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A selective NH_3 gas sensor based on Fe_2O_3–ZnO nanocomposites at room temperature

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Abstract

Gas sensors based on the Fe_2O_3–ZnO nanocomposites with different compositions of Fe:Zn was prepared by a sol–gel and spin-coating method. Morphology of the Fe_2O_3–ZnO nanocomposites was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD, D/max-rA) and energy dispersive X-ray analysis (EDX). The results of electrical and sensing measurement indicated that the sensor with Fe:Zn = 2% exhibited fairly excellent sensitivity and selectivity to NH_3 at room temperature. The response and recovery time of the sensor were both less than 20 s. Finally, the mechanism for the improvement in the gas sensing properties was discussed.
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Keywords: ZnO nanoparticles; Fe_2O_3; Gas sensor; NH_3

1. Introduction

Since many decades, the world awareness about environmental problems and human safety is increasing with the technological development. Therefore, sensors are required for many applications. Recently, the need to detect low ammonia concentrations has greatly increased in many fields of technological importance, such as food technology, chemical engineering, medical diagnosis, environmental protection, monitoring of car interiors and industrial processes.

Seiyama et al. proposed the gas sensors based on ZnO thin films for the first time [1]. ZnO is sensitive to many gases of interest, such as trimethylamine (TMA) [2–4], H_2 [5], oxygen [6–8], H_2O [9,10], ethanol [11] and NH_3 [12], etc. It also has a rapid response with a possibility of miniaturization. However, it has some drawbacks, such as high working temperature, normally between 400 and 500 °C, poor gas selectivity and relatively low gas sensitivity [13].

To overcome these disadvantages, considerable research and development are underway. There are various techniques to modify the sensing properties of the gas sensors. One critical approach is to modify the metal oxide surface by using noble metals (Au, Pt or Pd) [14,15] or rare earth metals (La, Y and Ce) [16,17]. ZnO(n)/CuO(p) heterocontact configuration also showed some possibility of improving the selectivity [18]. Nanto et al. have reported that a sensor based on a ZnO thin film doped with Al, In or Ga could detect the ammonia gas whose concentration was as low as 1 ppm [12]. But the working temperature was as high as 350 °C. Recently, Ivanovskaya et al. suggested that a sensor based on α-Fe_2O_3/In_2O_3 nanocomposites exhibited high sensitivity to NO_2 [19].

The present work was undertaken to investigate the gas sensing behavior of ZnO nanoparticle thin films doped with α-Fe_2O_3 nanoparticles prepared by a sol–gel and spin-coating method. Morphological, structural and sensing properties at room temperature were studied. The ultimate objective of this study is to improve the gas selectivity and sensitivity of the nano-sized ZnO-based sensors at room temperature.

2. Experimental

ZnO nanoparticles doped with α-Fe_2O_3 nanoparticles were prepared in a similar manner to the literature procedure [20]. The α-Fe_2O_3 nanoparticles were synthesized by a hydrothermal method [21]. Some of the α-Fe_2O_3 nanoparticles were ultrasonically dispersed into methanol (200 ml) at about 60 °C. Subsequently, 0.01 M $Zn(Ac)_2$ was dissolved into the above solution. Then, a 0.03 M solution of KOH (65 ml) in methanol

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was added dropwise. The reaction mixture was stirred for 2 h. The resulting solution was concentrated by the evaporation of the solvent. The resulting white product was centrifugalized, washed with deionized water and ethanol to remove the ions possibly remaining in the final product. The ZnO nanoparticles doped with α-Fe_2O_3 nanoparticles with different compositions (molar ratio) of Fe:Zn being 0, 1, 2, 3 and 4% were prepared. Finally, five ZnO nanoparticle solutions were obtained, labeled as sample 0, 1, 2, 3 and 4, respectively. The obtained samples were characterized by transmission electron microscopy (TEM), which was performed with a JEM 200 CX microscope operated at 160 kV. For X-ray diffraction (XRD) (D/max-rA) and energy dispersive X-ray analysis (EDX) (Phoenix) measurement, powder samples were used, which were prepared by annealing the final precipitates at 200 °C for 3 h.

Interdigitated Au electrodes were obtained by metal deposition on glass substrates. The final precipitate was redispersible in ethanol. The Fe_2O_3–ZnO nanocomposite films were fabricated on the top of the Au electrodes by spin-coating, followed by annealing at 200 °C for 3 h before electrical and sensing measurement. Gas sensing behavior of the ZnO nanosensors was measured at room temperature by using the Keithley 236 Source Measure Unit. The chamber was purged with N_2 until a steady baseline of the sensor resistance was reached. Then, the test vapor was injected at a fixed concentration of 0.4 ppm in N_2. In general, the dc voltage was fixed at 10 V, and the changes of current with time were recorded. The sensor response is given here as the current ratio I_g/I_a, where I_g and I_a are the current across the sensor in the test gas and in air, respectively [22,23]. The response-recovery time of the sensor is defined as the time needed to reach 90% of the original resistance.

3. Results

3.1. Morphology of Fe_2O_3–ZnO nanocomposites

Fig. 1 shows TEM images of the Fe_2O_3–ZnO nanocomposites with different compositions of Fe:Zn. Morphology of the pure α-Fe_2O_3 prepared by a hydrothermal method was nanoparticles (Fig. 1a). Size of the nanoparticles was about 10 nm. When 1% Fe_2O_3 (molar ratio) nanoparticles (sample 1) were doped into the ZnO nanoparticles, the morphology of the resulting sample was similar to that of the pure α-Fe_2O_3 (Fig. 1b). It is obvious that the prepared nanoparticles were crystalline

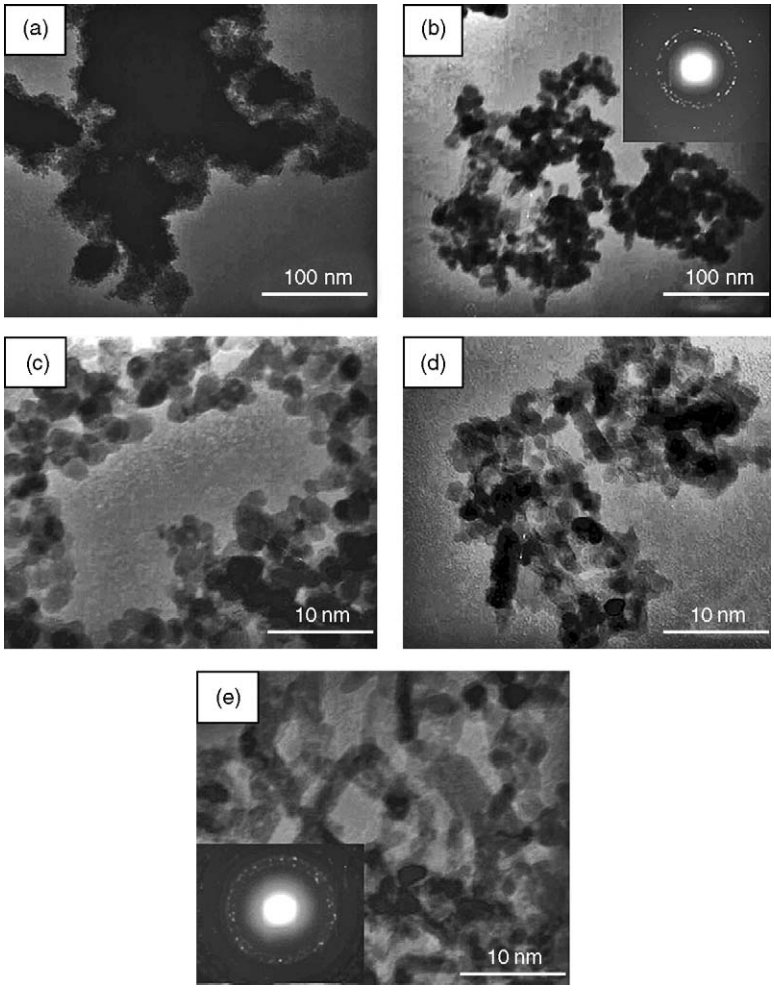

Fig. 1. TEM images of the ZnO–Fe_2O_3 nanocomposites with different compositions (molar ratios) of Fe:Zn: (a) pure α-Fe_2O_3 nanoparticles; (b) sample 1, inset is the selected area electron diffraction (SAED) pattern of the particles; (c) sample 2; (d) sample 3; (e) sample 4, inset is the SAED pattern of the nanorods.

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