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ARTICLE TYPE

Poly (3-amino phenyl boronicacid) functionalized carbon nanotubes based chemiresistive sensors for detection of sugars

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Polyanilineboronic acid (PABA) functionalized single walled carbon nanotube (SWNT) non enzymatic sensor was developed for detection of saccharides. The work involved electrochemical polymerization of 3-amino phenyl boronic acid (APBA) in presence of fluoride on the surface of SWNTs and their subsequent evaluation as chemiresistive sensors towards detection of D-fructose and D-glucose. By varying the sensor's synthesis conditions by charge controlled electropolymerization, the sensing performance was systematically optimized. Electrical characterization in terms of change in resistance, cyclic voltammetry confirmed the electrochemical deposition of PABA coating on SWNTs. The optimized sensors showed sensing response over a wide dynamic range of concentrations and a limit of detection of 2.92 mM for D-fructose and 3.46 mM for D-glucose. The hybrid sensors could be regenerated on the basis of the reversible nature of the binding between PABA and 1, 2 or 1, 3-diols at lower values of pH.

Introduction

Detection of saccharides is of prime importance in biomedical diagnostics and quality control in food industries. The conventional approach mostly employs techniques that use enzymatic assays to detect and quantify saccharides[1, 2]. However, the gradual degradation of their enzymatic activity calls for timely replenishment of the enzyme thereby limiting the lifetime and stability of these sensors. Furthermore, their need for frequent calibration, temperature and oxygen dependence [3, 4] limits their potential application pool and makes them unsuitable for easier and continuous monitoring of glucose concentrations.

Polyaniline is a popular conducting polymer in the field of molecular electronics owing to its attractive properties like low cost, facile nature of preparation, stability, easy processibility and high conductivity [5]. The ability to tune its electrical properties by reversible doping and undoping of the polymer backbone via chemical manipulation along with its well-behaved electrochemistry makes it an ideal sensing material. Numerous accounts in literature have reported the synthesis of functionalized polyaniline [6, 7]. Boronic acid substituted polyaniline synthesis route [8, 9] proves to be of great interest in the detection of saccharides [10-14]. Complexation of saccharides (as well as alkyl and aromatic diols) with aromatic boronic acids produces a stable boronate anion and a proton in the pH range 6-10 thus opening up possibilities of numerous electrochemical approaches to detect sugars based on saccharide-boronic acid functionality interactions [15, 16].

Single walled carbon nanotube (SWNT)-conducting polymer hybrid structures have provided an ideal platform for building reliable and highly sensitive sensors for a wide array of sensing applications [17]. Dai and coworkers synthesized and demonstrated conducting polymer-carbon nanotube (CP-NT) coaxial nanowires for amperometric detection of glucose [18].Apart from providing mechanical stability [19] and enhanced electrical conductivity in terms of efficient transduction [20] to and from the conducting polymer layer, the large surface area of the SWNTs leads to enhanced sensitivity towards detecting the analyte.

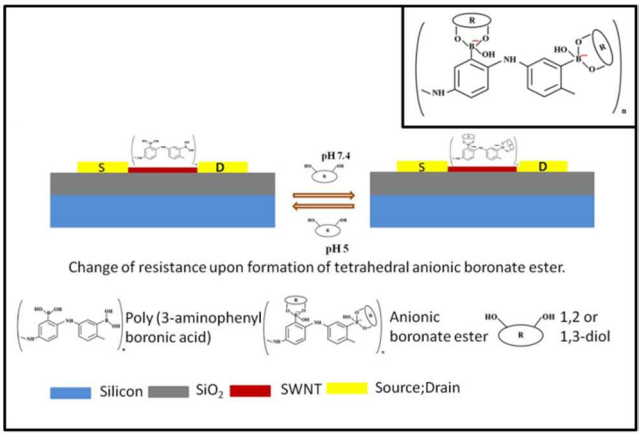

Fig. 1. Schematics of the chemiresistive PABA coated SWNT sensor.Structure of the anionic boronate ester (inset).

In this work, we have developed and demonstrated an enzyme-free PABA (poly 3-amino phenyl boronic acid) coated SWNT based sensor for detection of monosaccharides in solution. Our key strategy involves electropolymerization of PABA on the surface of SWNTs in a simplistic, reproducible and controllable manner at room temperature. By varying the electrodeposition time, PABA film of controlled thickness was developed over the SWNT surface.When exposed to sugar, the boronic acid-saccharide complexation brings about a change in the net electrical charge of the PABA coated SWNT sensor thereby resulting in a change of the overall conductance of the sensor. Unlike the enzymatic assays which consume the analyte in course of detection, this approach utilizes the pH dependant reversible nature of boronic acid-saccharide complexation wherein the sugar in released back to the solution at lower values of pH. This approach could be extended in the creation of large density of reproducible saccharide sensors that are easy to fabricate, cost effective and easily integrable for an all-electronic readout format.

Experimental

Materials

Carboxylated single-walled nanotubes (SWNT-COOH, 80–90% purity and 1.5 to 3 atomic %–COOH content) were procured commercially from Carbon Solution Inc (Riverside, CA, USA). 3-Aminophenylboronic acid hydrochloride salt 98% (3-APBA) was purchased from Sigma Aldrich (St Louis, Mo, USA). D-Fructose, D-Glucose were purchased from Alfa Aesar. Uric acid, Ascorbic acid and citric acid were purchased from Fisher Scientific. All buffer solutions were prepared in deionized water obtained by purifying distilled water through a Milli-Q plus (Millipore Inc) ultrapure water system.

Sensor design and fabrication

Microelectrodes Fabrication: An array of 16 source-drain gold electrodes pairs with 3 μm channel length was defined on SiO_2/Si substrate using standard photolithography technique as reported previously [21]. In brief, source-drain electrode patterns are predefined on a SiO_2 (300 nm)/Si substrate. at a distance of 3 μm.

DEP Deposition of SWNTs

SWNTs suspension was prepared as detailed in the supplementary material. A 0.1 μL drop of SWNTs suspension was placed between the electrodes using micropipette followed by applying an ac electric field of 3V p-p ($0.36V_{RMS}$) at 4 MHz frequency across the electrodes from 2 to 10 s as reported earlier [22]. The aligned SWNTs were then annealed at 300 ^{0} C for 1 hour in an atmosphere of 5% hydrogen and 95% nitrogen gas. This improved the contact resistance between the electrodes and the SWNTs and helped to remove DMF residues accumulated during the process of alignment.

Electropolymerization of PABA

Poly 3-amino phenyl boronic acid (PABA) was deposited electrochemically onto the aligned SWNTs electrodes. A three electrode configuration where the aligned SWNTs network with the gold electrodes, a Pt wire, and chlorinated silver wire (Ag/AgCl wire) were employed as working, counter, and reference electrodes, respectively was constituted. The monomer solution containing 40 mM 3-APBA and 300 mm NaF was prepared in the undiluted 0.1 M phosphate buffer saline (10X PBS) stock solution and under conditions where the pH was reduced to 5.0 by addition of 0.5 M HCl. A 0.1 μL drop of the electrolyte was placed on top of the SWNT networks followed by potentiostatic electropolymerization at 0.7 V (vs. Ag/AgCl). After electrodeposition, the sensors were rinsed with deionized water followed with PBS at pH 7.4 and then kept in PBS solution overnight to allow the electrochemical potential to stabilize.

Apparatus for device characterization and sensing

Electrical characterization was performed using a potentiostat (Model # 1202A, CHInstruments, Inc., TX, USA) in terms of the resistance of the sensors by measuring the current versus voltage response of the sensors. The initial or baseline resistance of the sensor was recorded by incubating the SWNT coated PABA device with a 20 ml of PBS and sweeping the voltage from -1 V to +1 V. For the purpose of better precision of measurements, the slope of the I-V was measured in a region near to the zero voltage preferably +/- 100 mV. Upon exposure to different concentrations of D-glucose and D-fructose solutions made in PBS, change in resistance was measured after incubating the sensor for 5 mins followed by washing with PBS twice.

Results and Discussions

Functionalization of SWNTs by aromatic boronic acid can be performed either by covalent attachment of APBA or non-covalent attachment routes [23]. In this work, non-covalent approach of attachment by electropolymerization of APBA in the presence of fluoride is performed. The complexation of fluoride with boronic acid leads to the formation of a negatively charged species [24, 25]. As discussed in literature fluoride catalyzed reaction results in poly (aminophenylboronic acid) to have a self-doped structure under acidic conditions[8]. The cyclic voltammogram (CV) obtained for 3-aminophenylboronic acid in the presence of 40 mM fluoride and 300 mM NaF in 10X PBS adjusted to pH 5.0 is provided in the supplementary material (Fig. S1). It has been reported earlier that increasing the concentration of sodium fluoride results in significant negative shifts in the oxidation potential, thereby enhancing polymerization rates with the polymer film thus formed exhibiting better stability and adhesion properties [13]. This high concentration of fluoride resulted in sustained polymerization and significant and continuous polymer growth. Thus, a self-doped polymer was produced on the surface of SWNT along with the formation of a tetrahedral anionic boronatespecies [26].

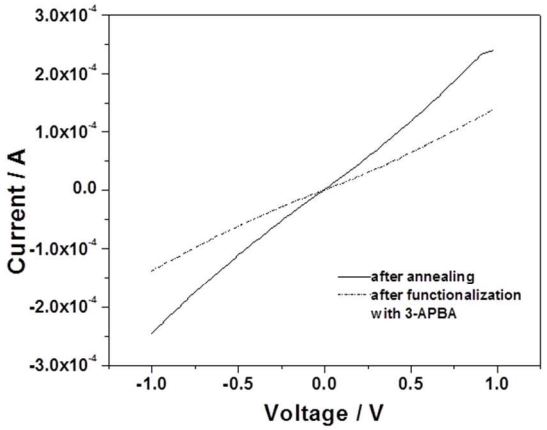

Fig. 2. I_{DS} vs. V_{DS} of AC dielectrophoretically aligned SWNTs network before and after electropolymerization of 3-APBA.

Electrical characterization in terms of I-V characteristics after electropolymerization of PABA on theSWNT surface shows that the PABA coated devices exhibited higher resistance as compared to bare SWNT devices (Fig. 2). This can be attributed to the fact that upon electropolymerization of 3-APBA, the amino functional groups which are protonated and therefore positively charged, reduce the overall hole concentration in p-type semiconducting SWNTs in a similar manner as applying a positive potential to the gate reduces the conductance in a p-type semiconductor channel [27]. As an additional confirmation of successful electropolymerization, CV was performed on the coated SWNT devices in the monomer solution as shown in Fig. 3 which showed peaks corresponding to PABA.In order to obtain consistent sensing results, devices which had resistance in the range of 20 KΩ to 30 kΩ after annealing were electropolymerized. Charge controlled electropolymerization of PABA was carried out and the sensing behavior towards a definite concentration (in this case 10 mM) of D-fructose was

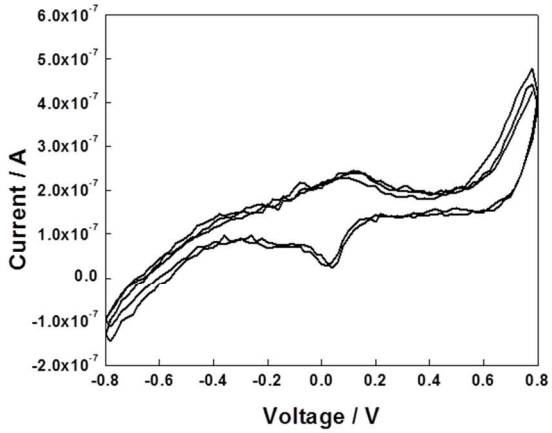

Fig. 3. CV of PABA coated SWNT device in 10X PBS plus 300 mMNaF; pH 5.0. Scan rate: 100 mV s^{-1}

recorded as shown in Fig. 4. Optimal charge for electropolymerization was determined to be around 25 μC i.e., devices electropolymerized at 25 μC yielded better sensitivity than the ones electropolymerized at charges lower/ higher than it. A suitable explanation to this phenomenon could be the difference in the thickness of the PABA coatings on the SWNTs on the basis of charge. Charge controlled electropolymerization at lower charges resulted in a thinner coating of PABA with lesser number of BA receptors which weren't adequate enough to bind with all the cis-diol groups present in the analyte. On the other hand, higher charges resulted in thicker coatings thereby offering some hindrance in the efficient charge transfer from the polymerized coating onto the SWNTs when the BA receptors attached with the cis-diol groups of the saccharide to form tetrahedral anionic cyclic esters.

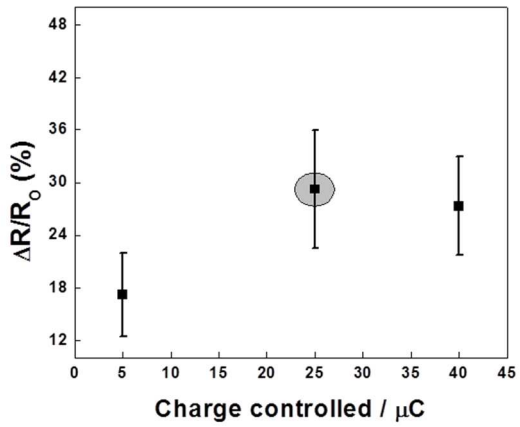

Fig.4. Response of PABA coated SWNT sensors electropolymerized at 5, 25 and 40 μC charge towards 10 mM D-fructose.

Upon exposed to saccharide, the presence of fluoride enhances the complexation of saccharides with the BA receptors by disrupting any B-N interactions and facilitates the formation of the anionic ester [25]. This ester formation leads to an increase in

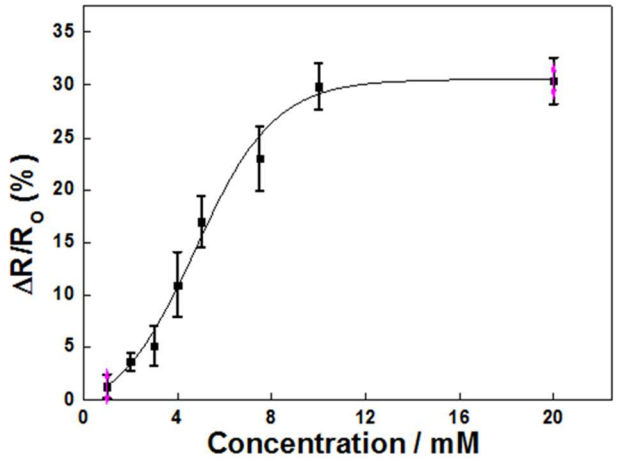

Fig. 5.Response of the PABA coated SWNT sensors towards D-fructose at pH of 7.4 with the corresponding sigmoidal fit.

relative negative charge on the surface of the p-type SWNTchannel thereby resulting in an increase in the resistance of the sensor. Thus the extent of binding event is detected and quantified by the PABA coated SWNT chemiresistive sensor. Fig. 5 and Fig. 6 show the nanosensor calibration plot for different concentrations of D-fructose and D-glucose, respectively. The sensors showed excellent intra- and inter-batch reproducibility with data points obtained from a total of 8-9 electrodes prepared in two batches. Each D-glucose/D-fructose concentration was measured on these 8-9 devices to ensure reproducibility.

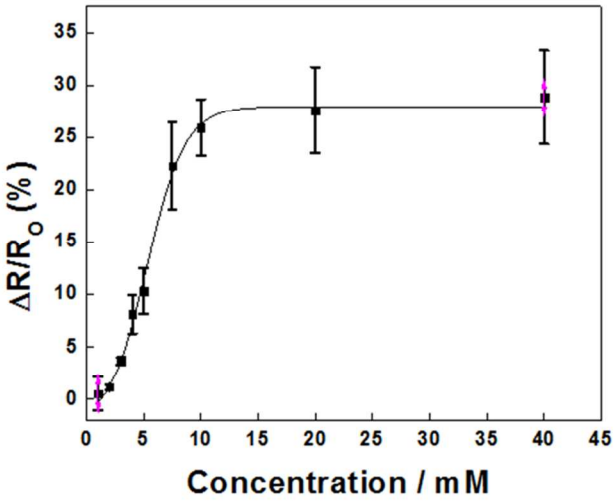

Fig. 6.Response of the PABA coated SWNT sensors towards D-glucose at pH of 7.4 with the corresponding sigmoidal fit.

The response of the sensor is measured in terms of its relative change in resistance, expressed in percentage, when exposed to a particular concentration of the saccharide. The sensor exhibited a fast response time of 4 min,a sensitivity (measured as the slope in the linear region) of 3.34×10^{-2} mg^{-1} l for D-fructose and 3.1×10^{-2} mg^{-1} l for D-glucose respectively. The estimated limit of detection (LOD) given by LOD = 3 SD/ m where m is the slope of the linear part of the calibration curve and SD is standard deviation of the blank measurement was found out to be 2.92 mM

and 3.46 mM for D-fructose and D-glucose respectively. The best fit to the calibration curves yieldsthe "S-shaped" sigmoidal profile. Sigmoidal curves for ligand-receptor bindingresulting in complex formation are observed in cases wherein low doses of ligand illicit small responses and high doses plateau at maximal (100%) complex formation/response.In such cases, both the dissociation constant (K_d) and the receptor concentration affect the curve's behaviour [28].In case of PABA coated SWNT sensor, sensing can be explained by the progressive saturation of the exposed binding sites of the functionalized PABA. Beyond saturation, the sensor shows no significant change with higher sugar concentration.The response curvesfor D-fructose and D-glucose with the corresponding sigmoidal fit exhibited correlation coefficient (R^2) of 0.9905 and 0.9930, respectively.The curves are mathematically defined by equations as detailed in the supplementary material. The degree of complexation depends on the binding constants (k) between 3-APBA and the monosaccharides. It has been found that fructose shows higher affinity to 3-APBA for all pH values owing to its higher binding constant (D-fructose > D-glucose > R-methyl-D-glucoside) [29]. This explains the higher sensitivity of the sensors towards D-fructose as compared to D-glucose.

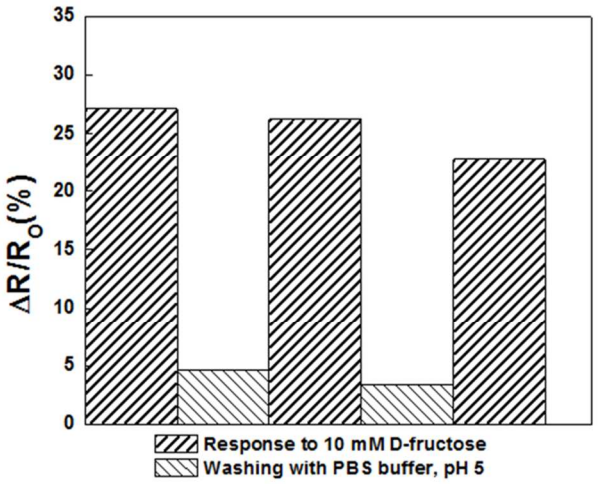

Fig. 7. Response of the PABA coated SWNT sensors towards 10 mM D-fructose and subsequent regeneration by washing with buffer at pH of 5.

Owing to the reversible nature of the binding between the BA receptors and the sugar media [10, 11, 14], the sensors could be regenerated by incubating them in buffer of pH 5 for 10 min as shown in Fig. 7. Lowering the pH results in the disruption of the binding between the BA moieties and the sugar thus releasingthe sugar back to the medium. Following the regeneration, for every subsequent use in detecting sugar at physiological pH, the sensor was washed twice and incubated for 10 min in PBS buffer of pH 7.4. The as-renewed sensor retained 81.4% of its initial conductivity after 2 regeneration cycles.

To investigate the effects of interference arising from redox-active species such as Ascorbic acid (AA), Uric acid (UA) and Citric acid (CA) that commonly coexist in food samples and beverages, physiological concentration levels of these samples were tested for their response to the PABA coated SWNT sensors. As seen in Fig. 8, while a certain higher concentration of ascorbic acid showed a higher response, the effects of other samples were found to be negligible. This response of AA can be attributed to its binding ability through its planar diol and to the fouling effect caused by the adsorption of the oxidized product of

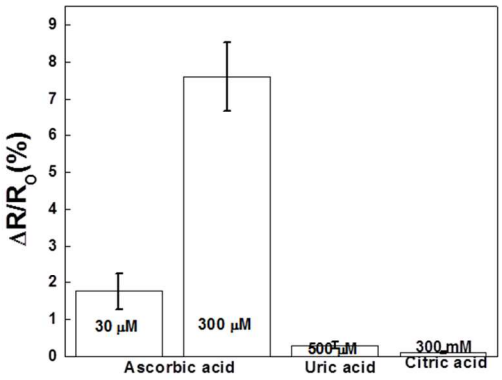

Fig. 8. Response of PABA coated SWNT sensors towards 30 μM ascorbic acid, 300 μM ascorbic acid, 500 μM uric acid and 300 mM citric acid.

the ascorbic acid (AA) on the gold electrode surface [30, 31]. One possible way to eliminate the interference effects of AA is to block the gold electrode with mercaptohexanol(MCH) for 30 min in buffer. Thus, the sensors can be used to selectively detect a monosaccharide like glucose or fructose while providing high immunity against other common interferences.

There have been several reports of boronic acid-modified CNT based electrochemical sensors for the detection of diol containing biomolecules such as dopamine [32,33] and D-glucose [34, 35].While the FET based detection technique [34]involves dropcasting high density of CNTs (150-300 nanotubes in the channel) for sensor fabrication and covalent functionalization of pyrene-1-boronic acid on CNT which results in higher sensitivity and lower LOD of 300 nM, our approach involves alignment of CNTs across the source-drain electrodes using dielectrophoresis and noncovalent attachment of PABA by electropolymerization on CNT. Our approach is advantageous as it allows for the precise manipulation of the baseline resistance of the sensor by deposition of a single or a bundle of SWNTs of controlled density between the electrodes thereby ensuring repeatability. In addition, sensor recovery in the former case is slow. When compared to the work of Vlandas et al. [35] which report a sensitivity of 5 nA/mM and LOD of 5 mM for D-glucose using impedance based technique, our sensors exhibit a better LOD of 2.92 mM and 3.46 mM for D-fructose and D-glucose, respectively. In addition, this current work employs chemiresistive mode of sensor configuration which can be easily integrated for an all-electronic readout signal for real time applications.

Conclusions

In summary, a simple, cost effective and enzyme-free approach of detection of saccharides in solution using PABA coated SWNT sensor was developed. Negligible interference from analytes like uric acid and citric acid and relatively small influence of ascorbic acid was observed while investigating the target specificity of the sensors during glucose detection. The reversible nature of the reaction between 3-amino phenyl boronic acid with 1, 2 or 1, 3 diols enables the release of sugar back to the medium at lower values of pH, thus providing a simpler, faster and regenerative way for detecting saccharides in solution. Due to the site-specific functionalization strategy of electropolymerization, it is foreseeable that a synthetic molecular receptor sensor array system can be constituted with each individual entity designed for specific analyte detection. This could lead to the development of cost effective and highly efficient lab-on-a-chip configurations.

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Notes and references

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