

Highly Sensitive NO₂ Detection and DMMP Sensing at Room Temperature using Flexible SWNT Thick Film Sensor

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ABSTRACT

Low cost; easy to fabricate and flexible single wall carbon nanotubes thick film resistor (SWNT-TFR) for detailed study of NO₂ detection is reported. SWNT-TFR was fabricated by vacuum filtration technique on flexible polycarbonate membrane. SWNT-TFR sensor shows selective response to NO₂. The response increases from 1.47 per cent to 17.34 per cent by increasing the concentration of NO₂ from 0.2 ppm to 10 ppm. Different energy sources, thermal and UV were explored for achieving fast recovery of the SWNT-TFR sensor. The results showed that the gas sensor shows fast recovery in the presence of UV radiation. The calculated detection limit (DL) is less than 764 ppt for NO₂. This work suggests the possibility to utilize SWNTs-TFR as extremely sensitive NO₂ sensor. We are also presenting sensing of Dimethyl methylphosphonate (DMMP), a simulant of chemical warfare agent sarin, using SWNT-TFR. The CNT based sensor gives repeatable response of ~2.7 per cent for 500 ppm of DMMP.

Keywords: Sensor, thick film resistor, carbon nanotubes, gas sensor, recovery

1. INTRODUCTION

Development of low cost, highly sensitive and selective, reproducible and low power gas sensor are always a hot topic for research because of potential application in different areas such as environmental studies, applications in detection of chemical warfare agents, explosives, environmental studies, industrial, automobile and indoor air quality supervision¹⁻⁴. Presently there are different types of gas sensing technologies such as ion-mobility spectrometry, semiconductor, metal oxide, polymer and SAW, etc.⁵⁻⁸ that are being used for detection of gases. Apart from the above established technologies, CNTs has received great attention due to their unique properties such as high surface area and aspect ratio, high sensitivity, low cost, and ability to detect the trace quantity of chemicals⁹⁻¹². CNTs are more chemically active due to curvature effect of nanotube which makes asymmetric π electron cloud around nanotube^{13,14}. SWNTs form bundle due to van der waals' interaction between these electron clouds¹⁵. There are various types of adsorption sites available on these bundle surface¹⁶. The adsorption on these sites depends on the size of target molecule, type of interaction, type of adsorption and activation energy. Researcher have reported detection of various gas molecules such as NO₂, O₂, CO, CH₄, and NH₃, etc. by SWNT^{17,18}.

Film of SWNT can be deposited using various methods like, spin coating, screen printing and dielectrophoresis (DEP)^{9,19-21}. Fabrication of the SWNT gas sensors by these techniques is not reproducible because density of the network,

SWNT diameter; SWNT bundle diameter; perfect alignment of the bundles cannot be controlled by these techniques. This may lead to variation in the resistance of the fabricated SWNT gas sensor^{22,23}, which, in turn, may affect reproducibility of the gas sensor. Vacuum filtration is a simple method to fabricate SWNT gas sensor with controlled network density over flexible substrate by filtration of uniform and homogeneous CNT dispersion²². Film thickness and resistance can be controlled by controlling the density of suspension^{24,25}.

Detailed study of NO₂ detection using SWNT-TFR. We have fabricated SWNT-TFR gas sensor by vacuum filtration of SWNT dispersion over flexible polycarbonate membrane. SWNTs in these sensors are pristine and sensing was performed at room temperature were presented in the paper. Sensing characteristic of SWNT-TFR is studied for different gases and it gives a selective response to NO₂. It shows repeatable response with detection limit below 1 ppb. This flexible SWNT-TFR gives higher sensitivity and faster response time as compared to reported flexible CNTs based sensors^{26,27}. Therefore, to the best of our knowledge, we are first time reporting repeatable sub-ppm level detection of NO₂ within 1 min of response time and with sub-ppt level of detection limit over flexible SWNT-TFR sensor. Sensing of DMMP has also studied as a simulant of sarin which is a chemical warfare agent (CWA).

2. EXPERIMENTAL WORK

As-produced SWNTs used for fabrication of gas sensor are procured from Carbon Solution Inc., USA. SWNT is dispersed in 50 per cent solution of dimethylformamide (DMF) and then ultrasonicated for 2 h. The gas sensor is fabricated

by vacuum filtration method. After making uniform dispersion, it is filtered through the polycarbonate membrane of 0.5 μm pore size. The prepared film then dried in oven at 65 $^{\circ}\text{C}$ to remove any residue of the solvent. Cr/Au contacts are made on this film using a shadow mask with RF sputtering system. This completes the fabrication of SWNT-TFR based gas sensor. We cut a piece of this SWNT-TFR for gas sensing study, which have a pair of electrodes and SWNT network in between them for sensing. This piece is mounted on transistor outline (TO) header and electrodes are connected to the pins of TO header using Au wire. The resistance of the gas sensor is studied by the Fluke 289 RMS multimeter.

3. GAS SENSING SETUP

Figure 1 illustrates schematic and photograph of the gas sensing set up which we have assembled. This sensing setup is capable of generating 0.5 ppm to 100 ppm concentration of NO_2 , NO , SO_2 , CO , and NH_3 gases, with N_2 being the dilutant gas. The gas sensing studies are carried out in a closed gas cell as shown in Fig. 1. The gas sensing cell has an effective internal volume of about $\sim 3.6 \text{ cm}^3$. The gas sensing setup has also a provision of thermal heating or UV light illumination for the desorption of analyte from the gas sensor surface.

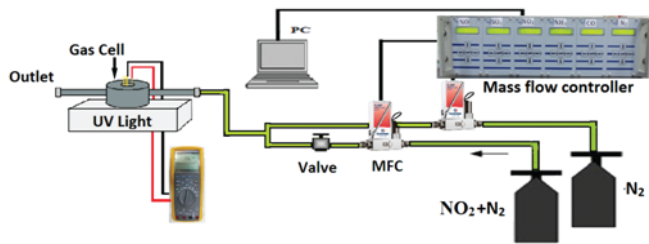


Figure 1. Gas sensing setup to carry out gas sensing study.

4 RESULTS AND DISCUSSION

4.1 Characterisation

For fabrication of SWNT gas sensor, DMF is used as a solvent to disperse and de-bundle SWNTs²⁸. The absorbance of the SWNTs dispersion is shown in Fig. 2(a), which shows absorbance peak at $\sim 290 \text{ nm}$ is closer to the π Plasmon frequency of the SWNTs²⁹. The structural properties of SWNT are evaluated with Raman spectrum as shown in Fig. 2(b). The radial breath mode (RBM) of SWNT lies between 130 cm^{-1} - 200 cm^{-1} and G peak lies^{30,31} at 1593 cm^{-1} . The intensity of

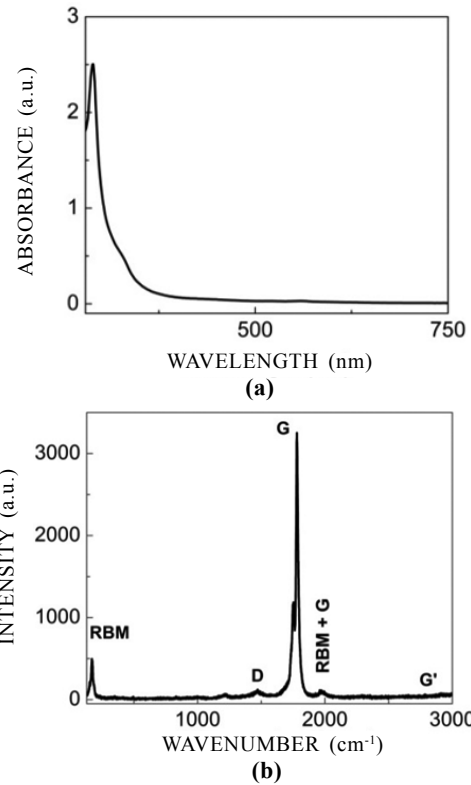


Figure 2. (a) UV spectrum of SWNT solution in DMF and (b) Raman spectrum of SWNT.

disorder induced D peak is very small and lies at about 1367 cm^{-1} and the ratio between I_d/I_g is 0.04 indicating few defects on SWNTs³². The diameter of SWNT is calculated using the formula $\omega_{rbm} = A_1/d_t + A_2$, where d_t is the diameter of SWNT and A_1 , A_2 are experimental constant with values 234 cm^{-1} and 10 cm^{-1} for SWNT bundles^{30,33}. The diameter of SWNT lies in the range from ~ 1.23 to 1.95 nm .

The structure and morphology of SWNT is studied by TEM and SEM as shown in Fig. 3(a) to 3(c). SWNTs are in bundle form as observed from Fig. 3(a). SWNTs form bundle due to high aspect ratio and large van der waals' interaction¹⁵. Two adjacent parallel lines represent the side wall of nanotube¹⁶. The continuous random network of SWNT bundles is observed from SEM image 3(c). The typical diameter of the bundle is about 22 nm to 43 nm . The amorphous carbon is also present in minute quantity on SWNT network as observed in SEM image.

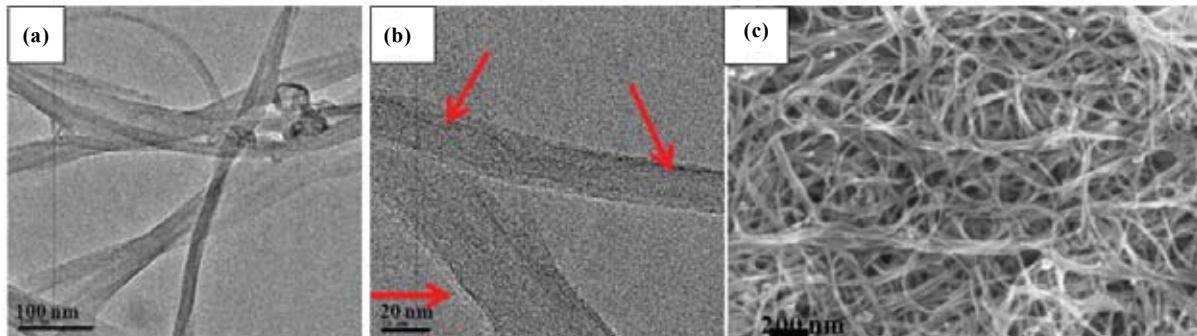


Figure 3. TEM image (a), (b) at low and high magnification and (c) SEM image of the SWNT network.

4.2 Gas Sensing

To check the response of SWNT-TFR gas sensor to different pollutant gases, it is exposed to different concentration ranging from 1 ppm to 20 ppm of five gases sequentially for 3 min each and the next cycle is exposed after 3 min recovery in the presence of N₂. Figure 4(a) shows that the gas sensor does not give any response to CO, SO₂ and NH₃, but it gives selective response to NO_x. The resistance of gas sensor decreases when exposed to NO_x. Sensing mechanism of SWNT-TFR sensor can be explained as charge transfer between SWNT and testing gas. SWNT is p-type in nature at atmospheric conditions^{34,35}. NO₂ and NO are oxidising gases; withdraw charge from nanotube structure^{36,37}. NO and NO₂ molecules have lesser activation energy as compared to CO, SO₂, and NH₃^{41,42}. Therefore, adsorption of NO_x is preferred on the SWNT surface⁴³.

Next desirable property of the gas sensor is repeatability. If a gas sensor is exposed to a fix concentration it should give the same response to multiple exposure. If the response of gas

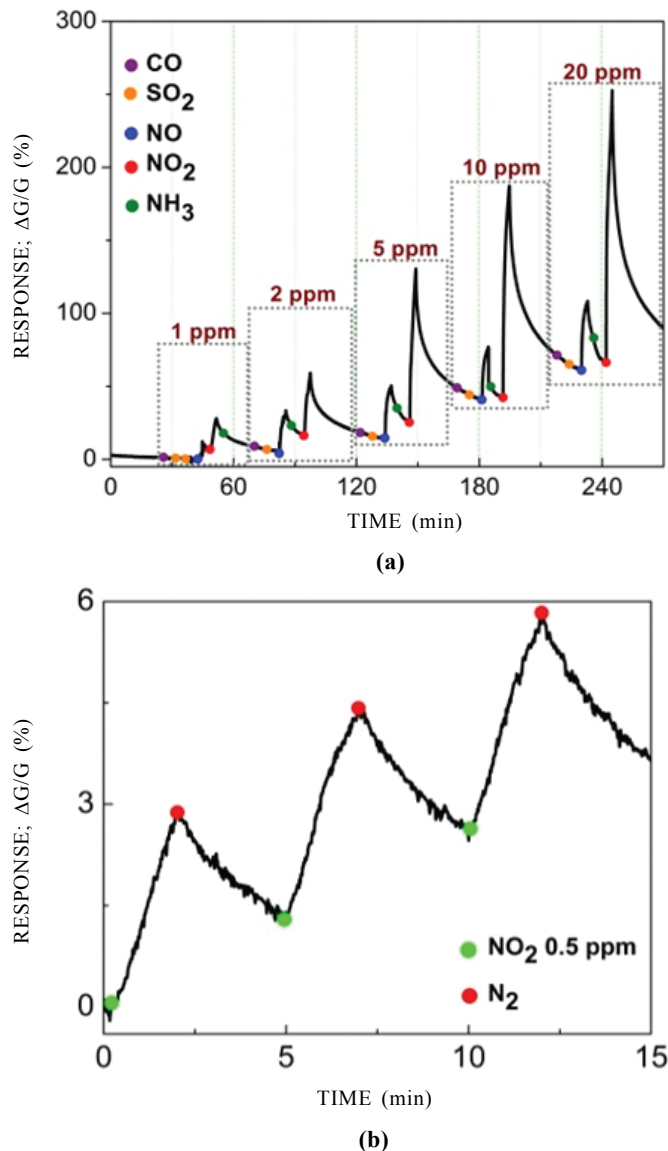


Figure 4. (a) Response of gas sensor towards different exposed gases and (b) repeatable response of the gas sensor for 0.5 ppm of NO₂.

sensor decreases with the multiple exposure or there is a shift in the baseline, it shows that some residue of the analyte is remaining over the gas sensor surface from previous exposure cycle. To check the repeatability, SWNT-TFR is exposed to 0.5 ppm of NO₂ for 1 min and then left for recovery for 1 min in the presence of N₂. The 'expose-recover' cycle is then repeated multiple times. Over the three cycles SWNT-TFR gave repeatable response of ~3 per cent. Although the response is repeatable, but the gas sensor is not recovering to its baseline. This is due to residual molecules on the gas sensor surface and shows that NO_x molecules are not desorbing completely, within the period of observation. Hence, to enhance the recovery rate, we tried different techniques to overcome the binding energy between SWNT and NO₂.

4.2.1 Recovery of Gas Sensor

It is observed from above graphs that the gas sensor does not recover to its baseline after removal of gas exposure due to chemisorption of NO₂ on SWNT surface with high binding energy^{36,37,44}. In case of chemisorption extra energy is needed for forced recovery of the gas sensor. The recovery of these gas sensors is investigated using different sources of energy such as N₂ flush, halogen lamp, thermal heating, UVB and UVC. For self-recovery of sensor, it is exposed to 0.5 ppm of NO₂ for 70 min and then the supply of NO₂ was halted. It does not recover to the baseline within the observation period. It recovers 90 per cent in 6 h and up to 96 per cent in 20 h. It takes more than 24 h for complete recovery of sensor to its original state. The gas sensor does not saturate even after exposure for 70 min as observed from Fig. 5(a), showing availability of huge number of sites for gas adsorption. For further, sensing study, the sensor is exposed to target gas for a fixed duration. SWNT-TFR is again exposed to 5 ppm of NO₂ for 5 min, then a halogen lamp (5 W power and having emission spectrum in the range 320 nm to 750 nm) is used as recovery source. The sensor does not recover to the baseline with halogen lamp as it emits mainly in the visible and infrared range, with only limited emission in the UV. Next, we tried thermal heating for recovery of the gas sensor. SWNT-TFR is kept at a particular temperature and then 5 ppm of NO₂ is introduced to gas sensor. It is observed that the response of the gas sensor increases with operating temperature up to 100 °C and decreases with further increase in temperature. The recovery increases slightly with the operating temperature but the sensor does not recover to its baseline within the period of observation. Further elevation of temperature is restricted due to use of polycarbonate filtration membrane.

Next, UVC ~ 4.6 eV is used for recovery of the gas sensor. The gas sensor recovers to its baseline when exposed to the UVC radiation. The sensor recovers to its baseline in the presence of UVC. As NO₂ chemisorbed on SWNT surface due to high binding energy and it takes more than 12 h to recover its baseline³⁷. UV provides the sufficient energy to overcome the barrier energy of desorption between SWNT and NO₂⁴⁵.

To check the recovery rate in the presence of N₂ or UV and N₂ source, the gas sensor is first exposed to 100 ppm of NO₂. The gas sensor is recovered with N₂ for 2 min then it is exposed to UVC radiation. The gas sensor gives fast recovery

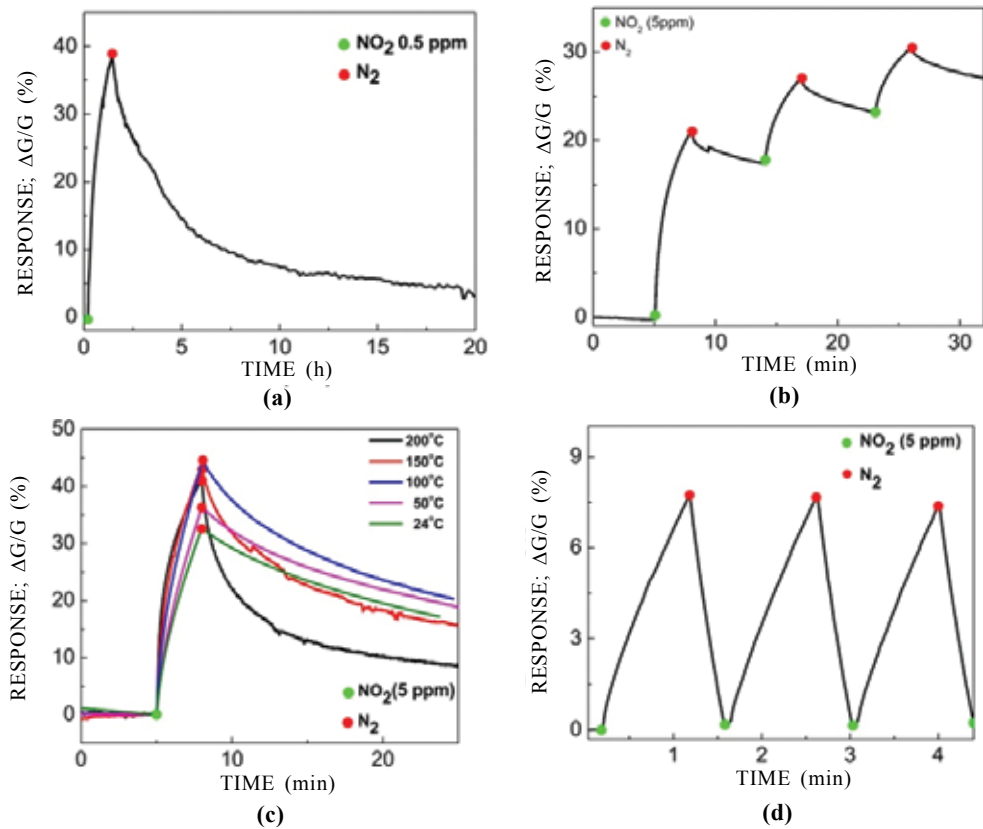


Figure 5. (a) Recovery of the gas sensor in the presence of (b) N_2 , (b) halogen lamp, (c) thermal heating, and (d) with UVC.

in the presence of UVC radiation. The recovery of this gas sensor is shown in Fig. 6(a). The extrapolated curve shown by dotted line in the Fig. 6(a) represents the recovery in N_2 , which is extracted to more than 24 h. Next, UVB and UVC radiation sources are used for gas sensor recovery. The gas sensor is exposed to 5 ppm of NO_2 and after exposed to these recovery sources, the gas sensor recovers to its baseline. There is a drift in the response of the gas sensor in the presence of UVB, which may be due to analyte residue remain on the gas sensor surface. The drift in the response is small in case of the UVC. SWNT-TFR gives a repeatable response when recovered in the presence of UVC and recovery rate is faster as compared to UVB for repeated exposure.

4.2.2 Response and Repeatability

Next, to check the gas sensor is able to distinguish the

different exposed concentration. It is exposed to different concentration ranging from 0.2 ppm to 10 ppm for fix duration of one minute. The response of the gas sensor increases from 1.47 per cent to 17.23 per cent, respectively. The response vs different exposed concentration is plotted in Fig. 7(a). The response of the gas sensor increases with different exposed concentrations due to more adsorption of analyte molecules present in the surrounding. The gas sensor shows saturation behavior at higher concentration due to the surface coverage⁴⁶. The response of SWNT-TFR gas sensor increases with increase in dose of the exposed gas due to the more adsorption of the gas molecules on gas sensor surface. Next to check the repeatability of gas sensor response, gas sensor is exposed to the same concentration of NO_2 for three times. An initial dip is observed in first cycle of the response; thereafter response

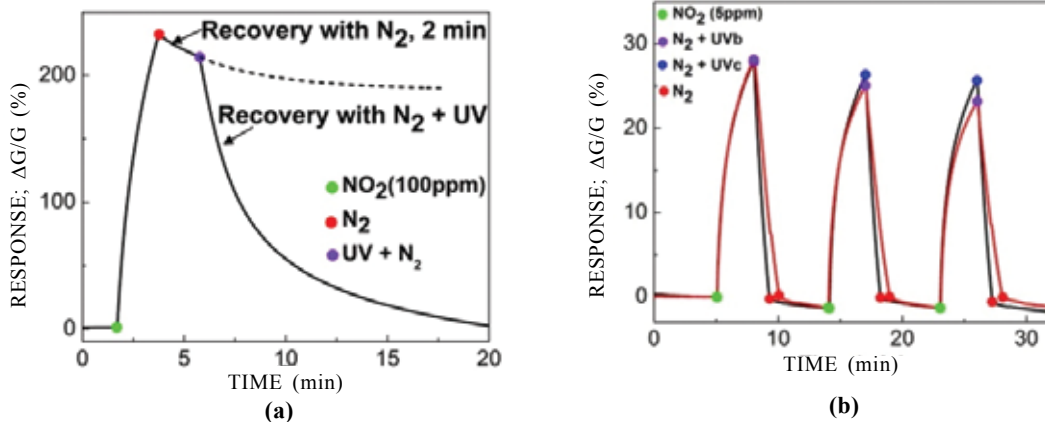


Figure 6. Recovery of gas sensor with (a) N_2 and UVC radiation, and (b) UVB and UVC sources.

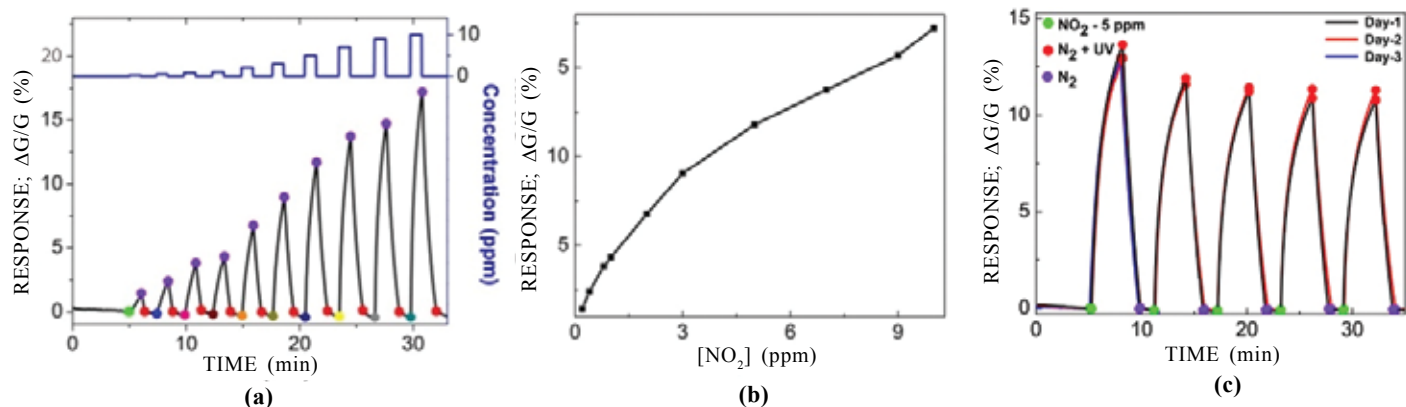


Figure 7. (a) Response of the gas sensor with respect to different exposed concentration ranging from 0.2 ppm to 10 ppm, (b) variation of response with respect to different exposed concentrations, and (c) repeatable response against multiple exposure of 5 ppm of NO₂.

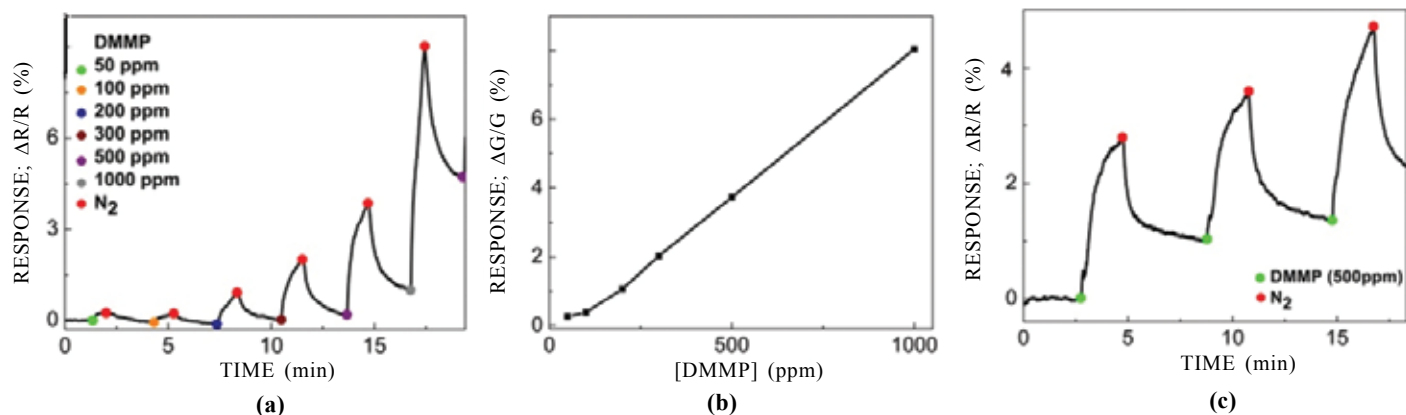


Figure 8. (a) Response of SWNT-TFR film for DMMP ranging from 50 ppm to 1000 ppm, (b) the variation of response with respect to exposed concentration of DMMP, and (c) repeatable response for 500 ppm of DMMP.

remains constant for a period of observation. The gas sensor gives good repeatable response.

Detection limit of the gas sensor is calculated for 3:1 signal to noise ratio using formula as given in literature⁴⁷. For calculation of detection limit, the gas sensor is kept in N₂ atmosphere until a stable baseline is formed. After a stable baseline, it is exposed to NO₂ gas for 5 min and change in resistance is measured against exposed gas. The signal to noise ratio is 200 for 50 ppb of NO₂ and detection limit of the gas sensor is less than 744 ppt.

4.2.3 Sensing of Chemical Warfare Agent

These high sensitive SWNT-TFR sensors are further used for sensing of DMMP. The gas sensor is exposed to different concentration of DMMP ranging from 50 ppm to 1000 ppm. The response of the gas sensor varies linearly with increase in the concentration as shown in Fig. 8(b). The gas sensor is exposed 500 ppm of DMMP for multiple times. It gives repeatable response of 2.7 per cent for exposed concentration. SWNT-TFR does not recover to its base line within period of observation.

5. CONCLUSION

We have fabricated flexible SWNT thick film gas resistor (SWNT-TFR) by vacuum filtration method. SWNT-TFR

gives selective response to NO_x. The response of the gas sensor increases from 1.47 per cent to 17.34 per cent with increase in NO₂ concentration ranging from 0.5 ppm to 10 ppm, respectively. The gas sensor gives repeatable response against the exposed gas and response of the gas sensor remains constant for period of observation. The recovery of the SWNT-TFR sensor can be accelerated by the use of UVC radiation. The gas sensor shows sub-ppb detection limit for sensing NO₂. This flexible SWNT-TFR gives higher sensitivity and faster response time as compared to reported flexible CNTs based sensors^{26,27}. SWNT-TFR was also shown to give repeatable response to 500 ppm of DMMP.

REFERENCE

1. Liu, X.; Cheng, S.; Liu, H.; Hu, S.; Zhang, D. & Ning, H. A survey on gas sensing technology. *Sensors*, 2012, **12**, 9635-9665. doi: 10.3390/s120709635
2. Lee, D.-D. & Lee, D.-S.; Environmental gas sensors. *IEEE Sensors J.*, 2001, **1**, 214-224. doi: 10.1109/jsen.2001.954834
3. Fleischer, M. & Lehmann, M. Solidstate gas sensors-industrial application. Springer Science & Business Media 2012. doi: 10.1007/978-3-642-28093-1

4. Rimai, L.; Visser, J. H.; Logothetis, E. M. & Samman, A. Gas sensors for automotive applications. *In* *Polymers in Sensors*. Chapter 9, pp. 102–118. doi: 10.1021/bk-1998-0690.ch009
5. Binions, R. & Naik, A.J.T.; Metal oxide semiconductor gas sensors in environmental monitoring. *In* *Semiconductor Gas Sensors*, Woodhead Publishing. Chapter 13, 2013, . 433-466. doi: 10.1533/9780857098665.4.433
6. Yamazoe, N. New approaches for improving semiconductor gas sensors. *Sensors Actuators B: Chemical*, 1991, **5**, 7-19. doi: 10.1016/0925-4005(91)80213-4
7. Bai, H. & Shi, G. Gas sensors based on conducting polymers. *Sensors*, 2007, **7**, 267-307. doi:10.3390/s7030267
8. Pentyala, V.; Davydovskaya, P.; Ade, M.; Pohle, R. & Urban, G. Metal–organic frameworks for alcohol gas sensor. *Sensors Actuators B: Chemical*, 2016, **222**, 904-909. doi:10.1016/j.snb.2015.09.014
9. Wang, Y. & Yeow, J.T.W. A review of carbon nanotubes-based gas sensors. *Journal Sensors*, 2009, **24**. doi: 10.1155/2009/493904
10. Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J. & Meyyappan, M. Carbon nanotube sensors for gas and organic vapor detection. *Nano Letters*, 2003, **3**, 929-933. doi: 10.1021/nl034220x
11. Zhang, T.; Mubben, S.; Myung, V. N. & Deshusses, A. M. Recent progress in carbon nanotube-based gas sensors. *Nanotechnology*, 2008, **19**, 332001. doi : 10.1088/0957-4484/19/33/332001
12. Iijima, S. Helical microtubules of graphitic carbon. *Nature*, 1991, **354**, 56-58. doi: 10.1038/354056a0
13. Li, J. & Lu, Y. Nanostructure-engineered chemical sensors for hazardous gas and vapor detection. *In* *Optics East*, International Society for Optics and Photonics, 2004, pp. 222-231. doi: 10.1117/12.570528
14. Goddard Iii, W. A.; Brenner, D.; Lyshevski, S.E. & Iafrate, G.J. Handbook of nanoscience, engineering, and technology. Chapter 18, CRC press, 2007.
15. Saether, E.; Frankland, S.J.V. & Pipes, R.B. Transverse mechanical properties of single-walled carbon nanotube crystals. Part I: determination of elastic moduli. *Composites Sci. Technol.*, 2003, **63**, 1543-1550. doi : 10.1016/S0266-3538(03)00056-3
16. Agnihotri, S.; Rostam-Abadi, M. & Rood, M. J. Temporal changes in nitrogen adsorption properties of single-walled carbon nanotubes. *Carbon*, 2004, **42**, 2699-2710. doi:10.1016/j.carbon.2004.06.016
17. Chikkadi, K.; Muoth, M.; Roman, C.; Haluska, M.; and Hierold, C. Advances in NO₂ sensing with individual single-walled carbon nanotube transistors. *Beilstein J Nanotechnol.* 2014, **5**, 2179–2191. doi: 10.3762/bjnano.5.227.
18. Misra, A. Carbon nanotubes and graphene-based chemical sensors. *Current Science*, 2014, **107**, 419-429. doi:10.18520/cs/v107/i3/419-429
19. Wang, R.; Li, H.; Pan, M. & Chen, D. A carbon nanotube gas sensor fabricated by dielectrophoresis and its application for NH₃ detection. *In* the Annual International Conference of the IEEE on Engineering in Medicine and Biology, 2009. EMBC 2009. pp. 6046-6049. doi: 10.1109/IEMBS.2009.5334531
20. Hines, D.; Zhang, H.; Rummeli, M. H.; Adebimpe, D. & Akins, D.L. Nanomolecular gas sensor architectures based on functionalized carbon nanotubes for vapor detection. SPIE Sensing Technology+ Applications, International Society for Optics and Photonics, 2015, pp. 948112-948112-948119. doi: 10.1117/12.2177204
21. Valentini, L.; Armentano, I.; Kenny, J.M.; Cantalini, C.; Lozzi, L. & Santucci, S. Sensors for sub-ppm NO₂ gas detection based on carbon nanotube thin films. *Applied Physics Letters*, 2003, **82**, 961-963. doi: 10.1063/1.1545166
22. Hu, L.; Hecht, D.S. & Grüner, G. Carbon nanotube thin films: Fabrication, properties, and applications. *Chem. Rev.*, 2010, **110** (10), 5790–5844. doi: 10.1021/cr9002962
23. Kanoun, O.; Müller, C.; Benchirouf, A.; Sanli, A.; Dinh, T. N.; Al-Hamry, A.; Bu, L.; Gerlach, C. & Bouhamed, A. Flexible carbon nanotube films for high performance strain sensors. *Sensors*, 2014, **14**, 10042-10071. doi: 10.3390/s140610042.
24. Hu, L.; Hecht, D. S. & Grüner, G. Percolation in transparent and conducting carbon nanotube networks. *Nano Letters*, 2004, **4**, 2513-2517. doi: 10.1021/nl048435y
25. Zhou, Y.; Hu, L. & Grüner, G.; A method of printing carbon nanotube thin films. *Applied Physics Letters*, 2006, **88**, 123109. doi: 10.1063/1.2187945
26. Jeong, H.Y.; Lee, D.-S.; Choi, H. K.; Lee, D.H.; Kim, J.-E.; Lee, J. Y.; Lee, W.J.; Kim, S.O.; Choi, S.-Y.; Flexible room-temperature NO₂ gas sensors based on carbon nanotubes/reduced graphene hybrid films. *Applied Physics Letters*, 2010, **96**, 213105. doi: 10.1063/1.3432446
27. Su, P.-G.; Lee, C.-T.; Chou, C.-Y.; Cheng, K.-H. & Chuang, Y.-S.; Fabrication of flexible NO₂ sensors by layer-by-layer self-assembly of multi-walled carbon nanotubes and their gas sensing properties. *Sensors and Actuators B: Chemical*, 2009, **139**, 488-493. doi: 10.1016/j.snb.2009.03.051
28. Liu, C.-X. & Choi, J.-W. Improved dispersion of carbon nanotubes in polymers at high concentrations. *Nanomaterials*, 2012, **2**, 329-347. doi: 10.3390/nano2040329
29. Yu, Z.; Brus, L.; Rayleigh and Raman scattering from individual carbon nanotube bundles. *J. Physical Chemistry B*, 2001, **105**, 1123-1134. doi: 10.1021/jp003081u
30. Cantalini, C.; Valentini, L.; Lozzi, L.; Armentano, I.; Kenny, J. M. & Santucci, S. NO₂ gas sensitivity of carbon nanotubes obtained by plasma enhanced chemical vapor deposition. *Sensors Actuators B: Chemical*, 2003, **93**, 333-337.

- doi: 10.1016/S0925-4005(03)00224-7
31. Dresselhaus, M.S.; Dresselhaus, G.; Saito, R. & Jorio, A. Raman spectroscopy of carbon nanotubes. *Physics Reports*, 2005, **409**, 47-99.
doi: 10.1016/j.physrep.2004.10.006
 32. Wang, L.-C.; Tang, K.-T.; Teng, I. J.; Kuo, C.-T.; Ho, C.-L.; Kuo, H.-W.; Su, T.-H.; Yang, S.-R.; Shi, G.-N. & Chang, C.-P. A single-walled carbon nanotube network gas sensing device. *Sensors*, 2011, **11**, 7763.
doi: 10.3390/s110807763
 33. Milnera, M.; Kürti, J.; Hulman, M. & Kuzmany, H. Periodic resonance excitation and intertube interaction from quasicontinuous distributed helicities in single-wall carbon nanotubes. *Physical Rev. Letters*, 2000, **84**, 1324-1327.
doi: 10.1103/PhysRevLett.84.1324
 34. Nonoguchi, Y.; Ohashi, K.; Kanazawa, R.; Ashiba, K.; Hata, K.; Nakagawa, T.; Adachi, C.; Tanase, T. & Kawai, T. Systematic conversion of single walled carbon nanotubes into n-type thermoelectric materials by molecular dopants. *Scientific Reports*, 2013, **3**, 3344. doi: 10.1038/srep03344
 35. Donghun, K.; Noejung, P.; Ju-hye, K.; Eunju, B. & Wanjun, P. Oxygen-induced p-type doping of a long individual single-walled carbon nanotube. *Nanotechnology*, 2005, **16**, 1048.
doi: 10.1088/0957-4484/16/8/008
 36. Kang, D.; Park, N.; Ko, Ju-h.; Bae, E.; Park, W.; Donghun, K.; Noejung, P.; Ju-hye, K.; Eunju, B. & Wanjun, P. Nanotube molecular wires as chemical sensors. *Science*, 2000, **287**, 622-625.
doi: 10.1126/science.287.5453.622
 37. Chikkadi, K.; Muoth, M.; Roman, C.; Haluska, M. & Hierold, C. Advances in NO₂ sensing with individual single-walled carbon nanotube transistors. *Beilstein J. Nanotechnol.*, 2014, **5**, 2179-2191.
doi: 10.3762/bjnano.5.227
 38. Nguyen, L.H.; Phi, T.V.; Phan, P.Q.; Vu, H.N.; Nguyen-Duc, C. & Fossard, F.; Synthesis of multi-walled carbon nanotubes for NH₃ gas detection. *Physica E: Low-dimensional Syst. Nanostruct.*, 2007, **37**, 54-57.
doi: 10.1016/j.physe.2006.12.006
 39. Hannon, A.; Lu, Y.; Li, J.; Meyyappan, M. Room temperature carbon nanotube based sensor for carbon monoxide detection. *J. Sens. Sens. Syst.* 2014, **3**, 349-354.
doi:10.5194/jsss-3-349-2014
 40. Yu, S. & Yi, W. Single-walled carbon nanotubes as a chemical sensor for SO₂ detection, *IEEE Trans. Nanotechnol.*, 2007, **6**, 545-548. doi: 10.1109/TNANO.2007.903800
 41. Ahlam, A.; Barbary, E.L.; Ismail, G.H. & Babeer, A.M. Effect of monovacancy defects on adsorbing of CO, CO₂, NO and NO₂ on carbon nanotubes: First principle calculations. *J. Surface Engineered Mat. Adv. Technol.*, 2013, **3**, 287.
doi: 10.4236/jseamat.2013.34039
 42. Sonawane, M.R.; Habale, D.; Nagare, B.J. & Gharde, R.; Interaction of O₂, CO₂, NO₂ and SO₂ on Si-doped carbon nanotube. *Int. J. Appl. Phy. Math*, 2011, **1**, 138-143.
doi: 10.7763/IJAPM.2011.V1.27
 43. Dai, J.; Giannozzi, P. & Yuan, J.; Adsorption of pairs of NO_x molecules on single-walled carbon nanotubes and formation of NO + NO₃ from NO₂. *Surface Science*, 2009, **603**, 3234-3238. doi: 10.1016/j.susc.2009.09.010
 44. W.-L. Yim, Gong, X. & Liu, Z.-F.; Chemisorption of NO₂ on carbon nanotubes. *J. Physical Chem. B*, 2003, **107**, 9363-9369.
doi: 10.1021/jp0276471
 45. Yang, L.; Ouyang, M.; Li, W.J. & Han, X.; UV-illumination induced desorption of CNT sensors. In the 8th IEEE Conference on Nanotechnology, 2008. NANO'08, pp. 284-287.
doi: 10.1109/NANO.2008.90
 46. Wang, Y.; Wang, Z.; Hu, N.; Wei, L.; Xu, D.; Wei, H.; Kong, E.S.-W. & Zhang, Y.; Hexafluorobisphenol a covalently functionalized single-walled carbon nanotubes for detection of dimethyl methylphosphonate vapor. *J. Nanosci. Nanotechnol.*, 2011, **11**, 4874-4881.
doi: 10.1166/jnn.2011.4193
 47. Chen, G.; Paronyan, T.M.; Pigos, E.M. & Harutyunyan, A.R. Enhanced gas sensing in pristine carbon nanotubes under continuous ultraviolet light illumination. *Scientific Reports*, 2012, **2**.
doi: 10.1038/srep00343

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