Área: ELE

Synthesis of platinum nanoparticles in deep eutectic solvent for application in electrochemical sensors

Paulo C. Gomes-Junior (PG),[1]* Karen K. L. Augusto (PG),[1] Renan O. Gonçalves (PG),[1] Gustavo P. Longatto (IC),[1] Júlio C. O. Almeida (IC),[1] Éder T. G. Cavalheiro (PQ),[2] Orlando Fatibello-Filho (PQ).[1]

paulojunior@estudante.ufscar.br

1 Department of Chemistry, Federal University of São Carlos, São Carlos 13565-905, SP, Brazil
2 São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP, Brazil
Keywords: *Platinum nanoparticles, Deep eutectic solvent, Electrochemical sensors.*

Highlights

Eutectic synthesis of PtNPs in reflux using reline as a stabilizing medium.
PtNPs and MWCNTs were incorporated into a Nafion film, increasing electrocatalytic activities for riboflavin detection.

Abstract

Deep eutectic solvents (DES) were introduced by Abbot et al.[1] in 2001 and proved to be alternatives to non-aqueous solvents and ionic liquids with various applications, mainly because the characteristics they present, such as low toxicity, biodegradability, and high thermal stability[2]. In this work, we synthesize platinum nanoparticles (PtNPs) by a reflux method using a DES based on choline chloride and urea (reline) in a 1:2 molar ratio. Then, the PtNPs were incorporated into a composite sensor based on multi-walled carbon nanotubes (MWCNTs) for electrochemical detection of riboflavin (RB). The synthesized PtNPs were characterized by transmission electron microscopy (TEM). The PtNPs were small-sized nanoparticles with an average diameter of (0.200 ± 0.001) nm. The cyclic voltammetry results showed that PtNPs-ChCl:U/MWCNTs/GCE sensor presented an increase of electrocatalytic activity in comparison to those of glassy carbon (GCE, inset (i)) and MWCNTs/GCE (inset (ii)) sensors (Figure 1a) for the RB determination. Then, the effect of potential scan rate, pH, supporting electrolyte, and square wave voltammetry (SWV) operational parameters were evaluated using the PtNPs-ChCl:U/MWCNTs/GCE sensor to establish the electrochemical behavior and optimal conditions to determine RB. The potential scan rate effect revealed that RB electro-reduction is an adsorptive-diffusion-controlled process. The pH effect (2.0 - 9.0 in BR 0.2 mol L^{-1} buffer) showed that peak potential (E_p) *vs.* pH was linear for RB (1.0 mmol L^{-1}) with a slope of -0.059 V pH^{-1}, suggesting an equal number of protons and electrons in the reduction process. In addition, pH 7.0 was chosen, and the supporting electrolyte effect showed that peak currents were higher in the phosphate buffer solution (PBS) than in the BR buffer solution at the same ionic strength and pH. The RB response in PBS was optimized by varying the SWV parameters with the selected conditions: frequency (*f*) = 8 Hz, amplitude (a) = 100 mV, and increment (ΔE_S) = 5 mV. Under these conditions, the analytical curve was constructed (Figure 1b) with the following equation: - Icp (μA) = - 3.2 + 247.1 [C_{RB}, μmol L^{-1}] (R^2 = 0.99). The detection (LOD) and quantification (LOQ) limits obtained were 1.8 nmol L^{-1} and 0.01 μmol L^{-1}, respectively. Intra (n = 15) and inter-day (n = 3) repeatability studies were performed for RB at 0.20, 0.50, and 0.98 μmol L^{-1}. The relative standard deviation (RSD) results were lower than 7 and 5%, respectively, suggesting good precision of the method by applying of the sensor in RB detection. The sensor efficiency was tested in samples of biological fluids fortified with RB at the following concentrations: 0.05, 0.25, and 0.73 μmol L^{-1} for synthetic urine and 0.12, 0.37, and 0.84 μmol L^{-1} for serum. The recoveries obtained ranged from 92.1 to 104.7% in the samples, which denotes a low matrix effect on the response with the PtNPs-ChCl:U/MWCNTs/GCE sensor, which suggests potentiality in the determination of RB in real biological samples.

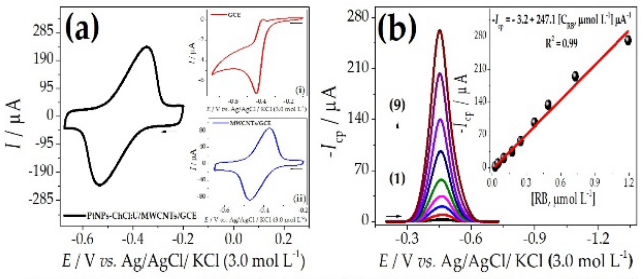

Figure 1: (a) Cyclic voltammograms obtained for RB at 1.0 mmol L^{-1} with PtNPs-ChCl:U/MWCNTs/GCE sensor in PBS 0.2 mol L^{-1} (pH 7.0), v = 50 mV s^{-1} and Insets: (i) CGE and (ii) MWCNTs/GCE. (b) Analytical curve obtained for RB at concentrations (1) 0.02 μmol L^{-1} to (9) 1.0 μmol L^{-1}, with the sensor PtNPs-ChCl:U/MWCNTs/GCE in PBS 0.2 mol L^{-1} (pH 7.0), using SWV with a = 100 mV, f = 8 Hz and ΔE_S = 5 mV.

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Acknowledgments

The authors gratefully acknowledge the financial support and scholarships granted by CAPES (Proc. 88887.597443/2021-00 and 88887.607018/2021-00), CNPq (#140406/2021-2) and FAPESP (2022/15513-3 and 2020/01050-5).