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Nanometric polythiophene films with electrocatalytic activity for non-enzymatic detection of glucose

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ABSTRACT

Electrochemical detection of glucose using simple polymeric electrodes without the assistance of enzymatic or inorganic catalysts (*i.e.* metals or metal oxides) has been issued a challenge to the scientific community. In this work we present the development of a potentiometric glucose sensor based on nanometric films of a very electroactive polythiophene derivative bearing a hydroxyl substituent per repeat unit. The sensor, which is enzyme free and does not require from additional catalytic nanoparticles, exhibits excellent tolerance against interferents, a low detection limit, and a deviation lower than 2% with respect to measures in human blood samples with commercial sensors. The excellent response of this highly electroactive polythiophene derivative, which exhibits a very simple chemical structure, has been attributed to the closeness between the hydroxyl substituents and the aromatic groups contained in the linear and rigid backbone. This particular chemical distribution favors the activation of the hydroxyl substituents, inducing their participation in the oxidation of glucose molecules.

1. Introduction

Regular monitoring of glucose levels in the human body is crucial for the diagnosis and management of diabetes, which has become a worldwide public health problem. In addition, monitoring of the glucose metabolism through the detection of changes in the concentration of this important chemical may improve the treatment of brain diseases (*e.g.* brain tumors and traumatic brain injuries) [1,2].

To date the most common glucose biosensors, which are based on amperometric detection, achieve specific recognition by immobilizing an enzyme called glucose oxidase (GOx) that catalyzes the oxidation of glucose to gluconolactone [3]. Within this context the application of conducting polymers (CPs) to bioelectronic surfaces has gained considerable attention due to a number of advantages, such as their easy preparation and direct deposition on the electrode surface [4]. Thus, CPs have been successfully used to increase the signal-to-noise ratio in the detection process and to immobilize and entrap the enzymes [5–10]. For the specific case of GOx, a large number of CPs have been either functionalized or modified at their surface to facilitate the effective chemical or physical immobilization of the enzyme, enabling their subsequent utilization

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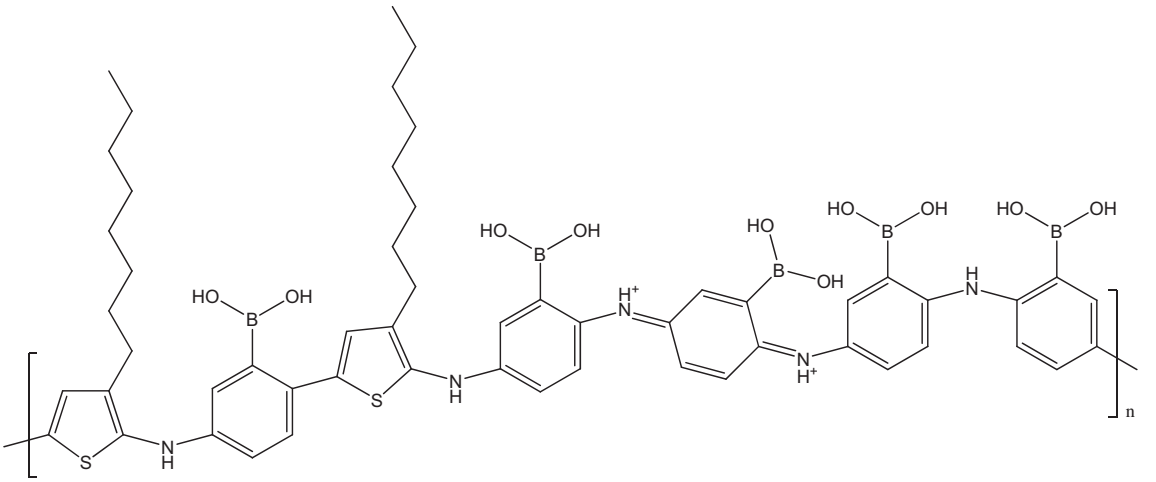


Scheme 1. Chemical structure proposed for PAPBAOT in Ref. 26.

as amperometric sensors [11–16]. Another important advantage of these CP-based materials is that they usually minimize the access of interfering compounds to the biosensor surface.

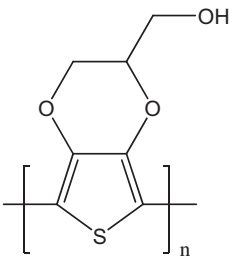
In order to solve the problems associated to enzyme-based sensors (*e.g.* poor reproducibility, complicated immobilization processes and high cost), the development of non-enzymatic glucose sensors (NEGSs) has attracted the interest of scientists. Most NEGSs are primarily based on the ability of Au, Cu, Ni, Pt and their oxides to catalyze glucose oxidation [17–22]. Carbon nanotubes and graphene have also been used to fabricate NEGSs [23–26]. In recent years some NEGSs have been fabricated by stabilizing catalysts with CPs, *e.g.* poly(hydroxyl-1,4-naphthoquinone) and poly(3-octylthiophene) (P3OTh) with Au, and polypyrrole (PPy) with magnetic $ZnFe_2O_4$ [17,18,27]. Although direct electrooxidation of glucose is kinetically very slow and, therefore, enzymatic or inorganic catalysts are required to speed up the process and to offer adequate selectivity, Çiftçi and Tarmer [28] recently developed a new CP able to detect glucose without the assistance of any catalytic agent. This sensor, which was based on poly(3-aminophenylboronic acid-co-3-octylthiophene) (PAPBAOT) deposited on glassy carbon, exhibited a detection limit of 0.5 mM and was selective against common interferents, *i.e.* uric acid (UA), ascorbic acid (AA) and dopamine (DA) [28]. In spite of this success, the commercial application of PAPBAOT is drastically limited by its complex chemical structure (Scheme 1), which includes boronic acid and alkyl spacer functional groups as molecular recognition and penetration agent, respectively.

In this work we present a new NEGS based on a very simple CP, which was recently designed to improve the amperometric detection of DA [29]. This CP, poly(hydroxymethyl-3,4-ethylendioxythiophene) (PHMeDOT), was chosen among the vast palette of poly(3,4-ethylendioxythiophene) (PEDOT) derivatives that can be prepared using commercial monomers because of the electrocatalytic activity of the exocyclic hydroxymethyl group (Scheme 2) [29]. The main advantages of PHMeDOT, which acts as glucose sensor without any special modification or treatment, with respect to other reported system are the lack of enzymatic or inorganic catalysts and the simplicity of its chemical structure, facilitating the synthesis process and reducing its economic cost.

2. Methods

2.1. Materials

Thieno[3,4-b]-1,4-dioxin-2-methanol (HMeDOT) monomer, anhydrous lithium perchlorate ($LiClO_4$), D-glucose, DA hydrochloride (3-hydroxytyramine hydrochloride), AA (L-configuration, crystalline) and UA (crystalline) of analytical reagent



Scheme 2. Chemical structure of PHMeDOT.