Aza[5]helicene/MWCNTs selective sensors

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Introduction

Organic materials based on π-conjugated molecules are intensively studied nowadays in the field of organic semiconductors as a complement to the shortcomings of inorganic semiconductors [1, 2]. Organic semiconductors offer, with respect to current inorganic-based technology, greater substrate compatibility, device processability, flexibility, large area coverage, and reduced cost. Recently, we prepared a composite resistive gas sensor based on diazabenzo[*ghi*]perylene / MWCNTs thin films on alumina [3], showing large variations of the electrical resistance with varying the relative humidity and acetic acid concentration. In this work we covalently bonded a derivatized monoaza[5]helicene to MWCNTs, realizing a composite material for phenol sensing. The three-dimensional helical π-system anchored on MWCNTs possesses a combination of chirality and electron transfer efficiency, which could lead to the development of novel electrode materials with inherently strong chiral properties.

Materials and methods

Preparation of the sensing material

Multi walled carbon nanotubes were treated with concentrated nitric acid and with $SOCl_2$ to obtain MWCNT-COCl. This material was then reacted with functionalized 5-aza[5]helicene (**2**), obtained by treating 5-aza[5]helicene (**1**) with the Fenton reagent (hydrogen peroxide/ $FeSO_4 \cdot 7\ H_2O$) in methanol as solvent (Fig.1).

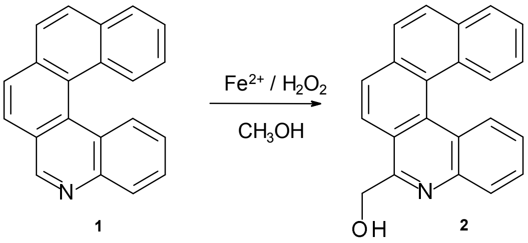

Figure 1. Functionalization of 5-aza[5]helicene.

An ester was formed between MWCNTs and compound (**2**), giving rise to the formation of the sensing material (Figure 2).

Figure 2. Modified nanotubes.

Sensor fabrication

The sensor was fabricated by using a commercial screen printed three-electrode consisting of a ceramic planar support equipped with a carbon working electrode, a carbon counter electrode and a silver pseudo-reference electrode. A dense solution of active material was obtained dispersing a suspension of the 5-aza[5]helicene-CH_2O-CO-MWCNTs in ethanol, casting this solution onto the surface of the working electrode and allowed it to dry at room temperature.

Results and discussion

CV curves were recorded in the presence of different hydroquinone concentrations. A reversible couple of peaks was detected after hydroquinone addition, and a remarkable increase in both the cathodic and anodic peak current was observed on the modified electrodes with increase in hydroquinone concentration. Further, the oxidation and reduction peak shifts to more positive and negative potential, respectively, as the concentration of hydroquinone increased. The current peak was found to increase linearly with the scan rate. These results indicate that in the scan range studied the electrode reaction is mainly an adsorption controlled process. The linear sweep voltammetry curves of the electrode show a linear relationship with HQ concentration. Under the reported conditions, the proposed voltammetric sensor could detect HQ in the linear range of 0−0.5 mM, with a sensitivity of 1872 μA $mM^{-1}cm^{-2}$, much larger than that obtained with bare SPCE electrode.

We then applied the electrode to the selective detection of epinephrine (EP, Fig.3), an important neurotransmitter. The electron transfer rate of EP at bare electrode is slow, because it is often adsorbed on the surface of bare electrode for subsequent passivation. Further, EP and ascorbic acid always exist together in biological environment and their close values of the oxidation potentials result in an overlapping voltammetric response. Interestingly, on our modified electrode, a large peak-to-peak separation was detected (0.250 V) accompanied by a larger enhancement of the peak anodic current, which is enough for avoiding undesired interferences. This is clearly due to the larger over potential of EP on the modified electrode surface, while the potential of ascorbic acid is not affected.

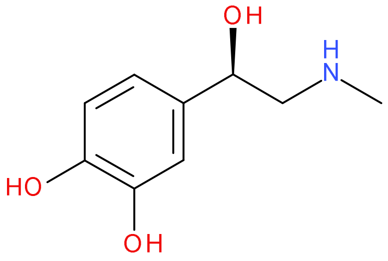

Figure 3. Epinephrine

Concluding, due to the enhanced electrocatalytic activity and enlarged separation of the anodic peak potential of epinephrine in the presence of ascorbic acid at the 5-aza[5]helicene-CH_2O-CO-MWCNTs/SPCE modified electrode, the linear sweep voltammetry (LSV) determination of EP, with detection limit (S/N = 3) of 5 μmol L^{-1}, was demonstrated.

Bibliografia

[1] H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W.Wu, and E. P. Woo, Science 290, 2123 (2000)
[2] D.R. Gamota, P. Brazis, X. Kalyanasundaram, J. Zhang, Printed Organic and Molecular Electronics, Kluwer Academic Publishers, NY, USA, 2004
[3] F.Fontana, T.Caronna, N.Donato, M.Latino, A.Bonavita, G.Rizzo, G.Neri “Novel Organic / MWCNTS Semiconductor Composite For Resistive Gas Sensors” AISEM2010 Messina, 8-10/2/2010