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Deposition of BiOBr thin films by thermal evaporation and evaluation of its photocatalytic activity

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ABSTRACT

Thin films of BiOBr were prepared by a sequential evaporation process in a thermal evaporation system (TES) starting from BiOBr powders previously synthesized by co-precipitation. The deposition rate was fixed at 1.2 Å s^{-1} to get a controlled evaporation of the material using glass slides as substrate. BiOBr thin films with a thickness of 300 nm were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The analysis by XRD of the thin film deposited confirmed the formation of BiOBr, showing a high degree of specific crystal orientation in {0 0 1} planes. In the same way, SEM analysis showed that the deposition of oxide took place by formation of plates and small particles with shape of flowers. The photocatalytic activity of BiOBr thin films was evaluated in the degradation reaction of rhodamine B (RhB) in aqueous solution under sun-like irradiation. BiOBr thin films were able to bleach a solution of RhB (5 mg L^{-1}) in 99% after 24 h, and to mineralize a solution of RhB (50 mg L^{-1}) in 38% after 96 h.

1. Introduction

The use of organic dyes has been extensively increased in the last decades by a great variety of industries, with the subsequent generation of important amounts of wastewater and contamination of the environment. Several decontamination technologies have emerged in order to solve this problem, such as those based in biodegradation, absorption or ultrasonic degradation process. These technologies have proved their limited efficacy in the past, with problems to be solved such as costs, real elimination of pollutants instead of a simple change of phase and degradation of pollutants in aqueous medium until low values of concentration. For these reasons, alternative methods have been proposed motivated to find more efficient technologies. In this sense, the photocatalysis seems to be a good option due to its low cost, efficiency and non-toxic nature, aspects that make this process a green technology [1–4].

TiO_2 oxide is the most used semiconductor material in the field of photocatalysis due to its low cost, high stability to corrosion process, innocuous character and high photocatalytic activity [5]. By the contrary, the major drawback in the use of this oxide is the fact that its activation as photocatalyst takes place only with UV radiation, which represents only a minor portion of solar radiation. For this reason, in the past, TiO_2 anatase polymorph has been doped with nitrogen in order to increase its absorption in the visible range [6–8]. In the same way, alternative oxides were proposed to get advantage of the visible region on solar spectrum [9–12]. In this direction, a special attention has been put in the family of oxyhalides of bismuth BiOX (X = F, Cl, Br or I) characterized by the chemical stability of the compounds and an outstanding photocatalytic activity under visible-light irradiation [13–17]. Different synthesis routes to produce powders of BiOX were successfully explored in the past such as co-precipitation [15], solvothermal method [18], reverse microemulsions [19], hydrolysis method [20] and hydrothermal synthesis [21]. These routes allow the synthesis of powders conformed of particles with different shapes like nanosheets, microspheres and microflowers.

From the point of view of a technological application, the use of the photocatalyst in powder form represents the inconvenient of its removal from aqueous medium when the decontamination process has been concluded. The use of the photocatalyst in thin film, instead of suspension, eliminates this complicated process. For this reason, an important goal in the field of photocatalysis applications is the deposition of thin films of photocatalytic materials on surfaces of interest, maintaining its high activity. From the different compounds of the family BiOX, the bromide oxyhalide BiOBr exhibits the higher activity in aqueous media due to an appropriate

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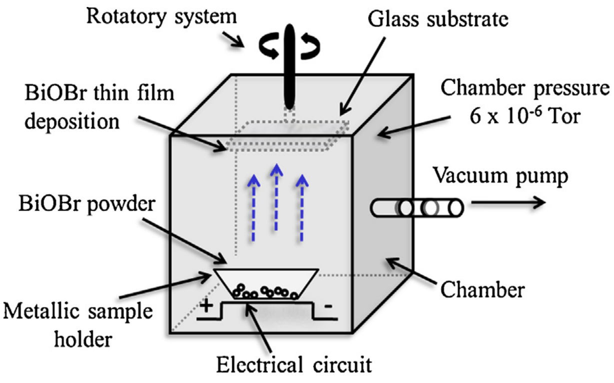

Fig. 1. Scheme of thermal evaporation system.

energy band gap value to adsorb an important portion of solar radiation [15]. It must be noted that films of BiOBr systems were previously obtained by solvothermal method by hydrolysis route [22].

In this work, BiOBr thin films with a controlled thickness of 300 nm were successfully obtained by thermal evaporation deposition following a similar procedure used to the deposition of thin films of γ-Bi_2MoO_6 photocatalyst [23]. The photocatalytic activity of thin films of BiOBr was evaluated in the degradation reaction of RhB in aqueous solution under sun-like irradiation. To determine the degree of mineralization of organic dye, total organic carbon (TOC) was analyzed during the photocatalytic process.

2. Experimental

2.1. Sample preparation

Crystalline BiOBr powders were used as evaporation source to produce BiOBr thin films. BiOBr powders were synthesized by co-precipitation method following the next procedure. A solution of 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved under strong stirring in 20 ml of ethanol. A second solution was prepared with 1 mmol of KBr dissolved in 20 ml of distilled water. The bromide solution was added to the bismuth solution drop by drop under stirring. After the reaction was completed, the resulting solid product was collected by filtration, washed several times with distilled water and dried for 12 h at 100 °C.

The deposition of BiOBr thin films was carried out by thermal evaporation of BiOBr powders in a Thermal Evaporation Åmod 204 Series System (TES) developed by the Angstrom Engineering Company. BiOBr powders were placed in a metallic crucible which was connected to the electrical circuit of the TES inside a chamber with an internal pressure lower than 6×10^{-6} Torr. The TES was operated in automatic mode, which means that the equipment controlled the power (%P) passing through the thermal resistive deposition source (TRDS) to fix the deposition rate (Å s^{-1}) of the oxide over the glass substrate. The deposition rate was measured with a sensor of quartz, and the TES controls the power in order to maintain constant this deposition rate. To avoid an abrupt evaporation of the powders, or a strong decomposition of the original BiOBr powder, a low deposition rate of 1.2 Å s^{-1} was selected. The deposition process was finalized when the automatic mode of the TES indicated 300 nm of thickness of the film deposited. A scheme of the system used to produce BiOBr thin films is showed in Fig. 1. The deposits were done on microscope glass slides of 12 mm × 75 mm.

2.2. Characterization

The formation process of BiOBr films was analyzed in a Bruker D8 Advanced diffractometer with Cu Kα radiation. The X-ray diffraction data were collected in the 2θ range from 10° to 70° with a scan rate of 0.05° in 0.05 s^{-1}. The morphology of the films and their composition were done by scanning electron microscopy (SEM) in an FEI Nova NanoSEM 200 operated at low vacuum to obtain images and in high vacuum for energy-dispersive spectrometry (EDS) analysis. The UV–vis diffuse reflectance absorption spectra of the films were obtained in an Agilent Technologies UV–vis–NIR spectrophotometer model Cary 5000 series equipped with an integrating sphere.

2.3. Photocatalytic experiments

The photocatalytic activity of the BiOBr semiconductor oxide in thin film was evaluated in the degradation reaction of RhB in aqueous solution under sun-like irradiation. A Xe lamp of 5600 K was used as irradiation source because this type of lamp reproduces better the energy balance coming from sun irradiation [24].

In a typical photocatalytic experiment, 12 glass slides with a total area of exposition of 108 cm^2 completely covered by BiOBr film were immersed in 200 mL of an aqueous solution of RhB (5 mg L^{-1}). The adsorption–desorption equilibrium of the organic dye on the surface of BiOBr film was reached by keeping the photocatalytic system in the dark for 1 h. During reaction, samples of 1.5 mL were taken at different time intervals of irradiation, and the concentration of RhB was determined in a Perkin Elmer Lambda 35 UV–vis spectrometer at $\lambda = 554$ nm.

The degradation degree (DE) of RhB by BiOBr thin films was calculated using the following equation:

$$DE = \frac{C_0 - C}{C_0} \times 100 \qquad (1)$$

where C is the concentration of RhB at the time t and C_0 is the concentration of organic dye after the adsorption–desorption equilibrium was reached before irradiation.

To determine the mineralization degree of organic dye, a photocatalytic experiment as was described above was performed but using an initial concentration of RhB of $C_0 = 50$ mg L^{-1}. After the adsorption–desorption equilibrium was reached by 60 min, the lamp was turned on and aliquots of 10 mL was taken each 24 h. The total organic carbon (TOC) content of the samples irradiated

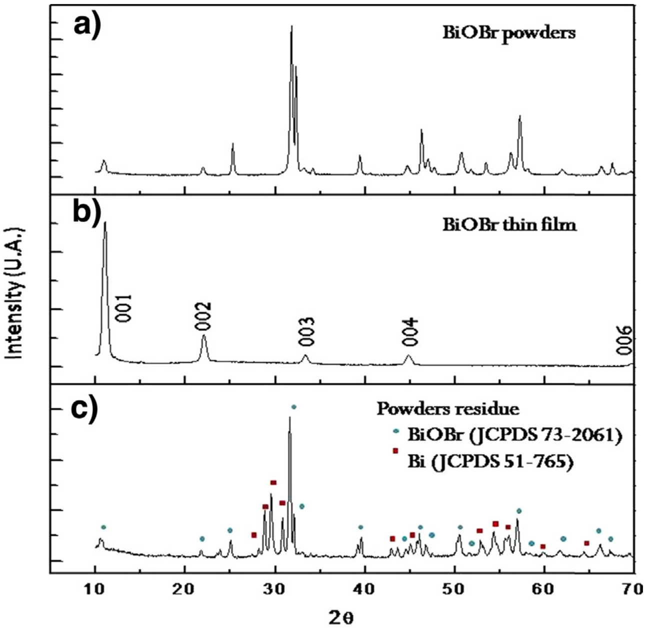

Fig. 2. XRD patterns: (a) BiOBr powders, (b) BiOBr thin film, (C) BiOBr residue.