single-atom doping, since the synergistic effects involved further enhance both catalytic activity and stability. In another case, Li et al. synthesized S and Fe co-doped CoP nanoneedle arrays on iron foam (S, Fe–CoP@IF). XPS analysis showed that the Co 2p peaks of S, Fe–CoP@IF exhibited the highest binding energies, indicating strong electronic interactions among S, Fe, and CoP. These interactions generated more empty d orbitals on CoP and facilitated hydrogen adsorption and electron transfer, improving the water-splitting performance of the catalyst. DFT calculations of ΔG_{H^*} at both Co and P sites further showed that the energy barriers of this catalyst were closest to the ideal value, suggesting a more suitable hydrogen adsorption free energy that significantly enhances HER activity.

5.5. Other strategies

Besides the strategies discussed above, depositing TMPs onto suitable supports is also an effective way to improve their performance. Catalyst supports such as graphene oxide, porous carbon, and MXene usually possess weak or no catalytic activity themselves; nevertheless, they serve as substrates that provide large specific surface areas and excellent electrical conductivity, regulate the adsorption/desorption of reactants on the TMP surface, and improve the utilization efficiency of active sites, thereby boosting both HER and OER activities. Taken together, a variety of modification strategies are available to enhance the electrocatalytic activity of TMPs, and among them elemental doping is one of the most commonly employed and readily achievable approaches for modifying transition metal-based catalysts.

6. Conclusions and outlook

This paper has reviewed the research landscape of transition metal phosphides (TMPs) for hydrogen production via water electrolysis, covering the multi-electron transfer reaction pathways and the underlying microscopic mechanisms of the two electrocatalytic half-reactions, namely cathodic hydrogen evolution and anodic oxygen evolution. The technical characteristics and application

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limitations of the mainstream preparation methods—liquid-phase synthesis, pyrolysis reduction, mechanical ball milling, electrodeposition, and gas–solid phosphidation—have been summarized. Particular attention has been paid to the regulatory logic of four modification strategies, i.e., interface engineering, vacancy introduction, morphological control, and heteroatom doping, in terms of modulating electronic band structures, active site density, and reaction intermediate adsorption energies. Overall, current modification strategies have proved effective in optimizing the intrinsic catalytic activity and acid-base stability of TMPs. Some modified materials can achieve low-overpotential HER, OER, and bifunctional overall water-splitting catalysis across the full pH range, with electrochemical performance comparable to that of noble metal benchmark catalysts under low-to-medium current density conditions.

Looking forward, future research may focus on multi-component co-doping composite modification, the precise synthesis of high-entropy metal phosphides, and the development of synergistic systems based on conductive composite supports. Guided by theoretical calculations for the targeted optimization of electronic structures, the simultaneous development of low-energy-consumption and scalable green synthesis routes will be essential to advancing TMP-based water-splitting catalysts toward industrial application.

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