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Short Communication

# Facile one-pot preparation of $Bi_6O_6(OH)_3(NO_3)_3$•$1.5H_2O$-$Bi_2WO_6$ heterostructure with superior photocatalytic activity

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ABSTRACT

Basic bismuth nitrate $Bi_6O_6(OH)_3(NO_3)_3$•$1.5H_2O$ (BBN) modified $Bi_2WO_6$ heterostructures was facilely synthesized by one-pot hydrothermal strategy. The modification of BBN effectively improves the photocatalytic activity of $Bi_2WO_6$ for degradation and mineralization of Rhodamine B. The enhanced photocatalytic performance is attributed to the increased surface area and effective separation of photogenerated carriers induced by the potential difference at BBN/$Bi_2WO_6$ interface. Furthermore, the micro-scaled heterostructure is easily recycled with excellent circulating stability. The work provides some new insights for the rational design and synthesis of basic salt modified Bi-system photocatalyst with high efficiency.

## 1. Introduction

Extensive attention has been directed on heterogeneous semiconductor photocatalysts for the green and cost-effective application in wastewater remediation [1,2]. Especially, the development of visible-light-driven photocatalysts has achieved great interest from the viewpoint of efficient utilization of solar energy. Bismuth tungstate ($Bi_2WO_6$) has been confirmed to be a promising alternative due to the response to visible-light up to 460 nm [3]. Great efforts have been made in the preparation of $Bi_2WO_6$ nanostructures [4,5] and various hierarchical structures [6–8] to achieve high photocatalytic activity and good retrievability. Especially, flower-shaped $Bi_2WO_6$ microspheres [9–11] with abundant mesopores presented much superior photocatalytic performance due to the allowance of light penetration and the reactive species transfer.

Despite great potential, fast recombination of photoinduced $e^-/h^+$ pairs still hinders its practical commercialization. The modification of noble metal [12,13] and metal oxides [14–16] has been employed to further enhance the photocatalytic behavior of $Bi_2WO_6$. The loading species influences the photoactivity by broadening the visible-light absorption or acting as carrier trappers to facilitate the separation and migration of $e^-/h^+$ pairs. However, the loading species are limited due to the high cost of noble metal or the matching band-edge of metal oxide. The modification of $Bi_2WO_6$ with basic salts has never been reported. Bi-based basic salts with rich crystal chemistry were preliminarily studied for medical application and as precursor for bismuth oxides [17]. Very recently, the basic bismuth (III) nitrate with composition of $Bi_6O_6(OH)_3(NO_3)_3 \cdot 1.5H_2O$ (BBN) was found to be a new type of photocatalyst [18,19]. But BBN only responses to UV light due to the wide band-gap of 3.38 eV, which significantly hinders the practical application. However, there is somewhat alike in the preparation parameters of our previously synthesized $Bi_2WO_6$ microflowers [11] and the novel BBN. It should be feasible to combine BBN with $Bi_2WO_6$ and investigate the co-catalysis effect.

Herein, BBN modified $Bi_2WO_6$ (BBN/BWO) heterostructure was facilely prepared by one-pot hydrothermal method. The structure and photocatalytic behavior for the degradation of RhB were systematically investigated. The composite exhibited much superior photocatalytic activity due to the enhanced surface area and promoted separation of photogenerated $e^-/h^+$ pairs at BBN/BWO interface. It is noteworthy that this is the first report regarding BBN/BWO hierarchical heterostructure for the degradation of organic compounds.

## 2. Experimental

### 2.1. Preparation of BBN/BWO

BBN/BWO composites were prepared by one-pot hydrothermal strategy. In a typical case, 1.0 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 0.4 mmol $Na_2WO_4 \cdot 2H_2O$ were mixed in 17.0 mL distilled water. After stirring for 30 min, the suspension was transferred into a 25 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h. After the autoclave cooled to room temperature, the product were collected, washed and dried at 60 °C to obtain BBN/BWO-0.08 (molar ratio, SI). Other BBN/BWO samples were prepared following the same procedure by

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adjusting the amount of Bi source. Pure $Bi_2WO_6$ and BBN were synthesized by using stoichiometric Bi and W resources and only with $Bi(NO_3)_3 \cdot 5H_2O$, respectively.

### 2.2. Characterization

The crystal phase was characterized by X-ray diffraction (XRD) on a Bruker D8-Advance diffractometer. Surface chemical state was recorded on a Thermo Fisher K-alpha X-ray photoelectron spectrometer (XPS). Morphology and microstructure were examined with a field-emission scanning electron microscopy (FEI, NOVA Nano SEM 230) and a transmission electron microscopy (FEI, Tecnai $G^2$ F20). $N_2$ adsorption-desorption isotherms were collected using a Micromeritics ASAP2020 surface area and porosity analyzer. Diffuse reflectance spectra (DRS) were recorded on a JASCO V-550/V-570 UV–vis spectrophotometer. Photoluminescence (PL) spectra were recorded with a F-4500 fluorescence spectrophotometer. Total organic carbon (TOC) was measured by a Shimadzu TOC-$V_{CPH}$ analyser.

### 2.3. Photocatalysis

Photocatalytic activity was evaluated by the degradation of RhB under simulated sunlight with a 500 W Xe lamp. In each experiment, 5.0 mg photocatalyst was added into 10 mL of RhB solution ($10^{-5}$ M) in a quartz tube. Before illumination, the suspension was magnetically stirred in dark for 30 min to establish an adsorption-desorption equilibrium. Then at given time intervals, a quartz tube was taken out and the photocatalyst was immediately separated to analyze the supernate by degradation efficiency (SI).

## 3. Results and discussion

The XRD patterns of $Bi_2WO_6$, BBN and BBN/BWO composites are shown in Fig. 1a. Pure orthorhombic $Bi_2WO_6$ (JCPDS 29-713) with high crystallinity is obtained with stoichiometric $Bi(NO_3)_3 \cdot 5H_2O$ and $Na_2WO_4 \cdot 2H_2O$ used in the preparation. By adjusting excess Bi source, the products present the dominant peaks of $Bi_2WO_6$ but with two new peaks appearing at 10.3° and 31.3°, respectively. The positions

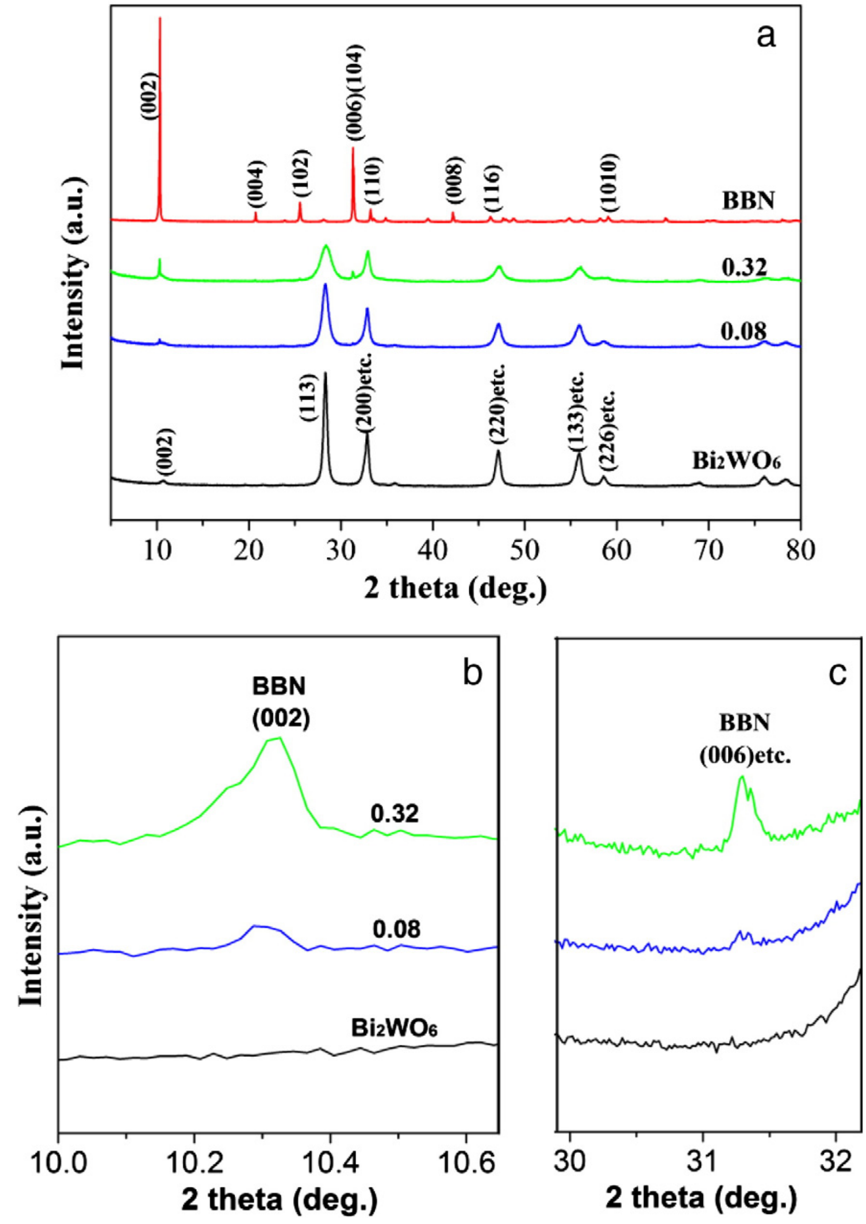

**Fig. 1.** XRD patterns of $Bi_2WO_6$, BBN and BBN/BWO composites: (a) wide angle diffraction, (b–c) partially enlarged diffractions.