Fabrication of Gas Sensors based on Carbon Nanotube for CH$_4$ and CO$_2$ Detection

Amin Firouzi, Shafreeza Sobri, Faizah Mohd Yasin, Fakhru’l-razi b. Ahmadun
Department of Chemical and Environmental Engineering
Universiti Putra Malaysia
Serdang, Malaysia
Firouzi.amin@gamil.com, eeza@eng.upm.edu.my, fmy@eng.upm.edu.my, fakhrul@eng.upm.edu.my

Abstract—This study was carried out to investigate the adsorption effect of CH$_4$ and CO$_2$ on carbon nanotubes (CNTs) based gas sensors by measuring the variation of their electrical resistance. The CNTs were synthesized by Floating Catalyst Chemical Vapor Deposition (FC-CVD) method on quartz substrate under benzene bubble at temperature of 700°C. Then, they were tested for gas detection. Upon exposure to gaseous molecules, the electrical resistance of CNTs dramatically increased for both CH$_4$ and CO$_2$ gases with short response time and high sensitivity. In addition, the recovery of the sensors and mechanism of gas sensing procedure are discussed.

Keywords—carbon nanotubes; chemical vapor deposition; gas sensor; quartz substrate

I. INTRODUCTION

Discovered in 1991 by Iijima [1] carbon nanotubes (CNTs) are being globally as a new dream material in the 21st century and broadening their applications to almost all the scientific areas, such as electrochemical actuators [2], hydrogen storage [3], emission display [4] and chemical sensors [5]. To utilize them in fundamental investigation and industrial application, synthesizing high quality CNTs on a large scale is necessary. Considering the production cost and application requirement, Chemical vapor deposition (CVD) technique is no doubt the most comprehensive one [6].

In the present report, CNTs were synthesized directly on a substrate by using a liquid reactants and the vapor of catalyst precursor that are bubbled into the reaction zone with carrier gas such as H$_2$ and/or Argon [7].

Recently, CNTs have been successfully applied as promising candidates for fabricating gas and chemical sensors, due to their high surface area, size and hollow geometry [5, 8]. The fabrication of sensors using CNTs was first reported by Dai and coworkers [9]. These authors demonstrated that small concentration of NO$_2$ are capable of producing large changes in the sensor conductance, shifting the Fermi level to the Valence band and generating hole enhanced conductance [9]. Also, CNTs based sensors for detection of gases such as H$_2$, NH$_3$, CO$_2$ or CH$_4$ have already been successfully demonstrated [8, 10, 11].

In this research, we present that the grown CNTs could be used in the fabrication of fast response gas sensor operating at room temperature.

II. EXPERIMENTAL

A. Synthesis of CNTs

Carbon nanotubes were synthesized in a conventional CVD apparatus consisted of double-stage electric furnace, a ceramic tube located horizontally inside both furnaces (50 mm OD, 40 mm ID and 1 m length) and gas flow controlling units [12].

In a typical experiment, we put a quartz substrate (1 cm × 1 cm) that was placed in the ceramic boat and 200 mg of Ferrocene (catalyst precursor) in furnace 2 and 1, respectively, as depicted in Fig. 1. At first, the ceramic tube was flushed with argon in order to eliminate oxygen from the reaction chamber during heating up the reactor [13]. When the second furnace reached to a temperature of 700°C, argon flow was stopped. Then the temperature of first furnace was raised to 120°C to sublimate the catalyst [14]. After 5 minutes, hydrogen carrier flow (150 ml/min) was bubbled into the benzene (200 ml) that used as a hydrocarbon source before mixing with Fe nanoparticles. Then, benzene decomposed in the presence of Fe nanoparticles in the second furnace to form CNTs. The reaction is over after 45 minutes and furnace was cooled down with argon flow.

![Figure 1. Schematic diagram of CVD apparatus.](image-url)
B. Gas Sensing Set up

Two types of gas (CH\textsubscript{4} and CO\textsubscript{2}) were employed for gas sensing application. Electrical contacts were made to the sensors by connecting two copper wires using silver paste. Fig. 2 Shows that the silver paste contact were made directly to the top of the nanotubes grown over quartz. Also, the wires from the CNTs film were connected to the digital Multimeter (ESCORT, 3145A) used to obtain and monitoring the values of resistance every second on the computer.

The sensors were placed in a sealed plexiglas chamber of 0.027 m\textsuperscript{3} volume with electrical feedthrough. Argon gas was used continuously as the carrier gas throughout the work. After purging of chamber with pure argon when the resistance of CNTs gave constant results, the tested gas, CH\textsubscript{4} or CO\textsubscript{2}, was injected into the chamber with concentration of 369 ppm.

The resistance of CNTs was recorded before and after injection at every one second. The experiments have been repeated three times with four times injection for each gas to get the precise results. All the measurements were taken at room temperature of 25°C.

III. RESULTS AND DISCUSSION

A. Morphology Observations

CNTs grown on quartz substrate were examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscope (TEM) to get the general view of the product formed such as morphology (alignment), topology (uniformity) and diameter.

Fig. 3a shows the SEM micrograph of synthesized CNTs on quartz. From SEM image, we can clearly see that the CNTs are mostly entangled and exhibit high accumulation with the shape of matchstick.

TEM image (Fig. 3b) indicates the presence of multi-walled CNTs type at reaction condition. Also, the image shows that the grown CNTs are long and uniform with relatively thick diameters of about 25-65 nm. Long reaction time of 45 minutes can be caused to synthesize large diameters in CNTs due to the fact that catalyst particles have sufficient time for more collisions, resulting in the increase of the Fe nanoparticles size and CNTs diameter [12].

B. Sensor Characteristics

In general, these sensors were reliable and exhibited good performance in terms of response time and sensitivity in the overall resistance.

Fig. 4 and Fig. 5 show the electrical resistance variations of p-type semiconductor CNTs [15] upon exposure to CH\textsubscript{4} and CO\textsubscript{2} filling and pumping environment, respectively.

For both gases, sensors showed a fast response of ca. 30 second. This indicates that the sensors are highly sensitive towards CO\textsubscript{2} and CH\textsubscript{4} adsorption at room temperature of 25°C. Also, it can be seen that the resistance of CNTs increases at the first injection of target gas. The same increment can be observed for the second, third and fourth injection.
In the case of CO$_2$, the recovery of sensor is not complete. It can be as a result of high adsorption energy between CO$_2$ molecules and CNTs molecules resulting in the incomplete CO$_2$ desorption in the short time [16]. Fabricated sensors have been highly electrical resistance, in the range of 1200 ohm. The increasing of resistance can be described as follows:

As we know CH$_4$ and CO$_2$ are reducing gases [17]. Exposure to these gases, impressively causes to move the valence band of CNTs away from the Fermi level thereby, the positive hole carrier of p-type semiconductor depleted and the electrical resistance increases [9].

The sensor sensitivity ($S$) is calculated using (1) [15]:

$$S(\%) = \left(\frac{R_g - R_0}{R_0}\right) \times 100$$  \hspace{1cm} (1)

Where, $R_g$ and $R_0$ are the resistance values of the sensor with and without gas exposure, respectively. Sensitivity of sensors to gas adsorption is summarized in Table 1.

![Figure 4](image1.png)

**Figure 4.** Electrical resistance variations of CNTs-based sensor upon injection of CH$_4$ gas.

![Figure 5](image2.png)

**Figure 5.** Electrical resistance variations of CNTs-based sensor upon injection of CO$_2$ gas.

### Table 1. Sensitivity, $S(\%)$, of Sensors to CH$_4$ and CO$_2$ Exposure

<table>
<thead>
<tr>
<th>Gas Exposure</th>
<th>CH$_4$ gas</th>
<th>CO$_2$ gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st injection</td>
<td>0.42</td>
<td>0.33</td>
</tr>
<tr>
<td>2nd injection</td>
<td>0.42</td>
<td>0.34</td>
</tr>
<tr>
<td>3rd injection</td>
<td>0.42</td>
<td>0.37</td>
</tr>
<tr>
<td>4th injection</td>
<td>0.42</td>
<td>0.30</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

We have obtained high density of uniform CNTs having diameters in the range of 25-65 nm by FC-CVD method of benzene at 700°C. The CNTs patterned on quartz substrate have been used for gas sensing application. These sensors are highly sensitive with fast response to CH$_4$ and CO$_2$ molecules and the recovery process is complete only for CH$_4$.

Our results have shown that CNTs have potential to be an excellent gas sensor at room temperature. Thus, future work will concentrate on further enhancing the performance of these CNTs-based gas sensors.

ACKNOWLEDGMENT

This work was supported by the research grant provided by the Malaysian Ministry of Science, Technology and Innovation.

REFERENCES


