Strategies for Developing Transition Metal Phosphides in Electrochemical Water Splitting

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Electrochemical water splitting involving hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is a greatly promising technology to generate sustainable and renewable energy resources, which relies on the exploration regarding the design of electrocatalysts with high efficiency, high stability, and low cost. Transition metal phosphides (TMPs), as nonprecious metallic electrocatalysts, have been extensively investigated and proved to be high-efficient electrocatalysts in both HER and OER. In this minireview, a general overview of recent progress in developing high-performance TMP electrocatalysts for electrochemical water splitting has been presented. Design strategies including composition engineering by element doping, hybridization, and tuning the molar ratio, structure engineering by porous structures, nanoarray structures, and amorphous structures, and surface/interface engineering by tuning surface wetting states, facet control, and novel substrate are summarized. Key scientific problems and prospective research directions are also briefly discussed.

Keywords: transition metal phosphides, hydrogen evolution reaction, oxygen evolution reaction, water splitting, modulated strategies

INTRODUCTION

In the past decades, global energy consumption has been growing dramatically, with fossil fuels still providing over 80% of energy consumption, resulting in severe energy crisis and greenhouse effect (Zhang et al., 2017a; Peng et al., 2016). To address the key issue of these energy sources, researchers have begun to exploit clean and renewable energy resources such as solar energy, geothermal energy, wind power, and hydropower (Gallagher et al., 2015; Hou et al., 2011). Since hydrogen is regarded as a pollution-free energy source with ultrahigh energy density, water electrolysis has attracted tremendous attention for producing hydrogen energy from water in abundance (Peng et al., 2014; Ying et al., 2017; Yu et al., 2019a). As shown in Figure 1, electrochemical water splitting consists of two half-cell reactions, namely, hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. The current state-of-the-art water electrolysis technology requires the use of precious metal (e.g., Pt and IrO₂) electrocatalysts (Fujishima et al., 2008; Stoerzinger et al., 2015). Nevertheless, the high cost and low abundance of precious metals are restricting the widespread application of water electrolysis technology (Ying et al., 2014a; Ying et al., 2018a; Xiao et al., 2019; Xiao et al., 2021a).

Accordingly, tremendous substantial efforts have been devoted to the development of sustainable alternative electrocatalysts, one of which involves high efficiency, high stability, and low cost. Thus, many nonprecious metal electrocatalysts including carbon/carbon-based nanomaterials (Lu et al., 2015; Han et al., 2019; Ji et al., 2019), metal chalcogenides (Li et al., 2016), carbides (Yang et al., 2019;
Lai et al., 2020), borides (Li et al., 2019), nitrides (Ye et al., 2018; Tareen et al., 2019), oxides (Song et al., 2018; Li et al., 2020), and especially phosphides (Ren et al., 2020; Sarkar et al., 2020) are currently representative electrocatalytic materials for both HER and OER. Among them, transition metal phosphides (TMPs) have been widely investigated and demonstrated to be very suitable for electrochemical water splitting (Dutta and Pradhan, 2017; Wang et al., 2018).

As the first nickel phosphate was prepared for vapor phase catalysis in the 1950s, it has been gradually depleted for a long time (Sweeney et al., 1958). In the 1990s, Kupka et al. first used metal phosphides as electrocatalysts (Kupka and Budniok, 1990). In 2005, Liu et al. presented the high HER activity of Ni2P(001) facet by density functional theory (DFT) calculations and suggested that the Ni-P bonds form a weak “ligand effect” that endows the fast dissociation of thiophene and hydrogen (Liu and Rodriguez, 2005). In 2013, Lewis et al. used nanostructured TMPs as HER electrocatalysts in acid media (Popczun et al., 2013). Until 2015, Yoo et al. made further progress demonstrating that the surface oxidized compounds are the true catalytic site of the metal phosphides (Ryu et al., 2015). Inspired by this work, massive research studies on TMPs for water electrolysis in the past several years have been reported. For example, Liu et al. reported an oxygen doping strategy to prepare an effective NiCoP electrocatalyst with optimized hydrogen adsorption energy and plentiful exposed active sites (Liu et al., 2018a).

Currently, the field of synthesis of TMP electrocatalysts for water splitting is experiencing a prosperous development with increasing achievements. It is necessary to timely provide a brief overview of this type of advanced material. In this minireview, we provide a general overview of the recent advances in efficient TMPs for electrochemical water splitting based on the understanding of their relationship between structure and performance. The developments in the design strategies based on composition engineering, structure engineering, and surface/interface engineering are summarized. Moreover, key scientific problems and prospective research directions are also proposed.

Composition Engineering
Considering the influence of electron structure and intermediate adsorption energy, the introduction of elements into TMPs, such as element doping, hybridization with other compositions, and tuning their molar ratios is often used to improve their electrocatalytic performance.

Element Doping
In general, doping foreign elements can boost the intrinsic activity of electrocatalysts (Niu et al., 2019; Song et al., 2021; Gao et al., 2019). What is more, the optimal ratio of doping elements can be predicted in advance via DFT calculations (Peng et al., 2021; Fu et al., 2019). Hence, the electrocatalytic behavior can be precisely regulated at the atomic scale. Most single metal phosphides have a limited intrinsic activity due to the difficulty in balancing the adsorption and desorption of reaction intermediates (Parra-Puerto et al., 2019; Read et al., 2016; Dutta et al., 2016). To solve the shortcomings, incorporating foreign atoms into the single TMPs has been studied by many research groups (Wu et al., 2018; Du et al., 2020; Yue et al., 2019; Shin et al., 2020; Lv et al., 2020). Liu et al. reported that doping element Zn into pristine CoP could significantly enhance HER performance (Liu et al., 2017). Because Zn had lower electron negativity as compared with Co, it could provide some electrons to nearby P atoms and generate some electron-deficient cations. As a result, the surrounding Co will lose more electrons, thus weakening H chemisorption strength with Co and improving HER performance (Figure 2A). Not only that many research studies have been achieved to explore the effects of introducing other elements such as N, S, or O into TMPs (Chang et al., 2018; Xi et al., 2018; Wang et al., 2019; Mu et al., 2021).

Hybridization
Hybridization with other compositions also remarkably increased catalytic activity because of the strong synergistic effect between multiple compositions and the improved mass transportation ability. In a multicomponent composite, the contacted components/phases show special interactions (Wang et al., 2018). By the rational design of the heterogeneous structure, the physicochemical properties of the interface can be obviously changed, thus presenting better performance than the single bulk phase (He et al., 2018; Saha et al., 2020). Li et al. developed a novel Fe@FeP core–shell nanoparticles on carbon nanotubes as an efficient HER catalyst (Li et al., 2017). The resulting Fe@FeP hybrid catalyst presented a low overpotential of 53 mV at a current density of 10 mA cm−2 and a Tafel slope of 55 mV dec−1 due to the presence of strong electron interactions and synergistic effects between Fe and FeP (Figure 2B). DFT calculations showed that the hydrogen adsorption energy on Fe@FeP is very close to that on Pt (111), revealing the enhancement effect of the Fe@FeP core–shell structure. In
addition, Yu et al. synthesized a FeP/Ni2P hybrid catalyst via the chemical vapor deposition method (Yu et al., 2018). The obtained hybrid catalyst showed excellent catalytic performance in HER because it preferentially exposed the most active facets compared to the FeP(001) crystal, which contributed to the high activity not observed in typical FeP crystals.

**Tuning the Molar Ratio of M/P**

Since the first use of TMPs in electrocatalysis, enormous efforts have been devoted to pursuing the optimal metal/phosphorus (M/P) molar ratios (Callejas et al., 2015). As studied before, different M/P molar ratios lead to variations in crystal structures, hence directly influencing the electrocatalytic properties (Pei et al., 2017). In some situations, tuning molar ratios of M/P could boost excellent enhancements on HER activity. For example, Laursen et al. have explored the superior HER activity of Ni3P4 nanoparticles by researching the different catalytic performances between Ni2P and Ni3P4 nanoparticles (Laursen et al., 2015). The combination of the Volmer–Tafel mechanism and DFT calculation disclosed that Ni3P4 displayed a faster reaction rate because of the increased binding energy of the first hydrogenic intermediate, which in turn increases the second proton affinity. Moreover, the bond length of Ni-P in Ni4P5 is also longer than that in Ni2P (Figure 2C), explaining that Ni4P5 exhibited much better catalytic activity compared to Ni2P.

**Structure Engineering**

Besides the composition engineering mentioned above, structure engineering is also an indispensable strategy to improve the water splitting performance of electrocatalysts. Three main aspects including porous structures, nanoarray structures, and amorphous structures are discussed in this section.
Porous Structures
It is well known that the electrocatalytic reactions proceed on the surface of electrocatalysts; tiny pore structure could lead to improving the surface area and exposing more active sites (Peng et al., 2018; Xiao et al., 2021b; Ying et al., 2018b; Ying et al., 2014b). Since Erlebacher’s group put forward a continuum model to explain the fundamental mechanism of nanoporosity formation in the dealloying process (Erlebacher et al., 2001), many scientists have continuously continued to explore this. In this regard, Xu et al. developed a facile technique to prepare a nanoporous (NiFe) xP y with controllable metal ratio (Figure 2D), which serves as a bifunctional catalyst for both HER and OER with an outstanding catalyst performance (Xu et al., 2018a). Sun et al. designed porous and multishelled Ni/P hollow spheres by using the carbon spheres as the template, subsequently phosphating along with thermal treatment (Sun et al., 2017). The hollow porous multishells and nanosized subunits endow Ni2P with short charge transport distances, abundant active sites, and high stability against agglomeration, representing outstanding OER catalytic performance.

Nanoarray Structures
The nanoarray-structured self-supported electrodes, growing on the free-standing substrates, with discontinuous phase contact areas are very attractive due to avoiding the negative effects of binders and generating excellent stability (Liang et al., 2016; Zhang et al., 2020; Hou et al., 2020). In contrast to swarming bubbles adsorbed onto the planar surface of bulk materials, these nanoarrays can always show very preeminent electrocatalytic activity. For example, Shen et al. reported a porous MoP nanoflake array grown on nickel foam (MoP/NF) with excellent performance in water electrolysis (Figure 2E) (Jiang et al., 2018). In contrast to MoP, the enhanced electrocatalytic performance of MoP/NF is ascribed to the reduced size and the special nanoflake array structure. Moreover, besides avoiding the use of binders, the porous MoP/NF could be directly treated as both current collector and electrocatalyst, which made the active sites fully exposed and conductive to gas penetration and mass transfer. For another example, Su et al. successfully prepared self-supported NiMoP2 with grain boundary rich nanowire architecture on a carbon cloth substrate, showing small overpotential and remarkable electrochemical durability for water splitting (Wang et al., 2017). Such impressive characteristics can be tracked to the hierarchical architecture of the NiMoP2 nanowire in situ grown on a 3D carbon cloth substrate weakening the disintegration tendency of catalyst, and the special grain boundary nanowire structure of NiMoP2 provides the maximum number of electroactive surface/active sites.

Amorphous Structures
Since vacancies and defects are often considered as active sites of catalysis, amorphous catalysts are widely researched because of the disordered domains containing lots of vacancies and defects (Yan et al., 2017; Chu et al., 2020). In general, amorphous structures are always rigorous to preparation conditions (Zhang et al., 2016; Anantharaj et al., 2017; Ray et al., 2017). For instance, Xiong et al. reported a high-efficiency OER electrocatalyst based on bulk amorphous NiFeP in both alkaline and acidic electrolytes (Hu et al., 2017). In this case, the element P with proper electronegativity has been utilized to stabilize Ni and Fe atoms as an amorphous metallic phase with high conductivity and may also form active species for enhancing OER performance. Besides, the metallic bonds facilitated the electron transfer, whereas the P atoms supplied suitable bonds with reaction intermediates (Figure 2F). At the same time, the coordination numbers of Ni and Fe in Ni30Fe70P30 were largely lower than those counterparts, indicating metal atoms in the Ni30Fe70P30 were unsaturated. Combining these features together, this Ni30Fe70P30 electrode manifested an outstanding performance in OER. Therefore, the amorphous NiFeP accomplishes unprecedentedly excellent OER performance.

Surface/Interface Engineering
Surface/interface engineering, including the tuning surface wetting states, facet control, and novel substrate, is another effective way to enhance the performance of electrocatalysts. Since both mass transfer and gas delivery play a crucial role during water splitting, modifying the surface wettability such as superhydrophilicity is beneficial to HER and OER. In addition, the facet control and novel substrate are also beneficial to electrocatalytic properties via exposing more catalytic active sites and facilitating the electrolyte transfer.

Tuning Surface Wetting States
During the electrolysis of water, the surface wettability such as superhydrophilicity and superaerophobicity of the electrocatalysts are key to the electrocatalytic process due to the evolution of gas bubbles in the solution (Hao et al., 2016; Tian et al., 2020). It is commonly thought that superhydrophilicity is advantageous for mass transfer inside the electrode and can improve the interaction between electrocatalysts and electrolytes (Kim et al., 2021; Riyajuddin et al., 2021). Likewise, the superaerophobicity can be beneficial to electrocatalysts by avoiding bubble effects (Sheng et al., 2020). The formed gas bubbles would adhere to the surface of the electrocatalyst during the water splitting process, which would be a barrier to the solution diffusing to the active sites and result in a dissatisfied performance (Xu et al., 2018b). Precise surface design can improve the surface’s superhydrophilicity and superaerophobicity to boost the interaction between electrodes and electrolytes and also solve the bubble adsorption issue during the electrocatalytic process. For example, Yu et al. prepare a Ni2P nanoray catalyst with a unique superaerophobic surface feature grown on a Ni foam substrate, which represents remarkable electrocatalytic activity and stability in basic media (Yu et al., 2019b). The special superaerophobicity endows an outstanding capability to withstand inside and outside forces and releases the in situ-formed H2 bubbles timely (Figure 2G), resulting in highly efficient electrocatalytic activity and outstanding stability of the Ni2P/NF.

Facet Control
While researching the composition of a nanostructure to TMPs that display reasonable electrocatalytic performance during water splitting progress, a large portion of research studies have focused
on enhancing the intrinsic activity of active sites on the surface of nanostructures (Dutta et al., 2016; Lei et al., 2018; Ying et al., 2018c). Hence, there have been enormous efforts to prepare facet-controlled TMP nanostructures restricted by special facets which exert excellent catalytic activity (Liu and Rodriguez, 2005; Popczun et al., 2013). For example, Zhang et al. reported the ultrathin CoP nanosheets with dominant active facets by a chemical transformation method (Zhang et al., 2017b). The as-prepared samples consist of porous nanosheets, which are in single crystalline structure with a preferential [100] orientation. DFT calculation disclosed that on CoP (Lv et al., 2021) facets, a near-zero Gibbs free energy could lead to high utilization efficiency of active sites, therefore endowing (Lv et al., 2021) highly active CoP. In addition to single crystalline, other crystallines are, of course, affected by the crystal surface. For instance, Feng et al. reported novel [2–10] facet-exposed Ni₃S₂ nanosheet arrays on nickel foam (NF) (Figure 2H), which can efficiently catalyze both HER and OER (Feng et al., 2015). The excellent electrocatalytic performance in water splitting can be attributed mainly to the synergistic effect between the nanosheet array architecture and exposed [2–10] high-index facets.

**Novel Substrate**

Until now, two novel substrates with good conductivity, high mechanical strength, and corrosion resistance in electrocatalysis fields have been developed, which can act as supporting materials for stabilizing electrocatalysts and facilitate the electron transfer from the external circuit to electrocatalysts (Liu et al., 2018b; Gao et al., 2021; Yu et al., 2020; Xiu et al., 2018). One of them is black phosphorus (BP), a kind of 2D material, which is well known for its intriguing physicochemical properties, such as high charge–carrier mobility, tunable bandgap, and highly anisotropic characters (Fei and Yang, 2014; Jiang and Park, 2014; Liu et al., 2014). In view of these merits of BP, Wu et al. designed novel Ni₃N-Ni₃P-BP heterostructure nanosheets with enhanced OER activity in alkaline conditions (Wu et al., 2019). The DFT calculation demonstrates that Ni₃P is very close to the ideal value compared to the Gibbs free energies of Ni₃N and BP. In addition, the electron transfer rate can be improved by the metallic nature of the Ni₃N-Ni₃P-BP catalyst. As a result, the heterostructure of Ni₃N-Ni₃P-BP catalysts can remarkably enhance the OER activity. As another promising 2D material, transition metal carbides and nitrides (known as MXenes) with the features of great mechanical stability, high conductivity, and wide chemical variety display great potential as substrates (Du et al., 2018; Yoon et al., 2019; Lv et al., 2021). For example, Yan et al. successfully prepared novel CoP nanosheet arrays on the surface of Ti₃C₂ MXene nanosheets (CoP/Ti₃C₂ MXene) (Figure 2I) (Yan et al., 2020). Benefiting from the unique structure and synergistic effect between the active CoP and Ti₃C₂ MXene nanosheets, the 3D MXene matrix not only prevents the self-aggregation of active sites but also significantly facilitates the electrolyte accessibility and enhances the charge/mass transfer. Hence, the CoP/Ti₃C₂ MXene heterostructure represents a largely improved electrocatalytic activity and remarkable stability in HER over a wide pH range.

**CONCLUSION AND OUTLOOK**

This review has summarized the reported strategies for developing TMP electrocatalysts in electrochemical water splitting, including composition engineering, structure engineering, and surface/interface engineering. These strategies can be utilized as common and efficient strategies for preparing high-performance electrocatalysts. Moreover, the strategies discussed above can be modified and/or extended to other systems although we only focused on a limited number of examples.

Although rapid and significant development has been made in the synthesis of TMP electrocatalysts with superior HER and/or OER performance, the research in this field is still at the exploration stage, and several issues need to be addressed, such as preparation of TMPs with a special facet, stabilization of TMPs in acidic OER, and surface oxidation of TMPs. To better understand the in-depth reason for the enhanced electrocatalytic performance, two research aspects are recommended: 1) in situ structural characterization for investigating the catalytic active sites and 2) theoretical reaction simulation for predicting the optimized structures/compositions. Combining these two aspects, the field of TMP electrocatalysts for water splitting will undoubtedly keep moving forward rapidly.

**AUTHOR CONTRIBUTIONS**

JY was in charge of organization and writing of this manuscript. HW contributed to the search of related literature studies.

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