

### Determination of noradrenaline using a glassy carbon electrode modified with cobalt ferrite nanoparticles on carbon nanotubes

Daniely F. Queiroz, Tony R.L. Dadamos, Sérgio A.S.

Machado and Marco A.U. Martines

Institute of Chemistry of São Carlos, University of São

Paulo, C.P. 780, 13560-970, São Carlos, SP, Brazil

Federal University of Mato Grosso of Sul, C.P. 79080-

190, Campo Grande, MS. E-mail:

address: [danielyqueiroz@iqsc.usp.br](mailto:danielyqueiroz@iqsc.usp.br)

Norepinephrine, also known as norepinephrine, is a monoamine that influence mood, anxiety, sleep and eating with serotonin, dopamine and epinephrine. Its main actions on the cardiovascular system are related to increased cellular calcium flow and maintaining blood pressure at normal levels. These effects are mediated by alpha adrenergic receptors. Besides being a hypertensive<sup>[1]</sup>. Thus was developed in this work an electrochemical sensor for quantification of norepinephrine through the modification of a glassy carbon electrode with nanoparticles of cobalt ferrite in carbon nanotubes.

The cobalt ferrite (FCo) were prepared from coprecipitation of ions  $\text{Co}^{2+}$  e  $\text{Fe}^{3+}$  from aqueous and chlorides in amounts stoichiometric molar ratio  $\text{Co:Fe}=1:2$ . Was added a solution of sodium hydroxide concentration  $5 \text{ mol L}^{-1}$  and agitation of 800 rpm until a pH 13 under temperature  $98^\circ\text{C}$ . After the precipitation the solution remained aging for a period of 1 hour under stirring. This material was placed at rest with the aid of a permanent magnet for settling the precipitate.

The precipitate was washed with ultrapure water for several times. The pH of the supernatant was analyzed, and the wash was carried out until achieving a pH of 7 to ensure the removal of excess base. The dark-colored precipitate started by oven drying at a temperature of  $120^\circ\text{C}$  for 24 hours. Figure 1 shows the XRD of the synthesized cobalt ferrite.

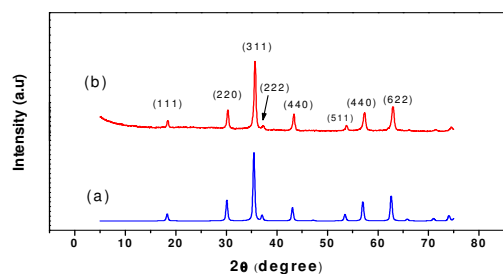


Figure 1: XRD pattern of magnetic nanoparticles, (a) JCPDS card No. 22-1086 de  $\text{CoFe}_2\text{O}_4$  e (b) FCo .

The investigation of magnetic behavior of sample FCo by vibrating sample magnetometer revealed a saturation magnetization  $M_s$  value ( $39,73 \text{ emu g}^{-1}$ ) indicating a behavior ferrimagnetic. According to data from transmission electron microscopy showed the sample FCo average diameter of  $42 \text{ nm} \pm 7 \text{ nm}$  and a degree of polydispersity of 18%. The adsorption isotherm of nitrogen temperature of 77 K ferrites showed values of surface area  $46 \pm 0,14 \text{ m}^2 \text{ g}^{-1}$ .

For the modification of the electrode was suspended 10 mg of carbon nanotubes multiple walls (MWCNT) and 10 mg de FCo in 2 mL of ethanol respectively. The suspension was dispersed by using ultrasonic 30 min. An aliquot of  $10 \mu\text{L}$  de MWCNT and  $4 \mu\text{L}$  of FCo were placed on the surface of the glassy

carbon electrode (CV). The study of the modification of glassy carbon electrode with nanoparticles of cobalt ferrite nanotubes and multi-walled carbon were performed using cyclic voltammetry with the redox couple ferrocyanide / ferricyanide potassium  $0.01 \text{ mol L}^{-1}$  in phosphate buffer  $0.1 \text{ mol L}^{-1}$  (pH = 7). Figure 2 shows the cyclic voltammograms of the electrode containing the changes.

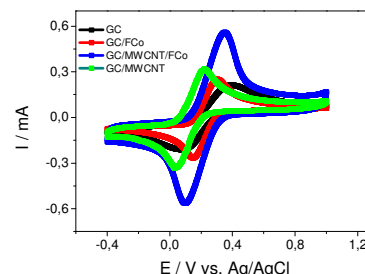


Figure 2: Cyclic voltammograms at ferrocyanide / ferricyanide potassium  $0.01 \text{ mol L}^{-1}$  in phosphate buffer  $0.1 \text{ mol L}^{-1}$  (pH = 7) with a scan rate of  $100 \text{ mV s}^{-1}$ .

As observed in the voltammograms of Figure 2 electrode modified with nanoparticles of cobalt ferrite nanotubes and multi-walled carbon has a better defined voltammetric profile with a decrease of overpotential of  $100 \text{ mV vs. Ag/AgCl}$  and an increase of the current of a factor 2.6 times.

A study was performed varying the speed of consecutive sweeps of potential (25 to  $200 \text{ mV/s}$ ) in the range of 0 a  $0,6 \text{ V vs. Ag/AgCl}$  of the modified electrode in the presence of noradrenaline. The linearity of the peak current ( $I_p$ ) as a function of the root of scan speed for both the peaks indicate that the process is controlled by diffusion. The linear relationship for straight anode was  $I (\mu\text{A}) = 2,94 + 7,0 v^{1/2} (\text{mV s}^{-1})$  and the line cathode was  $I (\mu\text{A}) = 7,14 - 6,08 v^{1/2} (\text{mV s}^{-1})$ .

In order to test the applicability of the developed sensor in analytical work, a calibration curve was constructed. The linear range for noradrenaline detection was from  $0.16$  to  $1.91 \text{ mmol L}^{-1}$ . The linear relationship between diffusion currents and analyte concentration was represented by  $I_{pa} (\text{A}) = 2.34 \times 10^{-6} (\text{A/mol L}^{-1}) + 0.82 \times 10^{-3} [\text{noradrenaline}] (\text{mol L}^{-1})$ , with a correlation coefficient of 0.9989 (for  $n = 12$ ). The detection limit was estimated as  $0.76 \mu\text{mol L}^{-1}$  by the IUPAC procedure.

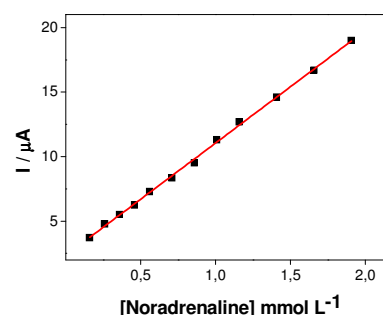


Figure 2: Analytical curve obtained for noradrenaline employing the electrode modified with CV/MWCNT/FCo in PBS (pH = 7) with scan rate of  $100 \text{ mV s}^{-1}$ .

The low value in the detection limit suggests that the CV/MWCNT/FCo biosensor is suitable for the detection of noradrenaline in matrices of interest.

### References

- <sup>[1]</sup> Zhang, X., and S. Wang. *Sensors* 3, no. 3 (2003): 61-68.