



Facile synthesis of a silver nanoparticles/polypyrrole nanocomposite for non-enzymatic glucose determination



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ABSTRACT

The present work describes the synthesis of a new conductive nanocomposite based on polypyrrole (PPy) and silver nanoparticles (PPy-AgNP) based on a facile reverse microemulsion method and its application as a non-enzymatic electrochemical sensor for glucose detection. Focusing on the best sensor performance, all experimental parameters used in the synthesis of nanocomposite were optimized based on its electrochemical response for glucose. Characterization of the optimized material by FT-IR, cyclic voltammetry, and DRX measurements and TEM images showed good monodispersion of semispherical Ag nanoparticles capped by PPy structure, with size average of 12 ± 5 nm. Under the best analytical conditions, the proposed sensor exhibited glucose response in linear dynamic range of 25 to 2500 $\mu\text{mol L}^{-1}$, with limit of detection of 3.6 $\mu\text{mol L}^{-1}$. Recovery studies with human saliva samples varying from 99 to 105% revealed the accuracy and feasibility of a non-enzymatic electrochemical sensor for glucose determination by easy construction and low-cost.

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1. Introduction

Electrochemical (bio)sensors for glucose detection have been widely employed as a tool for diabetes mellitus control due to its rapid response, accurate, selective and low cost per analysis [1]. In general, procedures for determining glucose with portable devices currently available are invasive, requiring the patient to remove a small amount of blood, making this common procedure uncomfortable and painful. An interesting alternative for a daily glucose monitoring is through saliva, that presents glucose concentration between 25 and 100 $\mu\text{mol L}^{-1}$. In general, biosensing devices are based on a selective site of recognition which provides a good selectivity, but the sensor stability could be severely affected by alterations of its biological activity which impairs the sensitivity and, consequently, the required limits for analysis of this kind of sample [2]. Alternatively, the use of non-enzymatic electrochemical sensors, especially noble metal interfaces (Au, Ag, Pt) can provide efficient and fast electrocatalytic response toward reaction between glucose and noble metal oxides formed in positive potentials [3–5]. In case of Ag, during the anodic sweep, the AgO so-formed chemically reacts with glucose to yield Ag₂O. Therefore, using a simple cyclic voltammetry experiment, glucose concentration can be directly related with Ag₂O peak in reverse sweep [6]. (See Scheme 1.)

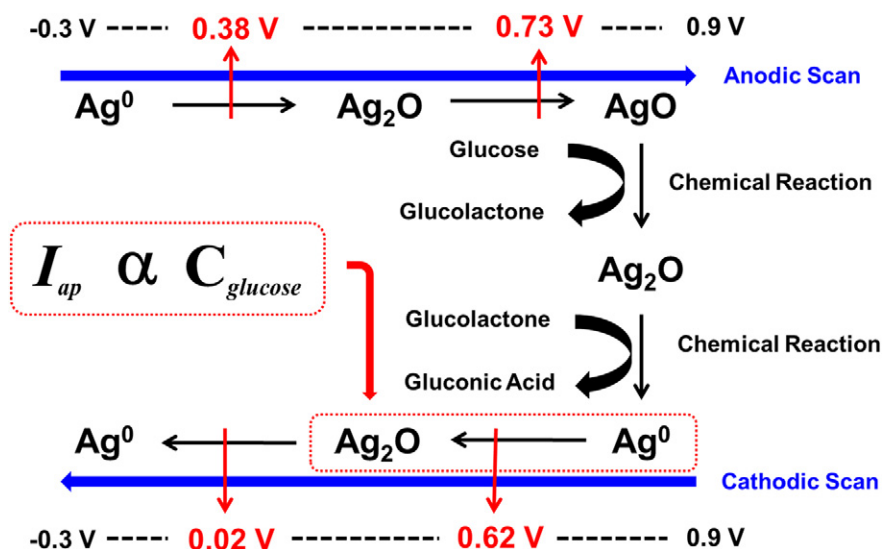
The present work describes for the first time, a non-enzymatic glucose sensor based on electrocatalytic properties of silver nanoparticles capped by conductive polypyrrole structure (PPy-AgNPs nanocomposite). Besides the synthesis of a “100% conductive” nanocomposite, the main novelty of this work is the optimization of synthetic parameters based on electrochemical measurements in presence of glucose, in order to obtain the best electrochemical performance for the proposed sensor.

Nanocomposites between conductive polymers (CPs) and noble metals nanoparticles (CPs-NPs) have presented as interesting systems because NPs can provide high electrocatalytic activity and increase in surface area [7,8]. Moreover, the synergistic properties of such nanocomposites can present superior selectivity and sensitivity toward the electrochemical detection [9,10]. PPy-AgNP composites have been widely explored due its electrochemical properties; they could be yielded using fast and easy routes in aqueous media based on chemical oxidation of pyrrole monomers (Py) by silver ions without addition of any chemical acceleration agent [11]. Synthetic routes and approaches are related in literature to increase reaction rate by varying temperature [12], hydrothermal reaction [13,14], UV irradiation [15], and also Py oxidation in organic medium [16,17].

Concerning of synthesis methodology, there are no reports citing PPy-AgNP synthesis based on reverse microemulsion method. Basically, the chemical approach consists in a water-in-oil microemulsion where reactants are caged into micelles and the size distribution can be

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Scheme 1. Proposed mechanism for glucose determination with PPy-AgNPs nanocomposite sensor.

adjusted by W_0 ($[H_2O]/[surfactant]$) [18]. Moreover, it becomes possible to obtain polymers with high molar mass and polymeric nanoparticles with diameters <50 nm and can present an assortment of nano or microstructures, which is reflected directly on polymer properties [19].

2. Experimental

2.1. Chemicals and materials

All the chemicals were of analytical reagent grade and used as received from Sigma Aldrich (USA) and Vetec (Brazil), without further purification, pyrrole was distilled before use. All the aqueous solutions were prepared using deionized water obtained from Milli-Q system.

2.2. Apparatus

Transmission electron microscopy (TEM) images were performed using JEOL JEM 1200 operated at 120 kV. The samples were prepared by dropping $5.0 \mu\text{L}$ of 1.0 mg mL^{-1} PPy-AgNPs dispersion on standard copper grids covered by thin film of amorphous carbon. The size and distribution of the PPy-AgNPs were determined by counting 1000 objects from TEM images for each sample. Electrochemical measurements (cyclic voltammetry and chronoamperometry) were carried out using a potentiostat/galvanostat μ -autolab Type III (EcoChemie) and a conventional three electrodes one-compartment cell with a modified GCE as working electrode, a platinum wire as auxiliary electrode and Ag/AgCl (3.0 mol L^{-1} KCl) as reference electrode. All experiments were carried out at room temperature.

2.3. Synthesis of PPy-AgNPs nanocomposites

PPy-AgNPs nanocomposites were prepared by reversed microemulsion approach according to procedure described below.

Two separated microemulsions were prepared; the first one (microemulsion 1) was composed by aqueous solution of 0.02 mol L^{-1} AgNO_3 and 20.0 mL of *n*-hexane (with 4.0 g of dodecyl sodium sulfate (DSS) and 8.0 g of buthanol, as surfactant and co-surfactant, respectively) as organic phase; the second one (microemulsion 2) was composed by 0.04 mol L^{-1} of pyrrole monomer (previously distilled) in aqueous media with the same cited-above organic phase. For both microemulsions, the ratio $W = [H_2O]/[Surfactant]$ was fixed in 5. After this, the microemulsions were mixed under magnetic stirring and after a suitable reaction time, 40 mL of a mixture of 1:1 (v/v) water-ethanol was added to promote micelles destabilization

and stop the reaction. After separation and purification steps, a colloidal dispersion in water was obtained. The reaction time and Ag:Py molar ratio were evaluated in order to obtain the best material for cyclic voltammetry glucose determination.

2.4. Electrode modification

Glassy carbon electrode (GCE) with 3.0 mm diameter was polished with 0.05 mm alumina powder and rinsed with Milli-Q water. Fresh dispersion of PPy-AgNPs nanocomposite was prepared for each experiment by dispersing 1.0 mg of nanocomposite in 1.0 mL of deionized water followed by sonication by 15 min . The modified electrode was prepared by dropping $3.0 \mu\text{L}$ of the nanocomposite suspension onto pre-cleaned GCE and dried at room temperature. Before glucose measurements, an electrochemical pre-treatment of working electrode was done by successive voltammetric cycles (130 cycles, potential range from -0.30 to 0.95 V vs. Ag/AgCl (3.0 mol L^{-1} KCl) in 0.1 mol L^{-1} NaOH solution.

2.5. Chronoamperometric measurements and glucose detection in saliva samples

After optimized procedure for synthesis of nanocomposite based on electrochemical measurements, the GCE/PPy-AgNPs was evaluated for glucose determination by chronoamperometry. Some parameters as applied potential and volume of PPy-AgNP suspension onto GCE surface were evaluated. In order to construct the analytical curves, anodic current values were sampled 10 s after glucose additions.

The practical application of the proposed sensor was carried out performed using artificial human saliva samples spiked in three levels of glucose concentration ($30, 50$ and $80 \mu\text{mol L}^{-1}$). The artificial human saliva called SAGF medium was prepared as described by Gal et al. [20] and diluted in NaOH solution before measurements.

3. Results and discussion

3.1. Structural and morphological characterization of PPy-AgNPs nanocomposite

In reverse microemulsion method, precursor salt (AgNO_3) and monomer (pyrrole) are caged into micelles composed by sodium dodecylsulfate and buthanol, dispersed in organic phase. During the synthesis, the random movement and collision of both micelles occurs promoting intermicellar exchange. As resulting product, nucleation

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