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Ethanol sensing properties of tungsten oxide nanorods prepared by microwave hydrothermal method

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Abstract

Tungsten oxide nanorods have been prepared by a simple microwave hydrothermal (MH) method via Na_2SO_4 as structure-directing agent at 180 °C for 20 min. The structure and morphology of the products are characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). The obtained nanorods are about 20–50 nm in diameter and several micrometers in length. The ethanol sensing property of as-prepared tungsten oxide nanorods is studied at ethanol concentration of 10–1000 ppm and working temperature of 370–500 °C. It was found that the sensitivity depended on the working temperatures and also ethanol concentration. The results show that the tungsten oxide nanorods can be used to fabricate high performance ethanol sensors.

Keywords: A. Microwave processing; B. Electron microscopy; D. Transition metal oxides; E. Sensors

1. Introduction

Gas sensors based on metal oxide semiconductors may be used in a wide variety of applications including gas monitoring and alarm applications [1–4]. Considerable research has been carried out on the development of chemical sensors based on semiconductor metal oxides such as SnO_2, ZnO, and TiO_2 [5,6]. WO_3, as an n-type semiconductor, has been proven to be a highly sensitive material for the detection of both reducing and oxidizing gases [7,8]. Recently, inspired by the advantages of small size, high density of surface sites and increased surface to volume ratios, synthesis of these semiconductor metal oxides with one-dimensional (1D) nanostructures and exploration of their properties are of current interest [9]. Up to now, many 1D nanostructures have been successfully synthesized and applied in various chemical sensors [10].

Many synthetic methodologies have been devoted to the growth of 1D tungsten oxides nanostructures such as sol–gel method [11], physical vapor deposition method [12], molten-salt method [13], thermal decomposition method [14], and hydrothermal route [15,16]. Among them, synthesis under hydrothermal conditions can provide a low-temperature, environmentally friendly and low-cost route to prepare nanosized oxide materials, and become an attractive method. However, this method usually requires prolonged reaction time for more than 10 h even for several days. An alternative synthesis process, the microwave hydrothermal (MH) method, has recently been developed to prepare nanoparticles [17]. The main advantages identified are that the MH process can offer the product rapidly within a short time with a high degree of control of particle size and morphology [18].

Recently, we have prepared $WO_3{\cdot}nH_2O$ nanospheres by a simple MH method [19]. Here, we successfully synthesized WO_3 nanorods by a MH method at 180 °C in 20 min. This method required a shorter synthesis time, and the reaction process employed here was also very simple. The sensor fabricated from the WO_3 nanorods exhibits good ethanol sensing properties under different ethanol concentration and temperature. The results demonstrate that the WO_3 nanorods are promising materials for fabricating high performance ethanol sensors.

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2. Experimental

Microwave reaction was performed in a Milestone ETHOS microwave system. All of the chemical reagents used in the experiment were of analytical grade. A typical synthesis process for the preparation of WO_3 nanorods was as follows: 1.5 g of $Na_2WO_4{\cdot}2H_2O$ and 2.5 g of Na_2SO_4 was dissolved in deionized water to form a transparent solution. Several milliliters of 3 M HCl were added to the solution to adjust the pH to 1.5 under continuous stirring. After 30 min of stirring, the mixture was transferred into a 100 mL Teflon container, which was filled with distilled water up to 66% of the total volume, sealed and treated in the microwave system at 180 °C for 20 min. The final products were obtained by centrifugation and washed with deionized water and pure alcohol to remove ions possibly remnant in the final products, and finally dried at 60 °C in air for 60 min.

The obtained samples were characterized by X-ray diffractiometer (XRD) using a Rigaku D/max-ga X-ray diffractometer at a scanning of 2° min^{-1} in 2θ ranging of from 10° to 80° with Cu Ka radiation ($\lambda = 1.54178$ Å). Transmission electron micrographs (TEM) were obtained on a JEOL JEM-2010 electron microscope. Gas sensing measurements were carried out on a computer-controlled WS-30A system (Zhenzhou, China). The WS-30A multimeter was used for continuously monitoring the electrical resistance of the sensors during the measurement process. The data acquired were stored in a PC for further analysis. It was attached with mass flow controllers for precise measurement of the gas flow at ppm level. A separate microheater of around 1 cm × 1 cm size was used in order to heat the sample and its working temperature was monitored with a thermocouple attached to the sensor.

WO_3 nanostructure gas sensors were sintered into side-heat device in traditional way [20,21]. A bit of the production was first milled in a mortar for 10 min. Each power was mixed with adhesive (Terpineol, from Tianjin, China) and stirred well so as to form a uniform slurry of adequate rheology. Then the slurry was printed on a ceramic tube with four gold electrodes. The ceramic tube was first dried in air and then was heated at 150 °C for 1 h in a muffle stove. The as-fabricated sensors were fixed into the gas sensing apparatus and aged at 300 °C for 240 h and then the sintered side-heating gas sensor was obtained.

3. Results and discussion

3.1. XRD and TEM analysis

The typical XRD pattern of the sample is shown in Fig. 1. All of the reflection peaks can be indexed to hexagonal WO_3 with lattice constants of $a = 7.298$, $b = 7.298$ and $c = 3.899$, which are consistent with the values in the standard card (JCPDS 33-1387). Fig. 2 shows energy dispersive X-ray spectroscopy (EDX) spectrum of the WO_3 nanorods. The peaks of the pattern correspond to W and O elements and the quantitative analysis of the EDX spectrum indicates that the atomic composition ratios of W:O is close to 1:3, which is in agreement with the stoichiometric proportion of WO_3.

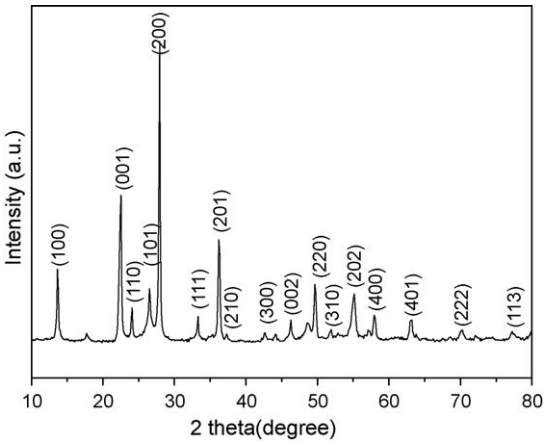

Fig. 1. Powder XRD pattern of WO_3 nanorods prepared by microwave hydrothermal process.

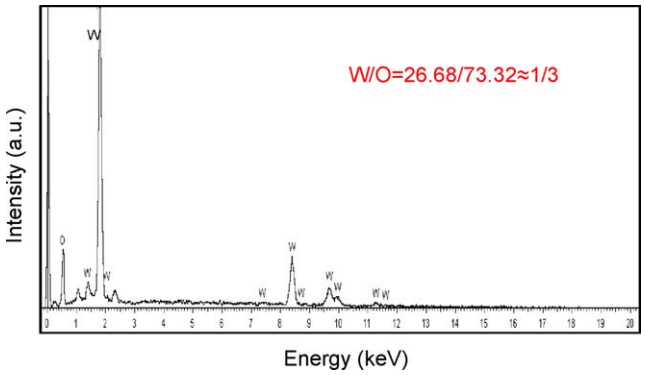

Fig. 2. EDX spectrum of WO_3 nanorods.

The morphology and microstructure of the products are examined by TEM. Fig. 3(a) and (b) shows the overall morphology of the sample, revealing that the resulting products are composed of a large quantity of rod-like nanostructures with diameters in the range 20–50 nm and lengths up to several micrometers. Those nanorods are straight and smooth with uniform diameter along their axial direction. It is worth noting that the nanorods prepared here are obviously thinner than those grown by the conventional hydrothermal method (their diameters are usually in the range of 100–200 nm) [16], which may be associated with microwave effect. Fig. 3(c) presents a high-resolution transmission electron microscopy (HRTEM) image of a single WO_3 nanorod with the diameter of 20 nm. The fringe spacing is about 0.3691 nm, which is close to the interplanar spacing of the (1 1 0) lattice planes of h-WO_3. This means that the axial direction of the prepared nanorods is along the direction of the (1 1 0) lattice planes of h-WO_3. The selected-area electron diffraction (SAED) pattern depicted in Fig. 3(d) can be indexed with the hexagonal structure of WO_3 (JCPDS 33-1387), which is consistent with the result of XRD.

3.2. Gas sensing properties

A lot of studies on the fabrication of metal oxide sensors for many gases have been reported in the literature. However, most of studies focused on WO_3 film made of large particles.

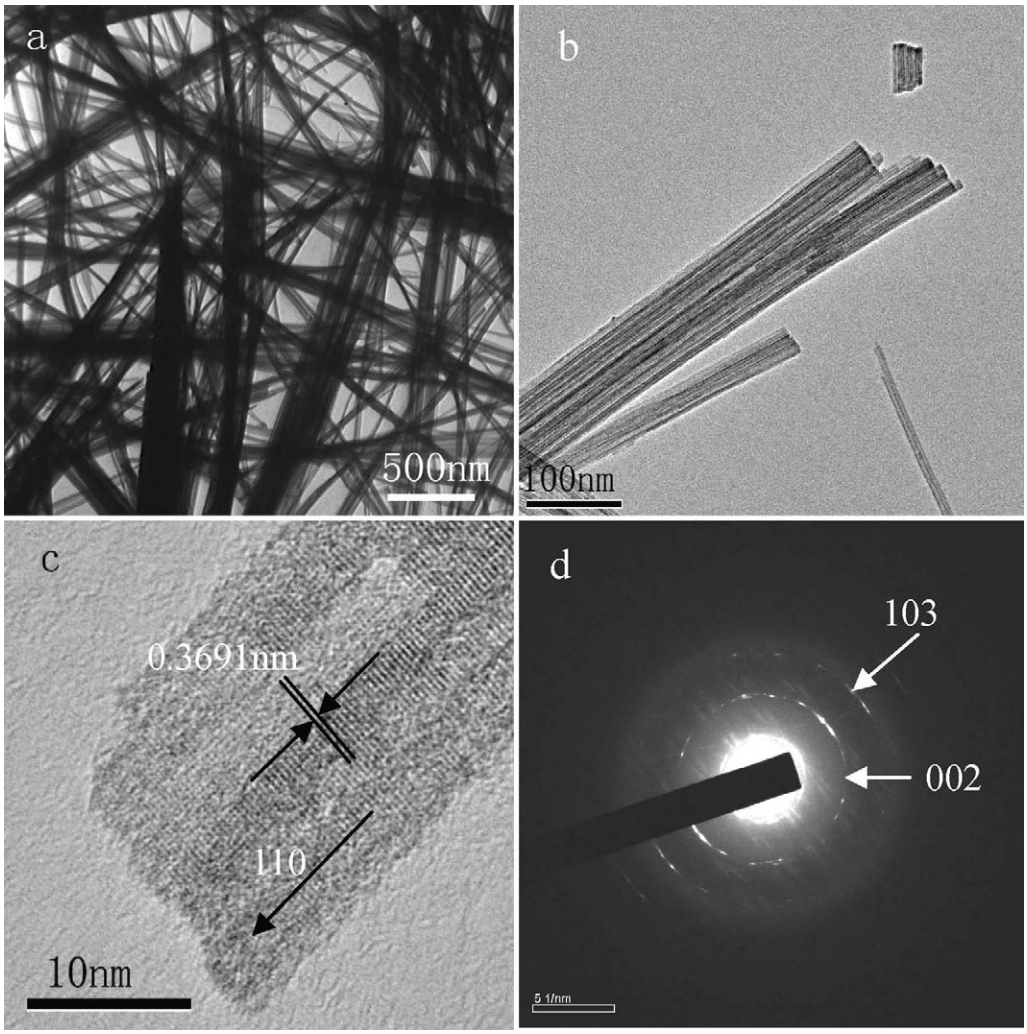

Fig. 3. TEM images of the *h*-WO_3 nanorods at different magnifications. (a) Low- and (b) high-magnification TEM images; (c) HRTEM image of a nanorod; (d) SAED pattern take on the *h*-WO_3 nanorods shown in (c).

Because of bigger particle size, the sensitivity of those sensors was poor [22–24]. Compared between the sensing characteristics of the samples, we could determine that the samples with higher surface areas were more sensitive to many gases [25,26]. In this work, we studied the ethanol sensing property of the WO_3 nanorods. The sensing characteristic of the WO_3 nanorods at temperatures of 370–500 °C with ethanol concentration of 1000 ppm is shown in Fig. 4(a), which reveals that the sensitivity of the sensors was greatly enhanced with the temperature increased and at 500°C, the sensitivity was up to

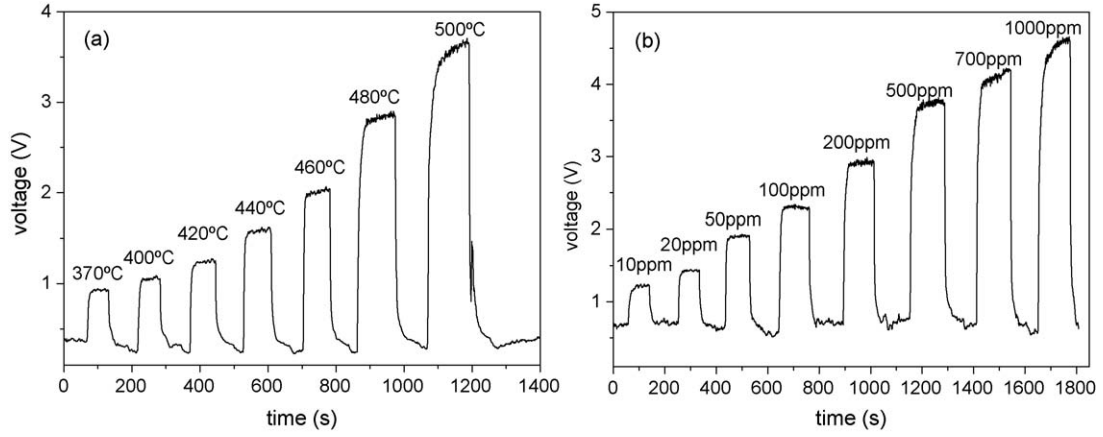

Fig. 4. Typical response curves of gas sensors made of WO_3 nanorods: (a) different working temperature with the ethanol concentration of 1000 ppm and (b) to the ethanol with different concentration at 500 °C.

maximization. When ethanol vapor was injected into or removed from the chamber, the resistance of the sensors was quickly increased or decreased. The dependence of the WO_3 nanorod sensor's sensitivity on the concentrations of ethanol (10–1000 ppm) was investigated at 500 °C, and the result is shown in Fig. 4(b). As shown in the image, the WO_3 nanorod sensors had good response to the alcohol gases even at low concentration of 10 ppm. Meanwhile, with increasing concentration of the gases, the sensitivity of the sensors sharply increased. We have also investigated the temperature-dependence behavior of the sensors. The response time and recovery time (defined as the time required to reach 90% of the final equilibrium value) were only 2∼4 s and 3∼7 s, respectively. Such a result indicates the good response speed of the sensors fabricated here.

The sensing mechanism of semiconducting oxide sensors is usually believed to be the surface conduction modulation by the absorbed gas molecules [8]. The excellent ethanol sensing property of the WO_3 nanorods could be interpreted by the high surface to volume ratio of the nanorods and the resultant faster adsorption and desorption kinetics [27]. The sensing process of the WO_3 nanorod sensors can be briefly depicted as follows. When the WO_3 nanorods are exposed to air, oxygen molecules adsorb on the surface of the WO_3 nanorods and form chemisorbed oxygen species by capturing electrons from the conductance band. Thus WO_3 nanorods will show a high resistance state in air ambient. When the nanorods are exposed to a reductive gas (such as ethanol) at moderate temperature, the gas may react with the surface oxygen species, which increases the electron concentration and eventually decreases the conductivity of the WO_3 nanorods.

4. Conclusions

In summary, WO_3 nanorods with an average diameter of 20–50 nm are synthesized by a MH method, and their ethanol sensing property is also investigated under different concentrations of ethanol (10–1000 ppm) at different temperature (370–500 °C). The results demonstrate that WO_3 nanorods have excellent potential applications for fabrication high performance ethanol sensors.

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