available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Environmental and Energy Catalysis)

In-situ transformation of Bi_2WO_6 to highly photoreactive $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ nanoplate via ion exchange

Tingting Huang ^a, Yuhan Li ^{a,b}, Xiaofeng Wu ^a, Kangle Lv ^{a,*}, Qin Li ^a, Mei Li ^{a,#}, Dongyun Du ^a, Hengpeng Ye ^a

^a Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, College of Resources and Environmental Science, South-Central University for Nationalities, Wuhan 430074, Hubei, China

^b Department of Science and Environmental Studies, The Education University of Hong Kong, Tai Po, N.T., Hong Kong, China

ARTICLE INFO

Article history:

Received 22 October 2017

Accepted 26 November 2017

Published 5 April 2018

Keywords:

 Bi_2S_3 Bi_2WO_6

Ion exchange

Photocatalytic degradation

Nanoplate

ABSTRACT

As a two dimensional (2D) visible-light-responsive semiconductor photocatalyst, the photoreactivity of Bi_2WO_6 is not high enough for practical application owing to its limited response to visible light and rapid recombination of photogenerated electron-hole pairs. In this paper, 2D core-shell structured $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ nanoplates were prepared by calcination of a mixture of Bi_2WO_6 (1.3 g) and a certain amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (0–3.0 g) at 350 °C for 2 h. The reactivity of the resulting photocatalyst materials was evaluated by photocatalytic degradation of Brilliant Red X-3B (X3B), an anionic dye, under visible light irradiation ($\lambda > 420 \text{ nm}$). As the amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was increased from 0 to 1.5 g, the degradation rate constant of X3B sharply increased from 0.40×10^{-3} to $6.6 \times 10^{-3} \text{ min}^{-1}$. The enhanced photocatalytic activity of $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ was attributed to the photosensitization of Bi_2S_3 , which greatly extended the light-responsive range from the visible to the NIR, and the formation of a heterojunction, which retarded the recombination rate of photogenerated electron-hole pairs. However, further increases in the amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (from 1.5 to 3.0 g) resulted in a decrease of the photocatalytic activity of the $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ nanoplates owing to the formation of a photo-inactive NaBiS_2 layer covering the Bi_2WO_6 surface.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Recently, photocatalytic degradation of harmful pollutants has become an increasingly important technology for water and air purification [1]. TiO_2 is considered to be an excellent photocatalyst because of its biological and chemical inertness, strong photo-oxidization power, cost effectiveness, and long-term stability to photo-induced and chemical corrosion [2]; however, TiO_2 has a broad bandgap (3.2 eV for anatase

TiO_2) and absorbs only a small fraction of solar energy [3,4]. Considering that UV light constitutes only 3%–5% of the solar spectrum, more efficient photocatalysts, which can be activated both by UV and visible light, are highly desired [5–7].

As one of the simplest Aurivillius oxides with a layered 2D structure, Bi_2WO_6 nanoplates are notable for their visible-light-response and photocatalytic performance [8–12]. The perovskite-like structure is defined by WO_6 units that form a layer perpendicular to the [100] direction and sandwich

* Corresponding author. Tel: +86-27-67841369; Fax: +86-27-67843918; E-mail: lvkangle@mail.scuec.edu.cn

Corresponding author. Tel: +86-27-67842752; Fax: +86-27-67842752; E-mail: limei@mail.scuec.edu.cn

This work was supported by the National Natural Science Foundation of China (51672312, 21571192, 21373275), the Science and Technology Program of Wuhan (2016010101010018, 2015070504020220), the Key Project in the National Science & Technology Pillar Program during the Twelfth Five-Year Plan Period (2015BAB01B01), and the Natural Science Foundation of South-Central University for Nationalities (XTZ15016, CZP17062).

DOI: 10.1016/S1872-2067(17)62913-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 4, April 2018

(Bi_2O_2) $^{2+}$ units [13,14]. These nanoplate materials are usually characterized by high crystallinity and well-defined chemical compositions as well as extremely high anisotropy, with ultrathin plates [8]. However, the photocatalytic activity of Bi_2WO_6 nanoplates is not yet high enough for practical applications because of the rapid recombination of photogenerated electrons and holes, and the limited visible-light-response range [15,16]. Unmodified Bi_2WO_6 nanoplates can only adsorb UV or visible light of wavelengths shorter than 450 nm [17,18].

To improve the photocatalytic activity of Bi_2WO_6 nanoplates and/or extend the range of light response, many strategies have been studied, including semiconductor coupling [19], metal/non-metal doping and noble metal deposition [20]. For example, Ge *et al.* [21] reported a red shift of the light absorption and strong absorbance of visible light region after coupling Bi_2WO_6 with g- C_3N_4 . The enhancement in the photocatalytic performance of the g- C_3N_4 @ Bi_2WO_6 composite materials was attributed to the combination of polymeric g- C_3N_4 and Bi_2WO_6 , which improved separation of photogenerated electron-hole pairs [21]. Similarly, our group [3] reported the coupling of Bi_2WO_6 with TiO_2 using a layer-by-layer deposition and calcination strategy. We found that a hybrid coated with four layers of TiO_2 (containing 20 wt% TiO_2) showed the highest photocatalytic activity, which was 10.45 and 3.20 times as high as that of pure Bi_2WO_6 and TiO_2 , respectively. Zhu *et al.* [22] reported that, doping Bi_2WO_6 by F resulted in a two-fold increase in the photocatalytic degradation activity of MB under visible-light irradiation ($\lambda > 420$ nm). The enhanced photocatalytic activity was attributed to increased mobility of photo-excited charge carriers and a positive shift of the valance band position. Yu *et al.* [1] reported the fabrication of high visible photoreactive plasmonic Ag and graphene co-modified Bi_2WO_6 nanosheets, combining the surface plasmon resonance (SPR) effect of Ag and the electronic properties of graphene at the surface of Bi_2WO_6 .

Bismuth sulfide (Bi_2S_3) has been reported to be a semiconductor with a narrow bandgap of approximately 1.3 eV [12,23–25], which has been used as a sensitizer because of its ability to absorb visible and even near infrared light [26–28]. Here, we propose a structure of Bi_2WO_6 nanoplates with a surface layer of Bi_2S_3 to improve the photoreactivity of the material. Considering that strong interactions between two semiconductors is of great importance for efficient separation of carriers [29], the Bi_2S_3 was designed to grow on the surface of the Bi_2WO_6 nanoplate *via* an in-situ ion-exchange strategy, to form core-shell structured Bi_2WO_6 @ Bi_2S_3 nanoplates (Scheme 1). The effects of the amount of Bi_2S_3 loading on the structure and photocatalytic activity of the Bi_2WO_6 @ Bi_2S_3 nanoplates were systematically studied.

2. Experimental

2.1. Preparation of Bi_2WO_6 @ Bi_2S_3 nanoplates

All reagents were of analytical purity and were used as received from the Shanghai Chem. Co., China. The Bi_2WO_6 @ Bi_2S_3 nanoplate hybridized photocatalyst was synthesized by an ion

Scheme 1. Proposed formation mechanism of Bi_2WO_6 @ Bi_2S_3 nanoplate *via* ion exchange and the photoreactivity enhancement mechanism.

exchange strategy using Bi_2WO_6 nanoplates as a precursor, which were synthesized by a simple hydrothermal process according to the literature [8]. To synthesize the Bi_2WO_6 @ Bi_2S_3 nanoplates, 1.3 g of square Bi_2WO_6 precursor was added to a beaker containing 40 mL of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution under magnetic stirring. This mixture was then evaporated to dryness in an oven at 60 °C for 4 h. The resulting powder was further calcined at 350 °C for 2 h in muffle furnace at a heating rate of 5 °C min^{-1} . Afterwards, the obtained samples were rinsed with anhydrous ethanol followed by drying in an oven at 80 °C for 2 h. The prepared hybridized photocatalysts are denoted as S_x , where x indicates the amount of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ used (0–3.0 g, Table 1). Thus, the S0 sample represents the 350 °C-calcined Bi_2WO_6 precursor without treatment by the Na_2S solution.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a D8-advance X-ray diffractometer (German Bruker) using $\text{Cu } K\alpha$ radiation at a scan rate of 0.02° s^{-1} . The accelerated voltage and applied current were 15 kV and 20 mA, respectively. The morphology of the catalysts was characterized with a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) operating at an accelerating voltage of 10 kV and a transmission electron microscopy (TEM: Tecnai G ^{2} 20, USA) with an accelerating voltage of 200 kV. The optical absorption properties of the samples were investigated through diffuse reflectance spectrum (DRS) with a UV-Vis spectrophotometer (Lambda, Bio 35, PE Co., USA). Powder photoluminescence (PL) spectrum were measured at room temperature on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan). The excita-

Table 1
Physical property of the photocatalyst.

Sample	A_{BET} ($\text{m}^2 \text{g}^{-1}$)	PV ($\text{cm}^3 \text{g}^{-1}$)	APS (nm)
S0	18.8	0.08	18.7
S0.75	30.3	0.12	15.7
S1.0	29.5	0.12	14.6
S1.5	42.6	0.18	15.6
S2.0	39.7	0.23	23.1
S3.0	17.8	0.16	35.2

tion wavelength was 240 nm with a scanning speed of 1200 nm min⁻¹ and a PMT voltage of 400 V. The excitation and emission slits were both set to a width of 10.0 nm. The surface photovoltage spectroscopy (SPS) measurements of the samples were performed with a home-built apparatus. The SPS signals reflect the change of the potential barrier of the tested electrode surface in the presence of light and that in the dark. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Multilab 2000 XPS system with a monochromatic Mg *K*_α source and a charge neutralizer. All the binding energies were referenced to the C 1s peak at 284.4 eV from adventitious carbon. The Brunauer-Emmett-Teller surface area (*A*_{BET}) of the samples was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA).

2.3. Evaluation of the photocatalytic activity

The photocatalytic activity of the as-prepared photocatalyst was evaluated by decomposition of Brilliant Red X-3B dye (X3B) under visible light irradiation at room temperature. The photocatalytic experiments were performed with the sample powder (50 mg) suspended in X3B solution (50 mL, 1.0 × 10⁻⁴ mol L⁻¹) with constant stirring. Prior to illumination, the suspensions were shaken at a constant rate in the dark for 12 h to achieve adsorption-desorption equilibrium. The suspension was then irradiated under a 350 W Xe lamp with a 420-nm cutoff filter. The reaction was performed at room temperature to prevent any thermal catalytic effects. At certain time intervals, 3.0 mL of the suspension was taken and centrifuged to remove the photocatalyst particles. The concentration of dye was monitored by UV-Vis spectroscopy at λ = 530 nm.

2.4. Photoelectrochemical performance

The photocurrents and electrochemical impedance spectroscopy (EIS) of the film electrode were measured on an electrochemical system (CHI-760e, Shanghai, China) with the use of a standard three-electrode cell. The working electrode was composed of a 2 cm × 1.5 cm ITO substrate onto which the sample was deposited, a Ag/AgCl electrode was used as a reference electrode and a platinum wire was used as the counter electrode. The ITO/sample working electrode was prepared by a dip-coating method: 50 mg of the photocatalyst was suspended in 1.0 mL of ethanol, which was then dip-coated onto the ITO glass electrode. The electrolyte was 0.1 mol L⁻¹ Na₂SO₄. The photoelectric response of the sample was measured with switching of an LED lamp (3 W) emitting mainly at 420 ± 10 nm. The EIS measurements were performed in the dark at open circuit voltage, and a sinusoidal ac perturbation of -0.3 V was applied to the electrode over the frequency range of 0.1–10000 Hz.

3. Results and discussion

3.1. Phase structure and morphology

The phase structure of the prepared photocatalyst was in-

Fig. 1. XRD patterns of the prepared samples.

vestigated by XRD. Fig. 1 shows that the XRD patterns of precursor (S0 sample) could be indexed to the russellite phase Bi₂WO₆ (PDF#26-1044) [3]. No impurity diffraction peaks were observed, indicating the high purity of the Bi₂WO₆ phase. After the treatment with Na₂S, the peak intensity corresponding to Bi₂WO₆ decreased, while some unknown impurity phase was found in the S0.5 and S1.0 samples. These results suggest that a reaction occurred between the Bi₂WO₆ and Na₂S. For the S1.5 sample, we identified the formation of Bi₂S₃. The reaction between Bi₂WO₆ and Na₂S to produce Bi₂S₃ proceeded through ion exchange (Eq. (1)):

This ion exchange reaction resulted in the transformation of the surface of the Bi₂WO₆ nanoplates to Bi₂S₃ to form a core-shell structure of Bi₂WO₆@Bi₂S₃. SEM (Fig. 2) and TEM (Fig. 3) images show the plate-like structure of the

Fig. 2. SEM images of pristine Bi₂WO₆ (a, b), S1.5 (c, d) and S3.0 (e, f).

Fig. 3. TEM images of pristine Bi₂WO₆ (a), S1.5 (b) and S3.0 (c).

Bi₂WO₆@Bi₂S₃ sample (S1.5). The Bi₂S₃ layer was produced by in-situ growth at the surface of the Bi₂WO₆ nanoplate, thus, interactions between the Bi₂WO₆ core and Bi₂S₃ shell should be strong. The close proximity of the two semiconductors should be beneficial for efficient separation of photogenerated electron-hole pairs and improve photocatalytic activity [30].

The TEM image of the S1.5 sample indicated that some holes formed in Bi₂WO₆@Bi₂S₃ nanoplate, which could be attributed to the attack of S²⁻, which resulted in the dissolution of Bi₂WO₆ units (Eq. (1)). Further increases of the amount of Na₂S·9H₂O to 3.0 g resulted in a sharp diffraction peak emerging at 31° in the XRD patterns of S3 sample, which was identified as NaBiS₂. This result indicates that some Bi₂S₃ was further transformed into NaBiS₂ in the high concentration Na₂S solution (Eq. (2)), and the S3 sample was a ternary composite of NaBiS₂/Bi₂S₃/Bi₂WO₆.

Fig. 2(e) and (f) show SEM images of the S3 sample, which indicate the formation of a porous structure. The TEM image (Fig. 3(c)) suggests that the S3 sample was an aggregate made up of smaller nanoplates, which resulted in the formation of porous coral-like structures.

Energy-dispersive X-ray spectroscopy (EDS) line scans and mapping analysis were used to study the composition of the photocatalyst. The elemental mapping images (Fig. 4) show that the content of S in the photocatalyst increased in the order: S0 < S1.5 < S3. The EDS elemental mapping results also show that the content of W decreased as the Na₂S content of the treatment was increased. These results further indicate that the reactions described by Eqs. (1) and (2) occurred during the preparation of the photocatalyst [31,32].

3.2. UV-vis diffuse reflectance spectrum

The UV-vis diffuse reflection spectroscopy (DRS) results of the as-prepared samples are compared in Fig. 5. Consistent with previous reports [33], the onset of the DRS for the pristine Bi₂WO₆ sample (S0) started at approximately 450 nm, corresponding to a bandgap of 2.76 eV. This reflects the poor visible light harvesting ability of the material. However, the light absorption of Bi₂WO₆ was greatly enhanced in the visible light region after the sulfur treatment of the surface and even extended to the NIR region (Fig. 5(b)–(f)). This can be attributed to the small bandgap and large absorption coefficient of Bi₂S₃

Fig. 4. EDS elemental mapping images of the photocatalysts for pristine Bi₂WO₆ (a), S1.5 (b) and S3.0 (c) samples.

Fig. 5. UV-vis diffuse reflectance spectra of the as-prepared samples.

[34]. Therefore, the in-situ formed Bi_2S_3 on the surface of the Bi_2WO_6 nanoplate can be used as a photosensitizer to excite Bi_2WO_6 , which might enable full use of the solar spectrum.

3.3. Photoluminescence and surface photovoltage spectrum

PL analysis is commonly used to analyze the recombination rate of photogenerated electrons and holes in a photocatalyst [35]. Herein, we conducted PL measurements for Bi_2WO_6 before and after treatment with Na_2S . The PL spectra shown in Fig. 6, indicate that the pristine Bi_2WO_6 (S0) sample possessed the highest light emission intensity among the three photocatalysts. This result also suggests the material has poor photocatalytic activity owing to the rapid recombination rate of carriers. The S1.5 sample exhibited the lowest light emission intensity, which suggests that the recombination of electron-hole pairs was substantially suppressed after deposition of Bi_2S_3 on the surface of the Bi_2WO_6 nanoplates. This result is attributed to the formation of a heterojunction between the two semiconductors (Bi_2WO_6 and Bi_2S_3), which facilitated efficient separation of photogenerated electrons and holes, retarding the recombination [36]. However, if the concentration of Na_2S was too high, the PL intensity started to increase, as for

Fig. 6. Room-temperature PL spectra of the as-prepared samples ($\lambda_{\text{ex}} = 240 \text{ nm}$).

Fig. 7. Comparison of the SPS spectra of pristine Bi_2WO_6 (S0) and $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplates (S1.5, S3.0).

the S3 sample.

SPS was also performed to confirm the separation efficiency of the photogenerated carriers of the photocatalyst. The SPS signal of pristine Bi_2WO_6 was negligible (Fig. 7), while the S1.5 sample exhibited the strongest SPS response, which was consistent with the PL characterization results (Fig. 6).

3.4. XPS analysis

XPS was used to investigate the chemical states and surface composition of the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ composite. The XPS survey spectra of the unmodified (S0) and the S-modified Bi_2WO_6 nanoplate (S1.5) are compared in Fig. 8(a). The unmodified Bi_2WO_6 nanoplates contained the elements Bi, W, O, and C. The carbon peak was attributed to residual carbon from the precursor solution and adventitious hydrocarbons from the XPS instrument itself [37]. Peaks with binding energies of 164.43 and 159.11 eV corresponded to photoelectron emission from $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$ of Bi (III), respectively (Fig. 8(b)), while the peaks with binding energies of 37.6 and 35.5 eV were attributed to $\text{W } 4f_{5/2}$ and $\text{W } 4f_{7/2}$ of W (VI), respectively, (Fig. 8(c)) [38].

After the Na_2S treatment, the signal from W decreased (Fig. 8(c)), and a weak signal from S was observed in the high resolution XPS spectrum (Fig. 8(d)). The peaks centered at 161.7 and 162.7 eV were attributed to the $\text{S } 2p_{3/2}$ and $\text{S } 2p_{1/2}$ of S^{2-} [39]. In addition, the binding energy of the spin-orbit Bi $4f$ could be deconvoluted into four peaks after the sulfur treatment. Two new weak peaks centered at 157.6 and 162.7 eV were related to the formation of Bi_2S_3 in the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplates. These results were consistent with the XRD results (Fig. 1), and further confirmed successful substitution of S^{2-} into WO_6^{6-} through an ion exchange reaction (Eq. (1)).

3.5. Nitrogen adsorption

To determine the BET specific surface area and microstructure of the photocatalyst, nitrogen adsorption-desorption isotherms were measured (Fig. 9). The nitrogen adsorption-desorption isotherms were similar and all possessed type

Fig. 8. XPS survey spectra (a) and corresponding high resolution XPS spectra in Bi 4f (b), W 4f (c) and S 2p (d) regions for S0 and S1.5 samples.

Fig. 9. Nitrogen adsorption-desorption isotherms of the catalysts (a) and the corresponding pore size distribution curves (b). Arrows in (a) indicate the beginning of the hysteresis loop.

IV isotherms (BDDT classification) with a hysteresis loop at high relative pressures, indicating the mesoporous character of the surface. The shape of the hysteresis loop was of H3 type, suggesting the presence of narrow slit-shaped pores, which are generally associated with plate-like particles [2], agreeing well with the nanoplate morphology of the particles (Figs. 2 and 3).

The adsorption isotherm of the S1.5 sample was shifted upward compared with those of the S0 and S3.0 samples, indicating its larger BET surface area. The BET surface areas of the S0, S1.5 and S3.0 samples were measured to be 18.8, 42.6, and

17.8 $\text{m}^2 \text{g}^{-1}$, respectively (Table 1). A larger BET specific area suggests that more active sites are available for adsorption and photocatalytic reactions, which might contribute to enhanced photocatalytic activity.

The hysteresis loop of the S1.5 sample begins at a relative pressure of 0.45, while those of S0 and S3 samples begin at higher relative pressures of approximately 0.9, indicating that the S1.5 sample possesses smaller mesopores than those of the S0 and S3 samples. This result was confirmed by the corresponding pore size distribution curves, as shown in Fig. 9(b).

Fig. 10. Photocatalytic degradation profiles of X3B as a function of irradiation time in the presence of different photocatalyst under visible light irradiation (a), and the corresponding rate constants (b).

The S1.5 sample possesses a larger pore volume (PV) and a smaller average pore size (APS) than those of the S0 and S3.0 samples. The larger PV and smaller APS of the $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ nanoplates can be attributed to the etching of Bi_2WO_6 by the S^{2-} to form a porous structure (Eq. (1) and Fig. 3).

3.6. Photocatalytic activity

We evaluated the photocatalytic degradation of X3B dye under visible light irradiation. Fig. 10(a) shows that the degradation of X3B was negligible under light irradiation without the addition of photocatalyst (control experiment). The photocatalytic activity of pristine Bi_2WO_6 (S0 sample) was very poor, owing to its limited response to visible light (Fig. 5) and rapid recombination of photogenerated electron-hole pairs (Fig. 6 and 7). As the amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was increased from 0 to 1.5 g, the X3B removal efficiency steadily improved, and the S1.5 sample showed the highest photocatalytic activity among all the photocatalysts. A further increase in the content of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ caused the reactivity of the photocatalyst to decrease, likely because of the formation of a photo-inactive Na-BiS_2 surface layer (Fig. 1), which prevented reactions between the substrate and photocatalyst.

The degradation profiles of X3B followed pseudo-first-order kinetics, and the related degradation rate constants are compared in Fig. 10(b). The rate constant of the S1.5 sample ($6.60 \times 10^{-3} \text{ min}^{-1}$) was 16.5 times as high as that of pristine Bi_2WO_6 ($0.40 \times 10^{-3} \text{ min}^{-1}$).

To account for the photocatalytic degradation mechanism of X3B on the core-shell structured $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ hybridized photocatalyst, we performed radical trapping experiments to detect the reactive oxidative species (ROSs) by introducing isopropyl alcohol (IPA), triethanolamine (TEOA), and 1,4-benzoquinone (BQ) into the degradation system to scavenge $\cdot\text{OH}$, h^+ , and $\text{O}_2^{\cdot-}$, respectively. After addition of IPA, TEOA, and BQ, the degradation rate constant of X3B decreased from 6.60×10^{-3} to 3.50×10^{-3} , 1.75×10^{-3} and $1.03 \times 10^{-3} \text{ min}^{-1}$, respectively (Fig. 11). Thus, the quenching effect of TEOA and BQ on the degradation of X3B was more pronounced than that of IPA.

This result indicates that both h^+ and $\text{O}_2^{\cdot-}$ are the main ROSs responsible for the oxidization of X3B.

3.7. Reactivity enhancement mechanism

According to previous reports, the potentials for the valence band (E_{VB}) and conduction band (E_{CB}) of Bi_2WO_6 are 3.38 and 0.40 V [40], while those for Bi_2S_3 are 1.42 and 0.12 V, respectively [33]. Therefore, a heterojunction between Bi_2WO_6 and Bi_2S_3 is formed owing to their staggered energy potentials (Scheme 1). Under visible light irradiation, photogenerated electrons in the CB of Bi_2S_3 can transfer to the CB of Bi_2WO_6 , while holes on Bi_2WO_6 can migrate to the VB of Bi_2S_3 . This semiconductor coupling effect can efficiently improve the separation rate of photogenerated electron-hole pairs to enhance the photocatalytic activity [41].

Fig. 12 compares the photocurrents [42,43] and EIS responses of the S0, S1.5, and S3 samples. The S1.5 sample featured the largest photocurrent (Fig. 12(a)) and the smallest arc radius in the EIS Nyquist plots (Fig. 12(b)), which further confirmed the efficient separation of photogenerated carriers at

Fig. 11. Effect of scavenger on the photocatalytic degradation of X3B using S1.5 as photocatalyst under visible light irradiation. (1) Without scavenger; (2) Isopropyl; (3) Triethanolamine; (4) 1,4-Benzoquinone.

Fig. 12. Comparison of the photocurrent (a) and EIS response (b) of the photocatalysts. R_s : solution resistance; R_t : charge transfer resistance; CPE: constant phase element.

the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplate owing to the formation of a heterojunction. The enlarged BET surface area and improved light harvesting ability owing to Bi_2S_3 sensitization should also benefit the photoreactivity of the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplate.

3.8. Stability of the photocatalyst

The stability of the photocatalyst is of great importance from the viewpoint of practical applications. Therefore, we studied the reusability of $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{WO}_6$ in the photocatalytic degradation of X3B over four consecutive cycles under visible light irradiation, and the results are shown in Fig. 13. It can be seen that the degradation profiles of X3B in the presence of the S1.5 photocatalyst remained almost unchanged from the first to the fourth run, reflecting the good stability of the $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{WO}_6$ composite. The high stability of the as-prepared $\text{Bi}_2\text{S}_3/\text{Bi}_2\text{WO}_6$ hybrid photocatalyst suggests promise for practical applications.

Fig. 13. Photocatalytic degradation profiles of X3B in solution for reusing of $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ photocatalyst for four consecutive runs under visible light irradiation using S1.5 sample as an example. Note that the initial concentration of X3B solution is $0.33 \times 10^{-4} \text{ mol L}^{-1}$, and the concentration of the photocatalyst is 50 mg in 50 mL X3B solution.

4. Conclusions

$\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplates were synthesized by ion exchange between Bi_2WO_6 and Na_2S . The photocatalytic activity of the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplates was 16.5 times as high as that of the pristine Bi_2WO_6 . The improved photocatalytic activity of the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplates was attributed to the formation of a heterojunction between Bi_2WO_6 and Bi_2S_3 , which facilitated efficient separation of photogenerated electrons and holes and retarded their recombination. The enlarged BET surface area and photosensitization of Bi_2S_3 also contributed to the enhancement of photocatalytic activity for the $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplate hybridized photocatalyst. The present study provides an alternative approach to the design of highly efficient and ultra-stable hybrid photocatalysts.

References

- [1] J. X. Low, J. G. Yu, Q. Li, B. Cheng, *Phys. Chem. Chem. Phys.*, **2014**, 16, 1111–1120.
- [2] R. W. Yang, J. H. Cai, K. L. Lv, X. F. Wu, W. G. Wang, Z. H. Xu, M. Li, Q. Li, W. Q. Xu, *Appl. Catal. B*, **2017**, 210, 184–193.
- [3] Y. Zheng, K. L. Lv, X. F. Li, K. J. Deng, J. Sun, L. Q. Chen, L. Z. Cui, D. Y. Du, *Chem. Eng. Technol.*, **2011**, 34, 1630–1634.
- [4] J. F. Lan, X. F. Wu, K. L. Lv, L. L. Si, K. J. Deng, *Chin. J. Catal.*, **2015**, 36, 2237–2243.
- [5] Y. H. Li, K. L. Lv, W. K. Ho, Z. W. Zhao, Y. Huang, *Chin. J. Catal.*, **2017**, 38, 321–329.
- [6] L. L. Yin, M. Zhao, H. L. Hu, J. H. Ye, D. F. Wang, *Chin. J. Catal.*, **2017**, 38, 1307–1314.
- [7] T. Wang, W. W. Li, D. D. Xu, X. M. Wu, L. W. Cao, J. X. Meng, *Chin. J. Catal.*, **2017**, 38, 1184–1195.
- [8] C. Zhang, Y. F. Zhu, *Chem. Mater.*, **2005**, 17, 3537–3545.
- [9] F. Amano, A. Yamakata, K. Nogami, M. Osawa, B. Ohtani, *J. Am. Chem. Soc.*, **2008**, 130, 17650–17651.
- [10] S. W. Liu, J. G. Yu, *J. Solid State Chem.*, **2008**, 181, 1048–1055.
- [11] H. B. Fu, L. W. Zhang, W. Q. Yao, Y. F. Zhu, *Appl. Catal. B*, **2006**, 66, 100–110.
- [12] C. J. Tang, Y. S. Zhang, J. F. Su, C. Q. Wang, R. R. Sun, J. Zhang, G. H. Li,

Graphical Abstract

Chin. J. Catal., 2018, 39: 718–727 doi: 10.1016/S1872-2067(17)62913-9

In-situ transformation of Bi_2WO_6 to high photoreactive $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplate via ion exchange

Tingting Huang, Yuhang Li, Xiaofeng Wu, Kangle Lv *, Qin Li,
Mei Li *, Dongyun Du, Hengpeng Ye
South-Central University for Nationalities;
The Education University of Hong Kong

$\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ nanoplates were fabricated by a simple ion-exchange reaction between Bi_2WO_6 and Na_2S . Visible light photocatalytic activity of $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ in degradation of X3B dye increased 16.5 times owing to the formation of a heterojunction between the two semiconductors.

- Solid State Sci.*, **2016**, 51, 24–29.
- [13] G. Colon, S. Murcia Lopez, M. C. Hidalgo, J. A. Navio, *Chem. Commun.*, **2010**, 46, 4809–4811.
- [14] B. Yuan, B. Zhang, Z. L. Wang, S. M. Lu, J. Li, Y. Liu, C. Li, *Chin. J. Catal.*, **2017**, 38, 440–446.
- [15] Y. H. Li, K. L. Lv, W. K. Ho, F. Dong, X. F. Wu, Y. Xia, *Appl. Catal. B*, **2017**, 202, 611–619.
- [16] M. J. Chen, Y. Huang, S. C. Lee, *Chin. J. Catal.*, **2017**, 38, 348–356.
- [17] L. Wu, J. H. Bi, Z. H. Li, X. X. Wang, X. Z. Fu, *Catal. Today*, **2008**, 131, 15–20.
- [18] Z. J. Zhang, W. Z. Wang, M. Shang, W. Z. Yin, *J. Hazard. Mater.*, **2010**, 177, 1013–1018.
- [19] L. Pan, J. W. Zhang, X. Jia, Y. H. Ma, X. W. Zhang, L. Wang, J. J. Zou, *Chin. J. Catal.*, **2017**, 38, 253–259.
- [20] L. Pan, S. B. Wang, W. B. Mi, J. J. Song, J. J. Zou, L. Wang, X. W. Zhang, *Nano Energy*, **2014**, 9, 71–79.
- [21] L. Ge, C. C. Han, J. Liu, *Appl. Catal. B*, **2011**, 108, 100–107.
- [22] C. Wang, D. Vander Vliet, K. C. Chang, H. You, D. Strmcnik, J. A. Schlueter, N. M. Markovic, V. R. Stamenkovic, *J. Phys. Chem. C*, **2009**, 113, 19365–19368.
- [23] T. Wu, X. G. Zhou, H. Zhang, X. H. Zhong, *Nano Res.*, **2010**, 3, 379–386.
- [24] R. Vogel, P. Hoyer, H. Weller, *J. Phys. Chem.*, **1994**, 98, 3183–3188.
- [25] Y. Bessekhouad, M. Mohammadi, M. Trari, *Sol. Energy Mater. Sol. Cells*, **2002**, 73, 339–350.
- [26] D. Robert, *Catal. Today*, **2007**, 122, 20–26.
- [27] Y. Bessekhouad, D. Robert, J. V. Weber, *J. Photochem. Photobiol. A*, **2004**, 163, 569–580.
- [28] C. F. Yu, K. Wang, P. Y. Yang, S. W. Yang, C. Lu, Y. Z. Song, S. Y. Dong, J. Y. Sun, *Appl. Surf. Sci.*, **2017**, 420, 233–242.
- [29] X. Jia, M. Tahir, L. Pan, Z. F. Huang, X. W. Zhang, L. Wang, J. J. Zou, *Appl. Catal. B*, **2016**, 198, 154–161.
- [30] L. Pan, S. B. Wang, J. W. Xie, L. Wang, X. W. Zhang, J. J. Zou, *Nano Energy*, **2016**, 28, 296–303.
- [31] D. H. Son, S. M. Hughes, Y. P. Yin, A. P. Alivisatos, *Science*, **2004**, 306, 1009–1012.
- [32] R. D. Robinson, B. Sadtler, D. O. Demchenko, C. K. Erdonmez, L. W. Wang, A. P. Alivisatos, *Science*, **2007**, 317, 355–358.
- [33] Z. Z. Zhang, W. Z. Wang, L. Wang, S. M. Sun, *ACS Appl. Mater. Interfaces*, **2012**, 4, 593–597.
- [34] Z. K. Cui, S. L. Li, J. Q. Zhou, J. L. Zhang, S. X. Ge, Z. Zheng, *Nano: Brief Rep. Rev.*, **2015**, 10, 1550021.
- [35] K. L. Lv, J. C. Hu, X. H. Li, M. Li, *J. Mol. Catal. A*, **2012**, 356, 78–84.
- [36] L. Pan, T. Muhammad, L. Ma, Z. F. Huang, S. B. Wang, L. Wang, J. J. Zou, X. W. Zhang, *Appl. Catal. B*, **2016**, 189, 181–191.
- [37] J. C. Yu, W. K. Ho, J. G. Yu, S. K. Hark, K. Iu, *Langmuir*, **2003**, 19, 3889–3896.
- [38] J. Di, J. X. Xia, Y. P. Ge, H. P. Li, H. Y. Ji, H. Xu, Q. Zhang, H. M. Li, M. N. Li, *Appl. Catal. B*, **2015**, 168–169, 51–61.
- [39] G. Wang, Y. K. Leng, H. Z. Guo, S. Song, Z. Q. Jiang, X. L. Yuan, X. B. Wang, K. Sun, H. J. Dou, *J. Mater. Chem. B*, **2014**, 2, 8310–8313.
- [40] L. Zhang, X. Zhang, Y. Q. Huang, C. L. Pan, J. S. Hu, C. M. Hou, *RSC Adv.*, **2015**, 5, 30239–30247.
- [41] W. J. Zhou, Y. H. Leng, D. M. Hou, H. D. Li, L. G. Li, G. Q. Li, H. Liu, S. W. Chen, *Nanoscale*, **2014**, 6, 4698–4704.
- [42] H. W. Huang, L. Y. Liu, Y. H. Zhang, N. Tian, *J. Alloys Compd.*, **2015**, 619, 807–811.
- [43] Z. X. Pei, S. X. Weng, P. Liu, *Appl. Catal. B*, **2016**, 180, 463–470.

离子交换法制备高光催化活性 $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{S}_3$ 异质结纳米片

黄婷婷^a, 李雨涵^{a,b}, 伍晓峰^a, 吕康乐^{a,*}, 李 覃^a, 李 玫^{a,#}, 杜冬云^a, 叶恒朋^a

^a中南民族大学资源与环境学院催化材料科学湖北省重点实验室, 湖北武汉430074

^b香港教育大学科学与环境系, 香港

摘要: 社会经济快速发展的同时, 也带来了日益严峻的环境污染问题。半导体光催化氧化技术因节能环保而在环境领域有广阔的应用前景。作为最具有代表性的半导体光催化材料, TiO_2 因为其禁带宽度(3.2 eV)比较大, 只能被紫外光激发, 因而

对太阳能的利用率较低。作为一种最简单的含铋层状氧化物, Bi_2WO_6 的禁带宽度(2.7 eV)相对较小, 可以部分利用太阳光中的可见光, 因而受到广大研究者的青睐。但是, Bi_2WO_6 光催化材料的可见光响应范围较窄, 仅能被波长小于450 nm的光激发, 且激发后的光生载流子容易复合, 导致光催化效率不高。因此, 迫切需要对 Bi_2WO_6 光催化材料进行结构修饰与改性, 采用拓展其光响应范围和抑制载流子复合, 来提高其光催化活性。

本文采用离子交换法原位合成了具有核-壳结构的 $\text{Bi}_2\text{S}_3@\text{Bi}_2\text{WO}_6$ 纳米片, 充分利用 Bi_2S_3 优良的可见光响应性能和半导体异质结光催化剂的构建, 来提高 Bi_2WO_6 的光催化活性。结果表明, 随着 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 用量从0增加到1.5 g, 所得催化剂的光活性不断提高, X3B的降解速率常数由 $0.40\times 10^{-3} \text{ min}^{-1}$ 增加到 $6.6\times 10^{-3} \text{ min}^{-1}$, 催化剂活性提高了16.5倍。当进一步增加 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 的用量时(1.5–3.0 g), 复合催化剂的光活性下降。这是由于过多 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 的引入导致在催化剂表面生成了没有光活性的 NaBiS_2 层($\text{Bi}_2\text{S}_3 + \text{Na}_2\text{S} = 2\text{NaBiS}_2$), 占据了催化剂的活性位点, 阻碍了染料分子与催化剂的直接接触。 $\text{Bi}_2\text{WO}_6@\text{Bi}_2\text{S}_3$ 异质结纳米片光活性的提高, 可归因于 Bi_2S_3 的敏化作用极大拓展了复合催化剂的光响应范围; 另一方面, Bi_2WO_6 和 Bi_2S_3 两者之间的半导体异质结效应有效促进了光生载流子在空间的有效分离, 抑制了光生电子-空穴的复合, 从而提高了复合催化剂的催化效率。本研究为其他半导体复合材料的原位生长制备提供了新的思路。

关键词: Bi_2S_3 ; Bi_2WO_6 ; 离子交换; 光催化降解; 纳米片

收稿日期: 2017-10-22. 接受日期: 2017-11-26. 出版日期: 2018-04-05.

*通讯联系人. 电话: (027)67841369; 传真: (027)67843918; 电子信箱: lvkangle@mail.scuec.edu.cn

#通讯联系人. 电话/传真: (027)67842752; 电子信箱: limei@mail.scuec.edu.cn

基金来源: 国家自然科学基金(51672312, 21571192, 21373275); 武汉市科技计划(2016010101010018, 2015070504020220); “十二五”国家科技支撑计划(2015BAB01B01); 中南民族大学自然科学基金(XTZ15016, CZP17062).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).