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Short communication

Surfactant (CTAB) assisted flower-like Bi_2WO_6 through hydrothermal method: Unintentional bromide ion doping and photocatalytic activity

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ABSTRACT

In addition to morphology control, the unnoticed doping effect of adding surfactant CTAB in hydrothermal synthesis of visible-light driven photocatalyst was also found. In the meantime of assisting the microstructure assembling to higher 'surface accessibility', a small amount of doped Br-lowered the band gap of Bi_2WO_6 and expanded its optical absorption in visible light region and thus further improved the photocatalytic performance. To our knowledge, this is the first study reporting this doping effect of surfactants. We expect to provide new insights into the roles of surfactants participating in photocatalyst synthesis.

1. Introduction

Heterogeneous visible-light driven photocatalysts have been widely studied for photocatalytic degradation of organic compounds due to their potential applications in wastewater purification [1]. With the advantages of simplicity, high efficiency and low cost, hydrothermal method is widely used to prepare the photocatalysts [2]. In order to further improve catalytic efficiency of prepared photocatalysts, two primary approaches have been mostly studied. One effective technique is doping with other elements to hinder the recombination of electron-hole pairs [3,4]. For photocatalytic and adsorption properties of photocatalyst are closed related to their microstructure and morphology, another method is morphology control by controlling experimental conditions or adding assistant additives in synthesis process [5,6]. In previous works, various surfactants have been reported to show effectiveness on fabricating visible-light driven photocatalysts with controllable crystal phases and morphologies and thus to enhance catalytic ability, such as polyethylene glycol (PEG), cetyltrimethyl ammonium bromide (CTAB), surfactant sodium dodecyl sulfate (SDS) [7–10].

It is widely accepted that surfactant hinders the crystal growth to control crystal morphology in preparation process, and there was no mention of whether the surfactants were consumed as element source in crystal growth [11]. Therefore, to clarify the current fuzzy perception of their whole functions in crystal synthesis, the roles of these surfactants in the preparation process would be investigated by systematical characterizations in this study.

Herein, we choose bismuth tungstate (Bi_2WO_6) as synthetic objects, which was an excellent frequently-studied visible-light driven photocatalyst with remarkable photocatalytic activity and some other special electrical properties [12–16]. We firstly prepared Bi_2WO_6 by a facile hydrothermal method with typical cationic surfactant CTAB and several other surfactants for comparison, such as CTAB, SDS, polyvinylpyrrolidone (PVP), sorbitan polyoxyethylene monooleate (Tween 80), PEG 600 and PEG 6000. Then the photodegradation of model pollutant Rhodamine B (RhB) was employed to evaluate the photocatalytic activities under visible-light illumination. Compared with other dispersants, CTAB was found to exhibit most excellent assistance performance in Bi_2WO_6 synthesis. The particle shape, surface area, size and crystal structure were examined to further understand the mechanism of enhanced photocatalysis efficiency. The comprehensive mechanism of CTAB participating in hydrothermal synthesis was discussed on the basis of the materials characterization and adsorption performance.

2. Experiment

2.1. Synthesis of photocatalysts

All the chemical reagents were commercially available and employed without further purification. All solutions were prepared

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with distilled water. The Bi_2WO_6 photocatalyst was synthesized by a typical hydrothermal process. 1.65 g (0.05 mol) of $Na_2WO_4 \cdot 2H_2O$ and 4.85 g (0.1 mol) of $Bi(NO_3)_3 \cdot 5H_2O$ were put into two beakers and dissolved with deionized water under magnetic stirring. After that, 1 g of polyvinylpyrrolidone (PVP), CTAB, SDS, sorbitan polyoxyethylene monooleate (Tween 80), PEG 600 and PEG 6000 were added to the Na_2WO_4 aqueous solution to form a homogeneous mixture, and then the mixture was dropped dropwisely to the $Bi(NO_3)_3$ aqueous solution. Then the mixture suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 20 h. After cooling, the resulting products were filtered off and washed three times with absolute alcohol and deionized water, and dried in a vacuum at 70 °C for 5 h. Samples Bi_2WO_6 will be named as BWO.

2.2. Photocatalytic and adsorption experiments

The photocatalytic activities of the prepared BWO powders were evaluated by the photo-degradation of RhB aqueous solution (initial concentration of 10 mg/L) in quartz photochemical reactor. A 300 W Xenon lamp (Nbet HSX-F300, Beijing) with a 400 nm cut-off filter was used as visible light source. The photo degradation was performed as follows: the 100 mL RhB solution containing 0.1 g BWO kept in ultrasonic process for 5 min and after in dark for 60 min to achieve adsorption-desorption equilibrium between catalysts and RhB, then the suspension transfer in a cylindrical photoreactor equipped with a water cooling system under magnetic stirring. Every 10 min of time intervals, 3 mL mixture was sampled, centrifuged and filtered using 0.45 m polytetrafluoroethylene (PTFE) filters to remove photocatalysts. The absorbance of RhB solution was analyzed by measuring the maximum absorbance at 554 nm using a UV–vis spectrophotometer (UV-2600, Shimadzu, Japan) [17].

The removal ratio of RhB was calculated by using the following equation:

$$R(\%) = \frac{C_0 - C}{C_0} \quad (1)$$

where R is the removal ratio of RhB. C_0 and C are initial and instantaneous concentrations of RhB (mg/L), respectively.

All batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks with 100 mL of RhB solutions and 0.1 g photocatalyst, performed under the conditions of 100 rpm shaking, 28 ± 0.5 °C, pH 7.5, in dark.

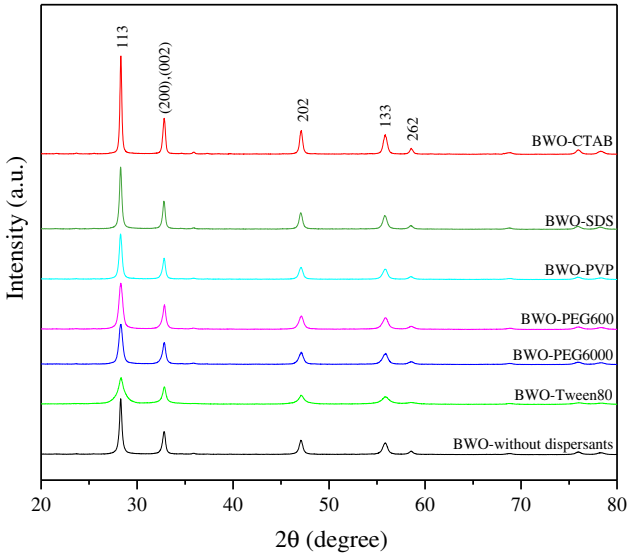

Fig. 1. XRD pattern of as-prepared BWO photocatalysts.

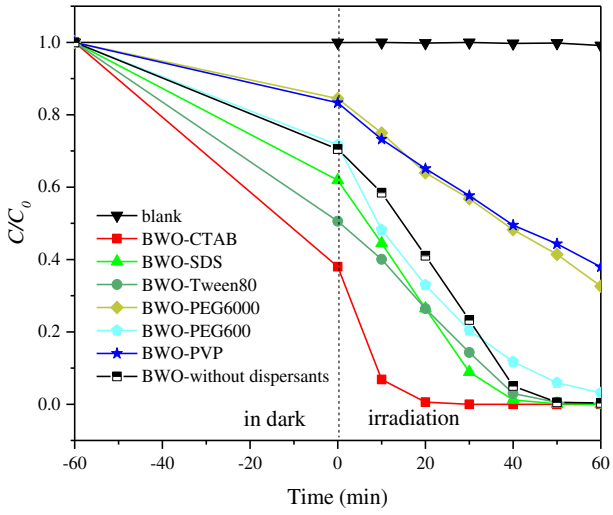

Fig. 2. Photocatalytic activities of various dispersant-assisted BWO samples.

2.3. Characterization methods

The composition of the products were analyzed by XRD (XRD, Rigaku, RXIII) in a range of 20–80° (2θ). XPS images were recorded on a XPS system (XPS, K-Alpha, Thermofisher Scientific Company, US). The morphology and microstructures were observed by using a SEM (FESEM, Model S-4300, Hitachi, Japan). Energy-dispersive X-ray spectroscopy (EDX) was following on FESEM image captured. UV–vis DRS were recorded using an UV–vis spectrophotometer (UV-2550, Shimadzu, Japan) in the range 220–800 nm using $BaSO_4$ as reference.

3. Results and discussion

3.1. Characterization and performance testing

The phase structure and phase composition of the obtained samples in the presence of different surfactants were characterized by XRD technique. As shown in Fig. 1, the XRD patterns of all the samples obtained in the presence of different surfactants readily indexed to the pure orthorhombic phase of Bi_2WO_6 (JCPDS No. 20-0172), which showed

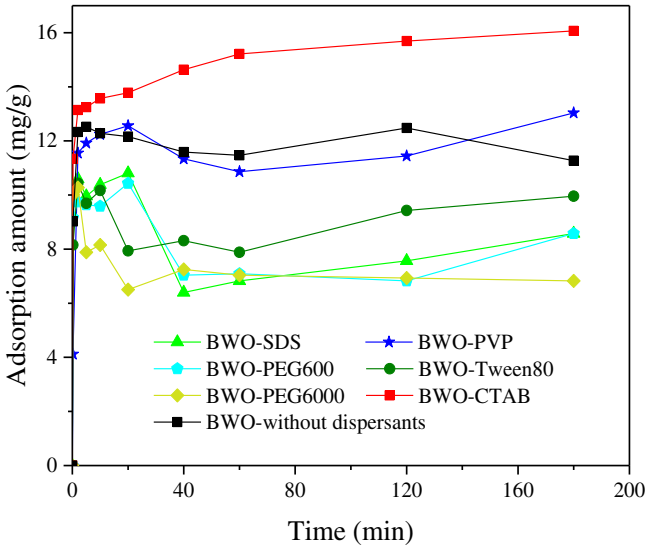

Fig. 3. Adsorption performance of as-prepared BWO samples.