Simple Hydrothermal Synthesis of g-C3N4/Ni9S8 Composites for Efficient Photocatalytic H2 Evolution

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Research Article

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Abstract

The prompt recombination between photogenerated electrons and holes is the common problem for improving the hydrogen evolution properties of a photocatalyst, which could be solved greatly by composite co-catalysis. Herein, a simple hydrothermal reaction was utilized to prepare g-C$_3$N$_4$/Ni$_9$S$_8$ composite photocatalysts. Through electroless nickel plating, Ni$_9$S$_8$ nanostructure was homogeneously grown onto the g-C$_3$N$_4$ surface by using sodium hypophosphite as reducing agent. With the optimum amount of Ni$_9$S$_8$, the acquired g-C$_3$N$_4$/Ni$_9$S$_8$ composite compared with the raw g-C$_3$N$_4$ which has an excellent increase in hydrogen evolution rate under visible light irradiation. Its rate of hydrogen evolution measured at 7 degrees Celsius was 355.7 $\mu$mol·g$^{-1}$·h$^{-1}$, being 21.2 time that of raw g-C$_3$N$_4$. The mechanism for the hydrogen evolution reaction over the present g-C$_3$N$_4$/Ni$_9$S$_8$ composite photocatalysts was discussed in detail.

1. Introduction

Nowadays, human beings are suffering from energy shortage, environmental pollution and extreme climate, because the increasing large-scale use of fossil energy will cause the depletion of easily available energy sources, which gives a pessimistic perspective for the reserve of fossil energy, together with a lot of waste gases and greenhouse gases, which have great impact on the earth's ecology [1-x]. Therefore, the development of new energy is very urgent for mankind. Hydrogen energy, as a pearl of new energy, has attracted much attention because of its high calorific value, no carbon emission and facile recyclability [2]. And since 1972 when Fujishima and Honda discovered that TiO$_2$ could decompose water into hydrogen and oxygen under ultraviolet light [3], it seems for human beings to find a shortcut to solve the energy problem once and for all. Thus now photocatalysis is such an exciting technology that attracts numerous researchers to study.

It is soon recognized by scientists that photocatalysis is based on the photoelectric conversion of semiconductors, and ultimately the conversion of light into chemical energy [4]. Therefore, the exploration of semiconductor photocatalysts has been rapidly launched. Today, many photocatalytic semiconductors such as ZnO, Ga$_2$O$_3$, SrTiO$_3$ and ZnS [5-8] have been found to be similar with TiO$_2$ in photocatalytic decomposition of water. However, these semiconductor photocatalysts can only respond to ultraviolet light because of their wide bandgap. To effectively make use of visible light, in which the sunlight (containing almost 96% visible light) is an inexhaustible energy source for human beings, researchers have developed CdS, MoS, Cu$_2$O and many other narrow bandgap semiconductors for photocatalytic hydrogen evolution [9-11]. But their poor photochemical stability, heavy metal pollution on water and less earth reserves limit their large-scale application [12].

In 2009, Wang et al. first found that g-C$_3$N$_4$ has the ability of photocatalytic decomposition of water under visible light [13]. Such ability of this kind of organic semiconductors has soon aroused the great interest of scientists. In literature, a large number of studies have shown that g-C$_3$N$_4$ owns a bandgap of roughly
2.78 eV, which can respond to light sources with wavelength below 460 nm [14]. At the same time, it has the advantages of strong photochemical stability, low cost, easy availability, non-toxicity and pollution free for environment [15]. In spite of these virtues, however, there are a large number of intrinsic defects in such organic semiconductors, which make the photogenerated carriers over g-C$_3$N$_4$ under light rapidly conform to these defects, thus seriously degrading its photocatalytic activity [12].

To reduce the recombination of photogenerated carriers (holes and electrons) in photocatalysts, co-catalysis is an excellent solution [16]. For example, noble metals like Au, Pt, Pd, Rh and so on have excellent catalytic effect due to their unique surface plasmon effect, which can also serve as good co-catalysts [17]. Regrettably, noble metals cannot widely be used in photocatalytic industry due to their high cost and scarce reserves. Therefore, it is very important to find low-cost co-catalysts for photocatalytic hydrogen evolution. In addition, by combining different semiconductor photocatalysts together to form a built-in electric field, photogenerated electrons are easily transferred from the optical semiconductor to the co-catalytic semiconductor. At this time, because of the Schottky barrier, the photogenerated electrons are difficult to return to the original photocatalyst, thus the separation of photogenerated carriers is realized [14]. Meanwhile, for this co-catalytic semiconductor, low overpotential and good conductivity are very helpful for hydrogen evolution. Therefore, it is a feasible idea to find a semiconductor with low overpotential and good conductivity to replace noble metals.

In literature, NiS has been regarded as an excellent co-catalyst in photocatalytic hydrogen evolution, and hopefully it can replace noble metals. This is due to the following advantages of NiS: (1) high conductivity due to low bandgap, (2) low surface work function that can effectively reduce the reaction activation energy or over potential, (3) high power conversion efficiency, and (4) easy preparation, low cost as well as environmental friendliness [18]. Therefore, a lot of researches have been executed on the co-catalysis of NiS in photocatalysis, such as CdS/NiS, TiO$_2$/NiS, g-C$_3$N$_4$/NiS and MoO$_3$/NiS [19-22]. However, since nickel sulfides can exist in different component including NiS, NiS$_2$, Ni$_3$S$_4$, Ni$_4$S$_3$, Ni$_9$S$_8$ and so forth [23], it is difficult for researchers to study them fully. Among them, Ni$_9$S$_8$ is less involved because it is not easily synthesized. As far as we know, no one has reported any composite of Ni$_9$S$_8$ and g-C$_3$N$_4$. Moreover, Ni$_9$S$_8$ has a near zero bandgap compared with NiS, which implies that Ni$_9$S$_8$ has better conductivity and is more conducive to the transmission of photogenerated electrons [24]. Therefore, it is much desirable to prepare the composite of g-C$_3$N$_4$ and Ni$_9$S$_8$ on photocatalytic hydrogen evolution.

In the present work, we adopt a facile green hydrothermal route to grow Ni$_9$S$_8$ nanostructures onto the pre-prepared g-C$_3$N$_4$ nanosheet, obtaining the g-C$_3$N$_4$/Ni$_9$S$_8$ composite. In the synthesis of g-C$_3$N$_4$/Ni$_9$S$_8$ composite, in order to form Ni$_9$S$_8$, NaHPO$_2$ was used, which is commonly used in electroless nickel plating, to reduce Ni$^{2+}$ to metal Ni, and then to conduct the redox reaction with S$^{2-}$ to obtain the g-C$_3$N$_4$/Ni$_9$S$_8$ composite. The results reveal that the as-acquired g-C$_3$N$_4$/Ni$_9$S$_8$ composite has a uniform dispersion of Ni$_9$S$_8$ nanostructures on the g-C$_3$N$_4$ nanosheet. Possessing the high conductivity, low surface work function and high electron mobility, the as-acquired composite photocatalyst has excellent photocatalytic performance for hydrogen evolution, presenting a H$_2$ evolution rate as high as 355.7
mmol·g⁻¹·h⁻¹ at 7 ℃. The successful preparation of the present composite will also provide a new perspective for developing other high-performance heterostructure photocatalysts for hydrogen evolution.

2. Experimental

2.1 Raw materials

Sodium hypophosphite (NaH₂PO₂, 99.0%), nickel acetate (Ni(CH₃COO)₂, 99.5%), melamine (99.5%), thiourea (CH₄N₂S, 99.5%), ethanol (C₂H₅OH, 99.9%), triethanolamine (TEOA, 99.5%), H₂PtCl₆·6H₂O (99.5%) and Na₂SO₄ (99.5%) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). During the experiments, all the raw materials are used without further treatment.

2.2 Synthesis of g-C₃N₄ particles

Bulk g-C₃N₄ samples were first synthesized by directly heating melamine [25]. Typically, in an open box furnace, a half-covered crucible with 5 g of melamine powder is heated from room temperature to 550 ℃ at a speed of 5 ℃/min, soaking at this temperature for 4 h. Afterwards, the furnace was cooled down to ambient temperature, and then the resultant bulk sample was ground, finally obtaining yellow g-C₃N₄ powders.

2.3 Synthesis of g-C₃N₄/Ni₉S₈ nanocomposites

A facile one-step hydrothermal approach was applied in this work to synthesize the proposed g-C₃N₄/Ni₉S₈ nanocomposites. Typically, in a beak with 50 mL deionized water, 100 mg of the as-obtained g-C₃N₄ powders was homogeneously dispersed through vigorous stirring for 30 minutes under sonicating. Then, in order to obtain g-C₃N₄/Ni₉S₈ composites with different loading amounts of Ni₉S₈, a series of designed amount of nickel acetate (0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 0.9 mmol, respectively) were added into the dispersion solution. And thiourea with an amount of three times that of nickel acetate was mixed in the dispersion solution together. After further strong stirring for 30 minutes, 300 mg sodium hypophosphite was mixed in the solution system. After stirring evenly, the solution was transferred into an autoclave (100 ml) and then kept in an oven at 140 ℃ for 8 h. By simply shutting the electricity of the furnace, it was cooled down to ambient temperature. And then the autoclave was taken out from the oven. The resultant precipitates were collected after centrifuging, washed twice with 30 ml deionized water as well as absolute ethanol respectively, and dried out at 60 ℃ for 8 h. Finally, the proposed, dark blue powders could be acquired.

2.4 Materials characterization

In this work, a Zeiss GEMINISEM 500 field emission scanning electron microscope (FE-SEM, Germany) was first applied to examine the morphology and microstructure of the samples. Then a Thermo ESCALAB MKII X-ray photoelectron spectroscope (XPS, Thermo VG Scientific Ltd., UK) was used to explore their elemental composition and chemical state. With the C1s line (284.8 eV) as reference, the
recorded results were corrected. In order to identify their phase compositions, X-ray diffraction (XRD) analysis was executed (GI-XRD, Japan; Cu Kα radiation, \( \lambda = 1.5418 \) Å). For the analysis, the corresponding scanning rate was set as 4 °/min with 1° of X-ray incidence angle in continuous scanning mode. Finally, with a Varian Cary 5000 UV-vis spectrometer (Agilent, America), the UV-visible absorption spectrum of the samples was collected.

2.5 Evaluation of photocatalytic hydrogen evolution

For the accurate date of hydrogen evolution, in each test 50 mg catalyst was first diffused into 100 ml TEOA aqueous solution with a concentration of 10 vol.%. Then, the prepared reaction mixture was settled in a Perfectlight LabSolar Photocatalytic Hydrogen Evolution System (Beijing, China). The system possesses a Xe lamp (300 W) with an UV cut-off filter (\( \lambda \geq 420 \) nm) for light source. Afterwards, the system is sealed. Before photocatalytic reaction, the system was first evacuated to a vacuum of -0.1 MPa, and throughout the photocatalytic reaction, the cooling system based on circulating water should work continuously to keep the reaction temperature at 7 °C. For the reaction, the applied light source was placed 20 cm far from the reaction vessel, and the area for effective irradiation was measured as 12.57 cm². During the reaction, the generated gas was characterized by a gas chromatography (GC-7900, Xuansheng Scientific Instrument Co. Ltd, Shanghai, China) on-line with nitrogen as carrier gas. Additionally, each of the cyclic tests for photocatalytic hydrogen evolution was executed for 3 hours and the gas products were taken for characterization every half an hour. After one round of tests, the reactor will be evacuated for 30 minutes, and then the subsequent round of tests is repeated without changing the reaction liquid.

2.6 Photoelectrochemical characterization

For each photoelectrochemical test, a working electrode was first fabricated, for which 50 μL ink prepared from 5 mg sample, 500 μL absolute ethanol together with 20 μL Nafion solution (5 wt.%) was coating onto a FTO glass substrate, finally forming an electrode with a size of 1 cm². The electrolyte is 0.2 M Na₂SO₄ aqueous solution.

The measurement on transient photocurrents was carried out by a standard three-electrode system on an electrochemical workstation (CHI 660E, Chenhua Instrument, Shanghai, China). For the measurement, a piece of Pt foil was used as counter electrode, Ag/AgCl (saturated KCl) was used as reference electrode, and the visible light (\( \lambda \geq 420 \) nm) was provided by a Xe lamp (300 W) using an UV cut-off filter. Prior to the tests, the system should be degassed by high-purity N₂ gas for about 30 minutes.

The samples’ electrochemical impedance spectra (EIS) were recorded with the same parameters as those in measuring transient photocurrents. During the EIS tests, the frequency falls in the range of 0.01-100000 Hz, and the applied AC amplitude is 5 mV (vs. Ag/AgCl).

3. Results And Discussion
3.1 Photocatalytic performance for H₂ evolution

To reveal the photocatalytic activity of the proposed g-C₃N₄/Ni₉S₈ composite, all the samples were tested for hydrogen evolution under the irradiation of visible light at 7 °C. Firstly, a series of samples prepared with different Ni/g-C₃N₄ feed molar ratios were tested to determine the optimal sample. Fig. 1a compares their hydrogen evolution rates (HERs). As can be seen in this figure, with the increase of feeding amount of nickel source, the HER value of the acquired samples can be improved. When the Ni/g-C₃N₄ feed molar ratio was 0.2, their HER value reached the highest, which was 355.7 μmol·g⁻¹·h⁻¹. With more nickel source added, the performance of the obtained photocatalysts declined again, possibly because that the excessive addition of nickel source would lead to a large amount of nickel sulfides coating on g-C₃N₄, which would hinder the absorption of light by g-C₃N₄, thus reducing the hydrogen evolution efficiency of the catalysts. So, the optimal Ni/g-C₃N₄ feed molar ratio for the present composite samples is 0.2. In Fig. 1b, the HER values of the raw g-C₃N₄, the pure Ni₉S₈, the raw g-C₃N₄ which loaded with Pt (1 wt.%) and the optimal g-C₃N₄/Ni₉S₈ composite are compared. Among them, the sample of g-C₃N₄ with Pt was obtained by adding 1 wt.% chloroplatinic acid into the photocatalytic reaction cell and irradiating it with a 300 W xenon lamp for 30 min. As is seen in the figure, the sample of raw g-C₃N₄ only has a very small HER and the pure Ni₉S₈ has no detectable photocatalytic hydrogen evolution ability. However, the HER value of the optimal composite sample can reach 355.7 μmol·g⁻¹·h⁻¹. This remarkable value is 21.2 times that of the raw g-C₃N₄, and only 22.1% less than the sample of raw g-C₃N₄ which loaded with Pt (1 wt.%). Therefore, it can be inferred that the compositing between g-C₃N₄ as well as Ni₉S₈ will present a synergistic effect, which can effectively transfer the photogenerated electrons on g-C₃N₄ to Ni₉S₈ through the interface charge transfer effect. And then the electrons on Ni₉S₈ can also combine with H⁺ to generate hydrogen, which greatly improves the photocatalytic efficiency of g-C₃N₄. Additionally, in order to determine the stability of the sample, the optimal sample was continuously reacted for 3*6 h in the light reaction cell. It can be seen from the cyclic test results of the composite sample as shown in Fig. 1c that the HER value of the sample has no obvious change after 18 h of cyclic test. Therefore, it can be concluded that the optimal composite has good cycling stability.

3.2 Compositional and structural properties

To elucidate the photocatalytic performance of the acquired samples, their composition and structure were investigated. Firstly, SEM imaging was carried out. Fig. 2a shows typical SEM micrograph of the optimal g-C₃N₄/Ni₉S₈ composite. As is seen, this composite sample has a similar morphology with that of the raw g-C₃N₄ sample. Therefore, the two-dimensional structure of raw g-C₃N₄ is not destroyed in the recombination process. To explore the distribution of nickel sulfides in the sample, EDS mapping scanning was executed in the same area for SEM imaging. And the results are displayed in Fig. 2b-d. It is easily seen that N, Ni as well as S atoms are homogeneously distributed over the sampling area. Therefore, it can be concluded that the nickel sulfides in the obtained composite is uniformly grown onto the g-C₃N₄ surface, rather than a simple mixture of both components. The uniform composition and
structure is one of the reasons why the proposed g-C$_3$N$_4$/Ni$_9$S$_8$ composite has high photocatalytic activity.

To determine the specimens’ phase composition, XRD analysis was carried out. Fig. 3 compares the recorded XRD patterns of the optimal composite, the raw g-C$_3$N$_4$ and pure nickel sulfides samples, in which the raw g-C$_3$N$_4$ specimen was acquired by the calcination of melamine, while the nickel sulfides sample was obtained under the similar conditions as done for the optimal composite but without the addition of g-C$_3$N$_4$. As is seen, the main XRD peaks of the pure nickel sulfides sample can be indexed to orthorhombic Ni$_9$S$_8$ phase (JCPDS no.22-1193), while a small amount of hexagonal NiS (JCPDS no.12-0041) can be also identified, indicating that it is a mixture of Ni$_9$S$_8$ as the main body with a small amount of hexagonal NiS. The XRD peaks of the raw g-C$_3$N$_4$ sample match perfectly with those of its predecessors, confirming its successful synthesis in this work [12]. And in the optimal composite, only the diffraction peaks of g-C$_3$N$_4$ and Ni$_9$S$_8$ can be identified, which proves that it is a relatively pure composite of g-C$_3$N$_4$ and Ni$_9$S$_8$.

The elemental composition as well as chemical state of the optimal g-C$_3$N$_4$/Ni$_9$S$_8$ composite was further detected by XPS analysis. The obtained results are shown in Fig. 4. XPS survey spectroscopy reveals that the optimal g-C$_3$N$_4$/Ni$_9$S$_8$ sample is composed of C, N, Ni and S, indicating that it is a composite of these elements as expected. The high-resolution C 1s spectrum as exhibited in Fig. 4a presents two distinct peaks at 282.8 and 286.0 eV. Literature survey reveals that the peak at 282.8 eV could be assigned to free carbon, while the one at 286.0 eV should be indexed to the binding energy of C atoms in g-C$_3$N$_4$ [26]. The N 1s spectrum (see Fig. 4b) can be fitted into four peaks at 396.5, 397.9, 399.2 and 402.3 eV, respectively. Among them, the three peaks at 396.5, 397.9 and 399.2 eV could be ascribed to the sp$^2$ hybrid nitrogen in C=N-C group, sp$^3$ hybrid nitrogen in N-(C)$_3$ structure and nitrogen in amino moiety in g-C$_3$N$_4$, respectively, while the one at 402.3 eV is owing to the dangling bond of N on the g-C$_3$N$_4$ surface [27]. The Ni 2p spectrum (Fig. 4c) exhibits two main peaks at 853.2 and 860.4 eV, in which the one at 853.2 eV can be attributed to Ni$^{2+}$ in Ni$_9$S$_8$, and that at 860.4 eV is assigned to Ni$^{2+}$ in the hydroxyl compound of nickel [24]. However, the phase of hydroxyl compound of nickel could not be identified from the XRD patterns, possibly because its content in the samples were too small. In a word, the main reason for the formation of this binding energy is the hydroxyl hanging bond on the surface of Ni$_9$S$_8$ during hydrothermal reaction [18]. Correspondingly, the S 2p spectrum presented in Fig. 4d displays two main peaks at 160.2 and 166.5 eV. The peak at 160.2 eV can be attributed to the S atom in Ni$_9$S$_8$ lattice, while that at 166.5 eV may be due to the attachment of some sulphate produced by thiourea hydrolysis on the surface of the sample [24].

In summary, the above-mentioned characterizations reveal that a g-C$_3$N$_4$/Ni$_9$S$_8$ composite with uniform composition and structure has been successfully synthesized in this work.
The formation mechanism of g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite as follow was proposed based on the above experimental results (Fig. 5). In the designed first step, the raw g-C<sub>3</sub>N<sub>4</sub> powder is dispersed in deionized water by ultrasonic stirring to form uniformly dispersed g-C<sub>3</sub>N<sub>4</sub> nanosheets. After nickel acetate and thiourea joined into the reaction system, because of the negative charges on the g-C<sub>3</sub>N<sub>4</sub> nanosheets, Ni<sup>2+</sup> could be adsorption on the surface of g-C<sub>3</sub>N<sub>4</sub>, while thiourea could form a complex with Ni<sup>2+</sup> to slow down the release of Ni<sup>2+</sup>. In the second step, during the hydrothermal reaction, sodium hypophosphite was first decomposed into PH<sub>3</sub>, which could be ionized into H<sup>-</sup> with strong reducibility. Then the H<sup>-</sup> can reduce Ni<sup>2+</sup> attached to g-C<sub>3</sub>N<sub>4</sub> surface into metal Ni. In the third step, the stable thiourea was thermally decomposed to produce a large amount of S<sup>2-</sup> and reacted with the metal Ni grown on the g-C<sub>3</sub>N<sub>4</sub> surface to obtain the proposed composite in the state full of unsaturated sulfur. Finally, the g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite in the state of unsaturated sulfur was obtained. We got this idea by referring to the method of electroless nickel plating [28].

3.3 Photocatalytic mechanism

To clarify the photocatalytic mechanism for H<sub>2</sub> evolution of the as-acquired g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite, its photoelectrochemical features were further explored. For comparison, the Ni<sub>9</sub>S<sub>8</sub> nanostructure and raw g-C<sub>3</sub>N<sub>4</sub> were also investigated. Fig. 6a compares the UV-visible absorption spectrum of the optimal g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite with those of raw g-C<sub>3</sub>N<sub>4</sub> and Ni<sub>9</sub>S<sub>8</sub> nanostructure. It can be seen that the starting point of the absorption edge for the raw g-C<sub>3</sub>N<sub>4</sub> is about 440 nm, which is well corresponding to the value reported in literature [29]. However, after g-C<sub>3</sub>N<sub>4</sub> was combined with Ni<sub>9</sub>S<sub>8</sub>, the absorption ability for visible light of the obtained composite was greatly enhanced, while the absorption capacity for ultraviolet and near ultraviolet spectrum below 450 nm was also significantly increased. This result reveals that after the Ni<sub>9</sub>S<sub>8</sub> co-catalyst was loaded onto the g-C<sub>3</sub>N<sub>4</sub> nanosheets, the optical absorption region of the composite sample could be effectively broadened. The enhanced ability in optical absorption could be owing to the existence of low bandgap black Ni<sub>9</sub>S<sub>8</sub> in the g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite. Such Ni<sub>9</sub>S<sub>8</sub> nanostructures have strong optical absorption to the light with a wavelength from 300 to 800 nm. Furthermore, the bandgaps of the as-acquired, optimal g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite together with the raw g-C<sub>3</sub>N<sub>4</sub> sample was estimated from their corresponding plots on (ahν)<sup>2</sup> versus E<sub>g</sub> (see Fig. 6b). As is seen, the E<sub>g</sub> values of the as-acquired, optimal g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite and the raw g-C<sub>3</sub>N<sub>4</sub> are 2.85 and 2.88 eV, respectively. This little difference in their E<sub>g</sub> values implies that there is almost no doping effect in the present composite.

Moreover, the transient photocurrents of the raw g-C<sub>3</sub>N<sub>4</sub>, pure Ni<sub>9</sub>S<sub>8</sub> together with the optimal g-C<sub>3</sub>N<sub>4</sub>/Ni<sub>9</sub>S<sub>8</sub> composite are compared in Fig. 7a. We can find out that the prepared raw g-C<sub>3</sub>N<sub>4</sub> sample has only 0.3 μA/cm<sup>2</sup> of transient photocurrent, which is far less than that of the optimal composite. This is because the photogenerated electrons and holes are easily recombined with each other in the raw g-C<sub>3</sub>N<sub>4</sub> sample. In addition, on the prepared pure Ni<sub>9</sub>S<sub>8</sub> nanostructure the detected photocurrent is not distinct,
indicating that although it has strong absorption to the light at the wavelength of 300-800 nm, it can not contribute to the transient photocurrent of the present composite independently. These facts prove that in the present g-C₃N₄/Ni₉S₈ composite, the Ni₉S₈ nanostructure is not a photocatalyst but a co-catalyst for g-C₃N₄. The Ni₉S₈ co-catalyst can boost the segregation of photogenerated electrons and holes, thus increase the efficiency of photogenerated carrier transfer.

Furthermore, the recorded EIS Nyquist curves (see Fig. 7b) reveal that among the three investigated samples, the raw g-C₃N₄ sample possesses the highest intrinsic impedance, indicating that there is a higher charge transfer rate in the composite g-C₃N₄/Ni₉S₈ samples after the loading of Ni₉S₈ onto g-C₃N₄. These phenomena may be due to the homogeneous combination of the relatively low-conductivity g-C₃N₄ nanosheets with the high-conductivity Ni₉S₈ nanostructures.

According to the above-mentioned experimental results, the possible photocatalytic mechanism over the present g-C₃N₄/Ni₉S₈ composite on hydrogen evolution was proposed (see Fig. 8). Under the irradiation of visible light, the photogenerated electron (e⁻) will leap into the conduction band (CB) of g-C₃N₄, which will leave hole (H⁺) in its valence band (VB). A part of photogenerated electrons could move to the g-C₃N₄ surface and directly reduce H⁺ ions in solution to produce H₂. More importantly, due to the close contact between the main body g-C₃N₄ and the high-conductivity Ni₉S₈ nanostructures in the present g-C₃N₄/Ni₉S₈ composite, the built-in electric field is formed after the combination between them. As a result, the photogenerated electrons would easily emigrate to the Ni₉S₈ surface, thus effectively suppressing the recombination between the photogenerated electrons and holes. Because of the high electrocatalytic activity of Ni₉S₈, the surface of the Ni₉S₈ nanostructure can also be used as the active site for electron reduction reaction, effectively reducing H⁺ to H₂ in the solution. In addition, triethanolamine can absorb the holes transferred from the valence band to the surface of g-C₃N₄, thus completing a complete set of redox reactions.

4. Conclusion
A interesting g-C₃N₄/Ni₉S₈ composite was prepared by using a novel hydrothermal method. Under visible light irradiation, the optimal g-C₃N₄/Ni₉S₈ nanocomposite has high photocatalytic activity. The hydrogen evolution rate of the optimal g-C₃N₄/Ni₉S₈ composite prepared with the Ni/g-C₃N₄ feed molar ratio of 0.2 could reach 355.7 μmol·g⁻¹·h⁻¹ at 7 °C, which is 21.2 times higher than the raw g-C₃N₄ sample, and only 22.1% less than the raw g-C₃N₄ with Pt (1 wt.%) loaded. The possible mechanism of photocatalytic H₂ evolution over the as-acquired g-C₃N₄/Ni₉S₈ composite was that: due to the close contact between g-C₃N₄ and Ni₉S₈ of high conductivity of Ni₉S₈, the photogenerated electrons during photocatalysis could easily emigrate from the relatively low-conductivity g-C₃N₄ surface to the high-conductivity Ni₉S₈ surface, thus effectively promoting the segregation of photogenerated electrons and holes and sponsoring the electrocatalytic activity of Ni₉S₈ via effectively reducing H⁺ to H₂ as well. The present study will supplied
a new approach for the construction of nano photocatalysts by co-catalysis for photocatalytic hydrogen evolution.

Declarations

Conflicts of interest

There is no conflict of interests regarding the publication of this paper.

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