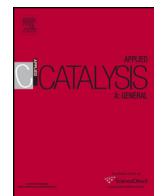




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# Fabrication of hexagonal/cubic tungsten oxide homojunction with improved photocatalytic activity

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### ABSTRACT

A homojunction with different phases of tungsten oxide photocatalyst was prepared via a hydrothermal method by adjusting the pH value. The structural analysis showed the homojunction consisted of tungsten bronze-type (hexagonal) and pyrochlore-type (cubic) structures. The rod-like hexagonal phase inserted into block cubic phase to form a well-defined homojunction structure under the proper pH condition. The activity of photocatalyst was tested through degrading RhB and water oxidation. The results indicated the homojunction photocatalyst displayed a higher photocatalytic activity compared with individual tungsten oxide under visible light and full sunlight spectra irradiation. The further investigations revealed the inner electric field at the interface of the homojunction facilitated the separation of electron-hole pairs, resulting in the improved photoelectrochemical performance. The design of favorable tungsten oxide homojunction structure in the present work provided a promising method for the development of other efficient photocatalysts.

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## 1. Introduction

Semiconductor photocatalysts have been intensively investigated in the last decades as it is potential in the applications to degradation of harmful pollutants and water splitting [1–3]. To further improve the photocatalytic activity, heterogeneous structures are considered as one of effective strategies to design new photocatalysts. Two major heterostructures, metal/semiconductor and semiconductor/semiconductor, are commonly applied in photocatalytic research [4–8]. Several factors are taken into consideration for an efficient heterojunction, such as proper material choice, surface properties, band structure matching and crystallinity of photocatalysts [9].

Recently, the homojunction constituted by the different phases of the same photocatalyst has attracted much attention for it is simple, controllable and usually of great photocatalytic activity [10–12]. Li and coworkers reported that an efficient homojunction formed between the anatase and rutile TiO<sub>2</sub> nanoparticles could greatly enhance the photocatalytic activity for hydrogen production, suggesting that the enhanced photocatalytic activity

was related to the efficient surface-phase junctions [13]. They also demonstrated another homojunction of  $\alpha/\beta$  Ga<sub>2</sub>O<sub>3</sub> and put forward that the promoted charge separation induced by the inner electric field between  $\alpha$  and  $\beta$  Ga<sub>2</sub>O<sub>3</sub> was the main reason for the improvement of photocatalytic activity [14]. Based on the matching band principle, Zhang's group selected the  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> to build a  $\alpha/\gamma$  Bi<sub>2</sub>O<sub>3</sub> homojunction photocatalyst through a controllable synthesis method, which showed better activity in the degradation of RhB than that of single phase Bi<sub>2</sub>O<sub>3</sub> [15]. Usai et al. reported the preparation of a highly active homostructured monoclinic/tetragonal-BiVO<sub>4</sub> system by yttrium doping, which noted the presence of yttrium and the formation of monoclinic/tetragonal homostructure would suppress the recombination of charge carriers and lead to a higher photon efficiency [16]. From these reports, it can be seen that the homojunction has been proposed as one of the effective and promising strategies to improve the activity of photocatalysts.

Tungsten oxide (including tungsten oxide hydrate), as a kind of n-type semiconductor material, has been intensively studied due to their good optical and electrical properties, and the potential applications in lithium batteries, electrochromic windows, gas sensors and photocatalysis [17–21]. Furthermore, the tungsten oxide-based materials appear some different crystal structures including tungsten bronze-type hexagonal, pyrochlore-type cubic

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and so on, which suggests a potential in constructing homojunction photocatalysts. In the previous studies, both tungsten bronze-type hexagonal phase and pyrochlore-type cubic phase have received attentions for application to photocatalyst and show a high activity for degrading pollution and splitting water [22–24]. It should be emphasized that the realization of efficient homojunction demands the energy structure match between two different phases, which has been used as the standard to constitute homojunction from a series of existing phases. In our work, the valence band spectra analysis indicates that the hexagonal and the cubic tungsten oxides are proper to constitute a homojunction.

In the present work, a tungsten bronze-type hexagonal/pyrochlore-type cubic homojunction has been prepared via a one-step hydrothermal method with an appropriate pH condition. This homojunction photocatalyst greatly improves the photocatalytic activity for degrading RhB and producing oxygen from water oxidation compared with individual tungsten oxide. The mechanism of improved photocatalytic activity of homojunction is discussed in detail. The work can provide a promising approach for the development of efficient homojunction photocatalysts.

## 2. Experimental

### 2.1. Preparation of photocatalysts

All reagents were of analytical grade and used as received without purification. The synthesis of photocatalysts was carried out using a facile manner via a hydrothermal method. In a typical procedure, 3.30 g  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  and 5.85 g NaCl were dissolved in 70 mL deionized water, and the above solution was vigorously stirred for 10 min. Then the pH values of the solution were adjusted to  $\sim 1.5$ ,  $\sim 2.5$  and  $\sim 3.5$  by drop-wise adding of concentrated HCl solution (11.8 mol/L) under constant stirring. The resulting mixture was transferred into 100 mL Teflon-lined stainless-steel autoclave, sealed, and maintained at 453 K for 24 h. The products were collected by centrifugation and washed for three times with deionized water and ethanol, then dried at 333 K for all night.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a D8 Advanced X-ray diffractometer (Bruker Germany), using  $\text{Cu K}\alpha$  radiation at a scan rate of  $0.02^\circ 2\theta \text{ s}^{-1}$ . Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray emission was carried out by using an S-4800 field emission SEM (FESEM, Hitachi, Japan) with an accelerating voltage of 5 kV. High-resolution transmission electron microscopy (HRTEM) analysis was conducted with the use of a JEM 2100 microscope at an accelerating voltage of 200 kV. Ultraviolet visible (UV–vis) diffuse reflectance spectra were recorded using a UV–vis spectrophotometer (Shimadzu UV-2550, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer equipped with an Al  $\text{K}\alpha$  source. All the binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon. Infrared absorption and Raman spectra were recorded by Thermo Nicolet NEXUS 670 FT-IR spectrophotometer. Nitrogen absorption isotherms were measured with an ASAP 2020 absorption analyzer at liquid nitrogen temperature. Prior to the measurements, the samples were degassed at a temperature of 77 K for 10 h. The Brunauer-Emmett-Teller (BET) surface area was determined from the relative pressure range of 0.05–0.3. The photoluminescence (PL) measurements were performed in a luminescence spectrophotometer (Hitachi F-4500) operate at room temperature with the excitation at 275 nm.

### 2.3. Photocatalytic experiments

The photocatalytic activities of the as-prepared samples were evaluated by decolorization of rhodamine B (RhB) under visible light irradiation from a 300 W metal-halide lamp equipped with a 420 nm cutoff filter. The 50 mg photocatalyst of each experiment was dispersed into 50 mL RhB (10 mg/L) aqueous solution. Prior to light irradiation, the solution was continuously stirred in the dark for 0.5 h to ensure the establishment of absorption-desorption equilibrium between the sample and RhB. At given time (30 min) intervals, 5 mL of each sample was taken, followed by centrifugation to remove the photocatalyst. The concentration of RhB was determined in terms of the change of optical absorption at 552 nm during the photoreaction using a Hitachi U-3500 UV–vis spectrometer.

Photocatalytic oxygen evolution was performed in a quartz reaction connected to a closed gas circulation system. A 300 W Xe lamp was employed to simulate sunlight spectra. Both simulated visible light ( $\lambda > 420 \text{ nm}$ ) and full sunlight spectra are considered to test the activity of the as-prepared samples. In each run, 0.1 g photocatalyst powder was suspended in 100 mL water with a constant magnetic stirring. Prior to irradiation, the system was vacuumized to remove air completely. The evolution of oxygen was measured by using an on-line gas chromatography with thermal conductivity detector (TCD).

### 2.4. Photoelectrochemical measurements

The photocurrents were carried out by an electrochemical workstation in a standard three electrode system, in which three electrodes were composed with the sample as the working electrode, a Pt foil as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. For the fabrication of the working electrode, samples were obtained by mixing 40 mg of as-prepared powder and a certain amount of Nafion solution homogeneously. The samples were then spread on an indium-tin oxide (ITO) conducting glass by spin coater and dried at 373 K for 1 h. A 300 W Xe lamp (PLS-SXE300C, Beijing Trusttech Co., Ltd) was used as the light source. The electrolyte was a 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution. It was bubbled with nitrogen for 30 min under vigorous stirring before measurement. The photocurrents with light on and off were measured at 0.5 V. In the electrochemical impedance spectroscopy (EIS) measurements, the frequency was scanned from 0.01 to 100,000 Hz at an applied under simulated sunlight irradiation.

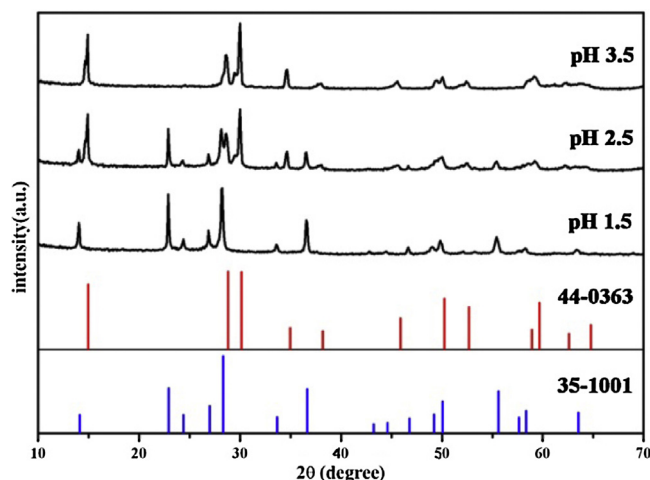


Fig. 1. XRD patterns of the three samples prepared at different pH values. The vertical lines are standard diffraction peaks from JCPDS no. 35-1001 and no. 44-0363.

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