available at www.sciencedirect.com

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

Article

SrTiO₃/BiOI heterostructure: Interfacial charge separation, enhanced photocatalytic activity, and reaction mechanism

Ruimin Chen^a, Hong Wang^a, Huizhong Wu^a, Jianping Sheng^{b,*}, Jieyuan Li^{b,c}, Wen Cui^{b,d}, Fan Dong^{a,b,#}

^a Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China

^b Research Center for Environmental Science & Technology, Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 611731, China

^c College of Architecture and Environment, Sichuan University, Chengdu 610065, Sichuan, China

^d The Center of New Energy Materials and Technology, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, Sichuan, China

ARTICLE INFO

Article history:

Received 10 September 2019

Accepted 12 October 2019

Published 5 April 2020

Keywords:

Heterostructure

SrTiO₃/BiOI

Charge separation

Photocatalysis

Reaction mechanism

ABSTRACT

Heterostructured photocatalysts provide an effective way to achieve enhanced photocatalytic performances through efficient charge separation. Although both wide- and narrow-band-gap photocatalysts have been widely investigated, the charge separation and transfer mechanism at the contacting interface of the two has not been fully revealed. Here, a novel SrTiO₃/BiOI (STB) heterostructured photocatalyst was successfully fabricated by using a facile method. The heterostructure in the photocatalyst extends the photoabsorption to the visible light range, and thus, high photocatalytic NO removal performance can be achieved under visible light irradiation. A combination of experimental and theoretical evidences indicated that the photogenerated electrons from the BiOI semiconductor can directly transfer to the SrTiO₃ surface through a preformed electron delivery channel. Enhanced electron transfer was expected between the SrTiO₃ and BiOI surfaces under light irradiation, and leads to efficient ROS generation and thus a high NO conversion rate. Moreover, in situ diffused reflectance infrared Fourier transform spectroscopy revealed that STB can better inhibit the accumulation of the toxic intermediate NO₂ and catalyze the NO oxidation more effectively. This work presents a new insight into the mechanism of the interfacial charge separation in heterostructures and provides a simple strategy to promote the photocatalytic technology for efficient and safe air purification.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Nitric oxide (NO) has caused extensive concerns as a major

contributor to photochemical smog, acid rain, and ozone depletion [1–3]. NO released in high concentrations in the form of industrial emissions can be treated by conventional techniques

* Corresponding author. E-mail: jpshengchn@163.com

Corresponding author. E-mail: dfctbu@126.com

This work was supported by the National Natural Science Foundation of China (21822601, 21501016, 21777011), the National R&D Program of China (2016YFC02047), the Innovative Research Team of Chongqing (CXTDG201602014), the Natural Science Foundation of Chongqing (cstc2017jcyjBX0052). The authors also acknowledge AM-HPC in Suzhou, China for computational support.

DOI: S1872-2067(19)63472-8 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 41, No. 4, April 2020

including physical adsorption, biofiltration, and thermal catalysis [4–6]. However, the traditional methods are not economically feasible for NO removal at parts per billion level [7–9]. Semiconductor photocatalysis as a green technology offers the advantage of direct utilization of the natural sunlight to purify air pollutants at low concentrations under ambient conditions, thus providing a promising alternative approach to NO purification [10–14].

Visible light accounts for nearly 50% of the solar spectrum and far exceeds the proportion of ultraviolet (UV) light (4%). However, wide-band-gap semiconductors primarily respond only to UV light [15]. Although narrow-band-gap semiconductor photocatalysts exhibit excellent visible light absorbing properties, they suffer from fast recombination of electron-hole pairs and low redox ability [16–18]. Therefore, narrow- and wide-band-gap photocatalysts can display high visible light adsorptions and strong redox abilities, respectively [19–21]. Consequently, various wide- and narrow-band-gap photocatalysts have been combined to enhance the photocatalytic performance, such as $\text{TiO}_2/\text{g-C}_3\text{N}_4$ [22], $\text{SrTiO}_3/\text{Cu}_2\text{O}$ [23], and $\text{BaCO}_3/\text{BiOI}$ [24]. SrTiO_3 is a typical n-type semiconductor with a wide band gap of approximately 3.2 eV that has been considered as a promising photocatalyst because of its physicochemical stability and non-toxicity [25–27]. The p-type narrow-band-gap semiconductor BiOI has been extensively studied because of its excellent visible light absorbing properties [28]. However, the photocatalytic activity of BiOI is normally low owing to fast recombination of its photogenerated carriers [29]. Considering the properties of SrTiO_3 and BiOI, fabrication of a p-n heterostructure by combining BiOI with SrTiO_3 can potentially promote charge separation and thus enhance the photocatalytic performance under visible light irradiation, in comparison with those of the pristine catalysts [30–33].

Most importantly, most of the reported literature solely focus on the efficiency of degradation of target pollutants (such as NO in air), while attention has rarely been paid to the toxic byproducts obtained during the transformation process of the target pollutant [34,35]. Therefore, it is desirable to explore novel photocatalysts that would simultaneously enhance the efficiency of NO purification under visible light irradiation and inhibit the generation of toxic intermediates [36–39]. Besides, the charge separation and transfer mechanism at the contacting interface of the two counterparts has not been fully revealed [40]. Exploration of the interfacial charge separation and electron transfer mechanism remains a great challenge. Therefore, the interfacial interaction of the heterojunction with the reactants requires investigation at the atomic level.

In this work, $\text{SrTiO}_3/\text{BiOI}$ (STB) composites were successfully prepared by a facile method, through which SrTiO_3 was compactly adhered to the surface of BiOI to fabricate a heterostructure. Although SrTiO_3 or BiOI alone shows negligible photocatalytic activity, the heterostructure with matching band gaps can extend the photoabsorption range and promote charge separation, thus achieving a high photocatalytic NO removal performance under visible light irradiation. An attempt was made to combine the theoretical and experimental approaches with the aim of disclosing the formation of electron

transfer channels at the interface between SrTiO_3 and BiOI. Moreover, in situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) technology was employed to dynamically monitor the photocatalytic NO oxidation process and investigate the generation and transformation of toxic intermediates. An effective electronic transmission channel was built to realize an exceptionally high charge-separation rate. Thus, the generation of ROS was enhanced for efficient photocatalytic oxidation of NO into the end products. This work presents a simple strategy that promotes efficient and safe air purification through photocatalytic technology.

2. Experimental

2.1. Synthesis of SrTiO_3 nanoplates

All the chemicals used in this study were of analytical grade and employed without further purification. SrTiO_3 was synthesized by hydrothermal method according to the following procedure. In a typical process, 5.0 mmol of tetrabutyl titanate was dissolved in 25 mL ethylene glycol. Then, 15.0 mL of 0.50 M $\text{Sr}(\text{NO}_3)_2$ solution was added to the above solution. After the two solutions were mixed, 20.0 mmol NaOH was added to the mixture solution and the resulting mixture was sealed in a 50 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. After cooling to room temperature, the obtained precipitates were washed several times with ultrapure water and alcohol and dried at 70 °C for 12 h to realize the final samples.

2.2. Fabrication of $\text{SrTiO}_3/\text{BiOI}$ heterojunction

The $\text{SrTiO}_3/\text{BiOI}$ heterojunction was constructed by the facile chemical bath method. 0.10 g SrTiO_3 and 1.0 mmol KI were ultrasonically dispersed in 40.0 mL distilled water to form a uniform solution A. Then, 1 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 mL ethylene glycol to form solution B. Solution B was added dropwise to solution A under vigorous stirring. Afterwards, the mixture was transferred into a water bath at 80 °C and held for 2 h. After cooling to room temperature, the obtained precipitates were washed several times with ultrapure water and alcohol and dried at 70 °C for 12 h. By changing the weight of SrTiO_3 added in the synthesis process, 22.12, 36.23, and 46.01 wt% STB composites were obtained. As will be discussed later, all the three STB samples revealed similar patterns in their photocatalytic activities and characterizations. Thus, STB-36.23 (labeled as STB) was presented as a prototype, and the corresponding results of STB-22.12 and STB-46.01 were listed in Supplementary Materials. Pure BiOI was prepared according to the same procedure as detailed above, but by not adding SrTiO_3 .

2.3. Characterization methods

The crystal structures of the samples were obtained using powder X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical compositions of

the samples. A UV-vis diffuse spectrophotometer was employed to analyze the optical properties of the samples with 100% BaSO₄. The morphological structures were revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electron spin resonance (ESR) spectra of the radicals that were spin-trapped using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) were also obtained. More details of the characterization methods are provided in text S1.

2.4. Photocatalytic activity tests

The photocatalytic performance was evaluated by removing NO (present at ppb levels) from a continuous stream reactor (Fig. S1). Details of the photocatalytic activity tests and analyses are provided in text S2 of Supporting Information.

2.5. In situ DRIFTS investigation

In situ DRIFTS measurements (Fig. S2) were performed with the help of a TENSOR II FT-IR spectrometer (Bruker Corp., Billerica, MA, USA), an in situ diffuse-reflectance cell (Harrick Scientific Products Inc., Pleasantville, NY, USA), a gas system, a light source (MVL-210; Mejiro Genossen Inc., Tokyo, JPN), and pretreatment equipment. The reaction chamber was equipped with three windows, two for the entry and detection of IR light and the third for illumination of the photocatalyst. A Xe lamp was used as the irradiation light source. The total gas flow rate was 100 mL/min (50 mL/min NO and 50 mL/min O₂). The prepared samples were pretreated at 80 °C for 20 min under high-purity He gas before the measurements.

2.6. Density functional theory (DFT) calculations

DFT calculations were performed using the “Vienna *ab initio* simulation package” (VASP5.4) and a generalized gradient correlation function [41–43]. A plane-wave basis set with a cut-off energy of 400 eV and the projector-augmented wave method framework were adopted. The Gaussian smearing width was set to 0.2 eV [44,45]. The Brillouin zone was sampled with a 3 × 3 × 2 Monkhorst Pack grid. All the atoms were allowed to converge to 0.01 eV/Å. The 15 × 18 × 20 supercell includes BiOI

with 16 O atoms, 12 Bi atoms, and 8 I atoms, and SrTiO₃ with 96 O atoms, 24 Sr atoms, and 24 Ti atoms. The supercells of BiOI and SrTiO₃ alone were first relaxed, before the BiOI supercell was placed on the plane of SrTiO₃ [46].

3. Results and discussion

3.1. Phase composition and morphology

The as-prepared SrTiO₃, BiOI, and STB composites were characterized by powder XRD (Fig. 1(a)). The diffraction peaks of the as-prepared pure BiOI and SrTiO₃ can be indexed to tetragonal BiOI (JCPDS 73-2062) and cubic SrTiO₃ (JCPDS 35-0734), respectively. Some characteristic peaks of SrTiO₃ and BiOI can be observed in the patterns of STB composites that confirm successful fabrication of the heterojunction. Notably, the (110) peak of BiOI in STB (at 31.7°) is right-shifted in comparison with that of pure BiOI (30.6°), which can be attributed to the interaction of SrTiO₃ with BiOI. Besides, the peaks of SrTiO₃ in the composites are weakened, which is a result of the high diffraction intensity of BiOI [47,48]. The other samples with different mass percentages of SrTiO₃ present similar phenomena (Fig. S3). The XPS survey spectra (Fig. 1(b)) show that all these samples contain Bi, O, I, Sr, and Ti elements, which further indicate that the STB composites have been successfully prepared [49].

The SEM and TEM images show the morphologies of the SrTiO₃, BiOI, and STB samples (Figs. 2 and S4). In Figs. 2(a) and 2(b), it is observed that the SrTiO₃ is composed of nanoparticles and the BiOI is constructed of nanosheets. The SEM images of STB (Figs. 2(c) and 2(d)) reveal that SrTiO₃ nanoparticles are dispersed on the surface of BiOI nanoplates. In Figs. 2(e) and 2(f), the lattice fringes observed with interplanar spacings of 0.36 and 0.30 nm can be indexed to the (011) and (012) planes of orthorhombic BiOI phase, respectively. The other lattice fringes with an interval of 0.275 nm are ascribed to the (110) planes of cubic SrTiO₃ perovskite. The EDX elemental maps (Fig. 2(g)) clearly show that SrTiO₃ is distributed on the surface of BiOI nanoplates. The BiOI and SrTiO₃ in the STB sample are tightly contacted with each other, which is consistent with the peak shifts observed in the XRD pattern of STB, which confirm that an interface is formed between BiOI and SrTiO₃ (Fig. 2(f)).

Fig. 1. Chemical compositions of the as-prepared samples. (a) XRD patterns, with the inset displaying partially enlarged profiles; (b) XPS survey spectra.

Fig. 2. Typical SEM images of SrTiO_3 (a), BiOI (b), STB samples (c, d); HR-TEM images (e, f) and EDX elemental maps (g) of STB.

3.2. Charge separation and electron transfer

In order to elucidate the interfacial interaction between BiOI and SrTiO_3 in STB heterojunction at the atomic level, the theo-

retical and experimental approaches were combined. The high-resolution XPS pattern reveals the chemical states of the samples. Fig. 3(a) shows that the Sr 3d and Ti 2p binding energies of the STB shift to higher values, compared to those of pure SrTiO_3 . On the other hand, the I 3d and Bi 4f (Fig. 3(b)) binding energies of the STB shift to lower values, in comparison with those of pure BiOI . The characteristic O 1s peaks are also offset to some extent (Fig. S5). These chemical shifts experimentally reveal that electrons are transferred from the Bi and I atoms of BiOI to the Sr and Ti atoms of SrTiO_3 in the STB compound. The shifts in the Sr 3d, Ti 2p, Bi 4f, and I 3d binding energies also confirm the strong interaction between SrTiO_3 and BiOI .

DFT was employed in calculations of the electronic structure to further confirm the nature of the interaction. The ELF indicates that covalent interactions exist at the contacting interface of STB (Fig. 3(c)), where electronic transmission channels are formed to reduce carrier recombination. The as-produced covalent bonds between SrTiO_3 and BiOI lead to the accumulation of localized excess electrons (e^-_{ex}), as depicted by the red dotted frame (Fig. 3(d)). These accumulated e^-_{ex} can further transfer through the interface with the covalent interaction channel [50]. It is apparent that the calculation results are consistent with the XPS results. More importantly, since the electron transfer channel is established, intensified electron exchange is expected across the interface under visible light irradiation, which leads to more efficient activation of the reactants and generation of ROS.

3.3. Visible light photocatalytic performance and ROS generation

The photocatalytic performances of the as-prepared samples in NO removal were investigated under visible light irradiation by using a house-customized continuous flow reaction

Fig. 3. Sr 3d and Ti 2p (a), and Bi 4f and I 3d (b) XPS patterns of the samples. (c) electron location function (ELF). (d) distribution of the charge difference between BiOI and SrTiO_3 : charge accumulation is shown in blue, whereas charge depletion is presented in yellow, and the isosurface is set to $0.002 \text{ eV}/\text{\AA}^3$.

system (Figs. 4(a) and S6). The NO purification performance on pure BiOI is negligible, although BiOI exhibits large visible light absorption. The STB displays a remarkably enhanced visible light photocatalytic activity, with a NO removal of 59.0%, compared with those of SrTiO₃ (33%) and BiOI. The UV-vis spectra reveal that the photoabsorption of the STB heterojunction is extended to the visible light range (Figs. 4(b) and S7). SrTiO₃ exhibits a decent visible light activity, which is attributed to the existence of O vacancies, as revealed by EPR (Fig. 4(c)) [51]. The DOS was subsequently calculated, and the results show that the O vacancies can form a defect energy level that lowers the photoenergy required for exciting the electrons (Fig. 4(d)) [52]. The limited NO removal activity of BiOI is a result of the rapid recombination of the photogenerated carriers and a feeble redox ability.

Typically, the photocatalytic performance is closely related to the generation of ROS. The ESR profiles were obtained to identify the changes in the ROS during the photocatalytic reaction, including those of DMPO-·OH, DMPO-·O₂⁻, TEMP-¹O₂, and e⁻, under visible light irradiation (Fig. 5). Compared with those of pure SrTiO₃ and BiOI, the ESR signal intensities of STB are all much stronger for ·OH, ·O₂⁻, and ¹O₂ radicals, which indicate the superior oxidation capacity of the STB heterojunction. This fact implies that the photogenerated charge carriers are efficiently separated in STB via the electron transfer channel. The accelerated accumulation of superoxide radical signals in STB suggests that the separated photoelectrons are prone to combine with O₂ molecules to produce more ·O₂⁻ (O₂ + e⁻ → ·O₂⁻) under visible light irradiation (Fig. 5(c)). Holes are left behind in the BiOI when the photogenerated electrons transfer from BiOI to SrTiO₃, which can promote the generation of ·OH radicals via

the oxidation of OH⁻ (OH⁻ + h⁺ → ·OH) [53]. Then, the singlet oxygen (¹O₂) produced by the oxidation of the superoxide radicals (·O₂⁻ + h⁺ → ¹O₂) is stronger than those of pure BiOI and SrTiO₃ (Fig. 5(c)). The electron sacrificial agent is rapidly consumed in STB under visible light irradiation to generate ROS, but it is still maintained in BiOI, as shown in Fig. 5(d). These ROS radicals can efficiently oxidize NO molecules into the final products. Hence, the outstanding photocatalytic performance of the STB compounds should be attributed to the establishment of electrons transfer channels that accelerate charge separation and ROS generation.

3.4. Photocatalytic mechanism and inhibition of toxic intermediates

In order to confirm the theoretical predictions and establish a comprehensive understanding of the photocatalytic mechanism, in situ DRIFTS was employed to dynamically track the primary reaction intermediates and products during the NO purification reaction. BiOI had been confirmed to exhibit negligible NO removal performance under visible light irradiation (Fig. 4(a)). Therefore, this section only compares SrTiO₃ with STB (Fig. S8). After the adsorption equilibrium is reached (Ads. Equ.), the DRIFTS pattern was recorded with light irradiation to explore the photocatalytic NO purification mechanism, especially for the generation and transformation of toxic intermediates. As shown in Fig. 6(a), the peak intensities of NO₂ (1616 cm⁻¹) and NO₂⁻ (1353 and 1303 cm⁻¹) on SrTiO₃ gradually increase, especially those of NO₂ [54,55]. As NO₂ is more toxic than NO, the conversion of NO into NO₂ should be largely inhibited.

Fig. 4. (a) Evaluation of the photocatalytic efficiency of NO degradation under visible light irradiation; (b) UV-vis diffuse reflectance spectra; (c) EPR profile of SrTiO₃ obtained in the dark and under visible light irradiation for 15 min; (d) density of states (DOS) of perfect SrTiO₃ and O-deficient SrTiO₃ with the Fermi level set to 0 eV.

Fig. 5. ESR profiles of DMPO-OH (a), DMPO-O₂⁻ (b), TEMP-O₂⁻ (c), and e⁻ (d) recorded under visible light irradiation.

Notably, the peak of NO₂ on STB was barely detected (Fig. 6(b)). The normalized evolution of species (Fig. 6(c)) implies that the amount of NO₂ on STB is kept at a low level. In addition, the peak at 1565 cm⁻¹ was evidently detected for STB under visible light irradiation, which can be assigned to NO₃⁻ [56]. Similarly, the final product NO₂⁻ (1366 cm⁻¹) was monitored on the STB. However, the peaks of the final products (i.e., NO₂⁻ and NO₃⁻) cannot be obviously detected on SrTiO₃. Based on these results, it is obvious that NO was smoothly converted into the target products (NO₂⁻ and NO₃⁻) and that NO₂ did not accumulate on STB. On SrTiO₃, NO dominantly transformed to NO₂. Acceleration of the charge separation and transfer process on STB promotes the generation of ROS. Thus, the toxic intermediate NO₂ cannot be further effectively converted into the target products. After a comprehensive comparison of the DRIFTS results of STB and SrTiO₃, it can be concluded that STB can inhibit the generation of toxic intermediates and enhance the

photocatalytic oxidation of NO. Based on these results, it can be summarized that the photocatalytic activity and the inhibition of toxic intermediates are simultaneously reinforced by the covalent interactions occurring at the interface of SrTiO₃ and BiOI, which can be attributed to the enhanced charge separation that increases the generation of ROS. The mechanism proposed in this work is illustrated in the form of a schematic in Fig. 7. The photoexcited electrons of BiOI can migrate to the CB of SrTiO₃ under the driving force of the energy difference between the CBs of BiOI and SrTiO₃. The electrons in the CB of SrTiO₃ can react with the O₂ to produce ·O₂⁻ radicals. The residual holes in the VB of BiOI in the heterojunction react with the OH⁻ to produce ·OH radicals. The SrTiO₃/BiOI heterostructure with matching band gaps can promote charge separation and enhance ROS generation, thus achieving a high photocatalytic activity under visible light irradiation.

Fig. 6. In situ DRIFTS patterns for NO adsorption and reaction: local in situ DRIFTS patterns (a, b) and changes in the normalized absorbances of the species (c) on the surface during the visible-light-driven photocatalytic reaction process (NO₂).

Fig. 7. Schematic diagram of the proposed mechanism that illustrates the band structure configuration and ROS generation under visible light irradiation.

4. Conclusions

SrTiO₃/BiOI heterojunction photocatalysts were designed and fabricated to simultaneously enhance the efficiency of NO purification in air under visible light irradiation and inhibit the generation of toxic intermediates. By combining experimental and theoretical approaches, we revealed the formation of electron delivery channels at the contacting interface of the two counterparts. The electrons photogenerated in the BiOI semiconductor can directly transfer to the SrTiO₃ surface through the preformed electron delivery channel. Therefore, the electron channels can facilitate the generation of ROS, which enhances the overall NO purification efficiency and inhibits the formation of toxic intermediates. This work presents a simple and novel strategy that promotes efficient and safe air purification through photocatalytic technology.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21822601, 21501016, 21777011), the National R&D Program of China (2016YFC02047), the Innovative Research Team of Chongqing (CXTDG201602014), the 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 AM-HPC in Suzhou, China for computational support.

References

- [1] Y. F. Xie, W. H. Yang, Y. Yang, X. L. Cai, J. Zhou, *Acta Ecol. Sin.*, **2007**, 27, 5193–5201.
- [2] D. H. Stedman, F. Stuhl, E. E. Daby, H. Niki, *J. Air Pollu. Control Associ.*, **1972**, 22, 260–263.

Graphical Abstract

Chin. J. Catal., 2020, 41: 710–718 doi: S1872-2067(19)63472-8

SrTiO₃/BiOI heterostructure: Interfacial charge separation, enhanced photocatalytic activity, and reaction mechanism

Ruimin Chen, Hong Wang, Huizhong Wu, Jianping Sheng*, Jieyuan Li, Wen Cui, Fan Dong*

Chongqing Technology and Business University; University of Electronic Science and Technology of China; Sichuan University; Southwest Petroleum University

SrTiO₃/BiOI heterojunction photocatalysts were designed and fabricated to simultaneously enhance the efficiency of NO purification in air under visible light irradiation and inhibit the generation of toxic intermediates.

- [3] D. M. Leahey, M. C. Hansen, *Atmos. Environ. A*, **1990**, 24A, 2533–2540.
- [4] P. F. Gay, M. W. Travers, *Nature*, **1936**, 138, 546–547.
- [5] M. Noris, M. Todeschini, F. Casiraghi, D. Roccatello, G. Martina, L. Minetti, B. Imberti, F. Gaspari, M. Atti, G. Remuzzi, *Am. J. Kidney Dis.*, **1998**, 32, 115–124.
- [6] J. M. Barnes, W. A. Apel, K. B. Barrett, *J. Hazard. Mater.*, **1994**, 41, 315–326.
- [7] F. Dong, Z. Wang, Y. Li, W. K. Ho, S. C. Lee, *Environ. Sci. Technol.*, **2014**, 48, 10345–10353.
- [8] W. Cui, J. Li, Y. Sun, H. Wang, G. Jiang, S. C. Lee, F. Dong, *Appl. Catal. B*, **2018**, 237, 938–946.
- [9] M. Sun, W. Zhang, Y. Sun, Y. Zhang, F. Dong, *Chin. J. Catal.*, **2019**, 40, 826–836.
- [10] M. Green, A. Tran, R. Smedley, A. Roach, J. Murowchick, X. Chen, *Nano Mater. Sci.*, **2019**, 1, 48–59.
- [11] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, *Adv. Mater.*, **2012**, 24, 229–251.
- [12] J. Li, W. Cui, Y. Sun, Y. Chu, W. Cen, F. Dong, *J. Mater. Chem. A*, **2017**, 5, 9358–9364.
- [13] J. Li, X. Dong, G. Zhang, W. Cui, W. Cen, Z. Wu, S. C. Lee, F. Dong, *J. Mater. Chem. A*, **2019**, 7, 3366–3374.
- [14] G. Williams, B. Seger, P. V. Kamat, *ACS Nano*, **2008**, 2, 1487–1491.
- [15] H. Wang, W. He, X. Dong, H. Wang, F. Dong, *Sci. Bull.*, **2018**, 63, 117–125.
- [16] R. Shen, J. Xie, Q. Xiang, X. Chen, J. Jiang, X. Li, *Chin. J. Catal.*, **2019**, 40, 240–288.
- [17] S. Luan, D. Qu, L. An, W. Jiang, X. Gao, S. Hua, X. Miao, Y. Wen, Z. Sun, *Sci. Bull.*, **2018**, 63, 683–690.
- [18] M. Chen, Y. Huang, S. C. Li, *Chin. J. Catal.*, **2017**, 38, 348–356.
- [19] Z. Zhang, W. Wang, L. Wang, S. Sun, *ACS Appl. Mater. Interfaces*, **2012**, 4, 593–597.
- [20] P. Lu, F. Wu, N. Deng, *Appl. Catal. B*, **2004**, 53, 87–93.
- [21] K. Yang, X. Li, C. Yu, D. Zeng, F. Chen, K. Zhang, W. Huang, *Chin. J. Catal.*, **2019**, 40, 796–818.
- [22] I. Papailias, N. Todorova, T. Giannakopoulou, S. Karapati, N. Boukos, D. Dimotikali, C. Trapalis, *Appl. Surf. Sci.*, **2018**, 430, 225–233.
- [23] Y. Xia, Z. He, K. Hu, B. Tang, J. Su, Y. Liu, X. Li, *J. Alloys Compd.*, **2018**, 753, 356–363.
- [24] H. Wang, Y. Sun, W. He, Y. Zhou, S. C. Lee, F. Dong, *Nanoscale*, **2018**, 10, 15513–15520.
- [25] K. M. Macounova, R. Nebel, M. Klusáčková, M. Klementova, P. Krtil, *ACS Appl. Mater. Interfaces*, **2019**, 11, 16506–16516.
- [26] A. Viernstein, M. Kubicek, M. Morgenbesser, G. Walch, G. C. Brunauer, J. Fleig, *Adv. Funct. Mater.*, **2019**, 29, 1900196.
- [27] X. Y. Lai, C. R. Wang, Q. Jin, B. R. Yu, D. Wang, *Sci. China Mater.*, **2015**, 58, 192–197.
- [28] I. Papailias, N. Todorova, T. Giannakopoulou, S. Karapati, N. Boukos, D. Dimotikali, C. Trapalis, *Appl. Surf. Sci.*, **2018**, 430, 225–233.
- [29] R. Sugrañez, J. I. Álvarez, M. Cruz-Yusta, I. Mármol, J. Morales, J. Vila, L. Sánchez, *Build. Environ.*, **2013**, 69, 55–63.
- [30] Z. Zhao, Y. Cao, F. Dong, F. Wu, B. Li, Q. Zhang, Y. Zhou, *Nanoscale*, **2019**, 11, 6360–6367.
- [31] J. Chen, J. Zhan, Y. Zhang, Y. Tang, *Chin. Chem. Lett.*, **2019**, 30, 735–738.
- [32] X. Li, J. Yu, M. Jaroniec, X. Chen, *Chem Rev*, **2019**, 119, 3962–4179.
- [33] X. Li, J. Xie, C. Jiang, J. Yu, P. Zhang, *Front. Environ. Sci. Eng.*, **2018**, 12, 14–1–14–32.
- [34] Y. Sun, J. Liao, F. Dong, S. Wu, L. Sun, *Chin. J. Catal.*, **2019**, 40, 362–370.
- [35] S. Liu, M. Zhao, Z. He, Y. Zhong, H. Ding, D. Chen, *Chin. J. Catal.*, **2019**, 40, 446–457.
- [36] C. Hu, H. X. Huang, Y. F. Lin, M. Yoshida, T. H. Chen, *J. Taiwan Inst. Chem. Eng.*, **2019**, 96, 264–272.
- [37] Y. Li, X. Wu, W. Ho, K. Lv, Q. Li, M. Li, S. C. Lee, *Chem. Eng. J.*, **2018**, 336, 200–210.
- [38] J. Li, Z. Zhang, W. Cui, H. Wang, W. Cen, G. Johnson, G. Jiang, S. Zhang, F. Dong, *ACS Catal.*, **2018**, 8, 8376–8385.
- [39] J. Li, R. Chen, W. Cen, P. Yan, K. Li, P. Wang, S. Shu, Y. Chu, F. Dong, *Chem. Eng. J.*, **2019**, 375.
- [40] X. J. Wen, C. G. Niu, L. Zhang, C. Liang, G. M. Zeng, *J. Catal.*, **2017**, 356, 283–299.
- [41] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **1996**, 54, 11169–11186.
- [42] J. P. Perdew, K. Burkner, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77, 3865–3868.
- [43] P. E. Blöchl, *Phys. Rev. B*, **1994**, 50, 17953–17979.
- [44] G. Kresse, J. Furthmüller, *Comp. Mater. Sci.*, **1996**, 6, 15–50.
- [45] G. Kresse, D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758–1775.
- [46] S. K. Bhatia, A. L. Myers, *Langmuir*, **2006**, 22, 1688–1700.
- [47] N. Liang, M. Wang, L. Jin, S. Huang, W. Chen, M. Xu, Q. He, J. Zai, N. Fang, X. Qian, *ACS Appl. Mater. Interfaces*, **2014**, 6, 11698–11705.
- [48] H. Cheng, B. Huang, Y. Dai, X. Qin, X. Zhang, *Langmuir*, **2010**, 26, 6618–6624.
- [49] X. Zhang, L. Zhang, T. Xie, D. Wang, *J. Phys. Chem. C*, **2009**, 113, 7371–7378.
- [50] J. Li, X. A. Dong, Y. Sun, G. Jiang, Y. Chu, S. C. Lee, F. Dong, *Appl. Catal. B*, **2018**, 239, 187–195.
- [51] S. Bai, N. Zhang, C. Gao, Y. Xiong, *Nano Energy*, **2018**, 53, 296–336.
- [52] Y. Sun, H. Wang, Q. Xing, W. Cui, J. Li, S. Wu, L. Sun, *Chin. J. Catal.*, **2019**, 40, 647–655.
- [53] X. Ding, W. Ho, J. Shang, L. Zhang, *Appl. Catal. B*, **2016**, 182, 316–325.
- [54] G. Ramis, G. Busca, F. Bregani, P. Forzatti, *Appl. Catal.*, **1990**, 64, 259–278.
- [55] K. I. Hadjiivanov, *Catal. Rev. Sci. Eng.*, **2000**, 42, 71–144.
- [56] J. Laane, J. R. Ohlsen, *Prog. Inorg. Chem.*, **1980**, 27, 465–513.

SrTiO₃/BiOI异质结构:界面电荷分离、增强光催化活性和反应机理

陈瑞敏^a, 王 红^a, 武慧中^a, 盛剑平^{b,*}, 李解元^{b,c}, 崔 雯^{b,d}, 董 帆^{a,b,#}

^a重庆工商大学环境与资源学院, 重庆市催化与新环境材料重点实验室, 重庆400067

^b电子科技大学基础与前沿科学研究院环境科学研究中心, 四川成都611731

^c四川大学建筑与环境学院, 四川成都610065

^d西南石油大学材料科学与工程学院, 新能源材料与技术中心, 四川成都610500

摘要: 异质结构光催化剂为实现高效的电荷分离, 提高光催化性能提供了一种有效的途径。虽然宽禁带和窄禁带光催化剂

已经得到了广泛的研究,但它们在接触界面上的电荷分离和转移规律尚未完全揭示.本文采用简便的方法成功地制备了一种新型 $\text{SrTiO}_3/\text{BiOI}$ (STB)异质结构光催化剂.该光催化剂中的异质结构可以将光吸收扩展到可见光范围,从而在可见光照射下获得较高的光催化NO去除性能.实验和理论证据表明,BiOI光生电子可以通过预成型的电子传递通道直接转移到 SrTiO_3 表面.

XRD和XPS结果表明, $\text{SrTiO}_3/\text{BiOI}$ 复合材料已成功制备.SEM和TEM图像显示了 SrTiO_3 、BiOI和STB样品的形貌.能量色散X射线(EDX)元素图清楚地表明 SrTiO_3 均匀分布在BiOI纳米片表面,证实BiOI与 SrTiO_3 形成了界面.高分辨率XPS表明,电子从BiOI中Bi和I原子转移到STB化合物中 SrTiO_3 的Sr和Ti原子.采用DFT进一步确定了BiOI与 SrTiO_3 相互作用的机制.电子局域函数(ELF)表明,STB的接触界面存在共价相互作用. SrTiO_3 和BiOI之间生成的共价键导致局域化超额电子(e^-_{ex})的积累.在可见光照射下,界面内的电子交换增强,从而提高反应物活化和ROS生成的效率.

采用自制的连续流反应体系,研究了在可见光照射下制备的样品对NO去除的光催化性能.与 SrTiO_3 和BiOI相比,STB具有显著增强的可见光光催化活性,去除率为59.0%.UV-vis DRS显示,STB异质结的光吸收扩展到可见光范围. SrTiO_3 具有可见光活性,这归因于EPR所描述的氧空位的存在.随后计算态密度(DOS),发现氧空位可以形成缺陷能级,降低激发电子所需的光能.利用ESR光谱发现,STB上的ESR信号强度都要强得多,说明STB异质结具有较好的氧化能力,也说明光生载流子可以通过电子传递通道被有效地分离.原位红外光谱表明,在 SrTiO_3 上,NO主要转化为 NO_2 .STB的加速电荷分离和转移特性,促进活性氧的生成,从而进一步有效地将有毒中间体 NO_2 转化为目标产物.

设计并制备的 $\text{SrTiO}_3/\text{BiOI}$ 异质结光催化剂在可见光辐照下净化空气中NO的效率提高,同时抑制了有毒中间体的生成.通过实验和理论相结合的方法揭示了在两种材料的接触界面上建立电子传递通道.来自BiOI的光生电子可以通过预先形成的电子传递通道直接转移到 SrTiO_3 表面,从而促进了ROS的生成,所以整体的NO净化效率和对有毒中间体的抑制作用提高.综上,本文提出了一种简单、新颖的促进空气污染物高效安全净化的策略.

关键词: 异质结构; $\text{SrTiO}_3/\text{BiOI}$; 电荷分离; 光催化; 反应机理

收稿日期: 2019-09-10. 接受日期: 2019-10-12. 出版日期: 2020-04-05.

*通讯联系人. 电子信箱: jpschengchn@163.com

#通讯联系人. 电子信箱: dfctbu@126.com

基金来源: 国家自然科学基金(21822601, 21501016, 21777011); 国家重点研发计划(2016YFC02047); 重庆市创新团队项目(CXTDG201602014); 重庆市自然科学基金(cstc2017jcyjBX0052).

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>).