

# Detection of organic chemical vapors with a MWNTs-polymer array chemiresistive sensor

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Organic chemical hazardous gases pose a significant threat to human life and the environment. An urgent need exists for the development of reliable chemical sensors that would be able to identify these hazardous gases. In a recent study, conductive carbon nanotubes were mixed with six polymers with various chemical adsorption properties to produce a composite thin film for the fabrication of a chemical sensor array. A silicon wafer was used as a microelectrode substrate for a resistance sensor fabricated using a typical semiconductor manufacturing process. This sensor array was then used to identify hazardous chemical gases at various temperatures. Results for two hazardous gases, ammonia (NH<sub>3</sub>) and chloroform (CHCl<sub>3</sub>), tested with the six polymers at different temperatures, indicated that the variation in sensitivity/resistance increased when the temperature increased. It was found that the MWNTs-PVP and MWNTs-PMVEMA sensing films had high sensitivity, excellent selectivity, and favorable reproducibility in detecting the two chemical agent vapors. In addition, we derived the solubility parameter ( $\Delta\delta$ ) to demonstrate the sensitivity of the polymers to ammonia (NH<sub>3</sub>). The results showed that smaller solubility parameter corresponds to a stronger interaction between NH<sub>3</sub> gas and polymers, and increased sensitivity. Additionally, we used the statistical methods of principal component analysis to identify the interaction of hazardous gases with the MWNTs-polymer sensor.

Keywords: *chemical hazardous gases; multi-walled carbon nanotube – MWNT; resistance sensor array; primary component analysis*

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## 1. Introduction

Volatile organic chemical vapors in our environment can affect human health and survival. The entire nitrogen content of all manufactured organic compounds is derived from ammonia. A major application of ammonia is the use in the manufacturing of explosives, whereby nitric acid is made by oxidizing ammonia. Chloroform is an organic compound and is a common solvent used in the laboratory. It is relatively unreactive, miscible with most organic liquids, colorless, conveniently volatile, but it is hazardous.

Therefore, the ability to accurately and quickly discriminate hazardous vapors is essential for protecting human health and safety. Many countries have developed industrial and environmental safety regulations to limit personal exposure concentra-

tions, and have set emission concentration standards for various hazardous and caustic gases. In response to these regulations and standards, we found that many efforts focus on the development of cheap, micro-chemical gas sensors with high reproducibility and fast reaction rates, which are light in weight and are applied in the testing, chemical manufacture, industrial safety, agriculture and the military industry [1–4]. At present, air quality is determined by collecting samples and analyzing them with analytical laboratory instruments, such as Raman surface spectroscopy [5], gas chromatography-mass spectrometry [6], nuclear magnetic resonance spectroscopy [7], neutron activation analysis [8], ion mobility spectrometry [9], cycle voltammetry [10], X-ray diffraction [11], and quartz-crystal microbalance sensors [12], electrochemical/conductive polymer nanostructure sensors, and surface acoustic wave sensors [13, 14]. These methods and equipment are expensive and

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require frequent calibration to maintain accuracy. The equipment is often too large for the terrain and the environmental conditions in which it is used. Therefore, a low cost, portable, durable, and real-time monitoring chemical sensor made of organic polymers would be the ideal of a protective detector.

Developing an electrochemical sensor that is light in weight, compact, robust, and is capable of real-time monitoring has become a popular research subject for institutes all over the world. Among all electrochemical sensors, the most representative type is a chemiresistor. The operating principle of a chemiresistor is based on the variation in its resistance when the polymer is coated on a circuit board. The polymer selectively adsorbs/desorbs chemical substances and swells when exposed to chemical gases. Polymer swelling increases the electrode resistance, and the variation of this resistance can be used to estimate the concentration of a tested gas. The most important element in the fabrication of a chemiresistor is the polymer material [15] of which the two major elements are made: (1) a sensor material produced by mixing conductive substances and polymers, and (2) a material made of intrinsically conducting polymers. The chemiresistor uses the semiconductor properties of a conductive polymer and performs sensing operations based on the resistance variation due to chemical gas adsorption/desorption. To produce a composite chemiresistor sensors, the conductive film mainly made of carbon mixed with an inorganic semiconductor or a metal powder is used.

Many researchers working on gas sensors which use polymer-carbon nanotube composite thin-films pay a lot of attention on the polymer material [16–18]. Few researchers focus on the theories of the interaction between the materials and molecules, and gas sensing at various temperatures and moisture levels. In our previous studies on MWNTs-polymers sensing films, we focused on the aspects of the process of film manufacturing, such as the multi-carbon nanotube content, and on measuring the sensor response to some explosive vapors under various operating conditions, including adsorption/desorption behavior and concentra-

tion [19–21]. Kim et al. demonstrated MWNTs and MWNT-PANI sensing films to detect  $\text{NH}_3$  gas. The results showed that the MWNT-polymer sensing films were more sensitive than the MWNT sensing films [22]. In another study, the polymer and solvent solubility theory (the Hansen and Hildebrand solubility parameters) was applied to the solution phase dispersion of single-walled carbon nanotubes. The results were compared with experimental extinction and adsorption coefficients for HiPco-SWNT suspended in organic solvents. A closer correlation was achieved with hydrogen bonding and polar forces, rather than with dispersion forces, although the relationship varied for chlorinated solvents [23, 24]. Until now, there has been an extensive theoretical investigation of the interaction between polymers and MWNTs [25], but without considering the solubility parameter, theoretically demonstrating the polymer-ammonia interactions in a chemoresistive sensor.

In this work we utilized MWNTs after surface modification. We used the semiconductor process to develop an interdigitated microelectrode (IME) chip and fabricated the nano-composite chemical-gas sensor with the drop-coating approach. The sensor films were designed to test two kinds of hazardous gases of various concentrations. Bar charts were used to illustrate the resistance variation. The reproducibility and stability of the thin-film sensors under the operation of the microelectrode resistance system was shown in the sensitivity chart of adsorption/desorption tendency. An information pattern was established based on the measured results of resistance variation. Furthermore, we used the polymer-solvent solubility parameter to demonstrate the polymer-ammonia composite interactions in a chemoresistive sensor. The statistical methods of principal component analysis (PCA) were used to identify the two tested gases at various concentrations.

## 2. Experimental section

### 2.1. Materials

Multi-walled carbon nanotubes with a nominal outside diameter (OD) of 30 – 40 nm were

produced using the chemical vapor deposition (CVD) method. For the device fabrication, a semiconductor manufacturing technique (photolithography) was used.

In this research, we selected six polymer materials with three different types of intermolecular bonds [21]:

- styrene/allyl alcohol copolymer (SAA), poly(methyl vinyl ether-alt-maleic acid) (PMVEMA), poly(vinylidene poly(alpha-methylstyrene) (PMS), chloride-co-acrylonitrile) (P(VDC-AN)) (no hydrogen-bond, NHB),
- polyvinylpyrrolidone (PVP) (hydrogen-bond basic, HBB) and
- poly(ethylene adipate) (PEA) (hydrogen-bond acidic, HBA).

The polymers,  $\text{NH}_3$  and  $\text{CHCl}_3$  were purchased from Aldrich Chemical Corp.

## 2.2. Fabrication of composite thin-film sensor

Wang et al. prepared MWNT-polymer composite membranes in one-layer and two-layer versions for ethanol sensing experiments. The two-layer membrane had higher sensitivity, faster recovery time, and better repeatability. Therefore, we adopted the two-layer version for fabrication of our composite sensing films [21]. The MWNTs layer-modified electrode was prepared by coating the surface of a IME device with 5 mg/ml of methyl-ethylketone dispersion, which was dried in air at room temperature. The polymer layer was then deposited on the MWNTs-layer by drop-casting with 1 wt.% of various polymer solutions, followed by drying in vacuum. The double-layer film sensor device was then formed.

The functionalized MWNT-polymer samples were characterized using scanning electron microscopy (SEM). JSM-6500F was used to observe the double-layer morphology.

## 2.3. Fabrication and measurement using the gas sensing system

A computer-interfaced multichannel multimeter was used to measure the lateral resistance of the

nanostructured coating on the IME. The IME devices were housed, and tubing was used to connect them to the vapor and air pump sources in a Teflon chamber (inner diameter of 1/8 inch). Sensor response was measured using a customized IME device, with 12 pairs of gold electrodes (1 mm wide, 1 mm spaced apart) on a  $\text{SiO}_2$  wafer (Fig. 1).

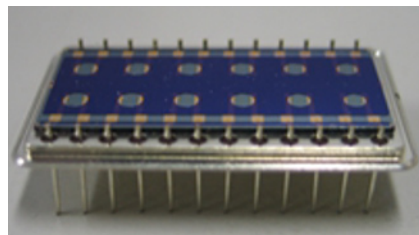


Fig. 1. Configuration of the interdigitated microelectrodes.

Resistance and frequency measurements were simultaneously performed with computer control. All experiments were performed at various temperatures (30, 40, 50 and 60 °C) and at approximately 50 % – 60 % humidity. The gas flow was controlled with a calibrated Aalborg mass-flow controller. The flow rate of the vapor stream was maintained at 100 ml/min. The vapor generating system relied on the Gas Standard Generator (KIN-TEK, Laboratories. Inc., 670C). The vapor stream was produced by drying the solvent vapor and using the controller to manipulate the vapor concentration. The vapor concentration (parts per million, ppm) in the unit was calculated from the weight loss and volume of the analyte at various temperatures (see Table 1), which can be expressed by Equation 1 [20]:

$$\text{Concentration} = (RK)/F(\text{v/v in ppm}) \quad (1)$$

where  $K = \{22.4(T + 273) \times 760\}/\text{MW} \times 273 \times P$ ,  $R(\text{mg/min})$  is the weight loss of the analyte, and  $F(\text{ml/min})$  is the flow ratio.

Fig. 2 shows the apparatus for determining resistance. Air was used as the carrier gas. Several vapor concentrations were generated with an impingement system. At the beginning of the experiment, the test chamber was purged of air for 30 min to ensure that no air existed in the chamber and to establish a baseline. Before every experiment, the

Table 1. Concentrations (ppm) of the two vapors.

Temperature °C	NH <sub>3</sub> ppm	CHCl <sub>3</sub> ppm
30	418	19381
40	465	32274
50	895	44225
60	1056	100639

chamber was purged of air for 10 min and then filled with the test vapor at the desired concentration for 5 min [20].

The sensitivity of a gas sensing thin film is extremely influential on the detection performance of the resistance gas sensor. Generally speaking, a sensor with higher sensitivity has a more efficient detection capability and a broader range of applications. The sensitivity of the resistance gas sensor ( $S\%$ ) is defined in Equation 2:

$$\begin{aligned} S\% &= [(R_{gas} - R_{air}) / R_{air}] 100\% \\ &= (\Delta R / R_{air}) 100\% \end{aligned} \quad (2)$$

where  $R_{air}$  is the resistance of the sensor in the air and  $R_{gas}$  is the resistance after adsorbing gases at various temperatures.

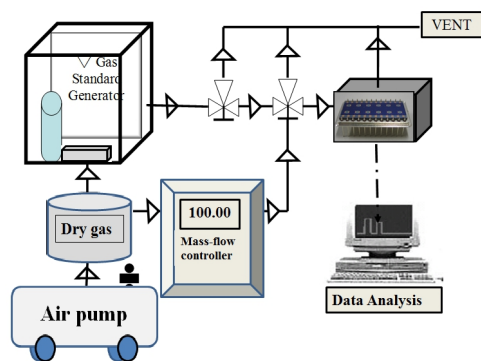


Fig. 2. Instrument for measuring resistance.

## 2.4. Solubility parameters

Solubility parameters were developed to describe the enthalpy of a mixture of sample liquids, but were extended to include polar solvents and

polymers. The Hildebrand and Scott [24, 26] methods were used to estimate the solubility parameter of the polymer and the analyzed substances. Dissolution of a polymer in a solvent is governed by the free energy of mixing:

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (3)$$

where  $\Delta G_M$  is the Gibbs free energy change of the polymer/solvent mixture,  $\Delta H_M$  is the enthalpy change of the polymer/solvent,  $T$  is the absolute temperature, and  $\Delta S_M$  is the entropy change of the polymer/solvent.

Equation 4 yields the heat of mixing of regular solutions, in which the components are mixed with: (a) no reaction between the components, (b) no volume change on mixing at a constant pressure, and (c) no complex formation or special associations:

$$\Delta H_M = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (4)$$

where  $V$  is the volume of the mixture and  $\phi$  is the volume fraction of the mixture. The heat of mixing must be smaller than the entropic term in Eq. 3 for polymer-solvent miscibility.  $\Delta G_M$  has to be negative to ensure mutual solubility of two substances, therefore  $\Delta H_M$  must be kept as small as possible. This means that  $(\delta_1 - \delta_2)^2$  or  $\|\Delta\delta\| = (\delta_1 - \delta_2)$  must be small so that it could be analyzed, explained, and predicted by the adsorption of a part of substances analyzed by the polymer. This is followed by an analysis and prediction of the Hildebrand solubility parameter ( $\text{MPa}^{1/2}$ ). The molar volume of the solvents and polymers can also be estimated by group contribution methods [27]. Group contribution methods are based on the assumption that the contributions of several functional groups to the thermodynamic properties are additive. The solubility parameter of polymers or solvents can be obtained with Equation 5:

$$\delta = (\sum n_j \Delta e_j / \sum n_j V_j)^{1/2} \quad (5)$$

where  $\Delta e_j$  is the energy of vaporization contribution of group  $j$ , and  $n_j$  is the number of type  $j$  in the polymer molecule.

### 3. Results and discussion

#### 3.1. Gas-sensing resistivity response characteristics

We used six kinds of MWNTs-polymer sensors to detect two kinds of industrial chemical gases ( $\text{NH}_3$  and  $\text{CHCl}_3$ ) at various temperatures. The array sensing films differed from each other in terms of chemical and physical characteristics of the mediator molecules, including hydrogen-bonding properties, hydrophobicity, and chain length or structure. Variations in resistance were measured with adsorption/desorption tests using several vapor concentrations at various temperatures. The sensitivity of the MWNTs-PMVEMA sensing film drastically increased by approximately 7 %, 10 %, 12 % and 45 % within 80 s after exposure to 418, 465, 895 and 1056 ppm  $\text{NH}_3$  vapor, respectively. Exposure of the first MWNTs-PVP then the MWNTs-PMVEMA film to  $\text{CHCl}_3$  vapor showed excellent sensitivity and reproducibility (data not shown). The responses of the films in the array to various vapors, differed for the chloride and amino groups.

After sampling saturated adsorption resistances for five times at different temperatures, we have derived the standard error (S.E) and change in resistance ( $\Delta R$ ) for the MWNTs-polymer exposure to ammonia vapor, ranging from 0.095 – 0.13 and 1 – 27 k $\Omega$ , respectively (Fig. 3A). The standard error and the change in resistance ( $\Delta R$ ) due to the MWNTs-polymer exposure to  $\text{CHCl}_3$  ranged from 0.13 – 2.91 and 1 – 22 k $\Omega$ , respectively (Fig. 3B). The resistance variation can be further explored via factors such as interaction forces among chemical gas molecules, vapor pressure of chemical gas molecules, and polymer solubility parameters.

According to the response data, we have compared the sensitivity responses of the tested polymer films (Fig. 4). From the bar chart in Fig. 4a it follows that the MWNTs-PMVEMA were highly sensitive to  $\text{NH}_3$  gases at various concentrations, showing the highest change in relative resistance  $\Delta R/R$  under the gas flow. However, the MWNTs-PMVEMA exposure to  $\text{CHCl}_3$  caused a sensitivity response that was lower than the responses of the MWNTs-PVP (Fig. 3b). Thus, the exper-

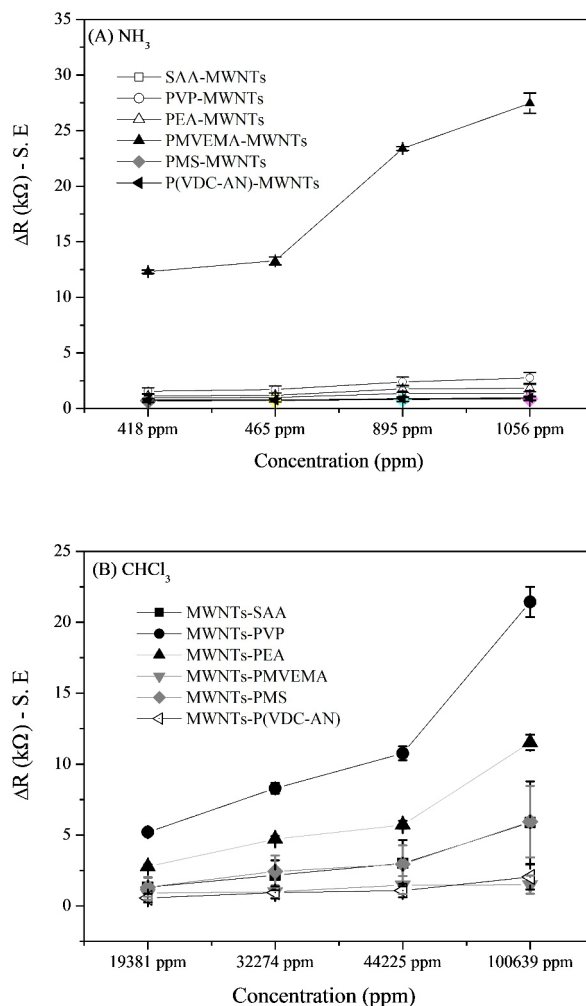


Fig. 3. Changes in resistance  $\Delta R$  (k $\Omega$ ) and standard error (S. E), denoted as error bars for MWNTs-polymer thin film with respect to two kinds of gases, calculated for five cycles. (A)  $\text{NH}_3$  and (B)  $\text{CHCl}_3$ .

imental results indicate that MWNTs-PMVEMA and MWNTs-PVP had the highest sensitivities for the  $\text{NH}_3$  and  $\text{CHCl}_3$  vapor analytes, respectively. Additionally, the increase in sensitivity response with high specificity for  $\text{NH}_3$  vapor is unprecedented, and results from the unique combination of the hydrogen-bonding donor/acceptor and hydrophobicity of the MWNTs-polymer structure [25]. These experimental results show that the MWNTs-polymer composite thin-film sensors respond selectively to the two hazardous gases at various temperatures.



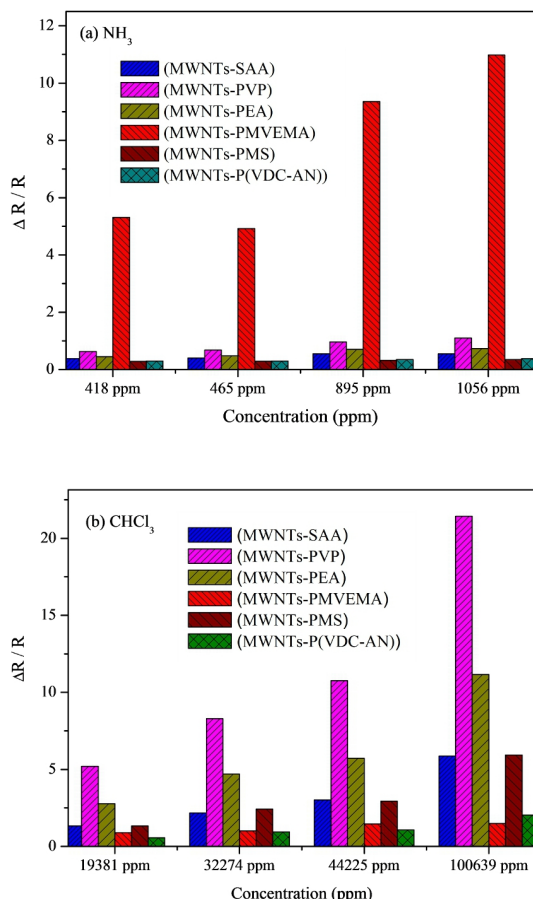


Fig. 3. The relative resistance bar chart of six MWNTs-polymers with respect to two kinds of gases at various concentrations.

### 3.2. SEM of double-layer sensing films

Fig. 4 shows a scanning electron micrograph of the MWNTs-PMS double-layer film, indicating that MWNTs with diameters of 30 to 80 nm are evenly distributed on the surface of small bundles or single tubes. These small bundles and single tubes, which are assembled homogeneously on the substrate, should improve the sensor performance because most of the well-dispersed MWNTs are electrochemically accessible. Furthermore, the deposition of PMS on the MWNTs film produced a multilayer morphology. The PMS particles are spherical and rough (the particles are approximately 100 nm wide), and agglomeration is also observed. This uneven surface is beneficial for gas adsorption. The anchoring of PMS covering the

MWNTs surface imparted compatibility and electron transfer which greatly improved the material responsiveness and reversibility.

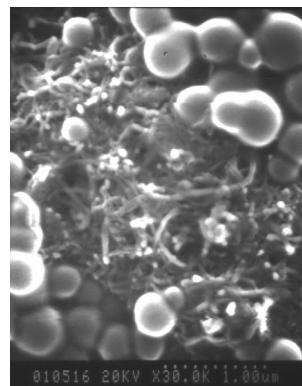


Fig. 4. Micrograph of the MWNTs-PMS.

### 3.3. Absorbance mechanism of gas-sensing film

The response mechanism of adsorption/desorption may be associated with the variations in the physical adsorption properties of the MWNTs and polymers for several organic chemical vapors.

The double-layered MWNTs-polymer composites have central hollow core structures, permitting analytes to permeate the MWNTs-polymer film through both the inner and outer layers. This enables the polymers to swell rapidly. In addition, it is likely that when the interlayer interactions between carbon nanotubes take place, the MWNTs-polymer changes from a metal-like to a semiconductor-like polymer, which results in an increase in resistance. Therefore, the issue whether  $\text{NH}_3$  and  $\text{CHCl}_3$  are able to induce a change in conductive performance through adsorption on the MWNTs-polymer surface requires further study. The polymeric “shrinking” and “swelling” destroys the configuration of the sensor film. At the same time, the volume of the polymer increases when it swells, and the interlayer distance between MWNTs increases, breaking the conducting network and leading to a large increase in the electrical resistance of the film. It is worth noting that the swelling behavior of polymer chains wrapped around MWNTs is not the same as that of a pure polymer matrix. The swelling

of polymer chains wrapped around MWNTs is influenced by the interactions on the surface of the MWNTs-polymer [28]. Aggregation occurs more easily when polymer chains in a pure polymer matrix interact. Therefore, the shrinking ability of the polymer alone is not sufficient to explain the aforementioned phenomenon. In our previous studies we used atomic force microscopy to demonstrate the MWNTs-PANI absorption of DMMP vapor, wherein the sensing film swelled and the film thickness increased from 0.8 to 1.3  $\mu\text{m}$  [20].

### 3.4. Analyzing the test results with the solubility parameter theory

Table 2 [26] and Table 3 show the solubility parameters ( $\Delta\delta$ ) of ammonia gas and outline three kinds of physical adsorption bonding polymers: weak dipolar (no hydrogen bond), hydrogen bond acidity, and hydrogen bond basicity interactions. Table 3 shows that we can apply the solubility parameter to estimate the order of sensitivity to detect  $\text{NH}_3$ , which is: PMVEMA > PVP > PEA. A smaller solubility parameter corresponds to a stronger interaction between  $\text{NH}_3$  gas and a polymer, resulting in increased sensitivity ( $S$ ). Therefore, we can provide solubility parameters to effectively predict the performance of a polymer in sensing chemical gases.

### 3.5. Pattern recognition using Principal Components Analysis (PCA)

The PCA statistical method was applied to the signal of the optimized sensor array. Normalized responses were the input data from the primary matrix, which were chosen to represent the relative resistance change ( $\Delta R/R_0$ ) of the MWNTs-polymer sensors. The PCA data (centered and standardized) were obtained with the correlation matrix [28]. The responses of the six MWNTs-polymer sensors were normalized by adding all the sensor response values for a given analyte. This normalization process reduced the array response dependence on vapor concentration and slightly reduced sensor drift effects. Fig. 6 depicts 3D plots for the four concentrations of  $\text{NH}_3$  and  $\text{CHCl}_3$  vapors. These data were obtained by applying PCA analysis to the normal-

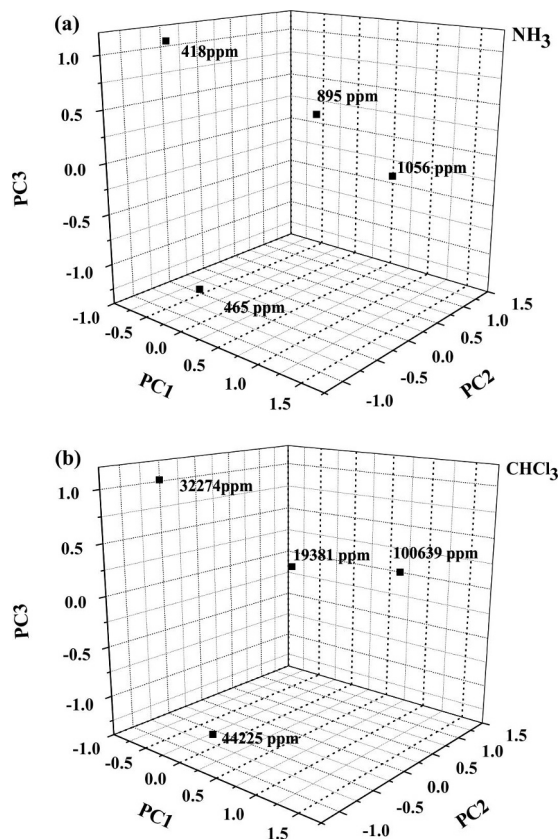


Fig. 5. PCA score plots of two groups of gases in the 3D PCA space (a)  $\text{NH}_3$  and (b)  $\text{CHCl}_3$ .

ized responses of the six MWNTs-polymer sensing films. As shown by the data points at the higher concentrations, the analytical results demonstrate that all vapors could be easily separated. Between the four dots of 418, 465, 895 and 1056 ppm (Fig. 6a), another evolved region of organic agents can be fixed in the feature plane ( $\text{PC}_1 - \text{PC}_2$ ) analyzed with a high cumulative variance exceeding 93.72 %. As previously noted, the largest portion of the variance was from the first principal component ( $\text{PC}_1$ ), which was also the most critical component in dot discrimination. The second principal component ( $\text{PC}_2$ ) contained less information (3.60 %), whereas the third principal component showed the smallest variation (2.68 %). Fig. 5b shows the four dots for 19381, 32274, 44225 and 100639 ppm. With the high cumulative variance exceeding 94.02 %,  $\text{PC}_2$  contained less information (4.99 %). The third principal component ( $\text{PC}_3$ ) had

Table 2. Solubility parametrs of three polymers and NH<sub>3</sub> [26].

Polymer/Solvent	Solubility parameters ( $\delta$ )		H-bonding group
	(MPa <sup>1/2</sup> )	(cal/cm <sup>3</sup> ) <sup>1/2</sup>	
Polyvinylpyrrolidone (PVP)	25.6	12.51	m
Poly[ethylene adipate] (PEA)	22.51	11.01	–
Poly[methyl vinyl ether-alt-maleic acid] (PMVEMA)	26.33	12.87	m
Ammonia (NH <sub>3</sub> )	33.34	16.3	s

Table 3. Comparison of solubility parameters and sensitivity of three polymers to NH<sub>3</sub>.

Polymers/Solvents	PVP/NH <sub>3</sub>	PMVEMA/NH <sub>3</sub>	PEA/NH <sub>3</sub>
Solubility parameters ( $\Delta\delta$ )	7.74	7.01	10.83
Sensitivity(S)	1.10	10.98	0.73

the smallest variation (0.99 %). Thus, no redundant sensors existed in the studied array.

## 4. Conclusions

In this study we demonstrated that the coating of the surface of MWNTs with six polymers can produce remarkable gas-sensing properties, for the detection of the chemical vapors of NH<sub>3</sub> and CHCl<sub>3</sub>. The sensitivities of the MWNTs-polymer films for discriminating NH<sub>3</sub> in decreasing order, are: MWNTs-PMVEMA > MWNTs-PVP > MWNTs-PEA > MWNTs-SAA > MWNTs-P(VDC-AN) > MWNTs-PMS. The order of sensitivity to the discriminate CHCl<sub>3</sub>, again in decreasing order, is: MWNTs-PVP > MWNTs-PEA > MWNTs-PMS > MWNTs-SAA > MWNTs-P(VDC-AN) > MWNTs-PMVEMA, which corresponds to the order of decreasing conductivity. The results show that the MWNTs-PVP sensor provides high sensitivity, excellent selectivity, effective reproducibility, and long duration stability for the investigated vapors at various concentrations. The modification of the electronic structure of MWNTs by chemical functionalization is a valuable method for the development of an advanced sensor material. We suggest that the adsorption and desorption behavior of the polymer chains covering the MWNTs as well as the interaction between the polymer chains and analytes, play important roles

in gas sensing. In summary, we have developed polymer-functionalized MWNTs sensor platforms for the detection of vapors from chemical agents at various temperatures. For the compatibility analysis, we used the solubility parameter to identify and analyze the interaction force between polymers and industrial chemical gas molecules. We determined the relationship between the solubility parameter  $\Delta\delta$  of three kinds of thin-film sensors with respect to NH<sub>3</sub>, and the sensitivity variation of actual resistance sensing. The compatible adsorption and the detection sensitivity improve when the solubility variation  $\Delta\delta$  decreases. We applied PCA to compare the performance of the as-fabricated films to two chemical agent exposures. The devices developed in this study can potentially be further extended to MWNTs/PVP and MWNTs-PMVEMA sensors for highly sensitive and specific molecular detection.

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