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Carbon Nanotubes-based Gas Sensor in Detection of Methane Gas at Room Temperature

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ABSTRACT

Room temperature carbon nanotubes (CNT)-based gas sensor was utilised in detection of methane, CH_4 gas. The CNT was functionalized with amide group via Fischer esterification process and labelled as CNT-Amide. Silicon dioxide, SiO_2 substrate with interdigitated prepatterned gold electrodes were employed as transducers and drop casting technique was used to deposit the multi walled-CNT samples. The electrical properties of the functionalized CNT samples in the exposure of CH_4 gas are studied by recorded the changes of resistance using digital multimeter. Concentration of CH_4 gas was varied from 1250 ppm to 10 000 ppm. The changes of electrical resistance of CNT-Amide increases with the concentration of tested gas. Sensor response of functionalized CNT are improved more than 10% as compared to pristine CNT. The sensitivity of CNT-Amide also better than CNT-Carboxyl due to the presence of nitrogen element in amide functional group which chemically active to react with CH_4 gas. Additionally, fast response of CNT-Amide towards CH_4 gas suggested that the functional group enhanced the rate of gas adsorption on sensing layer.

Introduction

Methane, CH_4 gas is an odourless and colourless gas, it is mainly used as natural gas resources for electricity generation by burning it as a fuel in a gas turbine or steam generator. Due to its extremely

flammable properties, National Institute of Occupational Safety and Health (NIOSH) had set safe limit in exposure to CH_4 gas for 0.1% in working environment. CH_4 can form as an explosive substance if the concentration level reach more than 10%. Thus, it is necessary to develop a reliable, fast response and low-cost device in detection of CH_4 gas. By far, numerous research of CH_4 sensors including metal oxide semiconductor gas sensor [1]–[3], photoacoustic-based gas sensor [4], graphene based gas sensor [5], [6] and tin oxide, SnO_2-based gas sensor [7]–[9] has been published at different concentration of CH_4 gas. However, these types of sensors required high power consumption, poor response and costly to be integrated in CH_4 monitoring industrial.

Carbon nanotubes, CNT are widely used as sensing material for detection of various gases. The unique characteristics of CNT including high surface area to volume ratio [10], highly sensitive and fast recover in short period, made CNT a good candidate in detection of CH_4 gas at ppm level. These characteristics are important in order to improve the interaction between gas analytes and sensing material, in this case, CNT. However, pristine CNT tend to agglomerate due to their strong sp^2 bonding in their hexagonal network [11]. The agglomeration morphology of CNT will limit their capability as CH_4 sensor. Modification of CNT with various functional group is one ways to overcome this disadvantage [12]. Moreover, electrical properties of CNT are sensitive towards chemical modification effects by functional group attached on surface of CNT.

In this study, we synthesized CNT modified with amide functional group using dodecylamine as functionalizing reactant. CNT was functionalized with carboxyl group via sulphonitric treatment. Then, pristine and functionalized CNT were characterized with Fourier Transform Infrared (FT-IR) spectroscopy and the morphology of the samples on interdigitated transducer (IDT) were characterized using Field Emission-Scanning Electron Microscopy (FESEM). Detection of CH_4 gas was conducted in air tight gas chamber and the electrical resistance of CNT sample was monitored by digital multimeter. Sensor response and sensitivity of pristine and functionalized CNT network were investigated.

Materials and Methodology

i. Modification of CNT

CNT was purchased from Nanostructured and Nanomaterials, USA with inner diameter 5 to 10 nm and purity more than 95%. Sulphuric acid (H_2SO_4), nitric acid (HNO_3) and dodecylamine ($CH_3(CH_2)_{11}NH_2$) were supplied by Merck, Germany in high purity and without any pre-treatment. First, CNT was immersed in solution of H_2SO_4 and HNO_3 in a mole ratio 3:1. The mixture was placed in sonicator water bath for 2 hours at 70^0C. Then, the mixture was diluted with deionised water, filtered, washed for several times until reached pH 7 and dried in vacuum oven for 24 hours at 80^0C and labelled as CNT-carboxyl. Fig. 1 shows schematic diagram of preparation of CNT-carboxyl.

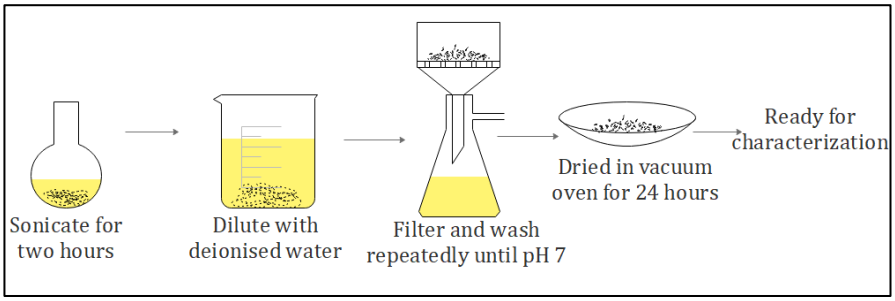

Fig. 1: Preparation of CNT-carboxyl

For further modification with amide functional group, 1.0g of CNT-Carboxyl and 0.5g $CH_3(CH_2)_{11}NH_2$ were mixed together and placed in sonicator water bath for 5 hours. The dilution, filtration and drying procedure of sample was carried out same as CNT-Carboxyl preparation and named as CNT-Amide. Each sample produced was characterized using Fourier Transform-Infrared (FT-IR) spectroscopy (Model Spectrum BX FTIR Perkin Elmer, England) and scanned between 4000 cm^{-1} to 400 cm^{-1}.

ii. Sensor fabrication and detection measurement

Pristine CNT and functionalized CNT were dispersed in dimethylformamide (DMF) solvent and drop casting method was chosen to deposit the sample onto silicon dioxide (SiO_2) substrate with interdigitated prepatterned gold electrodes. Then, gold ribbons (99.9%) was placed on gold plates by silver conductive paste and dried in oven at 60^0C for 10 minutes until it well solidified.

For detection of CH_4, the IDT with deposited of CNT sample on gold electrodes was placed in air tight gas chamber and synthetic air as carrier gas was purged into system for 1 hour to stabilize the sample properties. In order to compare the effect of functionalization towards detection of CH_4 gas, we compared the change of resistance of pristine and functionalized CNT. The electrical resistance of sample was monitored by digital multimeter (Fluke True RMS 289) when exposed to different gas concentration. CH_4 gas (1250 ppm, 2500 ppm, 5000 ppm, 7500 ppm and 10 000 ppm) were purged into the system in duration 5 minutes alternately with synthetic air to study the capability of CNT sample to recover to their initial state. Each of measurements were conducted in room temperature and controlled humidity environment (55%). Fig. 2 shows schematic diagram of gas sensor set-up for detection of CH_4 gas.

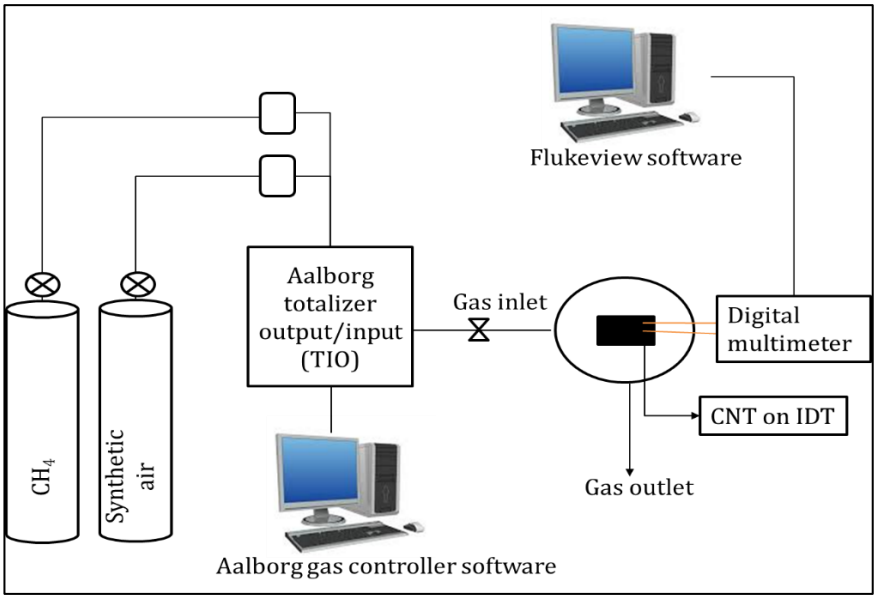

Fig. 2: Gas sensor set-up for detection of CH_4 gas

Findings and Discussions

i. Characterization of carbon nanotubes

FT-IR is the most widely used vibrational spectroscopic technique. FT-IR spectroscopy was used to obtain an infrared spectrum in a whole range of wavenumbers simultaneously to study the functional group attached on the functionalized CNT. Fig. 3 shows the FT-IR spectra for pristine and functionalized CNT.

The weak peaks appeared in the pristine CNT at 2903 cm^{-1} is corresponded to O-H band (stretching from hydroxyl group) and peak at 1648 cm^{-1} is corresponded to C=O band from carboxyl group. The CNT supplied by the manufacturer was treated by acid to get 95% purity. Thus, the presence of carboxyl functional group is expected as discussed by Abuilaiwi et al., 2010 and Nag et al., 2016. The signal occurred at 978 cm^{-1} is assigned to the deformation and bending of different C-H bonds and in agreement with the findings by Haniyeh et al., 2013.

The hydroxyl (O-H) band (3151 cm^{-1}) in the CNT-carboxyl spectrum is associated with the presence of various oxidations species from carboxylation treatment. The peak at 2987 cm^{-1} can be assigned to the O-H stretch from strongly hydrogen bonded -COOH as supported by Zhao et al.,

2013. The C=O band characteristics of carboxyl functional group (-COOH) appeared in the 1671 cm^{-1} and carboxylation treatment has confirmed successful due to the appearance of this C=O band. Well-constructed of hexagonal structure on the CNT was confirmed by the existence of band at 1522cm^{-1} interpreted as carbon double bond (C=C) aromatic and unsaturated structures [13]. Meanwhile, the band from 1352 cm^{-1} is attributed to the stretching modes of the C-O-H bonds of the carboxylic acid [14], [15]. As a result of carboxylation, number of functional groups should be increase after treatment with concentrated of H_2SO_4 and HNO_3 mixture as discussed by Yudianti et al., 2011. The CNT-carboxyl will then used as reaction precursor for further functionalization with amide group [10].

FT-IR spectrum for CNT-Amide shows that band of C-N stretching appeared approximately at 1034 cm^{-1}. Band at 2916 cm^{-1} is corresponded to C-H bonding indicated that the long hydrocarbon chain $(CH_2)_{11}$ of dodecylamine successfully attached on CNT-Amide and in agreement as reported by Le at al., 2013 and Silva et al., 2012. It was observed that the band at 1671 cm^{-1} has become weak and a new band at 1654 cm^{-1} has appeared, suggesting the formation of amide functional group (N-C=O) on CNT-Amide. Ferreira et al., 2017 and Zanganeh et al., 2016 also reported the same findings on appearance new band at 1600 cm^{-1}. Hence, FT-IR spectra of both functionalized CNT had confirmed that the surface of CNT were successfully modified with carboxyl and amide functional groups as predicted.

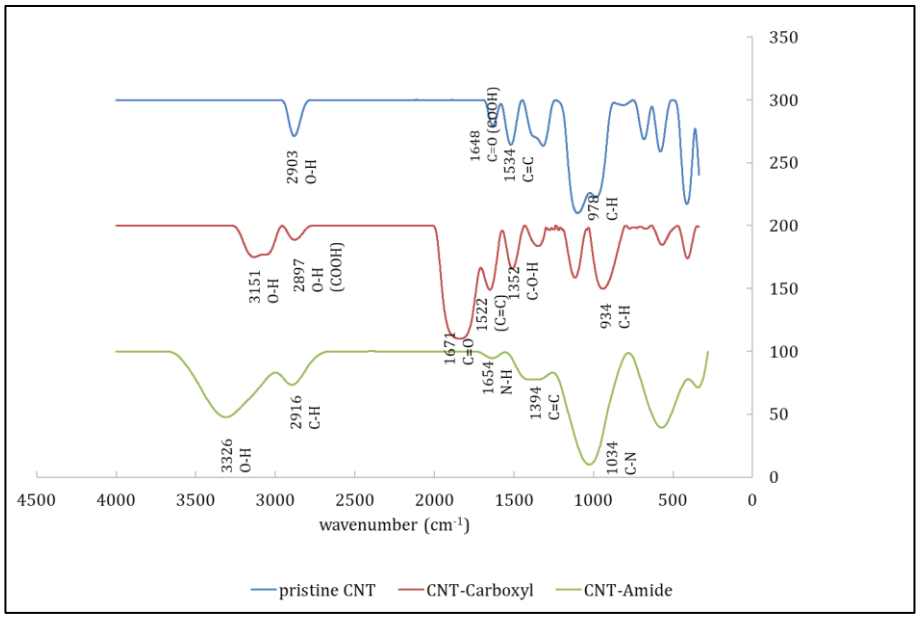

Fig. 3: FT-IR spectra of pristine CNT, CNT-carboxyl and CNT-Amide

ii. Characterization of CNT on IDT

CNT samples were deposited on IDT by drop-cast method. The morphology of CNT on gold electrodes was examined using FESEM (JEOL 7600F). The CNT paste was prepared by sonication process in organic solvent for 30 minutes and by using Eppendorf micropipette, 2.5µL of CNT paste was drop-cast on the IDT. Fig. 4 shows FESEM images of morphology of CNT on IDT. Based on the results, the CNT was in well dispersed condition even after the sonication process was conducted. The changes in tubes structure of functionalized CNT is caused by acid treatment as discussed in our previous article [18]. The well dispersed of CNT paste is caused by the presence of functional group on CNT[10]. Functionalization of CNT has improved the dispersion of CNT in solvent matrix, hence, the preparation of CNT-based gas sensor is easier and cheaper. Furthermore, it is confirmed that the existence of CNT on the IDT which is used as substrate in the experimental of detection of CH_4 gas.

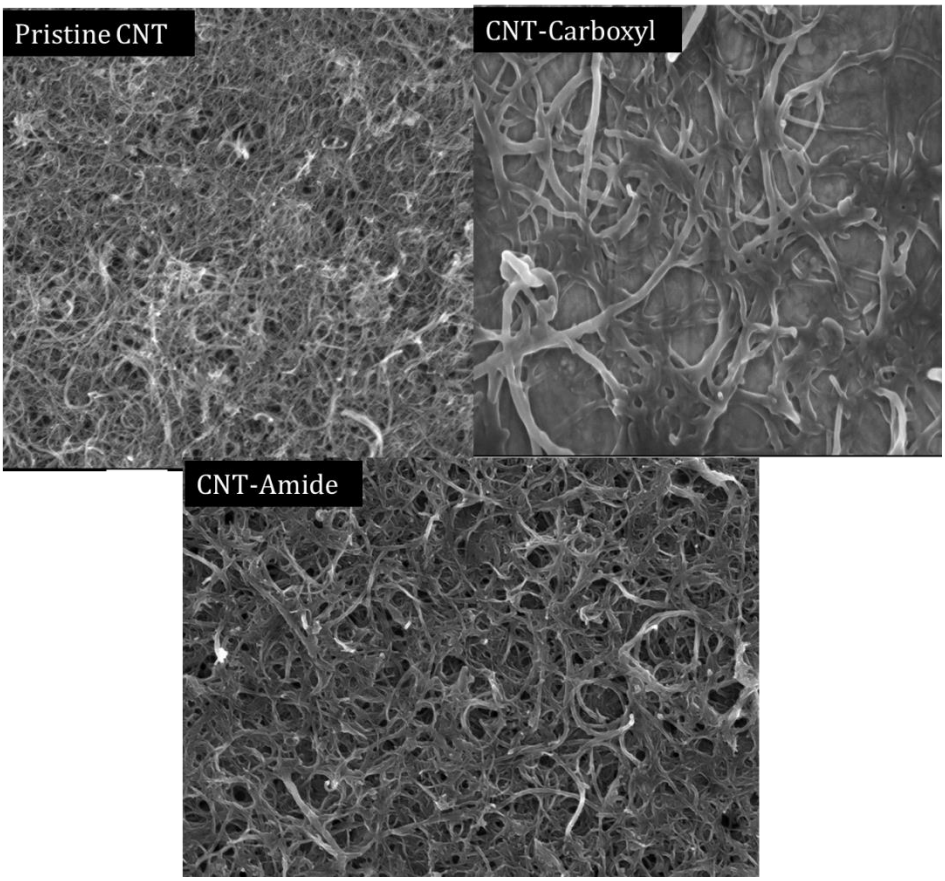

Fig.4: Morphology of pristine CNT, CNT-carboxyl and CNT-Amide on IDT

iii. Detection of methane

Based on the literature review, CNT owing semiconductor properties where insulator and conductor properties at same time which favourable for application as sensing layer [19]. In order to investigate performance and sensitivity of CNT network as sensing material, the detection of CH_4 gas test was carried out. Sensor response (S_R) of CNT network upon exposure of gas was presented in normalized data by using Eq. 1[20]:

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

Where, R_g indicated electrical resistance of CNT network with the presence of gas analytes and R_o indicated electrical resistance of CNT network with the presence of synthetic air. Then, sensitivity (S) of CNT network was analyzed using Eq. 2 [21]:

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

Where S_1 indicated the sensor response, S_1 of pristine CNT and S_2 indicated the sensor response of functionalized CNT.

Fig. 5 summarized the sensor response of CNT network versus time performance at different CH_4's concentration. At lower concentration of 1250 ppm, CNT-Carboxyl showed highest increment of sensor response, meanwhile response of pristine CNT has increased about 2% only. The poor response by pristine CNT was expected as the agglomeration occurred in their morphology had limit the interaction between CNT and gas analytes. Surprisingly, the sensor response has increased with increasing of CH_4 concentration in CNT-Amide network. CNT-Amide

network shown a better response as compared to CNT-Carboxyl due to the presence of monovalence electrons in amide functional group. The monovalence electrons are chemically active and could easily react with other element in their surroundings. Thus, gas analytes were more attracted to amide functional group and increased the sensor response in CNT-Amide sensing layer.

Fig. 5: Sensor response of pristine CNT and functionalized CNT

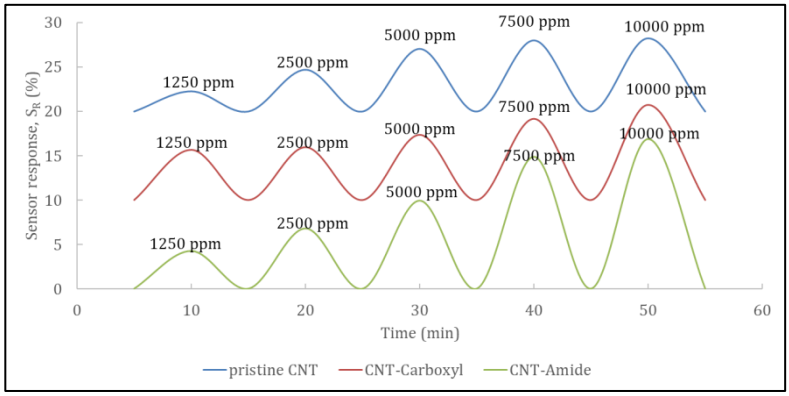

Fig. 6 displayed the sensitivity performance of CNT-Carboxyl and CNT-Amide. At lower concentration, CNT-Carboxyl showed better sensitivity than CNT-Amide. The high affinity of carboxyl group traps more electrons, consequently adsorbed high rate of gas analytes and resulting increased the sensitivity of CNT-Carboxyl network. This finding is in agreement with Pradip Kar and Arup Choudhury (2013) and K. Y. Doung et al., 2016. The carboxyl group acts as interaction site within the nanocomposite sensor which lead to faster the adsorption of gas analyte. However, the availability of carboxyl group is limited and fully occupied with gas analytes, thus the sensitivity reduced when concentration of CH_4 gas increased. This situation explained the pattern of sensitivity reduction in CNT-Carboxyl network.

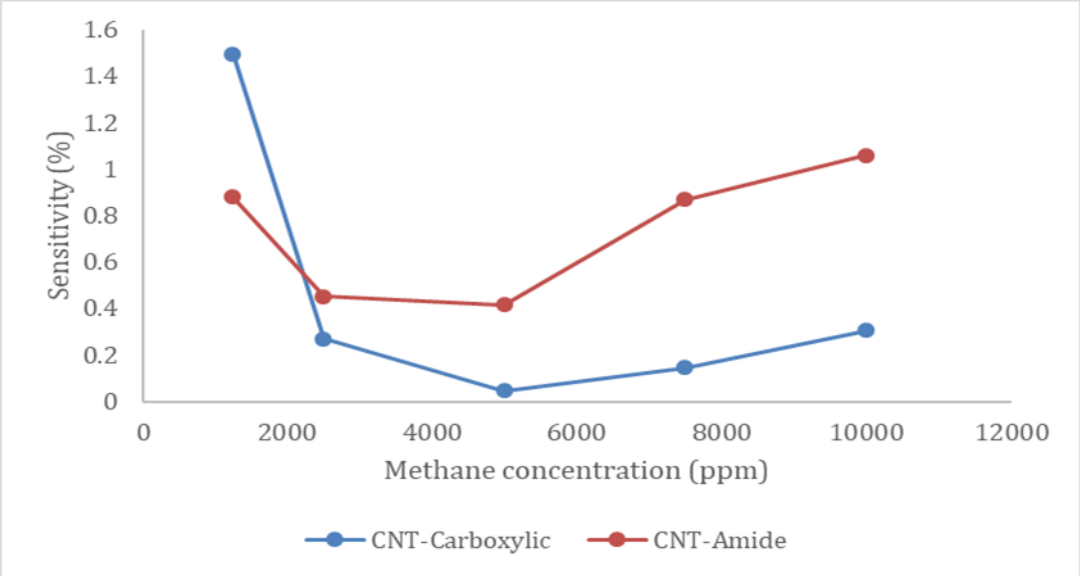

Fig. 6: Sensitivity of CNT-Carboxyl and CNT-Amide network

iv. Mechanism of methane detection by CNT-based gas sensor

The van der Waals interaction between CNT sample as sensing layer and methane gas is generally weak and can be denoted as:

Functionalized CNT+ Gas analytes $\rightarrow$Functionalized CNT$^{\Delta e}$ Gas analytes$^{\Delta h}$ [22]

Where "Δe" indicates the number of amount electron transferred and "Δh" indicates the number of amount hole carriers transferred during the interaction between the sensing material and gas analyte. Furthermore, due to CNT is extremely sensitive to the changes of charge transfer, hence, adsorption of gas analytes could induce change in the electrical properties of CNT [23]. CH_4 gas acts as electron donating group in both CNT sample, pristine and functionalized CNT. It will donate electron towards sensing layer and decrease the number of hole carrier. Hole carrier is the majority charge carrier in p-type semiconducting CNT material, the depletion of hole carrier will increase the resistance of sensor on exposure of CH_4 gas [24]. Additionally, interaction of oxidising gas with adsorption site of CNT leads to the shifting the Fermi level closer to the conduction band of CNT (seen Fig. 6). The functional group in the sensing layer efficiently enhanced rate of adsorption of CH_4 gas during the detection. They act as an active site and captured more electron from gas analyte and increased the sensor response. As a result, it significantly improved the sensor response and increased the sensitivity of functionalized CNT sample. The functional group accelerated the recovery process of sensing material to their initial condition as those interaction is physisorption only. Synthetic air as carrier gas would removed the gas analytes on the surface of CNT at room temperature. These results are important for CH_4 sensing application in which portability and reusability is required, since the sensor does not need any extra treatment such UV illumination or heating at high temperature to desorb the gas after measurements. It can readily reuse and avoid power hungry, costly and time-consuming device.

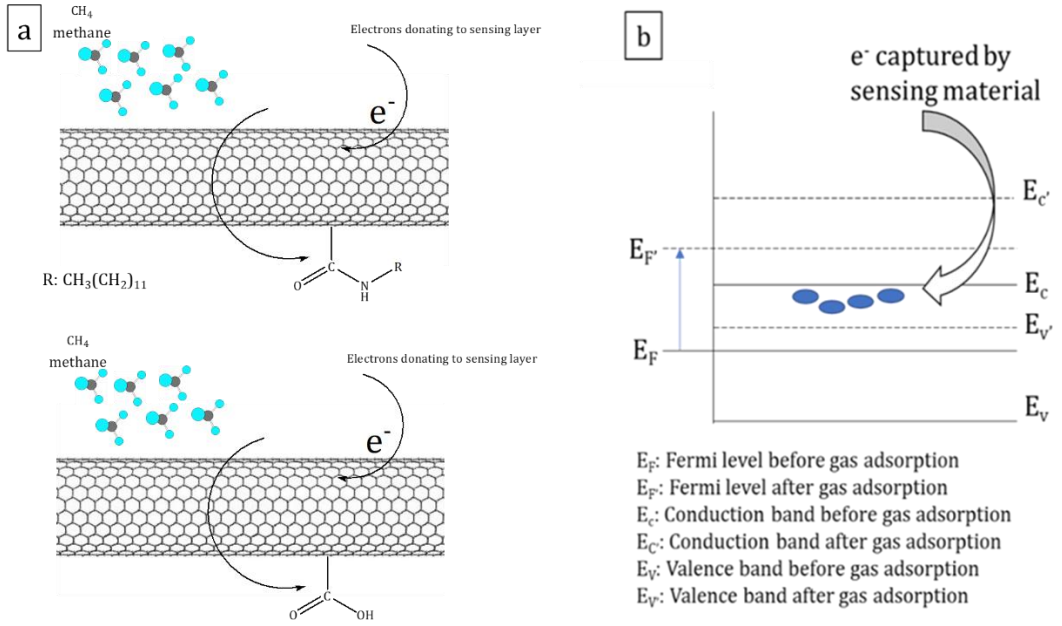

Fig. 6: (a) Schematic mechanism on adsorption of CH_4 gas on CNT sensing layer (b) band diagram of interaction between gas analytes and sensing layer (solid lines before gas adsorption, dashed lines after gas adsorption)

Conclusion

CNT functionalized with carboxyl group was prepared by a mixture of H_2SO_4 and HNO_3. It was further functionalized with amide group using $CH_3(CH_2)_{11}NH_2$ as functionalizing reactant. The attachment of functional group improved the sensor response and sensitivity performance of CNT network as sensing layer. All the measurements of CH_4 detection were carried out at room temperature, which significantly important in utilizing CNT as sensing layer for CH_4 gas monitoring in industrial environment as well as public health concern.

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