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Full Length Article

Study of $PbBiO_2X$ (X = Cl, Br and I) square nanoplates with efficient visible photocatalytic performance

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ABSTRACT

Three new type of single crystallite $PbBiO_2X$ (X = Cl, Br and I) square-like nanoplates with several hundreds nanometers in length are synthesized via a simple hydrothermal method. The band structure and behavior of charge carriers for the nanoplates are investigated experimentally and theoretically. The halogen elements are closely related to the indirect narrow band gap(2.61 eV, 2.51 eV and 2.38 eV for $PbBiO_2Cl$, $PbBiO_2Br$ and $PbBiO_2I$, respectively). The $PbBiO_2X$ square-like nanoplates exhibit improved photocatalytic performance on degradation of organic pollutant under visible irradiation, owing to their novel nanostructure and efficient photoelectric conversion. This work demonstrates that $PbBiO_2X$ nanoplates can be considered as a promising photocatalyst and offer a better understanding about other halogen group elements related semiconductors.

1. Introduction

Semiconductor photocatalysis is usually regarded as one of the most efficient and promising methods for solar energy conversion and environmental pollution [1–4]. Titanium dioxide has attracted lots of attention during the last few decades [5–8]. However, up to now, the photocatalytic application of TiO_2 is still limited by its large band gap and poor response to visible light. Hence, it is of great importance to develop new type of semiconductor photocatalysts which are sensitive to visible light. Recent years, $PbBiO_2X$ (X = Cl, Br and I) has drawn some attention owing to their narrow band gap and unique layer structures. Füldner et al. found $PbBiO_2X$ (X = Cl, Br and I) exhibit selective, clean and complete photocatalytic reduction of nitrobenzene derivatives[9]. Shen et al. synthesized RuO_2 over $PbBiO_2Cl$ with improved photocatalytic performance on degradation of MO (Methyl Orange) [10]. Xiao et al. prepared $PbBiO_2Br$ micro-spheres with improved photocatalytic activity on degradation of MO[11]. Li et al. prepared new $PbBiO_2Br$-SOF-$NbSe_2$ nanocomposite with enhanced photocatalytic activity under visible irradiation[12]. Recently, we reported a simple synthesis of $PbBiO_2Cl$ truncated bipyramid nanostructure with improved visible photocatalytic activity [13]. However, to my knowledge, it is still a great challenge to fabricate and develop uniform and well-defined $PbBiO_2X$ nanostructures with specific exposed facets. Moreover, it remains uninvestigated about the relationships between halogen elements and band structure, photocatalytic activity, behavior of charge carriers as well as the surface micro-structure for $PbBiO_2X$.

In this work, a series of $PbBiO_2X$ (X = Cl, Br and I) square nanoplates with exposed {001} facets are prepared by a simple hydrothermal method. The crystal structure, morphology and band structure as well as the behavior of photogenerated electrons and holes are investigated systematically. Moreover, the electronic band structures and density of states for $PbBiO_2X$ (X = Cl, Br and I) are also studied in details. It is found that $PbBiO_2Cl$ and $PbBiO_2Br$ exhibit improved photocatalytic activity on degradation of MO under visible irradiation, compared with $PbBiO_2I$.

2. Experimental details

2.1. Sample preparation

The $PbBiO_2X$ (X = Cl, Br and I) nanoplates are synthesized via a simple hydrothermal method. 0.191 g of lead acetate and 0.245 g of bismuth nitrate were added into the mixture of 15 mL of deionized

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water, 1.5 mmol of NaX (0.088 g of NaCl for $PbBiO_2Cl$; 0.155 g of NaBr for $PbBiO_2Br$; 0.227 g of NaI for $PbBiO_2I$) and 2 mL of ethylene glycol. Then 5 mL of sodium hydroxide (1 mol/L) was added into the mixture. After stirring for 30 min, the mixture was transferred into a 25 mL Teflon-lined stainless autoclave and heated at 180 °C for 24 h. After cooling to room temperature, the obtained participates were washed with deionized water for six times and then dried at 60 °C. For the $PbBiO_2X$ (X = Cl, Br and I) prepared by solid state method, the mentioned above mixtures are dried at 100 °C for ten hours and calcined at 800 °C for 2 h to obtain nanoparticles.

2.2. Calculation

The calculation was performed by using a first-principle calculation software package CASTEP. Generalized gradient approximation (GGA)-based density functional theory (DFT) was used to calculate electronic band structure band structure and density of states (DOS) for $PbBiO_2X$ (X = Cl, Br and I). The plane wave cutoff was set to be 340 eV and the k-point set was $6 \times 6 \times 2$. The valence electronic configurations for Pb, Bi, O, Cl, Br and I were $5d^{10}\ 6s^2\ 6p^2$, $6s^2\ 6p^3$, $2s^2\ 2p^4$, $3s^2\ 3p^5$, $4s^2\ 4p^5$ and $5s^2\ 5p^5$, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were acquired on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Kα, λ = 1.54056 Å). High-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL 3010, for which the samples were prepared by applying a drop of ethanol suspension onto an amorphous carbon-coated copper grid and dried naturally. The scanning electron microscopy images (SEM) were taken on a LEO 1530vp SEM. Diffuse reflectance UV–visible absorption spectra were collected on a UV–visible spectrometer (UV-1061PC, Shimadzu). Photoluminescence (PL) spectra and the time-resolved PL decay curve were acquired by using a time-resolved spectrofluorometer with the femtosecond (fs) laser system and an intensified CCD camera (ICCD) spectrograph (LAVISION, PicoStar HR12 Camera System). The fs laser pulse (800 nm, 120 fs, 1 kHz) was amplified to a fs laser pulse (400 nm, 120 fs, 1 kHz) by a regenerative amplifier. X-ray photoelectron spectroscopy (XPS) was carried out with a SECA Lab 220i-XL spectrometer using an unmonochromated Al Kα (1486.6 eV) X-ray source. Photocurrent measurements were performed on a CS 300 electrochemical workstation(CorrTest, Wuhan, China) in a conversional three electrode configuration with a Pt foil as the counter electrode and a Ag/AgCl (saturated KCl) reference electrode. A 500 W Xe arc lamp severed as a light source. A 1 M Na_2SO_4 aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 10 mg of the prepared photocatalyst was added into 1 mL of ethanol to make slurry under ultrasonic treatment. The slurry was then spread on a $2 \times 1\ cm^2$ ITO glass substrate with an active area of about $1\ cm^2$ by the doctor-blade method, using adhesive tape as the space. The film was dried in air and annealed at 400 °C for 60 min in air. The photoresponses of the samples as light on and off were measured at 0.0 V.

2.4. Evaluation of photocatalytic activity

The photocatalytic degradation of methyl orange (MO) was carried out in a 150 mL glass reactor with 50 mg amounts of catalysts suspended in MO solution (100 mg/L, 100 mL). A sunlamp (Philips HPA 400/30S, Belgium) was used as the light source. The reactor was perpendicular to the light beam and located 15 cm away from the light source and a 420 nm cutoff filter was applied to remove the UV light. The MO solution was continuously bubbled by O_2 gas at a flux of 5 mL min^{-1} under magnetic stirring at 25 ± 2 °C. Before irradiation, the suspensions were stirred at room temperature in the dark for half an hour. The residual concentration of MO was measured by a UV–visible spectrometer (UV-1061PC, SHIMADZU).

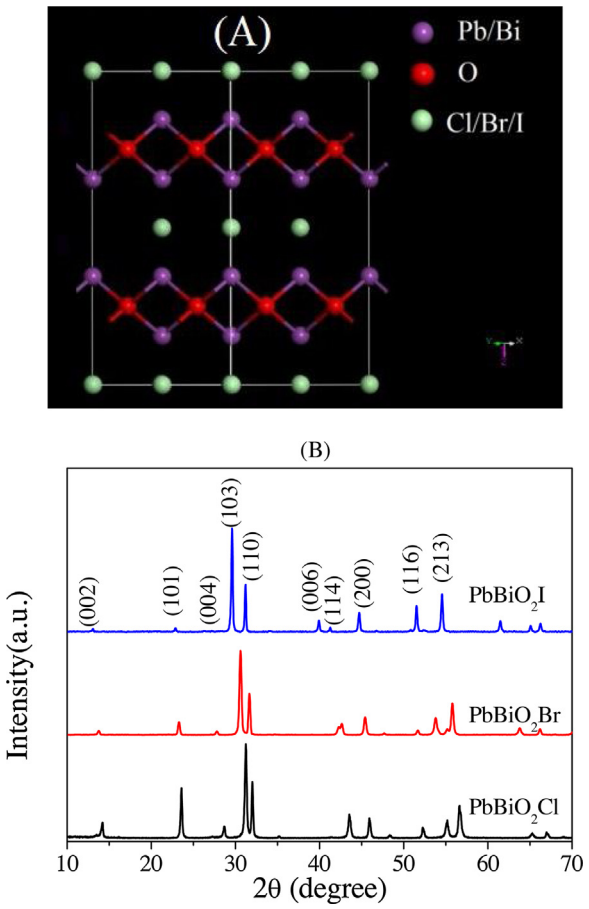

Fig. 1. Crystal structure along [110] and XRD patterns of $PbBiO_2X$ (X = Cl, Br and I).

3. Results and discussion

Fig. 1A shows the crystal structure of $PbBiO_2X$ (X = Cl, Br and I) along [110] direction. It is noted that $PbBiO_2Cl$, $PbBiO_2Br$ and $PbBiO_2I$ are isotypic and crystallize tetragonally in space group of *I4/mmm* (No.139) [9,14]. The $PbBiO_2X$ consists of a layered structure with [$PbBiO_2$] slab interleaved by a slab of halogen ions (Cl, Br and I) along the Z axis. For metal oxide slabs [$PbBiO_2$], lead and bismuth ions are distributed statistically at the same position with mixed occupancy (0.5:0.5). It is found from Fig. 1A that each metal ion (Bi^{3+} or Pb^{2+}) is surrounded by four oxygen atoms and four halogen atoms (Cl, Br or I) in a longer distance. XRD patterns are carried out to confirm these crystal structures of $PbBiO_2X$ (X = Cl, Br and I), which are plotted in Fig. 1B. All three samples can be indexed to the tetragonal structure of $PbBiO_2Cl$ (JCPDS No.39-0802), $PbBiO_2Br$ (JCPDS No.38-1008) and $PbBiO_2I$ (JCPDS No.78-0521), respectively. The high and sharp peak patterns for all samples suggest the high crystallinity of $PbBiO_2X$ (X = Cl, Br and I) prepared by this hydrothermal method. The lattice parameters, cell volumes and crystal sizes are also evaluated and shown in Table 1. It is found that the lattice parameters and cell volume increase in the order of $PbBiO_2Cl$ < $PbBiO_2Br$ < $PbBiO_2I$. This can be attributed to different sizes of ionic radius for halogen ions (Cl^- (181 pm) < Br^- (195 pm) < I^- (216 pm)).

The morphology of the $PbBiO_2X$ (X = Cl, Br and I) nanostructures are investigated by SEM and TEM, as shown in Fig. 2. Inset