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Facile Synthesis of Flower-like Superparamagnetic Fe_3O_4/BiOCl Nanocomposites as High Effective Magnetic Recyclable Photocatalyst under Visible Light

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In this paper, 10 nm Fe_3O_4 nanoparticles were modified on the surface of 2 μm flower-like bismuth oxychloride (BiOCl) spheres by a facile co-precipitation method. The results showed that the Fe_3O_4/BiOCl nanocomposites exhibited excellent photocatalytic activity and superparamagnetic property (M_s = 3.22 emu/g) under visible light for Rhodamine B (RhB) degradation. Moreover, the Fe_3O_4-BiOCl photocatalyst possessed magnetic recyclable property, which could maintain high photocatalytic effective even after 20 cycle times. These characteristic indicates a promising application for wastewater treatment.

Keywords : magnetic nanoparticles, bismuth oxychloride (BiOCl), photocatalysts, superparamagnetic

1. Introduction

Recently, semiconductor-based photocatalysts, such as titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS), and zirconium dioxide (ZrO_2), have been received much attention due to their highly efficient, non-polluting, and energy-saving characteristics [1-5]. These characteristics allow photocatalysts to convert solar light energy into chemical energy while degrading pollutants [6, 7].

Among numerous photocatalysts, bismuth oxychloride (BiOCl) has been extensively investigated because of its unique properties, including higher catalytic efficiency than many other photocatalysts [8, 9]. However, it is very hard to separate BiOCl from aqueous solution after photocatalytic reaction. To resolve that problem, ferriferrous oxide (Fe_3O_4) nanoparticles were selected to functionalize BiOCl. As-synthesized superparamagnetic nanocomposites could be directed by applying an external magnetic field, which was convenient to be fluidized and recycled [10-13].

It was found that Fe_3O_4/BiOCl composite was an effective photocatalyst to degrade the organic dyes, which was comparable with bare BiOCl system [14]. Tan *et al.* [15] demonstrated a chemical co-precipitation method for the synthesis of Fe_3O_4/BiOCl nanocomposite photocatalysts, which can be easily recovered after photodegradation process. Bai *et al.* [16] reported a solvothermal method to synthesize Fe_3O_4/BiOCl magnetic nanocomposites for the degradation of Rhodamine B (RhB) under simulated solar light irradiation.

In this paper, we report a facile and simple route to prepare flower-like Fe_3O_4/BiOCl nanocomposites via co-precipitation method. The nanocomposites exhibited high photocatalytic activity under visible light for RhB degradation. Moreover, the flower-like Fe_3O_4/BiOCl nanocomposites can be easily recovered and recycled after photodegradation process.

Materials and Experimental

$FeSO_4 \cdot H_2O$ (≥ 99%), $FeCl_3 \cdot 6H_2O$ (≥ 99%), $NH_3 \cdot H_2O$ (36-38%), $Bi(NO_3)_3 \cdot 5H_2O$, HNO_3, Hydrochloric acid (37%) were purchased from Chengdu kelong Chemical Reagent Company.

In a typical experiment, 30 mL $FeCl_3 \cdot 6H_2O$ (0.1 mol/L) and 15 mL $FeSO_4 \cdot H_2O$ (0.1 mol/L) were added into a 250 mL flask under vigorous stirring at 30 °C. Subsequently, $NH_3 \cdot H_2O$ (36-38%) was dropwised into the system with pH to be 10, and a black precipitate was immediately formed. Afterthat, the precipitate was collected by magnet and washed with deionized water several times, then dried in vacuum at 40 °C for 8 h.

After that, 0.3 g as-synthesized Fe_3O_4 powders were

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dispersed in 20 mL deionized water, then 30 mL $Bi(NO_3)_3 \cdot 5H_2O$ (0.2 mol/L) was injected into the solution with vigorous stirring. Subsequently, the pH of the reaction system was adjusted with HCl to 2. After reacted for 12 h, a brown precipitate was formed. Then the precipitate was washed with deionized water and ethanol for several times, and dried in vacuum for 24 h.

Powder X-ray diffraction (XRD) analysis of the samples were measured on an X'Pert PRO X-ray powder diffractometer with monochromatized Cu Kα radiation (λ = 0.15406 nm) at a setting of 40 kV and 40 mA. The scanning electron microscopy (SEM) images were obtained on a TM-1000, using an accelerating Voltage of 15 kV. The morphologies and microstructures of the samples were examined with transmission electron microscopy (TEM) by ZEISS Libra 200 FE, with 200 kV accelerating voltage. Room temperature magnetic properties of the composite were characterized using a vibrating sample magnetometer (BKT-4500Z). RhB was used as target dye to evaluate the photocatalytic activity of the as-prepared magnetic BiOCl samples. And the photocatalytic reaction is carried out in a homemade photocatalytic reactor.

The light source of the reaction device is a U-3010 UV-Vis lamp spectrometer with the wavelength range from 200 to 800 nm.

3. Results and Discussion

Figure 1 shows the XRD pattern of the flower-like Fe_3O_4/BiOCl nanocomposites. In Fig. 1, the most intensive diffraction peaks marked with "Δ" can be assigned to the (002), (101), (110), (102), (112), (200), (201), (113), (211), (212), (203), (220), (214), and (302) planes of

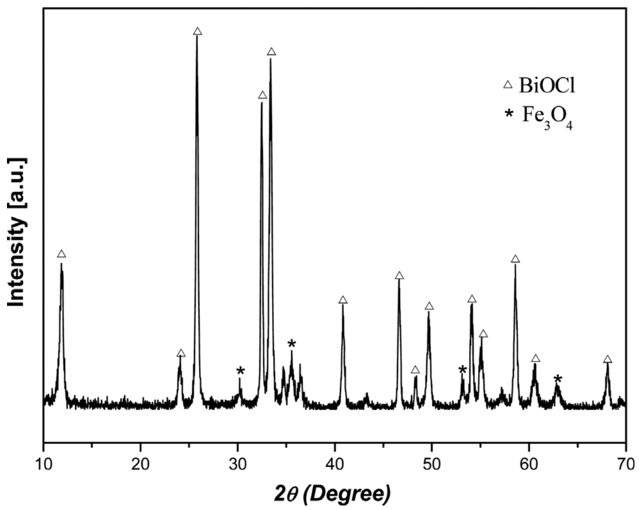

Fig. 1. XRD pattern of the as-synthesized Fe_3O_4/BiOCl nanocomposites.

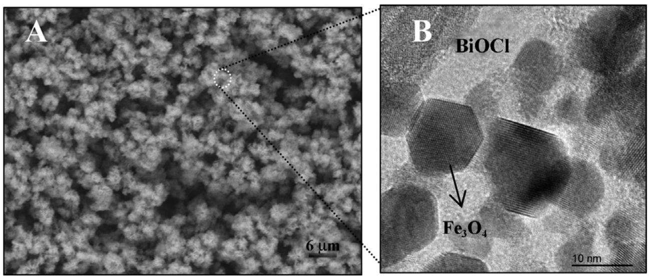

Fig. 2. SEM (A) and TEM (B) images of Fe_3O_4/BiOCl nanocomposites.

BiOCl, which correspond well to the tetragonal phase BiOCl (JCPDS 06-0249). The diffraction peaks marked with "*", can be assigned to the (220), (311), (511), and (440) planes of Fe_3O_4 (JCPDS Card No. 19-0629). These results prove the successful synthesis of Fe_3O_4/BiOCl nanocomposites.

Figure 2 displays the SEM and TEM images of the flower-like Fe_3O_4/BiOCl nanocomposites. As shown in Fig. 2 (A), the flower-like matrix of BiOCl was made up of BiOCl nanosheets, and the size of the Fe_3O_4/BiOCl is about 3 μm. Moreover, as can be seen in Fig. 2 (B), the 10 nm Fe_3O_4 nanoparticles are adsorbed on the surface of BiOCl.

Figure 3 shows the magnetization curves of Fe_3O_4 nanoparticles and the flower-like Fe_3O_4/BiOCl nanocomposites. The specific saturation magnetization (*Ms*) of Fe_3O_4 is 42.74 emu/g. After combined with BiOCl, the *Ms* of Fe_3O_4/BiOCl nanocomposites decreased to 3.22 emu/g. However, both Fe_3O_4 and Fe_3O_4/BiOCl exhibit superparamagnetic property, indicating the Fe_3O_4/BiOCl photocatalyst could be easily recovered by a magnetic field.

The photocatalytic activities of Fe_3O_4/BiOCl photocata-

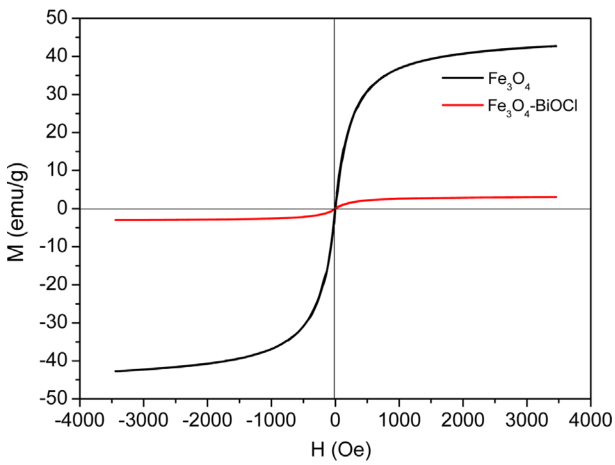

Fig. 3. (Color online) Magnetization loops of Fe_3O_4 nanoparticles flower-like Fe_3O_4/BiOCl nanocomposites.

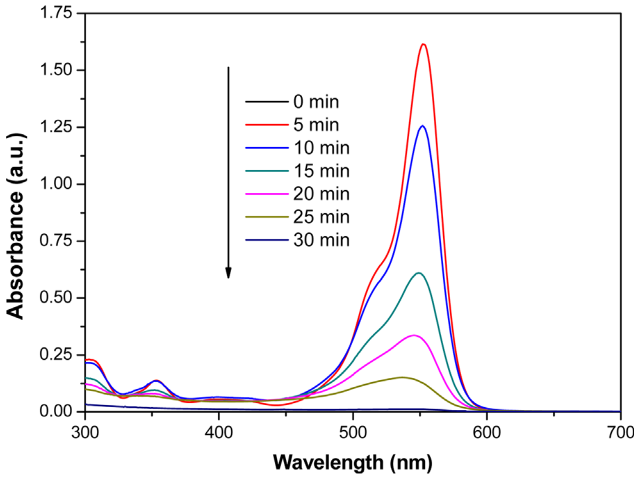

Fig. 4. (Color online) Absorbance spectra of Rhodamine B for the flower-like Fe_3O_4/BiOCl reused in different photocatalytic time.

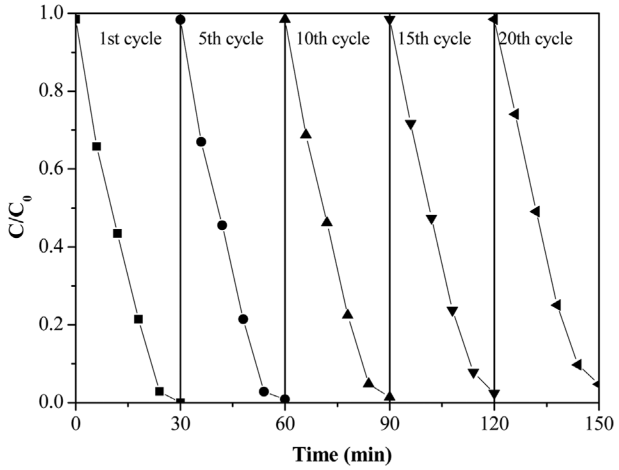

Fig. 5. Photocatalytic recycle efficiency of degrading RhB (40 mg/L) on the flower-like Fe_3O_4/BiOCl under visible irradiation.

lysts were evaluated by the degradation of RhB (40 mg/L) over the samples under visible light irradiation (k > 420 nm) at room temperature. Figure 4 shows the UV-Vis absorption spectra of the RhB solution at different degradation time. It is observed that the RhB can be completely degraded within 30 minutes. Moreover, the photocatalytic activity of Fe_3O_4/BiOCl nanocomposite was enhanced and the absorption range was extended by Fe_3O_4 for the degradation of RhB under visible light irradiation [15].

Twenty photodegradation recycle experiments were applied to study the reusability of Fe_3O_4/BiOCl nanocomposites under visible light irradiation. Figure 5 illustrates the photocatalytic ability of the successive RhB photodegradation cycles. The Fe_3O_4/BiOCl nanocomposite could be easily collected by applying an external magnetic field within 30 s. It should be noticed that the flower-like Fe_3O_4/BiOCl nanocomposite can degrade RhB completely within 30 min, which is much faster than reported Fe_3O_4/BiOCl nanospheres [16, 17]. Moreover, the nanocomposite retains its high photocatalytic ability in photodegradation cycles. Even after 20 successive cycles, the degradation rate of RhB was still 98 % of its initial value, indicating that Fe_3O_4/BiOCl possess excellent photocatalytic stability and reusability properties.

4. Conclusion

In summary, flower-like Fe_3O_4-BiOCl nanocomposites were successfully synthesized via a facile co-precipitation method. It was found that the nanocomposites showed excellent and stable photocatalytic activity in degradation of RhB under visible light. Moreover, the flower-like Fe_3O_4-BiOCl exhibited superparamagnetic property (M_s = 3.22 emu/g) at room temperature. It can be easily recovered and recycled by applying an external magnetic field. Most importantly, the Fe_3O_4-BiOCl could maintain above 98 % photocatalytic effective even after 20 cycle times, indicating highly promising in wastewater treatment.

Acknowledgments

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