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Rapid microwave-assisted solvothermal synthesis and visible-light-induced photocatalytic activity of Er^{3+}-doped BiOI nanosheets

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ABSTRACT

BiOI nanosheet photocatalysts with different Er^{3+} doping contents were rapidly synthesized by microwave-assisted solvothermal method using water and ethylene glycol as a mixed solvent. All synthesized photocatalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), N_2 adsorption, photoluminescence (PL) spectra, and UV–vis diffuse reflectance spectroscopy (DRS). The photocatalytic activities of the as-prepared Er^{3+}-doped BiOI nanosheets were investigated by the photodegradation of Rhodamine B (RhB) dye in aqueous solution under visible light irradiation. The photodegradation results indicate the optimal doping of 1 mol.% Er^{3+} in BiOI nanosheets (doping content is from 0 mol.% to 4 mol.%) to be the most beneficial for photodegradation of RhB. 1Er-BiOI nanosheets also possesses good photocatalytic activity for representative anionic methyl orange (MO). From the scavenger testing results, the reactive species of holes (h^+) and superoxide radical anions ($^{\cdot}O^{2-}$) show major impacts on the photodegradation progress of RhB and MO dyes over 1Er-BiOI photocatalyst under visible light irradiation.

1. Introduction

A clean, secure source of water is essential for all activities of organisms on earth. However, in the recent century clean water source is being polluted by anthropogenic activities [1]. With the development of various industries, such as chemical, electroplating and paper industries, a big amount of wastewater including organic molecules, heavy metal ions and other pollutants are discharged to the rivers and lakes without appropriate treatment, which can not only lead to serious water pollution but also harm human health [2,3]. With the growing industries, a serious attention is urgently needed for clean environment and human health, technologies with high-efficiency, clean and low cost to decrease the pollutant concentration of wastewater. In recent years, semiconductor photocatalysis has been deemed to be one of the best alternative green ways for the purification of environmental pollution [4,5]. Classically, TiO_2 (3.03 eV for rutile-type and 3.2 eV for anatase-type), as one of wide band gap materials having unique advantages, such as low cost, long-term stability, unique chemical and physical properties [6,7], has been employed for the photocatalytic degradation of organic pollutants, including methyl orange (MO) [8–10], methylene blue (MB) [11], Rhodamine B (RhB) [12,13] and the reduction of the heavy metal ion, such as Cr (VI) [14]. However, TiO_2 reveals unsatisfactory visible-light photocatalytic activity due to the restricted visible light absorbance and the low quantum yield caused by the high recombination rate of photogenerated electron-hole pairs, which limit the development of TiO_2 in the field of photocatalysis.

In recent years, developing high efficiency photocatalysts to extend the absorption wavelength range into the visible light region has attracted a remarkable attention. Among the bismuth oxyhalides (BiOX, X = Cl, Br, and I), bismuth oxyiodide (BiOI) has the smallest band gap (~1.7 eV) and has been demonstrated to be an efficient and promising visible-light-driven photocatalyst for the photodegradation of organic pollutants [15,16]. Nevertheless, the activity of pure BiOI is still far away from the practical application due to its high recombination rate of photogenerated

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electron-hole pairs [17,18]. Therefore, many methods have been developed to enhancing the photocatalytic activity of BiOI under visible-light irradiation. Among them, it has been widely reported that the lanthanide ions (Er^{3+} [19], Eu^{3+} [20], etc) doping can effectively improve the photocatalytic performance of the BiOI photocatalysts under visible-light irradiation. Han et al. [19] synthesized Er^{3+}-doped BiOI porous microspheres via ethylene glycol-assisted solvothermal method and discussed the detailed photodegradation mechanism for the excellent photocatalytic activities of degradating MB, RhB and MO organic dyes. Dash et al. [20] reported the synthesis of hydrophilic poly vinyl alcohol (PVA)-functionalized Eu^{3+}-doped BiOX (X = Cl, Br, I) for the first time via green synthetic route employing microwave irradiation and the as-prepared samples showed high efficient photocatalytic activity for the degradation of RhB dye under visible light using a solar simulator. In summary, lanthanide ions doping can effectively enhance the photocatalytic performance of photocatalysts, which maybe mainly attributed to the reason that the lanthanide ions as efficient scavengers could trap the photogenerated electrons and thus suppress the recombination of photogenerated carriers [21,22]. In addition, compared with manifold ordinary chemical synthesis routes, the microwave-assisted solvothermal method can has many advantages, such as molecular level stirring, high heating speed, uniform heating without temperature gradient, narrow size distribution, uniform morphology and composition which can be tuned facilely [20,23,24].

In this work, we report on the fast synthesis of BiOI nanosheets with different Er^{3+} ion doping contents using microwave-assisted solvothermal method with distilled water and ethylene glycol as mixed solvent. The photocatalytic performance of Er^{3+}-doped BiOI nanosheets were evaluated by the RhB and MO under visible light irradiation. The possible mechanism of enhanced photodegradation of dyes over the Er^{3+}-doped BiOI nanosheet photocatalysts was also discussed in this work.

2. Experimental

2.1. Synthesis

All chemical reagents bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), erbium nitrate ($Er(NO_3)_3{\cdot}6H_2O$), potassium iodide (KI), ethylene glycol (EG), Rhodamine B (RhB), methyl orange (MO), etc.) purchased from Sinopharm Chemical Reagent Corp (Shanghai, China) are analytical grade without further purification. In this work, the Er^{3+}-doped BiOI nanosheet photocatalysts (the doping content range is from 0 to 4 mol.%) were prepared by microwave-assisted solvothermal method using deionized (DI) water and EG as the mixed solvents. Firstly, 2.82 mmol (1.3682 g), 2.79 mmol (1.3544 g), 2.76 mmol (1.3405 g), and 2.74 mmol (1.3267 g) of $Bi(NO_3)_3{\cdot}5H_2O$ were dissolved in 15 mL of EG, and then magnetic stirring for 40 min. 0.3 mmol (0.125 g) of $Er(NO_3)_3{\cdot}6H_2O$ were dissolved in 10 mL of EG under magnetic stirring for 40 min. At the same time, four series of KI were dissolved in 10 mL of EG, respectively, under magnetic stirring for 40 min. After that, 1, 2, 3, and 4 mL of $Er(NO_3)_3{\cdot}6H_2O$ solution were added dropwise into the former Bi-based solution respectively, and then the KI solutions were also added into the mixed solutions under continuous stirring. A certain amount of DI water was added into the above each mixed solutions (the final total volume of each mixed solution was 50 mL) under magnetic stirring for 30 min. Finally, the obtained reddish-brown mixed suspensions were transferred into 100 mL Teflon-lined stainless steel autoclaves of microwave hydrothermal parallel synthesizer (XH-800S, Beijing Xianghu Science and Technology Development Co., Ltd.) and then heated at 160 °C for 30 min under microwave irradiation with the power of 800 W. After cooling down to room temperature, the resultant precipitates were collected by centrifugation and washed several times with deionized water and ethanol. Finally, the obtained products were dried at 80 °C for 12 h. Similarly, pure BiOI photocatalyst was also prepared under identical synthesis procedure. The as-synthesized samples doped with different contents of Er^{3+} (from 0 to 4 mol.%) were designated as pure BiOI, 1Er-BiOI, 2Er-BiOI, 3Er-BiOI, and 4Er-BiOI, respectively.

2.2. Characterization

The crystallinity and phase of the samples were analyzed by using X-ray diffraction (XRD) measurements using a D/Max2550 diffractometer (Rigaku, Japan) with Cu Kα (λ = 1.5406 Å) operating at 40 kV and 50 mA at a scanning rate of $5^\circ{\cdot}min^{-1}$ in the range of 10–80°. The morphologies and microstructures of the as-prepared samples were examined by a field emission scanning electron microscope (Hitachi S-4800, Japan). The surface elemental composition and chemical state of the samples were determined by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB MKII X-ray photoelectron spectrometer (VG Scienta, USA) with Mg Kα radiation. UV–vis diffuse reflectance (DRS) spectra of the obtained samples were measured by using a Cary 5000 UV–VIS-NIR spectrophotometer with a diffuse reflectance accessory in the region 200–800 nm. The Brunauer-Emmett-Teller (BET) specific surface areas of all the synthesized samples were measured by using a Micromeritics Tristar II 3020 adsorption analyzer. The photoluminescence (PL) spectra of the samples were obtained by sing a fluorescence spectrophotometer (PL, F-4600, Hitachi Japan) equipped with a 150 W Xenon lamp as excitation source (wavelength range of 585–605 nm) at room temperature. The photodegradation of dyes (RhB and MO) were analyzed in a U-3010 UV–vis spectrophotometer (Hitachi, Japan). RhB and MO were used as cationic dye and anionic target pollutant, respectively. A 400 W halogen lamp with a 400 nm cut-off filter was used as a visible-light source to evaluate the photocatalytic activity of the photocatalysts. The inceptive concentration of the photocatalyst and the RhB were $1.0\ g{\cdot}L^{-1}$ and $10\ mg{\cdot}L^{-1}$, respectively. Before irradiation the suspension was sonicated for 30 min and then continuously stirred in the dark for 30 min to ensure the establishment of an absorption–desorption equilibrium between the photocatalyst, dye and water. During visible-light irradiation, 3 mL of suspension was taken out at a given time interval for subsequent dyes concentration analysis. The dyes concentration was analyzed by using a UV-3100 UV–Vis spectrophotometer (Hitachi, Japan).

3. Results and discussion

Fig. 1a shows the XRD patterns of all the as-synthesized Er^{3+}-doped BiOI samples, and all the diffraction peaks of the samples were indexed according to the standard data of tetragonal BiOI (ICDD PDF# 73-2062) with a space group of $P4/nmm$. The XRD pattern of samples with sharp peaks, which show the good crystal quality of the Er^{3+}-doped BiOI samples, and no signals of impurity phases in the XRD patterns were noted even in the 4Er-BiOI sample. From Fig. 1a, compared with that of the pure BiOI, the diffraction peak intensity of the Er^{3+}-doped samples did not change significantly, implying that the Er^{3+} doping has no pronounced effect on the crystallinity of the as-synthesized samples. Compared with that of the pure BiOI, the (1 0 2) diffraction peaks of all the Er^{3+}-doped BiOI samples shifted to lower diffraction angles (Fig. 1b), indicating that their unit cell parameters become larger than that of the pure BiOI. Since the ionic radius of Er^{3+} (0.089 nm) is smaller than that of Bi^{3+} (0.103 nm), the unit cell parameters should be decreased if all Er^{3+} ions replace the Bi^{3+} ions [19]. How-

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