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Research paper

Facile fabrication and enhanced photocatalytic performance: From BiOCl to element-doped BiOCl

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ABSTRACT

Sulfur-doped BiOCl (BiOCl-S) photocatalysts were synthesized using a simple and effective method. The as-synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman scattering spectroscopy, photoluminescence (PL) spectroscopy and ultraviolet visible (UV–vis) absorption spectroscopy. During the photodegradation of rhodamine B and phenol, BiOCl-S exhibits higher activity than BiOCl. Sn, Mn doped BiOCl were also synthesized successfully with the same doping route. We provide a simple and effective method for doping element into bismuth oxyhalides. BiOCl-S photocatalyst may be one of the promising materials for the degradation of organic environmental pollution.

1. Introduction

Environmental pollution and energy crisis have become increasingly serious problems. In the face of these problems, it is urgent to find simple and effective solutions [1]. Since Fujishima first discovered photocatalytic splitting of water on TiO_2 photochemical electrodes in 1972, semiconductor photocatalysis has been considered as a potentially promising approach to solve current environmental and energy problems [2,3]. Therefore, semiconductor photocatalysis has attracted widespread attention because of its potential applications, and attracted a considerable number of people to participate in the research.

Varied types of semiconductor photocatalysts that can degrade organic pollutants or split water under solar radiation have been developed, such as ZnO [4], ZnS [5], Fe_2O_3 [6], Ag_3VO_4 [7], Bi_2WO_6 [8], BiOX (X = Cl, Br, I) [9–11]. Bismuth-based compounds have attracted widespread attention because of their high photocatalytic activity [12–18]. Among them, BiOCl has been widely studied due to its excellent stability, good electron transport properties, no-photo-corrosivity, high photocatalytic activity, and potential applications [19]. BiOCl is a layer structured compound with a crystal structure of $[Bi_2O_2]^{2+}$ layers interleaved with double slabs of Cl ions [20]. However, its photocatalytic activity has also been limited by its wide bandgap.

Up to now, many methods have been proposed to improve the photocatalytic activity of semiconductor photocatalysts, such as doping [21,22], semiconductor recombination [23–25], surface modification [26] and deposition of noble metals [27,28], etc. Numerous studies show that proper ion doping can improve the photocatalytic activity of photocatalysts. Among them, sulfur doping could be an effective way. Jimmy C. Yu and coworkers synthesized S-doped TiO_2 via one-step low-temperature hydrothermal route [29]. Jiang et al. synthesized S-doped BiOCl by one-pot solvothermal method [30]. These semiconductor photocatalysts doped with sulfur showed higher photocatalytic activity than before. Here, in our work, we explored another simple method for doping sulfur into BiOCl, and the photocatalytic activity of BiOCl was improved. The photocatalytic activity of the S-doped BiOCl was evaluated by the decomposition of rhodamine B (Rh. B) and phenol. Sn, Mn doped BiOCl were also synthesized successfully with the same doping route.

2. Experimental

All chemicals were of analytical grade and were used without further purification. Deionized water was used for all instrument and samples washes.

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2.1. Preparation of BiOCl

In a typical experiment, 0.01 mol $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 200 mL nitric acid (1 mol/L) solution. The mixture was stirred until it was completely dissolved and then 10 mL hydrochloric acid (6 mol/L) solution was added. A white precipitate formed immediately. After magnetic stirring for 2 h, the precipitate was centrifuged and washed with deionized water several times. Finally, the white powdered BiOCl was obtained by drying the precipitate at 100 °C overnight.

2.2. Preparation of S doped BiOCl and undoped BiOCl

3 mmol BiOCl was dissolved in 20 mL hydrochloric acid (6 mol/L) solution. The mixture was stirred until it was completely dissolved. After that, 0.15 mmol thioacetamide was added to the mixture to stir until completely dissolved. The resulting solution was added dropwise to 100 mL absolute ethyl alcohol. The mixture was washed several times and then dried at 100 °C to obtain S doped BiOCl (denoted as BiOCl-S). BiOCl-R sample was obtained using the same route without adding thioacetamide.

2.3. Characterizations

The morphologies of the as-prepared products were obtained via the Hitachi S4800 microscope with an accelerating voltage of 7.0 kV. The chemical element mapping was characterized through an energy dispersive X-ray spectrometer equipped in the scanning electron microscopy (SEM) machine. Powder X-ray diffraction (XRD) spectra measurements were carried out on a Bruker AXS D8 advance powder diffractometer with Cu Kα X-ray radiation. Raman spectra were performed using Horiba Lab RAM HR system, and laser radiation ($\lambda = 1064\ cm^{-1}$) served as excitation source. UV–vis diffuse reflection spectra (DRS) were measured using a Shimadzu UV 2550 recording spectrophotometer equipped with an integrating sphere. The photoluminescence (PL) properties of the samples were characterized by Spectro fluorometer with an excitation wavelength at 310 nm.

2.4. Photocatalytic activity measurement

A 300 W Xenon lamp with a 400 nm cutoff filter was used as the visible light source. 300 W mercury lamp was used as the UV–visible light source. Rh. B and phenol were chosen as the model pollutant to evaluate the photocatalytic activity of as-prepared samples. In a typical photocatalytic experiment, 0.08 g photocatalyst was mixed with 80 mL Rh. B (phenol) solution (0.02 mmol/L). The suspension was magnetically stirred in dark for 60 min to establish adsorption–desorption equilibrium. The suspension containing Rh. B (phenol) and the photocatalyst was then irradiated under the visible light. At a given time, 4 mL of the suspension was withdrawn after periodic intervals of irradiation. The Rh. B (phenol) concentrations during the photodegradation process were monitored at 554 nm (270 nm) using a UV–vis spectrophotometer.

3. Results and discussion

The crystallinity and phase purity of the products were confirmed by XRD analysis. As shown in Fig. 1, the diffraction peaks of pure BiOCl and BiOCl-S samples are both in good agreement with the characteristic Bragg diffraction of tetragonal crystal structure of BiOCl (JCPDS 73-2060), and no other diffraction peaks could be observed. It indicates that S doping did not affect the crystal structure of BiOCl.

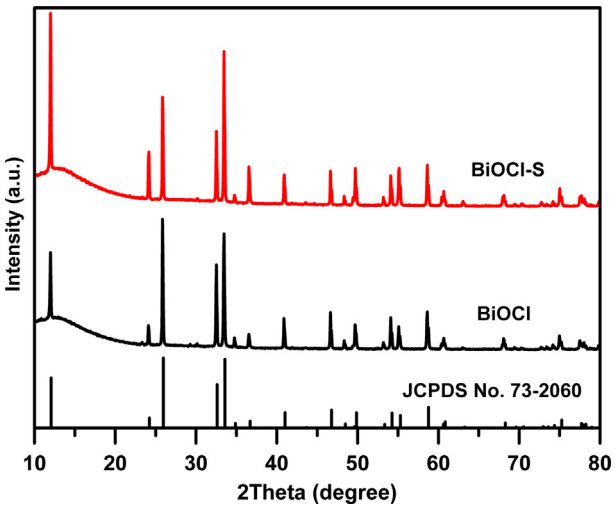

Fig. 1. The XRD patterns of BiOCl and BiOCl-S.

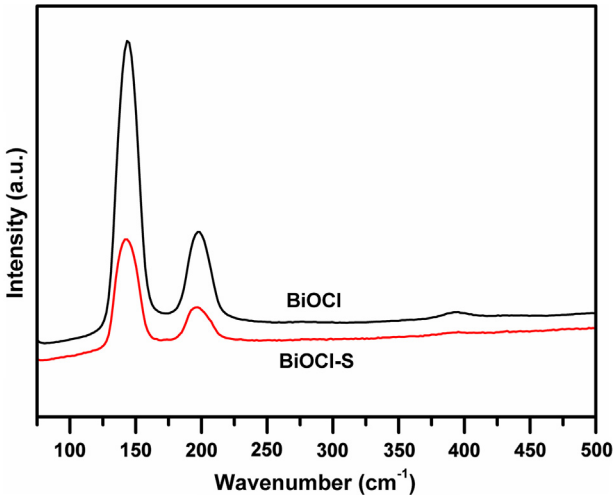

Fig. 2. Raman spectra for BiOCl and BiOCl-S.

Raman scattering spectroscopy is considered as a powerful molecular structural technique. Raman spectra of pure BiOCl and BiOCl-S were measured and shown in Fig. 2. It shows that the Raman peaks of pure BiOCl and BiOCl-S correspond to A_{1g} and E_g of Bi–X stretching mode and the vibration of Bi–O in BiOCl, respectively [31–33]. The characteristic Raman peaks of Bi_2S_3 (located at 236.7 and 259.8 cm^{-1} and between 70 and 150 cm=$^{-1}$) [30,34] are not found in BiOCl-S. It is also proved that there is no Bi_2S_3 in BiOCl-S, which is consistent with the results of XRD.

The morphological feature of as-prepared BiOCl and BiOCl-S was characterized by SEM and shown in Fig. 3(a–c). BiOCl and BiOCl-S both possess well-defined plate-shaped structure. The diameter size of BiOCl-S nanoscale is smaller than that of BiOCl. Since the binding energies of Bi $4f_{5/2}$ and S $2p$ state both locate at around 163 eV [35,36], it is difficult to distinguish sulfur from BiOCl-S by XPS analysis [37]. Chemical element mapping analysis (Fig. 3c) confirms the presence of S element and its homogeneous dispersion in BiOCl-S.

The optical absorption properties of the samples were measured using UV–visible absorption spectroscopy. Fig. 4 shows that BiOCl-S causes redshift at the absorption edge relative to BiOCl, and the absorption is enhanced. Optical bandgap of BiOCl-S and