GAS SENSOR APPLICATION OF CARBON NANOTUBES

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ABSTRACT

Gas sensors have a wide application in everyday life, whether in industry, medical, agriculture and environmental monitoring. A good sensor should be selective, sensitive, responsive, reliable and cost effective. Currently available gas sensors are lacking in one or more of these criteria. Therefore, there is a need to develop new sensing materials and technologies. Carbon nanotubes (CNTs) have the potential to be developed as a new gas sensing material due to their inherent properties such as their small size, great strength, high electrical and thermal conductivity, and high specific surface area. As a result, it is possible to create a miniaturized sensor, which can lead to low power consumption, lighter and low cost. This research was carried out to investigate the absorption effect of ammonia (NH_3) on the change in resistance of carbon nanotube pellets. Carbon nanotubes used in this research were synthesized using Floating Catalyst Chemical Vapor Deposition (FC-CVD). Benzene was used as a hydrocarbon source while ferrocene as a catalyst with Hydrogen and Argon as carrier and purge gas respectively. From the research, it was shown that carbon nanotubes show high sensitivity towards ammonia. It is expected that many applications of CNT-based sensors will be explored in future as the interest of the nanotechnology research community in this field increases.

***Keywords**: carbon nanotubes, ammonia, carbon dioxide, hydrogen sensor*

INTRODUCTION

Gas sensors are widely used in industry for environmental analysis, medical diagnostics and other various field applications. Common gas sensors are metal oxide semiconductor such as Tin Oxide, Zinc Oxide, Titanium Oxide and Aluminum Oxide. Problems encounter with these sensors are lack of flexibility, poor response times and operated at elevated temperature. Therefore a new material is needed to serve as a cheap, small, user-friendly and reliable gas sensing device [5].

Researches had been carried out to design small and cheap gas sensor which possess high sensitivity, selectivity and stability. This is where nanotechnology comes to the rescue. What is nanotechnology? Nanotechnology is the latest and advanced technology dealing with materials having at least one dimension in the range of about one to hundred nanometers.

Carbon nanotubes are new carbon materials discovered recently. They are cylindrical carbon molecules with properties such as low density, high tensile strength and elastic modulus. Metallic carbon nanotubes have a high electric current density, and all of these properties make carbon nanotubes potentially useful in extremely small-scale electronic and mechanical application. There are two main types of nanotubes; single walled carbon nanotubes (SWNTs) and multi walled carbon nanotubes (MWNTs). SWNTs can be considered as a sheet of graphene that has been rolled up into a seamless cylinder, while MWNTs consist of nested coaxial arrays of SWNT constituents. Their structures are unique, only a few nanometers in diameter, but up to hundreds of microns long [1-3].

Carbon nanotubes possess very unique characteristics due to their hollow center, nanometer size and large surface area, and are able to change their electrical resistance drastically when exposed to alkalis, halogens and other gases at room temperature. Hence, carbon nanotubes have the potential to be a better chemical sensor. [4]

MATERIALS AND METHODS

The production method employed in this study is Floating Catalyst Chemical Vapour Deposition (FC-CVD). Benzene was used as a hydrocarbon source while ferrocene as a catalyst with Hydrogen and Argon as carrier and purge gas respectively. The reaction temperature is in the range of 850°C-750°C, while the reaction time is 30 minutes.

A simplified schematic diagram for the apparatus used for carbon nanotubes production is shown in Figure1

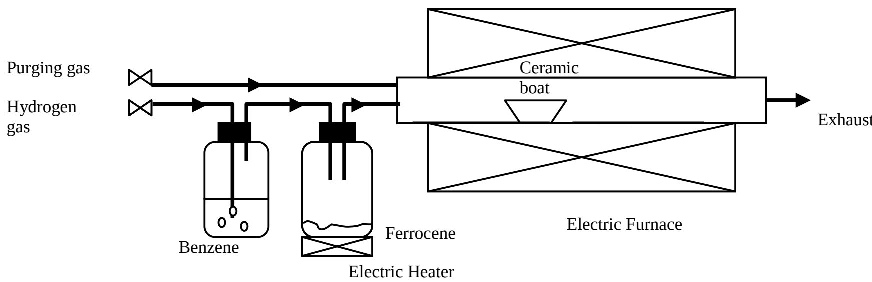

Figure 1: Schematic drawing of Chemical Vapour Deposition System used in this research

This study is carried out to investigate the potential application of carbon nanotubes as a gas sensor by measuring the change of electrical resistance of the carbon nanotubes upon ammonia (NH_3), carbon dioxide (CO_2) and hydrogen (H_2) absorption.

Sample Preparation

100mg of carbon nanotubes powder was mixed with a non-conductive binder (ethyl cellulose) to form a thick paste. The binder was prepared by dissolving one gram of ethyl cellulose powder in ethyl alcohol to produce a viscous liquid. The mixture of carbon nanotubes and binder was then placed in a rectangular mould (5 mm width, 15 mm length and 1.5 mm thick) and left for about 1 hour at room temperature to dry and solidify. A pellet sample is shown in Figure 2.

Figure 2: Carbon nanotube pellets with binder

Gas Sensor Setup

Two sets of carbon nanotubes pellets with binder were made for gas sensing application. Pellet S1 and S2 were made using bulk carbon nanotubes produced at temperatures of 850°C and 800°C, respectively. Silver paint was used to create contacts at both surfaces of the pellet. Four strips of copper wire were soldered onto the silver paint on the pellet surface.

The wires from the pellet were then connected to the Source Measurement Unit, SMU (Keithley 4200 SCS, Department of Electrical and Electronic Engineering, UPM) that was used to obtain I-V (current-voltage) curve and to extract the value of resistance, R and conductivity, G of the samples. The range of current source used was 0 – 50mA.

The pellet was placed in a sealed conical flask with an electrical feedthrough. Argon gas, which acts as a carrier gas was fed continuously into the flask. The resistances for the carbon nanotubes were recorded at ten second intervals until the system reached steady state, i.e. when the resistance of the carbon nanotubes gave a constant reading. Then, the tested gas was injected periodically for duration of three seconds into the flask. The resistance of the carbon nanotubes was recorded before and after the injection at ten second intervals. The interval time was chosen based on the time taken for the carbon nanotubes' resistance to revert to the original reading. All the measurements were taken at room temperature, 25°C. The tests were repeated three times for both samples, S1and S2, in order to get precise results.

RESULTS AND DISCUSSION

SEM and HRTEM Characterization

Scanning Electron Microscopy (SEM) and High Resolution Transmission Electron Microscopy (HRTEM) were used to characterize the carbon nanotubes produced.

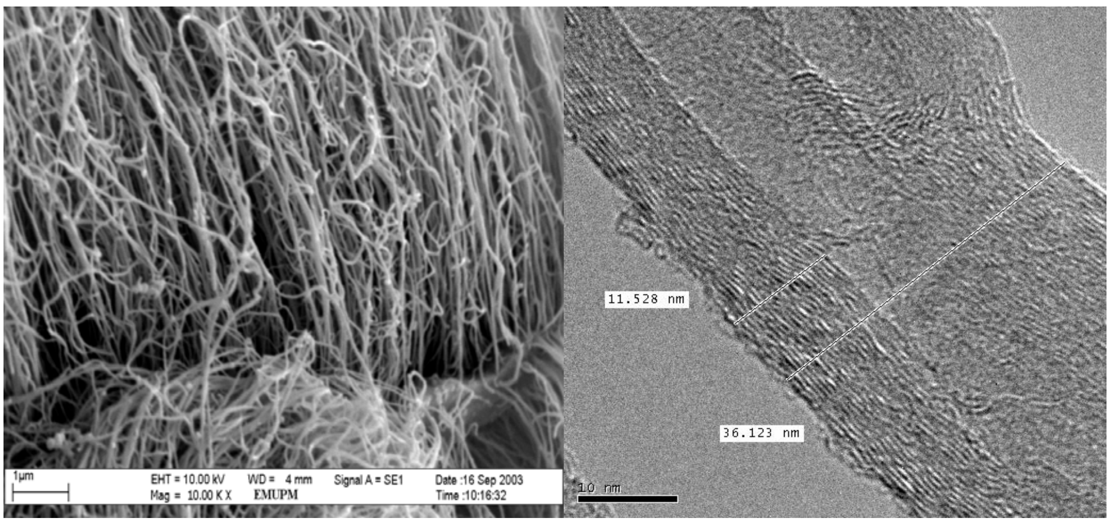

Figure 3: SEM and HRTEM micrograph of carbon nanotubes

SEM micrographs have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. In Figure 3, the SEM images show that the carbon nanotubes are of high purity, tens of microns long and effectively uniform in diameter. The bulk morphology of the long carbon nanotubes is film like, randomly oriented and in some cases entangled. From the HRTEM micrograph, it can be concluded that the carbon nanotube is a multiwalled nanotube with a diameter of 36.1nm and wall thickness of 11.5nm.

Ammonia Absorption

The results obtained indicate that the carbon nanotubes samples were sensitive to ammonia. Upon exposure to ammonia, the resistance of carbon nanotubes increased significantly. Figure 4 shows the results of samples S1 and S2 for three repetitions respectively. These two samples give the same pattern and are in good agreement with each other. For S1, the maximum resistance detected is 256 milliohm which is the increment of 5 milliohm from the resistance recorded in argon. From the graph, it can be seen that the first repetition, R1 had a lower value compare to R2 and R3. This indicates that the absorbed ammonia gas had interacted with carbon nanotube molecules and did not desorbed immediately. R3 had the highest reading due to accumulated ammonia gas in the sample.

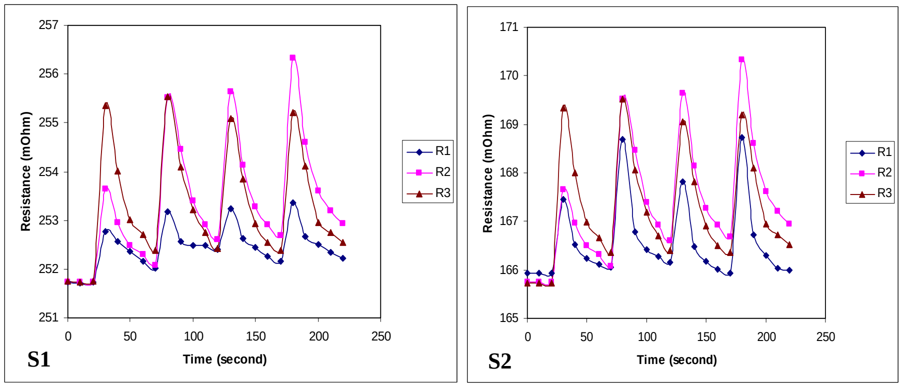

Figure 4: Electrical resistance variations of sample S1 and S2 upon injection of NH_3 gas

The same occurrence was observed with sample S2. All the four injections give rise to carbon nanotube resistance. Similarly R1 had the least value followed by R2 and R3.

This result indicates that carbon nanotubes have a high affinity for ammonia due to ammonia being a polar molecule with a dipole moment of 1.5 debye. When the samples are exposed to NH_3 gas, electrons are transferred from NH_3 to carbon nanotubes. NH_3 molecules donate electrons to the valence band of the carbon nanotubes, decreasing the number of holes, thereby increasing the separation between the conduction band and the valence band. This forms a space charge region at the surface of the semiconducting carbon nanotubes, increasing the electrical resistance. The increase in resistance proves that the carbon nanotubes are a p-type semiconductor.

This result is in mutual agreement with the work done by other researchers. It is reported that upon exposure to NH_3 gas, the resistance of the carbon nanotubes based sensor increased with an increase in gas concentration [8]. Multi-walled carbon nanotube based gas sensors for detecting ammonia were developed using microwave plasma-enhanced chemical vapor deposition [11]. The carbon nanotubes laid under the electrodes were fabricated using electron-beam lithography and lift-off techniques. They found out that the sensor was sensitive to NH_3 gas and the conductance of MWNTs decreases when exposed to NH_3 gas at room temperature of 25°C. This suggests that the MWNTs could be a good candidate material for NH_3 detection at room temperature.

Researchers noted that NH_3 absorbed into carbon nanotubes by replacing pre-adsorbed oxygen within the carbon atoms [10]. Oxygen, an oxidizing gas, increases the conductivity of p-type carbon nanotubes as it increases the holes concentration; hence the replacement of oxygen by ammonia should reduce the conductivity.

The work done previously [8], [10], [11] support the result obtained from this study. Absorption of gas ammonia onto the carbon nanotubes pellets had resulted in an increment in the carbon nanotubes resistance.

Carbon Dioxide Absorption

The results of carbon dioxide absorption into carbon nanotubes samples indicate that injection of carbon dioxide gas had similar effect as in ammonia absorption. This trend is showed in the Figure 5 whereby there are significant increments in the resistance when CO_2 gas is injected into the system. The same pattern was obtained for the second, third and fourth injection for all the three repetitions indicates by R1, R2 and R3.

Carbon dioxide is a reducing gas and its absorption resulted in injection of electrons to the carbon nanotubes and reduced number of holes in the material. Holes are the main charge carrier for p-type semiconductor, holes depletion will result in increase resistivity or decrease conductivity of the sample.

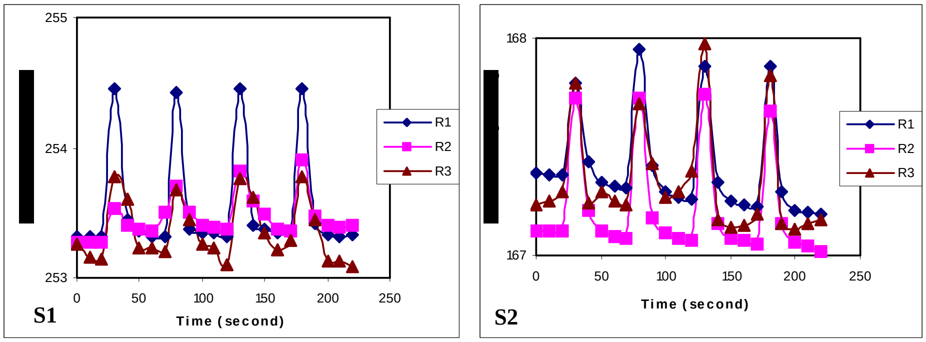

Figure 5: Electrical resistance variations of sample S1 and S2 upon injection of CO_2 gas

This result is in good agreement with the work done by other researchers [6], [7], [10]. They observed that absorption of carbon dioxide gas had significant effect on the resistance of carbon nanotubes. The sample resistance showed an increment upon exposure to carbon dioxide gas.

Hydrogen Absorption

Hydrogen is the lightest and most abundant element in universe. At standard pressure and temperature, it occurs as diatomic gas. Hydrogen absorption into carbon nanotubes samples at room temperature had no significant change in the resistance of carbon nanotubes. This is in a mutual agreement with results reported by other researchers. The carbon nanotubes need to be doped with other atoms or operated at higher temperature for them to be a good gas sensor for hydrogen.

The results from this study on the effect of hydrogen absorption on sample S2 is plotted in figure 6 and the circle on the graph indicates the injection of gas at 30, 80, 130 and 180 second.

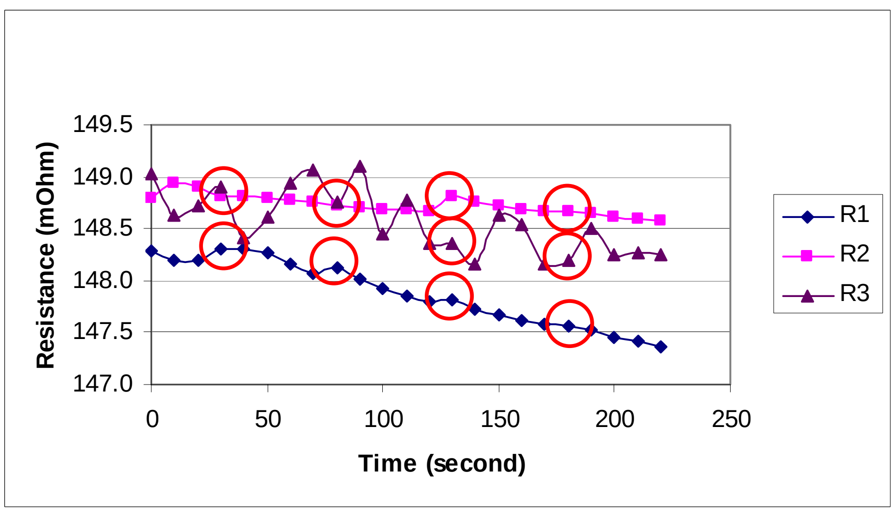

Figure 6: Electrical resistance variations of sample S2 upon injection of H_2 gas

Gas sensor utilizing carbon nanotubes in a thin layer Pd/CNTs/n^+-Si structure has a high sensitivity to hydrogen over a wide temperature range [12]. Raw and palladium doped carbon nanotubes sensors do not detect hydrogen at room temperature [9]. The sensing activity of raw carbon nanotubes started at temperatures higher than 200°C.

This finding [9], [12] is relevant with the result obtained in this study. It is confirmed that pure carbon nanotubes unable to detect hydrogen gas at room temperature.

Effect of Gases on Carbon Nanotubes Samples

Graphs of tested gas absorption into carbon nanotubes samples were plot as samples electrical resistance in milliohm against tested gas as shown in Figure 7 and 8 respectively. The graph shows that ammonia recorded the highest increment of electrical resistance followed by carbon dioxide. This indicates that carbon nanotubes have a higher affinity for ammonia due to ammonia being a polar molecule with a dipole moment of 1.5 debye.

The other tested gases are non-polar molecule with a zero dipole moment. However, carbon dioxide showed significant increment in the resistance, but not hydrogen. This is due to the reason that carbon dioxide possesses rich electron site in their molecules. Carbon dioxide has two sets of lone pairs contributing by two oxygen atoms, whereas hydrogen is non-polar molecules and had none electronegative atoms in the molecules which can contribute to electron rich site within the molecules.

Sensitivity of the carbon nanotubes sample is estimated by using the following equation [10];

$$S = \frac{(R_{gas}-R_{argon})}{R_{argon}} \times 100 \quad (1)$$

Where,

S	=	sensitivity
R_{gas}	=	resistance of sample in tested gas
R_{argon}	=	resistance of sample in argon gas

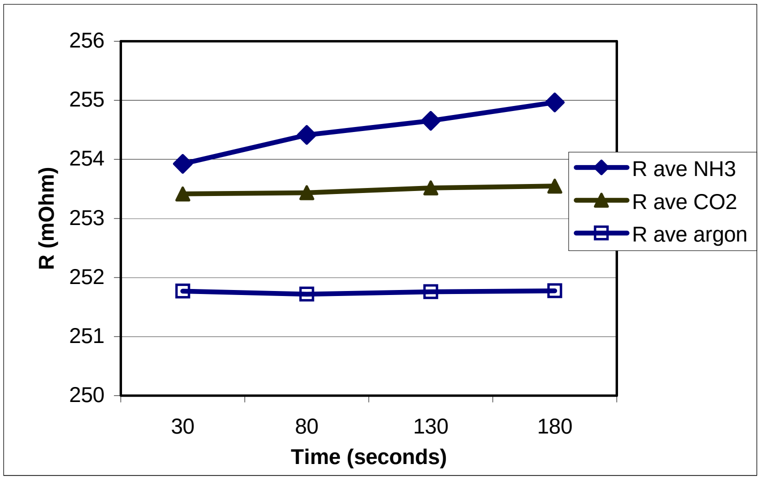

Figure 7: Overall results for gas absorption of S1

Table 1: Sensitivity of S1 in Ammonia and Carbon Dioxide

Time	Gas Ammonia				Gas Carbon Dioxide			
	R1	R2	R3	Ave	R1	R2	R3	Ave
30	0.43	0.79	1.47	**0.90**	0.91	0.54	0.64	**0.70**
80	0.62	1.55	1.56	**1.24**	0.91	0.63	0.62	**0.72**
130	0.63	1.58	1.36	**1.19**	0.91	0.66	0.64	**0.74**
180	0.67	1.84	1.41	**1.31**	0.91	0.69	0.64	**0.75**
Ave	**0.59**	**1.44**	**1.45**	**1.16**	**0.91**	**0.63**	**0.64**	**0.73**

Figure 7 shows the value of the electrical resistance of sample S1 at injection time of gases ammonia and carbon dioxide. It can be summarized that sample S1 response significantly to ammonia and carbon dioxide. However, ammonia had the more effect compare with carbon dioxide. As such, the sensitivity of S1 upon exposure of these gases is tabulated in Table 1. From the table, it can be concluded that ammonia has the highest sensitivity for sample S1.

Accordingly, Figure 8 and Table 2 summarized the response of S2 upon exposure of ammonia and carbon dioxide. The same pattern is observed, ammonia gave the maximum increment in resistance and also the highest sensitivity.

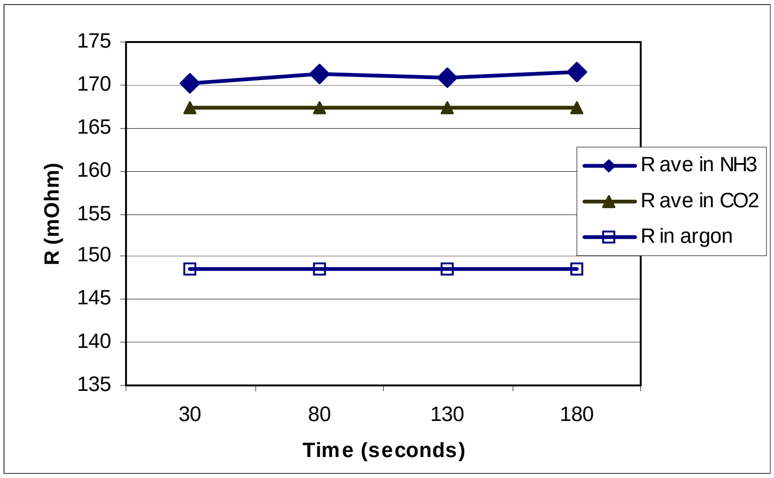

Figure 8: Overall results for gas absorption of S2

Table 2: Sensitivity of S3 in Ammonia, Acetylene and Carbon Dioxide

Time	**Gas Ammonia**				**Gas Carbon Dioxide**			
	R1	**R2**	**R3**	**Ave**	**R1**	**R2**	**R3**	**Ave**
30	12.71	12.85	13.98	**13.18**	12.60	12.55	12.60	**12.58**
80	13.58	14.14	14.14	**13.95**	12.75	12.59	12.58	**12.64**
130	12.96	14.20	13.80	**13.65**	12.66	12.57	12.73	**12.65**
180	13.55	14.64	13.87	**14.02**	12.65	12.51	12.62	**12.59**
Ave	**13.20**	**13.96**	**13.95**	**13.70**	**12.67**	**12.56**	**12.63**	**12.62**

Finally, from the results obtained, it can be concluded that carbon nanotube has a potential application for gas sensing technology operated at room temperature for ammonia and carbon dioxide. For hydrogen, modification had to be done to the carbon nanotubes to make it more sensitive towards the gas.

CONCLUSIONS

The aim of this study was to investigate the electronic sensor application of carbon nanotubes upon absorption of ammonia. Based on the experimental results, it was proven that the carbon nanotubes have the capability to detect ammonia and carbon dioxide at room temperature. Therefore, it can be concluded that the gas sensing characteristics carried out in this work has shown that carbon nanotubes have potential to be an excellent ammonia and carbon dioxide sensor material at room temperature.

ACKNOWLEDGEMENT

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