



# Nanoparticles functionalized with phenylboronic acid for the potentiometric detection of saccharides



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## ABSTRACT

We have proposed a concept for the analytical application of modified gold nanoparticles in potentiometric sensors. The main idea is to embed modified gold nanoparticles as receptor units during electropolymerization into a polymeric matrix which should serve as a transducer of the potentiometric signal. The concept was verified using a model system based on gold nanoparticles modified with mercaptophenylboronic acid (MPBA–AuNPs) as a receptor of saccharides in a pH-sensitive polymer matrix, namely polyaniline (PANI). The determination of saccharides, in particular D-glucose, is based on the determination of released protons as products of the reaction between mercaptophenylboronic acid and saccharides. Differential pulse voltammetry showed that approximately 33% of the MPBA–AuNPs present in the polymerization mixture were built into the PANI polymeric film. The absorption and reflectivity spectra confirmed the recognition process occurring between mercaptophenylboronic acid and D-glucose inside the pH-sensitive polymeric matrix. A potentiometric response of MPBA–AuNP-modified PANI electrodes towards D-glucose in the concentration range from 0.31 up to 33 mM with a sensitivity of +47 mV/decade was verified. The MPBA–AuNP-modified PANI film can be considered to be a saccharide-sensitive receptor layer exhibiting an indirect mechanism of signal generation.

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## 1. Introduction

Potentiometric detection is a promising read-out method for its relative technical simplicity and ease of miniaturization. The development of potentiometric sensors can be achieved through the introduction of new ion recognition chemistry that combines supramolecular design and an immobilization procedure. In a potentiometric sensor, the supramolecular receptor is involved either as a monomer or covalently attached to a polymeric matrix. The immobilization procedure should be performed in a way that does not change the recognition properties of the receptor. The idea of using nanomaterials as carriers of supramolecular receptors has been driven by the practical requirements for the compatibility of materials and improvement of sensor characteristics. Nowadays, nanotechnology offers many kinds of nanoparticles for the immobilization of biomolecules and supramolecular receptors. The unique chemical and physical properties of nanoparticles can make them suitable for designing new and improved sensing devices, in particular potentiometric sensors [1]. It should be emphasized that up to now, most systematic studies on the application of nanomaterials for potentiometric detection were focused on the

determination of heavy metals [2]. G. Jágorszki et al. demonstrated the potentiometric detection of Ag<sup>+</sup> ions with a nanomolar detection limit using an ionophore immobilized on inert gold nanoparticles (AuNPs) [3]. X.G. Li's group has shown that a significant improvement in the detection limit of a potentiometric sensor for Pb<sup>2+</sup> ions can be achieved by immobilizing copolyaniline nanoparticles as the ionophore in a vinyl resin matrix [4].

The ability of phenylboronic acid (PBA) and its derivatives to reversibly form esters with cis-diols has been a central theme in field sensor development and receptor design for saccharides. The latest advances in the field of saccharide and carbohydrate sensing with boronic acid derivatives are reviewed in [5,6]. The attachment of a receptor to an electrode surface is desirable, since such electrodes can be quickly developed into "real" analytical systems. Phenylboronic acid-modified electrodes should be an alternative to enzyme-based saccharide sensors. In this context, it is worth mentioning that the non-enzymatic electrochemical sensing of saccharides, particularly of glucose, might be based on the catalytic ability of the electrode surface [7]. However, the authors noted that the development of such sensors is far more complex and not always perfect. Nonetheless, the deposition of AuNPs on the surface of gold electrodes resulted in new electrochemical properties [8].

Self-assembled monolayers (SAMs) of thiol-modified PBA deposited on the electrode surface have been used for the development of electrochemical sensing [5,9–11]. A series of efforts by Takahashi et al. have

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been directed at the development of voltammetric sensors based on SAMs for the detection of saccharides [10,11]. The interaction between the saccharide and PBA has led to the formation of a negatively charged monolayer which blocked the access of  $[\text{Fe}(\text{CN})_6]^{3-}$  ions to the electrode surface due to electrostatic repulsion. Taking into account the selectivity of sensors, the authors suggested developing reagentless sensors that can be used without adding redox ions such as  $[\text{Fe}(\text{CN})_6]^{3-}$  to the sample. Afterwards, J. Li et al. used Prussian blue as the electrochemical indicator, which was co-deposited with Au nanoparticles (AuNPs) on an Au electrode [12]. To generate the binding sites for 4-mercaptophenylboronic acid (MPBA), a second AuNP layer was assembled on the Au/PB nanocomposite via electroless metallization, induced by the catechol group of polydopamine. The proposed non-enzyme glucose amperometric sensor exhibited a wide linear range from  $1.0 \times 10^{-7}$  to  $1.35 \times 10^{-5}$  M.

Molecular imprinting is a method that introduces specific binding sites into a polymer by copolymerizing functional monomers and a cross-linker in the presence of a template. The possibility of using an imprinted polymer for monitoring saccharides was demonstrated using a potentiometric approach. At alkaline pH, the imprinted polymer bound glucose and instantly released protons in proportion to the glucose concentration over a clinically relevant range (0 to 25 mM) [13]. B. Deore and M. S. Freund have shown a significant role of fluoride in saccharide imprinting in the polymerization of aniline boronic acid. Their results suggested that fluoride serves to disrupt intermolecular B–N interactions between monomers, which results in complexation [14].

Recent studies have also demonstrated that potentiometric sensors for saccharides can be constructed by coupling boronic acid groups to the backbone of conducting polymers [15–17]. Shoji and Freund were the first to propose a non-enzymatic potentiometric sensor based on a poly(aniline boronic) film on a glassy-carbon electrode for the recognition of saccharides [15]. The potentiometric signal was the result of the pKa changes of the poly(aniline boronic) film upon saccharide binding. Ciftci et al. prepared a copolymer of 3-aminophenyl boronic acid and 3-octylthiophene (PAPBAOT) to detect glucose potentiometrically [18]. The selective response of the copolymer was the result of the simultaneous action of both an octylthiophene and the phenyl boronic acid groups that performed the role of a partition layer and a complexing agent near the electrode surface for preconcentrating glucose, respectively. The main advantage of the PAPBAOT-based sensor was low interference from ascorbic acid, uric acid, and dopamine that can block the signal of glucose in real samples. As can be seen from the literature, the polyaniline matrix and its modification still continues to be attractive in the field of saccharide sensors.

Recently, J. Li et al. assumed that a polymer film with a porous structure and large surface could positively affect the sensitivity and response time of a saccharide sensor [19]. This group fabricated highly ordered poly(aniline boronic acid) (PABA) nanotubes by employing an anodic alumina oxide (AAO) membrane as a template. In contrast to conventional poly(aniline boronic acid) films, the as-synthesized PABA-nanotube-based sensor demonstrated a higher sensitivity to D-glucose (ca.  $1.5 \text{ mV mM}^{-1}$ ) and D-fructose (ca.  $3.5 \text{ mV mM}^{-1}$ ) with a rapid response time for both D-glucose (65 s) and D-fructose (23 s).

In this work we provide detailed investigations of the interaction of MBPA–AuNPs embedded into a PANI film with saccharides. The previous findings indicated that protons as products of the interaction between phenylboronic acid and saccharides may be monitored potentiometrically [20]. The main objectives of this study are:

- i) to demonstrate the release of protons as result of the interaction of MBPA–AuNPs in the PANI film using spectroscopic measurements,
- ii) to determine the amount of gold entrapped into the polyaniline film using differential pulse voltammetry, and subsequently to apply this information as a presumption of the optimal amount of gold to obtain an optimal potentiometric response,

- iii) to include the influence of important interferents on the determination of glucose, to determine the long-term properties of proposed potentiometric sensors,
- iv) to gain insight into the behavior of MPBA–AuNPs in the PANI film, taking into account our experimental findings and literature data.

## 2. Materials and methods

### 2.1. Reagents and materials

Aniline ( $\geq 99.5\%$ ), 4-mercaptophenylboronic acid (90%) (MPBA), potassium tetrachloroaurate(III) (98%), uric acid, dopamine and saccharides were obtained from Sigma–Aldrich (Germany–Czech Republic). Methanol (99.5%) and trisodium citrate dihydrate (99%) were from Penta (Czech Republic). Acids and various inorganic/organic salts of analytical grade were purchased from Lachema (Czech Republic). All solutions were prepared using distilled water. Borosilica glass slides were obtained from Marienfeld. The platinum sputtering target (purity 99.999%) was obtained from Safina a.s., argon (purity 99.999%) was from Linde Gas a.s. The epi-polished semiconductor quality silicon (111) used as a reflectance standard was bought from MaTeCK GmbH.

Gold nanoparticles (AuNPs) obtained according to [21] were further modified with MPBA. For the modification,  $1 \times 10^{-2}$  M methanol solution of MPBA (1 mL) was added to 99 mL of an aqueous solution of AuNPs. The vessel was capped and left to stand for a day in the dark at ambient temperature.

### 2.2. Polymerization of aniline

The electrochemical polymerization of aniline was carried out in a three-electrode electrochemical cell. A platinum wire (diameter 0.4 mm, length 7 mm) was used as the working electrode. Prior to polymerization, the polymerization solution was purged with nitrogen for 10 min. The electrochemical polymerization was achieved by cycling the potential of the working electrode from +1.2 to 0.0 V versus Ag/AgCl in the presence of  $2.96 \times 10^{-2}$  M aniline and 0.5 M  $\text{H}_2\text{SO}_4$ . After 10 cycles, the electropolymerization of aniline was continued in the presence of 500  $\mu\text{L}$  of MPBA–AuNPs solution. The electrochemically prepared film formed a blue–green porous layer on the electrode surface. Electrodes prepared in this way were subsequently used as indicator electrodes in the potentiometric measurements (Section 2.5). Before potentiometric measurements, the electrode surface was rinsed with water and then soaked with  $8 \times 10^{-3}$  M Britton–Robinson buffer, pH 12. After this soaking, the polymeric film turned blue.

The chemical polymerization of aniline in acryl cuvettes was carried out with 3 mL of an aqueous solution of aniline (0.08 M) and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0.08 M) in 1.5 M HCl at 0 °C in the absence and presence of 500  $\mu\text{L}$  of MPBA–AuNP solution for 3 h. Thereafter, green transparent films were formed inside the walls of the cuvettes.

### 2.3. Absorption and reflectivity spectra

Absorbance measurements of a chemically prepared PANI film unmodified and modified with MPBA–AuNPs were recorded and processed using Ocean Optics Spectrasuite software. Before measurement, the various polymer-coated surfaces were equilibrated for 10 min in each measured solution.

Absorbance measurements of chemically polymerized PANI film were carried out in acryl cuvettes (path length: 10 mm). UV–vis spectra of polymer-coated cuvettes were recorded when cuvettes were filled with acidic solution at pH 2, basic solution at pH 12, with and without the addition of  $1 \times 10^{-2}$  M D-glucose. The acidic and basic solutions were obtained by adding  $1 \times 10^{-3}$  M  $\text{H}_2\text{SO}_4$  and  $1 \times 10^{-3}$  M NaOH to deionized water.

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