11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Novel multi-walled carbon nanotubes paste electrode modified with Prussian blue: spectroelectrochemical study and its application as a hydrogen peroxide biosensor

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Abstract – A novel carbon paste/Prussian blue electrode was constructed from a single ferricyanide solution. The electrochemical feature of such electrode has been fully evaluated with cyclic voltammetric and Raman spectroelectrochemical experiments. Prussian blue nanotube paste electrode proved to possess a strong stability and showed high sensitivity towards hydrogen peroxide with a very low detection limit.

The ability of carbon nanotubes (CNTs) to promote the electron-transfer reactions of important molecules has made them attractive for several electrochemical and electroanalytical proposes, as in building of different kinds of modified electrodes. On the other hand, Prussian blue (PB - a mixed-valent iron(III) hexacyanoferrate compound with general formula $Fe^{III}_4[Fe^{II}(CN)_6]_3.nH_2O$ having a face-centered cubic lattice containing an open zeolite-like structure) presents very interesting redox properties, electrochromic behavior, ferromagnetic properties below its Curie temperature of 5.6 K, semiconducting electronic transport and application in several devices, including the amperometric detection of H_2O_2.[1]

Several efforts have been done recently to achieve novel nanocomposite materials formed by the combination of PB and CNTs.[2] In which concerns the application as amperometric sensor, the intrinsic characteristics of CNTs should provide better electrochemical stability and increase the stability of the PB to material in neutral pH solution, which corresponds to a great advance in this kind of device. Carbon nanotubes electrodes modified by PB have been prepared by different methods, generally based on two approaches: 1) the PB is chemically pre-synthesized and after mixed with CNTs; 2) the PB is electrodeposited *in situ* over a previously built CNT-electrode, by cycling a CNT-electrode within a suitable potential window (or applying a suitable potential) immerse in an aqueous solution containing both ferricyanide (usually from the dissolution of $[K_4Fe(CN)_6]$) and free iron ions (normally precedent from the dissolution of $FeCl_3$). In this paper we report a very simple and innovative route to prepare a Prussian blue-modified carbon nanotube paste electrode, based on a liquid/solid heterogeneous reaction between ferricyanide ions in aqueous solution and iron-based species (mainly metallic iron and the iron oxides hematite and magnetite) intrinsically present on the CNT sample. Also, we report the utilization of the obtained electrode as a hydrogen peroxide sensor showing the highest sensitivity to H_2O_2 ever described to this kind of electrode.

The MWCNTs were prepared through the ferrocene pyrolysis, and present has cavities filled with iron and iron oxide (Figure 1).[3] The Prussian blue occurrence was confirmed by cyclic voltammetry (Figure 2) and Raman spectroscopy. Raman spectroelectrochemical studies showed a strong interaction between the PB and the CNTs, causing an electrochemical p-doping modification of carbon nanotubes with PB. The Prussian blue-modified carbon nanotube electrode has been employed as amperometric sensor to H_2O_2, showing excellent results. The obtained values of detection limit and quantification limit were very low ($1{,}94.10^{-8}$ mol.L^{-1} e $6{,}46.10^{-8}$ mol.L^{-1}, respectively), and the sensibility was very high (Figure 3).

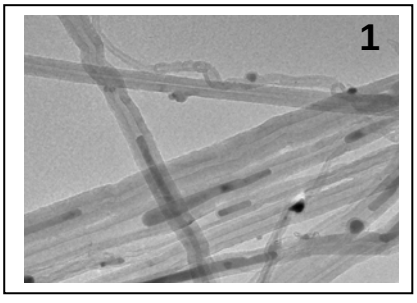

Figure 1: TEM image of ion oxide-filled multiwalled carbon nanotubes

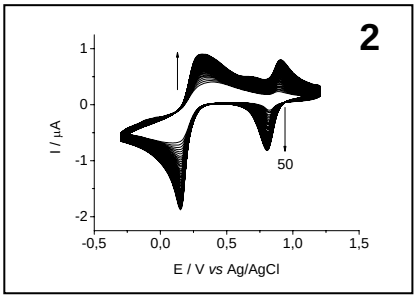

Figure 2: Cyclic voltamograms showing the formation of AP.

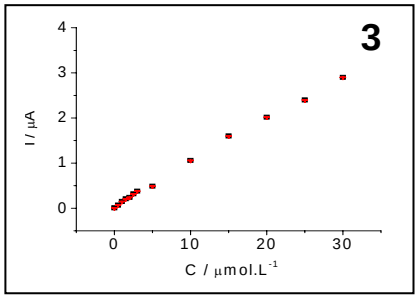

Figure 3: Calibration curve for the H_2O_2 determination using the modified electrode.

[1] N. R. Tacconi and K. Rajeshwar, Chem. Mater. 15, (2003) 3046.
[2] Y. Zhang, et. al., Electrochem. Commun. 6, (2004) 1180.
[3] M. C. Schnitzler, et. al., Phys. Rev. Lett. 381, (2003) 541.