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SnO_2 doped MoO_3 nanofibers and their carbon monoxide gas sensing performances

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ABSTRACT

SnO_2 doped MoO_3 nanofibers with an average diameter of 100 nm were synthesized by a wet-chemical method, and sensors were fabricated by screen printing the nanofibers on alumina ceramic substrates. Structural characterizations were carried out using X-ray diffractometer, scanning electron microscope and transmission electron microscope, and chemical state analyses by energy dispersive X-ray spectroscope, X-ray photoelectron spectroscope and Diffuse Reflectance Infrared Fourier Transform Spectroscope. The carbon monoxide (CO) sensing properties were characterized in the temperature range of 200 to 400 °C; comparing with α-MoO_3, both the sensitivity and the selectivity of the SnO_2 doped MoO_3 nanofibers were improved. The chemisorption and the oxidation of CO on the surfaces of the nanofibers are vital to the sensing performance; the addition of SnO_2 to MoO_3 enhanced the chemisorption and the oxidation of CO. The high sensitivity and vigorous repeatability demonstrate that the nanofibers are auspicious as sensitive and reliable chemical sensors.

1. Introduction

Carbon monoxide (CO) is a hazardous gas; it can cause harmful health effects by reducing oxygen delivery to the body's organs, and at high levels, CO can even cause death [1]. Generally, we cannot identify the CO gas in the atmosphere, because it is colorless, odorless and tasteless, thus human beings do not have timely awareness to its presence. For this reason, CO is often mentioned as a “silent killer”. Hence, the early detection of the CO gas is vital for industry and domestic purposes. It has enthused considerable research to develop simple and effective chemical sensors for detecting CO gas [2–4].

To detect CO gas, one can adopt the metal oxide technology based on the conductance variation of an oxide upon contact with the gas. The involved oxides comprise metals, such as Zn, Ti, W, Mo, Ga, Ce, Sn [5–9], and oxides with perovskite structure [10]. The sensitivity of such CO sensors is high, but the selectivity for the targeted gas (i.e. CO) is relatively poor. The electrochemical cell technology is well-developed, leading to highly sensitive CO detectors, but electrochemical sensors display low lifetimes [11,12].

Metal oxide (MO_x) semiconducting nanofibers (NFs) are the most auspicious material systems for conductometric gas sensors. In gas sensing, the one dimensional (1-D) single crystalline nanomaterials are currently of great significance. Their unique morphology can offer a direct pathway for the photogenerated charges, with reduced grain boundaries, resulting in superior charge transport properties [13–15]. Besides, the 1-D nanostructures are ideal for the gas sensing application due to the high surface-to-volume ratio [16,17]. Molybdenum oxide (MoO_3) is an important n-type semiconductor and attracts considerable interests due to its promising physical and chemical properties. As an n-type semiconductor, crystalline α-MoO_3 nanomaterials are good candidate for sensing devices, owing to their low cost, high resistance to corrosion, and environmental friendliness.

Tin oxide (SnO_2) is an n-type semiconductor with a wide band gap (~3.52 eV). It has been demonstrated as a highly sensitive material for the detection of both reducing gases (e.g., CO, CH_4 and H_2) and oxidizing gases (e.g., NO_x) [18–22]. Unfortunately, several problems occur with currently available semiconductor sensors based on SnO_2 and the other single component oxides. Their selectivity is usually poor at the presence of many gases [22,23]. When an inert gas is present in the environment, these commercially available sensors often give an undesired signal. The problem presents challenges that require best design of sensing materials, which involves treating advanced sensing material not only as electronic materials, but also as microstructural and catalytic ones. Therefore, we should consider the composition and microstructure of sensing materials in terms of electronic and chemical activity and reactivity.

Recent studies revealed that the addition of a secondary component in the form of surface additives or dopant can enhance the performance of SnO_2 gas sensor especially in the presence of reducing gases [19,24]. The electrical conductivity of SnO_2 in air can be reduced with the

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addition of MoO_3 by two orders of magnitude, which may be due to the transfer of electrons trapped at oxygen vacancy sites to Mo^{6+} [25]. SnO_2 addition to MoO_3 has also been proposed as an alternative to modify the sensor response towards certain gases, since the presence of Sn atoms on the MoO_3 surface changes its acidic nature [26]. Thus, SnO_2 and MoO_3, as a combined system, have the potential for superior sensitivity and selectivity for CO.

In this work, CO sensors based on SnO_2 doped MoO_3 NFs were fabricated by screen printing on Al_2O_3 substrates, while the NFs with tailored properties were synthesized by a two-step process. The doping of MoO_3 with SnO_2 improved the CO gas sensing activity, showing an impressive 2 times enhancement in sensitivity compared with that of undoped MoO_3. The SnO_2 doped MoO_3 NFs based gas sensors also displayed good selectivity to CO.

2. Experimental

2.1. Synthesis of SnO_2 doped MoO_3 NFs

Molybdenum powder (99.9% Aldrich) and $SnCl_2 \cdot 2H_2O$ (AR, Sinopharm) were used without further purification. The SnO_2 doped MoO_3 NFs were synthesized by a two-step method. Firstly, the pristine α-MoO_3 were prepared using the hydrothermal method [27]. In detail, 2 g of molybdenum powder was slowly added to 20 ml of H_2O_2 (30% AR, Sinopharm) and 15 ml de-ionized H_2O under water-cooling until the clear orange peroxomolybdic acid sol was obtained. The feeding rate of Mo powder should be slow because the reaction of Mo and H_2O_2 is a strong exothermic reaction with the product of $MoO_2(OH)(OOH)$. Then the sol was directly transferred into a Teflon-lined stainless steel autoclave and kept at 190 °C for 36 h. After hydrothermal reaction, the autoclave was left to cool down to room temperature and the precipitate of α-MoO_3 nanobelts (NBs) was filtered, and then rinsed with demineralized water and ethanol three times. Afterwards, the α-MoO_3 samples were dried at 60 °C overnight.

After that, α-MoO_3 samples were further doped with SnO_2 by a wet chemical method. 0.253 g α-MoO_3 was ultrasonically dispersed into 30 ml purified water for 30 min, then 2 ml HCl (AR, Sinopharm) and 0.017 g $SnCl_2 \cdot 2H_2O$ were added to the above solution. After ultrasonic treatment for 20 min and vigorous stirring for 6 h, the resulted precipitate was collected and washed with ethyl alcohol and distilled water. The light blue products were dried at 80 °C under vacuum for 12 h. Finally, the dried product was annealed at 500 °C for 4 h in a chamber furnace to obtain SnO_2 doped MoO_3 nanofibers (NFs). The dopant concentration of SnO_2 is 5 mol%.

2.2. Characterizations of SnO_2 doped MoO_3 NFs

The crystal structure was identified by X-ray diffraction (Philips Diffractometer PW 3050) using Cu Kα radiation ($\lambda = 0.15406$ nm). Field emission scanning electron microscope (SEM, Nova Nano SEM 450) equipped with EDS (EDAX genesis energy-dispersive X-ray spectroscopy) was employed to investigate morphology and the element distribution. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) investigations were conducted using JEOL-2100F electron microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) investigations were carried out with SECALab2200i-XL spectrometer by using an unmonochromated Al Kα (1486.6 eV) X-ray source. Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded by a VERTEX 70-FTIR spectrometer equipped with a SMART collector and a MCT detector.

2.3. Sensor fabrication with SnO_2 doped MoO_3 NFs

Screen printing technique was used to fabricate sensors. Initially, 70 wt% of SnO_2 doped MoO_3 NFs were mixed with 30 wt% of organic vehicle composing of terpineol (CP, Aldrich), diethylene glycol monobutyl ether acetate (98%, Aldrich) and dibutyl phthalate (98.5%, Aldrich). The mixture was then ground in a mortar for 2 h to obtain the printing paste. The paste was screen-printed onto Al_2O_3 substrates, and then calcined at 500 °C for 2 h to obtain thick films (area 14×5 mm^2, thickness ~ 10 μm) composed of SnO_2 doped MoO_3 NFs. Four 2 mm-wide platinum electrodes were screen-printed on the alumina substrate in a similar way, followed with calcination at 850 °C for 2 h in air. The electrodes were separated from each other by a space of ~4 mm, a sensor was thus fabricated.

2.4. Measurements of sensing properties

The sensor resistance was measured by the four-probe method to eliminate the contact resistance of the electrodes on the films, and the data were collected every second automatically using an Agilent B2901A Source Measurement Unit (SMU). A flow system comprising two mass flow controllers (MFC) was used to introduce gases with specified concentrations of CO gas in N_2 gas into the sample chamber at a flow rate of 100 SCCM. A thermocouple was placed near to the sample surface to accurately monitor the sensor temperature. The CO gas concentration was monitored by an Agilent 7890A Gas Chromatography System (GCS).

3. Results and discussion

The X-ray diffraction patterns of pristine α-MoO_3 NBs and SnO_2 doped MoO_3 NFs are shown in Fig. 1. The diffraction peaks are indexed to the orthorhombic MoO_3, with lattice parameters $a = 0.3966$ nm, $b = 1.3858$ nm and $c = 0.3693$ nm. These values are consistent with the standard values of bulk MoO_3 (JCPDS card No. 76-1003); no impurity phase is detected by XRD. The addition of SnO_2 does not change the crystal structure of the orthorhombic MoO_3, demonstrating that Sn is fully incorporated into the MoO_3 lattice.

The low and high magnification SEM images of the α-MoO_3 NBs are displayed in Fig. 2, showing randomly distributed nanobelts. The nanobelts exhibit a wide range of width from 50 to 150 nm. The length of nanobelts is about 1–5 μm. These nanobelts are straight and have rectangular flat tips with four sharp corners at ends.

The low and high magnification SEM images of the SnO_2 doped MoO_3 NFs are shown in Fig. 3(a) and (b). The SnO_2 doped MoO_3 NFs exhibit randomly oriented fibers in the form of nonwoven mats with diameter ranging from 20 to 100 nm and length of 2–8 μm. Fig. 3(c) shows the cross-section of the sensor based on SnO_2 doped MoO_3 NFs.

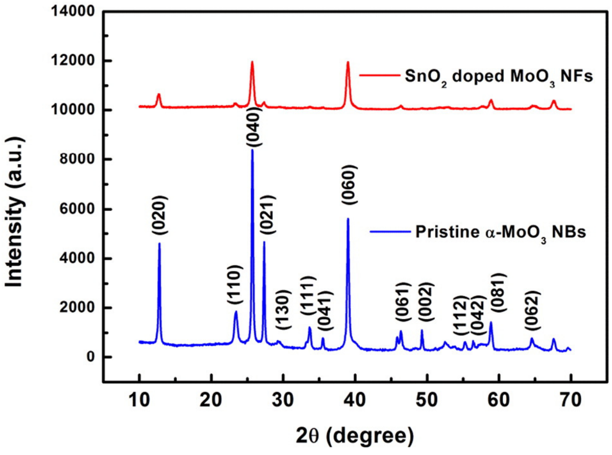

Fig. 1. XRD patterns of pristine α-MoO_3 nanobelts and SnO_2 doped MoO_3 nanofibers.