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Enhanced usage of visible light by $BiSe_x$ for photocatalytic degradation of methylene blue in water via the tunable band gap and energy band position

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ABSTRACT

The increasing demand for new materials with narrow bandgap energy, capable of harvesting the photons in the visible range, is central in the remediation of environmental pollutants by photocatalytic reactions. For the first time, we report a novel visible light driven photocatalyst of $Bi_2Se_3/Bi_{1.007}Se_{0.993}$ by the formation of solid solution composite. Both the individual Bi_2Se_3 and $Bi_{1.007}Se_{0.993}$ have very low photocatalytic efficiency under visible light irradiation; however, $Bi_2Se_3/Bi_{1.007}Se_{0.993}$ provides much higher efficiency in decomposing methylene blue (MB). Especially in the presence of H_2O_2, the reaction rate was enhanced by 15 times and 100% of MB degradation was obtained in 90 min. Characterization results confirmed that the bandgap of $Bi_2Se_3/Bi_{1.007}Se_{0.993}$ was greatly broadened to 1.38 eV compared with Bi_2Se_3 of 0.3 eV, which matched well with visible range. Moreover, the relative conduction band position vs. NHE of $Bi_2Se_3/Bi_{1.007}Se_{0.993}$ was −0.3 V, which was more negative than that of $Bi_{1.007}Se_{0.993}$ of +0.2 V. It was responsible to the excellent photocatalytic activity due to harvesting the photons in the visible range. Finally, N-type semiconductor based reduction O_2 to $O_2^{\bullet-}$ and photoreduction of H_2O_2 into $^{\bullet}OH$ involved reaction mechanism under the visible light irradiation was proposed based on all the experimental results.

1. Introduction

Environmental contamination caused by organic pollutants is one of the most pressing problems all over the world. Among the multifarious organic pollutants, textile dyes and other industrial dyestuffs constitute one of the largest groups(Chen et al., 2010). Most of the commercial dyes are designed to resist photo-degradation, and many of them cannot be decomposed by the applied microbial processes (Meehan et al., 2000). The great present interest is to use solar light which is free and inexhaustible (Lachheb et al., 2002). Hence, remediation of environmental pollutants by photocatalytic reaction has attracted extensive attention to address global challenges related to energy and water scarcity in the last few decades (Chen et al., 2010; Cheng et al., 2016; Ge et al., 2016; Liu et al., 2016; Shannon et al., 2008). TiO_2 is well known as the most efficient photocatalyst, but it can only use the photons in UV range (accounts for 5% of the sun's energy) due to its wide bandgap (3.2 eV) (Guo et al., 2016; Hadnadjev-Kostic et al., 2017; Hu et al., 2017; Safardoust-Hojaghan and Salavati-Niasari, 2017). Thus, it is desirable to develop a photocatalyst using the entire visible region of the solar spectrum (Dai et al., 2015; Zhang et al., 2015).

Narrow bandgap semiconductors capable of harvesting the photons in the visible range have drawn great attention and exhibit high visible light photocatalytic activity by formation of hetero-junction with TiO_2, such as $FeTiO_3$, Ag_3PO_4, $W_{18}O_{49}$,WO_3, Bi_2WO_6 and Sb-doped SnO_2 etc (Chen et al., 2016; Ju et al., 2014; Meng and Zhang, 2016; Sotelo-Vazquez et al., 2017; Xu et al., 2011). However, their utilization efficiency for visible light was limited due to their relative higher band gap (<3.0 eV) than the optimum theoretical value of about 1.5 eV (which can covers all the visible-light area of the solar spectrum).

Bismuth selenide has attracted great attention in physics and chemistry because of its remarkable thermoelectric, optical and photoelectric properties, which has been widely investigated in fields including topological insulators, thermoelectric devices and Li-ion batteries (Han et al., 2014; Jin et al., 2013; Kadel et al., 2011; Li et al., 2013; Min et al., 2013; Sun et al., 2010; Zhang et al., 2009b;

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Zheng et al., 2015). It is also biocompatible and then studied for simultaneous cancer imaging and therapy (Li et al., 2013). Bismuth selenide can be synthesized via different methods such as hydrothermal (Cui et al., 2004), solvothermal (Han et al., 2014), CVD (Yan et al., 2013), reduction and colloidal methods (Jiang et al., 2016; Liu et al., 2005). Among all these methods, solvothermal method needs a relative lower reaction temperature of about 160–200 °C and more easy to enlarged production, which was more commonly used. But few studies were reported about its direct application as a visible light driven photocatalyst due to the quick photo-generated electron-hole recombination as a result of narrow band gap (Chen et al., 2016). Hence, it is a big challenge to expand the band gap of bismuth selenide and increase its visible-light-driven photocatalytic activity.

To solve such problem, techniques such as transition-metal or chalcogens doping, combing with wide band gaps semiconductors and formation of solid solutions can be employed (Ji et al., 2009). Researchers have tried to enhance the photocatalytic performance of bismuth selenide by inducing cocatalysts of sulphur or nickel (Kulsi et al., 2017; Song et al., 2011). This strategy can increase the band gap energy of bismuth selenide, in which S and Ni may retard the recombination of photogenerated carriers by acting as electron trap (Kulsi et al., 2017; Song et al., 2011). The construction of heterostructure, such as Bi_2Se_3/CdS/TiO_2, also to help or coordinate the band-edge levels to infrared (NIR) light area (Hu et al., 2006; Zhang et al., 2012). However, the heavy metal such as Cd was also not environmentally friendly, which may cause secondary pollution (Tanong et al., 2017; Ward et al., 1977). However, at present, none of these reports gives sufficient information of controlling the band gap energy of bismuth selenide and the relationship between band gap energy and visible-light-driven photocatalytic activity. Moreover, the good photocatalytic activity depends not only on the suitable band gap energy, but also on the suitable band edge positions (Ji et al., 2009). For example, it is difficult for the photogenerated electrons to reduce the O_2 to $O_2^{\bullet-}$ if the conduction band position of the sample was more positive than the redox potential of $O_2/O_2^{\bullet-}$.

In this study, bismuth selenide was chosen as a representative to broaden the bandgap from 0.3 eV to 1.38 eV by the composition regulation between Se and Bi. Not only bandgap but also band edge position had a great effect on the catalytic activity. Methylene blue (MB) is a cationic dye which exhibits two major absorption bands at 293 (π-π^*) and 664 (n-π^*) nm in dilute aqueous solutions (Heger et al., 2005). It is a basic thiazine dye used in histologic and microbiologic staining with potential life-threatening toxicity (Albert et al., 2003). Thus methylene Blue (MB) was used as a model contaminant to evaluate the visible-light photocatalytic activity of as prepared samples (Chen et al., 2010). Compared with the individual Bi_2Se_3 and $Bi_{1.007}Se_{0.993}$, the Bi_2Se_3/$Bi_{1.007}Se_{0.993}$ showed a higher visible-light-driven photocatalytic activity, especially in the presence of H_2O_2, the MB degradation rate was enhanced by about 15 times. Plus, the synthesis temperature of the solid solution was 130 °C, which means a lower cost in production. Finally, the bismuth selenide based photocatalytic reaction mechanism was also proposed based on all the experimental results. In general, this study provides a novel strategy for the application of narrow bandgap semiconductors in visible-light-driven photocatalytic process.

2. Experiment

2.1. Materials

Potassium selenocyanoacetate ($NCSeCH_2COOK$) was purchased from Wuhan SunEn-Tech Co., Ltd. Other chemicals are from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade and used without further purification.

2.2. Synthesis of Bi_2Se_3/$Bi_{1.007}Se_{0.993}$ solid solution

Typically, the desired amount of hexahydrate bismuth nitrate ($Bi(NO_3)_3 5H_2O$) and cetanecyl trimethyl ammonium chloride (CTAC) were dispersed in 30 mL ethylene glycol (EG) with stirring under ambient temperature. Then 3 g/20 mL KOH/EG solution was dropwise added to obtain a colorless solution. After that, another 30 mL EG dissolved with 4.5 mmol potassium selenocyanoacetate ($NCSeCH_2COOK$) was dropwise added to the upper solution. The final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The crystallization process was carried out under autogenous pressure at 130 °C for 20 h. After the autoclave was cooled and depressurized, the products was taken out and washed 3 times by deionized water and ethanol, collected by centrifuge and dried in a vacuum oven at 50 °C for 12 h.

For comparison, Bi_2Se_3 and $Bi_{1.007}Se_{0.993}$ were synthesized as followed. Bi_2Se_3: 3 mmol of hexahydrate bismuth nitrate ($Bi(NO_3)_3 5H_2O$) and cetanecyl trimethyl ammonium chloride (CTAC) were dispersed in 3 g/50 mL KOH/EG solution with stirring under ambient temperature. After that, another 30 mL EG dissolved with 4.5 mmol sodium selenite (Na_2SeO_3) was dropwise added to the upper solution. The final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The crystallization process was carried out under autogenous pressure at 160 °C for 20 h $Bi_{1.007}Se_{0.993}$: 3 mmol of hexahydrate bismuth nitrate ($Bi(NO_3)_3 5H_2O$) and cetanecyl trimethyl ammonium chloride (CTAC) were dispersed in 3 g/50 mL KOH/EG solution with stirring under ambient temperature. After that, another 30 mL EG dissolved with 4.5 mmol potassium selenocyanoacetate ($NCSeCH_2COOK$) was dropwise added to the upper solution. The final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The crystallization process was carried out under autogenous pressure at 160 °C for 20 h.

2.3. Catalyst characterization

The chemical composition was determined by ICP-MS (iCAP Qc, Thermo Scientific) and AFS (230 E, Beijing Kechuang Haiguang Instrument Co., Ltd). The surface morphologies of the product were studied using Field Emission Scanning Electron Microscopy (FESEM, Hitachi S-4800). Low and high resolution transmission electron microscopy (TEM) images were taken on a high-resolution transmission electron microscope (HRTEM; Philips Tecnai G2 F30) with an energy dispersive spectrometer (EDX) analysis capability. X-ray diffraction (XRD) was used to characterize the crystalline structure of the product, which was carried out on a Rigaku D/max-βB diffractometer (Cu Ka X-ray radiation, $\lambda = 0.015432$ nm). The chemical compositions of these samples were investigated by X-ray photoelectron spectroscopy (XPS) (VG Multilab 2000 spectrometer with an Al Ka X-ray source, and the spectra calibrated to the C 1s peak at 284.8 eV). The specific surface areas of the samples were calculated by N_2 adsorption/desorption using the Brunauer-Emmett-Teller (BET, Micromeritics, ASAP 2020) method. A desorption isotherm was used to determine the pore size distribution by the Barrett-Joyner-Halenda (BJH) method. Prior to measurement the samples were degassed at 100 °C overnight under vacuum condition.

2.4. The catalytic activity of bismuth selenide evaluation

The catalytic activity of as-prepared bismuth selenide was evaluated by degradation of methylene blue (MB) solution