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RESEARCH ARTICLE

Highly Sensitive NO_2 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 NO_2 detection is reported. SWNT-TFR was fabricated by vacuum filtration technique on flexible polycarbonate membrane. SWNT-TFR sensor shows selective response to NO_2. The response increases from 1.47 per cent to 17.34 per cent by increasing the concentration of NO_2 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 NO_2. This work suggests the possibility to utilize SWNTs-TFR as extremely sensitive NO_2 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 supervision[1-4]. 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 chemicals[9-12]. 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 clouds[15]. There are various types of adsorption sites available on these bundle surface[16]. 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 NO_2, O_2, CO, CH_4, and NH_3, 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 dispersion[22]. Film thickness and resistance can be controlled by controlling the density of suspension[24,25].

Detailed study of NO_2 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 NO_2. 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 NO_2 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

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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 ºC to remove any residue of thesolvent. 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 to 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 ~3.6 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.

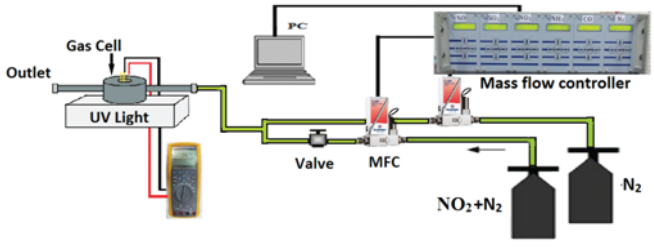


Figure 1. Gas sensing setup to carry out gas sensing study.

4 RESULTS AND DISCUSSION

4.1 Characterisation

For fabrication of SWNT gas sensor, DMF is used as a solvent to disperse and de-bundle SWNTs[28]. The absorbance of the SWNTs dispersion is shown in Fig. 2(a), which shows absorbance peak at ~ 290 nm is closer to the π Plasmon frequency of the SWNTs[29]. 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

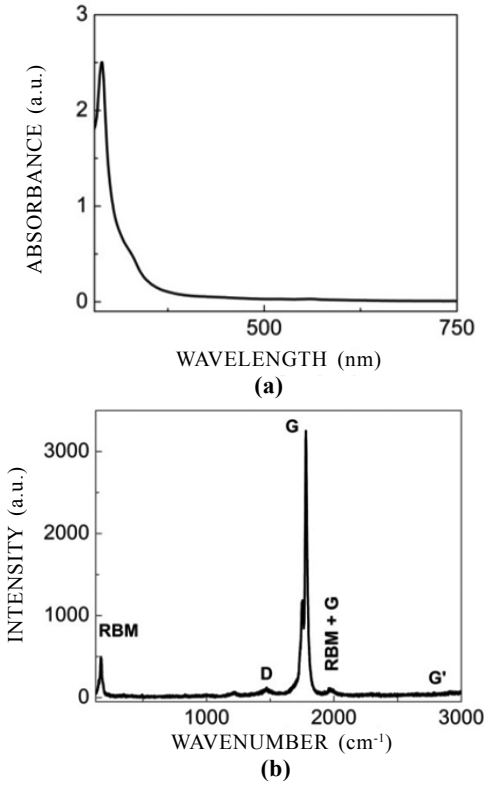


Figure 2. (a) UV spectrum of SWNT solution in DMF and (b) Raman spectrum of SWNT.

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 SWNTs[32]. 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' interaction[15]. Two adjacent parallel lines represent the side wall of nanotube[16]. 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.

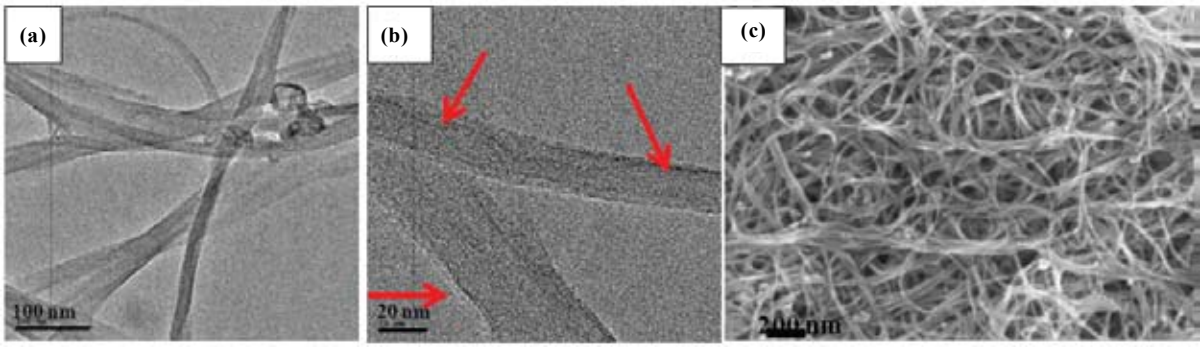
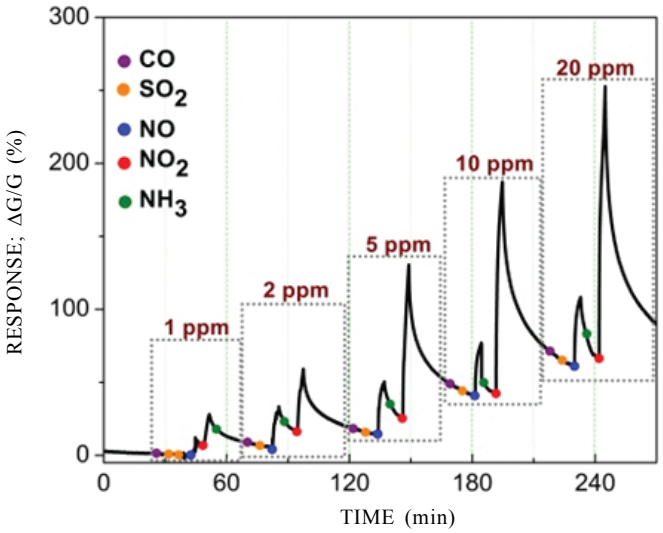


Figure 3. TEM image (a), (b) at low and high magnification and (c) SEM image of the SWNT network.

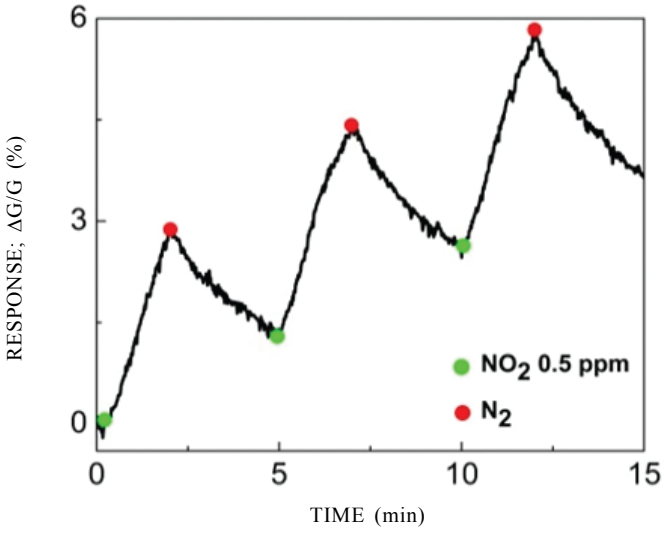
4.2 Gas Sensing

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 N_2. Figure 4(a) shows that the gas sensor does not give any response to CO, SO_2 and NH_3, 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]. NO_2 and NO are oxidising gasess; withdraw charge form nanotube structure[36,37]. NO and NO_2, molecules have lesser activation energy as compared to CO, SO_2, and NH_3 [41,42]. Therefore, adsorption of NOx is preferred on the SWNT surface[43].

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 sensor decreases with the multiple exposureor 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 NO_2 for 1 min and then left for recovery for 1 min in the presence of N_2. 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 NOx 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 NO_2.



(a)



(b)

Figure 4. (a) Response of gas sensor towards different exposed gases and (b) repeatable response of the gas sensor for 0.5 ppm of NO_2.

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 NO_2 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 N_2 flush, halogen lamp, thermal heating, UVB and UVC. For self-recovery of sensor, it is exposed to 0.5 ppm of NO_2 for 70 min and then the supply of NO_2 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 NO_2 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 NO_2 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 NO_2 chemisorbed on SWNT surface due to high binding energy and it takes more than 12 h to recover its baseline[37]. UV provides the sufficient energy to overcome the barrier energy of desorption between SWNT and NO_2[45].

To check the recovery rate in the presence of N_2 or UV and N_2 source, the gas sensor is first exposed to 100 ppm of NO_2. The gas sensor is recovered with N_2 for 2 min then it is exposed to UVC radiation. The gas sensor gives fast recovery

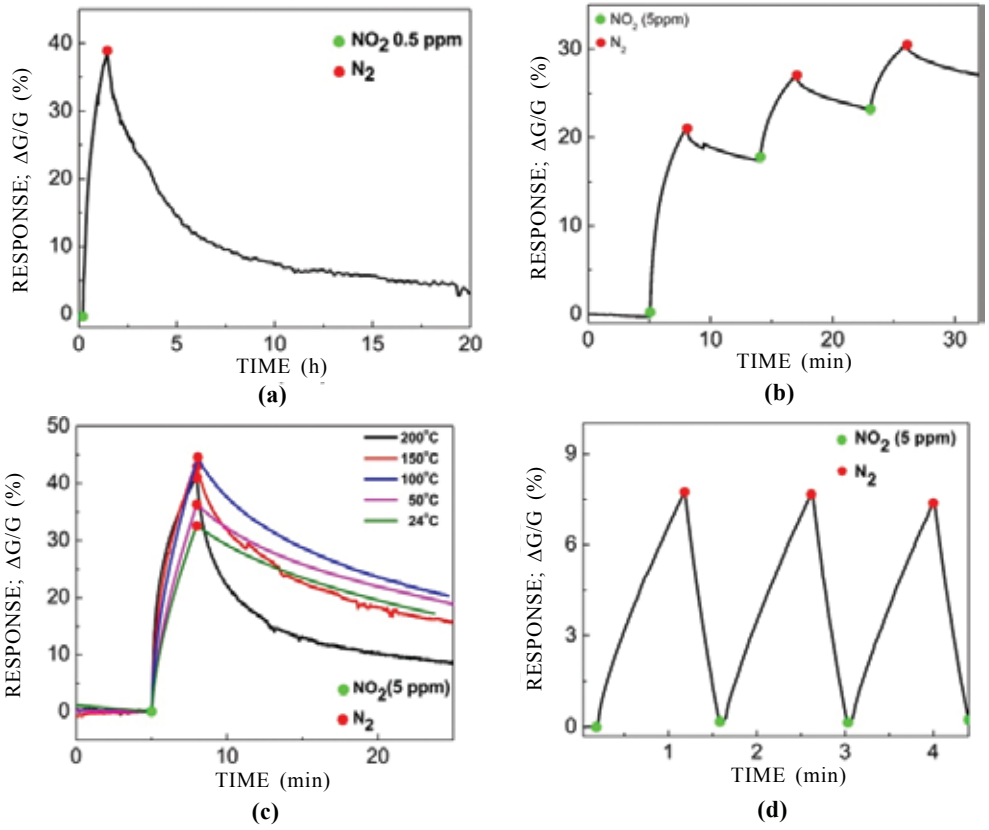


Figure 5. (a) Recovery of the gas sensor in the presence of (b) N_2, (b) halogen lamp, (c) thermal heating, and (d) with UVC.

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 coverage[46]. 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

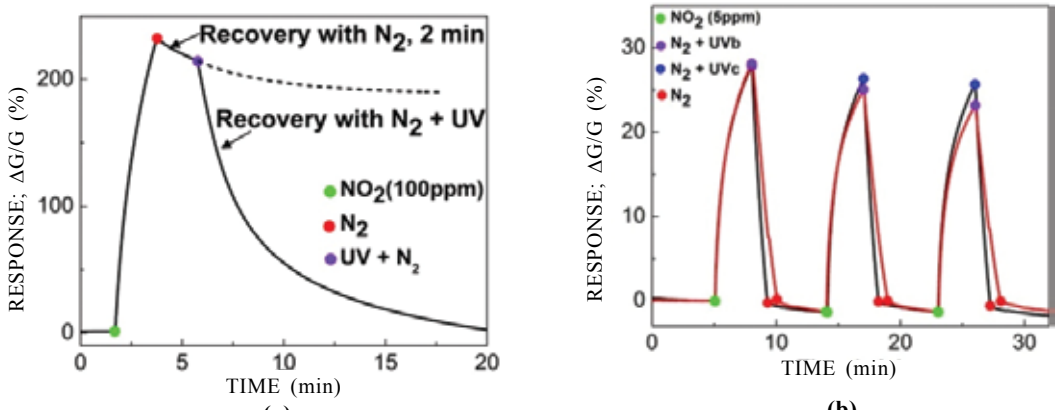


Figure 6. Recovery of gas sensor with (a) N_2 and UVC radiation, and (b) UVB and UVC sources.

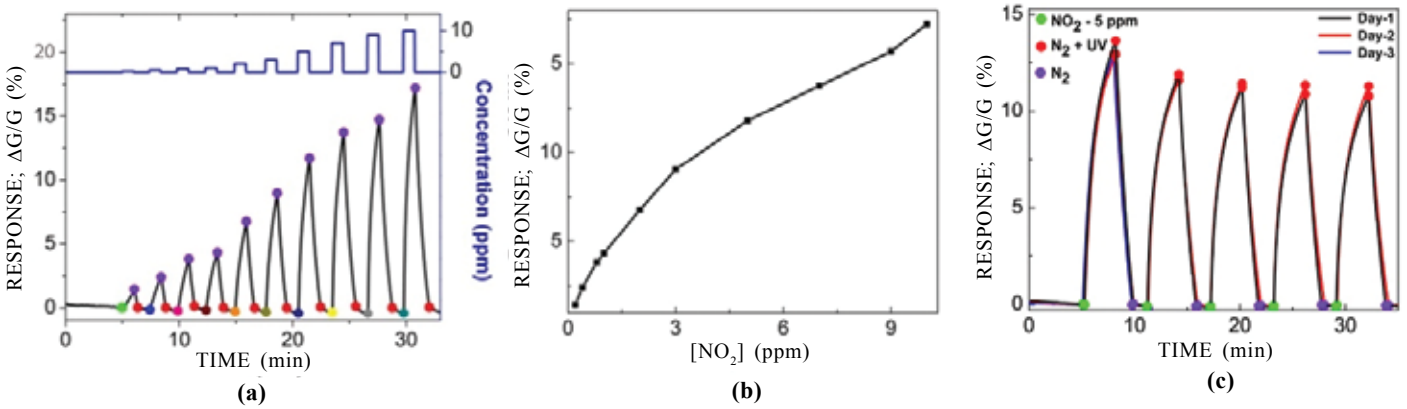


Figure 7. (a) Response of the gas sensor with respect to different exposed concentration ranging from 0.2 ppm to 10 ppm, (b) variation of response with respect to different exposed concentrations, and (c) repeatable response against multiple exposure of 5 ppm of NO_2.

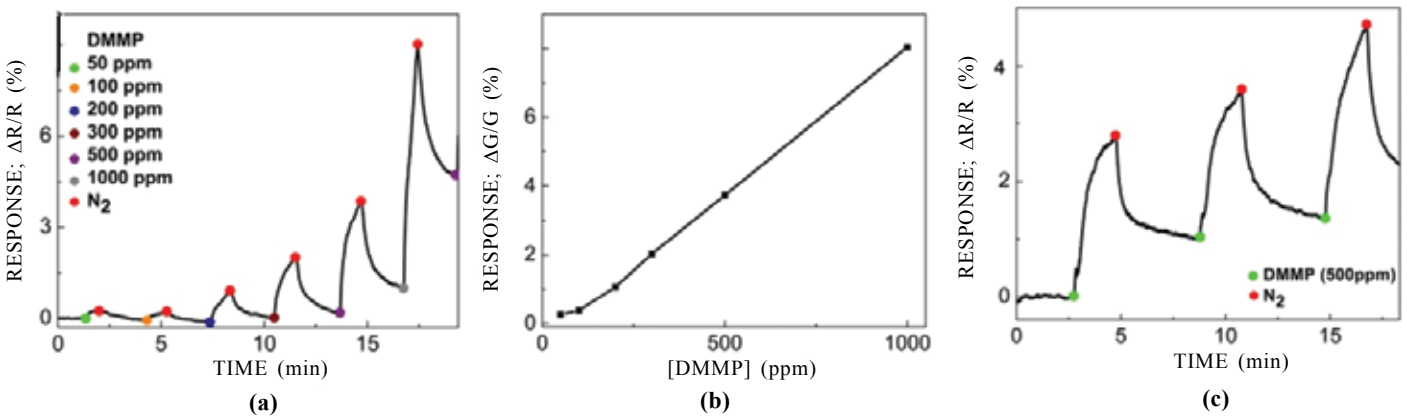


Figure 8. (a) Response of SWNT-TFR film for DMMP ranging from 50 ppm to 1000 ppm, (b) the variation of response with respect to exposed concentration of DMMP, and (c) repeatable response for 500 ppm of DMMP.

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 literature[47]. For calculation of detection limit, the gas sensor is kept in N_2 atmosphere until a stable baseline is formed. After a stable baseline, it is exposed to NO_2 gas for 5 min and change in resistance is measured against exposed gas. The signal to noise ratio is 200 for 50 ppb of NO_2 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 NO_2 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 NO_2. 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.

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