



# An enzyme free potentiometric detection of glucose based on a conducting polymer poly (3-aminophenyl boronic acid-co-3-octylthiophene)

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## ARTICLE INFO

### Article history:

Received 14 October 2012

Received in revised form 4 December 2012

Accepted 6 December 2012

Available online 17 December 2012

### Keywords:

Enzyme-free sensor

Glucose

Open circuit potential

Conducting polymer electrode

Poly (3-aminophenyl boronic acid-co-3-octylthiophene)

## ABSTRACT

An enzyme free potentiometric glucose sensor was developed through the electrochemical preparation of a new poly (3-aminophenyl boronic acid-co-3-octylthiophene) (PAPBAOT) organic electrode. A PAPBAOT conducting polymer film electrode was first synthesized electrochemically on glassy carbon electrode and the analytical performance of the developed sensor was evaluated using potentiometric measurements. Boronic acid and the alkyl spacer functional group were used as molecular recognition and penetration agent, respectively. The PAPBAOT film electrode was characterized using cyclic voltammetry, Scanning electron microscopy (SEM), UV–vis spectroscopy, Raman spectroscopy, and Differential scanning calorimetry (DSC). The potentiometric calibration plot showed a hydrodynamic range of 5–50 mM glucose within a range of blood glucose level. The detection limit was 0.5 mM, and the sensor exhibited no interference from common interference such as ascorbic acid, dopamine, and uric acid. The PAPBAOT film electrode was used for the determination of glucose in human plasma samples and the results were compared with commercial amperometric sensors.

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## 1. Introduction

Determination of glucose for patient suffering from diabetes mellitus is crucial, and an enduring analytical challenge [1]. Enzymatic assays have been widely used [2,3] and detection methods such as fluorometric [4], quartz crystal microbalance [5], electrochemical [5], SPR [6], and chromatographic [7] methods have been reported. Electrochemical methods, such as an amperometric glucose sensor, can also be used for minimal sample amounts, without any pre-treatment processing. Although the selective response of enzymatic sensor, the most serious problem is its lack of stability, due to the intrinsic nature of the enzyme, the activity of which can be easily affected by various factors such as temperature, pH, etc. [8,9]. Non-enzymatic sensors are not involved in enzymatic bioactivity, and are extremely stable; however, they need to overcome the high overpotential of glucose oxidation.

The selective response of conducting polymers toward organic molecules has made them ideal sensors in numerous applications [10,11]. The main advantage of electrochemical synthesis in conducting polymer films is that the procedure leads directly to a new electrode material in a single step process [12]. Recent studies have

also demonstrated that potentiometric sensors for saccharides can be constructed by coupling boronic acid groups to the backbone of polyaniline [13,14].

The molecular recognition systems are widely applied to various target molecule for selective binding [15–18]. A molecular recognition agent, boronic acids, recognise cis diol configuration in saccharides and form reversible covalent complexes in aqueous media, represent an ideal synthetic molecular receptor having the ability to selectively recognise saccharides [19,20]. Phenylboronic acid derivatives have been developed for saccharide sensing in various methods, based on piezoresistive microcantilevers [21], UV–vis absorption [22,23], fluorescence [24,25], electrochemistry [26–30], plasmonics [31], and holography [32] and SPR [33]. Consequently, boronic acids and phenylboronic acid derivatives can be used as the recognition moiety for the detection of saccharides in a solution. Various factors that affect the binding of phenylboronic acid derivatives on the surface of electrodes and optical devices, such as SPR [34]. The complexity of saccharides with aromatic boronic acids produces a stable ester, where the binding constant depends on pH, electrolyte concentration, and the pK<sub>a</sub> of aromatic boronic acid [35]. There is an electropolymerization study that illustrates the use of PAPBA as a glucose molecular recognition agent; recognition properties of PAPBA are mediated through reversible covalent and electrostatic interactions [13,28,36]. Recent work by the Duyne group demonstrated that the direct detection of glucose using

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surface-enhanced Raman scattering (SERS) is possible and glucose was partitioned into alkanethiolate monolayer, such as decanethiol and (1-mercaptoundeca-1(-yl) tri (ethylene)glycol) [37,38]. Norrild and Sotofte prepared the ferrocene modified phenylboronic acid for the construction of glucose selective redox sensors [27]. Okano et al. reported a glucose sensitive electrode based on a platinum electrode coated with a phenylboronic acid bearing polymer film [39]. Granot et al. reported co-electropolymerization of phenol and 3-hydroxyphenylboronic acid on the surface of gold electrode. Sugar imprinted film modified electrode exhibited enantioselective response to glucose and mannose [40,41].

A few studies have been published about the synthesis of copolymer for aniline and thiophene or their derivatives that were prepared electrochemical methods [42,43]. In previous studies from our laboratory, the electrochemical preparation of aniline–thiophene copolymer in acetonitrile was elucidated and a catalytic mechanism related to the role of thiophene cation radicals, which involves chemical and electrochemical oxidation step, is proposed [44]. Recently, we prepared poly(3-octylthiophene) film electrode that contains gold nanoparticles modified with 4-mercaptophenyl boronic acid. This electrode was used for glucose determination as potentiometric non-enzymatic glucose sensor. Calibration graphs were obtained in the concentration ranging between 5 and 30 mM glucose including the level of human blood glucose [45]. The approach described in this paper coating of poly(3-aminophenyl boronic acid-co-3-octylthiophene) copolymer film on the surface of GC electrode electrochemically for the first time. The potentiometric response to glucose concentration of poly(3-aminophenyl boronic acid-co-3-octylthiophene) copolymer film coated electrode was examined. Experimental parameters such as pH, alkyl spacer length, monomer ratio and film thickness were optimized. Also, in vitro determination of glucose in human plasma samples was demonstrated.

## 2. Experimental

### 2.1. Materials

3-Octylthiophene (OT), 3-methylthiophene (MT), 3-decylthiophene (DT), 3-dodecylthiophene (DDT), 3-aminophenylboronic acid (APBA), acetonitrile (HPLC grade), and tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) were used as received from Aldrich (Steinheim, Germany). Deionised water (18.2 MΩ cm), free from organic matter, obtained from a Millipore purification system, was used to prepare all solutions, which were then de-aerated with argon to remove present oxygen.

### 2.2. Instruments

A Gamry potentiostat (model reference 600, USA) in a conventional three-electrode arrangement, equipped with a glassy carbon (2.0 mm diameter) working electrode, a platinum wire counter electrode, and an Ag|AgCl reference electrode was used to perform electrochemical studies. Scanning electron microscopy (SEM) was used to examine morphologies of films. A JSM-6400 electron microscope (JEOL), equipped with IXRF, EDS2000 microanalysis system was used to produce scanning electron micrographs. Thermal analysis was conducted using a DSC 60 Shimadzu device, with a heating rate of 10 °C min<sup>-1</sup>. Bayer (USA) elite blood test strips were used as a commercial glucose sensor. Test strips of its contain 6% (w/w) FAD glucose dehydrogenase (*Aspergillus* sp., 2.0 U/test strip), 56% (w/w) potassium ferricyanide and 38% (w/w) non-reactive ingredients.

A DeltaNu Examiner Raman microscope (Deltanu Inc., Laramie, WY) with a 785-nm laser source, a motorised microscope stage

sample holder, and a cooled +CCD detector was used to produce the Raman spectra of polymers.

### 2.3. Preparation of the PAPBAOT film electrode

The polymer film was synthesized from a reaction medium containing a total monomer concentration of 0.1 M and 0.1 M TBABF<sub>4</sub> in acetonitrile, via repeated cycling between 0.00 V and +2000 mV vs. Ag|AgCl at a scan rate of 100 mV s<sup>-1</sup>. The number of cycles applied to electrodes permitted control of film thickness. Films were then undoped by subjecting the working electrode to an applied potential of -200 mV for one minute in the same synthesis solution. The electrode was removed from the synthesis cell, and was rinsed with water. It is important to indicate that the respective last scan ended at a final potential value of -200 mV vs. Ag|AgCl for all synthesised films, so that the film was left in neutral reduced state, prior to the potentiometric measurement step. Glassy carbon electrode was polished using a fine emery paper, and 0.1 μm alumina powder, after which it was ultrasonically rinsed with water for 5 min. All experiments were run three times at room temperature.

### 2.4. Spectroelectrochemistry

Indium-tin oxide (ITO, Delta Tech. 5–15 Ω, 0.7 cm × 5 cm) was coated with films to conduct spectroelectrochemical characterisation. A Perkin Elmer spectrometer was used to conduct spectroelectrochemical studies. A platinum wire was used as a counter electrode, and an Ag wire was used as a pseudo-reference.

### 2.5. Electrochemical measurements

Potentiometric measurements were carried out using a two electrode cell configuration. A PAPBAOT film electrode was used as the working electrode, and an Ag|AgCl electrode was employed as the reference electrode. Unless otherwise stated, all open circuit experiments were conducted in a stirred boric acid/borate buffer solution at pH 9. The electrode potential was allowed to settle in the buffer solution prior to performing all open circuit measurements. All studied solutions contained 1 mM NaCl, as an ionic strength adjuster. After the PAPBAOT electrode settled, the change in open circuit potential ( $E_{oc}$ ) was monitored before and after the addition of glucose. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a three electrode/one compartment glass cell in the boric acid/borate buffer solution at pH 9 with a CH Instruments System, Model 660B (USA). All electrochemical measurements were conducted at room temperature.

### 2.6. Determination of glucose in human blood serum

Serum samples were collected from normoglycemic individuals. 100 μL of serum samples were injected to 2.5 mL of constantly stirred solution of pH 9, and the potentiometric response was recorded. Thus, the response corresponds to an effective concentration of 1/25th of the original.

## 3. Results and discussion

### 3.1. Fabrication and characterisation of the PAPBAOT electrode

The conducting polymer layer was created on the glassy carbon electrode surface using an electropolymerization reaction of 3-Octylthiophene (OT) and 3-aminophenylboronic acid (APBA) monomers in an acetonitrile solution containing 30 mM OT, 70 mM APBA, 100 mM TBABF<sub>4</sub> by cycling the potential between 0.00 and +2000 mV up to twenty times, at a scan rate of 100 mV s<sup>-1</sup>. For comparison, electropolymerization of OT and APBA monomers were

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