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Morphology-controllable synthesis, characterization and sensing properties of single-crystal molybdenum trioxide

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ABSTRACT

Different morphologies of single-crystal molybdenum trioxide (MoO_3) were successfully synthesized by a novel, facile and low cost method using cotton as biotemplate. The morphology and structure of crystals were characterized by scanning electron microscopy and X-ray diffraction. Gas sensors have been fabricated using MoO_3 samples to examine the response to ethanol gas. The effects of cotton biotemplate and calcination condition, as well as morphologies obtained by different synthesized methods on ethanol sensing property were investigated. It is found that the sensor based on MoO_3 hollow microtubules calcined at 300 °C showed highly sensitive to ethanol with fast response, good selectivity and stability, indicating its potential applications for environment and food or the drinking status of drivers.

1. Introduction

Semiconductor metal oxide-based gas sensors have been a subject of extensive research because of their use in detecting several toxic, inflammable and odorless gases [1]. The sensing properties are based on the reaction between semiconducting metal oxides and gases in the atmosphere. Recently, there is an increasing trend to use specifically engineered structured materials as gas sensing elements. The use of such structured materials such as belts, rods and wires in micro-, meso- or nano-dimensions, offer high surface to volume ratios and unique structural features that are expected to enhance the properties and performance of gas sensors [2,3]. Molybdenum trioxide (MoO_3), an important n-type semiconductor with a band gap of approximately 2.39–2.9 eV, has been widely used in catalytic and electrochromic. Furthermore, MoO_3 has been attracted as a new gas sensing materials to detect H_2 [4], CH_4 [5], NH_3 [6], H_2S [7] and trimethylamine [8]. The high surface-to-volume ratio associated with nanostructures makes their electrical responses extremely sensitive to the species adsorbed on the surface. Morphologies of molybdenum trioxide crystals based on different procedures and synthesis techniques are now prepared such as MoO_3 nanorods [9], nanoplates [10], nanobelts [11], nanoflower [12], MoO_3 hollow spheres [13], MoO_3 fibers [14] and MoO_3 films [15]. However there remains much interest in morphology-controllable synthesis and novel properties.

Template-directed synthesis is an ideal approach to replication, for the fabrication of inorganic materials with predetermined structural properties. Recently, using natural biomaterials and their ramifications as templates, novel biomorphic products with fascinating designs could be produced for practical industrial applications, such as cotton, wood, paper, sponges, egg shell membrane, butterfly wings and ferritin [16,17]. In this paper, taking MoO_3 as an example, we present the use of commercial cotton as both the template and the stabilizer for the morphology-controllable synthesis of MoO_3. This work reports for the first time on a novel, facile and low cost method leading to MoO_3 consist of stratified long rectangles. The molybdenum trioxide samples were characterized by means of X-ray diffraction, scanning electron microscopy and field-emission scanning electron microscopy. And the gas sensing performance of the resulting lamellar MoO_3 toward ethanol was investigated.

2. Experimental

2.1. Synthesis

The morphology-controllable syntheses of MoO_3 were carried out by the infiltration and calcinations method. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (A. R. grade, Sinopharm Group Chemical Reagent Co., Ltd.) was used as the source of molybdenum. In a typical procedure, an aqueous solution of 200 mL was first prepared by dissolving $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (0.04 mol) in distilled water. Then, the dried and loose cotton fibers were infiltrated with the above solution for 24 h. After drying at 60 °C for 12 h, it was then

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placed in an alundum crucible, and fired in air at 300, 400, 500 and 600 °C for 3 h.

2.2. Characterization methods

The crystalline phase in the samples were characterized by an X-ray diffraction (XRD, Bruker D8 Advance) using Cu*Ka*1 radiation ($\lambda = 0.15406$ nm) at 30 kV and 40 mA at a scanning rate of 2° at 2θ min^{-1} ranging from 10° to 70°. The morphologies of the samples were observed by scanning electron microscopy (SEM, Hitachi S2500) and FEI Sirion 200 field emission gun scanning electron microscope (FESEM, Hitachi S4800). The adsorption and desorption isotherm studies with liquid nitrogen were performed using a Micromeritics ASAP 2010 M + C system. The specific surface area was examined using a single point Brunauer–Emmett–Teller (BET) method. Pore-size distribution was calculated from the adsorption branch of the nitrogen isotherm, using the Barrett–Joyner–Halenda method.

2.3. Sensor fabrication and test

The gas sensor was fabricated by coating aqueous slurry of the prepared MoO_3 material onto an alumina tube, which is positioned with a pair of Au electrodes and four Pt wires on both ends of the tube. A Ni–Cr alloy coil through the tube was employed as a heater to control the operating temperature. Gas sensing test was operated in a measuring system of WS-30A (Winsen Electronics Co. Ltd., Zhengzhou, China), and the measurement was processed by a static process. The gas concentration was controlled by changing the mixing ratio of the parent gases and air. The sensor's sensitivity was defined as

$$\text{response} = \frac{R_{air}}{R_{gas}} \quad (1)$$

where R_{air} is the resistance of the sensor in air and R_{gas} is the resistance of sensor in the presence of the test gas. Then, the slope coefficient of response value to the logarithm of the concentration was defined as sensitivity. The response time was defined as the time required for the variation in resistance to reach 90% of the equilibrium value after a test gas was injected, and the recovery time as the time necessary for the sensor to return to 10% above the original resistance in air after releasing the test gas.

3. Results and discussion

3.1. Micro-characterization results

The XRD patterns of MoO_3 samples are shown in Fig. 1. The results indicate that the final products were all pure orthorhombic α-MoO_3 (JCPDS card No. 35-0609, $a = 0.3963$ nm, $b = 1.3856$ nm, $c = 0.3697$ nm, space group *Pbnm*). The strong diffraction peaks of (0 2 0), (0 4 0) and (0 6 0) planes reveal a layered crystal structure or a highly anisotropic growth of the oxides [18]. In these patterns, it was also observed that the diffraction peaks became sharper with the increase in calcinations temperature, which confirmed that the crystallite size of the α-MoO_3 grow abruptly with the increase in calcinations temperature. The average crystallite sizes of MoO_3 samples were estimated according to the line width analysis of the diffraction peaks based on the Scherrer formula, $D = 0.89\lambda/\beta\cos\theta$, where D is the mean crystallite size, λ is the wavelength of the X-ray radiation ($\lambda = 0.154$ nm for CuKα1 radiation), and β is the full width at half-maximum of diffraction peak at 2θ. From the XRD spectrums, the average crystallite size were calculated (Table 1) to be about 23, 29, 37 and 46 nm for sample calcinations temperatures 300, 400, 500 and 600 °C, respectively.

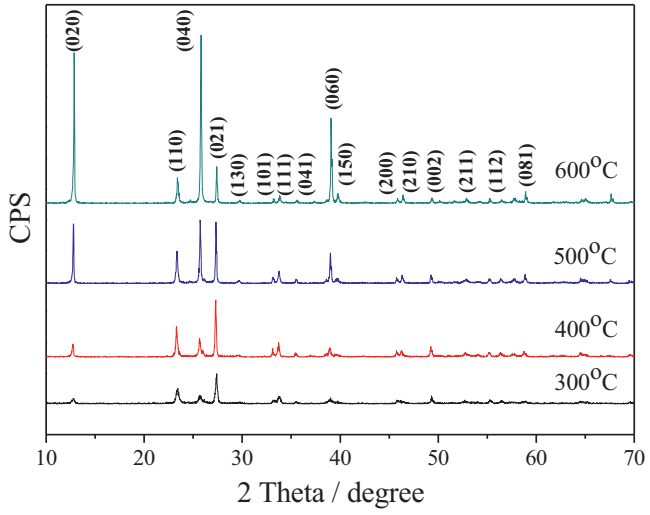

Fig. 1. XRD patterns of the samples calcined at different temperatures.

It is well known that gas sensing properties of a metal oxide strongly depends on its morphological features. Fig. 2 shows the SEM morphological characterization on the MoO_3 calcined at different temperatures. As can be seen in Fig. 2(a) and (b), the biomorphic MoO_3 microtubules very long, hollow, and retain the original fibrous cotton morphology with cotton body removal, their length are several centimeters and the diameter is basically in the range of 10–20 μm. The chemical composition of the samples were analyzed by energy dispersive X-ray spectroscopy (EDS). As shown inset of Fig. 2(a) and Table 1, the biomorphic MoO_3 samples were only composed of Mo and O, and while the Cu signal is derived from the supporting SEM copper conductive tape. The results show that the O/Mo atomic ratios approximately equal 3:1 within the accuracy of the technique, in good accordance with the stoichiometry of MoO_3. Such an observation was also reported by Di Zhang et al. [16,19]. Fig. 2(e) and (f) shows the FESEM images of MoO_3 hollow fibers calcined at 300 °C and 400 °C. It is clearly demonstrated that the framework of the biomorphic MoO_3 microtubules consists of a large amount of nanoplates. Since they are well interconnected, the orientated platelets can now be viewed as an integrated 3D stack. The calcination temperatures have remarkable effect on the grain size. It is found that the average nanoplates grain size of the walls calcined at 300 and 400 °C range from 200 to 400 nm and from 1 to 2 μm. In Fig. 2(c), numerous batten-like crystallites are formed with well-defined and smooth facets, serving as building blocks to construct a typical hierarchical patterning. It can be observed that the average size of the batten-like crystallites is ~2 μm in width and 10–15 μm in length (Fig. 2(c)) With the increasing of calcinations temperature, the MoO_3 battens grow into large rectangular plates with the average width and length of about 10 and 100 μm, respectively, which can be seen in Fig. 2(d). Such plates are also shown in the literatures [20,21]. The average sizes of the MoO_3 samples were consistent with the increase of crystallinity with increasing calcination temperature in X-ray diffraction patterns (Fig. 1). This

Table 1
Effect of calcination temperature on the structural properties of MoO_3.

Calcination temperature (°C)	BET area (m^2/g)	Pore size (nm)	Average crystallite size (nm)	O/Mo atomic ratio
300	50.8	16.82	23	3.09
400	36.4	20.92	29	3.12
500	27.6	26.89	37	3.05
600	20.3	29.86	46	2.96