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Enhancing biosensor properties of conducting polymers via copolymerization: Synthesis of EDOT-substituted bis(2-pyridylimino) isoindolato-palladium complex and electrochemical sensing of glucose by its copolymerized film

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ABSTRACT

1,3-Bis(2-pyridylimino)isoindoline derivative bearing 3,4-ethylenedioxythiophene (**EDOT-BPI**) and its palladium complex (**EDOT-PdBPI**) were synthesized and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, UV–Vis spectroscopies and via mass spectrometric analysis. Polymerization of **EDOT-PdBPI** and copolymerization with 4-amino-N-(2,5-di(thiophene-2-yl)-1*H*-pyrrol-1-yl)benzamide (**HKCN**) were carried out by an electrochemical method. In addition, P(EDOT-PdBPI-*co*-HKCN) modified graphite rod electrode was improved for amperometric glucose sensor based on glucose oxidase (GOx). In this novel biosensor matrix, amino groups in **HKCN** were used for the enzyme immobilization. On the other hand, **EDOT-PdBPI** used to mediate the bioelectrocatalytic reaction. Amperometric detection was carried out following oxygen consumption at −0.7 V vs. the Ag reference electrode in phosphate buffer (50 mM, pH 6.0). The novel biosensor showed a linear amperometric response for glucose within a concentration range of 0.25 mM to 2.5 mM (LOD: 0.176 mM). Amperometric signals at 1 mM of glucose were 17.9 μA under anaerobic conditions. Amperometric response of the P(EDOT-PdBPI-*co*-HKCN)/GOx electrode decreased only by 13% within eight weeks. The P(EDOT-PdBPI-*co*-HKCN)/GOx electrode showed good selectivity in the presence of ethanol and phenol. This result shows that, modification of the proposed biosensor by copolymerization of amine functionalized monomer, which is indispensable to the enzyme immobilization, with palladium complex bearing monomer, which is mediate the bioelectrocatalytic reaction, have provided to give perfect response to different glucose concentrations.

1. Introduction

The chemistry of isoindolines has been the key for the development of phthalocyanines as well as related macrocycles and chelating ligands (Tamgho et al., 2013; Bekaroğlu, 2000; Torres, 2000). Among the isoindoline-based chelating ligands, bis(2-pyridylimino)isoindolines (*BPI*) have been the focus of interest because they are readily synthesized and easily modified (Hanson et al., 2011; Kim et al., 2012; Selvi et al., 2005; Tran et al., 2014; Wen et al., 2011). *BPIs* have been shown to function as neutral, nondeprotonated and also as uninegative ligands. The ligands are capable of occupying three sites about a metal ion and forming either 1:1 or 2:1 (ligand:metal) complexes depending on the coordination number and geometry of the metal ion (Bakthavachalam and Reddy, 2013; Balogh-Hergovich et al., 2005; Dietrich et al., 2005; Meder et al., 2005; Pap et al., 2011a). Most of the published papers about bis(2-pyridylimino)isoindolines and their metal complexes focused on structural characterization and main application areas of these compounds are homogeneous catalysis and biomimetics (Csonka et al., 2015; Kaizer et al., 2008, 2007; Pap et al., 2011b; Sauer et al., 2012). Here we present first time a new bis(2-pyridylimino)isoindolato-palladium complex bearing electropolymerizable EDOT (3,4-(ethylenedioxy)thiophene) substituent and show it may be used for glucose sensing as heterogeneous catalytic system.

Most of enzymatic glucose biosensors are based on the immobilized glucose oxidase (GOx), which catalyzes the oxidation of glucose to gluconic acid and H_2O_2, and the concentration of

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