Synthesis of BiOBr\textsubscript{x}Cl\textsubscript{1-x} by Solvothermal Method and Its Photocatalytic Activity

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Abstract. In order to improve the activity of monohalide ruthenium oxide, different ratios of BiOBr\textsubscript{x}Cl\textsubscript{1-x} series samples (X=0, 0.2, 0.4, 0.6, 0.8, 1) were synthesized by solvothermal method. The synthesized BiOBr\textsubscript{x}Cl\textsubscript{1-x} samples were characterized by X-ray diffraction (XRD), ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS) and scanning electron microscopy(SEM). The photocatalytic degradation experiment for Rhodamine B showed that the BiOBr\textsubscript{0.2}Cl\textsubscript{0.8} sample had higher degradation efficiency under visible light and effectively improved photocatalytic activity.

1. Introduction

Today, environmental pollution and energy shortage have severely constrained the progress and development of human society. In this context, photocatalysis technology came into being and gradually developed. The photocatalytic reaction has relatively low requirements on the reaction conditions, which can be carried out at normal temperature. The removal effect of organic pollutants is good, and it has become a research hotspot at home and abroad.[1-3] However, as a conventional photocatalyst, TiO\textsubscript{2} has a large band gap (3.0-3.2 eV), which only exhibits photocatalytic activity under ultraviolet light which is less than 4% of the solar spectrum. There is no good light response in the visible light region[4-6]. Therefore, how to improve the performance of the conditioning material in the visible region is also very necessary.

In recent years, bismuth halide (BiOX, X = Cl, Br, I) has provided sufficient possibilities for atomic and atomic orbital polarization due to its unique layered crystal structure, promoted separation of photogenerated electrons and holes, and effectively improved photochemical properties[7, 8]. Therefore, as a new type of semiconductor material, BiOX, with its unique layered structure, has become an ideal choice for a new type of photocatalyst. Zhang et al. found that BiOCl had strong photocatalytic degradation of methyl orange in the ultraviolet region[9]. Zhang et al. synthesized 3D BiOBr by solvent thermal method, which had certain degradation properties to methyl orange[10].
However, the single bismuth halide oxide material still has some limitations. For example, BiOCl has a large band gap and only responds to the ultraviolet region, while the photogenerated electrons and holes of BiOBr are easy to compound, resulting in relatively limited applications in the field of photocatalysis. Therefore, trying to build composite materials has become a research hotspot, such as NaBiO$_2$/BiOCl\cite{[11]}, BiOCl/g-C$_3$N$_4$\cite{[12]}, SnS$_2$/BiOBr\cite{[13]}. For example, Li et al. synthesized BiOCl/BiOI semiconductor by hydrothermal method, and the degradation rate for RHB and MO in visible light region was significantly improved\cite{[14]}.

In view of the above two points, the bismuth oxyhalide with obvious hierarchical structure was selected as the research material. The solvothermal method was used to construct the BiOBr$_x$Cl$_{1-x}$ composite material, and the energy band was adjusted to achieve the appropriate band gap. RHB and norfloxacin were used as pollutant models to degrade under visible light. It was found that the degradation rate for RHB and norfloxacin was significantly increased, and the degradation mechanism was discussed.

2. Experimental

2.1 Synthesis of materials

The materials used were analytical grade reagents. BiOBr$_x$Cl$_{1-x}$ is made by solvothermal method. First, 80 ml of ethylene glycol was added to the beaker, and a certain proportion of KBr and KCl (the sum of the two moles was 4 mmol, X represents the ratio of the amount of KBr added) was added to the beaker to completely dissolve, and then 4 mmol Bi(NO$_3$)$_3$•5H$_2$O was added to the beaker to completely dissolve, and the solution was transferred to a 100 ml reaction vessel for solvent heat treatment at 140 °C for 24 h. After naturally cooling to room temperature, the sample was centrifuged and washed with deionized water and absolute ethanol for several times. Finally, the samples were dried overnight at 80 °C.

For comparison, pure BiOCl, BiOBr$_{0.2}$Cl$_{0.8}$, BiOBr$_{0.4}$Cl$_{0.6}$, BiOBr$_{0.6}$Cl$_{0.4}$, BiOBr$_{0.8}$Cl$_{0.2}$, BiOBr samples were prepared by changing the ratio of the amount of KBr added.

2.2 Characterization of materials

X-ray diffraction (XRD, D/MAX-2500/PC; Rigaku Co., Tokyo, Japan) was applied to analyze the crystal structures of prepared BiOBrXC11-X photocatalysts. The morphology of samples were tested by scanning electron microscopy (SEM, JSM-6700F, JEOL, Tokyo, Japan). UV–vis diffuse reflectance spectra (DRS) were collected using UV–Vis diffuse reflectance spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan).

2.3 Photocurrent measurement

Electrochemical workstation, 500W xenon lamp, three-electrode system were used for photoelectrochemical testing. The sample was uniformly suspended on the indium-tin oxide FTO glass as a working electrode, and a three-electrode test was performed (Pt as a counter electrode, saturated Ag / AgCl as a reference electrode), and Na$_2$SO$_4$(0.1 mol L$^{-1}$) was used as an electrolyte solution.

2.4 Photocatalytic assessments

In order to study the photocatalytic activity of the prepared catalyst, RHB was chosen as the representative pollutant. The sample prepared from 20 mg was added to the 10 mg/l RHB of 100 ml, and the dark state was adsorbed for half an hour. The solution was transferred to RHB of 10 ml at 100
ml, and the photocatalytic degradation was carried out until no adsorption effect was achieved. The light intensity of the light source was measured with an optical power meter and adjusted to 300 mW/cm². Through the condensate system, the distance between the light source and the degradation solution is 10 cm, and the temperature is kept at 25 °C. The samples are separated by centrifugation at a certain time interval. The absorbance of the solution is measured at 554 nm, and the concentration is obtained.

3. Results and Discussion

![Figure 1. XRD patterns of BiOBrₓCl₁₋ₓ](image)

To understand the crystal structure of the prepared series of samples, the XRD patterns of the BiOBrₓCl₁₋ₓ series of samples are shown in Figure 1. The prepared BiOCl and BiOBr sample diffraction peaks are coincided with the tetragonal standard cards BiOCl (JCPDS No. 85-0861) and BiOBr (JCPDS No. 73-2060), respectively, which confirms the preparation of relatively pure phase BiOCl and BiOBr samples. The XRD patterns of the other different ratios of BiOBrₓCl₁₋ₓ show that as the ratio of Br increases, the two diffraction peaks corresponding to the (110) and (102) crystal planes of BiOCl gradually weaken, and the (102) peak corresponding to BiOBr gradually appears, while the intensity of the diffraction peak corresponding to the (101) crystal plane of BiOCl is gradually weakened as the Br ratio increases. These results indicate that BiOBrₓCl₁₋ₓ may exhibit a good hybrid state.

![Figure 2. SEM images of (a) BiOCl, (b) BiOBr₀.₂Cl₀.₈, (c) BiOBr₀.₄Cl₀.₆, (d) BiOBr₀.₆Cl₀.₄, (e) BiOBr₀.₈Cl₀.₂, (f) BiOBr](image)
In order to study the topography of the sample, a SEM test was performed as shown in Figure 2. Figure 2a, b, c, d, e, and f correspond to SEM images of BiOCl, BiOBr0.2Cl0.8, BiOBr0.4Cl0.6, BiOBr0.6Cl0.4, BiOBr0.8Cl0.2, and BiOBr samples, respectively. From Figure 2a, we can see that the single-phase BiOCl exhibits a relatively regular microsphere-like structure with a particle size of about 1-2 μm. The single-phase BiOBr in Figure 2f also exhibits irregular microspheres, and the agglomeration phenomenon is more serious. Observing the b-e diagram, it is found that as the proportion of Br increases, the morphology of the material itself is not greatly affected. The samples are composed of different slices and have a regular composition of the chestnut-shaped particles, and the particle size is also about 1-2 μm.

![Figure 2: SEM images of BiOCl and BiOBr samples](image)

**Figure 3.** (a) UV-vis diffuse reflection spectra of BiOBrXCl1-X and (b) plot of (Ahv)1/2 vs the band gap (eV) for BiOCl, BiOBr, BiOBr0.2Cl0.8

The energy band structure of the sample is one of the key factors determining the photocatalytic performance of the sample. Figure 3 shows the UV-DRS results of the series samples. The absorption threshold of BiOCl is about 360 nm, and that of BiOBr is about 440 nm. The absorption thresholds of the other different ratios are between the above two values. The absorption threshold of BiOBr0.2Cl0.8 is about 390 nm, which is redshifted compared with that of BiOCl, and the absorption range is widened. The band gap of the sample can be obtained by Kubelka–Munk equation[15]. As shown in Figure 3b, the band gaps of BiOCl, BiOBr and BiOBr0.2Cl0.8 samples are 3.25 eV, 2.7 eV, and 3.1 eV, respectively.

![Figure 3: UV-vis diffuse reflection spectra and band gap for BiOCl, BiOBr, and BiOBr0.2Cl0.8](image)

**Figure 4 (a) kinetics of photocatalytic degradation of RHB and (b) visible light curves of NOR over BiOBr0.2Cl0.8**
In order to study the photocatalytic activity of the sample, we chose RHB as a simulated pollutant to degrade under visible light. Figure 4 shows the degradation results of the series samples for 10 mg/L RHB solution under visible light. When the degradation efficiency of RHB solution is above 95%, the time required for BiOBr and BiOCl is 60 min and 45 min, respectively. While for BiOBr$_{0.2}$Cl$_{0.8}$, it only takes 30 minutes. However, with the further increase of Br content, the degradation rate is gradually slowed down, and the degradation rate of BiOBr$_{0.8}$Cl$_{0.2}$ is the slowest. The photocatalytic degradation rate of BiOBr$_{0.2}$Cl$_{0.8}$ composite was the fastest in the prepared BiOBr$_X$Cl$_{1-X}$ series samples. In order to study whether the material has photocatalytic degradation rate for other pollutants, we chose norfloxacin as another simulated pollutant for degradation experiments and the results are shown in Figure 4b. NOR has two absorption peaks at 278 and 330 nm. As shown in Figure 4b BiOBr$_{0.2}$Cl$_{0.8}$ composites also have strong adsorption and degradation properties for NOR.

![Figure 5](image)

**Figure 5** (a) Electrochemical impedance (EIS) spectra of BiOCl, BiOBr$_{0.2}$Cl$_{0.8}$, BiOBr,
(b) Photoinduced current-time (i-t) curves of BiOCl, BiOBr$_{0.2}$Cl$_{0.8}$, BiOBr

In order to study the degradation mechanism, we carried out photoelectrochemical tests. Figure 5 shows the EIS and it curves of the samples. Figure 5a is the EIS diagram of the series samples. It is well known that the arc radius of the curve reflects the speed of electron transport. The smaller of the arc radius is, the faster the electron transport speed is. It can be clearly observed that the arc radius of BiOBr$_{0.2}$Cl$_{0.8}$ is significantly smaller than that of BiOI and BiOBr, which proves that the BiOBr$_{0.2}$Cl$_{0.8}$ has a good electron transport rate. The i-t curve is a test method used to characterize the separation efficiency of photogenerated electrons and holes. Figure 5b is the i-t diagram of the sample. The photocurrent density of BiOBr$_{0.2}$Cl$_{0.8}$ is slightly higher than that of BiOBr and BiOCl. The enhancement of photocurrent density indicates that the separation of photogenerated electrons and holes was improved and its transfer efficiency was improved, which was consistent with the results obtained by EIS. Therefore, the higher degradation performance of BiOBr$_{0.2}$Cl$_{0.8}$ material may be attributed to the formation of heterojunction structure, which increases the photogenerated electron-hole transfer pathway, and thus inhibits the recombination of the photogenerated electrons and holes. Therefore, BiOBr$_{0.2}$Cl$_{0.8}$ shows better degradation performance.

4. Conclusion

BiOBr$_X$Cl$_{1-X}$ series materials were prepared by solvothermal method using Bi(NO$_3$)$_3$·5H$_2$O, KBr and KCl as raw materials. The structure is composed of chestnut-shaped microspheres with regular
composition of different slices. The particle size is approximately 1 - 2μm. The material can degrade RHB and norfloxacin under visible light. It was found that BiOBr$_{0.2}$Cl$_{0.8}$ has high adsorption and degradation ability. Photoelectrochemical test shows that BiOBr$_{0.2}$Cl$_{0.8}$ has smaller impedance and higher photocurrent. The recombination of photogenerated electrons and holes are suppressed, thereby greatly improving its photocatalytic degradation ability.

References

[1] Zou JP, Wu DD, Luo J, Xing QJ, Luo XB, Dong WH, et al. A Strategy for One-Pot Conversion of Organic Pollutants into Useful Hydrocarbons through Coupling Photodegradation of MB with Photoreduction of CO2. Acs Catalysis. 2016;6(10):6861-7.

[2] Yan W, Shi Z, Fan C, Wang X, Hao X, Chi Y. ChemInform Abstract: Synthesis, Characterization, and Photocatalytic Properties of BiOBr Catalyst. Cheminform. 2013;199(19):224-9.

[3] Jing T, Chen Z, Deng X, Quan S, Sun Z, Li W. Improving Visible Light Driving degradation of norfloxacin over core-shell hierarchical BiOCl microspherical Photocatalyst by Synergistic Effect of Oxygen Vacancy and Nanostructure. Applied Surface Science. 2018;453:373-82.

[4] Michal R, Dworniczek E, Caplovicova M, Monfort O, Lianos P, Caplovic L, et al. Photocatalytic properties and selective antimicrobial activity of TiO 2 (Eu)/CuO nanocomposite. Applied Surface Science. 2016;371:538-46.

[5] Gou Y, Chen D, Zhixing SU. Photocatalyst of nanometer TiO2/conjugated polymer complex employed for depigmentation of methyl orange. Applied Catalysis A General. 2004;261(1):15-8.

[6] Ohno T. Preparation of visible light active S-doped TiO2 photocatalysts and their photocatalytic activities. Water Science & Technology. 2004;265(1):115-21.

[7] Jing C, Zhou C, Lin H, Xu B, Chen S. Surface modification of m -BiVO 4 with wide band-gap semiconductor BiOCl to largely improve the visible light induced photocatalytic activity. Applied Surface Science. 2013;284(11):263-9.

[8] Yang W, Bo MA, Wang W, Wen Y, Zeng D, Shan B. Enhanced photosensitized activity of a BiOCl—Bi2WO6 heterojunction by effective interfacial charge transfer. Physical Chemistry Chemical Physics Pccp. 2013;15(44):19387-94.

[9] Zhang KL, Liu CM, Huang FQ, Zheng C, Wang WD. Study of the electronic structure and photocatalytic activity of the BiOCl photocatalyst. Applied Catalysis B Environmental. 2006;68(3):125-9.

[10] Zhang J, Shi F, Lin J, Chen D, Gao J, Huang Z, et al. Self-Assembled 3-D Architectures of BiOBr as a Visible Light-Driven Photocatalyst. Chemistry of Materials. 2010;39(30):no-no.

[11] Chang X, Yu G, Huang J, Li Z, Zhu S, Yu P. Enhancement of photocatalytic activity over NaBiO3/BiOCl composite prepared by an in situ formation strategy. Catalysis Today. 2010;153(3):193-9.

[12] Bai Y, Wang PQ, Liu JY, Liu XJ. Enhanced photocatalytic performance of direct Z-scheme BiOCl-g-C3N4 photocatalysts. Rsc Advances. 2014;4(37):19456-61.

[13] Qiu F, Li W, Wang F, Li H, Liu X, Sun J. In-situ synthesis of novel Z-scheme SnS 2 /BiOBr photocatalysts with superior photocatalytic efficiency under visible light. Journal of Colloid & Interface Science. 2017;493:1-9.

[14] Li TB, Chen G, Zhou C, Shen ZY, Jin RC, Sun JX. New photocatalyst BiOCl/BiOI composites with highly enhanced visible light photocatalytic performances. Dalton Trans.
2011;40(25):6751-8.

[15] Tandon SP, Gupta JP. Measurement of Forbidden Energy Gap of Semiconductors by Diffuse Reflectance Technique. Physica Status Solidi. 2010;38(1):363-7.