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Synthesis and characterization of Cr-doped WO_3 nanofibers for conductometric sensors with high xylene sensitivity

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ABSTRACT

In this work, pure and 2, 4, 6 mol% Cr-doped WO_3 nanofibers were successfully synthesized via an electrospinning method. The morphological and microstructural properties of these nanofibers were analyzed by various kinds of techniques. The grain sizes of the WO_3 nanocrystal were greatly decreased by Cr doping. X-ray photoelectron spectroscopy results confirmed the existence of Cr^{3+} and the increased amount of both chemisorbed oxygen and oxygen vacancy after Cr doping. The gas-sensing properties of pure and Cr-doped WO_3 nanofibers were tested at the optimal operating temperatures. The results indicated that among all the samples (0, 2, 4 and 6 mol% Cr-doped WO_3 nanofibers), 4 mol% Cr-doped WO_3 nanofibers showed the highest response towards 100 ppm xylene. At the same time, the sensors based on 4 mol% Cr-doped WO_3 nanofibers also exhibited good repeatability, selectivity and long term stability, which were critical for designing high performance xylene gas sensor. The sensing mechanism of the enhanced gas sensing properties was also discussed. We suggest the increasing oxygen vacancies, surface chemisorbed oxygen species and defects in the lattice created after Cr doping to be the underlying reason for enhancement of charge carrier density and accelerated reactions with xylene.

1. Introduction

In recent years, toxic, corrosive and explosive gases from industrial effluents, agricultural chemicals and fertilizers, such as NO_x, ethanol, benzene, NH_3, are posing serious threats to human health and environmental sustainability [1–3]. Atmospheric environmental monitoring has aroused great concern worldwide. Several reports devoted to gas sensors based on metal oxide semiconductor (MOS) have shown great practical importance in gas sensing mainly because MOS are low-cost, good chemical reliability, real-time monitoring, and possess a Debye length corresponding to the target molecules [4–8]. As the basis of functional materials, including ZnO [9,10], In_2O_3 [11,12], CuO [13,14], SnO_2 [15,16] and NiO [17,18], have been applied in gas sensing due to their tunable chemical and physical properties in the past few decades. Among them, tungsten oxide (WO_3), as a kind of important semiconductor, has been intensively investigated as gas sensors [19,20]. However, how to enhance the gas sensing performance of pure WO_3 material is still a challenge. Recently, many studies have demonstrated that oxide semiconductor composites have importantly practical significance in gas sensing properties compared with pure material. For example, Bao designed the plate-like NiO/WO_3 nanocoposites, which showed excellent sensitivity towards NO_2 [21]. Chu synthesized graphene-WO_3 composites via a hydrothermal method which exhibited a high response to acetaldehyde at a relatively low operating temperature of 100 °C [22]. Wang et al. synthesized Cr-doped WO_3 microspheres for H_2S sensing at a low temperature of 80 °C [23]. The enhancement of sensing performance of material can be attributed to the incorporation of guest metal oxides used as "catalyst" [24,25]. In this work, Cr_2O_3 was introduced to design and synthesis WO_3/Cr_2O_3 composites for high performance gas sensors. Chromium oxide (Cr_2O_3) is a kind of important p-type semiconductor for widely practical application, such as gas sensors [26,27], lithium-ion batteries [28,29] and photocatalysts [30].

Recent investigations have suggested that the sensitivity of chemical sensors mainly depends on the large change of resistance caused by adsorption and desorption of gas molecules on the surface of nanograins [31–34]. Therefore, the nanostructure of sensing material plays an important role in gas sensing performance. It is found that gas sensors based on quasi one-dimensional nanos-

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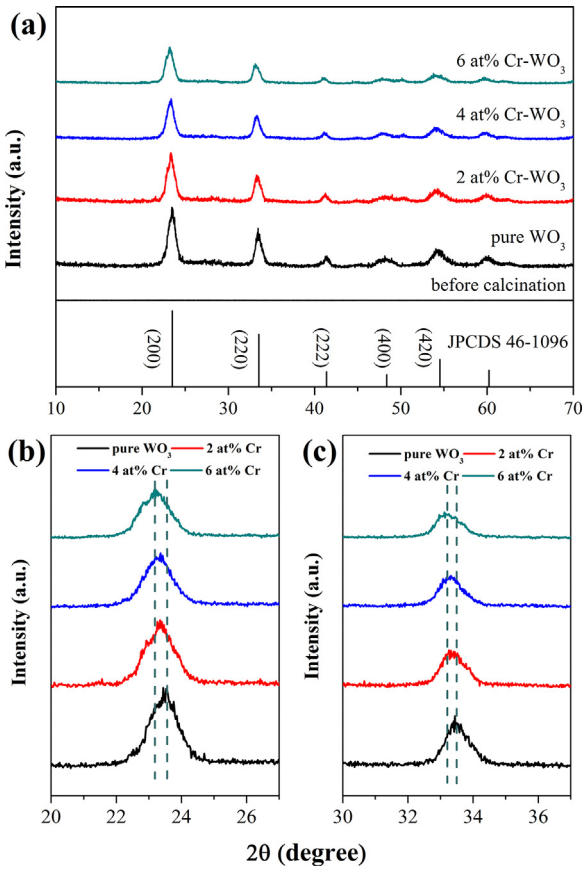

Fig. 1. (a) XRD patterns of WO_3 samples with 0 at%, 2 at%, 4 at% and 6 at% Cr doping; (b) (c) Comparison of (2 0 0) and (2 2 0) peaks from XRD patterns.

tructures, such as nanowires, nanorods, and nanobelts, present interesting advantages because of large surface-to-volume ratios, high loading capacity, surface permeability [35,36] as Kawi et al. demonstrated in the previous articles [37,38]. The unique electrical properties can be attributed to size reduction or quantum confinement because crystal size approximates to the wavelength of the electronic wave-function [39].

In this paper, we successfully prepared a repeatable and stable Cr-doped WO_3 nanofibers by a facile electrospinning route. A contrastive gas-sensing test between the pure WO_3 and Cr-doped WO_3 nanofibers was performed to demonstrate the potential application and the effect of Cr dopants. It was found that the gas sensor based on as-prepared Cr-doped WO_3 semiconductor composites showed improved gas-sensing properties. Especially, when the molar ratio was 4:100, the Cr doping sensors exhibited the highest response of 35.04–100 ppm xylene, and meanwhile had a good selectivity and fast response/recovery speed. The enhanced performance could be attributed to the increase of oxygen vacancies, surface chemisorbed oxygen species and defects in the lattice after Cr doping.

2. Experimental

2.1. Perparation of pure and Cr-doped WO_3 nanofibers

All the chemical reagents used in this work were of analytical grade without further purification. In a typical experiment, tungstic acid (H_2WO_4) and polyving akohol (PVA 1788) were purchased from Aldrich. Chromium acetylacetonate ($C_{15}H_{21}CrO_6$), citric acid ($C_6H_8O_7{\cdot}H_2O$) absolute ethanol (C_2H_5OH) and hydrogen peroxide (H_2O_2) were purchased from Beijing Chemicals Co., Ltd.

The pure and Cr-doped WO_3 composite nanofibers with various doping concentrations of 2, 4 and 6 mol% were synthesized by an electrospinning method. In a typical synthesis process, the electrospinning solution was prepared by dissolving 1.5 g H_2WO_4 in a mixed solution containing 9 ml hydrogen peroxide and 6 ml ethanol. The pH value of solution was adjusted (3–4) using ammonium hydroxide and citric acid and then the solution was under bath sonication for 40 min. After magnetic stirring for 25 min at 80 °C under reflux condensation, PVA (8 wt%) was added to form an appropriate viscous precursor solution for electrospinning. After fully stirring, the solution was loaded into 5 ml plastic syringe attached with a spinneret whose inner diameter was 1.64 mm. The PVA/H_2WO_4 or PVA/H_2WO_4/Cr^{+3} precursor composite nanofibers were deposited on the collector (a flat aluminum foil) with a distance of 20 cm to the needle by applying 20 kV. The feed rate was 1 ml/h by using a syringe pump. To remove organic polymer components, the as synthesized nanofibers were calcined at 500 °C for 2 h in air with a heating ratio (1 °C/min). Then the pure WO_3, 2, 4, 6 mol% Cr-doped WO_3 were obtained and labeled as S1, S2, S3, S4, respectively.

The X-ray diffraction (XRD) patterns were recorded to analyze the crystalline by using a Rigaku TTRIII X-ray diffractometer with Cu K radiation at a wavelength of 1.5406 Å in the range of 10–70° (2θ) at room temperature. Field emission scanning electron microscopy (FESEM) images were obtained with a JEOL JSM-7500F microscope with an acceleration voltage of 5 kV. The energy dispersive X-ray spectroscopy (EDS) spots pattern scanning analysis was carried out by the TEM attachment. Transmission electron microscopic (TEM) and high resolution transmission electron microscopic (HRTEM) images were obtained on a JEOL JEM-3010 transmission electron microscope. X-Ray photoelectron spectroscopy (XPS) data was obtained with a VG ESCALAB MK II spectrometer with an Mg KR excitation (1253.6 eV).

2.2. Fabrication and measurement of gas sensor

Gas sensors were fabricated as follows [40,41]: a small amount of the calcined nanofibers were mixed with the deionized water to form a paste. And then the paste was coated uniformly onto the surface of a ceramic tube by a small brush to form a sensing film with a thickness of about 100 μm between two parallel gold electrodes. After drying under air at room temperature for 30 min, the devices were sintered at 400 °C for 2 h. This process was used to stabilize the microstructure to improve long term stability of sensors [42]. The operating temperature of the gas sensor was tuned from 140 °C up to 360 °C by a heater of Ni-Cr coil which was inserted into the tube. The response of the sample was determined by monitoring the relative variation of resistance ($S = R_{gas}/R_{air}$ for oxidizing gas or $S = R_{air}/R_{gas}$ for reducing gas) with a CGS-8 gas-sensing characterization analyzer under laboratory conditions (30% relative humidity, 25 °C). The sensor was put into a chamber filled with air to get a constant value (R_{air}). Then the sensor was put into a closed chamber with a given amount of the test gas to obtain a constant resistance (R_{gas}). Soon afterward, the sensor was transferred into another chamber also full of air and began to recover. The response time (τ_{res}) is defined as the time to achieved 90% of the total resistance change in the case of adsorption, similarly, the recovery time (τ_{rec}) is defined as the time required to achieve 10% of full recovery to initial baseline value after the gas was removed.

3. Results and discussion

3.1. Structural and morphological characteristics

The crystallization of the samples was investigated by XRD. Fig. 1 displayed the XRD patterns of the synthesized pure and Cr-doped WO_3 nanofibers with different contents of Cr. It could be seen