



An initiative, simple vacancy remedy method and the effect on photochemical properties

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ARTICLE INFO

Article history:

Received 28 June 2016

Received in revised form 15 August 2016

Accepted 18 September 2016

Available online 20 September 2016

Keywords:

Defect remedy

Fluorination

H₂O₂

NH₄F

Tungstic oxide

ABSTRACT

Recently, an increasing attention is paid to crystal defects due to the significant influence on the catalytic properties of material. Herein, the WO₃ and fluorinated WO₃ (F-WO₃) samples have been prepared by an *in situ* hydrothermal method. On one hand, we have found that under visible light irradiation ($\lambda \geq 420$ nm), the photocatalytic activities of F-WO₃ samples are obviously reduced, which has been mainly attributed to the generation of W vacancies by fluorination. This finding is obviously distinct from the previous reports, in which the photocatalytic activities of semiconductors can be effectively improved by fluorination. On the other hand, after being further processed by H₂O₂ again, the generated W vacancies by fluorination can be remedied easily; moreover, the WO₃/WO₃·0.333H₂O heterojunctions have formed with a novel flower shape (H₂O₂-F-WO₃). It is amazing that under visible light irradiation ($\lambda \geq 420$ nm), the activity of H₂O₂-F-WO₃ sample is 4.3 and 3.0 times higher than that of F-WO₃ and WO₃, respectively. The significantly improved activity is mainly attributed to the remedy of W vacancy and the formation of the WO₃/WO₃·0.333H₂O heterojunction. Compared with conventional defect remedy method (e.g., calcination), this vacancy remedy method with H₂O₂ is facile, energy-saving, which could be extended to develop the other efficient photocatalysts.

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1. Introduction

As an advanced oxidation technology, solar energy-driven photocatalysis has drawn considerable attention. Unfortunately, its practical application is still limited by the low utilization of solar energy and low quantum efficiency. In the past decades, various strategies have been tried to solve the problems, such as band gap engineering, crystal modification, interfacial heterojunction, and

so on [1]. However, it is still a big challenge to develop efficient photocatalysts.

Recently, tungsten trioxide (WO₃) has attracted much attention due to its abundant reserves, nontoxicity and excellent optical property [2–6]. As an n-type semiconductor, WO₃ ($E_g = 2.5\text{--}2.8$ eV) exhibits approximately 12% absorption of solar energy [2]. Because of its low conduction band edge (0.3–0.5 vs. normal hydrogen electrode (NHE)), however, the conduction band electrons of WO₃ cannot react with O₂ ($E_0(\text{O}_2/\text{O}_2^{\bullet-}) = -0.33$ vs. NHE and $E_0(\text{O}_2/\text{HO}_2^{\bullet}) = -0.05$ vs. NHE) [7–9]. Consequently, its photocatalytic activity is significantly reduced by the fast recombination rate of electrons and holes. Hence, it is desirable to develop a new method to solve this disadvantage. To date, many studies have reported that the fluorination of semiconductor can efficiently enhance the photocatalytic activities [1,10–16], e.g., TiO₂ [10–13],

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Bi_2O_3 [14], BiPO_4 [15], ZnWO_4 [16], etc. Nevertheless, the fluorination of WO_3 has not been reported to date. Hence, it is still unknown for us whether fluorination can improve photocatalytic activity of WO_3 or not. It has been reported that the doping of fluorine can introduce special localized electronic and surface defect states [12,17]. For instance, the fluorine-doped TiO_2 shows a visible light activity due to the creation of surface oxygen vacancies [10,12]. In this work, W vacancies, instead of surface oxygen vacancies, are generated by the fluorination of WO_3 . However, we have found that the W vacancies are disadvantageous to the photocatalytic reaction. Generally, crystal defects can be repaired by a calcination method [18]. Nevertheless, the calcination method often brings about the significant changes in particle size and morphology [19], leading to a poor physicochemistry properties. Besides, the fluorine within crystal lattices is easy to be removed during calcination [20]. Thus, it is desirable to develop a mild method for the vacancy remedy, so as to obtain an efficient photocatalyst.

In this work, we have developed a new, mild approach to remedy W vacancies, in which the $[\text{O}_2]^{2-}$ chelating ligand can be provided by H_2O_2 [21]. It is found that after being processed with H_2O_2 , two interesting results are obtained as follows: (1) the W vacancies generated by the fluorination of WO_3 can be remedied by H_2O_2 ; (2) a heterojunction can form between monoclinic WO_3 and orthorhombic $\text{WO}_3 \cdot 0.333\text{H}_2\text{O}$ with a new flower shape. This facile post-synthesis defect remedy method may be extended to develop the other efficient photocatalysts.

2. Experimental

2.1. Sample preparation

All reagents were of analytical grade, purchased from Beijing Chemical Reagents Industrial Company of China, and were used without further purification.

2.1.1. Synthesis of WO_3 and F- WO_3

The WO_3 and fluorinated WO_3 (F- WO_3) samples were synthesized by a simple hydrothermal method. Typically, 1.3 g of ammonium tungstate, the measured amount of NH_4F and 5 mL 65 wt% nitric acid were added in 20 mL of deionized water in sequence. After being stirring for 30 min, the mixture was transferred into Teflon-lined stainless steel autoclaves and heated at 180°C for 24 h; then the resulting precipitate was collected by centrifugation, washed with deionized water for several times, and finally dried at 60°C . To investigate the effect of the NH_4F amount added, the atomic ratio (R_F) of F to W was varied from 0 to 0.1, 0.5, 1.0 and 2.0. Herein, the as-prepared sample at $R_F = 0$ is designated as WO_3 , while the as-prepared samples at $R_F = 0.1$ –2.0 are designated as F- WO_3 .

2.1.2. Post-synthesis processing with H_2O_2

Typically, the as-synthesized F- WO_3 ($R_F = 1.0$) or WO_3 ($R_F = 0$) above was added in the mixture solution containing both 10 mL of 30 wt% H_2O_2 and 5 mL of H_2O . Then, the mixture solution was transferred into Teflon-lined stainless steel autoclaves, and was processed at 180°C for 24 h. After reaction, the resulting precipitate was collected by centrifugation, washed with deionized water, and dried at 60°C . Herein, the as-processed WO_3 and F- WO_3 samples are designated as H_2O_2 - WO_3 and H_2O_2 -F- WO_3 , respectively.

2.2. Characterization

The crystal structures of the samples were determined by X-ray powder polycrystalline diffractometer (Rigaku D/max-2550VB), using graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$), operating at 40 kV and 50 mA. The XRD patterns were obtained in

the range of 10 – 80° (2θ) at a scanning rate of 7° min^{-1} . The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV. The samples were coated with 5-nm-thick gold layer before observations. The fine surface structures of the samples were determined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) equipped with an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were done on a VG ESCALAB MKII XPS system with $\text{Mg K}\alpha$ source and a charge neutralizer. All the binding energies were referenced to the $\text{C}1s$ peak at 284.8 eV of the surface adventitious carbon. Electron paramagnetic resonance (EPR) spectra were conducted on a Bruker ESP 500 spectrometer at room temperature. UV-vis diffused reflectance spectra of the samples were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO_4 was used as a reflectance standard in a UV-vis diffuse reflectance experiment. Nitrogen sorption isotherms were performed at 77 K and $<10^{-4}$ bar on a Micromeritics ASAP2010 gas adsorption analyzer. Each sample was degassed at 90°C for 5 h before measurements. Nitrogen adsorption-desorption isotherms were obtained at 77 K using the Autosorb-iQ physicoadsorption apparatus (Quantachrome). Surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

An electrochemical system (CHI-660B, China) was employed to measure the electrochemical impedance spectroscopy (EIS) and photocurrent. EIS was performed from 0.1 Hz to 100 kHz at an open circuit potential of 0.3 V and alternating current (AC) voltage amplitude of 5 mV. The data were analyzed by Zsimwin software. Photocurrent measurement was carried out in a conventional three-electrode system, in which indium-tin oxide (ITO) glass was used as the current collector to fabricate photo electrode, and 0.1 M Na_2SO_4 was used as the electrolyte solution. The sample/ITO photo electrodes were prepared by a dip-coating method. The photo electrode was implemented as the photo anode in a photoelectrochemical cell (PEC).

2.3. Theoretical calculations

The simulations of band structures, total and partial densities of states (T- and P-DOS) were calculated by density functional theory (DFT) as implemented in the CASTEP. The calculations were carried out using the generalized gradient approximation (GGA) level, and Perdew-Burke-Ernzerh (PBE) formalism for combination of exchange and correlation function. The cut-off energy is chosen as 380 eV, and a density of $(3 \times 2 \times 5)$ Monkhorst-Pack K -point was adopted to sample the Brillouin zone.

2.4. Photocatalytic activity measurements

The photocatalytic activity of the sample was performed under visible light irradiation ($\lambda \geq 420 \text{ nm}$). 0.1 g of photocatalyst was put into a 250-mL beaker containing 200 mL of 10 mol L^{-1} methyl blue (or rhodamine b) dye solution. A 500-W high pressure Xe lamp (Beijing ZhongjiaoJinyuan Science Co. Ltd. China) was used as light source. The breaker was placed in a sealed black box with the top opened, and the distance between the breaker and light source was 15 cm. Before the lamp was turned on, the suspension was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption-desorption equilibrium between the catalyst and dye. During degradation, 3 mL of the solution was collected using a pipette at intervals of irradiation, and subsequently centrifuged to remove the catalyst. UV-vis spectra were recorded using a Spectrumlab 722sp spectrophotometer to determine the concentration of dye.

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