Potentiometric Sensors Based on the Inductive Effect on the pKa of Poly(aniline): A Non-enzymatic Glucose Sensor

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Experimental

Reagents. 3-aminophenylboronic acid (ABA), Nafion (40 wt% alcohol-water mixed solution), sodium fluoride, D-glucose (GL), fructose (FR), and α-methyl-D-glucoside were purchased from Aldrich and used as purchased. Phosphate buffer saline (PBS) stock solution, pH 7.4, (x10 concentrated stock) was purchased from EM Science. The water that was used for all experiments was purified and deionized (18.3 mega ohm) by pure water system (Branstead, Model: Easy pure RF).

Instrumental setup. Glassy carbon electrodes (3 mm diameter) were purchased from Bioanalytical Science. The open circuit potential measurements were performed on an electrochemical workstation system (CH Instruments, model 660) connecting PC computer (Dell Optiplex GX-1). Cyclic voltammetry was performed with a potentiostat (EG&G Model: 362). In the voltammetric experiments, a three-electrode configuration was used including a platinum wire (length: 50 cm, diameter: 0.2mm) counter electrode and a saturated calomel electrode (SCE) as reference. XPS spectra were recorded with an M-Probe surface spectrometer (Surface Science Instruments). All spectra were recorded with focused and monochromatized Al $K\alpha_{1,2}$ irradiation (hv=1486.6 eV), and the X-ray beam was incident on the surface at an angle of 55° with respect to the surface normal. The analyzer was also positioned at an angle of 55° with respect to the surface normal.

Poly(aniline boronic acid) deposition. The oxidative polymerization of 3-aminophenylboronic acid was performed producing poly(aniline-3-boronic acid)(PABA) as follows: 3-aminophenylboronic acid (40 mM) and sodium fluoride (40 mM) were dissolved in 25 mL sulfuric acid aqueous solution(0.5 M) containing 5 mM Nafion (commercially available 40 wt% Nafion alcohol-water mixture solution was used); the potential of the GC electrode was scanned between 0.0 and 1.1 V vs. SCE at a scan rate of 100 mV/s; polymerization was halted when the charge passed for the reduction of the deposited polymer reached 0.34 mC. The production of the PABA layer had a deep greenish blue color similar to that obtained upon the formation of poly(aniline). After careful washing of the layer with pure water, the electrode was stored in pH 7.4 PBS buffer to settle its chemical potential.

Open circuit measurements. 25 mL of phosphate buffer saline (PBS, commercially available stock solution as 137 mM NaCl, 2.7 mM KCl, 10 mM phosphate buffer, pH 7.4) was placed in an electrochemical cell. A PABA electrode, equilibrated in PBS was placed in the cell and an open circuit measurement was made versus an SCE. The solution in the cell was stirred continuously during the measurements. Analyte was injected from a concentrated stock solution. For example, for glucose, 612.5 mg of D-glucose was dissolved in 4 mL PBS and the resulting solution was used as concentrated stock solution allowing 3.4 mM changes in concentration per 100 μL injection. Measurements were made under ambient conditions (ca.25 °C) with no strict control over temperature.

XPS of PABA

XPS was used to demonstrate that all fluoride had exchanged out of the PABA film once equilibrated in PBS. Figure 1s shows the survey scan of a film. The absence of a fluorine 1s peak at ~697 eV indicates that fluoride does not remain in the film.

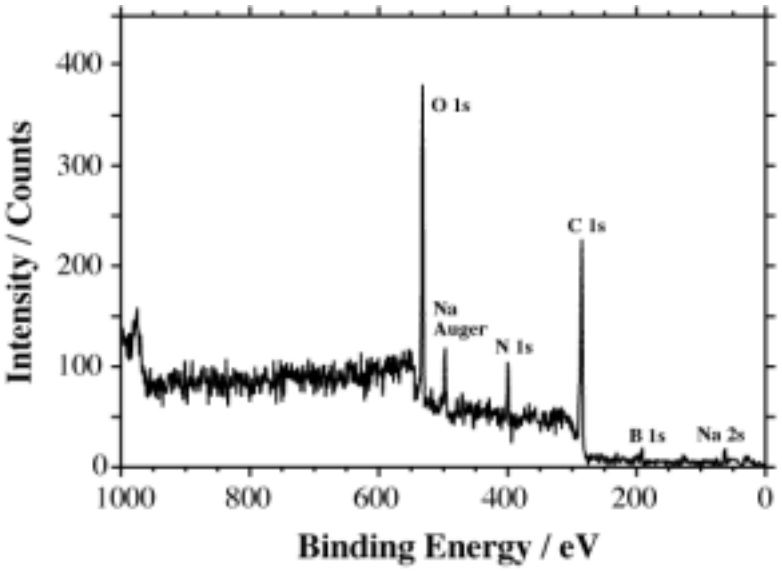

Figure 1s. XPS survey scan of electrochemically generated poly(aniline boronic acid) film on ITO.

Poly(aniline)/poly(vinylphenylboronic acid) response

An electrode consisting of a thin film of polyaniline coated with poly(vinylphenylboroinic acid) was exposed to fructose. Transient responses associated with Scheme 1 in the manuscript are seen in Figure 2s showing that the response of poly(aniline) to the pH change was quickly equilibrated with the bulk solution.

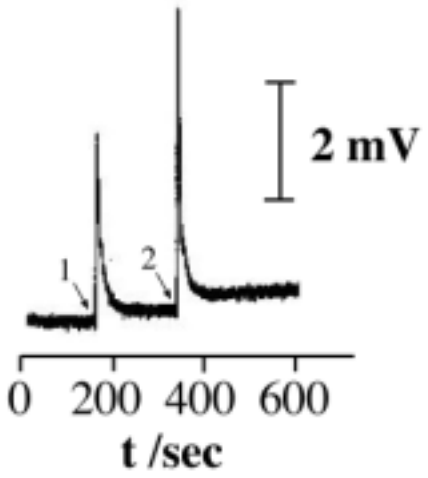

Figure 2s. D-Fructose response curve of poly(vinylphenylboronic acid)(containing 10 wt% of poly(hydroxyethyl methacrylate) coated poly(aniline) electrode in pH 7.4 PBS as a function of time. Additions of fructose resulted in 1) 3.4 and 2) 6.8 mM increments in concentration.