

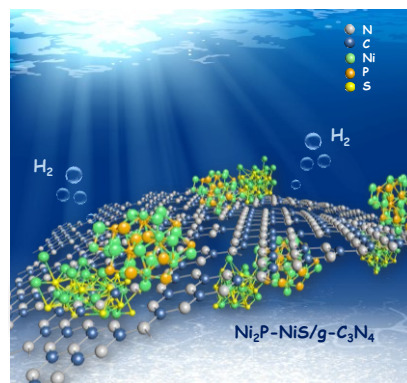
Enhancement of Photocatalytic H₂-Evolution Kinetics through the Dual Cocatalyst Activity of Ni₂P-NiS-Decorated g-C₃N₄ Heterojunctions

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Abstract: With rapid industrialization, issues pertaining to the environment and energy have become an alarming concern. Photocatalytic water splitting is considered one of the most promising green technologies capable of resolving these issues, as it can convert solar energy into chemical energy and have a positive impact on the realization of “carbon neutrality”. Current research focuses on the development of highly efficient catalysts to improve the photocatalytic H₂-production activity. Transition metal phosphides and sulfides are often used as photocatalysts owing to their low H₂-evolution overpotential and excellent electrical conductivity. Among them, Ni₂P and NiS have generally been used independently during photocatalytic H₂ production; however, it is necessary to study the synergistic effect when they are combined as a dual cocatalyst. In this work, we successfully prepared a Ni₂P-NiS dual cocatalyst for the first time *via* a simple hydrothermal method using red phosphorus (RP) and thioacetamide (C₂H₅NS) as the sources of P and S. Ni₂P-NiS was then introduced to the surface of g-C₃N₄ nanosheets through solvent evaporation to create a Ni₂P-NiS/g-C₃N₄ heterojunction. Furthermore, X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), ultraviolet-visible spectrophotometry (UV-Vis), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), linear sweep voltammetry (LSV), Mott-Schottky (M-S), and electrochemical impedance spectroscopy (EIS) were used to reveal the crystal structures, morphologies, element compositions, and photoelectric characteristics of the samples; thus, it was demonstrated that Ni₂P-NiS was successfully deposited on the surface of g-C₃N₄ and that together they exhibited better activity than their monomers. Moreover, the optimized 15% Ni₂P-NiS/g-C₃N₄ composite exhibits a H₂ generation rate of 6892.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is about 46.1, 7.5 and 4.4 times higher than that of g-C₃N₄ (150 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), 15% NiS/g-C₃N₄ (914.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), and 15% Ni₂P/g-C₃N₄ (1565.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), respectively. In addition, photoelectric performance tests show that Ni₂P-NiS/g-C₃N₄ has a stronger photocurrent intensity, smaller charge-transfer resistance, more positive H₂-evolution overpotential, and better charge-separation ability than the individual components (*i.e.*, Ni₂P and NiS), suggesting that the coexistence of Ni₂P and NiS can further boost the activity of g-C₃N₄ during H₂ evolution compared with their monomers. This is mainly due to the Schottky barrier effect between Ni₂P-NiS nanoparticles and g-C₃N₄ nanosheets, which can greatly promote charge separation and charge transfer at their interface. Additionally, Ni₂P-NiS can reduce the H₂-evolution overpotential, leading to the increased surface kinetics of H₂ evolution. This work offers a promising approach to obtaining a highly active and stable noble-metal-free dual cocatalyst for photocatalytic H₂ production.



Key Words: Ni₂P-NiS; g-C₃N₄; Cocatalyst; Schottky barrier; Photocatalytic water splitting

Received: October 29, 2021; Revised: November 12, 2021; Accepted: November 22, 2021; Published online: November 24, 2021.

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This work was supported by the National Natural Science Foundation of China (21676213, 11974276, 22078261), Natural Science Basic Research Program of Shaanxi (2020JM-422).

国家自然科学基金(21676213, 11974276, 22078261), 陕西省自然科学基金基础研究计划项目(2020JM-422)资助

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Ni₂P-NiS 双助剂促进 g-C₃N₄ 光催化产氢动力学

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摘要: 本文通过简单的一步水热法得到Ni₂P-NiS双助催化剂, 之后采用溶剂蒸发法将Ni₂P-NiS与g-C₃N₄纳米片结合构建获得无贵金属的Ni₂P-NiS/g-C₃N₄异质结。研究表明, 优化后的复合材料具有良好的光催化产氢活性, 其产氢速率最高可到6892.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 分别为g-C₃N₄ (150 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)、15%NiS/g-C₃N₄ (914.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)和15%Ni₂P/g-C₃N₄ (1565.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)的46.1、7.5和4.4倍。这主要归因于Ni₂P-NiS相比Ni₂P和NiS单体具有更好的载流子转移能力, 其与g-C₃N₄形成的肖特基势垒能有效促进光生载流子在二者界面上的分离, 同时Ni₂P-NiS能进一步降低析氢过电势, 进而显著增强了表面析氢反应动力学。本研究为开发稳定、高效的非贵金属产氢助剂提供了实验基础。

关键词: Ni₂P-NiS; g-C₃N₄; 助催化剂; 肖特基结; 光催化分解水

中图分类号: O643

1 Introduction

Nowdays, energy and environmental issues from the consumption of fossil resources have become two major problems for the sustainable development of the world. It is urgent to exploit new energy sources to solve above problems^{1,2}. “Zero carbonization of fuel” will play an important role in the future energy systems. Hydrogen (H₂) is considered as an ideal candidate to replace fossil fuels for its pollution-free and high-energy density features³. Photocatalytic H₂ evolution by water splitting can convert solar energy into chemical fuels, which is a promising way to produce H₂ through a cost-efficient and environment-friendly ways⁴⁻⁸.

Since 1972⁹, many photocatalysts have been explored for water splitting, however, the development of more excellent catalysts is still a hot spot. For the traditional catalysts, TiO₂ can only harvest ultraviolet light, leading to a lower energy conversion efficiency^{10,11}. Although CdS with narrow band gap can absorb visible light, it usually suffers from poor photostability^{12,13}. Since 2009¹⁴, g-C₃N₄ has been widely investigated for its superiorities, such as suitable bandgap (about 2.7 eV), good chemical stability, simple preparation process, large specific surface area and so on¹⁵⁻¹⁸. However, its H₂ evolution efficiency is seriously blocked to the quick recombination of electrons and holes induced by the incident light. Therefore, various strategies were used to facilitate the H₂ evolution process over g-C₃N₄, including morphology control^{19,20}, element doping^{21,22}, cocatalysts loading^{23,24} and heterojunction construction^{25,26}, etc. Among them, cocatalysts loading is an efficient way by increasing the active sites, inhibiting the charge recombination and accelerating the REDOX kinetics²⁷. The most effective cocatalysts are noble metals nanoparticles, including Pt²⁸, Au²⁹, Ag³⁰, however, the high cost makes their large-scale application impossible. Hence,

it is of significance to develop low-cost and high-efficiency cocatalysts in the view of economic.

Recently, transition metal phosphides and sulfides have become a hot spot due to their excellent chemical stability and conductivity, which are considered as ideal substitution of noble metals³¹⁻³³. For instance, Lu *et al.* found that highly dispersed Ni₂P QDs over g-C₃N₄ can effectively promote the photoelectric activity of g-C₃N₄³⁴. Wang *et al.* used NiS cocatalyst to promote the H₂ evolution activity of g-C₃N₄, and the maximum H₂ production rate over the ideal sample reached 244 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ³⁵. Further investigations showed that the transition metal thiophosphates exhibited better H₂ production activity³⁶. Zhang *et al.* reported that porous iron phosphosulfide (FePS₃) prepared by one-step sulfurphosphidation method exhibited a relative higher H₂ production rate of 305.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ ³⁷. Zhang *et al.* prepared two different of copper phosphosulfide (Cu₃P|S and CuS|P) by the solid-state reaction and the wet chemical processes respectively, the photocatalytic HER (Hydrogen Evolution Reaction) activities are dramatically enhanced over both Cu₃P|S and CuS|P, the H₂ evolution rates are 2085 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and 976 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively³⁸. However, the preparation processes of transition metal phosphorsulfides are slightly complex, which usually requires tubular furnace, harmful reagents and higher temperature.

Inspired by the works above, if transition metal phosphates and transition metal sulfides can be used as cocatalyst at the same time, the advantages of them might trigger a positive synergistic effect. For example, Xiao *et al.* obtained NiS/Ni₂P heterostructure on carbon cloth (NiS/Ni₂P/CC) by a three-step method with only an overpotential of 111 mV for the HER, which is superior to NiS and Ni₂P alone³⁹. Xu *et al.* found that NiS/Ni₂P nanoparticles is an efficient and durable dual-functional cocatalyst for the amorphous Ni(OH)₂ during the

photoelectric catalytic overall water splitting⁴⁰. Despite these advances, photocatalytic H₂ production over Ni₂P/NiS cocatalysts-related system has never been reported.

In this work, the Ni₂P-NiS nanoparticle was prepared through a hydrothermal approach using thioacetamide (C₂H₅NS) and red phosphorus (RP) as the S and P sources respectively, and then Ni₂P-NiS/g-C₃N₄ heterojunction was obtained by deposition of Ni₂P-NiS on the g-C₃N₄ using a solvent evaporation process. The as-prepared 15% (w, mass fraction) Ni₂P-NiS/g-C₃N₄ exhibits a superior H₂ production activity than 15% Ni₂P/g-C₃N₄ and 15% NiS/g-C₃N₄. According to a series of analysis, the Ni₂P-NiS can restrain the charge recombination of g-C₃N₄, and decrease H₂ evolution overpotential, sequentially a faster H₂ evolution kinetics.

2 Experimental

2.1 Synthesis of g-C₃N₄ nanosheets

g-C₃N₄ nanosheet was prepared using a simple high-temperature polymerization process followed by an ultrasonic treatment. In detail, first, 20 g of urea was heated at 550 °C for 2 h in a microwave muffle oven with tin foil wrapped tightly. After cooling down, the sample was gathered to acquire the bulk g-C₃N₄. Second, 2 g of obtained bulk g-C₃N₄ was put into 1000 mL of water and treated under ultrasonic. Finally, the g-C₃N₄ nanosheet with light-yellow color was obtained after centrifugation, washing and drying at 60 °C.

2.2 Preparation of Ni₂P-NiS nanoparticles

Ni₂P-NiS nanoparticles were prepared by a one-step hydrothermal method. Typically, 2 mmol of NiCl₂·6H₂O, 1.5 mmol of RP (the purification of RP is shown in Supporting Information) and 0.5 mmol of C₂H₅NS were added into 50 mL of water. Subsequently, the pH of the suspension was adjusted by adding 300 μL of 10 mol·L⁻¹ NaOH, after magnetic stirring, the mixture solution was sealed in a Teflon-lined stainless-steel autoclave and treated at 140 °C for 12 h. Finally, Ni₂P-NiS nanoparticles were acquired by centrifugal washing and dry at 60 °C for 8 h.

Moreover, pure Ni₂P nanoparticles were fabricated by a similar hydrothermal reaction. In detail, 2.5 mmol of NiCl₂·6H₂O, 25 mmol of RP were dispersed in 50 mL of water under stirring, which was sealed and treated at 140 °C for 12 h.

For pure NiS nanoparticles, 1 mmol of Ni(CH₃COO)₂·4H₂O was dispersed in 50 mL of ethyl alcohol, after stirring for 30 min and ultrasonic treatment for 20 min, then 1 mmol of C₂H₅NS was dispersed in the above solution under stirring, finally the above suspension was heated at 200 °C for 12 h in a sealed condition.

2.3 Preparation of Ni₂P-NiS/g-C₃N₄ composites

A simple solvent evaporation process was employed to synthesis of Ni₂P-NiS/g-C₃N₄ heterojunction, as shown in Fig. 1, 100 mg g-C₃N₄ nanosheet and an appropriate Ni₂P-NiS were added into 10 mL of ethyl alcohol respectively, after 2 h ultrasonic treatment, they were mixed and stirred at 60 °C to obtain gray powder by fully evaporation of ethyl alcohol.

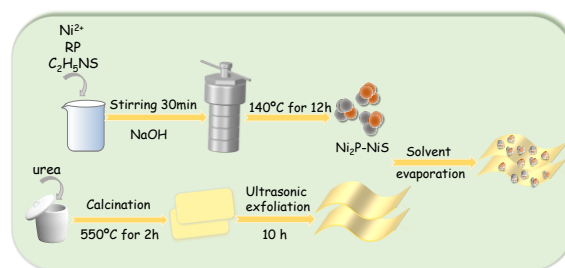


Fig. 1 Schematic diagram for the preparation of Ni₂P-NiS/g-C₃N₄ photocatalysts.

Herein, x% Ni₂P-NiS/g-C₃N₄ composites (x = 3, 5, 10, 15 and 20) were prepared by changing the loading amount of Ni₂P-NiS, x represents the experimental mass ratio of g-C₃N₄ and Ni₂P-NiS.

2.4 Characterization

More information about the XRD, SEM, TEM, XPS, UV-Vis, PL, LSV, M-S, EIS *etc.* tests are listed in Supporting Information.

3 Results and discussion

3.1 Structure and morphology

Fig. 2a presents the XRD of the pure Ni₂P, NiS and Ni₂P-NiS nanoparticles. The signals at 40.7°, 44.6°, 47.4° and 54.2° belong to (111), (201), (210) and (300) crystal planes of Ni₂P (PDF 74-1385), respectively⁴¹. For NiS, the signals at 18.4°, 32.2°, 35.7°, 40.5°, 48.8°, 52.6° are well-indexed to (110), (300), (021), (211), (131) and (401) crystal planes of NiS (PDF 86-2281)⁴². In

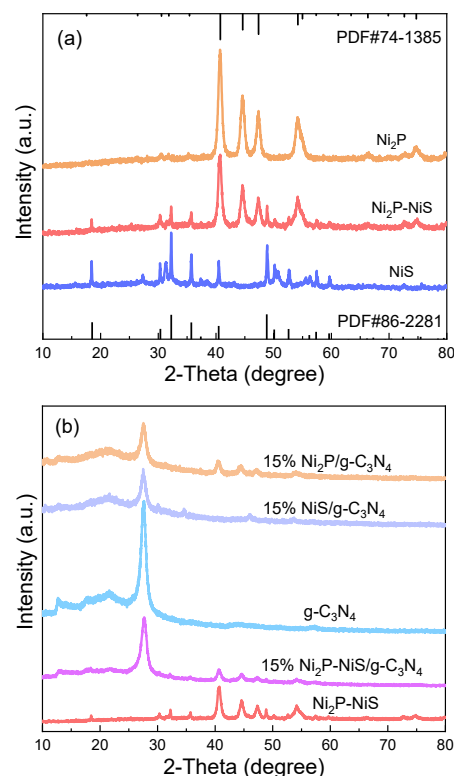


Fig. 2 XRD patterns of (a) Ni₂P, NiS and Ni₂P-NiS, (b) pure g-C₃N₄ and all composites.

addition, the XRD pattern of $\text{Ni}_2\text{P-NiS}$ is consistent with the standard cards of Ni_2P and NiS . The above results indicate that $\text{Ni}_2\text{P-NiS}$ has been obtained *via* the solvothermal approach in our work. In addition, two peaks at 27.4° and 13.0° are observed in Fig. 2b, which are belonging to the (100) and (002) planes of $\text{g-C}_3\text{N}_4$ (PDF 87-1526), respectively⁴³. It is clearly that the signals of $\text{g-C}_3\text{N}_4$ are preserved after loading $\text{Ni}_2\text{P-NiS}$, indicating $\text{g-C}_3\text{N}_4$ is not destroyed in the process of solvent evaporation. The characteristic peaks of $\text{Ni}_2\text{P-NiS}$, Ni_2P and NiS are obviously observed in the composites too, indicating $\text{Ni}_2\text{P-NiS}$, Ni_2P and NiS are introduced to the surface of $\text{g-C}_3\text{N}_4$, respectively.

In Fig. 3, the peak at 810 cm^{-1} belongs to the bending vibration of the tri-s-triazine ring. The peaks from 1000 cm^{-1} to 1800 cm^{-1} result from the typical stretching vibration of C-N and C=N bonds. And the wide signals from 3000 cm^{-1} to 3400 cm^{-1} is attributed to the $-\text{NH}$ stretching and $-\text{OH}$ from the surface-adsorbed H_2O ^{44,45}. In addition, there is no obvious difference among the spectra of 15% $\text{Ni}_2\text{P/g-C}_3\text{N}_4$, 15% $\text{NiS/g-C}_3\text{N}_4$, 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$ composites and pure $\text{g-C}_3\text{N}_4$, implying the basic chemical structure of $\text{g-C}_3\text{N}_4$ is reserved, which agrees with the above XRD results.

Fig. 4 shows the SEM image of the samples. In Fig. 4a, $\text{Ni}_2\text{P-NiS}$ particles presents an irregular shape and aggregates together. However, $\text{Ni}_2\text{P-NiS}$ is tightly attached with $\text{g-C}_3\text{N}_4$ nanosheet in Fig. 4b, indicating $\text{Ni}_2\text{P-NiS}$ is introduced to the $\text{g-C}_3\text{N}_4$. Furthermore, the corresponding SEM element mappings of 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$ are presented in Fig. 4c, and the evenly distribution of each element further indicates that $\text{Ni}_2\text{P-NiS}$ are decorated on the $\text{g-C}_3\text{N}_4$ uniformly. The EDS spectra in Fig. 4d shows the weight and atom percentage of each element. In addition, only a little $\text{Ni}_2\text{P-NiS}$ is introduced to the $\text{g-C}_3\text{N}_4$ during the physical recombination process, while most of $\text{Ni}_2\text{P-NiS}$ enters into the solution, therefore P, S, and Ni make up only ~3% of the total mass.

To further reveal the surface morphology and structure of the samples, TEM investigation was performed on $\text{Ni}_2\text{P-NiS}$ and 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$. As shown in Fig. 5a, $\text{Ni}_2\text{P-NiS}$ nanoparticles is dispersed evenly. In Fig. 5b, the spaces of 0.192 nm and 0.222 nm correspond to the (210) plane of Ni_2P and (211) plane of NiS , they are also observed in the XRD patterns in

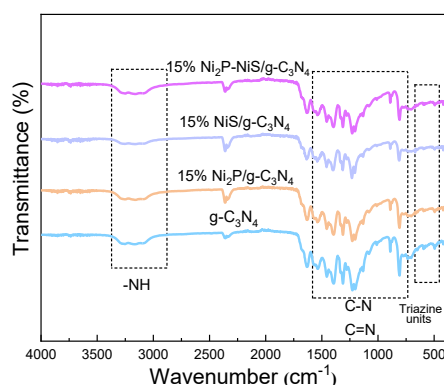


Fig. 3 FT-IR spectra of the samples.

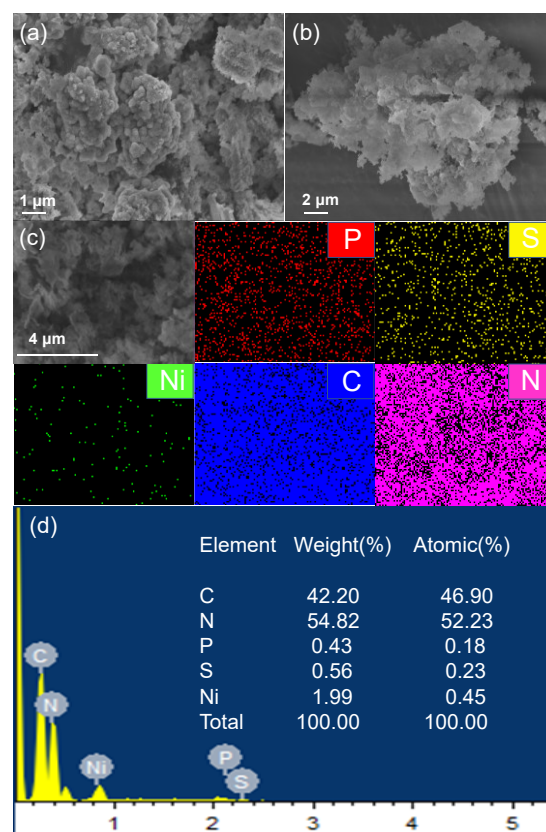


Fig. 4 SEM images of (a) $\text{Ni}_2\text{P-NiS}$ and (b) 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$, (c) elemental mapping images of each element in plane, (d) EDS spectra of 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$.

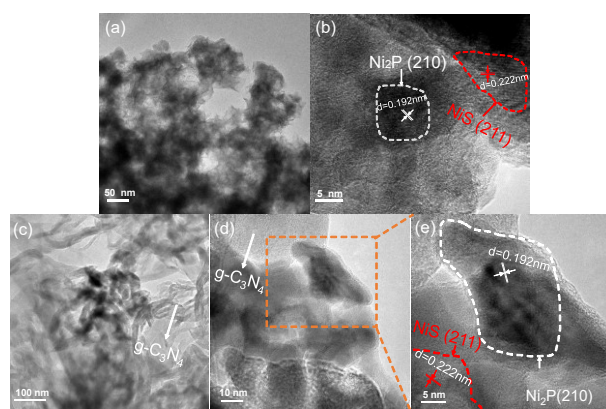


Fig. 5 TEM figures of (a, b) $\text{Ni}_2\text{P-NiS}$ and (c-e) 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$.

Fig. 2^{46,47}. From Fig. 5c-e, it can be seen that $\text{Ni}_2\text{P-NiS}$ nanoparticles is closely contacted with $\text{g-C}_3\text{N}_4$. Besides, as seen in Fig. 5e, the (211) crystal plane of NiS and the (210) crystal plane of Ni_2P are also corresponding to the spaces of 0.222 nm and 0.192 nm respectively.

The surface chemical state of the elements was analyzed using XPS. All the spectra are adjusted according to the $\text{C } 1s$ signal at 284.8 eV. Besides, the signals of $\text{C } 1s$, $\text{N } 1s$, $\text{O } 1s$, $\text{Ni } 2p$, $\text{P } 2p$ and $\text{S } 2p$ in 15% $\text{Ni}_2\text{P-NiS/g-C}_3\text{N}_4$ can all be detected as exhibited in the survey spectrum (Fig. 6a). The O element might originate from the surface adsorbed CO_2 and H_2O . As displayed in Fig. 6b, $\text{C } 1s$ high resolution spectrum could be divided into

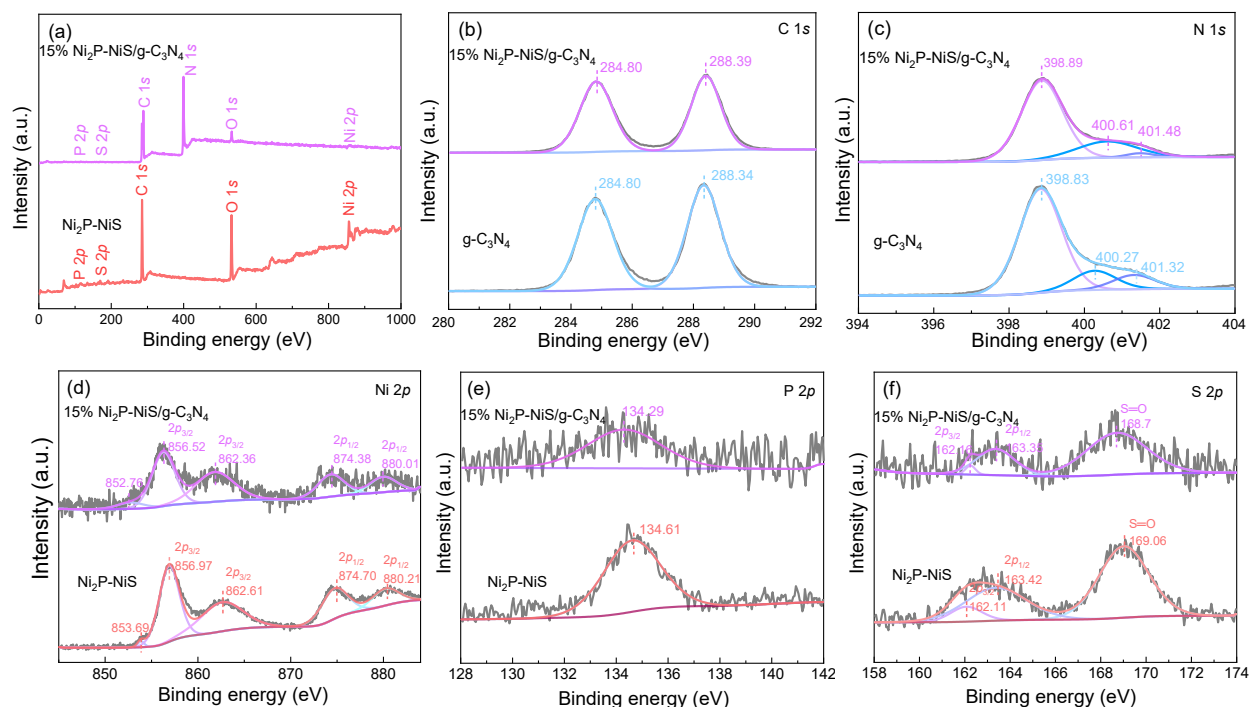


Fig. 6 (a) Full survey XPS spectrum of Ni₂P-NiS and 15% Ni₂P-NiS/g-C₃N₄, (b–f) high-resolution XPS spectra of g-C₃N₄, Ni₂P-NiS and 15% Ni₂P-NiS/g-C₃N₄.

two peaks at 284.80 and 288.34 eV, they correspond to the sp^2 C–C and sp^2 N–C=N bonds in g-C₃N₄ respectively. For N 1s spectra in Fig. 6c, three peaks could be resolved at 398.83, 400.27 and 401.32 eV, which belong to the sp^2 hybridized aromatic N atoms of C=N–C, the tertiary N atom bonded to C of N–(C)₃ and the terminal amino function groups of C–N–H, respectively⁴⁸. After introducing Ni₂P-NiS, the signals of C 1s and N 1s shift toward high energy obviously, indicating there is a powerful internal forces between g-C₃N₄ and Ni₂P-NiS⁴⁹. Fig. 6d exhibits the Ni 2p XPS spectrum, the two peaks at 874.38 and 856.52 eV are identified as Ni 2p_{1/2} and Ni 2p_{3/2}, and another two peaks at 880.01 and 862.36 eV result from the satellite peaks of Ni 2p_{1/2} and Ni 2p_{3/2}. What's more, the peak at 852.76 eV can be attributed to the Ni^{δ+} ($0 < \delta < 2$) species^{50,51}. For the P 2p (Fig. 6e), the peak at 134.29 eV in P 2p spectra results from the PO_x species for the oxidation in air⁴⁰. For the S

2p spectra in Fig. 6f, the signals at 163.42 and 162.11 eV are attributed to S 2p_{1/2} and S 2p_{3/2}⁵², and the peak at 169.06 eV belongs to S=O due to the oxidation of surface sulfide. Compared with the signals of Ni₂P-NiS, the peaks of 15% Ni₂P-NiS/g-C₃N₄ shift toward lower binding energy.

3.2 Photocatalytic experiment

Fig. 7 shows the activity of the samples during H₂ production in 20% (volume fraction) TEOA aqueous solution (TEOA is the sacrificial agent) under 300 W Xe-lamp irradiation. As displayed in Fig. 7a, g-C₃N₄ possesses a low H₂ production activity, after introducing Ni₂P-NiS, the H₂ production rate of g-C₃N₄ first obviously enhances with the increase the mass ratio of Ni₂P-NiS, and then it decreases for the shielding effect from the overloaded Ni₂P-NiS, which usually has excellent light harvesting ability⁵³. In addition, 15% Ni₂P-NiS/g-C₃N₄ achieves a highest H₂ production rate of 6892.7 μmol·g^{−1}·h^{−1}, which is about 46.1

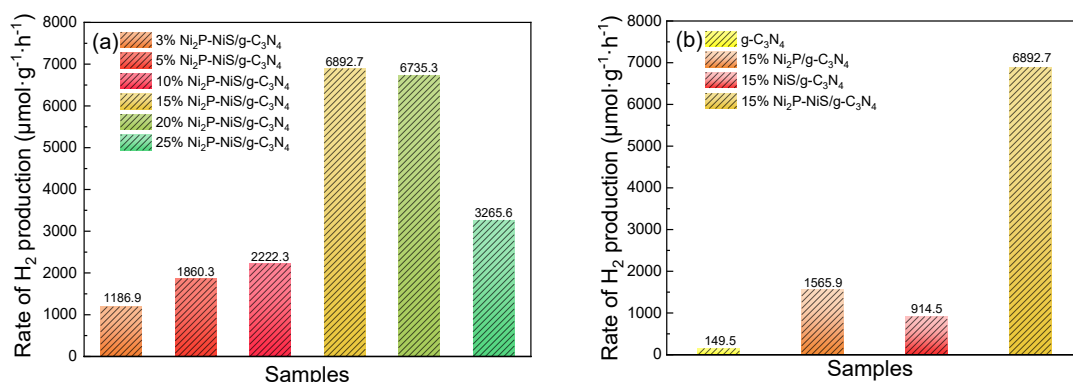


Fig. 7 (a) Effect of mass fraction of Ni₂P-NiS on the activity of g-C₃N₄, (b) H₂ production rates comparison over different samples.

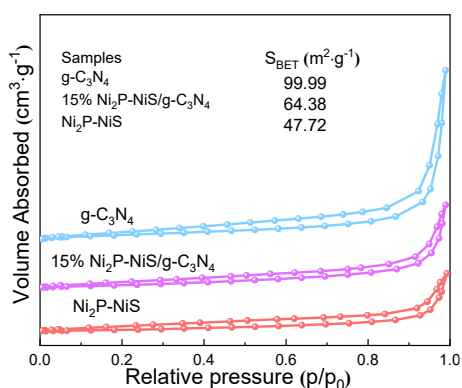


Fig. 8 N₂ adsorption-desorption isotherm curves with corresponding S_{BET} .

times higher than that of g-C₃N₄ (150 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). Besides, the rate of 15% Ni₂P-NiS/g-C₃N₄ is approximately 4.4 and 7.5 times higher than those of 15% Ni₂P/g-C₃N₄ and 15% NiS/g-C₃N₄ respectively (Fig. 7b). It's obvious that Ni₂P-NiS is an excellent H₂ evolution dual cocatalyst.

3.3 N₂ adsorption-desorption isotherm

N₂ adsorption-desorption isotherms can reflect the microstructure and the S_{BET} of the catalysts. All the curves share H3 adsorption hysteresis loops, resulting from the accumulation of sheet-like g-C₃N₄ in Fig. 8⁵⁴. The S_{BET} of 15% Ni₂P-NiS/g-C₃N₄ is 64.38 $\text{m}^2\cdot\text{g}^{-1}$, it is lower than the S_{BET} of pure g-C₃N₄ (99.99 $\text{m}^2\cdot\text{g}^{-1}$), but larger than the S_{BET} of Ni₂P-NiS (47.72 $\text{m}^2\cdot\text{g}^{-1}$), which may result from the hole blocking effect of Ni₂P-NiS nanoparticles after loading on the surface of g-C₃N₄⁵⁵. This indicates that the S_{BET} is not the key factor to determine the activity of the samples, but the active site from Ni₂P-NiS.

3.4 Photoelectric properties

Besides the structural features of the catalyst itself, the optical and electrical properties of the catalyst are also important factors

to the activity of the catalysts. Photoelectric properties tests were conducted to further reveal of the HER activity of Ni₂P-NiS/g-C₃N₄. The UV-Vis diffuse reflectance spectroscopy is exhibited in Fig. 9a, the g-C₃N₄ absorption edge of is approximately 455 nm. NiS, Ni₂P and Ni₂P-NiS cocatalysts exhibit excellent light absorption ability in the whole regions for its black color. That is why the absorption of the composites is better than the g-C₃N₄. It strongly proved that the introduction of cocatalysts such as NiS, Ni₂P and Ni₂P-NiS can affect the absorption capacity of g-C₃N₄. Furthermore, on the basis of the Mott-Schottky plots in Fig. 9b, g-C₃N₄ is a n-type semiconductor owing to the positive slope⁵⁶. Meanwhile, its flat band potentials (E_{fb}) is -1.24 V vs. SCE according to the horizontal intercept. In Fig. 9c,d, the E_{F} of Ni₂P and NiS are -0.85 V, -0.96 V respectively. According to Fig. 9e, the bandgap of g-C₃N₄ is calculated to be 2.67 eV based on the Kubelka-Munk plots. Furthermore, it is known to all that the flat band of n-type semiconductor is approximately more positive 0.2 eV than its CB position. On the basis of the formula ($E_{\text{NHE}} = E_{\text{SCE}} + 0.24$, standard hydrogen electrode conversion), the CB of g-C₃N₄ is -1.2 V vs. NHE. Therefore, the VB of g-C₃N₄ is 1.47 V base on the formula ($E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}}$) correspondingly.

Fig. 10a exhibits the $I-t$ curves of the samples, compared with 15% Ni₂P/g-C₃N₄ and 15% NiS/g-C₃N₄, the photocurrent intensities of 15% Ni₂P-NiS/g-C₃N₄ has a slight enhancement under the same bias voltage, indicating the superiority conductivity of Ni₂P-NiS/g-C₃N₄. The electrochemical impedance spectroscopy (EIS) of samples is described in Fig. 10b, the arc radius of semicircle of EIS can reflect the resistance of the systems, the smaller radius means the smaller resistance⁵⁷. Obviously, the radius of the composites is smaller compared with pure g-C₃N₄, suggesting a smaller charge transfer resistance of the composites, and further illustrating that Ni₂P-NiS can

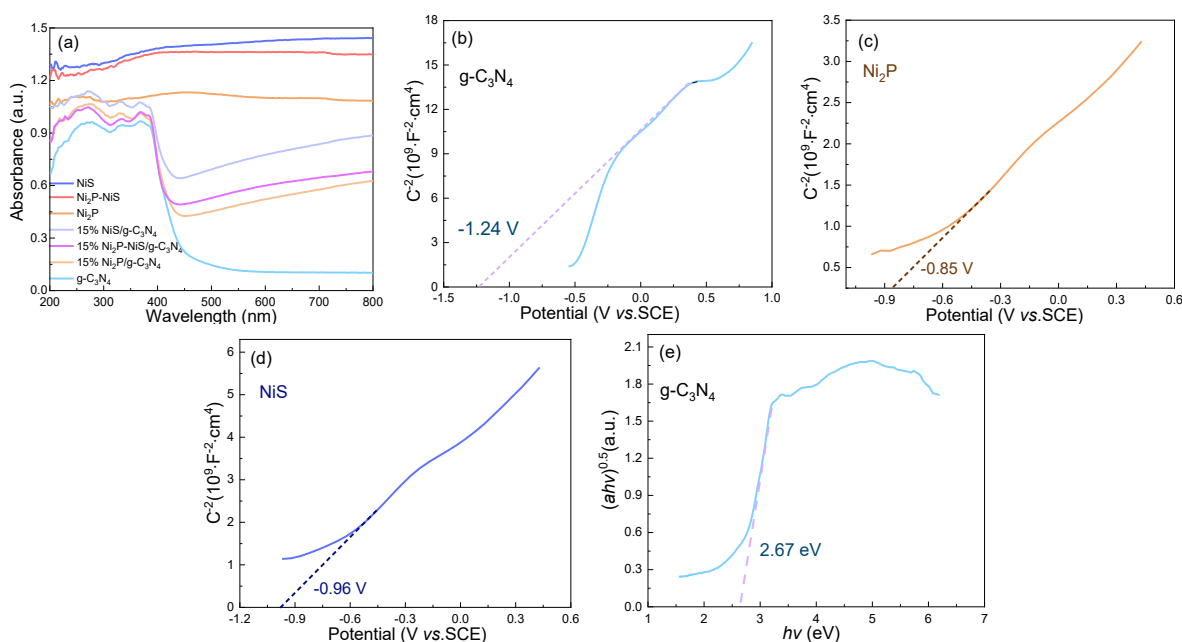
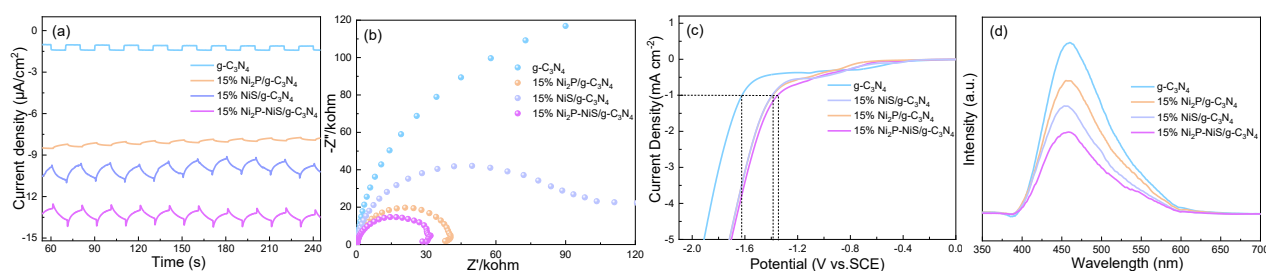


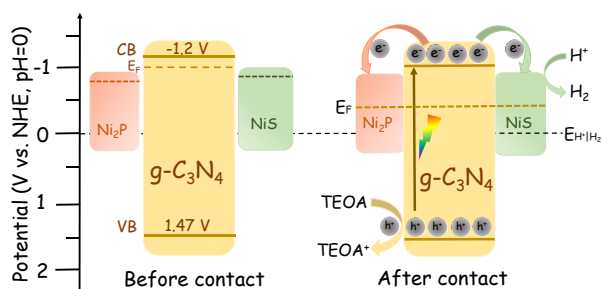
Fig. 9 (a) UV-Vis DRS, (b-d) Mott-Schottky plots of samples and (e) Kubelka-Munk plots of g-C₃N₄.

Fig. 10 (a) $I-t$, (b) EIS, (c) LSV and (d) PL spectra of the samples.

facilitate the charge transfer. To investigate the surface reduction ability of protons and the kinetics of H_2 evolution of the catalyst, the HER polarization curves were measured. As shown in Fig. 10c, Ni_2P-NiS can obviously enhance the H_2 evolution reduction ability of the sample. The corresponding potentials of $g-C_3N_4$, 15% $Ni_2P/g-C_3N_4$, 15% $NiS/g-C_3N_4$ and 15% $Ni_2P-NiS/g-C_3N_4$ are -1.9 , -1.71 , -1.71 and -1.69 V vs. NHE under $1\text{ mA}\cdot\text{cm}^{-2}$ current density, respectively. It is apparently that the H_2 evolution overpotential of the composites is lower than that of $g-C_3N_4$, that is more conducive to promote the H_2 evolution reaction kinetics. Finally, photoluminescence (PL) spectra is shown in Fig. 10d, the emission peak around 460 nm belongs to the light emission from the charge recombination⁵⁸. Furthermore, the PL intensity of 15% $Ni_2P-NiS/g-C_3N_4$ is significantly reduced in comparison to the $g-C_3N_4$, 15% $Ni_2P/g-C_3N_4$ and 15% $NiS/g-C_3N_4$, suggesting an effectively charge separation after loading Ni_2P-NiS .

3.5 Analysis of photocatalytic mechanism

Based on the analysis above, the charge transfer route between Ni_2P-NiS and $g-C_3N_4$ is proposed preliminary in Fig. 11. Before $g-C_3N_4$ and Ni_2P-NiS contacting, the Fermi level (E_F) of $g-C_3N_4$ is negative than H_2 evolution potential ($E_{H^+|H_2}$), while Ni_2P-NiS is more positive. Therefore, it is impossible for Ni_2P-NiS to produce H_2 from the view of thermodynamics. The electrons can transfer from $g-C_3N_4$ to Ni_2P-NiS until reaching an equilibrium after contacting, resulting in an internal electric field between them with a Schottky barrier formed⁵⁹. After light excitation, a large number of electrons on the CB of $g-C_3N_4$ can shift to Ni_2P-NiS in an irreversible way due to the existence of Schottky barrier, furthermore, the electrons in Ni_2P-NiS are able to quickly reduce H^+ to H_2 . While TEOA can quickly consume the holes on VB. On the one hand, the Schottky barrier can effectively restrain the charge recombination, on the other hand,

Fig. 11 Schematic diagram of photocatalytic H_2 evolution over $Ni_2P-NiS/g-C_3N_4$.

Ni_2P-NiS can reduce the H_2 evolution barrier to facilitate the H_2 evolution kinetics. Thus, Ni_2P-NiS as dual cocatalyst can effectively promote the H_2 production performance of $g-C_3N_4$.

4 Conclusions

In this work, Ni_2P-NiS dual cocatalyst was successfully fabricated *via* a facile hydrothermal method, subsequently, it was introduced to the surface of $g-C_3N_4$ through a solvent evaporation way. The 15% $Ni_2P-NiS/g-C_3N_4$ shows an excellent H_2 production rate of $6892.7\text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, that is about 46.1, 7.5 and 4.4 times higher than those of $g-C_3N_4$, 15% $NiS/g-C_3N_4$ and 15% $Ni_2P/g-C_3N_4$, respectively. The investigation demonstrates that dual cocatalyst modification is a good approach to improve the activity of $g-C_3N_4$ compared with the single ones. The introduction of Ni_2P-NiS not only can suppress the charge recombination and improve the electric conductivity, but also can lower H_2 evolution overpotential, leading to an excellent HER activity. This work sheds light on the fabrication of noble-metal-free dual cocatalyst to improve the photocatalytic H_2 evolution of a semiconductor.

Supporting Information: available free of charge *via* the internet at <http://www.whxb.pku.edu.cn>.

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