

## Regular Article

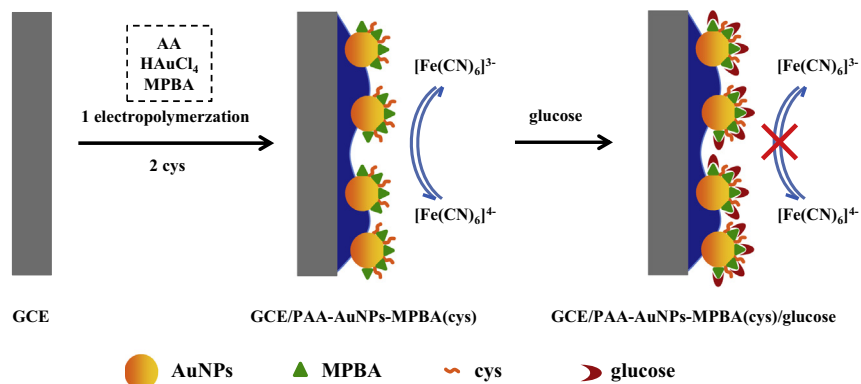
## One-pot preparation of conductive composite containing boronic acid derivative for non-enzymatic glucose detection



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The composite consisting of poly(azure A), gold nanoparticles and 4-mercaptophenylboronic acid (PAA-AuNPs-MPBA) was prepared on the glassy carbon electrode surface by using a one-pot electropolymerization protocol. The generation of poly(azure A) film, the reduction of HAuCl<sub>4</sub> and the binding of MPBA on metallic gold were simultaneously achieved in the cyclic voltammetric scan process, which was verified by scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy measurements. MPBA on the composite could capture glucose based on the specific boronic acid–diol binding and form a stable 5-membered cyclic boronate ester, which prevented the penetration and the charge transfer of the ferri-/ferrocyanide couple on the electrode surface. The peak-current change was found to be proportional to the logarithm of the glucose concentration in the range 10 nM–10 μM with a detection limit of 4 nM. The proposed sensor exhibited good immunity from interference of several physiological compounds, reliable reproducibility and satisfying stability and it was successfully used in the determination of glucose in human serum sample.

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## 1. Introduction

Conducting polymers are commonly functional  $\pi$ -conjugated materials. They are named as “synthetic metals” since their electric, electronic, magnetic and optical properties are quite similar to those of metals or semiconductors [1]. The frequently used

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conducting polymers include polyaniline [2], polypyrrole [3], polythiophene [4], organic dye-polymer [5–7], and so on. Due to their inherent charge-transport properties and biocompatibility, conducting polymers have been employed as immobilization matrixes, electron mediators and even receptors in some biosensors in which catalytic reactions or immunoreactions are involved.

Global report on diabetes issued by World Health Organization (WHO) demonstrates that alone diabetes caused 1.5 million deaths in 2012 and the global prevalence of diabetes among adults over 18 years of age has risen from 4.7% in 1980 to 8.5% in 2014 [8]. Monitoring of blood glucose concentration can play a significant role in the diagnosis and prevention of diabetes. Two types of common glucose electrochemical sensors are widely employed. One is enzymatic glucose sensor on which enzyme, such as glucose oxidase (GOx), is immobilized. It works based on the catalytic oxidation of glucose in the presence of oxygen or mediator [9–13]. The other is non-enzymatic glucose sensor on which the electro-oxidation of glucose can be achieved. Some special electrode substrates or modification materials, such as metals (Au, Pt, Ag, Pd, Ni, Cu, etc.) [14–19], metal alloys [20,21], metal oxides [22,23] and metal-complexes [24,25], are employed because they have important influence on either the sensitivity or the selectivity for glucose detection [26]. Non-enzymatic glucose sensor is extremely stable, however, it need to overcome the high overpotential of glucose oxidation.

Boronic acid and its derivatives, as small-molecule mimics of lectins, can bind reversibly with 1,2- and 1,3-diols and produce 5- and 6-membered cyclic boronic esters, respectively [27]. It has been reported that some boronic acid derivatives, such as mercaptophenylboronic acid [28], aminophenylboronic acid [29], methacrylamidophenyl boronic acid [30] and their polymer [31–33] can be immobilized on the electrode surface. The developed boronic acid-based sensors have been applied in the detection of saccharides including glucose by using voltammetric [28], amperometric [30], potentiometric [29,32,33] and electrochemical impedance spectroscopy [27,31] measurements. However, the assembly of these boronic acid derivatives requires relatively complicated procedure with multiple steps [27–30,34,35].

In the present work, the one-pot preparation of poly(azure A)-gold nanoparticles-4-mercaptophenylboronic acid composite was realized on the electrode surface based on the electropolymerization of azure A in the presence of HAuCl<sub>4</sub> and 4-mercaptophenylboronic acid. The composite-modified electrode surface was characterized with scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy, respectively. The effect of glucose on the redox reaction and charge transfer of the ferri-/ferrocyanide couple on the composite-modified electrode was investigated. The ultrasensitive and non-enzymatic electrochemical detection of glucose was performed. The linear range, detection limit, anti-interference performance, reproducibility, stability and actual application of the fabricated sensor were all evaluated.

## 2. Experimental

### 2.1. Materials and apparatus

Azure A (biological stain, BS, dye content >99%) was purchased from Xiya Chemical Industry Co., Ltd. (Linshu, China) and its stock solution (5 mM) was stored in the dark due to the sensitivity of the dye. HAuCl<sub>4</sub>, 4-mercaptophenylboronic acid (MPBA) and glucose (analytical reagent, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). L-cysteine (cys), bovine serum albumin (BSA), dopamine (DA), ascorbic acid (AA) and uric acid (UA) were used as received from Sigma-Aldrich. The buffer for

the assay was 0.1 M phosphate buffered saline (PBS), prepared by mixing stock standard solutions of Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub>. Other chemicals were of analytical reagent grade and all aqueous solutions were prepared in Milli-Q ultrapure water.

A CHI660C electrochemical workstation (CH Instruments, China) and a three-electrode electrolytic cell were used in electrochemical measurements. Glassy carbon electrode (GCE, 3 mm in diameter) acted as the working electrode. A KCl saturated calomel electrode (SCE) and a platinum plate served as the reference electrode (RE) and the counter electrode (CE), respectively. Scanning electron microscopy (SEM) analysis of the modified electrode surfaces was performed on a Nova NanoSEM 450 field-emission scan electron microscope (FEI, USA). A Nicolet Nexus 670 FTIR spectrometer (Nicolet, USA) was employed for the infrared spectral measurement. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Fisher, UK).

### 2.2. Preparation of the composite-modified electrode and measurement procedure

GCE was polished with 0.05 μm α-Al<sub>2</sub>O<sub>3</sub> power slurries until a mirror shiny surface was obtained, and then it was washed ultrasonically in acetone, HNO<sub>3</sub> (1:1, v/v), NaOH (1 M) and ultrapure water in sequence. The polished and cleaned electrode was scanned between –1.0 and 1.0 V versus SCE in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution for sufficient cycles until the reproducible cyclic voltammograms appeared. Finally the electrode was thoroughly rinsed with ultrapure water and dried under a nitrogen stream. As shown in Fig. 1, the preparation of poly(azure A)-gold nanoparticles-4-mercaptophenylboronic acid (PAA-AuNPs-MPBA) composite on GCE was initiated in N<sub>2</sub>-saturated 0.1 M pH 6.5 PBS containing 0.5 mM azure A and 0.1 M NaNO<sub>3</sub> in the presence of 2 mM HAuCl<sub>4</sub> and 5 mM MPBA by using cyclic voltammetry (CV) from –1.0 to 1.6 V for 3 cycles at a scan rate of 100 mV s<sup>–1</sup>. The composite-film was then grown on the electrode surface by the potential cycling between –0.6 and 0.5 V at 100 mV s<sup>–1</sup> for 30 cycles in the same solution. The solution used in the electropolymerization was thoroughly deoxygenated by bubbling pure nitrogen gas, and a continuous flow of nitrogen gas was maintained over the solution during the CV scan. Next, the prepared electrode, which was marked as GCE/PAA-AuNPs-MPBA, was immersed in 5 mM cys solution overnight to block the non-specific sites on the gold nanoparticles. The prepared electrode was defined as GCE/PAA-AuNPs-MPBA(cys) and it was employed to capture glucose based on the covalent binding of glucose with boric acid moieties in MPBA molecules. The CV measurements of GCE/PAA-AuNPs-MPBA(cys) in pH 6.5 PBS using the ferri-/ferrocyanide couple as the electrochemical probe before and after the addition of glucose were performed, respectively. The working electrode potential was fixed at the formal potential of the ferri-/ferrocyanide couple in electrochemical impedance spectroscopy (EIS) analyses. The impedance data were recorded in the frequency range between 1 mHz and 100 kHz with the amplitude of 5 mV. All electrochemical measurements were carried out at room temperature.

## 3. Results and discussion

### 3.1. Preparation and characterization of PAA-AuNPs-MPBA composite on the electrode surface

The MPBA-modified GCE was prepared by employing the electropolymerization of azure A in this work. The oxidation of NH<sub>2</sub> moieties in the azure A molecules and the generation of the cation

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