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Metalloporphyrins-functionalized carbon nanotube networked films for room-temperature VOCs sensing applications

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Abstract

Networked films of carbon nanotubes (CNTs) have been grown by Chemical Vapor Deposition (CVD) technology onto cost-effective alumina substrate, coated by Cobalt nanocatalyst for growing the CNTs. The sidewalls of the CNTs films have been functionalized by spray-coating with two different metalloporphyrins (MPP), consisting of a Tetraphenylporphyrin coordinated by a central metal of zinc (Zn-TPP) and manganese (Mn-TPP). The surface-modification of the CNTs with layers of Zn-TPP and Mn-TPP provides enhanced sensitivity and broad selectivity to volatile organic compounds (VOCs). The chemical interactions of these MPP-modified CNTs films with different tested VOCs (alcohols, esters, aromatics, ketones) have been investigated using the miniaturized two-pole chemiresistors technique. The sensor response in terms of p-type electrical conductance in the MPP-modified CNTs-chemiresistors exhibits a good sensing performance, at room temperature. The findings show a VOC adsorption occurring by sensing characteristics of response-concentration relationships as a combined Langmuir-Henry behaviour.

Keywords: Carbon nanotubes networks gas sensors; Metalloporphyrins; CNTs functionalizations; VOCs detection

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional nanostructures based on graphene sheets rolled up into hollow cylinders. Their outstanding properties of high surface area, hollow geometry, nanosized structure, high electronic mobility, make them ideal platforms for gas adsorption with high sensitivity and low temperature operations. The surface-modification of the CNTs networked films is a valid methodics to enhance the gas sensitivity and modify the chemical patterns of the selectivity. In fact, nanoclusters of noble metals (Au, Pt, Pd, Ag, etc.) have been used to enhance the gas sensitivity of the CNTs networked films, operating at a sensor temperature of 150-200°C [1,2]. This approach has been addressed to detect gas molecules of NO₂ and NH₃.

Metalloporphyrins (MPP), consisting of Tetraphenylporphyrins (TPP) coordinated by a central metal of zinc (Zn) and manganese (Mn), are functional materials used as highly-sensitive receptors for artificial olfaction [3,4].

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Recently, the authors [5] studied the sensing properties of the MPP-modified CNTs networked films by means of a two-pole chemiresistor for VOC detection, at room temperature. In this work, MPP-functionalized CNT-chemiresistors have been used to investigate at room temperature the VOC adsorption, in a wider range of concentration, including low gas concentrations. Furthermore, molecular film properties including the effect of the thickness of the functionalizing MPP layer have also been investigated. Generally, the sensor response increases with the applied MPP functionalization compared to unmodified CNT-chemiresistor. Adsorption isotherms are not linear in the whole tested gas concentration range and fit with a combined Langmuir-Henry isotherm, whose Langmuir part is more evident in MPP-coated CNT-sensors by suggesting an increase of the specific adsorption sites introduced by the metalloporphyrins. A different behaviour in the gas adsorption at low and high concentrations has been observed in the MPP-modified CNT-sensors. The sensing mechanisms in the two regimes at low and high gas concentrations are briefly discussed.

2. Experimental details

Multiwalled carbon nanotubes (MWCNTs) networked films were grown by chemical vapour deposition (CVD) technology onto low-cost alumina substrates coated with Cobalt (Co) sputtered nanosized catalyst of nominal thickness of 6 nm. The substrate size was 5 mm width x 5 mm length x 0.6 mm thickness. The substrates were placed in a quartz boat and then inserted into the center of a 1-inch diameter quartz tube reactor housed in a furnace. The tube was evacuated at a base pressure of \(5 \times 10^{-3}\) Torr by a rotative pump. Hence the substrates were heated up to 550°C in a \(H_2\) flux of 100 sccm at a working pressure of 100 Torr. Then, acetylene \((C_2H_2)\) was introduced at a flow rate of 20 sccm with \(H_2\) flow rate of 80 sccm. The flow rate was controlled using two separate mass flow controllers. The CNT growth was performed with a total pressure of 100 Torr for 30 minutes. After CNT growth, the furnace was cooled to room temperature in \(H_2\) atmosphere. A pair of metal strips of Cr/Au (20 nm/300 nm) was vacuum thermally evaporated onto CNTs films to serve as electrical contacts for the chemiresistor upon two-probe format. The Cr/Au electrode sizes were 1 mm width x 5 mm length. The gap between two electrodes was 3 mm.

\((5,10,15,20\text{-tetraphenylporphyrin})\text{zinc} \quad \text{[Zn-TPP]}\) and \((5,10,15,20\text{-tetraphenylporphyrin})\text{manganese chloride} \quad \text{[Mn-TPP]}\) have been synthesized according to the literature methods [6]. The sensing properties of these metalloporphyrins have been extensively investigated in the past [3], and manganese and zinc are sufficiently distant in the periodic table to provide different coordination interactions to the metalloporphyrin complex.

A layer of metalloporphyrins (MPP) with different thickness was deposited by spray-coating onto the surface of the CNT layer. Metalloporphyrins were not modified to be covalently anchored onto the surface of the carbon nanotubes, nonetheless an enough adhesion of the metalloporphyrin film was provided. Fig. 1 shows the scheme of the fabricated gas sensor. The electrical resistance, at room temperature and upon inert reference atmosphere, of the un-modified and MPP-functionalized CNT-sensors was measured as 1-2 kΩ. Fig. 2 shows the FE-SEM top-view image of the CNTs networked films. The carbon nanostructures are clearly characterized as a tangled net with a film thickness of 200-300 nm and a diameter of the mats of nanotubules in the range of 10-60 nm. The aspect ratio of the CNTs layer was estimated in the range of 40-300. The clusters of the MPP (Zn-TPP) onto CNT-sidewalls are clearly visible as islands randomly dispersed with partial coverage of the CNT-surface.

Fig. 1. Cross-sectional scheme of the two-pole CNT-based chemiresistor surface-modified with a spray-coated layer of metalloporphyrins.
Fig. 2. FE-SEM image of the CNTs surface-modified with a spray-coated layer of Zn-TPP porphyrins (2 spray-layers thickness).
3. Results and discussion

Fig. 3 shows the typical transient responses of the four sensors based on unmodified CNT and MPP-modified CNT with Mn-TPP layer at two various thicknesses and Zn-TPP layer at a single thickness. They are exposed at room temperature to increasing concentration of individual 5-minute VOC pulse, and recovered upon dry air. The resistance for all CNT-sensors increases upon single pulse of reducing VOC, thus the electrical character of p-type semiconductor of the CNTs, including MPP-modified CNTs, is confirmed. A charge transfer between CNTs and adsorbed molecules is the sensing mechanism for gas detection. The adsorption isotherms for the four sensors are shown in the Fig. 4 for five VOCs under test. These curves fit with a combined Langmuir-Henry isotherm, whose Langmuir part is more evident in MPP-coated CNT-sensors by suggesting an increase of the specific adsorption sites introduced by the metallorphyrins. The Langmuir-Henry isotherm is described by the following equation:

$$\Delta R/R = k_1 \cdot c + (k_2 \cdot c) / (k_3 + c)$$  \hspace{1cm} (1)

where $\Delta R/R$ is the sensor response in terms of percentage relative resistance change, $c$ is the gas concentration, and $k_1$, $k_2$, and $k_3$ are constants.

Fig. 3. Time responses of four-sensors based on unmodified CNT, MnTPP-modified CNT with two different thicknesses of Mn-TPP and Zn-MPP-modified CNT exposed towards various gas concentrations of (a) ethanol and (b) tetrahydrofuran, operating at room temperature.

Fig. 4. Room-temperature calibration curves of four-sensors based on unmodified CNT and MPP-modified CNT for (a) tetrahydrofuran, (b) methanol, (c) acetone, (d) ethylacetate, and (e) ethanol with the fitting of the adsorption isotherms by Langmuir-Henry curves.
By inspection of the calibration curves, generally, for a given VOC the gas sensitivity of the MPP-modified CNTs increases slightly at low concentrations compared to unmodified CNTs and exhibits greater enhancement at high concentrations considered. This behaviour could be attributed to a moderate increasing of the surface sites of MPP onto CNT-sidewalls, as confirmed by cluster distribution of the MPP shown in the FE-SEM image of Fig. 2. In the contrast, since the MPP clusters are VOC-permeative, there should be a higher amount of volume interactions with a consequent improvement of the gas sensitivity in the MPP-modified CNTs at high concentrations. This trend in the gas adsorption in the two regimes of sensitivity ($S$) at low concentrations and high concentrations has been elucidated in the Fig. 5 by Langmuir-Henry isotherms. These regimes are described by following equations:

$$S_{c=0} = \left[ \frac{d(\Delta R/R)}{dc} \right]_{c=0} = k_1 + \left( \frac{k_2}{k_3} \right)$$  \hspace{1cm} (2)

$$S_{c=\infty} = \left[ \frac{d(\Delta R/R)}{dc} \right]_{c=\infty} = k_1$$  \hspace{1cm} (3)

The chemical patterns demonstrate that for a given test VOC at low concentrations the sensitivity of the MPP-modified CNTs generally enhances slightly compared to unmodified CNTs; while at high concentrations the sensitivity of the MPP-functionalized CNTs improves remarkably compared to unmodified CNTs. This could be caused by enhanced volume interactions of the MPP tailored by their increasing thickness at high concentrations.

![Fig. 5. Sensitivity (a) at low concentrations and (b) high concentrations of four-sensors based on unmodified CNT and MPP-modified CNT for five VOCs measured by the fitted Langmuir-Henry adsorption isotherms.](image)

4. Conclusions

In summary, CNTs networked films have been grown by CVD technology onto miniaturized cost-effective alumina substrates for VOCs sensing applications at room temperature operations and low power consumption. The CNTs have been modified by spray-coating MPP layer based on Zn-TPP and Mn-TPP film. The MPP-modified CNTs-sensors exhibit enhanced VOC-sensitivity and broad selectivity for gas sensor array. The gas adsorption is regulated by Langmuir-Henry isotherms by distinguishing two different regimes at low and high gas concentrations.

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