available at www.sciencedirect.com

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

Article

A Bi/BiOI/(BiO)₂CO₃ heterostructure for enhanced photocatalytic NO removal under visible light

Yanjuan Sun ^{a,b,*}, Jiazhen Liao ^b, Fan Dong ^{b,c}, Sujuan Wu ^a, Lidong Sun ^{a,#}^a State Key Laboratory of Mechanical Transmission, School of Materials Science and Engineering, Chongqing University, Chongqing 400044, China^b Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China^c Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 611731, Sichuan, China

ARTICLE INFO

Article history:

Received 7 August 2018

Accepted 9 October 2018

Published 5 March 2019

Keywords:

BiOI

Oxygen vacancy

Heterojunction

Surface plasmon resonance effect

NO oxidation

ABSTRACT

Narrow-band BiOI photocatalysts usually suffer from low photocatalysis efficiency under visible light exposure because of rapid charge recombination. In this work, to overcome this deficiency of photosensitive BiOI, oxygen vacancies, Bi particles, and Bi₂O₂CO₃ were co-induced in BiOI via a facile *in situ* assembly method at room temperature using NaBH₄ as the reducing agent. In the synthesized ternary Bi/BiOI/(BiO)₂CO₃, the oxygen vacancies, dual heterojunctions (i.e., Bi/BiOI and BiOI/(BiO)₂CO₃), and surface plasmon resonance effect of the Bi particles contributed to efficient electron-hole separation and an increase in charge carrier concentration, thus boosting the overall visible light photocatalysis efficiency. The as-prepared catalysts were applied for the removal of NO in concentrations of parts per billion from air in continuous air flow under visible light illumination. Bi/BiOI/(BiO)₂CO₃ exhibited a highly enhanced NO removal ratio of 50.7%, much higher than that of the pristine BiOI (1.2%). Density functional theory calculations and experimental results revealed that the Bi/BiOI/(BiO)₂CO₃ composites promoted the production of reactive oxygen species for photocatalytic NO oxidation. Thus, this work provides a new strategy to modify narrow-band semiconductors and explore other bismuth-containing heterostructured visible-light-driven photocatalysts.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Photocatalytic technology is considered a promising solution to environmental pollution and energy shortages [1,2]. Numerous studies have focused on the use of semiconductor photocatalysts to address these challenges. Although this photocatalytic technology has been used for hydrogen production

[3] and environmental remediation [4], the development of highly active photocatalysts that can utilize solar energy efficiently is challenging. To obtain desirable photocatalytic efficiency, the photoinduced charge carriers must be effectively separated and rapidly migrate to the semiconductor surface to participate in redox reactions [5–11].

Amongst the various semiconductors, bismuth-containing

^{*} Corresponding author. Tel/Fax: +86-23-62769785; E-mail: syhsyj@163.com[#] Corresponding author. E-mail: lidong.sun@cqu.edu.cn

This work was supported by the National Natural Science Foundation of China (21501016, 21777011, 51871037, 51501024), the Innovative Research Team of Chongqing (CXTDG201602014), the Key Natural Science Foundation of Chongqing (cstc2017jcyjBX0052) and the Plan for "National Youth Talents" of the Organization Department of the Central Committee. The authors also acknowledge the AM-HPC in Suzhou, China for computational support.

DOI: 10.1016/S1872-2067(18)63187-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 3, March 2019

materials have shown superior photocatalytic properties on visible light exposure because of their suitable band gap and layered structure. Bismuth oxyhalides (BiOX , $X = \text{Cl}$, Br , and I), where $[\text{Bi}_2\text{O}_2]^{2+}$ slabs are sandwiched between double anion (X^-) layers, have shown good photocatalytic activity. In particular, bismuth iodide (BiOI) shows strong absorption in the visible light region because of its small band gap of 1.6–1.9 eV [12,13]. However, the high photoelectron recombination rate of BiOI limits its practical application as a visible light catalyst. To overcome this disadvantage of BiOI , various strategies, such as material design [14], decoration with noble metals [15], elemental doping [16], and heterojunctions [17,18], have been employed.

Recently, extensive work has been conducted on the introduction of oxygen vacancies (OVs) into photocatalysts to modulate their optical absorption, charge separation and transport, and surface reactions to enhance the photocatalytic activity [19–21]. The construction of a heterostructure can increase the photocatalytic efficiency of semiconductors because the band structures of the materials are matched, which can improve three vital photocatalytic processes: electron excitation, separation and transmission, and depletion. For example, $\text{Bi}/\text{Bi}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ [18], $\text{SrCO}_3/\text{BiOI}$ [17], and $\text{Bi}_2\text{O}_2\text{CO}_3/\text{BiOI}$ [22] have been reported to show highly enhanced photocatalytic activity. As a semimetal, bismuth has a very small band overlap and possesses surface plasmon resonance (SPR) properties, similar to those of the noble metals. Jiang et al. [23] prepared a Bi nanoparticle (NP)-decorated $\text{g-C}_3\text{N}_4$ composite and confirmed that the incorporation of the Bi NPs improved the photocatalytic activity of $\text{g-C}_3\text{N}_4$ via the combined heterojunction and SPR effect, both of which facilitated electron-hole (e^-/h^+) separation in $\text{g-C}_3\text{N}_4$. Thus, the simultaneous introduction of OVs and Bi NPs on BiOI effectively quenches the electron-hole recombination in BiOI and promotes photocatalytic activity.

In this paper, a ternary $\text{Bi}/\text{BiOI}/(\text{BiO})_2\text{CO}_3$ heterojunction was constructed via an *in situ* assembly method under mild conditions. This unique heterojunction contains Bi nanoparticles, BiOI with oxygen vacancies (OV- BiOI), and $(\text{BiO})_2\text{CO}_3$. The $\text{Bi}_2\text{O}_2\text{CO}_3$ and Bi metal deposited on BiOI can dramatically boost the NO removal efficiency via the formation of dual junctions (i.e., Bi/BiOI and $\text{BiOI}/(\text{BiO})_2\text{CO}_3$), which result in increased charge carrier separation and the production of reactive radicals for visible light photocatalysis.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade and were used without further purification. The $\text{Bi}/\text{BiOI}/(\text{BiO})_2\text{CO}_3$ composites were prepared by a facile *in situ* assembly method with pure BiOI as the substrate. The BiOI was obtained by precipitation. Briefly, 0.485 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added to 30 mL of deionized water and dispersed by magnetic stirring for 10 min, forming a homogeneous white suspension. Then, 0.166 g of KI was dissolved in 30 mL water and added dropwise to this mix-

ture. Next, the mixture was stirred for 30 min at room temperature. Subsequently, the resultant brown yellow suspension was left to stand for 20 min. The product (denoted BOI) was centrifuged and washed twice with distilled water and ethanol.

The $\text{Bi}/\text{BiOI}/(\text{BiO})_2\text{CO}_3$ samples were then synthesized using the produced BiOI as the precursor and NaBH_4 solution as the reducing agent. In detail, 0.352 g of BiOI powder was added to 100 mL polyvinylpyrrolidone (PVP, 0.1 g/L) solution with continuous stirring for 20 min. Then, 30 mL of NaBH_4 solution (70 mmol/L) was added dropwise to the above solution. After reaction for 1 h, the suspension was left to stand for 1 h. The resultant precipitate was centrifuged and washed twice with deionized water and absolute ethanol. Finally, the product was dried at 40 °C in a vacuum oven. The products are labeled based on the concentration of the NaBH_4 solution, that is, BOI-70 .

2.2. Characterization

The crystal phases of the samples were determined by X-ray diffractometry (XRD) with $\text{Cu K}\alpha$ radiation (D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out using an $\text{Al K}\alpha$ X-ray radiation source (Thermo Scientific ESCALAB 250, USA) to analyze the chemical composition of the samples. The morphologies and structures of the samples were observed by scanning electron microscopy (SEM, JSM-6490, Japan) and transmission electron microscopy (TEM, JEM-2010, Japan). Electron spin resonance (ESR, JES FA200) spectroscopy was used to obtain spectra of the spin-trapped radicals (trapping agent: 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO)). UV-vis diffuse reflectance spectroscopy (UV-vis DRS) measurements were carried out on dry-pressed disk samples. The UV-vis spectrometer (UV2550, Shimadzu, Japan) was equipped with an integrating sphere assembly, and 100% BaSO_4 was used as the reflectance sample. Photoluminescence (PL) spectra were recorded using an Aqualog Spectrofluorometer (F-7000, Hitachi, Japan).

2.3. Visible light photocatalytic NO removal

The visible-light-driven photocatalytic removal of NO was evaluated using a continuous-flow reactor. The rectangular reactor (30 cm $\times$ 15 cm $\times$ 10 cm) was made of polymeric glass and covered with Saint-Glass. To block UV light, a 150-W Xe commercial tungsten halogen lamp was fitted with a UV cutoff filter (420 nm), and the average light intensity was 0.16 W/cm². For the photocatalysis experiments, 0.20 g of the catalyst was coated onto two 12-mm diameter glass disks, which were placed in the reactor without irradiation when adsorption-desorption equilibrium had been reached. The initial concentration of NO was diluted to about 550 ppb by a zero air generator. The concentration of NO was continuously measured using a NO_x analyzer (Thermo Environmental Instruments Inc., 42c-TL) while analyzing the NO_x (where NO_x represents $\text{NO} + \text{NO}_2$) concentration. The NO removal ratio (η) was obtained using the following equation: $\eta(\%) = (1 - (C/C_0)) \times 100\%$, where C represents the NO concentration at the outlet of

the reactor after turning on the lamp, and C_0 represents the NO concentration when adsorption-desorption equilibrium is reached before turning on the lamp.

2.4. Density functional theory (DFT) calculations

DFT calculations were carried out using the "Vienna *ab initio* simulation package" (VASP 5.4) [24–26] and employed a generalized gradient correlation functional [27]. The projector-augmented wave method was used with a plane-wave basis set with a cut-off energy of 500 eV [28,29]. The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a $3 \times 3 \times 1$ Monkhorst–Pack grid. All atoms were allowed to converge to 0.01 eV/Å. The $8 \times 8 \times 8$ supercell of BiOI included eight oxygen atoms, eight bismuth atoms, and eight iodine atoms. The final optimization of the structural model resulted in the atomic energy converging to a minimum.

3. Results and discussion

3.1. Phase and morphological structure

As shown in Fig. 1(a), the crystal structure of tetragonal BiOI possesses a Sillén-like layered structure, which is composed of $[\text{Bi}_2\text{O}_2]^{2+}$ layers with I[−] ions between them. Fig. 1(b) depicts the powder XRD patterns of the as-prepared BOI and BOI-70 samples. All the diffraction peaks of BOI can be well indexed to the tetragonal phase of BiOI (JCPDS No. 10-0445). No other impurity peaks are present in the XRD pattern of BOI. After the addition of a certain amount of NaBH_4 , peaks corresponding to BiOI and $(\text{BiO})_2\text{CO}_3$ (JCPDS No. 25-1464) were observed in the XRD pattern of BOI-70. In addition, four diffraction peaks at 27.3° , 37.9° , 39.8° , and 48.7° of the metallic Bi phase (JCPDS No. 05-0519) are also present in the XRD pattern of BOI-70. These results indicate the coexistence of Bi, $(\text{BiO})_2\text{CO}_3$, and BiOI phases in the BOI-70 composites. Furthermore, the peaks of BiOI were weakened, and diffraction peaks corresponding to $(\text{BiO})_2\text{CO}_3$ and Bi appear. It is possible that the weak basicity of the NaBH_4 aqueous solution results in CO_2 from the air forming CO_3^{2-} , thus resulting in the conversion of $(\text{BiO})^+$ to $(\text{BiO})_2\text{CO}_3$. Simultaneously, in the presence of NaBH_4 , the $(\text{BiO})^+$ can be reduced to the metallic Bi phase. The signal arising from the OV in the BOI-70 sample is obvious in the solid state EPR spectra (Fig. 1(c)) [30], showing as a characteristic signal with

a g -factor of about 2.0 for BOI-70. Because of the special layered structure of BOI, the formation of oxygen vacancies on the surface during the reduction process is favorable. It can be inferred that the OVs of the as-prepared BOI-70 sample are located on the surface of BiOI (labeled OV-BiOI). These results confirm that the Bi/OV-BiOI/ $(\text{BiO})_2\text{CO}_3$ composites had been successfully prepared.

The surface composition and chemical states of the as-prepared samples were further analyzed by XPS measurements. Fig. 2(a) shows the elemental composition of the samples, which shows that BOI-70 contains O, C, Bi, and I. Fig. 2(b) shows the high-resolution XPS spectra of Bi. In the spectrum of BOI, the presence of Bi^{3+} is confirmed by the characteristic Bi $4f_{7/2}$ and Bi $4f_{5/2}$ peaks at 164.0 and 158.7 eV, respectively. In the spectrum of BOI-70, in addition to the two Bi $4f$ peaks of Bi^{3+} , peaks corresponding to metallic Bi^0 are detectable at 162.1 and 156.8 eV, suggesting that Bi^{3+} was partially reduced by NaBH_4 to form Bi metal in BOI-70. Fig. 2(c) shows the XPS spectra of the I $3d$ region, and the peaks at 618.5 and 630.1 eV can be ascribed to I $3d_{5/2}$ and I $3d_{3/2}$, respectively. The I $3d$ peaks in the spectra of the BOI-70 composites have binding energies similar to those of BOI, and the results further confirm the presence of BiOI in the as-prepared BOI-70 samples.

The morphology and structural changes of BOI and BOI-70 were investigated using SEM and high-resolution (HR)TEM measurements. The SEM images of BOI (Fig. 3(a)) and BOI-70 (Fig. 3(b)) show flower-like structures formed of nanosheets. In comparison with the smooth surfaces of the nanosheets in the BiOI sample, the surfaces of the flower-like microspheres are rough, and they are covered by some irregularly aggregated particles, as shown in Figs. 3(a) and (b). The TEM images (Figs. 3(c) and (d)) show the microstructure of the samples in detail. From the HRTEM image of BOI (Fig. 3(c)), a lattice spacing of 0.458 nm was determined, which is consistent with the (002) crystallographic plane of BiOI. As shown in Fig. 3(d), the HRTEM image clearly shows the lattice fringes with interplanar spacings corresponding to metallic Bi, tetragonal BiOI, and $(\text{BiO})_2\text{CO}_3$. The interplanar spacings of 0.328, 0.458, and 0.193 nm correspond to the (012) crystallographic plane of Bi, (002) crystallographic plane of BiOI, and (020) crystallographic plane of $(\text{BiO})_2\text{CO}_3$. The combined XRD, XPS, and HRTEM results show that the ternary Bi/OV-BiOI/ $(\text{BiO})_2\text{CO}_3$ composite can be constructed through the facile reduction of BiOI by NaBH_4 . In Fig. 3(d), two borders can be seen (of Bi/OV-BiOI and

Fig. 1. (a) Crystal structure of tetragonal BiOI; (b) XRD patterns of BOI and BOI-70; (c) EPR spectra of BOI and BOI-70.

Fig. 2. (a) XPS survey spectra of BOI and BOI-70; (b) Bi 4f spectra of BOI and BOI-70; (c) I 3d spectra of BOI and BOI-70.

OV-BiOI/(BiO)₂CO₃, which implies that an intimate interface had formed. This interface could optimize the path for charge carrier transfer in the ternary composite. The formation of Bi/BiOI/(BiO)₂CO₃ is represented by Eqs. (1)–(7).

When NaBH₄ is dissolved in water, the solution becomes weakly alkaline (Eqs. (1) and (2)). This results in ambient CO₂ becoming dissolved in the water and forming CO₃²⁻ (Eqs. (3) and (4)). During the chemical reduction process, some of the BiOI is transformed into (BiO)₂CO₃ by the presence of dissolved atmospheric CO₂ (the carbonate source) at room temperature during the long stirring process (Eqs. (5) and (6)). In addition, some of the (BiO)⁺ is reduced to Bi metal (Eq. (7)), simultaneously forming oxygen vacancies. Lastly, the Bi metal is deposited on the surface of the OV-BiOI/(BiO)₂CO₃ composite, forming a ternary heterojunction structure.

3.2. Photocatalytic performance under visible light irradiation

The photocatalytic removal of NO from a continuous flow of air was tested. The samples were kept in the dark until adsorption equilibrium was reached. Then, the activity was assessed under visible light ($\lambda > 400$ nm) illumination.

Fig. 4(a) shows the photocatalytic performance of BOI and BOI-70. Over the 30-min visible light photocatalytic reaction, the NO concentration decreased with increasing reaction time. The NO removal ratios (η) of BOI, P25, and BOI-70 are 1.2%, 11.5%, and 50.7% after 30 min, respectively. BOI exhibits low activity because of its high charge carrier recombination rate. Clearly, BOI-70 can remove NO more efficiently than BOI and P25, indicating that the ternary Bi/BiOI/(BiO)₂CO₃ composites can indeed improve the photocatalytic performance via the synergistic dual interface heterojunction and the introduced vacancies. On repeated testing, the photocatalytic activity of BOI-70 (Fig. 4(b)) was not reduced, implying that this catalyst is stable for NO removal and does not suffer obvious deactivation. The final products of photocatalytic NO oxidation are nitrates [17,18], which can be removed by washing with water.

Reactive oxygen species (ROS) are considered to be involved in the photocatalytic reaction, and these species play a crucial role in the oxidative removal of NO. Figs. 4(c) and (d) show the DMPO spin-trapping ESR spectra. In Fig. 4(c), a stronger DMPO-•O₂⁻ signal intensity for BOI-70 is observed compared to that of BOI. Similarly, stronger •OH signals were detected for BOI-70 (Fig. 4(d)). The catalytic performance of the sample is closely related to its charge carrier concentration and electronic transmission properties. The formed heterojunction and presence of OVs are beneficial for charge carrier transportation, increasing the production of reactive oxygen species and significantly improving the photocatalytic activity.

3.3. Photocatalysis mechanism

To reveal the mechanism behind the enhancement in photocatalytic efficiency, UV-vis diffuse reflectance spectra (DRS) of BiOI (BOI) and (BiO)₂CO₃ (BOC), and the ternary Bi/BiOI/(BiO)₂CO₃ composite (BOI-70) were examined, and the results are presented in Fig. 5(a). Compared to BOC, BOI-70 shows enhanced photo-absorption, indicating that the number

Fig. 3. SEM (a, b) and high-resolution HRTEM (c, d) images of BOI (a, c) and BOI-70 (b, d).

Fig. 4. (a) Photocatalytic activity of BOI, BOI-70 for NO removal; (b) photocatalytic stability of BOI-70; DMPO spin-trapping ESR spectra in a methanol dispersion for $DMPO \cdot O_2^-$ (c) and in an aqueous dispersion for $DMPO \cdot OH$ (d).

Fig. 5. (a) UV-vis DRS of BOI and BOC and BOI-70; (b) PL spectra of BOI and BOI-70.

of charge carrier increased in the ternary composite. As shown in Fig. 5(b), PL quenching was observed in the spectra of the BOI-70 composites. The $BiOI/(BiO)_2CO_3$ heterojunction contributes to the separation and transfer of photoelectrons and increases the number of charge carriers. Metallic Bi has SPR properties in the visible light range and concentrates the incident photon energy into plasmon oscillations, thus greatly extending the photoresponsive range of the ternary composite.

The local environment and fast transmission of charge carriers by the OV were confirmed by DFT calculations. To clarify the contribution of the OV to the electronic transmission, DFT calculations were used to model the adsorption and activation

of oxygen on the surface of the photocatalyst. The oxygen vacancies are located at the surface of the BiO^+ layer (Figs. 6(a) and (b)). To provide more information, we analyzed the charge difference distribution of BiOI (Figs. 6(c) and (d)). On the surface of the defective BiOI (Fig. 6(d)), an electron trap is formed at the OV, and the electron density around the oxygen atoms increases. Then, the electrons are transferred from the OVs to O_2 molecules. This phenomenon does not occur in the defect-free BiOI (Fig. 6(c)), which indicates that the recombination of photogenerated charges is inhibited by the OVs because they provides sites for the transfer of electrons to the reactants. The adsorption energy (E_{ads}) of O_2 on the surface decreases

Fig. 6. Optimized O_2 adsorption on BiOI (a) and BiOI containing oxygen vacancies (OV-BiOI) (b). Charge density difference of BiOI (c) and OV-BiOI (d). Electron accumulation is shown in blue and depletion in yellow.

from -0.29 to -0.76 eV from defect-free to defective BiOI, respectively, and the O–O bond length increases from 1.30 to 1.37 Å, respectively (Figs. 6(a) and (b)). This result implies that the OVs can promote the adsorption of O_2 molecules on the surface of the photocatalyst by reducing the oxygen adsorption energy and promote the activation of O_2 by weakening the O–O bonds. The results of the theoretical calculations are consistent with the ESR results (Figs. 4(b) and (c)), which confirm that more molecular oxygen is activated by the OVs on BOI-70 than those on BOI, generating more $\bullet O_2^-$ radicals for photocatalysis [31,32].

The valence band (VB) and conduction band (CB) energies of BiOI and $(BiO)_2CO_3$ were evaluated using Eqs. (9) and (10) [33].

$$E_{VB} = X - E^e + 0.5E_g \quad (9)$$

$$E_{CB} = E_{VB} - E_g \quad (10)$$

Here, E_g represents the band gap of the semiconductor, X is the electronegativity of the semiconductor calculated from the electronegativity of the constituent atoms, and E^e is the energy of free electrons on the hydrogen scale (approximately 4.5 eV). The X values of BiOI and $(BiO)_2CO_3$ are approximately 5.94 and 6.36 eV. The band gaps of BiOI and $(BiO)_2CO_3$ were calculated to be 1.80 and 3.40 eV, respectively. For BiOI, E_{VB} and E_{CB} were estimated to be 2.34 and 0.54 eV, respectively, and those of $(BiO)_2CO_3$ were estimated to be 3.56 and 0.16 eV, respectively.

BiOI is a typical p-type semiconductor where the Fermi level is located close to the valence band (VB) [34–36]. The Fermi level of n-type $(BiO)_2CO_3$ is close to the CB [37–39]. The coupling of an n-type semiconductor ($(BiO)_2CO_3$) to a p-type photosensitizer (BiOI) enables the Fermi level of $(BiO)_2CO_3$ and BiOI to shift to the same level, thus forming a p–n heterojunction [40–42]. Because the Fermi levels of BiOI and $(BiO)_2CO_3$ reach equilibrium, the CB of $(BiO)_2CO_3$ shifts to an energy level lower than that of BiOI. Because of the energy difference in the Fermi level of Bi NPs (-0.17 eV) [43] and the p–n heterojunction (OV-BiOI/ $(BiO)_2CO_3$), the three components form a perfect heterojunction structure. This synergistic interaction is illustrated in Fig. 7. Because of the intimate contact between Bi, $(BiO)_2CO_3$ and OV-BiOI (Fig. 1(b)) and the higher Fermi level of the Bi NPs, two interfacial heterojunctions, i.e., Bi/OV-BiOI and OV-BiOI/ $(BiO)_2CO_3$, are formed.

When the ternary composite is exposed to visible light, electron-hole pairs are excited and dissociated over the surface of the Bi NPs, as well as the BiOI semiconductor, leading to a much-increased charge carrier concentration. In addition to the injection of hot electrons from the Bi NPs into the BiOI, the concentrated resonance energy caused by the SPR effect of the Bi NPs can also be converted into a local electromagnetic field [44–46], which promotes e^-/h^+ separation in the ternary composite. The photoexcited electrons spontaneously migrate through the heterojunction from Bi to OV-BiOI and then to $(BiO)_2CO_3$ under the driving force of the energy difference between the dual heterojunction. The holes remain in the VB of BiOI, but the electrons in the CB of $(BiO)_2CO_3$ can react with the O_2 to produce $\bullet O_2^-$ radicals [47]. In addition, some of the elec-

Fig. 7. Schematic of the energy bands of Bi, BiOI, and $Bi_2O_2CO_3$ (a) and possible charge separation process at the heterojunction (b).

trons activate oxygen, generating $\bullet\text{O}_2^-$ radicals under the action of the OVs in the OV-BiOI. The residual holes in the VB of OV-BiOI react with OH^- to produce $\bullet\text{OH}$ radicals [48]. These reactive oxygen species are responsible for the prominent visible light photocatalytic NO removal ability of the composite [49–51]. In summary, because of the heterojunction and SPR effects of the Bi NPs and the presence of OVs, the Bi/BiOI/(BiO) $_2$ CO $_3$ ternary system shows highly enhanced photocatalysis with increased charge carrier concentration and rapid electron-hole separation [52,53].

4. Conclusions

A Bi/BiOI/(BiO) $_2$ CO $_3$ ternary heterojunction photocatalyst was synthesized by an *in situ* assembly method using NaBH $_4$ as the reducing agent. During the reaction, metallic Bi and (BiO) $_2$ CO $_3$ were produced from BiOI. Using both theory and experiment, we have revealed the role of each component in the ternary system in photocatalysis. This composite has a broad response range to visible light and high electron-transfer efficiency on account of the synergistic effect of the heterojunction, SPR, and OVs. The introduction of Bi, (BiO) $_2$ CO $_3$, and OVs provides abundant electrons for the activation of O $_2$ molecules, thus promoting the production of ROS for photocatalytic NO oxidation. As a result, the Bi/BiOI/(BiO) $_2$ CO $_3$ ternary composites demonstrate highly enhanced photocatalytic activity for the removal of NO under visible light irradiation. Thus, this study provides insights into the synergistic effect of the het-

eromaterial structure, SPR effect, and OVs for enhancing visible light photocatalysis, providing a new strategy to explore other bismuth-containing heterostructured visible-light-driven photocatalysts.

References

- [1] L. Chen, J. He, Y. Liu, P. Chen, C.T. Au, S.F. Yin, *Chin. J. Catal.*, **2016**, 37, 780–791.
- [2] K. L. He, J. Xie, X. Y. Luo, J. Q. Wen, S. Ma, X. Li, Y. P. Fang, X. C. Zhang, *Chin. J. Catal.*, **2017**, 38, 240–252.
- [3] R. B. Wei, Z. L. Huang, G. H. Gu, Z. Wang, L. X. Zeng, Y. B. Chen, Z. Q. Liu, *Appl. Catal. B*, **2018**, 231, 101–107.
- [4] X. Feng, W. Zhang, H. Deng, Z. Ni, F. Dong, Y. Zhang, *J. Hazard. Mater.*, **2017**, 322, 223–232.
- [5] Y. Li, K. Lv, W. Ho, Z. Zhao, Y. Huang, *Chin. J. Catal.*, **2017**, 38, 321–329.
- [6] W. Zhang, X. Liu, X. Dong, F. Dong, Y. Zhang, *Chin. J. Catal.*, **2017**, 38, 2030–2038.
- [7] H. An, B. Lin, C. Xue, X. Yan, Y. Dai, J. Wei, G. Yang, *Chin. J. Catal.*, **2017**, 39, 654–663.
- [8] R. He, D. Xu, B. Cheng, J. Yu, W. Ho, *Nanoscale Horiz.*, **2018**, 3, 464–504.
- [9] X. Xie, Y. Liu, X. Dong, C. Lin, X. Wen, Q. Yan, *Appl. Surf. Sci.*, **2018**, 455, 742–747.
- [10] M. Chen, Y. Huang, J. Yao, J. Cao, Y. Liu, *Appl. Surf. Sci.*, **2018**, 430, 137–144.
- [11] J. Niu, P. Dai, Q. Zhang, B. Yao, X. Yu, *Appl. Surf. Sci.*, **2018**, 430, 165–175.
- [12] J. Yang, L. Xu, C. Liu, T. Xie, *Appl. Surf. Sci.*, **2014**, 319, 265–271.

Graphical Abstract

Chin. J. Catal., 2019, 40: 362–370 doi: 10.1016/S1872-2067(18)63187-0

A Bi/BiOI/(BiO) $_2$ CO $_3$ heterostructure for enhanced photocatalytic NO removal under visible light

Yanjuan Sun *, Jiazhen Liao, Fan Dong, Sujuan Wu, Lidong Sun *

Chongqing University; Chongqing Technology and Business University; University of Electronic Science and Technology of China

Photoexcited electrons spontaneously migrate through the heterojunction from Bi to OV-BiOI and then to (BiO) $_2$ CO $_3$ under the driving force of the energy difference between the dual heterojunction. The holes remain in the VB of BiOI, and the electrons on the CB of (BiO) $_2$ CO $_3$ react with O $_2$ to produce $\bullet\text{O}_2^-$ radicals. The residual holes in the VB of OV-BiOI react with the OH^- to produce $\bullet\text{OH}$ radicals.

- [13] J. Hu, S. Weng, Z. Zheng, Z. Pei, M. Huang, P. Liu, *J. Hazard. Mater.*, **2014**, 264, 293–302.
- [14] Q. C. Liu, D. K. Ma, Y. Y. Hu, Y. W. Zeng, S. M. Huang, *ACS Appl. Mater. Interfaces*, **2013**, 5, 11927–11934.
- [15] W. J. Kim, D. Pradhan, B. K. Min, Y. Sohn, *Appl. Catal. B*, **2014**, 147, 711–725.
- [16] X. Zhang, L. Zhang, *J. Phys. Chem. C*, **2010**, 114, 18198–18206.
- [17] H. Wang, Y. J. Sun, G. M. Jiang, Y. X. Zhang, H. W. Huang, Z. B. Wu, S. C. Lee, F. Dong, *Environ. Sci. Technol.*, **2018**, 52, 1479–1487.
- [18] W. J. He, Y. J. Sun, G. M. Jiang, H. W. Huang, X. M. Zhang, F. Dong, *Appl. Catal. B*, **2018**, 232, 340–347.
- [19] J. Z. Liao, L. C. Chen, M. L. Sun, B. Lei, X. L. Zeng, Y. J. Sun, F. Dong, *Chin. J. Catal.*, **2018**, 39, 779–789.
- [20] Y. C. Huang, H. B. Li, M. S. Balogun, W. Y. Liu, Y. X. Tong, X. H. Lu, H. B. Ji, *ACS Appl. Mater. Interfaces*, **2014**, 6, 22920–22927.
- [21] W. J. Fan, H. B. Li, F. Y. Zhao, X. J. Xiao, Y. C. Huang, H. B. Ji, Y. X. Tong, *Chem. Commun.*, **2016**, 52, 5316–5319.
- [22] P. Y. Song, M. Xu, W. D. Zhang, *Mater. Res. Bull.*, **2015**, 62, 88–95.
- [23] G. M. Jiang, X. W. Li, M. N. Lan, T. Shen, X. S. Lv, F. Dong, S. Zhang, *Appl. Catal. B*, **2017**, 205, 532–540.
- [24] S. Grimme, *J. Comput. Chem.*, **2006**, 27, 1787–1799.
- [25] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **1996**, 54, 11169–11186.
- [26] G. Kresse, J. Furthmüller, *Comp. Mater. Sci.*, **1996**, 6, 15–50.
- [27] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77, 3865–3868.
- [28] P. E. Blöchl, *Phys. Rev. B*, **1994**, 50, 17953–17979.
- [29] G. Kresse, D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758–1775.
- [30] L. R. Grabstanowicz, S. Gao, T. Li, R. M. Rickard, T. Rajh, D. J. Liu, T. Xu, *Inorg. Chem.*, **2013**, 52, 3884–3890.
- [31] H. W. Huang, Y. He, X. Du, P. K. Chu, Y. H. Zhang, *ACS Sustain. Chem. Eng.*, **2015**, 3, 3262–3273.
- [32] D. Fukushima, A. Sasaki, H. Hirabayashi, M. Kitano, *Microelectron. Reliab.*, **2017**, 79, 1–4.
- [33] Y. Nosaka, A. Y. Nosaka, *Chem. Rev.*, **2017**, 117, 11302–11336.
- [34] M. Yan, Y. Q. Hua, F. F. Zhu, W. Gu, J. H. Jiang, H. Q. Shen, W. D. Shi, *Appl. Catal. B*, **2017**, 202, 518–527.
- [35] R. Dong, Y. Hu, Y. Wu, W. Gao, B. Ren, Q. Wang, Y. Cai, *J. Am. Chem. Soc.*, **2017**, 139, 1722–1725.
- [36] H. Wang, Y. Liang, L. Liu, J. Hu, P. Wu, W. Cui, *Appl. Catal. B*, **2017**, 208, 22–34.
- [37] Y. J. Sun, Z. W. Zhao, W. D. Zhang, C. F. Gao, Y. X. Zhang, F. Dong, *J. Colloid Interf. Sci.*, **2017**, 485, 1–10.
- [38] F. Mian, G. Bottaro, M. Rancan, L. Pezzato, V. Gombac, P. Fornasiero, L. Armelao, *ACS Omega*, **2017**, 2, 6298–6308.
- [39] M. Chen, J. Yao, Y. Huang, H. Gong, W. Chu, *Chem. Eng. J.*, **2018**, 334, 453–461.
- [40] X. Zou, Y. Dong, X. Zhang, Y. Cui, X. Ou, X. Qi, *Appl. Surf. Sci.*, **2017**, 391, 525–534.
- [41] H. Derikvand, A. Nezamzadeh-Ejehieh, *J. Colloid Interf. Sci.*, **2017**, 490, 314–327.
- [42] J. Sun, X. Li, Q. Zhao, M. O. Tadé, S. Liu, *Appl. Catal. B*, **2017**, 219, 259–268.
- [43] S. Yu, H. Huang, F. Dong, M. Li, N. Tian, T. Zhang, Y. Zhang, *ACS Appl. Mater. Interfaces*, **2015**, 7, 27925–27933.
- [44] T. Xiong, X. Dong, H. Huang, W. Cen, Y. Zhang, F. Dong, *ACS Sustain. Chem. Eng.*, **2016**, 4, 2969–2979.
- [45] J. Lv, J. Zhang, J. Liu, Z. Li, K. Dai, C. Liang, *ACS Sustain. Chem. Eng.*, **2017**, 6, 696–706.
- [46] Q. Wang, J. He, Y. Shi, S. Zhang, T. Niu, H. She, Y. Bi, *Chem. Eng. J.*, **2017**, 326, 411–418.
- [47] F. J. Corpas, J. B. Barroso, *Nitric Oxide*, **2017**, 68, 103–110.
- [48] X. Dong, W. Zhang, Y. Sun, J. Li, W. Cen, Z. Cui, H. Huang, F. Dong, *J. Catal.*, **2018**, 357, 41–50.
- [49] W. Cui, J. Li, Y. Sun, H. Wang, G. Jiang, S. C. Lee, F. Dong, *Appl. Catal. B*, **2018**, 237, 938–946.
- [50] X. Dong, J. Li, Q. Xing, Y. Zhou, H. Huang, F. Dong, *Appl. Catal. B*, **2018**, 232, 69–76.
- [51] P. Chen, F. Dong, M. Ran, J. Li, *Chin. J. Catal.*, **2018**, 39, 619–629.
- [52] J. Li, Z. Zhang, W. Cui, H. Wang, W. Cen, G. Johnson, G. Jiang, S. Zhang, F. Dong, *ACS Catal.*, **2018**, 8, 8376–8385.
- [53] W. He, Y. Sun, G. Jiang, H. Huang, X. Zhang, F. Dong, *Appl. Catal. B*, **2018**, 232, 340–347.

Bi/BiOI/(BiO)₂CO₃异质结可见光催化净化NO的性能增强

孙艳娟^{a,b,*}, 廖佳珍^b, 董帆^{b,c}, 吴素娟^a, 孙立东^{a,#}

^a 重庆大学材料科学与工程学院, 机械传动国家重点实验室, 重庆 400044

^b 重庆工商大学环境与资源学院, 催化与环境新材料重庆市重点实验室, 重庆 400067

^c 电子科技大学基础与前沿研究院, 四川成都 611731

摘要: 窄带隙BiOI光催化剂因电荷重组速率快而导致其可见光下的光催化效率较低。本文以NaBH₄为还原剂, 采用简单的常温原位组装法在BiOI上构建氧空位、金属Bi颗粒和Bi₂O₂CO₃共作用, 以克服BiOI的缺点。在合成的三元Bi/BiOI/(BiO)₂CO₃中, 氧空位、双异质结(即Bi/BiOI和BiOI/(BiO)₂CO₃)以及Bi粒子的表面等离子体共振效应均促进了电子-空穴分离和电荷载流子浓度的增加, 从而提高了可见光的整体光催化效率。将制备的催化剂用于可见光下去除连续流空气中的ppb级NO。结果表明, Bi/BiOI/(BiO)₂CO₃的NO去除率显著增强, 大约为50.7%, 并远高于BiOI(1.2%)。密度泛函理论计算和实验结果表明, Bi/BiOI/(BiO)₂CO₃复合材料可明显促进光催化NO氧化的活性氧生成。本文可提供一个新的策略来改性窄带隙半导体和探索其他含铋异质结构的可见光驱动光催化剂。

XRD结果发现, BOI-70中出现Bi和(BiO)₂CO₃的特征峰, 但BOI却很微弱; XPS结果表明, 高价态Bi³⁺被NaBH₄部分还原而形成低价态金属Bi颗粒, 且I 3d峰位结合能进一步证实了BOI-70样品中存在BiOI, 由此可见, 成功制备了三元Bi/BiOI/(BiO)₂CO₃异质结催化剂, EPR结果表明氧空位的产生。SEM和TEM结果表明, BiOI和三元Bi/BiOI/(BiO)₂CO₃催化剂为纳米片组装的花状结构。HRTEM的结果进一步显示了金属铋、正方晶相BiOI和(BiO)₂CO₃对应的晶格间距。紫外-可见光催化去除NO的测试结果表明, BOI-70(50.7%)的光催化活性明显高于BOI(1.2%)和P25(11.5%), 且在循环测试实验中表现出

优异的稳定性. UV-vis DRS测试结果显示, BOI-70具有更强的光吸收; PL结果表明, 其光生电子-空穴对的分离效率更高. ESR结果表明, 参与反应的主要活性物种为 $\bullet\text{O}_2^-$ 和 $\bullet\text{OH}$ 自由基. DFT计算结果证实了OVs对电荷载流子的局部环境和快速传输: OV为电子捕获陷阱, 使电子从OVs转移到 O_2 分子形成活性氧物种; O_2 表面的吸附能从无缺陷BiOI时的 -0.29 eV 降到有缺陷的 -0.76 eV , O–O键长从 $1.30\text{ \AA}$ 增至 $1.37\text{ \AA}$, 说明OVs通过降低氧的吸附能可促进 O_2 分子在光催化剂表面的吸附. 综上所述, 由于Bi NPs的异质结效应和SPR效应以及OVs的存在, Bi/BiOI/(BiO) $_2$ CO $_3$ 三元体系的原位组装通过增加载流子浓度和加速电子空穴分离使光催化活性显著增加.

关键词: BiOI; 氧空位; 异质结; 表面等离子体共振效应; NO氧化

收稿日期: 2018-08-07. 接受日期: 2018-10-09. 出版日期: 2019-03-05.

*通讯联系人. 电话/传真: (023)62769785; 电子信箱: syhsyj@163.com

#通讯联系人. 电子信箱: lidong.sun@cqu.edu.cn

基金来源: 国家自然科学基金(21501016, 21777011, 51871037, 51501024); 重庆市高校创新团队(CXTDG201602014); 重庆市自然科学基金重点项目(cstc2017jcyjBX0052); 中组部“万人计划”青年人才计划.

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).