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# Methanal and xylene sensors based on ZnO nanoparticles and nanorods prepared by room-temperature solid-state chemical reaction

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ABSTRACT

Easy synthesis of ZnO nanoparticles and nanorods were executed by solid-state chemical reaction between $ZnCl_2$ and NaOH under ambient condition. The methanal (HCHO) and xylene ($C_6H_4(CH_3)_2$) sensing characteristics of as-prepared ZnO products were investigated. The ZnO products exhibited good HCHO and $C_6H_4(CH_3)_2$ sensing properties at relatively low working temperature, which can be regarded as excellent potential candidates for HCHO and $C_6H_4(CH_3)_2$ sensors.



## 1. Introduction

Chemical sensors have attracted considerable attention owing to their application in public safety, emission detection, environment monitoring and chemical process controlling, which are coming into effect to reduce the emission and discharge of hazardous pollutants. Among the solid-state chemical sensors, gas sensors have widely been investigated and applied to detect harmful gases in pollutants for a long time. Semiconductor metal oxide sensors are the most promising due to simplicity in device structure, low fabrication cost, robustness in practical applications, and adaptability to a wide variety of toxic and inflammable gases [1–4].

Zinc oxide is an interesting chemically and thermally stable n-type semiconductor with high sensitivity to combustible and reducing gases. Various types of ZnO-based gas sensors, such as thick films [5], thin films [6], nanoparticles [7], nanoparticulate thin films [8], have been reported. Recent studies on ZnO gas sensors have been focused on the one-dimensional (1D) nanostructures in respect that it may be promised for highly sensitive gas sensors [9–12]. The fabrication of 1D ZnO nanostructures using various methods has been reported [13–15]. However, these reported preparation methods may involve complicated process control, high reaction temperature, and long synthesis time. Therefore, it is still desirable to obtain ZnO nanostructures in simple and highly efficient ways. Simultaneously, it is very necessary for 1D sensing materials to be applied to detection of more and more noxious pollutants that badly hurt our health, for example, HCHO and $C_6H_4(CH_3)_2$, which are released from the materials of building fitments.

The introduction of solid-state chemical reaction technique has provided a relatively simple and powerful method for controlling the size, shape and dimension of nanoparticles. It has been explored to achieve nanoparticles and hollow nanostructures in our laboratory [16–18]. The easy low-cost method provides a new technological route to fabricate gas sensor materials. In this paper, we report the synthesis of ZnO nanoparticles and nanorods via simple solid-state chemical reaction technique using a simple synthetic process under mild conditions, which has the advantages of short time, high yield, low cost and low power consumption. The gas-sensing properties of the ZnO nanoparticles and nanorods to HCHO and $C_6H_4(CH_3)_2$ have also been investigated.

## 2. Experimental

### 2.1. Synthesis

ZnO nanomaterials were synthesized using solid-state chemical reaction methods. All the reagents were analytically pure from commercial sources and used without further purification. Typical synthesis for ZnO nanoparticles and nanorods were as follows:

(a) ZnO nanoparticles-0

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Solid $ZnCl_2$ and NaOH with a molar ratio of 1:2 were apart weighed and ground in an agate mortar for about 5 min to ensure the evenness of starting materials, then mixed. The reaction started as soon as the reactants get in touch with each other, accompanied with the release of heat and evaporation of water vapor, and finished in a very short time less than 10 s. The color of mixture changed fleetly from white to yellow within 3 s and subsequently turned into white after 10 s. The color change from white to yellow indicated the generation of ZnO according to the physical property of ZnO that ZnO was yellow under heating condition. Finally, the mixture was washed with distilled water for a certain time to remove NaCl. The product was dried in air, and then ZnO nanoparticles were successfully obtained and named as nanoparticles-0. The reaction process can be described as follows:

$$ZnCl_2 + NaOH \rightarrow Zn(OH)_2 + NaCl \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO(nanoparticles) + H_2O \quad (2)$$

(b) ZnO nanorods-1

Solid $ZnCl_2$ was first ground and blended with an appreciable proportion of polyethylene glycol 600 (PEG 600) (about 3 mL PEG 600 for 10 mmol $ZnCl_2$) and deposited for 10 min, then NaOH powder was added at a 1:2 molar ratio between $ZnCl_2$ and NaOH. The mixture was ground for about 30 min to ensure the completeness of reaction. Compared with the synthetic reaction of nanoparticles-0, the speed of solid-state reaction obviously slowed down. Then the mixture was washed with distilled water and alcohol for a certain time to remove NaCl and PEG 600. The product was dried in air, and then ZnO nanorods was successfully synthesized and named as nanorods-1. The reaction process can be described as follows:

$$ZnCl_2 + NaOH \rightarrow Zn(OH)_2 + NaCl \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO(nanoparticles) + H_2O \quad (2)$$

$$ZnO(nanoparticles) \rightarrow ZnO(nanorods) \quad (3)$$

(c) ZnO nanorods-2

$ZnCl_2$ and $Na_2WO_4{\cdot}2H_2O$ were apart weighed at a molar ratio of 1:2 and ground in an agate mortar for about 5 min, then mixed and ground for 30 min. The phenomenon of deliquescence which was a typical feature of solid-state chemical reaction was obviously observed in the reaction process. Subsequently, the mixture was blended with an appreciable proportion of PEG 600 (about 3 mL PEG 600 for 10 mmol $ZnCl_2$) and deposited for 10 min, and then NaOH powder was added at a 1:2 molar ratio between $ZnCl_2$ and NaOH. The mixture was ground for about 30 min to ensure the completeness of reaction, then washed with distilled water and alcohol for a certain time to remove NaCl, $Na_2WO_4$ and PEG 600. The product was dried in air, and then ZnO nanorods was successfully fabricated and named as nanorods-2. The reaction process can be described as follows:

$$Na_2WO_4 + ZnCl_2 \rightarrow ZnWO_4 + NaCl \quad (1')$$

$$ZnWO_4 + NaOH \rightarrow Zn(OH)_2 + Na_2WO_4 \quad (2')$$

$$Zn(OH)_2 \rightarrow ZnO(nanoparticles) + H_2O \quad (3')$$

$$ZnO(nanoparticles) \rightarrow ZnO(nanorods) \quad (4')$$

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a MAC Science MXP18AHF X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 1.54056 Å). Energy disperse X-ray spectrum (EDS) was examined on an Oxford 2000 energy disperse X-ray spectroscope. Transmission electron microscopic (TEM) images were obtained on a Hitachi H-600 transmission electron microscope. High-resolution transmission electron microscopic (HRTEM) images and the selected area electron diffraction (SAED) patterns were obtained by a JEOL-2010 high-resolution transmission electron microscope. Scanning electron microscopic (SEM) images were obtained on a LEO1430VP scanning electron microscope.

### 2.3. Measurements of gas-sensing properties

Gas sensors were made in a conventional way [19,20]. The solid products were dispersed in terpineol which was used as a binder to form pastes. An alumina ceramic tube, which was assembled with platinum wire electrodes for electrical contacts, was dipped into the paste several times to form the gas-sensing films. Then the elements were annealed at 600 °C for 1 h to evaporate the terpineol. Finally, the alumina tube obtained with a Ni–Cr heater fixed inside was welded onto a bakelite substrate. To improve the stability and repeatability, the sensors were aged at 300 °C for 7 days in air prior to use. The test was operated in a glass test chamber using a gas-sensing measuring system of HW-30A (Hanwei Electronics Co. Ltd., PR China).

Response of a sensor was defined as follows:

$$\text{Response} = \frac{R_{air}}{R_{gas}}$$

$R_{air}$ is the resistance of the sensor in air, and $R_{gas}$ is that in a mixture of testing gases and air. Response time was defined as the time required for the conductance to reach 90% of the equilibrium value after a test gas was injected, which recovery time was the time necessary for a sensor to attain a conductance 10% above its original value in air.

## 3. Results and discussion

### 3.1. Structure of the products

Fig. 1 shows the XRD patterns of the products prepared by the solid-state chemical reaction of $ZnCl_2$ and NaOH. It can be seen that all of the diffraction peaks can be indexed as ZnO with a hexagonal phase (JCPDF Card File No. 36-1451). The EDS result of as-synthesized ZnO revealed the presence of Zn and O at an atomic ratio of 1:1.08 (see supporting information S1). Based on the results,

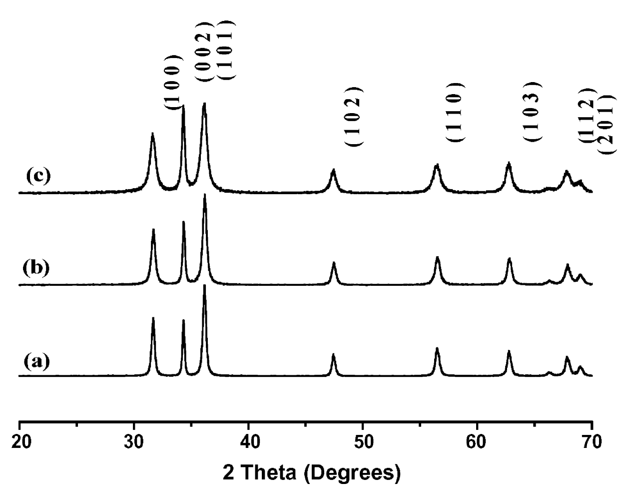


**Fig. 1.** XRD patterns of ZnO products of (a) nanoparticles-0, (b) nanorods-1 and (c) nanorods-2.