



Facile low-temperature co-precipitation method to synthesize hierarchical network-like g-C₃N₄/SnIn₄S₈ with superior photocatalytic performance

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Received: 26 February 2016

Accepted: 13 April 2016

Published online:
25 April 2016

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ABSTRACT

Hierarchical network-like graphitic carbon nitride/SnIn₄S₈ (g-C₃N₄/SnIn₄S₈) composites were prepared through a facile low-temperature co-precipitation method. The g-C₃N₄/SnIn₄S₈ composite showed enhanced visible-light absorption. The band gap energies of g-C₃N₄, pure SnIn₄S₈, and 15 % g-C₃N₄/SnIn₄S₈ are 2.58, 1.8, and 1.68 eV, respectively. The photocurrent and photocatalytic activity of the g-C₃N₄/SnIn₄S₈ composites firstly increased and then decreased with increasing g-C₃N₄ content, and it was found that the optimal 15 % g-C₃N₄/SnIn₄S₈ exhibited the highest photocurrent intensity and best photocatalytic performance with complete degradation of MO within 80 min under visible-light irradiation, which is much higher than that of pure SnIn₄S₈. The effect of main reactive species on the MO degradation follows the order of h⁺ > •O₂⁻ > •OH, and the possible degradation mechanism was proposed. Moreover, 15 % g-C₃N₄/SnIn₄S₈ exhibits excellent reusability and stability without an obvious decrease of photocatalytic activity after four consecutive photocatalytic degradation–regeneration cycles.

Introduction

Water pollution has posed a potential threat to human health by the food chain system, thus it is particularly significant to develop some reliable methods to resolve water pollution problem [1–4]. By far, adsorption, coagulation, biological treatment, chemical oxidation, electrochemical treatment, and

heterogeneous photocatalytic oxidation technology have been established for water purification [5–9]. Among the above techniques, TiO₂-based heterogeneous photocatalysis has received much attention due to its low cost, strong oxidation ability, nontoxicity, chemical stability, biocompatibility, and simplicity of operation [10–15]. However, TiO₂ has a wide band gap (3.2 eV for anatase and 3.0 eV for

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rutile) and can only respond in the ultraviolet (UV) light region, which restrict its practical application in wastewater treatment [16–20]. Therefore, it is imperative and challenging to develop new and efficient visible-light-responsive photocatalysts.

Ternary chalcogenide compounds possess narrow band gap, high stability, and strong visible-light absorption and thus have received tremendous attention in recent years [21–23]. Stannum indium sulfide (SnIn_4S_8) is a common ternary chalcogenide semiconductor and exhibits potential application in photocatalysis [24, 25]. However, single SnIn_4S_8 semiconductors usually possess a small specific surface area and fast electron–hole recombination, and the photocatalytic activity of silver-based catalysts is diminished during recycling process, which would depress their photocatalytic efficiency and restrict practical application. To solve these problems, integrating SnIn_4S_8 with other proper semiconductors or supports is an effective and feasible strategy for high photocatalytic efficiency.

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), a metal-free polymeric semiconductor, has drawn extensive attention due to its nontoxicity, low cost, suitable band position, excellent electrical conductivity, good thermal–chemical stability, excellent optical performance, and strong absorption of visible light, and has been regarded as a promising visible-light-responsive photocatalyst or an excellent support for many photocatalysts [26–30]. Herein, we first presented low-temperature co-precipitation strategy for the fabrication of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites in this study. The physicochemical and electrochemical properties of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites were studied. The effect of $\text{g-C}_3\text{N}_4$ content on PL intensity, photocurrent intensity, and the photocatalytic activities of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites under visible-light irradiation was also systematically investigated. Moreover, the possible photocatalytic mechanism of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ was provided.

Experimental

Materials

Tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and indium (III) chloride tetrahydrate ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Thioacetamide (TAA) was

purchased from China National Medicine Group Chemical Reagent Co., Ltd. (Shanghai, China). Dicyandiamide, urea, *p*-benzoquinone (BQ), isopropanol (IPA), and triethanolamine (TEOA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ethanol was supplied by Shantou Xilong Chemical Co., Ltd. (Shantou, China). Methyl orange (MO) was obtained from Shanghai Jingxi Chemical Technology Co., Ltd. (Shanghai, China). All the reagents were of analytical grade and used as received without further purification. Water was purified using a Milli-Q water system (Bedford, USA).

Preparation of $\text{g-C}_3\text{N}_4$

The $\text{g-C}_3\text{N}_4$ was prepared by pyrolysis of urea and dicyandiamide in air atmosphere. 3.5 g urea and 1.5 g dicyandiamide were firstly milled for 30 min, then transferred in a muffle furnace, and heated to 530 °C for 4 h to complete the reaction [31].

Preparation of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite via a low-temperature co-precipitation approach

0.421 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (1.2 mmol) and 1.409 g of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (4.8 mmol) were dissolved in 96 mL of anhydrous ethanol under continuous magnetic stirring, and then 0.9 g TAA (12 mmol) was added to the above solution. Afterwards, a certain amount of $\text{g-C}_3\text{N}_4$ was added to the solution. The mixture solution was stirred until a transparent solution was formed, then the above solution was transferred to a 150-mL round-bottom flask with a reflux condenser, placed in a thermostatic bath at 70 °C for 3 h under continuous magnetic stirring, and cooled to room temperature naturally. The obtained yellow precipitate was filtered, washed with distilled water and absolute ethanol several times, and finally dried at 80 °C for 12 h. The samples with different $\text{g-C}_3\text{N}_4$ content were designated as pure SnIn_4S_8 , 5 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, 10 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, 20 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, 30 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, and 40 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$.

Characterization

X-ray diffraction (XRD) patterns of samples were obtained using a Rigaku D/max 2200 PC automatic

X-ray diffractometer (Rigaku, Japan). Transmission electron microscopy (TEM, Hitachi, Japan) and scanning electron microscopy (SEM, Shimadzu, Japan) were used to observe the morphology of the samples. Energy-dispersive spectrometry (EDS, Shimadzu, Japan) was used to confirm the existence of SnIn_4S_8 and $\text{g-C}_3\text{N}_4$. The specific surface area and pore structures of samples were determined using a GEMINI VII 2390 surface area and porosity analyzer (Micromeritics, USA). The reflectance spectra were obtained using a UV-2550 scan UV-Vis spectrophotometer (Shimadzu, Japan) equipped with a Lab-sphere diffuse reflectance accessory. The photoluminescence (PL) emission spectra were obtained using F-7000 fluorescence spectrophotometer (Hitachi, Japan).

Photocatalytic activity measurement

The photocatalytic activities were evaluated by decomposing MO under visible-light irradiation. A 300 W Xe lamp with a 400 nm cut-off filter was used as the visible-light source. For the typical photocatalytic experiments, 30 mg of photocatalyst was added into 160 mL of 10 mg/L MO solution. Before irradiation, the suspensions were magnetically stirred in the dark for 40 min to reach adsorption-desorption equilibrium. In the dark reaction, 4 mL suspension was sampled at different time intervals and centrifuged immediately to remove suspended photocatalyst powders. The concentration of MO was analyzed using a UV-Vis spectrophotometer at 463 nm.

Regeneration and reuse of spent $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite photocatalyst

The spent $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ catalysts were recovered from the mixture solution by centrifugation, regenerated by washing with water and ethanol, and then dried at 80 °C for 4 h. The regenerated $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ catalysts were reused for MO degradation under similar reaction conditions as with the fresh catalysts.

Results and discussion

XRD analysis

The crystal structure of $\text{g-C}_3\text{N}_4$, pure SnIn_4S_8 , and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite was characterized

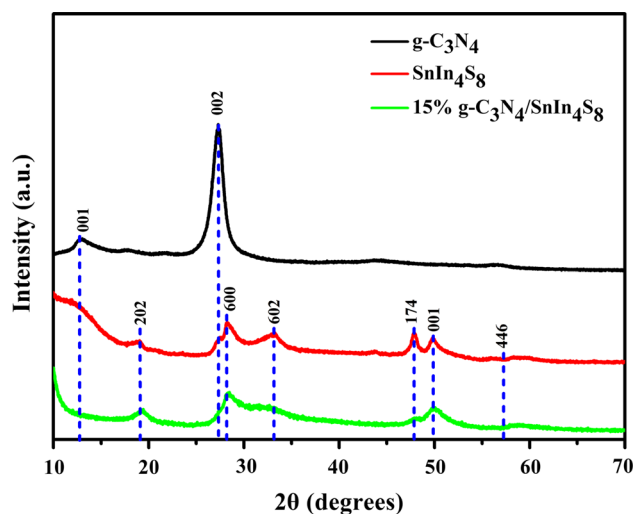


Figure 1 XRD patterns of $\text{g-C}_3\text{N}_4$, pure SnIn_4S_8 , and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$.

by XRD (Fig. 1). Pure SnIn_4S_8 and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ have similar XRD patterns. The main diffraction peaks at about $2\theta = 28.6^\circ$ and 50.4° are observed, which can be indexed to the (600) and (001) crystalline planes of tetragonal phase of SnIn_4S_8 , respectively. Moreover, it is interesting to note that no $\text{g-C}_3\text{N}_4$ diffractions are found in the XRD pattern of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite, possibly due to the low loading content of $\text{g-C}_3\text{N}_4$ or the highly dispersed $\text{g-C}_3\text{N}_4$ on SnIn_4S_8 .

Morphology analysis of pure SnIn_4S_8 and $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$

The morphologies of pure SnIn_4S_8 and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ are shown in Fig. 2. Pure SnIn_4S_8 is composed of a large amount of 3D hierarchical network-like spheres with a diameter ranging from 1 to 2 μm . An enlarged view of an individual SnIn_4S_8 sphere shows that the network-like superstructure of pure SnIn_4S_8 is constructed by numerous bending two-dimensional nanosheets with a thickness of about 20 nm. In case of 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, the thickness of nanosheets becomes obviously thinner, and hierarchical pores between nanosheets become obviously larger compared with pure SnIn_4S_8 . The thinner nanosheets and larger hierarchical pores are beneficial for the multiple scattering of light and light-harvesting capacity, thus it is expected that this structure would improve the photocatalytic activity of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$.

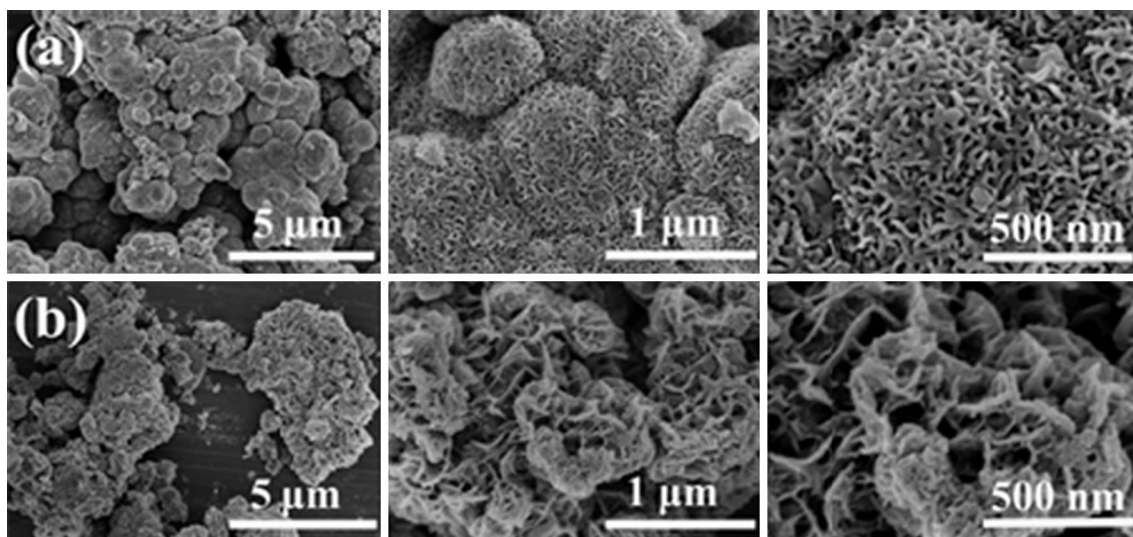


Figure 2 SEM images of **a** pure SnIn₄S₈ and **b** 15 % g-C₃N₄/SnIn₄S₈ with different magnifications.

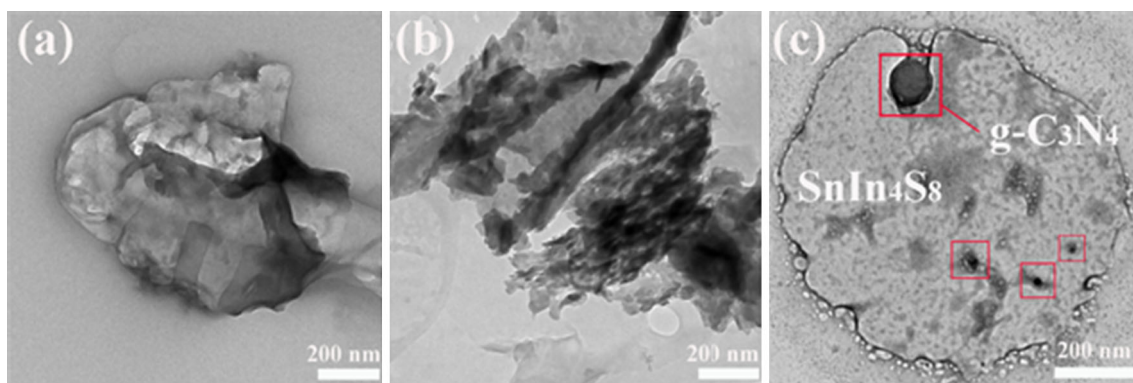


Figure 3 TEM images of **a** pure SnIn₄S₈, **b** g-C₃N₄, and **c** 15 % g-C₃N₄/SnIn₄S₈.

The microstructure of g-C₃N₄, pure SnIn₄S₈, and 15 % g-C₃N₄/SnIn₄S₈ composites was further studied by TEM (Fig. 3). The TEM images further confirmed the network-like structure of pure SnIn₄S₈, and g-C₃N₄ possessed a loose structure and nanopores with size in the range of 20–50 nm, and it is clear that g-C₃N₄ was successfully dispersed on SnIn₄S₈.

EDS analysis

The EDS analysis was used to analyze the chemical composition of pure SnIn₄S₈ and 15 % g-C₃N₄/SnIn₄S₈ (Fig. 4). It can be seen from Fig. 4 that pure SnIn₄S₈ is composed of Sn, In, and S elements. In case of 15 % g-C₃N₄/SnIn₄S₈, Sn, In, S, C, and N elements

were observed, confirming the formation of g-C₃N₄/SnIn₄S₈ composites.

Specific surface areas and porous structures

The nitrogen adsorption–desorption isotherm and the pore size distribution curves of pure SnIn₄S₈ and 15 % g-C₃N₄/SnIn₄S₈ composite are shown in Fig. 5. The isotherms of pure SnIn₄S₈ and 15 % g-C₃N₄/SnIn₄S₈ are classified as type IV according to the Brunauer–Deming–Deming–Teller (BDDT) classification, implying the presence of mesopores (2–50 nm). The shape of the hysteresis loop is of type H3, which is associated with aggregates of plate-like particles, giving rise to slit-like pores. Pure SnIn₄S₈

Figure 4 EDS patterns of **a** pure SnIn_4S_8 and **b** 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites.

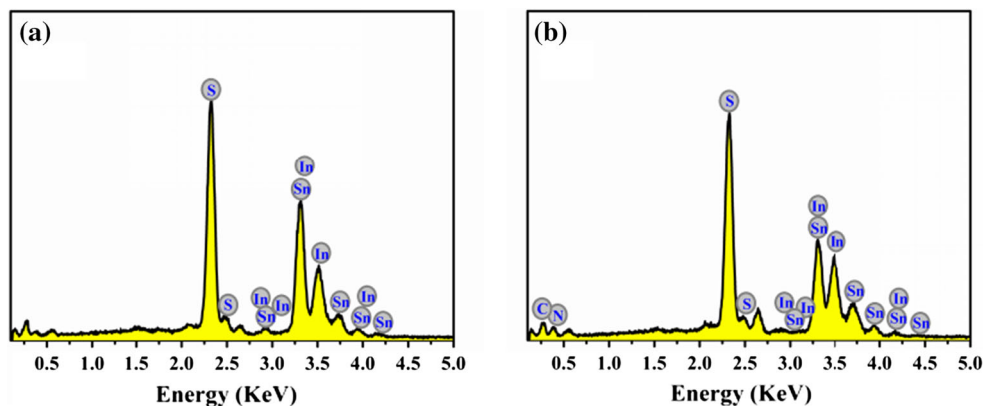
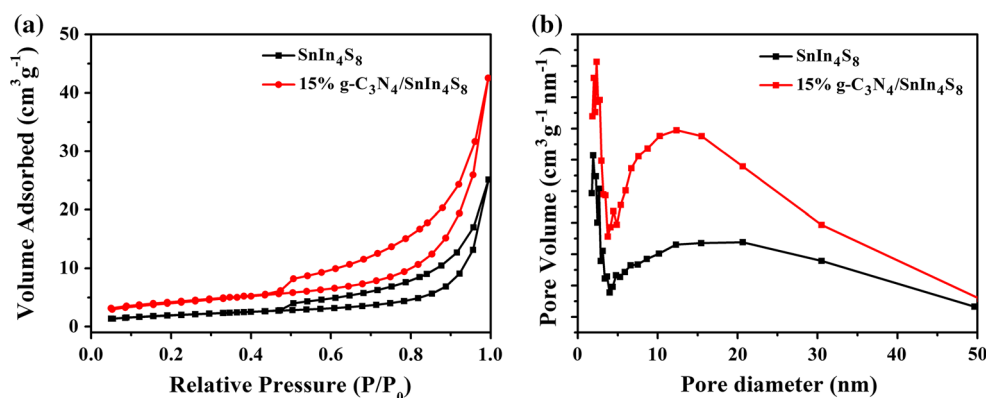


Figure 5 **a** Nitrogen adsorption–desorption isotherms and **b** pore size distribution curves of pure SnIn_4S_8 and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$.



and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites possessed broad and bimodal pore size distribution with small mesopores (2–3 nm) and larger ones (5–30 nm). The BET surface areas of pure SnIn_4S_8 and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites are 14.49 and 21.33 $\text{m}^2 \text{g}^{-1}$, respectively. A larger surface area of 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ provides more surface active sites for the adsorption of the reactive molecules, which is beneficial for the photocatalytic degradation of organic pollutants.

Optical properties

The UV–Vis diffuse reflectance spectra of pure SnIn_4S_8 , $\text{g-C}_3\text{N}_4$, and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite are shown in Fig. 6a. We can see that the absorption edges of 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite shift significantly to longer wavelength, and the absorption intensity of 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite is stronger than that of pure SnIn_4S_8 .

The band gap energies of pure SnIn_4S_8 , $\text{g-C}_3\text{N}_4$, and 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite can be estimated from the following equation: $(\alpha h\nu)^n = k(h\nu - E_g)$, where α is the absorption coefficient, k is a constant, $h\nu$ is the

photonic energy, E_g is the absorption band gap energy, and the value of n is 2 and 1/2 for a direct and an indirect band gap semiconductor, respectively. Plots of $(\alpha h\nu)^2$ versus $h\nu$ of the samples are shown in Fig. 6b, and the band gap energies of pure SnIn_4S_8 , 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$, and $\text{g-C}_3\text{N}_4$ are estimated to be about 1.8, 1.68, and 2.58 eV, respectively.

PL emission spectra

The separation efficiency of photogenerated electrons and holes can be investigated by PL emission spectra. Figure 7 represents the PL spectra of pure SnIn_4S_8 and $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites with different $\text{g-C}_3\text{N}_4$ content. Pure SnIn_4S_8 shows the highest PL intensity, indicating that pure SnIn_4S_8 exhibits the highest recombination of electrons and holes and the lowest separation efficiency under visible-light irradiation. Moreover, the PL emission intensity of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites is obviously influenced by the content of $\text{g-C}_3\text{N}_4$. With increasing the $\text{g-C}_3\text{N}_4$ content from 0 to 15 %, the emission intensity of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite decreased, but further increasing the $\text{g-C}_3\text{N}_4$ content results in a dramatic

Figure 6 **a** UV–Vis diffuse reflectance spectra and **b** plots of $(\alpha h\nu)^2$ versus $h\nu$ of pure SnIn₄S₈, g-C₃N₄, and 15 % g-C₃N₄/SnIn₄S₈.

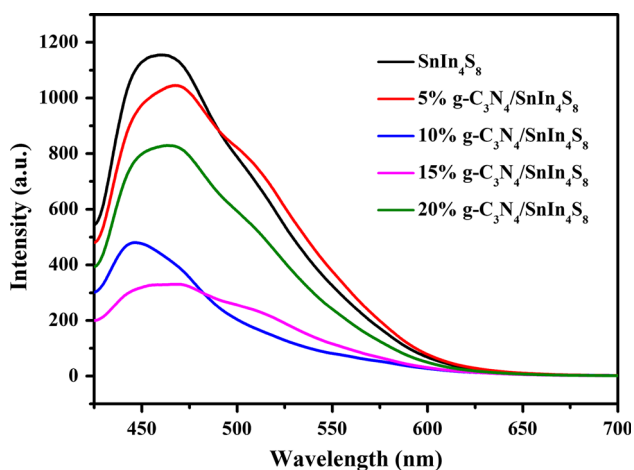
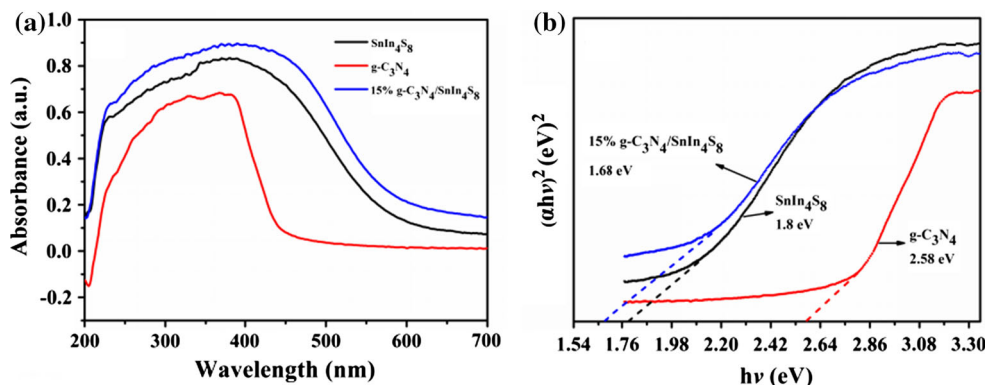


Figure 7 PL spectra of pure SnIn₄S₈ and g-C₃N₄/SnIn₄S₈ composites with different g-C₃N₄ content.

increase of PL emission intensity, leading to the lowest PL emission intensity for 15 % g-C₃N₄/SnIn₄S₈ composite. Therefore, it is implied that 15 % g-C₃N₄/SnIn₄S₈ composite could exhibit the highest separation efficiency of electron–hole pairs under visible-light irradiation.

Photocurrent analysis

To further confirm the separation efficiency of photogenerated electrons and holes, the transient photocurrent response versus time curves of g-C₃N₄, SnIn₄S₈, and g-C₃N₄/SnIn₄S₈ composite ITO electrodes under visible-light irradiation were measured (Fig. 8). The photocurrent intensity increased in the order of g-C₃N₄ < pure SnIn₄S₈ < 5 % g-C₃N₄/SnIn₄S₈ < 10 % g-C₃N₄/SnIn₄S₈ < 20 % g-C₃N₄/SnIn₄S₈ < 15 % g-C₃N₄/SnIn₄S₈, indicating that

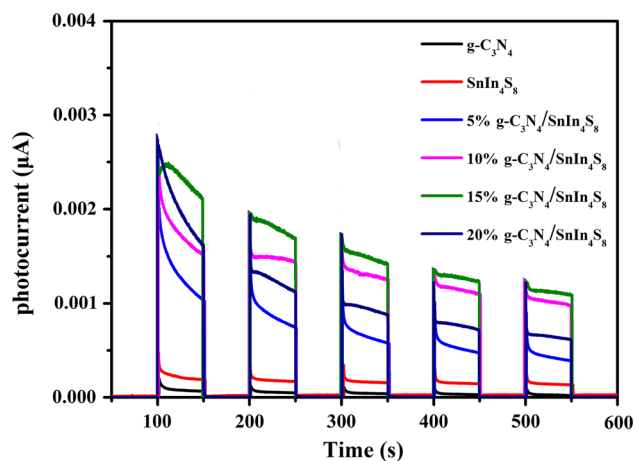


Figure 8 Transient photocurrent response for g-C₃N₄, pure SnIn₄S₈, and g-C₃N₄/SnIn₄S₈ composites with different g-C₃N₄ content.

g-C₃N₄ content in the composite has an obvious effect on the photocurrent intensity of g-C₃N₄/SnIn₄S₈ composite. The photocurrent intensity of g-C₃N₄/SnIn₄S₈ composite increased with increasing the g-C₃N₄ content from 0 to 15 %, but decreased with further increasing the g-C₃N₄ content from 15 % to 20 %, leading to the highest photocurrent intensity for 15 % g-C₃N₄/SnIn₄S₈ composite. The highest photocurrent intensity of 15 % g-C₃N₄/SnIn₄S₈ composite further confirmed its highest separation efficiency of electron–hole pairs under visible-light irradiation, which is consistent with PL results.

Photocatalytic activity

Figure 9 shows the adsorption process in the dark and photocatalytic degradation of MO over pure SnIn₄S₈, g-C₃N₄, and g-C₃N₄/SnIn₄S₈ composites

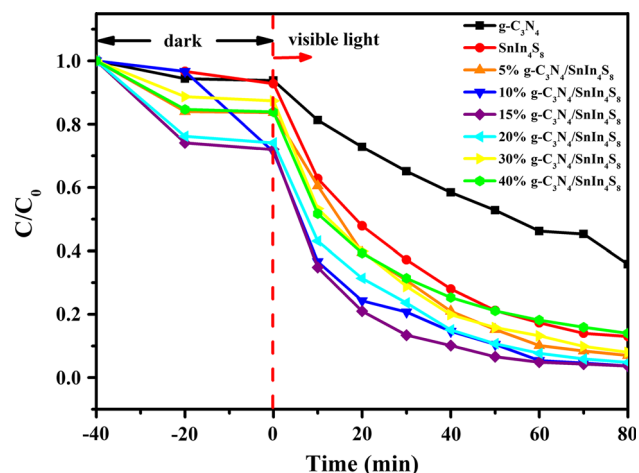


Figure 9 Temporal changes of MO concentration in the presence of pure SnIn_4S_8 and $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composites with different $\text{g-C}_3\text{N}_4$ content.

under visible-light irradiation. The photocatalytic activity of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite is higher than that of pure SnIn_4S_8 and $\text{g-C}_3\text{N}_4$ and is greatly influenced by the $\text{g-C}_3\text{N}_4$ content. The photocatalytic activity of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite is enhanced with increasing the $\text{g-C}_3\text{N}_4$ content from 5 % to 15 %. When the content of $\text{g-C}_3\text{N}_4$ reaches 15 %, it exhibits the highest photocatalytic activity, giving rise to the almost complete degradation of MO, which is much higher than that of pure SnIn_4S_8 . However, as the proportion of $\text{g-C}_3\text{N}_4$ further increases from 15 to 40 %, the photocatalytic activity decreases gradually though it remains higher than that of pure SnIn_4S_8 . Possible reason is that appropriate amount of $\text{g-C}_3\text{N}_4$ is beneficial for the generation and transfer of photogenerated electrons and holes, while excessive $\text{g-C}_3\text{N}_4$ could shield SnIn_4S_8 from light as well as promote electron–hole recombination. Therefore, due to the demands of both the charge transfer and light harvesting, the photocatalytic activity of $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ firstly increases and then decreases with increasing $\text{g-C}_3\text{N}_4$ content, which results in the best photocatalytic activity of 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$.

Photocatalytic mechanism

In order to detect the main reactive species (such as h^+ , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ radicals) of 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$ composite during photocatalytic process under visible-light irradiation, the trapping experiment of h^+ , $\cdot\text{OH}$, and $\cdot\text{O}_2^-$ radicals was investigated by adding

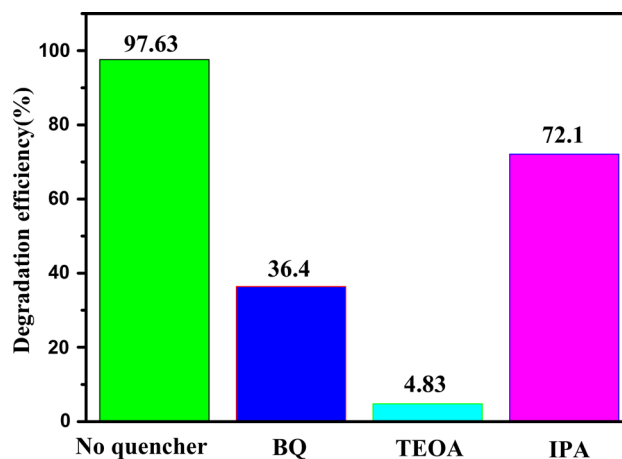


Figure 10 Effect of different scavengers on the MO photodegradation by 15 % $\text{g-C}_3\text{N}_4/\text{SnIn}_4\text{S}_8$.

1.0 mmol/L TEOA (a quencher of h^+), 1.0 mmol/L BQ (a quencher of $\cdot\text{O}_2^-$), and 1.0 mmol/L IPA (a quencher of $\cdot\text{OH}$), respectively. As shown in Fig. 10, the degradation efficiency of MO is 97.63 % in the absence of quenchers. When TEOA, BQ, and IPA scavengers were added, the MO degradation efficiency was reduced to 4.83, 36.4, and 72.1 %, respectively. The results indicated that the main reactive species which play crucial roles in the degradation of MO follow the order of $\text{h}^+ > \cdot\text{O}_2^- > \cdot\text{OH}$.

According to the band gap energy and Mott–Schottky plot of SnIn_4S_8 (Fig. 11), the conduction band potential (E_{CB}) and valence band potential (E_{VB}) of SnIn_4S_8 can be calculated. The flat-band potential (E_{fb}) of SnIn_4S_8 can be estimated from the Mott–Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 N_d} \left(E - E_{\text{fb}} - \frac{k_B T}{e} \right),$$

where C is the space charge capacitance, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of free space, N_d is the donor density, E is the applied potential, E_{fb} is the flat-band potential, k_B is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is the absolute temperature, and e is the electronic charge. The E_{fb} value can be determined by extrapolating the linear part of the curve to $\frac{1}{C^2} = 0$, and the E_{fb} value of SnIn_4S_8 is about -0.45 V versus the saturated calomel electrode (SCE), and is about -0.21 V versus NHE. Supposing the difference between flat-

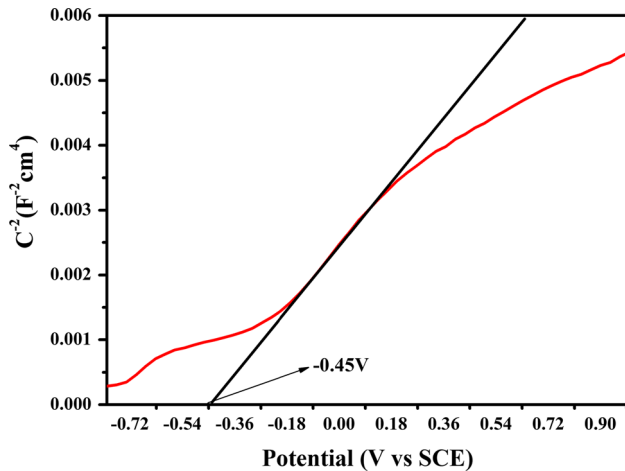


Figure 11 Mott–Schottky plots for SnIn₄S₈.

band potential and conduction band potential can be negligible for n-type semiconductors [32], the E_{CB} value (−0.21 V vs NHE) is approximately equal to the E_{fb} value. The E_{VB} of SnIn₄S₈ can be calculated by empirical equation ($E_{VB} = E_{CB} + E_g$), and the E_{VB} value of SnIn₄S₈ is about 1.59 V versus NHE.

Based on the trapping experiment results, E_{CB} and E_{VB} values of SnIn₄S₈, and the reported literatures, the generation and transfer of the photogenerated holes and electrons in g-C₃N₄/SnIn₄S₈ composites are illustrated in Fig. 12. As shown in Fig. 12, under visible-light illumination, the photogenerated

electrons (e^-) and holes (h^+) can be excited from the valence band (VB) and conduction band (CB) of g-C₃N₄ and then transferred to the VB and CB of SnIn₄S₈, respectively. The accumulated e^- on the surface of SnIn₄S₈ can react with adsorbed O₂ to form superoxide radicals ($\cdot O_2^-$). A majority of $\cdot O_2^-$ radicals play important roles in the MO degradation, and the rest of $\cdot O_2^-$ could further react with H₂O to generate hydroxyl radicals ($\cdot OH$), which also have some impact on the degradation of MO. The h^+ in the VB of SnIn₄S₈ can preferentially attack MO adsorbed onto the surface of g-C₃N₄/SnIn₄S₈ composites, and then MO can be transformed to degradation products.

Regeneration and reuse of spent g-C₃N₄/SnIn₄S₈ composite

To test the stability and reusability of 15 % g-C₃N₄/SnIn₄S₈, the 15 % g-C₃N₄/SnIn₄S₈ composite was reused four times for photocatalytic reaction under the same conditions, and the results are shown in Fig. 13a. There is no obvious decrease in the photocatalytic activity of the 15 % g-C₃N₄/SnIn₄S₈ after four consecutive photocatalytic degradation cycles, indicating that the 15 % g-C₃N₄/SnIn₄S₈ is stable and can be used repeatedly. Moreover, the structure of the regenerated 15 % g-C₃N₄/SnIn₄S₈ after four consecutive cycles was characterized by XRD, and the results are shown in Fig. 13b. It can be seen that

Figure 12 Photocatalytic mechanism of g-C₃N₄/SnIn₄S₈ composite under visible-light irradiation.

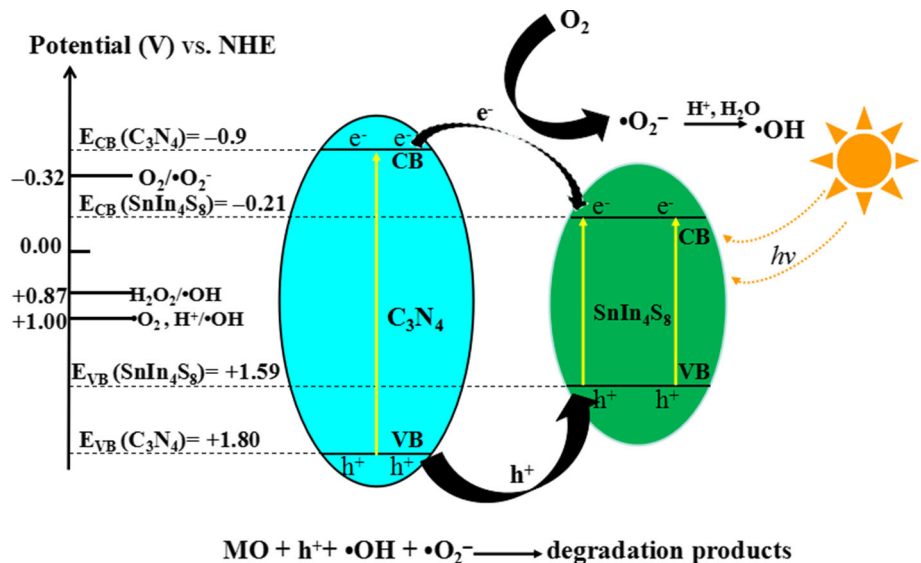
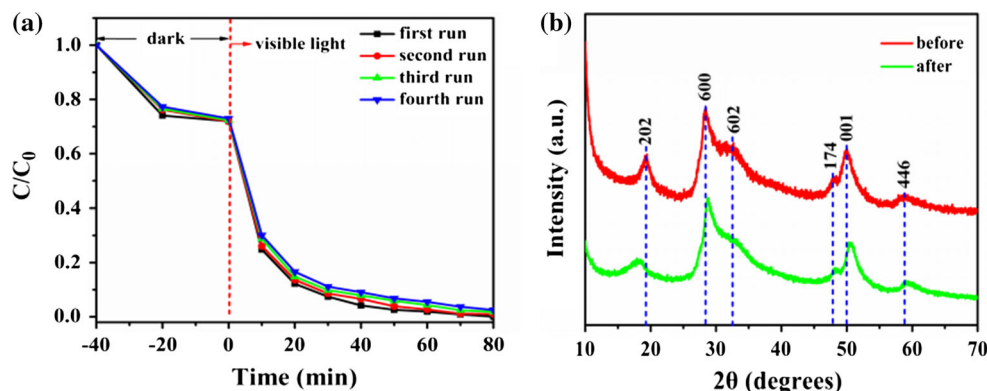


Figure 13 **a** Regeneration and reuse of 15 % g-C₃N₄/SnIn₄S₈ and **b** XRD patterns of the regenerated 15 % g-C₃N₄/SnIn₄S₈ after four consecutive cycles.



there is no significant change of crystal structure, and the main diffraction peaks of the regenerated 15 % g-C₃N₄/SnIn₄S₈ are approximately consistent with those of the fresh counterpart.

Conclusions

We first successfully prepared hierarchical network-like g-C₃N₄/SnIn₄S₈ composites with visible-light response and high photocatalytic activity by low-temperature co-precipitation method. The band gap energies of g-C₃N₄, pure SnIn₄S₈, and 15 % g-C₃N₄/SnIn₄S₈ are 2.58, 1.8, and 1.68 eV, respectively. The g-C₃N₄ content in g-C₃N₄/SnIn₄S₈ composites was optimized, and the optimal 15 % g-C₃N₄/SnIn₄S₈ composites showed the maximum photocurrent intensity and the best photocatalytic performance with complete degradation of MO within 80 min under visible-light irradiation, which is much higher than that of pure SnIn₄S₈. The main reactive species which affect MO degradation efficiency follow the order of $h^+ > \cdot O_2^- > \cdot OH$, and the possible degradation mechanism was proposed. Moreover, 15 % g-C₃N₄/SnIn₄S₈ exhibits excellent reusability and stability without an obvious decrease of photocatalytic activity after four consecutive photocatalytic degradation cycles.

Acknowledgements

This work was supported by the Natural Science Foundation of China (51422807, 51178213, 51238002, 51308278), the China Scholarship fund (201408360048), and the Innovation Fund Designated for Graduate Students of Jiangxi Province (100279315010).

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