Experimental Study on the Photocatalytic Reduction of CO₂ by Fe₂O₃/BiOIO₃ Composite Photocatalyst

Jianshu Zou, Jiang Wu*

College of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, China

*Corresponding Author: E-mail Address: wujiang@shiep.edu.cn

Mobile: +86-13761615154

Abstract. Photocatalytic reduction of CO₂ to produce renewable hydrocarbon fuels is of great significance for solving the greenhouse effect and energy crisis. However, due to some shortcomings of the photocatalyst itself, further research is needed to realize its industrial application. In this article, we prepared Fe₂O₃/BiOIO₃ composite photocatalyst by a simple one-step hydrothermal method, and discussed the photocatalytic activity and reaction mechanism of Fe₂O₃/BiOIO₃ composite photocatalyst through a series of characterization and photocatalytic reduction experiments. The band gap energy of the composite photocatalyst (2.32 ev) is smaller than that of pure BiOIO₃ (2.98 ev), so the composite photocatalyst can absorb visible light. Since the edge of the conduction band of BiOIO₃ is more positive than the edge of the Fe₂O₃ conduction band, the photogenerated electrons in the Fe₂O₃ conduction band can be transferred to the BiOIO₃ conduction band, which makes BiOIO₃ more reducible and can reduce CO₂ to CO. This study can provide some reference for the field of photocatalytic reduction of carbon dioxide.

1. Introduction

With the rapid development of human society, the demand for energy is increasing, which makes the excessive use of fossil fuels, which causes a large amount of greenhouse gases to be discharged into the air\(^{[1,2]}\). Carbon dioxide accounts for about half of the total greenhouse effect. Therefore, effective and innovative means are needed to keep the global net CO₂ emissions within an acceptable range. Among the semiconductors that have been studied for photocatalytic reduction of CO₂, BiOIO₃ has good product selectivity and photocatalytic activity\(^{[3]}\). Nevertheless, pure BiOIO₃ as a photocatalyst also has some limitations. For example, pure BiOIO₃ has a wide band gap width and a small specific surface area. In order to overcome these shortcomings, researchers often use the method of preparing composite photocatalysts to regulate and control BiOIO₃\(^{[4,5]}\). For example, Zeng et al. prepared Fe₂O₃/BiOIO₃ composite photocatalyst. In this study, the band gap energy of pure BiOIO₃ is 3.0 ev, and the band gap energy of the composite photocatalyst is 1.81 ev, which indicates that the photocatalytic activity of the composite photocatalyst is stronger than that of BiOIO₃\(^{[6]}\). Guan et al. successfully prepared BiOIO₃/γ-C₃N₄/MoS₂ ternary composite photocatalyst. In this study, due to the in-situ electronic channel, the internal electric field was formed through the corresponding band gap engineering to improve the photocatalytic reaction\(^{[7]}\). Huang Hedong reported a new type of dual nonlinear optical material BiOIO₃, the research is that the layered structure of BiOIO₃ leads to the formation of an internal automatic electric field, which enhances the charge separation efficiency\(^{[8,9]}\).
Due to the small size of Fe$_2$O$_3$ particles, the surface area occupies a large volume percentage, the bonding and electronic states of the surface are different from the inside of the particles, and the coordination of surface atoms is different, which leads to an increase in active sites on the surface. And the band gap energy of Fe$_2$O$_3$ (2.2 ev) is small, which can be activated under visible light.

Therefore, in this paper, Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst was prepared by a simple one-step hydrothermal method. A series of characterizations were used to analyze the microscopic morphology, band structure and optical properties of the composite photocatalyst. And the composite photocatalyst was used in the experimental study of photocatalytic reduction of CO$_2$, and the photocatalytic activity and reaction mechanism of the composite photocatalyst were discussed.

2. Preparation of sample
BiOIO$_3$ was prepared by hydrothermal method, and the hydrothermal condition is hydrothermal at 160°C for 10 h. A certain amount of iron oxide was added to deionized water and stirred for 30 minutes. After being fully dissolved, BiOIO$_3$ with different mass ratios was added, and stirring was continued for 30 minutes. Then the mixed solution was placed in a stainless steel high-pressure hydrothermal reactor lined with 100 Teflon and heated at 160°C for 10 hours. Finally, the obtained sample was washed three times with deionized water and ethanol, and then the above sample was placed in a drying box at 80°C for 12 h and ground into powder. The mass ratios of Fe$_2$O$_3$ and BiOIO$_3$ in the prepared catalyst were 1, 0.1 and 0.05, respectively, named FB-1, FB-0.1 and FB-0.05, respectively.

3. Results and discussion
The detailed crystal structure of the pure BiOIO$_3$ and Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst (FB-X, X = 1, 0.1, 0.05) sample was studied by XRD technology. The results are shown in Figure. 1. The diffraction peaks of pure BiOIO$_3$ are consistent with the diffraction peak data of orthorhombic BiOIO$_3$ crystals (ICSD # 262019) [10]. All patterns of the samples show sharp diffraction peaks, indicating that all samples are highly crystalline [11]. With the increase of Fe$_2$O$_3$, the intensity of the (121) peak first decreases and then increases. When the sample is FB-0.05, the diffraction peak intensity is the weakest. The results show that an appropriate amount of iron oxide will affect the crystallinity.

![XRD pattern of BiOIO$_3$ and Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst](image)

Figure. 1. XRD pattern of BiOIO$_3$ and Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst

Figure. 2a shows the microstructure of the sample FB-0.1 observed by TEM, indicating that most of the sample exhibits a flaky structure, and a small amount exhibits a striped structure. Figure. 2b shows the lattice fringes of the sample FB-0.1. Two kinds of lattice fringes are analyzed in Figure. 2b. The lattice fringe spacing in the upper part of the figure is 0.368 nm, and the corresponding crystal plane is the (017) crystal plane of Fe$_2$O$_3$ [12]. The lattice fringe spacing in the lower left corner of
Figure 2b is 0.289 nm, and the corresponding crystal plane is the (002) crystal plane of BiOIO$_3$ [13]. Figure 2c-f is the element map, showing the spatial distribution of atoms, corresponding to Figure 2a, the analysis shows that Fe$_2$O$_3$ and BiOIO$_3$ form a heterojunction.

Figure 3a shows the UV visible diffuse reflectance spectra (UV-vis DRS) of the sample BiOIO$_3$ and Fe$_2$O$_3$/BiOIO$_3$. The prepared samples shows strong absorption between 200-400 nm, and as the concentration of Fe$_2$O$_3$ increases, the absorption of Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst in the visible light region gradually increases. The sample FB-1 shows a stronger absorption between 300nm-400nm than BiOIO$_3$. The results show that the combination of Fe$_2$O$_3$ and BiOIO$_3$ can enhance the photoresponse ability of BiOIO$_3$. Since the recombination of Fe$_2$O$_3$ and BiOIO$_3$ will cause energy band transition, the introduction of a certain amount of Fe$_2$O$_3$ will increase the light response range of the sample. The optical band gap energy is estimated as formulas (1) and (2):

$$E_g = \frac{1240}{\lambda_{\text{Absorp. Edge}}} \quad (1)$$

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (2)$$

In the equation, the value of n is 4, which depends on the characteristics of the indirect optical transition in BiOIO$_3$ [14]. Then, by intersecting the tangent to the inflection point of the curve with the photon energy axis, the $E_g$ value of the sample can be determined from the graph of $(\alpha h\nu)^{1/2}$ vs. $h\nu$. Then, by stretching the linear part of the curve, the $E_g$ value of the sample can be fixed according to vs. As shown in Figure 3b, the $E_g$ values of BiOIO$_3$ and Fe$_2$O$_3$ are 2.98 eV and 1.8 eV, respectively. The results show that the band gap energy of the composite material is reduced compared with that of pure BiOIO$_3$, which makes the Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst more photosensitized.

Figure 3 (a) UV-vis DRS spectra of all samples, (b) all samples band gap energy value
4. Analysis of performance and mechanism of photocatalytic reduction of CO₂

4.1. Photocatalytic reduction of CO₂ activity test

In order to study the photocatalytic reduction of CO₂ activity of different samples, the experiment was carried out in a photocatalytic online analysis system. The light source used in the experiment was a 300 W xenon lamp and equipped with a filter with λ > 420 nm to simulate visible light. The product in the experiment was Gas chromatography (GC) for qualitative and quantitative analysis. At the same time, comparative experiments were carried out, 1) the photocatalysis experiment was carried out under the condition of no catalyst; 2) the photocatalysis experiment was carried out in the dark; 3) the photocatalysis experiment was carried out with nitrogen instead of CO₂. No CO product was detected in the above control experiment, indicating that the light source and photocatalyst were not replaceable in the CO₂ photocatalytic reduction process, and the CO product produced was derived from the gaseous CO₂ in the experiment. Figure 4a shows the product yield of the photocatalytic reduction of CO₂ by prepared samples without sacrificial agents. From the figure, we can see that the main products of composite photocatalytic reduction of CO₂ are CO. The composite material FB-0.1 showed the highest CO yield of 5.2 μmol g⁻¹h⁻¹, which was about 1.6 and 9.8 times higher than the CO yields of other materials BiOIO₃ and Fe₂O₃. It is consistent with the results of the analysis of the optical properties of the sample, which proves that the optical properties and electronic structure of the semiconductor affect its photocatalytic activity. In the cyclic test of the photocatalytic reduction of CO₂ with sample FB-0.1, as shown in Figure 4b, the output of the composite material did not decrease significantly under the 6 cyclic tests in 24 hours, which indicates that the photocatalyst is highly stable.

4.2. Analysis of the mechanism of photocatalytic reduction of CO₂

Under visible light irradiation, Fe₂O₃ can be excited to generate electrons and holes in the Fe₂O₃/BiOIO₃ composite material. A heterojunction is formed between Fe₂O₃ and BiOIO₃, which facilitates the separation of photo-generated electrons and holes. Since the edge of the conduction band of BiOIO₃ is more positive than that of Fe₂O₃, the photogenerated electrons in the conduction band of Fe₂O₃ can be transferred to the conduction band of BiOIO₃, which makes BiOIO₃ more reducible and can reduce CO₂ to CO. As shown in Figure 5, as a result, photogenerated electron transfer forms a path from Fe₂O₃ to BiOIO₃ conduction band (Fe₂O₃→BiOIO₃). At the same time, photogenerated electrons react with adsorbed carbon dioxide to produce CO, while holes react with water to produce O₂.
5. Conclusions
In this chapter, a one-step hydrothermal method is used to prepare Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst, and a series of characterizations are used to analyze its phase composition, microscopic morphology and optical properties. The analysis of the phase composition shows that with the increase of Fe$_2$O$_3$ content, the crystallinity of the composite material changes, and the micro morphology of the composite material also changes, which means that the adsorption capacity of the composite material changes. The analysis showed that the Fe$_2$O$_3$/BiOIO$_3$ composite photocatalyst formed a heterojunction after hydrothermal treatment. In the experimental study of visible light photocatalytic reduction of CO$_2$, the composite material FB-0.1 showed the highest carbon monoxide yield of 5.2 $\mu$mol g$^{-1}$h$^{-1}$, which was consistent with the results of the sample's optical characteristics analysis. The transfer of photogenerated electrons effectively enhances the charge separation. In this case, most electrons can be driven to the conduction band of BiOIO$_3$, selectively reducing CO$_2$ light to CO.

References
[1] An C, Feng J, Liu J, et al. NiS nanoparticle decorated MoS$_2$ nanosheets as efficient promoters for enhanced solar H$_2$ evolution over Zn$_x$Cd$_{1-x}$S nanorods[J]. Inorganic Chemistry Frontiers, 2017, 4(6): 1042-1047.
[2] Zhou Y, Xiao H, Zhang S, et al. Interlayer expanded lamellar CoSe$_2$ on carbon paper as highly efficient and stable overall water splitting electrodes[J]. Electrochimica Acta, 2017, 241: 106-115.
[3] Chen F, Huang H, Ye L, et al. Thickness-dependent facet junction control of layered BiOIO$_3$ single crystals for highly efficient CO$_2$ photoreduction[J]. Advanced Functional Materials, 2018, 28(46): 180-284.
[4] Zhang X, Wang D, Man X, et al. Influence of BiOIO$_3$ morphology on the photocatalytic efficiency of Z-scheme BiOIO$_3$/g-C$_3$N$_4$ heterojunctioned composite for Hg$^+$ removal[J]. Journal of colloid and interface science, 2020, 558: 123-136.
[5] Ling Y, Wu J, Man X, et al. BiOIO$_3$/graphene interfacial heterojunction for enhancing gaseous heavy metal removal[J]. Materials Research Bulletin, 2020, 122: 11-20.
[6] Zeng H, Liu X, Wei T, et al. Boosting visible light photo-/Fenton-catalytic synergetic activity of BiOIO$_3$ by coupling with Fe$_2$O$_3$[J]. RSC Advances, 2017, 7(38): 23787-23792.
[7] Guan Y, Wu J, Lin Y, et al. Solvent-exfoliation of transition-metal dichalcogenide MoS$_2$ to provide more active sites for enhancing photocatalytic performance of BiOIO$_3$/g-C$_3$N$_4$ photocatalyst[J]. Applied Surface Science, 2019, 481: 838-851.
[8] Dong F, Xiong T, Sun Y, et al. Controlling interfacial contact and exposed facets for enhancing photocatalysis via 2D–2D heterostructures[J]. Chemical Communications, 2015, 51(39): 8249-8252.
[9] Sun Y, Xiong T, Dong F, et al. Interlayer-I-doped BiOIO$_3$ nanoplates with an optimized electronic structure for efficient visible light photocatalysis[J]. Chemical Communications, 2016, 52(53): 8243-8246.
[10] Nguyen S D, Yeon J, Kim S H, et al. BiO(IO₃): a new polar iodate that exhibits an aurivillius-type (Bi₂O₂)²⁺ layer and a large SHG response [J]. Journal of the American Chemical Society, 2011, 133(32): 12422-12425.

[11] Zhang X, Wang D, Man X, et al. Influence of BiOIO₃ morphology on the photocatalytic efficiency of Z-scheme BiOIO₃/g-C₃N₄ heterojunctioned composite for Hg0 removal [J]. Journal of colloid and interface science, 2020, 558: 123-136.

[12] Jin M, Peng T, Zhang X, et al. Selective methanol production from photocatalytic reduction of CO₂ on BiVO₄ under visible light irradiation [J]. Catalysis Communications, 2012, 28:38-41

[13] Wan Z, Zhang G. Controlled synthesis and visible light photocatalytic activity of Bi12GeO20 uniform microcrystals [J]. Scientific Reports, 2014, 4:6298

[14] Yang Y Y, Zhang X G, Niu C G, et al. Dual-channel charges transfer strategy with synergistic effect of Z-scheme heterojunction and LSPR effect for enhanced quasi-full-spectrum photocatalytic bacterial inactivation: new insight into interfacial charge transfer and molecular oxygen activation [J]. Applied Catalysis B: Environmental, 2020, 264: 118-465.