Promotion effect of metal phosphides towards electrocatalytic and photocatalytic water splitting

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Abstract
Hydrogen evolution from water splitting over semiconductors has been considered one of the most promising ways to address energy shortages and environmental pollution. Searching for low-cost, highly efficient, and durable catalysts is the key to improve the hydrogen production rate. Expensive noble metals, such as Pt and Au, are generally loaded onto semiconductors to promote photocatalytic activity. Metal phosphides are promising candidates to replace noble metals in hydrogen generation via electrocatalytic or photocatalytic water splitting due to their low hydrogen-producing overpotential, tunable electronic structure, high electrical conductivity, and low price. In this review article, the characteristics and synthetic methods of metal phosphides are briefly introduced, and the development of metal phosphides for electrocatalytic or photocatalytic water splitting is presented. Finally, the challenges and future directions of metal phosphides are discussed.

KEYWORDS
electrocatalytic, metal phosphides, photocatalytic, water splitting

1 INTRODUCTION

Energy shortages and environmental pollution are scientific problems that urgently need to be solved in today’s society. As the global energy structure is transforming to clean and low carbonization, hydrogen energy, as a secondary energy source with abundant reserves, flexibility, efficiency, and zero emission, is an important breakthrough to address the energy crisis and environmental pollution and promote energy transformation and upgrading. The International Hydrogen Council forecasts that hydrogen (H₂) will account for 18% of global energy consumption by 2050. Solar energy with abundant reserves is clean energy that will not cause environmental pollution in the process of its utilization and can be developed locally without transportation problems. Hence, photocatalytic water splitting to produce H₂ under the irradiation of solar energy is an effective way to solve energy shortages and environmental pollution. The key to this process is to develop a photocatalyst with high activity and stability to achieve efficient and continuous H₂ production.

Since the first report of photoelectrochemical water splitting for H₂ evolution with TiO₂ photoanodes,¹ photocatalytic decomposition of water with semiconductors to produce H₂ has attracted increasing attention. Currently, different kinds of catalysts, such as TiO₂,² ZnO,³ BiVO₄,⁴ CdS,⁵ ZnIn₂S₄,⁶ Mn₉Cd₁₋ₓS₁₋₉,⁷ and g-C₃N₄,⁸ have been applied in photocatalytic water splitting. However, when these photocatalysts are used alone for the H₂ production
reaction, the electrons and holes are more easily recombined, inducing inferior photocatalytic performance. Hence, a series of modification methods, such as cocatalyst loading, semiconductor coupling, elemental doping, and defect engineering, are introduced to accelerate the reaction kinetics. Among them, cocatalyst loading is usually used to accelerate the separation and transfer of charge carriers. Metal phosphides are promising candidates to replace noble metals in photocatalytic H₂ production by water splitting due to their low hydrogen-producing overpotential, tunable electronic structure, high electrical conductivity, and low price. For example, Ni₃P⁹, CoP¹⁰, Cu₃P¹¹, MoP¹², and FeP¹³ have been demonstrated to be promising cocatalysts in photocatalysis.

Metal phosphides were first reported in the 18th century. After a long time, they gradually became popular with expanding application scope, such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydroprocessing (HPC)¹⁴. Since Liu et al.¹⁵ predicted the outstanding behavior of Ni₃P (001) towards the hydrogen evolution reaction (HER) by density functional theory (DFT) calculations, metal phosphides were widely used in the HER and oxygen evolution reaction (OER) with high reactivity and stability. The types of metal phosphides and their applications are presented in Figure 1. Currently, an increasing number of metal phosphides are employed in electrochemical water splitting and photocatalytic water splitting.

In this minireview, an overall summary of metal phosphides as promising bifunctional catalysts and highly active cocatalysts for overall electrochemical water splitting and photocatalytic water splitting is presented. Different kinds of metal phosphides acting as electrocatalysts and cocatalysts with excellent electrocatalytic and photocatalytic activities, respectively, are summarized in Tables 2 and 3. Finally, the existing problems, challenges, and future directions of metal phosphides are discussed. It is expected that this review could provide guidance for researchers to design and construct low-cost and high-efficiency metal phosphate systems.

2 CHARACTERISTICS OF METAL PHOSPHIDES

Metal phosphides are usually composed of metal and phosphorus. The outer valence electron configuration of phosphorus is 3s²3p³, and there are five valence electrons and five vacant 3D orbitals in the third shell. Its intrinsic activity determines that phosphorus can form compounds with most metals. Metal phosphides have shown superior catalytic activity, low H₂ evolution overpotential, and tunable composition and structure, which makes them popular among researchers.¹⁶ On the one hand, the electronegative P atoms in metal phosphides can capture the positively charged H⁺ in the electrolyte to produce H₂, leading to the enhancement of the catalytic activity. On the other hand, by properly adjusting the atomic ratio of metal and P, metal phosphides may have excellent electrical conductivity.¹⁷

Metal phosphides, labeled MₓPᵧ (for instance, Ni₃P, Ni₄P₅, Ni₂P₃, Ni₃P₄, NiP, Ni₅P₆, and NiP₃), with different molar ratios of M and P are divided into metal-rich (x/y ≥ 1) and phosphorus-rich (x/y < 1) metal phosphides. The former is ascribed to covalent compounds with metallic properties, which exhibit excellent thermal and electrical conductivity and high mechanical strength; the latter belongs to semiconductors, whose thermal stability and chemical stability are worse than those of the former.¹⁴,¹⁸ According to the Hagg rule, the crystal configuration depends largely on the atomic radius and electronegativity. To achieve geometric stability, the ratio of the atomic radius of the nonmetal to that of the metal is usually between 0.41 and 0.59. The atomic radius of phosphorus (0.100 nm) is larger than that of carbon (0.070 nm) or nitrogen (0.065 nm). The ratio of the atomic radius of phosphorus to that of the metal is not within this scope; hence, it is difficult for phosphorus to form stable structures with metal atoms. Metal phosphides with more coordination unsaturated surface atoms present a higher catalytic activity than carbides and nitrides.¹⁹ Metal phosphides with different crystalline phase structures present various

![Figure 1](image_url) Types and applications (photocatalysis, electrocatalysis, batteries, HDS, HDN, and HPC) of metal phosphides
electron conductivities, thermal and chemical stabilities, and catalytic reactivities.20

M and P in MₓPᵧ possess a partial positive charge (δ+) and a partial negative charge (δ−), respectively.21,22 P atoms in metal phosphides with more electronegativity can draw electrons from metal atoms, which can trap positively charged protons.23 The crystalline structures of representative metal phosphides are shown in Figure 2. The various crystal structures make metal phosphides show different catalytic activities. Monodispersed nickel phosphide nanocrystals (NCs) were prepared through a phase-controlled synthesis strategy by changing the molar ratio of P and Ni precursors. Hollow-structure NiₓPᵧ NCs with an average particle size of 17.55 ± 2.25 nm were obtained at a P:Ni precursor molar ratio of 0.65.24 When the molar ratio of the P:Ni precursors increased to 1.1, NiₓPᵧ and Ni₁₀P₄ coexisted in the products. Upon further increasing the P:Ni precursor ratio to 2.18, Ni₁₀P₄ presented a hollow structure with an average particle size of 9.19 ± 1.16 nm. Moreover, when the molar ratio of P:Ni precursors was increased to 8.75, Ni₁₀P₄ solid spheres with an average particle size of 600 nm were obtained. Ni₁₀P₄ displayed much better catalytic activity than NiₓPᵧ and Ni₁₀P₄ due to the larger positive charge of Ni and stronger ensemble effect of P in Ni₁₀P₄.

3 | PREPARATION OF METAL PHOSPHIDES

The synthesis of metal phosphides is more complex than that of metal sulfides, metallic oxides, and metal hydroxides. Some methods, such as in-situ phosphating transition metal oxides, hydroxides, and metal-organic frameworks (MOFs) with the PH₃ generated from the decomposition of sodium hypophosphate (NaH₂PO₂), the ion exchange strategy and the solvent thermal process with red phosphorus and white phosphorus, have been developed for the fabrication of metal phosphides. High temperature, the release of toxic gases, or the use of toxic materials was involved in this process, making it difficult to achieve large-scale preparation and application. Hence, it is necessary to develop a simple and environmentally friendly strategy for the preparation of metal phosphides.

Generally, the phosphorus source used in the high-temperature calcination preparation process is NaH₂PO₂, which decomposes to release PH₃ when heated over 250°C. Then, PH₃ can further react directly with a variety of metal oxides, hydroxides, and MOFs to form metal phosphides. Zhao et al21 fabricated g-C₃N₄/Ni₂P photocatalyst with NaH₂PO₂ as the phosphorus source and g-C₃N₄/Ni(OH)₂ as the precursor. Fe₂P nanoparticles were synthesized by annealing a mixture of Fe₂(SO₄)_3 and NaH₂PO₂ at 300°C for 2 hours in argon. Porous FeP nanosheets were also obtained by an anion exchange reaction of Fe₁₆S₂₇–TETAH (TETAH = protonated triethylenetetramine) nanosheets with P ions, which provided guidelines for the transformation of solid inorganic-organic hybrid precursors into nanoporous products while maintaining the original morphology. Single MOF precursor-derived Ni₃P catalysts were also constructed, in which triphenylphosphine organic ligands were inherently incorporated into the structure of

![Figure 2](image-url)
the phosphine coordination materials.31 Ni(NO₃)₂·6H₂O and yellow phosphorus were employed to fabricate Ni₂P.32 In addition, Mi et al29 selectively constructed Ni₁₂P and Ni₁₂P₅ via a solvent thermal process in the presence of sodium dodecylbenzene sulfonate with NiCl₂ and white phosphorus as the starting reactants. The formation process of Ni₂P and Ni₁₂P₅ was also proposed as follows:

\[ \text{P}_4 + 6\text{CH}_3\text{CH}_2\text{OH} \rightarrow 2\text{PH}_3 + 2\text{H}_3\text{PO}_3 + 6\text{C}_2\text{H}_4, \quad (1) \]

\[ \text{P}_4 + 12\text{H}_2\text{O} \rightarrow 5\text{PH}_3 + 3\text{H}_3\text{PO}_4, \quad (2) \]

\[ \text{Ni}^{2+} + \text{PH}_3 \rightarrow \text{Ni}_{12}\text{P}_5/\text{Ni}_2\text{P} + \text{H}^+. \quad (3) \]

However, the above preparation methods involve high temperature, the release of poisonous gases, such as PH₃, or the use of toxic substances, such as triphenylphosphine, white phosphorus, and yellow phosphorus, which makes the synthesis process very dangerous. To solve the above problems, researchers replaced white phosphorus with red phosphorus to synthesize Ni₂P, Ni₁₂P₅, and a mixture of them under mild conditions,33,34 avoiding the use of toxic substances and high temperature.

In addition, Ni₂P, Ni₁₂P₅, and Ni₂P/Ni₁₂P₅ biphase nanocomposites were successfully constructed by changing the initial molar ratio of phosphorus and NiCl₂·6H₂O.35 Compared with bare Ni₁₂P₅ and Ni₂P, Ni₂P/Ni₁₂P₅ biphase nanocomposites exhibited higher catalytic activity for the reduction of 4-nitrophenol. Nanosized nickel phosphides with controllable crystal structures and morphologies were fabricated by Deng et al35 through a solvothermal route. By changing the types of nickel sources (NiCl₂·6H₂O, Ni(CH₃COO)₂·4H₂O, NiSO₄·6H₂O, and Ni(NO₃)₂·6H₂O) and solvents (H₂O, methanol, ethanol, glycol, glycerol, and polyglycol) and using nontoxic red phosphorus as the P³⁻ ion source, pure crystal phases of Ni₂P and Ni₁₂P₅ with various morphologies were fabricated, as presented in Figure 3.

In addition, MOFs, a kind of functional material exhibiting large specific surface areas and pore size distributions, multiple active sites, and clipping structures, were usually used as precursors to prepare metal phosphides.36-38 MOF-derived nickel phosphate (Ni₂P) was prepared via a simple, cost-effective procedure using inexpensive and abundant elements.39 The synthetic process of Ni₂P is displayed in Figure 4. Ni-BTC MOFs were first prepared via hydrothermal treatment, and certain amounts of Ni-BTC and NaH₂PO₄ were mixed together, placed in a covered ceramic crucible, and heated to 275°C at a ramp rate of 1°C. In addition, MOF-derived nitrogen-doped FeP nanorods were fabricated through the combination of phosphorization and thermal decomposition. The P atoms in FeP could effectively attract electrons from Fe atoms, serving as the collector of protons. The incorporation of N into FeP could increase the bond strength between FeP and oxygen.40

Kang et al41 proposed a universal but facile and controllable sol-gel strategy (Figure 5) to fabricate carbon-supported metal phosphides with different metal ions as metal sources. During the sol-gel process, citric acid chelated with metal ions to form cross-linked networks in which the inorganic species were homogeneously dispersed. Through the universal strategy, a series of metal phosphides, such as CoP@C, MoP@C, FeP@C, Cu₂P@C, Ni₃P@C, PtP₂@C, NiFeP@C, NiCoP@C, FeNiP@C, CoNiP@C, and FeCoNiP@C, were successfully constructed. This work provided a general methodology for preparing carbon-supported metal phosphides.

### 4 METAL PHOSPHIDES AS BIFUNCTIONAL CATALYST FOR HER AND OER

Electrocatalytic water decomposition is regarded as an efficient and green method because of its convenience and high purity and involves two half reactions: the OER and HER of water. Freshwater has usually been employed as the raw material for water electrolysis in experiments and is scarce in some parts of the Earth. However, the reserves of seawater are enormous, accounting for approximately 97.5% of total water resources. Therefore, it is vital to develop an economical and feasible method for the electrocatalytic decomposition of seawater to produce hydrogen. Generally, catalysts with excellent catalytic activity are noble metals, such as Pt, IrO₂, and RuO₂; however, their high price and low content prevent their large-scale application. Therefore, researchers have replaced precious metals with non-precious metals to minimize cost and achieve sustainability.42 The electrocatalytic activities of metals in the periodic table for the HER (following Sabatier's
principle) and OER vary with the change in the atomic number.\textsuperscript{43} The relationship of logarithmic of exchange current densities (log $i_0$) vs bonding adsorption strength ($\Delta E_{M-H}$) was calculated by Trasatti (Figure 6A). A more thorough computation of the “volcano” curve (dotted line) for H$_2$ evolution ($-\log i_0$) is displayed in Figure 6B.\textsuperscript{44-46} An increasing number of theoretical calculations have confirmed nickel hydroxides, nickel phosphides, nickel oxides, and nickel sulfides to be effective catalysts. Currently, various metal phosphides have been demonstrated to be effective electrocatalysts for the HER and OER. In this section, we mainly introduce the application of metal phosphides in electrocatalytic water splitting.

In an electrolytic cell, the two-electron HER and four-electron OER proceed at the cathode and anode, respectively, and usually require at least a working potential of 1.23 V.\textsuperscript{47-49} Stable and efficient catalysts are highly desired for the HER and OER to reduce the overpotential. Generally, catalysts that work for both the HER and OER are often diverse, and their optimal operating conditions, such as electrolyte and pH, are also different; therefore, it is difficult to achieve overall water splitting in a system with two kinds of catalysts under optimal conditions. On the one hand, bifunctional catalysts can be used for both the HER and OER; on the other hand, the use of bifunctional photocatalysts greatly reduces the cost of material preparation. Consequently, the design of bifunctional
catalysts that are effective in an electrolyte for both the HER and OER is urgently needed.\textsuperscript{30,51}

For the decomposition of seawater, the seawater electrolysis rate is controlled by the sluggish OER accompanied by competitive side reactions, such as chloride electrooxidation reactions (CERs). Chloride is present in seawater at high concentrations (~0.5 M), and its oxidation products, such as Cl\texttwosc{} and OCl\texttwosc{}, are toxic and should be minimized to achieve maximum OER selectivity. The reactions are as follows:\textsuperscript{52}

\[
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \quad E = 1.23\text{V vs RHE (acidic media)} ,
\]

\[
4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \quad E = 1.23\text{V vs RHE (alkaline media)} ,
\]

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \quad E = 1.36\text{V vs RHE (acidic media)} ,
\]

\[
\text{Cl}^- + 2\text{OH}^- \rightarrow \text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- \quad E = 1.36\text{V vs RHE (alkaline media)}.
\]

The CER is more difficult than the OER to occur from a thermodynamic point of view; however, the CER has faster reaction kinetics than the OER. Hence, the OER and CER always proceed simultaneously.\textsuperscript{53,54} Hence, different methods have been employed to promote the catalytic activity of the HER and OER while avoiding the occurrence of side reactions. For example, Co\textsubscript{3}O\textsubscript{4} modified MnO\textsubscript{2} exhibited a smaller OER overpotential of only 450 mV, which is lower than that of hypochlorite formation (480 mV). Moreover, the iodine titration test also proved that no hypochlorite was produced during the OER process. Excellent catalytic activity was obtained in alkaline seawater splitting. The Tafel slope values and the current densities were \( \approx 40 \text{mV}\text{dec}^{-1} \) and 13 mA cm\textsuperscript{-2}, respectively, which was superior to those of most Mn\textsubscript{2}O\textsubscript{3}-based catalysts. This work provided guidelines for selective seawater electrolysis.\textsuperscript{52}

Metal phosphides such as Ni\textsubscript{3}P, Fe\textsubscript{3}P, and CoP have been demonstrated to be highly efficient electrocatalysts for a single HER or OER. Exploring novel materials with both superior HER and OER performances remains a top priority. Currently, there has been increasing attention on using metal phosphides such as Ni\textsubscript{2}P-Fe\textsubscript{2}P,\textsuperscript{17} NiCo-P,\textsuperscript{55} and Co\textsubscript{2}P\textsuperscript{56} as bifunctional catalysts towards overall electrochemical water splitting. However, when metal phosphides are used alone for water splitting, their activity is unsatisfactory. Researchers have devised various strategies, such as ion doping, noble metal loading, and microstructure regulation, to boost catalytic activity. Based on this, S-incorporated Co\textsubscript{2}P was constructed via an economical and ecofriendly urea-phosphate-assisted strategy, in which doping with S has a higher electronegativity than Co and P led to a more positive charge on Co\textsuperscript{3+} and a more negative charge on P\textsuperscript{3-} and S\textsuperscript{2-}, as supported by XPS results.\textsuperscript{56} DFT calculations confirmed the reduced density of states (DOS) of metallic Co, as observed from the contraction of the conduction/valence band near the Fermi level in S:Co\textsubscript{2}P compared with that in pure Co\textsubscript{2}P, as shown in Figure 7, which signified the enhanced hydride acceptor (Co\textsuperscript{3+} H\textsuperscript{δ-}) and proton acceptor (P/S\textsuperscript{δ-} H\textsuperscript{5+}) properties after the doping of S. Hence, a stable current density of 100 mA cm\textsuperscript{-2} at 1.782 V was obtained with S:Co\textsubscript{2}P@NF as both the cathode and anode in alkaline electrolytes, which was superior to that obtained with the Pt/C and IrO\textsubscript{2} systems. S-doped Co\textsubscript{2}P displayed smaller Tafel slopes and higher current densities (62 mV dec\textsuperscript{-1} and 0.133 mA cm\textsuperscript{-2} for the HER and 71-82 mV dec\textsuperscript{-1} and 1-3 mA cm\textsuperscript{-2} for the OER) than primary Co\textsubscript{2}P (113 mV dec\textsuperscript{-1} and 0.116 mA cm\textsuperscript{-2} for the HER and 94 mV dec\textsuperscript{-1} and 1.3 mA cm\textsuperscript{-2} for the OER) for the HER and OER, respectively, illustrating that significantly improved carrier transfer dynamics were achieved after the incorporation of S. This research provided a general approach to fabricate phase-pure Co\textsubscript{2}P without the use of expensive and toxic phosphines. In addition, Chen et al\textsuperscript{57} designed an ultralow Ru (1.08 wt%)-loaded transition metal phosphide supported by nickel foam (Ru-MnFeP/NF), which presented excellent electrocatalytic activity, requiring overpotentials of only 191 and 35 mV to obtain current densities of 20 mA cm\textsuperscript{-2} and 10 mA cm\textsuperscript{-2} for the OER and HER, respectively. The Tafel slope of Ru-MnFeP/NF for the HER (36 mV dec\textsuperscript{-1}) and OER (69 mV dec\textsuperscript{-1}) was the smallest among the Tafel slopes of all electrocatalysts, implying its outstanding HER and OER kinetics due to its intrinsic catalytic activity. The amount of H\textsubscript{2} and O\textsubscript{2} produced in 6 minutes was exactly in line with the theoretical value, implying that the Faradic efficiency was close to 100% and that the overall water splitting process was highly selective. DFT calculations indicated that Ru-loaded Fe\textsubscript{3}P or Mn\textsubscript{2}P possessed a lower *H adsorption capabilities, and the electronic structure between Ru and phosphides would change after the incorporation of Ru, inducing the improvement of HER activity due to the interaction of Ru and Fe\textsubscript{3}P/Mn\textsubscript{2}P.

It was reported that ternary bimetallic phosphides with the advantages of individual metal phosphides showed superior catalytic activity relative to the corresponding binary metal phosphides, which is beneficial for the configuration of electronic structures.\textsuperscript{58} For example, nanoporous (Ni\textsubscript{a}Fe\textsubscript{1-a})P\textsubscript{5} with a tunable Ni/Fe ratio was constructed by Xu et al\textsuperscript{59} via electrochemical
dealloying. A current density of 10 mA cm$^{-2}$ was obtained for the OER and HER over the np-(Ni$_{0.67}$Fe$_{0.33}$)$_4$P$_5$ catalyst at overpotentials of 245 mV and 120 mV in 1 M KOH, respectively, with corresponding Tafel slopes of 32.9 and 41.8 mV dec$^{-1}$ for the OER and HER, respectively. The CV curves confirmed that the current density increased as the number of aging cycles increased, implying that the catalytic activity was significantly boosted. Ni oxidation, such as Ni$_x$Fe$_{1-x}$OOH, was generated in the aging process, which indicated that Ni$_x$Fe$_{1-x}$OOH would be the real active site for the HER. However, the aged sample displayed lower catalytic activity than the fresh one towards the HER, which suggested that the metal phosphides might be the active sites for the HER. In addition, the aged sample displayed lower catalytic activity than the fresh one towards the HER, which suggested that the metal phosphides might be the active sites for the HER. In addition, the electrochemically active surface area demonstrated that amorphous (Ni$_x$Fe$_{1-x}$)$_4$P$_5$ showed superior catalytic activity than crystalline (Ni$_x$Fe$_{1-x}$)$_4$P$_5$ because of its abundant active sites and disordered atomic arrangement. The maximum shift in Ni 2p and P 2p caused the change in the electronic structure for both Ni and P atoms, which was beneficial for the improvement of catalytic activity.

Generally, catalytic reactions occur at the active sites on catalyst surfaces; the more active sites exposed, the faster the catalytic reaction rate. The number of exposed catalytic active sites is determined by the apparent morphology and microstructure of the catalyst. To increase the number of active sites exposed, researchers fabricated metal phosphides possessing structures including nanoparticles, nanofibers, nanoframes, and nanocubes with a large specific surface area and pore structure, which favors contact between the electrolyte and catalysts. For instance, Lv et al. fabricated doubly functionalized carbon carved hollow nanocubes, C-(Fe-Ni)P@PC/(Ni-Co)P@CC. The overpotentials required to attain a current density of 10 mA cm$^{-2}$ in 1 M KOH were 142 and 251 mV, with Tafel slopes of 98 and 56 mV dec$^{-1}$ for the HER and OER, respectively. The faradaic efficiency of C-(Fe-Ni)P@PC/(Ni-Co)P@CC was nearly 100%. The overpotential of C-(Ni-Co)P@CC was 308 mV at 10 mA cm$^{-2}$, which was much higher than that of C-(Fe-Ni)P@PC/(Ni-Co)P@CC (251 mV) and (Fe-Ni)P@PC/(Ni-Co)P@CC (280 mV), illustrating that the exterior (Fe-Ni)P was the main active substance for the OER. Meanwhile, the HER performance results proved that (Ni-Co)P was the dominant active material towards the HER. The synergistic effects between (Fe-Ni)P and (Ni-Co)P jointly promoted the improvement in HER and OER performance. In addition, the hollow structure of the catalyst could provide more electrocatalytic active sites, and the holes located at the eight vertices of the cube could reduce the transfer distance of electrolytes and bubbles. This novel bifunctional carved hollow nanocube structure provided guidelines for the design of...
bifunctional electrocatalysts. Using metal phosphides as bifunctional catalysts to design electrolysers has also achieved amazing results. Yu et al.\textsuperscript{62} constructed porous Ni\textsubscript{2}P and FeP supported on Ni foam with Fe(NO\textsubscript{3})\textsubscript{3}, Ni foam, and phosphorus as the Fe, Ni, and P sources, respectively. Ni\textsubscript{2}P and FeP supported on Ni foam required a very low cell voltage of 1.42 V to afford 10 mA cm\textsuperscript{-2} in alkaline water electrolysers. A voltage of only 1.72 V was needed to achieve a commercially practical current density of 500 mA cm\textsuperscript{-2} and superior catalytic stability for more than 40 hours. The lowest Tafel slope of FeP/Ni\textsubscript{2}P for the HER was only 24.2 mV dec\textsuperscript{-1}, which is even lower than that of Ni\textsubscript{2}P (117.3 mV dec\textsuperscript{-1}) and Pt (36.8 mV dec\textsuperscript{-1}) due to FeP/Ni\textsubscript{2}P having a larger active surface area and smaller resistance. The number of active sites in FeP/Ni\textsubscript{2}P was approximately 2.5 times that in Ni\textsubscript{2}P, demonstrating that the incorporation of FeP on Ni\textsubscript{2}P contributed to the improvement in HER activity. FeP/Ni\textsubscript{2}P displayed outstanding catalytic activity and stability, paving the way for promising large-scale H\textsubscript{2} generation.

In addition, the bimetallic heterostructure Ni\textsubscript{2}P-Fe\textsubscript{2}P was fabricated by dipping commercial Ni foam in HCl (3 M) and Fe(NO\textsubscript{3})\textsubscript{3}, 9H\textsubscript{2}O (0.1 M) aqueous solutions. The bifunctional Ni\textsubscript{2}P-Fe\textsubscript{2}P heterostructure displayed excellent catalytic activity and stability towards overall water/seawater splitting. The Ni\textsubscript{2}P-Fe\textsubscript{2}P electrocatalysts achieved current densities of 100 mA cm\textsuperscript{-2} in KOH (1 M) and KOH seawater (1 M) at voltages of 1.682 and 1.811 V, respectively, which were superior to those of the IrO\textsubscript{2}/Pt/C. The Tafel slopes of Ni\textsubscript{2}P-Fe\textsubscript{2}P/NF were 58 and 86 mV dec\textsuperscript{-1} for the OER and HER, respectively. In addition, the enhanced stability and corrosion resistance of Ni\textsubscript{2}P-Fe\textsubscript{2}P due to the alloying of Ni, Fe, and P atoms enable them to be highly efficient in seawater. Only H\textsubscript{2} and O\textsubscript{2} could be found by gas chromatography, the amount of H\textsubscript{2} and O\textsubscript{2} was consistent with the theoretical value, and no Cl\textsubscript{2} signal was observed, which demonstrated that the faradaic efficiency of Ni\textsubscript{2}P-Fe\textsubscript{2}P/NF in overall seawater splitting reached nearly 100%. In contrast to the hydrothermal and electrochemical deposition methods reported in other literature to prepare bimetallic compounds, the preparation of Ni\textsubscript{3}P-Fe\textsubscript{2}P could be carried out at room temperature, the loading of Fe was adjusted by the concentration of the Fe(NO\textsubscript{3})\textsubscript{3}, 9H\textsubscript{2}O solution, and the reaction solution could be reused, which was conducive to large-scale production. This study provided a new way for the large-scale synthesis of bifunctional catalysts for the efficient decomposition of water/seawater to produce hydrogen.\textsuperscript{17}

For electrocatalytic water splitting, the wettability of water is very important for catalytic reactions; the larger the contact angle with water is, the more favorable the contact between the electrolyte and the electrode surface. The high wettability can improve contact between the electrode and the electrolyte, promote the migration of photogenerated carriers and reduce ohmic losses.\textsuperscript{63,64} NiFePi and NiFePi/P possessed smaller contact angles (63 ± 3°, 69 ± 3°) than NiFe (100 ± 3°) and NiFeP (127 ± 3°), implying that the affinity of the catalyst for water remarkably improved after phosphorylation. In addition, NiFePi/P presented the lowest charge transfer resistance (Rct) (0.57 Ω) and the lower series resistance (Rs), as displayed in Figure 8, which confirmed that phosphorylation could greatly improve the electrical conductivity and charge transfer by improving the surface wettability. For NiFePi/P, Rct was the lowest, but Rs was not. NiFePi/P presented the lowest overpotential of 230 mV at 10 mA cm\textsuperscript{-2}, with a Tafel slope of 57 mV dec\textsuperscript{-1}, which further demonstrated that wettability is more vital than electrical conductivity in contributing to the OER catalytic activity. The XPS results confirmed that a synergistic effect between metal phosphates and phosphates can be achieved by changing the amount of P-O-P and M-O-P in NiFePi/P, leading to a change in the electron environment around metal ions, an improvement in catalytic activity, and an increased number of Fe\textsuperscript{3+} and Ni\textsuperscript{3+/4+} active sites.\textsuperscript{55}

Surface phosphorylation of metal phosphides is helpful in improving the wettability of water on metal phosphides. It was reported that the distorted-tetrahedral cobalt geometry derived from the phosphate/pyrophosphate groups was beneficial to water adsorption.\textsuperscript{66} The surface wettability of NiFe/NiFe:Pi (contact angle of 44 ± 3°) remarkably improved relative to that of NiFe hydroxide (contact angle of 129 ± 5°). Moreover, the electrochemical polarization also changed the surface wettability of the sample. NiFe/NiFe:Pi became superhydrophilic without a contact angle after long-term catalysis. For NiFe, the contact angle changed from ~129° to ~45° under electrochemical polarization conditions. The current density of NiFe/NiFe:Pi increased by two times at a potential of 1.65 V relative to that of the NiFe electrode, which confirmed the synergistic effect between NiFe and NiFe:Pi. The Tafel slope of NiFe/NiFe:Pi was 38 mV dec\textsuperscript{-1}, which is smaller than that of NiFe (48 mV dec\textsuperscript{-1}) and Ni:Pi (50 mV dec\textsuperscript{-1}).\textsuperscript{64}

5 METAL PHOSPHIDES AS OCCATALYSTS FOR PHOTOCATALYTIC WATER SPLITTING

The process of photocatalytic H\textsubscript{2} evolution from water splitting is as follows: (a) absorption of photons;
(b) separation and transfer of photoinduced electrons and holes; and (c) oxidation and reduction reactions. Currently, the major scientific issues of photocatalytic water decomposition are the low light absorption efficiency, severe photogenerated carrier recombination, and the slow surface reaction rate. Based on the main problems of photocatalytic water splitting, the catalyst was designed and modified in the following ways to improve the rate of H₂ production by researchers: (a) researchers introduced an impurity level between the forbidden bandwidth by metal- or nonmetal-doping or regulated the defects of materials to increase the response range of visible light, (b) designed the microstructure and surface morphology of catalysts to speed up the transport of carriers or reduce their migration distance, (c) loaded cocatalysts to accelerate surface chemical reactions and inhibit the fast recombination of charge carriers, (d) coupled two different semiconductors to take advantage of their respective advantages, such as the construction of Z-scheme heterojunctions and the formation of p-n junctions, (e) doped foreign atoms in semiconductors to induce the formation of vacancies or defects (Figure 9). Among them, loading cocatalysts on the surface of semiconductors has usually been employed to improve the surface reaction efficiency. Metal phosphides with excellent electrical conductivity, low H₂ production overpotentials, and high stability have been extensively studied by researchers.

Generally, metal phosphides have physical properties similar to those of metal carbides and nitrides, such as excellent thermal and electrical conductivity and high mechanical strength. Compared with carbon and nitrogen atoms, phosphorus atoms possess a larger atomic radius, and it is hard to reside in the interstitial spaces between metal atoms to form a simple mesenchymal crystal structure. Hence, metal phosphides tend to form a more isotropic crystal structure, as displayed in Figure 2, which makes them possess more unsaturated surface atoms for coordination. Consequently, metal phosphides exhibit much better catalytic activity than metal carbides, nitrides, and sulfides. Hence, metal phosphides with a lower hydrogen-producing
overpotential, tunable electronic structure, high electrical conductivity, and low price are promising candidates to replace noble metal cocatalysts in photocatalytic H₂ production by water splitting.

The work function (WF) refers to the minimum energy required to move an electron from the inside of a solid just to the surface, reflecting its ability to bind electrons. It affects the catalytic performance by affecting the injection of carriers. A high work function is an important index to evaluate the excellent catalytic activity of catalysts. The larger the work function is, the more favorable it is for the catalyst to capture electrons. The barrier layer and anti-barrier layer would form at the interface between the metal and semiconductor due to the difference in the work functions of the metal and semiconductor, as presented in Table 1. When a metal is in contact with an n-type semiconductor, if the work function of the metal (Wm) is greater than the work function of the semiconductor (Ws), electrons enter the metal from the semiconductor, and the energy band at the surface of the semiconductor bends upward to form a surface barrier, which is a high-resistance area called a barrier layer. The built-in electric field is oriented from the semiconductor to the metal, which is not conducive to the transfer of electrons from semiconductors to metals. Otherwise, if Wm is smaller than Ws, electrons enter the semiconductor from the metal, and the energy band at the surface of the semiconductor bends downward to form an anti-barrier layer, which is beneficial for electron migration from semiconductors to metals. Otherwise, if, the opposite is true, as displayed in Table 1. Hence, it is very important to choose metals and semiconductors with matching work functions.

For n-type semiconductors, choose a metal with small WF, and for p-type semiconductors, choose a metal with large WF, which can reduce the Schottky barrier height at the interface between the metal and the semiconductor, benefiting the injection of carriers. For example, the work function of Cu (111) was 4.99 eV, which perfectly matches that of WC (001) (5.11 eV) relative to Ag (111) (4.74 eV), Au (111) (5.31 eV), Al (111) (4.24 eV), Ni (111) (5.35 eV), and Fe (111) (4.74 eV). The absolute work function difference between Cu and WC was the smallest among these metals, implying the preservation of a high work function for the WC (001) surface. In addition, ΔG_H2 was reduced to −0.36 eV from −0.72 eV, which favored the improvement in HER performance.23 A Schottky junction will form at the interface when metal phosphides touch the semiconductor because of the difference in Wf, which will induce the bending of the conduction band. For example, when Fe_2P, Co_2P, and Fe_2P-Co_2P are coupled with g-C3N4, the electrons flow from metal phosphides to g-C3N4 because of the difference in Wf until their Fermi levels are equal, causing the band to bend downward for g-C3N4, as displayed in Figure 10.25

5.1 Nickel phosphide

Nickel phosphides are the metal phosphide cocatalysts most commonly combined with semiconductors in photocatalytic water splitting due to their low H₂ evolution overpotential and unique structural features. DFT calculations have shown that hollow Ni sites in Ni2P made Ni2P possess more active sites for anchoring reactants. Noble-metal-free Ni2P cocatalyst-decorated g-C3N4 composites were fabricated through a two-step hydrothermal and phosphidation method by Zhao et al.21 Under the optimal conditions, the H₂ evolution rate reached 5.67 μmol h⁻¹, which is approximately 1418 times greater than that of pure g-C3N4 and even higher than that of the noble metal Pt-loaded g-C3N4. The Ni and P in the Ni2P cocatalyst acted as the hydride-acceptor and proton-acceptor centers, respectively, inducing an increase in the rate of H₂ production. Similarly, Indra et al.77 prepared Ni2P-modified mesoporous graphitic carbon nitride (sg-CN) by a sol-gel method, which showed a much higher catalytic activity than the physical mixture of Ni2P and sg-CN or metallic nickel on sg-CN under similar conditions. In this integrated system, the loading of Ni2P not only decreased the charge recombination rate but also accelerated the surface chemical reaction. Zeng et al.78 developed a novel solution-phase method to construct highly monodisperse zero-dimensional (0D) nickel phosphide (Ni2P) nanoparticles and then anchored them on the surface of two-dimensional (2D) porous g-C3N4 nanosheets via a solution-phase self-assembly process. As presented in Figure 11, monodisperse Ni2P nanoparticles with good crystallization and small particle sizes were produced by the phosphorization of intermediate monodisperse Ni. Ni2P nanoparticles were tightly anchored on the surface of porous g-C3N4 nanosheets. g-C3N4/3.5% Ni2P presented the highest H₂ evolution rate of 474.7 μmol h⁻¹ g⁻¹ because Ni2P with excellent electrical conductivity was an effective cocatalyst for accelerating the separation of holes and electrons.

| TABLE 1 | Conditions for the formation of n-type and p-type barriers layer |
|-----------------|-----------------|-----------------|
| **n-Type semiconductor** | **p-Type semiconductor** |
| Wm > Ws | Barrier layer | Anti-barrier layer |
| Wm < Ws | Anti-barrier layer | Barrier layer |

Wm > Ws: 0.36 eV, which favored the improvement in HER performance. Wm < Ws: 0.72 eV, which favored the improvement in HER performance.
Sulfide photocatalysts with suitable conduction band and valence band positions and remarkable visible-light responsive capacity can meet the requirements of photocatalytic water splitting. However, the main problems that sulfides faced were the fast recombination of carriers and the phenomenon of severe photocorrosion.
In view of the above problems, Li et al.\textsuperscript{25} constructed 2D/2D Ni$_2$P/ZnIn$_2$S$_4$ nanohybrids to increase their contact area and reduce the carrier diffusion distance, which confirmed that Ni$_2$P was an effective cocatalyst to improve the photocatalytic performance of H$_2$ generation for sulfides. In addition, Ni$_2$P was also demonstrated to be an effective cocatalyst for Zn$_{0.5}$Cd$_{0.5}$S,\textsuperscript{79} CdS,\textsuperscript{80} g-C$_3$N$_4$,\textsuperscript{77} ZnO,\textsuperscript{81} and red phosphorus\textsuperscript{34} in the photocatalytic field. To solve the photocorrosion problem of sulfide and enhance its stability, Ni$_2$P@CdS composites with core-shell structures were constructed by Zhen et al.\textsuperscript{82} via a two-step solvent thermal process, as depicted in Figure 12. In this system, artificial gills were applied to remove the O$_2$ generated during the process of photocatalysis, and the occurrence of CdS photocorrosion was inhibited to a certain extent. Meanwhile, the reverse reaction of H$_2$ and O$_2$ was prevented. ICP results confirmed that the Ni$_2$P shell played a vital role in the protection of CdS from photocorrosion.

It has been reported that the microstructure of a material has a great effect on catalytic activity. Quantum dots (QDs) with smaller diameters possessed unique physical and chemical properties due to the quantum confinement effect, which could reduce the transfer distance of carriers. For example, Ni$_2$P QDs-modified ultrathin g-C$_3$N$_4$ nanosheets were fabricated by Lu et al.\textsuperscript{83} The maximum H$_2$ production rate was 1503 μmol h$^{-1}$ g$^{-1}$ at the optimal Ni$_2$P loading amount, which was much better than that of noble metal Pt-loaded g-C$_3$N$_4$ (560 μmol h$^{-1}$ g$^{-1}$). As displayed in the TEM images of Figure 13, ultrasmall Ni$_2$P QDs were tightly anchored on the surface of ultrathin g-C$_3$N$_4$ nanosheets, and the contact between them was close. According to the characterization results, the valence band value of g-C$_3$N$_4$ shifted up after the modification of Ni$_2$P QDs, enhancing the photocatalytic reduction ability. The light absorption capacity of Ni$_2$P/g-C$_3$N$_4$ was significantly enhanced relative to that of pure g-C$_3$N$_4$, which was beneficial for improving the H$_2$ evolution rate. In addition, the XPS results confirmed the formation of Ni–N chemical bonds between Ni$_2$P QDs and g-C$_3$N$_4$ nanosheets, which was favorable for the timely migration and separation of photonic carriers. Hence, the photocatalytic and photoelectric activity of g-C$_3$N$_4$ significantly improved after the incorporation of Ni$_2$P QDs. This work showed that metal phosphides are a promising and low-cost cocatalyst for the replacement of noble metals.

In addition, QDs have been regarded as one of the most promising structures due to their small particle size. On the one hand, a smaller particle size is advantageous to the timely transfer and separation of photocarriers, inhibiting the recombination of electrons and holes; on the other hand, QDs possess a large surface area, providing more catalytically active sites.\textsuperscript{83,84} Ni$_2$P QDs have also been employed as cocatalysts in combination with other semiconductors, such as TiO$_2$ and red phosphorus. A 0D/2D Ni$_2$P/TiO$_2$ architecture was fabricated by Luo et al.\textsuperscript{85} via a facile solvothermal method, and the H$_2$ generation rate of TiO$_2$ significantly improved after the introduction of Ni$_2$P. Ni$_2$P dispersed on ultrathin TiO$_2$ nanosheets acted as the electron acceptor, reducing H$^+$ into H$_2$, and the intimate interface between Ni$_2$P and TiO$_2$ was advantageous to the timely transfer and separation of photocarriers, accelerating the reaction rate. Liang et al.\textsuperscript{86} employed Ni$^{2+}$ as a chemical scissor to construct a 0D/2D Ni$_2$P/red P photocatalyst using a facile and mild in situ hydrothermal method. Ni$_2$P in the form of QDs was loaded on the surface of red P nanosheets. During the hydrothermal process, Ni$^{2+}$ not only served as a nickel source to fabricate Ni$_2$P but also functioned as a chemical scissor during the formation of red P nanosheets.

In addition to Ni$_2$P, Ni$_{12}$P$_5$ is usually employed as a cocatalyst and loaded on the surface of semiconductors for water splitting. Ni$_{12}$P$_5$/g-C$_3$N$_4$ composites were prepared by Wen et al.\textsuperscript{86} At the optimal Ni$_{12}$P$_5$ loading amount, the rate of H$_2$ generation was 126.61 μmol h$^{-1}$ g$^{-1}$, which was up to 269.4 times higher than that of g-C$_3$N$_4$. Ni$_{12}$P$_5$ nanoparticles on the surface of g-C$_3$N$_4$ trapped electrons from the conduction of g-C$_3$N$_4$, acted as the active sites to promote the separation of charge carriers and accelerated the H$_2$ evolution kinetics due to its low H$_2$ evolution over-potential.\textsuperscript{87} In addition, colloidal Ni$_{12}$P$_5$ nanoparticles were successfully embedded into porous g-C$_3$N$_4$ nanosheets through a facile solution-phase approach. The H$_2$ evolution rate reached 535.7 mmol h$^{-1}$ g$^{-1}$ at the optimal content of Ni$_{12}$P$_5$. As displayed in Figure 14, Ni$_{12}$P$_5$ nanoparticles evenly inserted into the porous g-C$_3$N$_4$ nanosheets, which acted as excellent catalytic activity sites for H$_2$ generation, inducing the improvement in H$_2$ evolution.\textsuperscript{88} This study was beneficial to the development of effective and robust g-C$_3$N$_4$-based photocatalysts.
Different crystal structures also lead to different H₂ production rates. Sun et al.²² fabricated three different crystalline phases of NiₓPₓ, Ni₁₂P₅ₓ, and Ni₃P-hybridized g-C₃N₄ composites and systematically investigated the effect of the phase structure of NiₓPₓ on H₂ production activity. It was demonstrated that the H₂ generation rate of all types NiₓPₓ/g-C₃N₄ composites obviously improved after the incorporation of NiₓPₓ, implying that NiₓPₓ was an effective cocatalyst for g-C₃N₄. In particular, Ni₂P/g-C₃N₄ hybrids showed the highest rate of H₂ evolution among them. Since the P atoms in NiₓPₓ played an essential role in trapping the positively charged proton and delivering H₂, NiₓP with more P atoms could provide more Ni–P bonds, leading to an increase in the photocatalytic activity, as displayed in Figure 15. In addition, amorphous NiₓP-modified CdS nanorods were constructed via a facile photoreduction method using NiCl₂ and NaH₂PO₂ as the nickel and phosphorus sources, respectively, in which NiₓP acted as a low-cost cocatalyst uniformly distributed onto the CdS nanorods. The presence of NiₓP in NiₓP/CdS improved the light absorption performance, boosted the photocurrent intensity, lowered the photoelectric impedance, reduced the fluorescence intensity, and prolonged the fluorescence lifetime of CdS, effectively promoting the migration and separation of charge carriers. The abovementioned research confirmed that NiₓPₓ was an inexpensive and efficient cocatalyst in the photocatalytic decomposition of water.⁸⁹

Unlike the above binary photocatalyst system, ternary photocatalysts can achieve the efficient and timely separation of electrons and holes in space, which can significantly increase the rate of H₂ production. In addition, ternary photocatalysts possess an enhanced light absorption capacity and a faster carrier transfer rate than binary photocatalysts. Thus, researchers designed ternary photocatalysts to enrich electrons and holes on different catalysts, inhibiting their recombination. NiO/Ni₂P/g-C₃N₄ (NiO/Ni₂P/CN) ternary photocatalyst was constructed by Shi et al.⁹⁰ via a one-step in situ phosphating strategy. As displayed in Figure 16, Ni₂P acted as a cocatalyst to receive electrons from the conduction band of CN, reducing H⁺ into H₂ because of its low H₂ evolution overpotential. Meanwhile, NiO accepted holes from the valence band of CN, inducing the timely transfer and separation of photocarriers in space. The maximum H₂ evolution rate (5.04 μmol h⁻¹) was 126 times higher than...
that of CN, which was ascribed to the intimate contact among NiO, Ni$_3$P, and CN and the timely transfer and separation of photocarriers. This work might provide guidelines for the construction of highly efficient ternary photocatalysts. Jiang et al.\textsuperscript{91} synthesized Ni$_3$P/Ni(NO$_3$)$_2$/g-C$_3$N$_4$ 3D heterojunction photocatalysts by the hydrothermal and calcination method, in which Ni$_3$P/Ni(NO$_3$)$_2$ nanoparticles were evenly dispersed on the surface of g-

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FIGURE 14  TEM images of A, g-C$_3$N$_4$; B, Ni$_3$P$_5$; and C-F, 5Ni$_{12}$P$_5$-g-C$_3$N$_4$. E, HAADF image and G-K, elemental mapping images of the C, N, Ni, and P of 5Ni$_{12}$P$_5$-g-C$_3$N$_4$. Reproduced with permission: Copyright 2017, The Royal Society of Chemistry\textsuperscript{88}
C₃N₄ nanosheets. When Ni₂P and Ni(PO₃)₂ existed together, the H₂ evolution rate of g-C₃N₄ reached the maximum, demonstrating the existence of a synergetic effect between them. In addition, an N-TiO₂/g-C₃N₄ heterostructure modified with a Ni₅P cocatalyst was fabricated by Wu et al²² via ammonia etching and photoreduction deposition method. N-doped TiO₂ nanosheets formed and stood upright on the surface of g-C₃N₄ nanosheets with a 3D structure. The loading of the Ni₅P cocatalyst and the formation of intimate nanoheterojunctions between TiO₂ nanosheets and g-C₃N₄ nanosheets promoted charge transfer. This work provided some perspectives for the design and construction of the microstructure of catalysts.

To inhibit the photocorrosion of sulfides, Qin et al⁹³ developed a Ni₂P-Cd₀.₉Zn₀.₁S/g-C₃N₄ core-shell heterostructure with Cd₀.₉Zn₀.₁S crystalline core and g-C₃N₄ shell layer, achieving timely effective carrier separation in space, as displayed in Figure 17. The electrons and holes transferred to Cd₀.₉Zn₀.₁S and g-C₃N₄, respectively, due to the formation of a type II heterojunction at their interface. Meanwhile, Ni₂P as a cocatalyst received electrons from g-C₃N₄, reducing H⁺ into H₂. The g-C₃N₄ layer covering the surface of Cd₀.₉Zn₀.₁S collected holes from Cd₀.₉Zn₀.₁S, which could effectively suppress the photocorrosion of Cd₀.₉Zn₀.₁S, inducing a significant improvement in H₂ production activity and stability. The maximum H₂ production rate was up to ~2100 μmol h⁻¹ mg⁻¹, with an apparent quantum yield of 73.2% at 420 nm and an excellent photocatalytic H₂ evolution stability of 90 hours. In addition, Yu et al⁹⁴ fabricated Ni₂P/Cd₀.₅Zn₀.₅S/Co₃O₄ (Ni₂P/CZS/Co₃O₄) composites that showed better photocatalytic activity than bare CZS. The electrons transferred from the CB of Co₃O₄ to the CB of CZS, the holes shifted from the valance band (VB) of CZS to the VB of Co₃O₄, and Ni₂P as a cocatalyst received the electrons from the CB of CZS and reduced H⁺ into H₂, achieving efficient space charge separation in time. This study provided a deep understanding of the fabrication of photocatalysts with unique microstructures to achieve timely space charge separation.

2D black phosphorus has a large surface area and excellent electrical conductivity, which makes it very attractive in the catalytic field. For example, 2D-black phosphorus (BP)-supported Ni₂P (2D-Ni₂P@BP) was integrated with 2D mesoporous graphitic carbon nitride (CN).⁹⁵ In the integrated system, BP acted not only as a catalyst but also as a source of phosphorus for the synthesis of Ni₂P, inducing close contact between Ni₂P and BP. The obtained 2D-Ni₂P@BP/CN displayed superb photocatalytic activity, which was attributed to the synergetic effect of fast carrier separation, the fast transfer of electrons from CN to Ni₂P@BP and rapid H⁺ reduction into H₂ on Ni₂P. Meanwhile, 2D Ni₂P@BP combined
with CN led to a greater interface contact area, significantly reducing the carrier transfer distance. Yan et al.\textsuperscript{96} designed ternary Ni$_2$P/rGO/g-C$_3$N$_4$ nanotubes with a maximum H$_2$ generation rate of 2921.9 mmol h$^{-1}$ g$^{-1}$, which was approximately 35, 16, and 9 times higher than that of g-C$_3$N$_4$, rGO/g-C$_3$N$_4$, and Ni$_2$P/g-C$_3$N$_4$, respectively. In this integrated system, rGO acted as an electron transfer medium, and Ni$_2$P worked as a reaction site. This work confirmed that Ni$_2$P was an effective cocatalyst in photocatalytic H$_2$ evolution and that the fabrication of ternary photocatalysts was beneficial to the improvement of H$_2$ generation.

MOFs have attracted much attention due to their unique physical and chemical properties. Ni-based MOFs were employed as the source of nickel to fabricate Ni$_2$P/Ni nanoparticles encapsulated in carbon/g-C$_3$N$_4$ composites via in situ pyrolysis and phosphidation.\textsuperscript{97} The maximum H$_2$ evolution rate was up to 18.04 mmol h$^{-1}$ g$^{-1}$ with eosin Y (EY)-sensitization, which was 13 times higher than that of pristine g-C$_3$N$_4$. In this system, carbon acting as an electron transport bridge accepted the electrons from excited EY and g-C$_3$N$_4$ and then transferred them to Ni$_2$P and Ni. The rapid separation of carriers, intimate contact interface, and matching bandgap array among g-C$_3$N$_4$, Ni, and Ni$_2$P, as well the accelerated proton reduction reaction promoted by Ni$_2$P/Ni NPs, were the main reasons for the improvement in catalytic activity. The CdS/MoS$_2$@Ni$_2$P ternary photocatalyst was prepared via a hydrothermal and MOF template strategy. The optimal CdS/MoS$_2$@Ni$_2$P displayed an excellent H$_2$ production rate, which was 69.29 times that of pure CdS. In this system, MoS$_2$ and Ni$_2$P acted as electron acceptors and cocatalysts, respectively, and the electrons captured by MoS$_2$ transferred to Ni$_2$P and then reacted with H$^+$ to generate H$_2$.\textsuperscript{98} In addition, a g-C$_3$N$_4$/C@Ni$_3$S$_4$/Ni$_2$P hybrid photocatalyst was fabricated via the in situ sulfuration and phosphidation of g-C$_3$N$_4$/Ni-MOF, and the highest photocatalytic H$_2$ evolution rate was 14.49 mmol h$^{-1}$ g$^{-1}$ with EY as the sensitizer, which was ascribed to the staggered band alignment among each component and the synergistic effect between Ni$_2$P and Ni$_3$S$_4$.\textsuperscript{99} The above research supplied some guidance for the construction of MOF-derived cocatalysts.

\section*{5.2 Cobalt phosphide}

It has been reported that the photocatalytic reaction mechanism of Co-based phosphides is similar to what hydrogenases naturally do.\textsuperscript{100} DFT simulations confirmed that the rate-limiting step in the process of H$_2$ generation was the H$_2$ desorption energy from the cobalt phosphide (CoP) surface, which needed an energy input of 0.63 eV, as shown in Figure 18. This value is lower than that of the noble metal Pt (0.74-0.86 eV), which indicated that noble metal-free CoP is a promising candidate for H$_2$ evolution.\textsuperscript{101} Furthermore, DFT calculations also confirmed that the electrical conductivity of CoP was mainly derived from Co atoms.\textsuperscript{102} Luo et al.\textsuperscript{10} constructed CoP/g-C$_3$N$_4$ composites via the phosphorization of the Co$_3$O$_4$ QDs/g-C$_3$N$_4$ precursor. The highest H$_2$ generation rate was 1.074 mmol h$^{-1}$ g$^{-1}$, which is 283-fold higher than that of pure g-C$_3$N$_4$. The characterization results showed that the formation of a new electron transfer route created by the interaction of Co with N atoms promoted the fast transfer and separation of carriers, that the lower energy barrier of CoP than Pt for H$_2$ generation made CoP a robust and low-cost H$_2$ production cocatalyst, and that the homogeneously dispersed CoP nanoparticles offered many more reaction sites for H$_2$ evolution, which together promoted the H$_2$ production rate. This work offered an effective method to fabricate highly dispersed cocatalysts in the matrix of host catalysts.

In addition, CoP combined with a CdS photocatalyst was fabricated by Xu et al.\textsuperscript{103} and applied for the oxidation of aryl alcohols to form aromatic aldehydes, which was accompanied by H$_2$ evolution in water. The species driving the catalytic reaction were hydroxyl free radicals derived from the decomposition of water. Meanwhile, the isotope labeling experiment confirmed that water worked as a hydrogen source. Qiu et al.\textsuperscript{104} successfully combined...
Cd$_x$Zn$_{1-x}$Se nanotubes with CoP nanoparticles via a facile mechanical mixing method. The bandgap width and CB position of Cd$_x$Zn$_{1-x}$Se could be tuned by changing the Cd concentration, which was beneficial for the acceptance of electrons by CoP.

The rapid recombination of electrons and holes was the main factor hindering the improvement in the H$_2$ production rate; reducing the transfer distance of carriers and accelerating the migration rate of carriers were efficient methods for promoting photocatalytic performance. For example, a 2D/2D CoP/g-C$_3$N$_4$ interface was designed to shorten the transmission distance of the photogenerated charges. Theoretical calculations confirmed that the Schottky effect existed between CoP and g-C$_3$N$_4$. The unique 2D/2D CoP/g-C$_3$N$_4$ heterostructure enlarged the Schottky effect and shortened the transmission distance of the photogenerated charges, inducing the promotion of catalytic activity. The construction of a 0D/2D CoP/black phosphorus (CoP/BP) heterostructure was also an effective strategy for increasing the intimate interface contact area between CoP and BP, which effectively reduced the carrier transfer distance. Xiang et al. fabricated 2D-2D CoP/ZIS nanohybrids via an electrostatic self-assembly method. The unique 2D structure of CoP and ZIS made the large intimate contact interface between them, effectively reducing the diffusion distance of carriers. In addition, CoP QDs were also employed as cocatalysts loaded on the surface of g-C$_3$N$_4$ via a simple pyrolysis-based method and electroless plating. This work provided a simple and feasible method of synthesizing metal phosphide QDs.

The intimate contact between each component was crucially important for the timely transfer of carriers. Based on this, Co$_2$P-modified CdS was fabricated by Li et al. via an in situ hydrothermal strategy. In the integrated system, the Co$_2$P nanoparticles were homogeneously dispersed on the surface of CdS with unique intimate contact. The characterization results confirmed that great bonding occurred between the interface of Co$_2$P and CdS during the in situ hydrothermal process, which was beneficial to the improvement in photocatalytic H$_2$ evolution. Dong et al. loaded Co$_2$P onto CdS nanorods by a photochemical strategy with Co salt and NaH$_2$PO$_2$ as the Co and P sources, respectively. The whole process was completed within an hour, which was safe, rapid, and energy saving. The optimized H$_2$ production rate of Co$_2$P/CdS was approximately 500 mmol h$^{-1}$ g$^{-1}$, which was attributed to the fact that the Co$_2$P cocatalyst could effectively prevent the recombination of electrons and holes. This study supplied a fast and feasible strategy for fabricating metal phosphides. In addition, photochemical synthesis strategies have also been applied for the synthesis of amorphous Co-P alloy-modified ZnIn$_2$S$_4$, and the test results showed that ZnIn$_2$S$_4$ presented improved photocatalytic activity after modification with an amorphous Co-P alloy, which was attributed to the elevated photocurrent density, reduced impedance, weakened fluorescence intensity and extended carrier life. This work demonstrated that an amorphous Co-P alloy was a robust and efficient cocatalyst in the photocatalytic field.

MOFs are often employed as precursors for the synthesis of metal phosphides due to their excellent physical and chemical properties. For example, CoP/g-C$_3$N$_4$ composites were constructed by Sun et al. via a two-step calcination procedure. The preparation process is shown in Figure 19. ZIF-67 and g-C$_3$N$_4$ were prepared via simple precipitation and thermal condensation processes, respectively, in which the precursor mixed with NaH$_2$PO$_2$ was heated to 300°C. The introduction of CoP could obviously boost the photocatalytic activity of g-C$_3$N$_4$ due to the enhanced light absorption ability, accelerated carrier migration, and separation rates. Zhang et al. constructed CoP/CEVO$_4$ nanohybrids through a simple one-step chemical precipitation method, in which CeVO$_4$ particles were firmly attached to the surface of CoP particles derived from ZIF-9 to form a “small point” to “large point” heterojunction. Mechanistic studies showed that the Schottky barrier led to the bending of the bands of CoP and CeVO$_4$ and the formation of an internal electric field created by the heterojunction between CoP and

![The energy profile for H$_2$ production on the CoP (101) surface and the optimized structures of the initial states (IS), transition state (TS), and final state (FS). Reproduced with permission: Copyright 2018, Elsevier](image1.png)
CeVO₄. Hence, the synergistic effect between CoP and CeVO₄ promoted the improvement in photocatalytic activity. This study presented some guidelines for modulating the electronic structure and carrier behavior of transition metal phosphide-based photocatalysts.

In practice, the recombination of electrons and holes was still the main factor hindering the improvement in photocatalytic H₂ production activity. It is vital to increase the H₂ evolution rate to improve the timely transfer and separation of photogenerated carriers in space. Based on this, Lin et al. developed dual cocatalyst-modified photocatalysts by selectively loading Au nanoparticles and CoP nanosheets onto the inside and outside surfaces of a three-dimensionally ordered macroporous (3DOM) g-C₃N₄ framework. In the CoP/3DOM g-C₃N₄/Au sample, the spatially separated dual cocatalyst could provide two paths for electron migration in opposite directions to dramatically boost the rate of electron migration. As shown in Figure 20, one was electron movement from g-C₃N₄ to CoP nanosheets on the outside surface of g-C₃N₄, and the other was electron transfer from g-C₃N₄ to Au nanoparticles on the inside surface of g-C₃N₄. Meanwhile, the holes were consumed by scavengers, which could achieve fast carrier separation at different reactive sites, resulting in an obvious improvement in photocatalytic H₂ evolution.

A p-n-n tandem heterostructure was constructed by combining n-type CdS with n-type WS₂ nanosheets and p-type CoP nanoparticles, which acted as a bifunctional photocatalyst for simultaneously degrading pollutants and generating H₂. Reddy et al. designed multicomponent hierarchical dandelion-flower-like Cds/RGO-MoS₂@CoP composites with a maximum H₂ generation rate of 83 907 μmol h⁻¹ g⁻¹. In this composite, the covered RGO nanosheets acted as good electron collectors and transporters. At the same time, the CoP and MoS₂ nanostructures worked as electron acceptors and cocatalysts, respectively, achieving the effective separation of charge carriers.

5.3 Iron phosphide

Iron phosphide (FeP) as a cocatalyst has become increasingly popular in photocatalytic reactions since iron is the most abundant transition metal. In addition, the vacant 3d orbital and/or 3p lone pair electrons of P atoms regulate the surface charge state of Fe atoms, facilitating electron transfer to the surface of FeP nanoparticles. Zhao et al. designed ultrasmall 0D FeP nanodots anchored on layered 2D g-C₃N₄ nanosheets by the low-temperature phosphidation method, and the resulting composites had well-defined nanostructures and an intimate 0D/2D interface. The FeP nanocrystals in the composites played a cocatalyst role, accelerating the transfer and separation of charge carriers. The presence of FeP improved the visible light response capability and accelerated the charge carrier transfer dynamics of g-C₃N₄.

The particle size and dispersibility of cocatalysts are also one of the main factors affecting the catalytic activity; the smaller the particle size is, the higher the dispersity, the more active sites exposed, and the better the catalytic activity. Sub-5 nm ultrafine FeP nanodot-modified porous graphitic carbon nitride (g-C₃N₄)
composites were fabricated by Zeng et al. via the gas-phase phosphorization of a FeO$_2$/g-C$_3$N$_4$ precursor in an argon atmosphere. The introduction of sub-5 nm FeP nanodots with uniform sizes and a high dispersity boosted the transfer rate of electrons and acted as reactive sites for reducing H$^+$ into H$_2$. In addition, the DFT calculations showed that the FeP/g-C$_3$N$_4$ hybrids exhibited a moderate adsorption-desorption capacity ($\Delta G_{\text{ads}}^\circ = -0.09$ eV), as displayed in Figure 21, which was similar to that of the noble metal Pt, suggesting superior HER kinetics.

Sun et al. fabricated FeP nanoparticle-coupled CdS nanosheets via an in situ phosphorization method. In the synthesized heterojunction photocatalysts, 0D FeP NPs, were tightly attached to the surfaces of 2D CdS nanosheets, achieving efficient photocatalytic H$_2$ evolution. The characterization results demonstrated that the fabrication of 0D/2D heterojunctions with close contact between FeP and CdS could boost the transfer and separation of carriers, promoting the improvement in photocatalytic performance. FeP nanoparticle-modified CdS nanocrystal photocatalysts were applied for photocatalytic H$_2$ generation and achieved a maximum H$_2$ evolution rate of 202 000 $\mu$mol h$^{-1}$ g$^{-1}$, which is 3-fold higher than that of Pt/CdS. In addition, the system presented excellent stability for more than 100 hours.

In addition to binary FeP composites, Qi et al. designed a g-C$_3$N$_4$/FeO$_2$@FeP hybrid material by annealing and phosphidation of g-C$_3$N$_4$/Fe MOFs. During the preparation process, as shown in Figure 22, heterogeneous structure construction and cocatalyst loading were realized with compact contact between each component. The optimized g-C$_3$N$_4$/FeO$_2$@FeP sample presented a maximum H$_2$ evolution rate of 12.03 mmol h$^{-1}$ g$^{-1}$ in the presence of EY, which was ascribed to the following reasons: (a) improved light absorption capacity; (b) efficient separation and transfer of electrons and holes due to the formation of a type-II heterojunction between FeO$_2$ and g-C$_3$N$_4$; and (c) increased numbers of H$_2$ production sites provided by FeP.

5.4 | Copper phosphide

Copper phosphide (Cu$_3$P), a p-type semiconductor with a bandgap of 1.3-1.4 eV, has been applied to lithium-ion batteries, HER and photocatalytic H$_2$ evolution by water splitting due to its abundant reserves. In particular, Cu$_3$P functioned as a p-type semiconductor coupled with an n-type semiconductor, forming p-n heterojunction photocatalysts. For example, Yue et al. developed an earth-abundant Cu$_3$P-modified TiO$_2$ “P-N” heterojunction by mechanical mixing and calcining processes. An optimized H$_2$ generation performance was obtained over Cu$_3$P/TiO$_2$ (7940 $\mu$mol h$^{-1}$ g$^{-1}$), which was attributed to the fast separation and transfer of charge carriers due to the presence of a built-in electric field created by the p-n heterojunction. In addition, Shen et al. constructed Cu$_3$P nanoparticle-decorated g-C$_3$N$_4$ nanosheets. The study found that Cu$_3$P functioned as a cocatalyst at a low content (1.5 wt%) and served as a p-type semiconductor when its content reached 20 wt%, as shown in Figure 23. Comparatively speaking, the role of the p-type semiconductor for Cu$_3$P in increasing the photocatalytic H$_2$ production rate in Cu$_3$P/g-C$_3$N$_4$ composites was more obvious than that of the cocatalyst for Cu$_3$P. A maximum H$_2$ evolution rate of 159.41 $\mu$mol h$^{-1}$ g$^{-1}$ was achieved over Cu$_3$P/g-C$_3$N$_4$, which was 1014-fold higher than that of g-C$_3$N$_4$.

Hua et al. fabricated a p-type Cu$_3$P/n-type g-C$_3$N$_4$ heterojunction via phosphorization of a CuCl(OH)$_3$/g-C$_3$N$_4$ precursor. In this system, Cu$_3$P performed the following two functions: accelerating the separation of carriers and lowering the hydrogen evolution overpotential. In addition, control experiments confirmed that the electrons accumulated on Cu$_3$P nanoparticles and that holes were enriched on g-C$_3$N$_4$ nanosheets, which demonstrated that the carrier transfer path was Z scheme. Rauf et al. designed Bi$_2$WO$_6$-Cu$_3$P Z-scheme composites through a simple ball-milling complexation strategy, producing a mediator- and cocatalyst-free photocatalyst system. The study demonstrated the significant role of interfacial solid-solid contact and the well-matched energy level positions between Bi$_2$WO$_6$ and Cu$_3$P for solar-water splitting.

5.5 | Other metal phosphides

In addition to the metal phosphides mentioned above, other metal phosphides have been developed for
photocatalytic H₂ evolution. Nanosized MoP was fabricated via a phosphorylation process under an ambient air atmosphere. The optimal MoP/g-C₃N₄ photocatalyst possessed an H₂ evolution rate of 3868 μmol h⁻¹ g⁻¹. In this system, the introduction of MoP into g-C₃N₄ could broaden the absorption range of visible light and build a conducive highway (Mo (δ⁺)-N (δ⁻) bond) for electron transfer from g-C₃N₄ to MoP, inducing an improvement in the H₂ production rate. In addition, Chen et al. anchored ruthenium on the CN framework and then further phosphorized it, acquiring the target product Rh-P/g-C₃N₄. Structural analysis showed that Rh-P was atomically dispersed on the framework of CN, and theoretical calculations confirmed that the single Rh-P site on g-C₃N₄ provided convergence centers for photogenerated electrons and reduced the H₂ evolution potential.

In addition, Zhang et al. synthesized tungsten phosphide (WP) nanoparticles through the traditional temperature programming reduction method, and then, they were loaded on the surface of CdS. After the incorporation of WP at a content of 4.0 wt%, the H₂ generation rate of CdS reached a maximum of 155.2 μmol h⁻¹, which was 11.67 times higher than that of CdS. Jin et al. designed EY-sensitized EY-UiO-66(Zr)/WP photocatalysts via the ultrasound-assisted impregnation method. In the integrated system, 3D UiO-66 with a large specific surface area, porosity, and adsorption capacity was favorable for the loading of WP nanoparticles and the adsorption of a large amount of EY molecules. EY dye molecules acting as photosensitizers extended the absorption range of visible light. WP nanoparticles acting...
as efficient cocatalysts boosted the transfer rate of electrons, leading to the improvement in \( \text{H}_2 \) evolution.

### 5.6 Bimetallic phosphides

It was reported that the high catalytic activity of metal phosphides is mainly attributed to the unbalanced surface charge distribution derived from partially positively charged Ni (\( \text{Ni}^{\delta^+} \)) and partially negatively charged P (\( \text{P}^{\delta^-} \)) due to the electronegativity difference between Ni and P.\(^{129} \) Bimetallic phosphides possess a more unbalanced surface charge distribution than single metal phosphides.\(^{130} \) For example, bimetallic phosphide NiCoP-modified g-C\(_3\)N\(_4\) exhibited an obviously improved \( \text{H}_2 \) evolution rate compared with Ni\(_2\)P/g-C\(_3\)N\(_4\) and Co\(_2\)P/g-C\(_3\)N\(_4\), which was mainly attributed to the synergistic effect of the Schottky barrier and the lower overpotential relative to that of the Ni\(_2\)P or Co\(_2\)P counterparts.\(^{131} \) Ternary metal phosphide Ni\(_x\)Co\(_{1-x}\)P-decorated Zn\(_{0.5}\)Cd\(_{0.5}\)S nanorod photocatalysts were constructed by Li et al.\(^{132} \) through an in situ phosphating method, in which Ni\(_x\)Co\(_{1-x}\)P nanoparticles were homogeneously dispersed on the surface of Zn\(_{0.5}\)Cd\(_{0.5}\)S nanorods. DFT calculations confirmed that the proposed photocatalytic mechanism agreed well with the experimental results. The formation of a coordination bond between Zn\(_{0.5}\)Cd\(_{0.5}\)S and Ni\(_{0.1}\)Co\(_{0.9}\)P at their contact interface played a vital role in the separation and transfer of charges during the photocatalytic process.

In addition, bifunctional NiCoP-modified g-C\(_3\)N\(_4\) photocatalysts were successfully fabricated by Qin et al.\(^{133} \) In the integrated system, a crystalline NiCoP core was surrounded by an amorphous nickel cobalt phosphate (NiCo-Pi) shell. The mechanistic study suggested that the NiCoP core acted as a reductive reaction site and that the NiCo-Pi shell behaved as an oxidative reaction site for separate photocatalytic \( \text{H}_2 \) and \( \text{O}_2 \) generation, as presented in Figure 24. It was demonstrated that the NiCoP@NiCo-Pi core/shell cocatalyst accelerated the
| Photocatalyst          | Light source | Sacrificial reagent | Catalyst dose | H₂ evolution rate | Efficiency | Ref.  |
|------------------------|--------------|---------------------|---------------|-------------------|------------|-------|
| 2D-Ni₂P@BP            | 300 W Xe lamp (λ ≥ 420 nm) | Triethanolamine (TEOA) | 20 mg | 858.2 μmol h⁻¹ g⁻¹ | QE = 2.8% (λ = 420 nm) | 95    |
| Cd₀.₅Zn₀.₅S/Ni₂P      | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 50 mg | 41.26 mmol h⁻¹ g⁻¹ | 143        |
| Ni₂P/Cd₀.₅Zn₀.₅S/Co₂O₄ | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 50 mg | 39.66 mmol h⁻¹ g⁻¹ | 94         |
| Ni₂P/g-C₃N₄           | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 0.01 g | 2337.09 μmol h⁻¹ g⁻¹ | EQE = 3.98% (λ = 420 nm) | 144   |
| 0D/2D Ni₂P/g-C₃N₄    | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 20 mg | 1503 μmol h⁻¹ g⁻¹ | AQE = 4.6% (λ = 420 nm) | 83    |
| 2D/2D Ni₂P/CdS       | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 10 mg | 17.95 mmol h⁻¹ g⁻¹ | AQE = 4.2% (λ = 420 nm) | 145   |
| CdS/Ni₂P/g-C₃N₄      | 300 W Xe lamp (λ ≥ 420 nm) | No sacrificial reagent | 50 mg | 15.56 μmol h⁻¹ g⁻¹ | AQE = 0.18% (λ = 420 nm) | 146   |
| Ni₂P/g-C₃N₄          | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 40 mg | 362.4 μmol h⁻¹ g⁻¹ | AQE = 1.8% (λ = 420 nm) | 147   |
| Ni₂P/Ni(PO₃)₂/g-C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | Methanol | 0.1 g | 508.3 μmol h⁻¹ g⁻¹ | 91         |
| Ni₂P/Zn₁In₁S₆        | 300 W Xe lamp (λ ≥ 400 nm) | Formic acid | 0.1 g | 45.73 μmol h⁻¹ | AQE = 1.8% (λ = 400 nm) | 148   |
| g-C₃N₄/Ni-P          | 350 W Xe lamp (λ ≥ 400 nm) | TEOA | 10 mg | 1051 μmol h⁻¹ g⁻¹ | 149        |
| MoS₂/g-C₃N₄/Ni₂P     | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 50 mg | 298.1 μmol h⁻¹ g⁻¹ | AQE = 2.51% (λ = 420 nm) | 150   |
| Ni₂P@CdS             | 300 W Xe lamp (λ ≥ 420 nm) | No sacrificial reagent | 100 mg | 251.4 μmol/180 min | AQE = 3.89% (λ = 430 nm) | 82     |
| Ni₁₂P₅/CdS           | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 10 mg | 13.89 mmol h⁻¹ g⁻¹ | 151        |
| Ni₂P/CdS             | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 1 mg | 1200 μmol h⁻¹ mg⁻¹ | AQY = 41% (λ = 450 nm) | 32     |
| 2D/2D Ni₂P/Zn₁In₁S₄ | 300 W Xe lamp (λ ≥ 400 nm) | Lactic acid | 50 mg | 2066 μmol h⁻¹ g⁻¹ | AQY = 7.7% (λ = 420 nm) | 25     |
| Ni₂P/g-C₃N₄          | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 30 mg | 3344 μmol h⁻¹ g⁻¹ | QE = 9.1% (λ = 420 nm) | 152   |
| Ni₂P/TiO₂             | 300 W Xe lamp (λ ≥ 420 nm) | Methanol | 20 mg | 9.38 mmol h⁻¹ g⁻¹ | AQE = 11.6% (λ = 360 nm) | 153   |
| g-C₃N₄/Ni₃P          | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 10 mg | 5.67 μmol h⁻¹ | 21         |
| Ni₂P/CdS             | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 20 mg | 44.65 mmol h⁻¹ g⁻¹ | AQY = 37.09% (λ = 420 nm) | 80     |
| Zn₁In₂S₄/Ni₁₂P₅     | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 50 mg | 2263 μmol h⁻¹ g⁻¹ | AQY = 20.5% (λ = 420 nm) | 154   |
| Ni₂P/g-C₃N₄          | 500 W Xe lamp (λ ≥ 420 nm) | TEOA | 3 mg | 561 μmol h⁻¹ g⁻¹ | 155        |
| Ni₂P-Zn₀.₅Cd₀.₅S     | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 0.1 g | 912.57 μmol h⁻¹ | AQE = 37.5% (λ = 420 nm) | 156   |
| Zn₀.₅Cd₀.₅S/Ni₂P     | 18 W LED lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 5 mg | 21.19 mmol h⁻¹ g⁻¹ | AQY = 21.16% (λ = 450 nm) | 157   |
| Photocatalyst | Light source | Sacrificial reagent | Catalyst dose | H₂ evolution rate | Efficiency | Ref. |
|--------------|--------------|---------------------|---------------|-------------------|------------|-----|
| Ni₂P-CdS     | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 2 mg | 68.47 mmol h⁻¹ g⁻¹ | AQE = 1.03% (λ = 450 nm) | 158 |
| Ni₂P/g-C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 20 mg | 82.5 μmol h⁻¹ g⁻¹ | AQE = 31% (λ = 313 nm) | 159 |
| Ni₂P/TiO₂    | 300 W Xe lamp | Methanol | 10 mg | 3.966 mmol h⁻¹ g⁻¹ | AQE = 1.03% (λ = 450 nm) | 85 |
| Ni₂P/Ni@C/g- C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 10 mg | 18.04 mmol h⁻¹ g⁻¹ | AQE = 58.1% (λ = 420 nm) | 97 |
| 2D Ni₂P/red phosphorus | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 30 mg | 2183 μmol h⁻¹ g⁻¹ | AQE = 28% (λ = 420 nm) | 28 |
| Ni₂P/Ni₂P/g- C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 10 mg | 14.49 mmol h⁻¹ g⁻¹ | AQE = 46.7% (λ = 420 nm) | 99 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 2 mg | 69.2 mmol h⁻¹ g⁻¹ | AQE = 4.2% (λ = 475 nm) | 89 |
| Ni₂P/CdS     | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 5 mg | 34.9 mmol h⁻¹ g⁻¹ | AQE = 21.7% | 160 |
| Ni₂P/red P   | 300 W Xe lamp (λ ≥ 420 nm) | Methanol | 10 mg | 265.43 μmol h⁻¹ g⁻¹ | AQE = 0.46% (λ = 420 nm) | 34 |
| NiO/Ni₂P/g- C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 10 mg | 5.04 μmol h⁻¹ | AQE = 0.22% (λ = 400 nm) | 90 |
| Ni₂P/Zn₀.₅Cd₀.₅S | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 50 mg | 1173 μmol h⁻¹ g⁻¹ | AQE = 18.95% (λ = 420 nm) | 79 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 1 mg | 33 480 μmol h⁻¹ g⁻¹ | AQE = 4.67% (λ = 420 nm) | 88 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 5 mg | 44 450 μmol h⁻¹ g⁻¹ | AQE = 46.3% (λ = 420 nm) | 163 |
| Ni₂P/300 W Xe lamp (λ ≥ 400 nm) | TEOA | 2 mg | 162 μmol h⁻¹ g⁻¹ | AQE = 4.67% (λ = 420 nm) | 22 |
| Ni₂P/g-C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | TEOA | 50 mg | 126.61 μmol h⁻¹ g⁻¹ | AQE = 0.46% (λ = 420 nm) | 86 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 7.2 mg | 1567 μmol h⁻¹ g⁻¹ | AQE = 3.2% (λ = 420 nm) | 161 |
| Ni₂P/300 W Xe lamp (λ ≥ 400 nm) | Lactic acid | 50 mg | 486 μmol h⁻¹ g⁻¹ | AQE = 4.6% (λ = 420 nm) | 162 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | TEOA | 60 mg | 535.7 μmol h⁻¹ g⁻¹ | AQE = 4.6% (λ = 420 nm) | 88 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 5 mg | 44 450 μmol h⁻¹ g⁻¹ | AQE = 46.3% (λ = 420 nm) | 163 |
| Ni₂P/300 W Xe lamp (λ ≥ 400 nm) | TEOA | 2 mg | 162 μmol h⁻¹ g⁻¹ | AQE = 4.6% (λ = 420 nm) | 22 |
| N-TiO₂/g- C₃N₄@Ni₂P | 300 W Xe lamp (λ = 350-780 nm) | TEOA | 50 mg | 5438 μmol h⁻¹ g⁻¹ | AQE = 0.46% (λ = 420 nm) | 92 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Lactic acid | 1 mg | 33 480 μmol h⁻¹ g⁻¹ | AQE = 4.6% (λ = 420 nm) | 39 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 1 mg | ~2100 μmol h⁻¹ mg⁻¹ | AQE = 73.2% (λ = 420 nm) | 93 |
| Ni₂P/300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃ | 100 mg | 6.4 mmol h⁻¹ g⁻¹ | AQE = 20.1% (λ = 400 nm) | 164 |
| g-C₃N₄/CoP | 300 W Xe lamp (λ ≥ 420 nm) | Formic acid | 100 mg | 6.4 mmol h⁻¹ g⁻¹ | AQE = 20.1% (λ = 400 nm) | 164 |
| CoP QD/P/g- C₃N₄ | 300 W Xe lamp (λ ≥ 420 nm) | Methanol | 12.5 mg | 724 μmol h⁻¹ g⁻¹ | AQE = 8.5% | 165 |
| Zn₀.₃Cd₀.₇S/CoP | Solar simulator | Ascorbic acid | 100 mg | 12 175.8 μmol h⁻¹ g⁻¹ | AQE = 4.37% (λ = 420 nm) | 166 |

(Continues)
| Photocatalyst                  | Light source          | Sacrificial reagent      | Catalyst dose | H₂ evolution rate | Efficiency             | Ref. |
|-------------------------------|-----------------------|--------------------------|---------------|-------------------|------------------------|------|
| CoP/CdS/WS₂                  | 300 W Xe lamp (λ ≥ 420 nm) | No sacrificial reagent   | 0.05 g        | 9.16 μmol h⁻¹ g⁻¹ | AQE = 1.34% (λ = 420 nm) | 113  |
| CoP₆/CdS                     | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃             | 1 mg          | ~500 μmol h⁻¹ mg⁻¹ | AQE = 35% (λ = 450 nm)  | 140  |
| Pt-CoP/g-C₃N₄                | 300 W Xe lamp         | Methanol                 | 80 mg         | 2.1 μmol h⁻¹      |                        | 141  |
| g-C₃N₄-Co₃P-Κ₂HPO₄            | 300 W Xe lamp         | TEOA                     | 50 mg         | 27.81 μmol h⁻¹    |                        | 167  |
| g-C₃N₄/CoP                   | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 10 mg         | 840 μmol g⁻¹      |                        | 168  |
| CdS/RGO-MoS₂@CoP              | 150 W Xe lamp (AM 1.5G filter) | Lactic acid              | 1 mg          | 83 907 μmol h⁻¹ g⁻¹ | AQE = 22.5% (λ = 450 nm) | 114  |
| CoP/BP                       | 300 W Xe lamp (λ ≥ 420 nm) | Oxalic acid              | 2 mg          | 694 μmol h⁻¹ g⁻¹  |                        | 106  |
| Co-P/g-C₃N₄                  | 300 W Xe lamp (λ ≥ 400 nm) | Methanol                 | 0.1 g         | 19.48 μmol h⁻¹    |                        | 169  |
| Co₃P-CdS                     | 300 W Xe lamp (λ ≥ 400 nm) | Lactic acid              | 50 mg         | 0.356 mmol h⁻¹    | AQE = 13.88% (λ = 420 nm) | 108  |
| CoP/Zn₀.₃Cd₀.₅S              | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid              | 50 mg         | 734 μmol h⁻¹      |                        | 136  |
| CoP/g-C₃N₄                   | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 0.1 g         | 474.4 μmol h⁻¹ g⁻¹|                        | 170  |
| g-C₃N₄/CoP                   | 350 W Xe lamp         | TEOA                     | 10 mg         | 936 μmol h⁻¹ g⁻¹  |                        | 100  |
| Co/P/ZnIn₂S₄                 | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid              | 20 mg         | 7.84 mmol h⁻¹ g⁻¹| AQY = 4.3% (λ = 420 nm) | 110  |
| Co₃P/CdS                     | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid              | 3 mg          | 500 mmol h⁻¹ g⁻¹  |                        | 109  |
| Cd₀.₅Zn₀.₅S/Cu₃P             | 300 W Xe lamp (AM 1.5G filter) | Na₂S/Na₂SO₃              | 1 mg          | 45.1 mmol h⁻¹ g⁻¹ | QY = 13.8% (λ = 420 nm) | 104  |
| CoP/g-C₃N₄/Au                 | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 50 mg         | 11 820.1 μmol h⁻¹ g⁻¹ | AQE = 18.0% (λ = 435 nm) | 112  |
| CoP/g-C₃N₄                   | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 10 mg         | 1.074 mmol h⁻¹ g⁻¹| AQY = 6.1% (λ = 420 nm) | 10   |
| Co/P/Fe₂O₃@g-C₃N₄            | 300 W Xe lamp         | TEOA                     | 10 mg         | 444.6 μmol h⁻¹ g⁻¹|                        | 111  |
| FeP/g-C₃N₄                   | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 10 mg         | 215 μmol h⁻¹ g⁻¹  |                        | 116  |
| FeP/CdS                      | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid              | 25 mg         | 1.39 mmol/5 h     | EQY = 18.63% (λ = 450 nm) | 118  |
| FeP/Zn₀.₃Cd₀.₅S-P            | 300 W Xe lamp (λ ≥ 420 nm) | Lactic acid              | 10 mg         | 24.45 mmol h⁻¹ g⁻¹| AQY = 10% (λ = 470 nm)  | 13   |
| Cd₀.₅Zn₀.₅S/Cu₃P             | 300 W Xe lamp (λ ≥ 420 nm) | Na₂S/Na₂SO₃              | 0.025 g       | 321 μmol h⁻¹      | AQE = 17.5% (λ = 420 nm) | 171  |
| g-C₃N₄/FepO₃@FeP              | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 10 mg         | 12.03 mmol h⁻¹ g⁻¹| AQE = 38.8% (λ = 420 nm) | 120  |
| FeP/g-C₃N₄                   | 300 W Xe lamp (λ ≥ 420 nm) | TEOA                     | 60 mg         | 177.9 μmol h⁻¹ g⁻¹| AQY = 1.57% (λ = 420 nm) | 117  |
| g-C₃N₄/Cu₃P                  | 300 W Xe lamp         | TEOA                     | 50 mg         | 159.41 μmol h⁻¹ g⁻¹|                        | 122  |
transfer and separation of carriers and promoted the surface reaction.

Shen et al.\(^{134}\) constructed carbon black (CB)- and Co\(_{1.4}\)Ni\(_{0.6}\)P-commodified graphitic CN via sonochemical loading and high-temperature phosphatizing. In the integrated system, the synergetic effect between the Schottky heterojunctions and Co\(_{1.4}\)Ni\(_{0.6}\)P could improve the separation efficiency of photogenerated electron-hole pairs, inducing the improvement in activity and stability. Fe-Ni-P nanotubes derived from Fe-Ni-MIL-88 nanorods presented superior photocatalytic H\(_2\) and O\(_2\) evolution activity in the presence of different dyes.\(^{135}\) Moreover, the catalytic activities of such dye-sensitized systems could be regulated by changing the molar ratio of Fe and Ni in Fe-Ni-P nanotubes.

### 6 | DISCUSSION

Generally, metal phosphides reported in most literature are covered by metal phosphates since metal phosphides are easily oxidized when exposed to air. CoP cocatalyst-decorated Zn\(_{0.5}\)Cd\(_{0.5}\)S exhibits a 20-fold higher H\(_2\) production rate than the primary Zn\(_{0.5}\)Cd\(_{0.5}\)S catalyst. Although the phosphide in topic is in the form of CoP, the XPS results demonstrated that the peak area of oxidized P species was significantly larger than that of metal phosphides due to the superficial oxidation of CoP, as shown in Figure 25A.\(^{136}\) The peak of oxidized P at 133.8 eV was in accordance with that of phosphate (133.7 eV) in the Co-Pi cocatalysts, further confirming the presence of Co-Pi on the surface of Zn\(_{0.5}\)Cd\(_{0.5}\)S.\(^{137}\) A similar phenomenon was observed in other studies,\(^{105}\) which suggested that most superficial metal phosphides were oxidized into metal phosphate. However, there is little explanation of the action of phosphates in the article, so it is confusing which part plays a major role in the improvement in H\(_2\) production activity. However, Di et al\(^{137}\) considered that Co-Pi deposited on the surface of CdS acted as an oxidation cocatalyst to capture the holes derived from CdS, inducing the partial oxidation of Co\(^{2+}\) to Co\(^{3+}\) due to the more positive valence band potential of CdS than the oxidation potential of Co\(^{2+}/Co^{3+}\), and then, Co\(^{3+}\) was reduced into Co\(^{2+}\) by lactic acid with a perfect cycle (Figure 25B). Meanwhile, the electrons at the CB of CdS participated in the reduction reaction to reduce H\(^+\) into H\(_2\). The function of metal phosphates covering the surface of metal phosphides was indistinct, and the true source of the improvement in catalytic activity was not clear. Similar reports have been provided by other researchers.\(^{138}\) Hence, it is urgent to explore the main reasons for the improvement in photocatalytic activity.

| Photocatalyst | Light source | Sacrificial reagent | Catalyst dose | H\(_2\) evolution rate | Efficiency | Ref. |
|--------------|--------------|---------------------|---------------|-----------------------|------------|-----|
| Cu\(_3\)P/CdS | 300 W Xe lamp (\(\lambda \geq 420 \text{ nm}\)) | Na\(_2\)S/Na\(_2\)SO\(_3\) | 1 mg | 200 \(\mu\)mol h\(^{-1}\) mg\(^{-1}\) | AQY = 25\% (\(\lambda = 450 \text{ nm}\)) | 11 |
| g-C\(_3\)N\(_4\)/Cu\(_3\)P/UIO-66 | 5 W LED white light (\(\lambda \geq 420 \text{ nm}\)) | TEOA | 10 mg | 79 \(\mu\)mol/5 h | | 172 |
| Bi\(_2\)WO\(_6\)-Cu\(_3\)P | Xe lamp (AM 1.5G filter) | Na\(_2\)HPO\(_4\)/NaH\(_2\)PO\(_4\) | 100 mg | 3.5 \(\mu\)mol g\(^{-1}\) | | 124 |
| Cd\(_{0.7}\)Zn\(_{0.3}\)S/Cu\(_3\)P | 300 W Xe lamp (\(\lambda \geq 420 \text{ nm}\)) | Na\(_2\)S/Na\(_2\)SO\(_3\) | 0.025 g | 321 \(\mu\)mol h\(^{-1}\) | AQE = 17.5\% (\(\lambda = 420 \text{ nm}\)) | 171 |
| Cu\(_3\)P/TiO\(_2\) | 300 W Xe lamp (\(\lambda \geq 420 \text{ nm}\)) | TEOA | 0.1 g | 7940 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) | AQE = 4.6\% | 121 |
| MoP/g-C\(_3\)N\(_4\) | 300 W Xe lamp (\(\lambda \geq 400 \text{ nm}\)) | TEOA | 10 mg | 3868 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) | AQY = 21.6\% (\(\lambda = 405 \text{ nm}\)) | 125 |
| RuP/g-C\(_3\)N\(_4\) | 300 W Xe lamp (\(\lambda \geq 400 \text{ nm}\)) | TEOA | 20 mg | 166.28 \(\mu\)mol/4 h | | 126 |
| WP/CdS | 300 W Xe lamp (\(\lambda \geq 420 \text{ nm}\)) | (NH\(_4\))\(_2\)SO\(_3\) | 50 mg | 155.2 \(\mu\)mol h\(^{-1}\) | | 127 |
| WP-g-C\(_3\)N\(_4\)/CdS | 5 W LED white light (\(\lambda \geq 420 \text{ nm}\)) | Lactic acid | 10 mg | 18 238.89 \(\mu\)mol h\(^{-1}\) g\(^{-1}\) | AQE = 4.55\% (\(\lambda = 475 \text{ nm}\)) | 173 |
production under visible light. This work showed that amorphous CoPₓ served as an important substitute for precious Pt in photocatalytic H₂ production. Nevertheless, the XPS results confirmed that phosphate species were not the active sites and could be dissolved during the process of photocatalytic H₂ evolution. However, Pan et al. considered that CoP and Pt nanoparticles on the surface of g-C₃N₄ nanosheets served as proton reduction sites and O₂ evolution sites, respectively, which is contradictory to the above discussion and other reports. No conclusive conclusions have been reached regarding the role of phosphates in photocatalysis. Hence, it is absolutely imperative to explore the role of metal phosphides in photocatalysis and electrocatalysis.

7 CONCLUSION AND OUTLOOK

In summary, metal phosphides can lower the H₂ evolution overpotential and accelerate the transfer and separation of charge carriers in the photocatalytic process; hence, they served as cocatalysts and electrocatalysts for improving the photocatalytic H₂ generation performance and electrocatalytic H₂ evolution reaction, respectively. This review summarizes the promotion of metal phosphides in electrocatalytic and photocatalytic H₂ evolution. As presented in Tables 2 and 3, different kinds of transition metal phosphides have been explored for electrocatalytic and photocatalytic H₂ production by the decomposition of water. Although some progress has been made, the actual rate of H₂ production is still too low for industrial use. The ultimate goal of these efforts is to seek stable, efficient, and low-cost catalysts for commercial electrocatalytic and photocatalytic H₂ evolution from water splitting.

At present, metal phosphides applied to electrocatalytic and photocatalytic H₂ evolution by water splitting have attracted wide attention and have good development prospects in dealing with energy shortages and environmental pollution due to their low cost, abundance, and low H₂ evolution potential. However, they still fall far short for the large-scale application required for industrialization. A stable and efficient catalyst is one of the key factors necessary to realize the conversion of solar energy into hydrogen energy. In recent years, numerous metal phosphides have been employed as effective catalysts displaying stable and highly efficient H₂ evolution activity, and some of them are even superior to traditional noble metals, such as Pt and Pd. However, metal phosphides also have the following problems.

1. Metal phosphides supported on the surface of photocatalysts are more easily oxidized when exposed to air. Most of the metal phosphides reported in the literature were covered by some metal phosphates due to the oxidation of partial metal phosphides. The role of metallic phosphates during the photocatalytic process is unclear and unexplored.

2. It has been reported that the morphology and microstructure of catalysts have a great influence on the catalytic activity. Few studies have focused on the effect of morphology and the microstructure of phosphide-decorated photocatalysts on H₂ production activity.

3. There is a lack of research on the root cause of the improvement in the H₂ production rate of phosphide-decorated photocatalysts. The mechanism of improving the photocatalytic H₂ production performance of phosphate-based photocatalysts is still unclear. The function of metal phosphides and metal phosphates is not definite.

Based on the problems mentioned above, metal phosphide photocatalysts should be modified to further improve their solar-to-hydrogen conversion efficiency. In future studies, the design, preparation, and modification of metal phosphides can be carried out based on the following aspects:

1. New methods and synthetic strategies should be explored to fabricate phosphide-modified photocatalytic systems to prevent the oxidation of the metal phosphide surface in the air. In addition, the role of metal phosphates in the photocatalytic process should also be explored.

2. Nanostructure design and the optimization of metal phosphides should be achieved to improve their activity and stability in photocatalytic H₂ production. The effect of the apparent morphology and microstructure of the catalyst on the rate of H₂ production should be systematically studied.

3. In situ analytical techniques, such as XPS, scanning probe microscopy, Raman spectroscopy, and the corresponding theoretical calculations of metal phosphides, should be implemented to thoroughly understand the mechanism of the enhancement in photocatalytic activity.

4. Due to their distinctive properties, metal phosphides exhibit superior photocatalytic activity. More theoretical calculations should be conducted for metal phosphide materials to further understand the inherent mechanism to boost photocatalytic water splitting.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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REFERENCES
1. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972;238:37-38.
2. Yue X, Yi S, Wang R, et al. A novel architecture of dandelion-like MoO3/α-TiO2 heterojunction photocatalysts towards high-performance photocatalytic hydrogen production from water splitting. J Mater Chem A. 2017;5:10591-10598.
3. Ma D, Shi J, Sun D, et al. Au decorated hollow ZnO@ZnS heterostructure for enhanced photocatalytic hydrogen evolution: the insight into the roles of hollow channel and au nanoparticles. Appl Catal Environ. 2019;244:748-757.
4. Zou L, Wang H, Wang X. High efficient photodegradation and photocatalytic hydrogen production of CdS/β-V2O5 heterostructure through Z-scheme process. ACS Sustain Chem Eng. 2016;5:303-309.
5. Xiao R, Zhao C, Zou Z, et al. In situ fabrication of 1D CdS nanorod/2D Ti3C2 MXene nanosheet Schottky heterojunction toward enhanced photocatalytic hydrogen evolution. Appl Catal Environ. 2020;268:118382.
6. Xu B, He P, Liu H, et al. A 1D/2D helical CdS/ZnIn2S4 nano-heterostructure. Angew Chem Int Ed. 2014;53:2339-2343.
7. Han Y, Dong X, Liang Z. Synthesis of Mn0.5Cd0.5S nanorods and modification with CuS for extraordinarily superior photocatalytic H2 production. Catal Sci Technol. 2019;9:1427-1436.
8. Zhang X, Zhang X, Li J, et al. Exceptional visible-light activities of g-C3N4 nanosheets dependent on the unexpected synergistic effects of prolonging charge lifetime and catalyzing H2 evolution with H2O. Appl Catal Environ. 2018;237:50-58.
9. Ye L, Han C, Ma Z, et al. Ni3P loading on CdO-ZnO nanosheets for exceptional photocatalytic nitrogen fixation under visible light. Chem Eng J. 2017;307:311-318.
10. Luo B, Song R, Geng J, et al. Towards the prominent cocatalytic effect of ultra-small CoP particles anchored on g-C3N4 nanosheets for visible light driven photocatalytic H2 production. Appl Catal Environ. 2019;256:117819.
11. Sun Z, Yue Q, Li J, et al. Copper phosphide modified cadmium sulfide nanorods as a novel p-n heterojunction for highly efficient visible-light-driven hydrogen production in water. J Mater Chem A. 2015;3:10243-10247.
12. Song Y, Li N, Chen D, et al. 3D ordered MoP inverse opals deposited with CdS quantum dots for enhanced visible light photocatalytic activity. Appl Catal Environ. 2018;238:255-262.
13. Zhu X, Yu S, Gong X, et al. In situ decoration of Zn0.5Cd0.5S with FeP for efficient photocatalytic generation of hydrogen under irradiation with visible light. ChemPlusChem. 2018;83:825-830.
14. Oyama ST, Gott T, Zhao H, et al. Transition metal phosphide hydroprocessing catalysts: a review. Catal Today. 2009;143:94-107.
15. Liu P, Rodriguez JA. Catalysts for hydrogen evolution from the [NiFe] hydrogenase to the Ni3P (001) surface: the importance of ensemble effect. J Am Chem Soc. 2005;127:14871-14878.
16. Li Y, Dong Z, Jiao L. Multifunctional transition metal-based phosphides in energy-related electrocatalysis. Adv Energy Mater. 2019;10:1902104.
17. Wu L, Yu L, Zhang F, et al. Heterogeneous bimetallic phosphide Ni3P-Fe2P as an efficient bifunctional catalyst for water/seawater splitting. Adv Funct Mater. 2021;31:2006484.
18. Gopalakrishnan S, Alheid S, Rangan K. Convenient route for the synthesis of transition-metal pnictides by direct reduction of phosphate, arsenate, and antimonate precursors. Chem Mater. 1997;9:2113-2116.
19. Furimsky E. Metal carbides and nitrides as potential catalysts for hydrosprocessing. Appl Catal Gen. 2003;240:1-18.
20. Cao S, Wang CJ, Fu W, et al. Metal phosphides as co-catalysts for photocatalytic and photoelectrocatalytic water splitting. ChemSusChem. 2017;10:4306-4323.
21. Zhao H, Sun S, Jiang P, et al. Graphitic C3N4 modified by Ni3P cocatalyst: An efficient, robust and low cost photocatalyst for visible-light-driven H2 evolution from water. Chem Eng J. 2017;315:296-303.
22. Sun Z, Zhu M, Fujitsuka M, et al. Phase effect of Ni3P hybridized with g-C3N4 for photocatalytic hydrogen generation. ACS Appl Mater Interfaces. 2017;9:30583-30590.
23. Shi Y, Zhang B. Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. Chem Soc Rev. 2016;45:1529-1541.
24. Pan Y, Liu Y, Zhao J, et al. Monodispersed nickel phosphide nanocrystals with different phases: synthesis, characterization and electrocatalytic properties for hydrogen evolution. J Mater Chem A. 2013;5:1656-1665.
25. Li X, Wang X, Zhu J, et al. Fabrication of two-dimensional Ni3P/ZnIn2S4 heterostructures for enhanced photocatalytic hydrogen evolution. Chem Eng J. 2018;353:15-24.
26. Zhang B, Huang C, Huang Y, et al. Potential-tuned selective electrocatalysis of azoxy-, aza- and amino-aromatics over a CoP nanosheet cathode. Natl Sci Rev. 2020;7:285-295.
27. Xu Y, Wu R, Zhang J, et al. Anion-exchange synthesis of nanoporous FeP nanosheets as electrocatalysts for hydrogen evolution reaction. Chem Commun. 2013;49:6656-6658.
28. Liu E, Qi L, Chen J, et al. In situ fabrication of a 2D Ni3P/red phosphorus heterojunction for efficient photocatalytic H2 evolution. Mater Res Bull. 2019;115:27-36.
29. Mi K, Ni Y, Hong J. Solvent-controlled syntheses of Ni12P5 and Ni3P nanocrystals and photocatalytic property comparison. J Phys Chem Solid. 2011;72:1452-1456.
30. Sun Z, Chen H, Huang Q, et al. Enhanced photocatalytic hydrogen production in water under visible light using noble metal-free ferrous phosphate as an active cocatalyst. Cat Sci Technol. 2015;5:4964-4967.
31. Dunning SG, Nandra G, Conn AD, et al. A metal-organic framework with cooperative phosphines that permit post-synthetic installation of open metal sites. Angew Chem Int Ed. 2018;57:9295-9299.
32. Sun Z, Zheng H, Li J, et al. Extraordinarily efficient photocatalytic hydrogen evolution in water using semiconductor nanorods integrated with crystalline Ni3P cocatalysts. Energ Environ Sci. 2015;8:2668-2676.
33. Tian F, Hou D, Zhang W, et al. Synthesis of a Ni₃P/Ni₆P₅ bi-phase nanocomposite for the efficient catalytic reduction of 4-nitrophenol based on the unique n-n heterojunction effects. *Dalton Trans.* 2017;46:14107-14113.
34. Liang Z, Dong X, Han Y, et al. In-situ growth of 0D/2D Ni₃P quantum dots/red phosphorus nanosheets with p-n heterojunction for efficient photocatalytic H₂ evolution under visible light. *Appl Surf. Sci.* 2019;484:293-299.
35. Deng Y, Zhou Y, Yao Y, et al. Facile synthesis of nanosized nickel phosphides with controllable phase and morphology. *New J. Chem.* 2013;37:4083.
36. Du L, Chen W, Zhu P, et al. Applications of functional metal-organic frameworks in biosensors. *Biotechnol. J.* 2021;16:1900424.
37. Feng L, Wang K, Lv X, et al. Hierarchically porous metal-organic frameworks: synthetic strategies and applications. *Nat Sci Rev.* 2020;7:1743-1758.
38. Xu Q, Pang H, Xue H, et al. A highly alkaline-stable metal oxide@metal-organic framework composite for high-performance electrochemical energy storage. *Nat Sci Rev.* 2020;7:305-314.
39. Kumar DP, Choi J, Hong S, et al. Rational synthesis of metal-organic framework-derived noble metal-free nickel phosphide nanoparticles as a highly efficient cocatalyst for photocatalytic hydrogen evolution. *ACS Sustain Chem Eng.* 2016;4:7158-7166.
40. Yang M, Xie J, Lin Z, et al. N-doped FeP nanorods derived from Fe-MOFs as bifunctional electrocatalysts for overall water splitting. *Appl Surf Sci.* 2020;507:145096.
41. Kang Q, Li M, Shi J, et al. A universal strategy for carbon-supported transition metal phosphides as high-performance bifunctional electrocatalysts towards efficient overall water splitting. *ACS Appl Mater Interfaces.* 2020;12:19447-19456.
42. Bigiani L, Barreca D, Gasparotto A, et al. Selective anodes for seawater splitting via functionalization of manganese oxides by a plasma-assisted process. *Appl Catal Environ.* 2021;284:119684.
43. García-Garcia R, Ortega-Zarzosa G, Rincón ME, et al. The hydrogen evolution reaction on rhenium metallic electrodes: a selected review and new experimental evidence. *Electrocatalysis.* 2014;6:263-273.
44. Trasatti S. Work function, electronegativity, and electrochemical behaviour of metals III electrolytic hydrogen evolution in acid solutions. *Electroanal. Chem Interfacial Electrochem.* 1972;39:163-184.
45. Jaksic JM, Ristic NM, Krstajic NV, Jaksic MM. Electrocatalysis for hydrogen electrode reactions in the light of fermi dynamics and structural bonding factors individual electrocatalytic properties of transition metals. *Int J Hydrogen Energy.* 1998;23:1121-1156.
46. Trasatti S. Chemical and electrochemical surface reactivity: role of the competition between solvent and reaction intermediate adsorption. *Process Electrochem Soc.* 1982;82-2:73-91.
47. Yu J, Li Q, Li Y, et al. Ternary metal phosphide with triple-layered structure as a low-cost and efficient electrocatalyst for bifunctional water splitting. *Adv Funct Mater.* 2016;26:7644-7651.
48. Wu L, Yu L, Xiao X, et al. Recent advances in self-supported layered double hydroxides for oxygen evolution reaction. *Research.* 2020;2020:3976278.
49. Zhao J, Li C, Shi Z, et al. Boosting lattice oxygen oxidation of perovskite to efficiently catalyze oxygen evolution reaction by FeOOH decoration. *Research.* 2020;2020:6961578.
50. Zou X, Zhang Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chem Soc Rev.* 2015;44:5148-5180.
51. Cheng Z, Huang B, Pi Y, et al. Partially hydroxylated ultrathin iridium nanosheets as efficient electrocatalysts for water splitting. *Nat Sci Rev.* 2020;7:1340-1348.
52. Gayen P, Saha S, Ramani V. Selective seawater splitting using pyrochlore electrocatalyst. *ACS Appl Energ Mater.* 2020;3:3978-3983.
53. Karlsson RK, Cornell A. Selectivity between oxygen and chlorine evolution in the chlor-alkali and chlorate processes. *Chem Rev.* 2016;116:2982-3028.
54. Dionigi F, Reiter T, Pawolek Z, et al. Design criteria, operating conditions, and nickel-iron hydroxide catalyst materials for selective seawater electrolysis. *ChemSusChem.* 2016;9:962-972.
55. Shuai C, Mo Z, Niu X, et al. Nickel/cobalt bimetallic phosphides derived metal-organic frameworks as bifunctional electrocatalyst for oxygen and hydrogen evolution reaction. *J Alloys Compd.* 2020;847:156514.
56. Anjum MAR, Bhatt MD, Lee MH, et al. Sulfur-doped dicobalt phosphate outperforming precious metals as a bifunctional electrocatalyst for alkaline water electrolysis. *Chem Mater.* 2018;30:8861-8870.
57. Chen D, Pu Z, Lu R, et al. Ultralow Ru loading transition metal phosphides as high-efficient bifunctional electrocatalyst for a solar-to-hydrogen generation system. *Adv Energy Mater.* 2020;10:2000814.
58. Lian Y, Sun H, Wang X, et al. Carved nanoframes of cobalt-iron bimetal phosphate as a bifunctional electrocatalyst for efficient overall water splitting. *Chem Sci.* 2019;10:464-474.
59. Xu W, Zhu S, Liang Y, et al. A nanoporous metal phosphate catalyst for bifunctional water splitting. *J Mater Chem A.* 2018;6:5574-5579.
60. Surendran S, Shanmugapriya S, Sivanantham A, et al. Electrospun carbon nanofibers encapsulated with NiCoP: a multifunctional electrode for supercapattery and oxygen reduction, oxygen evolution, and hydrogen evolution reactions. *Adv Energy Mater.* 2018;8:1800555.
61. Lv C, Zhang L, Huang X, et al. Double functionalization of N-doped carbon carved hollow nanocubes with mixed metal phosphides as efficient bifunctional catalysts for electrochemical overall water splitting. *Nano Energy.* 2019;65:103995.
62. Yu F, Zhou H, Huang Y, et al. High-performance bifunctional porous non-noble metal phosphate catalyst for overall water splitting. *Nat Commun.* 2018;9:2551.
63. Qiu Y, Xin L, Li W. Electrocatalytic oxygen evolution over supported small amorphous Ni-Fe nanoparticles in alkaline electrolyte. *Langmuir.* 2014;30:7893-7901.
64. Li Y, Zhao C. Enhancing water oxidation catalysis on a synergistic phosphorylated NiFe hydroxide by adjusting catalyst wettability. *ACS Catal.* 2017;7:2535-2541.
65. Zhang Q, Li T, Liang J, et al. Highly wettable and metallic NiFe-phosphate/phosphide catalyst synthesized by plasma for highly efficient oxygen evolution reaction. *J Mater Chem A.* 2018;6:7509-7516.
66. Kim H, Park J, Park I, et al. Coordination tuning of cobalt phosphates towards efficient water oxidation catalyst. *Nat Commun.* 2015;6:8253.
67. Sun T, Fan J, Liu E, et al. Fe and Ni co-doped TiO₂ nanoparticles prepared by alcohol-thermal method:
application in hydrogen evolution by water splitting under visible light irradiation. *Powder Technol.* 2012;228:210-218.

68. Feng J, Huang H, Fang T, et al. Defect engineering in semiconductors: manipulating nonstoichiometric defects and understanding their impact in oxynitrides for solar energy conversion. *Adv Funct Mater.* 2019;29:1808389.

69. Han Y, Zhang Q, Liang Z, et al. Mn3O4CdS-S nanorods modified with NiS clusters as photocatalysts for the H2 evolution reaction. *J Mater Sci.* 2020;55:5390-5401.

70. Han Y, Liang Z, Dang H, et al. Extremely high photocatalytic H2 evolution of novel Co0.67O2CO2.67S p-n heterojunction photocatalyst under visible light irradiation. *J Taiwan Inst Chem E.* 2018;87:196-203.

71. Meng A, Zhang L, Cheng B, et al. Dual cocatalysts in TiO2 photocatalysis. *Adv Mater.* 2019;31:1807660.

72. Sun K, Liu M, Pei J, et al. Incorporating transition-metal phosphides into metal-organic frameworks for enhanced photocatalysis. *Angew Chem Int Ed.* 2020;59:22749-22755.

73. Yao M, Wang B, Sun B, et al. Rational design of self-supported Cu@WC core-shell mesoporous nanowires for pH-universal hydrogen evolution reaction. *Appl Catal Environ.* 2021;280:11451.

74. Bai S, Jiang J, Zhang Q, et al. Steering charge kinetics in photocatalysis: intersection of materials syntheses, characterization techniques and theoretical simulations. *Chem Soc Rev.* 2015;44:2893-2929.

75. Cheng L, Xie S, Zou Y, et al. Noble-metal-free Fe3P-Co3P cocatalyst boosting visible-light-driven photocatalytic hydrogen production over graphitic carbon nitride: the synergistic effects between the metal phosphides. *Int J Hydrogen Energy.* 2019;44:4133-4142.

76. Kim B, Kim T, Lee K, et al. Recent advances in transition metal phosphide electrocatalysts for water splitting under neutral pH conditions. *ChemElectroChem.* 2020;7:3578-3589.

77. Indra A, Acharyya A, Menezes PW, et al. Boosting visible-light-driven photocatalytic hydrogen evolution with an integrated nickel phosphate-carbon nitride system. *Angew Chem Int Ed.* 2017;56:1653-1657.

78. Zeng D, Ong W, Zheng H, et al. Ni12P5 nanoparticles embedded into porous g-C3N4 nanosheets as a noble-metal-free hetero-structure photocatalyst for efficient H2 production under visible light. *J Mater Chem A.* 2017;5:16171-16178.

79. Zhu S, Wang J, He Y, et al. In situ photodeposition of amorphous Ni3P on Cds nanorods for efficient visible-light photocatalytic H2 generation. *Cat Sci Technol.* 2019;9:5394-5400.

80. Shi J, Zou Y, Cheng L, et al. In-situ phosphating to synthesize Ni3P decorated NiO/g-C3N4 p-n junction for enhanced photocatalytic hydrogen production. *Chem Eng J.* 2019;378:122161.

81. Jiang H, Zhao T, Yang Z, et al. Earth-rich Ni3P/Ni(PO3)2 co-catalysts promoted electron-hole separation for g-C3N4 nanosheets visible light photocatalysts. *J Taiwan Inst Chem E.* 2019;104:160-167.

82. Wu M, Zhang J, Liu C, et al. Rational design and fabrication of noble-metal-free Ni3P cocatalyst embedded 3D N-TiO2/g-C3N4 heterojunctions with enhanced photocatalytic hydrogen evolution. *ChemCatChem.* 2018;10:3069-3077.

83. Qin Z, Xue F, Chen Y, et al. Spatial charge separation of one-dimensional Ni3P-CdS2ZnSxS1-x/g-C3N4 heterostructure for high-quantum-yield photocatalytic hydrogen production. *Appl Catal Environ.* 2017;217:551-559.

84. Yu T, Li Z, Lv Z, et al. Constructing Ni3P/CdS2ZnSxS/CoO4 ternary heterostructure for high-efficient photocatalytic hydrogen production. *Appl Surf Sci.* 2020;509:145371.

85. Boppella R, Yang W, Tan J, et al. Black phosphorus supported Ni3P co-catalyst on graphitic carbon nitride enabling simultaneous boosting charge separation and surface reaction. *Appl Catal Environ.* 2019;242:422-430.

86. Yan J, Peng W, Zhang S, et al. Ternary Ni3P/reduced graphene oxide/g-C3N4 nanotubes for visible light-driven photocatalytic H2 production. *Int J Hydrogen Energy.* 2020;45:16094-16104.

87. Xu J, Qi Y, Wang L. In situ derived Ni3P/Ni encapsulated in carbon@g-C3N4 hybrids from metal-organic frameworks@g-C3N4 for efficient photocatalytic hydrogen evolution. *Appl Catal Environ.* 2019;246:72-81.

88. Choi J, Amaranatha Reddy D, Han NS, et al. Modulation of charge carrier pathways in CdS nanospheres by integrating MoS2 and Ni3P for improved migration and separation toward...
enhanced photocatalytic hydrogen evolution. *Cat Sci Technol*. 2017;7:641-649.

99. Qi Y, Xu J, Zhang M, et al. In situ metal-organic framework-derived c-doped Ni$_x$S$_2$/Ni$_x$P hybrid co-catalysts for photocatalytic H$_2$ production over g-C$_3$N$_4$ via dye sensitization. *Int J Hydrogen Energy*. 2019;44:16336-16347.

100. Qi K, Lv W, Khan I, et al. Photocatalytic H$_2$ generation via CoP quantum-dot-modified g-C$_3$N$_4$ synthesized by electroless plating. *Chin J Catal*. 2020;41:114-121.

101. Cao S, Chen Y, Wang H, et al. Ultrasmall Co$_x$P nanoparticles as efficient cocatalysts for photocatalytic formic acid dehydrogenation. *Joule*. 2018;2:549-557.

102. Sun X, Yang D, Dong H, et al. ZIF-derived CoP as a cocatalyst for enhanced photocatalytic H$_2$ production activity of g-C$_3$N$_4$. *Sustain Energ Fuels*. 2018;2:1356-1361.

103. Xu Y, Zeng L, Fu Z, et al. Photocatalytic oxidation of arylalcohols to aromatic aldehydes promoted by hydroxyl radicals over a CoP/CdS photocatalyst in water with hydrogen evolution. *Cat Sci Technol*. 2018;8:2540-2545.

104. Qiu B, Zhu Q, Xing M, et al. A robust and efficient catalyst of Cd$_x$Zn$_{1-x}$Se motivated by CoP for photocatalytic hydrogen evolution under sunlight irradiation. *Chem Commun*. 2017;53:897-900.

105. Wang X, Tian X, Sun Y, et al. Enhanced Schottky effect of a 2D-2D CoP/g-C$_3$N$_4$ interface for boosting photocatalytic H$_2$ evolution. *Nanoscale*. 2018;10:12315-12321.

106. Liang Q, Shi F, Xiao X, et al. In situ growth of CoP nanoparticles anchored on black phosphorus nanosheets for enhanced photocatalytic hydrogen production. *ChemCatChem*. 2018;10:2179-2183.

107. Xiang Z, Guan H, Zhang B, et al. Electrostatic self-assembly of 2D-2D CoP/ZnIn$_2$S$_4$ nanosheets for efficient photocatalytic hydrogen evolution. *J Am Cerum Soc*. 2021;104:504-513.

108. Li S, Wang L, Liu S, et al. In situ synthesis of strongly coupled Co$_x$P-CdS nanohybrids: An effective strategy to regulate photocatalytic hydrogen evolution activity. *ACS Sustain Chem Eng*. 2018;6:9940-9950.

109. Dong Y, Kong L, Wang G, et al. Photochemical synthesis of Co$_x$P as cocatalyst for boosting photocatalytic H$_2$ production via spatial charge separation. *Appl Catal Environ*. 2017;211:245-251.

110. Liu Q, Wang M, He Y, et al. Photochemical route for synthesizing co-P alloy decorated ZnIn$_2$S$_4$ with enhanced photocatalytic H$_2$ production activity under visible light irradiation. *Nanoscale*. 2018;10:19100-19106.

111. Zhang L, Hao X, Li J, et al. Unique synergistic effects of ZIF-9 (Co)-derived cobalt phosphide and CeVO$_4$ heterojunction for efficient hydrogen evolution. *Chin J Catal*. 2020;41:82-94.

112. Lin B, Li J, Xu B, et al. Spatial positioning effect of dual cocatalysts accelerating charge transfer in three dimensionally ordered macroporous g-C$_3$N$_4$ for photocatalytic hydrogen evolution. *Appl Catal Environ*. 2019;243:94-105.

113. Zhong Y, Wu Y, Chang B, et al. A CoP/CdS/WS$_2$ p-n-n tandem heterostructure: a novel photocatalyst for hydrogen evolution without using sacrificial agents. *J Mater Chem A*. 2019;7:14638-14645.

114. Reddy DA, Choi J, Lee S, et al. Hierarchical dandelion-flower-like cobalt-phosphide modified CdS/reduced graphene oxide-MoS$_2$ nanocomposites as a noble-metal-free catalyst for efficient hydrogen evolution from water. *Cat Sci Technol*. 2016;6:6197-6206.

115. Wu F, Chen Z, Wu H, et al. In situ catalytic etching strategy promoted synthesis of carbon nanotube inlaid with ultrasmall FeP nanoparticles as efficient electrocatalyst for hydrogen evolution. *ACS Sustain Chem Eng*. 2019;7:12741-12749.

116. Zhao C, Tang H, Liu W, et al. Constructing 0D FeP nanodots/2D g-C$_3$N$_4$ nanosheets heterojunction for highly improved photocatalytic hydrogen evolution. *ChemCatChem*. 2019;11:6310-6315.

117. Zeng D, Zhou T, Ong WJ, et al. Sub-5 nm ultra-fine FeP nanodots as efficient co-catalysts modified porous g-C$_3$N$_4$ for precious-metal-free photocatalytic hydrogen evolution under visible light. *ACS Appl Mater Interfaces*. 2019;11:5651-5660.

118. Sun K, Shen J, Yang Y, et al. Highly efficient photocatalytic hydrogen evolution from 0D/2D heterojunction of FeP nanoparticles/CdS nanosheets. *Appl Surf Sci*. 2020;505:144022.

119. Cheng H, Lv X, Cao S, et al. Robustly photogenerating H$_2$ in water using FeP/CdS catalyst under solar irradiation. *Sci Rep*. 2016;6:19846.

120. Qi Y, Xu J, Fu Y, et al. Metal-organic framework templated synthesis of g-C$_3$N$_4$/Fe$_2$O$_3$@FeP composites for enhanced hydrogen production. *ChemCatChem*. 2019;11:3465-3473.

121. Yue X, Yi S, Wang R, et al. A novel and highly efficient earth-abundant Cu$_x$P with TiO$_2$ “P-N” heterojunction nanophotocatalyst for hydrogen evolution from water. *Nanoscale*. 2016;8:17516-17523.

122. Shen R, Xie J, Lu X, et al. Bifunctional Cu$_3$P decorated g-C$_3$N$_4$ nanosheets as a highly active and robust visible-light photocatalyst for H$_2$ production. *ACS Sustain Chem Eng*. 2018;6:4026-4036.

123. Hua S, Qu D, An L, et al. Highly efficient p-type Cu$_3$P/n-type g-C$_3$N$_4$ photocatalyst through Z-scheme charge transfer route. *Appl Catal Environ*. 2019;240:253-261.

124. Rauf A, Ma M, Kim S, et al. Mediator- and co-catalyst-free direct Z-scheme composites of Bi$_2$WO$_6$-Cu$_3$P for solar-water splitting. *Nanoscale*. 2018;10:3026-3036.

125. Cheng C, Zong S, Shi J, et al. Facile preparation of nanosized Mo$_3$P as cocatalyst coupled with g-C$_3$N$_4$ by surface bonding state for enhanced photocatalytic hydrogen production. *Appl Catal Environ*. 2020;265:118620.

126. Chen Z, Bu Y, Wang L, et al. Single-sites Rh-phosphide modified carbon nitride photocatalyst for boosting hydrogen evolution under visible light. *Appl Catal Environ*. 2020;274:119117.

127. Zhang J, Yao W, Huang C, et al. High efficiency and stable tungsten phosphide cocatalysts for photocatalytic hydrogen production. *J Mater Chem A*. 2017;5:12513-12519.

128. Jin Z, Zhang Y, Ma Q. Orthorhombic WP co-catalyst coupled with electron transfer bridge UiO-66 for efficient visible-light-driven H$_2$ evolution. *J Colloid Interface Sci*. 2019;556:689-703.

129. Peng C, Kang L, Cao S, et al. Nanostructured Ni$_3$P as a robust catalyst for the hydrolytic dehydrogenation of ammonia-borane. *Angew Chem Int Ed*. 2015;54:15725-15729.

130. Grosvener AP, Cavell RG, Mar A. Next-nearest neighbour contributions to P 2p3/2 X-ray photoelectron binding energy shifts of mixed transition-metal phosphides Mn$_x$M$_{3-x}$P with the MnP-type structure. *J Solid State Chem*. 2007;180:2702-2712.
131. Jin C, Xu C, Chang W, et al. Bimetallic phosphide NiCoP anchored g-C3N4 nanosheets for efficient photocatalytic H2 evolution. J Alloys Compd. 2019;803:205-215.

132. Li S, Wang L, Xiao N, et al. In-situ synthesis of ternary metal phosphides Ni1Co1-xP decorated Zn0.5Cd0.5S nanorods with significantly enhanced photocatalytic hydrogen production activity. Chem Eng J. 2019;378:122220.

133. Qin Z, Chen Y, Huang Z, et al. A bifunctional NiCoP-based core/shell cocatalyst to promote separate photocatalytic hydrogen and oxygen generation over graphitic carbon nitride. J Mater Chem A. 2017;5:19025-19035.

134. Shen R, Liu W, Ren D, et al. Co1-xNi1-xP cocatalysts modified metallic carbon black/g-C3N4 nanosheet Schottky heterojunctions for active and durable photocatalytic H2 production. Appl Surf Sci. 2019;466:393-400.

135. Li S, Tan J, Jiang Z, et al. MOF-derived bimetallic Fe-Ni-P nanotubes with tunable compositions for dye-sensitized photocatalytic H2 and O2 production. Chem Eng J. 2020;384:123354.

136. Dai D, Xu H, Ge L, et al. In-situ synthesis of CoP co-catalyst decorated Zn0.5Cd0.5S photocatalysts with enhanced photocatalytic hydrogen production activity under visible light irradiation. Appl Catal B: Environ. 2017;217:429-436.

137. Di T, Zhu B, Zhang J, et al. Enhanced photocatalytic H2 production on CdS nanorod using cobalt-phosphate as oxidation cocatalyst. Appl Surf Sci. 2016;389:775-782.

138. Cao S, Chen Y, Hou C, et al. Cobalt phosphate as a highly active non-precious metal cocatalyst for photocatalytic hydrogen production under visible light irradiation. J Mater Chem A. 2015;3:6096-6101.

139. Gai Q, Zheng X, Liu W, et al. 2D-2D heterostructured CdS-CoP photocatalysts for efficient H2 evolution under visible light irradiation. Int J Hydrogen Energy. 2019;44:27412-27420.

140. Sun Z, Lv B, Li J, et al. Core-shell amorphous cobalt phosphide/cadmium sulfide semiconductor nanorods for exceptional photocatalytic hydrogen production under visible light. J Mater Chem A. 2016;4:1598-1602.

141. Pan Z, Zheng Y, Guo F, et al. Decorating CoP and Pt nanoparticles on graphitic carbon nitride nanosheets to promote overall water splitting by conjugated polymers. ChemSusChem. 2017;10:87-90.

142. Zhao Z, Schipper DE, Leitner AP, et al. Bifunctional metal phosphide FeMnP films from single source metal organic chemical vapor deposition for efficient overall water splitting. Nano Energy. 2017;39:444-453.

143. Yu T, Si Y, Lv Z, et al. Cd0.5Zn0.5S/Ni1P noble-metal-free photocatalyst for high-efficient photocatalytic hydrogen production: Ni1P boosting separation of photocarriers. Int J Hydrogen Energy. 2019;44:31832-31840.

144. Chen Z, Yu Y, She X, et al. Constructing Schottky junction between 2D semiconductor and metallic nickel phosphide for highly efficient catalytic hydrogen evolution. Appl Surf Sci. 2019;495:143528.

145. Liu C, Xiong M, Chai B, et al. Construction of 2D/2D Ni1P/CdS heterojunctions with significantly enhanced photocatalytic H2 evolution performance. Cat Sci Technol. 2019;9:6929-6937.

146. He H, Cao J, Guo M, et al. Distinctive ternary CdS/Ni1P/g-C3N4 composite for overall water splitting: Ni1P accelerating separation of photocarriers. Appl Catal Environ. 2019;249:246-256.

147. Wang W, An T, Li G, et al. Earth-abundant Ni1P/g-C3N4 lamellar nanohybrids for enhanced photocatalytic hydrogen evolution and bacterial inactivation under visible light irradiation. Appl Catal Environ. 2017;217:570-580.

148. Duan S, Zhang S, Chang S, et al. Efficient photocatalytic hydrogen production from formic acid on inexpensive and stable phosphide/Zn1In2S6 composite photocatalysts under mild conditions. Int J Hydrogen Energy. 2019;44:21803-21820.

149. Qi K, Xie Y, Wang R, et al. Electroless plating Ni-P cocatalyst decorated g-C3N4 with enhanced photocatalytic water splitting for H2 generation. Appl Surf Sci. 2019;466:847-853.

150. Liang G, Waqas M, Yang B, et al. Enhanced photocatalytic hydrogen evolution under visible light irradiation by p-type MoS2/n-type Ni1P doped g-C3N4. Appl Surf Sci. 2020;504:144448.

151. Guo X, Cao J, Guo M, et al. Excellent visible light photocatalytic H2 evolution activity of novel noble-metal-free Ni12P5/CdS composite. Catal Commun. 2019;119:176-179.

152. Liu E, Jin C, Xu C, et al. Facile strategy to fabricate Ni1P/g-C3N4 heterojunction with excellent photocatalytic hydrogen evolution activity. Int J Hydrogen Energy. 2018;43:21355-21364.

153. Chen Y, Qin Z. General applicability of nanocrystalline Ni1P as a noble-metal-free cocatalyst to boost photocatalytic hydrogen generation. Cat Sci Technol. 2016;6:8212-8221.

154. Zeng D, Lu Z, Gao X, et al. Hierarchical flower-like ZnIn2S4 anchored with well-dispersed Ni1P nanoparticles for high-quantum-yield photocatalytic H2 evolution under visible light. Cat Sci Technol. 2019;9:4010-4016.

155. Zhao Z, Wang D, Pu Y, Wang JX, Zhang LL, Chen JF. High-gravity-assisted engineering of Ni1P/g-C3N4 nanocomposites with enhanced photocatalytic performance. Green Energy Environ. in press, https://doi.org/10.1016/j.gee.2020.09.006.

156. Shao Z, He Y, Zeng T, et al. Highly efficient photocatalytic H2 evolution using the Ni1P-Zn0.5Cd0.5S photocatalyst under visible light irradiation. J Alloys Compd. 2018;769:889-897.

157. Dhingra S, Nagaraja CM. Highly efficient visible-light-assisted photocatalytic hydrogen generation from water splitting catalyzed by Zn0.5Cd0.5S/Ni1P heterostructures. Int J Hydrogen Energy. 2018;43:22917-22928.

158. Yuan X, Shen D, Zhang Q, et al. Highly exposed (001) facets Ni(OH)2 induced formation of nickel phosphate over cadmium sulfide nanorods for efficient photocatalytic hydrogen evolution. Int J Hydrogen Energy. 2020;45:9397-9407.

159. Ye P, Liu X, Iocozzia J, et al. A highly stable non-noble metal Ni1P co-catalyst for increased H2 generation by g-C3N4 under visible light irradiation. J Mater Chem A. 2017;5:8493-8498.

160. Wang J, Wang P, Hou J, et al. In situ surface engineering of ultrafine Ni1P nanoparticles on cadmium sulfide for robust hydrogen evolution. Cat Sci Technol. 2018;8:5406-5415.

161. Zhu L, Yue Q, Jiang D, et al. Metal-free graphene quantum dots photosensitizer coupled with nickel phosphate cocatalyst for enhanced photocatalytic hydrogen production in water under visible light. Chin J Catal. 2018;39:1753-1761.

162. Wang X, Li X, Liu C, et al. Metalloid Ni1P and its behavior for boosting the photocatalytic hydrogen evolution of CaIn2S4. Int J Hydrogen Energy. 2018;43:219-228.

163. Wu T, Wang P, Qian J, et al. Noble-metal-free nickel phosphide modified CdS/C3N4 nanorods for dramatically
enhanced photocatalytic hydrogen evolution under visible light irradiation. Dalton Trans. 2017;46:13793-13801.

164. Chu L. Synthesis of Ni2P/Zn3In2S6 hierarchical heterostructure for improving photocatalytic H2 evolution. Catal Commun. 2019;128:105705.

165. Hua Q, Zhou X, Zhang B, et al. Band modulation and interfacial engineering to generate efficient visible-light-induced bifunctional photocatalysts. ACS Sustain Chem Eng. 2020;8:2919-2930.

166. Wang P, Zhan S, Wang H, et al. Cobalt phosphate nanowires as efficient co-catalyst for photocatalytic hydrogen evolution over Zn0.3Cd0.7S. Appl Catal Environ. 2018;230:210-219.

167. Shen R, Xie J, Zhang H, et al. Enhanced solar fuel H2 generation over g-C3N4 nanosheet photocatalysts by the synergetic effect of noble metal-free Co2P cocatalyst and the environmental phosphorylation strategy. ACS Sustain Chem Eng. 2017;6:816-826.

168. Zhao H, Jiang P, Cai W. Graphitic C3N4 decorated with CoP co-catalyst: enhanced and stable photocatalytic H2 evolution activity from water under visible-light irradiation. Chem Asian J. 2017;12:361-365.

169. Ge L, Han C, Xiao X, et al. In situ synthesis of cobalt-phosphate (Co-Pi) modified g-C3N4 photocatalysts with enhanced photocatalytic activities. Appl Catal B: Environ. 2013;142-143:414-422.

170. Yi S, Yan J, Wulan B, et al. Noble-metal-free cobalt phosphate modified carbon nitride: an efficient photocatalyst for hydrogen generation. Appl Catal Environ. 2017;200:477-483.

171. Cheng L, Zhang D, Fan J, et al. Metal phosphate modified Cd,Zn1−xS solid solutions as a highly active visible-light photocatalyst for hydrogen evolution. Appl Catal Gen. 2020;590:117336.

172. Pu J, Jin Z, Cheng Y, et al. g-C3N4/CdBP/UiO-66 ternary composites for enhanced visible light photocatalytic H2 evolution. ChemistrySelect. 2019;4:5459-5469.

173. Jian Q, Jin Z, Wang H, et al. Photoelectron directional transfer over a g-C3N4/CdS heterojunction modulated with WP for efficient photocatalytic hydrogen evolution. Dalton Trans. 2019;48:4341-4352.

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