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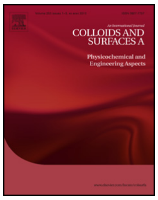

Synthesis of erbium ions doped BiOBr via a reactive ionic liquid with improved photocatalytic activity

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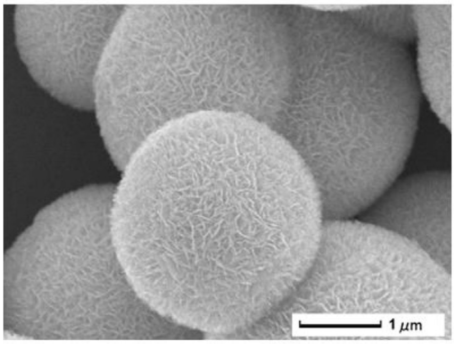
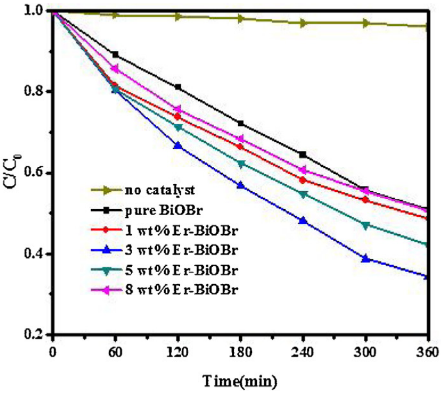
HIGHLIGHTS

- Novel Er ions doped BiOBr microspheres have been synthesized in the present of [C_{16}mim]Br.
- The Er/BiOBr composites exhibited higher visible light photocatalytic activity than pure BiOBr on the degradation of CIP.
- The enhanced photocatalytic performance could be attributed to the improved separation efficiency of electron–hole pairs and reduced band gap.

GRAPHICAL ABSTRACT

Erbium ions doped BiOBr has been synthesized through a solvothermal method in the presence of reactable ionic liquid 1-hexadecyl-3-methylimidazolium bromide ([C_{16}mim]Br). The sphere-like Er/BiOBr hierarchical structures were formed with an average diameter of 2–3 μm. The photocatalytic activities of pure BiOBr and Er/BiOBr samples were evaluated by the degradation of ciprofloxacin (CIP) under visible-light irradiation, in which 3 wt% Er/BiOBr showed the highest photocatalytic activity. The enhanced photocatalytic performance could be attributed to the improved separation efficiency of electron–hole pairs and reduced band gap.





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ABSTRACT

Erbium (Er)-doped BiOBr with different Er ions doping concentrations has been synthesized through a solvothermal method in the presence of reactive ionic liquid 1-hexadecyl-3-methylimidazolium bromide ([C_{16}mim]Br). The as-prepared samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform spectrophotometer (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and UV–vis diffuse reflectance spectroscopy (DRS). The photocatalytic activities of the Er ions doped BiOBr samples were evaluated by the degradation of ciprofloxacin (CIP) under visible-light irradiation. The results assumed that doping of Er ions over BiOBr led to the increase of the photocatalytic activity under visible light irradiation and 3 wt% Er/BiOBr showed the highest photocatalytic activity. The enhanced photocatalytic performance could be attributed to the improved separation efficiency of electron–hole pairs and reduced band gap.

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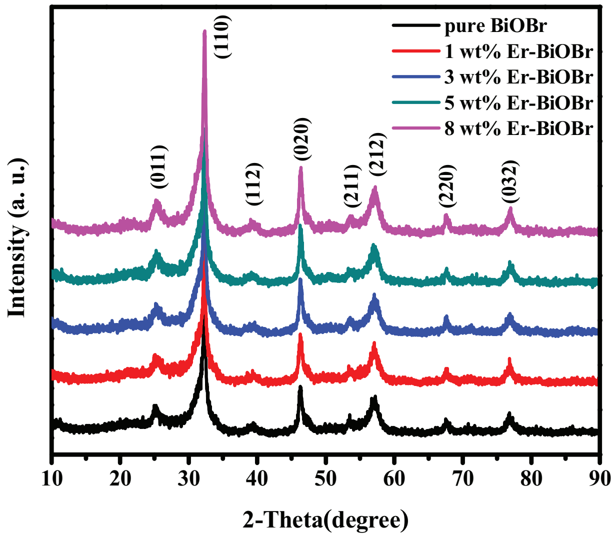

Fig.1. The XRD pattern of the Er ions doped BiOBr samples and pure BiOBr synthesized by ionic liquids solvothermal treatment at 160 °C for 24 h.

1. Introduction

In recent years, the semiconductor photocatalysts have showed great potential applications in elimination of organic pollutants [1–3]. TiO_2 as a semiconductor photocatalyst was in-depth studied due to its high efficiency, good stability and nontoxicity [4,5]. However, the pure traditional TiO_2 shows the low efficiency in utilizing of sunlight [6]. In this sense, recent research is focused on the development of novel alternative materials to replace traditional TiO_2 capable of using more solar energy as green energy resources [7,8].

Bismuth oxybromide (BiOBr) was found to be a promising material for organic contaminants decomposition under visible-light irradiation [9,10]. The unique layered structure feature with $[Bi_2O_2]$ slabs interlacing with double halogen slabs result in the production of self-built internal static electric fields in BiOBr. However, the photocatalytic activity of pure BiOBr is still limited by the high recombination of photogenerated electron–hole pairs. In this sense, many studies have committed to modify pure BiOBr [11,12]. Wang et al. [13] synthesized a novel four-leaf clover-shape BiOBr microstructure by EDTA-modified hydrothermal method. And the as-synthesized BiOBr sample exhibited excellent photocatalytic activity for the degradation of rhodamine B (RhB) in aqueous solution under visible-light irradiation. It shows that the control of morphology can improve the photocatalytic activity. Li et al. [14] reported a facile hydrothermal route to prepare BiOBr–Bi_2WO_6 mesoporous nanosheet composites in the presence of titanium isopropoxide. The BiOBr coupled with Bi_2WO_6 have high surface areas, increased light harvesting and enhanced electron–hole separation, thus exhibited high photocatalytic efficiency. The result indicates that BiOBr compound with other semiconductors could show the enhanced photocatalytic efficiency. Jiang et al. [15,16] indicated that metal ion-doping to the light-excited semiconductors such as Ti-doped BiOBr and Fe-doped BiOBr could enhance the photoabsorption and interfacial charge transfer. In these cases, the electron–hole separation efficiency and photocatalytic activity can be improved.

Rare earth elements have drawn more and more attention in the application of photocatalysis [17–19]. Doping of rare earth ions into the host semiconductors can impact its stability, phase and photocatalytic activity. For example, Cao et al. [20] synthesized a series of Sm^{3+}-doped TiO_2 and the result showed that the Sm^{3+} ions doping can not only suppress the phase transition from anatase to rutile of TiO_2, but also inhibit the growth of TiO_2 nanoparticles. The rare earth ions doped $BiVO_4$ has also been reported, Sergio Obregón et al. [21] reported that Er doped $BiVO_4$ exhibited enhanced photocatalytic activity for the degradation of methylene blue. It suggests that doping rare earth ions plays an important role in photocatalysis. Inspired by this, we aim to synthetize a novel erbium-doped BiOBr semiconductor so as to achieve the enhanced photocatalytic activity.

Ionic liquids (ILs) are non-volatile and non-flammable organic salts. Recently, ILs have attracted a great interest in the preparation of inorganic materials due to their high ionic conductivity, good thermal stability, good dissolving ability, wide electrochemical window, nonflammability and negligible vapor pressure [22,23]. In our previous work, we have synthesized a series of BiOX (X = Cl, Br, I) composites with reactive ionic liquids by a solvothermal process [24–26]. The result showed that ILs played important roles of solvent, reactant and template at the same time. Inspired by this, we expect that the Er-doped BiOBr will have enhanced photocatalytic activity if the Er-doped BiOBr can be controllable synthesized in the presence of ionic liquids.

Herein, we demonstrated a serious of Er ions doped BiOBr photocatalysts via a facile one-pot solvothermal method in the presence of reactive ILs $[C_{16}mim]Br$. The ILs played important roles in solvent, reactant and template at the same time during the reactive process. The photocatalytic activities of Er-doped BiOBr composites were tested by the degradation of ciprofloxacin (CIP) under visible-light irradiation, and the Er-doped BiOBr showed enhanced photocatalytic activity compared with the pure BiOBr. Further more, a possible mechanism for the photocatalytic activity of Er-BiOBr on the enhancement of visible light performance was proposed.

2. Experimental

2.1. Material and sample preparation

All chemicals were analytical grade and used as received without purification. The ILs 1-hexadecyl-3-methylimidazolium bromide ($[C_{16}mim]Br$) (99%) was purchased from Shanghai Chengjie Chemical Co., Ltd.

In a typical procedure (in Fig. S1.), 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved into 20 mL 2-methoxyethanol solution containing 1 mmol $[C_{16}mim]Br$, and then erbium nitrate ($Er(NO_3)_3{\cdot}5H_2O$) as a source of Er was added into the solution. The concentration of erbium ions was chosen as 1 wt%, 3 wt%, 5 wt% and 8 wt%, in which the wt% was the corresponding mass percent of as-prepared BiOBr. Furthermore, the wt% in this system was represented the original addition content of Er element. The mixture was stirred for 30 min, and then transferred into 25 mL Teflon-lined autoclave up to 80% of the total volume. The autoclave was then heated at 160 °C for 24 h and cooled down to room temperature naturally. The final product was separated by centrifugation, washed with distilled water and absolute ethanol for four times, respectively, and dried at 50 °C for 24 h before further characterizations. Pure BiOBr were also prepared under the same conditions. The as-obtained samples were named as *x* wt% Er/BiOBr, where *x* represents the content of Er ions.

2.2. Characterization

X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu Kα ($\lambda = 1.54$ Å). X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI5300 with a monochromatic Mg Kα source to explore the elements on the surface. The field-emission scanning electron microscopy (FE-SEM) measurements were carried out with a field-