Revised: 26 March 2018



In situ synthesis of C_3N_4/Bi_2S_3 composites with enhanced photocatalytic degradation performance under visible light irradiation

Jian Yin^{1,2} | Zhenyu Wu¹ | Min Fang^{1,3} | Ying Xu¹ | Weiju Zhu^{1,3} | Cun Li^{1,2}

¹School of Chemistry and Chemical Engineering, Anhui University, Hefei, China

²AnHui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Anhui University, Hefei, China

³Anhui Province Key Laboratory of Environmentfriendly Polymer Materials, Anhui University, Hefei, China

Correspondence

Cun Li, School of Chemistry and Chemical Engineering, Anhui University, Hefei 230601, China.

Email: cun_li@126.com

Funding information

Graduate Academic Innovation Research Project Fund of Anhui University, Grant/Award Number: yqh100085; Natural Science Foundation of Education Department of Anhui Province, Grant/Award Number: KJ2017A008; Dr. Research Project Fund of Anhui University, Grant/Award Number: 33190213; National Natural Science Foundation of China, Grant/Award Numbers: 51472001, 21404001 Carbon nitride/bismuth sulfide (C_3N_4/Bi_2S_3) nanocomposites were prepared by a facile one-step in situ calcination method using ammonium thiocyanate and bismuth chloride as reagents. The crystal structure, composition, and morphology of the nanocomposites were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The photocatalytic degradation of rhodamine B (RhB) was carried out to evaluate the photocatalytic activity of the nanocomposites under visible light irradiation. The as-prepared C_3N_4/Bi_2S_3 nanocomposites displayed enhanced visible light absorption. These photocatalysts exhibited superior photodegradation performance under visible light irradiation compared to pure C_3N_4 . Meanwhile, the C_3N_4/Bi_2S_3 nanocomposites exhibited remarkably stable photocatalytic efficiency after five cycles of photodegradation of RhB. The C_3N_4/Bi_2S_3 heterostructure improved the separation and transfer efficiency of the photogenerated electron–hole pairs. It played an important role for the enhanced photocatalytic performance of the nanocomposite photocatalysts.

KEYWORDS

bismuth sulfide, carbon nitride, photocatalyst, photodegradation

1 | INTRODUCTION

Photocatalysis using nanomaterials holds extensive potential applications in the energy and environmental fields. Wang et al.^[1] first reported that graphitic carbon nitride (g-C₃N₄) could be used as a photocatalyst to produce hydrogen from water using visible light. Since then, g-C₃N₄ with a π -conjugated inorganic polymer semiconductor has drawn much attention, especially as a promising semiconductor photocatalyst for use in environmental and energy photocatalysis.^[2–5] However, owing to the high exciton binding energy and low mobility of carriers, the photogenerated electron–hole pair separation efficiency in C₃N₄ semiconductor is low, which leads to high recombination rate of the photo-induced electrons and holes and low quantum

efficiency during the photocatalytic reaction.^[6–8] In addition, g-C₃N₄ can absorb and utilize only ultraviolet and visible light in a narrow wavelength range of less than 460 nm because of its bandgap of ~2.7 eV.^[9] These main drawbacks limit its practical application as an efficient photocatalyst in the visible light region.

It is well known that the formation of a heterojunction structure with two different coupled semiconductors is an efficient method to accelerate the separation of photogenerated electron–hole pairs. It has been reported that the coupling of C_3N_4 with TiO₂ is a simple technique to improve its photocatalytic performance.^[10] Sun et al. reported that the C_3N_4/ZnO heterojunction showed higher photodegradation activity and cyclic stability than those of the individual components.^[11] Therefore, in order to extend the range of visible

© 2018 The Chemical Society Located in Taipei & Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

light absorption and overcome the disadvantages of $g_{3}N_{4}$,^[6] the novel photocatalyst composites with narrowbandgap semiconductors were considered.

Bismuth sulfide (Bi₂S₃) is a promising inorganic semiconductor material because of its good photocatalytic activity, nontoxicity, chemical stability, and visible light response.^[12,13] It has been investigated and exploited largely for optoelectronic applications.^[14,15] C₃N₄/Bi₂S₃ composites are advanced materials for photocatalytic applications. Recently, a nanocomposite of C₃N₄ coupled to the narrowbandgap semiconductor Bi₂S₃ was synthesized by a two-step method.^[16] The photocatalytic efficiency of this nanocomposite was much higher than that of the individual components. Zhou et al.^[17] obtained C₃N₄/Bi₂S₃ composites by using the microwave-assisted method and found that its visible light photocatalytic degradation activity with methyl orange increased significantly. The well-matched bandgap of the C_3N_4/Bi_2S_3 heterojunction could be constructed to improve the separation and transfer efficiency of photo-induced carriers and visible light response. All these results demonstrate that C₃N₄/Bi₂S₃ composites are efficient photocatalysts for the photocatalytic degradation of environmental pollutants.

It has been reported that ammonium thiocyanate could be used as a precursor to synthesize C_3N_4 by pyrolysis polymerization,^[18] but sulfur is lost during the synthesis process. It has been found that in situ growth could not only greatly increase the specific surface area but also reduce the size of the nanoparticles.^[19] Here we report a simple onestep in situ calcination method by using ammonium thiocvanate and bismuth chloride mixture to prepare C₃N₄/Bi₂S₃ nanocomposites. Bi₂S₃ nanoparticles are produced from the reaction of BiCl₃ and sulfur, and the sulfur is produced from the pyrolysis polymerization of NH₄SCN; this is one of the novel strategies to utilize the sulfur source of NH₄SCN. The photocatalytic activity of the nanocomposites on the environmental contaminant rhodamine B (RhB) was carried out and investigated in detail. We found that C₃N₄/Bi₂S₃ nanocomposites exhibited superior photocatalytic performance and higher stability toward RhB degradation under visible light irradiation compared to those with the C₃N₄ component alone. The obtained results show that C₃N₄-based nanocomposite photocatalysts with high efficiency and stability can be developed for practical applications in the environmental and energy fields.

2 | RESULTS AND DISCUSSION

2.1 | Structure and morphology study

Figure 1 shows the X-ray diffraction (XRD) patterns of the C_3N_4/Bi_2S_3 nanocomposites prepared at 550 °C with different Bi_2S_3 contents. For all samples, the diffraction peaks appeared at 12.9° and 27.6°, which can be assigned to the g- C_3N_4 layers,^[20] corresponding to the (100) and (002) planes

FIGURE 1 XRD patterns of different C₃N₄/Bi₂S_{3(X)} samples

of hexagonal g-C₃N₄ (JPCDS No.87-1526).^[17] It can also be seen that with increasing amounts of Bi₂S₃ in composites, the diffraction peaks of Bi₂S₃ become obvious and coexist with those of g-C₃N₄. The new high-intensity diffraction peaks at 24.9° and 28.7° correspond to the (130) and (211) planes of the orthorhombic phase Bi₂S₃ (JCPDS No. 17-320). This indicates that the Bi₂S₃ nanocrystals are embedded in the bulk C₃N₄ from this one-step in situ synthesis route. These results also indicate that the in situ produced Bi₂S₃ nanocrystals might have deposited on the surface of graphite-like layer structure of g-C₃N₄.

Fourier transform infrared (FT-IR) spectra of the assynthesized C_3N_4/Bi_2S_3 nanocomposites are displayed in Figure 2. It is worth noting that bulk C_3N_4 and C_3N_4/Bi_2S_3 samples show similar FT-IR absorption peaks. The broad absorption band at 3100-3300 cm⁻¹ can be assigned to the stretching modes of the secondary and primary amines as well as the stretching vibration of O-H of the absorbed water molecule and their intermolecular hydrogen-bonding interactions.^[6,21] All the samples are characterized by a series of bands in the 1200–1600 cm^{-1} region and a strong peak at about 800 cm⁻¹. The bands at 1200–1600 cm⁻¹ are characteristic of the aromatic carbon nitride heterocycles.^[22] The band around 806 cm⁻¹ corresponds to the stretching vibrations of the triazine ring.^[23] These IR bands are typical molecular vibration modes of the triazine and heptazine rings in g- C_3N_4 . The results indicate that the layer structure of $g-C_3N_4$ is not changed upon the formation of Bi₂S₃ nanocrystals.

To investigate the morphology of the as-prepared C_3N_4/Bi_2S_3 samples, scanning electron microscopy (SEM) images of pure C_3N_4 and $C_3N_4/Bi_2S_{3(0.5\%)}$ samples were taken, which are shown in Figure 3. It can be seen from Figure 3a that pure C_3N_4 is composed of irregular lamellar particles of micrometer size. Figure 3b shows the morphology of $C_3N_4/Bi_2S_{3(0.5\%)}$ composites. The composites also display the major characteristic layer morphology of C_3N_4 . Meanwhile, the surfaces of the composites are relatively smooth,





FIGURE 2 FT-IR spectra of different $C_3N_4/Bi_2S_{3(X)}$ samples

indicating that the nanoparticles of Bi_2S_3 are dispersed uniformly in the C_3N_4 bulk. The corresponding energy dispersive X-ray spectrum (EDS) result of $C_3N_4/Bi_2S_{3(0.5\%)}$ is displayed in Figure 3c. It can be seen that $C_3N_4/Bi_2S_{3(0.5\%)}$ consists of C, N, Bi, and S. This indicates that the in situ growth of a small number of Bi_2S_3 nanoparticles does not influence the structure of graphite-like C_3N_4 .

Transmission electron microscopy (TEM) and highresolution (HR)TEM were used to characterize the morphology and crystalline structure of the Bi₂S₃ nanoparticles in the nanocomposites. Figure 4a and b show typical TEM images of pure C₃N₄ and C₃N₄/Bi₂S_{3(0.5%)}, respectively. The Bi₂S₃ nanoparticles with size 5–7 nm are embedded in the C₃N₄ matrix, as seen from the TEM image of C₃N₄/Bi₂S_{3(0.5%)} (Figure 4b). Figure 4c presents the HRTEM photograph of the nanocomposite. Some Bi₂S₃ nanocrystallites of several nanometers show clear fringe spacing with an interval of 0.36 nm, which could be indexed to the (130) lattice plane of Bi₂S₃.^[24,25] The lattice fringes at the interface of the composites are discontinuous, and the interfacial edge of Bi₂S₃ nanoparticles displays the obscure flake folds of C₃N₄, indicating that special heterostructures have been formed.

X-ray photoelectron spectroscopy (XPS) gives the structural environment of the elements of C_3N_4/Bi_2S_3 sample. Figure 5 shows the XPS spectra of $C_3N_4/Bi_2S_{3(0.5\%)}$. There are some peaks due to C, N, S, and Bi in the survey spectrum (Figure 5a), which is consistent with the elements of the C_3N_4/Bi_2S_3 composite. The higher resolution spectra of the C 1s, N 1s, Bi 4f, and S 2p regions were also obtained. The C 1s spectrum contains two peaks at 288 and 284.6 eV. The peak of 288 eV is ascribed to the sp² hybrid carbon in the aromatic ring. The C 1s peak at 284.6 eV is usually assigned into graphitized carbon or sp² C–N.^[26] The N 1s peak can be deconvoluted into three peaks. The main peak at 398.2 eV is attributed to the sp² hybrid N on the triazine ring, while the peak at 400 eV corresponds to the bridging N atoms connected to three triazine rings N–(C)₃.^[27] The high3



FIGURE 3 SEM images of (a) pure C_3N_4 and (b) $C_3N_4/Bi_2S_{3(0.5\%)}.$ (c) EDS results

energy peak at 404.1 eV comes from the charging effect or positive charge localization in the heterocycles.^[28] In addition, the characteristic Bi 4f peaks were present at 158.4 and



 $\label{eq:FIGURE4} \begin{array}{l} \text{TEM images of (a) pure C_3N_4 and (b) C_3N_4 / $Bi_2S_{3(0.5\%)}$}. \\ \mbox{(c) HRTEM images of C_3N_4 / $Bi_2S_{3(0.5\%)}$} \end{array}$

163.6 eV. These peaks are lower in energy compared to the standard XPS binding energy (158.8 and 164.3 eV) for Bi³⁺ 4f, which indicates an increase in the electron density of Bi₂S₃.^[29] This may have originated from the electron transfer between C_3N_4 and Bi_2S_3 in the composites. Meanwhile, the XPS spectrum also confirms the existence of sulfur species from the appearance of an S 2p peak at 163.7 eV, which is consistent with the literature.^[30] The results show that the existence of Bi₂S₃ nanoparticles does not change the basic chemical structure of C_3N_4 . The formation of the heterojunction composites may favor the electron transfer between C_3N_4 and Bi₂S₃.



FIGURE 5 XPS survey spectrum of $C_3N_4/Bi_2S_{3(0.5\%)}$ (a) and the corresponding high-resolution XPS spectra of C 1s (b), N 1s (c), Bi 4f (d), and S 2p (e)

2.2 | Optical characterization

The UV–vis–NIR absorption spectra of the as-prepared C_3N_4/Bi_2S_3 nanocomposites are shown in Figure 6. It is obvious that all the curves have a stronger absorption edge at about 460 nm, which corresponds to the bandgap of C_3N_4 of ~2.7 eV. All the C_3N_4/Bi_2S_3 nanocomposite samples show a distinct absorption band at ~950 nm, which corresponds to the bandgap of Bi_2S_3 , which is ~1.3 eV.^[31,32] With increasing the Bi_2S_3 content, the



FIGURE 6 UV–vis–NIR spectra of the C_3N_4 and different $C_3N_4/Bi_2S_{3(X)}$ samples



FIGURE 7 PL spectra of C₃N₄ and C₃N₄/Bi₂S₃ samples

absorption of C_3N_4/Bi_2S_3 in the visible and near-infrared (NIR) regions increases, which is attributed to the good optical absorption ability of Bi_2S_3 . The increase in light absorption can improve the utilization of the visible



FIGURE 8 (a) Nitrogen adsorption–desorption isotherms and (b) the corresponding pore size distribution curves of the as-prepared samples

 TABLE 1
 Surface area, total pore volume, and average pore diameter of the as-prepared samples

Samples	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
X = 0	18.003	0.772	46.171
X = 0.1%	31.657	0.19	40.131
X = 0.3%	40.752	0.225	42.147
X = 0.5%	44.029	0.48	47.366
X = 1%	27.325	0.323	43.692

spectral region of sunlight. This is attributed to the narrow bandgap of Bi_2S_3 nanoparticles and the heterojunction between C_3N_4 and Bi_2S_3 .

The efficiency of recombination of the photogenerated electron-hole pairs in the nanocomposites was investigated from the photoluminescence (PL). It can be seen in Figure 7 that all the samples exhibit a broad emission peak centered at ~480 nm, which can be attributed to the electron-hole recombination PL phenomenon with the photon energy approximately close to the bandgap energy (2.7 eV) of C₃N₄.^[33] The PL intensity of C₃N₄ significantly decreases when it is blended with the Bi_2S_3 , and it reduces with the increase in Bi_2S_3 content. But X = 1% was abnormal, indicating that Bi₂S₃ plays a leading role in the composites as the Bi₂S₃ content increases.^[16] The PL intensity of C₃N₄ in $C_3N_4/Bi_2S_{3(0.5\%)}$ sample is the lowest. The fluorescence quenching effect indicates that the C₃N₄ coupled with Bi₂S₃ will inhibit the recombination of photogenerated electronhole pairs. The main advantage of the heterojunction structure is to promote the separation of the electrons and holes and the mobility of free carriers.^[34-36] This will lead to high separation efficiency and low recombination rate of the photogenerated charge carriers, which is of great benefit to photocatalytic reactions.



FIGURE 9 Photocatalytic degradation of RhB over different $C_3N_4/Bi_2S_{3(X)}$ samples obtained at 550 °C under visible light irradiation

2.3 | Specific surface area analysis

The nitrogen adsorption–desorption isotherms of the asprepared samples are presented in Figure 8a. Type-III isotherms with a sharp capillary condensation step at high relative pressures with H3 hysteresis loops are observed. The H3 hysteresis loops might be ascribed to the slits due to the aggregation of plate-like particles. Figure 8b shows the corresponding pore size distribution curves centered at ~45 nm. Table 1 gives the surface area, total pore volume, and average pore diameter in detail. It is found that $C_3N_4/Bi_2S_{3(0.5\%)}$ exhibits the highest surface area of 44.029 m²/g, with a total pore volume of 0.48 cm³/g and an average pore diameter of 47.366 nm. The larger surface area favors heterogeneous photocatalysis reaction. Therefore, this sample is expected to exhibit the highest photocatalytic activity.

2.4 | Photocatalytic activity

The photocatalytic activity of the C₃N₄/Bi₂S₃ nanocomposites with different Bi₂S₃ contents was evaluated by the photodegradation of the organic dye RhB under visible light irradiation. The results are displayed in Figure 9. It can be seen that all nanocomposites demonstrate enhanced photodegradation performance compared to pure C3N4 and pure Bi_2S_3 . The photocatalytic degradation activity of $C_3N_4/$ Bi_2S_3 was significantly improved with increase in the Bi_2S_3 content. The $C_3N_4/Bi_2S_{3(0.5\%)}$ sample showed the best photodegradation activity, while the photocatalytic activity of $C_3N_4/Bi_2S_{3(1\%)}$ was slightly reduced. In our experiments, the Bi_2S_3 nanoparticles dispersed uniformly in the C_3N_4 bulk instead of depositing on the surface of C₃N₄ as reported earlier. Hence, heterojunction structures exist throughout the composites, not only on the surface of the catalyst. The photocatalyst with the higher Bi_2S_3 content did not possess higher activity. It might be due to the formation of some recombination centers of photo-induced electron-hole pairs in the bulk of the catalyst. This is consistent with the results of the PL investigation (Figure 7). On the other hand, excessive Bi₂S₃ in the composites increased the agglomeration of the nanoparticles.

The effects of the preparation conditions on photocatalytic activity of C_3N_4/Bi_2S_3 nanocomposites were investigated. The corresponding photocatalytic activity of pure C_3N_4 and $C_3N_4/Bi_2S_{3(0.5\%)}$ samples synthesized at different temperatures was measured, and the results are shown in Figure 10a and b. It can be seen that the photodegradation of RhB by pure C_3N_4 and C_3N_4/Bi_2S_3 was influenced obviously by the calcination temperature. The results reveal that the photocatalytic activity of pure C_3N_4 and C_3N_4/Bi_2S_3 samples synthesized at 500 and 450 °C was poor. However, when the calcining temperature exceeded 500 °C, the activity of these two kinds of catalysts improved significantly. Especially, the photocatalytic activity of C_3N_4/Bi_2S_3 samples was much higher than that of pure C_3N_4 prepared at the same temperature. It has been reported that defects would increase in bulk C_3N_4 prepared at higher temperature, which can promote electron localization.^[37] The RhB degradation process was fitted using quasi-first-order kinetics, and the apparent rate constants are shown in Figure 10c. Compared to that of



FIGURE 10 Photocatalytic activity of (a) C_3N_4 and (b) $C_3N_4/Bi_2S_{3(0.5\%-T)}$ prepared at different temperatures. (c) Photocatalytic degradation rate constant of RhB for the first-order kinetics (the "°C" had been modified in (c))



FIGURE 11 Stability of $C_3N_4/Bi_2S_{3(0.5\%)}$ for RhB photodegradation under visible light irradiation

pure C_3N_4 , the photocatalytic reaction of C_3N_4/Bi_2S_3 nanocomposites was accelerated significantly. For the samples synthesized at 550 °C, the apparent rate constant of RhB photodegradation of C_3N_4/Bi_2S_3 was 1.5 times that of pure C_3N_4 . $C_3N_4/Bi_2S_{3(0.5\%-600)}$ sample shows the largest reaction rate, which is 2 times that of pure C_3N_4 . This apparent kinetic constant is higher than that of the best composite sample (Bi₂S₃/g-C₃N₄-4) synthesized by two steps.^[16]

2.5 | Photocatalytic stability

To determine the photostability of the nanocomposite catalysts, the photodegradation of RhB by $C_3N_4/Bi_2S_{3(0.5\%)}$ was repeated for five cycles under the same conditions. After five recycling experiments, the catalyst still maintained its high photodegradation activity and no apparent reduction in photocatalytic performance was detected (Figure 11). The results show that the nanocomposite photocatalyst was stable under the experimental conditions. This is important for the practical application of the photocatalyst.

2.6 | Photocatalytic mechanism

A plausible mechanism of the separation and transport of the photogenerated charges of C_3N_4/Bi_2S_3 during the photodegradation is shown in Figure 12. The conduction band (CB) and valence band (VB) potentials of Bi_2S_3 are estimated to be -0.2 and 1.1 eV, while those of C_3N_4 are -1.3and 1.4 eV.^[16] When a C_3N_4/Bi_2S_3 sample is irradiated by visible light ($\lambda > 400$ nm), C_3N_4 and Bi_2S_3 can be excited to produce photogenerated electrons (e⁻) and holes (h⁺). Because of the connected heterojunction interface and the well-matched VB structure, some holes in the VB of C_3N_4 can easily transfer to the VB of Bi_2S_3 spontaneously. This will promote the separation of electrons and holes. The active free-radical species of superoxide radical ($O_2^{\bullet-}$) can react with H₂O to generate active hydroxyl radical (OH[•]), and abundant OH[•] can oxidize organic substrates to



FIGURE 12 Schematic of photogenerated charge transfer in the C_3N_4/Bi_2S_3 system under visible light irradiation

decomposition products.^[10,16,38] In the process, the acceleration in charge separation reduces the probability of charge recombination. The photo-erosion of Bi_2S_3 can be prevented by the encapsulated C_3N_4 sheets. As a result, the photocatalytic activity and stability of the composites material are increased.

The impacts of active species such as $O_2^{\bullet-}$, OH^{\bullet} , h^+ , and e^- in the photocatalytic degradation process are shown in Figure 13. When isopropanol (10^{-3} M, 5 mL) was selected as the scavenger for the OH[•] radicals, the degradation rate only slightly decreased, indicating that OH[•] did not play an important part during the photocatalytic process. This may be because the generation of OH[•] radicals was very fast, so isopropanol did not have enough time to take part in the reaction. Thus the influence of isopropanol was



FIGURE 13 Effects of $O_2^{\bullet-}$, OH^{\bullet} , h^+ , and e^- during the degradation of RhB with the addition of different scavengers

not obvious. However, after adding N2 and EDTA-2Na $(10^{-3} \text{ M}, 5 \text{ mL})$, respectively, the photocatalytic activity was greatly suppressed, indicating that the $O_2^{\bullet-}$ and/or h⁺ were the main oxidative species in the degradation of RhB. Oxygen was reduced with the purging of nitrogen, which limited the generation of the superoxide radical. This led to more recombination of electron and holes, as seen from Figure 12. EDTA-2Na can act as an effective electron donor to trap holes produced from the VB of nanoparticles due to irradiation by visible light,^[39] thus inhibiting the oxidation capacity of holes in the nanocomposites (as shown in Figure 12). In addition, it is found that the degradation rate is drastically promoted by the addition of the electron capture agent silver nitrate $(10^{-3} \text{ M}, 5 \text{ mL})$, which further shows that electrons play an important role in the organic contaminant degradation process. It could be considered that the Ag⁺ was reduced by the electrons. Then, the advantage of Ag to act as an electron storage increases, minimizing the electronhole pair recombination rate while enhancing the performance of photocatalysis.[40]

3 | CONCLUSIONS

 C_3N_4/Bi_2S_3 nanocomposite catalysts with different Bi_2S_3 contents were successfully prepared by a one-step in situ technique using NH₄SCN and BiCl₃ as precursors. Small Bi₂S₃ nanocrystals were uniformly distributed in the bulk of the C₃N₄ matrix. A well-constructed heterojunction between C_3N_4 and Bi_2S_3 of the nanocomposites resulted in enhanced visible light absorption and acceleration of the separation rate of the photoexcited charger carriers. Under visible light irradiation, the photocatalytic degradation of RhB by the nanocomposites was more efficient compared to that with the pure C_3N_4 photocatalyst. The content of Bi_2S_3 and the preparation temperature had significant influence on the photocatalytic activity of the C₃N₄/Bi₂S₃ catalyst. C₃N₄/ $Bi_2S_{3(0.5\%-550)}$ demonstrated good photocatalytic activity and reusability under the experimental conditions. The experimental results prove that one-step in situ synthesis of carbon nitride-based composites modified with small amounts narrow-bandgap semiconductors of metal sulfides with high photocatalytic efficiency and good stability is feasible.

4 | EXPERIMENTAL

All the reagents were purchased from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China) and used as received without further purification.

4.1 | Synthesis of C₃N₄/Bi₂S₃ nanocomposites

 C_3N_4/Bi_2S_3 samples were synthesized by a one-step in situ calcination method from a mixture of NH₄SCN and BiCl₃.

First, 15 g NH₄SCN was mixed with different amounts of BiCl₃ in 20 mL ethanol solution. Then, ethanol was removed by evaporation at 80 °C. After thorough drying in an oven, the solid mixtures were calcined at 550 °C for 2 hr at a ramp rate of 5 °C/min in N₂ atmosphere to acquire yellow samples. The obtained samples were denoted as C₃N₄/Bi₂S_{3(X-T)}, where *X* (*X* = 0, 0.1, 0.3, 0.5, 1%) refers to the initial mass ratio of BiCl₃/NH₄SCN, and *T* refers to the calcination temperature. The productivity of C₃N₄ acquired using NH₄SCN as a precursor was about 6%, and according to the inductively coupled plasma (ICP) test results, the real mass ratio of Bi₂S₃ to C₃N₄ in the composites was about 5% for C₃N₄/Bi₂S_{3(0.5%-550)}. The letter "*T*" of the samples prepared at 550 °C was omitted unless otherwise noted.

4.2 | Characterization

XRD measurements were carried out on a DX-2700 diffractiometer using Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and with a 30 mA flux, at the scanning rate of 4°min⁻¹. FT-IR spectra were recorded using a Vertex80 FT-IR spectrometer in KBr pellets. Field-emission (FE)SEM measurements were performed on a Hitachi S-4800 scanning electron microscope. HRTEM images were obtained on a JEM-2100 high-resolution TEM (Japan Electron Co.) at an accelerating voltage at 200 kV. The UV–visible–near infrared (UV–vis– NIR) adsorption spectra were recorded on a Hitachi U-4100 spectrometer in the range 240–1800 nm. The roomtemperature PL spectra were recorded on a fluorescence spectrophotometer (Hitachi F-4500). XPS data were obtained on a ESCALAB 250Xi instrument. ICP tests were carried out on an iCAP 7400 Duo device.

4.3 | Photocatalytic test

The photodegradation activity of C_3N_4/Bi_2S_3 nanocomposite photocatalysts were evaluated using RhB solution $(1.0 \times 10^{-5} \text{ mol/L})$ as a simulation of wastewater. The light source for the photocatalytic reaction was a 300 W Xe lamp combined with a cutoff filter to remove light wavelengths below 400 nm. Fifty milligrams of the photocatalyst was added to 100 mL of the model pollutant solution. After stirring in the dark for 30 min to ensure adsorption–desorption equilibrium, the solution was exposed to visible light radiation. The RhB concentration was analyzed by the UV–vis spectrophotometer at certain irradiation time intervals.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (no. 21404001, 51472001), the Dr. Research Project Fund of Anhui University (no. 33190213), the Natural Science Foundation of Education Department of Anhui Province (No. KJ2017A008), and

JOURNAL OF THE CHINESE CHEMICAL SOCIETY

the Graduate Academic Innovation Research Project Fund of Anhui University (no. yqh100085).

REFERENCES

- X. C. Wang, K. Maeda, X. F. Chen, K. TakaNabe, K. Domen, Y. D. Hou, X. Z. Fu, M. Antonietti, J. Am. Chem. Soc. 2009, 131, 1680.
- [2] S. Cao, J. Low, J. Yu, M. Jaroniec, Adv. Mater. 2015, 27, 2150.
- [3] Y. Wang, X. C. Wang, M. Antonietti, Angew. Chem. Int. Ed. 2012, 51, 68.
 [4] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Z. Qiao, Environ. Sci. 2012, 5,
- 6717.
- [5] S. W. Cao, J. G. Yu, J. Phys. Chem. Lett. 2014, 5, 2101.
- [6] Y. J. Cui, Chin. J. Catal. 2015, 36, 372.
- [7] S. Kumar, T. Surendar, A. Baruah, V. Shanker, J. Mater. Chem. A 2013, 1, 5333.
- [8] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J. O. Muller, R. Schlogl, J. M. Carlsson, J. Mater. Chem. 2008, 18, 4893.
- [9] J. Chen, S. H. Shen, P. H. Guo, M. Wang, P. Wu, X. X. Wang, L. J. Guo, *Appl. Catal.*, B 2014, 152, 335.
- [10] J. G. Yu, S. H. Wang, J. X. Low, W. Xiao, Phys. Chem. Chem. Phys. 2013, 15, 16883.
- [11] J. X. Sun, Y. P. Yuan, L. G. Qiu, X. Jiang, A. J. Xie, Y. H. Shen, J. F. Zhu, *Dalton Trans.* **2012**, *41*, 6756.
- [12] J. F. Chao, S. M. Xing, J. Z. Zhao, C. H. Qin, D. G. Duan, Y. L. Zhao, Q. He, *RSC Adv.* **2016**, *6*, 55676.
- [13] L. Cademartiri, R. Malakooti, P. G. Brien, A. Migliori, S. Petrov, N. P. Kherani, G. A. Ozin, Angew. Chem. Int. Ed. 2008, 47, 3814.
- [14] G. Konstantatos, L. Levina, J. Tang, E. H. Sargent, Nano Lett. 2008, 8, 4002.
- [15] A. K. Rath, M. Bernechea, L. Martinez, G. Konstantatos, Adv. Mater. 2011, 23, 3712.
- [16] X. S. Rong, F. X. Qiu, J. Yan, H. Zhao, X. L. Zhu, D. Y. Yang, RSC Adv. 2015, 5, 24944.
- [17] X. Zhou, S. Y. Yao, Y. M. Long, Z. S. Wang, W. F. Li, *Mater. Lett.* 2015, 145, 23.
- [18] Y. J. Cui, Y. X. Wang, H. Wang, F. Cao, F. Y. Chen, *Chin. J. Catal.* 2016, 37, 1899.
- [19] X. H. Wu, F. Y. Chen, X. F. Wang, H. G. Yu, Appl. Surf. Sci. 2018, 427, 645.
- [20] Y. J. Cui, J. H. Huang, X. Z. Fu, X. C. Wang, Catal. Sci. Technol. 2012, 2, 1396.
- [21] L. Y. Chen, W. D. Zhang, Appl. Surf. Sci. 2014, 301, 428.
- [22] B. V. Lotsch, W. Schnick, Chem. Mater. 2006, 18, 1891.
- [23] X. S. Rong, F. X. Qiu, J. Qin, J. Yan, H. Zhao, D. Y. Yang, J. Ind. Eng. Chem. 2014, 20, 3808.

- [24] F. Jiang, T. T. Yan, H. Chen, A. W. Sun, C. M. Xu, X. Wang, *Appl. Surf. Sci.* 2014, 295, 164.
- [25] Y. M. Cui, Q. F. Jia, H. Q. Li, J. Y. Han, L. J. Zhu, S. G. Li, Y. Zou, J. Yang, *Appl. Surf. Sci.* 2014, 290, 233.
- [26] S. M. Lyth, Y. Nabae, S. Moriya, S. Kuroki, M. Kakimoto, J. Ozaki, S. Miyata, J. Phys. Chem. C 2009, 113, 20148.
- [27] J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen, J. Mater. Chem. 2011, 21, 14398.
- [28] D. Foy, G. Demazeau, P. Florian, D. Massiot, C. Labrugere, C. Goglio, J. Solid State Chem. 2009, 182, 165.
- [29] Z. Fang, Y. F. Liu, Y. T. Fan, Y. H. Ni, X. W. Wei, K. B. Tang, J. M. Shen, Y. Chen, J. Phys. Chem. C 2011, 115, 13968.
- [30] J. M. Wang, X. Zhang, J. Wu, H. Chen, S. Sun, Nanoscale 2017, 9, 15873.
- [31] X. H. Gao, H. B. Wu, L. X. Zheng, Y. J. Zhong, Angew. Chem. Int. Ed. 2014, 53, 5917.
- [32] Y. Wu, Q. F. Han, L. Wang, Mater. Chem. Phys. 2017, 187, 72.
- [33] X. F. Chen, Y. S. Jun, K. Takanabe, K. Maeda, K. Domen, X. Z. Fu, M. Antonietti, X. C. Wang, *Chem. Mater.* **2009**, *21*, 4093.
- [34] J. S. Zhang, X. F. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Z. Fu, M. Antonietti, X. C. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 441.
- [35] J. S. Zhang, M. W. Zhang, R. Q. Sun, X. C. Wang, Angew. Chem. Int. Ed. 2012, 51, 10145.
- [36] G. G. Zhang, M. W. Zhang, X. X. Ye, X. Q. Qiu, S. Lin, X. C. Wang, Adv. Mater. 2014, 26, 805.
- [37] Y. J. Cui, Z. X. Ding, P. Liu, M. Antonietti, X. Z. Fu, X. C. Wang, *Phys. Chem. Chem. Phys.* 2012, 14, 1455.
- [38] S. Kumar, A. Baruah, S. Tonda, B. Kumar, V. Shanker, B. Sreedharc, Nanoscale 2014, 6, 4830.
- [39] J. J. Wang, L. Tang, G. M. Zeng, Y. C. Deng, H. R. Dong, Y. N. Liu, *Appl. Catal. B-Environ.* 2018, 222, 115.
- [40] W. D. Oh, L. W. Lok, A. Veksha, A. Giannis, T. T. Lin, *Chem. Eng. J.* 2018, 333, 739.

How to cite this article: Yin J, Wu Z, Fang M, Xu Y, Zhu W, Li C. In situ synthesis of C_3N_4/Bi_2S_3 composites with enhanced photocatalytic degradation performance under visible light irradiation. *J Chin Chem Soc.* 2018;1–9. <u>https://doi.org/10.1002/jccs.</u> 201800002