Carboxyl functionalized Carbon Nanofibers as Active Sensing Material for Detection of Benzene

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Abstract

Carbon nanofibers (CNF) have been exhibited to be one of the most desirable material for gas sensing. This research applies a simple and low-cost method for the detection of benzene at room temperature. CNF was functionalized using sulphonitric mixture to attach carboxyl functional group to CNF as active site for interaction between gas analyte and sensing material. The flexible gas sensor demonstrated high sensitivities of 23.64 % at room temperature for ambient benzene gas concentration of 0.125 %, respectively. Moreover, the gas response of CNF-based resistivity sensor is being caused by p-type conductivity in the Au-modified semiconducting substrate. The recovery time, repeatability and reusability of sensor to gas concentration are demonstrated, indicating a major improvement towards the low-cost large-scale production of this type of device.

Keywords

Carbon nanofibers, benzene, gas sensor, acid functionalization

Introduction

The rapid and sensitive detection of toxic and hazardous airborne pollutants such as toxic industrial wastes (TICs) and chemical warfare agents (CWAs) has become critically

important to homeland security. There are huge possible ways for exposure, for TICs, including the spillage in chemical plants or during transportation [1] and for CWAs, terrorists attack or unnecessary incidents. The increasing risks and dangers become key factor of this area to focus on developing chemical and biological sensor device. A high precision device with sensitivity, selectivity, very less false positivity, good accuracy should be available to detect, identify and quantified a wide range of these compounds [2]. Thus, this important device plays an important role to protect homeland security in terms of responding and recovering from unexpected situations. The emergence of nanosized material as sensor device currently offering a good solution for this problem. Nanomaterial is excellent candidate as active sensing material due to their high surface area to volume ratio which crucial to develop a high sensitivity and precision sensor device [3]. Furthermore, nanosized-based gas sensor makes them portable and low-cost for large-scale production.

In the past few decades, researchers have focusing on carbon nanotubes (CNT) as active sensing material. However, high quality of CNT is quite expensive caused by complicated processing methods [4]. Recently, an explosion of interest has been seen on producing carbon nanofibers (CNF) as replacement of CNT in numerous applications include as sensing material. CNF is dimensionally like CNT but differs in diameter size and production methods. CNT can be synthesizing using 3 methods which is chemical vapour deposition method [5], laser ablation [6] and arc discharge [7], while CNF could be synthesizing using 2 methods which is catalytic chemical vapour deposition and electrospinning [8]. The unique characteristics of CNF such as high energy efficiency, wider surface area and high defects which promotes many available sites for adsorbing gas analytes. The defects site is an advantage as it accelerate the adsorption process and produce signal transformation with high efficiency and speed [9]. However, to maximize the capability of CNF, it needs to overcome the weaknesses such as low dispersibility and improve the reactivity of CNF. Functionalization of CNF with organic functional group include carboxyl, amide and ester had proven improve the performance of CNF as sensing material [10], [11].

In this paper, CNF has been exhibited as sensing material for detection of benzene gas at room temperature. The dispersibility and reactivity of CNF were improved by functionalized with carboxyl group using sulphonitric mixture. CNF functionalized was characterized using several techniques and implemented in benzene gas detection. The gas response, sensitivity, recovery time, repeatability and reusability were explored to analyse the performance of carboxyl functionalized CNF.

Experimental

Materials

Carbon nanofibers (purity: 70 %, length: 5 – 50 μm) was purchased from Nanostructure and Amorphous Materials, Inc (USA), sulphuric acid (H_2SO_4, 98 %), nitric acid (HNO_3, 65 %) were obtained from Merck company (Germany) and for detection of benzene, benzene gas in 1.0 % mixed with nitrogen gas was purchased from Airgas Scientific company (Singapore).

Carboxyl functionalization

A 50.0 mg of pristine CNF was immersed in a mixture of sulphuric acid and nitric acid (sulphonitric) with a ratio 3:1 at room temperature. The mixture was treated in an ultra-sonication water bath for 2 hours at 70 °C. When the reaction process was ended, the product was diluted, filtered, washed several times to ensure all excess reagents were removed completely and dried in vacuum oven at 80 °C for 24 hours. These samples are labelled as CNF-carboxyl. CNF was characterized using Field Emission Scanning Electron Microscopy-Energy Dispersion X-ray spectroscopy (FESEM-EDX).

Detection of benzene by CNF

Gold, Au pre-patterned interdigitated transducer (IDT) with CNF was fixed in a customized gas chamber and connected to a digital multimeter and temperature controller. The digital multimeter was connected via RS232 port to a computer installed with FlukeView form software to record resistance change of CNF in real time. The normalized sensor response of CNF, S_R was calculated using eq. 1[12].

(1)

Where R is denoted as resistance of CNF when exposed to benzene gas and R_o is denoted as resistance of CNF when exposed to nitrogen gas as carrier gas. To compare sensitivity, S of pristine CNF and CNF-carboxyl, the sensor response, S_R ratio was calculated at lowest concentration (0.125%) using eq. 2 [13].

(2)

Where, S_1 is denoted as sensor response of pristine CNF and S_2 is denoted as sensor response of CNF-carboxyl. The gas chamber was attached to a gas calibration system with a computer-controlled mass flow controller, which regulated gas flow at 200 sccm. Benzene gas

concentration was varied by controlling the dilution of 1.0 % gas with carrier gas. Resistance measurement was conducted while the sample was exposed to benzene gas with different concentration (0.125 %, 0.25 %, 0.5 %, 0.75 % and 1.0 %). The dynamic response of the sample was observed through the change in resistance as the system alternately purged benzene gas into the chamber with carrier gas. The measurements were carried out at room temperature and in controlled humidity environment (~55 %). Repeatability of CNF as sensing material was exhibited by purged benzene gas at 1.0 % at same sample for five times within a day. While, reusability of CNF was exhibited by purged benzene gas at 1.0 % at same sample for five different days. The response time and recovery time of CNF was recorded to compare their performance.

Results and discussion

Field Emission-Scanning Electron Microscopy-Energy Dispersion X-Ray

Fig. 1 (a) and (b) represent FESEM images of pristine CNF and CNF-carboxyl, respectively. It can be seen clearly that the surface of pristine CNF was quite smooth. The diameter distribution is in the range of 70 nm to 145 nm. After chemical treatment using sulphonitric mixture, the morphology changes dramatically and increased the diameter distribution of CNF. The arrangement of CNF-carboxyl is also more aligned and denser as shown in Fig. 1 (b) which some of CNF-carboxyl surface are partly damaged and roughed. The acid mixture between H_2SO_4 and HNO_3 are usually used to cut the highly tangled long fiber of nanotubes [14]. Elemental percentage of pristine CNF and CNF-carboxyl are in Table 1. Based on the result, it showed that percentage of oxygen element content in CNF-carboxyl increases moderately as compared to the pristine CNF. This indicated that oxygenated functional group (i.e. hydroxyl, carboxyl) successfully attached on CNF by acid treatment.

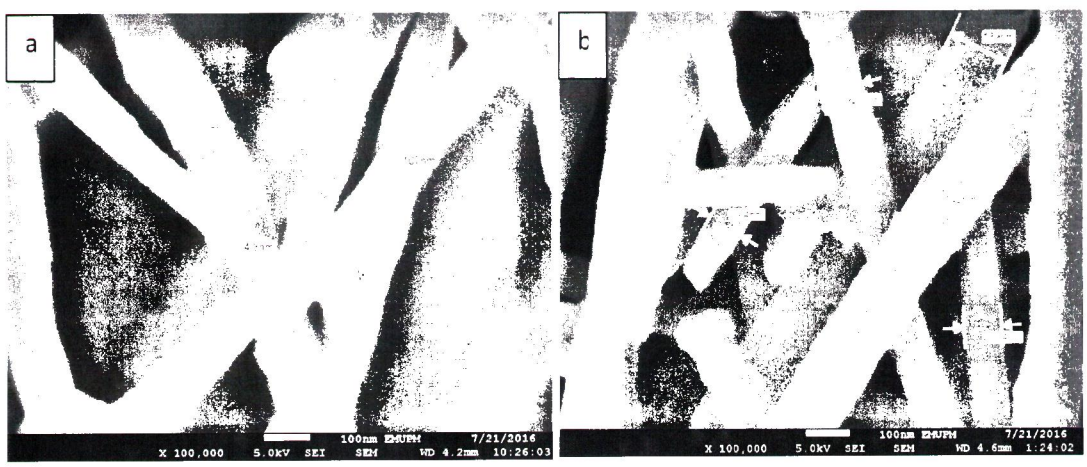

Fig. 1 FESEM image of (a) pristine CNF and (b) CNF-carboxyl

Table 1 Elemental analysis of pristine CNF and CNF-carboxyl

Element	Pristine CNF (%)	CNF-Carboxyl (%)
C	93.34	93.24
O	6.51	6.64

Detection of benzene gas

Fig. 2 shows sensor response, S_R of pristine CNF and CNF-carboxyl. The S_R of pristine CNF showed a poor response when the concentration of benzene gas was increased. This could be due to lack of active sites for adsorption of gas analytes in pristine CNF. CNF-carboxyl displayed high response towards benzene gas which caused by increasing of active sites available in CNF-carboxyl. Active site plays important role for adsorption of gas during exposure of benzene gas towards sensing material [15]. Results from the response of sensor shows that the detection was attributed to the p-type semiconducting of CNF-based gas sensor which hole is their majority carrier. The electrical charge transfer is found to be main sensing mechanism at room temperature. Benzene gas is electron donating group, which they tend to donate their electron towards sensing network. This will reduce the hole density in sensing network. As a result, the carriers concentration increase and the resistance of sensor increased as well [16]. Pristine CNF showed increment of sensor response less than 1.0 % while, CNF-carboxyl more than 3.0 %. The high increment of CNF-carboxyl most likely due to high defects distributions on CNF surface [17]. The defects act as adsorption sites and increased the sensor response. Sensitivity of CNF-carboxyl is shown in Fig. 3. Based on the graph, after 0.50 % of benzene concentration, sensitivity of CNF-carboxyl decreased. This is because the availability of active sites is limited. Even the interaction between gas analyte and sensing network is weak interaction, some of gas molecule could not fully desorb by carrier gas during recovery phase. Thus, the number of active sites decreased resulting of gas adsorption decreased and sensitivity of sensor also decreased. This indicated that at 0.50 % of benzene concentration is saturation point of CNF sensor.

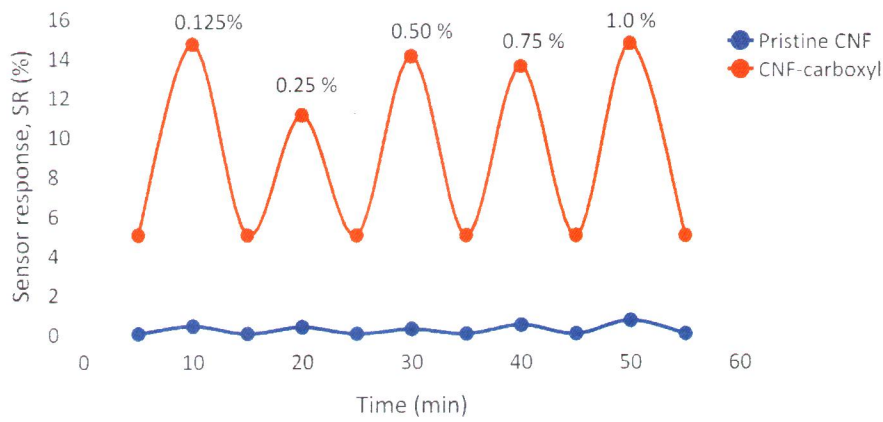

Fig. 2: Sensor response of pristine CNF and CNF-carboxyl towards benzene gas

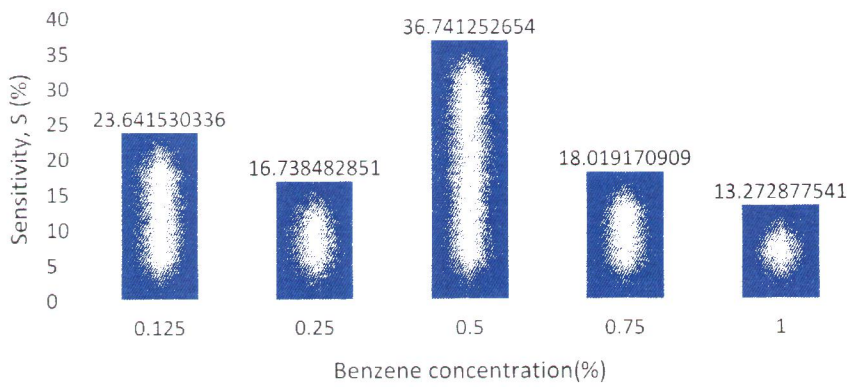

Fig. 3 Sensitivity of CNF-carboxyl towards benzene gas

The repeatability and reusability of CNF network based on the highest sensitivity upon exposure of benzene gas shown in Fig. 4 (a) and Fig. 4 (b). Table 2 shows the response time, R_T and recovery time, R_C of pristine CNF and CNF-carboxyl. Response time of pristine CNF is more than a minute even though it has good repeatability. The pristine CNF network also unable to regain their initial resistance value. As discussed earlier, the carrier gas only could not fully desorb all gas molecules on CNF network. Heat treatment or UV illumination are some of alternatives to improve the recovery phase of pristine CNF network. In this study, the measurements are conducted in room temperature only. The pristine CNF also exhibited some increment of resistance value after few days of measurements. This is most probably due to degradation of sensing properties which indicates that the pristine CNF is not suitable for a long period of time. Thus, the functionalization of CNF could improve the poor performances of pristine CNF. CNF-carboxyl displayed excellent. Moreover, the composited

used are not easy degradable material such as polymers or metals. The chemical treatment that applied in functionalization procedure is stable and reusable for a long period of time. CNF-carboxyl also showed fast response by exhibiting the response time in 30 seconds and fast recover with recovery time less than 60 seconds.

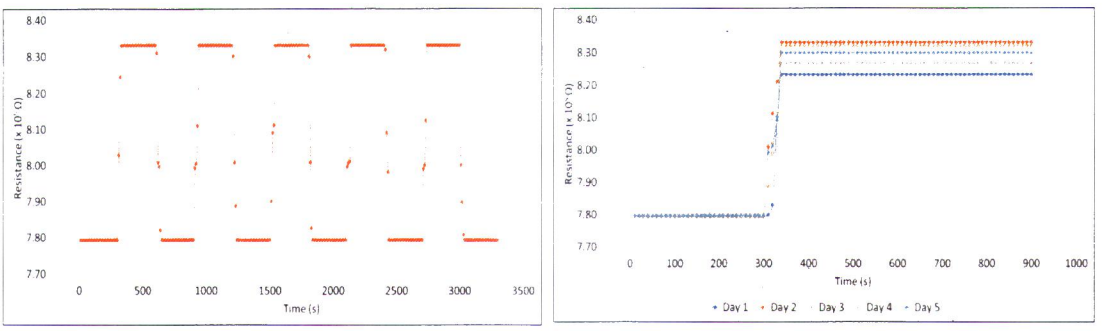

Fig. 4 (a) Repeatability and (b) Reusability of CNF-carboxyl towards benzene gas

Table 2 Response time and recovery time of pristine CNF and CNF-carboxyl

Sample	Response time (s)	Recovery time (s)
Pristine CNF	60	70
CNF-carboxyl	30	50

Conclusion

CNF was functionalized with carboxyl group using simple and low-cost technique. The sulphonitric mixture was used to attach carboxyl group on CNF surface. The characterization revealed that the attachment of carboxyl group was successful and further used as active sensing material in benzene detection. Results shown that the sensor response by CNF-carboxyl was higher than pristine CNF and achieved sensitivity of 36.74 % at room temperature for 0.125% benzene. The functional group acts as active site for adsorption of gas analyte. The fast response, stability and recovery of the sensor also favourable. The results clearly demonstrate the feasibility of manufacturing flexible and portable gas sensor based on functionalized CNF using simple and low-cost procedures.

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