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PABA-assisted hydrothermal fabrication of $W_{18}O_{49}$ nanowire networks and its transition to WO_3 for photocatalytic degradation of methylene blue

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ABSTRACT

$W_{18}O_{49}$ nanowire networks have been fabricated by a facile hydrothermal method. In this method, *p*-aminobenzoic acid (PABA) was used as an assistant agent to control the morphology transformation. $W_{18}O_{49}$ and its products annealed at different temperature were characterized by XRD, SEM, TEM, UV–vis absorption spectroscopy, XPS, TGA, and FTIR. Formation mechanism and thermal stability of $W_{18}O_{49}$ nanowire networks were studied in detail. The experiment data showed that PABA played an important role in the induced crystal growth of $W_{18}O_{49}$ nanowires along [0 1 0] axis. In transformation, the structure of samples was controlled: from irregular particles to nanowire networks. $W_{18}O_{49}$ nanowire networks were annealed at different temperature. The nanowire networks collapsed at 450 °C, while WO_3 nanocrystals were obtained. The $W_{18}O_{49}$ nanowire networks annealed at 400 °C have a superior photocatalytic performance to degrade methylene blue and its specific surface area was up to 147 $m^2\ g^{-1}$.

1. Introduction

Nowadays, nanomaterials have achieved a widespread attention due to their enhanced physical and chemical properties [1–5]. Among all kind of nanomaterials, one dimension nanostructure has attracted extensive interests due to the unique electronic and optical properties [6–8]. Tungsten oxide nanowires and nanorods, as one of the crucial transition metal oxide semiconductors, have a wide applications in electrochromic devices, gas sensors, optical devices, hydrogen reduction, and photocatalysts [9–15]. Specially, tungsten oxide is well-known for its nonstoichiometric properties, as the lattice can withstand a considerable amount of oxygen vacancy [12,16,17]. In particular, monoclinic $W_{18}O_{49}$ is of special interest for its unique defect structure and distinct physical and chemical properties in the nanometer regime [4,18–20].

Hitherto, $W_{18}O_{49}$ based materials have exhibited excellent performance in various fields, such as catalysis [21], gas sensing property [22], optical property [23], magnetic and near-infrared adsorption properties [24,25]. Recent research shows that the reductivity of $W_{18}O_{49}$ can realize the direct growth of metal particles on metal oxides in situ [26]. Furthermore, the acidic surface of the $W_{18}O_{49}$ porous nanomaterials enhances their adsorption on basic dyes [27,28]. Guangcheng Xi and co-workers have reported the preparation of ultrathin $W_{18}O_{49}$ nanowires with diameters below 1 nm that are efficient in the photochemical reduction of carbon dioxide by visible light [4]. Y.M. Zhao and Y.Q. Zhu have researched the room temperature ammonia sensing properties of ultra-thin $W_{18}O_{49}$ nanowires with diameter less than 5 nm, and the nanowire was prepared by a solvothermal technique [18]. Chongshen Guo et al. have investigated the morphology-controlled synthesis and near-infrared (NIR) absorption properties of $W_{18}O_{49}$ which applied to innovative energy-saving windows [25].

The general method to fabricate $W_{18}O_{49}$ nanomaterials is alcoholysis of WCl_6, $W(CH_3CO)_6$, or $W(CO)_6$ [18,26,29]. However, the reagents are expensive and unstable, which are disadvantageous for practical applications. Therefore, it is highly desirable and challenging to develop a facile and economical method to produce $W_{18}O_{49}$ with porous nanostructures for their large scale applications in water treatment and others.

Once, we have reported a communication about the hydrothermal fabrication of $W_{18}O_{49}$ nanowire networks with $Na_2WO_4{\cdot}2H_2O$ as tungsten resource [30]. In that work, tungsten acid was used as precursor while *p*-amino-benzoic acid (PABA) was utilized as a reductive and structure-directing agent, respectively. Herein, the

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formation mechanism of the $W_{18}O_{49}$ nanostructure has been studied in detail by discussing the amount of PABA, the reaction time. Furthermore, the surface feature of the samples has been characterized by FT-IR spectrum and XPS spectrum. The thermal stability research shows that the product has a high stability and the $W_{18}O_{49}$ nanowire networks can transform to monoclinic WO_3 nanocrystals at 450 °C and is of an excellent hydrophilicity. The $W_{18}O_{49}$ nanowire networks have an excellent visible-light photocatalytic activity in present work.

2. Experimental

In this experiment, all chemical reagents were of analytical grade and used without further purification.

2.1. Synthesis of tungsten acid precursor

The basic synthetic process is listed as follows: 10 g of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 1 mol L^{-1} HNO_3 to form tungsten acid ($H_2WO_4 \cdot nH_2O$) precipitate, and precipitate was dried with a vacuum freeze dryer.

2.2. The fabrication of $W_{18}O_{49}$ nanowire networks

Four group experiments were conducted to investigate the role of PABA in synthesizing $W_{18}O_{49}$ nanowire networks by using different amount of PABA.

1 g of $H_2WO_4 \cdot nH_2O$ and PABA (0/0.5/1/2/4 g) were mixed into 60 mL of deionized water with continuous stirring for 2 h, respectively. Then the mixture was transferred into a 90 mL Teflon-lined stainless steel autoclave. Hydrothermal treatment of mixture was carried out at 180 °C for 24 h, and then the autoclave was cooled down naturally. The final products were washed with deionized water and ethanol several times, and dried in air at 60 °C. The samples prepared at different amount of PABA (0/0.5/1/2/4 g) were noted as S-0, S-0.5, S-1, S-2, S-4.

S-2 was selected for researching the formation mechanisms of $W_{18}O_{49}$ nanowire networks by controlling the hydrothermal time (0/4/8/12/24 h).

2.3. Thermal stability analysis

S-2 was chosen for investigating the thermal stability of $W_{18}O_{49}$ nanowire networks. A certain amount of S-2 was heated at 400 °C, 425 °C, and 450 °C for 30 min with the heating rate of 2 °C min^{-1}. The products were denoted as $W_{18}O_{49}$-400, $W_{18}O_{49}$-425, and $W_{18}O_{49}$-450, respectively. Moreover, S-2 was further annealed at 400 °C for 60/90/150/210/300 min, respectively, with the heating rate of 2 °C min^{-1}.

2.4. Characterization

The crystal phase of the obtained samples was studied with powder X-ray diffraction (XRD) analysis (Bruker, D8-Advance X-ray Diffractometer, Cu Ka, λ = 1.5418 Å). Scanning electron microscopy (SEM) images were recorded with a field emission scanning electron microscopy (S-4800, Hitachi, Japan). Transmission electron microscope (TEM) images were obtained on a Hitachi H-600 with an accelerating voltage of 100 kV. HRTEM characterizations were performed with a JEOL JEM-2100 (JEOL, Japan) transmission electron microscope. UV/Vis absorption spectra were recorded with a Shimadzu UV-4802S. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher Scientific XPS ESCALAB 250Xi instrument with an Al Kα (1486.8 eV) X-ray source. Thermogravimetric analysis (TGA) was performed on a SDT Q600 instrument and measured from 20 to 800 °C with a heating rate of 10 °C min^{-1} in air. Fourier transform infrared spectra (FTIR) were recorded with a Bruker Equinox 55 in the range of 400–4000 cm^{-1}. Before the FTIR spectra test, the pretreatment process of samples was as follows: about 2 mg of each sample was grounded into fine particles and mixed with 100 mg potassium bromide (KBr), then the mixed powder was dried and pressed into tablets for test. The Brunauer-Emmett-Teller (BET) surface area and pore volume were measured by the nitrogen gas adsorption-desorption method using a Micromeritics ASAP (accelerated surface area and porosimetry) 2020 system. The samples were degassed under vacuum at 180 °C for 6 h, and the N_2 adsorption/desorption isotherms were measured at 77 K.

2.5. Contact angle measurement

The contact angle measurements were conducted using a JJ200B2 (provided by Shanghai Zhongchen Digital Technology Apparatus Co., Ltd) in a water environment. Before examination, the powder of samples was pressed into a hard plate and then were put into contact angle meter. Subsequently, 2 μL of ultrapure water was directly released onto the surfaces carefully. The final contact angle values were attained by averaging at least five points at different positions on the same surface.

2.6. Photocatalytic degradation experiments

The photocatalytic activities of the samples were evaluated by degradation of methylene blue (MB) in an aqueous solution under visible light from 800 W Xe lamp. 50 mg of photocatalysts ($W_{18}O_{49}$-400/$W_{18}O_{49}$-450) was well-dispersed into 50 mL of MB aqueous solution (10 mg L^{-1}) with a constant stirring in a quartz tube at room temperature. Before light was turned on, the solution was continuously stirred for 60 min in dark to ensure the establishment of an adsorption-desorption equilibrium. Then, when light was turned on, samples were drawn from solution at predetermined time intervals, and centrifuged to measure the MB removal via a UV–vis spectrometer (Shimadzu UV-2500 PC).

3. Results and discussion

Recently, we have reported $W_{18}O_{49}$ nanowire networks fabricated by the PABA-assisted method. The product exhibited an excellent water treatment performance. Here, we performed a further research to understand the formation mechanism and thermal stability of the $W_{18}O_{49}$ nanowire networks. The influencing factors, such as PABA amount, hydrothermal time and annealing temperature have been systematically studied in present work.

3.1. Structure and morphology characterization

In the reported communication we put forward a thought that PABA may play an important role on the formation of $W_{18}O_{49}$ nanowire networks. Here, the influence of PABA amount has been studied by changing the PABA amount from 0 g to 4 g. Fig. 1 showed the XRD patterns of the products derived from different PABA amount. It was obvious that S-0 was monoclinic WO_3 (JCPDS card No. 72-0677). S-0.5 was a mixture of WO_3 and $WO_3 \cdot 0.33H_2O$ (JCPDS card No. 43-1035 and 35-0270). With the increase of PABA to 1 g, WO_3 (S-1) was obtained (JCPDS card No. 72-0677). When the amount of PABA reached to 2 g or more than it (4 g), oxygen-deficient monoclinic $W_{18}O_{49}$ phase was obtained (JCPDS card No. 36-101). So, it was evident that the amount of PABA played an important role on the fabrication of non-stoichiometric tungsten oxide.

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