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Shuttle-like ZnO nano/microrods: Facile synthesis, optical characterization and high formaldehyde sensing properties

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ABSTRACT

Shuttle-like ZnO nano/microrods were successfully synthesized via a low temperature (80 °C), "green" (without any organic solvent or surfactant) and simple hydrothermal process in the solution of zinc chloride and ammonia water. X-ray diffraction and Raman spectroscopy indicated that the ZnO nano/microrods are a well-crystallized hexagonal wurtzite structure. Yet photoluminescence analysis showed that abundant intrinsic defects (52.97% electron donor defects and 45.49% electron acceptor defects) exist on the surface of ZnO crystals. Gas sensors based on the shuttle-like ZnO nano/microrods exhibited high sensitivity, rapid response–recovery and good selectivity to formaldehyde in the range of 10–1000 ppm at an optimum operating temperature of 400 °C. Through applying linear fitting to the plot of sensitivity versus formaldehyde concentration in logarithmic forms, the chemisorbed oxygen species on the ZnO surface were found to be O^{2-} (highly active among O_2, O_2^- and O^- species). Notably, formaldehyde can be easily distinguished from acetaldehyde with a selectivity of about 3. The high formaldehyde sensitivity is mainly attributed to the synergistic effect of abundant electron donor defects (52.97%) and highly active oxidants (surface adsorbed O^{2-} species) co-existed on the surfaces of ZnO.

1. Introduction

As one of the vital wide-band-gap (3.4 eV at 2 K) metal oxide semiconductors (MOS), ZnO has been proven to be a promising gas-sensitive material for detecting both oxidative and reductive target molecules at ppm (parts per million) level and above [1]. Especially, it has been found that the gas-sensing properties (e.g., sensitivity, response–recovery, reproducibility and stability) were substantially improved by reducing the grain size to nanoscale dimensions commonly due to the nano-size effects leading to high density of surface active sites and large surface-to-volume ratios in comparison with their bulk counterparts [2]. Various ZnO nanostructures have been synthesized and utilized as gas sensors, such as nanoparticles [3], nanorods [4], nanowires [5], nanobelts [6], nanoplates [7] and hollow spheres [8]. But regrettably, not a general principle could have been obtained yet for directing the design of efficient MOS nanostructures with high sensitivity and selectivity of a specific target gases mainly because of the complexity of sensing procedures and the lack of deep understanding of the relations between physico-chemical properties of sensitive materials and sensing performances. Based on grain contact and related band structures of MOS powers, Morrison summarized a grain boundary barrier model to explain the gas-sensing principle [9]. Subsequently, Xu and co-workers put forward an empirical model to elucidate how to enhance sensitivity through controlling the grain size of sensing materials [10]. However, the theoretical research on gas-sensing mechanism develops much more slowly than the great progress has been made on experimental results. Recently, several elaborate researches have revealed new discoveries uncovering that some of the physico-chemical properties of MOS nanomaterials determined the sensing performance strongly. For example, highly gas-sensing performance was reported based on 3D porous ZnO architectures, as the gas diffusion and mass transportation were significantly enhanced by their unique structures [11]. Through controlling the morphology of nano/microstructured ZnO crystallites, nanocrystal with more contents of high-energy surfaces exhibited higher gas sensitivity, due to their better chemisorption ability [12]. Gas response of ZnO nanorods was enhanced by introducing more donor- and less acceptor-related intrinsic defects because more oxygen could be adsorbed and ionized on the surface of semiconductor sensing materials [4]. Based on these findings, synthesis of MOS nanostructures with specific spatial configurations, controllably exposed crystal faces and defect structures is the key to enhancing gas sensing performances.

Formaldehyde is an important chemical used most widely by industry to manufacture plastics, medicine, dyes, synthetic fibers, building materials and numerous household products. In view

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of its volatility, irritability and toxicity, exposure to formaldehyde is very harmful to human health. Therefore, detection of formaldehyde in environment is an urgent need with great realistic significance. Although great progress has been made for ZnO nanostructured formaldehyde sensors, the performances, such as sensitivity, response–recovery and selectivity, are still required to be further improved [13,14]. Moreover, for the MOS formaldehyde gas sensors, acetaldehyde is a common interfering gas, which is often difficult to be differentiated from formaldehyde due to their quite similar chemical properties [15–17]. Hence, highly selective formaldehyde gas sensors, especially to acetaldehyde, are of great meaningful in practical application.

In this work, we reported a kind of shuttle-like ZnO nano/microrods which were successfully synthesized by a facile and "green" hydrothermal method under mild conditions through utilizing aqueous solutions of zinc chloride and ammonia water. Crystal structure, defects, surface oxygen species and gas sensing performances of the as-obtained ZnO nano/microrods were mainly studied. Furthermore, the reason of high formaldehyde sensitivity was investigated through photoluminescence analysis and linear fitting the plot of sensitivity versus formaldehyde concentration in logarithmic forms.

2. Experimental

2.1. Preparation and characterization of materials

Shuttle-like ZnO nano/microrods were synthesized via a facile hydrothermal method at low temperatures. In a typical synthesis procedure, 0.5457 g $ZnCl_2$ (0.004 mol) was dissolved in 40 mL deionized water. Then 20 mL 25% ammonia water added dropwise under mild magnetic stirring for 10 min. After that, a 50 mL Teflon-lined stainless steel autoclave was filled with the above solution, sealed and maintained at 90 °C for 16 h. Finally, the white product was washed several times with deionized water and ethanol, and dried at 80 °C for 12 h.

X-ray diffraction (XRD) was conducted on a D8 Advance Bruker X-ray diffractometer with CuKα radiation (λ = 0.15406 nm) operating at 40 kV. Raman-scattering spectrum was measured by a JY LabRam-HR confocal Raman microscope with a backscattering configuration, excited by the 514 nm line of an argon-ion laser at room temperature. Field emission scanning electron microscope (FE-SEM) images were performed on a JEOL JSM-6700F microscope operating at 5 kV. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained on a JEOL JEM-2010 microscope with an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectrum was measured on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer at room temperature. The photoluminescence (PL) measurement was carried out on a Hitachi F-7000 FL Spectrophotometer by a 325 nm excitation from Xe lamp at room temperature.

2.2. Fabrication and measurement of sensors

The shuttle-like ZnO nano/microrods were ground with Triton X-100 in a weight ratio of about 1:1 to form a homogeneous paste. Then, the paste was coated on an alumina ceramic tube on which a pair of gold electrodes was previously printed, followed by sintering at 500 °C for 1 h to remove Triton X-100 and provide good mechanical strength. After that, a Ni–Cr wire was inserted into the tube to assemble a side-heated gas sensor. The structure and photograph of an as-fabricated sensor are shown in Fig. 1(a) and inset in Fig. 1(b), respectively.

The gas-sensing properties were measured using a HW-30A gas sensitivity instrument (Hanwei Electronics Co. Ltd., PR China). The measurement followed a stationary state process: a given amount of target gas was injected into a glass chamber and fully mixed with air. In the measuring electric circuit (Fig. 1(b)), a load resistor (R_L: 47 kΩ) was connected in series with a gas sensor. The circuit voltage (V_c) was 5 V, and output voltage (V_{out}) was the terminal voltage of the load resistor. The working temperature of the sensor was adjusted by changing the heating voltage (V_h). The sensor resistance in air or a target gas was measured by monitoring V_{out}. Through measuring V_{out}, the sensor resistance (R_S) can be calculated according to formula (1):

$$R_S = \frac{(V_c - V_{out})}{V_{out}} \times R_L \quad (1)$$

For reducing and oxidizing gases, the sensitivity (S) is defined by formulas (2) and (3), where R_a and R_g are the resistances of the gas sensor in air and target gases, respectively.

$$S = \frac{R_a}{R_g} \quad (2)$$

$$S = \frac{R_g}{R_a} \quad (3)$$

Selectivity of formaldehyde to the other gases (K) is defined by formula (4), where S_{ig} is the sensitivity of the sensor to a certain interfering gas.

$$K = \frac{S}{S_{ig}} \quad (4)$$

Here, the response or recovery time is defined as the time taken for the sensor to achieve 90% of its final equilibrium resistance in the case of adsorption or desorption.

3. Results and discussion

3.1. Structure and morphology characteristics

The structure of the ZnO samples was first characterized by XRD as shown in Fig. 2(a). All reflection peaks of the XRD pattern can be indexed to hexagonal wurtzite ZnO (JCPDS card no. 36-1451), indicating high purity and crystallinity of the as-synthesized products.

Room temperature micro-Raman spectrum was measured to further confirm the crystallinity and structure as shown in Fig. 2(b). The peaks at 330 and 437 cm^{-1} are attributed to the second-order Raman spectrum arising from the zone-boundary phonons $3E_{2H} - E_{2L}$ and E_{2H} mode of ZnO crystal [6], respectively. Thereinto, the strong peak at 437 cm^{-1} corresponds to the band characteristic for the hexagonal wurtzite ZnO, indicating the high crystallinity of the products [18]. The peak at 579 cm^{-1} is assigned to the E_1 (LO) mode, which is caused by the defects such as oxygen vacancies (V_O) and zinc interstitials (Zn_i) [18]. It is reported that the gas response could be enhanced remarkably by introducing more electron donors (V_O and Zn_i) because more adsorbed oxygen would be ionized on the surface of gas sensing materials [4]. As for the peak at 383 cm^{-1}, it corresponds to the A_1 (TO) mode.

The morphology of the as-formed ZnO was characterized by FE-SEM. Fig. 3(a) shows the panorama of the ZnO crystals, which consists of shuttle-like nano/microrods with two sharp tips and six symmetrically grown smooth surfaces. The shuttle-like ZnO nano/microrods exhibit a length of 5–10 μm and a width of 1–2.5 μm in the middle section, respectively.

Detailed morphology and structure analysis of ZnO rods was carried out using TEM and SAED. TEM image (Fig. 3(b)) of a single ZnO nano/microrod further presents the shuttle-like profile. High-resolution TEM (HRTEM) image (Fig. 3(c)) displays resolved fringes separated by 0.260 nm corresponding to the (0 0 0 2) lattice planes of hexagonal ZnO. SAED pattern was recorded by focusing the election beam along the [1 $\bar{1}$ 0 0] axis to further determine the