



Efficient visible light photocatalytic heterostructure of nonstoichiometric bismuth oxyiodide and iodine intercalated $\text{Bi}_2\text{O}_2\text{CO}_3$



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ABSTRACT

Bismuth oxide based (BOB) materials display strong potentials in visible light photocatalytic applications, but are greatly restricted by the poor stability for organic degradation in aqueous solutions. Herein, a unique heterostructural photocatalyst, nonstoichiometric bismuth oxyiodide $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$ ($x = 0.243$) covered with iodine intercalated $\text{Bi}_2\text{O}_2\text{CO}_3$, were developed through a treatment of $\text{Bi}_7\text{O}_9\text{I}_3$ in urea solution and subsequent calcinations. The interesting formation chemistry of this heterostructure were revealed and their dramatically enhanced photoresponse properties were studied. The lower amount of iodine in $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$ contributes a higher oxidation potential of photogenerated holes, while the presence of outlayer of iodine intercalated $\text{Bi}_2\text{O}_2\text{CO}_3$ retards the transformation of inner bismuth oxyiodide. We anticipate this strategy can be generalized to tune iodine contents and to fabricate delicate BOB photocatalytic heterostructures with desirable performance for environmental applications.

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1. Introduction

Bismuth oxide based (BOB) materials are promising candidates for photocatalytic applications, because of the relative abundance of elementary bismuth and the possibility of visible light driven reactions. Among these materials, bismuth oxyiodide and bismuth oxide have attracted increasing attention. The former is a family of V–VI–VII ternary oxides, including BiOI and other oxygen rich compounds, such as $\text{Bi}_4\text{O}_5\text{I}_2$, $\text{Bi}_7\text{O}_9\text{I}_3$ and $\text{Bi}_5\text{O}_7\text{I}$ [1–5]. The formula of these compounds can be generalized as $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$ ($x = 1, 0.5, 0.428, 0.2$, etc.), in which iodine anions are regarded as the intercalators in the interweaved space of bismuth oxides. Meanwhile, most bismuth oxide polymorphs display visible light photocatalytic activity, including α , β , γ and δ - Bi_2O_3 [6–12]. However, these $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$ or Bi_2O_3 compounds are greatly restricted by the poor stability during the photocatalytic degradation of organic pollutants. The frequent transformation product is bismuth oxide carbonates ($\text{Bi}_2\text{O}_2\text{CO}_3$), because of its relatively negative formation enthalpy and the available carbonates generated from dissolved CO_2 or the mineralization of organics in aqueous solution [13]. However, the appearance of the wide bandgap $\text{Bi}_2\text{O}_2\text{CO}_3$ ($E_g = 3.31$ eV) would

significantly decrease the visible light photocatalytic activity. However, $\text{Bi}_2\text{O}_2\text{CO}_3$ is a more stable photocatalyst with a similar layered crystal structure as BiOI , in which carbonate anions intercalate in the interlayer of $[\text{Bi}_2\text{O}_2]^{2+}$ structure [14,15]. It can be expected that the intercalation of iodine anions is possible to tune the band structure of $\text{Bi}_2\text{O}_2\text{CO}_3$. Such anion intercalation strategy has been regarded as a promising way to develop novel photocatalysts, such as $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ [16].

Some BOB compounds, like δ - Bi_2O_3 , have the potential to incorporate iodine anions and transform into iodine containing BOB compounds, which is represented by the technology to capture and store radioactive iodine in nuclear waste [17–19]. On the other hand, upon calcinations the bounded iodine anions in the lattice of bismuth oxyiodide tend to diffuse out and produce a series of nonstoichiometric $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$ compounds with defects [1]. Generally, the decrease of iodine in bismuth oxyiodides would result in the downward shift of valence band potentials and the increase of oxidation ability of photogenerated holes, while also enlarge band gaps and decrease the ranges of responsive light [1,4]. Among bismuth oxyiodides, $\text{Bi}_7\text{O}_9\text{I}_3$ and $\text{Bi}_4\text{O}_5\text{I}_2$ display the highest photocatalytic activity [4]. However, there is a great potential to further optimized x value to balance the oxidation power and optical absorption, but a strategy is demanded to realize it before the production of $\text{Bi}_5\text{O}_7\text{I}$.

Fabricating semiconductor heterostructures is an important way to develop photocatalysts with minimized weakness and

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maximized strength [20–27]. Comprising of hetero components with matchable band potentials but random contact forms show improved photogenerated charge separation, such as β - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{O}_2\text{CO}_3$ [23], $\text{Bi}_2\text{O}_2\text{CO}_3/\text{BiOI}$ [24]. Moreover, confining the intrinsically unstable material with a layer of hetero compound is an effective strategy to enhance the stability [28]. Herein, according to the interaction between inner bismuth oxyiodide and surface carbonate at elevated temperatures, a heterostructure of nonstoichiometric $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$ covered with iodine intercalated $\text{Bi}_2\text{O}_2\text{CO}_3$ was developed through a treatment of $\text{Bi}_7\text{O}_9\text{I}_3$ in urea solution and subsequent calcinations. Benefiting from the unique structural feature and the proper iodine content in $\text{Bi}_2\text{O}_{3-x}\text{I}_{2x}$, the synthesized heterostructure exhibits significantly enhanced photocatalytic activity and stability in organic degradation.

2. Experimental

2.1. Sample synthesis

$\text{Bi}_7\text{O}_9\text{I}_3$ was synthesized by a solvothermal method [1–3]. Briefly, 2.5 mmol bismuth nitrate dissolved in 24 mL ethylene glycol, then an equal amount of KI was added into the mixture. The final solution was sealed in a 30 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 12 h. The final orange powder was filtered, washed with de-ionized water repeatedly and then dried in an oven. As prepared $\text{Bi}_7\text{O}_9\text{I}_3$ was performed an in situ transformation by introducing $\text{Bi}_7\text{O}_9\text{I}_3$ powder into a 0.2 M urea solution and stirring at 90 °C for different durations. The obtained products were dried and assigned as BCOI-*t* (*t* is the treating time). BCOI-*t* precursors were calcined by ramping to temperature *T* at a rate of 1 °C/min and holding for 2 h. The resulting products were assigned as BCOI-*t-T*. The untreated $\text{Bi}_7\text{O}_9\text{I}_3$ and the calcined $\text{Bi}_7\text{O}_9\text{I}_3$ at 350 °C (assigned as $\text{Bi}_7\text{O}_9\text{I}_3$ -350) were used as control samples. Moreover, $\text{Bi}_2\text{O}_2\text{CO}_3$ was synthesized for comparisons through a precipitation method [24]. Briefly, 2.425 g bismuth nitrate was dissolved in a 5 mL nitric acid aqueous solution (1 M) to obtain the solution A, and 0.25 g cetyltrimethyl ammonium bromide (CTAB) and 40 mmol sodium carbonate were dissolved in 70 mL water to obtain the solution B. Solution A was dropwise added into solution B to obtain the precipitation, which was filtered, washed and dried at 80 °C for 4 h.

2.2. Characterizations

Ratios of Bi to I were calculated from the data of elemental analyses, which were collected on an X-ray fluorescence analyzer (XRF-1800, Shimadzu). The thermal stability was investigated by a thermogravimetric-differential thermal analyzer (TG-DTA, TGA/DSC 1, Mettler Toledo) in an air atmosphere at a flow rate of 50 mL/min. The heating program was set as: ramping at 5 °C/min to 200 °C, 350 °C, 400 °C and 450 °C continuously, and holding at each point for 30 min; finally ramping to 600 °C at the same rate. The crystal phases of catalysts were analyzed using powder X-ray diffraction (XRD, D/max-2200, Rigaku Corp.) with Cu K α radiation, operating at 40 kV 30 mA ($\lambda = 0.154$ nm). Diffuse reflectance spectra (DRS) were recorded on a Lambda 950 UV/vis spectrophotometer (PerkinElmer Instrument Co., Ltd.), and the reflectance was converted into absorption by the Kubelka–Munk method. X-ray photoelectron spectroscopy (XPS) measurements were performed

on a Kratos AXIS Ultra DLD instrument with the monochromatic Al K α radiation ($h\nu = 1486.6$ eV). A high resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL, Japan) was used to observe the morphology of catalysts.

2.3. Photoelectrochemical and photocatalytic tests

Photoelectrodes were prepared by coating the pastes of BCOI-1-350 or $\text{Bi}_7\text{O}_9\text{I}_3$ -350 onto a slice of FTO glass through the doctor blade method [29,30]. The photoelectrochemical test system was composed of a CHI 606E Potentiostat/Galvanostat, a 500 W xenon lamp, and a homemade three-electrode cell. The as prepared photoelectrode, a platinum wire and a Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. The exposed area of the photoelectrodes under illumination was 0.785 cm². The electrolyte solution was a 0.5 M Na₂SO₄ aqueous solution, which was bubbled with N₂ gas for 30 min before tests. A 420 nm cutoff filter was utilized in specific conditions. The photocurrent transients were taken at a bias of +0.2 V vs. Ag/AgCl.

The photocatalytic activity was evaluated by phenol degradation under visible light from a 1000 W xenon lamp with a cutoff filter ($\lambda > 400$ nm). In a typical test, 0.05 g catalyst was added into a 50 mL phenol solution (initial concentration 10 mg/L). The suspension was stirred in the dark for 15 min to reach adsorption equilibrium before being exposed to visible light irradiation. During irradiation, the samples were taken at regular time intervals, filtered, and then monitored using a colorimeter on a UNICO UV-2102 spectrometer.

2.4. Theoretic calculations

First-principles calculations were performed by density functional theory (DFT) method using a plane-wave basis set, and implemented using Quantum ESPRESSO [31]. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional, and norm-conserving pseudopotentials are used for all calculations. Wave functions were expanded in plane-waves with a kinetic energy cutoff of 80 Ry and 320 Ry for the smooth and augmented part of density, respectively. Orthorhombic $\text{Bi}_2\text{O}_2\text{CO}_3$ ($a = 3.865$; $b = 3.862$; $c = 13.675$; $\alpha = \beta = \gamma = 90^\circ$) and their corresponding compounds with iodine substitute for carbonate (the ratio of Bi/I is 64 or 32) were modeled and calculated. Calculations were carried out on $2 \times 1 \times 2$ supercells at the Γ point of the Brillouin zone for the calculations of iodine containing cases. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) geometry optimization scheme was performed until forces and total electron energy converged below 0.005 eV Å⁻¹ and 10⁻⁵ Ry, respectively.

3. Results and discussion

3.1. Characterizations of BCOI-*t*

Microsphere nanocrystal $\text{Bi}_7\text{O}_9\text{I}_3$ was synthesized by ethylene glycol solvothermal method, whose Bi/I ratio was determined as 2.36 by XRF analyzer, and whose characteristic peak at 28.9° was quite different from the (1 0 2) plane of tetragonal phase BiOI (JCPDS 10-0445) at 29.7° (Fig. 1) [32]. Subsequently, $\text{Bi}_7\text{O}_9\text{I}_3$ powder was stirred in a urea solution at 90 °C. The hot urea solution is known

Table 1
Bismuth and iodine molecular ratios and $\text{Bi}_7\text{O}_9\text{I}_3$ percentages.

Catalysts	$\text{Bi}_7\text{O}_9\text{I}_3$	BCOI-05	BCOI-1	BCOI-2	BCOI-4	$\text{Bi}_7\text{O}_9\text{I}_3$ -350	BCOI-1-350	BCOI-2-350
Molecular ratio (Bi/I)	2.36	3.81	4.60	7.08	21.32	2.80	5.14	6.95
$\text{Bi}_7\text{O}_9\text{I}_3$ molecular percentage (%)	100	31.1	22.7	12.3	3.4	–	–	–

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