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Letter

Preparation of WO_3 network squares for ultrasensitive photodetectors

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ABSTRACT

Three-dimensional WO_3 network squares have been fabricated on a large scale by a hydrothermal method at 160 °C without any template or surfactant. The characterization of the network squares with X-ray diffraction, scanning electron microscopy, and transmission electron microscopy indicates a single crystalline hexagonal structure with a square of side length up to 20 μm. The influence of pH value on the morphology of the final product has been studied, indicating that more uniform WO_3 network squares can be obtained at pH 1.7. A possible growth mechanism involves the Ostwald ripening, oriented attachment and etching effect. The UV–vis reflection spectrum indicates a band gap of ~3.2 eV. The photodetector based on a single WO_3 network square shows remarkable photosensitivity under intermittent illumination of the simulated sunlight, which could mainly be attributed to the specific network structure of WO_3 and the Schottky contacts.

1. Introduction

In the past two decades we have witnessed amazing advances in the synthesis of one-dimensional (1D) nanostructures and the assembly of those building blocks into ordered superstructures or complex functional architectures [1–3]. Among these architectures, network structures can function as both devices and interconnections, and thus are expected to play a key role in the production of next generation of nanoscale electronic and optoelectronic devices [4–6]. Moreover, the networks usually show some novel and interesting properties superior to those of simple nanostructures. For instance, carbon nanotube networks are synthesized for their good physical properties and chemical functionalization [7]. Thermoelectrical characterization of lead chalcogenide networks has shown that the structure could promote the upper limits of their ZT values [8].

As an important fundamental material, tungsten oxides (WO_{3-x}) have recently attracted great interest due to their wide-ranging application as electrochromic devices, gas sensors and photocatalysts [9–11]. To date, substantial efforts have been devoted to the development of various synthetic methods of 1D WO_{3-x} nanostructures [12–14]. Hydrothermal method is commonly used to the synthesis of WO_{3-x} nanostructures, such as, $W_{18}O_{49}$ nanorods synthesized by Zeng et al. using Na_2SO_4 to control the morphology and phase [15], h-WO_3 hierarchical structure microspheres made of nanorods/nanowires, synthesized by Gu et al. using SO_4^{2-} ions to direct the structure [16] and also h-WO_3 nanowires prepared via pH value control [17]. In addition, WO_3 square platelets with smooth surfaces have also been synthesized by an organic acid-assisted hydrothermal process [18], and $WO_3{\cdot}H_2O$ square platelets have been obtained via low temperature hydrothermal treatment [19]. A few groups have reported the synthesis of WO_{3-x} networks, such as, three-dimensional tungsten oxide nanowire networks growing on a substrate by Zhou et al. [20], Chi et al. [21] and Li et al. [22] via thermal evaporation/vapor deposition at temperature of 750–1450 °C, and two-dimensional tungsten oxide nanowire networks obtained by Zhao et al. via thermally evaporating a WS_2 powder under a controlled moist atmosphere at temperature of 1400–1500 °C [23]. However, hierarchical networks in separate squares of WO_{3-x} have not yet been reported. It is still a challenge to assemble WO_{3-x} nanoscale building blocks into well-defined multidimensional networks under mild experimental conditions.

Herein, we report the synthesis of novel three-dimensional (3D) WO_3 networks in separate squares for the first time via the hydrothermal approach in which Na_2SO_4 was used as the structure-directing agent. The morphology evolution and growth mechanism of the products were studied in detail. The photodetector of a single WO_3 network square was fabricated, which exhibited remarkable photosensitivity. It should be mentioned that within last a few years, tremendous progress has been achieved in photodetector applications of one-dimensional (1D) ZnO nanostructures [24,25], whereas research has seldom been focused on the photosensitivity of WO_3 materials. The phototconductive

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gain of the WO_3 network-based device has been calculated and compared with that of the ZnO nanowire-based photodetector. Furthermore, a mechanism of the photosensitivity has been proposed.

2. Experimental

2.1. Preparation of WO_3 network squares

All the chemicals were of analytical grade and used without further purification. In a typical synthesis, the solution of 0.2 mmol sodium tungstate (Na_2WO_4) and 0.8 mmol sodium sulfate (Na_2SO_4) was prepared in a beaker with 20 mL of deionized water. Under stirring, an aqueous solution of nitric acid (HNO_3) (3 M) was added dropwise to the beaker until the pH value of the solution reached 1.7. The mixture was then transferred into a Teflon-lined stainless autoclave and heated at 160 °C for 48 h. After this step, the autoclave was taken out and allowed to cool to room temperature. The final products were obtained by centrifugation and washing with deionized water and pure alcohol to remove possible ions remaining in the final products, and let them dry at 60 °C.

2.2. Fabrication of photodetector

Au electrode patterns were defined with photolithography on a SiO_2 substrate. The as-synthesized WO_3 network squares were ultrasonicated in ethanol for 15 min to get sufficiently dispersed. A droplet of the suspension was placed onto the electrodes. By precisely controlling the concentration of the network squares in the solution, a device with only a single network across two electrodes can be achieved.

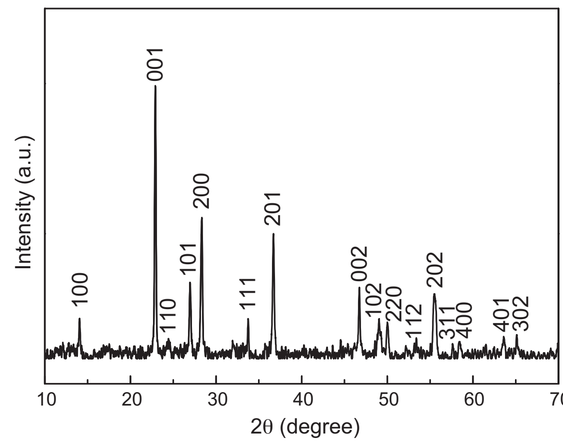

Fig. 1. XRD pattern of the WO_3 network squares synthesized at 160 °C and pH 1.7 for 48 h, indicating hexagonal phase of the WO_3.

2.3. Characterization and photoelectric measurement

The structure and morphology of the as-synthesized products were characterized with X-ray diffraction (XRD, BDX3200 with Cu Kα radiation), scanning electron microscope (SEM, Tescan Vega II and FEI Nova 400), transmission electron

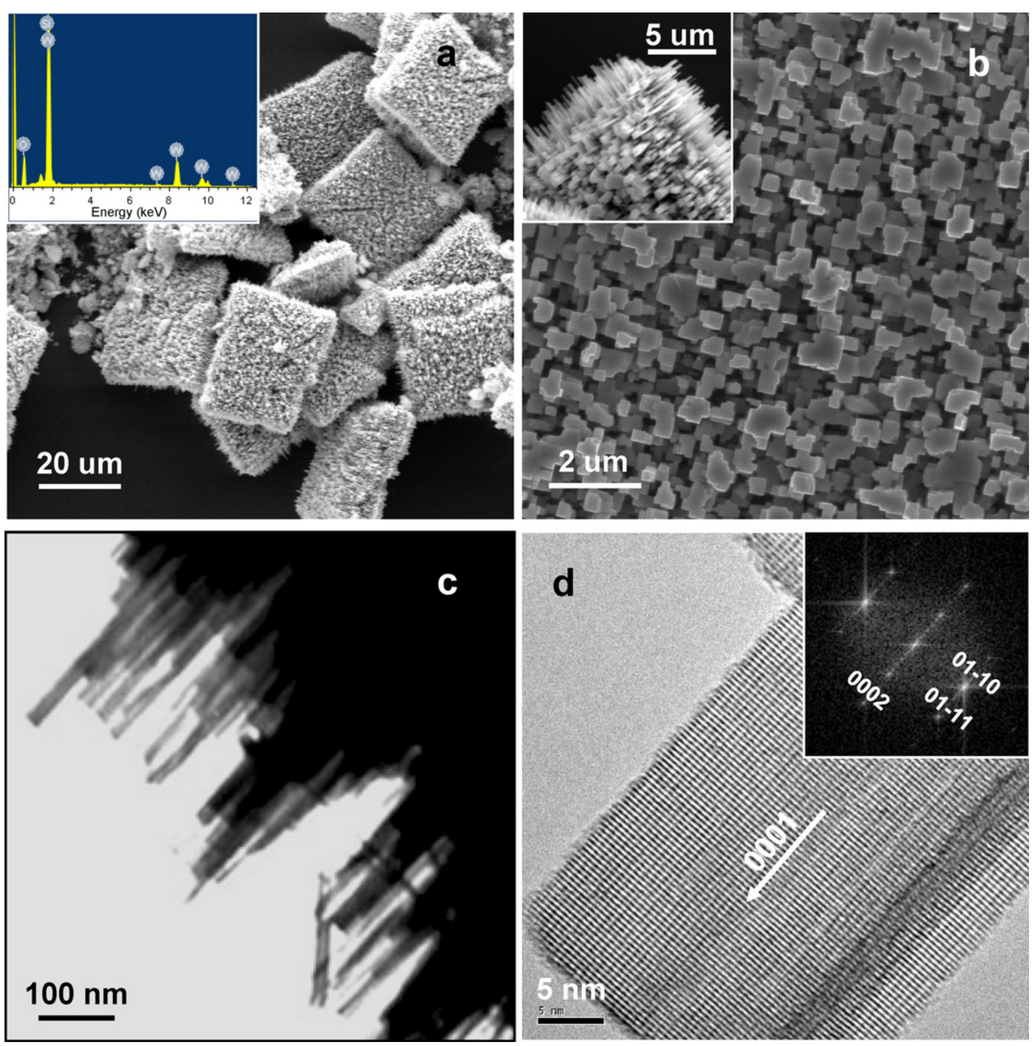

Fig. 2. (a) Low-magnification SEM image of the WO_3 network squares obtained at 160 °C for 48 h and its EDS spectrum in the inset. (b) High-magnification SEM images of the surface and the edge (inset) of one single network. (c) TEM image of the edge of an individual network. (d) HRTEM image of one nanorod and corresponding FFT pattern (inset).