International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:12, 2014

Hydrogen Gas Sensing Properties of Multiwalled Carbon Nanotubes Network Partially Coated with SnO_2 Nanoparticles at Room Temperature

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***Abstract*—**In the present work, hydrogen gas sensor of modest sensitivity utilizing functionalized multiwalled carbon nanotubes partially decorated with tin oxide nanoparticles (F-MWCNTs/SnO2) has been fabricated. This sensing material was characterized by scanning electron microscopy (SEM). In addition, a remarkable finding was that the F-MWCNTs/SnO_2 sensor shows good sensitivity as compared to F-MWCNTs for low concentration (0.05-1% by volume) of H_2 gas. The fabricated sensors show complete resistance recovery and good repeatability when exposed to H_2 gas at the room temperature conditions.

***Keywords*—**F-MWCNTs, SnO_2 nanoparticles, Chemiresistor, I-V Characteristics, H_2 Sensing.

I. Introduction

NOWADAYS, hydrogen (H_2) gas is rising as a promising fuel source to replace available fossil fuels. H_2 based fuel finds many applications in civil transportation and in rockets for space vehicles, so fabrication of H_2 gas sensor is very necessary for its safe and controlled use [1], [2]. Therefore, H_2 gas sensors has been extensively developed using metal/metal oxides nanoparticles, carbon nanotubes (CNTs) and their nanostructure with metal/metal oxides nanoparticles [3]. Among these, CNTs are well known to behave as p-type semiconductors and respond to both oxidizing (electron withdrawing, e.g. NO_2 & O_2) and reducing (electron donating, e.g. NH_3 & H_2) gases under ambient conditions [4]-[6]. However, gas sensors based on pristine CNTs exhibit certain limitations such as low sensitivity, irreversibility, long recovery time, and particularly lack of response toward many important molecules, such as H_2, CO, NH_3 and CH_4 [4]. To overcome these shortcomings, several physical or chemical modifications of CNTs have been proposed with a wide range of materials such as acids, conducting polymers (like and catalytic metal nanoparticles (Pd & Pt) and metal oxides nanoparticles [7]. These functionalized CNT sensors offer an improved gas sensing performance with a better selectivity at room temperature conditions. In addition, the nanoparticles give a continuous pathway for moving carriers, between the nanotubes, where sensitivity is enhanced by the existence of both the nanoparticles surface and the charge transfer between the nanotubes and nanoparticles induced by gas adsorption/desorption [8], [9]. However, agglomeration of these attached nanoparticles on the tubes surface produce poor sensitivity of the gas sensors.

In our previous work we compared the sensing response of pristine MWCNTs with functionalized MWCNTs at room temperature [3]. However, the objective of present work is to fabricate sensors, which show excellent resistance recovery and low recovery time for the detection of H_2 gas at room temperature using 2% by wt. partially attached SnO_2 nanoparticles functionalized MWCNTs. Here, we have used only 100x120 μm^2 area of fabricated interdigitated electrodes (IDEs) to detect the low concentrations (0.05 to 1% by volume) of H_2 gas. In addition, a simple approach has been used for to fabricate SnO_2 coated nanotubes composites.

II. Experimental

A. Sample Preparation

Pristine multiwalled carbon nanotubes (P-MWCNTs) were purchased from JK-impex (Mumbai, India) with a purity level >95%. These nanotubes have been synthesized by chemical vapor deposition (CVD) method. The average outer diameter of P-MWCNTs were ~11-15 nm and length ~10–30 μm. Firstly, P-MWCNTs were heated at 350°C for 2 h to remove impurities and then functionalized by different acids. The detail of functionalization process has been published in our previous work [3]. Further, adequate amount of functionalized nanotubes were mixed with the solution of tin chloride pentahydrate($SnCl_4 \cdot 5H_2O$) and stirred for 4-5 h at room temperature conditions. Then solution of NH_4OH was added drop wise into above solution so as to achieve pH 8-8.5. After precipitation, the sediment is kept at 50ºC for 24 h stirred and washed with distilled water many times to remove chlorine-ions and then dried at 100-120ºC for few hours. This prepared sample was called F-MWCNTs/SnO_2. Afterwards, to measure the electrical and sensing properties, 2% by wt. solutions of both samples was prepared in N, N-dimethyl formamide (DMF) solvent. These solutions were drop-casted on fabricated IDEs by using micropipette and then dried at 60-70°C

B. Samples Characterization

The morphology of the samples was investigated by scanning electron microscopy (SEM, model Raith 150-TWO). The current-voltage characteristics of the samples were recorded by using two probe configurations.

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C. Experimental Set Up of Sensing

Sensor response of the samples was measured in home-made system. In the whole experiment, N_2 gas was used as a carrier gas. The gas sensor response has been taken using multimeter and the flow rates of the gases were controlled by mass flow controllers attached to the inlets to the chamber. A small amount of oxygen (0.1%) was added to nitrogen gas to facilitate the recovery of the sensor. For studying the H_2 sensing performance, the important physical parameters were, the sensitivity factor S, complete resistance recovery and the low recovery time. Among these, S was defined as the relative variation of the resistance and calculated according to formula:

$$S\ (\%) = 100\left[\frac{(R_H - R_N)}{R_N}\right]\ \%$$

where R_N is resistance of sensor exposed in N_2 gas and R_H is the resistance of sensor after exposing to H_2 gas.

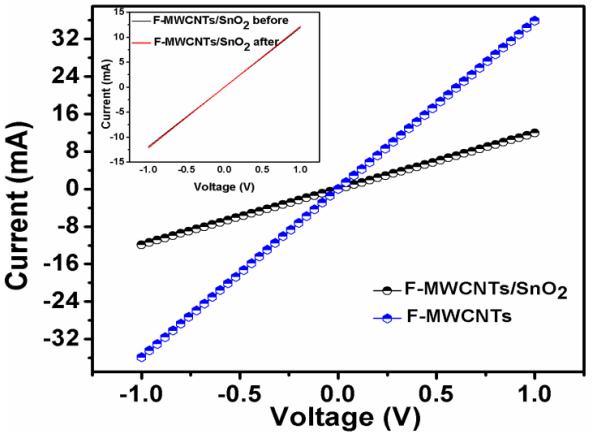


Fig. 1 Comparison in I-V characteristics of F-MWCNTs and F-MWCNTs/SnO_2 composite

III. Results and Discussion

The current-voltage (I-V) measurements of both samples at room temperature were performed between -1V to +1V and the results were plotted in Fig. 1. In this experiment, to check the reliability/repeatability of the device and also to separate out the role of current-induced annealing in the electrical current improvement, the I-V of the devices was measured at 1V after applying every higher bias, which means that first it was recorded at 1 V, and then at 2 V and again measured at 1 V and so on up to 8V. The inset of Fig. 1 shows the comparison in I-V before and after current induced annealing of F-MWCNTs/SnO_2. The current in F-MWCNTs/SnO_2 nanostructure at 1V was 11.7 mA and increased to 12.3 mA when measured after 8V, hence only 0.05% improvement was observed in the current. The absence of significant hetero-junction at all stages of the composite formation (F-MWCNTs/SnO_2) is confirmed by linear I–V characteristics [10]. In addition, the linear I–V curve of F-MWCNTs/SnO_2 indicates the formation of ohmic contacts between SnO_2 nanoparticles and nanotubes.

The morphology of pristine MWCNTs and SnO_2 nanoparticles attached functionalized MWCNTs composite as elucidated by SEM are shown in Figs. 2 (a) and (b) respectively. It indicates that, SnO_2 nanoparticles of different sizes were dispersed on the nanotubes network.

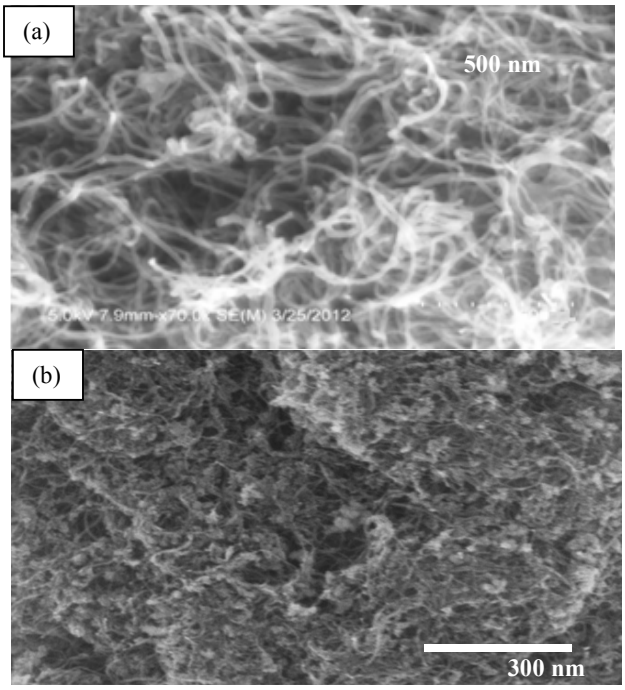


Fig. 2 (a) SEM image of P-MWCNTs (b) SEM image of F-MWCNTs/SnO_2 composite

In the present work, we have investigated the sensing properties by observing the resistance change, caused by adsorption and desorption of gas molecules on the surface of the sensing materials. The experimental set up used for the purpose is shown in Fig. 3. The system utilizes Keithley 2000 multimeter for recording the sensing response. The flow rates of N_2 and H_2 gases were controlled by mass flow controllers (MFC). Generally, the resistance of n-type semiconductor attached CNTs gas sensors decreases on exposure to reducing gas (H_2 and NH_3) and increases when kept in oxidizing gas (O_2 and NO_2). However, the resistance of these sensors increase as the amount of nanotubes increases in the sensing layer. Similar type of behavior is observed in the present gas sensor, such as, an increase in electrical resistance of the tested sensor in H_2 atmosphere and then reaching a maximum value. Fig. 4 (a) shows the sensing characteristics of F-MWCNTs/SnO_2 composite. The sensitivity of this sensor is found to increase to 2.8% for 0.05% concentration of H_2 gas as compared to the F-MWCNTs with sensitivity 0.8% for same amount of H_2 gas, which is well discussed in our previous work [3]. This increment in the sensitivity is due to high surface/volume ratio of F-MWCNTs/SnO_2 sensor as compared to F-MWCNTs. In addition, the good

reproducibility and baseline stability of the sensor is observed upon repeated exposure and removal of H_2 gas in N_2 atmosphere. Furthermore, a relationship between the sensitivity and H_2 concentrations is also obtained, as seen in Fig. 4 (b). The recovery time of F-MWCNTs/SnO_2 sensor (Fig. 4 (b)) is increased from 9 s for 0.05% H_2 to 30 s for 1% H_2 gas. The same type of increment in the recovery time has been observed for F-MWCNTs sensor which recovers in 100s for 1% H_2 gas. The inset of Fig. 4 (b) shows the comparison in sensitivity for 0.05% concentration of H_2 gas for various materials. The repeatability of this sensor for the low concentration (0.05%) of H_2 gas indicates that, the sensitivity of the sensor does not deteriorate after repeated exposure to H_2 gas, which confirms that sensing characteristics are reproducible.

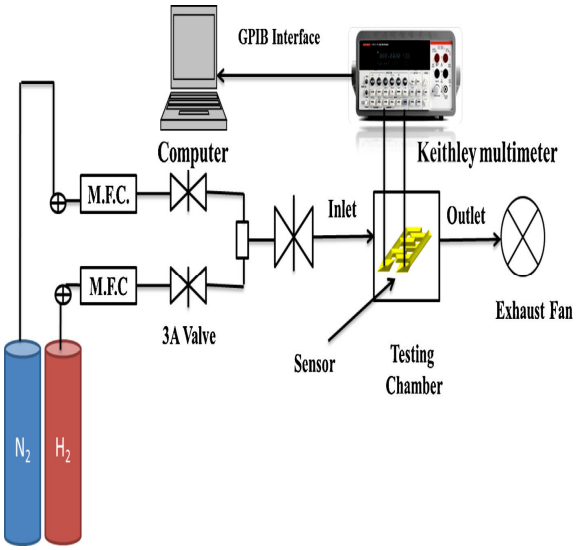
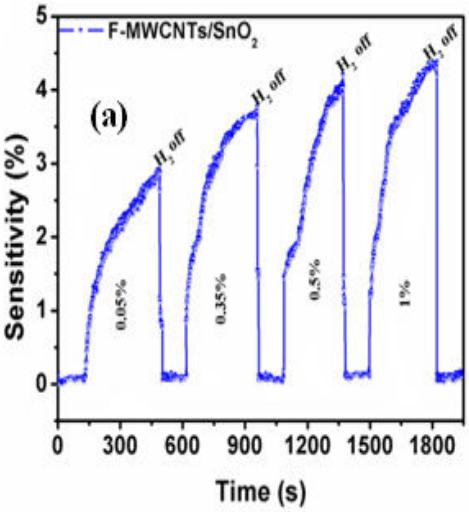


Fig. 3 Experimental setup of gas sensing



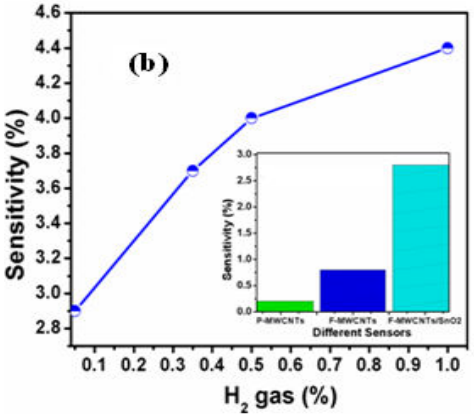


Fig. 4 (a) Sensitivity of F-MWCNTs/SnO_2 at different concentrations of H_2 gas (b) variations in sensitivity with H_2 gas concentrations

In the present case, two types of mechanisms can be possible; one between F-MWCNTs and second in partially covered nanotubes by SnO_2 nanoparticles. As we know the reducing H_2 gas molecules have lone electrons pair that are donated to the nanotubes and oxides nanoparticles when sensors are exposed to H_2 gas. Thus, H_2 gas acts as electron-donor or hole-acceptor in the presented sensors. Furthermore, the sensitivity of F-MWCNTs depends on functional groups attached on the tubes during functionalization process which act as catalytic sites for the dissociation of H_2 gas molecules with the following reaction:

$$OH + H_2 + F \rightarrow H + H_2O + F$$

Here F represents functional groups attached on the functionalized nanotubes. On the other hand, when H_2 gas is off these functional groups again help in desorption process by the following reaction:

$$H_2O + F \rightarrow O + H_2 + F$$

The coated material SnO_2 is n-type semiconductor, so majority charge carriers are electrons. However, it is partially covering on the nanotubes, therefore, the majority carriers are still holes in F-MWCNTs/SnO_2. Fig. 5 shows the schematic representation of sensing mechanism of the reported sensors. When this sensor exposed to H_2 gas, the O^- adsorbates react with H_2 gas molecules and release electrons to the conduction band of SnO_2, which are transferred to F-MWCNTs and hence lower the holes carrier concentration. As a result, the resistance of the F-MWCNTs/SnO_2 network sensor increases, as observed in Fig. 4 (a). Similar type of observation was reported by other researchers [11].

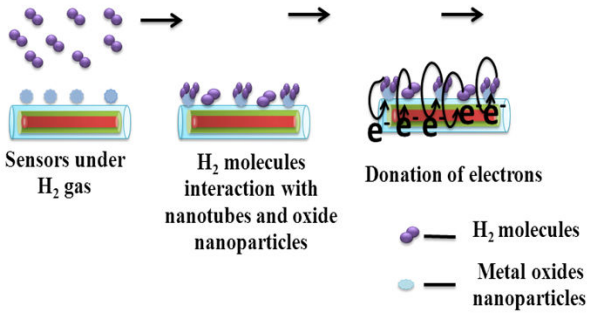


Fig. 5 Schematic representation of sensing mechanism

ACKNOWLEDGEMENT

Authors acknowledge the support and help for the fabrication of the devices and sensing measurements carried out at the Center of Excellence in Nanoelectronics (CEN) under Indian Nanoelectronics Users' Programme at Indian Institute of Technology (IIT), Bombay which has been sponsored by Department of information Technology (DIT), Government of India.

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