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Morphology, phase structure and acetone sensitive properties of copper-doped tungsten oxide sensors

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ABSTRACT

Cu-doped WO_3 hollow fibers were prepared by electrospinning technique, combined with the sol–gel method and reasonable sintering procedure. The morphology and crystal phase structure were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The gas-sensing properties were investigated as functions of the amount of Cu element, concentration of acetone and cooling method. The 3 mol% Cu-doped WO_3 hollow fibers using quenching for cooling exhibit high response and good selectivity to acetone. The response of the hollow fibers to 20 ppm of acetone was 6.43, which could be attributed to their high surface-to-volume ratio and junction structure. Partial substitution of W^{6+} in WO_3 with Cu^{2+} and quenching treatment could lead to a triclinic phase structure, which has a low symmetry, large dipole moment and strong interaction with acetone molecules and results in a good selectivity to acetone gas. Therefore, Cu-doped WO_3-based materials show the potential application for semiconducting gas sensors in the diagnosis of diabetes.

1. Introduction

It is known that certain diseases are associated with specific inorganic gases and volatile organic compounds (VOCs) present in human breath [1], for example, volatile sulfur compounds in breath are widely accepted as the main cause of oral malodor [2]; cancers are associated with 3-hydroxyl-2-butanono and styrene; and acetone gas, as an important breath marker of diabetes, could be used to reflect metabolic products of diabetes [1]. Diabetes is seriously harmful to human health and there are about 150 million patients all over the world and the number is continually increasing [3]. Medical investigations have shown that the acetone concentration in exhaled breath from a healthy human body is lower than 0.8 ppm, while that for a diabetic patient is higher than 1.8 ppm [4–6]. Therefore, the accurate analysis of breath acetone gas is extremely beneficial to diabetes treatment and is highly desirable.

The rapid, sensitive and accurate analysis of acetone in human breath is a key technique for noninvasive diagnosis of diabetes. The traditional detecting apparatus is expensive and requires special knowledge for operation [7], which is not suitable for real-time measurements. The semiconductor gas sensors work by changing resistance of active material due to the surface adsorption and desorption of gas molecules and the related space charge effects. The sensing properties are supposed to be enhanced with decreasing the grain size and increasing the surface-to-volume ratio [8]. The metal oxide semiconducting sensors, such as SnO_2 [9], TiO_2 [10] and ZnO [11], have certain advantages including high sensitivity, fast response and easy operation [12,13], though their gas selectivity is still a great challenge. Moona et al. [14] have synthesized Pd-doped TiO_2 nanofiber mats using electrospinning and subsequent calcination method and the as-prepared sensor showed a low working temperature (180 °C) and high gas response (R/R_0 = 38–2.1 ppm of NO_2). A novel micro gas sensor based on the SnO_2 nanofibers, which was successfully fabricated by Zhang et al. [15], exhibited short response and recovery times (<14 s to 10 ppm of ethanol) and low detection limit (<10 ppb). One-dimensional nanostructure materials are widely used in fabrication of gas sensors due to their high specific surface area, which provides more active sites for gas adsorption. Recently, WO_3 has attracted much interest for gas sensing applications and been considered as the most promising material for detecting gases like NO_2, H_2S, acetone and NH_3 [16–19].

In order to further improve the gas sensitivity and selectivity of WO_3, doping, dimension control and phase structure design are several effective methods. Till now, many scientific and technological efforts in relation to doping and size control methods have been made to improve the gas sensing properties of WO_3, whereas the phase design method is rarely studied. WO_3, which is best described as a three-dimensional network of corner-sharing WO_6 octahedra, has several crystal phases. For nanoscale WO_3, it has several phases

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such as triclinic (δ phase, −40 to 30 °C), orthorhombic (β phase, 500–950 °C) and tetragonal (α phase, >950 °C) [20]. The phase transition temperatures of nanoscale WO_3 are lower than that of WO_3 bulk and the phase transition is reversible because of its small grain size, large surface-to-volume ratio and ultrahigh surface energy [8]. In recent years, there are some reports about the phase transition of WO_3 [21–25], however, few of them are about the crystal phase design and acetone sensing properties, especially the research of one-dimensional WO_3 hollow fibers.

In this paper, one-dimensional WO_3 hollow fibers have been successfully prepared by electrospinning technique and their acetone sensing properties were investigated in detail. The effect of morphology, crystal phase structure and a possible gas sensing selective mechanism were also discussed.

2. Experimental details

2.1. Preparation of Cu-doped WO_3 hollow fibers and gas sensors

In our experiment, an electrospinning method was used to synthesize Cu-doped WO_3 hollow fibers. All the chemicals were of analytical grade and were used as received without further purification. In a typical synthesis, 1.5 g of H_2WO_4 was added into a mixed solvent of 6 ml ethanol and 9 ml H_2O_2 with ultrasonication for 35–40 min to form a homogeneous solution. Subsequently, citric acid and $NH_3{\cdot}H_2O$ aqueous solution, which was used to adjust pH to ca. 3–4, were dissolved into the solvent while stirring. After refluxing at 80 °C for 25 min, the solutions were transparent. Then different contents of $Cu(NO_3)_2{\cdot}3H_2O$ (3, 6 and 9 mol% corresponding to 0.045, 0.090 and 0.135 g $Cu(NO_3)_2{\cdot}3H_2O$, respectively) and 3 g PVP were added while vigorously stirring for 4 h and the sol solutions were obtained. The viscous sol solutions were then loaded into a glass syringe which was placed on a syringe pump horizontally. The pinhead of the syringe and a collector in front of it were connected to the positive and negative electrodes of a high voltage supply that was capable of generating direct current (DC) voltages of up to 30 kV. In our experiment, a voltage of 20 kV was applied for electrospinning, a tin foil served as the collector, and the distance between the pinhead and the collector was 10 cm.

The hollow fibers were sintered in air at 500 °C for 1 h and cooled in furnace. Then, the Cu-doped WO_3 hollow fibers were obtained. Especially, we quenched the fibers after sintering in order to keep the WO_3 at specific phases. The gas sensor was fabricated as follows: the as-prepared sample was mixed with distilled water and ground in an agate mortar to form a paste. Then the paste was coated on an alumina tube, on which two platinum wires had been previously installed at each end. A small Ni—Cr alloy wire was placed through the tube as a heater, which provided operating temperature, and the temperature is 300 °C in this experiment.

2.2. Microstructure analysis and gas sensing properties test

The morphological features of the synthesized hollow fibers were investigated using field emission scanning electron microscopy (FE-SEM: Hitachi, S4800, Japan) and transmission electron microscopy (TEM: JEOL, JEM-2100F, Japan). The crystalline structure including the phase purity was examined by X-ray diffraction (XRD: Rigaka, D/max 2500 v/pc, Japan) using the Cu Kα X-ray (λ = 0.15418 nm). Diffraction peaks of the crystalline phase were compared with the standard compounds reported in the JCPDS Data Files. Thermal analyses including thermogravimetric and differential scanning calorimetry (TG-DSC: NETZSCH, STA 449C, Germany) were used to determine the calcination temperature.

The acetone vapor sensing properties of the side-heated gas sensors were measured in a static gas system connected with a computer which was used to measure the resistances of the sensors. The response to acetone was defined as:

$$\text{Response} = \frac{R_a}{R_g} \quad (1)$$

where R_a and R_g were the electric resistances in air and test gas, respectively. The resistance measurements were carried out at 300 °C which was controlled by adjusting the heating voltage. The ambient temperature was 20 °C and RH 20%.

3. Results and discussion

3.1. Morphology analysis

The morphologies of the 3 mol% Cu-doped WO_3 fibers are shown in Fig. 1. The as-spun fibers form a net-like structure and a smooth surface due to the polymeric features before calcination (Fig. 1(A)). The network is constituted by randomly oriented micro fibers with diameters of 1.5–2.5 μm. After sintered at 500 °C in air, the fibers shrink due to the decomposition of PVP (Fig. 1(B)), and the diameters of the calcined WO_3 fibers are 1.0–2.0 μm, which are smaller than those of the as-spun fibers. Meanwhile, as shown in the high magnification image of the calcined WO_3 fibers (Fig. 1(C)), the structure of the 3 mol% Cu-doped WO_3 fibers is hollow and the wall thickness is about 300–500 nm. The TEM image (Fig. 1(D)) shows clearly that the wall of WO_3 hollow fiber is comprised by numerous nanocrystals with the size of ca. 20–30 nm.

The hollow structure of the calcined WO_3 fibers is resulted from the evaporation effect of PVP, which induces the component segregation of fibers during the calcination process, as reported by Wei et al. [26]. The formation mechanism is illustrated in Fig. 2.

In the precursor sol solution, H_2O_2, citric acid and ethanol served as dispersant, chelating agent and solvent, respectively. H_2WO_4 and $Cu(NO_3)_2$ as the metal precursors are enwrapped in the sol solution. During the process of electrospinning, ethanol evaporates rapidly which makes citric acid chelation and PVP have a tendency to move to the edge of the fibers. However, PVP moves slowly for its much bigger molecular weight than citric acid and H_2WO_4. Hence, there is a concentration gradient of PVP along the diameter of the fibers and the concentration in the center is higher than that at the edge of the fibers. As a result, the enwrapped H_2WO_4–$Cu(NO_3)_2$ chelation will move to the outer layer of the fibers easily and the component segregation occurs with the evaporation effect of PVP. After calcination at 500 °C, PVP decomposes completely and hollow fibers are formed. At the same time, the citric acid at the edge of fibers evaporates and decomposes, which results in the formation of porous wall of hollow fibers. The porous feature of the fibers was characterized by nitrogen adsorption method and the result shows that the BET surface area of the 3 mol% Cu-doped WO_3 fibers is 16.9 m^2/g. The high surface-to-volume ratio of the Cu-doped WO_3 fibers makes them have more active adsorption sites and more gas diffusion channels compared to the solid fibers. The gases can permeate into the hollow fibers and adsorb (or desorb) on the inside and outside surface of the hollow fibers easily, and the gas sensing properties can be improved accordingly.

3.2. Cu element doping effects on the gas sensing properties

Fig. 3 displays the X-ray patterns of the pure and Cu-doped (3, 6, 9 mol%) WO_3 hollow fibers calcined at 500 °C. The patterns of pure and 3 mol% Cu-doped WO_3 hollow fibers show peaks those are in good agreement with the orthorhombic WO_3 phase (JCPDS Card No. 20-1324). With the increasing of the Cu doping content,