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Synthesis of flower-like ZnO microstructures for gas sensor applications

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In the present work, flower-like ZnO microstructures were used for solid state gas sensor applications. Well-dispersed flower-like ZnO microstructures were synthesized by hydrothermal method. The size of flower-like ZnO microstructures was about 5–7 μm in radius and they were made up of dozen of ZnO nanorods building block units. Gas sensing device was prepared by thick film technology and tested primarily for NO_2 gas at different testing temperatures as well as concentrations. Response increased with gas concentration as well as temperature (except 400 °C). Further, it showed response for 10 ppm of NO_2 gas at room temperature. The response for NO_2 was higher than the CO, ethanol and acetaldehyde at low operating temperatures. These flower-like ZnO microstructures showed some sort of selectivity for NO_2 below 300 °C.

1. Introduction

In past few decades due to fast industrialization and urbanization, the risk of environmental pollution is increased. The level of toxic gases, releasing from industries and vehicles, is reached at alarming point in our ecosystem. Some toxic gases such as NO_x can affect human life and health even at part per million (ppm) levels. In recent years, the monitoring of NO_2 emitted from automobiles and various industrial processes has become an important issue. Current scientific results show that short-term exposure to NO_x gases, even at ppm level, can cause adverse respiratory effects such as inflammation, while long-term exposure is correlated to pulmonary edema and death [1–3]. The Occupational Safety and Health Administration (OSHA) have set a permissible exposure levels for NO_x by 5 ppm [4]. The NO_x gases mostly released from combustion of fossil fuels. The study of the European Environment Agency (EEA) suggests that 40% of total NO_x emissions in EU-27 Member States' was contributed from transport sector, in 2008 [5]. Therefore, there is a strong demand for developing high performance sensors for monitoring NO_2.

Metal oxide semiconductor (MOS) based gas sensors, such as SnO_2, ZnO, TiO_2, WO_3 and In_2O_3 have been extensively studied due to their industrial and domestic applications in toxic and flammable gas detection [6–10]. Among various MOS, ZnO, which is widely known as a kind of wide-band gap semiconductor, has been proved to be an excellent gas sensing material for both oxidative and reductive gasses [11–13]. Many exciting results on ZnO based gas sensors have been reported [14,15]. Recently, many efforts have been made to improve the gas sensing properties of ZnO-based gas sensors. In gas sensor, it has been found that the gas sensing properties of devices are strongly dependent on the morphology of the sensing materials. Recently, one-dimensional (1D) ZnO nanostructures (rods, wires, tubes and belts) have been attracting a great deal of research interest due to their high, aspect ratio, surface to volume ratio, electron mobility, etc. which play an important role in gas sensor [16]. The assembly and integration of these 1D ZnO nanomaterials into three-dimensional arrays or hierarchical structures are desirable for further improving their sensing property [12,17]. However, development of highly sensitive and selective gas sensors at low temperature is still remained a big challenge for researcher. Basically MOS gas sensors are operated above 300 °C for their practical application which means we need to supply power throughout their use. This exercise increases the cost if we are using MOS gas sensor. Therefore, development of MOS gas sensor operating at room temperature is needed to reduce the cost for their practical application [18–20]. In this study, a sensing device is fabricated from flower-like ZnO microstructures for room temperature NO_2 sensing. These flower-like ZnO have shown higher response for NO_2 as compared to CO, ethanol and acetaldehyde gases at low operating temperatures.

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2. Experimental

2.1. Synthesis of flower-like ZnO microstructures

Flower-like ZnO microstructures were synthesized in two steps using similar method reported in our previous work [21]. In first step, ZnO nanorods were grown by a simple hydrothermal reaction of $Zn(NO_3)_2·6H_2O$ (Reagent Grade, 98% Sigma–Aldrich) in the presence of cetyltrimethylammonium bromide (CTAB; Aldrich) as the promoter. In a typical procedure $Zn(NO_3)_2·6H_2O$ (9 mmol) was dissolved in 40 ml of deionized water and pH was maintained at 7 by adding ammonia followed by vigorous stirring for 1 h. A white precipitate was produced which was collected by centrifugation and washed thoroughly with deionized water. The precipitate was transferred in a 50 ml capacity autoclave with Teflon liner followed by uniform heating at 200 °C for 10 h. After completion of the reaction, it was cooled to room temperature and powdered samples were collected by centrifugation. Powdered sample was thoroughly washed with deionized water and ethanol and dried at 80 °C for 12 h.

In second step, a solution saturated with $[Zn(OH)_4]^{2-}$ was prepared by dissolving analytical grade ZnO (Sigma–Aldrich) in 5 M NaOH solution for growing the flower-like ZnO microstructure. Three milliliters of the obtained $[Zn(OH)_4]^{2-}$ solution was mixed with 0.01 g of ZnO nanorods prepared as described above and diluted with deionized water to a total volume of 25 ml. The mixture was transferred into an autoclave of 50 ml capacity and kept at 100 °C for 10 h. After completion of the reaction, it was cooled to room temperature and powdered samples were collected by centrifugation. Powdered sample was thoroughly washed with deionized water and ethanol and dried at 80 °C for 12 h.

2.2. Characterization

The crystallographic structures of the solid samples were determined using a X-ray diffractometer (XRD; D/Max 2005 Rigaku) equipped with graphite monochromatized high-intensity Cu Kα1 radiation (λ = 1.5405 Å). The particle morphology was investigated by scanning electron microscope (SEM; JSM-5900, JEOL) and transmission electron microscope (TEM; JEM-2010, JEOL). Photoluminescence (PL) spectroscopy property was studied by Cd–He laser at 325 nm excitation wavelength. Surface area was analyzed by BET-surface area analyzer using TriStar, Micromeritics.

2.3. Gas sensing measurement

Sensing device was fabricated by similar method reported in our previous works [11–13]. Flower-like ZnO powder (0.1 g) was mixed with α-terpineol (500 μl) and grinded in agate mortar for 30 min to make paste. The ZnO paste was pasted by doctor blading method onto the cleaned alumina circuit board with interdigitated platinum electrodes. The size of alumina circuit board was 15 mm × 15 mm. In this circuit board platinum electrodes were interdigitated in the area of 10 mm × 10 mm. For making sensor device, gold wire electrode was attached to circuit board using gold paste and sintered at 600 °C for 1 h. The circuit board was taped with Sellotape on four sides and ZnO paste was pasted by doctor blading method. Finally, tape was removed and device was dried at 80 °C for 5 h. The ZnO loaded device was sintered at 500 °C in a muffle furnace for 5 h.

The device was tested at desired temperature for desired concentration of test gas in a temperature-controlled environment. The total gas flow rate was 100 cm^3/min. The balance gas was N_2, and air was mixed to be 10.5% of oxygen. The device was tested at the temperature range of 27–400 °C for various concentrations of CO (200–1000 ppm), ethanol/acetaldehyde (50–250 ppm) and NO_2 (5–100 ppm) in a temperature-controlled environment. Before injection of test gas, device was heated in air at testing temperature to stabilize the baseline. The change in resistance of the device due to the presence of test gas was measured using a high resistance meter (Agilent 34970A). For NO_2 the resistance was very high below 100 °C and it was beyond the limit of resistance meter hence, 10 MΩ resistor was used parallel to sensing device. The sensor response (R_s) was calculated using (R_a/R_g) for reducing gases (CO, ethanol and acetaldehyde) and R_g/R_a for oxidizing gas (NO_2). Here, R_a is the resistance in air with 10.5% O_2, and R_g is the resistance in the test gas.

3. Results and discussion

Fig. 1a shows the XRD profile of flower-like ZnO microstructure in which all the peaks are indexed to typical wurtzite ZnO consistent with the standard values for bulk ZnO (JCPDS card No. 36-1451). The sharp diffraction peaks indicate the good crystallinity of the prepared crystals and no peaks for other impurities are detected in the spectra.

SEM images of flower-like ZnO microstructures are shown in Fig. 2a and b. It shows that the size of flower-like ZnO microstructures is about 5–7 μm in radius and they are uniformly distributed. A single flower-like ZnO microstructure is build from dozen of ZnO nanorods and they are radiated through the center to form flower-like structures. These radially oriented ZnO nanorods have diameters and lengths ranging from 250 to 500 nm and from 3 to 5 μm, respectively. Fig. 2c is the TEM image of the individual ZnO nanorods of flower-like assembly. It shows that the diameter of the rod is not uniform throughout the length and it is tapered at the top. Fig. 2d shows the high resolution TEM (HRTEM) image of the ZnO nanorods. Clear lattice fringes are seen in HRTEM without any stacking fault. The image clearly reveals only the fringes of (1 0 −1 0) planes with a lattice spacing of about 0.28 nm can be observed. The single crystalline nature of ZnO nanorods is confirmed by selected area electron diffraction (SAED) pattern (inset Fig. 2c) which is characterized by the symmetrical stripes justifying the presence of some ordered arrangement of crystallites in this terrain. BET surface area is calculated by using nitrogen adsorption data in the BET region (P/P_0 < 0.3). The surface area of these flower-like ZnO microstructures is 4.9 m^2/g.

Fig. 3 shows the PL spectrum of flower-like ZnO microstructures. As sensing property is tested after sintering the film at 500 °C for 5 h in the presence of air hence the PL spectrum is also taken for the powder after annealing at 500 °C for 5 h. It has two emitting bands including a weak emission band in UV region (390 nm) and

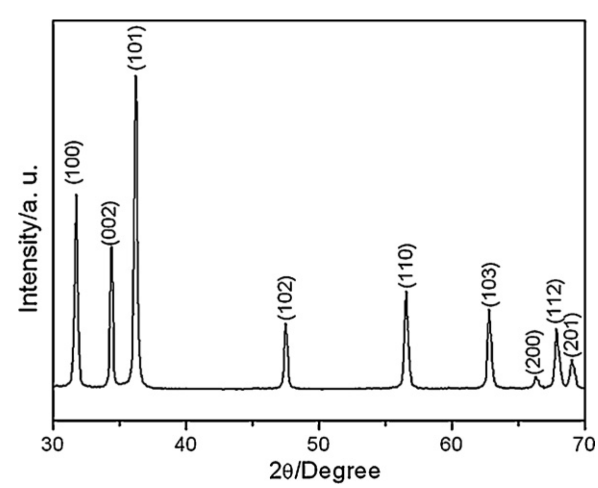

Fig. 1. XRD profile of flower-like ZnO microstructures.