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Synthesis and characterization of ZnO nanospheres sensitized BiOBr plates with enhanced photocatalytic performances

Yonglei Xing [a], Zuoli He [a,b], Wenxiu Que [a,*]

[a] Electronic Materials Research Laboratory, International Center for Dielectric Research, Key Laboratory of the Ministry of Education, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, PR China
[b] School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, South Korea

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ABSTRACT

ZnO nanospheres sensitized BiOBr plates (ZnO/BiOBr) were synthesized by combining hydrothermal, hydrolysis and post-thermal process. The ZnO nanospheres with the diameter about 20–40 nm grew on the BiOBr plates' surface and formed such ZnO/BiOBr plates. The degradation of Rhodamine B (RhB) solution in visible light was carried out to study such unique structured products' photocatalytic properties. Compared with pure BiOBr, ZnO and P25, the ZnO/BiOBr exhibits the highest photocatalytic performances, which is relative to the existence of BiOBr-ZnO heterojunction that acted as an effective separation of photo-generated electrons and holes.

1. Introduction

Many research issues have been focused on the environmental use of semiconductor materials so far, which can be employed to degrade the toxic organic compounds, split water, produce fuel and fabricate the photo-electrochemical cells [1–5]. Bismuth oxyhalide compounds (BiOX (X=Cl, Br, I)), as typical p-type semiconductors, have also gained more and more attentions owing to their characteristic internal structures of $[Bi_2O_2]^{2+}$ layers and unique optical properties [6–10]. Especially, BiOBr (Eg=2.50–2.91 eV), shows a stronger absorption in the visible light range [7,11,12]. However, the application is limited by the low separation efficiency of the photogenerated electrons and holes. As a result, many attempts have been made to overcome this disadvantage [13,14]. Some researchers combined ZnO and BiOBr to increase their photocatalytic activities [15,16]. Yi et al. reported that a class of novel p-n heterostructures comprising p-type BiOBr and n-type ZnO was successfully constructed by loading amounts of BiOBr nanoflakes onto the surface of ZnO nanoflowers, which show remarkably enhanced photocatalytic performances, higher than those of pure BiOBr and ZnO materials [15]. Duo et al. also reported that a kind of BiOBr/ZnO composites formed by the combination of BiOBr and ZnO, the high-efficiency separation of photogenerated electron-hole pairs through BiOBr/ZnO p-n junction was benefit for photocatalysis [16].

In this communication, the synthesis and characterization of the ZnO nanospheres sensitized BiOBr plates (ZnO/BiOBr) were reported. BiOBr plates were synthesized through a facile hydrothermal method, ZnO nanospheres were formed on the BiOBr plates's surface by the hydrolysis of zinc salt. Physicochemical features of such as-synthesized ZnO/BiOBr products were characterized by XRD, SEM, TEM and UV/VIS/NIR spectrometry. We also evaluated the photocatalytic degradation of RhB under visible light irradiation. Furthermore, a possible photocatalytic mechanism of such ZnO/BiOBr products was also discussed.

2. Experimental section

2.1. Synthesis

All the reagents were analytical grade and used without further treatment. At first step, stoichiometric amounts of $Bi(NO_3)_3 \cdot 5H_2O$ and cetrimonium bromide (CTAB) were dissolved in 25 mL distilled water. After stirring for 2 h, the solution was transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. The as-obtained product was collected by centrifugation, rinsed with water and ethanol, thus, the BiOBr plates were obtained after drying. In the second step, 0.305 g as-obtained BiOBr plates was dispersed into 120 mL mixed solvent(1:2 vol ratio of diethylene glycol and ethanol), 0.659 g $Zn(CH_3COO)_2 \cdot 2H_2O$ was add into the solution. After stirring for 2 h, the solution was treated at 180 °C

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[*] Corresponding author.
E-mail address: wxque@mail.xjtu.edu.cn (W. Que).

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for 20 min. The products were collected by centrifugation and washed with absolute ethanol. Finally, ZnO nanospheres sensitized BiOBr plates (ZnO/BiOBr) were obtained after annealing the as-obtained products at 500 °C for 1.5 h. ZnO microspheres were also prepared by the hydrolysis of zinc salt for comparison, which had described in our previous work [12].

2.2. *Characterization*

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200 diffractometer with Cu Kα radiation(Voltage: 40 kV; Current: 100 mA; Scanning rate: 10°/min). The morphological properties of the samples were observed by emission scanning electron microscopy (SEM, Quanta F250, FEI, USA) and high-resolution transmission electron microscopy (TEM JEM-2100, JEOL Inc., Japan) coupled with an energy-dispersive X-ray (EDAX) spectrometer. UV-Vis diffuse reflectance spectra (DRS) of the samples were studied by a UV/vis/NIR spectrometer (JASCO V-570) equipped with a diffuse reflectance accessory.

2.3. *Photocatalytic activity measurement*

The photocatalytic activities of the samples were estimated by observing the RhB degradation under visible light, which uses a 300 W Xenon lamp equipped with a 420 nm cutoff filter as the light source. For each experiment, 50 mg of photocatalyst was added into a 50 mL aqueous solution of RhB (5 mg L^{-1}). Prior to irradiation, the suspensions were magnetically stirred in the dark for 1 h to reach adsorption-desorption equilibrium. At certain time intervals, 5 mL of the suspension was sampled and centrifuged to separate the photocatalyst particles. The concentration of RhB aqueous solution was analyzed by measuring the absorbance at 554 nm. Such photocatalytic activity of P25(bought from Nippon Aerosil Co. Ltd) was also measured for comparison. Total organic carbon (TOC) analysis during the degradation of RhB was performed with a TOC-V CSH analyzer (Shimadzu).

3. Results and discussion

The morphologies of as-obtained ZnO/BiOBr plates are shown in Fig. 1a. Obviously, the BiOBr were kept plates-like structure after the second step. The ZnO nanospheres were deposited on the surface of the BiOBr plates and we will further confirm this by TEM next. By the way, the morphologies of ZnO and BiOBr were shown in Fig. S1 (in the Supporting information). In addition, the selected EDS of the ZnO/BiOBr plates is shown in Fig. 1b, indicating that the sample is composed of Bi, O, Br and Zn element(Bi: 14.71 at%; O: 56.9 at%; Br: 15.67 at%; Zn: 12.72 at%). XRD patterns of BiOBr, ZnO and ZnO/BiOBr products are shown in Fig. 1c. It can be seen that the diffraction peaks of ZnO microspheres and BiOBr plates can be indexed to and the hexagonal phase ZnO (JCPDS 36-1451) and the tetragonal phase BiOBr (JCPDS 09-0393), respectively [15,16]. For the ZnO/BiOBr samples, XRD diffraction peaks of ZnO and BiOBr phase can be clearly observed. Moreover, nor any other phases are detected in the ZnO/BiOBr products, indicating that no any impurities are formed between BiOBr and ZnO phase structure.

TEM were also used to further confirm the construction of the ZnO/BiOBr plates. As shown in Fig. 2a, the ZnO microspheres are composed of many small nanospheres with the diameters about 20–40 nm. BiOBr plates' unique structure was also present in Fig. 2b. The TEM images of ZnO/BiOBr plates were show in Fig. 2c-f. It could be seen the ZnO nanospheres tightly attached to the surface of BiOBr plates. The ZnO and BiOBr lattice fringes can be distinctly observed from Fast Fourier Transformation (FFT) patterns in Fig. 4f. The lattice spacing is determined as 0.26 and 0.281 nm, corresponding to the (002) plane of ZnO and the (012) plane of BiOBr, respectively. The BET specific surface area of the composites is 24.267 $m^2 g^{-1}$, that calculated from N_2 isotherms (Fig. S2a) and pore diameters of small and large mesopores are 2.0 and 22.5 nm, determined by using the BJH method as shown in Fig. S2b.

The optical absorption properties of these samples were measured by using DRS technique as shown in Fig. 3a. Obviously, the absorption edges of pure BiOBr and pure ZnO samples are located at 470 nm and 396 nm, respectively, which are consistent with the results as reported in Refs. [15,16]. In contrast, the absorption edges of the ZnO/BiOBr plates are well fallen between those of BiOBr and ZnO, showing an obvious absorption in the visible light region due to an introduction of BiOBr. Moreover, a gradual red shift of the wavelength edge appears as BiOBr content increases, it should be ascribed to an interaction between BiOBr and ZnO [17]. The band gap energy of all the as-prepared samples can be calculated by using the following equation [18], $ahv = A(hv - E_g)^{n/2}$, the value of n is 4 here. The plots of $(\alpha hv)^{1/2}$ versus photon energy (hv) are shown in Fig. 3b. The estimated band gap energies of BiOBr and ZnO are 2.60 eV and 3.00 eV, while the ZnO/BiOBr products show band gap energies at 2.70 eV.

Fig. 4 shows the photocatalytic activities of all samples for the degradation of RhB aqueous solution under the simulative sunlight irradiation with a 420 nm cutoff filter. Fig. 4a shows the variation curves of absorption spectra of RhB aqueous solution versus irradiation time in the presence of ZnO/BiOBr products. More strikingly, a blue-shift of the maximum absorption band of RhB aqueous solution from 554 to 522 nm can be also observed, which may be related to the step-by-step de-ethylation of RhB [18]. ZnO/BiOBr plates exhibit higher photocatalytic activities than the P25, pure ZnO and pure BiOBr samples as shown in Fig. 4b. After

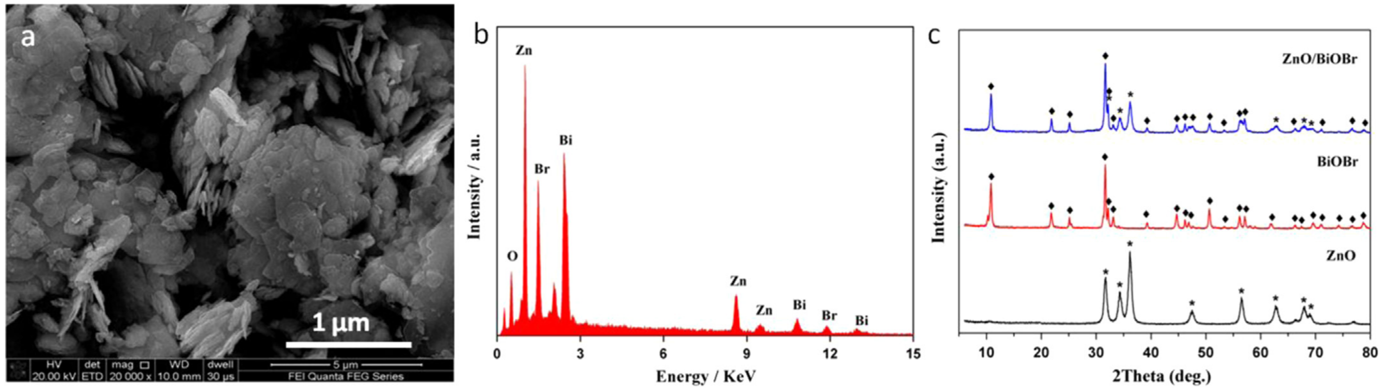

Fig. 1. (a) SEM images, (b) EDX spectrum of ZnO/BiOBr sample and (c) XRD patterns of ZnO, BiOBr, ZnO/BiOBr samples.