Sensors and Actuators B 160 (2011) 364–370

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

High sensitive and selective formaldehyde sensors based on nanoparticle-assembled ZnO micro-octahedrons synthesized by homogeneous precipitation method

Lexi Zhang[a,b], Jianghong Zhao[a,*], Haiqiang Lu[a,b], Liming Gong[a,b], Li Li[a], Jianfeng Zheng[a], Hui Li[a,b], Zhenping Zhu[a,*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taoyuan South Road 27, Taiyuan 030001, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

ARTICLE INFO

Article history:
Received 31 May 2011
Received in revised form 18 July 2011
Accepted 28 July 2011
Available online 4 August 2011

Keywords:
Homogeneous precipitation
ZnO micro-octahedron
Gas sensor
Formaldehyde
Defect
Oxygen species

ABSTRACT

Nanoparticle-assembled ZnO micro-octahedrons were synthesized by a facile homogeneous precipitation method. The ZnO micro-octahedrons are hexagonal wurtzite with high crystallinity. Abundant structure defects were confirmed on ZnO surface by photoluminescence. Gas sensors based on the ZnO micro-octahedrons exhibited high response, selectivity and stability to 1–1000 ppm formaldehyde at 400 °C. Especially, even 1 ppm formaldehyde could be detected with high response (S = 22.7). It is of interest to point out that formaldehyde could be easily distinguished from ethanol or acetaldehyde with a selectivity of about 3. The high formaldehyde response is mainly attributed to the synergistic effect of high contents of electron donor defects (Zn_i and V_O) and highly active oxygen species (O^{2-}) on the ZnO surface.

1. Introduction

Metal oxide semiconductor (MOS) gas sensors, including SnO_2, ZnO, In_2O_3, WO_3, and so on, have attracted considerable attention owing to their ability of detecting trace gases [1]. As one of the key wide bandgap (~3.4 eV at 1.2 K) [2] semiconductors, ZnO has been proved to be an excellent gas-sensing material for measuring both oxidative and reductive target gases at ppm (parts per million) level and above [3]. Taking advantages of the small size, large surface-to-volume ratios and high density of surface active sites compared to their bulk counterparts, great interest has been focused on performance-enhanced gas sensors based on ZnO nanostructures, such as nanoparticles [4], nanorods [5], nanobelts [6], nanotubes [7] and nanosheets [8]. Recently, hierarchical structures constructed by low-dimensional nanomaterials, for example, nanoparticle-organized hollow spheres [9], nanorod-combined flower-like structures [10], nanosheet-assembled 3D architectures [11,12], have began to catch much of researchers' attention, because they exhibited enhanced gas-sensing performances which originated from the improvement in exposing more available surface, facilitating gas diffusion and transportation, and so forth. However, great efforts are still needed to further develop their synthesis processes, since hard templates, surfactants or relative high temperature is usually necessary for fabricating these hierarchical structures. Accordingly, it is significantly important to develop template-free, facile and low temperature methods to synthesize novel hierarchical nanostructures, and to carry out in-depth research on their gas sensing properties. Compared with other methods, homogeneous precipitation is a more economic (no need for special apparatus) and environment-friendly (no need for surfactants or organic solvents) method to prepare metal oxides for sensor applications [13] in large scale at low temperature. In spite of its advantages in preparation, based on this method, it is usually difficult to controlled synthesize metal oxide nanostructures [14] (except for nanoparticles), to say nothing of nano-building block assembled hierarchical architectures.

As an important industrial chemical, formaldehyde has been widely used to manufacture plastics, medicine, synthetic fibers and household products. Regrettably, formaldehyde is very harmful to human health because of its volatility, irritability and toxicity, thus is considered as one of the main indoor air pollutants in residential and industrial occupational environments. It is of great practical importance to detect formaldehyde rapidly and accurately in the atmosphere. Till now, significant progress has been

* Corresponding authors. Tel.: +86 351 4048715; fax: +86 351 4041153.
E-mail addresses: zjh_sx@sxicc.ac.cn (J. Zhao), zpzhu@sxicc.ac.cn (Z. Zhu).

0925-4005/$ – see front matter
doi:10.1016/j.snb.2011.07.062

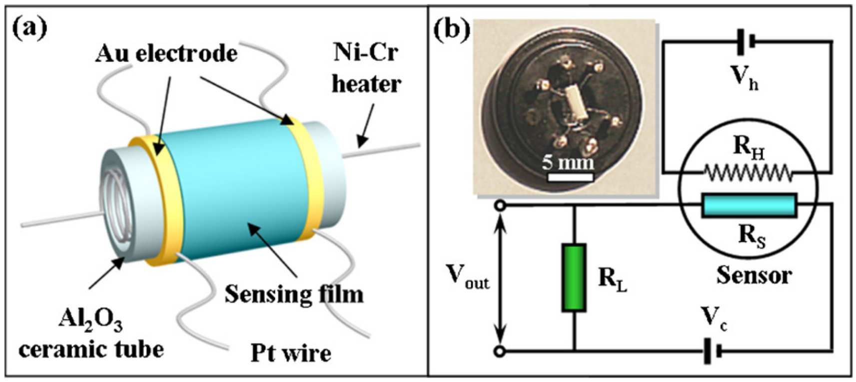

Fig. 1. (a) Scheme of the gas sensor structure. (b) The measuring electric circuit. Inset: photograph of a sensor.

made to formaldehyde sensors based on ZnO nanostructures; however, their gas-sensing performance is still required to be further improved in sensitivity, especially in selectivity. This is because for the practical MOS formaldehyde gas sensors, acetaldehyde is a common interfering gas [15], and formaldehyde is usually difficult to be distinguished from ethanol especially in indoor air detection [16]. Hence, highly selective formaldehyde gas sensors, in particular, to acetaldehyde and ethanol, are of great meanings in practical application.

In this work, ZnO micro-octahedrons assembled by nanoparticles were successfully synthesized through a facile homogeneous precipitation method. Their structure, morphology, surface defects and chemisorbed oxygen were investigated. Gas sensors using ZnO micro-octahedrons were tested and represented excellent formaldehyde sensing properties. Furthermore, the reason of high formaldehyde selectivity and response was also demonstrated.

2. Experimental

2.1. Preparation and characterization of materials

All the chemicals are analytical grade reagents and used as received without further purification. In a typical synthesis, 0.2195 g $Zn(CH_3COO)_2 \cdot H_2O$ was dissolved in 20 mL deionized water under magnetic stirring. Then aqueous ammonia (25–28 wt.%) was added until the pH value was adjusted to 10. After another 2 h stirring, the white precipitation was filtered, washed with deionized water, dried at 80 °C for 12 h and finally calcinated at 500 °C for 1 h.

Powder X-ray diffraction (XRD) was recorded on a D8 Advance Bruker X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) operating at 40 kV. Raman spectrum was performed 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 carried out 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 spectrum was measured on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer at room temperature. Photoluminescence (PL) was measured on a Hitachi F-7000 FL spectrophotometer by a 325 nm excitation from Xe lamp at room temperature. X-ray photoelectron spectrometry (XPS) was carried out using Al Kα ($h\nu$ = 1486.6 eV) X-ray beams as the excitation source. Binding energies were calibrated relative to the C1s peak at 284.6 eV.

2.2. Fabrication and measurement of sensors

The ZnO sample was ground with Triton X-100 in a weight ratio of 1:1 to obtain a fine paste. The paste was coated onto an alumina ceramic tube, on which a pair of gold electrodes was previously installed at each end, followed by sintering at 500 °C for 1 h to remove the organic binder and provide good mechanical strength. Then, a Ni–Cr wire was inserted into the tube and used as a heater. The structural diagram and photograph of a sensor are shown in Fig. 1(a) and inset of Fig. 1(b), respectively.

The gas-sensing properties were measured using a HW-30A gas sensitivity instrument (Hanwei Electronics Co. Ltd., PR China). The gas concentration was determined by 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

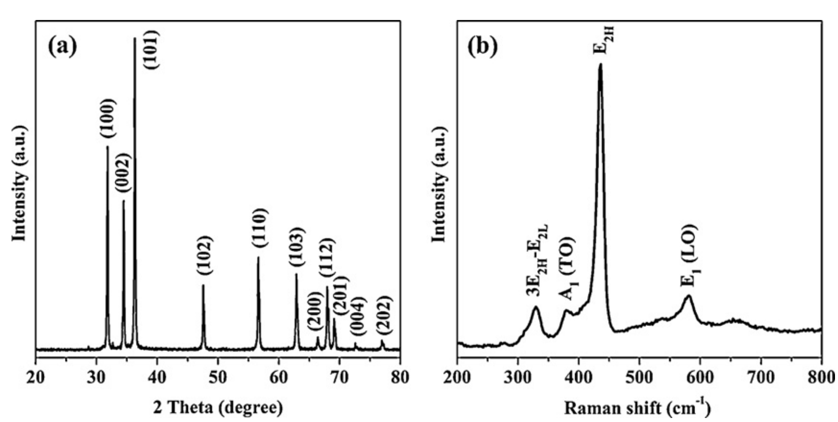

Fig. 2. XRD pattern (a) and Raman spectrum (b) of ZnO products.