The Detection Properties of Bulky Wrapped MWCNTs Towards Hazardous Gases

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ABSTRACT

The present paper investigates the bulk detection properties of low cost Multi-Wall Carbon Nanotubes (MWCNTs) towards gas analytes. The MWCNTs were physically functionalized based on a polymeric wrapping process to enhance their selectivity. Here, Polyetherglycol (PEG), Polyetherimide (PEI), and Nafion were the polymers used. Two-way based electrodes were manufactured and exposed to hazardous gases and the detection measured through changes in their electrical resistivity. It was shown that the wrapping process induces a degree of selectivity on the CNTs. It has been observed that while the CNTs-PEG complex is selective towards NH_3, the CNTs-PAN conjugate is sensitive to NO_2. The CNTs-Nafion matrix showed selectivity towards NO_2 and NH_3. Here, it was observed that the electrical resistance decreased in contact with NO_2, whereas it increased when exposed to NH_3. Detection of CO was also carried out and observations show that the degree of selectivity can be tailored based on the selection of wrapping material used.

Keywords: carbon nanotubes, sensors, polymers, wrapping and hazardous gases.

1 INTRODUCTION

The objective of this research is to develop an NO_2 detection platform using carbon nanotubes, (CNTs). CNTs inherently have very low resistances, whereas most polymers have very high resistances. Hence, the junction of these two materials appears to yield a conjugate CNTs-polymer complex with semi-conductor properties that can detect hazardous gases [1]. The change in the electrical properties of the conjugated polymer-CNTs appears to be due to the gas absorption, the swelling of the polymer, or the charge transfer between the polymer and the molecules of the analyte [1]. Previous efforts in the area of CNT based sensors have concentrated on the detection of gases [2,3]. Kong et al. studied the electrical response of CNTs as chemical detectors for NO_2 and NH_3 and found that whereas the conductivity of the nanotubes increases when in contact to NO_2, it decreases in the presence of NH_3 [4]. In such study, a voltage gate was used to shift the Fermi levels of the nanotubes in order to modulate the resistance of the nanomaterial. Someya et al. have also worked on detecting alcohol vapors using carbon nanotube based (field-effect transistor) FETs, and found that CNTs are sensitive to a wide range of alcohols [5]. They also show that the change in the electrical properties of the nanotubes, due to the analytes, depends strongly on the gate voltage applied to the nanodevice. Additional research using a two terminal CNTs-film based resistor approach has been studied by Valentini et al [6]. They showed that carbon nanotubes are capable of sensing several gases including NO_2, NH_3 and C_2H_5OH. Further research work on detection has been done by coating CNTs with specific polymers [7]. Philip et al developed a CNT-PMMA (Polymethylmethacrylate) sensor for detecting a range of gases and found that detection takes place at room temperature based on the polymer volume expansion and polar vapor-nanotube interaction [8]. Li et al. have introduced organic coating to detect Cl_2 and HCl, suggesting that the detection properties of nanotubes can be tailored based on the polymer used [9]. Although the sensing properties of CNTs have been continuously studied, most of the works have concentrated on individual single wall carbon nanotubes, (SWCNTs), as well as on chemical modifications in order to introduce selectivity into the nanotubes. However, sensors based on individual SWCNTs require complex instruments as well as an expensive nanotubes source. Additionally, chemical treatments can introduce damage to the sidewall structure of the nanotube leading to latent damage of the entire system [3]. Hence, the present project will investigate the sensing properties of a bed of relative, non-expensive nanotubes (MWCNTs) with properties based on physical polymer functionalization. Here, several polymers will be investigated in order to study their effects on the detection properties of the nanotubes.

2 EXPERIMENTAL METHODOLOGY

The investigated MWCNTs were synthesized using Chemical Vapor Deposition (CVD) with an incorporated spray pyrolysis process using alpha-pinene, a renewable biological agent, as the carbon source and ferrocene as a catalyst. The synthesized CNTs were subjected to Transmission Electron Microscopy (TEM) and Raman spectroscopy analysis in order to characterize their structural properties. Figure 1 shows the TEM image of the CNTs here investigated after being subjected to a chemical treatment for removing impurities. The figure shows a multi-wall structure with no apparent presence of amorphous carbon. Indeed, Raman spectroscopy also confirmed the high percentage of purity of the nanotubes by exhibiting a relatively high G/D peaks ratio (see Figure 2).

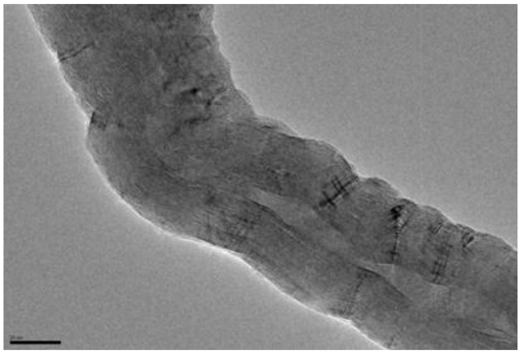


Figure 1: TEM image of the MWCNTs investigated.

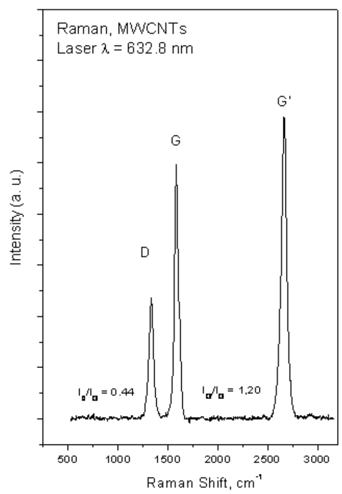


Figure 2: Raman spectra of the synthesized MWCNTs.

Subsequently, the MWCNTs were physically functionalized to enhance their selective properties through a polymeric wrapping process. Aqueous solutions of polymers and CNTs were prepared at various ratios and subjected to ultrasonic treatment proceeded by a thermal "cooking" process. The polymer matrices used for functionalization included Polyetherglycol (PEG), Polyethyleneimide (PEI), Polyanilyne (PAN) and Nafion, a sulfonated tetrafluoroethylene based fluoropolymer-copolymer. The CNT/Polymer conglomerate was then layered on the electrode (see Figure 3), and encapsulated in gas desiccators (see Figure 4). Here, the mass ratio of CNTs to polymers used for coating the electrodes was varied from 1:8 to 16:1.

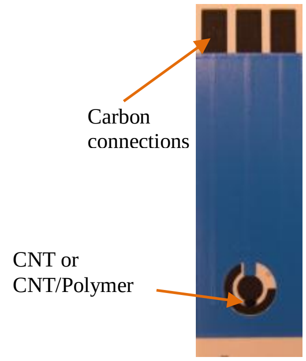


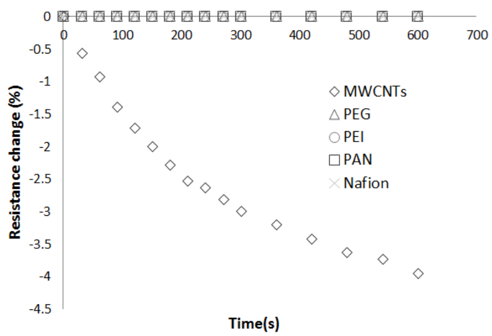
Figure 3: CNT:Polymer based two-way electrode.

Duplicates of all electrodes were prepared and tested concurrently to allow for detection of false positives. The NO_2 gas used for exposure was prepared by reacting nitric acid with copper while the NH_3 was produced by the redox reaction of NaOH and NH_4Cl. In the case of CO, the carbon monoxide was produced by reacting formic acid with sulfuric acid. To convert to parts per million in air, the volume of the desiccator was measured and the reaction was assumed to reach completion. Although the extent of the reaction is not measured this assumption allows for the upper limit of exposure to be measured and used for comparison. In order to measure the electrical gain/loss in response to gas exposure, the electrodes were wired to an InstruNet Data Acquisition device with corresponding software. Once the electrodes reached a stable baseline resistance the data acquisition unit began recording and after approximately one minute the gas was produced in the enclosed container. Gas mixtures were also here investigated by adding a second gas into the chamber. Changes in resistance across the electrode were measured continuously throughout. Figure 4 shows the apparatus set up used in this research work including the gas desiccators, data acquisition device and electrical connections.

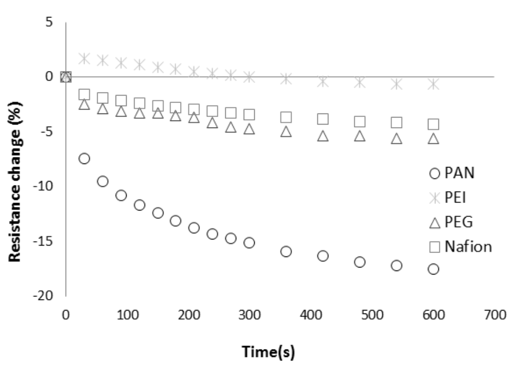
Fig 4. Experimental set up for gas detection

3 RESULTS AND DISCUSSIONS

The results showed definite changes in electrical output in response to gas exposure. Figure 5a shows the change in resistance of the plain polymers as well as the plain MWCNTs when exposed to approximately 9 ppm of NO_2. From Figure 5a, it can be observed that whereas the plain polymers are unable to detect the presence of the NO_2, the nanotubes showed 4% reduction from their original baseline, suggesting the detection of the gas. Indeed, previous studies have seen that CNTs are able to detect hazardous gases [7,9]. Figure 5b shows the electrical resistance of the different CNTs:Polymer (1:1 ratio) complexes studied. From Figure 5b it can be observed that PEG appears to slightly enhance the selectivity of the nanotubes, since the conjugated system showed a resistance change around 5%. The figure also shows the results of the nanotubes coated with PAN, and it can be observed that this conjugated complex yielded a notable change in its resistance outcome, over a 10% change in resistance, thus suggesting a high degree of selectivity towards NO_2. This affinity could be associated to the positive charge present in the PAN polymer.



a.)



b.)

Figure 5: Electrical response of the systems studied when subjected to approximately 9 ppm of NO_2. (a) Plain MWCNTs and polymers. (b) CNTs: Polymer (1:1 ratio)

The coated carbon nanotubes were also exposed to a maximum of 5500 ppm NH_3 in air. Figure 6 shows the electrical resistance output of the different CNTs-coated systems here tested. From Figure 6, it can be observed that PEG seems to have yielded the highest selectivity, 1.4% change in resistance. This pattern could be associated to the positive affinity of NH_3 towards the negative electrical cloud present in the PEG polymer. It is worth noting that whereas the PEG induced a slight decrease in the electrical resistance of the nanotubes when exposed to NO_2, it yielded an opposite response in the NH_3 environment. These are encouraging results for they suggest that a single wrapping material can detect gases with unique responses.

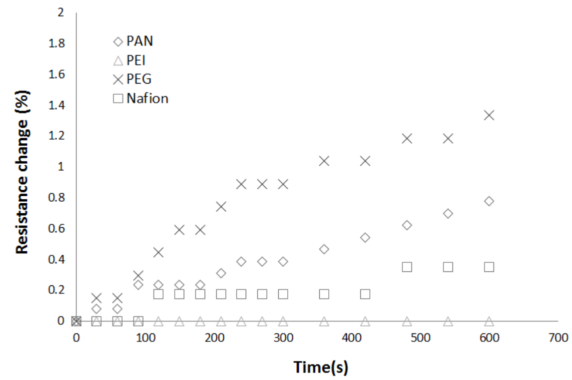


Figure 6: Electrical response of MWCNTS based sensors towards 5500 ppm of NH_3.

The wrapped MWCNTs were also exposed to 12% CO in air by volume and it was observed that the PEI appeared to have a remarkable induced affinity towards it, as seen below in Figure 7. It seems that the negative cloud charge of the CO gas interacted with the (positively charged) imide groups of the PEI polymer. It should be noted that the changes in resistance of the remaining CNT:Polymer systems were negligible. These results are again encouraging since show that selective analytes can be detected using specific physical functionalizations on the CNTs.

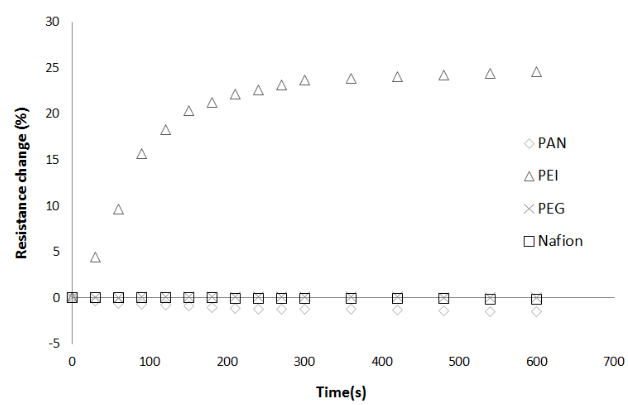


Figure 7: Electrical response of MWCNTS based sensors towards 12% CO in air by volume.

Mixtures of gases were also investigated and Figure 8 shows that the polymeric functionalization can result in a selective detection. Here, the CNTs coated with PEI resulted in a slight resistance decrement when exposed to NH_3, while the CNTs coated with Nafion showed an opposite outcome when subjected to the ammonia gas. The results suggest that the electronegativity of the polymers contribute to the selectivity of the gases detected. Indeed, PEI and Nafion have oppositely charged functional groups thus allowing for different responses between like charged gases.

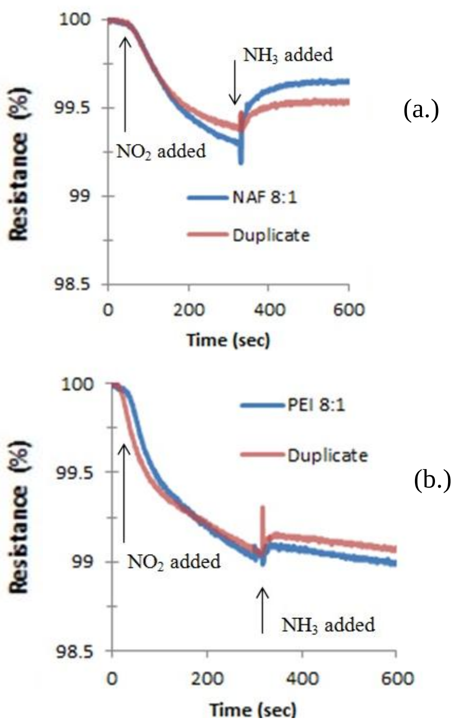


Figure 8: Electrical response of MWCNTS based sensors towards 9 ppm NO2 and excess NH3. (a) Nafion wrapped CNT. (b) PEI. The wrapped nanotubes complex was based on a 8:1 (CNTs:Polymer) ratio.

Again these results show promise for they suggest that particular polymers can allow for selective detection of the CNT based sensors and can be selective for specific analytes.

4 CONCLUSIONS

Here, the presented work shows that physically functionalized MWCNTs are capable of selectively detecting gas analytes with relative sensitivity in real time. By wrapping MWCNTS with a variety of polymer matrices it is seen that through a selective process polymers can be chosen to tailor the detection properties of a CNT based sensor. Polymer functionalization has been shown to be a promising alternative to chemical treatment and specialized synthesis conditions for creating CNTs with attractive electrical properties. The ability to use MWCNTs, which are more readily available at lower costs than SWCNTs, for the selective and sensitive detection of chemical agents has been demonstrated, showing great potential for the commercialization of carbonaceous detecting devices.

ACKNOWLEDGMENTS

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REFERENCES

[1] Vaseashta, A & Irudayaraj, J 2005. “Nanostructured and nanoscale devices and sensors,” Journal of Optoelectronics and Advanced Materials, vol 7, no.1,pp. 35-42.

[2] J. Li, Y. Lu, Q. Ye, et al., “Carbon nanotubes sensors for gas and organic vapour detection,” Nano Letters, vol. 3, no. 7, pp. 929–933, 2003.

[3] J. Suehiro, G. Zhou, and M. Hara, “Fabrication of a carbon nanotube-based gas sensor using dielectrophoresis and its application for ammonia detection by impedance spectroscopy,” Journal of Physics D, vol. 36, no. 21, pp. L109–L114, 2003.

[4] J. Kong, N. R. Franklin, C. Zhou, et al., “Nanotube molecular wires as chemical sensors,” Science, vol. 287, no. 5453, pp. 622– 625, 2000.

[5] T. Someya, J. Small, P. Kim, C. Nuckolls, and J. T. Yardley, “Alcohol vapor sensors based on single-walled carbon nanotube field effect transistors,” Nano Letters, vol. 3, no. 7, pp. 877–881, 2003.

[6] L. Valentini, C. Cantalini, I. Armentano, J. M. Kenny, L. Lozzi, and S. Santucci, “Highly sensitive and selective sensors based on carbon nanotubes thin films for molecular detection”. Diamond and Related Materials, vol. 13, no. 4–8, pp. 1301–1305, 2004.

[7] M. C. Petty and R. Casalini, “Gas sensing for the 21st century: the case for organic thin films,” Engineering Science and Education Journal, vol. 10, no. 3, pp. 99–105, 2001.

[8] B. Philip, J. K. Abraham, and A. Chandrasekhar, “Carbon nanotube/PMMA composite thin films for gas-sensing applications,” Smart Mater. & Struct., vol. 12, pp. 935–939, 2003.

[9] J. Li, Y. Lu, and M. Meyyappan, “Nano chemical sensors with polymer-coated carbon nanotubes,” IEEE Sensors Journal, vol. 6, no. 5, pp. 1047–1051, 2006.

[10] T. Ueda, M. M. H. Bhuiyan, H. Norimatsu, S. Katsuki, T. Ikegami, and F. Mitsugi, “Development of carbon nanotubebased gas sensors for NOx gas detection working at low temperature,” Physica E, vol. 40, no. 7, pp. 2272–2277, 2008.