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Preparation of magnetic $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr hybrids for the visible-light-driven degradation of methyl orange

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ABSTRACT

$Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr hybrids with p-n heterojunction were prepared by a facile sol-gel and hydrothermal method. And the samples with different AgBr contents were characterized by XRD,[1] SEM,[2] UV–vis DRS[3] and FT-IR.[4] The degradation capability of the photocatalysts were evaluated under visible light and used methyl orange (MO) as a target contaminant. All the composites possessed the magnetic properties of $Co_{0.5}Zn_{0.5}Fe_2O_4$ and also exhibited high photocatalytic activity of AgBr. Among the prepared photocatalysts, the hybrids prepared with 0.5 g $AgNO_3$ exhibited the highest photocatalytic efficiency. The increase photocatalytic activity of $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr hybrids might be associated with the formation of suitable internal structures between $Co_{0.5}Zn_{0.5}Fe_2O_4$ and AgBr. And a possible photocatalytic mechanism of the $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr hybrids was proposed.

1. Introduction

Semiconductor photocatalysis technology, which is believed to be a green and efficient method for the elimination of organic contaminants present in the environment [1–3]. Many research efforts have focused on the development of visible light responsive photocatalysts to maximise the utilization of clean, safe, and abundant solar energy, considering environmental protection and sustainable development [4,5]. AgBr, as an efficient photocatalyst and visible light sensitive agent, has aroused extensive concern, owing to its high activity, visible-light response, narrow band gap and environmentally friendly feature [6]. The study found that AgBr exhibited excellent visible light activity for its narrow band gap [7], so it could absorb photons under the illumination and generated lively electrons and holes easily. Xing and his coworkers [8] obtained the AgBr/TiO_2 nanocomposite photocatalyst via an ion exchange-calcination method, the result showed that the efficiency of the photodegradation of methyl orange (MO) had largely enhanced compared to pure TiO_2. However, AgBr is unstable and easy to decompose when absorbing light [9,10]. Also, nano-sized AgBr is not easy recycling. Therefore, AgBr combined with materials such as $BiPO_4$ [11], SiO_2 [12], TiO_2 [9,13] and other carriers [14,15] for the purpose of improving the photocatalytic performance, also obtaining a light stability composite photocatalyst. And it is an important investigative field that catches researcher's attention on reacquainting and studying of AgBr.

$Co_{0.5}Zn_{0.5}Fe_2O_4$ is a kind of spinel ferrite, meanwhile has spinel structure as $ZnFe_2O_4$ and inverse spinel structure as $CoFe_2O_4$ [16], with high saturation magnetization and coercivity, strong magnetic anisotropy, strong mechanical hardness, stable chemical properties [17]. But it was rarely reported as the magnetic substrate.

In this paper, easily recycled and visible-light driven photocatalysts $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr were prepared by a facile sol-gel and hydrothermal method. MO was used to evaluated the photocatalytic efficiency of the composites under the visible light. The results showed that $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr composites had a high photocatalytic property and magnetic separable.

2. Experimental

2.1. Materials

The chemicals used in this paper were all analytical grade (A.R.) and achieved from Tianjin Kermel Chemical Reagents development center (PR China). The reagents were used without further purification. And

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[1] X-ray diffraction.

[2] Scanning electron microscope.

[3] UV–vis diffuse reflectance spectrum.

[4] Fourier transfer infrared spectroscopy.

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the water used in the experiment was deionized water.

2.2. Preparation of photocatalysts

2.2.1. Preparation of $Co_{0.5}Zn_{0.5}Fe_2O_4$

According to the molar ratio of Co, Zn to Fe for 1:1:4, $Co(NO_3)_2 \cdot 6H_2O$ (2.5 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (2.5 mmol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.01 mol) were dissolved in just the right amount of deionized water. Otherwise, 3.6 g citric acid was dissolved in 30 mL of deionized water and then they were added dropwise into the above dispersion under vigorous stirring. The mixture was kept for 3 h in 80 °C and then was kept in drying oven at 105 °C. The product was then dried in a vacuum oven at 150 °C for 2 h. The magnetic substrate was kept for use [18].

2.2.2. Preparation of $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr

The $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr composites were synthesized by a facile hydrothermal method. Briefly, solution A was prepared by adding 0.1500 g of $Co_{0.5}Zn_{0.5}Fe_2O_4$ into 100 mL deionized water and was kept in the ultrasonic instrument for uniform dispersion. Solution B was prepared by dissolving 0.1 g $AgNO_3$ into 20 mL glycerin. Solution C was obtained by dissolving stoichiometric amount of KBr powder in 30 mL glycerin. The solution B was added in drops into solution A and got a further ultrasound for 30 min in order to allow as many Ag ions adsorb on the surface of $Co_{0.5}Zn_{0.5}Fe_2O_4$. Then solution C was added dropwise into the above suspension. After ultrasound for 1 h at room temperature, the final mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 160 °C. Natural cooling after hydrothermal reaction for 4 h, the obtain products were washed with distilled water and ethanol, and dried at 120 °C for 12 h. Different $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr samples were obtained by adjusting the weight of $AgNO_3$, the amount of $AgNO_3$ was 0.1 g, 0.2 g and 0.5 g, the obtained products were grinded and numbered as $1^{\#}$, $2^{\#}$ and $3^{\#}$, respectively.

2.3. Characterization of photocatalysts

The crystalline phases of the samples were obtained on X-ray Diffraction (XRD, X′Pert PRO, PANalytical, Holland) using a Cu Kα radiation (λ = 0.15406 Å) at a scanning rate of 10°/min in the 2θ range of 5–90° at room temperature. Morphological

analysis was performed with Scanning electron microscopy (SEM, TM-1000). UV–vis diffuse reflectance spectroscopy (UV–vis DRS, Cary 5000, Agilent, USA), its analysis ranged from 200 to 800 nm, equipped with an integrating sphere attachment and $BaSO_4$ was used as a reflectance standard. And fourier transfer infrared spectroscopy (FT-IR, Nicolet iS50, Thermo, USA) using KBr pellets.

2.4. Photocatalytic performance

The photocatalytic performance of the prepared samples was estimated by the photocatalytic degradation of MO under the condition of visible light irradiation. A 350 W Xe lamp was served as the visible light source. 0.05 g of photocatalyst was added into the MO solution (50 mL, 20 mg L^{-1}). Before the photocatalytic reaction, the suspension was continuously stirred for 30 min in the dark condition for the system reaching an adsorption-desorption equilibrium between the photocatalyst and dye. During irradiation, the absorbance of the solution was detected at a given time intervals, the clarified catalyst-free MO solution was analysed with a Shimadzu UV-2450 UV–vis spectrophotometer at 473 nm. The residual rate of MO was calculated as follows:

$$\eta\% = (C_t/C_O)*100 \tag{1}$$

where C_t is the concentration of MO at time t and C_0 is the initial concentration [19].

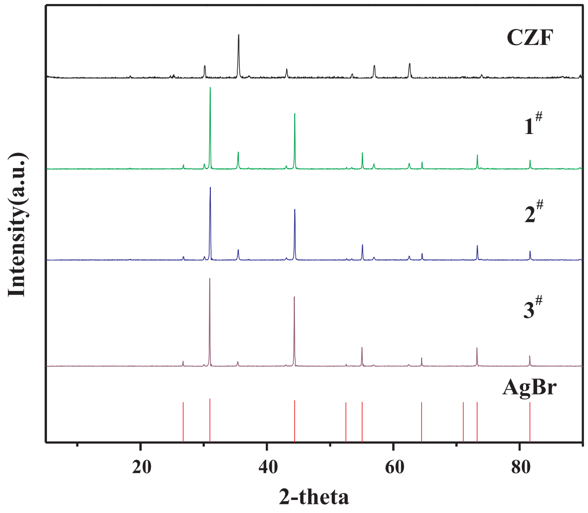

Fig. 1. XRD patterns of samples.

3. Results and discussion

3.1. Results of XRD characterization

Fig. 1 shows the XRD diffraction patterns of the as-synthesized $Co_{0.5}Zn_{0.5}Fe_2O_4$, AgBr and $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr composites with different amount of AgBr. Based on Fig. 1, the diffraction peaks of $Co_{0.5}Zn_{0.5}Fe_2O_4$ at 2θ values of 30.0°, 35.5°, 36.3°, 43.2°, 53.5°, 57.0°, 62.7° was indexed to the (220), (311), (222), (400), (422), (511) and (440) planes, respectively, which matches well with the reports for $Co_{0.5}Zn_{0.5}Fe_2O_4$ [20]. As can be seen from the Fig. 1, the patterns all $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr hybrids showed the coexistence of $Co_{0.5}Zn_{0.5}Fe_2O_4$ and AgBr (PDF#06-0438). Moreover, when the content of AgBr in composites increased to 0.5 g, the intensity of the characteristic peak increases slightly.

3.2. SEM analysis

The surface morphology of $Co_{0.5}Zn_{0.5}Fe_2O_4$, AgBr, and $Co_{0.5}Zn_{0.5}Fe_2O_4$/AgBr hybrids are shown in Fig. 2. In Fig. 2a and b, the magnetic substrate $Co_{0.5}Zn_{0.5}Fe_2O_4$ exhibited irregular shape and uneven agglomerate, AgBr showed irregular blocky structure and exhibited clumped distribution. Fig. 2c shows that the surface of AgBr was covered partly by $Co_{0.5}Zn_{0.5}Fe_2O_4$. While Fig. 2d and e shows that the surface of AgBr was almost uniformly covered by $Co_{0.5}Zn_{0.5}Fe_2O_4$, which indicated that $Co_{0.5}Zn_{0.5}Fe_2O_4$ and AgBr were composited successfully. The results above illustrated that after combining with AgBr, the agglomeration of $Co_{0.5}Zn_{0.5}Fe_2O_4$ was reduced largely.

3.3. FT-IR analysis

The infrared spectra of the as-prepared $Co_{0.5}Zn_{0.5}Fe_2O_4$ (Fig. 3) showed a broad band at around 3400 cm^{-1} belonged to the liquid H_2O molecule stretching vibration due to the absorbed water molecules on the surface. And the peak at 1656.98 cm^{-1} was assigned to Variable Angle vibration of the water molecules. The band at 1107.8 cm^{-1} for -C-O-C- belonged to citric acid during the preparation of $Co_{0.5}Zn_{0.5}Fe_2O_4$. The two absorption bands at 423.97 cm^{-1} and 575.82 cm^{-1} were related to the vibration of the mental ions at the octahedral and tetrahedral sites, respectively. Involving M–O bonds (M = Zn, Co and Fe) in $Co_{0.5}Zn_{0.5}Fe_2O_4$ [21]. The IR data confirmed the formation of cobalt zinc ferrous complex.