Materials Science in Semiconductor Processing xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Enhanced photocatalytic performance of visible-light-driven BiOBr/$BiPO_4$ composites

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ARTICLE INFO

Keywords:
BiOBr/$BiPO_4$ composites
Photocatalysis
Electrochemical impedance spectroscopy (EIS)

ABSTRACT

Photocatalytic activity of $BiPO_4$ was successfully improved by loading with different contents of BiOBr. The as-synthesized products were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, Raman spectrophotometry, ultraviolet (UV)-visible spectroscopy and photoluminescence (PL) spectroscopy. The analytical results certified that the pure products were hexagonal $BiPO_4$ with rice-grain-like particles, tetragonal BiOBr with flower-like particles, and mixed phases and morphologies of the two individual constituents. Electrochemical impedance spectroscopy (EIS) and photocatalysis were evaluated and found that 50 mol% BiOBr/$BiPO_4$ was the best composites for wastewater treatment.

1. Introduction

At present, semiconducting photocatalysts are very important materials used for environmental purification and energy conversion. They are extensively applied to degrade pollutants through a green route without producing secondary by-products and are considered as scavengers of organic substances containing in surrounding environment [1,2]. Recently, much attention has been given to new type of photocatalysts with the visible light active Bi-based composites. They have been proved to be promising semiconductors due to their excellent reaction performance in degradation of organic pollutants [3–5]. In this research, bismuth phosphate ($BiPO_4$) is a new type of inorganic photocatalyst [6] which shows high photocatalytic ability for decomposition of organic dyes [7–9]. $BiPO_4$ has three different allotropes: hexagonal $BiPO_4$, low-temperature monoclinic $BiPO_4$ and high-temperature monoclinic $BiPO_4$ [10–12]. It can display higher photocatalytic activity than P25 because its electrostatic field formed by PO_4 tetrahedrons on its surface favors the separation of photo-generated electron-hole pairs. It has much attractive properties such as low-cost, nontoxicity, stable chemical structure including exceptional optical and electronic properties [11–13]. $BiPO_4$ has attracted more attention on photocatalytic degradation of organic pollutants. It stills need to be further improved photocatalytic performance by forming composites with Bi_2WO_6 [3], BiOX (X = Cl, Br, I) [4,5,10], graphene oxide [14], g-C_3N_4 [15], CuTCPP [16], CdS [17], AgBr [7] and Ag_3PO_4 [6,8]. Energy band gap of $BiPO_4$ is quite wide. It needs to be coupled with other narrow band gap materials. Researchers focused on the combination of two different bismuth composites to establish heterojunctions which can effectively separate charged carriers. Thus the semiconductor can be improved to have low recombination rate of electrons and holes, and photocatalytic activity of the composites was significantly improved under visible light [4].

Among the different semiconducting photocatalysts, Bi-based oxyhalide materials have been extensively studied in recent years because they have unique properties and potential applications in catalysis [18]. Bismuth oxybromide (BiOBr), one of bismuth oxyhalide compounds, has been aroused great attention owing to its special chemical and physical structure, and potential photocatalytic application [19,20]. It

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https://doi.org/10.1016/j.mssp.2017.11.002
Received 23 May 2017; Received in revised form 7 September 2017; Accepted 1 November 2017

has tetragonal structure built up from tetragonal (Bi_2O_2) positively charged slabs between double slabs of bromine atoms by forming (Br–Bi–O–Bi–Br) layers along the c-axis. The self-built electric field between positive layer (Bi_2O_2) and Br negative layer can be effectively separated the photo-induced electron–hole pairs. Electrons and holes diffuse to the surface of BiOBr, which enhances the photocatalytic activity for environmental purification [21–25]. Over the past few years, BiOBr-based composites for using as photocatalytic materials were prepared by different methods: wet impregnation [1], hydrothermal [2,26], solvothermal [27], sol-gel and precipitation [28,29]. They are simple process, easy solution manipulation and inexpensive method. $BiPO_4$/BiOBr composites were prepared by a facile one-step hydrothermal method [10]. The $BiPO_4$/BiOBr composites displayed much higher photocatalytic performance for degradation of RhB and MO than single $BiPO_4$ and BiOBr under visible light and simulated sunlight irradiation. The finding of simple and cost-effective route is the most challenge for present synthesis of nanocomposites. Consequently, microwave-assisted hydrothermal synthesis is used for synthesizing of the composite materials. This method requires shorter time and the product has higher purity.

The microwave-assisted hydrothermal method is a hybrid process of microwave radiation and hydrothermal route, and is a closed system. The solutions in closed vessels are heated by microwave radiation. Pressure inside the vessels is uniformly controlled [30]. The kinetics of reaction is greatly increased with a small increase of temperature. New metastable products form and are generally single crystal. The microwave hydrothermal route can be continuously processed. It is fast, simple, effective, environmentally friendly, low reaction temperature and low cost [31–33]. Based on our knowledge, there was no report on the synthesis of BiOBr/$BiPO_4$ composites by one-step microwave hydrothermal method for improvement of visible-light-driven photocatalyst for wastewater treatment.

Thus, the BiOBr/$BiPO_4$ composites synthesized by one-step microwave-assisted hydrothermal method were studied and reported for the photocatalytic degradation of rhodamine B (RhB) under visible light of Xe lamp. The BiOBr/$BiPO_4$ composites show higher photodegradation efficiency than pure $BiPO_4$ under visible light irradiation.

2. Experiment

2.1. Synthesis of pure $BiPO_4$, pure BiOBr and BiOBr/$BiPO_4$ composites

$BiPO_4$, BiOBr and BiOBr/$BiPO_4$ composites were synthesized by microwave-assisted hydrothermal method. Typically, 0.005 mol Bi$(NO_3)_3{\cdot}5H_2O$, 0.005 mol Na_2HPO_4 and different contents (0%, 10%, 30% and 50% by mole) of KBr were dissolved in 40 ml deionized (D.I.) water and adjusted the pH to 0.2 by 65% HNO_3 with continued stirring until homogeneous solutions were obtained. Then, each of the solutions was transferred to glass lab-made autoclaves which were tightly closed and irradiated by 270 W microwave for 30 min. In the end, the as-synthesized products were filtered, washed with deionized water and ethanol, and dried at 80 °C for 12 h.

2.2. Characterization

Crystallinity and phases of the products were analyzed by X-ray diffraction (Philips X'Pert MPD XRD) operating at 20 kV and 15 mA with Cu-K_α radiation in the range of 10–80°. The structural morphology was carried out by field emission scanning electron microscopy (JEOL JSM-6335F FE-SEM) operating at 35 kV and transmission electron microscopy (JEOL JEM-2010 TEM) operating at 200 kV. Fourier transform infrared spectroscopy (Perkin Elmer RX FTIR) was carried out at room temperature in the range of 400–4000 cm^{-1}. The analyzed pellets were prepared by 40 times KBr dilution for FTIR testing. Raman spectroscopy (T64000 HORIBA Jobin Yvon) was operated using a 50 mW and 514.5 nm wavelength Ar green laser. The optical properties were studied by a Perkin Elmer, Lambda-900 UV–visible spectrometer and a Perkin Elmer LS50B fluorescence spectrophotometer using 345 nm excitation wavelength. The electrochemical impedance spectroscopy (EIS) was measured at V_{oc} one-sun illumination with 0.1 M Na_2SO_4 electrolyte between Pt-coated film counter electrode and sample film coated on fluorine-doped tin oxide (FTO) as a working electrode, held by two heavy-duty clips. The EIS was also measured using an electrochemical spectrometer (Autolab PGSTAT302N Metrohm) in a three-electrode mode which contains a Pt sheet and Ag/AgCl as counter and reference electrodes. The powder sample as a slurry was coated on a FTO glass as a working electrode in 0.5 M Na_2SO_4 electrolyte.

2.3. Photocatalysis

The photocatalytic activities were tested by measuring photodegradation of rhodamine B (RhB) under visible light from 35 W Xe lamp. 0.2 g photocatalyst was suspended in 200 ml of 1×10^{-5} M RhB solution which was stirred for 30 min in the dark at room temperature. To initiate photocatalysis, the visible light of 35 W Xe lamp was irradiated on the solutions which were stirred throughout the test. For every a certain time interval, 4 ml suspension was sampled and centrifuged to remove residual photocatalyst. The concentration of RhB was investigated by a UV–visible spectrometer at λ_{max} of = 554 nm. The decolorization efficiency (%) was calculated by the equation

$$\text{Decolorization efficiency}(\%) = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 is the initial concentration of RhB and C_t is the concentration of RhB when the photocatalysis was proceeding within the elapsed time (t).

3. Results and discussion

3.1. XRD

XRD characterization was performed to identify the structural detail of as-synthesized samples. The XRD patterns of the as-synthesized $BiPO_4$, BiOBr and BiOBr/$BiPO_4$ with different mole percent of BiOBr loading material are shown in Fig. 1. The XRD pattern of pure $BiPO_4$ contained strong peaks at 2θ = 14.6°, 20.0°, 25.4°, 29.2°, 29.6°, 31.3°, 37.9°, 39.6°, 41.8°, 47.3° and 48.7° which were respectively assigned to the (100), (101), (110), (111), (200), (102), (112), (210), (211), (301) and (212) planes of hexagonal $BiPO_4$ phase comparing to the JCPDS file No. 15-0766 [34]. The strong XRD diffraction peaks of pure BiOBr at 2θ = 10.9°, 22.0°, 25.3°, 31.7°, 32.3°, 39.6° and 46.4° can be assigned to the (001), (002), (101), (102), (110), (112) and (200) planes of tetragonal BiOBr structure (JCPDS file No. 09-0393) [34], respectively. For the BiOBr/$BiPO_4$ composites, their characteristic peaks were composed of both $BiPO_4$ and BiOBr phases. They should be noted that the XRD intensity of BiOBr was increased with the increase of BiOBr loading content. These results certify that the BiOBr/$BiPO_4$ composites were successfully synthesized by a one-step microwave-assisted hydrothermal method.

3.2. SEM and TEM

The SEM images and EDS spectra (Fig. 2) show different morphologies of pure $BiPO_4$, pure BiOBr and BiOBr/$BiPO_4$ composites. The pure $BiPO_4$ product was composed of a number of rice-grain-like particles with the length of 400–1300 nm. For the pure BiOBr product, it shaped like flowers composed of nanoplate petals. During synthesizing these products by microwave-assisted hydrothermal method, nucleation and growth proceeded with the controlled shape and size [35]. For the 10 mol% BiOBr/$BiPO_4$ composites, they contained only rice-grain-like particles. The mixed rice-grain-like and flower-like particles were detected in the 30 mol% and 50 mol% BiOBr/$BiPO_4$ composites, mixed