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Fe(III) ions enhanced catalytic properties of $(BiO)_2CO_3$ nanowires and mechanism study for complete degradation of xanthate

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HIGHLIGHTS

- The growth orientation and morphology of $(BiO)_2CO_3$ changed due to the doped Fe^{3+} ion.
- The photodegradation of xanthate followed a pseudo-second-order kinetics model.
- The xanthate could be completely degraded into CO_2 and SO_4^{2-} ions.
- The formed Bi–S bond on the surface of $(BiO)_2CO_3$ broadened the light response region.

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ABSTRACT

The wire-like Fe^{3+}-doped $(BiO)_2CO_3$ photocatalyst was synthesized by a hydrothermal method. The photocatalytic property of Fe^{3+}-doped $(BiO)_2CO_3$ nanowires was evaluated through degradation of sodium isopropyl xanthate under UV–visible light irradiation. The as-prepared Fe^{3+}-doped $(BiO)_2CO_3$ nanowires were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), UV–visible diffuse reflectance spectroscopy (UV–vis DRS), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) in detail. The results of XRD showed that the crystallinity of $(BiO)_2CO_3$ nanowires decreased when Fe^{3+} ions were introduced into the solution system. XPS results illustrated that xanthate could be absorbed on the surface of Fe^{3+}-doped $(BiO)_2CO_3$ nanowires to produce Bi–S bond at the beginning of the reaction, which could broaden the visible light absorption. FTIR spectra confirmed the formation of SO_4^{2-} after photocatalytic decomposition of xanthate solution. The Fe^{3+}-doped $(BiO)_2CO_3$ nanowires showed an enhanced photocatalytic activity for decomposition of xanthate due to the narrower band gap and larger BET surface area, comparing with pure $(BiO)_2CO_3$ nanowires. By the results of UV–vis spectra of the solution and FTIR spectra of recycled Fe^{3+}-doped $(BiO)_2CO_3$, the xanthate was oxidized completely into CO_2 and SO_4^{2-}. The photocatalytic degradation process of xanthate followed a pseudo-second-order kinetics model. The mechanism of enhanced photocatalytic activity was proposed as well.

1. Introduction

Xanthate is a widely used flotation agent in the flotation process of non-ferrous metal ore and is a critical sulfhydryl collector. The wastewater from ore-dressing process contains significant amounts of residual xanthate, which can cause serious harm to the surrounding ecological environment of mining area (Chen et al., 2011a; Shu et al., 2009). Many methods, such as chemical precipitation (Mielczarsk, 1986), chemical oxidation (Silvester et al., 2002; Fagadar-Cosma et al., 2003; Chen et al., 2015; Fu et al., 2016), adsorption (Mikhlin et al., 2015; Huang et al., 2012), and biodegradation (Chen et al., 2011b; Chockalingam et al., 2003), have been developed in recent years to degrade xanthate and its by-products from wastewater.

Recently, bismuth-containing photocatalysts, which can be activated by UV–visible light to degrade organic pollutants efficiently, have attracted increasing attention (Dong et al., 2011a; Chen et al., 2006; Cheng et al., 2010a). These bismuth-containing

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photocatalysts including BiOX (X = Cl, Br, I) (Chen et al., 2013), $BiVO_4$ (Xiao et al., 2011), Bi_2O_3 (Qiu et al., 2011), Bi_2MoO_6 (Tian et al., 2011), Bi_2WO_6 (Fu et al., 2005), $(BiO)_2CO_3$ (Selvamani et al., 2013), Bi_3NbO_7 (Zhang et al., 2009), and Bi_2S_3 (Wu et al., 2010) exhibit high photocatalytic performance in degrading organic pollutants. Among them, $(BiO)_2CO_3$ has been widely studied due to its unique Sillén-layered structure, adjustable band gap, outstanding stability and reusability (Sillén, 1942; Zhao et al., 2014). $(BiO)_2CO_3$ with different morphologies, such as sponge (Zhao et al., 2011), nanosheet (Liu et al., 2010a), nanotube (Qin et al., 2012), nanobar (Chen et al., 2012), nanowire (Cui et al., 2016), and microflower (Zhao et al., 2011), were prepared by different methods and showed decent photocatalytic activity. However, the various synthesized $(BiO)_2CO_3$ structures with large band gap (3.2–3.5 eV) could only be excited by UV light irradiation when they were used as photocatalysts, resulting in a low photocatalytic activity. For enhancing the photocatalytic activity of $(BiO)_2CO_3$, two strategies have been adopted. One is combining $(BiO)_2CO_3$ with other chemicals to improve the electron-hole separation efficiency, such as $(BiO)_2CO_3$/MoS_2 (Xiong et al., 2016), Ag clusters-grafted $(BiO)_2CO_3$ (Feng et al., 2017), $Bi_2O_2CO_3$/Bi_3NbO_7 (Gan et al., 2013). The other is doping ions into $(BiO)_2CO_3$ to modify the electronic structures, resulting in a broadened light response region. Until now, several ion-doped $(BiO)_2CO_3$ has been successfully synthesized, such as Sb-doped $(BiO)_2CO_3$ nanoplates (Zhao et al., 2015), N-doped $(BiO)_2CO_3$ hierarchical microspheres (Dong et al., 2012), C-doped $(BiO)_2CO_3$ microspheres (Xiong et al., 2015). As expected, the photocatalytic activity of these doped $(BiO)_2CO_3$ were enhanced under visible light irradiation. However, the organic contaminants could only be photodegraded into small molecules, which are also harmful to the environment. It is urgent to synthesis photocatalyst that can photodegrade organic pollutant completely. It is known that ionic iron can vary between bivalent or trivalent status under different condition, which could show different property. Moreover, doping Fe ions can enhance the activity by trapping e^-/h^+ pairs and inhibit the recombination of e^-/h^+ pairs. By far, various photocatalysts doping with Fe ions, such as Fe-doped TiO_2 nanotubes (Deng et al., 2010), Fe-doped ZnS nanoparticles (Dixit et al., 2015), and Fe-doped β-Bi_2O_3 porous microspheres (Liang et al., 2014), have been prepared and showed an enhanced UV–visible light photocatalytic activity. Fe^{3+} ions play an intermediate role for the efficient separation of photo-generated electron–hole pairs. Thus, it is reasonable that Fe^{3+}-doped $(BiO)_2CO_3$ can show an enhanced photocatalytic activity as well as degrade organic pollutant completely.

Herein, the effects of Fe^{3+} ions on the structure, band gap, and photocatalytic activity of $(BiO)_2CO_3$ nanowires were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–Vis spectra, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). The end-products of xanthate-containing wastewater after photodecomposition by the as-prepared Fe^{3+}-$(BiO)_2CO_3$ were also studied, and a photocatalytic mechanism was proposed.

2. Experimental

2.1. Synthesis of $(BiO)_2CO_3$ nanowires

All the reagents were of analytical grade and were used without any further purification. Deionized water was used in all the experiments. In the typical synthesis process, sodium chloride (2.380 g) and sodium carbonate (0.212 g) were first dissolved in deionized water (70 mL) in a 100-mL autoclave Teflon vessel. The pH value was then adjusted and kept to 3.0 using a 1 mol/L HCl solution. β-Bi_2O_3 (0.932 g) and $FeCl_3 \cdot 6H_2O$ (0.011 g) were added to the above solution. The autoclave was sealed and heated at 160 °C for 6 h agitatedly, and then cooled to room temperature naturally. Next, the resulting solid was filtered and washed with deionized water for three times and ethanol once. Fe^{3+}-doped $(BiO)_2CO_3$ samples were obtained after drying at 60 °C. According to the amount of $FeCl_3 \cdot 6H_2O$ (0 and 0.011 g), the resulting $(BiO)_2CO_3$ materials were labeled as BOC and F-BOC.

2.2. Structure characterization

The crystal phases of $(BiO)_2CO_3$ nanowires were analyzed by XRD with Cu Kα radiation. The XRD measurements were recorded on a DX-2700-Ray diffraction system (Fangyuan Instrument Co., China) with λ = 1.54187 Å and scanning range of 10°–80°. The FEI Nova NanoSEM 230 field-emission scanning electron microscope was used to characterize the morphology of the obtained products with accelerating voltage of 30 kV. The UV–Vis diffuse reflectance spectra (UV–Vis DRS) were obtained for the dry-pressed disk samples using a scan UV–Vis spectrophotometer (UV–Vis DRS: UV-2600, Shimadzu, Japan), equipped with an integrating sphere assembly. $BaSO_4$ powders were used as a reference. The XPS measurements were used to investigate the surface properties of the products in an ultrahigh vacuum electron spectrometer (K-Alpha 1063, Thermo Scientific, UK) using the Al Kα X-ray radiation source (operating at 72 W). The FTIR of the samples were obtained on an FTIR spectrometer (Nicolet 6700, Nicolet, USA) using a KBr pellet method. The BET specific surface areas of BOC and F-BOC were calculated to be 16.05 and 21.52 m^2/g, respectively, based on a nitrogen adsorption apparatus (ASAP 2020, Micrometrics, USA).

2.3. Determination of photocatalytic activity

The photocatalytic activities of the as-prepared samples were investigated through the photocatalytic degradation of sodium isopropyl xanthate under UV–visible light irradiation, which was provided by a 250 W metal halide lamp. An estimated 0.06 g of photocatalyst was added into a 150 mL xanthate solution (20 mg/L = 1.264×10^{-4} mol/L). The solution was exposed to the lamp under magnetic stirring under room temperature. After irradiation for a given interval, 3 mL of the solution was collected by syringe filters. The intensity change of the absorption peak was measured at 301 nm using a UV–Vis spectrophotometer (UV–2600). The degradation ratio (η) of xanthate was calculated by $\eta(\%) = (C_0 - C)/C_0 \times 100\%$, where C and C_0 denotes the xanthate concentration after a reaction of t and at the initial state, respectively.

3. Results and discussion

3.1. Phase structure and morphology of Fe^{3+}-doped $(BiO)_2CO_3$ nanowires

The XRD patterns of the as-prepared samples derived from Fe^{3+}-doped $(BiO)_2CO_3$ nanowires are shown in Fig. 1. All the diffraction peaks of the F-BOC and BOC samples can be indexed to $(BiO)_2CO_3$ (JCPDS-ICDD No. 41-1488). No impurity peaks were detected, suggesting that the BOC and F-BOC samples were highly phase pure and had excellent crystallinity. The sharp and strong peaks of the BOC sample illustrated good crystallinity and large crystal size of the $(BiO)_2CO_3$ nanowires. Compared with that of the BOC sample, the full width at half maximum (FWHM) of the XRD peaks broadened for the F-BOC sample, especially for the (002) crystal plane, (004) crystal plane, and (006) crystal plane. This result indicates a smaller size along the *c* axis of the as-prepared F-BOC sample. In addition, the relative intensity ratio of the (110) peak to the (013) peak of the F-BOC sample was significantly higher