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In situ fabrication of a 2D Ni₂P/red phosphorus heterojunction for efficient photocatalytic H₂ evolution

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Graphical abstract



Highlights:

- Ni₂P/red phosphorus heterojunction was fabricated by a simple in situ hydrothermal strategy.
- Ni₂P/red phosphorus with 2D nanostructure has good contact interface and stability.
- The surface edge of red phosphorus is the active sites during the photocatalytic reaction.
- Ni₂P as co-catalyst can induce more active sites and improve the charge separation.
- Ni₂P can greatly enhance the photocatalytic H₂ production efficiency of red phosphorus.

Abstract: Highly available and active photocatalysts and cocatalysts play key roles in the of efficient and stable visible-light-driven photocatalytic systems. In this work, a nickel phosphide (Ni₂P)/red phosphorus (RP) heterojunction composite was fabricated for the first time by an in situ hydrothermal method using nanosized RP and nickel chloride as the starting materials. The results indicated that the heterojunction exhibits a two-dimensional (2D) nanostructure with a good contact interface and stability. The surface edges of pure RP are the active sites during the photocatalytic reaction. The introduction of Ni₂P could improve the light-harvetsing ability of RP and facilitate charge separation, leading to an enhanced photocurrent intensity and excellent photocatalytic performance for H₂ evolution. The H₂ production rate of the 3% Ni₂P/RP sample was 2183 μ mol²g⁻¹h⁻¹ under visible light irradiation, which was higher than that of Pt/RP, indicating that Ni₂P could be used as an efficient noble-metal-free cocatalyst. In addition, a possible mechanism for H₂ production was proposed for Ni₂P/RP composite. Further work should be conducted in the exploration of P-based transition metal cocatalysts and RP-based photocatalysts.

Keywords: Red phosphorus; Nickel phosphide; Heterojunction; Cocatalyst

1. Introduction

Energy shortages and environmental pollution have become major global challenges, with a profound impact on sustainable development worldwide [1-11]. The replacement of fossil resources with green and renewable sources is the most effective

way to alleviate the above problems. Hydrogen energy is one of the best choices because of its high-energy intensity and pollution-free features [12-17]. However, hydrogen is usually produced by steam reforming of natural gas, involving high temperatures and energy-consuming separation processes. There is an urgent need to develop energy-saving and eco-friendly H₂ production processes.

Since the discovery of H₂ evolution from water splitting on a TiO₂ electrode under UV light irradiation by Fujishima and Honda, it has provided a way to convert solar energy directly into sustainable H_2 energy [18]. During the past few decades, a substantial amount of effort has been devoted to the development of efficient photocatalytic systems with the aim of improving the H₂ evolution efficiency. The major obstacles to achieving high solar-to-hydrogen energy conversion efficiency are the lack of visible light harvesting materials and the recombination of charge carriers due to the inherent defects in photocatalysts. For instance, the traditional TiO₂ photocatalyst has a large band gap (~ 3.2 eV), which results in TiO₂ only being active under ultraviolet light, leading to a low usage of solar energy [19-20]. Therefore, visible-light-driven (VLD) photocatalysts have received a substantial amount of attention, such as g-C₃N₄ [21], CdS [22], BiVO₄ [23], Cd_xZn_(1-x)S [24], and ZnInS₄ [25]. However, the absorption edge of most photocatalysts is below 500 nm, and photocatalysts cannot fully utilize visible light. In addition, the high recombination rate of charge carriers during the reaction limits the quantum efficiency of the excited electrons and holes. Many strategies have been developed to solve the above problems, such as constructing heterojunctions [26-27], elemental doping [28-29], structural regulation [30], photosensitization [31], and cocatalyst loading [32-33]. The exploration of photocatalysts with excellent visible light harvesting and H₂ production abilities is still a very active and interesting field.

In 2012, Wang et.al reported that red phosphorus (RP), which has a narrow band gap smaller than 2.0 eV, could achieve photocatalytic water splitting under visible light, and H_2 and O_2 were obtained over RP due to the suitable positions of its conduction and valence band edges. The nontoxic, stable and easily available properties of RP make it

a promising candidate for photocatalytic H₂ production. Most investigations have focused on improving charge carrier separation and increasing the specific surface area of RP. Additionally, YPO₄ [34], g-C₃N₄ [35], Ni(OH)₂ [36], black phosphorus (BP) [37], TiO₂ [38], CdS [39], MoS₂ [40], Cr₂O₃ [41] and graphene [42] have been employed to improve the activity of RP by constructing heterojunctions. However, most heterojunction composites with microsized structures suffer from small contact areas and a low number of active sites, leading to poor photocatalytic performance[43]. Zhang et al. increased the specific surface area of RP by heating amorphous RP in a vacuum tube furnace, but the maximum specific surface area was only 39 m²/g [44]. In our previous work, we successfully prepared nanosized RP by a hydrothermal method, its specific surface area was 54.3 m²/g, and the obtained nanosized RP exhibited excellent photocatalytic activity and adsorption performance. However, RP-based photocatalysts are still far from satisfactory for large-scale application. Developing highly active RP-based photocatalysts is an urgent need.

Extensive experiments have shown that introducing appropriate cocatalysts can not only enhance light harvesting but also favor the desired reactions and hinder the back reaction[45-46]. Introducing cocatalysts may create enough reactive sites for efficient utilization of the charge carriers and ensure the long-term stability of the composite [47-50]. Pt is the most commonly used cocatalyst for H₂ evolution, whereas its scarcity and high cost greatly limit the wide application of Pt-containing photocatalysts. Consequently, a substantial amount of attention has been focused on developing cocatalysts with earth-abundant nonprecious elements.

Recently, the use of transition metal phosphatides (such as Ni₂P and Co₂P) as nonprecious metal cocatalysts has sparked wide attention. For example, Cao et al. discovered that nickel phosphide (Ni₂P) is an efficient cocatalyst for photocatalytic H₂ evolution, and its hybrid system exhibited enhanced photocatalytic hydrogengenerating activity and excellent stability in an aqueous lactic acid solution [50]. Sun et al. prepared Ni₂P/CdS NRs in ethylenediamine by a solvothermal method, the highest H₂ production rate was 1200 mmol $g^{-1} \cdot h^{-1}$, and the apparent quantum yield was 41% at

450 nm [51], In addition, Zhao et al. reported g-C₃N₄ modified by a Ni₂P cocatalyst, which exhibited enhanced H₂ production activity under visible light irradiation, the photoinduced electron in the CB of g-C₃N₄ could rapidly transfer to the metallic Ni₂P through the heterostructured interfaces between g-C₃N₄ and Ni₂P. [52]. Chen et al. employed dispersed Ni₂P cocatalysts to boost the photocatalytic hydrogen generation of TiO₂, the photogenerated electrons can also transfer to the Ni₂P cocatalyst, since the conduction band edge of Ni₂P (0 V vs. RHE) is much lower than that of anatase TiO₂ (-0.26 V vs. RHE)[53]. In addition, Ni₂P has been employed to construct heterojunctions with Cd_xZn_(1-x)S [54], ZnO [55], CaIn₂S₄ [56] and graphene [57]. It is commonly believed that Ni₂P has the potential to replace Pt as a H₂-releasing cocatalyst. (the use of Ni₂P as a cocatalyst in the literature is summarized in Table 1). However, Ni₂P is mainly fabricated via high temperature calcining method with inert gas protection, and then it was combined with the semiconductor to form heterogeneous junction, leading to a poor contact interface, which can't take full advantage of Ni₂P.

In this work, Ni₂P/RP heterojunctions with 2D nanostructures were synthesized for the first time by an in situ hydrothermal method using nanosized red phosphorus as the phosphor source. The light-harvesting ability of RP and the separation of the charge carriers can be improved after the introduction of Ni₂P. The composites exhibit an obviously enhanced H₂ evolution rate under visible light irradiation (λ >420 nm) compared to those of pure RP and Pt/RP. The interfacial charge transfer between Ni₂P and RP was investigated, and a reasonable photocatalytic mechanism was proposed for the Ni₂P/RP system during the H₂ evolution reaction.

Table 1 The photocatalytic systems containing Ni_2P as a cocatalyst that have been reported in the literature

| Materials | Preparation method | Phosphorus source | Application | Sacrificial agent | AQY [%] | Results | Ref. |
|---|--|--|---|---|------------------|---|------|
| Ni ₂ P/CdS nanorods (NRs) | It was prepared in ethylenediamine by a solvothermal method. | Yellow Phosphorous | Photocatalytic water splitting under visible light irradiation (λ > 420 nm). | Na ₂ S, Na ₂ SO ₃ | 41 (450 nm) | Ni_2P/CdS exhibited a better photocatalytic H ₂ evolution rate than that of both of the components. The rate of 0.5 wt% Ni_2P loaded sample was approximately 22 times higher than that of the CdS NRs alone, providing an extraordinary H ₂ evolution rate of ~553 µmol·h ⁻¹ ·mg ⁻¹ . | [48] |
| Ni ₂ P/CdS hybrid | The composite was fabricated by grinding CdS and Ni ₂ P nanoparticles using a mortar in a certain ratio to form a uniform powder. | NaH ₂ PO ₂ | Photocatalytic reduction of 4- nitrotoluene into its corresponding amino organics under 30×3 W LED light (λ > 420 nm). | Na2S, Na2SO3 | No | For the system containing 5 wt% Ni ₂ P, the reaction rate for nitro reduction was determined to be 7146 μ mol·h ⁻¹ ·mg ⁻¹ in the first 10 h. | [58] |
| Ni ₂ P@CdS | Ni ₂ P was prepared by a simple solvothermal method. CdS were suspended in the process of preparing Ni ₂ P. | White phosphorous | Photocatalytic water splitting under visible light irradiation (λ > 420 nm). | No | 3.89 (430 nm) | The $10\%Ni_2P@CdS$ photocatalyst displayed the best photocatalytic activity for hydrogen production of the samples, $251.4 \mu mol of H_2$ was evolved over the $10\%Ni_2P@CdS$ catalyst within 180 min, which was 28.7 times higher than that of $1\%Pt@CdS$ (8.7 μmol) under the same reaction conditions. | [59] |
| 15 nm Ni ₂ P/g- C ₃ N ₄ | Ni ₂ P with an average size of 10.3 nm was blended with $g-C_3N_4$ by a simple ultrasonication method. | NaH ₂ PO ₂ and NH4H ₂ PO ₄ | Photocatalytic water splitting under visible light irradiation (λ > 420 nm). | Ethanol | 3.2 (435 nm) | The 3.5 wt% sample exhibited the highest photocatalytic activity of the samples, which achieved a H_2 evolution rate of 474.7 µmol·h ⁻¹ ·g ⁻¹ . | [60] |

| | - | | | - | - | | |
|--|---|---|--|---|------------------|---|------|
| Ni ₂ P/g-C ₃ N ₄ | The Ni ₂ P decorated g-C ₃ N ₄ composite was calcined at 300° C for 2 h at a heating rate of 2°C/min in an Ar atmosphere. | Monohydrat e sodium hypophosph ite | Photocatalytic water splitting under visible light irradiation (λ > 400 nm). | TEOA | No | H ₂ evolution rate over $Ni_2P/g-C_3N_4-0.48\%$ was approximately 1418 and 29 times higher than that over the pure g- C_3N_4 and $Ni(OH)_2/g-C_3N_4$ precursors, which represented a better H ₂ evolution activity compared with that of g-C ₃ N ₄ /Pt-0.48%. | [49] |
| Ni ₂ P/Fe ³⁺ - doped g-C ₃ N ₄ | It was obtained by an in situ growth process, which contained solvent heat evaporation and calcination at 543 K in an Ar atmosphere. | NaH ₂ P-O ₂ | Photocatalytic water splitting under visible light irradiation (λ > 420 nm). | TEOA | No | The 5% Ni ₂ P/Fe-CNN composite had a high H_2 evolution rate of 397 µmol g ⁻¹ h ⁻¹ , which is 71 times higher than that of BCN. | [61] |
| Ni2P /Cd _{0.5} Zn _{0.5} S | The composite was synthesized by a solvothermal method at 140°C for 12 h. | Yellow phosphorous | The fixation of N_2 to prepare NH_3 ($\lambda > 400$ nm). | No | 4.32 (420 nm) | After Ni ₂ P was loaded onto the surface of $Cd_{0.5}Zn_{0.5}S$, the NH ₃ generation rate was 101.5 µmol g ⁻¹ h ⁻¹ (35.7 times higher than that of $Cd_{0.5}Zn_{0.5}S$) under visible light. | [62] |
| $\begin{array}{c} Ni_2P\text{-} \\ Cd_{0.9}Zn_{0.1}S/ \ g\text{-} \\ C_3N_4 \end{array}$ | Ni ₂ P-Cd _{0.9} Zn _{0.1} S was prepared through a two-step hydrothermal method. Ni(NO ₃) ₂ ·6H ₂ O and red phosphorus (the molar ratio of Ni to P was 1:5) were mixed in an ethylenediamine solution and maintained for 24 h at 200°C. | Red phosphorus | Photocatalytic water splitting under visible light irradiation (λ > 420 nm). | Na ₂ S, Na ₂ SO ₃ | 73.2 (420 nm) | The composite showed a great performance for photocatalytically splitting water, and a high hydrogen production rate of 2100.3 μ mol mg ⁻¹ h ⁻¹ , which was ~ 17 times higher than that of Cd _{0.9} Zn _{0.1} S/g-C ₃ N ₄ . | [63] |
| Ni ₂ P/TiO ₂ | Ni ₂ P nanoparticles were synthesized via a solution-based method. Ni ₂ P/Ti NRs were synthesized by a thermally decomposing metal method. | Trinoctylph osphine | Photocatalytic water splitting under ultraviolet light. | Methanol | 11.6 (360 nm) | 0.4 wt% Ni ₂ P/TiO ₂ had a high hydrogen production rate of 9.38 mmol h^{-1} g ⁻¹ , which is ~85 times higher than that of the pure TiNR photocatalyst (0.11 mmol g ⁻¹ h^{-1}). | [50] |

2 Experimental

2.1. Synthesis of RP

The nanosized RP was synthesized by a facile hydrothermal method using commercial microsized RP as the raw material. The detailed preparation process is shown in a previous report [64].

2.2. Preparation of 2D Ni₂P-decorated RP (Ni₂P/RP)

Ni₂P/RP with a 2D nanostructure was synthesized by an in situ hydrothermal method using nanosized (RP) and (NiCl₂·6H₂O) as the raw materials. All reagents were of analytical grade and were used without further purification. First, NiCl₂·6H₂O (*x* g) and 1.30 g of RP were dissolved in a mixture containing 50 mL of ethanol under magnetic stirring for 3 h; then, the mixture was transferred into a Teflon-lined stainless steel autoclave with a volume of 100 mL, heated and maintained at 180 °C for 1 h. After cooling to room temperature, the solid samples were washed several times by vacuum filtration and then dried at 60°C for 6 h. Finally, different composites with weight ratios of NiCl₂·6H₂O to RP of 0.0001:1.3, 0.0003:1.3, 0.0005:1.3, 0.001:1.3, 0.003:1.3, 0.0005:1.3, 0.01:1.3, 0.6:1.3 and 1:1.3 were fabricated and labeled as 0.1% Ni₂P/RP, 0.3% Ni₂P/RP, 0.5% Ni₂P/RP, 1% Ni₂P/RP, 3% Ni₂P/RP, 5% Ni₂P/RP, 10% Ni₂P/RP, 60% Ni₂P/RP and 100% Ni₂P/RP.

2.4. Characterization techniques

A Shimadzu XRD-6000 powder diffractometer (Cu K α radiation) was used to characterize the crystalline structures of the samples. The microstructures of the samples were observed using scanning electron microscopy (SEM, Carl Zeiss SIGMA) and a Tecnai G2 F20S-TWIN for transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS, Kratos AXIS NOVA spectrometer) was performed on a Kratos AXIS NOVA spectrometer. The UV-Vis diffuse reflectance spectra were obtained on a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. The Brunauer– Emmett–Teller (BET) surface area was measured by a Quantachrome NOVA 2000e sorption analyzer based on N₂ adsorption-desorption isotherms at 77 K. The photoelectrochemical performance was measured with an electrochemical system (CHI 660E, China) and a mixed electrolyte containing 0.5 M Na₂SO₄. The sample electrodes

were illuminated with a 300 W Xe lamp.

2.5. Photocatalytic hydrogen production

The photocatalytic H₂ production experiments were carried out by a closed on-line detection system (Lab Solar-IIIAG, Beijing Perfect Light Technology Co. Ltd, China) using a 300 W Xe lamp equipped with a UV cut-off filter ($\lambda > 420$ nm) as the light source. Typically, 30 mg of each sample was dispersed in a 100 mL aqueous solution containing a mixed sacrificial agent (0.35 M Na₂S and 0.25 M Na₂SO₃). The evolved hydrogen was measured by gas chromatography (Tianmei, GC7900). To test the stability of the samples, a cycling experiment was performed in which the residual H₂ was removed by purging with nitrogen gas for 30 min before starting every new cycle.

3 Results and discussion

3.1 Formation mechanism of the Ni₂P/RP sample

A possible formation mechanism was proposed to understand the evolution of the RP and nickel ions during the hydrothermal process, as shown in Fig. 1, during the hydrothermal process, nickel ions are absorbed onto the surface of RP, then it can be reduced to metal nickel particles as the increase of reaction temperature (Equation1-1)[65], XPS indicates the existence of very small metal Ni (Fig. 5). which can be attributed to the excellent adsorption and reduction performance of RP. Besides, it well known that RP can react with water under high temperature to produce PH₃ and H₃PO₄ (Equation 1-2)[26], the obtained PH₃ may react with Ni particle to form intermediate (Ni-PH₃), and then Ni₂P (Equation 1-3)[65].

| $Ni^{2+} + 2e^- \rightarrow Ni^{$ | ······Equation 1-1 |
|--|--------------------|
| $8P+12H_2O \xrightarrow{O_2} 5PH_3 + 3H_3PO_4 \cdots \cdots \cdots \cdots$ | ······Equation 1-2 |
| $Ni + PH_3 \rightarrow Ni_2P + (Ni - PH_3)$ | Equation 1-3 |

3.2 Structural and compositional analysis

The X-ray diffraction (XRD) patterns of the Ni₂P/RP samples with different ratios of Ni₂P were carried out to reveal their crystal structures. As displayed in Fig. 2., it can be observed that the five distinct diffraction peaks of Ni₂P in the 100% Ni₂P/RP sample were located at 40.71°, 44.61°, 47.36°, 54.20° and 55.00°, which can be accurately

indexed to the (111), (201), (210), (300) and (211) planes, respectively, of the hexagonal structure of Ni₂P (JCPDS#74-1385) [66]. In addition, a characteristic diffraction peak at 20=14.95°, belonging to amorphous RP, was also detected, suggesting that Ni₂P/RP was successfully constructed. However, the characteristic diffraction peaks of Ni₂P in the Ni₂P/RP composites gradually weakening with decreasing Ni₂P content, and finally, only the diffraction peak of RP could be seen. The above results reveal that the Ni₂P/RP composite was successfully obtained (see SEM and TEM results below for more detailed information).

3.3 SEM and TEM analysis

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized to visualize the surface morphology and microstructure of the 3% Ni₂P/RP sample. Fig. 3A displays the typical microstructure of bare nanosized RP. Fig. 3B shows the SEM image of the as-obtained 3% Ni₂P/RP composite at the same magnification. It can be seen that irregularly shaped Ni₂P was uniformly grown across the surface of RP. Additionally, the original microscopic morphology of RP was well preserved. As shown in Fig. 3C-D, the elemental mapping results of the 3% Ni₂P/RP sample further demonstrate that Ni and P coexisted and were uniformly distributed.

The typical TEM images of RP and 3% Ni₂P/RP are given in Fig. 4. As shown in Fig. 4A, pure RP possesses a two-dimensional porous structure. Fig. 4B and Fig. 4C show that Ni₂P nanoparticles were uniformly grown and distributed across the surface of the RP, forming a tight interface with RP. To further visualize the crystal lattice on the surface of the sample, high-resolution TEM (HRTEM) was employed, as shown in Fig. 4D. Highly crystalline individual Ni₂P nanosheets with an average diameter of 5 nm can be clearly observed. The spacing of the lattice fringes is 0.22 nm, which corresponds to the (111) plane of Ni₂P [62]. Importantly, Ni₂P with a 2D structure was embedded onto the surface of RP due to the above in situ preparation process. It can be clearly seen that Ni₂P also has a 2D structure, suggesting that a tightly connected 2D heterojunction formed between Ni₂P and RP.

For comparison, a Pt/RP composite was prepared using a photochemical reduction method (see the supporting materials). As shown in Fig. 4E and 4F, Pt nanoparticles with diameters of approximately 3 nm were mainly distributed along the surface edges of pure RP. This result means that the surface edges are the active sites of pure RP during photocatalytic processes. In contrast to the Pt deposition, Ni₂P was uniformly distributed across the RP nanosheets by in situ growth, which may greatly increase the number of active sites on the surface of the RP.

3.4 XPS analysis

To further obtain the surface chemical composition and the chemical state, the Xray photoelectron spectroscopy (XPS) survey spectra of the 3% Ni₂P/RP were analyzed. As displayed in Fig. 5A, P, Ni, O and C were detected, and the existence of C and O originate from surface adsorbed impurities and oxygen (Fig. 5A), which is attributed to the adsorption performance of RP. The C 1s peak at 284.6 eV was used to correct all the binding energies. In the high-resolution XPS spectrum of the P 2p peak, shown in Fig. 5B,the peak located at 129.6 eV (P $2p_{3/2}$) was assigned to $P^{\delta-}$ in the form of metal phosphides (i.e., Ni₂P) [67]. Notably, as shown in Fig. 5C, the RP has a peak at 130.4 eV (P 2p_{3/2}), which is consistent with the characteristic peak position of elemental phosphorus (see Fig. 5E), In addition, the peak at a binding energy of 133.4 eV originated from P 2p1/2, which was ascribed to oxidized P species, likely due to surface oxidation or the interaction between RP and H₂O at room temperature [67]. The highresolution XPS spectrum of the Ni 2p region (Fig. 5C) shows peaks centered at 853.1 eV (Ni $2p_{1/2}$) and 870.0 eV (Ni $2p_{3/2}$), which are consistent with Ni^{$\delta+$} in the Ni₂P phase. The peaks at 856.2 eV and 874.1 eV were possible to attribute to the oxidized Ni species (Ni^{2+}) of the Ni $2p_{1/2}$ and Ni $2p_{3/2}$ peaks. Moreover, two satellite peaks appeared at 860.5 eV and 880.2 eV [68].

3.5 UV-Vis analysis

UV-Vis diffuse reflectance spectroscopy was used to evaluate the optical properties

of RP with different amounts of Ni₂P. As displayed in Fig. 6A, pure RP had an absorption edge at approximately 690 nm, corresponding to a band gap of 1.8 eV for RP. After introducing the Ni₂P cocatalyst, the composites exhibited significantly enhanced absorption in the 650-1200 nm region compared with that of RP, which can be attributed to the introduction of black Ni₂P, which has an excellent optical absorption [48]. In addition, the results are in good accordance with the color change from red (RP) to black (Ni₂P) with increasing Ni₂P content. The favorable optical absorption properties of Ni₂P greatly increased the visible light absorption of RP. The N₂ adsorption-desorption isotherms of RP and 3% Ni₂P/RP are presented in Fig. 6B. The calculated specific surface areas of RP and 3% Ni₂P/RP were 54.3 and 40.8 m²/g, respectively. It should be noted that the loading of Ni₂P led to a slight decrease in the surface area compared to that of pure RP. This might be due to the Ni₂P filling and blocking the pores of RP [69].

3.6 Transient photocurrent response

To validate the photoelectronic performance of the samples, the photocurrents and electrochemical impedance spectroscopy (EIS) behaviors of 3% Ni₂P/RP and RP were studied, and the results are displayed in Fig. 7A and B. The photocurrent density of the 3% Ni₂P/RP electrode was 11.96 μ A/cm², which is approximately 2.26-fold greater than that of the bare RP electrode (5.30 μ A/cm²). As shown in Fig. 7B, the EIS Nyquist plots of 3% Ni₂P/RP have a much smaller arc radius than that of RP, indicating that loading of the Ni₂P cocatalyst onto RP greatly reduced the charge transfer resistance, thus significantly improving the charge transfer and separation efficiencies of RP. This result is in good agreement with the results of the transient photocurrent responses.

3.7 3.7 Photocatalytic hydrogen production

The visible-light-induced ($\lambda \ge 420$ nm) photocatalytic activity for H₂ generation of the different photocatalysts was measured under a 300 W Xe lamp irradiation using Na₂S and Na₂SO₃ as sacrificial agents. Fig. 8A shows the H₂ evolution rates of the *x*% Ni₂P/RP (*x*=0.1, 0.3, 0.5, 1, 3, 5, 10, 60 and 100) catalysts after 3 h of irradiation. Notably, the rate of H₂ evolution increased with increasing Ni₂P loading (from 0.1 to

3%). In addition, it is worth noting that the 3% Ni₂P/RP photocatalyst had the highest photocatalytic activity of all the samples. However, a decay in the rate is observed when the amount of Ni₂P was further increased to 5% and 10%. For both the 60% Ni₂P/RP and 100% Ni₂P/RP composites, the H₂ production rates are below that of RP, which was ascribed to a "shielding effect" from the excess Ni₂P loaded on RP [70-71]. In addition, the average rate of H₂ evolution was calculated and is shown in Fig. 8B. The average H₂ production rate of 3% Ni₂P/RP was 2183.32 µmol·g⁻¹·h⁻¹, which is 7.41 times higher than that of RP (294.76 μ mol^{·g⁻¹·h⁻¹}). To compare the H₂ evolution ability of Ni₂P with that of Pt, 3wt% Pt/RP and 3% Ni₂P/RP, using TEOA (triethanolamine) as a scavenger, were tested by a 300 W Xe lamp equipped with a UV cut-off filter ($\lambda > 420$ nm). As displayed in Fig. 8C, the average photocatalytic H₂ evolution rate of 3% Ni₂P/RP (240.93 µmol·g⁻¹·h⁻¹) was approximately 2.95 times higher than that of 3wt% Pt/RP (81.63 µmol·g⁻¹·h⁻¹). In addition, the rate of 3% Ni₂P/RP was 17.33 times higher than that of RP (13.90 µmol·g⁻¹·h⁻¹). The above results clearly indicated that Ni₂P was an effective noble-metal-free and HER cocatalyst compared to RP. The enhanced photocatalytic activity was attributed to the abundance of active reaction sites caused by the introduction of Ni₂P and its charger transfer properties. The stability of a photocatalyst during photocatalytic reactions is an essential factor for its practical application. Therefore, a cycling experiment for 3% Ni₂P/RP was carried out, as shown in Fig. 8D. The 3% Ni₂P/RP sample still retains high H₂ evolution activity after five cyclic photoreactions. The Fig. 9 shows a comparison of the XRD patterns of 3% Ni₂P/RP before and after the photocatalytic reaction, which indicated that the crystal structure of 3% Ni₂P/RP composite did not change.

3.8 Photocatalytic mechanism

The band gap energy of RP was estimated to be 1.8 eV based on the results of a Kubelka-Munk plot (Fig. 10A). Furthermore, the valence band was calculated to be 1.59 eV by XPS analysis (Fig. 10B); therefore, the corresponding conduction band was -0.21 eV. These results are in agreement with those reported in the literature [42]. Consequently, a possible photocatalytic mechanism for the Ni₂P-decorated RP is

depicted in Fig. 11. Under visible light illumination, the excited electrons of RP were transferred from the valence band (VB) to the conduction band (CB), leaving holes in the valence band (VB). On the one hand, the photogenerated holes can be effectively consumed by S^{2-}/SO_3^{2-} . On the other hand, the electrons can be quickly transferred to Ni₂P due to its electron capture property and good interfacial contact. Therefore, photogenerated charge separation can be achieved, and the recombination process of the electron-hole pairs is restrained. In addition, Ni₂P, which has an abundance of active sites, can reduce the activation potentials for H₂ evolution, thus easily reducing H⁺ into H₂.

4. Conclusions

In conclusion, the 2D Ni₂P cocatalyst-decorated RP was successfully synthesized by an in situ hydrothermal method and exhibited an excellent ability to photocatalytically evolve H₂ from water under visible light irradiation. The introduction of Ni₂P could produce a greater number of active sites on the surface of RP for H₂ evolution, and the tightly combined 2D heterojunction can shorten the transmission distance of the photoelectrons. Therefore, the enhanced photocatalytic activity could be attributed to the effective separation of the charge carriers and greater number of exposed active sites for promoting the reaction of solar-driven water splitting. The 3% Ni₂P/RP sample exhibited an average H₂ production rate of 2183 μ mol·g⁻¹·h⁻¹, which was 7.41 times higher than that of RP (S²/SO₃²⁻ was used as the sacrificial agent). In addition, the H₂ production rate over 3% Ni₂P/RP was 2.95 times greater than that of Pt-modified RP under visible light irradiation (TEOA was used as the sacrificial agent). This work demonstrates that Ni₂P is a potential substitute for noble metal-based cocatalysts for photocatalytic H₂ production.

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References

- [1] H.L. Wang, L.S. Zhang, Z.G. Chen, J.Q. Hu, S.J. Li, Z.H. Wang, J.S. Liu, X. C. Chem Soc. Rev.
 3 (2014) 5234-5244.
- [2] Q.J. Xiang, B. Cheng, J.G. Yu, Angew Chem Int. Edit. 54 (2015) 11350-11366.
- [3] Y. Zhang, J. Zhang, Z. Zhu, N. Yan, Q. Liu, Mater. Res. Bull. 48 (2013) 4872-4876.
- [4] Y.N. Ma, J. Li, E.Z. Liu, J. Wan, X.Y. Hu, J. Fan, Appl Catal. B: Environ. 219 (2017)467-478.
- [5] J.R. Ran, T.Y. Ma, G.P. Gao, X.W. Du, S.Z. Qiao, Energ Environ. Sci. 8 (2015) 3708-3717.
- [6] F. Raziq, C. Li, M. Humayun, Y. Qu, A. Zada, H. Yu, L. Jing, Mater. Res. Bull. 70 (2015) 494-499.
- [7] T. Nakajima, Y. Tamaki, K. Ueno, E. Kato, T. Nishikawa, K. Ohkubo, Y. Yamazaki, T. Morimoto,O. Ishitani, J Am Chem. Soc. 138 (2016) 13818-13821.
- [8] S.P. Kim, M.Y. Choi, H.C. Choi, Mater Res Bull. 74 (2016) 85-89.
- [9] J.X. Low, S.W. Cao, J.G. Yu, S. Wage, Chem Commun. 50 (2014) 10768-10777.
- [10] R. Xu, X.S. Wang, H. Zhao, H. Lin, Y.B. Huang, R. Cao, Catal Sci Technol, 8 (2018) 2224-2230.
- [11] N. Li, Y.R. Wang, D.M. Tang, H.S. Zhou, Angew Chem Int. Edit. 54 (2015) 9271-9274.
- [12] B. Peng, S. Zhang, S. Yang, H. Wang, H. Yu, S. Zhang, F. Peng, Mater Res Bull. 56 (2014) 19-24.
- [13] Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, C. Wang, Y. Li, Nat Mater. 15 (2016) 611.
- [14] P. He, L. Song, S. Zhang, X. Wu, Q. Wei, Mater Res Bull. 51 (2014) 432-437.
- [15] A.K. Singh, S. Singh, A. Kumar, Catal Sci. Technol. 6 (2016) 12-40.
- [16] A. Nakamura, Y. Ota, K. Koike, Y. Hidaka, K. Nishioka, M. Sugiyama, K. Fujii, Appl Phys Express. 8 (2015) 107101.
- [17] E. L. González, F. I. Llerena, M. S. Pérez, F. R. Iglesias, J. G. Macho, Int J Hydrogen Energ. 40 (2015) 5518-5525.
- [18] A. Fujishima, K. Honda, Nature. 238 (1972) 37.
- [19] C. Peng, H. Wang, H. Yu, F. Peng, Mater Res Bull. 89 (2017) 16-25.

- [20] J. Tian, Y.H. Leng, Z.H. Zhao, Y. Xia, Y.H. Sang, P. Hao, J. Zhan, M.C. Li, H. Liu, Nano Energy. 11 (2015) 419-427.
- [21] Q. Li, B.D. Guo, J.G. Yu, J.R. Ran, B.H. Zhang, H.J Yan, J. R. Gong, J Am Chem Soc. 133 (2011) 10878-10884.
- [22] X. Li, T. Xia, C.H. Xu, J. Murowchick, X.B. Chen, Catal. Today. 225 (2014) 64-73.
- [23] Y.C. Deng, L. Tang, C.Y. Feng, G.M. Zeng, J.J. Wang, Y.Y. Zhou, Y. Liu, B. Peng, H.P. Feng, J hazard mater. 344 (2018) 758-769.
- [24] G. Gogoi, S. Keene, A. S. Patra, T. K. Sahu, S. Ardo, M. Qureshi, Acs Sustain Chem Eng. 6 (2018) 6718-6729.
- [25] F. Haque, T. Daeneke, K. Kalantar-zadeh, J.Z. Ou, Nano-Micro Lett. 10 (2018) 23.
- [26] N. Ding, L.S. Zhang, M. Hashimoto, K. Iwasaki, N.Chikamori, K. Nakata, Y.Z. Xu, J.J. Shi, H.J.Wu, Y.H. Luo, D.M. Li, A. Fujishima, Q.B. Meng, J. Colloid Inter. Sci. 512 (2018) 474-479.
- [27] Y. Shen, Z. Zhu, X. Wang, J. Gong, Y. Zhang, Mater Res Bull. 107 (2018) 407-415.
- [28] P. Kanhere, P. Shenai, S. Chakraborty, R. Ahuja, J. Zheng, Z. Chen, Phys Chem Chem Phy. 16 (2014) 16085-16094.
- [29] Z. Jiao, Y. Tang, P. Zhao, S. Li, T. Sun, S. Cui, L. Cheng, Mater Res Bull. (2019)
- [30] X.G. Zhang, X.B. Ke, J.F. Yao, J Mater Chem A. 6 (2018) 1941-1966.
- [31] L.Q. Liu, P. Li, B. Adisak, S.X. Ouyang, N. Umezawa, J.H. Ye, R. Kodiyath, T. Tanabe, G.V. Ramesh, S. Uedad, H. Abe, J Mater Chem A. 2 (2014) 9875-9882.
- [32] L. Yang, W. Duan, H. Jiang, S. Luo, Y. Luo, Mater. Res. Bull. 70 (2015) 129-136.
- [33] E. Liu, L. Qi, J. Bian, Y. Chen, X. Hu, J. Fan, Q. Wang, Mater Res Bull. 68 (2015) 203-209.
- [34] Q.J. Xiang, J.G. Yu, M. Jaroniec, J Am Chem Soc. 134 (2012) 6575-6578.
- [35] Y.P. Yuan, S.W. Cao, Y.S. Liao, L.S. Yin, C. Xue, Appl. Catal. B: Environ. 140 (2013) 164-168.
- [36] H.F. Dang, X.F. Dong, Y.C. Dong, H.B. Fan, Y.F. Qiu, RSC Advances. 4 (2014) 44823-44826.
- [37] Z.R. Shen, S.T. Sun, W.J. Wang, J.W. Liu, Z.F. Liu, J.C. Yu, J. Mater. Chem. A. 3 (2015) 3285-3288.
- [38] S. A. Ansari, M. H. Cho, Sci rep-uk. 6 (2016) 25405.
- [39] Z.S. Shi, X.F. Dong, H.F. Dang, Int J Hydrogen Energ. 41 (2016) 5908-5915.
- [40] X. Bai, J. Wan, J. Jia, X.Y. Hu, Y.D. He, C.L. He, E.Z. Liu and J. Fan, Mater. Lett. 222 (2018)

187-191.

- [41] H.P. Zhou, S.X. Xu, D.K. Zhang, S.J. Chen, J.K. Deng, Nanoscale. 9 (2017) 3196-3205.
- [42] W.B. Li, Y.P. Zhang, G.D. Tian, S.Y. Xie, Q.Q. Xu, L. Wang, J.M.Tian, Y.Y. Bu, J. Mol. Catal. A: Chem. 423 (2016) 356-364.
- [43] Z.S. Liu, B.T. Wu, J.N. Niu, P.Z. Feng, Y.B. Zhu, Mater Res Bull. 63 (2015) 187-193.
- [44] F. Wang, W.K.H. Ng, J.C. Yu, H.J. Zhu, C.H. Li, L. Zhang, Z.F. Liu, Q.Li, Appl. Catal. B: Environ. 111-112 (2012) 409-414.
- [45] B.B. Çırak, B. Caglar, T. Kılınç, S.M. Karadeniz, Y. Erdoğan, S. Kılıç, Ç. Çırak, Mater Res Bull. 109 (2019) 160-167.
- [46] T. Gao, Z. Chen, Y. Zhu, F. Niu, Q. Huang, L. Qin, Y. Huang, Mater Res Bull. 59, (2014) 6-12.
- [47] W.J. Ong, L. K. Putri, Y. C. Tan, L. L. Tan, N. Li, Y. H. Ng, S. P. Chai, Nano Research. 10 (2017) 1673-1696.
- [48] D.Q. Zeng, W. J. Ong, H.F. Zheng, M.D. Wu, Y.Z. Chen, D. L. Peng, M. Y. Han, J Mater Chem A. 5 (2017) 16171-16178.
- [49] W. J. Ong, J. J. Yeong, L. L. Tan, B. T. Goh, S. T. Yong, S. P. Chai, RSC Advances. 4 (2014) 59676-59685.
- [50] S. Cao, Y. Chen, C. J. Wang, P. He and W. F. Fu, Chem. Commun. 50 (2014) 10427-10429.
- [51] Z.J. Sun, H.F. Zheng, J.S. Li, P.W. Du, Energ Environ Sci. 8 (2015) 2668-2676.
- [52] H. Zhao, S.N. Sun, P.P. Jiang, Z.J. Xu, Chem Eng J. 315 (2017) 296-303.
- [53] Y.B. Chen, Z.X. Qin, Catal Sci Technol. 6 (2016) 8212-8221.
- [54] Z.X. Qin, F. Xue, Y.B. Chen, S.H. Shen, L.J. Guo, Appl. Catal. B: Environ. 217 (2017) 551-559.
- [55] S.L. Liu, L.B. Ma, H.Z. Zhang, C.L. Ma, Materials Science and Engineering: B. 207 (2016) 33-38.
- [56] X.J. Wang, X.L. Li, C. Liu, F.T. Li, Y.P. Li, J. Zhao, R.H. Liu, G.D. Li, Int J Hydrogen Energ. 43 (2018) 219-228.
- [57] Y. Lu, X.L. Wang, Y.J. Mai, J.Y. Xiang, H. Zhang, L. Li, C.D. Gu, J.P. Tu, S.X. Mao, J Phys Chem C. 116 (2012) 22217-22225.
- [58] W. Z.Gao, Y. Xu, Y. Chen, W. F. Fu, Chem. Commun. 51 (2015) 13217-13220.
- [59] W.L. Zhen, X.F. Ning, B.J. Yang, Y.Q. Wu, Z. Li, G.X. Lu, Appl. Catal. B: Environ. 221 (2018)

243-257.

- [60] D.Q. Zeng, W.J. Xu, W. J. Ong, J. Xu, H. Ren, Y.Z. Chen, H.F. Zheng, D. L. Peng, Appl. Catal. B: Environ. 221 (2018) 47-55.
- [61] C. Liu, K.L. Wu, G.H. Meng, J.N. Wu, B.H. Peng, J. Hou, Z.Y. Liu, X.H. Guo, Mol. Catal. 437 (2017) 80-88.
- [62] L.Q. Ye, C.Q. Han, Z.Y. Ma, Y.M. Leng, J. Li, X.X. Ji, D.Q. Bi, H.Q.Xie, Z.X. Huang, Chem Eng J. 307 (2017) 311-318.
- [63] Z.X. Qin, F. Xue, Y.B. Chen, S.H. Shen, L.J. Guo, Appl. Catal. B: Environ. 217 (2017) 551-559.
- [64] L.L. Qi, K.Y. Dong, T. Zeng, J.Y. Liu, J. Fan, X.Y. Hu, W.L. Jia, Catal. Tod. 314 (2018) 41-42.
- [65] B. Tian, Z. Li, W.L. Zhen, G.X. Lu, J Phys Chem C. 120 (2016) 6409-6415.
- [66] Z.Z. Luo, Y. Zhang, C.H. Zhang, H.T. Tan, Z. Li, A. Abutaha, X.L. Wu, Q.H Xiong, K. A. Khor,K. Hippalgaonkar, J.W. Xu, H. H. Hng, Q.Y. Yan, Adv Energy Mater. 7 (2017) 1601285.
- [67] C. Tang, R. Zhang, W.B. Lu, Z. Wang, D.N. Liu, S. Hao, G. Du, A. M. Asiri, X.P. Sun, Angew Chem. 129 (2017) 860-864.
- [68] W.J. Wang, T.C. An, G.Y. Li, D.H. Xia, H.J. Zhao, J. C. Yu, P. K. Wong, Appl Catal B: Environ. 217 (2017) 570-580.
- [69] L.F. Xiao, T. Su, Z. Wang, K. Zhang, X.N. Peng, Y.B. Han, Q. Li, X.N. Wang, Nanoscale Res Lett. 13 (2018) 31.
- [70] A. Nezamzadeh-Ejhieh, Z. Salimi, Applied Catalysis A: General. 390 (2010) 110-118.
- [71] L. Jing, R.X. Zhu, D. L. Phillips, J. C. Yu, Adv Funct Mater. 27 (2017) 1703484.



Fig. 2 XRD patterns of the pure RP, 3% Ni₂P/RP, 10% Ni₂P/RP, 60% Ni₂P/RP, and

100% Ni₂P/RP samples.



Fig. 3 SEM images of the (A)pure RP, and (B)3% Ni₂P/RP, and (C) and (D) the



corresponding EDS mapping of the 3% Ni₂P/RP sample for the region in image B.

Fig. 4 TEM images of (A) pure RP, and (B) and (C) 3% Ni₂P/RP (D) HRTEM images of 3% Ni₂P/RP, (E) TEM image of Pt/RP and (F) HRTEM images of Pt/RP.



Fig. 5 XPS spectra of the as-prepared 3% Ni₂P/RP including the (A) survey spectrum, (B) high-resolution spectrum of the Ni 2p region, (C) high-resolution spectrum of the P 2p region, (D) Survey spectrum of pure RP and (E) high-resolution spectrum of the P 2p region.



Fig. 6 (A) UV-vis diffuse reflectance absorption spectra of the samples, (B) Nitrogen adsorption-desorption isotherms of the pure RP and 3% Ni₂P/RP sample.



Fig. 7 (A) Transient photocurrent responses (I–t curves) of the photocatalysts in an aqueous 0.5 M Na₂SO₄ aqueous solution under visible-light irradiation, and (B) the Nyquist plots of different electrodes in an aqueous 0.5 M Na₂SO₄ aqueous solutions.



Fig. 8 (A) Photocatalytic H_2 evolution rate of the samples under visible light irradiation using Na₂S and Na₂SO₃ as sacrificial agents, (B) the average H_2 production rates after 3 h, (C) photocatalytic generation of H_2 over Pt/RP and 3% Ni₂P/RP using TEOA as a sacrificial agent, and (D) cyclic H_2 evolution curves over the 3% Ni₂P/RP sample under visible light irradiation.



Fig. 9 The XRD patterns of 3% Ni₂P/RP before and after the photocatalytic reaction.



Fig. 10 (A) Kubelka-Munk plots of bare RP and (B) XPS valence band spectrum of RP



Fig. 11 A possible schematic diagram for the charge carrier transfer in the Ni_2P/RP catalyst.