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Highly sensitive CO sensor based on ZnO/MWCNT nano sheet network grown via hydrothermal method

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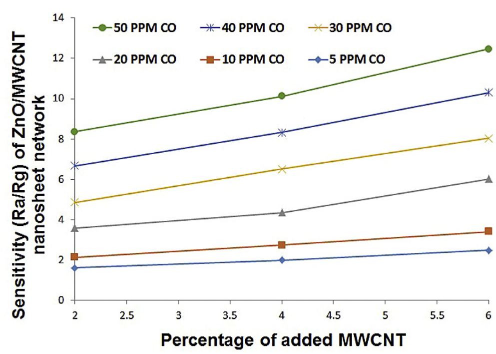
HIGHLIGHTS

- Growth of ZnO/MWCNT nanosheet network being mostly aligned perpendicular to the surface.
- More porous structure and lower width of ZnO nanosheets with increasing the additive MWCNT percentage.
- Strong response as well as fast recovery for CO as analyte.
- Low working temperature in the range of 70–100 C.
- Decrease in response time and almost linear increase in sensitivity by increasing the percentage of MWNCT additive.

GRAPHICAL ABSTRACT



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ABSTRACT

Zinc Oxide/Multiwall Carbon Nanotube (ZnO/MWCNT) nano sheet network is grown by an in situ hydrothermal method on glass substrate. MWCNT is added to ZnO precursors during hydrothermal process with different percentage of additive MWCNTs. Interdigitated Ag electrode is deposited on glass substrate beforehand. CO gas is used as the target gas and sensitivity of the sensors is tested with dry air as carrier gas. The sensors show considerable high sensitivity and fast response to CO at around 100 °C operating temperature which is promising for industrial applications. This sensor is having advantage of being small in size, very thin structure, very low working temperature, fast response and recovery time and sensitive to low ppm CO gas. Sensors with more additives MWCNTs show stronger responses to CO gas. Sensors with 2 wt% additive MWCNTs showed the sensitivity of 1.6 and sensors with 6 wt% additive MWCNTs showed the sensitivity of 2.5–5 ppm of CO gas. Samples were characterized utilizing Field Emission Scanning Electron Microscopy (FE-SEM), X-Ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) surface area measurement.

1. Introduction

It was discovered that semiconducting oxides are able to show gas sensing characteristics in 1960s, plenty of studies have been focused on this field. This potentiality is due to the adsorption of reducing gases on the surface of semiconductors that could result

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in change in the electrical conductivity [1,2]. This phenomenon attracts extensive attention to the development of gas sensors using various semiconducting oxides [3]. Most of the metal oxides are investigated and seem to be suitable choice to produce gas sensors for detecting various target gases [4,5]. Among them, ZnO, a typical n-type metal oxide semiconductor with merit features such as wide band gap (3.37 eV), good morphology tailoring properties, high electron mobility, good chemical stability and low production cost, has been studied by large number of research groups and the results demonstrate that ZnO exhibits excellent response characteristics to many toxic gases [6–8] like H_2S [9], NO_2 [10] and CO [11] etc.

Considering the sensing mechanism of ZnO, it can be concluded that quantities like surface-to-volume ratio, surface and interface states as well as oxygen adsorption mechanism play critical role in the response of gas sensors [12]. Thus, optimizing the morphologies to achieve high-performance gas sensors became popular and challenging subject in gas sensor field and due to high surface-absorption ability and active surface charge-transfer properties plenty of efforts have been focused on the preparation of ZnO nanostructures such as nanoparticles, nano sheets [13], nanobelts [14], nanorods, nanowires [15,16] and nanotubes [17].

CNTs are rolled graphene sheets which based on their chirality can take the form of metal, semiconductor and insulator [18]. CNT's unique properties such as highly developed surface, many dangling bond and defects make it an attractive material for different gass sensing intention. Sensing properties of materials containing carbon nanotubes are associated with an alteration in CNTs conductivity due to gas absorption [19]. Recently, it has been reported that MWCNTs demonstrate a p-type semiconducting character when they are exposed to sub-parts per million concentrations of reducing gases with decreasing resistance [20].

More recently, CNTs/metal oxide composites based on either SWCNTs or MWCNTs have been reported to be able to detect NH and NO at room temperature and higher temperatures with acceptable sensitivity. It has been reported that this observation could be related to the presence of a p-n junctions [21–23]. The electrical conductivity of these composites can be changed by alteration in amount of surrounding gases. Therefore, these structures present a great potential as new gas sensing materials [24].

In another research MWCNT/SnO_2 gas sensors were synthesized and was reported that addition of 0.05 wt% MWCNTs to SnO_2 sensors increases the sensitivity of the sensor to ethanol, CO, NO and CH_4 in quiet low operating temperature due the low Schotcky barrier between MWCNTs and SnO_2 particles as well as high conductivity of carbon nanotubes network which provides low resistance nanopathways for electrons transfer through the SnO_2 matrix [25]. In a recent research a ZnO/MWCNT gas sensor was synthesized with quite high sensitivity to volatile organic compounds such as ethanol, methanol, acetone and ether. Significant sensitivity and relatively low response and recovery times were reported for ZnO/MWCNTs gas sensors. It was reported that enhanced gas adsorption and diffusion due to existence of well dispersed MWCNTs in the ZHSs matrix as well as enhancement of depletion layer due to the formation of hetero-junctions between ZHSs (n-type) and MWCNTs (p-type) might be the reasons of the observed high sensitivity of synthesized ZnO/MWCNTs gas sensor [26].

In this paper, we present highly sensitive ZnO/MWCNTs gas sensors, constructed by hydrothermal method. ZnO/MWCNTs nano sheet network was grown on the surface of glass substrate with deposited Ag interdigitated electrodes. The morphology of the deposited layer is a network of ZnO nano sheets structure with MWCNTs on the sheets and between them. Samples were characterized by Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) surface area measurement. Responses to different CO concentrations with dry air as carrying gas were measured.

2. Experimental details

ZnO seeds were grown on the surface of glass substrate. The process was carried out as following: 15 mM zinc acetate dehydrate ($Zn(CH_3COOH)_2 \cdot 2H_2O$) was dissolved in 80 ml ethanol (C_2H_6O). The solution was subjected to magnetic stirring at room temperature for 6 h and then was sonicated for 30 min before deposition. The satisfactorily cleaned glass substrate was used for deposition of interdigitated Ag Electrodes (IDEs) with active area of 3×3 mm, via Physical Vapor Deposition (PVD) technique. ZnO seeds were deposited on substrate through steps of spin-coating then it was annealed at 350 °C for 25 min.

After depositing the seed layer, ZnO sensing film was coated on glass substrate via hydrothermal method. First, combination of 0.6 mol $Zn(NO3)_2 \cdot 6H_2O$ and 0.2 mol Hexamine (HMT) solution was dissolved in 40 ml deionized water, and 0.75 ml $NH_3 \cdot H_2O$ was added to the resulting mixture until the PH of solution reaches 10. Second, MWCNTs were dispersed properly for 1 min with Ultrasonic radiation probe (Bandelin sonopulsHD3200) and were added to the mixture with 2%, 4% and 6% in wt.% of Zinc Nitrate. Third, the seed-coated substrate was horizontally immersed in this solution at 100 °C for 1 h while the temperature was kept at 100 °C. Finally after hydrothermal procedure, the resulting devices were annealed at 200 °C for 2 h in furnace (Exciton 1400).

Sensing measurements were performed by a gas sensing set up. For gas sensing measurement purpose, dry air was used as carrying and recovery gas and CO was employed as analyte. Chamber of gas testing device was free of H_2O which may interfere with the gas sensing test results. Gas flow was controlled with a Mas Flow Control (MFC) and organic glass chamber was used as the container. The circuit voltage was set to 4V (AC source with frequency of 80 Hz served). Using Sanwa5000 multimeter, Output signals were transferred to a PC and the resistance of sensors was monitored during gas sensing procedure. A Ni-Cr coil as electric heater was placed under the glass substrate along with a (Pt-100) thermocouple. A temperature controller apparatus adjusted the sensor temperature on desired temperature with the accuracy of ±1 °C. The response and recovery times of the sensor were defined as the time required for the sensor resistance to reach 90% of final value. Sensitivity of sensor was defined as R_a/R_g in which R_a represents the resistance of sensors when exposed to recovery gas and R_g represents the resistance of sensors when exposed to analyte.

3. Results and discussion

3.1. Characterization of the samples

The synthesized samples were characterized by XRD using Panalytical Xpert Pro MPD. The corresponding XRD pattern of samples is shown in Fig. 1 (a). All the diffraction peaks can be indexed as the hexagonal wurtzite ZnO. In XRD pattern one can see that no MWCNTs peaks (Fig. 1 (b)) are observed. This absence is a result of very low amount of MWCNTs present in composite, which makes the peak intensity of MWCNTs negligible compared to the ZnO peak intensity [26].

The Brunauer–Emmett–Teller (BET) model was developed in 1938, and it is applied to isothermal N_2 desorption measured at 77 K which is liquid N_2 temperature [27]. BET model broadens the Langmuir adsorption theory to describe multilayer adsorption of N_2 on the surface of a specified material. BET theory equates the rate of condensation of one monolayer of adsorbate to the rate of desorption of the previous monolayer coverage on the surface of