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Zinc oxide hollow micro spheres and nano rods: Synthesis and applications in gas sensor

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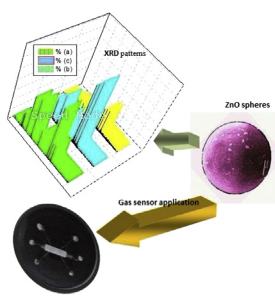
HIGHLIGHTS

- Zinc oxide spheres were prepared by using solvothermal method.
- Detailed description of the morphology of microspheres assembled by nano rods.
- Formation mechanism of zinc oxide spheres assembled by nano rods.
- Zinc oxide spheres and nano rods displayed very good gas sensing ability.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc oxide nano rods and micro hollow spheres are successfully fabricated by adopting a simple solvothermal approach without employing any surfactant/template by keeping heating time as variable. The prepared products are characterized by using different instruments such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In order to investigate the morphological dependence on the reaction time, analogous experiments with various reaction times are carried out. Depending upon heating time, different morphological forms have been identified such as hollow microsphere (4 μm to 5 μm) and nano rods with an average diameter of approximately 100 nm. The fabricated materials are also tested for ethanol gas sensor applications and zinc oxide hollow microsphere proven to be an efficient gas sensing materials. Nitrogen adsorption–desorption measurement was performed to understand better performance of zinc oxide micro hollow spheres as effective ethanol gas sensing material.

1. Introduction

Zinc oxide (ZnO) micro/sub micro sized spheres are versatile and technologically attention grabbing materials owing to their unique physical, acoustic, and electronic properties [1]. All these properties and controlled morphology as well as dimensionality have made it significant material for the applications in the field of room-temperature UV lasers, light-emitting diodes (LED), field-effect transistors, solar cells, sensors, and optoelectronics [2]. Their definite structures and distinctive properties, core/shell structured materials, together with their hollow structures have attained considerable attention in physics, chemistry, and materials

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science [3]. Zinc oxide (ZnO) is an eco-friendly semiconductor which has a sustainable growth into the wide range of nano and micro structures (e.g., Rods, wires, belts, spheres, etc.) [4].

To develop ZnO micro spheres and nano rods, various synthetic strategies have been explored including vapor–liquid–solid (VLS) growth, chemical vapor deposition, and electrochemical deposition but these methods require rigorous conditions or a catalyst for growth [5]. The solution phase method has numerous merits which includes growth of ZnO nano materials at low temperature [6].

Hollow-shell microspheres have potential to accomplish both high response and kinetics due to their high surface areas and reduced agglomerated configurations [7]. A number of hollow-structured materials including silica, Co_3O_4, Fe_3O_4, and CuS, have been engineered by utilizing sacrificial templates. Hollow ZnO structures have also been synthesized by using different methods. The use of a template results in high cost, low yield and a time-consuming synthesis process. All of these aspects strongly suggest that template-directed approach is not appropriate for large-scale preparations [8,9]. The main purpose of this research is to develop a simple and straightforward approach that leads to the formation of hollow spheres without the involvement of any surfactant to avoid the complexity interrelated with template removal and to make it economically beneficial for the use of bulk scale applications [10].

The high surface areas of nano and micro structured materials are also valuable for chemical sensing [11,12]. Chemical sensors are extensively used for engineering process control and security applications such as smoke detectors [13]. Zinc oxide at micro and nano scale, especially hollow spheres and rods have gained much attention in the field of gas sensing due to their controlled morphology, unique properties and large surface area [14].

The prime objective of proposed study is to analyze the synthesis of zinc oxide without using any template or surfactant. This article presents the synthesis of zinc oxide micro spheres and nano rods, the effect of reaction time on the morphology, formation mechanism and their applications in ethanol gas sensors.

2. Experimental section

2.1. Materials

Diethylene glycol (DEG), deionized water, Zinc acetate (Zn $(CH_3COO)_2.2H_2O$) as zinc source. The chemicals used in the fabrication process were purchased commercially and used without any further purification.

2.2. Synthesis

The zinc oxide precursors are prepared as follows; 7 mmol of zinc acetate dihaydrate (Zn $(CH_3COO)_2\cdot 2H_2O$) was dissolved in 25 ml of deionized water under vigorous magnetic stirring for 10 min followed by the addition of 55 ml of DEG. The mixture was ultrasonicated for half an hour to disperse the contents into solvent completely. A Teflon lined stainless steel autoclave was pierced with argon gas for 30 min and as prepared mixture was charged into that autoclave of 100 ml capacity. The autoclave was maintained at 150 °C for varied time intervals ranging from 12 to 48 h. After specific time spans, the autoclave was allowed to cool down at room temperature naturally. White precipitates of zinc oxide were collected by centrifugation at the rate of 3000 rpm. The collected precipitates were washed several times with deionized water and absolute alcohol, dried in vacuum at 60 °C for 10 h. The samples are further subjected to characterization by means of different instruments in order to investigate their morphology and applications.

2.3. Structure characterization

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/max Ultima III X-ray diffractometer with a Cu-Kα radiation source ($\lambda = 0.15406$ nm) operated at 40 kV and 150 mA at a scanning step of 0.02° in the 2θ range 10–80°. Scanning electron microscopy (SEM) observation was performed on a JEOL JSM-6480A scanning electron microscope. Transmission electron microscopy (TEM) observation was performed on an FEI Tecnai G^2 S-Twin transmission electron microscope (TEM) with an accelerating voltage of 200 kV.

2.4. Gas response test

To form gas sensors, ZnO powder was dispersed in ethanol to form slurry that was coated onto alumina tube with a diameter of 1 mm and a length of 4 mm, a film of ZnO with 50 mm thickness was developed on the tubes. One pair of gold electrodes and four platinum wires were fixed on both ends of the tube. Afterwards, a Ni–Cr alloy coil through the tube was utilized to heat the ZnO sensitive film. The gas-response test procedure was performed at 25 °C. The electrical response of the sensor was measured with an automatic test system controlled by a personal computer (PC). Ethanol was employed as an example, and introduced into the testing box by a micro-syringe [15]. The total voltage of the test circuit was 5 V and the operating temperature was 320 °C. Then, the sensor response of the sample was obtained by calculations. The internal structure of the gas sensor of ZnO and schematic diagram are given in Fig. 1.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The powder X-ray diffraction (XRD) patterns of as-prepared products are shown in Fig. 2. All diffraction peaks are indexed to wurtzite-structured (hexagonal) ZnO (JCPDS No. 75-0576). No extra peaks were observed in the XRD patterns, which validate the excellent purity of the product and non-existence of impurity phases.

The strong and sharp diffraction peaks demonstrate that the products are well crystallized. Fig. 2 depicts the XRD pattern for the products prepared at different heating times. The first pattern (black color) shows that peak at 31.7, 34.4, and 36.2 are indexed to (100), (002) and (101) respectively. Pattern 2 and pattern 3 showed

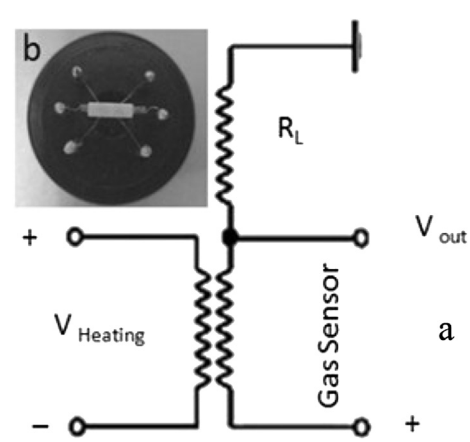

Fig. 1. (a) Internal structure of the gas sensor of ZnO (b) Electrical schematics of gas-response test system.