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Hydrothermal synthesis, characterization of h-WO_3 nanowires and gas sensing of thin film sensor based on this powder

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ABSTRACT

The monodisperse hexagonal WO_3 (h-WO_3) nanowires were synthesized using hydrothermal treatment through the acidification of $Na_2WO_4 \cdot 2H_2O$ by addition of K_2SO_4 and Na_2SO_4. The obtained products were characterized using X-ray powder diffraction, field emission scanning electron microscopy and transmission electron microscopy. It showed a high crystallinity and good dispersity of nanowire structure with the exposure of <200> crystal facets. Based on h-WO_3 products, thin film sensors were prepared. The gas-sensing properties to various concentrations (10, 20, 50, 100, and 200 ppm) of ethanol and formaldehyde were investigated. The h-WO3 nanowires exhibited high responses to both ethanol and formaldehyde gas. The sensor exhibited remarkably good response and fast response/recovery time, which were as short as 6–8 s. A possible reason for the influence of oxide structure on the sensing properties of thin film sensors is proposed. This work shows great potential for the preparation of 1D h-WO_3 nanostructures and their application in the detection of toxic gases.

1. Introduction

Tungsten oxides have been studied extensively for various applications including electrochromic devices, photochromic devices, photocatalysis and gas sensors [1–5]. The morphological parameters such as size, shape, and porous nature of tungsten oxide particles are found to be critically important in modulating its surface as well as sensing properties [6,7]. In recent years, the control synthesis of tungsten oxide with certain shape and size has been paid tremendous attentions [8–10]. Many techniques such as sputtering, reactive thermal evaporation, plasma-assisted approach and chemical vapor deposition, hydrothermal synthesis and sol–gel method have been applied in the synthesis of tungsten oxide particles [11–15]. Among these methods, hydrothermal method is considered advantageous due to its simplicity and low processing cost [16,17].

The synthesis of h-WO_3 monodisperse nanowires in room temperature remains challenging due to the existence of its various crystal phases (e.g. α-WO_3 (Tetragonal), β-WO_3 (Orthorhombic), γ-WO_3 (Monoclinic), δ-WO_3 (Triclinic) and h-WO_3 (Hexagonal) etc.) [18–23]. However, h-WO_3 has attracted much attention during the past few years because of its hexagonal and trigonal tunnels, which makes it a promising material for electro-catalyst and gas sensors [24,25]. In recent years, one-dimensional (1D) nanostructures have attracted considerable academic and technological interests owing to their interesting chemical and size-dependent properties for various applications [26,27]. Compared with bulk WO_3, 1D h-WO_3 nanostructures exhibit higher gas-sensing properties. Therefore, many efforts have been focused on the synthesis of 1D WO_3 nanostructures such as nanowires, nanorods, and nanotubes and their application to gas sensors [28–30]. Although, the addition of sulfate-ions have been proved to be an effective way to prepare 1D h-WO_3 nanostructure [31–33], no one has reported an economic way to prepare monodiperse h-WO_3 nanowires in low particle size and its exposure to ethanol and formaldehyde gas-sensing properties.

The presence of various volatile toxic gases such as, ethanol and formaldehyde can severely cause harmful effects on the environment and human health. Breathing or touching to ethanol and formaldehyde vapors can affect the immune system and irritate the eyes, nose, and throat, and further expedite the formation of cough and wheeze [34,35]. The sensitive detection of these organic pollutants using low cost sensors seems to be highly demanding. Among all the sensors, MOS (Metal Oxides Semiconductors) sensors show high sensitivity, good stability, long lifetime, and short response/recovery times. By using WO_3 nanostructures based gas-sensors, it can be very effective to detect these toxic gases.

The synthesis of h-WO_3 nanowires using hydrothermal route and the subsequent investigation on their crystal structure, ethanol and formaldehyde sensing properties are rarely reported. In this paper, the thin film sensor base on the as-prepared h-WO_3 nanowire powder is promising for the detection of ethanol and formaldehyde in low concentration (~10 ppm). An attempt is made to understand the underlying relationship between the crystal structure characteristics and the higher response of the h-WO_3 nanowires based on thin film sensors. The

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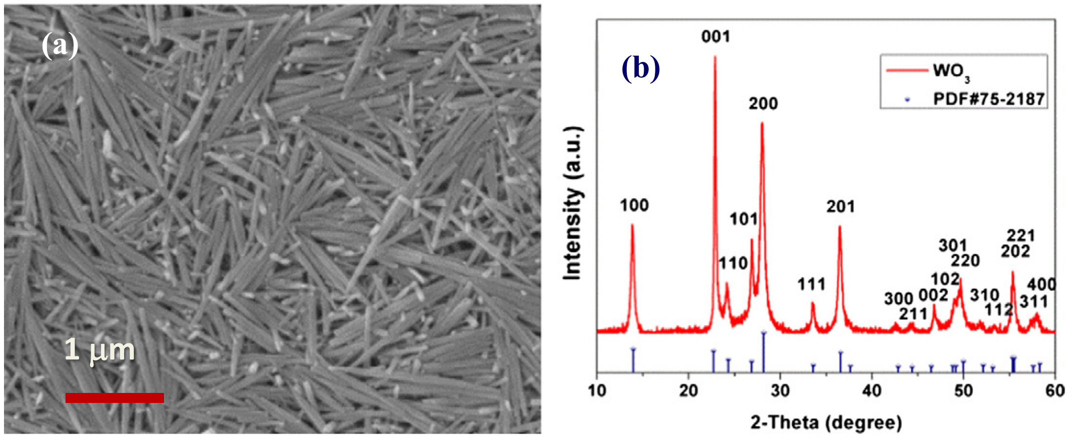

Fig. 1. (a) SEM image and (b) XRD pattern of the obtained h-WO_3 nanowires by hydrothermal route with the presence of Na_2SO_4 and K_2SO_4.

present study is therefore significant for the preparation of tungsten oxide as well as the application to MOS gas sensor.

2. Experimental details

2.1. Syntheses and characterizations

All chemical reagents were of analytic purity and used directly without any further purification. At room temperature, 7 mmol of $Na_2WO_4 \cdot 2H_2O$, 1.75 mmol of Na_2SO_4 and 1.75 mmol of K_2SO_4 were dissolved in 40 ml of deionized water. Then the pH value was adjusted to 1.5–2.0 by the drops of 2 M HCl solution until the appearance of yellow precipitates. After continuous stirring of 30 min, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h in an oven. The obtained white precipitates were collected by centrifugation, washed with deionized water and ethanol for several times, and dried in vacuum at 60 °C for more than 4 h.

The morphologies and crystal phase of the as-prepared products were observed by X-ray powder diffraction (XRD, Rigaku D/max-1200X) with Cu-Kα radiation ($\lambda = 0.15{,}406$ nm) at 50 kV/200 mA, field emission scanning electron microscopy (FE-SEM, Nova 400 Nano, 10 kV), transmission electron microscopy (TEM, ZEISS LIBRA200, 200 kV), high resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED). The specific surface areas of the powders were measured by Brunauer–Emmett–Teller (BET) (Gemini VII, Micromeritics Co. Ltd.).

2.2. Gas-sensing measurements

Gas-sensing properties were carried out using CGS-1TP Intelligent Gas Sensing Analysis System (Beijing Elite Tech. Co. Ltd., China). It consists of a heating system, gas distribution system, probe adjustment system, vacuum system, measurement and data acquisition system, and measurement control software. The heating system offers an external temperature control (from room temperature to about 500 °C with a precision of 1 °C), which could adjust the sensor temperature directly. All the samples were preheated at different working temperatures about 30 min. When the resistances of the sensors were stable, target gas was injected into the test chamber (18 L in volume) by the dynamic gas distributing system. As the sensor resistances reached new constant values, the test chamber was opened to recover the sensors in air. The whole process was performed in a super clean room at a constant humidity (25% relative humidity) and temperature (20 °C). The working temperature of the sensors was reported by the analysis system automatically [36].

Thin film sensors were prepared by employing the as-prepared tungsten oxide powders and then applied to the testing system. The gas response in this research is defined as Ra/Rg, where Ra is the sensor resistance in air (base resistance) and Rg is sensor resistance in target gas. Response time is defined as the time taken by the sensor resistance changing from Ra to Ra − 90% × (Ra − Rg) when the target gas was in. Similarly, recovery time is the time taken from Rg to Rg + 90% × (Ra − Rg) when gas was out [37].

3. Results and discussions

3.1. Structural and morphological characteristics

The XRD patterns and SEM images of the as-prepared h-WO_3 nanowires are shown in Fig. 1. A large scale of monodisperse nanowires is prepared by hydrothermal method in the presence of Na_2SO_4 and K_2SO_4. The diameter and length of the as-prepared nanowires is about 80 nm and 2.5 μm, respectively as shown in Fig. 1(a). These nanowires with an aspect ratio of 30 are highly monodisperse and uniform. According to the result of XRD in Fig. 1(b), the characteristics of XRD peaks corresponding to hexagonal phase of WO_3 (JCPDS 75-2187, a = b = 7.298 Å c = 3.899 Å) are observed. The h-WO_3 nanowires have high purity for no other peaks can be seen, and show good crystallinity due to the narrow and strong peaks.

Morphological and structural results are shown in Fig. 2. The TEM image of the synthesized single WO_3 nanowire is shown as Fig. 2(a). These nanowires show unsmooth peripheral face, a lot of linear pits appeared with an uneven end-face, are different with the earlier reported nanowires [33,38]. On the other hand, the directional growth of the nanowire can be visualized. The high resolution TEM (HRTEM) image and the corresponding fast Fourier transformed (FFT) pattern recorded on the boundary face are given in Fig. 2(b, c). HRTEM results shows the lattice fringes with an inter-planar spacing of about 0.391 nm, which is corresponding to the (002) plane of h-WO_3. Then it can be indicated that the nanowire grows along the crystal direction of [001] with the exposure of <200> crystal facets. To further illustrate the structural characteristic, the crystal structure of h-WO_3 is built according to the XRD result (P6/mmm (191), Z = 3), as show in Fig. 2(c, d). These structures show that the WO_3 crystal grows along the *c*-direction by the stacking of W–O atoms layered in ab planes. This process might be influenced by the addition of sulfate-ions addition.

3.2. Gas-sensing properties

The gas-sensing properties were measured by measuring the change of the resistance of sensing element which depends on the gas atmosphere and the working temperature of the sensing materials exposed