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Article

Sulfur-mediated photodeposition synthesis of NiS cocatalyst for boosting H₂-evolution performance of g-C₃N₄ photocatalyst

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ABSTRACT

Modification of nickel sulfide cocatalysts is considered to be a promising approach for efficient enhancement of the photocatalytic hydrogen production performance of g-C₃N₄. Providing more NiS cocatalyst to function as active sites of g-C₃N₄ is still highly desirable. To realize this goal, in this work, a facile sulfur-mediated photodeposition approach was developed. Specifically, photogenerated electrons excited by visible light reduce the S molecules absorbed on g-C₃N₄ surface to S²⁻, and subsequently NiS cocatalyst is formed in situ on the g-C₃N₄ surface by a combination of Ni²⁺ and S²⁻ due to their small solubility product constant ($K_{sp} = 3.2 \times 10^{-19}$). This approach has several advantages. The NiS cocatalyst is clearly in situ deposited on the photogenerated electron transfer sites of g-C₃N₄, and thus provides more active sites for H₂ production. In addition, this method utilizes solar energy with mild reaction conditions at room temperature. Consequently, the synthesized NiS/g-C₃N₄ photocatalyst achieves excellent hydrogen generation performance with the performance of the optimal sample (244 $\mu\text{mol h}^{-1} \text{g}^{-1}$) close to that of 1 wt% Pt/g-C₃N₄ (316 $\mu\text{mol h}^{-1} \text{g}^{-1}$, a well-known excellent photocatalyst). More importantly, the present sulfur-mediated photodeposition route is versatile and facile and can be used to deposit various metal sulfides such as CoS_x, CuS_x and AgS_x on the g-C₃N₄ surface, and all the resulting metal sulfide-modified g-C₃N₄ photocatalysts exhibit improved H₂-production performance. Our study offers a novel insight for the synthesis of high-efficiency photocatalysts.

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1. Introduction

Graphitic carbon nitride (g-C₃N₄) has attracted attention of a wide range of researchers since Wang first reported its application in photocatalytic hydrogen evolution in 2009 [1]. As a nonmetallic polymer semiconductor consisting of tri-s-triazine units connected via bridging nitrogen, g-C₃N₄ possesses excel-

lent properties including strong visible light adsorption, narrow bandgap (2.7 eV), chemical stability due to the van der Waals interlayer interactions, and thermal stability due to the high degree of condensation and the strong C–N bond [2–6]. In addition, g-C₃N₄ can be easily fabricated at low cost because it is composed of the abundant carbon and nitrogen elements. Nevertheless, rapid photogenerated carrier recombination

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leads to its poor photocatalytic H_2 production performance [7–14]. To date, the substantial research effort devoted to $g-C_3N_4$ has revealed that the use of an appropriate cocatalyst such as Pt can remarkably improve its photocatalytic H_2 -production rate because the cocatalyst not only facilitates interfacial charge migration and separation but also provides reaction sites for the H_2 production reaction [15]. It is clear that the high cost and the limited sources of noble-metal cocatalysts severely limit their practical use [16–19]. Therefore, the development and use of cost-effective and high-efficiency cocatalysts with long-term stability is important for the practical application of $g-C_3N_4$ in photocatalytic H_2 production [20–23].

Recent studies have shown that nickel sulfide (NiS) cocatalyst can effectively increase the photocatalytic hydrogen production activity of $g-C_3N_4$ [24,25]. The main reasons for this effect are as follows. (1) NiS cocatalyst displays high electrical conductivity due to the metallic character of its electronic structure, and such high conductivity promotes interfacial charge transport and carrier separation [26,27]. (2) NiS cocatalyst displays smaller Ni–H bond activation energy and lower overpotential for the hydrogen production reaction, and thus it can remarkably increase the H_2 -production rate [28,29]. (3) NiS cocatalyst can act as an electron-trapping agent and a reactive site for H_2 production, and therefore promotes interfacial charge transfer and separation [30,31]. Additionally, nontoxicity, abundant mineral resources and relatively strong stability enable its use in practical applications [32]. Therefore, NiS cocatalyst is considered to be an ideal substitute for noble metal cocatalysts. During past several years, an increasing number of studies have been carried out for the synthesis of NiS-modified $g-C_3N_4$. Various synthetic methods including the precipitation approach, the hydrothermal method and the calcination method have been developed [33–35]. Compared to the above approaches, photodeposition possesses unique advantages [36–38]. For example, photodeposition is a green and mild method because only solar energy and room temperature are needed. Additionally, photodeposition can realize in situ and solid cocatalyst modification on the surface of the photocatalysts because the cocatalysts are formed by utilizing the corresponding photogenerated electrons or holes on the surface of the photocatalysts. However, the use of photodeposition to modify the NiS cocatalyst on the $g-C_3N_4$ surface has been rarely reported. This may be due to the difficulty of the design of a suitable photodeposition system for NiS cocatalyst because the strong reduction and oxidation ability of the photogenerated electrons and holes of $g-C_3N_4$ can give rise to side reactions such as Ni^{2+} reduction and S^{2-} oxidation.

In this study, a novel and facile sulfur-mediated photodeposition approach is designed and used to achieve the modification of NiS cocatalyst on $g-C_3N_4$ surface using nickel nitrate hexahydrate, sulfur and $g-C_3N_4$ as the precursors. Here, sulfur molecules combine with Ni^{2+} and the photogenerated electrons to produce NiS cocatalysts when $g-C_3N_4$ is irradiated by visible light, because the potential of NiS/S (0.096 V vs. NHE) is more positive than those of Ni^{2+}/Ni (−0.23 V vs. NHE) and S/S^{2-} (−0.45 V vs. NHE). It is clear that the sulfur-mediated strategy restrains the side reaction such as metallic Ni formation.

Moreover, the NiS cocatalyst formed by using this approach can remarkably boost the hydrogen-evolution rate of $g-C_3N_4$. More importantly, our present synthetic strategy can be used as a versatile approach to achieve the modification of other metal sulfide cocatalysts (CoS_x , CuS_x , AgS_x , etc.) on $g-C_3N_4$.

2. Experimental

All of the reagents used in this study were of analytical grade, were supplied by Shanghai Chemical Reagent, Ltd. (China) and were used without further purification. Deionized water was used in all of the experiments.

2.1. Synthesis of $g-C_3N_4$ photocatalyst

The bulk $g-C_3N_4$ photocatalyst was synthesized by a thermal polycondensation approach according to the previous reported procedure [39,40]. Typically, melamine precursor was calcined at 550 °C for 4 h and the heating rate was set to 5 °C min^{−1}. Subsequently, a light-yellow product was obtained and ground into the $g-C_3N_4$ powder.

2.2. Synthesis of NiS/ $g-C_3N_4$ photocatalyst

The NiS/ $g-C_3N_4$ photocatalyst was synthesized via a facile sulfur-mediated photodeposition method. In this process, a certain amount of S powder was first dissolved in ethanol (80 mL) by heating at 60 °C in the water bath. Next, a certain amount of $Ni(NO_3)_2$ ethanol solution (0.1 mol L^{−1}) was injected to the above solution with stirring for 30 min at room temperature (the molar ratio of S to Ni is fixed to 2). Subsequently, $g-C_3N_4$ powder (0.3 g) was dispersed in the above solution with continuous stirring for 1 h. The above suspension was bubbled with N_2 for 30 min to remove the dissolved oxygen and was irradiated by LED lamps ($\lambda = 420$ nm) for 3 h. Finally, the NiS/ $g-C_3N_4$ samples were obtained by centrifuging at 8000 r min^{−1} for 30 min, washing three times with ethanol, and drying overnight in an oven at 60 °C. In this study, the theoretical mass ratios of Ni to $g-C_3N_4$ were controlled to be 0.05, 0.1, 0.3, 0.5, 1, and 3 wt%, and the corresponding samples were denoted as NiS/ $g-C_3N_4$ (X wt%).

For comparison, the NiS/ $g-C_3N_4$ photocatalysts were also synthesized via a wet-chemistry method at room temperature [33]. First, $g-C_3N_4$ powder (0.3 g) was dispersed in deionized water (80 mL). A certain amount of 0.1 mol L^{−1} $Ni(NO_3)_2$ solution was first dropped into the above-mentioned suspension with stirring for 20 min. Then, 0.1 mol L^{−1} Na_2S solution was dropped into the above suspension (the molar ratio of S to Ni is fixed to 1.2), and the suspension solution was stirred for another 2 min. The NiS/ $g-C_3N_4$ photocatalyst was obtained by centrifuging at 8000 r min^{−1} for 1 min and washing three times with ethanol. Finally, the sample was dried overnight in an oven at 60 °C.

2.3. Characterization

The morphology and microstructure of the photocatalysts

were revealed by FESEM electron microscopy (JEOL, Japan) and TEM (Thermo Fisher, USA), respectively. The phase compositions were investigated by XRD (RIGAKU, Japan) using Cu $K\alpha$ radiation. The surface information was obtained using a KRATOA XSAM800 XPS system with Mg $K\alpha$ source radiation, and binding energies were adjusted using the standard C 1s peak (284.8 eV). The Fourier transform infrared (FTIR) spectra were obtained using a Nexus FTIR spectrophotometer (Thermo Nicolet, USA), and the UV-vis diffuse reflectance spectra (DRS) were acquired using a UV-2450 instrument (Shimadzu, Japan). BaSO₄ was used as the reflectance standard in the UV-vis diffuse reflectance experiments.

2.4. Photocatalytic H₂-evolution activity

The photocatalytic H₂ production experiments were performed in a three-necked Pyrex flask (100 mL) at ambient temperature. Four 420 nm LED lamps (3 W, 80 mW cm⁻², Shenzhen Lamplic Science Co. Ltd., China) served as the irradiation sources of the photocatalytic reaction. They were located at 1 cm from the reactor in four different directions. In this experiment, the photocatalyst (50 mg) was dispersed in triethanolamine (10 vol%, 80 mL). Prior to each experiment, the system was first bubbled with nitrogen for 30 min to remove the dissolved gas impurities. During the irradiation, continuous stirring enabled the photocatalytic system to maintain the suspension. Gas (0.4 mL) was intermittently sampled and the H₂ production amount was tested using a gas chromatography system (Shimadzu GC-14C, Japan, with nitrogen as a carrier gas) equipped with a 5 Å molecular sieve column and a thermal conductivity detector.

2.5. Photoelectrochemical measurements

The photoelectrochemical performance measurements were performed in a standard three-electrode configuration with a platinum wire as the counter electrode, saturated Hg/Hg₂Cl₂ (in saturated KCl) as the reference electrode, sample-loaded FTO conductor glass as the working electrode and Na₂SO₄ (0.5 mol L⁻¹) aqueous solution as the electrolyte. The

test results were obtained using an electrochemical workstation (CHI660E). The light source was provided by a 420 nm LED lamp (3 W, 80 mW cm⁻²). Typically, the samples (10 mg) were added into anhydrous ethanol (2.5 mL) and Nafion D-520 dispersion (2.5 mL, 5% w/w, in water and 1-propanol, Alfa Aesar) and then uniformly dispersed by ultrasound to obtain a suspension. The suspension was spread on a fixed 1 × 1 cm FTO glass with the side protected by Scotch tape and then dried overnight at 60 °C. Prior to each measurement, the electrolyte was bubbled with nitrogen for 15 min to remove the dissolved oxygen. During each measurement, the electrolyte was bubbled with nitrogen continuously. Finally, the transient photocurrent responses of the working electrodes as a function of time (*i*-*t* curve) were measured at a 0.5 V bias potential during repeated ON/OFF illumination cycles. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.001–10⁶ Hz.

3. Results and discussion

3.1. Synthetic strategy of NiS/g-C₃N₄ photocatalyst

The schematic illustration of our facile sulfur-mediated photodeposition approach is shown in Fig. 1(A). First, S molecules and Ni²⁺ are absorbed on the g-C₃N₄ surface in the ethanol system (Fig. 1(A), (1)). Second, S²⁻ ions are formed by the reduction of the S molecules with the photogenerated electrons of g-C₃N₄ under visible-light irradiation (Fig. 1(A), (2)). Consequently, the NiS cocatalyst is deposited on the g-C₃N₄ surface by combining the S²⁻ and Ni²⁺ ions. Clearly, in our strategy, S molecules play an important role in mediating the formation of the NiS cocatalyst. As shown in Fig. 1B, g-C₃N₄ possesses the conduction band (CB) potential of approximately -1.1 V vs. NHE [2] and the corresponding photogenerated electrons can easily reduce S to S²⁻ (-0.45 V vs. NHE) and Ni²⁺ to Ni (-0.23 V vs. NHE). As shown in Figs. 1(B) (a) and (b), since g-C₃N₄ sample only reduces the S molecules to S²⁻ ions, the color of suspension does not change. However, it is found that the light yellow g-C₃N₄ sample (Fig. 1(B), (a)) becomes light green after the introduction of the Ni(NO₃)₂ ethanol solution under visi-

Fig. 1. (A) Schematic illustration of the synthesis of NiS/g-C₃N₄ in an ethanol system; (B) Schematics of g-C₃N₄ suspension (a), S²⁻/g-C₃N₄ suspension (b), Ni/g-C₃N₄ suspension (c), and NiS/g-C₃N₄ suspension (d) and corresponding redox potentials; (C) Schematic illustration of the formation of the NiS/g-C₃N₄ sample and the proposed photocatalytic hydrogen-generation mechanism of NiS/g-C₃N₄.

ble-light radiation (Fig. 1(B), (c)). Considering that $E^0(\text{S}/\text{S}^{2-})$ is more negative than $E^0(\text{Ni}^{2+}/\text{Ni})$, it is expected that Ni^{2+} should be preferentially reduced to Ni in the presence of both S molecules and Ni^{2+} ions. However, different from the above analysis, when S and Ni^{2+} co-exist, the suspension clearly changes to black color under visible-light irradiation (Fig. 1(B), (d)), suggesting that NiS cocatalyst is formed while the formation of metallic Ni is suppressed. The above results indicate that a S-mediated effect facilitates the formation of the NiS cocatalyst since $E^0(\text{S}/\text{NiS})$ (0.096 V) is more positive than $E^0(\text{Ni}^{2+}/\text{Ni})$ according to $E^0(\text{S}/\text{NiS}) = E^0(\text{S}/\text{S}^{2-}) + (RT/2F)\ln K_{\text{sp}}$ ($K_{\text{sp}}(\alpha\text{-NiS}) = 3.2 \times 10^{-19}$), as shown in the Eq. (1) of Fig. 1(B). Additionally, according to the formation process of the NiS cocatalyst, it is clear that the above NiS cocatalyst can be only selectively and preferentially deposited on the electron-enriched active sites of the g-C₃N₄ surface. In this case, during the following photocatalytic H₂-evolution process, the resulting NiS cocatalyst can act as the effective active sites to further increase the number of the electrons photogenerated from bulk g-C₃N₄, boosting the interfacial H₂-evolution rate (Fig. 1(C)).

3.2. Morphology and microstructure of NiS/g-C₃N₄

To verify the effectiveness of our synthetic strategy, the morphology and elements of the as-prepared samples were first observed by FESEM and EDS. As observed from Fig. 2(A), g-C₃N₄ shows an irregular blocky morphology that is attributed to the stacking of lamellar structures. NiS/g-C₃N₄ samples show similar morphology to that of g-C₃N₄ (Fig. 2(B)–(D)), demonstrating that our approach does not alter the structure of g-C₃N₄. However, no NiS cocatalyst is observed in the NiS/g-C₃N₄ samples, which may be due to their small particle sizes. Nevertheless, the EDS spectra of NiS/g-C₃N₄ clearly re-

veal the S and Ni signals in addition to the C and N signals, suggesting the existence of Ni and S elements in the as-prepared samples. Additionally, the EDS results show that the content of Ni and S elements gradually increases from NiS/g-C₃N₄(0.3 wt%) to NiS/g-C₃N₄(3 wt%). To further obtain the microstructure of NiS/g-C₃N₄, TEM/HRTEM images of the NiS/g-C₃N₄(1 wt%) were obtained. As shown in Fig. 2(E), some nanoparticles with the size range of 10–90 nm (shown in red circles) are dispersed on the g-C₃N₄ surface. As displayed in Fig. 2(F), the lattice spacing for the nanoparticles is *ca.* 0.196 nm and can be assigned to the (102) plane of hexagonal NiS ($\alpha\text{-NiS}$) [30,41].

To obtain their phase structures, the as-prepared samples were characterized by XRD (Fig. 3), and the two diffraction peaks observed at 27.6° and 13.2° were assigned to the (002) and (100) crystal planes of g-C₃N₄, respectively [42–47]. For NiS/g-C₃N₄(*X* wt%), the intensities and positions of the diffraction peaks do not show an obvious shift relative to g-C₃N₄, implying that this approach does not affect the structure of g-C₃N₄. However, no NiS peak was detected most likely due to its low degree of crystallinity deduced from the HRTEM image of the NiS/g-C₃N₄(1 wt%).

XPS measurements were used to analyze the surface chemical status of the NiS/g-C₃N₄ samples. It was observed that g-C₃N₄ samples are mainly composed of the C, N and O elements, and NiS/g-C₃N₄(*X* wt%, *X* = 0.3, 1 and 3) mainly consists of the C, N, Ni and S elements (Fig. 4(A)). The high-resolution XPS spectra of C 1s, N 1s, O 1s, Ni 2p, and S 2p further demonstrate the state of the elements in NiS/g-C₃N₄ (Fig. 4(B)–(F)). The C 1s peaks at 283.4 and 286.7 eV observed in Fig. 4(B) are attributed to impure carbon and the *sp*²-bonded carbon in the N–C=N triazine rings, respectively [48,49]. Four fitted characteristic peaks with binding energies of 397.2, 398.0, 399.4 and 403.1 eV are observed in the N 1s XPS spectra (Fig. 4(C)), cor-

Fig. 2. FESEM/EDS images of various samples. (A) g-C₃N₄; (B) NiS/g-C₃N₄(1 wt%); (C) NiS/g-C₃N₄(3 wt%); (D) NiS/g-C₃N₄(5 wt%). TEM (E) and HRTEM (F) images of NiS/g-C₃N₄(1 wt%).

Fig. 3. XRD patterns of various samples. (a) g-C₃N₄; (b) NiS/g-C₃N₄(0.1 wt%); (c) NiS/g-C₃N₄(0.3 wt%); (d) NiS/g-C₃N₄(1 wt%); (e) NiS/g-C₃N₄(3 wt%).

responding to the characteristics of the sp^2 -bonded nitrogen (C–N=C) in the triazine rings, tertiary nitrogen bonded to carbon (N–(C)₃), unreacted amino groups (C–N–H) and the charging effects in heterocycles, respectively [50–52]. For the O 1s spectra, the peak at 532.5 eV originates from the oxygen-containing intermediates [53,54]. The Ni 2p spectra exhibit two main peaks located at 855.5 and 873.1 eV (Fig. 4(E)) that are consistent with Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺. Another two peaks at 860.9 and 879.2 eV are attributed to the satellite peaks of Ni 2p_{3/2} and Ni 2p_{1/2} of Ni²⁺. The above results indicate that the nickel element of NiS/g-C₃N₄ exists in the Ni²⁺ form according to the reports in the literature [55,56]. In addition, two weaker peaks of NiS/g-C₃N₄(3 wt%) at 852.2 and 869.6 eV are observed that can be attributed to Ni⁰ 2p_{3/2} and Ni⁰ 2p_{1/2}, respectively [57,58]. This indicates the presence of metallic Ni due to the partial reduction of Ni²⁺ under a large loading [59].

Table 1

Elemental content (at%) of the various samples based on the XPS results.

Sample	C	N	O	Ni	S
g-C ₃ N ₄	43.95	53.06	2.99	0	0
NiS/g-C ₃ N ₄ (0.3 wt%)	44.78	49.77	4.07	0.65	0.73
NiS/g-C ₃ N ₄ (1 wt%)	44.33	45	7.30	1.7	1.67
NiS/g-C ₃ N ₄ (3 wt%)	42.62	43.96	8.46	2.18	2.78

In Fig. 4F, two local peaks for S 2p at 160.4 and 161.6 eV are assigned to S²⁻ [60–62]. An examination of the data presented in Table 1 shows that the atomic percentages of Ni and S increase with increasing loading amounts. Based on the above analysis, the XPS measurements confirmed that NiS cocatalyst was successfully anchored on the g-C₃N₄ photocatalyst.

The functional groups of the NiS/g-C₃N₄ samples can be studied by the FTIR spectra (Fig. 5(A)), and the g-C₃N₄ includes the tri-s-triazine structure (808 cm⁻¹), the CN heterocycles (1242, 1410 and 1635 cm⁻¹) and the unreacted amino functional groups (in the range of 3100–3300 cm⁻¹). Those peaks are in agreement with the FTIR spectra of g-C₃N₄ synthesized melamine calcining in previous studies [63,64]. The characteristic peaks of NiS cannot be detected in all of the NiS/g-C₃N₄ samples due to the low content of the NiS cocatalyst. The optical properties of various samples were characterized by UV-vis DRS. As shown in Fig. 5(B), g-C₃N₄ displays an absorption edge at ca. 460 nm, in agreement with the band gap of g-C₃N₄ (2.7 eV). Moreover, other NiS/g-C₃N₄ samples exhibit an additional absorption region (450–800 nm) due to the modification of the NiS cocatalyst. Moreover, the light absorption intensity gradually increases with increasing content of the NiS cocatalyst. The

Fig. 4. (A) Full-range XPS spectra and the high-resolution XPS spectra of C 1s (B), N 1s (C), O 1s (D), Ni 2p (E) and S 2p (F) for various samples. (a) g-C₃N₄; (b) NiS/g-C₃N₄(0.3 wt%); (c) NiS/g-C₃N₄(1 wt%); (d) NiS/g-C₃N₄(3 wt%).

Fig. 5. (A) FTIR spectra, and (B) UV-vis absorption spectra and photographs (inset) of various samples: (a) g-C₃N₄, (b) NiS/g-C₃N₄(0.05 wt%), (c) NiS/g-C₃N₄(0.1 wt%), (d) NiS/g-C₃N₄(0.3 wt%), (e) NiS/g-C₃N₄(1 wt%) and (f) NiS/g-C₃N₄(3 wt%).

above results were verified by the color change. It is clearly observed from the inset in Fig. 5(B) that the color of NiS/g-C₃N₄ transforms into dark black from initial light yellow of g-C₃N₄, demonstrating the successful loading of the NiS cocatalyst on the g-C₃N₄ photocatalyst.

3.3. Photocatalytic H₂-evolution performance of NiS/g-C₃N₄ photocatalyst

The H₂-evolution rates of various samples were measured under visible-light irradiation ($\lambda = 420$ nm). For comparison, the hydrogen generation performance over the Pt/g-C₃N₄(1 wt%) sample synthesized by photodeposition was also tested under the same conditions. It is clear that NiS/g-C₃N₄ samples exhibit superior photocatalytic H₂ evolution performance compared to the pristine g-C₃N₄ (Fig. 6(A)), demonstrating that NiS is a high-efficiency cocatalyst. Specifically, NiS/g-C₃N₄(0.3 wt%) reaches the maximum H₂-production rate (ca. 244 $\mu\text{mol h}^{-1} \text{g}^{-1}$) that approaches that of 1 wt% Pt/g-C₃N₄ (ca. 316 $\mu\text{mol h}^{-1} \text{g}^{-1}$).

However, the hydrogen generation rate of NiS/g-C₃N₄(0.3 wt%) synthesized via the wet-chemistry method is only approximately 111 $\mu\text{mol h}^{-1} \text{g}^{-1}$, which is clearly lower than that of our NiS/g-C₃N₄(0.3 wt%). Moreover, a recycling test of NiS/g-C₃N₄(0.3 wt%) sample was conducted to confirm the hydrogen production stability of the NiS/g-C₃N₄ samples (Fig. 6(B)). Notably, the NiS/g-C₃N₄ samples still maintain relatively stable photocatalytic performance after five cycles, implying that NiS/g-C₃N₄ possesses excellent stability. To understand the origin of the enhanced photocatalytic performance, the PEC (*i-t*) curves of g-C₃N₄ and NiS/g-C₃N₄(0.3 wt%) were measured to determine their charge separation characteristics. The PEC (*i-t*) curves for g-C₃N₄ and NiS/g-C₃N₄(0.3 wt%) under intermittent irradiation ($\lambda = 420$ nm) are shown in Fig. 6(C). It is observed that the photocurrent density of NiS/g-C₃N₄(0.3 wt%) is higher than that of g-C₃N₄. That is to say, the photogenerated electrons and holes are separated effectively due to the electron transfer from g-C₃N₄ to the NiS cocatalyst [65]. The accumulated electrons on the NiS

Fig. 6. (A) Photocatalytic H₂-evolution rate of various samples. (B) Recycling test of NiS/g-C₃N₄(0.3 wt%) sample; (C) Transient photocurrent responses; (D) Electrochemical impedance spectra curves. (a) g-C₃N₄; (b) NiS/g-C₃N₄(0.05 wt%); (c) NiS/g-C₃N₄(0.1 wt%); (d) NiS/g-C₃N₄(0.3 wt%); (e) NiS/g-C₃N₄(1 wt%); (f) NiS/g-C₃N₄(3 wt%); (g) NiS/g-C₃N₄(0.3 wt%, wet-chemistry method); (h) Pt/g-C₃N₄(1 wt%).

Fig. 7. FESEM/EDS results for various samples. (A) $\text{CoS}_x/\text{g-C}_3\text{N}_4$; (B) $\text{CuS}_x/\text{g-C}_3\text{N}_4$; (C) $\text{AgS}_x/\text{g-C}_3\text{N}_4$.

Fig. 8. (A) UV-vis absorption spectra and photographs (inset) and (B) Photocatalytic H_2 evolution rate for various samples. (a) $\text{g-C}_3\text{N}_4$; (b) $\text{CoS}_x/\text{g-C}_3\text{N}_4$; (c) $\text{CuS}_x/\text{g-C}_3\text{N}_4$; (d) $\text{AgS}_x/\text{g-C}_3\text{N}_4$.

cocatalyst act as active sites and accelerate the surface catalytic reaction for H_2 production. The separation of the photogenerated carriers and the collection of electrons on NiS will favor improved photocatalytic performance. In addition, the EIS curves for $\text{g-C}_3\text{N}_4$ and $\text{NiS}/\text{g-C}_3\text{N}_4$ (0.3 wt%) are shown in Fig. 6(D). It is found that the $\text{NiS}/\text{g-C}_3\text{N}_4$ displays a smaller arc radius than $\text{g-C}_3\text{N}_4$. In other words, $\text{NiS}/\text{g-C}_3\text{N}_4$ exhibits lower charge transfer resistance than $\text{g-C}_3\text{N}_4$, which is also beneficial for improving the photocatalytic performance.

More importantly, the present synthetic strategy can be a versatile approach for the modification of other metal sulfide cocatalysts on the $\text{g-C}_3\text{N}_4$ surface. As a demonstration, $\text{MS}_x/\text{g-C}_3\text{N}_4$ ($\text{M} = \text{Co}, \text{Cu}, \text{and Ag}$) were synthesized in similar conditions using $\text{Co}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and AgNO_3 instead of $\text{Ni}(\text{NO}_3)_2$. According to the FESEM/EDS results (Fig. 7), the Co and S, Cu and S, and Ag and S elements are present in the corresponding samples, respectively, implying the possible presence of CoS_x , CuS_x , and AgS_x in $\text{MS}_x/\text{g-C}_3\text{N}_4$ samples. Furthermore, the UV-vis DRS results and the images of the samples presented in Fig. 8(A) and its inset, respectively, also suggest the deposition of the above cocatalysts on the $\text{g-C}_3\text{N}_4$ photocatalyst due to the appearance of additional absorption in the visible light region (450–800 nm) and the color change of the corresponding samples. Figure 8(B) reveals that all of the $\text{MS}_x/\text{g-C}_3\text{N}_4$ samples exhibit enhanced photocatalytic H_2 production performance relative to the pure $\text{g-C}_3\text{N}_4$ sample. Further study of $\text{MS}_x/\text{g-C}_3\text{N}_4$ is ongoing and will be described in a future report.

4. Conclusions

In summary, the $\text{NiS}/\text{g-C}_3\text{N}_4$ photocatalyst was successfully synthesized via the sulfur-mediated photodeposition approach and exhibits excellent photocatalytic H_2 -production performance. The optimal performance of the $\text{NiS}/\text{g-C}_3\text{N}_4$ photocatalyst is close to that of the 1 wt% $\text{Pt}/\text{g-C}_3\text{N}_4$ photocatalyst. More importantly, this approach is versatile and can be applied to the synthesis of other $\text{MS}_x/\text{g-C}_3\text{N}_4$ ($\text{M} = \text{Co}, \text{Cu}, \text{and Ag}$) photocatalysts with enhanced photocatalytic hydrogen-production activity. Considering that the synthetic approach is facile and mild, the as-prepared $\text{NiS}/\text{g-C}_3\text{N}_4$ photocatalyst is promising for practical application in water splitting.

Conflicts of interest

The authors declare no competing financial interest.

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Graphical Abstract

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Sulfur-mediated photodeposition synthesis of NiS cocatalyst for boosting H₂-evolution performance of g-C₃N₄ photocatalyst

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NiS is deposited on the electron transfer sites of g-C₃N₄ by a sulfur-mediated photodeposition approach and provides active sites to improve the photocatalytic H₂-production of g-C₃N₄.

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NiS助催化剂的硫调控光沉积合成及其增强g-C₃N₄的光催化产氢性能

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摘要: 作为一种非金属聚合半导体, 石墨相氮化碳(g-C₃N₄)具有特殊的能带结构、可见光响应能力以及优良的物理化学性质以及生产成本低等特点, 因而已成为目前光催化领域的研究热点。然而, 由于g-C₃N₄被光激发的电子与空穴极易复合, 导致g-C₃N₄材料的光催化性能并不理想。而助剂修饰是实现光生载流子有效分离以提高光催化活性的有效途径。众所周知, 贵金属Pt可以作为光催化产氢的反应位点, 但高昂的成本限制了它的实际应用。所以, 开发高效的非贵金属助剂很有必要。近年来, NiS作为优良的电子助剂在光催化领域受到广泛关注。大量研究表明, NiS可以作为g-C₃N₄的产氢活性位点用于提高其光催化产氢性能。NiS助剂主要是通过水热、煅烧和液相沉淀的方法修饰在g-C₃N₄的表面上。相较而言, 助剂的光沉积方法具有一些独特的优势, 例如节能、环保、简易并且能够实现其原位牢固地沉积在光催化剂的表面。然而g-C₃N₄光生电子和空穴强还原和氧化能力容易导致像Ni²⁺的还原和S²⁻的氧化等副反应发生, 因此NiS助剂很难光沉积在g-C₃N₄材料表面。

本文采用硫调控的光沉积法成功合成了NiS/g-C₃N₄光催化材料, 该法利用g-C₃N₄在光照条件下产生的光生电子结合S以及Ni²⁺生成NiS, 然后原位沉积在g-C₃N₄表面。由于E⁰(S/NiS)(0.096 V)比E⁰(Ni²⁺/Ni)(-0.23 V)更正, 所以NiS优先原位沉积在g-C₃N₄表面。因此, 硫调控的光沉积法促进了NiS的生成, 并抑制了金属Ni等副反应的形成。

通过X射线光电子能谱分析NiS/g-C₃N₄的表面化学态, 表明该方法能成功地将NiS修饰在g-C₃N₄的表面, 这也得到透射电镜和高分辨透射电镜结果的证实。光催化产氢的结果表明, NiS/g-C₃N₄光催化剂实现了良好的光催化性能, 其最优产氢速率(244 μmol h⁻¹ g⁻¹)接近于1 wt% Pt/g-C₃N₄(316 μmol h⁻¹ g⁻¹)。这是因为硫调控的光沉积法实现NiS助剂在g-C₃N₄表面的修饰, 从而促进光生电子与空穴的有效分离, 进而提高光催化制氢效率。此外, 在该方法中, NiS的形成通常在g-C₃N₄光生电子的表面传输位点上, 因此也能够使NiS提供更多的活性位点以提高界面产氢催化反应速率。电化学表征结果也进一步证明NiS/g-C₃N₄光催化剂加快了电子与空穴的分离和转移。更重要的是, 这种简易且通用的方法还可以实现CoS_x, CuS_x, AgS_x对g-C₃N₄的助剂修饰, 并且都提高了g-C₃N₄的光催化产氢性能, 表明该方法具有一定的普适性, 为高效光催化材料的合成提供了新的思路。

关键词: g-C₃N₄; NiS; 助剂; 硫调控的光沉积法; 氢气; 光催化

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