Materials Science-Poland, Vol. 27, No. 2, 2009

Fabrication of MWNTs–PANI composite – a chemiresistive sensor material for the detection of explosive gases

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A chemiresistive sensor was fabricated by the chemical modification of multi-walled carbon nanotubes (MWNTs) and chemical oxidation of polyaniline (PANI). The resistances of the sensing film samples against 100, 250, 500, 1000 ppm explosives (picric acid (PA), 2,6-dinitrotoluene (2,6-DNT) and 2,4,6-trinitrotoluene(TNT)) agents were investigated. The MWNTs with various wt. % PANI agents were characterized by TGA, SEM, FTIR and Raman spectroscopy, respectively. The experimental results showed that 1wt. % MWNTs and 10, 5, 1wt. % PANI sensor samples provided high sensitivity, excellent selectivity and good reproducibility to PA and 2,6-DNT vapours. In addition, principal component analysis (PCA) was applied to distinguish the performance of PA, 2,6-DNT and TNT agents. Our results indicate that the electric detection of explosive agents is possible with simply fabricated MWNTs–PANI devices.

Key words: *multi-walled carbon nanotubes; polyaniline; explosive; PCA*

1. Introduction

During recent years, explosives-based terrorism has grown enormously because explosive-based weapons are simple to make, easy to deploy, and can cause extremely large damage. Detecting explosives is a challenging task, because of a number of factors such as the low mass of explosives, frequent introduction of novel explosive compositions, and variety of concealment techniques [1]. Recently, many researchers have

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attempted to detect explosive gases using various methods, including electrical conductivity of metal oxide semiconductors, quadrupole resonance, X-ray diffraction, electron capture detection and ion mobility spectrometry. Those techniques, however, are expensive and require frequent calibration [2]. Therefore, the fabrication of a more reliable and inexpensive technique with stable sensors, and the ability to adjust the pattern recognition routine according to the variation in the explosives adsorptive matrix such as electrochemical/chemical polymer and nanostructure sensors is needed. Chemical sensors for the rapid detection of explosives are important because they have potential applications, such as tactical and humanitarian demining, remediation of explosives manufacturing sites and forensic and criminal investigations [3].

Since fast and accurate detection of explosives is essential to protect human beings, many researchers have already attempted to detect nitro-aromatic explosive gases using various kinds of sensors. The explosives are mainly classified into four specific types such as trinitrotoluene (TNT), tetryl, picric acid and dinitrotoluene (DNT). Investigations using MEMS explosive sensors based on piezoresistive silicon microcantilevers to the desorption of explosive TNT, PETN and RDX vapours from under ambient air have also been carried out [4].

Carbon nanostructures show unique properties and morphological flexibility which makes them multifunctional and compatible with organic and inorganic systems. In other words, the gas sensor fabricated with multi-walled nanotubes (MWNTs) may work at room temperature [5]. But it did not receive much attention due to its low sensitivity.

At present, analyses of this kind are possible exclusively within the confines of sophisticated research laboratories. “Nanostructure–polymer” detectors of explosives have to be portable, fast-acting, cheap, simple to operate, and they have to be very sensitive and selective to gases under detection. The sensor array described consists of various highly sensitive electrode carbon nanotube based sensors with metal assemblies, and carbon nanotubes coated with polymers. The viability has been established of semiconductor metal oxides (SMO) thick-film gas sensors prepared using cheap commercial sensor platforms and a very simple drop-coating technique accompanied with *in situ* annealing of the deposited films by integrated heaters [6]. In addition, MWNTs and polyaniline films deposited on glassy carbon (GC) electrodes by the layer-by-layer method and have shown to be excellent amperometric sensors for H_2O_2 [7].

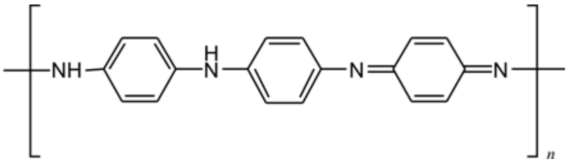
Conducting polymers are an important and interesting class of organic conductors for molecular electronic devices. Polyaniline (PANI) is regarded as one of the most technologically promising conducting polymers because of its ease of preparation, low cost, high environmental stability and relatively stable electrical conductivity [8–10].

The aim of this study is to analyze the suitability of multi-walled carbon nanotubes (MWNTs)–PANI sensor arrays for the identification of certain gases, which swell reversibly and cause changes of resistance with a wide variety of chemical explosives in the gas/vapour concentrations at 1000, 500, 250, 100 ppm levels. Thereafter, the responses are examined to simulate the gases of trinitrotoluene (TNT), 2,6-dinitrotoluene (2,6-DNT) and picric acid (PA). Principal component analysis (PCA), one of the statistical classification methods, was performed, in order to classify these three test gases [11].

2. Experimental

Materials. Multi-walled carbon nanotubes were produced by the chemical vapour deposition (CVD) method, with the nominal outside diameter (OD) of 10–20 nm. All chemicals (aniline, acetonitrile, methanol, 1-methyl-2-pyrrolidone) used were AR grade, The explosive agents (Cerilliant) were fabricated in our laboratory. Ammonium persulphate was used as an oxidizing agent for the preparation of the polyaniline.

Preparation of polyaniline. 2.0 moles of dodecylbenzenesulfonate were dissolved in 1 cm^3 of aniline and allowed to stand at room temperature for 1 h. The ammonium persulphate ($(NH_4)_2S_2O_8$) solution was then added to 20 cm^3 of deionized water, with constant stirring, over a period of 30 min. The resulting deep-blue solution was removed and allowed to stand at room temperature for 12 h, then it was vacuum filtered and rinsed several times with deionized water (1.0 dm^3) followed by rinsing with methanol (1.0 dm^3). Polyaniline (Scheme 1) was allowed to remain under vacuum until it became a dark blue powder.



Scheme 1. Polyaniline (PANI)

Preparation of thin film (layer-by-layer), The first MWNTs (1 wt. %) layer-modified electrode was prepared by casting 5mg/cm^3 methylethylketone (MEK) of the dispersion on the surface of an interdigitated microelectrode device, which was air-dried at room temperature. When the methylethylketone had volatilized, an MWNTs film was formed. The PANI layer was then formed from the PANI solution (5 mg/cm^3, 1 M NMP) ultrasonicated for 10 min and deposited on the MWNT-modified microelectrode, which was vacuum-dried to form the sensing film.

Sensor measurements and characterization. Sensor response was measured using a customized interdigitated microelectrode (IME) device, having 12 pairs of gold electrodes 1 mm wide with the 1 mm spacing on an SiO_2 wafer substrate. A computer-interfaced multi-channel home-made multimeter was used to measure the lateral resistance of the nanostructured coating on IME. The resistance and frequency measurements were performed simultaneously under a computer control. All experiments were performed at room temperature. The gas flow was controlled by a calibrated Aalborg mass-flow controller (GFM-17), and the flow rates of the vapour stream were 100 cm^3/min. The vapour generating system followed the gas standard generator (KIN-TEK, Laboratories Inc. 670C). The vapour stream was produced by bubbling dry gas through a bubbler of the vapour solvent using a controller to manipulate vapour concentration. We measured the resistance percentage, and used the relative differential resistance change $\Delta R/R_0$ for the evaluation of the vapour sorption responses. ΔR is the difference of the maximum and minimum values in the resistance response, and R_0 is the initial resistance of the film. The gas devices were housed_in a Teflon chamber (inner diameter of 1/8 inch) with tubing connections to vapour and air pump sources. The setup of the vapour generating system followed the standard protocol. The vapour concentration in the unit was calculated from the weight loss and the volume of the analyte in the air.

The resistance measurement apparatus. An air pump was used for supplying/removing the carrier gas. Various concentrations of vapours were generated using an impingement system. At the beginning of the experiment, the test chamber was purged with air for 30 min to ensure the absence of air and also to establish the baseline. During the experiments, the test chamber was purged with air for 10 min and then with test vapour for 5 min at the desired vapour concentration.

The functionalized MWNTs–PANI samples were characterized using several techniques. A Fourier-transform infrared (FTIR, Brucher VECTOR22 spectrometer of Varian) spectrometer was used to examine the types of functional groups present in those samples. Raman spectra, with the excitation in the visible range of a HeNe 633 nm laser, were captured on a Renishaw inVia Reflex Raman microscope using an objective of the 50× magnification and 10 s accumulation time. The power was always kept low to avoid destruction of the samples. A thermo-gravimetric analyzer (TGA), manufactured by the TA Co. of America, was used to determine the content of MWNTs–PANI under air flow at the heating rate of 10 °C/min. The observation of polyaniline morphology was performed by a JSM-6500F scanning electron microscope (SEM).

3. Results and discussion

The TGA analyses have been carried out on carbon nanotubes to investigate the content of PANI on the MWNTs surface. Figure 1 shows the TGA curves of MWNTs–PANI and of pure PANI samples. In curve a, the weight loss of 18.72% can be attributed to the decomposition of PANI in the MWNTs–PANI. In contrast, the 57% weight loss of pure PANI occurred at 972 °C, resulting from thermal decomposition of the PANI sample (Fig. 1, curve b). The weight loss of the MWNTs–PANI is mainly due to the depolymerization of PANI chains; we can therefore assume that, the weight percentage of PANI on the MWNTs surface can be estimated to be 18.72%.

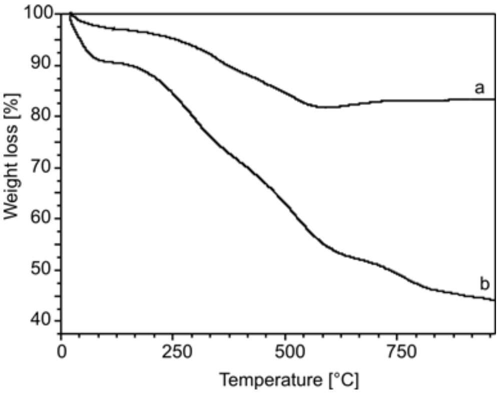


Fig. 1. TGA traces of 1 wt. % MWNTs –10 wt. % PANI (a) and pure PANI (b)

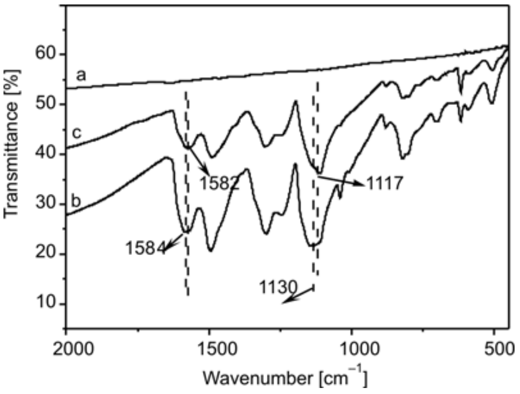


Fig. 2. FTIR spectra of MWNTs (a), MWNTs–PANI (b), pure PANI (c)

While the TGA data allows one to determine shows the concentration of PANI on the MWNTs surface, it does not provide any significant evidence as to the chemical bonding of the PANI onto the MWNT surface. Fortunately, it can be shown from FTIR spectra that the PANI was attached to the MWNTs. Figure 2 depicts the FTIR spectra of MWNTs, PANI and MWNTs–PANI. The characteristic absorption band of PANI is 1582 cm^{-1} (N=Q=N) and 1117 cm^{-1} (C–N) (Fig. 2, curve c), while the absorption peaks of MWNTs–PANI composite shift to 1584 cm^{-1} and 1130 cm^{-1} (Fig. 2, curve b). The absorption peak of the MWNTs–PANI composite is thus shifted by ca. 2 cm^{-1} and 13 cm^{-1} when compared to that of the pure PANI. These results indicate that intermolecular interactions exist between MWNTs and PANI. As shown in Fig. 2, curve a, pure MWNTs has no peak between 2000 cm^{-1} and 600 cm^{-1}.

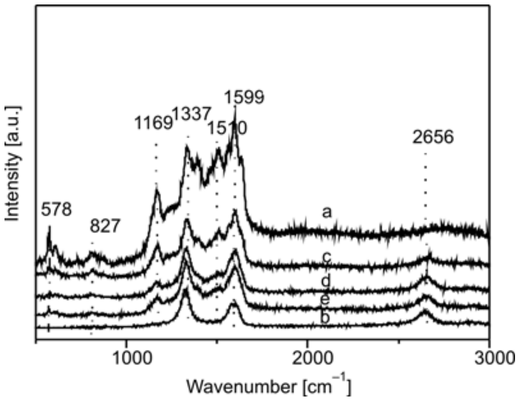


Fig. 3. Raman spectra of carbon nanotubes covered with PANI: pure PANI (a), pure MWNTs (b), 5 wt. % PANI–1 wt. % MWNTs (c), 10 wt. % PANI–1 wt. % MWNTs (d), 1 wt. % PANI–1 wt. % MWNTs (e)

Figure 3 shows that Raman spectroscopy is a useful tool for the characterization of PANI and MWNTs composite materials. A typical G-band (derived from the graphite-like mode) is situated at 1599 cm^{-1} in the spectrum of neat CNT. In contrast with the graphite G-band, which exhibits a single Lorentzian peak, the band for CNT has a shoulder extending to higher wavenumbers. The disorder-induced D-band is situated at 1337 cm^{-1} and its second-order harmonic D_0 band is found at 2656 cm^{-1} (Fig. 3, curve b). After coating of CNT with PANI, the spectrum of this polymer is dominant in all samples. This observation confirms that good coverage of CNT with PANI has been achieved. The peaks in the spectra are typical of protonated PANI and are located at 1599, 1510, 1337, 1169, 827 and 578 cm^{-1} (Fig. 3, curve a). Their positions remain practically unchanged for all contents of CNT. We have observed a relative decrease and a shift of the second-order of the disorder-induced band D_0 which indicates a less perfect structure for the nanotubes embedded in the polymer (Fig. 3, curves c–e) [12].

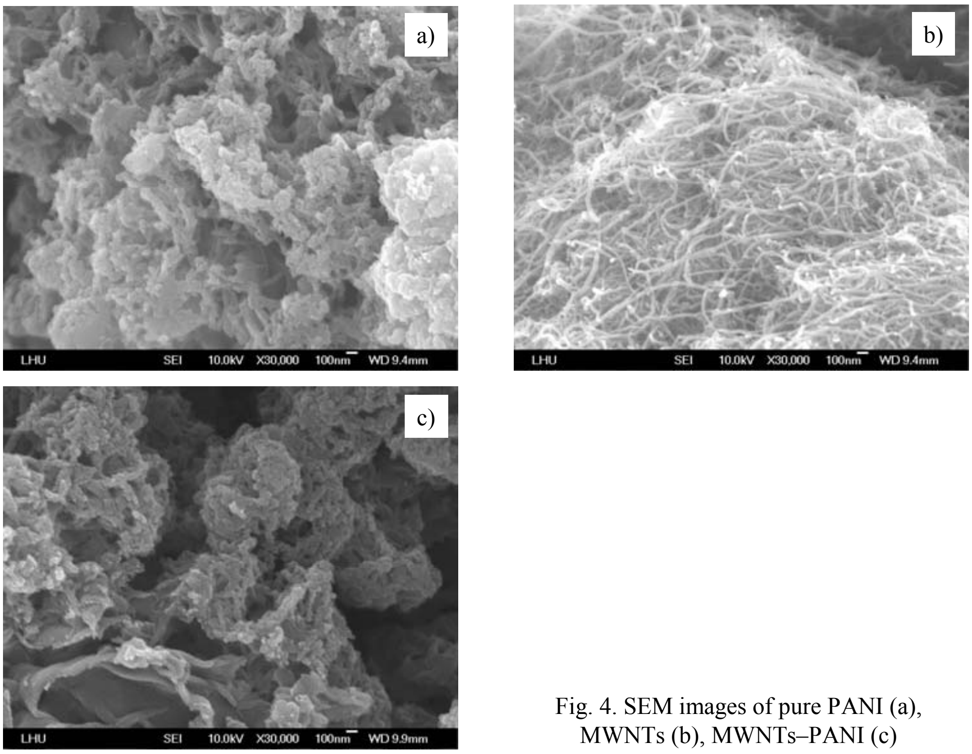


Fig. 4. SEM images of pure PANI (a), MWNTs (b), MWNTs–PANI (c)

Scanning electron micrographs (SEM) of the MWNTs and PANI are shown in Fig. 4. In these micrographs, PANI can be seen as an amorphous region. The surface of the particles is not smooth; lumps and holes (about 100 nm) in the material are visible (Fig. 4a). This uneven surface is a good property for gas adsorption. As shown in Fig. 4b, the SEM images also reveal that the MWNTs, with the diameter ranging from 30 to 80 nm, are well distributed on the surface and that most of the MWNTs are in the form of small bundles or single tubes. Such small bundles and single tubes assembled homogeneously on the substrate are believed to improve sensor performance because most of well-dispersed MWNTs are electrochemically accessible. In contrast,

Fig. 4c shows that depositing PANI on MWNTs film produces a layer-by-layer morphology : agglomeration and holes on the surface of the film were also observed. The larger diameter of PANI covered MWNTs compared with the neat MWNTs is visible.

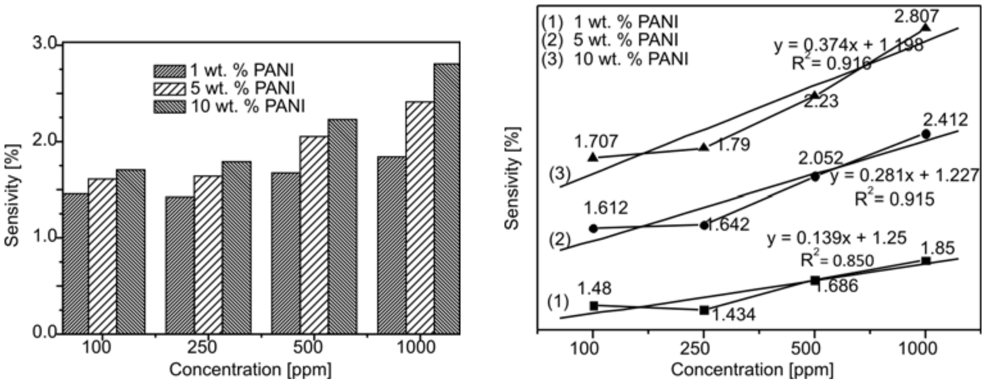


Fig. 5. Sensor response patterns (left) and fit-linear values (right) to TNT with an array of three weight percentages MWNTs/PANI sensing films

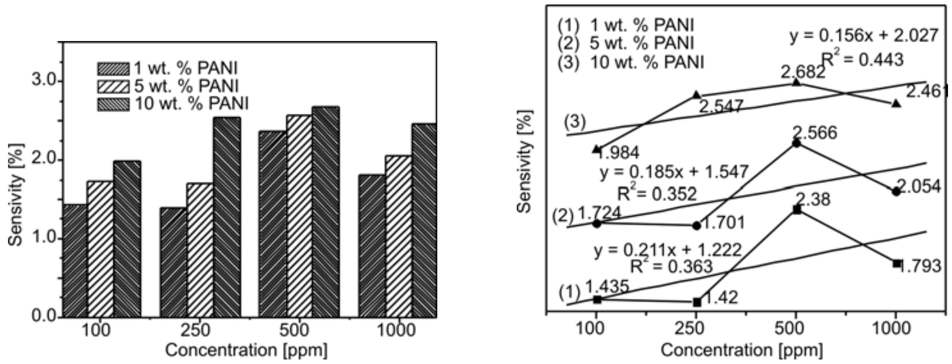


Fig. 6. Sensor response patterns (left) and fit-linear values (right) to 2,6-DNT with an array of three weight percentages MWNTs/PANI sensing films

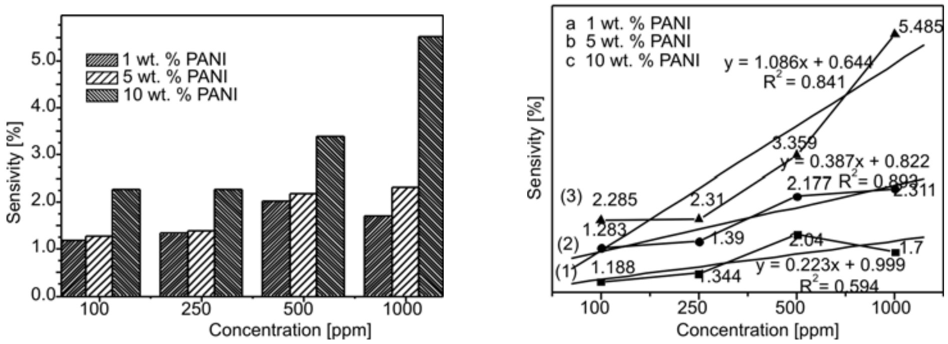


Fig. 7. Sensor response patterns (left) and fit-linear values (right) to picric acid with an array of three weight percentages MWNTs/PANI sensing films

The anchoring of PANI covering the MWNTs surface can impart its compatibility and transfer the electron, which greatly improves the responsiveness and reversibility of the materials. The response of the MWNTs–PANI composite film to three explosive vapours has been examined, as shown Figs. 5–7. Herein, the relative resistance responsivity is defined as $S = ((\Delta R)/R_0)\times100\%$, where R_0 and R are the original resistance and the maximum resistance of the film upon exposure to the above explosive vapours, respectively. The resistance of the sensors was in the range of 20–100 kΩ.

As shown in Figs. 5–7, the responsivities of the MWNTs- PANI systems to TNT, 2,6-DNT, PA are about 1.18 and ca. 5.51, respectively. However, only very small responsivities to any other explosive vapours were observed, for example to TNT. All these facts mean that the 10 wt. % MWNTs–PANI sensor has a stronger anti-jamming capacity and high sensitivity to PA vapour, and is therefore considered to be an ideal candidate for potential selective sensor applications.

The phenomenon may be associated with the differences in physical properties of MWNTs and polyaniline (PANI) conductive polymers. A high polar surface energy component was found for multi-walled carbon nanotubes, which significantly differs from that of carbon black particles [13], leading to different interaction of MWNTs and PANI sensing films. Moreover, the MWNTs–PANI film with centrally hollow core structures enables the analytes to permeate both the inner-layer and the outer-layer of the polymer nanotube, thus swelling the polymers rapidly. Additionally, it is likely that when the interlayer interactions of nanotubes were introduced, MWNTs –PANI could induce changes from metal to semiconductor, resulting in an increase in resistance. Of course, whether PA can definitively induce a change in conductive performances by adsorption on the MWNTs–PANI surface needs further investigation.

In fact, the PANI chain consisting of aniline anion and $C_{18}H_{29}$ SO_3 cation units may be responsible for the unique characteristics of the composite samples. This structure allows the formation of inter- and intramolecular hydrogen bonds [14], and the electronic transitions from the valence band into the mid-band gap states occur through the polaron state, containing one electron; the bipolaron state (i.e., containing two holes) is completely empty. In this case, the polymer material appears to "swell" and "dissolve" so that the original structure or configuration of the film will be destroyed. At the same time, the polymer volume increases under swelling and the interlayer distance between MWNTs is enlarged, which breaks the conducting network, leading to a large increase in the electrical resistance of the film.

It is worth noting that the swelling behaviour of PANI chains wrapped around MWNTs is very different from that of a pure PANI matrix. The former is concerned with the influence of interactions on the surface of MWNTs–PANI. The interactions among polymer differ from the latter that is easy to aggregate. Thus, only the dissolution ability to polymer is not a sufficient criterion to throw light on the aforementioned phenomenon. Up to now, there has been no extensive theoretical investigation into the interaction between polymer and MWNTs [15]. One viewpoint suggests that the polymer molecular structure and atomic interactions at CNT interfaces are likely to significantly influence the properties of sensor systems [16]. The other viewpoint is that weak electrostatic or noncovalent interactions between highly delocalized electron system of nanotubes and polymer may affect the molecular recognition of PANI to solvent molecules. For covalently functionalized MWNTs, the polymer is individually anchored onto the tube surface, forming a nanoscale layer of coating, especially in the case of higher conducting polymer proportions. A hopping mechanism is responsible for intertube charge transfer between CNTs and an intertube modulation of the CNTs network *in lieu* of a conductivity change [17]. This leads one to conclude that PANI molecules form an assembly domain around MWNTs with a large radius (Fig. 8) being a plausible structure model, suggested to explain the response mechanism.

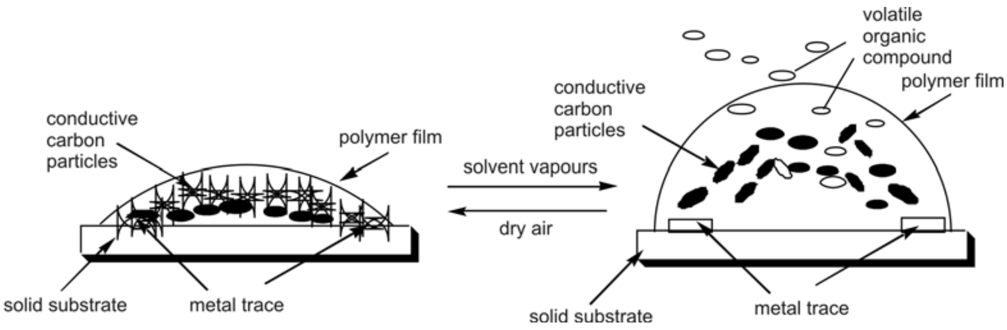
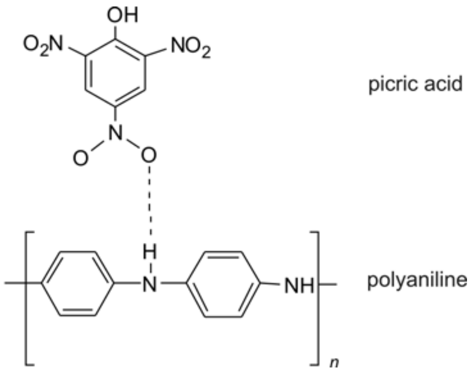


Fig. 8. Schematic representation of a possible structural model of MWNTs–PANI for explaining the response mechanism

In our study, explosive nitroaromatic compounds possess multiple basic sites at the nitro group oxygen atoms and the hydrogen-bond acidity of the polymer group is complimentary to these basic sites oriented to interact with electron rich oxygen atoms of the nitro groups on the nitro aromatic analytes. Here, hydrogen bonds may play an important role, and 2,6-DNT molecules act as good agents of MWNTs–PANI film. On the other hand, explosive agents such as TNT and PA, clearly induce an excellent response. Especially, PA vapour molecules act as a good agent of MWNTs–PANI film.



Scheme 2. Possible scheme of MWNTs–PANI interactions

Because the PA structure has –NO and –OH groups with strong electron donor properties, the sensor adsorption of a PA agent results in a partial charge transfer between the analyte and MWNTs–PANI that changes its electrical resistance, and speeds the motion and swelling of the polymer chains; it thereby breaks the conductive path and leads to an increase in resistance. The possible interaction is presented in Scheme 2.

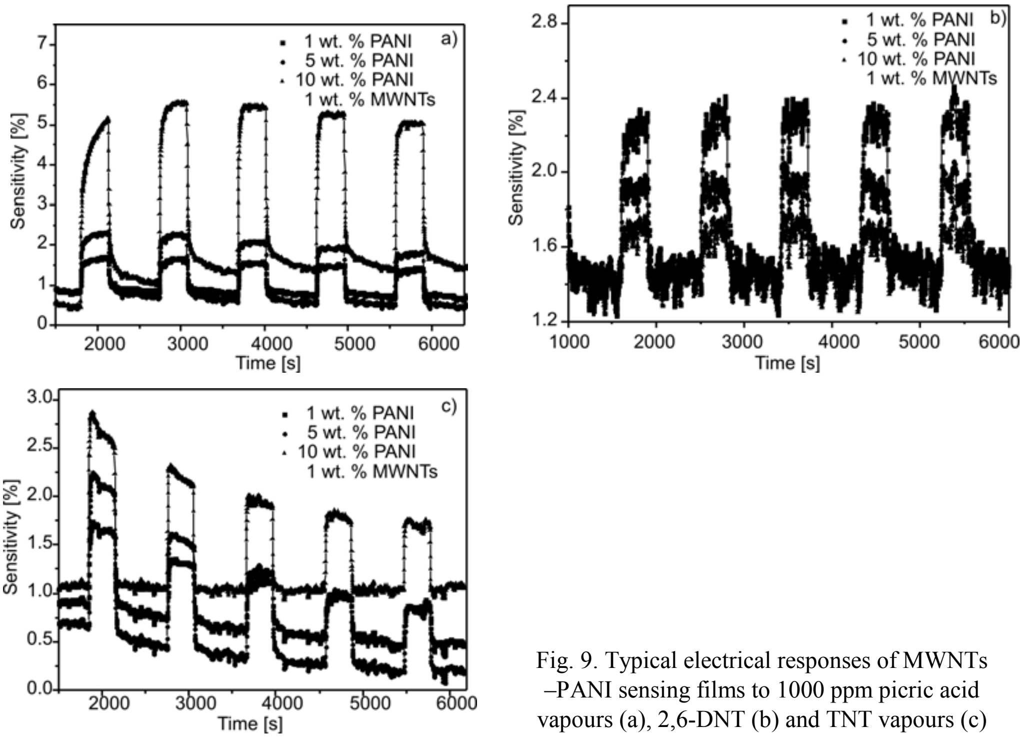


Fig. 9. Typical electrical responses of MWNTs –PANI sensing films to 1000 ppm picric acid vapours (a), 2,6-DNT (b) and TNT vapours (c)

We have contrasted the response patterns of the sensors in Figs. 5–7, based on the MWNTs–PANI materials. The resistance of the MWNTs–PANI (10 wt. %) sensing film drastically increased to over 5.5 of % within 1 s upon exposure to PA vapour (Fig. 9a). When it was transferred from the solvent vapour into dry air, the electrical resistance returned to the original value rapidly, showing a significant improvement in the restoring performance. This is also attributed to the weak hydrogen bond interaction between 2,6-DNT vapour and a polymer, which results in an abrupt adsorption of analyte molecules in a short time. The TNT adsorption resistance increased by about 1.73 of magnitude and the resistance could return to the original value (see also Fig. 9b). This further suggests that the rate of reversible response of the former is apparently superior to the latter. Therefore, a highly selective explosive gas sensor based on the MWNTs–PANI can be obtained. Figure 9 shows that the sensor developed from various weight ratios of MWNTs–PANI conductive material exhibits a better resistance reproducibility and stability five-fold exposure to the explosive vapours and dry air. Over a 6000 s period, the maximized variation in the baseline resistivity is less than 0.6 %. Such minor shifts did not significantly affect the response patterns and therefore do not affect sensor functionality. And the sensor film can be reused at least 12 times in this way. These results imply that the MWNTs–PANI material is a highly promising vapour sensor candidate, with excellent stability.

In the principle component analysis (PCA) study [18], the input data of the primary matrix are the normalized responses, chosen as the relative MWNTs–PANI resistance change ($\Delta R/R_0$), and processed by the correlation matrix (centred and standardized data). The response of the three MWNTs–PANI sensors array is normalized by the sum of all the sensor response values towards a given analyte. Such a normalization process reduces the dependence of the array response to the PA, 2,6-DNT and TNT concentrations, and also reduces slightly the effects of sensor drifts.

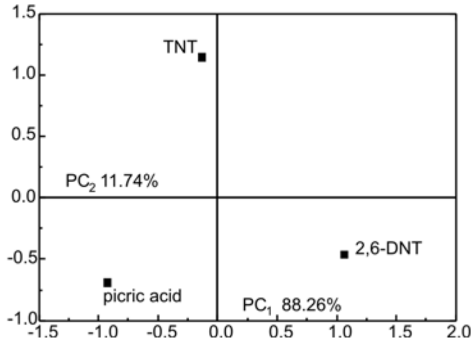


Fig. 10. PCA scores plot of the TNT, 2,6-DNT and PA in the PC_1–PC_2 plane of the original dataset obtained from the normalized responses of the all three deferent concentration MWNTs –PANI sensors of the IME

Figure 10 shows the scores plot in the PC_1–PC_2 class plane of two distinct clusters of PA, DNT and TNT with a spread of data points related to explosive agents with various graduated mixing ratios. The separate regions including the measurements of single simulantes indicate that the two different simulantes under test can be clearly discriminated from each other, and the first PCA value, 88.26, indicates the importance of the specific axis from the whole axis. In other words, if the sum of a whole axis importance was assumed to be 100, 88.26 means that the *X*-axis occupies about 88._As shown in Fig. 10, test gases can be easily distinguished by using a sensor array. The second principal component provides less information (11.74%), while the third principal component the lowest amount of information, by summing the overall information content of 100%. The results obtained indicate that the MWNTs–polymer composite sensors are the most appropriate option for the detection of a low concentration of an explosive.

4. Conclusion

We have demonstrated that chemical polymerization of PANI to the surface of MWNTs could endow devices with remarkable gas sensing properties with regard to both PA and DNT. The MWNTs–PANI sensor samples were afforded high sensitivity, excellent selectivity and good reproducibility or long stability. Thus the modification of the electronic structure of MWNTs–PANI by chemical functionalization provided a valuable route for the development of advanced sensor materials. To explain the selective responsiveness, we suggest swelling of PANI chains covering MWNTs. The interaction among PANI chains, MWNTs–PANI and analytes may also play an important role in gas sensing. The change in resistance of the film is caused by the interlayer distance change induced by the polymer swelling via gas absorption. On the other hand, the response on the MWNTs–PANI film to PA and 2,6-DNT differed from that to TNT, which is attributed to hydrogen bond interaction between explosive molecules and PANI chains. This interaction greatly affects the properties of MWNTs. In summary, we have developed a simple MWNTs, functionalized with a PANI sensor platform, for detecting explosive vapours at room temperature. The application of the PCA can be used to distinguish between the performance of PA, 2,6-DNT and TNT agents. The progress made here could be used as the basis for developing MWNTs –PANI sensors for highly sensitive and specific molecular detection.

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Received 5 May 2008
Revised 3 November 2008