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Specific NH_3 Gas Sensor Worked at Room Temperature Based on MWCNTs-OH Network

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Abstract. Functionalized Multi-Walled Carbon Nanotubes (MWCNTs-OH) network with thickness 4μm was made by the vacuum filtration from suspension (FFS) method. The morphology, structure and optical properties of the MWCNTs film were characterized by SEM and UV-Vis. spectra techniques. The SEM images reflected highly ordered network in the form of ropes or bundles with close-packing which looks like spaghetti. The absorbance spectrum revealed that the network has a good absorbance in the UV-Vis. region. The gas sensor system was used to test the MWCNT-OH network to detect NH_3 gas at room temperature. The resistance of the sensor was increased when exposed to the NH_3 gas. The sensitivities of the network were 1.3% at 14ppm, 3.3% at 27ppm and 6.13% at 68ppm. The sensor is specifically sensitive to NH_3 gas and does not affect by the amount of ambient air.

Introduction

Gas sensors, or chemical sensors, are attracting tremendous interest because of their widespread applications. Gas sensors with high sensitivity and selectivity are required for leakage detections of explosive gases such as hydrogen, and for real-time detections of toxic or pathogenic gases in industries. In general, there are some basic criteria for good and efficient gas sensors: (i) high sensitivity and selectivity; (ii) fast response time and recovery time; (iii) low analyst consumption; (iv) low operating temperature and temperature independence; (v) stability in performances [1]. CNTs are the strongest and most flexible molecular material known according to the unique C–C covalent bonding and seamless hexagonal network. The CNTs have electrical conductivity or semiconductivity, and high thermal conductivity in the axial direction [2].

The electronic properties of CNTs are extremely sensitive to the chemical environment, so they are ideal candidates for gas/chemical sensors. The electrical detection of a gas with CNTs depends on the change in electrical characteristics of nanotubes upon their interactions with gas molecules. The charge transfer between gas species and CNTs may be responsible for the conductivity change in the tubes [3]. The electrical properties of nanostructure are dramatically changed when exposed to the target gas analysis. The resistivity change of the sensors is related with the oxidation-reduction of gas adsorbed on the sensor surface [4]. CNTs composites have been found to act as a gas sensor by possessing electrical conductance highly sensitive to minimum amounts of ammonia (NH_3) and other gaseous [5]. Functionalization of CNTs has been proposed to promote the charge transfer between specific gas species and CNTs [3]. NH_3 and NO_2 gases are very useful for industries and agricultural, but exposure to these gases effects on the health of human beings as well as harmful to the surrounding. Proper detection of these gases will be very useful. Development of highly sensitive devices for monitoring and controlling purposes continued intensively around the world [6].

Sensitivity can be measured in different ways, such as through the electrical resistance [7- 9], conductivity [10] and density functional theory (DFT) calculations [4].

Experimental Work

MWCNTs-OH network with thickness 4μm was prepared by using short MWCNTs functionalized with 5.3-5.86% OH from Nanostructured and Amorphous Materials, Inc (with purity of > 95.0%, the outside diameter of the tubes was < 8 nm and the length ~ 0.5-2 μm) by filtration from suspension method (FFS).

To prepare CNTs suspension, adding 15 mg of functionalized nanotubes to 5 ml of N, N Dimethylformamide (DMF) solution (with the formula C_3H_7NO, molecular weight 73.09 and density 0.945 gm/ml (at 25 °C) which supplied by Biosolve Company) and sonication for 5min by an ultrasonic probe for a homogeneous distribution. At the same time and on the other side, 60 mg of benzoquinone (P- Benzoquinone (BQ) with the formula $C_6H_4O_2$ supplied by Sigma –Aldrich with purses > 95.5% (HPLC),) was dissolved in 10 ml of DMF. While the CNTs under sonication the solvent of BQ were added slowly and gradually. The cross-linker is effective for interactions breaking up the CNTs agglomeration and produces a small network. This is achieved by sonicating the mixture for 15 min. using an ultrasonic probe until the mixture becomes homogenous. Finally, the homogeneous mixture was filtered by Millipore filtration from suspension system with the aid of filter cake, by applying vacuum and temperature. The filter paper was purchased from Chm Company, F1001 grad, cat No. 1001-150 with medium porosity.

The structure of MWCNTs-OH network was observed by JSM-7610F scanning electron microscopy (SEM) while the optical properties of the prepared network were tested by UV-1650PC double beam UV-Vis. spectrophotometer from Shimadzu Co. with scanning range (200-1100 nm). The vibrational and rotational modes of MWCNTs-OH network was studied by VENTANA 532 Raman spectrometer from Ocean Optics Co. with CW laser of 100mW power.

Small films of MWCNTs-OH networks (length 8 mm, width 6 mm and thickness 4μm) were exposed to the NH_3 gas at room temperature to be tested as a gas sensor. The electrical resistance of the film's network was measured along the specimen length by the two-point technique using digital multimeter victor 70C. The film was placed on a plate inside a stainless steel vacuum chamber. Stainless steel chamber connected with separate gas inlet and outlet as in figure (1).

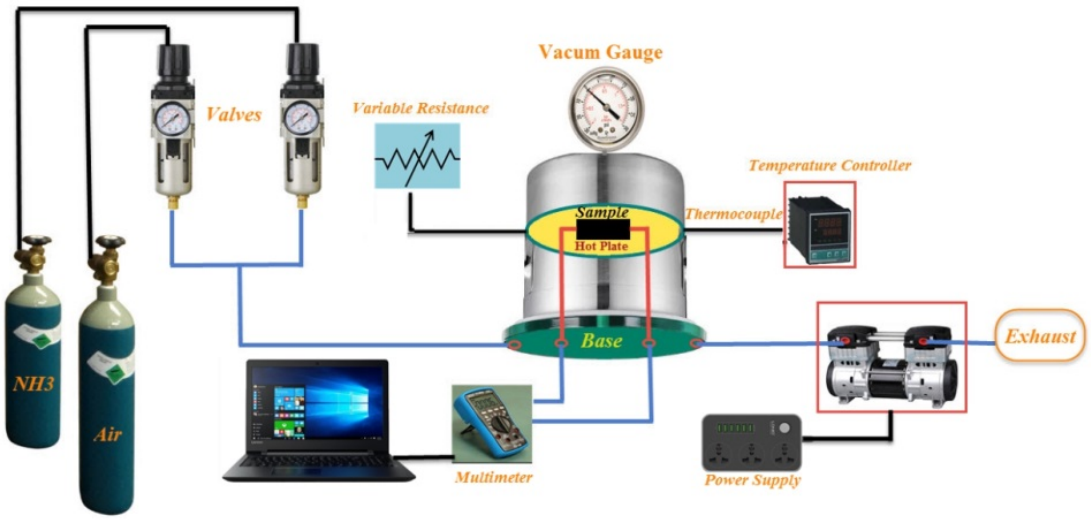

Figure 1: Schematic diagram of the gas sensor system.

Ambient air and NH_3 gas were used as the carrier and test gases, respectively. The two gases were mixed and fed into the chamber from separated lines through the gas inlet line. Valves and gauges were used to control the flow rates of air and NH_3 gas or gas-air mixture. The sensitivity of the film was measured by evacuation the chamber for 10min and reached to initial steady resistance value under ambient conditions. The sensor was exposed to the laboratory air and the resistance had been recorded for 10 min. After evacuation the chamber for 10 min again, the film firstly exposed to the NH_3 gas and secondly to the NH_3-air mixture and recording the resistance again. This cycle was repeated several times to confirm the validity of the results and take the average values.

Results and Discussion

The MWCNTs-OH network of 4µm thickness, which prepared using the FFS method is shown in figure (2-a). The prepared discs which appeared stuck on the filter paper were uniform, smooth and crack-free, with a regular and consistent structure that made it easy to use as a gas sensor. Figure (2b and c) shows the SEM images of MWCNTs-OH network for 1µm and 500nm magnification respectively.

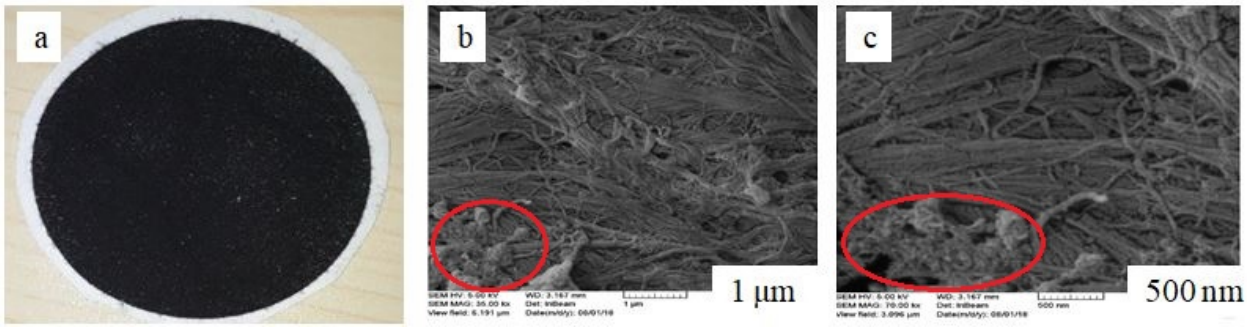

Figure 2: Film of MWCNTs-OH network (a), SEM images of MWCNTs-OH network for (b) 1µm, (c) 500nm magnification.

It observes that the CNTs film composed of randomly entangled structures which look like spaghetti. Because of the strong inter-tube Van der Waals forces, MWCNTs-OH network arranged in ropes or bundles with close-packing stacking.

This affected on the homogeneity of the suspension and caused agglomerations in the network were appearing in some areas (because the ultrasonic probe does not reach to the end of the suspension's tube) surrounded by the red line of the morphology image.

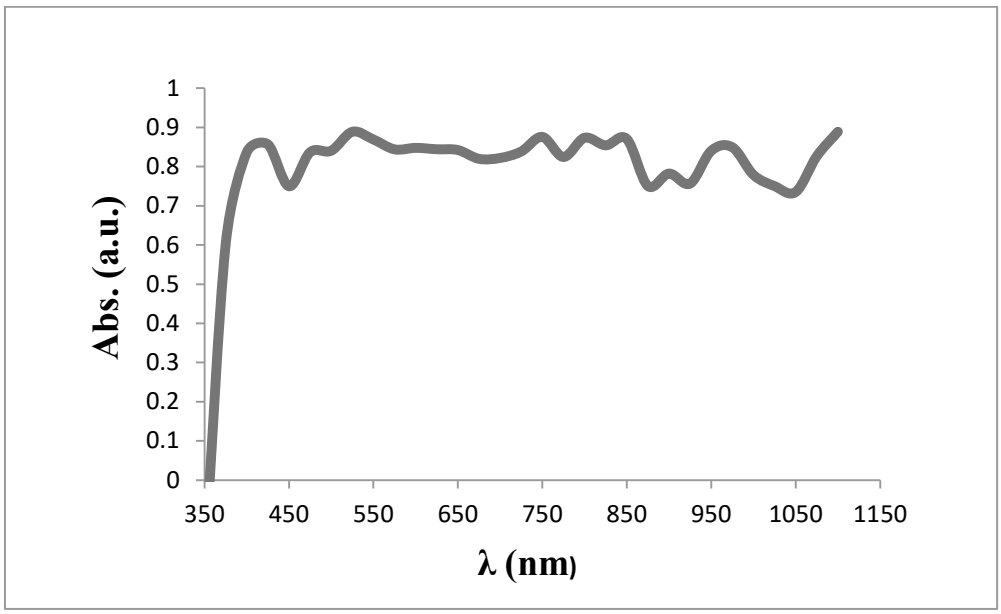

Figure 3: Absorbance spectrum for the film of MWCNTs-OH network prepared by FFS method.

Figure (3) shows the absorbance spectrum as a function of wavelength in the range (350-1100) nm of MWCNTs-OH network. The figure shows that the maximum absorption wavelength is in the range of 400 –1100 nm, which is mean the network absorbed the spectrum in Vis-NIR region. This result in agreement with [11]. Many sharp peaks have appeared in the absorbance spectrum, such as 400, 475, 525, 750, 800, 850, 950 and 1100 nm, respectively, these peaks may be attributed to the network structure as a mat.

The Raman shift spectra for the MWCNTs-OH network is shown in figure (4) with excitation wavelength 532nm at room temperature.

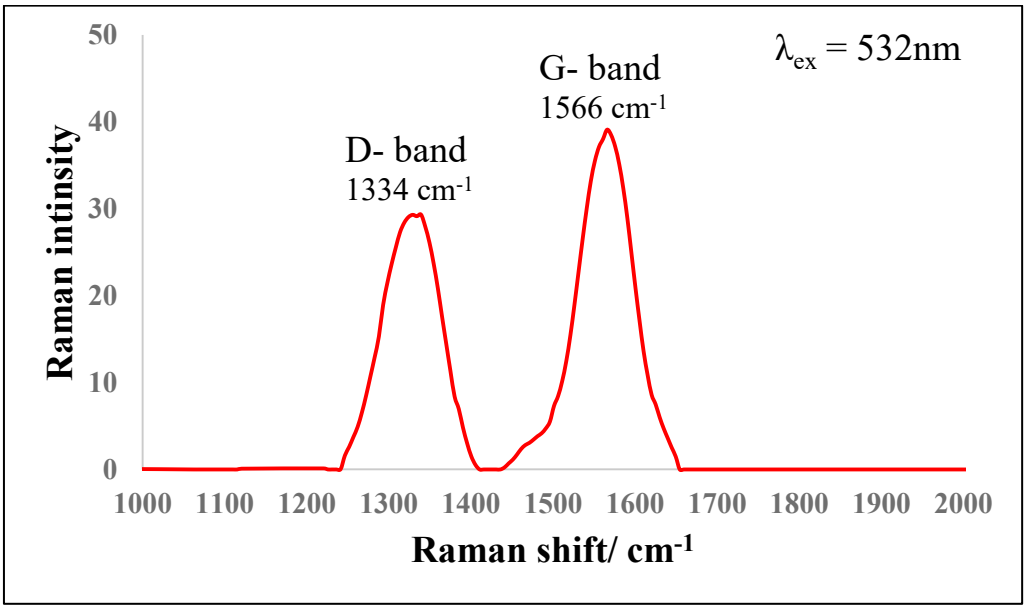

Figure 4: Raman spectra for the film of MWCNTs-OH network prepared by FFS method.

Figure (4) appears the two major peaks D (disordered sp^2 carbon) and G (graphite or crystalline sp^2 carbon) bands for MWCNTs-OH network. D band which is referring to a structural disorder of the CNTs around 1334 cm^{-1}. The second peak G band is identified at 1566 cm^{-1}.

The quality of the sample can be evaluated from the ratio of intensities of D band to G band. The smallest value of this ratio refers to the small structural defects in CNTs. The I_D/I_G ratio of MWCNT-OH network is about 0.74 that is illustrating the disorder estimation (qualitative) which suggests good crystallinity. These results are in agreements and nearly from the results of [12- 14]. The typical adsorption/desorption behavior of MWCNTs-OH network exposed to the NH_3 gas had been studied in this work. The sensitivity of the prepared devices is measured using the normalized electric resistance equation [15- 17]:

$$S\% = \frac{R_g - R_\circ}{R_\circ} \times 100\% \quad (1)$$

where R_g represents the gas resistance interaction with the sensitive material, and R_o refers to the ambient air resistance.

The resistance change was used because the film has high electrical resistance reach to some KΩ. Therefore, the resistance change has been cleared after exposure to the gas.

Figures (5-7) shows the resistance of the sensor as a function of time for different exposed NH3 gas concentration. Figure (5) shows the response of MWCNTs-OH to 14 ppm of pure NH3 gas and mixture of different ratios of ambient air represented as air: gas ratio.

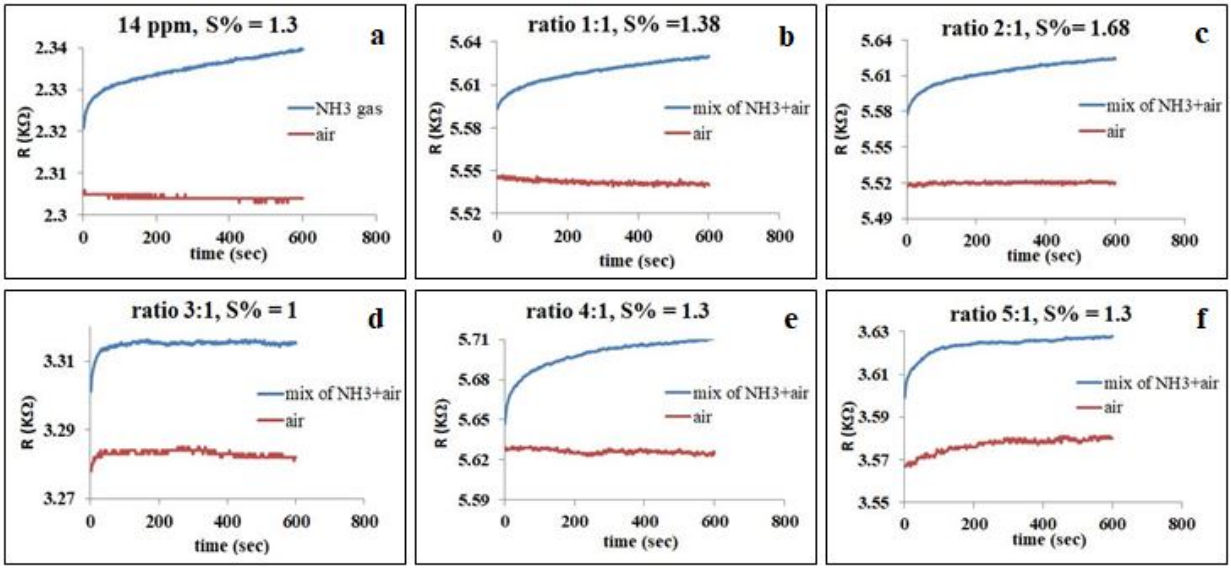

Figure 5: MWCNTs-OH sensor resistance as a function of time when exposed to a) 14ppm of pure NH_3 gas, a mixture of ambient air with 14ppm of NH_3 gas as a ratio air:gas b)1:1, c) 2:1, d) 3:1, e) 4:1 and f) 5:1.

It's clear that the resistance of the sensor after exposure to ambient air for 10 min. was an approximately constant comparison with the resistance of the sensor when exposed to the NH_3 gas of concentration 14ppm and/or a mixture of air with NH_3 which is exponentially increased with time. Increasing the sensor resistance return to the unique electronic properties of CNTs, which is extremely sensitive to their local chemical environment, making them ideal candidates for gas/chemical sensors. The electrical detection of a gas with CNTs is based on the change in electrical characteristics of CNTs upon their interactions with gas molecules [3]. In general; oxidizing gases (e.g., NO_2) withdraw electrons from CNTs, whereas reducing gases (e.g., NH_3, H_2, and CO) donate electrons to CNTs, which could lead to opposite changes in the electrical conductivity of CNTs [3, 16]. The electronic property changes of CNTs upon exposure to gas molecules are attributed to the charge transfer between the molecules and the nanotubes (the molecules act as electron donors or acceptors) [1]. A rich π- electron conjugation forms outside of the CNTs, making them electrochemically active, sensitive to charge transfer and chemical doping effects by various molecules and impurities [18]. The adsorption of electron-donating (e.g., NH_3) molecules onto the surface of CNTs causes a charge transfer between CNTs and the gas molecules with a typical *p*-type electrical behavior of semiconducting carbon nanotubes. Hole carriers are decreased in the CNTs when exposed to NH_3 gas, causing an increase in their resistance [19].

By applying equation (1), the sensitivity of the sensor for 14ppm of pure NH_3 gas was 1.3% and the sensitivities of the sensor, when exposed to the mixture of air-NH_3, were 1.38%, 1.68%, 1%, 1.3% and 1.3% for ratios 1:1, 2:1, 3:1, 4:1and 5:1, respectively. According to the results, MWCNTs-OH network not affected by the ratio of ambient air and can be detected even with a small concentration of gas pollution. This is approving that the prepared network is stable, active and specific for NH_3 detection at room temperature. The behavior of MWCNTs-OH network, when exposed to high concentration of gas and/or a mixture of gas and air, has been shown in figures (6-7).

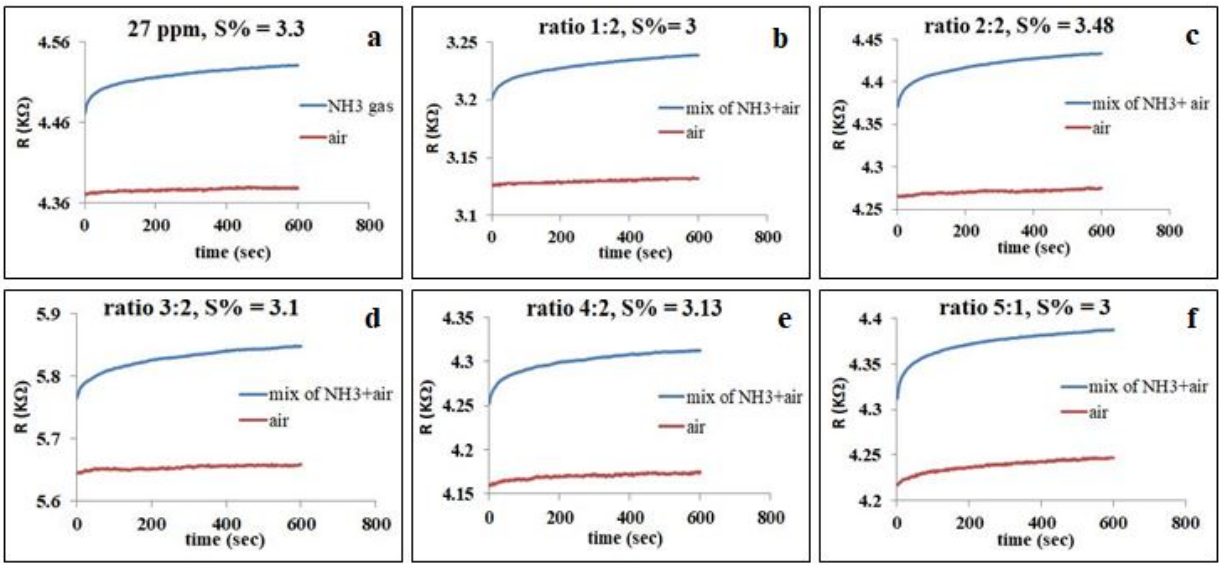

Figure 6: MWCNTs-OH sensor resistance as a function of time when exposed to a) 27ppm of pure NH_3 gas, a mixture of ambient air with 27ppm of NH_3 gas as a ratio air:gas b)1:2, c) 2:2, d) 3:2, e) 4:2 and f) 5:2.

Figure (6) shows that the resistance of the sensor after exposed to ambient air for 10 min was approximately constant while it rapidly increased when the sensor exposed to the gas of concentration 27 ppm and/or a mixture of air and gas. Sensitivity of the sensor for pure NH_3 was 3.3%, and for mixture of air and gas were 3%, 3.48%, 3.2%, 4.2%, and 3% for ratios of mixture 1:2, 2:2, 3:2, 4:3 and 5:2, respectively. These values of sensitivity for the mixture proved that the sensor was not affected by ambient air when it is doubled the gas concentration. When the gas concentration increased to five times from the previous concentration, the increase in resistance will be faster and smoother than the low concentrations.

One can observe that the resistance curve at low concentration has some aliasing. This aliasing was reduced by increased the concentration of gas exposure as shown in figure (7).

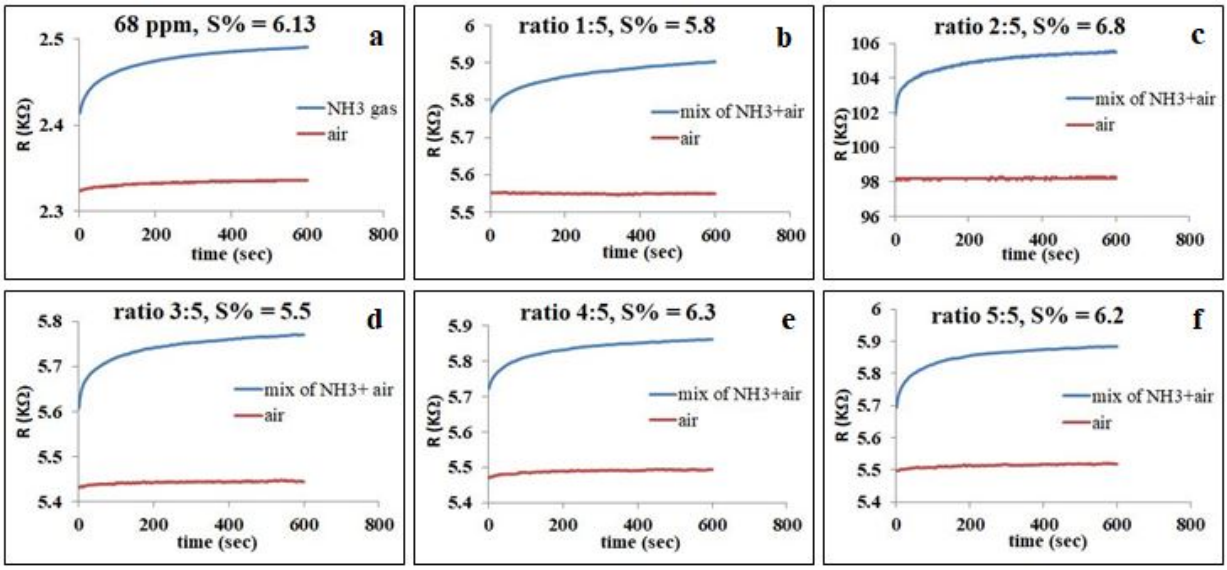

Figure 7: MWCNTs-OH sensor resistance as a function of time when exposed to:a) 68ppm of pure NH_3 gas, a mixture of ambient air with 68ppm of NH_3 gas as a ratio air:gas b)1:5, c) 2:5, d) 3:5, e) 4:5 and f) 5:5.

It is clear that the behavior of increasing the sensor resistance underexposed to a mixture of air with gas has the same behavior underexposed the sensor for pure gas only. The sensitivity of the sensor, when exposed to 68ppm of pure NH_3 gas, was 6.13% which were closed to the sensitivities of the sensor when exposed to a mixture of different ratios of ambient air and NH_3 gas.

Table (1) revealed that the sensor sensitivity for NH_3 gas is lower for low gas concentration (14ppm), while at high concentrations this sensitivity increased two to four times with increasing the gas concentration. All the sensitivity measurements hold at room temperature. These results were better than the results of [20], whose recorded device sensitivity 1.5% at 14-70 ppm concentration of NH_3 and better than the results of [21], where the membrane sensitivity for NH_3 gas was only 0.5% at 75ppm.

Table 1: The sensitivity values of the sensor to pure NH_3 and air:gas mixture.

Gas concentration (ppm)	Air:gas mixture ratio	Sensitivity% for pure gas	Sensitivity% for mixture
14	1:1	1.3	1.38
	2:1		1.68
	3:1		1
	4:1		1.3
	5:1		1.3
27	1:2	3.3	3
	2:2		3.48
	3:2		3.1
	4:2		3.13
	5:2		3
68	1:5	6.13	5.8
	2:5		6.8
	3:5		5.5
	4:5		6.3
	5:5		6.2

The average sensitivities of the mixture cases for (14, 27, and 68) ppm were around 1.33%, 3.14%, and 6.12%. These results are close to the sensitivities of the sensor when exposed to the pure gas. This makes the sensor specific and not affected by the amount of ambient air and can sense the pollution in the environment in the same efficiency.

Figure (8) shows the calibration sensitivity curve of MWCNTs-OH network sensor with a film thickness of 4μm prepared by FFS method when exposed to NH_3 gas at room temperature.

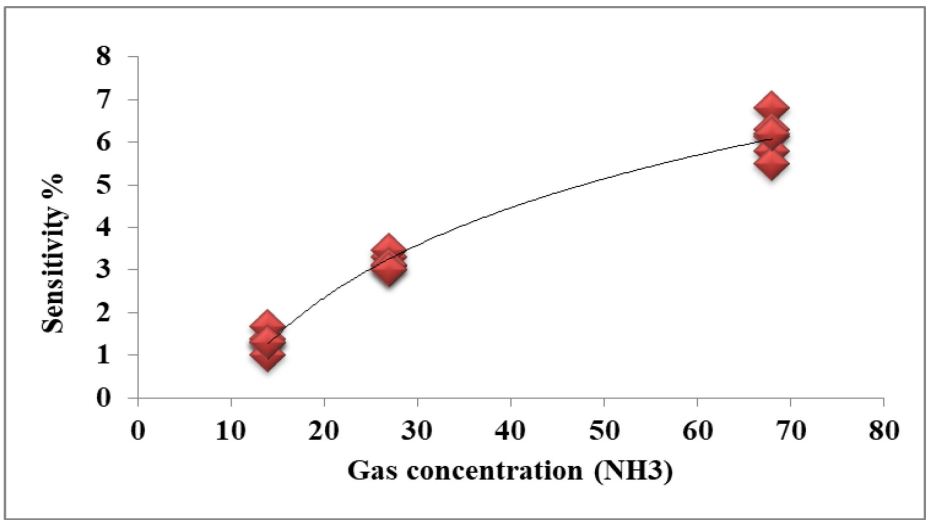

Figure 8: The calibration sensitivity curve of MWCNTs-OH network sensor with the film thickness of 4μm for different concentration (14- 68) ppm of NH3 gas at room temperature.

The calibration curve obeyed to logarithmic relation represents the increase the sensitivity through the increase in gas concentration. The calibration curve was extracted from the sensitivity values of the sensor to the exposure to different concentration of the NH_3 gas and a mixture of gas and air. The minimum value of the gas detection from the curve was 14ppm while the maximum value was 68ppm.

Conclusions

Gas sensing devices using hydroxyl functionalized multiwall carbon nanotubes (MWCNTs-OH) network with 4μm thickness was fabricated successfully using a simple and perfect (FFS) method. SEM measurements show that the network composed of randomly entangled structures which look like spaghetti. UV-Vis. analysis proved that MWCNTs-OH network absorbed the spectrum in Vis-NIR region. The gas sensing measurements appeared that the MWCNTs-OH gas sensor of film thickness 4μm can detected NH_3 gas with specific values of sensitivity without affected by the ambient air to the wide range of gas concentrations. The sensor sensitivity increased two to four times with increasing the gas concentration from low concentration of14ppm to high concentration of 68 ppm. The measurements proved that the fabricated gas sensor is specific and work at room temperature perfectly.

References

[1] Y. Wang and J.T.W. Yeow. A Review of Carbon Nanotubes-Based Gas Sensors. Journal of Sensors 2009; 2009: 24.

[2] I. Kang, Y. Heung , J. H. Kim, J. Won Lee, R. Gollapudi, S. Subramaniam et al. Introduction to carbon nanotube and nanofiber smart materials. Composites 2006; 37: 382–394.

[3] S. Mao, G. Lub, J. Chen. Nanocarbon-based gas sensors: progress and Challenges. Journal of Materials Chemistry A 2014; 2: 5573–5579.

[4] H. Jin, H. Zhou, Y. Zhang. Insight into the Mechanism of CO Oxidation on WO3 (001) Surfaces for Gas Sensing: A DFT Study. Sensors 2017; 17: 1898.

[5] C. Occhiuzzi, A. Rida, G. Marrocco, M.M. Tentzeris. CNT-based RFID Passive Gas Sensor. IEEE C2011; 978-1-61284-757-3/11.

[6] V. Mahalleh, E. Karimpour, F. Davoudifar, A. Hosseingholipourasl. Carbon Nanotubes-Based Gas Sensor. International Journal of Pharmaceutical Science Invention 2013; 2:115-120.

[7] P. Su, T. Pan. Fabrication of a room-temperature NO2 gas sensor based on WO3 films and WO3/MWCNT nanocomposite films by combining polyol process with metal organic decomposition method. Materials Chemistry and Physics 2011; 125: 351–357.

[8] S. Abdulla, T. Mathew and B. Pullithadathil. Highly sensitive, room temperature gas sensor based on polyaniline-multiwalled carbon nanotubes (PANI/MWCNTs) nanocomposite for trace-level ammonia detection. Sensors and Actuators B: Chemical 2015; 221: 1523-1534.

[9] S. Hernandez, D. Chaudhuri, W. Chen, N. Myung, A. Mulchandani. Single Polypyrrole Nanowire Ammonia Gas Sensor. Electroanalysis 2007; 19: 2125 -2130.

[10] Chapter 15: E. Jesús, J. Li and C. Cabrera. Latest Advances in Modified/Functionalized Carbon Nanotube-Based Gas Sensors. In: Syntheses and Applications of Carbon Nanotubes and Their Composites. INTECH 2013. 337- 366.

[11] J. Baral, A. Sharma, D. Wang, D. Ma, V. Truong, R. Izquierdo. Enhanced photovoltaic conversion efficiency in bulk heterojunction solar cells upon incorporating nanohybridized PbS Quantum Dots/Multiwall Carbon Nanotubes. Eur. Phys. J. Appl. Phys. (2014); 65: 10201.

[12] S. Roy, T. Das, L. Zhang, Y. Li, Y. Ming, S. Ting, et al. Triggering compatibility and dispersion by selective plasma functionalized carbon nanotubes to fabricate tough and enhanced Nylon 12 composites. Polymer 2015; 58: 153-161.

[13] X. Chen, A. Gross, F. Giroud, M. Holzinger, S. Cosnier. Comparison of Commercial and Lab-Made MWCNT Buckypaper: Physicochemical Properties and Bioelectrocatalytic O2 Reduction. Electroanalysis 2018; 30: 1-11.

[14] I. Chen, R. Liang, H. Zhao, B. Wang, C. Zhang. Highly conductive carbon nanotube buckypapers with improved doping stability via conjugational cross-linking. Nanotechnology 2011; 22: 7.

[15] H. Wang, J. Li, X. Zhang, Z. Ouyang, Q. Li, Z. Su, et al. Synthesis, characterization and drug release application of carbon nanotube-polymer nanosphere composites. RSC Advances 2013; 3: 9304- 9310.

[16] R. Olejnik, P. Slobodian, P. Saha. Multi-wall Carbon Nanotube Network Sensing Element for Organic Vapor Detection. Journal of Materials Science and Engineering 2011; 1: 937-941.

[17] R. Afrin, N. Shah. Room temperature gas sensors based on carboxyl and thiol functionalized carbon nanotubes buckypapers. Diamond & Related Materials 2015; 60: 42–49.

[18] V. Aruotiounian. Gas Sensor Based on Carbon Nanotubes. Journal of Contemporary Physics (Armenian Academy of Sciences) 2015; 50: 333–354.

[19] M. Penza, R. Rossi, M. Alvisi, G. Cassano, M. A. Signore, E. Serra, et al. Surface Modification of Carbon Nanotube Networked Films with Au Nanoclusters for Enhanced NO2 Gas Sensing Applications. Journal of Sensors 2008; 2008: 8.

[20] L. Nguyen, P. Phan, H. Duong, C. Nguyen and L. Nguyen. Enhancement of NH3 Gas Sensitivity at Room Temperature by Carbon Nanotube-Based Sensor Coated with Co Nanoparticles. Sensors 2013; 13: 1754-1762.

[21] Z. Wang, Z. Chen, J. Zhang, N. Tang and J. Cai. Fabrication of sensor based on MWCNT for NO_2 and NH_3 detection. Proceedings of the 13th IEEE International Conference on Nanotechnology (China) 2013; 686-689.