Synthesis, characterization and photocatalytic properties of BiOBr/amidoxime fiber composites

Ting-Xian Tao *, Jun-Sen Dai, Ren-Chun Yang, Jia-Bin Xu, Wei Chu, Zhi-Chuan Wu

School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu 241000, China

A R T I C L E   I N F O

Article history:
Received 27 January 2015
Received in revised form
29 May 2015
Accepted 14 June 2015
Available online 15 July 2015

Keywords:
BiOBr/fiber
Recycling performance
Coordination interactions

A B S T R A C T

BiOBr/amidoxime fiber composite photocatalysts have been successfully prepared via ions chelating on fibers. The structure and composition of the products were characterized by XRD, EDS, SEM, FT-IR, XPS and TG. The results indicated that BiOBr was successfully immobilized on the modified commercial fibers. Photocatalytic testing showed that the BiOBr/amidoxime fiber composites exhibited an excellent recycling performance owing to the coordination interactions between BiOBr and amidoxime fiber.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Over the past decade, semiconductor materials have attracted considerable attention owing to their intriguing potential for diverse applications, such as environmental and energy issues [1,2]. The photocatalytic degradation of toxic organic pollutants is expected as an important approach to solve environmental problems [3–6]. It is reported that the performance of these materials are closely related to their microstructures, particularly for their composition [7], size [8], and morphology [9], etc. Thus, much effort has been devoted to design the microstructures, especially for their compositions.

Recently, studies indicate that bismuth oxyhalides (BiOX, X=Cl, Br, and I), as a new type of semiconductor materials, have aroused great attention owing to their especial chemical and physical structure and potential photocatalysis applications [10–15]. Among those BiOx catalysts, BiOBr is of great research interest owing to its outstanding active and stability [16–22]. Although BiOBr shows relatively high stability, the application of them is limited due to its relatively poor regeneration performance. To solve the above mentioned problem, much effort was explored to immobilize the active component via the loading method. However, most of the immobilizations are a physical adsorption process. Thus, relative poor regeneration still existed. Motived by above mentioned question, it should be interesting to explore a more effective way to immobilize the active component. Here, a facile and low cost synthesis method was explored to immobilize BiOBr on fiber via ions chelating. The structure and composition of the products were investigated in detail. Moreover, the photocatalytic activity and the stability of the prepared catalysts were also tested for the degradation of RhB.

2. Experimental

2.1. Preparation of BioBr/amidoxime fiber

Polyacrylonitrile (PAN) fibers are obtained from commercial resource. All the reagents were purchased from Shanghai Chemical Company and used without further purification. In a typical process, the PAN fibers (1 g) were
first immersed in NH₂OH aqueous solution (200 mL, 1 mol/L) at 65 °C for 1.5 h and named AOCF [23]. After that, the AOCF were filtrated off and then washed with distilled water for several times. Subsequently, 1 mmol Bi(NO₃)₃·5H₂O were dissolved in 30 mL of ethylene glycol under magnetic stirring for 30 min, followed by the addition of 0.1 g AOCF fibers and 0.5 g CTAB (Br source). After stirring for 15 min, the mixture was then transferred to a 50 mL Teflon-lined stainless autoclave. The autoclave was allowed to be heated at 100 °C for 24 h under autogenous pressure, and then cooled down to room temperature. The product was collected, washed with deionized water and absolute ethanol and then dried in a vacuum at 60 °C for 8 h and named BiOBr/AOCF.

2.2. Structural characterizations

The samples were characterized by X-ray powder diffraction (XRD) with a Bruker AXS-D8 X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å), recorded with 2θ ranging from 10° to 80°. SEM images and EDS of the samples were obtained on field-emission scanning electron microscope (Hitachi S-4800). IR spectra were recorded on an Alpha-Centuart FT-IR spectrometer. X-ray photoelectron spectrum was recorded on a Thermo ESCALAB 250 XPS operating at the Al Kα radiation of 1486.6 eV, and all binding energy were referenced to the neutral C 1s peak at 284.6 eV. Thermal gravimetric (TG) was carried out on a NETZSCH STA 449C thermoanalyzer in air atmosphere. The samples are heated with temperature increasing rate of 10 °C/min.

2.3. Catalytic testing

The photocatalytic degradation of RhB was investigated by a BL-GHX-V photochemical reactor (Bilang Co., Shanghai, China) equipped with a 500 W high-pressure mercury lamp. The system was cooled by circulating water and kept at room temperature. In a typical experiment, 0.15 g of BiOBr/AOCF photocatalyst was dispersed into a quartz cuvette containing 150 mL of RhB aqueous solution (0.02 g/L) under air at room temperature. The solution was continuously stirred for 60 min in the dark before the light was turned on to ensure the establishment of an adsorption–desorption equilibrium. During irradiation, ~5 mL of the suspension was continually collected from the cuvette at the intervals of given time. The RhB concentration was investigated through a UV–vis spectrophotometer (YUAN XI, UV-5500) by checking the absorbance at 553 nm. The trapping experiments of active species were carried out by separately adding 0.5 ml isopropanol (IPA), 0.5 mmol p-benzoquinone (p-BQ) and 0.5 mmol ammonium oxalate ((NH₄)₂C₂O₄) into 50 ml RhB solutions with 50 mg BiOBr/AOCF composites photocatalyst, respectively. The experimental conditions were similar as the former photocatalytic activity tests. In addition, after the photocatalytic tests, the reproducibility of the catalyst was also studied only by washing and drying the catalyst for next cycle.

3. Results and discussion

The textural analysis about the phase, composition and superficial area of the samples were examined by XRD, EDS and N₂ adsorption–desorption. Fig. 1a shows the XRD patterns of the BiOBr/AOCF, pure BiOBr and AOCF. As can be seen, for the BiOBr/AOCF sample, only one relative weak peak can be found at 2θ = 18°, corresponding to amidoamide fiber. For the BiOBr sample, from the JCPDS Card 73-2061, one can easily find the sample can be indexed to a tetragonal phase of BiOBr. For the BiOBr/AOCF, not only the BiOBr diffraction peaks but also the amidoamide fiber diffraction peaks were all presented on the XRD pattern. Moreover, the very distinct phenomenon is that the peak intensity of the amidoamide fiber in the AOCF sample is higher than that of the BiOBr/AOCF sample. Such result should be due to the covering of BiOBr on the surface of the amidoamide fiber, which may promote the chemical combining of the BiOBr and AOCF. To further study the composition, the BiOBr/AOCF sample was analyzed by EDS; result is shown in Fig. 1b. As can be seen, the peaks of Bi, Br and O can be easily found. Besides, the C and N peaks were also presented, corresponding to amidoamide fiber. Such results indicate that the prepared BiOBr/AOCF sample is a typical composite of BiOBr/amidoamide fiber. The textural characteristics of the BiOBr and BiOBr/AOCF samples were studied by the nitrogen adsorption–desorption and shown in Fig. 1c and d. The isotherms of the two samples presented in Fig. 1c can be classified as type IV with an H5 hysteresis loop, indicating that the obtained samples are mesoporous materials.[24,25] From the pore-size distributions of the samples (Fig. 1d), one can find that the pore-sizes of the samples all focused in 5–30 nm. According to analysis, the surface areas of the BiOBr/AOCF and BiOBr samples are 2.9 and 12.3 m² g⁻¹, respectively. The surface area of the sample is relative small, which should be ascribed to the stacking of the particles. Obviously, the surface area of the BiOBr sample is high than that of the BiOBr/AOCF sample.

The morphology of the as-prepared AOCF, BiOBr/AOCF, BiOBr were observed by SEM. As can be seen in Fig. 2a, the amidoamide fibers have relatively smooth surfaces. After the BiOBr nanosheets (Fig. 2d) loading, the surfaces of amidoamide fibers were no longer smooth. As shown in Fig. 2b and c, one can easily find that the amidoamide fibers are decorated with many irregular particles. Such particles should be ascribed to the stacking of the particles. Obviously, the surface area of the BiOBr sample is high than that of the BiOBr/AOCF sample.

The FT-IR spectra of samples were shown in Fig. 3. For the support AOCF, one can find some prominent peaks at 2244, 1455, 1085 and 921 cm⁻¹, corresponding to stretching vibration of nitrile groups (–CN), bending vibration of methylene (–CH₂–), stretching vibration of C–N bonds, stretching vibration of N–O bonds, respectively [26,27]. For the pure BiOBr, a prominent peak at 520 cm⁻¹ can be found which is attributed to Bi–O stretching mode [28]. For the BiOBr/AOCF composites, all the characteristic vibration bonds of AOCF and pure BiOBr were observed. Notably, the peak from Bi–O bond vibration was broadened and the stretching vibration of N–O bonds was shifted to short wavenumber. Moreover, the
The stretching vibration of C–N bonds was also shifted to short wavenumber. Such results indicate that the BiOBr particles were combined successfully with the fiber support by chemical effect. [28]

The XPS spectrum of BiOBr/AOCF composite was shown in Fig. 4. Distinctly, the C, N, O, Br, Bi, O and C elements can be observed in the spectrum (Fig. 4a). As shown in Fig. 4b and Table 1, the values of binding energy of N 1s in AOCF...
were 399.3 and 400.5 eV, consistent with the two different nitrogen atoms of the C—N and N—H for amidoxime groups, respectively [29]; however, these two values were 399.0 and 400.7 eV in BiOBr/AOCF. The binding energies located at 164.1 and 158.8 eV were attributable to the Bi 4f5/2 and Bi 4f7/2 spin–orbital splitting photoelectrons, respectively (Fig. 4c). The splitting between these bands was 5.3 eV, which indicates the normal state of Bi3+ in BiOBr nanoparticles [30]. The peak located at 68.3 eV can be ascribed to Br 3d signal (Fig. 4d). Compared with the binding energy of Bi 4f in BiOBr/AOCF and pure BiOBr, no change can be found in the binding energy of Bi 4f. Fig. 4e shows the O 1s region of the X-ray photoelectron spectra. The sample shows three peaks around at 529.5, 531.5 and 532.5 eV. The characteristic line at 529.5 eV and 531.5 should be attributed to surface lattice oxygen (O_{lat})
species and adsorbed oxygen ($O_{ads}$) species of the BiOBr, respectively, whereas the peak located at 352.5 eV was ascribed to the O species of N–O bond. Fig. 4d shows the C 1s region of the X-ray photoelectron spectra. The sample presents three peaks around at 284.6 eV, 285.9 and 288.2 eV. Clearly, the characteristic line at 284.6 eV should be attributed to adsorbed water. For the BiOBr/AOCF, the weight loss is about 13% from 35 to 650°C, which should be ascribed to the bound-water. For the BiOBr/AOCF, the weight loss of amidoxime fiber was almost 100% when the temperature reached to 650°C, indicating that the fiber was completely decomposed. For the pure BiOBr, the weight loss is about 13% from 35 to 650°C, which should be ascribed to the bound-water. For the BiOBr/AOCF composites, the weight loss is about 73% when the temperature reached to 650°C. Therefore, the value of the mass ratio of BiOBr in BiOBr/AOCF composite was about 31%. Clearly, the BiOBr/AOCF sample is consisted of the two constituents of BiOBr and AOCF, confirming that BiOBr particles were successfully on the surface of the AOCF.

To ascertain the optical property of the samples, the optical experiment was investigated by UV–vis DRS spectroscopy. As shown in Fig. 6a, the peaks of BiOBr and AOCF samples present very distinct absorption around 200–380 nm. It is almost no response at visible light region for them. However, the BiOBr/AOCF sample exhibits absorption from 200 to 650 nm. Distinctly, the optical absorption of the BiOBr/AOCF sample is stronger than that of the pure BiOBr and AOCF sample at the visible light region. Such phenomenon should be assigned to the existence of coordination effect, indicating that the BiOBr/AOCF sample is more effective visible light response material.

The equation $(\alpha h \nu)^2 = K(h \nu - E_g)$ was used to calculate the band gap of the samples, where $\alpha$ is the absorption coefficient, $K$ is a proportionality constant, and $E_g$ is the band-gap energy. As can be seen in Fig. 6b, the $E_g$ values are estimated to be about 3.0, 2.9 and 1.7 eV for the pure BiOBr, AOCF and BiOBr/AOCF composites, respectively. Obviously, the optical band gap of the BiOBr/AOCF samples is less than those of the pure BiOBr and AOCF samples, indicating that the band gap depends on the coordination effect. The decrease of band gap for the BiOBr/AOCF sample indicates that light harvest and charge carrier separation can be achieve more easily, which should be helpful to improve photocatalytic reaction efficiencies.

The photocatalytic activity of BiOBr/AOCF composite for the degradation of RhB was evaluated under UV light illumination, results are shown in Fig. 7. The absorption peak of RhB at $\lambda_{max}$ = 553 nm was used to monitor the photocatalytic destruction process. As can be seen in Fig. 7a, with the prolonging of the irradiation time, the main absorption peak weakens. Moreover, a remarkable blue-shift of the maximum absorption occurred, suggesting that the conjugated structure of Rhodamine B was destructed and the formation of some new intermediates may exist in the process of destruction, deethylation of the fully N, N', N'-tetraethylated rhodamine molecule (i.e., RhB) has the wavelength position of its major absorption band moved toward the blue region, $\lambda_{max}$, RhB, 553 nm; N, N, N'-triethylated rhodamine, 541 nm; N, N'-diethylated rhodamine, 528 nm; N-ethylated rhodamine, 503 nm; and rhodamine, 492 nm. RhB formed rhodamine after being fully demethylated, and the rest was degraded through destruction of the conjugated structure [31,32]. The completely disappearance of the absorption peaks after illumination for 60 min indicated the complete decolorization of the RhB solution. As RhB is quite stable and its self-photolysis can be neglected (Fig. 7b), the present decomposition of RhB mainly originated from the photocatalysis induced by the BiOBr/AOCF composites photocatalyst. Furthermore, the comparative experiments of photocatalytic degradation of RhB by BiOBr/AOCF composites and pure BiOBr were performed under the same experimental conditions. The mass of pure BiOBr and the BiOBr in BiOBr/AOCF composites are identical. The results were displayed in Fig. 6b. The degradation efficiencies

![Fig. 5. TG curves of samples: pure BiOBr, AOCF and BiOBr/AOCF composites.](image)

![Scheme 1. Synthesis of BiOBr/AOCF composites.](image)
were about 100% and 87% for as-prepared and pure BiOBr at 60 min, respectively. Obviously, the photocatalytic activity of BiOBr/AOCF composites was higher than that of the pure BiOBr. This may be because the coordination between BiOBr and AOCF is in favor of the separation of photogenerated electron–hole pairs, increasing the photocatalytic activity of composites.

To analyze the mechanism of photodegradation of RhB by BiOBr/AOCF composites, the trapping experiments of active species were carried out; results are shown in Fig. 8a. Isopropanol (IPA, a quencher of ·OH), p-benzoquinone (p-BQ, a quencher of ·O₂⁻) and ammonium oxalate ((NH₄)₂C₂O₄, a quencher of h⁺) were generally used to detect the main active species in the photocatalytic reaction [33]. From Fig. 8a, it was found that the degradation of BiOBr/AOCF composites on RhB was 97% and the addition of isopropanol system did not change the photocatalytic activity of BiOBr/AOCF composites in degrading
RhB, which indicates that the hydroxyl radicals are not the main active species in BiOBr/AOCF composite photocatalysts for the degradation of RhB [34]. In contrast, the photocatalytic degradation percentage 28% and 34% of RhB decreased obviously when ammonium oxalate and p-benzoquinone were added, respectively. The above experimental results indicate that $h^+$ and $O_2^-$ played more important roles than OH in the photodegradation of RhB [35,36]. A proposed photocatalytic mechanism for the degradation of RhB over the BiOBr/AOCF composite photocatalysts is presented in Fig. 8b. From the foregoing analysis, one can easily find that the AOCF not only plays a support but also acts as the ligands, which should be helpful to increasing the separation efficiency of photo-generated electron–hole pairs.

We noted that BiOBr/AOCF composites could be easily separated and recovered from solution because of their large length to diameter ratios and flexible property. This character confirmed their well reusable property which was also investigated by collected, washed with deionized water and absolute ethanol and reusing for multiple cycles. Each reusability experiment was carried out under the identical condition. As shown in Fig. 9, the photocatalytic activity of BiOBr/AOCF composites was almost not changed after 5 cycles of photodegradation of RhB. Such result confirmed that the microstructure of BiOBr/AOCF composites is stability. The excellent stability of photocatalysts might be attributed to the strong coordination between BiOBr and amidoxime fiber molecules. The good stability and recoverable property is very helpful to enhancing the practical applications of BiOBr/AOCF composites in eliminating organic pollutants from wastewater.

4. Conclusion

In summary, BiOBr/amidoxime fiber composite photocatalysts have been successfully prepared via a facile solvothermal synthesis approach. The photocatalytic activity of the as-obtained photocatalysts was evaluated by the photodegradation of RhB. The photocatalysts exhibited a significant enhancement of photocatalytic performance in the degradation of RhB. Notably, the BiOBr/amidoxime fiber composite photocatalysts not only facilitate the separation of photocatalyst from dye solution because of their large length to diameter ratios but also retain high photocatalytic stability after several cycles owing to the coordination between BiOBr and amidoxime fiber molecules.

Acknowledgments

We gratefully acknowledge financial support from the Natural Foundation of Anhui Province (KJ2014ZD03) and the National Natural Science Foundation of China (21171003 and 51202003).

References