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Article

Accelerated separation of photogenerated charge carriers and enhanced photocatalytic performance of g-C₃N₄ by Bi₂S₃ nanoparticles

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ABSTRACT

Employing photothermal conversion to improve the photocatalytic activity of g-C₃N₄ is rarely reported previously. Herein, different ratios of g-C₃N₄/Bi₂S₃ heterojunction materials are synthesized by a facile ultrasonic method. Advanced characterizations such as X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy are employed to analyze the morphology and structure of the prepared materials. Compared with sole counterparts, the heterojunction materials CN-BiS-2 exhibit significantly enhanced photocatalytic performance, which is 2.05-fold as g-C₃N₄ and 4.42-fold as Bi₂S₃. A possible degradation pathway of methylene blue (MB) was proposed. Based on the photoproduced high-energy electrons and photothermal effect of Bi₂S₃, the transfer and separation of electron-hole pairs are greatly enhanced and more active species are produced. In addition, the relatively high utilization efficiency of solar energy has synergistic effect for the better photocatalytic performance.

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1. Introduction

Photocatalytic technology is a kind of advanced oxidation technology, which uses light to excite electrons to produce highly oxidizing species [1–4]. It can mineralize organic molecules to carbon dioxide and water, thus eliminating organic pollutants from water completely [5,6]. Traditional photocatalyst such as titanium dioxide (TiO₂), zinc oxide (ZnO) and bismuth phosphate (BiPO₄) have outstanding photocatalytic per-

formance for water splitting and/or organic pollutant degradation [7–10]. However, their application is highly limited by their wide bandgap (e.g. 3.2 eV, that can only be excited by UV light) and low utilization ratio of solar energy (i.e., UV light accounts for about only 4% of solar light) [11].

In recent years, visible light response photocatalysts arise increasing interests. A series of new photocatalyst such as bismuth oxide (Bi₂O₃) [12–14], bismuth vanadate (BiVO₄) [15,16], cadmium sulfide (CdS) [17,18], ferric oxides (Fe₂O₃) [19,20] or

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graphitic carbon nitride (g-C₃N₄) [21–23] were developed to overcome the shortages of UV light response photocatalysts. Among these semiconductors, g-C₃N₄ attracted extreme attentions due to its advantages of metal-free, wide resource, non-toxicity and facile preparation [24–27]. However, the bandgap of g-C₃N₄ is about 2.7 eV, which means that it can only absorb the light lower than 460 nm and its utilization ratio of solar light is still not high [28,29]. In addition, the rapid recombination of photogenerated charge carriers is another aspect limiting the application of g-C₃N₄ [30].

Constructing heterojunctions with other semiconductors is an efficient way to improve the photocatalytic performance of g-C₃N₄. Several g-C₃N₄ based heterojunctions such as BiOCl/g-C₃N₄, TiO₂/g-C₃N₄, Bi₂MoO₆/g-C₃N₄, Al₂O₃/g-C₃N₄, Ag₃PO₄/g-C₃N₄ have been developed previously, nevertheless, the poor light absorption is still limiting their application [31–35]. Therefore, better g-C₃N₄ based heterojunction materials should be synthesized to facilitate its high-efficient application. Sulfur-based materials have been widely used to improve the performance of photocatalysts [36–39], Bismuth sulfide (Bi₂S₃) is the main component of bismuth glance that belongs to orthorhombic crystal system with a narrow-bandgap of 1.3–1.7 eV [40]. Because of its distinctive electron structure and optical property, Bi₂S₃ has wide application prospect in different areas such as photocatalyst [41,42], photodetector [43,44] or medical imaging [45]. Due to the Peltier effect of Bi₂S₃, it can be used in thermoelectric-cooling technologies [46,47]. The excellent photothermal conservation effect also makes Bi₂S₃ a unique material in photothermal cancer treatment [48,49].

In fact, combining Bi₂S₃ with g-C₃N₄ to create heterojunction has been demonstrated to be a highly efficient way to improve the photocatalytic activity of g-C₃N₄. However, the reported methods in literature are rather complicated. For instance, Xuan et al. [50] used the microwave-assisted method to prepare g-C₃N₄/Bi₂S₃, in which microwave oven and nitrogen must be used. Chen et al. [51] put g-C₃N₄ and the precursor of Bi₂S₃ in a Teflon-lined steel autoclave and heated it at 160 °C for 30 h. After that, the product was collected, washed and dried in a vacuum oven. The final product includes g-C₃N₄/Bi₂S₃ and Bi. Yin et al. [52] reported another method to prepare g-C₃N₄/Bi₂S₃ composite materials, through calcining the mixture of ammonium thiocyanate (NH₄SCN) and bismuth chloride (BiCl₃) at 550 °C in nitrogen atmosphere. In addition, the potential mechanisms for the enhanced photocatalytic activity of g-C₃N₄/Bi₂S₃ heterojunctions in these previous studies remained unclear or even contradictory. In particular, Xuan et al. [45] claimed that the enhanced separation of electron and hole pairs should be assigned to the transfer of electrons rather than holes. In contrast, Chen et al. [46] stated that the transfer of holes should be the key reason for the better photocatalytic performance. Thus, the questions remained to be answered include: Can g-C₃N₄/Bi₂S₃ heterojunctions be synthesized more facilely? How does Bi₂S₃ influence the photocatalytic performance of g-C₃N₄? What is the transfer path of electrons and holes?

Herein, we employed a facile coprecipitation method to prepare Bi₂S₃ at low temperature. Bi₂S₃ was induced to g-C₃N₄

nanosheets by ultrasonic and the obtained g-C₃N₄/Bi₂S₃ heterojunctions exhibited better photocatalytic performance than g-C₃N₄ nanosheets and Bi₂S₃ particles. The morphology and structure of the prepared materials are comprehensively characterized. The potential mechanisms for the enhanced catalytic performance are then analyzed. The findings of this work are expected to provide insights into the synthesis and application of g-C₃N₄ based heterojunction photocatalysts.

2. Experimental

2.1. Reagents

Bismuth ammonium citrate was bought from Tianjin Guangfu Fine Chemical Research Institute. Thioacetamide and melamine were bought from Sinopharm Chemical Reagent Beijing Co., Ltd. All the chemicals were analytical reagent and used without further purification.

2.2. Preparation of materials

g-C₃N₄ nanosheets were prepared as follow. Firstly, 2 g of melamine was located in a 50 mL corundum crucible and heated to 540 °C for 4 h. The heating rate was 4 °C/min and the atmosphere was air. After that, the product (bulk g-C₃N₄) was ground uniformly and reheated at 500 °C for 2 h in air. Then g-C₃N₄ nanosheets are obtained [53].

Bi₂S₃ was synthesized by using the coprecipitation method. Firstly, 30 mL of bismuth ammonium citrate solution (0.0075 M) and 30 mL of thioacetamide solution (0.005 M) was put into two 100 mL flasks. Then the flasks were stirred for 10 min at 90 °C in water bath. After that, the thioacetamide solution was slowly added to the bismuth ammonium citrate solution. The mixture was kept at 90 °C for 2 h to form Bi₂S₃. Finally, the prepared Bi₂S₃ was washed by water and ethanol, and freeze-dried.

The g-C₃N₄/Bi₂S₃ heterojunctions were prepared by the ultrasonic method. The details are as follow: 1 g of g-C₃N₄ nanosheets, a certain amount of Bi₂S₃, 60 mL of water and 60 mL of ethanol were put in a 200 mL beaker. Then the mixture was strong stirred for 10 min and sonicated for 8 h. Afterwards, the powder was collected, washed 3 times and dried at 60 °C for 12 h. The amount of Bi₂S₃ was 2, 20 and 50 mg, besides, the samples were named as CN-BiS-1, CN-BiS-2 and CN-BiS-3 respectively.

2.3. Characterization of materials

The X-ray diffraction (XRD) of the samples was tested with a D/max-2400 X-ray diffractometer at 25 °C with intense Cu K α radiation. A Bruker V70 Fourier transform infrared spectrometer was employed to test the Fourier transform infrared spectroscopy (FTIR) of C₃N₄/Bi₂S₃ heterojunction samples and the wavenumber range was from 4000 to 600 cm⁻¹. X-ray photoelectron spectroscopy (XPS) of the prepared samples was obtained from a PHI Quantera XPS microprobe. JEOL2100F thermal field high resolution scanning transmission electron mi-

croscopy (STEM) with an Oxford M-max 80 energy-dispersive X-ray spectroscopy (EDS) was used to explore the morphology and structure of CN-BiS-2. The UV-vis diffuse reflectance spectroscopy (DRS) of the samples was obtained from a Hitachi U-3900 scan UV-vis spectrophotometer from 800 to 250 nm, the blank baseline of which was tested with high purity barium sulfate (BaSO_4). Photoluminescence (PL) spectra were tested with a Hitachi F-4600 fluorescence spectrometer excited at 325 nm and the wavelength range was from 300 to 700 nm. The electrochemical impedance spectroscopy (EIS) and photocurrent of the samples were tested by using a CHI 760E electrochemical workstation. A platinum (Pt) wire was used as counter electrode, a saturated calomel electrode (SCE) was used as reference electrode and the solution was 0.1 M sodium sulfate (Na_2SO_4). The preparation of working electrodes was as follow: 1 mL of water and 5 mg of samples were put into 5 mL cuvettes; then the cuvettes were sonicated 4 h to disperse the samples in the solvent evenly; then the suspension was evenly coated on indium-tin-oxide (ITO) glasses (5×2 cm) and dried in air for 12 h. The light resource of photocurrent was provided by a 300 W xenon lamp (PLS-SXE-300) and the light intensity was 50 mW/cm^2 . The frequency of EIS was from 1 to 1×10^5 Hz; the initial voltage was 0 V and the amplitude was 0.005 V. The electron spin resonance (ESR) spectra of pure g- C_3N_4 and CN-BiS-2 were tested with a Bruker ESR 300E spectrometer and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as the radical scavenger. Thermal images were gained from Xinsite HT02 thermography with a 300 W Xe lamp (PLS-SXE300) irradiation.

2.4. Photocatalytic activity and product tests

Methylene blue (MB) was used as the molecular probes to evaluate the photocatalytic activity of the prepared samples. The photocatalytic reaction test was carried out with a PhchemIII photochemical reactions instrument and the light resource was a 500 W xenon lamp with average light intensity being 35 mW/cm^2 . Firstly, 50 mg of the samples were weighted and located in five 50 mL quartz cuvettes. Then 50 mL of MB solution (5 ppm) was added to the cuvettes and the suspension was strong stirred for 2 h to reach the adsorption-desorption equilibrium. Afterwards, 3 mL of suspension was collected and the light was turned on. The photodegradation process lasted for 5 h and 3 mL of suspension was sampled per hour. The concentration of MB solution was measured with a Hitachi U-3900 scan UV-vis spectrophotometer at the wavelength of 664 nm. The total organic carbon (TOC) of the solutions during the photocatalytic degradation process was analyzed with a Shimadzu TOC-L. The degradation products were analyzed by a Shimadzu LCMS-8060 liquid chromatograph with tandem mass spectrometry (LCMSMS).

3. Results and discussion

3.1. Structure and morphology

Bi_2S_3 belongs to orthorhombic crystal system, crystallizing

Fig. 1. The crystal structure of Bi_2S_3 .

in the space group of Pnma (62) with the unit cell parameters $a = 11.2690 \text{ \AA}$, $b = 3.9717 \text{ \AA}$, $c = 11.1290 \text{ \AA}$, and $Z = 4$ [54]. Fig. 1 shows the crystal structure of Bi_2S_3 . The formation of Bi_2S_3 presents a serrated chain-like structure, which is formed by the connection of the trigonal pyramid structure of $[\text{Bi}_2\text{S}_3]$. This structure grows along the (001) direction and two chains can connect with each other and form $[\text{Bi}_4\text{S}_6]_n$. The strong and short Bi-S in the chains are between 2.584 to 2.7439 $\text{\AA}$, while the longer Bi-S between the chains are 3.056 $\text{\AA}$ [55].

Firstly, XRD patterns were used to explore the component and crystallinity of prepared materials. Fig. 2 is the XRD patterns of g- C_3N_4 , Bi_2S_3 and g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ heterojunction samples. The two peaks of g- C_3N_4 at 13.1 and 27.1° can be attributed to the (100) and (002) crystal plane diffraction respectively (JCPDS 87-1526). The XRD pattern of Bi_2S_3 well matches the reference card (ICSD 153946) that has not strong crystallinity like g- C_3N_4 . After sonicated with Bi_2S_3 in water and ethanol solution, the diffraction intensity of g- C_3N_4 gradually decreased, which illustrates that the crystallinity of the g- C_3N_4 was decreased. The effect of ultrasonic and solution can help further nanosize g- C_3N_4 and the Bi_2S_3 nanoparticles have a positive effect on the tailor of g- C_3N_4 [56,57].

Fig. 2. XRD patterns of g- C_3N_4 , Bi_2S_3 and g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{S}_3$ heterojunction samples.

Fig. 3. FTIR spectra of g-C₃N₄, Bi₂S₃ and g-C₃N₄/Bi₂S₃ heterojunction samples.

Afterwards, FTIR were employed to explore the surface functional groups of g-C₃N₄, Bi₂S₃ and g-C₃N₄/Bi₂S₃ samples (Fig. 3). The inorganic Bi₂S₃ had no obvious peaks in FTIR. For the g-C₃N₄ based samples, the wide peak at around 3400 cm⁻¹ was attributed to the hydroxyl form water, which was adsorbed on the surface of the samples. The peaks at 1200, 1234, 1317 1457 and 1631 cm⁻¹ were all assigned to the skeletal vibration peaks of (C₆N₇). [58] The peak at 1400 cm⁻¹ belonged to the stretching vibration of C₃N₃ and the vibration peaks of the out-of-plane skeleton of triazine rings showed a strong and sharp peak at 808 cm⁻¹ [59]. Compared with g-C₃N₄, no new peak appears in the FTIR of g-C₃N₄/Bi₂S₃ samples, indicating that the interaction between g-C₃N₄ and Bi₂S₃ is physical interaction.

Then, STEM and EDS mapping images were tested to ex-

Fig. 4. The STEM image (a) and the EDS mapping images of Bi (b), C (c), N (d) and S (e) of CN-BiS-2.

plore the morphology and structure of CN-BiS-2. According to Fig. 4(a), Bi₂S₃ particles (the bright part) in CN-BiS-2 were about 50 nm with irregular morphology. Some of the Bi₂S₃ particles were at the surface of g-C₃N₄ nanosheets, while the others were sandwiched in the g-C₃N₄ layers. As for g-C₃N₄, it showed a soft layer structure. The EDS mapping could further confirm the component and morphology of this sample.

Fig. 5(a) is the XPS narrow spectra of Bi and S of Bi₂S₃ and CN-BiS-2. For the low spectra intensity of CN-BiS-2, we enlarged this image and showed it in Fig. 5(b). In Bi₂S₃, two distinct peaks at 163.6 and 158.3 eV can be assigned to the 4f_{5/2} and 4f_{7/2} of Bi³⁺, respectively [13]. The weak peak at 160.1 eV is the 2p_{3/2} of S²⁻ [60]. For the peaks of Bi 4f_{5/2} and 4f_{7/2} of CN-BiS-2, the binding energy shifted to 163.2 and 157.9 eV, which is probably caused by the strong interaction between

Fig. 5. XPS narrow spectra of Bi and S of Bi₂S₃ and CN-BiS-2 (a), and enlarged spectrum of CN-BiS-2 (b). XPS narrow spectra of N of g-C₃N₄ (c) and CN-BiS-2 (d).

Fig. 6. Photocatalytic activity of g-C₃N₄, Bi₂S₃ and CN-BiS composite samples. (a) pseudo-first-order rate constant k ; (b) the TOC removal of g-C₃N₄ and CN-BiS-2.

Bi₂S₃ and g-C₃N₄. As the concentration of Bi₂S₃ in sample CN-BiS-2 is quite low, it is difficult to judge the narrow spectra of S from this image. As shown in Fig. 5(c), N1s has two peaks. The peak at 400.5 eV is attributed to the bridging N atoms in N(C)₃ or N bonded with H atoms. The other peak at 398.7 eV is assigned to the *sp*² hybridized N involved in triazine rings of g-C₃N₄. Due to the interaction between Bi₂S₃ and g-C₃N₄, the binding energy of N1s peaks of CN-BiS-2 also showed some shift.

Based on the above results, we can conclude that g-C₃N₄/Bi₂S₃ heterojunction samples are successfully fabricated. The Bi₂S₃ particles were either at the surface of g-C₃N₄ nanosheets or sandwiched in the g-C₃N₄ layers. After sonicated with Bi₂S₃ in water and ethanol solution, the crystallinity of the g-C₃N₄ clearly decreased. The effect of ultrasonic and solution can further nanosize the g-C₃N₄ and the Bi₂S₃ nanoparticles have a positive effect on the tailor of g-C₃N₄.

3.2. Photocatalytic activity

MB was used as molecular probes to evaluate the photocatalytic activity of prepared samples. Fig. S1 shows the concentration change of MB under simulated solar light irradiation. It is obvious that the concentration of MB solution gradually decreased during the time course. Among all the samples, CN-BiS-2 had the highest photocatalytic activity and the total removal of MB is 92.11% in 6 h. The pseudo-first-order rate constant k of CN-BiS-2 is 0.521 h⁻¹, which is 2.05-fold as g-C₃N₄ and 4.42-fold as Bi₂S₃ (Fig. 6(a)). To further confirm the mineralization of MB, the TOC was tested. As shown in Fig. 6(b), during 6 h, the TOC of MB reduced 82.03% by CN-BiS-2 and it is much higher than that of g-C₃N₄. However, the reduce of TOC is lower than the removal of MB concentration, indicating there are some intermediate and incompletely mineralized products. Then, LC-MSMS was employed to analyze the degradation products (Fig. S2) and a possible degradation path was proposed (Fig. 7). There are two major degradation pathways of MB by CN-BiS-2. Firstly, the oxygen in water can form S=O with MB [61]. Then a C–N is broken and 2,5-diamino-4-hydroxybenzenesulfonate was formed, which may be further degraded to ((2*E*,4*Z*)-5-amino-4-hydroxypenta-2,4-dien-2-yl) amide and

2,4-dimethylpent-2-en-3-ide. With increasing reaction time, these organic molecules can finally be converted to CO₂ and H₂O. In the other pathway, MB firstly lose two –CH₃ and then form 5λ⁴-phenothiazin-3-ol. It may also be gradually mineralized by the photocatalytic active species.

3.3. Photocatalytic mechanism

Solar light utilization ratio has crucial influence on the application of photocatalysts. Firstly, UV-vis DRS was employed to test the light absorption ability of prepared samples. Fig. 8 is the UV-vis DRS of g-C₃N₄, Bi₂S₃ and CN-BiS heterojunction samples. The g-C₃N₄ could only absorb the light lower than 460 nm and its bandgap was about 2.7 eV. When Bi₂S₃ was introduced to g-C₃N₄ nanosheets, the light absorption of the composite samples improved significantly both in the ultraviolet and visible light region. Besides, the absorption edges of the composite samples showed an obvious red-shift, which was caused by the strong interaction between g-C₃N₄ and Bi₂S₃. The wave-band absorption in the visible light region was also enhanced. The stronger light absorption can favor the samples to utilize more solar energy.

Photocurrent is an efficient way to prove the separation and

Fig. 7. A possible degradation path of the methylene blue molecule.

Fig. 8. UV-vis DRS of g-C₃N₄, Bi₂S₃ and CN-BiS composite samples.

transfer efficiency of photogenerated charge carriers. Fig. 9(a) is the photocurrent of g-C₃N₄ and CN-BiS-2. It was obvious that both g-C₃N₄ and CN-BiS-2 have strong photocurrent response when the light was turned on. The photocurrent intensity of CN-BiS-2 was much higher than that of g-C₃N₄, indicating that the separation and transfer efficiency of electrons was enhanced. Moreover, the EIS Nyquist plots arc radius of CN-BiS-2 was smaller than that of g-C₃N₄ (Fig. 9(b)), which could further confirm the higher separation and transfer efficiency of photogenerated electron as well as hole pairs.

Afterwards, PL spectra were used to further determine the separation and transfer efficiency of photogenerated charge carriers. As shown in Fig. 10(a), the CN-BiS-2 showed much lower PL spectra intensity than g-C₃N₄, illustrating that the introduction of Bi₂S₃ can restrain the recombination of photogenerated electron and hole pairs.

Then radical trapping experiments were also carried out to explore the main radicals in the photochemical reaction process of CN-BiS-2 (Fig. 10(b)). When IPA or N₂ was added to the reaction system, the photocatalytic activity reduced, while the extent was minor. In contrast, KI had a distinct influence on the photocatalytic performance of CN-BiS-2, which meant that holes were the most important radicals during the photodegradation process of CN-BiS-2.

After that, ESR spectra were used to compare the effect of

hydroxyl radicals and superoxide radicals of g-C₃N₄ and CN-BiS-2 (Figs. 10(c) and 10(d)). In a dark environment, neither g-C₃N₄ nor CN-BiS-2 showed obvious ESR signal. After light irradiation, both the samples had hydroxyl radical and superoxide radical ESR signal. The hydroxyl radical ESR spectra intensity and superoxide radical ESR spectra intensity of CN-BiS-2 were both stronger than that of g-C₃N₄, which indicated that CN-BiS-2 can provide more electrons and holes. As a result, more radicals were generated.

Photothermal conversion materials can accumulate solar radiation energy and convert it to thermal energy. Under solar light irradiation, Bi₂S₃ can absorb light energy and improve its temperature [49]. Fig. 11 is the temperature-time curve of g-C₃N₄ and CN-BiS-2 under simulated solar light irradiation. The temperature of g-C₃N₄ and CN-BiS-2 both increased rapidly, and it gradually became stable. At 27 min, the temperature of CN-BiS-2 reached about 82.4 °C, while that of g-C₃N₄ was about 68.4 °C. These results indicated that the introduction of Bi₂S₃ is beneficial to the photothermal conversion effect of CN-BiS-2, which can provide more energy to electrons and make them transfer much faster to vitally enhance photocatalytic reaction [62,63].

In brief, the UV-vis DRS of CN-BiS-2 had obvious red-shift and it can confirm the light utilization is greatly enhanced. The stronger photocurrent response, the smaller EIS Nyquist plots arc radius, and the lower intensity of PL all indicated the separation and transfer of photogenerated charge carriers was clearly improved. The results of trapping experiments concluded that the most important active species in the photodegradation process are holes. The hydroxyl radical ESR spectra intensity and superoxide radical ESR spectra intensity of CN-BiS-2 were both stronger than that of g-C₃N₄, which indicates that CN-BiS-2 can provide more electrons and holes, as a result, more radicals are generated. Due to the photothermal effect of Bi₂S₃, the carrier mobility was enhanced, which was also important for the photocatalytic reaction.

Based on all the above results, a possible mechanism for why g-C₃N₄/Bi₂S₃ heterojunction showed better photocatalytic performance was proposed (Fig. 12). The conduction band (CB) and valence band (VB) of g-C₃N₄ are at −1.13 and +1.57 eV respectively [24]. The CB of Bi₂S₃ is 0.10 eV and its VB is +1.45 eV [51]. Generally, electrons carry negative charges and trend to migrate to more positive potential; holes carry positive charges

Fig. 9. Photocurrent response (a) and EIS Nyquist plots (b) of g-C₃N₄ and CN-BiS-2 in 0.1 M Na₂SO₄ solution.

Fig. 10. (a) Photoluminescence spectra of g-C₃N₄ and CN-BiS-2; (b) radical trapping experiment results of CN-BiS-2 during the photodegradation process of MB; ESR spectra of hydroxyl radicals (c) and superoxide radicals (d) trapped by DMPO.

Fig. 11. Thermal images of g-C₃N₄ (a–c) and CN-BiS-2 (d–f) under simulated solar light irradiation for 0, 12 and 27 min; (g) the temperature-time curve of g-C₃N₄ and CN-BiS-2 under simulated solar light irradiation in 27 min.

and trend to migrate to more negative potential. Judging from the band structure of g-C₃N₄ and Bi₂S₃, electrons and holes both have the tendency to transfer to the CB and VB of Bi₂S₃, which may lead to reduction of the redox ability. As a result, g-C₃N₄ and Bi₂S₃ may not form a highly efficient heterojunction. However, when high-energy electrons are produced, this circumstance can be changed [64,65]. Based on the results of photocurrent, EIS, PL and ESR, it can be concluded that the transfer and separation of photogenerated charge carriers are accelerated, besides the photocatalytic performance of CN-BiS-2 is 2.05-fold as g-C₃N₄ and 4.42-fold as Bi₂S₃. The gap between the VB top of Bi₂S₃ and the CB bottom of g-C₃N₄ is 2.58 eV, corresponding to the light energy of about 480 nm, which means

that high-energy electrons of Bi₂S₃ excited by light shorter than 480 nm can energetically transfer to the CB of g-C₃N₄. The light range of xenon lamp we used is 200–1100 nm, indicating that the electrons on the VB of Bi₂S₃ can be excited to the maximum of −4.73 eV.

Firstly, under simulated sunlight irradiation, both g-C₃N₄ and Bi₂S₃ are excited; electrons can transfer to the CB and holes are produced on the VB. Electrons can react with oxygen to produce superoxide radicals. Holes can react with water and produce hydroxyl radicals. Superoxide radicals, hydroxyl radicals and hole are all strong oxidative species in photocatalytic reactions. Due to the high energy of simulated sunlight, a larger quantity of high-energy electrons are produced, which can

Fig. 12. Schematic diagram for possible charge separation in g-C₃N₄/Bi₂S₃ heterojunctions.

transfer to the CB of g-C₃N₄, at the same time holes can migrate from the VB of g-C₃N₄ to the VB of Bi₂S₃. As a result, the separation of photogenerated charge carriers is accelerated. Besides,

the introduction of Bi₂S₃ greatly enhanced the light absorption both in the ultraviolet and visible light region (Fig. 8). Finally, the photothermal effect of Bi₂S₃ can provide more energy to electrons and make them transfer much faster. Based on the above results, the g-C₃N₄/Bi₂S₃ heterojunction materials exhibit better photocatalytic performance.

4. Conclusions

In this work, a series of g-C₃N₄/Bi₂S₃ heterojunction materials with effective photocatalytic performance was constructed. The results of photocurrent, EIS, PL and ESR can confirm that transfer and separation of photogenerated charge carriers were promoted. The introduction of Bi₂S₃ can enhance the absorption of light energy and convert it to thermal energy, which can provide more energy to electrons and make them transfer much faster. Due to the high energy of simulated sunlight, a large quantity of high-energy electrons were produced, which can transfer to the CB of g-C₃N₄, at the same time holes can migrate from the VB of g-C₃N₄ to the VB of Bi₂S₃. As a result, the separation of photogenerated charge carriers is accelerated. The findings of this work provide a new facile way to develop highly efficient heterojunction photocatalysts via high-energy electrons and photothermal effect.

Graphical Abstract

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Accelerated separation of photogenerated charge carriers and enhanced photocatalytic performance of g-C₃N₄ by Bi₂S₃ nanoparticles

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Accelerated separation of photogenerated charge carriers and enhanced photocatalytic performance of g-C₃N₄ by Bi₂S₃ nanoparticles.

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利用硫化铋纳米颗粒增强类石墨相氮化碳的光生载流子分离效率和光催化活性

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摘要: 二氧化钛, 氧化锌, 磷酸铋等传统的紫外光响应光催化剂虽然具有良好的光催化性能, 但是对太阳能利用率很低(紫外光只占太阳光能量的4%左右)。近年来, 类石墨相氮化碳(g-C₃N₄)受到了广泛的关注。g-C₃N₄的带隙约2.7 eV, 它只能吸收460 nm以下的光, 对太阳能的利用率依然比较低。构筑异质结是一种有效的提高光催化活性的方法。BiOCl/g-C₃N₄, TiO₂/g-C₃N₄, Bi₂MoO₆/g-C₃N₄, Al₂O₃/g-C₃N₄, Ag₃PO₄/g-C₃N₄等异质结光催化剂曾被广泛的报道。硫化铋是属于正交晶系的窄带隙半导体, 它的带隙约1.3–1.7 eV。由于其独特的电子结构和光学特性, 硫化铋在光催化, 光检测器和医药成像等领域有着广泛的应用。另外, 硫化铋还具有优异的光热转换性能, 在光热癌症治疗领域有显著的效果。微波辅助法, 水热法, 惰性气体下高温煅烧法等都被用来合成g-C₃N₄/Bi₂S₃异质结光催化剂。不同的文献也提出了不同的催化机理。如何使用更简单环保的方法来合成g-C₃N₄/Bi₂S₃异质结光催化剂? 电子和空穴的转移路径是怎样的? 本文利用简单的低温方法合成了硫化铋, 利用超声法得到了g-C₃N₄/Bi₂S₃异质结光催化剂, 分析了其微观形貌, 结构, 并探讨了光催化的反应机理和提高光催化性能的因素。

X射线衍射, 傅里叶变换红外光谱, X射线光电子能谱和透射电子显微镜的结果表明, 硫化铋纳米颗粒被成功地引入到g-C₃N₄中。使用亚甲基蓝为分子探针研究了所制材料在模拟太阳光下的光催化活性。结果发现, CN-BiS-2表现出最佳的光催化活性, 是g-C₃N₄的2.05倍, 是Bi₂S₃的4.42倍。利用液相色谱二级质谱联用分析了亚甲基蓝的降解路径。

硫化铋的引入拓展了复合材料的吸收边, 使其向可见光区红移, 且在整个可见光区的光吸收能力都有明显的增强。光电流的增强和交流阻抗谱圆弧半径的减小, 表明光生载流子的迁移与分离速率得到了增强。自由基捕获试验表明, 最主要的活性物种是光生空穴, 次之是羟基自由基和超氧自由基。在CN-BiS-2样品中羟基自由基和超氧自由基的电子顺磁共振信号都比g-C₃N₄有明显的增强, 表明复合样品中能够产生更多的羟基自由基和超氧自由基。基于光电流, 交流阻抗, 荧光光谱, 自由基捕获和电子顺磁共振的结果, 我们提出了高能电子由硫化铋转移到g-C₃N₄, 同时空穴由g-C₃N₄转移到硫化铋的电子空穴转移机制。此外, 红外热成像的结果表明, g-C₃N₄/Bi₂S₃异质结材料具有更强的光热转换能力, 从而有利于加速光生载流子分离。

关键词: 类石墨相氮化碳; 硫化铋; 光催化; 水处理; 高能电子

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