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Low Cost and Room Temperature Methane Detection using Multi Walled-Carbon Nanotubes Functionalized with Octadecanol

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ABSTRACT

Multi walled-carbon nanotubes (CNT) functionalized with ester was used for detecting methane, CH_4 gas at room temperature. Quartz substrate with interdigitated prepatterned gold electrodes was employed as transducers and drop casting method was used to deposit the CNT samples. The electrical properties of the functionalized CNT samples in the presence of CH_4 gas were studied and the changes of resistance were recorded using digital multimeter. Concentration of CH_4 gas was varied from 0.125 % to 1.0 %. The resistance variation of functionalized CNT increased with the concentration of tested gas. Sensor response of functionalized CNT was improved more than 10 % as compared to pristine CNT. CNT-Ester gives the higher sensitivity due to the presence of ester functional group which act as active site to react with CH_4 gas. The fast response of functionalized CNT towards CH_4 gas suggested that the functional group enhanced the rate of gas adsorption on sensing layer.

Introduction

Methane or CH_4 is a simplest alkane compound also known as greenhouse gas (Lou et al., 2016) which contains one carbon atom and four hydrogen atoms. At room temperature and standard pressure, CH_4 exists as colourless and odourless gas that has extremely flammable properties. National Institute of Occupational Safety and Health (NIOSH) has set the safe CH_4 exposure at 1000 ppm (0.1%) in 8 hours period for workers. At higher concentration (more than 500 000 ppm), CH_4 can be asphyxiated and can replace oxygen in blood vessel (Brodny & Tutak, 2018). Thus, appropriate sensing material is required with good sensitivity, stability, fast response, low power consumption and can be operated in room temperature for being integrated in affordable detectors in CH_4 monitoring industry.

Carbon nanotubes (CNT) is an ideal sensing material due to the high surface area to volume ratio which significantly important for the interaction between gas analyte and sensing layer(Tung et al., 2015). Furthermore, the electrical properties of CNT are extremely sensitive to charge transfer and chemical modification effects by various functional groups (Hafaiedh et al., 2013). However, the main drawback of pristine CNT is due to its high van der Waals forces and strong sp^2 bonding in the hexagonal graphene network (Zaki et al., 2017). Due to these disadvantages, they tend to agglomerate and reduce the sensitivity of CNT as sensing material. One way to overcome this disadvantage is by modification of the edge and sidewall of CNT with new functional group. The functional group will detangle the agglomerated CNT and enhance the interaction between CNT and gas analyte (Pisal et al., 2014).

There are few literatures on detection of methane gas using CNT. S. Sattari et al.,2014 had developed polyaniline/MWCNT (PANI/MWCNT) for CH_4 detection using two different substrates; glass and silicon, Si. Resistance changes of sensor were observed upon exposure of CH_4 gas at room temperature. PANI/MWCNT showed higher sensitivity compared to pure PANI for both substrates. Moreover, PANI/MWCNT deposited on Si substrate exhibits good response due to p-type Si substrates gains more hole as carriers to enhance the conductance of sensor. Thus, PANI doped MWCNT on Si substrates have good potential in gas sensor field (Sattari et al., 2014). Chimowa et al., 2017 fabricated CH_4 sensor using MWCNT filling with vanadium oxide using simple capillary technique. The capability as CH_4 sensor was compared with unfilled MWCNT. MWCNT-Vanadium oxide showed great performance such as improved response time from 138 s to 16 s, shorten recovery time from 234 s to 120 s and increased sensitivity from 0.5% to 1.5% (Chimowa et al., 2017). Xiaoyu Chen et al., 2018 had investigated CH_4 gas sensing behaviour by lithium doped CNT sensor (Li-CNT). Concentration of CH_4 was varied from 50 – 500 ppm. Li-CNT sensor showed good response towards CH_4 gas with sensitivity 14.5 % at 500 ppm.

Polymer and metal decorated CNT was found to provide room temperature, sensitive, selective and good stability of CH_4 detectors (Hannon et al, 2016). However, such a device needs complicated preparation, high maintenance and produced large amount of solid waste that need to be landfilled, which adding cost of the detectors. Hence, CNT functionalized with chemical treatment may possess the requirements as good sensor with environmentally friendly approaches. In this study, the potential of CNT functionalized with octadecanol as the sensing material for the detection of CH_4 gas was investigated. Resistance changes upon exposure to methane gas were recorded to study the interaction between CNT with the gas analyte. Response time, sensitivity, repeatability and reusability of sensing material were also considered in order to verify the performance of functionalized CNT. The interaction of sensing layer and gas analytes was discussed further based on the variation of dipole moment of molecular substances.

Experimental Method

i. Functionalization of CNT

CNT used in this experiment was obtained from Nanostructured and Nanomaterials, USA with purity >95%, inner diameter 5 – 10 nm and outer diameter around 10 – 30 nm. The nanotubes were used in four type of forms: as a pristine CNT, CNT treated with sulphonitric mixture (as reaction precursor for further functionalization), CNT functionalized with ester group. All the functionalization process was assisted via sonication method to minimize the extremely damages on CNT structure. The carboxylated CNT was prepared by mixture of concentrated sulphuric acid and nitric acid in a molar ratio 3:1 in order to improve their dispersion in solvent and enhanced surface reactivity (Pisal et al., 2014). Carboxylated CNT became reaction precursor for further modification

with octadecanol to attach ester group. Basically, the carboxylation treatment involved ultra-sonication method at 70 °C for 2 hours. Once the reaction end, the product was diluted with deionised water, washed and filtered several times until reached pH 7. This product was labelled as CNT-Carboxyl (Janudin et al., 2017). For further functionalization, 0.5 mg of octadecanol was melted on hotplate before mixed with CNT-Carboxyl and sonicated for 15 minutes. Concentrated sulphuric acid was added dropwise as catalyst and the reaction was continued sonicated for five hours. Upon completion of reaction, the mixture was washed and filtered several times until it reached pH 7. The functionalized CNT produced was dried in vacuum oven for 24 hours and named as CNT-Ester.

ii. Fabrication of CNT-based gas sensor

Functionalized CNT were dispersed in polar solvent, dimethylformamide (DMF), sonicated for 30 minutes at room temperature and subsequently, deposited onto quartz sensor substrates using micropipette via drop cast method. Drop cast method is a favorable method due to it is low cost, simple and quick technique for deposition sample on substrate. These quartz substrates consist of prepatterned of indigitated gold electrodes with electrodes gap in 50 µm line/space provided by MARDI. The substrate was then heated in oven at 80 °C to ensure excess solvent was fully evaporated. Gold ribbons (purity: 99.9%) were attached to gold pads using silver conductive paste and left to dry and solidify at heated environment for 15 minutes. CH_4 gas sensing experiments were performed in customized chamber with electrical feedthrough occupied with temperature controller to maintain operating temperature at 25 °C. The gold ribbon was connected to True RMS Fluke 289 digital multimeter to record changes of resistance upon injection of tested gas. The electrical measurement was performed during adsorption and desorption cycles. A gas calibration system was employed to deliver specific concentration of CH_4 gas balanced in synthetic air into chamber during experiments. The sensing material was exposed to synthetic air as carrier gas at 200 standards cubic centimeters per minute (sccm) until stable resistance reading was reached. Then, the IDT was exposed to CH_4 gas at concentration 0.125%, 0.25%, 0.5%, 0.75% and 1.0% at room temperature. The duration of gas exposure was fixed at five minutes for each CH_4 concentration and chamber was purged with synthetic air in between each tested gas exposure, allowing the sensing material to recover to their initial state. A detailed schematic diagram of the measurement set-up can be seen in Fig. 1.

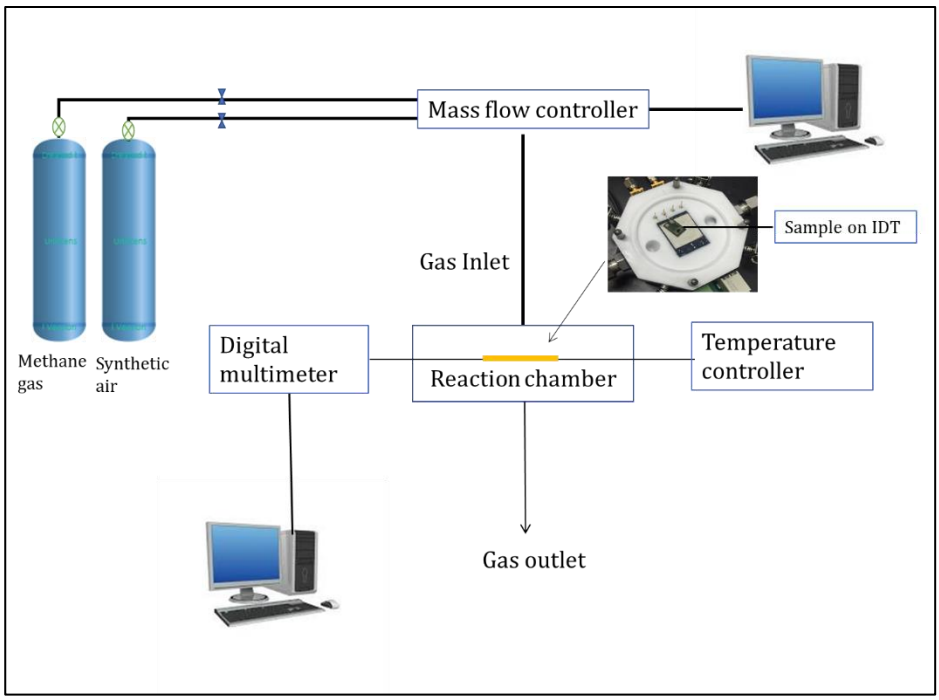

Fig. 1: Schematic diagram of measurement set up

Results and discussion

i. Material Characterization

The morphology of functionalized CNT was investigated by using FESEM. Fig. 2(a), (b) and (c) shows that pristine CNT, CNT-Carboxyl and CNT-Ester, respectively. The surface morphology of pristine CNT shown the highly entanglement between their tubes and the diameter was not uniform. Meanwhile, CNT-Carboxyl and CNT-Ester showed the less entanglement and the diameter distribution slightly increased due to functionalization by carboxyl and ester group. The tubes are appeared to be shorten, and the surface are rough. The changes of morphology of CNT surface suggested that carboxylic and ester group was successfully attached on the end and sidewalls of CNT. However, further characterization needs to be done to verify the attachment of ester group on CNT-Carboxyl.

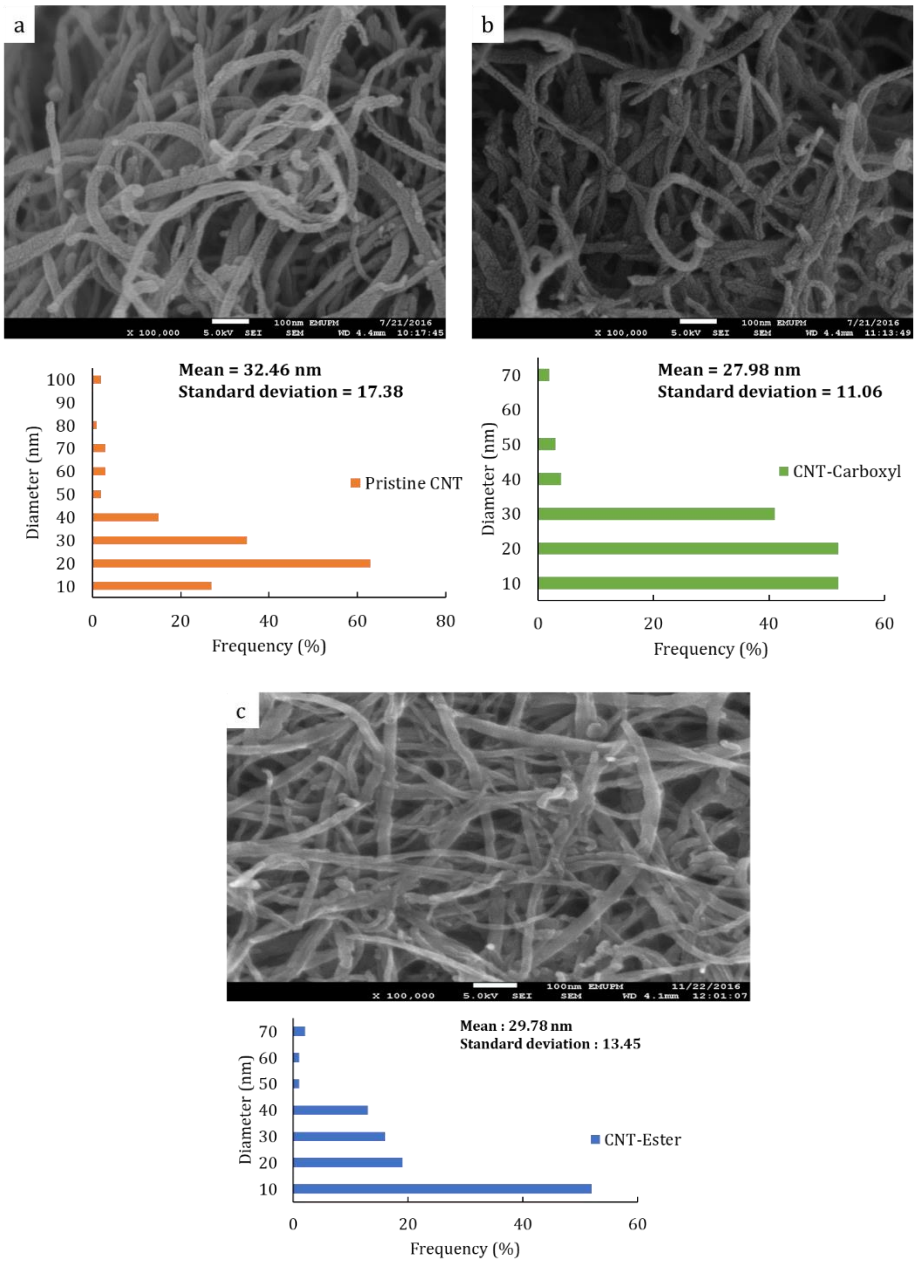

Fig. 2: FESEM image (a) pristine CNT, (b) CNT-Carboxyl and (c) CNT-Ester

Fig. 3 (a-c) shows the Raman spectra of pristine CNT, CNT-Carboxyl and CNT-Ester, respectively. In the high-frequency region of spectrum, two bands were observed showing the characteristics of CNT; these bands point the graphitic band (G band) and the disorder or defects of the structure, named D band. The ratio between the intensity of the D band and the G band, noted I_D/I_G, is related to the degree of disorder of the CNT. An increase in I_D/I_G value corresponds to a higher proportion of sp^3 carbon, which is generally attributed to the presence of more structural defects (Gómez et al., 2016). As can be observed in Raman spectra of CNT sample, the characteristic peaks of CNT, named the D band at 1344 cm^{-1} and 1350 cm^{-1} were appeared in pristine CNT and functionalized CNT, respectively. While, peaks at 1576 cm^{-1} , 1584 cm^{-1} and 1576 cm^{-1} is assigned to G band appeared at Raman spectrum of pristine CNT, CNT-Carboxyl and CNT-Ester, respectively. (Bokobza & Zhang, 2012). When carboxylation of CNT was performed, these characteristic peaks still can be observed, proving that the acid treatment does not damage the structure of CNT. Comparing the ratio I_D/I_G values of carboxylated and pristine CNT, it was observed that after functionalization, the ratio values increase as expected (Table 1). The oxidation of CNT breaks some of its bonds and inserts chemical groups that can be interpreted as defects on the structure (Osswald, Havel, & Gogotsi, 2007). Carboxylation treatment via sulphonitric mixture show a relevant change on the intensity of band D. The result indicates certain insertion of defects and/or break on the structure of CNT. This proves that the attachment of carboxyl group on CNT was successful via acid treatment. However, when the CNT-Carboxyl was further functionalized with ester, the G band shifted downfield ~6-14 cm^{-1} as compared to the CNT-Carboxyl. The shifted is due to the attachment of ester functional group on the surface of CNT. The ratio of I_D/I_G values of pristine CNT and CNT-Carboxyl was increased, but after functionalization with ester group the value was decreased (seen Table 1). It is proven that the inner graphitic layers of CNT were not affected by the ester functionalization and kept their highly oriented structure. This is in line with the lower intensity of D-band (level of defects in the sample) of CNT-Ester as compared to the CNT-Carboxyl (Kargarzadeh, 2017).

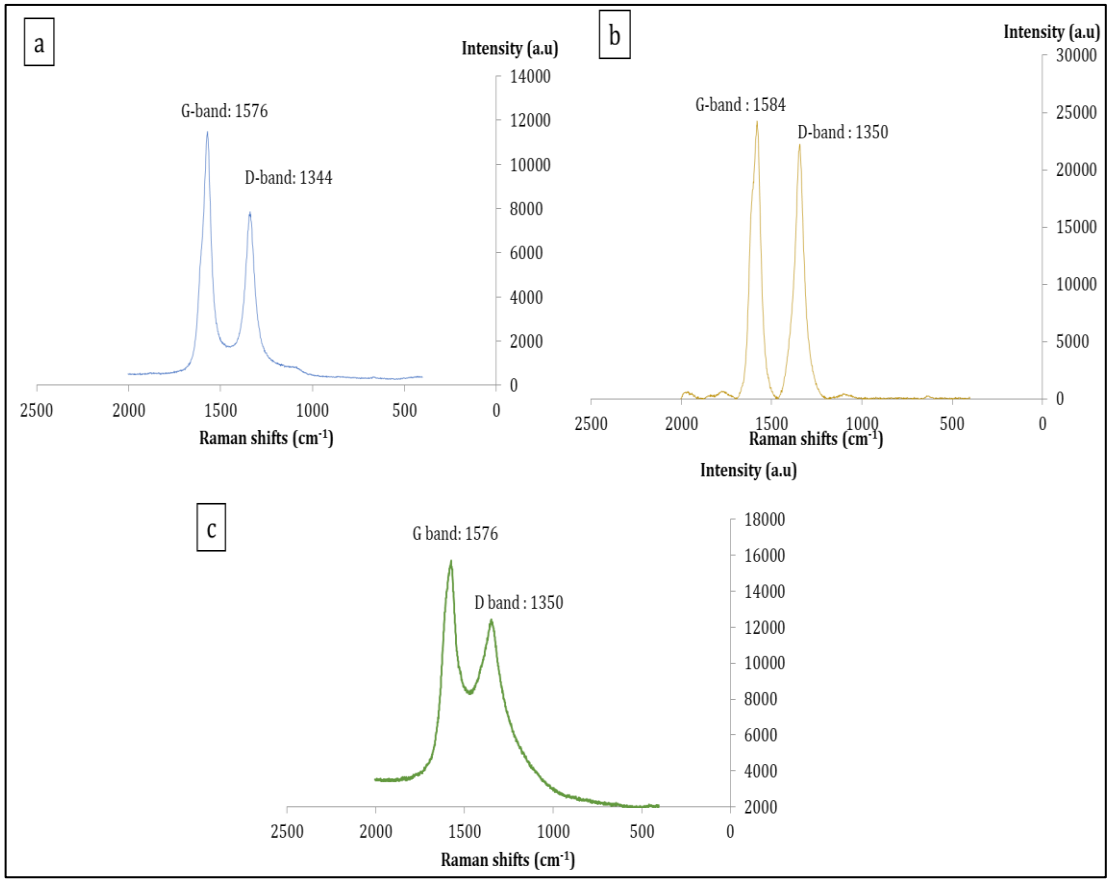

Fig. 3: Raman spectra of (a) pristine CNT, (b) CNT-Carboxyl and (c) CNT-Ester

Table 1: Intensity ratio of pristine CNT and functionalized CNT

Carbon Nanotubes	G band (cm^{-1})	D band (cm^{-1})	I_D/I_G
Pristine CNT	1576	1344	0.85
CNT-Carboxyl	1584	1350	0.96
CNT-Ester	1576	1350	0.80

Drop casting methods are commonly used to distribute a variety of substrate materials to the interdigitated transducers (IDT) surface (Muangrat et al., 2016), therefore, the same approach was used in this work. However, to minimize the multilayers and bundles of CNT, sonication is utilized at room temperature. In order to confirm that the CNT was remained on the IDT surface after the sonication process, FESEM was used to compare the surfaces of IDT after the preparation step. Fig. 4 (a-c) shows the surface of IDT deposited with carbon nanotubes. Based on the figures, the morphology of pristine CNT and functionalized CNT showed the good dispersion on IDT. The diameter of pristine CNT was in the range between 18 nm to 30 nm. The diameter of functionalized CNT slightly increased around 10 nm to 20 nm. Based on characterization result as discussed earlier, this was due to insertion of the new functional group on the carbon surface. It is also confirmed that the morphology of CNT-Carboxylic and CNT-Ester were unchanged after sonication treatment during dispersion in DMF. Besides that, FESEM images also proved the existence of CNT on the IDT which is used as a substrate in the investigation of gas sensing capability of CNT.

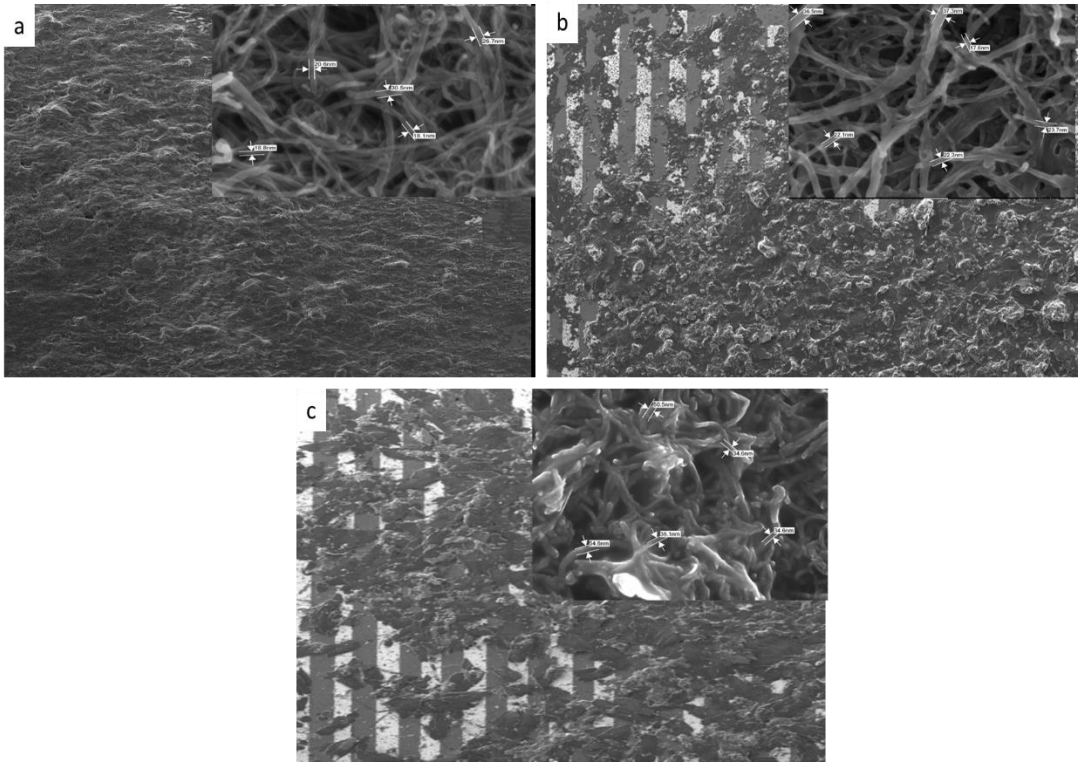

Fig. 4: FESEM micrograph images of (a) pristine CNT (b) CNT-Carboxyl and (c) CNT-Ester on gold interdigitated substrate

ii. Room temperature detection of CH_4 gas by CNT

Chemical treatments can lead to the p-doping which can shift Fermi level in sensing layer and resultant strengthen or weaken of all interband transitions in semiconducting material causing decrement or increment in resistance value, respectively (Afrin & Shah, 2015). This variation of

resistance value was observed in gas sensing measurements in terms of normalized sensor response. The normalized sensor response, S_R was calculated based on Eq. 1(Rigoni et al., 2014):

$$\boldsymbol{S_R}\ (\%) = \frac{\mathbf{R_g - R_o}}{\mathbf{R_o}} \times \mathbf{100} \quad (1)$$

Where R_g denotes for the resistance of CNT in the presence of CH_4 gas and R_o denotes for the resistance of CNT in the presence of synthetic air. Synthetic air was purged into the system for 30 minutes to 1 hour to stabilize sensing material properties. Table 2 shows the initial resistance of each CNT sample. The high initial resistance value in functionalized CNT suggested that the defect density was existed after functionalization treatment. By increasing the defect density, the conductivity of CNT sample was decreased accordingly (Afrin & Shah, 2015). Notable, the CNT sample are semiconducting material which owing both metallic and conductor properties in the same time which favourable properties as sensing material.

Table 2: Initial resistance value of pristine CNT and functionalized CNT

Sample	Resistance (Ω)
Pristine CNT	42.40 – 42.60
CNT-Carboxyl	1650.00 – 1680.00
CNT-Ester	6.71×10^7 – 7.07×10^7

To compare the sensitivity, S of pristine and functionalized CNT samples, the sensor response ratio was calculated at each concentration using Eq. 2 (Marshall, Popa-nita, & Shapter, 2006):

$$\boldsymbol{S} = \frac{(\boldsymbol{S_2 - S_1})}{\boldsymbol{S_1}} \quad (2)$$

Where S_1 denotes the sensor response of pristine CNT network and S_2 denotes the sensor response of functionalized CNT network. Fig. 5 shows the sensor response of CNT upon exposed to CH_4 gas at room temperature. Based on the figures, both CNT network showed an increase of resistance reading upon exposure of CH_4 gas. However, the response of pristine CNT increased about 2-7 % with increased of concentration. The poor response of pristine CNT was expected as the pristine CNT owing strong sp^2 bonding hexagonal network. This structure made the pristine CNT chemically inactive and prevent them to form chemical reaction with surrounding molecules (Afrin & Shah, 2015). Meanwhile, response of functionalized CNT was increased more than 10 % with increased of CH_4 concentration. This show that functional group in the CNT-Carboxyl and CNT-Ester acts as significant role in improving CNT response (Afrin & Shah, 2015; Marshall et al., 2006). CH_4 is a reducing gas which will donate electrons towards sensing layer. The increasing number of electrons on sensing layer will lead to reduction number of holes and therefore, increased the resistance value of CNT sample (Kumar, Sahatiya, & Dubey, 2014). This phenomenon suggests that CNT sample acts as p-type semiconducting sensor, where holes are their majority carriers. By recombination or restructuring of holes concentration, it will change the resistance of sensing layer (Chen et al., 2018).

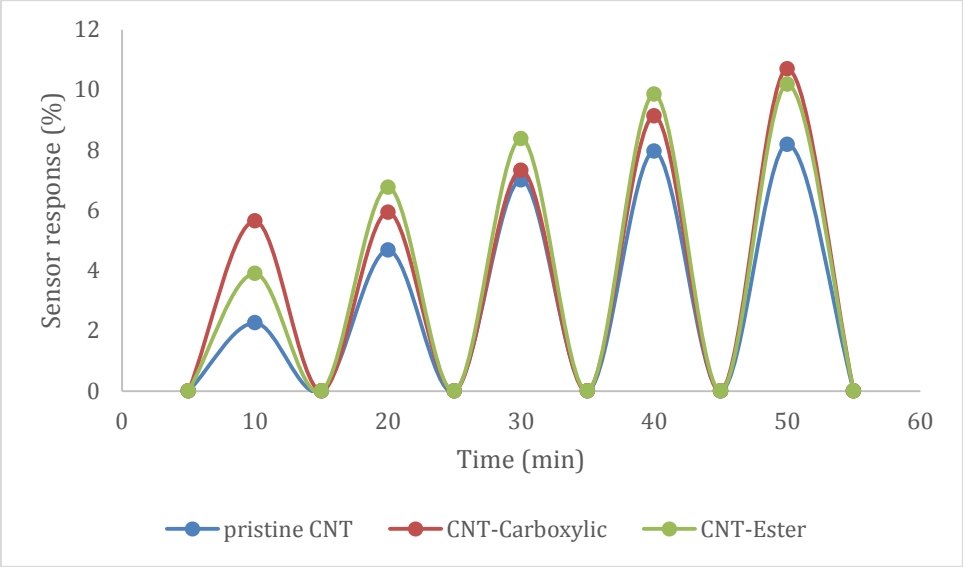

Fig. 5: Response of CNT sample towards detection of CH_4 gas at different concentration

Sensitivity of CNT sample was measured according to Eq. 2 and plotted as plotted in Fig. 6. Based on the graph, CNT-Carboxyl showed highest sensitivity as compared to CNT-Ester network at concentration 0.125 %. However, better sensitivity performance with increasing of CH_4 concentration was shown by CNT-Ester. It is most likely due to saturation effect. Functional group including carboxyl and ester acts as active site for the adsorption of gas analytes. The gas analytes were adsorbed on the surface of CNT and presence of functional group increased the rate of gas adsorption. Upon exposure of CH_4 gas at lowest concentration, the gas analytes fully adsorbed on the active sites exists in CNT-Carboxyl, resulting better sensitivity than CNT-Ester. However, the availability of active site is limited and interaction between gas analytes and sensing layer was decreased with increment of CH_4 concentration and hence, the sensitivity of CNT-Carboxyl was decreased. This is because the gas analytes were saturated on the surface of CNT-Carboxyl. As compared to CNT-Ester, the sensitivity was increased as CH_4 concentration increased proved that saturation effect did not exists in CNT-Ester network which make the CNT-Ester sensing layer is more favourable for methane detection.

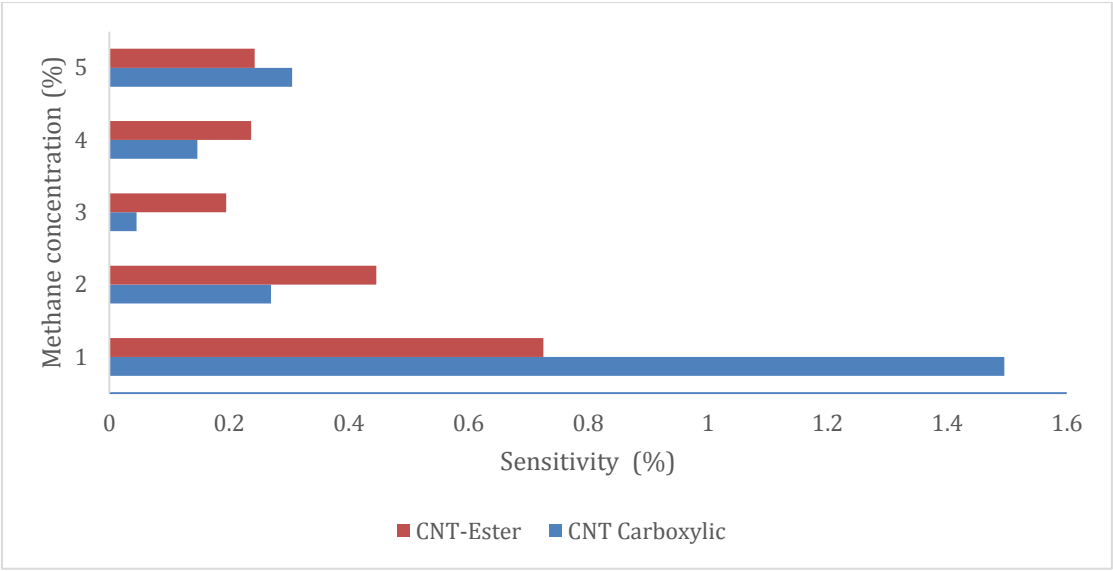

Fig. 6: Sensitivity of CNT sample at different concentration of CH_4 gas

Repeatability of CNT sample towards CH_4 detection was investigated by taking five measurements of 1.0% of CH_4 gas in sensing chamber within a day. Meanwhile, reusability of CNT sample was studied by purged 10 minutes of CH_4 gas in sensing chamber within a week. Fig. 7 (a),

(b) and (c) shows the repeatability and reusability of pristine CNT, CNT-Carboxyl and CNT-Ester, respectively. Based on the figure, it was clearly showed that pristine CNT network had poor response due to first injection of 1.0% was achieved within a minute. The pristine CNT also need more than a minute to back to their initial resistance in recovery phase. The inertness of pristine CNT network limits the potential of CNT as nanostructure gas sensor (Some et al., 2013). Meanwhile, all functionalized CNT showed good stability, fast response and short recovery time. Average time that the functionalized CNT took to achieve 90 % of CH_4 concentration was 40 s. They also managed to regain their baseline resistance value less than 50 s. Functional group on the edge and sidewalls of CNT contributed to the fast response of CNT network. They act as extra active area for gas adsorption, thus improved the response during the exposure of target gas. Excellent performances of functionalized CNT make them good candidate to develop as miniature gas sensor especially in CH_4 monitoring at room temperature.

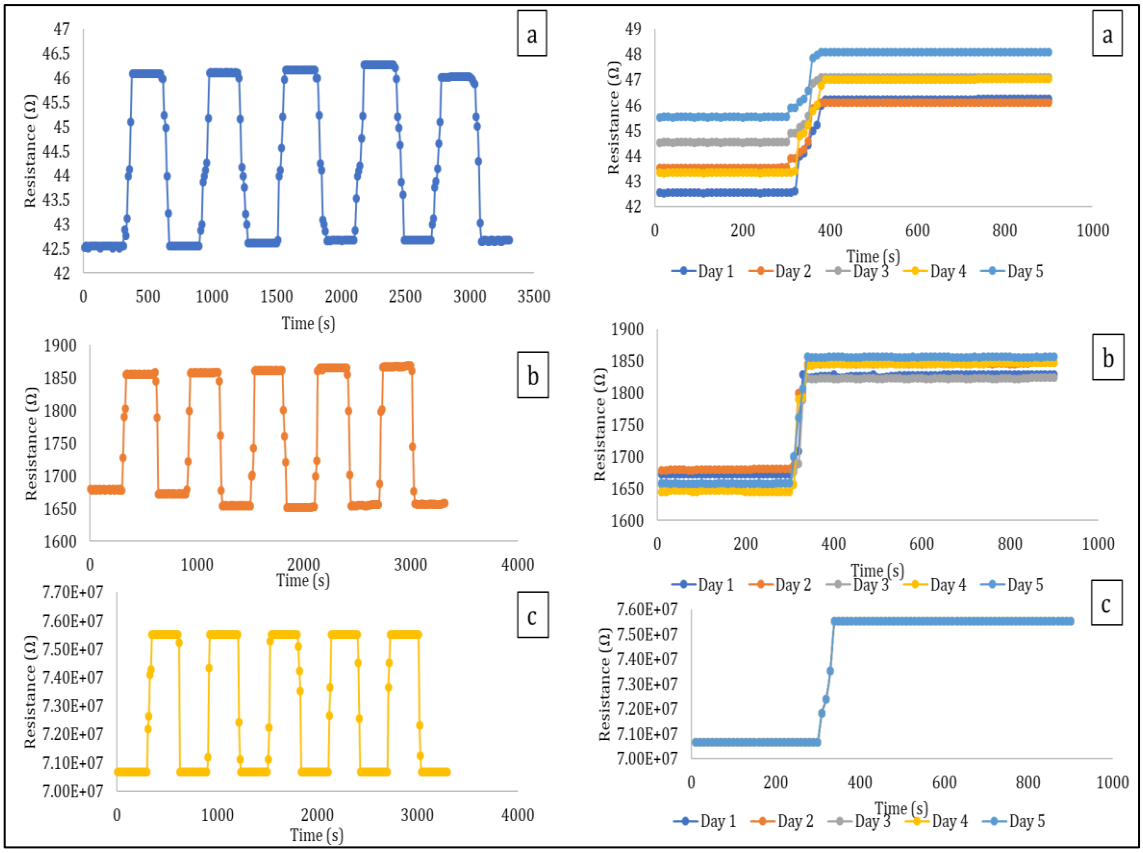

Fig. 7: Repeatability and reusability of (a) pristine CNT (b) CNT-Carboxyl (c) CNT-Ester

Conclusion

Multi walled CNT functionalized with carboxyl and ester group have been used for the detection of CH_4 gas at room temperature. Quartz substrate with interdigitated gold electrode were implemented as transducers and the drop casting method was used to deposit them with CNT sample. The electrical properties of CNT sample as sensing material were studied based on resistance changes with the presence of CH_4 gas at different concentration.

The resistance of CNT sample increased with concentration of CH_4 gas. The functionalized CNT showed high sensitivity and excellent recovery time during the desorption process. The response time also around 40 s for all functionalized CNT, in despite of their type of functional group. At lowest concentration of CH_4 gas, CNT-Carboxyl showed highest sensitivity which is 1.5 % as compared to CNT-Ester, but CNT-Ester showed better sensitivity as CH_4 gas concentration increased. Functional group act as active site to capture more gas analyte which results the enhancement of sensor response. These findings will give huge contribution on development of CH_4 gas sensor that is cost effective, portable and low power consumption which can applied in environmental monitoring or workplace protection.

The performance of CNT as sensing material was presented in this work, and the greater sensitivity may lead to another result of many kinds of gases. Gases that categorised in same type of CH_4 gas group which is electron donating group will give similar response as CH_4 gas which may contribute to false detection. Hence, multiple sensor arrays that consists different sensing material characteristics could overcome the false detection and improved the selectivity issue.

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