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New nanostructured platforms based on niclosamide immobilized on multi-wall carbon-nanotubes for electrocatalytic NADH oxidation

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Abstract – A new nanostructured platform was developed based on GCE modified with 5-chloro-*N*-(2-chloro-4-nitrophenyl)-2-hydroxybenzamide (niclosamide) immobilized on multi-wall carbon nanotubes (MWCNT) for electrocatalytic NADH oxidation. After *in situ* electrochemical reduction of the niclosamide by potential cycling between −0.8 and +0.5 V *vs.* Ag/AgCl, scan rate of 20 mV s^{-1}, PBS 0,1 M, pH 5 and 10 scans, the voltamogram showed two stable redox couples with formal potential of about -0.100 V and +0.100 V *vs.* Ag/AgCl for Ar-NO/Ar-NHOH and the latter reversible peak, possibly corresponding to the pair azoxy/azo, respectively. This electroactivated mediator Ar-NO/Ar-NHOH from niclosamide (NIC) showed electrocatalytic activity toward NADH oxidation in 0.0 V *vs.* Ag/AgCl (PBS 0.1M, pH 7.0 and ν = 5.0 mV s^{-1}), suggesting it as a very interesting transducer candidate in dehydrogenase-based biosensors.

Nanomaterials have attracted much attention, in special carbon nanotubes (CNT) due to their interesting properties and potential applications in sensors, biocatalysis and others [1]. Furthermore, a wide variety of compounds has been incorporated into CNT, as electron transfer mediators for NADH electrooxidation. However, some of these catalysts present a series of limitations like poor sensitivity, reproductibility, high overpotentials and modest rate constants. In this sense, the present work describes, for the first time, the preparation and use of a simple and efficient nanostructured platform based on glassy carbon electrode modified with a new redox mediator based on activated niclosamide (NIC), immobilized on MWCNT, towards electrocatalytic NADH oxidation. After cleaning the electrode, a suspension was prepared mixing by sonication 1.0 mg of MWCNT with 1 mL of DMF. Then, 10 µL of this suspension and 10 µL of 1.0 mg/mL NIC solution were directly placed on GCE surface, let to dry at 80ºC and rinsed with milli-Q water to remove the excess of NIC. Initially, the electroactive species was electrogenerated *in situ* by placing the modified electrode in 0.1 mol L^{-1} PBS (pH 5.0) and cycling in the potential range from -0.8 to 0.5 V *vs.* Ag/AgCl (10 scans), using a scan rate of 20 mV s^{-1}(Fig. 1). After that, the GCE/MWCNT/NIC 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). A new potential range was chosen, from -0.4 to 0.4 V and the cyclic voltammograms showed stable redox couples with $E^{0'}$ of about -0.100 V and +0.100 V *vs.* Ag/AgCl for Ar-NO/Ar-NHOH and possibly, to the pair azoxy (obtained from the reaction of ArNHOH and ArNO)/azo, respectively [2]. The GCE/MWCNT/NIC, in the presence of NADH (PBS 0.1M, pH 7.0 and ν = 5.0 mV s^{-1}), showed electrocatalytic activity toward NADH oxidation: the oxidation peak (relative to ArNHOH) is drastically increased and the reduction peak decreased (related to Ar-NO) (actually it vanished) and the second peak (azo/azoxy) the liquid current is unaffected, indicating a very efficient electrocatalytic effect by Ar-NO/Ar-NHOH from the activated nanostructured platform based on MWCNT/NIC (Fig.2), suggesting it as a very interesting transducer candidate in dehydrogenase-based biosensors.

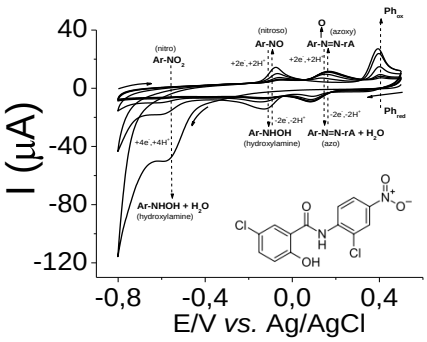

Figure 1. Activation process.

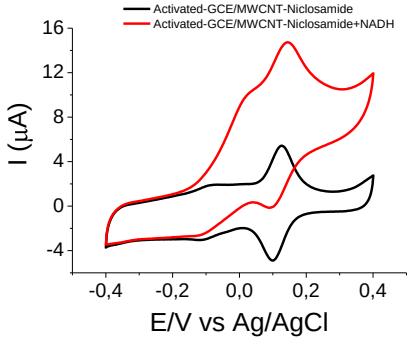

Figure 2. NADH catalysis.

References

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