

MWNTs/Polyaniline Composite Chemoresistive Sensor Array for Chemical Toxic Agents Detection

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ABSTRACT

Chemoresistive multi-layer sensor was fabricated by drop-coating polyaniline (PANI) solution on MWNTs of chemically modifying. The sensor response were investigated by exposing it to methanol MeOH, CHCl₃, dimethoxyl methylphosphonate (DMMP) and DCM. The morphology of MWNTs, PANI, MWNTs/PANI was studied using SEM. The structural characterization of the MWNTs/PANI and PANI were investigated with FTIR and UV-Vis spectrometer. The experimental results showed that 1wt % MWNTs and 10, 5, 1 wt % PANI sensor samples exhibited high sensitivity, excellent selectivity and good reproducibility to DMMP and DCM vapors. In addition, the principal component analysis (PCA) was applied to distinguish the performance of MeOH, CHCl₃, DMMP and DCM.

Keywords: Multi-walled carbon nanotubes, PANI, Chemical toxic agents, PCA

多壁式奈米碳管/聚苯胺組成化學電阻感測器對化學毒劑偵測

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摘要

以化學製成的聚苯胺(PANI)，用滴入-塗佈方式置於多壁式奈米碳管(MWNTs)上，建置雙層化學電阻感測膜，對甲醇、氯仿、DMMP、二氯甲烷做化學電阻回應之研究。以掃描式電子顯微鏡觀察 MWNTs/PANI、MWNTs、PANI 的型態，傳立葉紅外光譜儀和紫外光-可見光譜儀對多壁式奈米碳管/聚苯胺及聚苯胺作特性分析。實驗結果顯示 1 wt % MWNTs 和 1、5、10 wt % PANI 對於 DMMP 和 DCM 蒸氣顯現出較佳的靈敏性、高選擇性及好的再現性。另外，以主成分分析法去對甲醇、氯仿、DMMP 和 DCM 進行辨別。

關鍵詞：多壁式奈米碳管，聚苯胺，化學毒劑，主成分分析法

I. INTRODUCTION

Chemical warfare agents are colorless, toxic and very harmful to human health and the environment. These agents usually exist as liquids, but their vapors can be inhaled or absorbed through the skin. Exposure to nerve, blood and choking agents can cause a wide range of problems to central nervous system (CNS), cardiovascular collapse, chest discomfort, dyspnea and cough effects [1]. Fast and accurate detection of chemical warfare agents is essential for protecting human health. During recent years, many researchers have already attempted to detect toxic gases [2]. The kinds of sensors that have been used in the past to detect these gases include metal oxide semiconductors, colorimetric indicators, quartz-crystal microbalance sensors, electrochemical/chemical polymer nanostructure sensors and surface acoustic wave sensors [3–7].

Carbon nanostructures show unique properties and morphological flexibility, which make 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 [8]. But it did not receive much attention due to low sensitivity. At present, analyses of this kind are possible exclusively within the precincts of sophisticated research laboratories. Alexey et al, have demonstrated the viability of semiconductor metal oxides (SMO) thick-film gas sensors prepared using inexpensive commercial sensor platforms and a very simple drop-coating technique accompanied by in situ annealing of the deposited films by integrated heaters [9]. In addition, MWNTs and polyaniline films on glassy carbon (GC) electrodes prepared by the layer-by-layer methodology are shown to be excellent amperometric sensors for H_2O_2 concentrations. Therefore, “Nanostructure-polymer” detectors for chemical warfare agents and toxic industrial chemical reagents have to be portable, fast-acting, inexpensive, simple to operate, sensitive and selective to certain gases in question. [10]

This work is to analyze the ability of multi-layer MWNTs-Polyaniline (PANI) sensing films to identify chemical agent vapors, which

swell reversibly and cause resistance changes upon exposure to a wide variety of 2,122, 2,238, 481 and 332 ppm levels of methanol, chloroform, dichloromethane (DCM) and simulation chemical warfare agent (dimethyl methylphosphonate (DMMP) as a nerve agent), respectively. Principal component analysis (PCA) is used, one of the statistical classification methods, was conducted to classify four test gases [11].

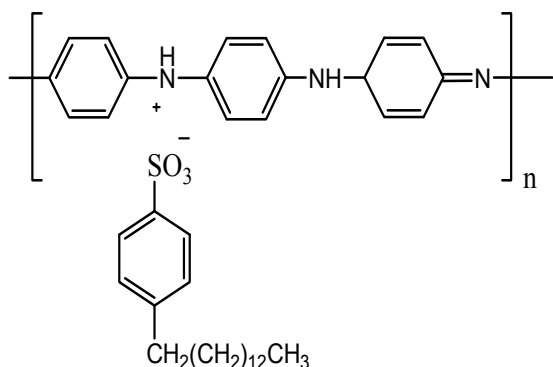
II. EXPERIMENTAL

2.1 Materials

Multi-walled carbon nanotubes were produced by the chemical vapor deposition (CVD) method with a nominal outside diameter (OD) of 20 ~30 nm. All the chemical reagents used (dimethyl methylphosphonate, dichloromethane, acetonitrile, aniline, methanol, chloroform and 1-methyl-2-pyrrolidone, sodium dodecylbenzenesulfonate) were of A.R. grade and distilled before use. Ammonium persulphate was used as an oxidizing agent for the preparation of polyaniline.

2.2 Preparation of Polyaniline

An amount of 2.0 mol sodium dodecylbenzenesulfonate (NaDBs), was dissolved in 1.0 mol aniline and allowed to stand at room temperature for 1 h. The ammonium persulphate $((NH_4)_2S_2O_8)$ solution was then added to the distilled water, with constant stirring, over a period of 30 min. The resulting deep-blue solution was removed from stirring and allowed to stand at room temperature for 12 h. The viscous solution was vacuum filtered and rinsed several times with deionized water and methanol. The deep-blue powder obtained was dried under a vacuum at 90 °C for 24 h (Scheme 1). [12]



Scheme 1. Preparation of a polyaniline structure.

2.3 Preparation of Thin Film

MWNTs (1wt%) layer-modified electrode was prepared by casting 5mg/ml methyl-ethyl-ketone (MEK), and the dispersion on the surface of a interdigitated microelectrode device (IME) and air-drying at room temperature. A PANI /solution (PANI: 5 mg/ml, 1 M NMP) was ultrasonicated for 10 min and then drop-coating deposited on the MWNTs / IME surface. After vacuum-drying, the double-layer sensing film was formed.

2.4 Measurements and Characterization

Sensor response measurements were performed using a customized interdigitated microelectrode (IME) device, which has 12 pairs of gold electrodes of 1mm width and 1mm spacing on a SiO₂ wafer substrate. A computer-interfaced multi-channel multimeter (in house) was used to measure the lateral resistance of the nanostructured coating on the IME. The resistance and frequency measurements were performed simultaneously with 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 vapor stream were 100 ml / min. The vapor generating system followed the Gas Standard Generator (KIN-TEK, Laboratories, Inc. 670 C). The vapor stream was produced by bubbling dry gas through a bubbler of the vapor solvent using the controller to manipulate the vapor concentration. We measured the resistance percentage and used the relative differential resistance change $\Delta R/R_0$ for the evaluation of the

vapor sorption responses. Where 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 transmission of gas devices were housed in a Teflon chamber (inner diameter of 1/8 inch) with tubing connections to vapor and air pump sources. The setup of the vapor generating system followed the standard protocol. The vapor concentration in the unit of ppm moles per liter was calculated from the weight loss and volume of analyte in the air.

Fig. 1 shows the resistance measurement apparatus. An air pump was used as gas carrier. Different concentrations of vapors were generated using an impinge 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. The test chamber was purged with air for 10 min and test vapor for 5 min at the desired vapor concentration.

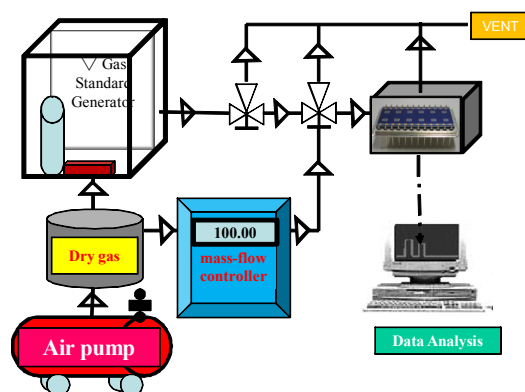


Fig. 1. Resistance measurement instrument.

The functionalized MWNTs/PANI samples were characterized using several instrumental techniques. A Fourier transform infrared (FTIR, Bruker VECTOR22 spectrometer of Varian) spectrometer and was used to examine the types of functional groups present on those samples. The observation of polyaniline, MWNTs and MWNTs / PANI morphology was performed by a JSM-6500F Scanning electron microscope (SEM). The ultra-visible spectra were obtained on a Cary 50 UV-Vis spectrophotometer (Varian). was used to determine the content of the MWNTs/PANI.

III. RESULTS AND DISCUSSION

3.1 FTIR and UV-Vis Spectral Analysis

The results of FTIR and UV-Vis spectra were shown in Figs.2 and 3 supports this conclusion also. The FTIR spectra show the attachment of PANI on MWNTs. Figure 2 shows the FTIR spectra of PANI, MWNTs/PANI and MWNTs. A weak peak at $3,446\text{ cm}^{-1}$ is ascribed to the N-H stretching vibration. The characteristic absorption band of PANI is $1,582\text{ cm}^{-1}$ ($\text{N}=\text{Q}=\text{N}$) and $1,117\text{ cm}^{-1}$ ($\text{C}-\text{N}$) (Fig. 2(c).), while the absorption peaks of MWNTs/PANI composited shift to $1,584\text{ cm}^{-1}$ and $1,130\text{ cm}^{-1}$ (see Fig.2(b).). The absorption peak of composite with MWNTs/PANI is that about 2 cm^{-1} and 13 cm^{-1} shift when compared to that of the pure PANI. These results indicate that there are some degree of intermolecular interaction between MWNTs and PANI. As shown on Fig. 2(a), the pure MWNTs will not show any peak appearing between 2000 cm^{-1} and 600 cm^{-1} absorption.

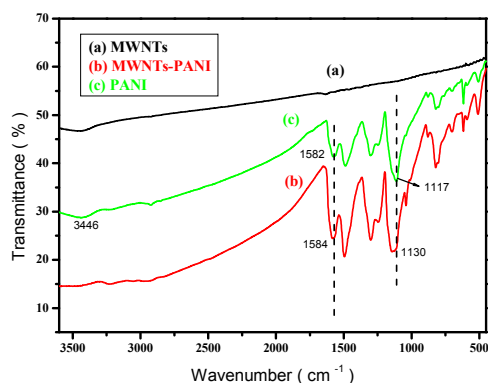


Fig. 2. FTIR spectra : (a) MWNTs, (b) MWNTs/PANI, (c) pure PANI.

Fig. 3 shows the UV-Vis spectra of the PANI and MWNTs/PANI films dissolved in NMP solvent are dominated by four absorption peaks at 328, 334, 615 and 642 nm, respectively. The peak of composite with 1wt % MWNTs/PANI films has a red shift about 6 nm than that of parent PANI, shown in Fig. 3(a). The peak of parent PANI around 328 nm is based on the $\pi-\pi^*$ transition of the benzenoid structure (due to hydrogen-bonding between the $\text{C}=\text{O}$ group in NMP and the N-H groups in the benzenoid units), where the peak of MWNTs/PANI is at 334 nm. The absorption in

the visible range, at 615 nm, is ascribed to exciton formation in the quinoid rings, where the peak of MWNTs/PANI is at 642 nm and has a red shift about 27 nm than that of parent PANI (see Fig. 3(b)). These results indicated that there are some interaction between MWNTs and polyaniline [13].

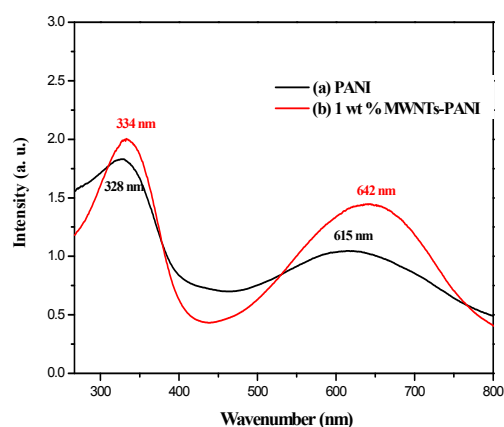


Fig. 3. UV-Vis spectrum of (a)PANI and (b)1 wt % MWNTs/PANI nanocomposite.

3.2 SEM Observation

Scanning electron micrographs (SEM) of the MWNTs and polyaniline are shown in Fig. 4. In these micrographs, polyaniline can be seen as an amorphous region. The surface of the particles is not smooth; lumps and holes (about 100 nm) in the material can be seen (Fig. 4(a)). This uneven surface is a good property for gas adsorptions. As shown in Fig. 4(b) the SEM images also reveal that the MWNTs, with a 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 benefit sensor performance because most of the well-dispersed MWNTs are electrochemically accessible. In contrast, Fig. 4(c) show depositing PANI on MWNTs film produces a layer-by-layer morphology, which the surface of the film is holes and the agglomeration also were observed. The larger diameter of PANI covered MWNTs compared with the neat MWNTs is visible.

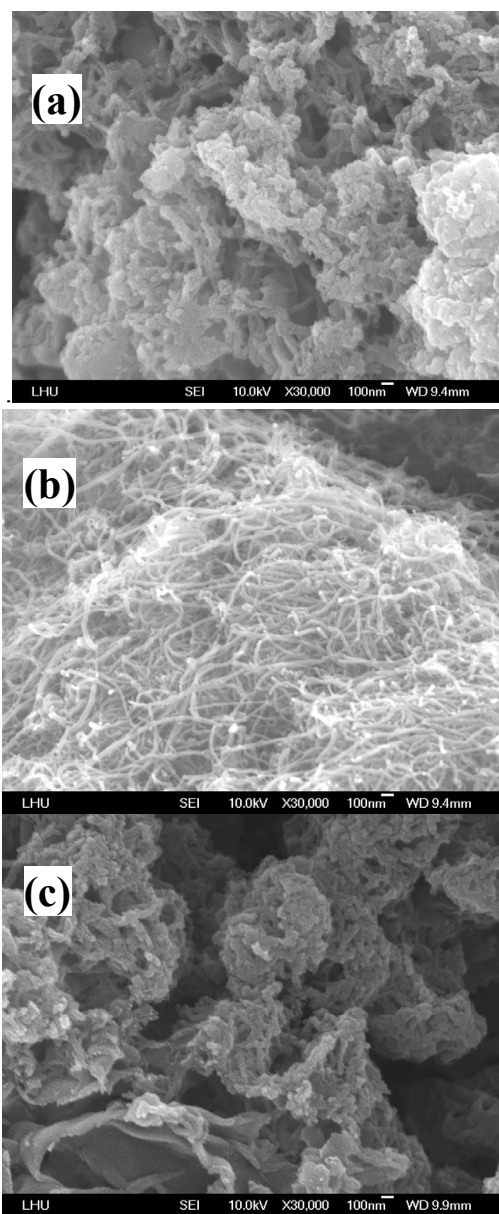


Fig. 4. SEM images of (a) pure PANI, (b) MWNTs (c) MWNTs/PANI.

3.3. Gas-Sensing Resistivity Behavior

The resistance characteristics in air of typical weight percentages of PANI (1, 5, 10 wt %) and 1 wt% MWNTs films are shown in Fig. 5. The resistance of the sensors was in the range of 20–100 k Ω . We compared the response of the three MWNTs/PANI composite sensing films to four solvent vapors, and the results are shown in Fig. 5. The time dependence of the change in the normalized resistance is shown for three polymers exposed to vapors of DMMP, DCM, MeOH and CHCl₃. The relative

sensitivity resistance responsiveness is defined as $\Delta R \% = [R/R_0] \times 100\%$, where R_0 and R are an original resistance and a maximal resistance of the film upon exposing to the above module chemical warfare solvent vapors, respectively.

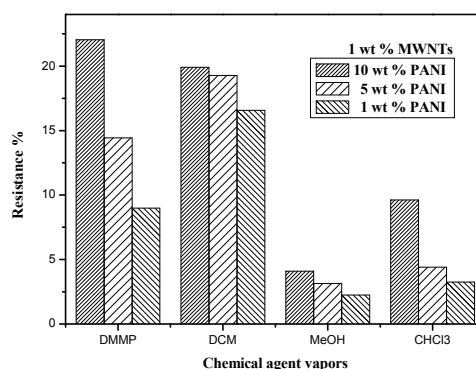


Fig. 5. Relative resistance responsivity of MWNTs/polymers multi-layer films against various chemical agent vapors.

As shown in Fig. 5 the resistivity of the MWNTs/PANI sensing films toward DMMP, DCM, MeOH and CHCl₃ are about 2.1 to ~22.02 % of magnitude, respectively. However, only very small responsivities to any other agent vapors were observed, for example, MeOH. All these manifest that the 10 wt % MWNTs/PANI sensor has a strong anti-jamming ability and high sensitivity to DMMP vapor, and should be considered an ideal candidate for a potential selective sensor application.

According to absorption/desorption the phenomena may be associated with the differences in physical adsorption properties of MWNTs and polyaniline (PANI) conductive polymers for simulated chemical warfare and organic agents. A high polar surface energy component was found for MWNTs that was significantly different from that of a carbon black particle [14], leading to the different interactions of MWNTs and PANI multi-layers. Moreover, the MWNTs/PANI sensing film has central hollow core structures that permit analytes to permeate the MWNTs/polymer from both the inner and outer layers, thus allow the polymers to swell rapidly. Additionally, it is likely that when the interlayer interactions of carbon nanotubes were introduced, the MWNTs/PANI could be induced to change from metal-like to semiconductor-like, resulting in an

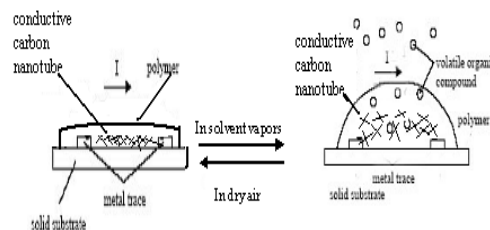
increase in resistance. Of course, whether DMMP can induce a change in conductive performance by adsorption on the MWNTs/PANI surface still needs to be shown in detail.

In fact, the PANI chain consisting of the aniline cation and $C_{18}H_{29}SO_3$ anion units, may be responsible for the unique characteristics of the composite samples. This structure allows the formation of inter- and intermolecular hydrogen bonds [15], and electronic transitions from the valance band to the mid-band gap states occur when the polaron state contains one electron and the bipolaron state is completely empty (i.e. contains two holes). In this case, “swelling” and “dissolution” of the polymer material appears so that the original structure or configuration of the film is destroyed. At the same time, the volume of polymer increases when it swells, and the inter-layer distance between MWNTs increase, breaking the conducting network and leading to a large increase in electric resistance of the film.

It is worth noting that the swelling behavior of PANI chains wrapped around MWNTs is very different from a pure PANI matrix. The former is concerned with the influence of the interactions on the surface of MWNTs/PANI. The interaction among polymers differs in the latter, which is easy to aggregate.

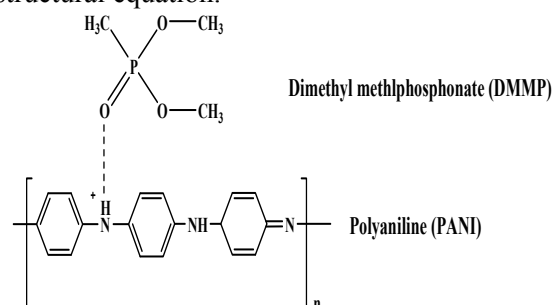
So the dissolution ability of polymer alone is not a sufficient criterion to explain the aforementioned phenomenon. Blau et al and Wei et al, suggests that polymer molecular structure and atomic interactions at CNT interfaces are expected to significantly influence the properties of the sensor system [16]. The other is that the weak electrostatic or noncovalent interactions between the highly delocalized electron system of carbon nanotubes and the polymer may affect the molecular recognition of PANI by solvent molecules. For covalently functionalized MWNTs, the polymer is individually anchored onto the tube surface, forming a nanoscale layer of coverage (thickness dependent on polymer amount), 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]. From this study, we conclude that the PANI molecules form an

assembly domain around MWNTs with a large radius. Scheme 2 depicts a plausible structural model that we suggest can explain the responsive mechanism.



Scheme 2. Schematic representation of a possible structural model of MWNTs/PANI for explaining the responsive mechanism.

In this study, although methanol and chloroform as good solvent for MWNTs/PANI, therefore hydrogen bonds may play an important role, but they induces no excellent response. On the other hand, they simulated chemical warfare agent DMMP and organic agent DCM clearly induce excellent responses. DMMP vapor molecules are especially good agents of MWNTs/PANI film. Because the simulated chemical nerve agent (DMMP) has strong electron donor properties, the sensor adsorption of a DMMP 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 the following structural equation.



In Fig. 6 we contrast the response patterns of the sensors based on the double-layer MWNTs/PANI materials. The sensitivity of the MWNTs/PANI sensing films drastically increased by 8 ~ 22% within 300s of exposure to DMMP and DCM vapors (Fig. 6(A) and (B)). When it was transferred from the solvent vapor into dry air, the electrical resistance returned to

the original value rapidly, demonstrating a good restoring performance. Fig. 6(C) to ~6(D) shows exposure to CHCl_3 and MeOH vapors for MWNTs/PANI sensing films, the sensitivity range are 0.4 ~ 0.9%. We attribute this behavior to the weak hydrogen bond interaction between the chloroform, and MeOH vapors, and the polymer that can result in a rapid adsorption of analyte molecules. This resistance could also return to the original value upon exposure to air. These results further suggests that the response speed and reversibility of the former are apparently superior to the latter. Therefore, a highly selective chemical organic solvent gas sensor based on MWNTs/PANI was obtained. Fig. 6 clearly shows that the sensor from the MWNTs/PANI conductive material exhibits a better resistance reproducibility and stability after four cycles of exposure to solvent vapors and a dry air. Over a period of 4,500 s, the maximum variation in the baseline resistivity was less than 22%. Such minor shifts did not significantly affect the response pattern and use of the sensors. These results imply that the MWNTs/PANI material is a very promising candidate for a vapor sensor with excellent stability.

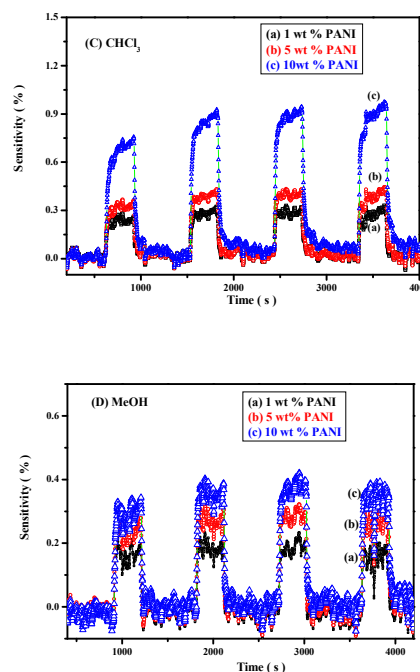
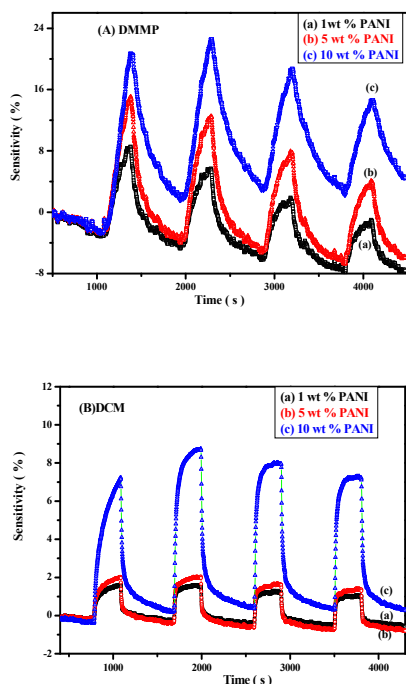


Fig. 6. Typical electrical responses of MWNTs/PANI films to simulate chemical agent (A) DMMP and organic agent vapors (B) DCM, (C) CHCl_3 , (D) MeOH.



3.4 Principle component analysis method

We used the principle component analysis (PCA) statistical method was applied to the signal of optimized sensor array [18-21], the input data of the primary matrix were the normalized responses, chosen as the relative MWNTs/PANI resistance change ($\Delta R/R_0$) and processed by the correlation matrix (centered and standardized data). The responses of the three MWNTs/PANI sensors were normalized by the sum of all the sensor response values towards a given analyte. This normalization process reduced the dependency of the array response on the concentration of vapor and also slightly reduced the effects of sensor drift.

Fig. 7 shows the score plot in the PC_1 - PC_2 class plane of two distinct clusters of DMMP and DCM plus a spread of data points related to methanol, chloroform agents with a different graduated mixing ratios. The fact that separate regions included the measurement of a single simulate indicate that two different simulates in the same test can be clearly discriminate from

one another. Between the two dots of DMMP and DCM, as indicated in Fig. 7, another evolved region of MeOH, CHCl₃ agents can be fixed in the feature plane analyzed (PC₁–PC₂) with a high cumulative variance exceeding over 99.885%. As noted, the largest portion of the variance was included in the first principal component (94.304%), which is also the most important in the discrimination of the dot. The second principal component comprised a lower amount of information (5.582%), while the third principal component included the least amount of the variation (0.115%). We can conclude that there were no redundant sensors in the studied array.

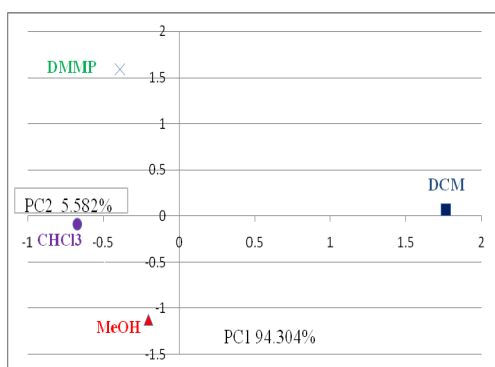


Figure 7. PCA score plot of the DMMP, DCM and organic agents.

IV. CONCLUSION

We have demonstrated that the chemical polymerization and coating of different wt% PANI on the surface of MWNTs can impart remarkable gas sensing properties for the detection of simulate chemical warfare agent DMMP and dichloromethane as well as organic agents methanol, chloroform. The 10 wt % MWNTs/PANI sensor provided high sensitivity, excellent selectivity and good reproducibility or long stability. The structure characterized and thermal properties of the MWNTs/PANI film were measured by SEM, FTIR and UV-Vis. We suggest that the swelling behavior of the PANI chains covering MWNTs as well as the interaction among PANI chains, MWNTs/PANI and analytes may play important roles in the gas sensing. The change in resistance of the film is caused by the change in inter-layers distance that is induced by polymer swelling upon gas absorption. The response on the MWNTs/PANI

film to DMMP, DCM, and methanol, chloroform differed from that of any other solvent, which we attribute to a hydrogen bond interaction between solvent molecules and PANI chains. This interaction is greatly affected by properties of PANI. In summary, we have developed a simple MWNTs functionalized with a PANI sensor platform for chemical warfare agents and methanol, chloroform agents vapors detection at room temperature. We applied PCA to distinguish the performance of DMMP, DCM, methanol and chloroform agents. The progress made here shall prepare us for developing MWNTs/PANI sensors for highly sensitive and specific molecular detection.

Appendix

1. wt%: weight percentage.
2. ppm: part per million
3. k Ω : unit of electrical resistance (kilo ohm)

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袁俊龍等

多壁式奈米碳管/聚苯胺組成化學電阻感測器對化學毒劑偵測