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Facile synthesis and enhanced photocatalytic H₂-evolution performance of NiS₂-modified g-C₃N₄ photocatalysts

Feng Chen^a, Hui Yang^a, Xuefei Wang^{a,*}, Huogen Yu^{a,b,#}^a School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, Hubei, China^b State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, Hubei, China

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ABSTRACT

NiS₂ is a promising cocatalyst to improve the photocatalytic performance of g-C₃N₄ for the production of H₂. However, the synthesis of the NiS₂ cocatalyst usually requires harsh conditions, which risks destroying the microstructures of the g-C₃N₄ photocatalysts. In this study, a facile and low-temperature (80 °C) impregnation method was developed to prepare NiS₂/g-C₃N₄ photocatalysts. First, the g-C₃N₄ powders were processed by the hydrothermal method in order to introduce oxygen-containing functional groups (such as -OH and -CONH-) to the surface of g-C₃N₄. Then, the Ni²⁺ ions could be adsorbed near the g-C₃N₄ via strong electrostatic interaction between g-C₃N₄ and Ni²⁺ ions upon the addition of Ni(NO₃)₂ solution. Finally, NiS₂ nanoparticles were formed on the surface of g-C₃N₄ upon the addition of TAA. It was found that the NiS₂ nanoparticles were solidly and homogeneously grafted on the surface of g-C₃N₄, resulting in greatly improved photocatalytic H₂ production. When the amount of NiS₂ was 3 wt%, the resultant NiS₂/g-C₃N₄ photocatalyst showed the highest H₂ evolution rate (116.343 μmol h⁻¹ g⁻¹), which is significantly higher than that of the pure g-C₃N₄ (3 μmol h⁻¹ g⁻¹). Moreover, the results of a recycling test for the NiS₂/g-C₃N₄ (3 wt%) sample showed that this sample could maintain a stable and effective photocatalytic H₂-evolution performance under visible-light irradiation. Based on the above results, a possible mechanism of the improved photocatalytic performance was proposed for the presented NiS₂/g-C₃N₄ photocatalysts, in which the photogenerated electrons of g-C₃N₄ can be rapidly transferred to the NiS₂ nanoparticles via the close and continuous contact between them; then, the photogenerated electrons rapidly react with H₂O adsorbed on the surface of NiS₂, which has a surficial metallic character and high catalytic activity, to produce H₂. Considering the mild and facile synthesis method, the presented low-cost and highly efficient NiS₂-modified g-C₃N₄ photocatalysts would have great potential for practical use in photocatalytic H₂ production.

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1. Introduction

Photocatalytic water splitting for H₂ generation by means of solar energy and semiconductor photocatalysts provides an

eco-friendly pathway to utilize renewable energy sources [1,2]. For practical water splitting, it is necessary to develop new and efficient photocatalysts to meet all the requirements, which include utilizing visible light (~43% of the solar spectrum) and

* Corresponding author. Tel: +86-13387570017; Fax: +86-27-87879468; E-mail: xuefei@whut.edu.cn

Corresponding author. Tel: +86-27-87871029; Fax: +86-27-87879468; E-mail: yuhuogen@whut.edu.cn

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possessing both a suitably sized band gap and a suitable position of the band gap [3,4]. Recently, various visible-light-driven photocatalysts, such as multicomponent oxides [5,6] and polymers [7–9], have been developed for H₂ generation. Among them, polymeric graphite-like carbon nitride (g-C₃N₄) is considered to be one of the most ideal photocatalysts and has received extensive attention since it was first reported by Wang et al. [10,11] for H₂ production under visible-light irradiation. g-C₃N₄ possesses several promising characteristics, including a narrow indirect band gap ($E = 2.7$ eV) to absorb visible light, a strong reduction potential (-1.3 V vs. normal hydrogen electrode) for H₂ evolution and good thermal stability resulting from its aromatic C–N heterocyclic structure [12,13]. Nevertheless, the performance of pure g-C₃N₄ for photocatalytic H₂ production is poor because of the fast recombination of the photogenerated electron-hole pairs and high overpotential [14,15]. To solve these problems, a number of strategies, such as coupling with other semiconductors [16–22], doping with metal or nonmetal elements [23,24], forming mesoporous or nanosheet structures [25,26], and loading cocatalysts [27–34] have been successfully applied to improve the photocatalytic activity of pure g-C₃N₄. Among these, the loading of suitable cocatalysts is regarded as one of the most effective strategies to enhance photocatalytic H₂ evolution over g-C₃N₄ [35], as the cocatalysts improve the charge separation and accelerate the surface catalytic reaction. Although rare and expensive noble metals, such as Pt, Au and Ag, can serve as highly efficient cocatalysts for enhancing the H₂-evolution rate over g-C₃N₄ [36,37], their widespread application is severely restricted by their rarity and cost. Therefore, it is desirable to develop low-cost, earth-abundant and high-performance cocatalysts to further improve the H₂-evolution performance and economy of g-C₃N₄.

Inspired by [NiFe] hydrogenases for catalytic H₂ production, nickel-based compounds have long been sought as promising cocatalysts for the production of H₂ by reduction [38–40]. They are considerably less expensive than noble metal cocatalysts and their preparation is usually facile. Among nickel-based compounds, NiS₂ has received particular attention for several reasons. First, it is one of the commonest natural minerals [41]. Second, it maintains relatively long-term stability in both acidic and alkaline operating environments. More importantly, its surface electronic structure exhibits a remarkable tendency toward a metallic character, attributed to lattice relaxation near the surface [42]; therefore, as a cocatalyst, it can facilitate interfacial charge transfer and provide catalytic active sites, similarly to MoS₂ [43,44]. Indeed, recent research has indicated that NiS₂ can effectively improve the photocatalytic activity of H₂ production when used to modify the surfaces of semiconductor photocatalysts. For example, Xue and co-workers [45] reported that a CdLa₂S₄ photocatalyst loaded with 2 wt% NiS₂ *via* a hydrothermal method achieved a H₂ production rate of 2.5 mmol h^{−1} g^{−1}, which was 3 times higher than that of the pristine CdLa₂S₄ photocatalyst. Furthermore, NiS₂ as a cocatalyst can be integrated with polymeric g-C₃N₄ through a hydrothermal process to improve the photocatalytic performance of H₂ production [46]. To maximize photocatalytic activity, it is well estab-

lished that cocatalysts must be prepared under mild reaction conditions to prevent destruction of the photocatalyst structure. The aim is to obtain a homogeneous dispersion of the cocatalyst on the surface of the photocatalyst, leading to close and continuous contact between them. However, this requirement is incompatible with the conventional preparation of the NiS₂ cocatalyst, which requires relatively rigorous reaction conditions, as in the above-cited examples. Therefore, it is highly desirable to explore mild and facile synthesis methods to realize the modification of the NiS₂ cocatalyst on the surface of semiconductor photocatalysts.

In order to develop a milder synthetic method for NiS₂-modified g-C₃N₄ to make a comparison with previous studies, NiS₂ nanoparticles as a cocatalyst were successfully modified on the surface of polymeric g-C₃N₄ photocatalysts by a mild and facile impregnation approach for the first time. Firstly, oxygen-containing functional groups were introduced onto the exterior of g-C₃N₄ by a hydrothermal treatment. Secondly, by electrostatic attraction, Ni²⁺ ions were strongly adsorbed onto the surface of the g-C₃N₄ after the addition of a Ni(NO₃)₂ precursor. Finally, when thioacetamide was added to a g-C₃N₄ suspension under low-temperature treatment conditions of 80 °C, the NiS₂ cocatalyst was strongly and homogeneously attached to the surface of g-C₃N₄. It was found that the presence of the NiS₂ nanoparticles on the g-C₃N₄ surface greatly enhanced the photocatalytic activity of g-C₃N₄ for H₂ generation under visible-light irradiation. A possible photocatalytic mechanism was proposed. Compared with the high-temperature synthesis, the present low-temperature impregnation method of NiS₂-modified g-C₃N₄ photocatalysts can be considered an economic and facile synthetic method for the design and preparation of high-efficiency photocatalytic materials.

2. Experimental

All chemicals were of analytical grade and supplied by Shanghai Chemical Reagent Ltd. (P.R. China) and used as received without further purification. Distilled water was used in all experiments.

2.1. Preparation of g-C₃N₄ photocatalyst

The bulk g-C₃N₄ was synthesized via a simple calcination-hydrothermal procedure, using melamine powder as the precursor [47]. In a typical procedure, 10 g of melamine was calcined at 550 °C in a muffle furnace for 4 h in ambient atmosphere. After cooling to room temperature, the yellow product was collected and ground into powder for further use. In order to increase its specific surface area and form additional oxygen-containing functional groups on the surface, 0.5 g of g-C₃N₄ powder was dispersed into 70 mL of distilled water with constant stirring for 1 h, and then the mixture was autoclaved in a Teflon-lined stainless-steel autoclave at 180 °C for 2 h. After naturally cooling to room temperature, the precipitation was washed with distilled water three times, and dried at 60 °C overnight. Finally, the yellowish product was ground into powder.

2.2. Preparation of $\text{NiS}_2/\text{g-C}_3\text{N}_4$ composites

The $\text{NiS}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts were prepared by an impregnation method. In brief, 0.2 g of the above prepared $\text{g-C}_3\text{N}_4$ powder was uniformly dispersed into 10 mL of deionized water, and then stirred at room temperature for 10 min. Then, a known volume of $\text{Ni}(\text{NO}_3)_2$ solution (0.1 mol L^{-1}) was injected into the above suspension. After stirring for 10 min, a known amount of thioacetamide (TAA) solution (1 mol L^{-1}) was injected into the above suspension. After stirring again for another 10 min, the mixture was maintained at 80°C for 12 h. In this study, the weight ratio of Ni to $\text{g-C}_3\text{N}_4$ was variously controlled to be 0, 0.1, 0.5, 1, 2, 3, 5 and 10 wt%, and the corresponding samples were denoted $\text{NiS}_2/\text{g-C}_3\text{N}_4$ ($X \text{ wt}\%$), where X refers to the weight ratio of Ni to $\text{g-C}_3\text{N}_4$.

2.3. Characterization

X-ray diffraction (XRD) measurements were obtained on a Rigaku Ultima III X-ray Diffractometer (Japan) using $\text{Cu K}\alpha$ radiation. The morphology was observed by a JEM-7500F field emission scanning electron microscope (FESEM, JEOL, Japan). Further morphological and structural characterizations were based on transmission electron microscopy (TEM) and high-resolution transmission microscopy (HRTEM) using a JEM-2100F transmitting electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOA XSAM800 XPS system with $\text{Mg K}\alpha$ source. All of the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. Ultraviolet-vis (UV-vis) absorption spectra were obtained using a UV-vis spectrophotometer (UV-2450, Shimadzu, Japan). BaSO_4 was used as the reflectance standard in the UV-vis diffuse reflectance experiments.

2.4. Photocatalytic activity

Each photocatalytic H_2 -production experiment was conducted in a 100 mL three-necked Pyrex flask at ambient temperature and atmospheric pressure, and the outlets of the flask were sealed with a silicone rubber septum. Four low-power LEDs (3 W, 420 nm, Shenzhen Lamplic Science Co. Ltd., China) were used as the irradiation light sources to trigger the photocatalytic reaction. In a typical photocatalytic experiment, 50 mg of $\text{NiS}_2/\text{g-C}_3\text{N}_4$ photocatalytic powder was dispersed in 80 mL of 10 vol% lactic acid solution. Before each experiment, the system was bubbled with nitrogen for 30 min to remove the dissolved oxygen. During the process of irradiation, continuous stirring was applied to keep the photocatalyst particles in the suspension state. Finally, H_2 evolution was analyzed by a gas chromatograph (Shimadzu GC-1240, Japan, with nitrogen as a carrier gas) equipped with a 0.5 nm molecular sieve column and a thermal conductivity detector [48,49].

2.5. Photoelectrochemical measurements

Photoelectrochemical (PEC) measurements and electro-

chemical impedance spectra (EIS) were recorded using a standard three-electrode configuration with a platinum wire as the counter electrode, saturated $\text{Hg}/\text{Hg}_2\text{Cl}_2$ (in saturated KCl) as a reference electrode, and Na_2SO_4 (0.5 mol L^{-1}) aqueous solution as the electrolyte. The test results were recorded with an electrochemical workstation (CHI660E). The visible irradiation was provided by one 3-W LED (420 nm light source with a 90 mW cm^{-2} power). A fluorine-doped tin oxide (FTO) conductor glass was used as the working electrode. Typically, the sample powders (10 mg) were added into 1 mL of anhydrous ethanol and 1 mL of Nafion D-520 dispersion (5% w/w, in water and 1-propanol, Alfa Aesar) and then evenly dispersed by ultrasonication to obtain a suspension. The suspension was spread on $1 \text{ cm} \times 1 \text{ cm}$ FTO glass with the sides protected by Scotch tape, and then dried at 60°C for 24 h. A copper wire was linked to the side of the working electrode via conductive tape and the uncoated parts of the electrode were isolated with epoxy resin. Lastly, the transient photocurrent responses as a function of time ($i-t$ curves) of the working electrodes were measured at a 0.5 V bias potential during repeated ON/OFF illumination cycles, and the EIS were recorded over the frequency range of $0.01\text{--}10^5 \text{ Hz}$ with an ac amplitude of 10 mV at the open-circuit voltage.

3. Results and discussion

3.1. Synthesis and characterization of $\text{NiS}_2/\text{g-C}_3\text{N}_4$ photocatalyst

The synthetic procedure of the $\text{NiS}_2/\text{g-C}_3\text{N}_4$ photocatalyst is mild and facile, as schematically illustrated in Fig. 1. First, oxygen-containing functional groups (such as $-\text{OH}$ and $-\text{CONH}-$) were introduced to the surface of $\text{g-C}_3\text{N}_4$ after the $\text{g-C}_3\text{N}_4$ powders are processed by the hydrothermal method at 180°C for 2

Fig. 1. Schematic illustration of the synthesis of the $\text{NiS}_2/\text{g-C}_3\text{N}_4$ photocatalyst. (step 1) hydrothermal treatment of $\text{g-C}_3\text{N}_4$ to obtain $\text{g-C}_3\text{N}_4$ with various oxygen-containing groups; (step 2) electrostatic interaction between Ni^{2+} and $\text{g-C}_3\text{N}_4$ to obtain $\text{g-C}_3\text{N}_4/\text{Ni}^{2+}$; (step 3) addition of thioacetamide to produce NiS_2 on the surface of $\text{g-C}_3\text{N}_4$.

Fig. 2. XRD patterns of various samples. (1) g-C₃N₄; (2) NiS₂/g-C₃N₄(0.1 wt%); (3) NiS₂/g-C₃N₄(1 wt%); (4) NiS₂/g-C₃N₄(3 wt%); (5) NiS₂/g-C₃N₄(5 wt%).

h (step 1) (as confirmed by the XPS results). Subsequently, a g-C₃N₄/Ni²⁺ suspension was obtained via strong electrostatic interaction between g-C₃N₄ and Ni²⁺ ions upon the addition of Ni(NO₃)₂ solution (step 2). Moreover, the Ni²⁺ ions could also be easily adsorbed near the tri-s-triazine ring of g-C₃N₄ by attraction to N atoms with lone pairs of electrons. As a consequence, a tight coupling interaction between the g-C₃N₄ and Ni²⁺ was formed. Finally, NiS₂ nanoparticles were formed on the surface of g-C₃N₄ upon the addition of TAA followed by low-temperature treatment (80 °C) (step 3). Considering that the Ni²⁺ ions were homogeneously distributed on the surface of g-C₃N₄, and strongly bound to it, it is reasonable to deduce that the resultant NiS₂ cocatalyst was well dispersed on the surface of g-C₃N₄, forming the NiS₂/g-C₃N₄ photocatalyst.

The phase structure and composition of the as-prepared NiS₂/g-C₃N₄ and the pure g-C₃N₄ photocatalysts were analyzed by XRD, as shown in Fig. 2. The pure g-C₃N₄ exhibits two characteristic diffraction peaks, which are consistent with previous

literature [10]. Specifically, the weak peak at 13.2° represents typically-oriented melons (i.e., polymerized tri-s-triazine units), which can be indexed to the (100) facet, and the strong peak at 27.6° represents the interplanar stacking of aromatic units, corresponding to the (002) facet. In addition to the diffraction peaks of g-C₃N₄, further peaks can be detected for NiS₂/g-C₃N₄(1–5 wt %), as shown in Fig. 2. More specifically, peaks are clearly identified at 31.4°, 35.3°, 45.1°, 48.0° and 53.4°, which can be well indexed to pyrite-type NiS₂ (JCPDS No. 89-1495), with the lattice constant $a = 0.5678$ nm (space group: Pa3̄ (205)) [50]. Furthermore, no shift of the g-C₃N₄ diffraction peaks was observed, suggesting that no Ni or S doping occurred in the g-C₃N₄ structure under the low-temperature treatment. In the case of NiS₂/g-C₃N₄(0.1 wt%), no obvious diffraction peaks of NiS₂ can be seen, possibly resulting from the low content and high dispersion of NiS₂. From the analysis of the above results, it is evident that the NiS₂ nanoparticles were successfully modified on the surface of g-C₃N₄.

To further demonstrate the successful loading of NiS₂ on the surface of g-C₃N₄, the NiS₂/g-C₃N₄ samples were characterized by FESEM and HRTEM (Fig. 3). It can be seen that the morphology of the g-C₃N₄ sample was irregular, with a lamellar structure (Fig. 3(a)), which was produced during the hydrothermal synthesis of bulk g-C₃N₄. For the NiS₂/g-C₃N₄ samples, despite the presence of NiS₂ cocatalysts modified on the surface of g-C₃N₄, they still exhibited similar morphologies to the pure g-C₃N₄ sample because of the mildness of the modification process (Fig. 3(b)–(d)). Furthermore, in the EDS results (inset in Fig. 3), characteristic S and Ni peaks can be detected in the selected area, implying the presence of NiS₂ in these samples. By EDX analysis, the calculated atomic ratio of S to Ni is close to 2, verifying the presence of NiS₂. With increasing weight ratios of NiS₂ from 1 to 5 wt%, the amount ratio of Ni in the NiS₂/g-C₃N₄ samples gradually increased. To further illustrate the morphology and phase structure of the NiS₂ nanoparticles, their corresponding TEM images are shown in Fig. 3(e) and (f).

Fig. 3. FESEM images of g-C₃N₄ (a), NiS₂/g-C₃N₄(1 wt%) (b), NiS₂/g-C₃N₄(3 wt%) (c), NiS₂/g-C₃N₄(5 wt%) (d); TEM (e) and HRTEM (f) images of NiS₂/g-C₃N₄(3 wt%).

It is clear that the NiS₂ nanoparticles were homogeneously dispersed on the g-C₃N₄ surface, with sizes of less than 50 nm. The HRTEM image of NiS₂/g-C₃N₄(3 wt%) in Fig. 3(g) illustrates a lattice fringe spacing of 0.284 nm, which is associated with the (200) plane of NiS₂. Therefore, the above results strongly indicate that the NiS₂ nanoparticles were homogeneously loaded on the g-C₃N₄ surface by the facile impregnation method developed herein to form the NiS₂/g-C₃N₄ photocatalyst.

XPS was used to further confirm the surface microstructures of NiS₂ on the surface of g-C₃N₄. Fig. 4(a) shows the XPS survey spectra of the pure g-C₃N₄ and NiS₂/g-C₃N₄(3 wt%) samples, indicating that both samples contained the main peaks of the elements C and N, which arise from the g-C₃N₄ phase according to previous reports [51]. In addition to C, N and O, the elements Ni and S were found in the NiS₂-modified g-C₃N₄ samples. More detailed information on the elemental composition of the samples can be obtained from the corresponding high-resolution XPS spectra of C 1s, N 1s, O 1s, Ni 2p and S 2p. For C 1s, the samples show two distinct peaks at approximately 284.9 and 288.5 eV (Fig. 4(b)). Therein, the peak at 284.9 eV can be attributed to *sp*²-hybridized C–C bonds and arises from interference from the experimental equipment. The other peak, at 288.5 eV, can be ascribed to the *sp*²-bonded carbon in the triazine rings (N–C=N), indicating that this was the major carbon environment in the g-C₃N₄ [52–54]. The N 1s spectra of the samples (Fig. 4(c)) contain two main peaks centered at approximately 398.8 and 400.4 eV, corresponding to the *sp*²-bonded nitrogen in the N-containing aromatic rings (C–N=C) and tertiary nitrogen (N–(C)₃), respectively [51]. In the XPS spectra of O 1s (Fig. 4(d)), from the location of the peak at 532.5 eV it is evident that the valence state of O in the samples was –2, which can be ascribed to oxygen-containing functional groups (such as –OH and –CONH–) [55]. The Ni 2p and S 2p spectra of NiS₂/g-C₃N₄(3 wt%) (Fig. 4(e) and (f)) each contain clear peaks of those elements. The binding energies of Ni 2p_{3/2} and Ni 2p_{1/2} are ca.

Fig. 5. UV-vis spectra and corresponding photographs (inset) of various samples. (1) g-C₃N₄; (2) NiS₂/g-C₃N₄(0.1 wt%); (3) NiS₂/g-C₃N₄(1 wt%); (4) NiS₂/g-C₃N₄(3 wt%); and (5) NiS₂/g-C₃N₄(5 wt%).

856.2 and 873.8 eV, respectively, suggesting that the valence state of Ni was +2 [46]. The XPS spectrum of S 2p shows the two typical peaks at 162.5 and 163.7 eV that imply the presence of S–S bonds. The above results indicate the formation of NiS₂ on the surface of g-C₃N₄ in NiS₂/g-C₃N₄(3 wt%) [56,57].

The optical properties of the various samples are shown in Fig. 5. The absorption edge of pure g-C₃N₄ is at 460 nm, corresponding to a band gap of ca. 2.7 eV. After surface loading of the NiS₂ nanoparticles, the NiS₂/g-C₃N₄ samples showed no shift in the absorption edge, suggesting that neither Ni nor S had been doped into g-C₃N₄. However, the absorption at wavelengths above 460 nm was gradually enhanced with increasing content of NiS₂ in the NiS₂/g-C₃N₄ samples, which can be attributed to absorption by the NiS₂ cocatalyst [45]. In addition, the absorption intensity of the NiS₂/g-C₃N₄ samples in the visible region accorded well with the corresponding color of the as-prepared samples, which changed from yellow to black. The above results clearly suggest that the NiS₂ cocatalysts were successfully

Fig. 4. XPS survey spectra (a) and high-resolution XPS spectra of C 1s (b), N 1s (c), O 1s (d), Ni 2p (e) and S 2p (f) for g-C₃N₄ (1) and NiS₂/g-C₃N₄(3 wt%) (2).

modified on the surface of g-C₃N₄.

3.2. Photocatalytic performance and mechanism

The photocatalytic performances of the various samples were compared by quantifying the evolution of H₂ under visible light, as shown in Fig. 6(a). From this histogram, we can see that the pure g-C₃N₄ sample had only a trace ability to photocatalyze H₂ evolution. However, the photocatalytic performances of all the synthesized NiS₂/g-C₃N₄ samples exhibited obvious enhancements compared with the pure g-C₃N₄ sample because of the presence of the highly efficient cocatalyst, which is in good agreement with previously reported results [46]. Specifically, the photocatalytic performance reached its maximum value of 116.343 $\mu\text{mol h}^{-1} \text{g}^{-1}$ when the Ni content was 3 wt%, a considerable improvement over the pure g-C₃N₄. Further increasing the amount of NiS₂, however, led to a slight decline in the photocatalytic performance, which is consistent with many previously reported cocatalyst-modified photocatalysts [45,58–61]. To evaluate the stability of the photocatalytic H₂-evolution performance of the NiS₂/g-C₃N₄ samples, and hence their reusability, a recycling test of the NiS₂/g-C₃N₄(3 wt%) sample performance was performed, as shown in Fig. 6(b). The results showed that this sample could maintain a stable and effective photocatalytic performance under visible-light irradiation for 12 h.

On the basis of the above results, it can be clearly seen that NiS₂/g-C₃N₄ photocatalysts obtained by the mild and facile synthesis method showed improved photocatalytic H₂-evolution activity compared with the g-C₃N₄ photocatalysts. We therefore investigated the mechanism of the improved photocatalytic performance of our samples; the proposed mechanism is shown in Fig. 7. Under visible-light irradiation, the excitation of g-C₃N₄ generated electron-hole pairs. Evidently, owing to the rapid recombination of the photogenerated electrons and holes and the lack of sufficient reactive sites, the pure g-C₃N₄ exhibited a poor ability to photocatalyze the pro-

Fig. 7. Schematic diagram illustrating the photocatalytic H₂-evolution mechanism of NiS₂/g-C₃N₄ photocatalyst. (1) rapid transfer of photo-generated electrons from g-C₃N₄ to the NiS₂ cocatalyst via the close and continuous contact between them; (2) rapid reaction of the photogenerated electrons with H₂O adsorbed on the surface of NiS₂, which has a surficial metallic character and high catalytic activity, to produce H₂.

duction of H₂. In our modified photocatalysts, the photogenerated electrons in g-C₃N₄ could rapidly transfer to the NiS₂ nanoparticles via the close and continuous contact between them. Then, the photogenerated electrons rapidly reacted with H₂O adsorbed on the surface of NiS₂, which has a surficial metallic character and high catalytic activity, to produce H₂. As a result, our NiS₂/g-C₃N₄ photocatalysts exhibited high photocatalytic activity during H₂ production. Thus, the improved H₂-evolution performance of the NiS₂/g-C₃N₄ accrued from the rapid interfacial charge transfer and catalytic reaction. Furthermore, because of the mild synthesis method, the possibility can be excluded that the improved photocatalytic performance was derived from changes of the g-C₃N₄ microstructures during the preparation of NiS₂/g-C₃N₄.

The above photocatalytic mechanism can be further verified

Fig. 6. (a) Photocatalytic H₂-evolution activities of various samples. (1) g-C₃N₄; (2) NiS₂/g-C₃N₄(0.1 wt%); (3) NiS₂/g-C₃N₄(0.5 wt%); (4) NiS₂/g-C₃N₄(1 wt%); (5) NiS₂/g-C₃N₄(2 wt%); (6) NiS₂/g-C₃N₄(3 wt%); (7) NiS₂/g-C₃N₄(5 wt%); and (8) NiS₂/g-C₃N₄(10 wt%). (b) Cycling stability of photocatalytic H₂ evolution by the NiS₂/g-C₃N₄(3 wt%) photocatalyst.

Fig. 8. Typical transient photocurrent responses (a) and electrochemical impedance spectra (b) of g-C₃N₄ (1) and NiS₂/g-C₃N₄(3 wt%) (2).

by PEC analysis under visible light, which is one of the most powerful techniques to study the interfacial charge transfer and recombination rates occurring in three-electrode systems. The transient photocurrent–time (i – t) curves recorded for two samples under intermittent visible-light irradiation ($\lambda > 420$ nm) are presented in Fig. 8(a). It can be clearly seen that the photocurrent of the NiS₂/g-C₃N₄ sample was higher than that of the g-C₃N₄, indicating that the NiS₂ cocatalyst efficiently enhanced the interfacial charge transfer. These PEC results suggest that the NiS₂-modified g-C₃N₄ photocatalysts could achieve markedly improved separation and transfer of the photogenerated electron-hole pairs, thus greatly contributing to the enhanced photocatalytic performance. Moreover, it can be seen that the arc radius on the EIS plots of the NiS₂/g-C₃N₄(3 wt%) photocatalyst was smaller than that of g-C₃N₄ under visible light (Fig. 8(b)), suggesting a smaller charge-transfer resistance on the electrode surface of the NiS₂/g-C₃N₄ photocatalyst. This again facilitated the rapid transfer of the photoinduced electron-hole pairs through an interfacial interaction between g-C₃N₄ and the NiS₂ nanoparticles.

4. Conclusions

A mild and facile impregnation method was developed to prepare NiS₂/g-C₃N₄ photocatalysts. The NiS₂ cocatalysts were closely and continuously deposited on the surface of g-C₃N₄. The NiS₂/g-C₃N₄ photocatalysts showed markedly greater photocatalytic performance during H₂ production than pure g-C₃N₄ under visible-light irradiation. The improved photocatalytic performance of NiS₂/g-C₃N₄ accrued from the rapid interfacial charge transfer and catalytic reaction. Considering the facile and economic synthetic method presented here for NiS₂ modification on the surface of g-C₃N₄ photocatalysts, the as-prepared NiS₂/g-C₃N₄ photocatalysts show promise for practical use in water splitting to produce H₂.

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Graphical Abstract

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Facile synthesis and enhanced photocatalytic H₂-evolution performance of NiS₂-modified g-C₃N₄ photocatalysts

Feng Chen, Hui Yang, Xuefei Wang *, Huogen Yu *

Wuhan University of Technology

NiS₂-modified g-C₃N₄ photocatalysts were synthesized by a low-temperature impregnation method. The resultant NiS₂/g-C₃N₄ photocatalysts showed improved photocatalytic performance resulting from the rapid transfer of the photogenerated electrons of g-C₃N₄ to the NiS₂ nanoparticles.

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NiS₂ 助剂修饰 g-C₃N₄ 光催化剂的简易合成及光催化制氢性能增强研究

陈 峰^a, 杨 慧^a, 王雪飞^{a,*}, 余火根^{a,b,#}

^a武汉理工大学化学, 化工与生命科学学院, 湖北武汉 430070

^b武汉理工大学硅酸盐国家重点实验室, 湖北武汉 430070

摘要: g-C₃N₄ 是一种新型的稳定的半导体光催化材料, 它可以通过热缩聚法、固相反应法、电化学沉积法和溶剂热法等制备. g-C₃N₄ 禁带宽度约为 2.7 eV, 吸收边在 460 nm 左右, 具有合适的导带位置, 可用作可见光响应制氢的光催化材料, 但在实际应用中 g-C₃N₄ 光催化性能较低, 其原因可归纳为: (1) g-C₃N₄ 在吸收光子产生电子和空穴对后, 光生载流子的传输速率较慢, 容易在体相或表面复合, 致使 g-C₃N₄ 的量子效率较低; (2) 材料在合成过程中易于结块, 使 g-C₃N₄ 的比表面积远小于理论值, 严重削弱了 g-C₃N₄ 光催化材料的制氢性能. 目前已有许多关于 g-C₃N₄ 改性的报道, 但一些方法对材料的处理过程耗时较长或者合成过程较难控制. 用助剂改性是提高光催化制氢活性的半导体材料的主要策略之一. 合适的助剂可改进电荷分离和加速表面催化反应, 从而提高光催化剂的制氢活性. 虽然稀有金属或贵金属, 如铂、金和银可大大提高 g-C₃N₄ 的制氢速率, 但由于其昂贵和稀缺性, 因而应用严重受限. 因此, 开发成本低、储量丰富、高性能助剂来进一步提高制氢性能具有重要意义.

NiS₂ 来源丰富、价格低廉. 它可在酸性和碱性的环境保持相对较高的稳定性, 且其表面电子结构表现出类金属特性. 但它较难与半导体光催化剂形成强耦合和界面, 通常需要水热等条件下合成. 实验表明, g-C₃N₄ 表面存在着大量的含氧官能团及未缩合的氨基基团, 为表面接枝提供了丰富的反应活性位点, 因而可利用 g-C₃N₄ 表面均匀分布的含氧官能团等和 Ni²⁺ 结合, 再原位与 S²⁻ 反应, 从而在 g-C₃N₄ 上负载耦合紧密的 NiS₂ 助剂, 进一步提高复合材料的光催化制氢活性.

本文采用低温浸渍法制备了 NiS₂/g-C₃N₄ 光催化剂. NiS₂ 助剂在温和的反应条件下与 g-C₃N₄ 光催化剂复合, 可以防止催化剂结构的破坏, 同时使得助剂均匀地分散, 并紧密结合在催化剂表面, 从而大大提高光催化剂的制氢性能. 该样品制备过程为: (1) 通过水热处理制备含氧官能团和较大比表面积的 g-C₃N₄; (2) 添加 Ni(NO₃)₂ 前驱体后, Ni²⁺ 离子由于静电作用紧密吸附在 g-C₃N₄ 表面; (3) 在 80 °C 加入硫代乙酰胺 (TAA), 可在 g-C₃N₄ 的表面紧密和均匀形成助剂 NiS₂. 表征结果证实成功制备 NiS₂ 纳米粒子修饰的 g-C₃N₄ 光催化剂. 当 Ni 含量为 3 wt%, 样品表现出最大的制氢速率 (116 μmol h⁻¹ g⁻¹), 明显高于纯 g-C₃N₄. 此外, 对 NiS₂/g-C₃N₄ (3 wt%) 的样品进行光催化性能的循环测试结果表明: 该样品在可见光照射下可以保持一个稳定的、有效的光催化制氢性能. 根据实验结果, 我们提出一个可能的光催化机理: 即 NiS₂ 促进了物质表面快速转移光生电子, 使 g-C₃N₄ 光生电荷有效分离. 基于 NiS₂ 具有成本低和效率高的优点, 因而有望广泛应用于制备高性能的光催化材料.

关键词: 光催化; NiS₂; 石墨化氮化碳; 助剂; 可见光催化制氢

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*通讯联系人. 电话: 13387570017; 传真: (027)87879468; 电子信箱: xuefei@whut.edu.cn

#通讯联系人. 电话: (027)87871029; 传真: (027)87879468; 电子信箱: yuhuogen@whut.edu.cn

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