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Article

Controllable design of Zn-Ni-P on g-C₃N₄ for efficient photocatalytic hydrogen production

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ABSTRACT

Synthesizing a stable and efficient photocatalyst has been the most important research goal up to now. Owing to the dominant performance of g-C₃N₄ (graphitized carbonitride), an ordered assemble of a composite photocatalyst, Zn-Ni-P@g-C₃N₄, was successfully designed and controllably prepared for highly efficient photocatalytic H₂ evolution. The electron transport routes were successfully adjusted and the H₂ evolution was greatly improved. The maximum amount of H₂ evolved reached about 531.2 μmol for 5 h over Zn-Ni-P@g-C₃N₄ photocatalyst with a molar ratio of Zn to Ni of 1:3 under illumination of 5 W LED white light (wavelength 420 nm). The H₂ evolution rate was 54.7 times higher than that over pure g-C₃N₄. Moreover, no obvious reduction in the photocatalytic activity was observed even after 4 cycles of H₂ production for 5 h. This synergistically increased effect was confirmed through the results of characterizations such as XRD, TEM, SEM, XPS, N₂ adsorption, UV-vis DRS, transient photocurrent, FT-IR, transient fluorescence, and Mott-Schottky studies. These studies showed that the Zn-Ni-P nanoparticles modified on g-C₃N₄ provide more active sites and improve the efficiency of photogenerated charge separation. In addition, the possible mechanism of photocatalytic H₂ production is proposed.

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1. Introduction

The constant consumption of fossil-based energy has brought about two major problems: energy shortages and environmental problems, which pose a great threat to human survival and development. Therefore, the universal goal has been to develop low-cost, efficient, environmentally friendly, recyclable, and renewable (clean) energy to alleviate the pinch of the existing resources. Hydrogen is considered as one of the best options because of its overwhelmingly high utilization value and non-polluting nature [1]. Meanwhile, the use of solar energy with great power has evinced great interest. Since the

discovery of the phenomenon of water decomposition by using TiO₂ [2], the field of semiconductor photocatalysis has been attracting wide attention and has developed rapidly, providing the required technology for the use of solar energy. However, it is still a daunting task to efficiently convert solar energy [3,4]. If solar energy can be used to satisfy the needs of the world and for its development, this will greatly alleviate the energy crisis and environmental quality problems and potentially save a lot of cost. However, how to effectively use solar energy to split water to produce H₂ is still a very difficult challenge [5]. Up to now, many semiconductor materials for splitting water to generate H₂ have been reported, such as TiO₂ [2], graphene [6], and

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g-C₃N₄ [7]. Before the discovery of the photocatalytic decomposition of water, H₂ was mainly generated from non-renewable resources such as oil, coal, and natural gases [8]. In turn, this has exacerbated the energy crisis and environmental contamination.

Carbon nitride (C₃N₄) materials having graphite-like structures, also known as graphite nitride carbon, are composed of C and N with *sp*² hybridization in a seven-triazine-ring structure, and exhibit semiconducting properties that are similar to those of non-metallic polymers. The seven-triazine-ring is connected through the ends of the N atoms and a large π bond is formed through an infinite expansion of the seven-triazine-ring; these structures are then stacked into a layered graphite-like structure [9]. Meanwhile, graphitic carbon nitride (g-C₃N₄) can decompose water to produce H₂ under visible light irradiation, which was first reported by Wang et al. [7]. Since this discovery, g-C₃N₄ has been extensively researched in the field of photocatalysis. Subsequently, it was found that g-C₃N₄ has an excellent electronic band structure and considerable physical and chemical stabilities [10–15]. There are many types of raw materials available for synthesizing g-C₃N₄, such as urea [16], thiourea [17], and melamine [18]. Pure g-C₃N₄ has a bandgap of 2.7 eV, and can directly decompose water to produce H₂ under visible light irradiation, but, owing to its low quantum efficiency and high recombination rate of electron-hole pairs, the catalytic activity is significantly limited [19,20]. Therefore, g-C₃N₄ is modified with a variety of metallized materials. For example, the photocatalytic activity can be enhanced by compounding precious metals, oxides, sulfides, phosphating compounds, etc. The photocatalytic activity of semiconductors can also be improved by compounding metal organic frameworks (MOFs) with increased surface areas and electrochemical energy storage capacities [21]. Nickel phosphide (Ni₂P) nanoparticles are not only a highly active cocatalyst that can accelerate the transfer of the photogenerated electron-hole pairs, but also a good semiconductor displaying a dominant performance [22]. Cao et al. [23] reported an efficient Ni₂P/CdS cocatalyst for H₂ evolution. Although ZnP₂ has not been reported in the field of H₂ evolution up to now, both ZnS and ZnO have been reported [24]. Therefore, Zn is a respectably available element for the preparation of efficient photocatalysts.

A heterojunction [25] refers to the interface formed when different semiconductors are brought in close contact with each other. Owing to the difference in the properties of the energy bands of different materials, a difference in space potential would be formed on both sides of the interface. The existence of this difference is advantageous for the separation of photogenic electrons and holes. Thus, the photocatalytic efficiencies of materials can be improved. In recent years, a large number of studies have shown that the construction of a heterojunction-based photoelectric conversion system can effectively improve the ability to separate and transfer electrons and holes. A binary or polybasic semiconductor composite-based heterojunction system is one of the effective methods to improve solar energy conversion efficiency and photocatalytic activity. When semiconductors and metals or semiconductors and semiconductors are compounded, because of the difference

in the Fermi energy level, an electric field would be generated at the heterojunction when the Fermi energy levels balance with each other; the existence of such an electric field can effectively improve the efficiency of separation of the light-generated electrons and holes, apart from improving the migration ability of the photogenerated electrons [26]. This phenomenon is advantageous for the photocatalytic decomposition of water to produce H₂. This was also confirmed by obtaining the Mott-Schottky curves of the sample. In the catalytic system of Zn-Ni-P@g-C₃N₄, we also believe that the existence of an electric field plays a crucial role in the separation and transfer of electrons and holes.

In this study, we aimed to prepare a special structure of Zn-Ni-P-decorated g-C₃N₄ nanosheets to accelerate the transfer of electrons and holes, which can significantly improve the H₂ production efficiency. We successfully obtained g-C₃N₄, Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄ catalysts through an experimental method that was extremely easy to implement, and it was discovered that the catalytic activity of Zn-Ni-P@g-C₃N₄ was higher than that of pure g-C₃N₄. Through an analysis of the H₂ production kinetics of the composite catalysts, it was found that the Zn-Ni-P@g-C₃N₄ showed excellent catalytic activity in a photosensitive system. At the same time, both fluorescence spectra and photoelectrochemical analysis showed that Zn-Ni-P could accelerate the transfer of g-C₃N₄ electrons, which greatly enhanced the efficiency of the photocatalytic decomposition of water to produce H₂. Based on our characterizations, we speculated the possible reaction mechanism of the catalytic system.

2. Experimental

2.1. Preparation of g-C₃N₄

During the preparation process, 15 g of urea was added to 50 mL of a porcelain crucible covered with a cap, placed in a muffle furnace at a rate of 5 °C/min was heated to 550 °C, then maintained at this temperature for 2 h and cooled naturally to room temperature. All the process was carried out in air. The resulting product was pale yellow g-C₃N₄ and grinded and collected for further use.

2.2. Preparation of composite catalysts Zn-P@g-C₃N₄ and Ni-P@g-C₃N₄

The Zn-P@g-C₃N₄ sample was prepared by heating zinc acetate (0.1098 g) and g-C₃N₄ (0.13 g) at 300 °C for 2 h in N₂ at the rate of 2 °C/min. The product was washed with distilled water three times and dried at 80 °C for 6 h.

The Ni-P@g-C₃N₄ sample was prepared by heating nickel acetate (0.2488 g) and g-C₃N₄ (0.13 g) at 300 °C for 2 h in N₂ at the rate of 2 °C/min. The product was washed with distilled water three times and dried at 80 °C for 6 h.

2.3. Preparation of the composite catalyst Zn-Ni-P@g-C₃N₄ with a Zn to Ni molar ratio of 1:3

In a typical procedure, 0.1098 g of zinc acetate, 0.3733 g of nickel acetate, 1.0000 g of sodium hypophosphite, and 0.13 g of g-C₃N₄ were grinded into powders and mixed evenly. Afterwards, a sample was prepared by heating the mixture to 300 °C for 2 h at the rate of 2 °C/min and cooling it naturally to room temperature; this calcination process was carried out in N₂. Then, the samples were washed with distilled water at least three times and dried in an oven at 80 °C for 6 h, resulting in the composite catalyst Zn-Ni-P@g-C₃N₄ ($n_{\text{Zn}}: n_{\text{Ni}} = 1:3$). Over the entire process, the molar ratio was adjusted such that the total number of moles of Zn and Ni was unchanged (2 mmol). In the characterizations performed subsequently, the molar ratio of Zn to Ni in Zn-Ni-P@g-C₃N₄ was 1:3.

2.4. Characterization of catalysts

The crystallization conditions of the components of the resulting photocatalyst and the crystal phases present were investigated by X-ray diffraction (XRD; Rigaku RINT-2000) with Cu K α radiation at 40 kV and 30 mA, with the scan range being 5° to 80° and the scanning rate 10°/min. XRD could also reveal the states of the various elements present in the crystal, their bonding states, the grain size, the mesoporous structure, and the structural defects, and is hence an important method for studying the microstructures of photocatalysts. The chemical bonds present in the obtained sample molecules were analyzed by Fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet Avatar 380 FT-IR spectrometer). In addition, FT-IR could analyze the structural defects of photocatalysts. X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi) can be used to analyze the surface composition, semiquantitatively examine the surface elements, the valence states, and the valence band structure of the sample. The geometrical morphology of photocatalytic materials, the dispersion state of powders, the size and distribution of nanoparticles, and the element composition and phase structure of specific topography regions were characterized by scanning electron microscopy (SEM; JSM-6701F, JEOL), performed under the acceleration voltage of 50 kV, and transmission electron microscopy (TEM; JEM1200EX, JEOL), carried out at the acceleration voltage of 100 kV. The solid light absorption of the photocatalyst was characterized through ultraviolet-visible diffuse reflectance spectroscopy (UV-vis; UV-2550) by using BaSO₄ as the reference. The fluorescence data was used to analyze the energy levels of defects and the kinetic process of charge separation and migration. The fluorescence lifetimes of the photocatalytic materials were obtained by using a FLUOROMAX-4 spectrophotometer at room temperature. Photoelectrochemical experiments were performed and Mott-Schottky curves were obtained by using a standard three-electrode system that was operated with an electrochemical workstation (VersaStat4-400, Advanced Measurement Technology, Inc.). A Pt electrode was used as the counter electrode and the reference electrode was a saturated calomel electrode (SCE). The electrolytic solution was 0.2 mol/L aqueous Na₂SO₄ solution and the area of the working electrode immersed in the electrolyte was about 1 cm². A 300 W Xe lamp was used as the light source and a 420 nm cut-off

filter was used to filter the ultraviolet light. The weight percent of the g-C₃N₄ sample in Zn-Ni-P@g-C₃N₄ was determined by thermogravimetric analysis (TGA; NETZSCH STA449F3) with a sampling rate of °C/min at 800 °C in Ar gas.

2.5. Photocatalytic H₂ evolution

The reactor used in this experiment was a quartz glass reaction bottle with a capacity of 50 mL, and a 5 W white-light multichannel photocatalytic reaction system served as the simulated solar light source. An aqueous solution of triethanolamine (TEOA; 15% v/v, pH = 10) was used as the sacrificial reagent. 10 mg of the sample and 20 mg of eosin Y (EY) were added to the quartz glass reaction bottle, along with 35 mL of the 15% TEOA (pH = 10). Subsequently, the bottle was placed in a numerically controlled ultrasonic cleaner for 10 min to obtain a sample that was evenly dispersed in the aqueous TEOA solution. Then, by using prepared N₂ for 10 min to eliminate O from the reaction system until the peak area corresponding to the O detected in the reaction system was less than 1000, the amount of H₂ produced could be examined, or continue to be excluded until all the O was discharged. After replacement, the reaction bottle was placed in a multichannel photocatalytic reaction system for illumination, and the time per reaction bottle was recorded; the H₂ content was determined by using a gas chromatograph (Tianmei GC7900, TCD, 13X column, N₂ carrier) every half an hour and the peak area corresponding to the H₂ production was recorded. The total illumination time per reaction bottle was 5 h and the entire H₂ production experiment was performed at room temperature. The apparent quantum efficiency (AQE) under different wavelengths was measured and calculated according to the following equation:

$$AQE = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photon}} \times 100\%$$

3. Results and discussion

3.1. Morphology and structure

The morphology of the photocatalyst is one of the important factors affecting its performance. Many important physical and chemical properties of a material are determined by its morphological characteristics. In order to gain insights into the morphology and the mechanism of generation of g-C₃N₄ and Zn-Ni-P@g-C₃N₄, the sample was characterized by SEM and TEM, and the results are shown in Fig. 1. As revealed in Fig. 1(A), g-C₃N₄ exhibits an obviously irregular structure of stacked sheets. It can be seen from Fig. 1(B) and Fig. 1(C) that Ni₂P and ZnP₂ nanoparticles are evenly attached to the g-C₃N₄ surface. However, when Zn-Ni-P was loaded on g-C₃N₄, the structural changes were considerably obvious, and compared with pure g-C₃N₄, the presence of elemental Zn and Ni in Zn-Ni-P@g-C₃N₄ composite implied the formation of Zn-Ni-P@g-C₃N₄ hybrid, as shown in Fig. 1(D). From Fig. 1(D), it can be seen that Zn-Ni-P@g-C₃N₄ reveals a relatively uniform granular structure in which the particles are very evenly and closely arranged with each other, thereby creating a favorable condition for the

Fig. 1. SEM images of (A) pure $g\text{-C}_3\text{N}_4$, (B) $\text{ZnP}_2@g\text{-C}_3\text{N}_4$, (C) $\text{Ni}_2\text{P}@g\text{-C}_3\text{N}_4$, and (D) $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$; (E) TEM image of $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$; (F) HRTEM image of $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$.

simultaneous transfer of large amounts of electrons. Therefore, it can be deduced that the structure of Zn-Ni-P comprised bigger nanoparticles than those of Ni_2P and ZnP_2 , based on the above discussion.

The TEM image of $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$ (Fig. 1E) not only further proves the layered stacking structure of $g\text{-C}_3\text{N}_4$ but also reveals that the ZnP_2 and Ni_2P nanoparticles are tightly loaded on the surface of the $g\text{-C}_3\text{N}_4$ nanolayer. The lattice fringes of ZnP_2 and Ni_2P can be seen from the high-resolution TEM (HRTEM) image in Fig. 1(F), and the spacings corresponding to these fringes are 0.355 and 0.217 nm for the (110) plane of ZnP_2 and the (111) plane of Ni_2P , respectively, which are in good agreement with the XRD results.

3.2. XRD studies

The crystal phases of the pure $g\text{-C}_3\text{N}_4$, $\text{Zn-P}@g\text{-C}_3\text{N}_4$, $\text{Ni-P}@g\text{-C}_3\text{N}_4$, and $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$ photocatalytic materials were studied by XRD. As shown in Fig. 2(a), pure $g\text{-C}_3\text{N}_4$ reveals two characteristic diffraction peaks, a low-angle diffraction peak around $2\theta = 13.0^\circ$ and a high-angle diffraction peak around $2\theta = 27.4^\circ$, that represent the in-plane repeated units of tri-s-triazine and the interlayer stacking reflection of $g\text{-C}_3\text{N}_4$ [27,28], respectively, and correspond to the (100) and (002) crystal faces of $g\text{-C}_3\text{N}_4$ (JCPDS #87-1526). It was obvious that there were other similar diffraction peaks of pure $g\text{-C}_3\text{N}_4$ in $\text{Zn-P}@g\text{-C}_3\text{N}_4$, $\text{Ni-P}@g\text{-C}_3\text{N}_4$, and $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$ composites, which showed that the crystal structure of $g\text{-C}_3\text{N}_4$ still exists in the abovementioned catalysts. When Zn-P and $g\text{-C}_3\text{N}_4$ were combined, there was no diffraction peak of Zn-P in the spectrum, which might be due to the smaller amount of Zn added. When Ni-P and $g\text{-C}_3\text{N}_4$ were compounded, they showed prominent diffraction peaks corresponding to the composite. The characteristic diffraction peaks were obtained at $2\theta = 40.8^\circ$, 44.6° , 47.3° , 54.2° , 54.9° , 66.2° , 72.7° , and 74.9° , corresponding to the (111), (201), (210), (300), (211), (310), (311), and (400) crystal faces of Ni_2P (JCPDS #3-953), respectively. From this, it could be inferred that the $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$ composite photocatalyst generates a plurality of different active crystal faces, which was quite favorable for improving its photocatalytic activity. At the same time, this was consistent with the design concept of this catalyst. Fig. 2(b) presents the XRD diffraction pattern of pure Zn-P prepared under the same conditions; characteristic peaks around $2\theta = 18.11^\circ$, 19.10° , 26.65° , 28.80° , 29.73° , 31.22° , 35.72° , 38.77° , 46.44° , 47.42° , 55.53° , and 69.78° that correspond to the (101), (004), (112), (113), (105), (104), (201), (008), (118), (109), (110), and (324) crystal faces of ZnP_2 (JCPDS #65-1678) could be seen, with the peaks at $2\theta = 20.2^\circ$ and 33.2° corresponding to the phosphide of the impurity Na. Compared with the XRD diffraction peak of $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4$ showed weak diffraction peaks in the $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$ complex, which might be due to the lower crystallinity of pure $g\text{-C}_3\text{N}_4$.

3.3. XPS analysis

Fig. 2. (a) XRD patterns of pure $g\text{-C}_3\text{N}_4$, $\text{Zn-P}@g\text{-C}_3\text{N}_4$, $\text{Ni-P}@g\text{-C}_3\text{N}_4$, and $\text{Zn-Ni-P}@g\text{-C}_3\text{N}_4$ catalysts and (b) XRD pattern of ZnP_2 .

The surface elements of Zn-Ni-P@g-C₃N₄ were characterized by XPS. From the XPS survey pattern (Fig. 3A), the presence of C, N, P, Zn, Ni, and O can be clearly observed. The presence of Na though was mainly a result of incomplete washing of the catalyst during the preparation process. In the high-resolution C 1s XPS pattern of (Fig. 3B) pure g-C₃N₄, two deconvolution peaks located at 284.7 and 288.1 eV, respectively, are observed. The peak at 284.7 eV was used as the reference to correct the binding energies that represent the C–C coordination, including the adventitious hydrocarbon from the XPS instrument itself, and reveal the presence of *sp*²-hybridized C atoms in g-C₃N₄; on the other hand, the peak at 288.1 eV was ascribed to the N=C–N groups of the triazine rings on g-C₃N₄ [29,30]. The N 1s spectrum of pure g-C₃N₄ (Fig. 3C) could be fitted to three peaks that are centered at 394.5, 399.1, and 401.1 eV, which could be assigned to the *sp*²-hybridized aromatic N atoms (C=N=C), tertiary nitrogen, i.e., N–(C)₃, and amino groups (C–N–H), respectively [31,32]. In Fig. 3D, the high-resolution XPS pattern of P 2*p* shows a P 2*p*_{3/2} peak at the binding energy of 133.6 eV. This peak is usually assigned to the typical P–N species [33]. The high-resolution spectrum of the Zn 2*p* (Fig. 3E) of Zn-Ni-P@g-C₃N₄ shows two peaks at 1021.6 and 1044.8 eV, which are assigned to Zn 2*p*_{3/2} and Zn 2*p*_{1/2}, respectively [34]. The main binding energy values of Ni 2*p* (Fig. 3F) were determined to be around 852.5, 856.1, and 869.5 eV, corresponding to Ni 2*p*_{3/2} and Ni 2*p*_{1/2}, which was consistent with those of the Ni 2*p*_{3/2} and Ni 2*p*_{1/2} of Ni₂P, respectively [35,36]. At the same time, the existence of divalent Ni ions was also confirmed. The peaks located at 874.2 and 861.9 eV were assigned to 2*p*_{1/2} and 2*p*_{3/2} satellite peaks, respectively.

3.4. BET and FT-IR studies

Table 1

*S*_{BET}, pore volume, and pore diameter of g-C₃N₄ and Zn-Ni-P@g-C₃N₄.

Sample	<i>S</i> _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
g-C ₃ N ₄	44.2069	0.1096	15.5835
Zn-Ni-P@g-C ₃ N ₄	1.5282	0.0024	86.4768

The Brunauer-Emmett-Teller (BET) specific surface area (*S*_{BET}) and the pore size distributions of pure g-C₃N₄ and Zn-Ni-P@g-C₃N₄ were calculated based on N₂ adsorption-desorption isotherms, and the results are shown in Table 1. Fig. 4(a) shows the adsorption isotherm of type II, which indicates that the adsorption heat of the first layer of the multimolecular layer adsorbed was greater than the condensation heat; this can be described by the following BET formula:

$$\frac{V^a}{V_m^a} = \frac{c(p/p^*)}{(1 - p/p^*)[1 + (c - 1)p/p^*]}$$

where *V*^a represents the amount adsorbed under pressure *p*, *V*_m^a is the saturation adsorption amount of the monolayer, *p*^{*} is the saturated vapor pressure of the liquid adsorbed at the adsorption temperature, and *c* is the adsorption constant that is related to the adsorption heat.

It is seen clearly from the test results that the specific surface area of g-C₃N₄ is 44.2069 m²/g, which is significantly larger than that of Zn-Ni-P@g-C₃N₄ (1.5282 m²/g). Further, it can be observed from the pore size distribution curves that the g-C₃N₄ and Zn-Ni-P@g-C₃N₄ catalysts exhibit mesopore and macropore structures. Meanwhile, the pores of g-C₃N₄ in Zn-Ni-P@g-C₃N₄ of sizes 0–25 nm disappeared, which indicated that Zn-Ni-P was successfully deposited onto the g-C₃N₄ surface or embedded in its holes. However, the pore volume of Zn-Ni-P@g-C₃N₄ was smaller than that of g-C₃N₄, from which it

Fig. 3. XPS patterns of Zn-Ni-P@g-C₃N₄.

Fig. 4. (a) N_2 adsorption-desorption isotherms of $\text{g-C}_3\text{N}_4$ and $\text{Zn-Ni-P@g-C}_3\text{N}_4$; (b) FTIR spectra of pure $\text{g-C}_3\text{N}_4$, $\text{Zn-P@g-C}_3\text{N}_4$, $\text{Ni-P@g-C}_3\text{N}_4$, and $\text{Zn-Ni-P@g-C}_3\text{N}_4$ catalysts.

could be further inferred that more Zn-Ni-P nanoparticles were embedded in the porous structure of $\text{g-C}_3\text{N}_4$. The existence of $\text{g-C}_3\text{N}_4$ in $\text{Zn-Ni-P@g-C}_3\text{N}_4$ was verified by FT-IR, as shown in Fig. 4(b). The main absorption range of pure $\text{g-C}_3\text{N}_4$ was $3000\text{--}3500\text{ cm}^{-1}$, corresponding to the N-H stretching vibration and the surface-adsorbed OH. There were also distinct absorption peaks in the significant band of $1240\text{--}1640\text{ cm}^{-1}$, with the peak at 1635 cm^{-1} corresponding to the heterocyclic stretching vibration of C-N and those at 1243, 1323, 1414, and 1570 cm^{-1} corresponding to the stretching vibration modes of the aromatic C-N; the peak observed at 807 cm^{-1} represents a particular breathing mode of the triazine unit [37,38].

3.5. Optical properties of the photocatalysts

Photoabsorption is a necessary condition for ensuring the activity of semiconductor photocatalysts, and the optical properties of pure $\text{g-C}_3\text{N}_4$, $\text{Zn-P@g-C}_3\text{N}_4$, $\text{Ni-P@g-C}_3\text{N}_4$, and $\text{Zn-Ni-P@g-C}_3\text{N}_4$ were investigated by UV-vis diffuse reflectance spectroscopy, with the results being shown in Fig. 5(a). It can be clearly seen from the spectrum that the absorption band edges of pure $\text{g-C}_3\text{N}_4$ and $\text{Zn-Ni-P@g-C}_3\text{N}_4$ are 436 and 490 nm, respectively. In the wavelength range $300\text{--}700\text{ nm}$, the light

absorption density significantly increases when Zn-P and Ni-P are combined with $\text{g-C}_3\text{N}_4$. Furthermore, when Zn-P and Ni-P were combined with $\text{g-C}_3\text{N}_4$, the light absorption density increased the most, which further confirmed that Zn-Ni-P and $\text{g-C}_3\text{N}_4$ were successfully compounded together. This increase in the light absorption density was directly related to the change in the color after the successful compounding of $\text{g-C}_3\text{N}_4$ with Zn-P and Ni-P . In addition, it could be observed from the spectrum that the light absorption density of $\text{Zn-Ni-P@g-C}_3\text{N}_4$ was slightly increased from 400 nm to 700 nm , which enhanced its photocatalytic H_2 generation activity. However, the light absorption density of $\text{Zn-P@g-C}_3\text{N}_4$ was obviously decreased in the same wavelength range, which was not conducive for enhancing the photocatalytic activity of the composite itself.

To obtain the mass percent of the $\text{g-C}_3\text{N}_4$ product, TGA of the $\text{Zn-Ni-P@g-C}_3\text{N}_4$ composite was performed. The $\text{Zn-Ni-P@g-C}_3\text{N}_4$ hybrid was heated from room temperature to $800\text{ }^\circ\text{C}$ at the rate of $10\text{ }^\circ\text{C/min}$ in N_2 , and the TGA curve obtained is shown in Fig. 5(b). It can be seen that the purity of $\text{g-C}_3\text{N}_4$ in the sample is high (91%–93%). The weight loss observed at $48\text{--}175\text{ }^\circ\text{C}$ can be attributed to the evaporation of the water bound in the composite. The weight loss observed be-

Fig. 5. (a) UV-vis diffuse reflectance spectra of pure $\text{g-C}_3\text{N}_4$, $\text{Zn-P@g-C}_3\text{N}_4$, $\text{Ni-P@g-C}_3\text{N}_4$, and $\text{Zn-Ni-P@g-C}_3\text{N}_4$; (b) TGA curve of $\text{Zn-Ni-P@g-C}_3\text{N}_4$.

tween 450 and 610 °C was ascribed to the decomposition of g-C₃N₄ in the Zn-Ni-P@g-C₃N₄ hybrid. Thus, it was estimated that the weight percent of g-C₃N₄ in Zn-Ni-P@g-C₃N₄ was about 43.19%. In addition, it was observed that the increase in weight observed beyond 700 °C (700–800 °C) for the resulting composite might be due to the oxidation of the impurities [39].

3.6. Photocatalytic H₂ evolution performance

Fig. 6(a) shows the H₂ production activities of eosin-sensitized catalysts under visible light. It can be seen clearly that the photocatalytic H₂ production activity of pure g-C₃N₄ is the lowest in 30 mL 15% aqueous TEOA and that the yield is only 9.7 μmol after visible light irradiation for 5 h. This is mainly attributed to the very low separation efficiency of the electron-hole pairs of pure g-C₃N₄ as a result of significant recombination of the electrons and holes during the transfer process; the number of electrons that migrated to the semiconductor surface was so small that eventually no more electrons reacted with the H⁺ to generate H₂. Meanwhile, the H₂ yields of Zn₂P and NiP₂ were only 0.156 and 5.527 μmol, respectively, under the same conditions. After elemental Zn or Ni was introduced to g-C₃N₄, the photocatalytic activity was improved slightly. The amounts of H₂ generated on the composite photocatalysts Zn-P@g-C₃N₄ and Ni-P@g-C₃N₄ reached 34.46 and 212.94 μmol under the same lighting conditions and reaction system, which were 3.55 and 21.95 times that of pure g-C₃N₄, respectively. The result also indicated that the presence of Zn-Ni-P in Zn-Ni-P@g-C₃N₄ played a key role in improving

the photocatalytic activity of the composite photocatalyst. Fig. 6(b) shows a test curve of the photocatalytic H₂ production with different molar ratios of Zn and Ni added. It can be seen that the photocatalytic activity of Zn-Ni-P@g-C₃N₄ is much higher than that of pure g-C₃N₄, and is also higher than those of Zn-P@g-C₃N₄ and Ni-P@g-C₃N₄. When the molar ratio of the Zn and Ni added is 1:3, the Zn-Ni-P@g-C₃N₄ composite catalyst showed the highest photocatalytic activity and the H₂ yield reached 531.2 μmol, which was 54.76, 15.41, and 2.49 times those of pure g-C₃N₄, Zn-P@g-C₃N₄, and Ni-P@g-C₃N₄, respectively. It was reported that the improvement in the activity of the photocatalyst indicated the existence of the Zn-Ni-P structure [40]. It was obvious that the key factor in improving the photocatalytic activity of the Zn-Ni-P@g-C₃N₄ composite photocatalyst is the presence of the Zn-Ni-P structure.

Fig. 6(c) shows the effect of the 15% aqueous TEOA solution of different pH values on the photocatalytic activity for the H₂ produced over the composite catalyst with the molar ratio of 1:3 of Zn to Ni under eosin sensitization. From the experimental results, it can be seen that the different pH systems have a very important influence on the H₂ production. The results also indicate that the activity of the photocatalyst increases with the increase in the pH from 8 to 10. However, the photocatalytic activity gradually reduced as the pH further increased from 10 to 12. In summary, the H₂ production activity of Zn-Ni-P@g-C₃N₄ (*n*_(Zn) : *n*_(Ni) = 1:3) composite photocatalyst was the highest when pH = 10, and the amounts of H₂ produced reached 531.2 μmol after visible light illumination for 5 h. Correspondingly, the H₂ production reaction of the

Fig. 6. (a,b) H₂ production performance, (c) pH effect, and (d) the results of the stability test of the samples.

Fig. 7. AQE of Zn-Ni-P@g-C₃N₄ at different wavelengths (420–600 nm).

Zn-Ni-P@g-C₃N₄ ($n_{\text{Zn}}:n_{\text{Ni}} = 1:3$) catalytic system became less favorable when the acid or alkali was stronger. The main reason was the triple excited eosin could be further reduced and quenched by the TEOA in the reaction system of pH = 10, and eosin dyes could be effectively adsorbed onto the different active crystal surfaces of the composite catalyst for participation in the catalytic H₂ production reaction. In the acid catalyst system, TEOA was easily protonated, which hindered its oxidation and thereby greatly weakened its ability to reduce and quench the eosin (in the triple excited state), thus decreasing the ability to generate H₂. In a strong alkaline environment, the content of H⁺ is drastically reduced, which greatly weakens the ability to generate H₂, therefore, such a condition is rather unfavorable for catalyzing H₂ production in this reaction system.

In addition, the stability of Zn-Ni-P@g-C₃N₄, with the highest catalytic activity, was studied under the condition of eosin sensitization for the 15% TEOA (pH = 10) system. Four cyclic stability tests were conducted on the Zn-Ni-P@g-C₃N₄ composite catalyst and the illumination time for each cycle was 5 h, as shown in Fig. 6(d). The results show that the amount of H₂ produced over the Zn-Ni-P@g-C₃N₄ composite catalyst hardly decreased during the 20-hour stability test, from which it could be inferred that the eosin-sensitized composite catalyst had

good stability.

To investigate the photocatalytic H₂ evolution of Zn-Ni-P@g-C₃N₄ under different wavelengths, the AQE was measured under visible light irradiation (420–600 nm). The result is shown in Fig. 7; the AQE largely decreases as the wavelength gradually increases, and the highest apparent quantum efficiency, which was obtained for the Zn-Ni-P@g-C₃N₄ sample, is 23.05% at the monochromatic wavelength of 420 nm.

3.7. PL spectra

In this study, the recombination of the photogenerated electron-hole pairs of the samples and the underlying mechanism of the photocatalytic H₂ production were investigated by steady-state fluorescence spectroscopy. The steady-state fluorescence spectrum might reflect the secondary recombination efficiency of the photogenerated electrons and holes to a certain extent. Under 480 nm light excitation, the eosin (1×10^{-6} mol/L) solution produced the strongest fluorescence emission peak in the range 500–600 nm, with the tallest emission peak observed at 538 nm, as shown in Fig 8(a); this is consistent with the electron regeneration process of the excited eosin. When pure g-C₃N₄ was added to the eosin solution, the fluorescence intensity decreased slightly. The fluorescence intensity decreased obviously when Zn-P@g-C₃N₄ and Ni-P@g-C₃N₄ existed in the eosin solution; the main reason for this was that the two types of semiconductor materials were closely combined, resulting in the formation of a heterojunction structure; this interface mutually helped the photogenerated electrons in the two materials to migrate to the conduction band of the catalyst. Moreover, the Schottky barrier formed during the electron transfer process became an effective trap for the photogenerated electrons, therefore, the photogenerated carriers were effectively separated and their recombination suppressed, which ultimately led to the improvement of the photocatalytic activity. When Zn-Ni-P@g-C₃N₄ was added to the eosin solution, the fluorescence intensity of the composite catalyst decreased to a great extent, which showed that the existence of the Zn-Ni-P structure in Zn-Ni-P@g-C₃N₄ could effectively inhibit the recombination of the photogenerated elec-

Fig. 8. (a) Steady-state fluorescence and (b) transient fluorescence measurements of samples.

trons and holes produced by g-C₃N₄ and increase the lifetimes of the photogenerated electrons. The cause of this phenomenon may be the Zn-Ni-P structure, which has a strong ability to capture and transfer electrons. The recombination of the photogenerated electron-hole pairs was suppressed to a great extent, which dramatically improved the photocatalytic H₂ production efficiency.

To further investigate the separation and transfer mechanism of the electrons and holes between the excited state eosin and the catalysts and determine the fluorescence lifetimes of Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄, we used the transient fluorescence spectroscopy technique. Fig. 8(b) shows that for all the samples, the fluorescence intensities exponentially decreased, which could be well fitted by using the three radiative lifetimes: $I(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2} + A_3e^{-t/\tau_3}$ [41]. The different lifespan changes are shown in Table 2. The longest lifetime increased from 26.34 ns for pure g-C₃N₄ to 63.68 ns for Zn-Ni-P@g-C₃N₄, whereas the medium lifetime increased from 4.34 ns to 4.94 ns, which showed that the combination of Zn-Ni-P and g-C₃N₄ effectively increased the lifetime of the charge carriers [42]. The result could also explain the good separation efficiency of the photogenerated electron-hole pairs and the effective electron transfer that occurred between Zn-Ni-P and g-C₃N₄, which was beneficial for improving the photocatalytic H₂ production activity. The average life could be calculated by the theoretical formula [43]:

$$\langle \tau \rangle = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

where τ_1 , τ_2 , and τ_3 represent the emission lifetimes, and A_1 , A_2 , and A_3 are the corresponding amplitudes.

The average lifetimes of g-C₃N₄, Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄ were calculated as 22.01, 49.36, 45.23, and 55.91 ns, respectively, by using the above formula. It shows that the average lifetime of Zn-Ni-P@g-C₃N₄ was the highest. It also indicates the existence of Zn-Ni-P, which effectively hindered the recombination of the photogenerated electron-hole pairs, thereby improving the photocatalytic activity by increasing the number of electrons that participate in the reduction reaction. The extension of the lifetime of a photocatalyst usually implies that the excited electrons or holes are more likely to be involved in the photocatalytic reaction. In combination with the

steady-state fluorescence test, it can be concluded that Zn-Ni-P effectively restrained the recombination of the electron-hole pairs of g-C₃N₄ and enhanced the conversion efficiency of the incident visible light, which was the reason for Zn-Ni-P@g-C₃N₄ showing a high catalytic activity for H₂ production.

3.8. Photoelectrochemical experiments (*I*-*t*, LSV, EIS, and Mott-Schottky)

Photoelectrochemical performance is considered as a strong metric for the separation and transfer efficiency of photogenerated electron-hole pairs [44]. At the same time, the photocurrent can also reflect the ability of a semiconductor catalyst to produce charge carriers under visible light irradiation [41]. Therefore, in order to further understand the phenomenon of the Zn-Ni-P-accelerated separation and transfer of electron-hole pairs, the samples were studied by obtaining the transient photocurrent-time curves (*I*-*t*). Fig. 9(a) shows the *I*-*t* curves of the samples coated on FTO conductive glass for several on/off cycles, from which it can be easily found that the Zn-Ni-P@g-C₃N₄ composite catalyst shows a stronger photocurrent response than pure g-C₃N₄; this suggested that the existence of Zn-Ni-P effectively improved the separation and transfer efficiency of the photoelectron-hole pairs. Thus, the photocatalytic H₂ production activity was enhanced.

With a view to understanding the key role of Zn-Ni-P in photocatalytic H₂ production, the voltammetric characteristics of pure g-C₃N₄, Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄ were obtained. As shown in Fig. 9(b), a weak current response is observed on the low-voltage FTO conductive glass, which is mainly due to the cathode current generated by the reduction of H⁺ to H₂ in a strongly negative pressure environment [9]. Under the same voltage environment, the current responses of Zn-P@g-C₃N₄ and Ni-P@g-C₃N₄ are obviously higher than that of pure g-C₃N₄, though the current response of the Zn-Ni-P@g-C₃N₄ catalyst is the highest. At the same time, the initial current of pure g-C₃N₄ is obviously lower than that of the Zn-Ni-P@g-C₃N₄ composite catalyst. These test results show that the introduction of Zn-Ni-P could significantly enhance the current response. Compared to pure g-C₃N₄, Zn-P@g-C₃N₄, and Ni-P@g-C₃N₄, Zn-Ni-P@g-C₃N₄ exhibits the best electron transport performance and transmission efficiency, hence, the photocatalytic H₂ production activity is improved.

The EIS Nyquist diagram that is related to the electrolyte and the interfacial electron transfer resistance [45] is important for studying the electron transfer across the interface and the associated reorganization [46]. The arc observed in the high-frequency region corresponds to the electron transfer process, with its diameter representing the interfacial electron transfer resistance [44]. The arc radius is reflective of the reaction rate on the electrode surface. If this radius is smaller, it implies better detachment of the photoelectron-hole pairs and a higher charge transfer efficiency between the electrolyte and the electrode interfaces. If the radius is larger, the converse is true [47]. Fig. 9(c) shows the Nyquist plots of g-C₃N₄, Zn-Ni-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄ in 0.2

Table 2

Decay parameters of EY in aqueous TEOA solution upon the introduction of Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄ (the excited and emission wavelengths were 369 and 538 nm, respectively).

System	Lifetime, τ (ns)	Rel (%)	χ^2
EY-g-C ₃ N ₄	$\tau_1 = 4.34$	$A_1 = 40.33$	1.71
	$\tau_2 = 26.34$	$A_2 = 29.36$	
	$\tau_3 = 0.37$	$A_3 = 30.31$	
EY-Zn-P@g-C ₃ N ₄	$\tau_1 = 4.35$	$A_1 = 16.48$	1.42
	$\tau_2 = 57.86$	$A_2 = 8.88$	
	$\tau_3 = 0.31$	$A_3 = 74.64$	
EY-Ni-P@g-C ₃ N ₄	$\tau_1 = 4.86$	$A_1 = 22.10$	1.49
	$\tau_2 = 53.29$	$A_2 = 12.43$	
	$\tau_3 = 0.34$	$A_3 = 65.46$	
EY-Zn-Ni-P@g-C ₃ N ₄	$\tau_1 = 4.94$	$A_1 = 20.82$	1.47
	$\tau_2 = 63.86$	$A_2 = 13.13$	
	$\tau_3 = 0.34$	$A_3 = 66.05$

Fig. 9. (a) Photocurrent responses of pure g-C₃N₄, Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄; (b) LSV curves of pure g-C₃N₄, Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄; (c) Electrochemical impedance spectra of pure g-C₃N₄, Zn-P@g-C₃N₄, Ni-P@g-C₃N₄, and Zn-Ni-P@g-C₃N₄; (d) Mott-Schottky curves of pure g-C₃N₄ and Zn-Ni-P@g-C₃N₄.

mol/L Na₂SO₄ solution. The Nyquist plots in the entire frequency range are composed of two fault-tolerant semicircular curves at high and low frequencies. The contact area half capacitor (C1) in the high-frequency region is a parallel nanoparticle with a contact resistance (R1), whereas the charge transfer resistance (R2) in the low-frequency semicircle corresponds to the capacitance of a parallel electric double layer (C2). The experimental data were modeled by using nonlinear least squares and an equivalent circuit was fitted, as illustrated in Fig. 9(c). It can be seen that the conductivity of the material is very low. Further, g-C₃N₄, Zn-P@g-C₃N₄, and Ni-P@g-C₃N₄ in the high-frequency zone display an obvious semicircle corresponding to the resistance. It is clearly seen from Fig. 9(c) that Zn-Ni-P and g-C₃N₄ are not simply mixed physically, therefore, the contact resistance is very small. There is only one circle between Zn-P@g-C₃N₄ and Ni-P@g-C₃N₄ in the low-frequency region, indicating that the resistance follows the order Zn-P@g-C₃N₄ > Zn-Ni-P@g-C₃N₄ > Ni-P@g-C₃N₄. Therefore, the method of mixing did not change the internal electron transfer mode, but effective blending reduced the contact resistance, which created a good condition for enhancing the H₂ production kinetics.

Fig. 9(d) shows the Mott-Schottky curves of g-C₃N₄ and Zn-Ni-P@g-C₃N₄. It can be seen that both g-C₃N₄ and Zn-Ni-P@g-C₃N₄ exhibit positive slopes of the E - C^{-2} plots, indicating that they are n-type semiconductors [48]. In other words, the Fermi levels are closer to the respective conduction bands, i.e., the probability that the electrons occupy an energy

level near the conduction band is higher, which provides good conditions for improving the efficiency of electron transfer. Furthermore, according to the physical meaning, the flat band potentials of g-C₃N₄ and Zn-Ni-P@g-C₃N₄ are about $E_{fb} = -1.06$ V and $E_{fb} = -1.12$ V, respectively. At the same time, based on the relation $E_{fb} = E_F$, the Fermi level could be obtained. Compared with g-C₃N₄, the flat band potential of the Zn-Ni-P@g-C₃N₄ system experiences a negative shift, which suggests an increase in the Fermi level of the semiconductor. Therefore, from the solution side, the particles can more easily capture the electrons on the conduction band of the semiconductor so that the photo-reduction reaction can occur. In terms of the thermodynamics, it implies that the photoinduced electrons have a stronger reducing power after illumination. For aqueous systems, the semiconductor is more likely to produce photoinduced electrons in order to generate H₂, which is beneficial for increasing the photocatalytic H₂ production activity.

3.9. Photocatalytic mechanism of H₂ evolution

Based on the above analysis and discussion, the possible mechanism of H₂ production by eosin-sensitized Zn-Ni-P@g-C₃N₄ under visible light illumination was proposed, as shown in Fig. 10. g-C₃N₄ could produce electron-hole pairs under light excitation, but its catalytic efficiency was greatly reduced because of their rapid recombination. However, when Zn-Ni-P and g-C₃N₄ were combined, the catalytic activity increased rapidly. Therefore, the existence of Zn-Ni-P was the

Fig. 10. H_2 production mechanism of eosin-sensitized Zn-Ni-P@g- C_3N_4 photocatalyst under visible light illumination.

main reason for the efficient electronic separation and transmission observed in Zn-Ni-P@g- C_3N_4 , which could accelerate the rapid transfer of the electrons and the depletion of the holes through the sacrificial reagent (TEOA). Thus, the recombination of the photoelectrons and photoholes was inhibited, and the photocatalytic activity was enhanced. At the same time, Zn-Ni-P and g- C_3N_4 could be together excited to produce electrons and holes through visible light irradiation, therefore, there was a synergistic effect of multiple photocatalytic H_2 productions in the catalytic system. The EY molecules that were adsorbed on the surfaces of Zn-Ni-P and g- C_3N_4 absorbed the light energy to form the single-excited state EY^1* , and the more stable triple-excited state EY^{3*} was formed through intersystem transition. Then, in the TEOA system, EY^{3*} was reduced and quenched to produce $\text{EY}^{\bullet-}$ with reductive capacity and oxidation states TEOA^+ . Some of the electrons of $\text{EY}^{\bullet-}$ could be transferred directly to the active sites of the Zn-Ni-P catalyst, while the remaining electrons were transferred to the conduction band of g- C_3N_4 , before being further transferred to the active sites of Zn-Ni-P to reduce water to H_2 . In addition, we believe that the presence of an electric field in the catalytic system plays an important role in the separation and transfer of electrons and holes.

4. Conclusions

A new type of Zn-Ni-P@g- C_3N_4 composite catalyst was successfully prepared by direct high-temperature calcination. The photocatalytic H_2 production experiments showed that Zn-Ni-P@g- C_3N_4 exhibited excellent photocatalytic activity. When the molar ratio of Zn to Ni was 1:3, the catalytic activity was the highest. The amount of H_2 generated reached 531.2 μmol after illumination for 5 h, which was 54.76 times that obtained with pure g- C_3N_4 . Further, it was found that Zn-Ni-P@g- C_3N_4 had a higher catalytic effect under alkaline conditions and that the highest H_2 production efficiency was observed at pH = 10. It can be seen from the SEM images that Zn-Ni-P@g- C_3N_4 has the morphology and structure of small particles that are arranged uniformly. Compared with pure

g- C_3N_4 , its structure has changed completely. It is also difficult to observe the existence of g- C_3N_4 nanosheets in the Zn-Ni-P@g- C_3N_4 structure, which strongly proved that a successful composite was formed between Zn-Ni-P and g- C_3N_4 . Then, by studying the UV-vis, electrochemical, transient-state, and steady-state fluorescence results of the samples, it was found that Zn-Ni-P@g- C_3N_4 could provide more active sites that could promote the catalytic reaction process. The introduction of Zn-Ni-P played an irreplaceable role in accelerating the separation and transfer efficiency of the electrons. Through a series of characterizations, we finally speculated on the possible photocatalytic reaction mechanism of the Zn-Ni-P@g- C_3N_4 material system.

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Graphical Abstract

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Controllable design of Zn-Ni-P on g-C₃N₄ for efficient photocatalytic hydrogen productionYanbing Li, Zhiliang Jin *, Lijun Zhang, Kai Fan
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The existence of Zn-Ni-P was the main reason for the efficient electronic separation and transmission observed in Zn-Ni-P@g-C₃N₄, which could accelerate the rapid transfer of electrons and the depletion of holes through the sacrificial reagent TEOA. Thus, the recombination of the photoelectrons and photo-holes was inhibited, and the photocatalytic activity was enhanced.

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可控设计Zn-Ni-P修饰g-C₃N₄催化剂光催化产氢性能李彦兵^{a,b}, 靳治良^{a,b,*}, 张利君^{a,b}, 樊凯^{a,b}^a北方民族大学化学与化学工程学院, 宁夏银川750021^b北方民族大学国家民委化工技术基础重点实验室, 宁夏银川750021

摘要: 光催化分解水制氢是应对能源危机和环境污染问题的途径之一, 也是实现太阳能转化和储存的有效方法. 其中, 应用层面的一个关键制约因素是高效光催化剂的开发和制氢反应体系的构建, 理论层面的一个关键科学问题是光生电子-空穴的高效分离及光生电子定向迁移, 这两个层面的问题构成当前光催化分解水制氢研究的重大挑战. 因此, 稳定、高效催化剂的制备成为光催化领域重要的研究目标.

类石墨烯氮化碳(g-C₃N₄)的结构与石墨相似, 其层与层之间的范德华力使其具有良好的热稳定性和化学稳定性.

$\text{g-C}_3\text{N}_4$ 是一种聚合物非金属半导体, 由于具有与碳材料相似的层状堆积结构和 sp^2 杂化的 π 共轭电子能带结构, 因此被认为是最有可能代替碳材料用于光催化分解水制氢的新型光催化材料. $\text{g-C}_3\text{N}_4$ 的室温禁带宽度为2.7 eV左右, 其价带和导带的位置完全覆盖了水的氧化-还原电位, 因此理论上 $\text{g-C}_3\text{N}_4$ 不仅能够氧化水为氧气, 而且能够将水还原产氢, 从而表现出优良的光电特性, 成为新型太阳能转换材料. 然而, $\text{g-C}_3\text{N}_4$ 在展示了良好研究前景的同时也存在一些缺陷, 如比表面积较小及稳定性差等, 这制约了 $\text{g-C}_3\text{N}_4$ 在光催化领域的应用. 为此, 通过各种化学修饰对 $\text{g-C}_3\text{N}_4$ 进行改性以提高其光催化活性和稳定性成为一个重要的研究方向.

本文采用高温煅烧方法成功制备了 $\text{Zn-Ni-P@g-C}_3\text{N}_4$ 催化剂. 将一定量的 $\text{g-C}_3\text{N}_4$ 、乙酸镍、乙酸锌和次亚磷酸钠均匀混合在一起并研磨成粉末, 然后以3 °C/min的速率升温至300 °C并在此温度下保持2 h, 自然冷却至室温后即得到 $\text{Zn-Ni-P@g-C}_3\text{N}_4$ 催化剂, 整个制备过程在氮气环境中进行. 研究表明, 在Zn与Ni摩尔比为1:3的 $\text{Zn-Ni-P@g-C}_3\text{N}_4$ 催化剂上, 当反应体系 $\text{pH} = 10$, 在420 nm光照下反应5 h产氢量可达531.2 μmol , 是纯 $\text{g-C}_3\text{N}_4$ 上的54.7倍. 20 h循环实验表明催化剂具有较好的光催化稳定性. 对催化剂进行了XRD、TEM、SEM、XPS、 N_2 吸附、UV-vis DRS、瞬态光电流、FT-IR、瞬态荧光和Mott-Schottk等一系列表征, 证明Zn-Ni-P的参与有效调变了电荷传输机制. SEM表征表明, $\text{Zn-Ni-P@g-C}_3\text{N}_4$ 为均匀排列的小颗粒, 与纯 $\text{g-C}_3\text{N}_4$ 相比其结构发生了改变, 在 $\text{Zn-Ni-P@g-C}_3\text{N}_4$ 结构中未发现 $\text{g-C}_3\text{N}_4$ 纳米片的存在, 说明Zn-Ni-P和 $\text{g-C}_3\text{N}_4$ 成功复合. 在上述研究基础上推测了可能的反应机理.

关键词: Zn-Ni-P; $\text{g-C}_3\text{N}_4$; 产氢; 可控设计; 光催化剂

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