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Efficient solar-driven photocatalytic performance of BiOBr benefiting from enhanced charge separation rate

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ABSTRACT

In this work, novel BiOBr photocatalyst (IL-BiOBr) with enhanced solar-driven photocatalytic activity was fabricated by a facile hydrothermal method with the assistance of ionic liquid (IL) 1-ethyl-3-methylimidazolium nitrate ([EMIm]NO_3). BiOBr and IL-BiOBr were characterized by the Brunauer–Emmett–Teller (BET) method, X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), particle size analyzer and surface photovoltage spectroscopy (SPS), respectively. The results reveal that [EMIm]NO_3 increases the specific surface area, decreases the particle size, and greatly enhances separation rate of the photo-induced charge of BiOBr. The photocatalytic activity of IL-BiOBr for decolorization of rhodamine B aqueous solution was evaluated. The results illustrate that the photocatalytic performance of IL- BiOBr is more than 2.3 times of that of the reference BiOBr and the possible reason was suggested.

1. Introduction

As a lamellar-structured p-type semiconductor, bismuth oxybromide (BiOBr) has received increasing interest in the potential application as a visible light photocatalyst due to its medium band gap energy (2.8 eV), nontoxicity, facile preparation and chemical stability in photocatalytic process [1]. It was reported that BiOBr has unique layered structures characterized by [Bi_2O_2] slabs interleaved by double slabs of bromine atoms, which can effectively reduce the recombination of the photo-generated carriers and is beneficial to the photocatalytic activity [2]. However, it is still a great challenge to further boost the photocatalytic activity in order to meet the practical applications. Tremendous approaches have been developed to promote the photocatalytic activity of BiOBr, in which the hydrothermal method is more applicable due to its outstanding advantages [3].

Ionic liquids (ILs) have attracted considerable interests because of their properties. Recently, ILs have been applied to fabricate BiOBr [4–6]. However, the effect of [EMIm]NO_3 on the photo-induced charge separation rate of BiOBr prepared by the hydrothermal method has been seldom addressed. The primary objective of this paper is to study the effect of [EMIm]NO_3 on the photo-induced charge separation rate and the relation with the photocatalytic activity of BiOBr.

2. Experimental section

[EMIm]NO_3 was purchased from Lanzhou Institute of Chemical Physics. All other chemicals (analytical grade reagents) were supplied from Chengdu Kelong Chemical Reagent Factory. IL-BiOBr was fabricated by a hydrothermal method. 5 g $Bi(NO_3)_3 \cdot 5H_2O$ and 0.1 g [EMIm]NO_3 were dissolved in 20 mL glacial acetic acid. After the mixture became clear solution, KBr aqueous solution (1.23 g KBr + 10 mL H_2O) was added dropwise to the above solution under stirring, resulting in precipitate. The above mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was maintained at 453 K for 24 h and then cooled to room temperature naturally. The product was collected by filtration, washed several times with deionized water and absolute ethanol, and then dispersed in absolute ethanol and dried at 353 K in air overnight. BiOBr was also prepared as the same procedure mentioned above without the presence of [EMIm]NO_3. The specific surface area and pore size measurement were carried out on a SSA-4200 automatic surface analyzer (Builder, China). XRD patterns were performed on a DX -2600 X-ray diffractometer using Cu Kα (λ = 0.15406 nm) radiation equipped with a graphite monochromator. The X-ray tube was operated at 40 kV and 20 mA. The UV–vis spectra of photocatalysts in the 300–850 nm range were recorded using a TU-1907 UV–vis spectrophotometer equipped

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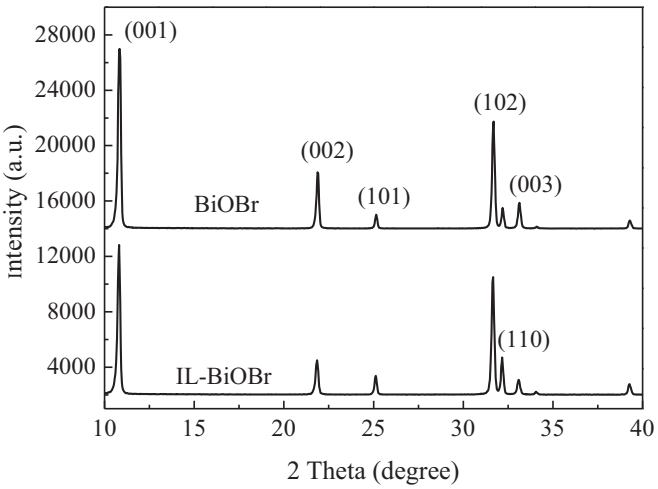

Fig. 1. XRD patterns of photocatalysts.

with an integrating sphere using $BaSO_4$ as the reference. SEM images were taken with a JSM-7500F scanning electron microscope, using an accelerating voltage of 5 kV. HRTEM (Tecnai TEM G2) were used to study the microstructure of the samples using an accelerating voltage of 300 kV. The distribution of particle size was measured on a BH-9300H Bettersize particle size analyzer using water as media and laser as light source. The SPS measurements were conducted with a home-built apparatus. The photocatalytic performance of BiOBr (50 mg) was investigated by decolorization of 50 mL rhodamine B aqueous solution (the concentration is 10 mg L^{-1}) under the identical conditions. The light source was a 500 W xenon lamp.

3. Results and discussion

3.1. Characterization of photocatalysts

The XRD patterns of the photocatalysts are shown in Fig. 1. All of the diffraction peaks can be assigned to the tetragonal phase of the BiOBr crystal (JCPDS no. 09-0393). No other patterns can be observed, suggesting high purity of the as-prepared BiOBr samples. Furthermore, the half maximum (FWHM) of IL-BiOBr sample is wider than that of BiOBr. According to the Scherrer equation, the wider the FWHM is, the smaller the crystal size of BiOCl is. Thus, IL-BiOBr has smaller crystal size than that of BiOBr. The decreased crystal size leads to the BET surface area increase, which fits well with the result of BET surface area and distribution of the particle size. The smaller crystal size can increase the specific surface area of BiOCl and the photocatalytic reaction active sites, which can improve the photocatalytic activity.

The SEM images of photocatalysts prepared are shown in Fig. 2.

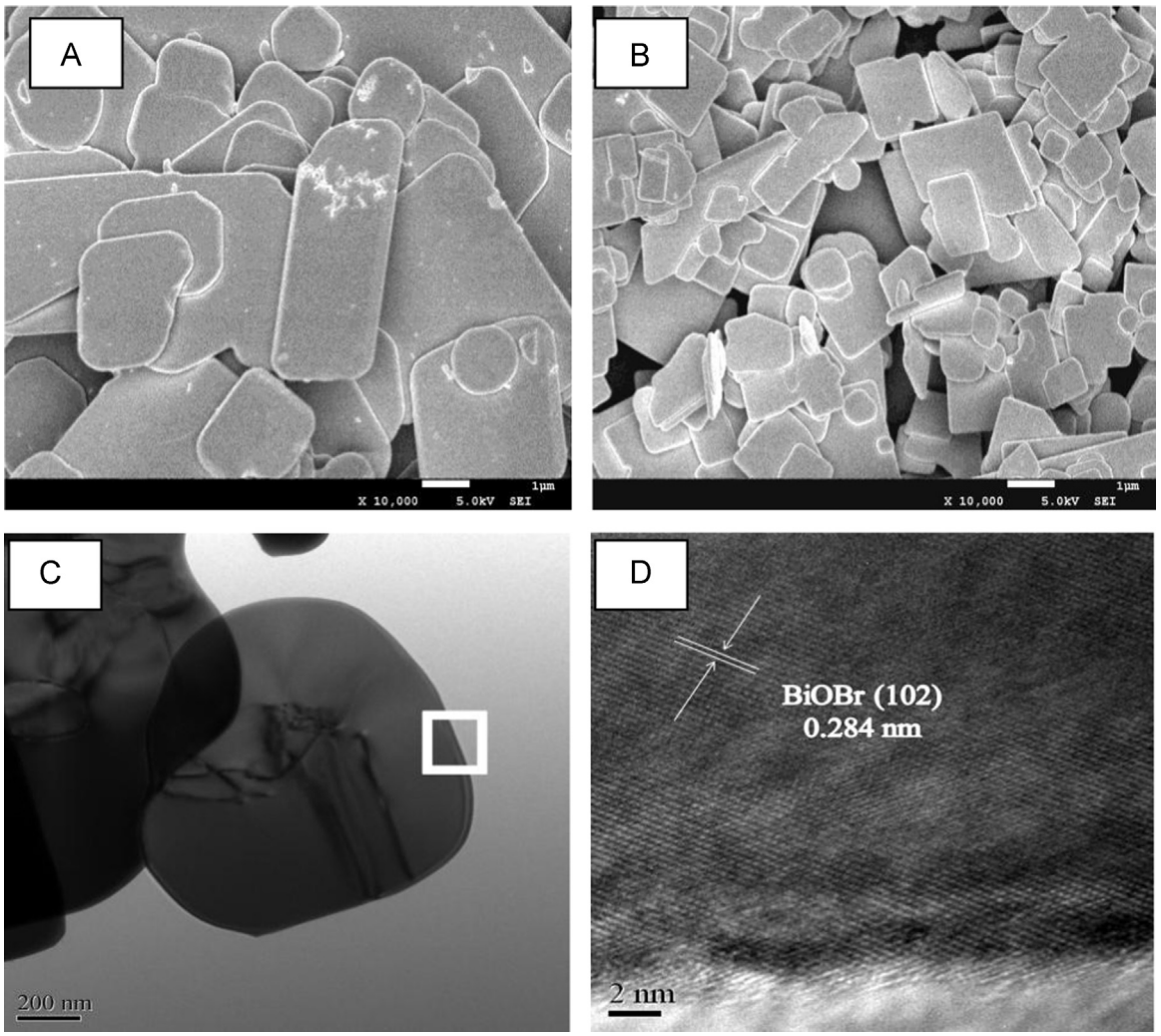

Fig. 2. SEM of photocatalysts (A) BiOBr; (B) IL- BiOBr; (C) TEM image of BiOBr; (D) the HRTEM image recorded from the white framed area indicated in C.