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Modulation of valence band maximum edge and photocatalytic activity of BiOX by incorporation of halides

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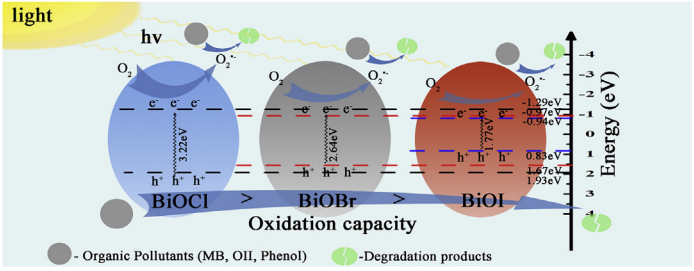
HIGHLIGHTS

- The characteristics of as-prepared BiOX (X = Cl, Br, I) nanosheets were compared.
- Catalyst's structures and chemical properties of organic contaminants influence the photocatalytic activity of BiOX.
- The formation of HO• was in the order of BiOBr > BiOI > BiOCl and formation of $O_2^{\bullet-}$ was in the order of BiOCl > BiOBr ≈ BiOI.
- The incorporation of halide influences the photoactivity of BiOX through mediating VB maximum edge.

GRAPHICAL ABSTRACT



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ABSTRACT

To better know the photocatalytic performance of bismuth oxyhalides (BiOX, X = Cl, Br, I) regulated by incorporation of halides within nanostructures, BiOX nanosheets were synthesized through morphology controllable solvothermal method and characterized systematically. The organic structural property greatly influences the photocatalytic activity of BiOX: 1) as for neutral molecular phenol, BiOX shows photocatalytic activity in the order of BiOCl > BiOBr > BiOI under simulated sun light irradiation, and the photo-oxidation kinetics follow Eley–Rideal mechanism; and 2) for adsorbed anionic orange II (OII) and cationic methylene blue (MB), BiOX shows photocatalytic activity in the order of BiOCl > BiOBr > BiOI, and the photo-oxidation kinetics follow Langmuir-Hinshelwood mechanism. The crystal structure of the catalyst also greatly influences the photocatalytic activity of BiOX: 1) The relative photo-oxidation power of $O_2^{\bullet-}$ radicals or HO• radicals involved in this study were different which were quantitatively detected using typical radical trapping agent, separately; 2) The relative oxidation power of photogenerated holes (h^+) in this study were in the order of BiOCl > BiOBr > BiOI, which may be ascribed to lowering the valence band maximum edge of BiOX through incorporation of halides as the atomic number of halides decreased. This study provides novel explanation for fabricating BiOX heterojunctions with tunable photocatalytic reactivity via regulating the halides ratio.

1. Introduction

On account of its high toxicity, ecological and environmental

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importance, refractory organic contaminants and their corresponding breakdown products from wastewater has been attracting a great deal of attention (Gulshan et al., 2010; Yu et al., 2016). Comparing with the traditional methods which have many disadvantages, advanced oxidation processes (AOPs) have been known as efficient alternatives in dye wastewater treatment due to their strong oxidizing capacity and environmentally friendly features, for instance, the Fenton degradation systems (Guo et al., 2016; Liu et al., 2017) and the semiconductor photocatalytic degradation systems (Li et al., 2014a). Semiconductor photocatalysis, such as TiO_2 (Hu et al., 2016; Liu et al., 2015), Fe_2O_3 (Qiu et al., 2015) and ZnO (Choo et al., 2015; Josephine and Sivasamy, 2014), could utilize the abundant solar energy for water splitting into H_2 gas (Li et al., 2015a; Liu et al., 2014), harmful pollutant decomposition (Hu et al., 2016) and selective organic transformations. Photocatalytic oxidation has been regarded as an efficient, green and promising solution to energy replacement and environmental decontamination.

Bismuth oxyhalides (BiOX, X = Cl, Br and I), as a new family of promising photocatalysts, have been attracting much attention because of its unique physical and chemical properties. The BiOX series crystallize in the tetragonal Matlockite structure shown in Fig. 1 (Keramidas et al., 1993). The crystal lattice consists of fluorite-like $[Bi_2O_2]$ layers sandwiched between double halide $[X_m]$ layers, to form [X-Bi—*O*—Bi-X] sheets with the structure held together by nonbonding van der Waals interactions along the [001] direction. It has been proposed that this structure type imparts an internal static electric field between the $[Bi_2O_2]^{2+}$ and double $[X]^-$ slab along the [001] direction, which aids efficient separation of the photogenerated electron-hole pairs (Ganose et al., 2016; Zhang et al., 2006, 2008a). The BiOX catalysts possess extraordinary photocatalytic activities under ultraviolet or visible light irradiation.

However, the evaluation of the photocatalytic degradation efficiencies of the three series BiOX (X = Cl, Br, I) materials are still controversial. There are many factors that will influence the photocatalytic performance of BiOX, such as crystalline, morphology, surface area, preparation methods, starting materials and organic structures, etc. Among these factors, halides anions play a crucial role in determination the photocatalytic reactivity of BiOX due to its various electronegativity and ionic radius.

In Lang Chen's research, all of the BiOX (X = Cl, Br, I) with 3D architectures show higher photocatalytic activities than their sheet-like counterparts (Chen et al., 2013). Li et al. fabricated BiOX (X = Cl, Br, I) with different sizes and morphologies by mannitol-mediated microwave synthesis method. And the flower-like BiOX hierarchical nanostructures show the highest photocatalytic activity, which is mainly ascribed to their unique hierarchical structure, wide band gap, and large BET surface area (Li et al., 2013a). Wang et al. prepared BiOX (X = Cl, Br, I) by the hydrothermal method and demonstrated that BiOBr exhibits the highest degradation rate of microcystin-LR mainly due to its intermediate valence band potential (E_{vb} = 3.02 eV) so that it can avoid occurrence of side-reaction of H_2O splitting to O_2 (Wang et al., 2015). Zhang et al. synthesized BiOX (X = Cl, Br, I) microspheres by one-pot solvothermal process and the photocatalytic activity was in the order of BiOI > BiOBr > BiOCl for methyl orange elimination without knowing the dominant degradation pathway and photodegradation mechanism (Zhang et al., 2008b). In Chang's communication about BiOX (X = Cl, Br, I) photocatalysts, it implied that BiOI exhibits the best activity under Xenon-light irradiation towards four kinds of typical phenolic environmental endocrine disruptors because of its narrow band gap (Chang et al., 2010). Furthermore, to the best of our knowledge, the effects of halides on the photocatalytic performance of BiOX and the relative reactive oxygen species (ROS) evolution in BiOX series have not been discussed.

In order to explore the regulation role of halides on BiOX structure and provide theoretic base for fabricating hybrid BiOX nanocomposites, a series of BiOX, (X = Cl, Br, I) nanosheets were synthesized by a facile solvothermal method and were characterized systematically. We compared the photocatalytic activity of the BiOX towards oxidation of different charged OII, MB and phenol under simulated solar light. The radical trapping experiments were employed to examine the relative roles of photogenerated holes (h^+) and the ROS within BiOX photocatalytic systems, such as $O_2^{\bullet-}$ and HO•. The involved radicals were evaluated via photocatalytic degradation of different organic pollutants and mediation role of halides on BiOX structures in detail. Although a lot of studies have reported the hydrothermal synthesis method (Tian et al., 2015; Zhang et al., 2015), different morphologies (Wu et al., 2015; Chang et al., 2015), or modification (Li et al., 2017; Chen et al., 2017; Zhang et al., 2017) of BiOX. While in this paper, we mainly elucidate the mediation role of halides within three kinds of BiOX and their influence on mediation of photocatalytic activity towards different chemical structural organic pollutants.

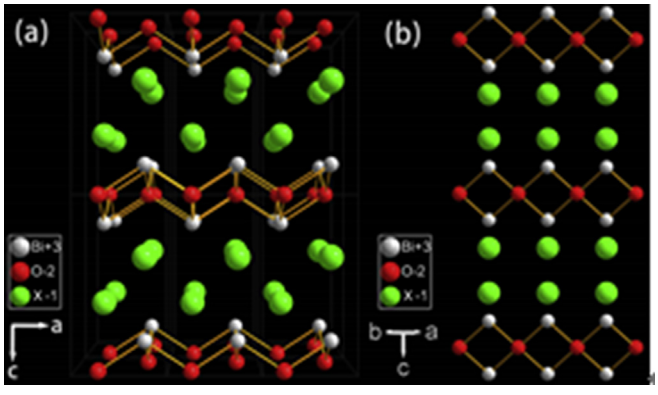

Fig. 1. Structure model illustration of BiOX crystals (3 × 2 lattices). (a) three-dimensional projection; (b) Perspective from {110} facets.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), sodium chloride (NaCl), sodium bromide (NaBr), potassium iodide (KI), ethyl alcohol (C_2H_6O, ≥99.7%), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), ascorbic acid (Vc), iso-propanol (IPA), orange II ($C_{16}H_{11}N_2NaO_4S$), methylene blue ($C_{16}H_{18}ClN_3S$), phenol (C_6H_5OH) were purchased from Shanghai Chemical Reagents Company, China. Polyethylene glycol ($HO(CH_2CH_2O)_nH$, average MW 10000), tetranitromethane ($C(NO_2)_4$), coumarin ($C_9H_6O_2$), 7-hydroxycoumarin ($C_9H_6O_3$) were purchased from Sigma-Aldrich Company. All chemicals were of analytical grade without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of BiOX samples

The BiOX (X = Cl, Br, I) powders were synthesized by solvothermal method. In detail, 1.290 g sample of $Bi(NO_3)_3 \cdot 5H_2O$ and 0.3 g polyethylene glycol was added into a 20 mL ethanol containing stoichiometric amounts of NaCl, NaBr and KI respectively, with the Bi/X molar ratio of 2. The mixture was stirred for 20 min at