ICAM2009
11th International Conference
on Advanced Materials

Rio de Janeiro Brazil
September 20 - 25

A new chemical sensor for NADH based on multi-walled carbon nanotubes and xanthurenic acid

*F.A.S. Silva(1), C.B. Lopes(1), E.O. Costa(1), P.R. Miranda(1), M.O.F. Goulart(1), P.R. Lima(2), L.T. Kubota(2)

(1)Instituto de Química e Biotecnologia, UFAL, Maceió, AL, 57072-970,
(2)Instituto de Química, UNICAMP, Campinas, SP, Brazil.
*Corresponding author. Tel.: +55-82-3214-1393; Fax: +55-19-3214-1389
E-mail address: fradeassis@hotmail.com

Abstract – A new electroactive material based on xanthurenic acid was electrogenerated *in situ* on a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNT) by cycling the potential (10 scans) between −0.5 and +1.0 V *versus* Ag/AgCl at a scan rate of 50 mV s^{-1}. The GCE/MWCNT-XA in the presence of NADH (PBS 0.1 M, pH 7.0 and ν = 5.0 mV s^{-1}) showed electrocatalytic activity toward NADH oxidation: the oxidation peak is drastically increased and the reduction peak decreased (actually it vanished) indicating a very efficient electrocatalytic effect. The MWCNT-XA-modified electrode enables sensitive, robust, stable measurements of NADH, suggesting it as a very interesting transducer candidate in dehydrogenase-based biosensors.

Xanthurenic acid (XA) is a product of tryptophan–NAD pathway. The role of XA in mammals is not well defined. It has been described as a chromophore capable of photosensitization and photo-oxidation of lens proteins and it accumulates in organs with ageing. It participates in apoptotic events in vascular smooth muscle and retinal pigment epithelium cells with modifications in mitochondrial Ca^{2+} transport and oxygen consumption.[1]

The present work describes, for the first time, the preparation and use of a simple and efficient glassy carbon electrode (GCE) modified with multi-wall carbon nanotubes (MWCNT) and an electrochemically activated-XA towards electrocatalytic NADH oxidation. After cleaning the electrode, a suspension was prepared mixing by sonication 2.0 mg of MWCNT and 1 mL of DMF. Then, 8 µL of this suspension was directly placed on GCE surface and let to dry at 80ºC to form a MWCNT nanocomposite on GCE surface. Initially, the electroactive species, probably a quinone-like redox group, was electrogenerated *in situ* from XA (120 μM) dissolved in 0.1 mol L^{-1} PBS (pH 5.5), onto MWCNT-modified electrode, after cycling in the potential range between -0.5 and 1.0 V *versus* Ag/AgCl, using a scan rate of 50 mV s^{-1} and 10 scans (Figure 1). After that, the GCE/MWCNT-XA was removed from the solution and rinsed thoroughly with milli-Q water and put in a new 0.1 mol L^{-1} PBS (pH 7.0), in absence of XA.

After optimizing the operational conditions, the observation of well-defined and persistent cyclic voltammetric peaks for the activated GCE/MWCNT-XA ($E^{0'}$= 0.1 V *vs.* Ag/AgCl) for various scan rates (5-4000 mV s^{-1}) indicates that the GCE/MWCNT-XA exhibits characteristics of redox species confined on the electrode surface. Furthermore, a linear correlation obtained for $E^{0'}$ *versus* pH with a slope of 0.06 V/pH from pH 5.0 up to 8.0 (Figure 2), is close to that expected for an electrodic reaction with the ratio e^-/H^+ equal to one (0.0592 (n_p/n_e) V/pH, where $n_p = n_e$ at 25 ◦C. Thus, the number of protons and electrons involved in this process should be the same. The GCE/MWCNT-XA in the presence of NADH (PBS 0.1 M, pH 7.0 and ν = 5.0 mV s^{-1}) showed electrocatalytic activity toward NADH oxidation: the oxidation peak is drastically increased and the reduction peak decreased (actually it vanished) indicating a very efficient electrocatalytic effect (figure 3). The MWCNT-XA-modified electrode enables sensitive, robust, stable measurements of NADH, suggesting it as a very interesting transducer candidate in dehydrogenase-based biosensors.

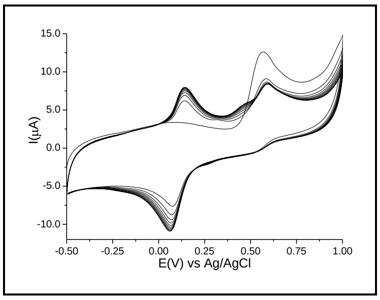

Figure 1: Activation process

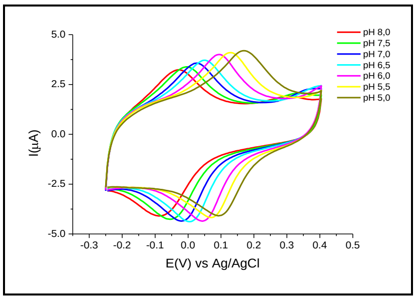

Figure 2: pH peak dependence

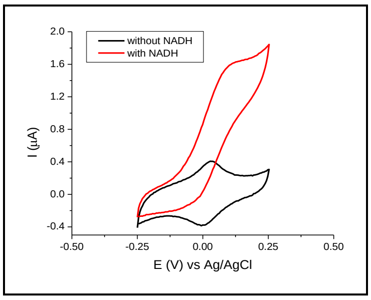

Figure 3: Catalyses with NADH

Acknowledgements: PROCAD/CAPES, INCT Bioanalítica, FAPESP, FAPEAL, CNPq. We also thank Dr. Vitor Lima for helpful discussions about xanthurenic acid.

References: [1]. Gobaille, S. Kemmel,V., Brumaru,D., Dugave,C., Aunis, D., Maitre, M. J. Neurochem. 105 (2008) 982.