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Room-temperature gas sensor using carbon nanotube with cobalt oxides

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ABSTRACT

Hydrogen gas (H_2) sensors are fabricated using a carbon-nanotube (CNT) sheet decorated with cobalt oxide (Co_3O_4) nanoparticles. The proposed hybrid sensor is fabricated by electrodepositing Co_3O_4 on CNT sheets. With an annealing treatment, the CNTs/Co_3O_4 composite sensors exhibit a much higher response to H_2 gas at room temperature than sensors that have not undergone the annealing treatment. The functional groups and oxygen defects that are formed during annealing serve as chemisorption sites for H_2 at room temperature. Moreover, the annealing treatment results in strong interaction between Co_3O_4 and the CNTs, which allows carriers to easily diffuse from the Co_3O_4 nanoparticles to the CNTs.

1. Introduction

Hydrogen (H_2) is considered a promising source of heat and power because of its high power efficiency, renewability, and environmental friendliness [1]. However, one of the main challenges in using H_2 is safety because of its properties such as being odorless, colorless, and flammable. Because H_2 can cause explosions at concentrations higher than 4% in air, early detection of hydrogen leakage is critical to ensure the safe operation of a H_2-based infrastructure [2]. Metal-oxide-based gas sensors are widely used for gas detection. However, most of them have the notable drawback of a high operating temperature, which leads to a high power consumption, safety concerns, a lack of flexibility, and an instability in the sensing materials [3,4]. Therefore, high-efficiency H_2 sensors with reliable gas response and fast response time, stability for long-term use, the ability to operate at room temperature, and low-power consumption are essential for H_2-based energy generation, H_2 storage, and filling stations.

Over the last decade, the use of carbon nanotubes (CNTs) as a sensing layer has drawn considerable attention owing to their outstanding properties such as high aspect ratio and excellent electrical, chemical, and environmental stability [5–7]. These properties make them an ideal candidate for gas-sensing applications. CNT-based gas sensors work by detecting changes in the electrical conductivities induced by charge transfer between the gas molecules and the CNTs [8,9]. However, pristine CNTs do not interact with H_2 molecules at room temperature because of their high activation energy [10].

Various approaches are currently being investigated to improve the physical and chemical properties of H_2 sensors [11]. Recently, hybrid materials consisting of semiconductor metal oxides and CNTs have attracted much attention in many applications [12,13]. The unique geometries and structures of the hybrid materials show potential for use as high-performance gas sensors. Recent our work reported a resistive gas sensor based on CNTs using manganese oxide as an active material for detecting H_2 in an inert atmosphere [14]. It was found that the size of the nanoparticles and the operating temperature significantly affected the performance of the sensor. The measured output characteristics were stable, reliable, and reproducible. However, the sensors share a common shortcoming with metal-oxide gas sensors, which is a high operating temperature (220 °C) that leads to increased power consumption to maintain the high gas response. Moreover, a high operating temperature poses a safety problem when used around H_2-based energy equipment such as H_2 gas stations or fuel-cell vehicles. Therefore, operation of the sensor at room temperature is desirable for practical environmental monitoring.

Previous studies reported the ability to detect hydrogen at room temperature by combining CNTs with some noble metals such as Pd, Pt, or Au [15–18]. However, the metals are very expensive and fabrication process is complex and time-consuming, thereby, their commercial use is limited. Therefore, it is essential to find alternative sensing materials for detecting H_2 with low-cost and easy fabrication at room temperature.

Cobalt oxide (Co_3O_4) is regarded as one of the most representative p-type semiconductors and is the most promising

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functional material for many technological applications such as heterogeneous catalysis, supercapacitors, lithium-ion batteries, and especially gas sensors [19,20]. In this paper, we report the room-temperature gas-sensing properties of a CNTs/Co_3O_4 hybrid composite sensor. The sensor was fabricated by electrodepositing Co_3O_4 onto CNT sheets. The shape of the electrodeposited Co_3O_4 on a CNT sheet was developed in the form of nanoparticles, which provide a large surface area to detect gas molecules. In order to improve the room-temperature gas response, annealing treatments were carried out in oxidizing environments at different temperatures. The hybrid composite sensors exhibited a high gas response and fast response time, stability, and reliable sensing performance at room temperature.

2. Experimental details

2.1. Growth of spin-capable CNTs

Previous experiments produced transparent conductive CNT sheets by using a simple MWCNT spinning method [21–24]. A 5–6 nm thick iron film was deposited on a 330-μm-thick p-type silicon wafer using electron beam (e-beam) evaporation. The thickness was monitored by a quartz-crystal sensor fixed inside the e-beam evaporation chamber. Catalyst annealing and CNT growth were performed in a chamber shaped like a vertical cylinder at atmospheric pressure. The flow rates of He (5 slm), C_2H_2 (100 sccm), and H_2 (100 sccm) were controlled by electronic mass-flow controllers (MFCs). After purging the tube with He for 10 min, the chamber was heated to 780 °C within 15 min (ramping rate: 50 °C/min), after which the growth of CNTs was carried out at 780 °C by adding acetylene gas to the flow for 5 min. Then, the C_2H_2 and H_2 gas flows were turned off, and the sample was rapidly cooled. As shown in Fig. 1, a super-aligned CNT film is continuously drawn from the CNT arrays. The fabrication process for the super-aligned CNT films is highly efficient and compatible with semiconductor technology for mass production.

2.2. Electrodeposition of Co_3O_4 on a CNT sheet

Co_3O_4 was deposited on the CNT sheet by electrodeposition, which was carried out in a fresh aqueous solution of 0.1-M $CoSO_4 \cdot 7H_2O$, 0.1-M NaOAc, and 0.1-M Na_2SO_4 (pH ~ 5.6) in the 263A Princeton Applied Research Potentiostat/Galvanostat. The CNT sheet, a platinum foil, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. Nitrogen gas was bubbled into the solution before the experiments. Co_3O_4 nanoparticles were electrodeposited with different times. After electrodeposition of Co_3O_4 on the CNT sheets, an annealing treatment was performed in an air environment at 300 °C for 30 min.

2.3. Sensor measurements

The sensing measurements were conducted in a conventional gas flow apparatus. The gas chamber had a gas inlet and an outlet. Air and H_2 were used as the carrier and test gases, respectively. The two gases arriving from separate lines were mixed and fed into the chamber through the gas-inlet line. MFCs were used to control the flow rates of air and H_2. The variation in the electrical resistance of the sensors with time and concentration was measured by a Keithley 2400.

3. Results and discussion

3.1. Annealing treatment and material characterization

The surface morphology of the CNT/Co_3O_4 composite was studied from SEM images. Circle-shaped Co_3O_4 nanoparticles

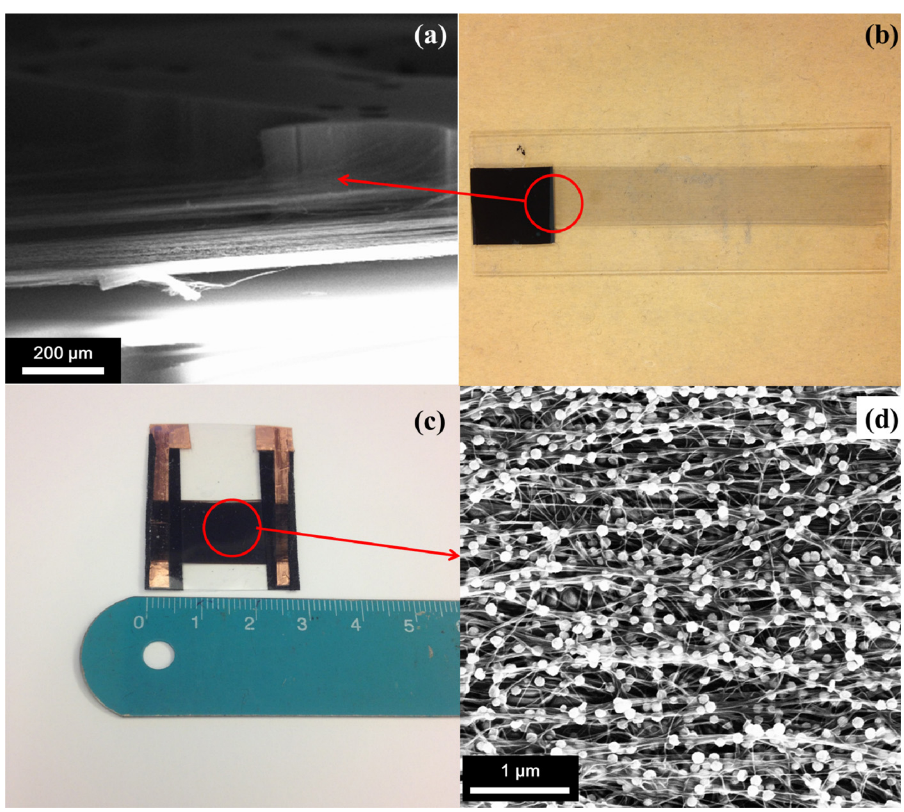

Fig. 1. SEM Images and pictures of (a) and (b) a CNT sheet pulled from the CNT forest, (c) fabricated sensor, and (d) CNTs/Co_3O_4 composite.