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Low Temperature Ethanol Gas Sensor based on SnO_2/MWNTs Nanocomposite

O. Alizadeh Sahraei, A. Khodadadi, Y. Mortazavi, M. Vesali Naseh, and S. Mosadegh

***Abstract*—**A composite made of plasma functionalized multiwall carbon nanotubes (MWNTs) coated with SnO_2 was synthesized by sonochemical precipitation method. Thick layer of this nanocomposite material was used as ethanol sensor at low temperatures. The composite sensitivity for ethanol has increased by a factor of 2 at room temperature and by a factor of 13 at 250˚C in comparison to that of pure SnO_2. SEM image of nanocomposite material showed MWNTs were embedded in SnO_2 matrix and also a higher surface area was observed in the presence of functionalized MWNTs. Greatly improved sensitivity of the composite material to ethanol can be attributed to new gas accessing passes through MWNTs and higher specific surface area.

***Keywords*—**Carbon nanotube, Functionalized, Gas sensor, Low temperature, Nanocomposite, Tin oxide.

I. Introduction

SnO_2 is an n-type semiconductor oxide with wide band gap energy and is always applied as gas sensing material to detect combustible, toxic and pollutant gases because of high sensitivity, simple design and low cost [1].

One of the disadvantages of tin oxide gas sensors is that they typically operate at elevated temperatures (higher than 200˚C). Operating at high temperatures may cause coalescence and structural changes [2] which leads to sensor instability and response variation. Fabricating sensing materials with low operating temperatures can inhibit structural changes, reduces the power consumption and enables safer detection of combustible gases.

Since the sensing mechanism of these devices is based on the chemisorption reaction that take place at the surface of the metal oxide, so increasing specific surface area of the sensitive materials leads to more sites for adsorption of surrounding gases [3], [4].

Some recent researches have been concentrated on improving gas sensitivity as well as reducing operating temperature by introducing dopants or decreasing SnO_2 particle size to nanoscale lower than 10 nm [5]-[8].

On the other hand, carbon nanotubes (CNTs) have become amazing nanostructured materials. Because of their high specific surface area and hollow interior, CNTs can be served as nanometer sized capillaries, mould or template in material fabrication. A number of modifications by functionalizing, doping or coating either in part or completely have been suggest to further improve the properties of CNTs [9]-[16]. The high surface area of CNTs with narrow pore size distribution is also very important to applications used as substrates for external coating.

However, there are some reports about coating of MWNTs with a thin and uniform layer of SnO_2 and using this nanocomposite material as chemical gas sensor [17]-[19]. According to these researches the nanocomposite material gas sensing property has improved in comparison to blank SnO_2 but many of them still operate at elevated temperatures and it seems that experimental data on SnO_2/MWNTs nanocomposite based gas sensors operating at room temperature are still low.

In this paper we synthesized SnO_2/MWNTs nanocomposite by sonochemical precipitation of tin oxide on CNTs dispersed in an aqueous solution. Sensitivity of the nanocomposite to ethanol is compared with that of SnO_2.

II. Experimental Procedure

A. Functionalization of Multiwall Carbon Nanotube

MWNTs grown by chemical vapor deposition (CVD) of methane on ferrocene, as a floating catalyst at 800°C, were used for the preparation of the composite. The as-prepared nanotubes were functionalized by plasma treatment in a dielectric barrier discharge (DBD) quartz chamber at atmospheric pressure, using a voltage of 8 kV and the treatment time of 4 min. A controlled flow of air was introduced inside the chamber.

B. Coating of MWNTs with SnO_2

In a typical precipitation reaction, 0.3 mg DBD plasma functionalized MWNTs were sonicated in 50 Ml of 0.15

O. Alizadeh Sahraei is a M.Sc. student and a research assistant in the Catalysis and Reaction Engineering Laboratory, University of Tehran since 2006. Email: baninalizadeh@gmail.com

A. Khodadadi is with Department of Chemical Engineering, P.O. Box 11365/4563, University of Tehran, Tehran, Iran; E-mail: Khodadad@ut.ac.ir.

Y. Mortazavi is with Nanoelectronics Center of Excellence, University of Tehran, Tehran, Iran. .(corresponding author to provide phone: +98 21 66967793 ; fax: +98 2166967793. Email: mortazav@ut.ac.ir

M. Vesali Naseh is a M.Sc. student and a research assistant in the Catalysis and Reaction Engineering Laboratory, University of Tehran since 2006. Email: *masood.vesali@gmail.com*

S. Mosadegh is an M.Sc. student and a research assistant at the Catalysis and Reaction Engineering Laboratory, University of Tehran since 2006. Email:sanaz.mosadegh@gmail.com

mol/L tin (IV) chloride solution with Heilscher 250 UL ultrasound system for 2 h at 70˚C. During the reaction ammonia was added to keep a constant PH of about 9. The resulting precipitate was collected by centrifugation and washed with distilled water for several times and dried at 70˚C overnight. Finally the MWNTs/SnO_2 nanocomposite material was obtained by calcination of the dried sample at 400˚C for 2 h. The concentration of MWNTs in nanocomposite material was approximately 0.026 wt%.

C. Material Characterization

A Philips XL 30 scanning electron microscope (SEM) was used to investigate the morphology of the materials. Brunauer–Emmett–Teller (BET) surface area of the samples was measured by using a Quantachrome CHEMBET 3000.

D. Gas Sensing Measurements

The nanocomposite sample was dispersed in water by ultrasonic vibration, and then a drop of the well mixed suspension was coated between two Au printed electrodes on to the surface of an alumina substrate. Fig. 1 shows the structure of the as-prepared gas sensor, thereafter the coating layer were heated in air at approximately 100˚C for 1 h, to evaporate the water in the coating layers. Finally, the coating layer was sintered at 400˚ C for 1 h. The electrodes of the sensors were then connected to signal Pt wires to enable electrical measurement.

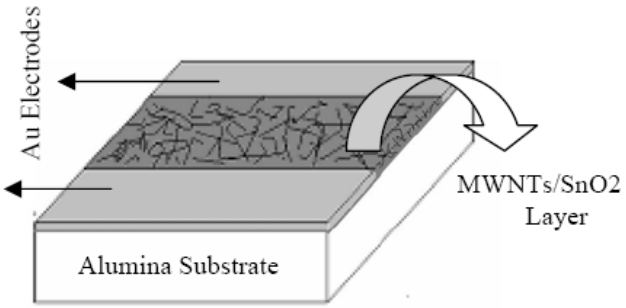

Fig. 1 Schematic diagram of MWNTs/ SnO_2 sensor lay-out

III. RESULTS AND DISCUSSION

A. Material Characterization

An SEM micrograph of the nanocomposite sample is shown in Fig. 2. MWNTs are imbedded tightly in the SnO_2 matrix. The MWNTs were well dispersed and there is no obvious agglomeration of MWNTs, i.e. the tubes are uniformly distributed inside the SnO_2 substrate.

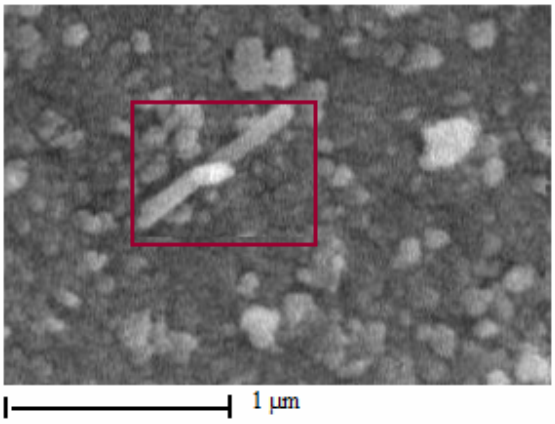

Fig. 2: SEM images of nanocomposite MWNTs/SnO_2.

Specific surface area of SnO_2 and its nanocomposite with MWNTs are 43 and 87 m^2/g, respectively. Two times increase in BET area of the nanocomposite can be attributed to the introduction of functionalized carbon nanotubes with high surface area of 382 m^2/g and smaller size tin oxide nanoparticles formed on the carbon nanotubes. Because of inert property, nanosized structure and high surface energy of carbon nanotubes, dispersion of them in any composite material is difficult. To overcome this problem, chemical functionalization is used. It has been reported that functional groups on carbon nanotubes can act as nucleation center for metal ions [20]. With the help of the functional groups attached to the surface by functionalization, carbon nanotubes could be well dispersed due to the electrostatic force repulsion from the charged functional groups such as carboxylic and hydroxyl groups. J. Xie and V. Vardan [21] have reported that functional carbon nanotubes play a critical role for nucleation and anchoring of fine tin oxide nanoparticles and also prevent the following possible coagulation and flocculation process.

B. Gas Sensing Performance

Fig. 4 plots a typical response curve of 0.026 wt% MWNTs/SnO_2 nanocomposite sensor to 1000 ppm ethanol at 80˚C. The sensor first exposed to air and its resistance was measured (R_{Air}) then it was exposed to 1000 ppm ethanol and the resistance reached quickly to a stable value of R_{gas}. Then the sensor was exposed to air at temperatures higher than 250^{o}C for about 30 min to recover.

Fig. 4 shows that the resistance of the sensor decreases upon exposure to ethanol. Ethanol is an electron donating gas. Therefore, the nanocomposite can be assumed to be an n-type semiconductor.

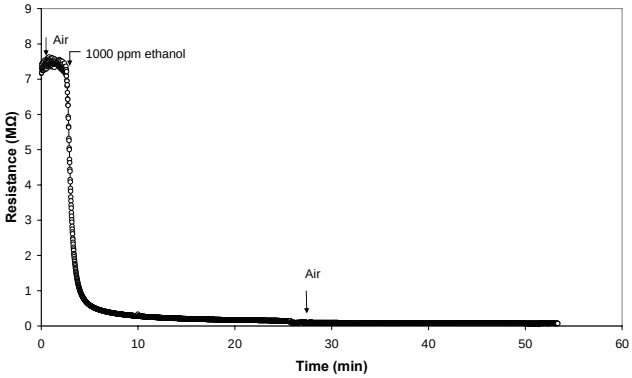

Fig. 4 Response curve of MWNTs/SnO_2 nanocomposite to 1000 ppm ethanol at 80˚C

The sensitivity (S) of the sensor defined by the relative resistance, R_{Air}/ R_{gas}, where R_{Air} and R_{gas} are defined before.

Fig. 5 plots the sensitivity versus temperature of nanocomposite MWNTs/SnO_2 and blank SnO_2 sensors. Clearly nanocomposite sensor has a higher sensitivity to ethanol than the blank one. For example at 80˚C the sensitivity of nanocomposite sensor is 8.8 times higher than blank one, this results suggest that doping with MWNTs effectively enhances the sensitivity to ethanol gas at different temperatures.

C. Discussion

Due to BET analysis test results, compared with blank tin oxide, much higher surface area were observed in the presence of functionalized carbon nanotubes in MWNTs/SnO_2 composite. This higher surface area plays an important role in sensitivity improvement of MWNTs/SnO_2 nanocomposite material compared with blank SnO_2.

On the other hand, in MWNTs/SnO_2 composite, carbon nanotubes are embedded within the SnO_2 matrix. Since SnO_2 behaves as n-type semiconductors and carbon nanotubes as p-type semiconductors [22], the n-p hetrostructure are formed at the interface between tin oxide and carbon nanotubes. The formation of such n-p hetrostructure are reported by different others [23], [24]. In nanocomposite sensitive films, two different depletion layers co-exist. One is on the surface of SnO_2 particles and the other is in the interface between MWNTs and SnO_2.The adsorption of ethanol at the tin oxide changes the depletion layer at the surface of SnO_2 particles and also at the p-MWNTs/n-SnO_2 hetrostructure. These two effects may be the other reason for improvement in sensitivity of tin oxide based nanocomposite sensors.

IV. Conclusion

Oxygen functionalized MWNTs, by dielectric barrier discharge plasma, were introduced during the formation of tin oxide nanoparticles by sonochemical precipitation method. BET analysis showed that the surface area of MWNTs/SnO_2 nanocomposite is much higher than blank SnO_2 nanoparticles.

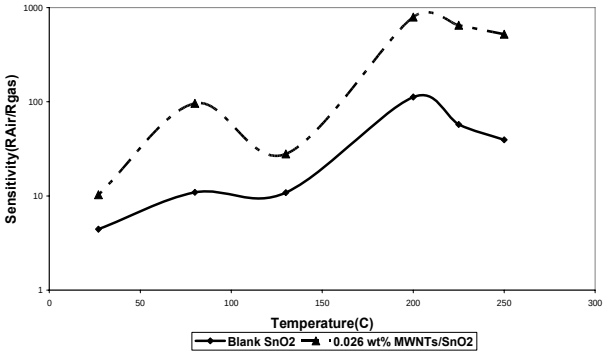

Fig. 5 Sensitivity comparison of blank SnO_2 with MWNTs/SnO_2 nanocomposite at different temperatures

This nanocomposite could be used as a high performance ethanol sensor. It is observed that adding a small quantity of oxygen functionalized MWNTs to SnO_2 matrix can drastically improve the sensitivity of tin oxide based sensor at low temperatures.

It is assumed that two different depletion layers co-exist in nanocomposite material, one is on the surface of SnO_2 particles and the other is in the interface between MWNTs and SnO_2 and modulation of the width of these two depletion layers is postulated as the mechanism of enhanced ethanol sensitivity of nanocomposite MWNTs/SnO_2 in comparison with SnO_2 blank nanoparticles.

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