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Facile synthesis and NO_2 gas sensing of tungsten oxide nanorods assembled microspheres

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ABSTRACT

Tungsten oxide nanorods assembled microspheres were synthesized by a facile hydrothermal process at 180 °C using ammonium metatungstate and oxalic acid as starting materials. The morphology and structural properties were investigated using scanning electron microscopy, powder X-ray diffraction, and transmission electron microscopy. The as-synthesized microspheres are composed of orthorhombic $WO_3 \cdot xH_2O$ nanorods with diameter less than 100 nm. These microspheres lose water gradually during annealing and transfer to monoclinic WO_3 when annealed at 550 °C. The gas sensing properties of the microspheres annealed at different temperatures were studied by exposing the gas sensors made from microspheres to NO_2 gas. The results indicated that the crystalline phase of the microspheres has no obvious effect on the gas sensing performance. The microspheres annealed at 350 °C showed fast and the highest response to NO_2 gas due to the three-dimensional network based on the nanorods and the high effective surface area.

1. Introduction

Nanostructured materials are considered as good candidates for gas sensing applications due to their large surface area-to-volume ratio and the size effect. Since the report of enhanced gas sensing performance of tin oxide nano-crystallites in 1990s [1], nanomaterials based gas sensors attracted more and more attentions [2,3]. Nanostructures of well-established gas sensing materials like tin oxide [4–6], zinc oxide [7], tungsten oxide [8–10], titanium oxide [11,12], and indium oxide [13,14] have shown higher sensitivity, faster response, lower operating temperature, and/or enhanced capability to detect low concentration gases compared with the thin film counterparts.

Tungsten oxides are a class of versatile materials that offer manifold technological applications including gas sensors [15,16], opto-electrochromic and optical modulation devices [17,18], photocatalysis [19], hydrophilic surface design [20], etc. Gas sensors based on tungsten oxide are sensitive to a variety of gases such as NO_2, O_3, H_2, H_2S, and NH_3 [21]. In particular, tungsten oxide showed superior sensitivity and selectivity in detecting NO_2 gas [22,23]. On the other hand, nanostructural tungsten oxide such as nanorods [24], nanowires [25], nanotubes [26], nanoflakes [27], nanodisks [28], and nanotrees [29] have been synthesized using high temperature evaporation, precipitation, hydrothermal reaction, and electrochemical or template assisted methods. These nanostructures provide good blocks for developing high performance gas sensors. Herein, we report the synthesis of tungsten oxide nanorods assembled microspheres by a facile hydrothermal method. To our knowledge, there is no report on the gas sensing of the microsphere-like tungsten oxide nanostructures. We expect that this kind of microsphere with nanorod substructure will benefit to the gas sensing performance of their based gas sensors.

2. Experimental

2.1. Synthesis

A facile hydrothermal process was employed to synthesize the samples. Ammonium metatungstate and oxalic acid (99.9%, Wako Pure Chemicals Co.) were used as starting materials. In a typical experiment, 0.53 g ammonium metatungstate and 0.72 g oxalic acid (OA) (the mole ratio of OA/W is 4:1) were dissolved in 50 ml deionized water. Clear solution was obtained after stirring for 30 min. Then, the mixture solution was transferred into a 100 ml Teflon-lined stainless autoclave. The autoclave was sealed and maintained at 180 °C for 8 h. After the reaction completed, the resulting product was centrifuged and washed with deionized water for three times, and then dried at 60 °C overnight. Part of the product thus treated was annealed at 350, 450, and 550 °C for 5 h, respectively,

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for investigating the crystal structure, morphology change, and the gas sensing properties. For comparison, samples were also synthesized at OA/W ratios of 2:1, 3:1, and 5:1 with a fixed tungsten ion concentration by the same synthesis process.

2.2. Structural characterization

X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (Rigaku, Ultrax 18SF) with an imaging plate detector using Cu Ka radiation. A Hitachi S-4800 field emission scanning electron microscope (FESEM) was used to investigate the morphology of the samples. Transmission electron microscopy (TEM) characterization was carried out on a Hitachi S-9000 transmission electron microscope. The effective surface area was measured using physical adsorption/desorption of Kr on a Quantachrome AUTOSORB-1-MP facility.

2.3. Gas sensing measurements

The gas sensors were made by drop-casting method. Briefly, desired amount of the synthesized powder was dispersed in methanol with the assist of ultrasonic. Then, the suspension was dispensed dropwise onto the oxidized Si substrate with a pair of interdigitated Pt electrodes. The gas sensors were ready for characterization after dried and then aged at 350 °C for 2 h. The gas sensing properties were measured in a tube system with a coil resistance heater. The carrier gas (dry synthetic air) mixed with a desired concentration of NO_2 gas was flowed at 200 ml/min through the quartz tube (45 mm in diameter and 400 mm in length) kept at a set temperature. The electrical measurement was performed by a voltamperometric method at a constant bias of 10 V, and a multimeter (Agilent 34970A) was used to monitor the change of electrical resistance upon turning the target gas on and off. The sensor response is defined as $(R_a - R_o)/R_o$, where R_o is the resistance in air and R_a is the maximum resistance after the NO_2 gas was introduced.

3. Results and discussion

3.1. Structure and morphology

All the as-synthesized products are powders with white blue color. The XRD patterns of the samples dried at 60 °C are shown in Fig. 1. The results indicate that the products synthesized with OA/W ratio of 2:1, 3:1, 4:1, and 5:1 are all crystallized and have the same crystalline structure. The peaks of the XRD patterns can match well with the documented diffraction pattern of orthorhombic $WO_3 \cdot 0.33H_2O$ (JCPDS card no. 35-0270). Considering the possibility of the variation of water in the structure during drying and annealing, we assign the formula of $WO_3 \cdot xH_2O$ to the samples containing water in our experiments.

Despite of the same phase composition, the morphology of the products synthesized with different OA/W ratio is very different. Fig. 2 presents the FESEM images of the samples synthesized with OA/W ratio of 2:1, 3:1, 4:1, and 5:1. The sample synthesized with OA/W ratio of 2:1 shows sphere-like aggregate with nanoplatelet substructure. The nanoplatelet substructure can still be observed when the ratio of OA to tungsten is increased to 3:1. However, the products change to nanorod-like morphology when the ratio of OA to tungsten is 4:1. These nanorods assemble to microspheres with average diameter of around 3 μm. For the sample synthesized at an OA/W ratio of 5:1, radial nanorod aggregates are obtained. Since no other templates or assistant agents were used in our experiments, the formation of various microstructures at different OA/W ratios should be ascribed to the interaction between tungsten ions and OA. It is known that OA can stabilize the hydrolyzed tungsten oxide

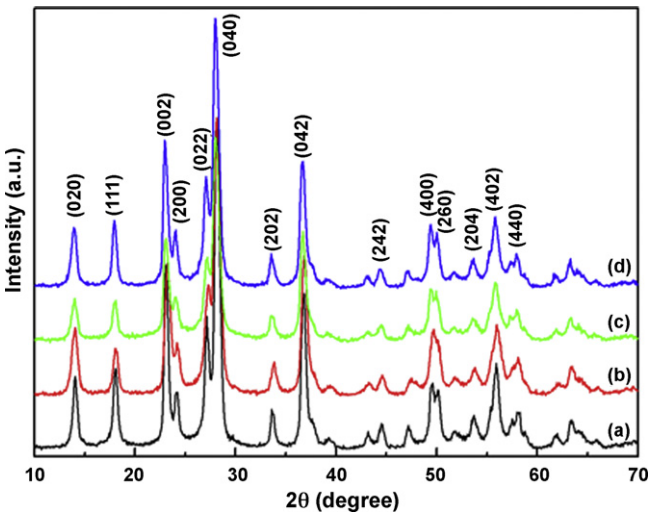

Fig. 1. XRD patterns of the products synthesized with oxalic acid/tungsten mole ratios of (a) 2:1; (b) 3:1; (c) 4:1; and (d) 5:1.

nanocrystals in aqueous solution by forming coordination complex [30]. The OA ligand would affect the growth direction of the nanocrystals by binding to specific surface of the nanocrystals. The $WO_3 \cdot xH_2O$ nanocrystals can grow in the platelet habit in the presence of a small amount of OA. However, in the presence of large amount of OA, for example when the OA/W ratio is 4, the crystallization habit is changed by the surrounding OA ligands, leading to the formation of rods like morphology. On the other hand, the intermolecular force among the OA molecules may contribute to the formation of the microsphere morphology [31]. The NH_4^+ ions in the solution may also affect the microstructure formation [32]. More detailed work should be done to clarify the self-assembly mechanism of the microspheres.

Fig. 3 shows a typical TEM image of the nanorods obtained with OA/W ratio of 4:1. These nanorods have an average diameter less than 100 nm and length in micrometer level. A corresponding diffraction pattern of the nanorods is also presented in Fig. 3. Diffraction rings can be clearly seen. The diffraction pattern, which can be indexed to orthorhombic phase, is consistent with the XRD results.

3.2. Effect of annealing on structural properties

Here we choose the microspheres synthesized with OA/W ratio of 4:1 to investigate the gas sensing properties. Since gas sensor requires a material to work continuously at high temperature condition, the microspheres were annealed to stabilize the microstructure. Fig. 4 represents the XRD patterns of the microspheres annealed at 350, 450, and 550 °C, respectively. The sample lost the crystalline water after annealed at 350 °C and transferred to hexagonal WO_3 (JCPDS card no.33-1387). With the increase of the annealing temperature, the diffraction peaks at 23–25° and the peaks at 26–30° separate gradually, indicating that the phase changed after annealing at higher temperature. The sample completely transferred to monoclinic WO_3 (JCPDS card no. 43-1035) after annealed at 550 °C for 5 h.

The FESEM images of the samples annealed at different temperatures are shown in Fig. 5. For the samples annealed at 350 and 450 °C, the nanorods on the microsphere surface were damaged to some extent. However, the nanorods inside the microspheres can still be clearly seen. The nanorod substructure was totally destroyed for the sample annealed at 550 °C and these nanorods changed to nanoparticles. However, it was noticed that the microsphere morphology still exists for the samples annealed at all conditions.