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Intrinsic characteristic and mechanism in enhancing H_2S sensing of Cd-doped α-MoO_3 nanobelts

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ABSTRACT

Pure and Cd-doped orthorhombic molybdenum trioxide (α-MoO_3) nanobelts with width of 200–800 nm and length of several micrometers have been successfully synthesized by a facile and low temperature (120 °C) hydrothermal method without any surfactant or template. The crystal structure and morphology of the products were characterized by XRD and FESEM. The sensing measurements reveal that the synthesized samples not only exhibit high response to H_2S but also small cross-sensing to other reducing gases. The change of intrinsic defects in Cd-doped sample is responsible for the enhancement of the sensing properties, which has been confirmed by the room temperature PL, Raman and XPS. The response transients of the sensors under different gas concentrations were measured and modeled using L–H heterogeneous reaction mechanism. Origin and mechanism of the enhanced gas sensing for 5 wt% Cd-doped sample were analyzed in detail according to the characteristic of PL and XPS.

1. Introduction

H_2S, as a toxic gas, presenced in air pollution not only destroys the environment, but also is badly harmful to human body [1,2], so, H_2S is an important target gas for α-MoO_3 gas sensors. One-dimensional (1D) α-MoO_3 [3,4] along with most of other semiconducting metal oxides, such as WO_3, ZnO, and SnO_2, etc. [5–9], have become promising candidates for detection of toxic gases in air, because their large surface-to-volume ratio and the congruence of the carrier screening length with their lateral dimensions make them highly sensitive and efficient transducers of surface chemical processes into electrical signals. In addition to sensing materials, 1D α-MoO_3 nanostructures are also applied to cathode material in batteries, conductive glass fiber, catalyst, precursor for the synthesis of intercalated compounds and many others. Wide range applications lead to numerous efforts in preparation of crystalline MoO_3 by different methods including hydrothermal synthesis, spray pyrolysis, thermal evaporation and deposition of vapor phase [10–13]. Among them, the hydrothermal process is recognized to be the most promising method for preparing well-defined 1D α-MoO_3 crystalline. However, most of the reported hydrothermal processes of 1D α-MoO_3 need high temperature (over 170 °C) and long reaction time (over 20 h) [10,14,15]. In this work, we present the preparation method of pure and Cd-doped α-MoO_3 nanobelts via a facile hydrothermal synthesis without any surfactant or template at lower temperature (120 °C). Many researchers have showed that gas sensing of pure MoO_3 nanomaterial is not ideal for high operating temperature [1]. So, various attempts have been employed to improve the gas sensing properties of MoO_3.[1,16,17]. Doping of metal elements already has been proved to be one of the most facial and effective methods in improving the sensing performances of semiconductor metal oxides, because doping can effectively modulates the parameters of crystal structure and band structures of oxide nanocrystals. Apart from expensive noble metals, the transition metal and rare-earth ion can be used as dopants [17]. The Cd doping of nanostructured semiconductor metal oxides has been a very active research area in the last few years, mostly due to the interesting photocatalytic properties of them. For example, porous Cd-doped ZnO nanorods prepared by two-step route (ethanol-thermal technique and following by annealing at 420 °C for 2 h) exhibits high photocatalytic activity to some dyes [18]. However, there have been only a few reports on the effects of Cd doping on the sensing properties of semiconductor metal oxides [19]. Herein, an attempt was made to synthesize pure and Cd-doped α-MoO_3 nanobelts, furthermore, the samples obtained were used as sensing material of H_2S sensor to examine their sensing properties to H_2S.

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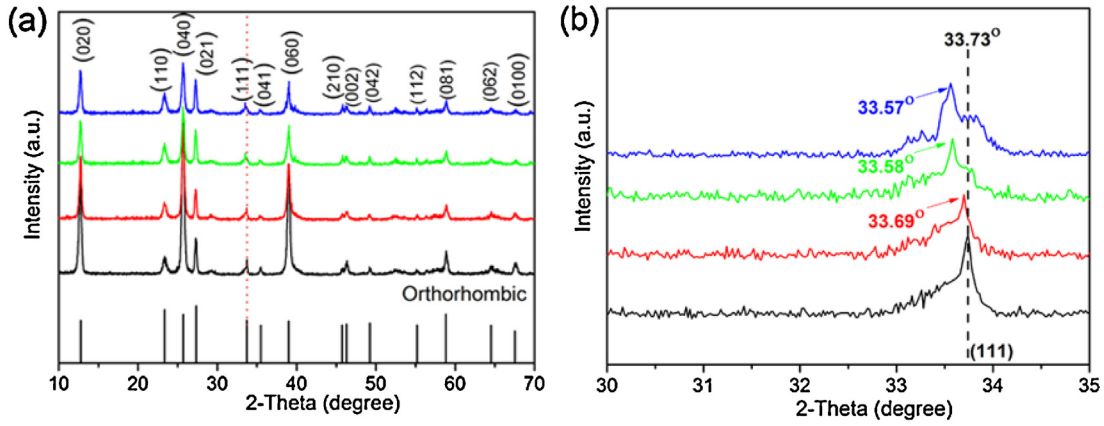

Fig. 1. (a) XRD patterns of the samples annealed at 300 °C: pure α-MoO_3 (black), 3 wt% (red), 5 wt% (green) and 7 wt% (blue) Cd-doped α-MoO_3 nanobelts and (b) high magnification of the (111) peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The response transients for these sensors under different gas concentrations were measured and modeled using L–H heterogeneous reaction mechanism. The sensing mechanism of the material to H_2S and the key factor of enhancing gas sensing were discussed by PL and XPS spectra.

2. Experimental

2.1. Synthesis of Cd-doped α-MoO_3 nanobelts

In a typical experimental procedure, 0.6180 g of ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) was dissolved in 25 mL distilled water. After continuous stirring for 30 min, 2.5 mL of nitric acid (HNO_3) (67%) was slowly added dropwise into the above solution. After stirring for 10 min, stoichiometric amounts of $Cd(NO_3)_2{\cdot}6H_2O$ (Cd/Mo = 0, 3, 5, 7 wt%, respectively) were dissolved into the above solution to form a transparent solution B. The reaction solution B was transferred into a Teflon-lined stainless steel autoclave of 100 ml capacity and followed by the heating of the Teflon-lined stainless steel autoclave to 120 °C for 24 h. After the reaction was completed, and then cooled down to room temperature naturally. White precipitations were formed at the bottom of the autoclave. The white precipitates were centrifuged, washed with distilled water and ethanol several times, and finally dried at 60 °C overnight. The as-synthesized products were then annealed at 300 °C for 2 h and examined their gas-sensing properties to H_2S.

2.2. Characterization

The product morphology was examined by field emission scanning electron microscopy (FESEM, Hitachi S-4700, 20.0 kV). Crystallographic information for the samples was collected using powder X-ray diffraction (XRD, Shimadzu XRD-600 diffractometer, copper Kα radiation with λ = 0.154 nm), operated at 45 kV and 40 mA. Scanning rate of 10° min^{-1} was applied to record the patterns in range of 10–70° (2θ). UV–vis absorption spectra were recorded with a UV/vis spectrometer (PerkinElmer, Lambda 35) in the range of 200–700 nm at room temperature. Surface elemental analysis was performed using an ESCALAB250 X-ray photo-electron spectrometer. PL spectrum was recorded from 350 to 600 nm at room temperature with a 325 nm excitation (RF-5301PC spectrometer). The Raman spectroscopy was performed on a laser Raman spectrometer (LabRAM ARAMIS) using a visible laser (λ = 532 nm) at room temperature.

2.3. Sensor fabrication and response measurement

The pure and Cd-doped MoO_3 samples were mixed with ethanol to form paste, and then drop-coated onto the surface of a ceramic tube with Pt electrodes and a Ni-Cr heating coil that was inserted through the ceramic tube to construct a sensor. The sensor was aged at the certain temperature for several days. The sensing responses of aged samples were measured to different concentrations of H_2S (5–100 ppm) using a JF02E gas sensor test system. The operating temperature of the sensor was adjusted by varying the voltage through an electric heating system. The resistance of the sensor in air (R_{air}) and in the air–test gas mixture (R_{gas}) was recorded, respectively. The response for H_2S is defined as the ratio of R_{air}/R_{gas}. The response and recovery times of the sensor were measured as the time for the sensor output to reach 90% of its maximum response after applying and switching off the gas in a step function.

3. Results and discussion

3.1. Structure and morphology of samples

X-ray powder diffraction analysis was carried out to investigate the crystallographic structure of the obtained products, XRD patterns of 0 wt%, 3 wt%, 5 wt% and 7 wt% Cd-doped α-MoO_3 nanobelts annealed at 300 °C were shown in Fig. 1a, respectively. All of the diffraction peaks in Fig. 1a can be exactly indexed to the orthorhombic structure of MoO_3 with lattice constants: a = 3.962 Å, b = 13.858 Å and c = 3.697 Å, which is in good agreement with the literature values (JCPDS 05-0508) [20], and no characteristic peaks of other impurities were observed. Additionally, according to estimation of XRD data, it was found that the positions of (1 1 1) peak of Cd-doped α-MoO_3 samples (Fig. 1b) slightly shift to lower angle compared to the pure α-MoO_3 sample. While the cell volume expansion with Cd doping is due to the ionic radius of Cd^{2+} (0.97 Å) being larger than that of Mo^{6+} (0.65 Å) [18].

Fig. 2a illustrates typical FESEM images of the as-synthesized pure MoO_3. From the overall morphology, one can find that the products consist almost entirely of nanobelts with width of 200–800 nm and length of several micrometers. From Fig. 2b, the morphology of 5 wt% Cd-doped α-MoO_3 nanobelts has almost not changed greatly. In order to further prove the existence of Cd in the doped samples, EDX was used to observe the elemental composition of the doped samples. The peaks of the Mo, Cd and O elements are presented in the spectrum of Fig. 3. The concentration of Cd component is about 5.21 wt% corresponding to Cd doping