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Immobilized Heteropolyacids with zeolite (MCM-41) to enhance photocatalytic performance of BiOBr

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ABSTRACT

BiOBr composites modified phosphotungstic acid immobilized with zeolite have been synthesized via impregnation method in which BiOBr is the primary light-absorber and phosphotungstic acid acts as an electron accepter. Photocatalysts were characterized by X-ray diffractometry (XRD), Scanning electron microscopy (SEM) and UV–vis diffuse reflectance spectra (DRS). Photodegradation experimental results on the degradation of methyl orange showed that the samples exhibited superior photocatalytic property under visible light irradiation.

1. Introduction

Semiconductors especially TiO_2 have received considerable attention for its practical applicability aiming to solve environmental and energy points [1]. However, the photocatalytic efficiency of TiO_2 is limited by its large band-gap energy and rapid recombination of photo-exited electron–hole pairs [2]. In recent years, Bi-based photocatalysts such as BiOBr has become the top-performer among the all metal oxide photocatalysts due to its attractive physical properties: intrinsic indirect band-gap, high refractive index, dielectric permittivity, and photoconductivity [3–6]. And numerous efforts have reported to enhance its photocatalytic activities. For example, Wang et al. have prepared visible light-driven Ag_2CO_3/BiOBr photocatalysts to broaden its visible light region [7], Lin et al. fabricated Bi-based semiconductors composites to enhance its photocatalytic properties [8,9].

Heteropolyacids (HPAs) is a well-defined transition metal oxygen clusters with structural diversity, showing many applications in catalysis, electronics, optics, medicine, biology, etc. [10]. Among these, $H_3PW_{12}O_{40}$(PTA) has received lots of attention as catalysts for redox processes involving organic substrates, since it is a good electron acceptor which can store several electrons per molecule [11]. However, this material has poor thermal stability, so, many researchers prefer to support HPAs on solid surfaces such as carbon, SiO_2, SBA-15 zeolites, aiming to increase its thermal stability [12–15].

Herein, to implement aforementioned concepts, we synthesized the composites of phosphotungstic acid immobilized with zeolite to modify BiOBr. Because of the porous structural feature of zeolite, the composites exhibit significantly enhanced photocatalytic activity for degradation of MO due to a larger specific surface area. And as due to a perfect electrons acceptor, photogenerated electrons were trapped by PTA under visible light irradiation, which cooperated resulting in an excellent quantum efficiency.

2. Experimental

2.1. Preparation of the samples

0.5 g Zeolite and different stoichiometric amount of phosphotungstic acid were initially dissolved in 30 mL distilled water, stirring for 0.5 h at 40 °C and were of ultrasonic for 0.5 h to be dispersed well. Then, the mixture was treated in water bath at 60 °C to evaporate. Resultant precipitates were washed with

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distilled water and ethanol for several times and finally dried at 60 °C for 10 h. The amount of added phosphotungstic acid (PTA) 0.125 g, 0.33 g, 0.75 g and 2.0 g were marked as MP-1, MP-2, MP-3, MP-4, respectively. Synthesis of MP–BiOBr is same with MPs. 0.5 g MPs and 0.5 g BiOBr were dissolved in 30 mL distilled water, stirring for 0.5 h at 40 °C and were of ultrasonic for 0.5 h to be dispersed well and finally evaporate at 60 °C. The composites of MP-1, MP-2, MP-3, MP-4 and BiOBr were defined to be MPB-1, MPB-2, MPB-3, MPB-4, respectively. Preparation of MCM-41 and BiOBr were shown in the Supplementary information.

2.2. Materials characterization

The morphologies, crystal structures and photo-response range were characterized by scanning electron microscopy (SEM, JSM-6701F, 5 kV), parallel beam X-ray diffraction (XRD, D/MAX-2200/PC, Cu-Kα, 40 kV, 20 mA) and X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-2200/PC equipped with graphite monochromatized Cu-Kα radiation (40 kV, 20 mA). SEM micrographs were observed using JSM-5600LV and UV–vis diffuse reflectance spectroscopy (DRS) of powder samples was carried out at room temperature using a Shimadzu Model 3100 (200–800 nm).

2.3. Measurements of photocatalytic activities

The photocatalytic experiments were carried out in a reactor containing 0.6 g photocatalysts and 60 mL 10 mg/L aqueous solution of methyl orange (MO). A high pressure xenon short arc lamp (CHF-XM35-500W, Beijing Changtuo Co.) was served as the visible light source, a glass filter (ZUL0400, Asahi Spectra Co.) was added to allow visible light ($\lambda > 420$ nm) to pass through. The suspensions were stirred for 0.5 h to reach adsorption–desorption equilibrium of MO molecules on the surface of catalyst. The concentration of MO was determined by recording the variations of supernatant at 464 nm using UV–vis spectrophotometer (TU-1901, Beijing Pgeneral).

3. Results and discussion

SEM imaging was used to study the surface morphology of MPBs composites. As shown in Fig. 1a, the ordered macropore structure with channels in 1–2 μm of MCM-41 can be observed and uniform dispersed nanoplates of pure BiOBr are also visible in Fig. 1b. As shown in Fig. 1c–f, the BiOBr plates and $H_3PW_{12}O_{40}$ (PTA) are strongly stacked to the highly porous structure of MCM-41, not only to the outermost surface of the particles but also to their interior.

X-ray diffraction (XRD) analysis was conducted to investigate the crystallographic structure of the prepared samples. As shown in Fig. 2a, all the characteristic diffraction peaks of BiOBr can be well-indexed to the tetragonal phase (JCPDS 09-0393) and no other impurities were indexed. Compared to MPB-3, the marked peaks can be perfectly indexed to (222), (611), (550) reflections of the $H_3PW_{12}O_{40}$ (JCPDS 50-0657). In addition, the photocatalytic activity is closely related to the absorption capacity of the photocatalysts, as shown in Fig. 2b, it can be clearly observed that the band gap adsorption edge of pure BiOBr is lower than about 430 nm. And the MPBs samples show a systematical red shift of absorbance region, which indicate that the MPBs could be candidate as visible-light catalysts. The band gap energy can also be estimated [16] and the estimated band gap energy of BiOBr was 2.80 eV, which are comparable with those of BiOBr reported before [17].

The photocatalytic experiments were evaluated via degradation

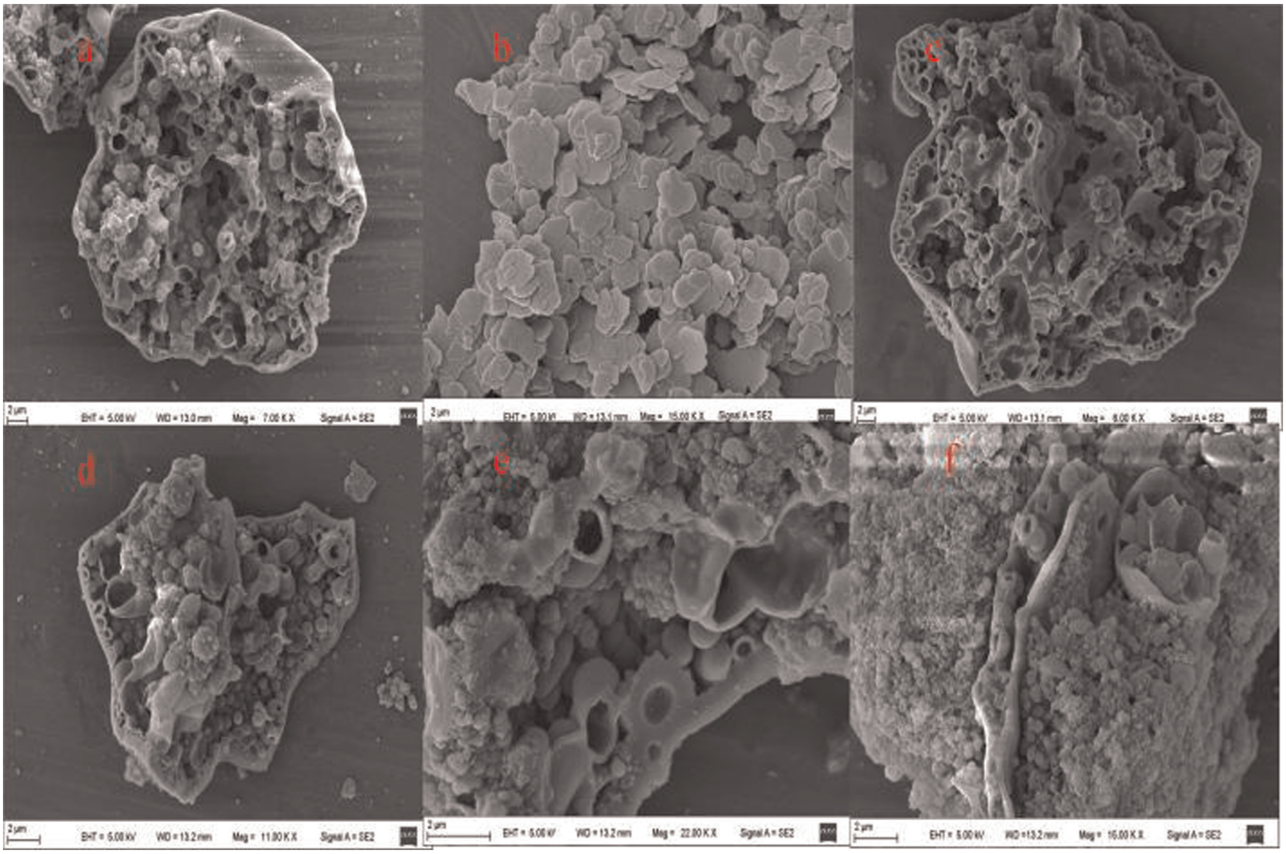

Fig. 1. SEM images of (a) MCM-41, (b) pure BiOBr, (c) MPB-1, (d) MPB-2, (c) MPB-3, and (e) MPB-4 of as-prepared samples.