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Fabrication of hierarchical bismuth oxyhalides (BiOX, X = Cl, Br, I) materials and application of photocatalytic hydrogen production from water splitting

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ABSTRACT

In this article, bismuth oxyhalides (BiOX) have been demonstrated to have remarkable photocatalytic activities due to their uniquely layered strusctures. Hierarchical BiOX (X: Cl, Br, I) microspheres were successfully synthesized by a microwave-assisted solvothermal method from bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) using ethylene glycol and ethanol as solvents. The structures, morphology, and optical properties of the grown BiOX nanostructures were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), UV–visible diffuse reflectance spectra (DRS), electrochemical impedance spectroscopy (EIS), photoluminescence spectra (PL), and Brunauer-Emmett-Teller (BET) surface area. SEM revealed BiOX to have flower-like structures of microspheres and the as-synthesized photocatalysts were tested for the photocatalytic hydrogen evolution from water splitting via the irradiation of visible light. Among BiOXs as synthesized, BiOI can achieve the maximum hydrogen produciton rate (1316.9 $\mu mol\ h^{-1}\ g^{-1}$) in 360 min under visible light irradiation because BiOI not only has a lowest PL intensity than the other BiOX group of materials to better separate the photogenerated electrons and holes, but also a sufficient over-potential of conduction band to achieve the conversion from H^+ to H_2.

1. Introduction

The technology of semiconductor-based photocatalytic water splitting, photoelectro-chemically splitting water into H_2 and O_2, has been considered as one of the most important approaches to achieve the conversion from solar energy to hydrogen energy [1]. In addition, much effort has been devoted in recent years to develop high activity heterogeneous photocatalysts for environmental applications, such as air purification, water disinfection, hazardous waste remediation, and wastewater treatment [2]. Bismuth oxyhalides (BiOX, X = F, Cl, Br, and I) have been studied recently due to their hierarchical structures (unique layered structure), adequate chemical stability, and superior photocatalytic activity as photocatalysts for water splitting and their ability to decompose toxic pollutants into harmless inorganic substances upon solar light irradiation [3–5]. The combination of $NaBiO_3$ and BiOCl has a higher photocatalytic activity compared with single $NaBiO_3$ or BiOCl photocatalyst, due to more effective photo-excited electron-hole separation by the heterojunction semiconductor structure [6]. Thin film of BiOBr showed high photocatalytic activity in the degradation of RhB due to {001} facets, which are the more active planes [7]. The CNT-BiOI electrode would have an advantage for simultaneously achieving an enhanced electricity generation efficiency and degradation efficiency for recalcitrant organic pollutants [8]. BiOI also has a tetragonal crystal structure with exposed {001} facets, which is favorable to enhance the visible-light photocatalytic reaction [9]. In addition, the photocatalytic activities of the composite photocatalysts, such as $BiOCl_xBr_{1-x}$, $BiOCl_xI_{1-x}$, and $BiOBr_xI_{1-x}$, were much stronger than the of the individual compounds (BiOCl, BiOBr, and BiOI) [10]. Up to now, the synthesis of the bismuth oxyhalide composite photocatalysts is still challenging because of the difficulty to obtain the tunable band gaps and the controllable morphological structures by an inexpensive and simple-operation method [10]. The microwave-assisted hydrothermal/solvothermal process is advantageous over the conventional hydrothermal process in synthesizing some metal oxide phases. Some significant advantages are: (i) it can increase the reaction rate by one to two orders of magnitude, (ii) it can lead to novel phases, (iii) it can eliminate metastable phases, and (iv) it can lead to a rapid heating. Rapid heating along with rapid kinetics can also lead to energy savings [11]. Therefore, bismuth oxyhalide hierarchical microspheres (BiOX, X = Cl, Br, and I) and composite photocatalysts ($BiOCl_xBr_{1-x}$, $BiOCl_xI_{1-}$

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$_x$, and $BiOBr_xI_{1-x}$) were prepared in this work via a facile one-pot microwave-assisted solvothermal synthesis using the solvent mixture containing EG and EtOH at the ratio of 75%:25%, where it has been reported at our earlier publication [12]. In addition, we explored its catalytic performance by photocatalytic splitting of water via the irradiation of visible light. The major factors, such as the pH values of water, the dosages of bismuth oxyhalide photocatalyst, and the different types of bismuth oxyhalide composite photocatalysts, to affect hydrogen evolution efficiency via photocatalytic splitting of water were also evaluated. To the best of our knowledge, this is the first report by comparing the photo-splitting of water with bismuth oxyhalide composite photocatalysts.

2. Experimental details

2.1. Materials

All chemicals were of the highest purity available and were used as received without further purification. Bismuth (III) nitrate pentahydrate [$Bi(NO_3)_2 \cdot 5H_2O$], potassium chloride (KCl), potassium bromide (KBr), and potassium iodide (KI) were respectively obtained from Acros. Yakuri Pure Chemical, Merck, and Shimakyu. Ethylene glycol ($HOCH_2CH_2OH$, EG), polyethylenglycol (PEG, molecular weight = 20,000), and ethanol (C_2H_5OH, EtOH) were purchased from FERAK Inc. Unless otherwise specified, all the reagents used were of analytical grade and the solutions were prepared by using de-ionized water from Millipore water purification system (18.2 MΩ).

2.2. Synthesis of hierarchical BiOX microspheres

Under vigorous stirring, 3 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 3 mmol KX (X = Cl, Br, I) were completely dissolved in 80 mL of the solvent mixture containing EG and EtOH at the volume ratio of 75%:25%. Subsequently, 0.05 g PEG was added into the solution by continuous stirring to achieve complete reaction. Then, the obtained mixture was heated in the microwave reaction system (2450 MHz, 1800 W, MARS 6, CEM) at 450 W for various irradiation time (10, 20, 30, and 60 min) and temperature (120, 140, and 160 °C). Thus, formed precipitate was collected and washed with deionized water and ethanol several times, then dried at 60 °C in a vacuum oven overnight.

2.3. Synthesis of bismuth oxyhalide $BiOA_xB_{1-x}$ composite photocatalysts

In the synthesis of $BiOA_xB_{1-x}$ (A, B = Cl, Br, or I) composite photocatalysts, 3 mmol $Bi(NO_3)_3 \cdot 5H_2O$, 3 mmol KX (X = Cl, Br, I) (derived from two different kinds of sodium halides), and 0.05 g PEG were completely dissolved in 80 mL of the solvent mixture containing EG and EtOH at the ratio of 75%:25%. Then, the obtained mixture was heated in the microwave reaction system (2450 MHz, 1800 W, MARS 6, CEM) with the operating power of 450 W and working temperature of 160 °C for 20 min. Thus, formed precipitate was collected and washed with deionized water and ethanol several times, then dried at 60 °C in a vacuum oven overnight.

2.4. Characterization of bismuth oxyhalide photocatalysts

The morphologies of the photocatalysts were examined by using JEOL, JSM-7401F field emission scanning electron microscope (FE-SEM). The X-ray diffraction (XRD) patterns were recorded using Rigaku Ultima III diffractometer (Japan) with Cu-Kα radiation, in the scan angle 2θ ranged from 10° to 80°. High resolution transmission electron microscopic (HR-TEM) images were recorded using JEOL JEM-2010 model. The UV–vis diffuse reflectance spectra were recorded using a Shimadzu UV-2600 spectrophotometer with integrated sphere attachment and barium sulfate was used as a reference. The flat-band potential of as-synthesized product was measured by electrochemical impedance spectroscopy (EIS) recorded using a multichannel Potentiostat/Galvanostats with optional modularity instrument (PGSTAT302N, Metrohm, Autolab). As synthesized catalyst deposited on the indium tin oxide conductive glass (ITO), Pt wire, and Ag/AgCl electrode were employed as working electrode, counter electrode, and reference electrode, respectively. Photoluminescence (PL) properties were measured at room temperature using a Shimadzu RF-3501 spectrometer excited at 400 nm. The Brunauer-Emmett-Teller (BET) surface area, pore size, and pore volume of the catalysts were measured by a nitrogen adsorption method using a Micrometrics ASAP-2020 instrument. Prior to analysis, 0.5 g of powder was degassed at 120 °C for 15 h.

2.5. Hydrogen evolution

The reaction was performed in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. The varying amounts of catalysts from 0.1 g/L to 0.4 g/L were dispersed in 100 mL deionized water. The experiments were carried out at different pH (3, 5, 7, and 9) under ambient condition. Before light irradiation, argon was purged through the reactor to remove dissolved air including nitrogen and oxygen. For light irradiation, the photocatalytic reactor was illuminated with a 350 W xenon light source having a cutoff filter that only allows visible light ($\lambda \geq 400$ nm) to pass. The evolved hydrogen amount was determined by an on-line TCD gas chromatography (GC-2014, SHIMADZU). The photocatalytic activities were compared by the average hydrogen evolution rate in the first 6 h.

3. Results and discussion

3.1. Characterization of bismuth oxyhalide composite photocatalysts

According to our previous report, many factors in the reaction, such as reaction time, reaction temperature, and solvent ratio, can affect the morphology of the self-assembled BiOBr particles [12]. In this work, the obtained solution was transferred into a 100 mL EasyPrep Teflon vessel via a facile one-pot microwave-assisted solvothermal procedure with various irradiation time and temperature. The morphologies of self-assembled BiOI particles in time sequence are shown in Fig. 1. From the FE-SEM image, results can be known for the formation of rough microspheres in 10 min. When the irradiation time was used for 20 min, the flower-like hierarchical BiOI microspheres were formed as shown in Fig. 1b. However, as the reaction time prolonged at 30 min to 60 min, the morphology of BiOI particles became more irregular, even agglomerated particles were formed as shown in Fig. 1c and d. Reaction temperature is the other key factor for fabricating BiOX (X = Cl, Br, I) particles. Fig. 2 displays the FE-SEM images of BiOI carried out from 120 to 160 °C, the amount of BiOI particles gradually formed homogeneous microstructure and uniform size particles as the reaction temperature rose. Based on the results, experimental condition at 160 °C for 20 min at microwave-assisted solvothermal synthesis was selected to produce bismuth oxyhalide composite photocatalysts.

From the XRD results as shown in Fig. 3, the observed major diffraction peaks at 19.64°, 25.46°, 33.04°, 42.56°, 46.82°, and 58.36° belong to (-111), (021), (-122), (122), (-302), and (-143) planes of Bi_2O_3 nanostructure and it is matching well with the monoclinic bismite phase structure (JCPDS card No. 41-1449, the cell parameters of a = 5.8499 Å). Furthermore, the major diffraction peaks of the BiOCl nanostructure clearly shows the crystalline nature with assigned to the major diffraction angles 25.80°, 32.54°, 33.46°, 40.88°, and 46.70° for (011), (110), (012), (112), and (020) planes, respectively. The diffraction peaks indicate the tetragonal phase of BiOCl structure (JCPDS card No. 73-2060, the cell parameters of a = 3.883 Å). The major diffraction peaks at 25.22°, 31.66°, 32.24°, 46.34°, and 57.20° belong to (101), (102), (110), (200), and (212) planes of BiOBr nanostructure and it is matching well with the tetragonal phase structure (JCPDS card No. 85-