

Quantum resistive vapour sensors made of polymer coated carbon nanotubes random networks for biomarkers detection

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Abstract

We report a straightforward approach to develop vapour quantum resistive sensors (vQRS) from polymer coated multi-walled carbon nanotube (CNT) random networks. A well controlled conducting architecture has been structured in two steps, firstly a random network of CNT was sprayed layer by layer (sLbL) and secondly CNT were coated by a nanometric layer of drop-casted polymer. The chemo-resistive behaviour of sensors exposed to several volatile organic compounds such as acetone, isopropanol, tetrahydrofuran, dichloromethane, chloroform, butanol, toluene or ethanol (which are also biomarkers for lung cancer detection from breath analysis) has been investigated. This new technique was found to be very effective to develop arrays of vapour transducers (possibly tuned by the amount of polymer deposited on CNT network) with fast, stable and reversible responses, highly selective and capable to discriminate biomarkers through a PCA treatment.

Keywords: Carbon nanotube; Random network; Polymer sheath; Volatile vapour compounds (VOC); Sensor array; Cancer biomarkers

1. Introduction

The development of miniaturized sensors arrays for the detection and discrimination of volatile organic compounds (VOC), which can be marker of food degradation [1, 2], disease [3, 4], air pollution [5, 6] or threat [7, 8] is a major concern for associated industries. Various nanomaterials such as carbon nanotube [9-15], metal oxides nanowires [16-17], carbon nanoparticles [18-20], and graphene sheets [8, 21] have been successfully used for the detection a wide range of gases and vapours. Among them carbon nanotube (CNT) and carbon nanotube filled conductive polymer nanocomposites (CPC) have focused a lot of attention due to their very high specific surface ($1600 \text{ m}^2 \cdot \text{g}^{-1}$ for SWCNT), small size, high electrical conductivity, and thermal stability. The quick change of their intrinsic properties such as conductivity, capacitance and dielectric constant with the adsorption of vapour/gas molecules, makes CNT very attractive candidates for sensing [9, 22-26]. Moreover, CPC based sensors can operate at room temperature and can be designed to selectively detect polar [20] or non-polar [4] volatile organic compounds (VOC).

However, the direct use of pristine carbon nanotubes to design vapour transducers is limited by the difficulty to change their selectivity, resulting from their surface chemistry and to improve their sensitivity towards vapour molecules due their small junction gaps leading to weak tunnelling effect [27-29]. Moreover, as the CNT network is not protected from pollution by adsorption of non-desirable molecules or structural changes by unexpected deformation, it is likely that their sensing performances will be altered and not durable [27]. Additionally, the use of single walled carbon nanotubes (SWCNT) is not necessarily a good way to obtain transducers with reproducible chemoresistive properties, as they are often penalized, apart their cost, by a distribution of chirality, diameter and electronic velocity, and a degradation of their conductivity due to the damage of their structure if a covalent

functionalization of their surface is tempted [30, 31]. These issues are much less concerning multi walled carbon nanotubes (MWCNT) for which surface functionalization has been found to favour dispersion in polymer matrices and enhance sensitivity to vapours. For instance, poly(ϵ -caprolactone) PCL-grafted-CNT sensors, resulting from the assembly of MWCNT functionalized by in-situ ring opening polymerization of caprolactone, were found highly sensitive and selective towards organic vapours [32]. Nevertheless, to make sure that functionalization will not degrade SWCNT surface, it is possible to use non-covalent bonding, as proposed by STAR et al. [33] who have adsorbed 1-pyrenesulfonic acid (PSA) on CNT prior to the polymerization of poly(aniline) to form a continuous film on their surface, or Johnson et al. [34] who have decorated SWCNT with DNA strands. Moreover, Feller et al. proposed to control directly CNT/CNT junction gap by either coiling amylose chains around CNT [35] or cross-linking a thin layer of chitosan around CNT [36], which resulted in stable responses with enhanced sensitivity and selectivity. Additional solutions to stabilize the architecture of CNT networks can be found through the use of exclusion volumes with hard [37] or soft spheres [38].

However, these approaches require several steps of fabrication and associated skills that can limit their further industrial development. For instance, the good control of the state of dispersion of nanofillers and the reproducibility of their association into a percolated architecture, were indentified as major hindrances toward the fabrication of high-performance CPC sensors [26, 39, 40]. Some developments of functionalized CNT random networks engineered by solution casting have been reported as smart approach to find a comparatively straightforward technique and to build up precisely selective vapour sensors. Such arrays of chemoresistors composed of quasi-2D random networks of CNT and organic layers are reported to detect organic vapours generated by breath or lung cancer patient [4, 41-44]. Compared to drop

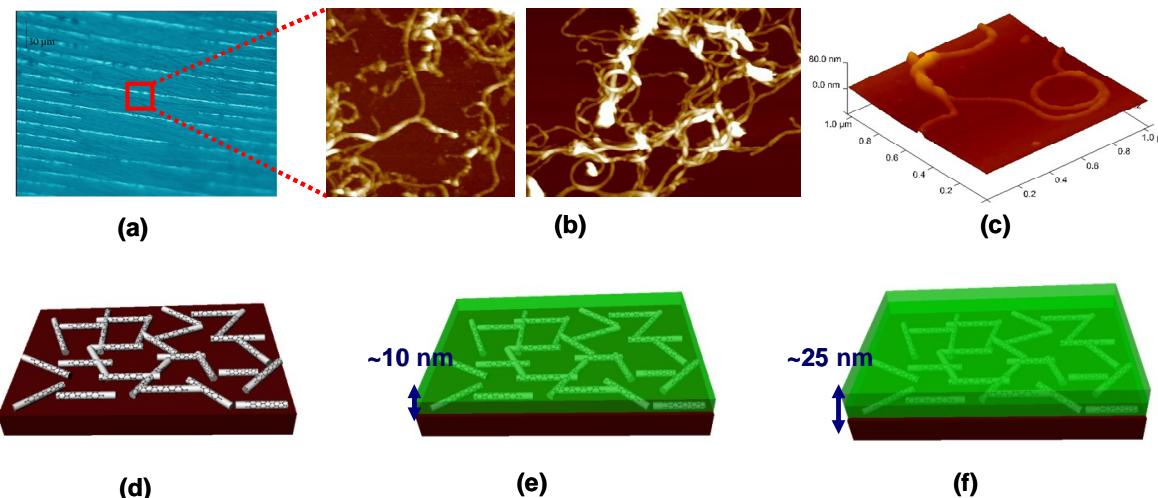


Figure 1. Steps of fabrication of vQRS (a) Optical microscope of interdigitated electrodes' surface (b) AFM height image of CNT random network ($2 \times 2 \mu\text{m}^2$) (c) 3D AFM image of single CNT (d) Schematic diagram of pristine random network of CNT (e) Random network of CNT coated by drop casting of a $2 \text{ g}\cdot\text{dm}^{-3}$ solution of polymer and (f) Random network of CNT coated by drop casting of a $5 \text{ g}\cdot\text{dm}^{-3}$ solution of polymer.

casting or spin coating, spray layer by layer (sLbL) is an interesting tool to develop conductive random network of partially made of individual or nano bundles of CNT. Actually, it has been successfully used to develop conductive polymer nanocomposite based sensors with controlled thickness and hierarchical network structure [45-47].

Here we report a simple technique of fabrication of vQRS, which consists in making firstly a sprayed LbL hierarchical random network of CNT, and secondly bringing chemical functionality by sheathing CNT with a thin polymer layer, deposited by drop casting. The sensitivity and selectivity of sensors can be optimized by adjusting both the polymers' sheathing thickness and nature, which makes this process versatile for applications. Eight volatile organic compounds (VOC), considered as biomarker for lung cancer anticipated diagnosis via breath analysis, were selected: Acetone, isopropanol, tetrahydrofuran (THF), dichloromethane (DCM), chloroform, butanol, toluene and ethanol [48]. Since moisture is highly present in exhaled breath, water vapour was added to the previous set of vapours. An e-nose composed of an array of CNT functionalized transducers was assembled to discriminate between the VOC by using a classical pattern recognition technique, principal component analysis (PCA) implemented into TANAGRA software [49].

2. Experimental Details

2.1. Materials

Multiwall carbon nanotubes (CNT) NANOCYL 7000® were kindly provided by NANOCYL S. A. (Belgium). These CNT with a purity of 90% were produced by CVD process, having a mean diameter of 10 nm, and an average length of 1.5 μm . CNT were used as received from the production source without additional purification. Subsequently, CNT were dried under vacuum at 60 °C for 24 h prior to solution preparation. Poly(carbonate) LEXAN 141R (PC) was purchased from GE PLASTICS (France). Poly(caprolactone) CAPA 6800 (PCL) was obtained from SOLVAY (Belgium). Poly(L-lactic acid) (PLA), L9000 was ordered from BIOMER (Germany). Poly(methyl methacrylate) (PMMA), VQ 101S was obtained from RHÖM (Germany). All volatile organic compounds (VOC), i.e.,

isopropanol, tetrahydrofuran (THF), dichloromethane (DCM), n-heptane, cyclohexane, methanol, ethanol and toluene were grade used for analytical and high-pressure liquid chromatography (HPLC) and purchased from ALDRICH (France).

2.2. Fabrication of polymer coated CNT random network transducers

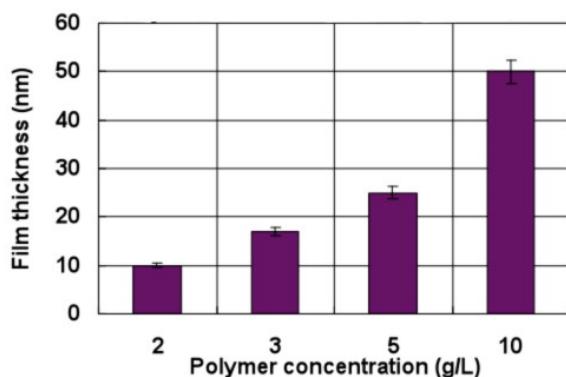
Firstly CNT (2 mg) were dispersed in 20 cm^3 chloroform via sonication (30 min) at room temperature. In the next step, CNT suspension was sprayed layer by layer (sLbL) onto interdigitated electrodes (IDE) obtained by cleavage of capacitors. IDE are composed of 25% Ag/75% Pd tracks separated by a 15 mm ceramic gap and prepared by cleaving 22-nF capacitors [16]. The shape of conducting tracks is clearly visible as shown in Figure 1a. Spraying was done with a homemade device [37] allowing to precisely control spraying conditions such as nozzle flow rate (index 2), air pressure ($p_s = 0.20 \text{ MPa}$), sweep speed ($V_s \approx 10 \text{ cm}\cdot\text{s}^{-1}$) and target to nozzle distance ($d_{tn} = 8 \text{ cm}$). In order to obtain reproducible transducers with relatively low resistance the LbL process was monitored by following the evolution of electrical resistance as a function of layers deposition. Figure 1b gives an idea about the network structure as CNT are entangled with each other and make conductive network architecture. The rope like morphology has been highlighted in Figure 1c illustrating real basic structure of bare CNT. After spray deposition, samples were vacuum dried at room temperature for 24 h prior to chemical vapour testing. In addition polymer solutions (known concentration - $2 \text{ g}\cdot\text{dm}^{-3}$ and $5 \text{ g}\cdot\text{dm}^{-3}$) were prepared by dissolving in suitable solvent (chloroform). A drop (2 mm^3) of polymer solution was deposited on the CNT random network covering the interdigitated electrode and dried in ambient condition. Figure 1d demonstrates the CNT network, which has been covered by thin polymer layer [Figure 1e - $2 \text{ g}\cdot\text{dm}^{-3}$ and Figure 1f - $5 \text{ g}\cdot\text{dm}^{-3}$].

2.3. Morphological characterization by AFM

AFM experiments were performed under ambient conditions using light tapping mode AFM (TM-AFM) on a multimode scanning probe microscope (NANOSCOPE IIIa,

Table 1. Samples code and description.

No.	Sample Code	Sample Description	Initial Resistance (kΩ)
1	CNT	Pristine CNT network	1.5±0.2
2	PLA	CNT net. + film of PLA (2 g.dm ⁻³)	125±5
3	PEO	CNT net. + film of PEO (2 g.dm ⁻³)	27±1.5
4	PC	CNT net. + film of PC (2 g.dm ⁻³)	15±2
5	PCL	CNT net. + film of PCL (2 g.dm ⁻³)	32±2
6	PMMA	CNT net. + film of PMMA (2 g.dm ⁻³)	20±1.3

**Figure 2.** Evolution of layers' thickness with PMMA concentration in solutions.

VEECO). The ratio of the set point amplitude to the free amplitude was maintained approximately at 0.9. RTESP AFM tips (VEECO), with typical resonance frequency between 300 and 400 kHz and tip radius between 5 and 15 nm were used. Both curvature and the surface roughness (0.5 - 1 μm) of interdigitated electrodes prohibited the direct and clear observation by AFM. As a consequence new samples were prepared for nanoscale characterization, using the same spray LbL protocol, but on the silicon wafers (MATERIALS TECHNOLOGY, France) and samples were washed with deionised water to remove any contamination and dried with filtered nitrogen. The thickness of PMMA films was measured by topographical AFM images by producing artificial scratches on the film using sharp wooden stick. Each thickness value reported in Figure 2 corresponds to the average of five measurements in different locations. The thickness variations between PMMA films prepared in similar conditions was found to be less than 5%. Figure 2 presents the evolution of PMMA films thicknesses deposited on silicon wafers with polymer concentration in solution using previously described experimental conditions. It is interesting to notice from samples thickness is regularly increasing with the concentration of polymer in solution making possible a very good control of CNT sheathing. All samples characteristics are summarized in Table 1.

2.4. Chemoresistive responses measurement

Chemo-electrical properties of CNT random network and polymer coated CNT random network sensors were investigated by recording their electrical responses when submitted to 5 min successive alternated cycles of dry nitrogen and vapours streams. The dynamic system consisting in mass flow controllers, solvent bubblers and electrical valves was controlled by LABVIEW software. The sensing device is

presented in supporting information (Figure 7S) and described in a previous paper [37]. The design of the device allows to keep constant the total flow rate at $Q_v = 100 \text{ cm}^3.\text{min}^{-1}$, where the analyte's flow rate is set to $Q_v = 20 \text{ cm}^3.\text{min}^{-1}$, $40 \text{ cm}^3.\text{min}^{-1}$, $60 \text{ cm}^3.\text{min}^{-1}$, $80 \text{ cm}^3.\text{min}^{-1}$ or $100 \text{ cm}^3.\text{min}^{-1}$ (which corresponds to 20, 40, 60, 80 and 100 % respectively of the saturated vapour concentration). The investigation of the effect of VOC concentration on the transducers chemo-resistive response amplitude was done using a KEITHLEY 6517A multimeter.

3. Results and Discussion

3.1. Chemo-resistive behaviour of transducers

In first step, the chemo-resistive behaviour of sensors was investigated by exposing them to different vapours. The resistance changes recorded during experiments were converted into relative amplitude, calculated from Equation 1, which allows to quantify the sensor's performances more easily, as it is a more sensitive and normalized parameter.

$$A_r = \frac{R_v - R_{ini}}{R_{ini}} \quad (1)$$

Where R_v is the resistance of sensors when exposed to vapour and R_{ini} is the initial resistance in dry nitrogen at room temperature [37]

Figure 3 provides a direct observation of effect of polymer concentration, thickness and vapour content on the amplitude of sensors' response. The graph illustrates well that all sensors (CNT, CNT-PMMA - 2 g.dm⁻³ and CNT-PMMA - 5 g.dm⁻³) exhibit a strong positive vapour coefficient (PVC) effect when exposed to acetone vapour, which means that their resistivity increases with analyte's sorption and decreases with its desorption in dry nitrogen. It is also remarkable that all sensors' responses have significant amplitudes (excepted CNT), and respond in a timescale of a couple of seconds, which is very quick for such sensor. Moreover all QRS perform at room temperature, which a striking advantage compared to metal oxide based sensors. The absence of any drift between successive cycles also suggests a weak retention of solvent molecules in the conductive network of transducers. This stable behaviour is thus promoting the durability of the QRS.

Interestingly, the thickness of the polymer layer that has been deposited on the CNT random network has a strong effect on the transducers' sensing performances. For instance, the transducer made of a CNT random network, which has been covered with a 2 g.dm⁻³ PMMA thin film, exhibits a much larger response than all the other transducers, based on

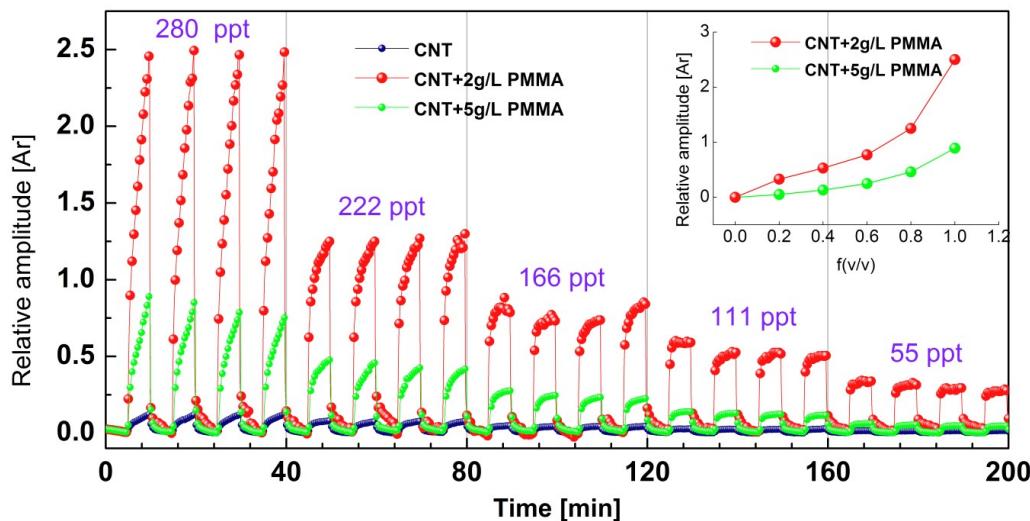


Figure 3. Response amplitudes Ar of CNT based QRS to successive cycles of acetone vapour and pure nitrogen for decreasing contents of 280, 222, 166, 111 and 55 parts per thousand; (inset) Reduction of Figure 5.

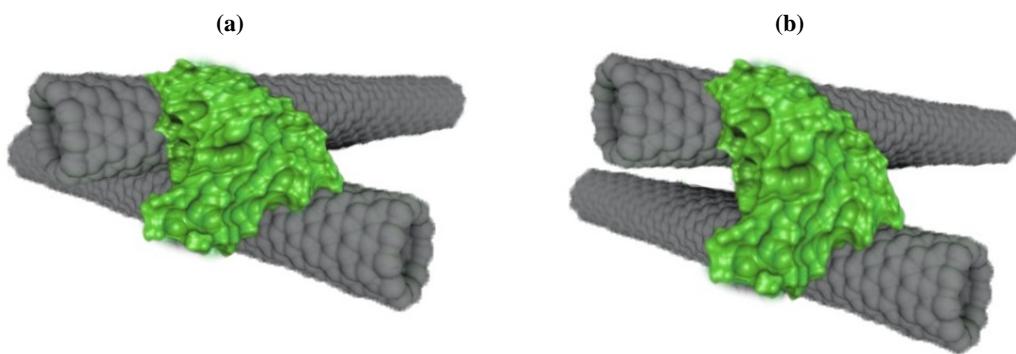


Figure 4. Schematic drawing of sensing mechanism due to junction gap variation (a) initial gap in dry nitrogen (b) Increased gap state in presence of vapour molecules.

CNT random network and CNT random network coated with a 5 g.dm⁻³ PMMA thin film. However, the sensing mechanism of such QRS seems more complex than that of pristine CNT based sensors, in which electrons' transfer mechanism occurs due to simple adsorption of vapour molecules on CNT surface [13]. We have interpreted this trend by the fact that macromolecules can sheath CNT preferably creating a thin insulating coating [50], which is, in particular, driving the electronic transfer at CNT-CNT junctions by tunnelling [38]. This hypothesis is supported by the observable changes in initial resistances, which vary from # 1.5 kΩ (CNT network), # 20 kΩ, and to # 59 kΩ after PMMA - 2 g.dm⁻³ and PMMA - 5 g.dm⁻³ solutions deposition respectively. The swelling of this thin polymer layer due to solvent molecules' diffusion is assumed to be responsible for the strong PVC signal observed and must find its origin at the nano-scale. The sensing principle proposed to explain that an increase in CNT-CNT junction gap in the presence of VOC can trigger an important macroscopic resistance variation is schematized in Figure 4. In the presence of a gap at CNT-CNT junction, the electrons can jump provided that they have enough potential energy to do so and if the gap is less than some tens of nm [51], depending on the systems. Thus, in QRS the electrons' circulation is mainly driven by quantum tunnelling, which leads the contact resistance between CNT to increase exponentially with the gap

at CNT/CNT junctions according to the quantum resistive conduction model of Equation 2.

$$\frac{\Delta R}{R_0} = a e^{b \Delta Z} \quad (2)$$

Where $\Delta R/R_0$ is the tunnel relative resistance variation, a and b are positive constants and ΔZ is the gap variation between two vicinal CNT [37].

Therefore, the polymer layer swelling caused by analyte molecules, yields an increasing proportion of conduction by tunnelling as the conducting network is progressively disconnected. Nevertheless, the increase of the polymer layer thickness can increase accordingly to the diffusion time of analytes to CNT-CNT junction and slow down their disconnecting dynamics [45]. Therefore, this can explain why CNT-2 g.dm⁻³ PMMA exhibit sharper and larger response than CNT-5 g.dm⁻³ PMMA transducers. However, the effect of the initial resistance R_0 , characteristic of the ease of disconnection of the percolated network must also be considered to explain the sensitivity of QRS. In fact, it is often observed that there is an optimum in R_0 that leads to the best sensitivity [18]. Thus there is a necessary compromise to find between sensitivity and stability.

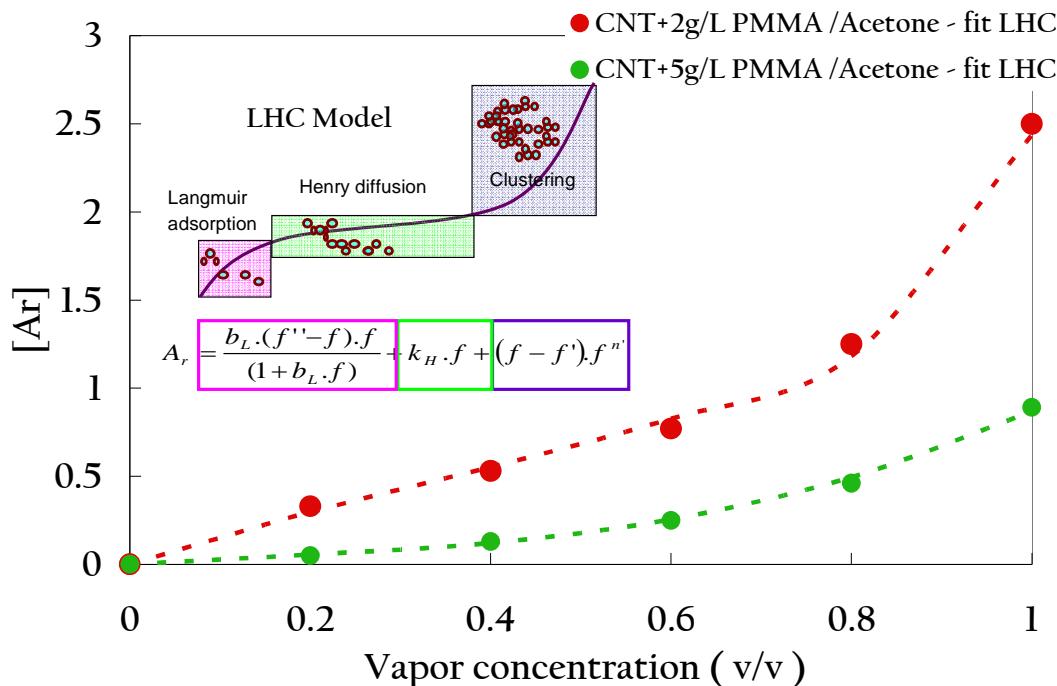


Figure 5. Langmuir-Henry-Clustering (LHC) model fitting [17] for CNT-2 g.dm⁻³ PMMA and CNT-5 g.dm⁻³ PMMA in the presence of acetone vapour (from 20 to 100 cm³.min⁻¹). In the expression of A_r , b_L is the Langmuir affinity constant, k_H the Henry's diffusion parameter, n the average number of solvent molecules per cluster and f the solvent fraction; f' and f'' correspond to transitions between different regimes of diffusion.

3.2. Quantitativity of sensors' responses

Figure 3 also shows the dependency of A_r towards acetone vapour concentration when it was varied from 20% to 100% successively (a concentration of 100% corresponds to the saturated vapour). Interestingly, sensors give responses proportional to the amount of organic molecules in their surrounding alike previously reported. A_r instantly increases in the presence of vapours but no equilibrium is observed within the experiment time for high vapour concentration. However, for low vapour concentration (55 or 111 parts per thousand) a plateau has been observed, confirming that an equilibrium in vapour diffusion has been reached. The different chemo-resistive behaviours that can take place in QRS can be well described by the Langmuir-Henry-Clustering (LHC) model [18-26], which is recalled in Figure 5 (inset), which can predict the evolution of sensors response in a wide range of vapour concentrations. In this equation, all parameters are derived from sorption laws: (b_L) the Langmuir affinity constant, (k_H) the Henry's diffusion parameter, (n) the average number of solvent molecules per cluster and (f) the solvent fraction. This makes a more physical interpretation of their values possible, even if the way their determination is different from that of classical sorption experiments. Other parameters, such as f' & f'' , mark the boundary between the three modes of diffusion, also linked to the three terms of the equation in Figure 5. This empirical model describes effectively which kind of diffusion regime takes place in the CPC sensor: Simple adsorption, diffusion, clustering, corresponding respectively to the three terms of the equation [37]. The main feature of this graph is the absence of the first step of diffusion called LANGMUIR's adsorption, compared to the classical three steps shape of the LHC model. This is certainly due to the fact that such behaviour takes place mostly at ppb and ppm concentrations, whereas here only parts per thousand level is studied.

Therefore, it can be concluded from the shape of LHC curve in Figure 5, that the dominant phenomenon at concentrations between 55 and 222 parts per thousand is HENRY's diffusion. This kind of diffusion is characterised by a linear evolution, suitable for easy calibration of QRS. When the concentration in acetone vapour rises over 222 parts per thousand, the analytes can rush into the polymer free volumes massively, forming clusters that will cause both swelling and expansion of the transducing material, which results in an exponential chemo-resistive response. Further experiments are ongoing to check the possible LANGMUIR's behaviour of these hierarchical structured sensors at lower concentration down to ppm/ppb levels, and determine at the same time their limit of detection for the different biomarkers.

3.3. Selectivity of sensors' responses

A quick outlook in Figure 6a shows the many differences between QRS responses for the whole set of VOC biomarkers. Although there is no universal law able to explain the selectivity of single polymer based QRS, it was found a good correlation between polymer solubility parameters and transducers selectivity [45-47]. Additionally, it can be seen that each transducer is broadly responsive to a variety of vapours and pertain its own distinct fingerprint. The unique sensing pattern resulting from the combination of all responses from the sensors array will lead to an e-nose with very good discrimination ability. It is meaningful to analyse the output of such e-nose with a pattern recognition algorithm such as PCA, which is a simple and effective method of classification allowing a quick interpretation of the data produced by an array of n-sensors exposed to m-studied vapours [49]. Despite some weaknesses, this technique allows the mapping of multi-dimensional data onto 2 or 3D axis with a minimum loss of information. Figure 6b is a good illustration of a two

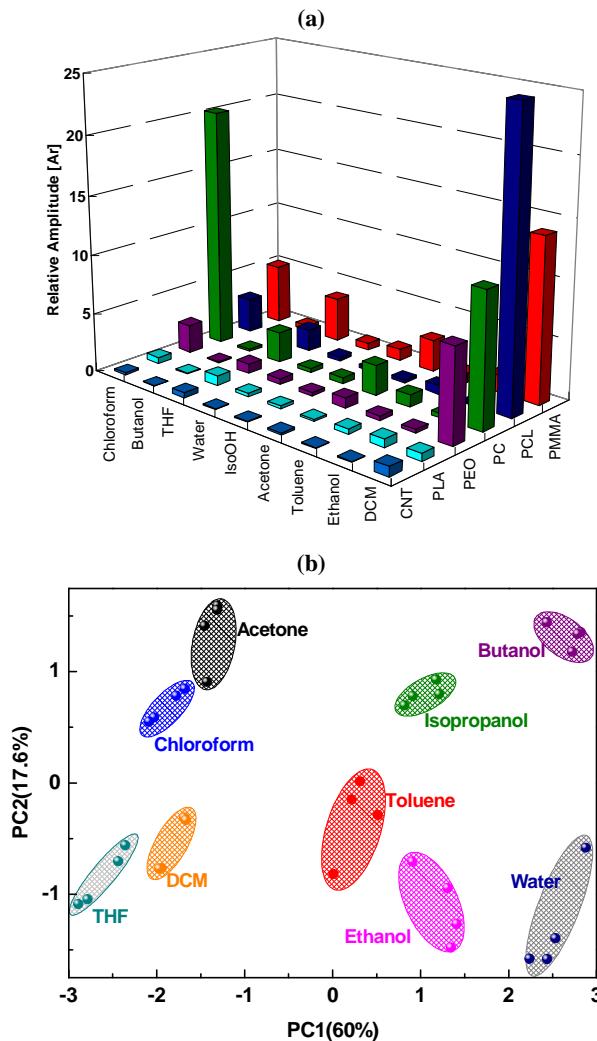


Figure 6. (a) Summary of relative amplitude for all sensors (the X, Y, Z axis represent respectively the names of solvents, polymers coating and responses), (b) 2D PCA map showing vapour discrimination ability of sensors.

dimensional plot (PC1-PC2), obtained by the collection of maximum relative amplitudes of each sensor exposed simultaneously to the set of vapours, recorded during five cycles and converted into an m by n matrix (m being the number of measurements and n the number of sensors). Finally 78% of the total variance within the data is contained in the two first principal components, which corresponds to fairly good discrimination ability between clusters of vapours which are elementary components of cancer patient breath [42–45].

4. Conclusions

It has been demonstrated in this paper that combining sLbL for the fabrication of random networks of CNT with drop casting for the coating of CNT by a functional polymer film was an elegant process of fabrication leading to QRS with fast response, high sensitivity and selectivity. Quantum resistive sensors have proved to give quantitative and reversible responses to a set of VOC considered as potential biomarkers for the anticipated diagnostic of lung cancer. The LHC model was found able to describe their chemo-resistive behaviour on a range of vapour concentrations comprised between 55 and 280 parts per thousand. The most sensitive/reactive QRS were

obtained with a polymer sheathing of about 10 nm derived from 2 g·dm⁻³ polymer solutions, which was found to be the best compromise between junction gap and diffusion time. The combinations of all sensors into an array and the subsequent treatment of their sensing pattern by PCA, has led to an e-nose with good discrimination ability of the selected VOC. The relatively simple fabrication of coated CNT random network sensors, combined with their good sensing performances, provides a cost-effective tool. Once QRS have been assembled into an e-nose, PCA makes possible the discrimination of biomarkers for an anticipated diagnostic of diseases. However, their limit of detection must reach the sub-ppm level and pattern recognition has to be effective with vapour blends including water as a major component, which is the focus of ongoing work.

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