Effect of F/O atomic ratio on photocatalytic activity of $\text{Bi}_x\text{O}_y\text{F}_z$

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Abstract

We have, for the first time, prepared $\text{BiO}_{0.9}\text{F}_{2.35}$ as a new photocatalyst by a simple hydrothermal method. It is found that at different ratios of fluorine to oxygen (F/O), the $\text{Bi}_x\text{O}_y\text{F}_z$ samples have the varied internal electric field (IEF) and electrical conductivities, thus showing different photochemistry properties for the degradation of RhB. The bulk IEF and conductivity can be conveniently controlled by the F/O ratio, thus improving the photochemistry properties of layered $\text{Bi}_x\text{O}_y\text{F}_z$. This study provides a new strategy to develop efficient photocatalysts.

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1. Introduction

Since the first report by Fujishima and Honda [1], photocatalysis as an advanced oxidation technology has attracted increasing attention [2,3]. However, the practical applications of photocatalysis are still limited by its low quantum efficiency, low light utilization and low photoactivity [4,5]. Thus, it remains a big challenge to develop efficient photocatalysts for the practical applications.

Recently, bismuth-based compounds, as efficient photocatalysts, are investigated widely [6-10]. In particular, the layered bismuth oxyhalides (BiOX , $\text{X}=\text{F}$, Cl , Br , I), which are comprised of $[\text{Bi}_2\text{O}_2]$ and anion slabs, have attracted interests [9-11]. It has been reported that the charge separation efficiency of BiOX can be effectively improved by the internal electrostatic field (IEF) between the slabs [12]. Thus it is reasonable that the IEFs of layered bismuth oxyhalides could be affected by the atom kind and ratio. Compared with BiOX (Cl , Br , I), fewer studies [13,14] have been performed on BiOF . Moreover, the synthesis of $\text{BiO}_{0.9}\text{F}_{2.35}$ has not been reported so far. Thus, it is desirable to investigate the photocatalytic activities of $\text{Bi}_x\text{O}_y\text{F}_z$ with different atom ratios.

In this work, we have synthesized the $\text{BiO}_{0.9}\text{F}_{2.35}$, $\text{Bi}_7\text{O}_5\text{F}_{11}$ and BiOF photocatalysts with different F/O ratios and investigated as their photocatalytic activities for the degradation of RhB under UV light irradiation. Moreover, the correlation of photocatalytic properties with conductivity and IEF has been mainly revealed.

2. Experimental section

2.1. Sample preparation

BiO_{0.9}F_{2.35}. In a typical procedure, 2 mmol Bi₂O₃ (0.48596 g) was dissolved in 24 mmol HF (1.08 mL, 20%); then, 10 mL H₂O and 10 mL alcohol were added to the above solution under magnetic stirring. After being stirred for 1 hour, the resulting suspension was transferred into a Teflon-lined autoclave and maintained at 160 °C for 12 h. The resultant precipitate was washed with distilled water and absolute ethanol for several times, respectively. Finally the sample was dried at 60 °C for 6 h.

Bi₇O₅F₁₁. 1 mmol Bi(NO₃)₃·5H₂O (0.485 g) was dissolved in 2 mmol HF (0.09 mL, 20 wt%). Then, 25 mL HAC and 5 mL H₂O were added to the above solution under magnetic stirring. After being stirred, the resulting suspension was transferred into a Teflon-lined autoclave and maintained at 160 °C for 12 h.

BiOF. In a typical synthesis, 1 mmol Bi(NO₃)₃·5H₂O was dissolved in 15 mL mixture of C₂H₅OH-H₂O (the volume ratio is 14:1) under magnetic stirring at room temperature. Then, 6 mmol NH₄F was added into the above solution under stirring. After stirring for 1 h, 15 mL of 2 mol/L NH₃·H₂O was added into the above solution. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at the 160 °C for 12 h.

2.2. Characterization

The samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis diffused reflectance spectra, Brunauer-Emmett-Teller (BET) method, the electrochemical impedance spectroscopy (EIS) from 0.1 Hz to 100 kHz.

2.3. Activity evaluation

Under UV light irradiation ($\lambda \leq 420\text{nm}$), the photo catalytic activities of the samples were evaluated using RhB as the probing molecule. Typically, 0.1 g of powder was added into the dye solution (200 mL, 10 mg L^{-1}). Under darkness, the suspension was stirred for 30 min to reach an adsorption–desorption equilibrium of dye molecules on the photo catalyst, then it was irradiated with a 500 W Xe arc lamp equipped with ultraviolet light ($\lambda \leq 420\text{ nm}$). During photoreaction, 4 mL of suspension was collected at a given interval time and centrifuged to remove the solids. The concentration of dye was determined by using UV–vis spectrophotometer.

3. Results and discussion

Fig. 1 (a) X-ray diffraction patterns (XRD) and (b-d) SEM images of the samples: (b)

$\text{Bi}_7\text{O}_5\text{F}_{11}$; (c) $\text{BiO}_{0.9}\text{F}_{2.35}$; (d) BiOF

Fig. 1a confirms that all the diffraction peaks of the samples can be well indexed to standard JCPDS-ICDD Card No. 89-4572, 50-0003, 73-1595, confirming the formation of phase-pure $\text{BiO}_{0.9}\text{F}_{2.35}$, $\text{Bi}_7\text{O}_5\text{F}_{11}$ and BiOF , respectively. Fig. 1(b-d) shows the SEM micrographs of the samples. In Fig. 1b, the $\text{Bi}_7\text{O}_5\text{F}_{11}$ octahedrons with the clear boundaries and apexes form, whose rhombic edge length is $1.2\ \mu\text{m}$; at the same time, some irregular nanoparticles also exist on the surfaces of octahedrons. Fig.s 1c and 1d show that the $\text{BiO}_{0.9}\text{F}_{2.35}$ and BiOF samples are composed of octahedrons and plates, respectively.

Fig. 2(a,b) shows the degradation curves and apparent reaction kinetic curves of RhB dye over the samples under ultraviolet light irradiation ($\lambda \leq 400\ \text{nm}$). The degradation of RhB can be simplified as a pseudo-first-order kinetic reaction (1) as follows.

$$\ln(C_0/C) = k_a t, \quad (1)$$

where C is the concentration of RhB remained in solution after irradiation, and C_0 is the initial concentration of RhB before irradiation. The apparent rate constants (k_a) over

Fig. 2 (a) Degradation curves and (b) apparent reaction kinetic curves of the samples for the degradation of RhB under ultraviolet light irradiation ($\lambda \leq 400\ \text{nm}$).

Bi₇O₅F₁₁, BiO_{0.9}F_{2.35} and BiOF are 0.005 min⁻¹, 0.0047 min⁻¹ and 0.0104 min⁻¹, respectively. Their degradation activities follow the order of BiOF(F/O=1) > Bi₇O₅F₁₁(F/O=2.2) > BiO_{0.9}F_{2.35}(F/O=2.6). The BET areas of the Bi₇O₅F₁₁, BiO_{0.9}F_{2.35} and BiOF samples are 1.5, 2.3 and 2.1 m²g⁻¹. Compared with BiO_{0.9}F_{2.35}, the higher activities of Bi₇O₅F₁₁ and BiOF may be decided by other factors, instead of the BET area.

As reported by Lv et al. [15], internal electric field (IEF) plays a key role in improving the activity for the layered BiOX photocatalysts. Herein, we mainly considered the role of IEF of the layer structure. For Bi₇O₅F₁₁, BiO_{0.9}F_{2.35} and BiOF, there are strong covalent bonds in the [Bi₂O₂] intralayer and weak van der Waals forces in the [Bi₂O₂] interlayer. Fig 3a shows a schematic diagram of IEF, which is perpendicular to the [BiO]⁺ slabs and F⁻ slabs. As a result, the non-uniform charge distribution will polarize the relative atoms and atomic orbitals to induce an internal electric field (IEF) [15]. As reported in ref. 16, IEF plays a key role in improving the activity for layered BiOX photocatalysts. The IEF could facilitate the separation and transfer of photogenerated charges. Typically, BiO_{0.9}F_{2.35} (F/O=2.6), Bi₇O₅F₁₁ (F/O=2.2) and BiOF (F/O=1) have the different F/O ratios, which could be responsible for the different intensities of IEFs. It is obvious that with the decrease of F/O ratio, the photocatalytic activities increase gradually, suggesting that the intensity of IEF may increase with the decrease of F. Hence, the different photocatalytic activities of Bi₇O₅F₁₁, BiO_{0.9}F_{2.35} and BiOF can be significantly decided by IEF.

Fig. 3b shows the ultraviolet visible diffuse reflectance spectra (UV-DRS) of Bi₇O₅F₁₁, BiO_{0.9}F_{2.35} and BiOF. The absorption edges of Bi₇O₅F₁₁, BiO_{0.9}F_{2.35} and BiOF occur at 322, 296 and 284 nm, and their band gap energies are demonstrated to be 3.85, 4.18 and 4.37 eV, respectively (Fig. 3c). As we all know, the transfer and

Fig. 3. (a) Schematic diagram of internal electric field (IEF), (b) UV-visible diffuse reflectance spectra (UV-DRS), (c) Tauc plot (absorption² vs. energy), (d) Nyquist plots of the samples

separation efficiencies of photo-generated charges have a significant influence on photocatalytic activity [17,18].

To understand the high activity of BiOF, electrochemical impedance spectroscopy (EIS) has been performed to investigate the electron transfer ability. The arc radius in the EIS spectra reflects the solid state surface charge transfer resistance, namely, a smaller semicircle radius in the EIS Nyquist plot means a smaller electrical resistance for electron transportation [19]. As a result, the fast electron transfer rate favors for an efficient separation of photo-generated electrons and holes [15,20]. As

shown in Fig 3d, the Nyquist radii follow the order of BiOF (F/O=1) < Bi₇O₅F₁₁(F/O=2.2) < BiO_{0.9}F_{2.35}(F/O=2.6), indicating that their conductivities follow the order of BiOF (F/O=1) > Bi₇O₅F₁₁(F/O=2.2) > BiO_{0.9}F_{2.35}(F/O=2.6), which favors for the transportation and separation of photo-generated carries. The results well agree with photocatalytic activity order. On one hand, fluorine with a high electronegativity can strongly attract electrons, thus leading to an uneven electron distribution. On the other hand, the lattice distortion could occur due to the repulsive force between the 6s² lone electron pairs of Bi(III) [21]. As a result, an internal electric field (IEF) would generate [12]. It is reasonable that the internal electric field (IEF) will vary with the F/O ratios.

4. Conclusions

The BiOF, Bi₇O₅F₁₁ and BiO_{0.9}F_{2.35} samples with different F/O ratios can be prepared by the simple hydrothermal methods. Under UV light irradiation ($\lambda \leq 420\text{nm}$), the samples show the different photocatalytic activities for the degradation of RhB dye, which has been mainly attributed to the different IEFs and electrical conductivities.

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Graphic abstract

The photocatalytic activity of $\text{Bi}_x\text{O}_y\text{F}_z$ is mainly controlled by the internal electric field (IEF) that varies with F/O ratio.