

Hydrogen Gas Sensing Properties of Multiwalled Carbon Nanotubes Network Partially Coated with SnO₂ Nanoparticles at Room Temperature

Neena Jaggi, Shivani Dhall

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/SnO₂ sensor shows good sensitivity as compared to F-MWCNTs for low concentration (0.05-1% by volume) of H₂ gas. The fabricated sensors show complete resistance recovery and good repeatability when exposed to H₂ gas at the room temperature conditions.

Keywords—F-MWCNTs, SnO₂ nanoparticles, Chemiresistor, I-V Characteristics, H₂ Sensing.

I. INTRODUCTION

NOWADAYS, hydrogen (H₂) gas is rising as a promising fuel source to replace available fossil fuels. H₂ based fuel finds many applications in civil transportation and in rockets for space vehicles, so fabrication of H₂ gas sensor is very necessary for its safe and controlled use [1], [2]. Therefore, H₂ 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. NO₂ & O₂) and reducing (electron donating, e.g. NH₃ & H₂) 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 H₂, CO, NH₃ and CH₄ [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 H₂ gas at room temperature using 2% by wt. partially attached SnO₂ nanoparticles functionalized MWCNTs. Here, we have used only 100x120 μm² area of fabricated interdigitated electrodes (IDEs) to detect the low concentrations (0.05 to 1% by volume) of H₂ gas. In addition, a simple approach has been used for to fabricate SnO₂ 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(SnCl₄•5H₂O) and stirred for 4-5 h at room temperature conditions. Then solution of NH₄OH was added drop wise into above solution so as to achieve pH 8-8.5. After precipitation, the sediment is kept at 50°C for 24 h stirred and washed with distilled water many times to remove chlorine-ions and then dried at 100-120°C for few hours. This prepared sample was called F-MWCNTs/SnO₂. 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.

Neena Jaggi is with the, National Institute of Technology, Kurukshetra, Haryana, India (Corresponding author phone: +918950263809; fax: +9111744238050; e-mail:neena_jaggi@rediffmail.com).

Shivani Dhall is with the, National Institute of Technology, Kurukshetra, Haryana, India (e-mail: shivani.dhall24@gmail.com).

C. Experimental Set Up of Sensing

Sensor response of the samples was measured in home-made system. In the whole experiment, N₂ 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 H₂ 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 N₂ gas and R_H is the resistance of sensor after exposing to H₂ gas.

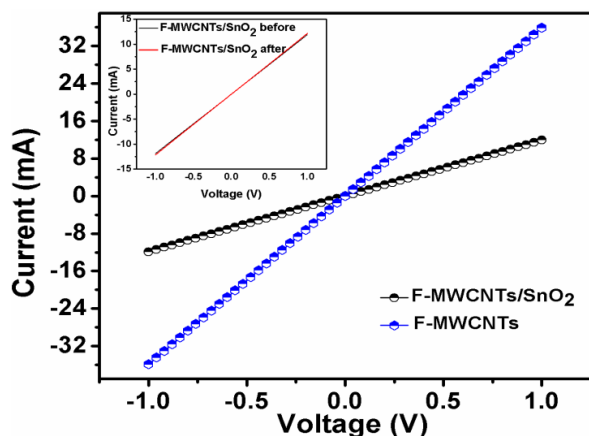


Fig. 1 Comparison in I-V characteristics of F-MWCNTs and F-MWCNTs/SnO₂ composite

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/SnO₂. The current in F-MWCNTs/SnO₂ 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/SnO₂) is confirmed by linear I-V characteristics [10]. In addition, the linear I-V curve of F-MWCNTs/SnO₂

indicates the formation of ohmic contacts between SnO₂ nanoparticles and nanotubes.

The morphology of pristine MWCNTs and SnO₂ nanoparticles attached functionalized MWCNTs composite as elucidated by SEM are shown in Figs. 2 (a) and (b) respectively. It indicates that, SnO₂ nanoparticles of different sizes were dispersed on the nanotubes network.

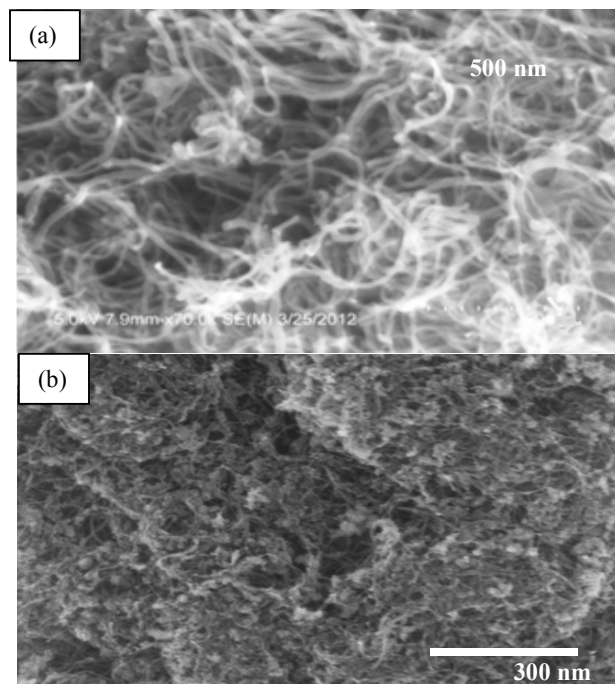


Fig. 2 (a) SEM image of P-MWCNTs (b) SEM image of F-MWCNTs/SnO₂ composite

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 N₂ and H₂ 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 (H₂ and NH₃) and increases when kept in oxidizing gas (O₂ and NO₂). 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 H₂ atmosphere and then reaching a maximum value. Fig. 4 (a) shows the sensing characteristics of F-MWCNTs/SnO₂ composite. The sensitivity of this sensor is found to increase to 2.8% for 0.05% concentration of H₂ gas as compared to the F-MWCNTs with sensitivity 0.8% for same amount of H₂ 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/SnO₂ 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 H₂ gas in N₂ atmosphere. Furthermore, a relationship between the sensitivity and H₂ concentrations is also obtained, as seen in Fig. 4 (b). The recovery time of F-MWCNTs/SnO₂ sensor (Fig. 4 (b)) is increased from 9 s for 0.05% H₂ to 30 s for 1% H₂ gas. The same type of increment in the recovery time has been observed for F-MWCNTs sensor which recovers in 100s for 1% H₂ gas. The inset of Fig. 4 (b) shows the comparison in sensitivity for 0.05% concentration of H₂ gas for various materials. The repeatability of this sensor for the low concentration (0.05%) of H₂ gas indicates that, the sensitivity of the sensor does not deteriorate after repeated exposure to H₂ gas, which confirms that sensing characteristics are reproducible.

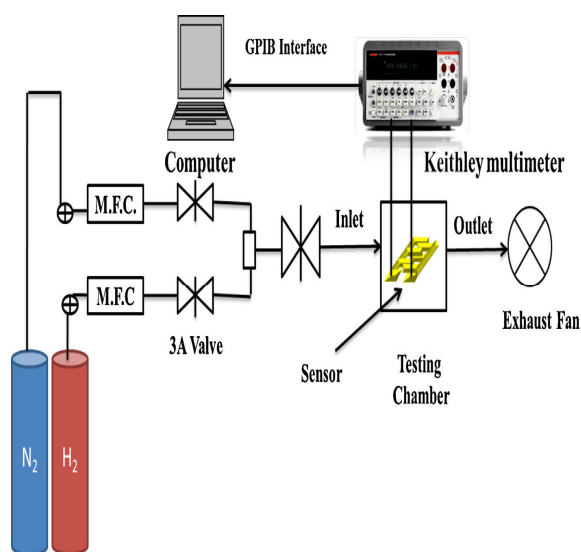


Fig. 3 Experimental setup of gas sensing

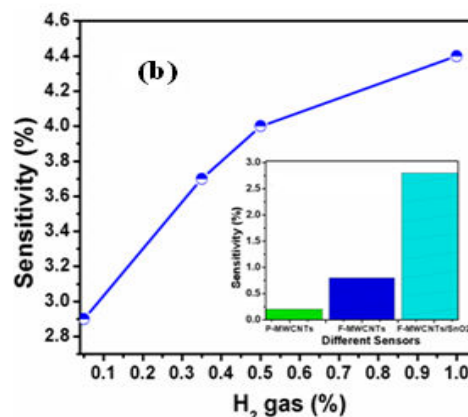
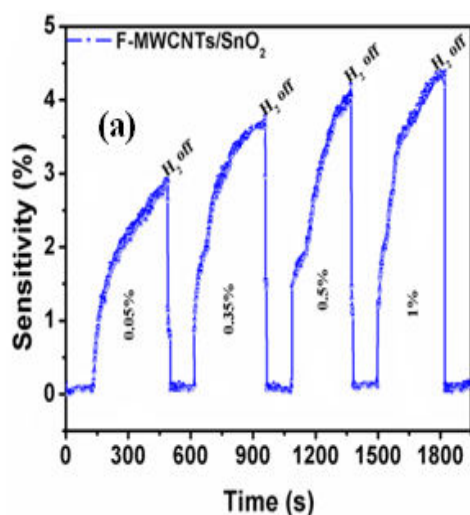
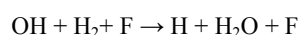
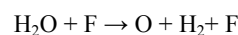


Fig. 4 (a) Sensitivity of F-MWCNTs/SnO₂ at different concentrations of H₂ gas (b) variations in sensitivity with H₂ gas concentrations

In the present case, two types of mechanisms can be possible; one between F-MWCNTs and second in partially covered nanotubes by SnO₂ nanoparticles. As we know the reducing H₂ gas molecules have lone electrons pair that are donated to the nanotubes and oxides nanoparticles when sensors are exposed to H₂ gas. Thus, H₂ 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 H₂ gas molecules with the following reaction:



Here F represents functional groups attached on the functionalized nanotubes. On the other hand, when H₂ gas is off these functional groups again help in desorption process by the following reaction:



The coated material SnO₂ 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/SnO₂. Fig. 5 shows the schematic representation of sensing mechanism of the reported sensors. When this sensor exposed to H₂ gas, the O⁻ adsorbates react with H₂ gas molecules and release electrons to the conduction band of SnO₂, which are transferred to F-MWCNTs and hence lower the holes carrier concentration. As a result, the resistance of the F-MWCNTs/SnO₂ network sensor increases, as observed in Fig. 4 (a). Similar type of observation was reported by other researchers [11].

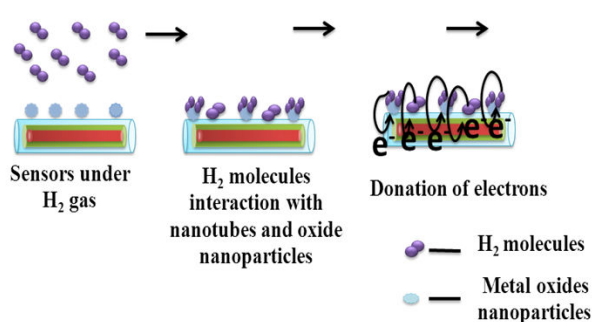


Fig. 5 Schematic representation of sensing mechanism

Spectroscopy and Nanotechnology focused on fabrication of composite materials of carbon nanotubes for hydrogen gas sensing at room temperature.

Shivani Dhall is pursuing Ph.D. at National Institute of Technology, Kurukshetra Haryana, India. Her current research interests include structural, spectroscopic and electrical studies of carbon materials and fabrication of nano devices for application as Hydrogen gas sensors.

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.

REFERENCES

- [1] V.M. Aroutiounian, "Hydrogen detectors," *Int J of Alternative Energy Ecol.*, vol. 23, pp 21-31, 2005.
- [2] V.M Aroutiounian, "Metal oxide hydrogen, oxygen, and carbon monoxide sensors for hydrogen setups and cells," *Int J Hydrogen Energy*, vol. 32, pp 1145-58,2007.
- [3] S. Dhall, N. Jaggi and R. Nathawat, "Functionalized multiwalled carbon nanotubes based hydrogen gas sensor," *Sens. and Actu. A*, vol. 201, pp 221-227, 2013.
- [4] L.D. Luca, A. Donato, S.Santangelo, G. Faggio, G. Messina, N. Donato and G. Neri, "Hydrogen sensing characteristics of Pt/TiO₂/MWCNTs composites," *Int. J. Hydrogen Energy*, vol.37, pp 1842-47, 2012.
- [5] C. Wongchoosuk, A. Wisitsoraat, D. Phokharatkul, A. Tuantranont and T. Kercharoen, "Multi-Walled Carbon Nanotube-Doped Tungsten Oxide Thin Films for Hydrogen Gas Sensing," *Sensors*, vol.10, pp 7705-15, 2010.
- [6] S. Trocino, A. Donato, M. Latino, N. Donato, S. G. Lenonardi and G. Neri Pt-TiO₂/MWCNTs "Hybrid composites for monitoring low hydrogen concentrations in air," *Sensors*, vol. 12, pp 12361-73, 2012.
- [7] S. Dhall and N. Jaggi, "Hydrogen Sensing of NiO and Cu₂O/Multiwalled Carbon Nanotubes Nanostructures at Room Temperature," *Sensor Lett.*, vol. 12, pp 1-6, 2014.
- [8] A. Star, V. Joshi, S. Skarupo, D. Thomas and J.C.P. Gabriel, "Gas Sensor Array Based on Metal-Decorated Carbon Nanotubes," *Phys. Chem. B*, vol.110, pp 21014-20, 2006.
- [9] A. Kaniyoor and S. Ramaprabhu, "Hybrid carbon nanostructured ensembles as chemiresistive hydrogen gas sensors," *Carbon*, vol. 49, pp 227-236, 2011.
- [10] V. V. Bolotov, V. E. Kan, P. M. Korusenko, S. N. Nesov, S. N. Povoroznyuk, I. V. Ponomareva, V. E. Roslikov, Yu. A. Sten'kin, R. V. Shelyagin and E. V. Knyazev, "Formation mechanisms of nanocomposite layers based on multiwalled carbon nanotubes and non-stoichiometric tin oxide," *Physics of the Solid State*, vol. 54, pp. 166-173, 2012.
- [11] M. Yang, D. H. Kim, W. S. Kim, T. J. Kang, B. Y. Lee, S. Hong, Y. H. Kim and S. H. Hong, "H₂ sensing characteristics of SnO₂ coated single wall carbon nanotube network sensors," *Nanotechnology*, vol. 21, pp 215501, 2010.

Neena Jaggi is working as Professor in Physics at National Institute of Technology, Kurukshetra Haryana, India. She has a long teaching and research experience of about 25 years. Her present areas of research are