Gas Sensing Properties of 3D Graphene Nanotubes (GNT)@ZnO at Room Temperature

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Abstract. In this study, nickel nanowires (Ni-NWs) were first grown by chemical method and then graphene was grown on the as-obtained Ni-NWs by CVD route to yield graphene nanotubes (GNTs). The GNTs were then hydrothermally combined with ZnO to construct a gas sensor for detection of NO\textsubscript{2}. The as-prepared GNT@ZnO sensor displayed high sensitivity towards the detection of NO\textsubscript{2} reaching up to 47.5\% per 50 ppm NO\textsubscript{2}. In addition, the sensor exhibited relatively fast response time of 300 s and recovery time of around 200 s under UV light. The sensor also showed good repeatability, making it promising for future applications.

1. Introduction

Gas sensors are important in many application fields for detection of toxic, harmful, flammable and explosive gases in the environment, as well as to monitor air pollution and industrial waste gas [1-5]. Gas sensors convert information related to outside air environment into electrical signals, which are then transmitted to monitoring centers for analysis. Gas sensors are also useful in food quality inspection, identification of counterfeit products, and traffic safety. Compared to traditional gas detection methods, gas sensors are advantageous in terms of simple working circuits, continuous monitoring, real-time use, on-site monitoring, feedback control, easy to carry, facile operation, and low-cost [6-8].

Graphene materials are widely used in field-effect transistors, lithium-ion batteries, solar cells, supercapacitors, sensors, and many other fields. The reason for graphene as the gas sensor’s material is related to the structure and P-type semiconductor property of graphene, which makes the hole carriers in the material determine its resistance. Graphene is a monolayer two-dimensional material composed of sp\textsuperscript{2} hybrids between carbon-carbon bonds. This two-dimensional structure exposes each carbon atom in graphene to its surface. Thus, adsorption of gas molecules on the graphene surface would induce electron transport. The resulting changes in electrical properties can then be translated into electric signals and used for detection of trace gases [9-12].

Numerous studies have shown that the three-dimensional structure of graphene combines the inherent characteristics of two-dimensional graphene with the high adsorption performance, strong mechanical properties, high electrical conductivity, low transmission resistance, fast electron transport
performance, large specific surface area, and relevant plasticity of the three-dimensional structure. In addition, the introduction of graphene materials into conventional semiconductor metal materials improves the gas sensing performance, which is generally reflected in lower operating temperatures, shorter response recovery times, and improved sensitivities [13-16].

The gas sensing properties of ZnO were first reported in the 1960s. ZnO nanomaterials possess good gas-sensitivity and high response towards flammable and explosive gases due to their high electron mobility, good chemical and thermal stability, high detection sensitivity, and low-cost. However, ZnO micro/nano materials require high operating temperatures (usually 200-500 °C), leading to consumption of substantial power [17-19]. In addition, they are not conducive to real-time and outdoor monitoring. Therefore, combination of graphene with ZnO to yield composites with reduced operating temperature, low response recovery time and improved sensitivity has been investigated [20].

In this paper, 3D (GNT)@ZnO nanospheres were prepared by a simple route. Nickel nanowires prepared by chemical reduction under water-bath heating and magnetic field conditions were used as substrates for the deposition of graphene nanotubes (GNTs). The GNTs were grown by ambient-pressure CVD on Ni-NWs. ZnO nanospheres were prepared by hydrothermal method. The as-obtained materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy. They were then tested as gas sensors for the detection of NO2, and the results were promising in terms of sensitivity, response time, and repeatability.

2. Experimental

2.1. Preparation of three-dimensional graphene
The graphene nanotubes (GNTs) were grown by ambient-pressure chemical vapor deposition (CVD) on Ni-NWs. Nickel nanowire substrate was suspended in constant temperature chemical vapor deposition chamber, and then sealed under Ar gas at 900 °C. Graphene was grown under CH4 and H2 atmosphere for 15 min and then cooled to room temperature under H2 and Ar atmosphere. Then a certain amount of polymethyl methacrylate (PMMA) was added to acetone and ultrasonicated for 30 min to form a clear solution. The as-obtained solution was then dropped onto the graphene nanotubes grown on the Ni nanowire substrate previously etched in 3 M HCl solution for 24 h. The graphene nanotubes were finally obtained by dropping acetone on PMMA-coated surface.

2.2. Preparation of GNT@ZnO nanospheres
ZnO nanospheres were prepared by the hydrothermal method. In a typical procedure, 0.27 g ZnCl2 was ultrasonicated in 30 ml ethylene glycol for 1 h. Next, certain amounts of sodium citrate and sodium acetate were added to the solution and the mixture was stirred for 3 h, followed by hydrothermal reaction at 180 °C for 14 h. The resulting product was centrifuged and dried. Then, 4 mg ZnO nanospheres and 2 mg graphene nanotubes were dissolved in ethanol to yield ZnO@GNT composite structure after ultrasonic mixing.

2.3. Characterization
The morphologies were characterized by scanning electron microscopy (SEM, Sigma300, Carl Zeiss, Oberkochen, Germany) at 3 kV. X-ray diffraction (XRD: Bruker, Germany Cu-Kα radiation, λ= 1.5418 Å) was used to analyze the crystalline structures of the prepared products. Further structural identification was carried out by Raman spectroscopy (HR-800, HORIBA JobinYvon, France) with a 632.8 nm He-Ne laser.

3. Results and Discussion
To verify the successful formation of GNTs, Raman spectroscopy was carried out and results are displayed in Fig.1. The Raman spectrum of graphene contained three characteristic peaks at 1323, 1579, and 2670 cm⁻¹. The G-band was produced by the first-order scattering of E2g phonon plane
vibration in sp² domain, indicative of crystallization degree of graphene. The D-band was produced by discontinuity in crystal plane of graphene or doping of foreign atoms. The intensity of D-band can reflect the defect density in graphene. The most intense peak in graphene was the 2D peak produced by double phonon resonance Raman peak, suggesting that defects were produced during synthesis. The ratio of 2D/G was recorded as 1.51, indicating the formation of few graphene layers or single layers.

Fig. 1. Raman spectra of GNT deposited on Ni Nanowires.

Fig. 2 shows the XRD patterns of ZnO nanospheres. The XRD pattern of ZnO nanostructures displayed diffraction peaks at 2θ of 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.7°, 66.3°, and 67.8°, which can be attributed to ZnO according to international standard cards. The nanometer-scale of ZnO was confirmed by the presence of diffraction peaks of (100), (002), (101), (102), (110), (103), and (112) crystal planes. The ZnO nanospheres showed a hexagonal wurtzite structure.

Fig. 2. XRD pattern of ZnO nanospheres.

The morphologies and microstructures of GNT@ZnO nanocomposites were analyzed by SEM. As shown in Fig. 3, ZnO appeared spherical with diameter around 2 μm, graphene appeared tubular with diameter around 300 nm, and GNTs were slightly damaged.
Fig. 3. SEM images of GNTs and ZnO nanospheres.

Two adsorption and desorption cycles were carried out to test the repeatability of the sensors. In Fig. 4, the resistance of the device reduced rapidly at room temperature as soon as the sensor came in contact with 50 ppm NO$_2$. The response of GNT@ZnO sensor reached 47.5%. In addition, the sensor recovered within 200 s under UV light. The successful adsorption and desorption processes showed good repeatability.

Fig. 4. Repeatability test of GNTs and ZnO composite structure gas sensor towards 50 ppm NO$_2$.

4. Conclusions
A novel sensor based on GNT@ZnO was reported for the detection of NO$_2$ gas. The gas sensing response towards 50 ppm NO$_2$ reached 47.5% due to the three-dimensional structure, which increased the contact between the material and NO$_2$ molecules. In addition, p-n junction was formed between ZnO and GNT, accelerating the electron-hole recombination and increasing the response. In addition, the prepared gas sensor showed good repeatability.

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