



Enhanced UV–visible response of bismuth subcarbonate nanowires for degradation of xanthate and photocatalytic reaction mechanism



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HIGHLIGHTS

- (BiO)₂CO₃ nanowires had well photocatalytic activity and recyclability for xanthate.
- Bi₂S₃@(BiO)₂CO₃ core–shell structure generated during photocatalytic reaction period.
- Bi₂S₃@(BiO)₂CO₃ core–shell structure enhanced photodegradation activity.
- A probable photocatalytic mechanism was proposed.

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ABSTRACT

(BiO)₂CO₃ nanowires were prepared by simple hydrothermal treatment of commercial Bi₂O₃ powders and characterized by X-ray diffractometry, scanning electron microscopy, transmission electron microscopy (TEM), high-resolution TEM, and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of (BiO)₂CO₃ nanowires was studied through degradation of sodium isopropyl xanthate. Photocatalytic experimental results indicated that the as-prepared (BiO)₂CO₃ nanowires show high photocatalytic efficiency. Photocatalytic activity increased after two cycles. Time-dependent UV–vis spectra demonstrated that the final degradation products included isopropyl alcohol and carbon disulfide. UV–vis diffuse reflection spectra showed that the band gap of the as-prepared (BiO)₂CO₃ nanowires and recycled (BiO)₂CO₃ nanowires were 2.75 eV and 1.15 eV, respectively. XPS results indicated that formation of Bi₂S₃@(BiO)₂CO₃ core–shell nanowires occurred after recycled photodegradation of isopropyl xanthate owing to existence of two types of Bi configurations in the recycled (BiO)₂CO₃ nanowires. A probable degradation mechanism of isopropyl xanthate was also proposed.

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1. Introduction

Xanthates are widely used as collectors in sulfide mineral flotation. Although most of the xanthates enter into the floated product, residual xanthate in the wastewater obtained from flotation processing presents serious environmental consequences because xanthate is not only toxic to aquatic fauna but also harms the liver, nervous system, and hematopoietic system of humans and animals (Liu et al., 2015). Thus, wastewater containing xanthate must be treated properly before discharge. Conventional treatment

methods for xanthates include physical, chemical, and biological processes. Physical processes, such as coagulation (Amuda and Amoo, 2007; Yang et al., 2010), activated carbon adsorption (Zietzschmann et al., 2014), and membrane filtration (Van Der Bruggen et al., 2003), are limited in practical application because of their poor reusability and high operational cost, among others. While conventional chemical treatment (Molina et al., 2013) to decompose xanthate using chlorine or permanganate as an oxidant is a simpler approach, toxic by-products are generated during chemical oxidation, thereby resulting in secondary pollution. Biological treatment methods make use of microorganisms to decompose the organic pollutant but usually require over 30 days to achieve adequate removal (Cheng et al., 2012), which makes them unsuitable for practical applications.

Advanced oxidation processes (AOPs) (Sauer et al., 2006), as a

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special category of oxidation techniques, have recently attracted considerable research interest because of their highly efficient production of hydroxyl radicals (OH·) with high oxidative ability. AOPs utilize ozone, hydrogen peroxide, Fenton's reagent, and photocatalyst to oxidize by-products. Among the currently available AOP processes, photocatalytic techniques are considered the most practical for degrading organic pollutants, including xanthate, because they feature high efficiency and low cost (Chen et al., 2010; Kitano and Hara, 2010). Most photocatalytic systems use nanostructured TiO₂-based photocatalysts, which can only absorb UV light because of their large band gap (3.2 eV); unfortunately, the UV region accounts for only 4% of the solar spectrum (Ohtani, 2010; Xiang et al., 2011). Therefore, TiO₂-based photocatalytic systems are difficult to develop for commercial application because of their low utilization rate of sunlight. Although non-TiO₂ semiconductors, such as ZnO-based semiconductors and BiVO₄ nanoparticles (Xiao and Ouyang, 2009; Xiao et al., 2011a; Xiao and Yao, 2011b), have attracted increased attention for treatment of potassium ethyl xanthate-containing wastewater through photocatalysis because of their wide adsorption band, the degradation efficiency of xanthate in these systems remains low. In addition, complicated separation and deactivation procedures during photocatalyst circulation further limit the applications of nanoscale photocatalysts. Consequently, discovering novel photocatalysts and exploring non-TiO₂ semiconductors with strong absorbance in the visible light spectrum and high efficiency for degrading wastewater containing xanthate are of great importance.

Bismuth subcarbonate [(BiO)₂CO₃], has recently attracted considerable research attention as a novel alternative photocatalyst because of its unique layered structure, which aids in the separation of photo-generated electron–hole pairs and achieves high photocatalytic performance (Selvamani et al., 2013; Gan et al., 2013). (BiO)₂CO₃ photocatalysts with different morphologies have been prepared through hydrothermal or solvothermal methods and show high efficiency for photodegrading rhodamine B, methyl orange, methyl blue, and toxic gases (e.g., NO). The morphologies and properties of (BiO)₂CO₃ photocatalysts are listed in Table 1. The band gap of this material, which is directly related to its light response range, crucially depends on its morphology and size distribution. Most of the synthesis experiments on (BiO)₂CO₃ photocatalysts thus far have focused on 3D structures and their band gaps in relation to dye degradation in wastewater. The poor recyclability

of (BiO)₂CO₃ photocatalyst has resulted in its application in non-commercial processes. Moreover, (BiO)₂CO₃ nanowires with large length/diameter ratios have not been employed to treat xanthate-containing wastewater, and their band gaps have not been reported yet.

This work aimed to investigate (BiO)₂CO₃ nanowires to assess their photocatalytic activity for xanthate degradation and recyclability. A probable photocatalytic mechanism was also proposed through measurement of UV–vis diffuse reflection spectra (UV–vis DRS) and determination of the degradation products.

2. Experimental

2.1. Materials and preparation of (BiO)₂CO₃ nanowires

The bismuth trioxide particles (Bi₂O₃) were purchased from Changde Fine Chemical Co. Ltd. Sodium chloride (NaCl) and sodium carbonate (Na₂CO₃) were bought from Tianjin Kernel Chemical Reagent Co. Ltd. Isopropyl xanthate (C₄H₇NaOS₂) was obtained from Shanghai Life Science & Technology Co., Ltd. All chemicals were used as received without further purification. Deionized water was used in the experiments.

In a typical synthesis of (BiO)₂CO₃ nanowires, 2.338 g NaCl and 0.212 g Na₂CO₃ were firstly dissolved into 70 mL deionized water and the solution was adjusted to pH 3.0 using 1M HCl. After that, 0.932 g Bi₂O₃ was added into the solution under magnetic stirring condition. Then the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, stirred magnetically for 6 h at 160 °C, and subsequently cooled to room temperature. Afterwards, the products were collected by filtration, washed several times with deionized water and ethanol, and dried in an oven overnight at 60 °C. The specific surface area of as-prepared powders was 19.67 m²/g according to the Brunauer–Emmett–Teller analysis measured by nitrogen adsorption–desorption isotherms at 77 K (BET, ASAP 2020, Micromeritics, USA).

2.2. Characterization of (BiO)₂CO₃ nanowires

The phase composition of the as-synthesized (BiO)₂CO₃ nanowires was identified by powder X-ray diffractometry (XRD, D/max, Rigaku, Japan) with Cu K α as a radiation source. The morphology was characterized by scanning electron microscopy (SEM, FEI Nova

Table 1
Survey of different morphologies and its reactive studies on (BiO)₂CO₃ nanostructures.

Morphology	Band gap (eV)	Size distribution	Description of studies	Ref.
Nanotubes	3.00	Diameter: 7 nm	Removal of Cr ⁶⁺ and photocatalytic activity for degradation of RhB under visible light	(Qin et al., 2012)
Nanosheets/ Nanoplates	3.34	Thickness: 50 nm	Photocatalytic degradation of RhB	(Zhao et al., 2011)
	3.39	Thickness: 70–80 nm	Photodegradation of RhB and 2-propanol under UV–vis light	(Liu et al., 2010)
	3.45	Thickness: ~110 nm	Photocatalytic degradation of the fully N,N,N',N'-tetraethylated rhodamine under visible light	(Zheng et al., 2010)
Sponge-like microspheres	2.87	Nanosheet thickness: <10 nm; Microsphere diameter: 2–3 μ m	Photocatalytic activity for degradation of RhB, MB and MO under artificial light; the photocatalytic activity declined at the third run	(Zhao et al., 2011)
	2.91	Nanosheet thickness: 12 nm; Microsphere diameter: 1 μ m	Photocatalytic degradation of MO under UV–vis light; the degradation efficiency decreased at the third run	(Peng et al., 2013)
Flower-like hierarchy structure	3.10	Nanosheet thickness: ~30 nm; Flower diameter: 2 μ m	Photocatalytic degradation of the fully N,N,N',N'-tetraethylated rhodamine under visible light	(Zheng et al., 2010)
Rose-like microspheres	3.20	Nanosheet thickness: 20 nm; Microsphere diameter: 2–3 μ m	Photocatalytic degradation of RhB, MB, MO and mixed aqueous dye solution of MO and MB under visible light	(Madhusudan et al., 2013)
Hierarchical hollow Microspheres	3.40	Nanosheet thickness: 20 nm; Microsphere diameter: 1.2 μ m	Photocatalytic removal of NO in air under simulated solar light	(Dong et al., 2012)
Microflower	3.55	Nanosheet thickness: 20 nm; Microflower diameter: 3 μ m	Photocatalytic degradation of MO under UV irradiation	(Cheng et al., 2010)

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