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Enhanced photocatalytic performance of tungsten oxide through tuning exposed facets and introducing oxygen vacancies

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ABSTRACT

It is known that the exposed facet and defect state are crucial to the photocatalytic performance. Here, we report that the exposed facets of the building blocks in the tungsten oxide hierarchical nanostructures could be controlled by adjusting the amount of formamide in the hydrothermal precursor solution and the oxygen vacancies were successfully introduced through the post-air annealing. It is found that exposing high percentage (020) facet is unbeneficial for the photocatalytic performance and (200) and (002) facets should be the photocatalytic active facets of the hexagonal tungsten oxide. The hexagonal tungsten oxide with oxygen vacancies and maximum (200) and (002) facets archives highest photocatalytic performance in degrading rhodamine B under simulated solar light irradiation, which the rate constant per specific surface area (k/SBET) is 7.3 times as high as the sample without oxygen vacancies and minimum (200) and (002) facets. Both introducing oxygen vacancies and exposing (200) and (002) facets can enhance the separation efficiency of photo-generated charges, thus improving the photocatalytic performance.

1. Introduction

Photocatalysis is an effective strategy to deal with the increasingly serious environment problems. Tungsten oxide has received considerable attention in the field of photocatalysis due to its earth-abundance, highly tunable composition, high chemical stability at appropriate pH value, and excellent electrical conductivity [1]. Tungsten oxide is made up of perovskite units and is one of the most-attractive candidates for photocatalysis, as it exhibits approximately absorption of 12% of the solar spectrum (Eg = 2.5–2.8 eV), a moderate hole-diffusion length (150–500 nm) compared with α-Fe_2O_3 (2–4 nm), and better electron transport (~12 $cm^2\ V^{-1}\ s^{-1}$) compared with TiO_2 (~0.3 $cm^2\ V^{-1}\ s^{-1}$) [1,2]. However, bulk tungsten oxide often has some drawbacks such as insufficient quantum efficiency and high recombination rate of the photoproduced electron-hole pairs, which limit its practical application on photocatalytic field.

The reactivity of a photocatalyst is basically influenced by its surface atomic and linked electron structure. Tuning exposed facet is becoming an important strategy to optimize the reactivity of a photocatalyst [3,4]. Abundant references have reported the determinant effects of exposed facets on the performance of TiO_2 [3,5–7]. However, the photocatalytic activity dependent on the exposed facets of tungsten oxide has been preliminarily investigated [8–21]. The photoactive facets are usually phase-dependent. Among the different crystal structures of tungsten oxides, the previously reported highly active facets for tungsten oxides were mainly toward monoclinic tungsten oxide [8–16], it may because monoclinic tungsten oxide is the most stable tungsten oxides in the room temperature and easily prepared [12]. Recently, hexagonal tungsten oxide (h-WO_3) are received great attention in many fields especially photocatalysis due to its unique structural features such as long, hexagonal prism channels parallel to the c-axis and layered oxygen octahedral [17,22–26]. Moreover, h-WO_3 is also stable in the room temperature [27]. However, exposed facet-dependent photocatalysis of tungsten oxides especially hexagonal tungsten oxide is still not well established or systematically studied.

Besides exposed facets, defect state especially oxygen vacancy is another important factor that influencing the photocatalytic performance, because the electronic configurations, charge transfer and surface properties of semiconductor based photocatalyst are

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closely related to the oxygen vacancies [28]. Many researchers reported that oxygen vacancies especially surface oxygen vacancies would appear above and partly overlap the valence band (VB), thus leading to the rising of the valence band maximum (VBM) and the narrowing of the band gap width, expanding the photoresponse wavelength range [29–33]. The rising of VBM can also expand the VB width, which would increase the transport rate of photogenerated carriers, resulting in the enhancement of the separation efficiency of photoinduced electron-hole pairs [31]. There are many approaches to introduce oxygen vacancies, such as hydrogen treatment [34,35], ball milling [36] and air annealing [37,38]. Among them, air annealing through control the annealing temperature and time is a very convenient and effective method for introducing oxygen vacancies.

Herein, the hexagonal tungsten oxide hierarchical nanostructures synthesized via hydrothermal reaction for application in photocatalysis is reported. The exposed facets of the building block were controlled by adjusting the amount of formamide and the oxygen vacancies were introduced through post-air annealing. The exposed facets and oxygen vacancies dependent-photocatalytic performance and photoelectrochemical property were investigated.

2. Experimental

2.1. Synthesis of materials

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. Deionized water was used for all experiments.

The tungsten oxide hierarchical nanostructures were synthesized through hydrothermal reaction by adjusting the amount of formamide. Typically, 0.875 g tungstic acid was added into 18 mL H_2O_2, stirred at 90 °C for 1.5 h before converting into a transparent sol. The resulting clear sol was diluted using deionized water to 210 mL, and then 14 mL of 3 M HCl was added to the as-prepared solution. After stirring for another 20 min, 30 mL of the precursor solution was transferred into a 50 mL Teflon-lined autoclave followed by adding a certain volume of formamide. Finally, the autoclave was sealed and maintained at 180 °C for 12 h. The as-synthesized precipitate was washed with deionized water for three times and ethanol for two times, and then dried in vacuum at 80 °C for 5 h. The as-prepared tungsten oxide was subsequently annealed in air at 350 °C for 2 h. The samples prepared by adding different amount of formamide were devoted as WF40 (40 μL formamide), WF120 (120 μL formamide), and WF160 (160 μL formamide) and the corresponding samples annealed in air at 350 °C were marked as WF40-A350, WF120-A350 and WF160-A350.

2.2. Measurements of photocatalytic property and photoelectrochemical property

The photocatalytic properties of the samples were evaluated by measuring the concentration of rhodamine B (RhB) in aqueous solution after irradiation with simulated solar light produced by a 300 W Xenon lamp. Typically, 20 mg sample was dispersed in 40 mL RhB aqueous solution (15 mg L^{-1}). Prior to irradiation, the suspension was stirred over night to ensure the equilibrium of dye adsorption on the surfaces of the sample. The RhB concentration was measured by UV–Vis spectroscopy.

The photocurrent and electrochemical impedance spectrum (EIS) were measured on an electrochemical workstation (CHI-660E, China) and carried out in a three-electrode system with a working electrode, a platinum wire as counter electrode and a standard calomel electrode (SCE) as reference electrode. 0.1 M Na_2SO_4 was used as the electrolyte solution. The photoelectric responses of the photocatalysts were measured at 0.0 V (vs. SCE). The working electrodes were prepared by a dip-coating method: 10 mg photocatalyst was suspended in 1 mL 1-methyl-2-pyrrolidinone (NMP) to make a slurry, and the slurry was then dip-coated onto a 2 × 3.5 cm fluorine-tin oxide (FTO) glass. The as-prepared electrodes were dried at 80 °C for 10 h in air.

2.3. Characterization of materials

The X-ray diffraction patterns were obtained on a Rigaku D/max-V2500 (Cu Kα radiation). The morphology and microstructure were studied by scanning electron microscopy (SEM, Zeiss, Germany) and transmission electron microscopy (TEM, JEOL-2100, Japan). UV–Vis spectrophotometer (U-3010, Hitachi, Japan) were used to record UV/Vis absorption spectra. The surface areas of the samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption-desorption isotherms at 77 K with a Contador QuadraSorb SI-MP instrument. High-resolution Raman spectroscopy (HR800, Horiba Jobin Yvon, France) were used to collect the Raman spectra. Electron spin resonance spectroscopy (ESR) measurements were performed with a JEOL FA200 ESR spectrometer.

3. Results and discussion

3.1. Structure and morphology

The XRD patterns of the as-prepared tungsten oxides are presented in Fig. 1. The peaks of the sample WF40 can be indexed to the orthorhombic structure of $WO_3 \cdot 0.33H_2O$ (JCPDS no. 72-0199). When adding160 μL formamide, the sample WF160 yields a

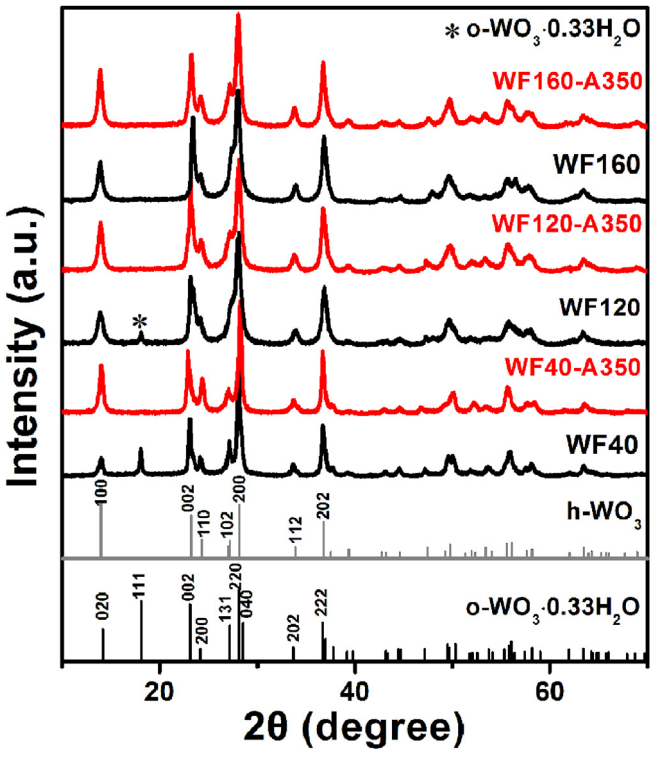

Fig. 1. XRD patterns of the tungsten oxides prepared with different amount of formamide and post-air annealed at 350 °C in air.