Bifunctional Nanostructured Hybrid Surface Pt/Au-SAM for Biosensing Analysis

Paulo A. Raymundo-Pereira[1,*] (PG), Dyovani Coelho[1], Flávio M. Shimizu[2] (PQ), Osvaldo N. Oliveira Jr.[2], Sergio A. S. Machado[1] (PQ).

[1] Grupo de Materiais Eletroquímicos e Métodos Eletroanalíticos (GMEME) – Instituto de Química de São Carlos (IQSC) – Universidade de São Paulo (USP). [2] Grupo de Polímeros – Instituto de Física de São Carlos (IFSC) – Universidade de São Paulo (USP). E-mail: paulo.raymundo@uol.com.br.

Palavras Chave: *Electrochemical (bio)sensors, Pt/Au, Nanoestructured, SAM, Bifunctional Hybrid Surface, Glucose.*

Introduction

Bimetallic nanostructures (Bi-MNSs) have drawn special attention due to their particular properties related to catalytic, electronic, mechanic, optic and magnetic characteristics which are tuned by the combination of the fine structures of each metal constituent. The result is a new surface (hybrid surfaces) which distinguished characteristics when compared to any its counterparts [1]. Among the several choices of bifunctional metals, gold is a unique due to its biocompatibility, which is a desirable property for biomolecules immobilization, however, platinum present excellent electrocatalytic property for oxidation/reduction towards H_2O_2 [1,2]. Thus, the motivation of this work was developed a new nanostructured hybrid surface based on Pt/Au-SAM for biosensing applications. We report the fabrication, characterization and applicability of the bifunctional nanostructured hybrid surface Pt/Au-SAM-GOx. The oxidation of H_2O_2 was monitored by measuring the increase in oxidation current of H_2O_2 on to the platinum surface.

Results and Discussions

Nanostructured interdigitated microelectrode array (IMA) of platinum/gold (Pt/Au) was fabricated by photolithographic and lift-off process [3]. Then, self-assembled monolayer (SAM) was immobilized by immersion of IMA in a solution containing 5 mM of 11-mercaptoundecanoic acid (11-MUA) by 20 h.

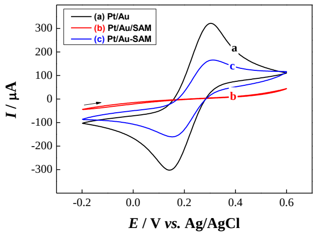

Figure 1. Cyclic voltammograms obtained in 0.1 mol L^{-1} KCl solution containing 5.0 mmol L^{-1} $[Fe(CN)_6]^{4-/3-}$, v = 50 mV s^{-1}.

Cyclic voltammograms shown in Figure 1, the anodic and cathodic peaks at 0.303 and 0.152 V, respectively, and can be attributed to electron-transfer between nanostructured bimetallic hybrid surface Pt/Au and redox probe $[Fe(CN)_6]^{4-/3-}$ (curve **(a)**). Curve **(b)** not presents redox peaks indicating SAM immobilization on the nanostructured hybrid surface. After electrochemical polishing in H_2SO_4 solution 0.5 mol L^{-1} at potential range between -0.23 and 1.1 V, the voltammogram **(c)** Figure 1 show the anodic and cathodic peaks at 0.313 and 0.152 V, respectively, attributed to electron-transfer between the redox probe $[Fe(CN)_6]^{4-/3-}$ and platinum surface but a decrease in the currents peaks was observed when compared to curve **(a). This** confirms that the procedure developed promote the SAM desorption only on platinum surface and remaining on the gold nanostructures. Thus, the surface can be called of bifunctional nanostructured hybrid surface Pt/Au-SAM. The ratio platinum/gold on the hybrid surface nanostructured bimetallic was estimated in 65% and 35%, respectively.

To achieve our goal, we have used the unique properties of the bifunctional nanostructured hybrid surface Pt/Au-SAM, by using the enzyme glucose oxidase (GOx) approach for the determination of H_2O_2. This novel system has been developed by immobilization of the SAM only on gold surface, of the hybrid surface nanostructured Pt/Au. Thus, the GOx was immobilized on the hybrid surface nanostructured Pt/Au-SAM by adsorption method. In this enzyme system, the glucose is subsequently oxidized by GOx and oxygen peroxide was produced, and finally H_2O_2 was detected on the platinum surface in the range concentration between 0 to 14.8 mmol L^{-1} glucose.

Conclusions

The bifunctional nanostructured hybrid surface Pt/Au-SAM (only on the gold nanostructures) was developed successfully and it was applied in the glucose determination.

Ackonowledgements

Angelo L. Gobbi and Maria H. Piazzeta by the use of Laboratory of Microfabrication (LMF/LNNano-LNLS). FAPESP (2012/17689-9 and 2013/17053-0).

[1]Upadhyay, S.; Rao, G.R.; Sharma, M.K.; Bhattacharya, B.K.; Rao, V.K.; Vijayaraghavan, R. Bios. bioelectronics, **2009**, *25*, 832.
[2]Iost, Jia, H.; Gao, P.; Ma, H.; Wu, D.; Du, B.; Wei, Q. Bioelectrochem. **2015**, *101*, 22.
[3]Huanga, H.M.; Liua, C.H.; Leeb, V.; Leea, C. Sens. Act. B, **2010**, *149*, 59.