



Preparation and first-principles study for electronic structures of BiOI/BiOCl composites with highly improved photocatalytic and adsorption performances

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ABSTRACT

The BiOI/BiOCl composites with high photocatalytic and adsorption abilities were prepared via a facile ionic liquid assisted ultrasonic method in several hours at room temperature. The BiOI/BiOCl composites with different contents of BiOI can be conveniently synthesized via changing the amount of 1-ethyl-3-methylimidazolium iodide precursor during the preparation process. Microstructures, morphologies, porosities and bandgaps of the as-prepared samples were determined through various experimental methods. A first-principles calculation was employed to explicate electronic structures of the complex. Photocatalytic results suggest that the obtained BiOI/BiOCl composite with 40% BiOI has the highest photoactivity for the degradation of rhodamine-B and quinoline blue under visible light irradiation. All the rhodamine-B and quinoline blue can be degraded in 25 min and 15 min, respectively. To observe the universality of the BiOI/BiOCl, the degradation results of colorless target pollutant (tetracycline) was also investigated. Based on experimental and computational results, origins of the photocatalytic abilities leading to the observed results were proposed.

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1. Introduction

The bismuth oxyhalides (BiOX, X=Cl, Br, I), a sequences of ternary semiconductors, have been found as promising materials for organic matter degradations due to their unique and excellent electrical, magnetic, optical, luminescent and catalytic properties [1–8]. Recently, considerable attentions have been paid to prepare BiOX with variety of morphologies and structures [9–24]. However, photocatalytic efficiencies of pure BiOX are unsatisfactory for the further applications under irradiation of visible light. This is mainly due to its wide band gap and the high recombination of the photogenerated electron-hole pairs. To enhance the degradation efficiency, various strategies have been designed and developed, such as the deposition of noble metals [25], and doping with metal or nonmetal elements [26–33].

Among the material manipulation routes, preparation of BiOI/BiOCl composites is an effective approach to improve degradation efficiency. Easy formations of the composites are contributed to the BiOX (X=Cl, Br, I) compounds crystallized tetragonal matlockite structure where a layer structure characterized by [Bi₂O₂] slabs is interleaved by double slabs of halogen atoms. Moreover, the BiOI is a coral red material, meaning that it has strong photoabsorption under irradiation of visible light [34]. So far, there are a few reports on the preparation of BiOI/BiOCl composites. For example, Li et al. has synthesized hierarchical BiOI/BiOCl composites by hydrothermal method with enhanced photocatalytic performance, but the preparation conditions require relative high temperature and use of organic solvent. Moreover, its need long reaction time. Besides, undesirable organic byproducts would be produced, which is not environmentally friendly [35]. Nan et al. synthesized 3D BiOI/BiOCl composite microspheres by solvothermal method, and it's also need long reaction time and high temperature [36]. Although BiOI/BiOCl composites have been synthesized by soft chemical method [37,38], the preparation conditions require relative long reaction time and need to control the reaction pH. In addition, dyes, such as rhodamine B and methyl orange have

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Table 1

The synthetic conditions of BiOI/BiOCl composites.

samples	[EMIM]I g ⁻¹	[BMIM]Cl g ⁻¹	[EMIM]I/[BMIM]Cl (mol:mol)	Contents of BiOI (%)
S1	1.190	0	1:0	100
S2	0.893	0.218	3:1	75
S3	0.714	0.349	3:2	60
S4	0.595	0.437	1:1	50
S5	0.476	0.524	2:3	40
S6	0.298	0.655	1:3	25
S7	0	0.873	0:1	0

been chosen as target pollutants for degradation studies; however, visible-lightinduced photocatalysis from dye sensitization may easily mislead result interpretation. Therefore, the investigation of the visible-light photodegradation colorless solution is necessary.

Herein, we developed a novel and simple method namely ionic liquid assisted ultrasonic method to prepare BiOI/BiOCl composites at room temperature. Through this method, BiOI/BiOCl composites can be obtained in one hours at room temperature. The contents of BiOI can be conveniently adjusted via the simple change of the amount of 1-ethyl-3-methylimidazolium iodide ([EMIM]I) used during the preparation process. Besides RhB and QB, the degradation result of colorless target pollutant (tetracycline) was also investigated. The results suggested that the obtained BiOI/BiOCl composite with 40% BiOI have highest photoactivity for the degradation of RhB and QB under visible light irradiation at room temperature. A first-principles investigation was carried out to explicate the impact of the composite electronic structures on the photocatalytic abilities.

2. Experimental

2.1. Materials

All the reagents in the present work were analytical grade and used without further purification.

2.2. Preparation of BiOCl-BiOI

A typical synthetic procedure was as follows. To the suspension of Bi(NO₃)₃·5H₂O (2.42 g, 5 mmol) in water (10 mL), the water solutions (10 mL) of 1-ethyl-3-methylimidazolium iodide ([EMIM]I) (0.595 g, 2.5 mmol) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) (0.437 g, 2.5 mmol) were added dropwise. The reaction mixture was kept stirring for 30 min at room temperature, and then ultrasonically irradiated 1 h. The precipitate was separated by filtration, and washed with de-ionized water and alcohol several times, and then dried at 50 °C in vacuum for 12 h. As shown in Table 1, depending on the molar ratio of [EMIM]I to [BMIM]Cl (1:0, 3:1, 3:2, 1:1, 2:3, 1:3, 0:1), different BiOI/BiOCl composites can be synthesized and labelled as S1–S7, respectively.

2.3. Characterizations

Crystal microstructures of the as-prepared samples were characterized by powder X-ray diffraction (XRD) on a D8 ADVANCE apparatus diffractometer. The operation voltage and currents were 40 kV and 40 mA. The K α lines from the Cu anodes were employed as radiation sources. Compositions of the as-prepared product were analysed by an energy-dispersive X-ray spectroscopy (EDS). The X-ray photoelectron spectra (XPS) were measured on a Thermo ESCALAB 250 spectrometer where the Al K α X-rays ($h\nu = 1486.6$ eV) were monochromized as the incident source. They were used to specify the species and chemical states of the elements. Energy calibrations of the XPS were performed by using the adventitious C1s

level at 284.75 eV as an internal standard. Sample morphologies and microstructures were determined through scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL JEM-2100F, accelerating voltage 200 kV). Nitrogen adsorption–desorption isotherms were obtained on a nitrogen adsorption apparatus (TRISTRAR II3020, USA). The UV–vis diffuse reflectance spectra (DRS) were recorded on a UV2501PC (Shimadzu) using BaSO₄ as the reference, while UV–vis absorption spectra on a Lambda 25 UV–vis spectrophotometer (Perkin-Elmer, USA) in the range of 300–800 nm.

2.4. Photocatalytic activity measurement

Photocatalytic activities of the products (50 mg) were evaluated by the degradation of the rhodamine-B (RhB) solution (10 mg L⁻¹, 50 mL), quinoline blue (QB) solution (10 mg L⁻¹, 50 mL) and tetracycline (TC) solution (20 mg L⁻¹, 50 mL) under visible light irradiations (a 350-W Xe lamp equipped with a 400 nm cut-off filter) for fixed time intervals. To eliminate the adsorption/desorption equilibrium effects of the RhB or QB, all of the samples were magnetically stirred in dark for 30 min before the irradiation. Part of the solution (5 mL) was taken out and centrifuged to remove the catalysts for 30 min. The UV–vis absorption spectra were recorded on a Lambda 25 UV–vis spectrophotometer (Perkin-Elmer, USA). The maximum absorption peak of RhB, QB and TC were at 553 nm, 638 nm and 362 nm, respectively. The scan range was 400–800 nm.

3. Theory

The present band structure calculations were performed by using the Cambridge Serial Total Energy Package (CASTEP) package [39] which is based on density functional theory (DFT). The exchange–correlation functional is treated within the generalized gradient approximation (GGA), in the form of Perdew–Burke–Ernzerhof (PBE) functional [40]. The convergence tolerance of the energy was set to 10⁻⁶ eV and the energy cutoff of the plane wave basis set was set to 450 eV. The structure of BiOX belongs to the tetragonal space group P4/nmm (number 129). The experimental lattice constants and atomic positions [41,42] were applied to the species of BiOCl and BiOI in the present calculations.

4. Results and discussion

The preparation process of BiOI/BiOCl composite is very simple under mild reaction conditions. As shown in Experimental section, the composites can be obtained at room temperature in several hours via the ionic liquid assisted ultrasonic method. Depending on the molar ratio of the [EMIM]I to the [BMIM]Cl used in the preparation process, different BiOI/BiOCl composites were synthesized. The synthesis conditions and product compositions were tabulated in Table 1.

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