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Facile synthesis of α-MoO_3 nanorods with high sensitivity to CO and intrinsic sensing performance

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ABSTRACT

Orthorhombic molybdenum trioxide (α-MoO_3) nanorods with well-defined morphology and high crystalline have been synthesized by a facile and fast hydrothermal method under 85 °C for 1.5 h without employing surfactants or templates. The controlling of stirring time, thermostatic time and HNO_3 amount is crucial for the growth of α-MoO_3 nanorods. The morphology and structure of α-MoO_3 were characterized by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The obtained α-MoO_3 nanorods as a novel sensing material exhibit high sensitivity, the highest response to 40 ppm CO is 239.6 at operating temperature of 292 °C. The intrinsic sensing performance arises from the non-stoichiometry of the α-MoO_3 due to the presence of Mo^{5+} in MoO_3 lattice, that is, the molecular formula of MoO_3 should be expressed as MoO_{3-x} ($x = 0.08$), which has been confirmed by X-ray photoelectron spectroscopic (XPS) analysis and room temperature photoluminescence (PL). The sensing mechanism of α-MoO_3 to CO was also discussed in terms of lattice oxygen in MoO_3.

1. Introduction

Molybdenum trioxide (MoO_3), as an n-type wide band gap semiconductor, has been widely applied to sensors, Li-ion batteries and photocatalysts [1–4]. MoO_3 usually has three structures: the thermodynamically stable orthorhombic α-MoO_3, the metastable monoclinic β-MoO_3 and hexagonal h-MoO_3 [5]. The most important structural characteristic of α-MoO_3 is its anisotropy and unusual chemistry of multiple valence states, where highly asymmetrical MoO_6 octahedra are interconnected with their edges along [0 0 1] direction and interlinked with their corners along [0 0 1] and [1 0 0], resulting in a so-called double-layer planar structure [6]. Nowadays, the development of one-dimensional (1D) nanostructures, such as nanorods, nanobelts and nanowires [2,7–10], has become a focal area to improve gas-sensing performance because of their large surface-to-volume ratio, various morphologies and excellent electronic radial transport. A number of techniques for synthesizing 1D α-MoO_3 nanostructures have been reported, including hydrothermal synthesis, spray pyrolysis, thermal evaporation and deposition of vapor phase etc. [11–14]. Among them, the hydrothermal process is recognized to be the most promising method for preparing well-defined morphology and crystalline α-MoO_3. Chen et al. [15] synthesized 1D α-MoO_3 using hydrothermal method at 170 °C for 45 h and investigated their sensing properties to ethanol. Wang et al. [16] prepared α-MoO_3 nanobelts at hydrothermal temperature of 180 °C for 20 h using cetyltrimethylammonium bromide (CTAB) as cationic surfactant. However, most of the reported hydrothermal processes need high temperature (over 170 °C) and long reaction time (over 20 h) [16,17]. Herein, we not only developed a facile and fast hydrothermal method for producing α-MoO_3 nanorods with well-defined morphology and high crystalline but also investigated their sensing properties to CO, which has rarely been reported in literatures.

2. Experimental

2.1. Synthesis of α-MoO_3 nanorods

In a typical experiment, 0.3 g $(NH_4)_6Mo_7O_{24}$ powder was added into distilled water (5 mL) in the conical flask with plug under stirring at room temperature. Then, nitric acid (67%, 20.0 mL) was added to the solution by stirring and the mixture was maintained at 85 °C under stirring. After stirring for 0.5 h, stopped stirring and

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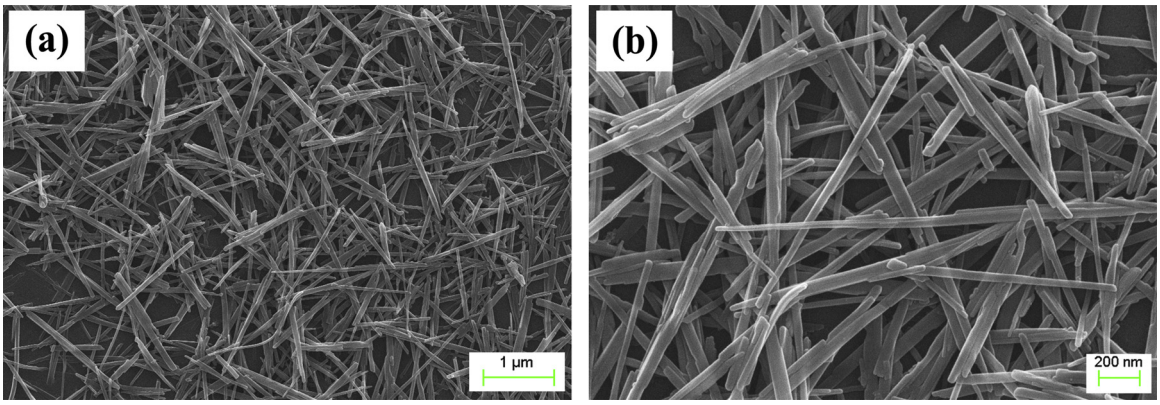

Fig. 1. FESEM image of the as-synthesized α-MoO_3 nanorods at different magnifications.

held another 1 h at 85 °C. The resulting precipitates were collected and washed several times with distilled water and ethanol, and finally dried in a vacuum oven at 60 °C for 12 h.

2.2. Characterization

The crystal structure of samples was characterized by X-ray diffraction (XRD) recorded on a Shimadzu XRD-6000 diffractometer with copper Kα1 radiation (λ = 0.15406 nm), using a scanning speed of 10° min^{-1} for 2θ in a range from 10° to 80°. Field emission scanning electron microscopy (FESEM) images were obtained with a Hitachi S-4700 instrument operated at 20.0 kV. Surface elemental analysis was performed using a PerkinElmer phi-5400 X-ray photoelectron spectroscopy (XPS). Photoluminescence spectra (PL) were investigated by florescence spectrophotometer (Shimadzu, RF-5301 PC) at room temperature by a 325 nm excitation.

3. Results and discussion

3.1. Morphology of α-MoO_3

It is well known that the gas sensing properties of semiconductor metal oxides are related to their morphologies. Fig. 1 shows the FESEM images of as-synthesized α-MoO_3 products. It can be clearly seen that the sample exhibits uniform rod-like morphology with average diameter of ca. 40 nm and length of 2 μm (i.e., aspect ratio of 50).

3.2. Crystal type and structure of α-MoO_3

Typical X-ray diffraction patterns are shown in Fig. 2. All diffraction peaks of the samples annealed at different temperatures can be perfectly indexed to the orthorhombic MoO_3 with lattice parameters: a = 3.962, b = 13.858 and c = 3.697 Å compared with standard JCPDS # 05-0508 [16]. There is no phase transition during annealing process but the diffraction peaks become stronger and sharper with the increase of annealing temperature, demonstrating that the sample crystallinity becomes better but the crystallite size becomes larger (decrease of specific surface). Besides, the peaks of (0 k 0) planes exhibit stronger intensity compared to that of other (h k l) planes of the α-MoO_3 nanorods, which indicates the highly anisotropic growth as well as the preferred orientation of the nanorods.

3.3. Thermogravimetric and differential thermal analysis of α-MoO_3

To preliminarily select an annealing temperature, the as-synthesized sample was thermal analyzed through thermogravimetric and differential thermal analysis (TG–DTA) at temperature ranges of 30–600 °C, the results are shown in Fig. 3. There are two obvious peaks from DTA, one is strong endothermic peak at 129 °C with a mass loss of 0.70% corresponding to TG curve, which is caused by the loss of the absorbed water on the surface of the as-prepared α-MoO_3. The other is strong exothermal peak at

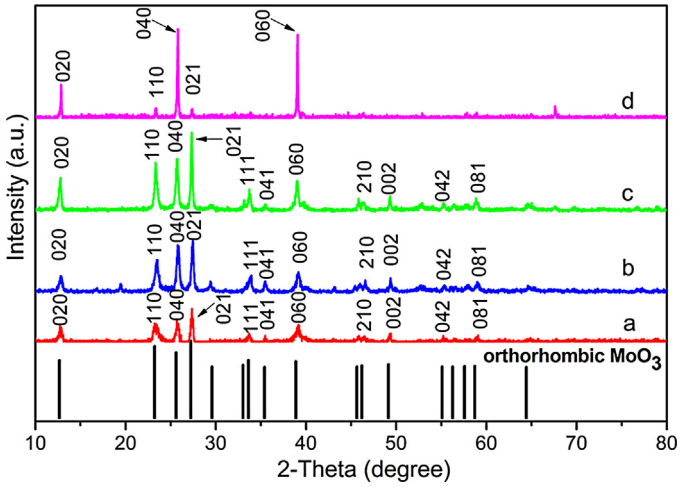

Fig. 2. XRD patterns of α-MoO_3 nanorods annealed at different temperatures (a) as-synthesized, (b) 300 °C, (c) 500 °C and (d) 700 °C.

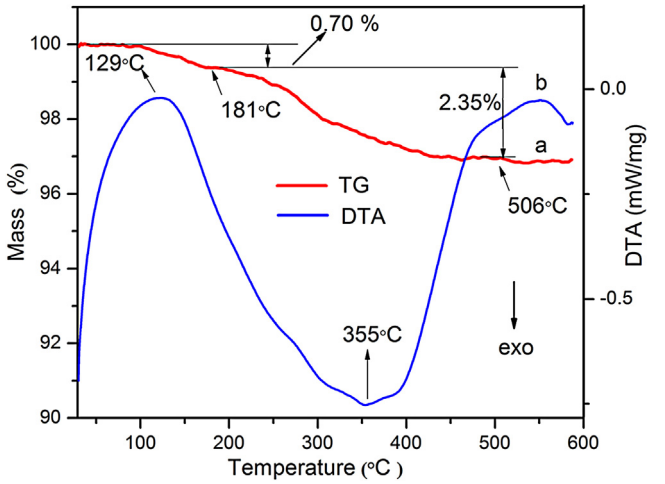

Fig. 3. TG–DTA curves obtained via thermogravimetric and differential thermal analysis of α-MoO_3 sample.