



Sensitive sugar detection using 4-aminophenylboronic acid modified graphene

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ABSTRACT

A sensitive electrochemical active interface for sugar sensing based on the specific boronic acid–diol binding was established. The sensing matrix was formed by stirring a suspension of graphene oxide (GO) with 4-aminophenylboronic acid (APBA). The resulting composite consists of a water insoluble precipitate of reduced graphene oxide (rGO) with APBA incorporated into the rGO matrix. Differential pulse voltammetry (DPV) on glassy carbon electrodes modified with rGO/APBA was used for the detection of fructose, mannose and glucose. The fabricated sensor exhibited a wide linear range with detection limits of 100 nM for fructose, and around 800 nM for mannose and glucose.

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1. Introduction

Diabetes has been assigned next to cancer, cardiovascular and chronic respiratory diseases as the most leading causes of death and disability. A close monitoring of blood glucose concentrations plays a significant role in the diagnosis and prevention of diabetes. Tremendous efforts have been put into the development of efficient, reliable and sensitive methods to determine blood glucose and electrochemical-based sensors have been considered as excellent analytical tools for rapid and inexpensive glucose-recognition (Park et al., 2006; Wang, 2008). The most serious problem connected with enzyme-based glucose sensors is the insufficient stability of the enzyme. The electrochemical determination of glucose concentrations without using glucose oxidase is one goal that many research teams have been trying to make come true. Initial research focused on the use of noble metals, such as mesoporous platinum (Park et al., 2003). The desire for better and cheaper electrocatalysts has resulted in the development of bimetallic systems (Bai et al., 2008; Wang et al., 2008) or in the fabrication of diamond nanowires (Luo et al., 2009) and diamond nanowires coated with nickel nanoparticles (Yang et al., 2013) for direct glucose oxidation in alkaline solutions.

A different approach in exploiting enzyme-less electrochemical sensor designs is based on the use of boronic acid compounds (Shoji and Freund, 2001; Choi et al., 2002; Takahshi and Anzai, 2005; Tiwari et al., 2010; Das et al., 2011a, 2011b; Takahshi et al., 2011). Boronic acid derivatives are important ligands for specific recognition of *cis*-diol containing molecules such as saccharides by forming five or six-membered cyclic esters in alkaline solutions, while the cyclic esters dissociate when the medium is changed to acidic pH.

Multi-walled carbon nanotubes (MWCNT) have been reported as an ideal supporting matrix for the electrocatalytic oxidation of glucose (Ye et al., 2004). Unfortunately, the electrocatalytic effect of MWCNT was observed only under basic conditions. Another carbon-based material that has received much attention in recent years is reduced graphene oxide (rGO) (Park and Ruoff, 2009; Pumera, 2010; Pumera et al., 2010; Ratinac et al., 2011). The large surface area of rGO together with its good electrical conductivity, possibility of production in bulk quantities and ease of processing have made it particularly attractive for electrochemical-based enzymatic glucose sensing (Kang et al., 2009; Shan et al., 2009; Alwarappan et al., 2010; Wu et al., 2010; Gao et al., 2011; Wang et al., 2011; Yang et al., 2011; Zeng et al., 2011; Dong et al., 2012). There are however only some reports on non-enzymatic graphene based glucose sensors using rGO (Mu et al., 2011; Kong et al., 2012; Wang et al., 2012) operated in alkaline media. Herein, we report on the fabrication of reduced graphene oxide-aminophenyl boronic acid (rGO/APBA) hybrid material which can directly detect sugars

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such as fructose, mannose or glucose with high sensitivity without the need for any enzyme using differential pulse voltammetry (DPV).

2. Material and methods

2.1. Materials

Graphite powder (< 20 μm), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), Potassium permanganate (KMnO_4), dimethylformamide (DMF), 4-aminophenylboronic acid hydrochloride, phosphate buffered saline (PBS), potassium ferrocyanide ($[\text{K}_4\text{Fe}(\text{CN})_6]$), ruthenium hexamine ($[\text{Ru}(\text{NH}_3)_6]^{3+}$), D-(+)-Glucose, ruthenium hexamine ($[\text{Ru}(\text{NH}_3)_6]^{3+}$), D-(+)-Mannose, and D-(-)-Fructose were purchased from Aldrich and used as received.

2.2. Preparation of reduced graphene oxide (rGO) modified with 4-aminophenylboronic acid (rGO/APBA)

Graphene oxide (GO) was synthesized from graphite powder by a modified Hummers' method (Hummers and Offerman, 1958) and the detailed experimental conditions are reported in (Das et al., 2011a, 2011b). To 1 mL of a homogeneous GO suspension (0.5 mg/mL) in distilled water was added 1 mL aminophenylboronic acid (10 mM in ethanol) and stirred for 12 h at 100 $^\circ\text{C}$. The resulting black precipitate was separated from the supernatant by centrifugation (20 min at 14000 rpm), washed with ethanol (three times) and water (three times), and then dried in an oven at 80 $^\circ\text{C}$ for 6 h.

2.3. Determination of sugar content in apple juice (colorimetric approach)

A standard calibration curve for fructose was generated by mixing aliquots of aqueous phenolic solution (5 wt%, 60 mL) and concentrated H_2SO_4 (900 mL) to a series of 60 mL aliquots of aqueous fructose solutions (0–200 $\mu\text{g}/\text{mL}$). After reaction for 10 min the absorption spectrum was recorded using as a blank a phenol- H_2SO_4 mixture containing only 60 mL of water. The absorbance of the solution was measured at two wavelengths: $\lambda_{\text{max}}=495$ (absorption band of fructose complex) and $\lambda_{\text{max}}=570$ nm (background) and the absorbance difference (A495–A570) was plotted against the concentration of fructose. For determining the sugar content in apple juice the sample was diluted 1050 times.

2.4. Instrumentation

2.4.1. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) experiments were performed in a PHI 5000 VersaProbe-Scanning ESCA Microprobe (ULVAC-PHI, Japan/USA) instrument. Monochromatic AlK_{α} radiation was used and the X-ray beam at an operating power of 25 W (15 kV). Photoelectron survey spectra were acquired using a hemispherical analyzer at pass energy of 117.4 eV with a 0.4 eV energy step. Core-level spectra were acquired at pass energy of 23.5 eV with a 0.1 eV energy step.

2.4.2. UV/vis measurements

Absorption spectra were recorded using a Perkin-Elmer Lambda UV-vis 950 spectrophotometer in a spectrometric quartz cuvette with an optical path of 10 mm. The wavelength range was 400–800 nm.

2.4.3. Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed using an Autolab 20 potentiostat (Eco Chimie, Utrecht, The Netherlands). The electrochemical cell consisted of a working electrode, Ag/AgCl (Bioanalytical Systems, Inc.) reference electrode, and platinum wire as counter electrode. The rGO/APBA modified GC electrodes were prepared by casting 30 μL of rGO/APBA-DMF suspension (0.5 mg/mL) onto the GC substrate followed by heating at 70 $^\circ\text{C}$ until full DMF evaporation.

3. Results and discussion

3.1. Formation and characterization of rGO/APBA nanocomposite

We (Kaminska et al., 2012a, 2012b, 2012c) and others (Xu et al., 2010) have recently shown that the direct reaction of GO with dopamine or tetrathiafulvalene (TTF) allows not only the reduction of GO to rGO in an easy manner, but results also in the simultaneous modification of the rGO nanosheets with the dopamine or tetrathiafulvalene ligand through π - π stacking interactions. Motivated by the fact that boronic acid modified electrodes have been successfully employed for the electrochemical detection of sugars, we investigate here, if 4-aminophenylboronic acid (APBA) can be used in a similar manner like dopamine or TTF for simultaneous reduction and incorporation of APBA moieties on the graphene skeleton (Scheme 1). The direct reaction of an aqueous mixture of GO (0.5 mg/mL) and APBA (5 mM) for 12 h at 100 $^\circ\text{C}$ resulted in the formation of a black water insoluble precipitate. The chemical composition of GO before and after reaction with APBA was determined by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 1). The C1s core level XPS spectrum of GO nanosheets is displayed in Fig. 1A(a) and can be deconvoluted into four components with binding energies at about 283.8, 284.7, 286.7 and 287.9 eV assigned to sp^2 -hybridized carbon, C-H/C-C, C-O and C=O species, respectively. The C/O ratio of GO is 1.73 comparable to reported data in the literature (Fellahi et al., 2011; Lia et al., 2011). After reaction of GO with APBA, XPS analysis of the resulting product indicates significant changes in the C1s core level spectrum (Fig. 1A(b)). The band at 283.9 eV due to sp^2 -hybridized carbon became predominant, suggesting the reconstitution of the graphitic network. The bands at 284.7 and 285.5 eV can be attributed to C-H/C-C/C-B and C-N of APBA, while the band at 287.3 eV is due to some remaining oxygen functionalities on the rGO. The C/O ratio increased to 3.8.

The success of the incorporation of the 4-aminophenylboronic acid derivative is in addition confirmed by the presence of B1s and N1s contributions in the XPS spectrum (Fig. 1B and C) with an atomic percentage of B1s of 4.51 and a B/N ratio of 1.1. The B1s high resolution XPs spectrum shows a band at 191.1 eV corresponding to $-\text{C}-\text{B}(\text{OH})_2$ bond (Fig. 1B) in accordance with the chemical composition of 4-aminophenylboronic acid. The N1s band of the nanocomposite (Fig. 1C(b)) can be deconvoluted into two bands at 398.2 eV and 399.7 eV with a ratio 2/1. This is rather different from the N1s band of the initial APBA (Fig. 1C(a)) where two bands at 399.1 eV and 400.96 eV (ratio=1/1.5) due to $-\text{NH}_2$ and protonated NH_3^+ groups are observed. The band at 399.7 eV of the rGO/APBA matrix is due to amine ($-\text{NH}-$, NH_2) bonds, while the lower binding energy band at 398.2 eV is most likely due to imine ($=\text{N}-$) groups, resulting from APBA oxidation and the formation of oligomeric side products. It is indeed well known that while graphene is a good electron acceptor, aniline and its derivatives is on the other hand very good electron donor (Vallés et al., 2011). As a result GO nanosheet are readily reduced by aniline at elevated temperature, accompanied by simultaneous *in situ* polymerization of aniline monomers (Xu et al., 2011).

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