Functionalized Carbon Nanofibers as Sensing Material for Acetone Gas

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Abstract. This article proposes a new sensing material made from carbon nanofibers (CNF) that were first functionalized with a carboxyl group before being further modified with an amide functional group. At room temperature, this sensing material was used to detect acetone gas. Fischer Esterification was used to create modified CNF with dodecylamine as the functionalizing reactant. FT-IR analysis was used to confirm the attachment of the carboxyl and amide functional groups to the modified CNF. As per the results of the characterization, CNF was successfully modified with the carboxyl and amide functional groups, as evidenced by the presence of new peaks in the FT-IR spectra. The modified CNF was then dropped cast onto IDT and placed in a customised chamber with an electrical feedthrough occupied with outlet/inlet gas. The resistance of modified CNF upon injection of ammonia gas was monitored with a digital multimeter and compared with the resistance of pristine CNF. Based on the result, modified CNF showed a better response and higher sensitivity than pristine CNF at room temperature. The resistance of modified CNF to acetone gas injection was measured using a digital multimeter and compared to the resistance of pristine CNF. Result shown that, modified CNF performed better and had higher sensitivity than pristine CNF at room temperature.

INTRODUCTION

Carbon nanofibers (CNF) have recently attracted a lot of attention in sensor application areas due to their unique properties such as excellent chemical and mechanical stability, high energy-efficiency because the carbon material on fibres has a fine graphite crystalline structure, and the possibility of mass production [1]. CNF has emerged as a promising material in a variety of applications due to its high performance. CNF, on the other hand, is hydrophobic and difficult to disperse homogeneously in most matrices, which limits its production applications [2]. It has been discovered that surface-bound functional groups on carbon nanostructures can improve their dispersibility, wettability, surface reactivity in fluids, and the degree of carbon/matrix interfacial binding within the composite material. Non-covalent functionalization, covalent functionalization, physical chemistry such as mechanochemical and electrochemical reactions, and outer wall/inner wall functionalization are the different types of carbon nanomaterial functionalization. Heating in a mixture of concentrated sulphuric acid and nitric acid (H_2SO_4: HNO_3) in a mol ratio of 3:1 or in concentrated nitric acid, HNO_3 solution is one of the main approaches to CNF functionalization [3].

Organic compound, acetone has the most basic ketone and is colourless, mobile, and flammable. Acetone's most dangerous characteristic is its extreme flammability [4]. Acetone vapours can be ignited by static discharge. Acetone has been extensively studied and is widely accepted to have low acute and chronic toxicity when ingested and/or inhaled. In humans, inhaling high concentrations of air caused throat irritation. Acetone is not currently considered a carcinogen, a mutagenic chemical, or a source of chronic neurotoxicity. Thus, the development of novel and feasible technologies for detection of acetone is become huge demand.

Objectives of this paper are to study the effect of functionalization of CNF towards the detection of acetone gas. Amide functional group was attached into CNF and characterized using Fourier Transform-Infrared analysis. Then, CNF occupied with amide functional group was used in the customized system to investigate the performance of CNF upon exposure to acetone gas. All of the measurements was performed at room temperature.

EXPERIMENTAL METHOD

High quality and purity of materials were purchased by the various supplier. Carbon nanofibers was purchased from Nanostructured & Amorphous Materials, Inc., USA. Sulphuric acid (98% purity), nitric acid (65% purity), N,N-dimethylformamide for analysis and dodecylamine (99% purity) were purchased from Merck company (Germany). Acetone gas (1% concentration) and nitrogen gas were produced by AGS company. All the chemicals and materials were used without any pre-treatment or purification process. Functionalization of carbon nanofibers with carboxyl and amide and detection of acetone are depicted in Fig. 1, 2 and 3, respectively. Details of functionalization CNF has been published in here [5].

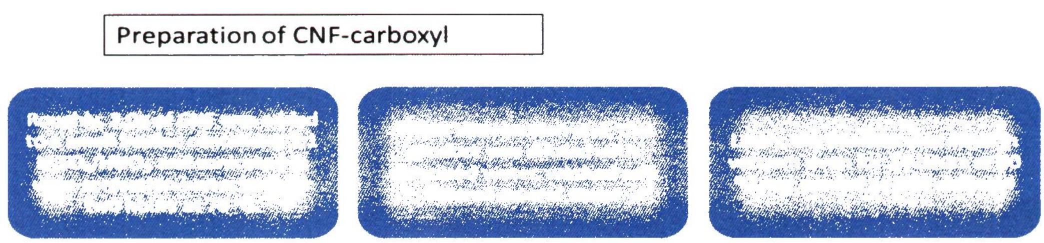

Fig. 1 Preparation of CNT-carboxyl

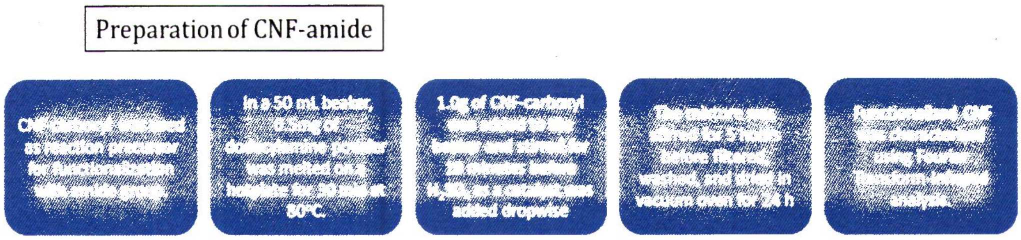

Fig. 2 Preparation of CNF-amide using dodecylamine

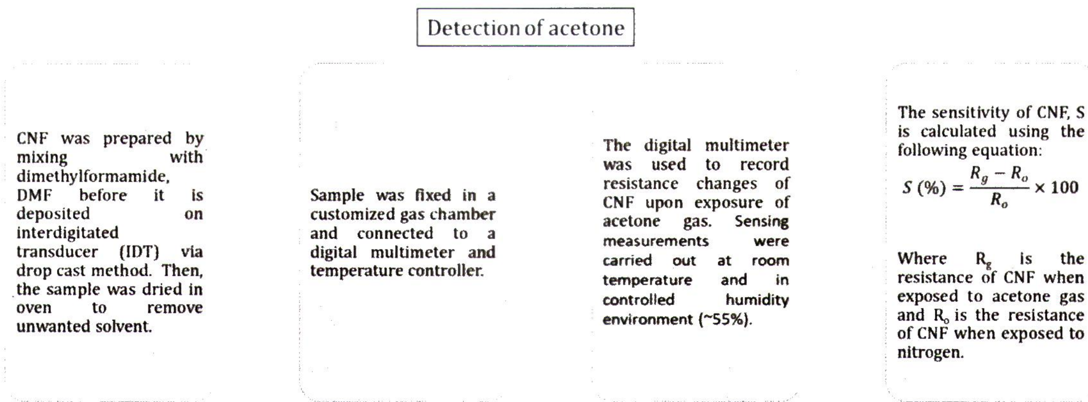

Fig. 3 Detection of acetone at room temperature

RESULT AND DISCUSSION

Characterization of CNF

Figure 4 represents FT-IR spectra of pristine CNF, CNF-carboxyl and CNF-amide. In the FT-IR spectrum of pristine CNF, peak at 3167 cm^{-1} is associated with the stretching of free hydroxyl group (O-H). The peak at 2821 cm^{-1} is corresponded to the C-H stretching modes of H-C=O in the carboxyl group, while band C=O of carboxyl group appeared at 1640 cm^{-1}. The present of carboxyl group is due to pre-treatment by manufacturer [6] to improve the purity of CNF sample (~75%). The C=C stretching bands of the aromatic ring can be observed at 1506 cm^{-1} and peak at 1320 cm^{-1} is associated with C-O from various chemical surroundings [7]. FT-IR spectrum shows identical peaks for carboxylation on the sidewalls of CNF. Peak at 3164 cm^{-1} is associated to the O-H stretching band which confirmed the oxidations occurred in the functionalized CNF [8]. The presence of =C-H stretching band from carboxyl group appeared at peak 2795 cm^{-1} is assigned to the deform benzene rings of CNF. This is in agreement as reported by Yudianti *et al.*, (2011). The indication of C=C from aromatic ring is observed at peak 1549 cm^{-1} as discussed by Huang *et al.*, (2012). Peaks appeared at 1339 cm^{-1} and 1159 cm^{-1} are assigned to C-O stretching band from carboxyl groups. The intensity of C-H stretching band of 2795 cm^{-1} increased in the CNF-carboxyl spectrum as compared to C-H band in the pristine CNF. This had confirmed that oxidation process occurred. The intensity is due to the presence of hydroxyl and carboxyl group covalently attached to the CNF during the surface modification by acid treatment [10]. Peak appeared at 931 cm^{-1} at both spectra including pristine CNF indicated the deformation and bending of different C-H bonds and parallel to the study by Haniyeh *et al.*, (2013). At FT-IR spectrum of CNF-amide, C-N stretching appeared approximately at 1034 cm^{-1} and 1174 cm^{-1}. Band at 2916 cm^{-1} is from C-H bonding indicated that the long carbon hydro chain $(CH_2)_{11}$ of dodecylamine is successfully attached on CNF-amide as reported by Le *et al.*, (2013) and Silva *et al.*, (2012). It is observed that the band at ~1700 cm^{-1} has become weak and a new band at 1654 cm^{-1} and 1626 cm^{-1} has appeared, suggesting the formation of amide functional group (N-C=O) on CNF-amide. Ferreira *et al.*, (2017) and Zanganeh *et al.*, (2016) also found an appearance of a new band at 1600 cm^{-1} [12], [13]. Hence, FT-IR spectra of both functionalized CNT and CNF had confirmed that the surface of CNT and CNF are successfully modified with ester and amide functional groups.

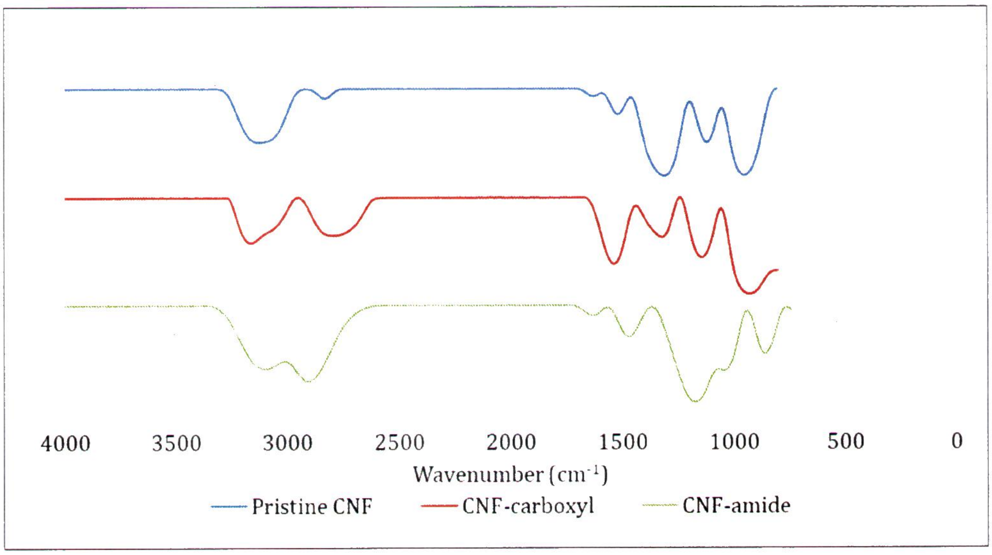

Fig. 4 FT-IR spectra of pristine CNF, CNF-carboxyl, and CNF-amide

Acetone detection using functionalized CNF as sensing material

Fig. 5 and 6 show the sensor response, S_R, and sensitivity of pristine CNF and functionalized CNF for acetone gas. The sensor response of pristine CNF showed a poor response when the concentration of gas is increased. This could due lack of active sites for adsorption of gas analytes in pristine CNF. CNF-carboxyl, and CNF-amide exhibited higher response towards acetone gas. The higher sensing response with gas concentration is caused by increasing of the active sites of functionalized CNF. The findings are consistent for all concentration levels of acetone gas. This indicates that the interaction between gas analytes and sensing layers is weak bonding, which is physisorption, instead of strong chemical interaction [14]. The sensitivity of sensor network towards the exposure of acetone gas at room temperature is 6.23% as compared to CNF-carboxyl which is 3.95%. The highest sensitivity achieved by CNF-amide in detection of acetone gas are attributed to the presence of amide functional group. Sayago et al., (2008) stated that functional group plays significant role as an extra active area for gas adsorption by CNF network as sensing material [15]. It allows more gas molecules to interact and eventually releasing free electron to adsorb. The free electrons move to conduction band of oxide group (carboxyl and amide) in the functionalized CNF altered the hole concentration. These processes reduce hole-electron carriers and increased the number of charge electron carriers in sensing layers. Therefore, it increased the resistance of CNF and improved the sensitivity of CNF.

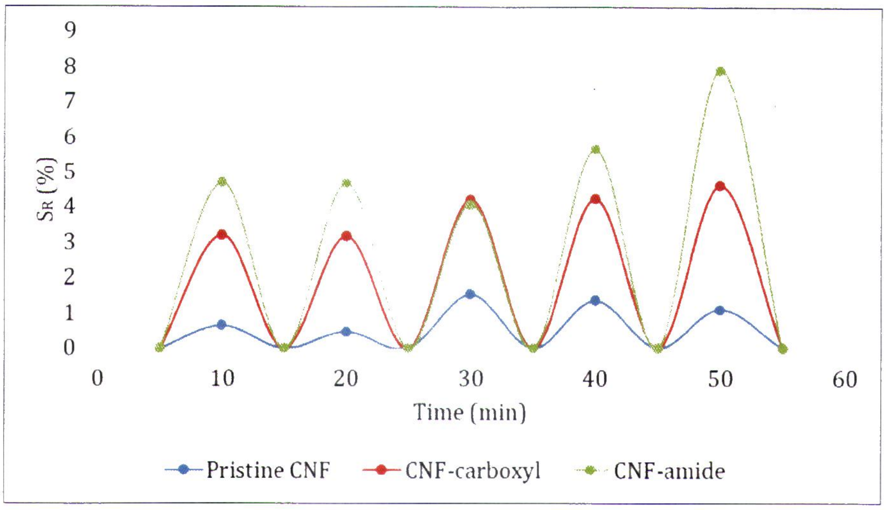

Fig. 5 Sensor response of pristine CNF, CNF-carboxyl and CNF-amide

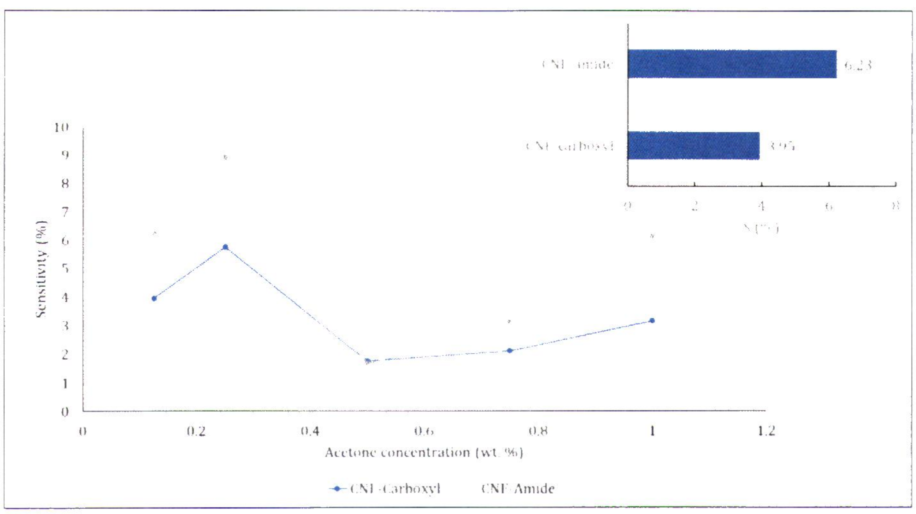

Fig. 6 Sensitivity of functionalized CNF as sensing material for detection acetone gas

CONCLUSION

In this study, CNF was successfully modified with carboxyl and amide functional group by oxidation using a mixture of concentrated sulphuric acid and nitric acid and Fischer Esterification, respectively. The appearance of new peaks indicated the successful attachment of new functional group on pristine CNF. CNF with functional group showed great potential as sensing materials in the detection of acetone gas at room temperature.

ACKNOWLEDGMENT

These works were supported by Ministry of Higher Education (KPT) under Fundamental Research Grant Scheme (FRGS, Code Grant: **FRGS/1/2016/STG01/UPNM/02/1**). The authors also would like to acknowledge UPNM and UPM for their tremendous support.

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