STRETCHABLE GLUCOSE SENSOR VIA CONJUGATED POLYMER CONFORMALLY-COATED CNT ELECTRODES PARTIALLY EMBEDDED IN PDMS

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ABSTRACT

This paper presents a stretchable glucose sensor composed of dodecylbenzenesulfonate-doped polypyrrole (PPy(DBS))-coated vertically aligned carbon nanotube (VACNT) forests partially embedded in a polydimethylsiloxane (PDMS) substrate. VACNTs are grown via chemical vapor deposition (CVD) and transferred onto partially cured PDMS. A conformal PPy(DBS) layer is electropolymerized on the nanotubes to create PPy(DBS)-coated VACNTs. Next, dip-coating is performed in glucose oxidase (GOx) solution to immobilize GOx with glutaraldehyde (GA) as a crosslinking agent onto the PPy(DBS) surface. The PDMS/CNT/PPy(DBS)/GOx is exposed to varying glucose concentrations to measure its amperometric response. The sensor exhibits a sensitivity of 10 mA cm^{-2} M^{-1}, a linear range of 0.1 mM to 12 mM, and a response time shorter than 5 seconds. Strain is applied to the sensor device, demonstrating its stable sensing function up to 75% strain and with coefficients of determination large than 0.975.

KEYWORDS

Flexible electrode, glucose sensor, electrochemical sensing, carbon nanotubes, polypyrrole

INTRODUCTION

Carbon nanotube (CNT) based electrodes are suitable for diverse biosensing applications owing to their high performance, inherent miniaturization, and low cost [1], [2]. Incorporating sensing materials with flexible and stretchy materials enables sensors to impact a wide range of applications, including electronic skins [3], smart sensor bandages [4], and wearable medical devices [5]. The wearable or skin-attachable flexible sensors can be subjected to various lateral strains via stretching. Therefore, these sensors need to be capable of accommodating various mechanical disturbances such as large bending, twisting, and stretching. Wearable or skin-attachable can be subjected to various lateral strains and need to be capable of accommodating various mechanical disturbances such as large bending, twisting, and stretching. To achieve flexibility, flexible electrodes are often synthesized with elastomeric polymer substrates, including polyimide, polydimethylsiloxane (PDMS), poly (methyl methacrylate) (PMMA), and polyethylene (PE). To achieve conductive transducer functionality, flexible substrates are conventionally deposited with conductive metal thin films, including Au, Ag, and Pt [6]–[8]. Fabrication of these thin metal films on flexible substrates has been demonstrated via established MEMS techniques, such as thermal evaporation, electron beam evaporation, sputtering, and inkjet printing. Upon application of sufficient mechanical deformation, however, metal thin films can lead to crack propagation and/or delamination from the underlying flexible substrate, causing inconsistent readings and premature device failure.

In attempts to bypass these issues, novel strategies are being pursued to combine conductive materials that can undergo strain on par with the capability of their underlying flexible substrates. Owing to their remarkably superior carrier mobility, stability, inherent miniaturization, and outstanding mechanical flexibility, CNTs are promising nanomaterials for flexible or stretchable microelectronics [9]. A highly conductive network is formed from the combined high conductivity of individual nanotubes as observed by forests of vertically aligned CNTs (VACNTs). In contrast, the charge carrier transport is limited by the large intertube electrical resistance caused by the intrinsic charge barriers at tube–tube junctions [10]. For perspective, nanotube film conductivity is reported up to 6000 S cm^{-1}, which is three orders of magnitude lower than the conductivity of a single nanotube [11]. For fabrication of CNT-based flexible electrodes, CNTs are usually deposited or embedded onto flexible or stretchable elastomer polymer substrates such as Polyethylene terephthalate (PET), polycarbonate (PC), or Polydimethylsiloxane (PDMS) [12], [13]. CNT-based flexible electrodes on elastomeric substrates have demonstrated high flexibility, limited only by the cohesive fracture of elastomeric substrates [14]–[16]. We previously demonstrated a flexible electrode design of VACNTs embedded in PDMS as a template that has been extended towards applications of energy storage [17] and pressure sensing [18]. In addition, a conjugated polymer, polypyrrole (PPy), acts as an anti-interference and anti-fouling barrier for glucose sensors [19]–[21]. Due to their synergistic properties, many efforts have been pursued to develop PPy and CNT in glucose sensors; however, current literature does not report their use in high strain applications, such as required by flexible sensors that undergo mechanical deformations in wearable or implantable electronics.

To this end, we adapt the flexible electrode composed of VACNTs embedded in PDMS into a glucose sensor, with PPy(DBS) conformally deposited on individual CNTs as an adherent film with the ease of incorporating glucose oxidase (GOx). We demonstrate a reliable electrochemical performance under strains up to 75% and correlation coefficients greater than 0.976. A wide linear range of 0.1 mM to 12 mM and sensitivity of 10 mA cm^{-2} M^{-1} is achieved, in addition to a response time of shorter than 5 seconds, indicating its potential use for continuous monitoring of physiological fluids with flexible application in wearable sensor applications.

FABRICATION

Figure 1 illustrates the fabrication process of the stretchable platform composed of vertically aligned carbon nanotubes (VACNTs) grown via chemical vapor deposition (CVD) embedded onto suspended polydimethylsiloxane (PDMS).

The PDMS/CNT electrode was reported in our previous work [17], [18]. Atmospheric pressure chemical vapor deposition (APCVD) in a 4-inch diameter quarts tube was pursued to deposit VACNT forests on Si/SiO2, with layers of Al and Fe (5 nm and 3 nm, respectively) deposited via physical vapor deposition (PVD) to serve as a solid catalyst. The furnace temperature was increased from atmosphere to a 750°C growth temperature with Ar gas flow at a gas flow rate of 500 sccm. At 750°C, the temperature was held constant with introduction of H_2 and C_2H_4 gas flows of 60 sccm and 100 sccm, respectively, for 15 minutes. The chamber was then rapidly cooled to ambient temperature with only Ar gas flow, resulting in VACNTs.

The as-grown VACNTs were transferred onto PDMS that was synthesized from 10:1 ratio of base to curing agent (Sylgard 184 Silicone Elastomer, Dow Corning). First, the PDMS was dispensed onto a glass slide and heated on a hot plate at 65°C to achieve a

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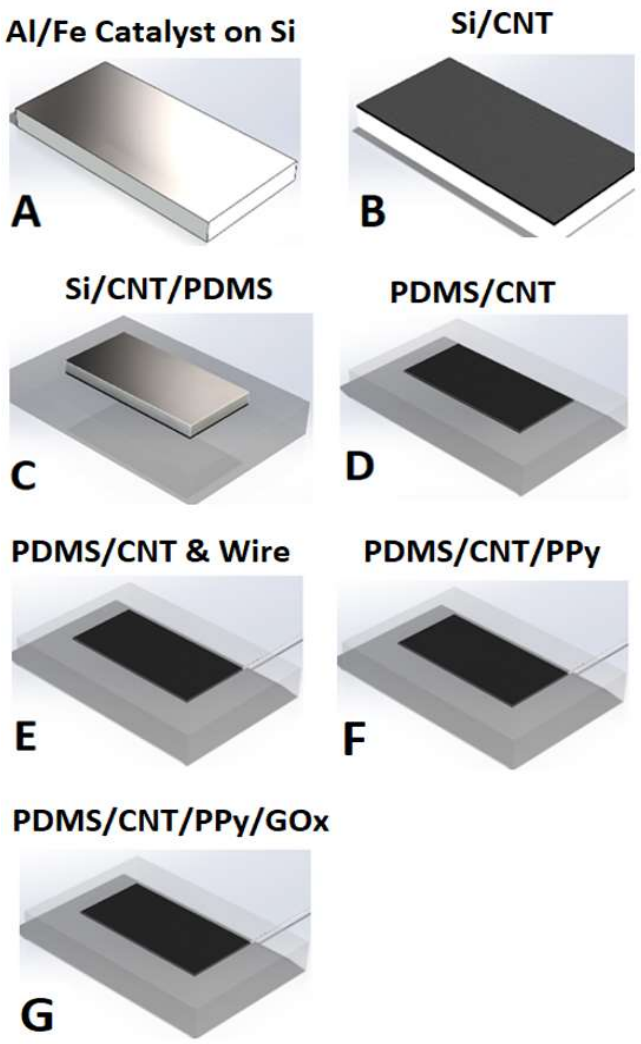

Figure 1: Illustration of the fabrication process: (a) PVD of Al/Fe catalyst onto silicon Si, (b) CVD of CNT forests, (c) CNT transfer onto partially cured PDMS, (d) Si removal after PDMS is fully cured, (e) Wiring from the PDMS/CNT electrode to potentiostat, (f) PPy(DBS) electropolymerization onto CNTs, (g) Electrode dipcoating into solutions of GA and GOx.

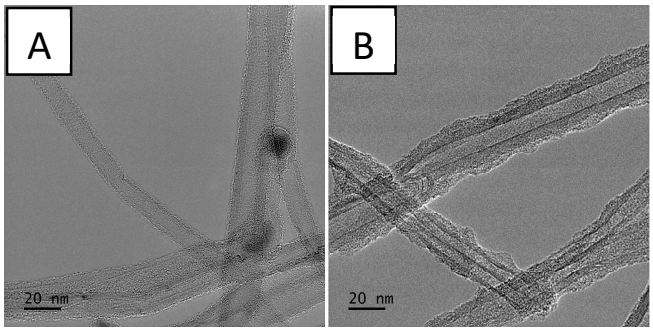

Figure 2: TEM images of: (a) bare CNT, and (b) CNT/PPy(DBS)

partially cured PDMS phase after approximately 30 minutes. The VACNT was placed face down onto the partially cured PDMS surface to fully wet the tips, and the PDMS was left in ambient condition for 12 h to complete the curing process, resulting in VACNT anchored into fully cured PDMS with exposed ends. Due to the strong bonding between CNTs and PDMS, the Si substrate was removed with ease and the exposed CNTs were vertically aligned and interwoven, enabling charge transfer as a flexible conductive electrode.

The PDMS/CNT electrode was conformally coated with PPy(DBS) via electropolymerization, which occurred in a solution consisting of 1 mL pyrrole monomer (Sigma-Aldrich, reagent grade, 98%) and 150 mL of 0.1 M NaDBS (Sigma-Aldrich, technical grade) and the PDMS/CNT acts as the working electrode. An Au-coated SiO_2 substrate was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Voltage of 0.7 V versus SCE was applied to the working electrolyte to achieve a PPy(DBS) coating with a surface charge density of 50 mC cm^{-2}. The PDMS/CNT/PPy(DBS) was rinsed thoroughly with water and allowed to dry overnight. The conformal PPy(DBS) layers on individual CNTs are shown in Figure 2.

The PDMS/CNT/PPy(DBS) was first dipped in 0.25 wt.% glutaraldehyde (GA) solution as a crosslinking agent for the immobilization of GOx. The dip-coating was achieved in 1.5 hours at room temperature, and then the PDMS/CNT/PPy(DBS) was washed 2-3 times with 0.1 M potassium phosphate buffer. Next, the sample was dipped into a solution of GOx (2 mg/mL) in 0.1 M potassium buffer (pH 7) for 2 hours at 4°C, followed by washing 2-3 times with 0.1 M potassium phosphate buffer.

CHARACTERIZATION

For imaging of CNT and CNT/PPy(DBS), transmission electrode microscopy (TEM) was used. A potentiostat (236A, Princeton Applied Research, Oak Ridge, TN) was used to measure the current response of the sensors with an applied voltage of 0.65 V. Various concentrations of glucose solution were added into a phosphate buffer solution using a syringe for concentration-dependent sensing. Experiments were performed with as-grown PDMS/CNT (without PPy(DBS), PDMS/CNT/PPy(DBS), and PPy(DBS) film coating on flat Au-coated Si/SiO_2. The above procedures were pursued to fabricate each sample, in addition to GA and GOx immobilization via dip coating. Each sample acted as a working electrode with a CNT counter electrode and an Ag/AgCl reference electrode, all inserted into 20 mL of 0.1 M phosphate buffer (pH 7). A constant voltage of 0.65 V was applied and current changes were observed with the addition of glucose solution at intervals of 50 s. For the application of strain, a clamping device was used to apply 15%, 30%, 45%, 60%, and 75% strains. A singled PDMS substrate containing CNT as counter electrode and CNT/PPy(DBS)/GOx as working electrode space apart several mm was used for testing with an Ag/AgCl wire reference electrode. 2 mL of 0.1 M phosphate buffer solution was placed centrally on the

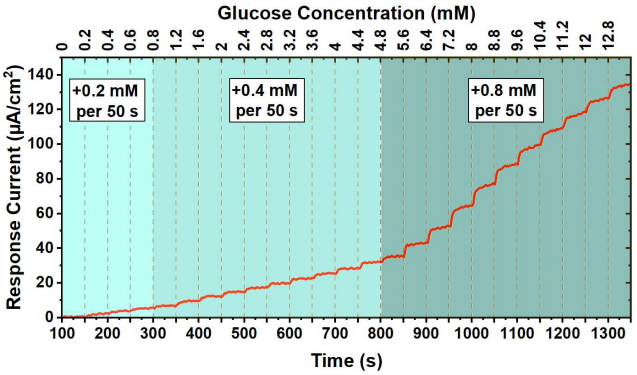

Figure 3: Current response of the fabricated biosensor upon successive addition of glucose at 50 second intervals, without application of strain.

sensor, and successive additions of glucose were added to the solution to observe glucose concentration-dependent current changes.

RESULTS & DISCUSSION

The fabricated electrode was dip-coated into solutions of glutaraldehyde (GA) and glucose oxidase (GOx) to form the glucose-sensitive layer. Alternative sensing can be accomplished such as through the use of immobilization of other enzymes. The biosensor was exposed to iterative concentrations of glucose, and GOx reacts in the presence of glucose, resulting in a concentration-dependent change of measurable current, as shown in Figure 3. The amount of glucose can be determined by measuring the current produced by the following two-step reaction:

$$Glucose + O_2 \xrightarrow{GOx} Gluconic\ acid + H_2O_2 \quad (1)$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (2)$$

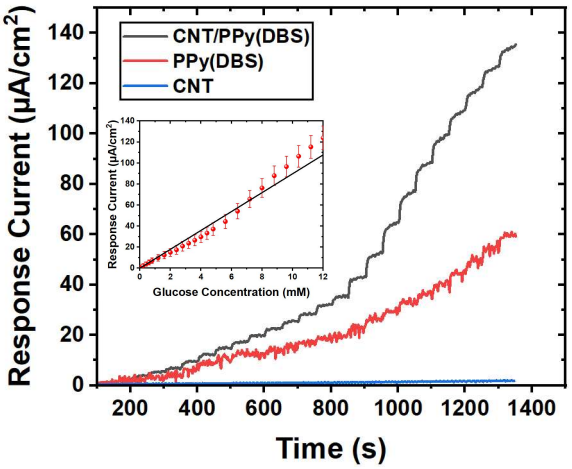

Figure 4: Current response of PPy(DBS)-coated CNTs, PPy(DBS), and CNTs upon successive addition of glucose; inset shows CNT/PPy(DBS) linear calibration curve between the current and the glucose concentration.

Sensitivity of ~10 mA cm^{-2} M^{-1} and a wide linear range WEre observed with glucose concentrations as low as 0.1 mM to 12 mM. The combination of PPy(DBS) coated on CNTs resulted in improved sensing than either material independently with a linear calibration curve between the current and the glucose concentration, as shown in Figure 4. CNTs forests offer high conductivity, commonly ranging from 7 to 14 S cm^{-1} along with the array at 300 K [12], in addition to geometric favorability of high specific surface area. Conformal coating of PPy(DBS) onto individual CNT surfaces results in increased reaction sites, resulting in at least 4x higher sensitivity than observed with independent PPy(DBS) films. The current response upon successive addition of 0.8 mM of glucose under strain shown in Figure 5 demonstrates the use of the sensor for wearable applications which undergo strain. Reliable electrochemical performance under various strains (i.e., stretching up to 75%) was demonstrated with correlation coefficients greater than 0.972, indicating a reliable linear sensing capability of glucose concentrations with strain up to 75%. The response time of shorter than 5 s enables the sensor for continuous monitoring systems [22], [23].

The flexible biosensor can be subjected to various lateral strains via stretching, while providing reliable electrochemical sensing of biomarkers on a patient's skin. We have developed CNT-based sensing electrodes on flexible substrates that exhibit reliable and stable glucose-sensing under stretching up to 75%. Skin-attachable devices for continuous monitoring of patients will enable potential applications for smart sensor bandages, critical wound monitoring, and glucose detection for diabetes.

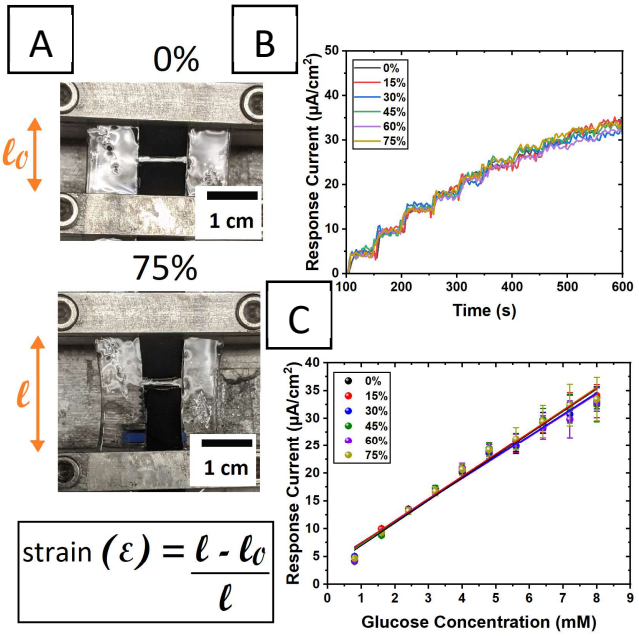

Figure 5: (a) Photographs showing the sensor under 0% and 75% strain, (b) current response upon successive addition of 0.8 mM of glucose, under strain, and (c) linear calibration curves between the current and the glucose concentration

CONCLUSIONS

This paper demonstrates a stretchable glucose sensor composed of PDMS/CNT/PPy(DBS)/GOx. The PDMS substrate enables the application of strain, and VACNTs embedded into the partially cured PDMS allowed the exposed individual CNTs to interconnect, enabling electron transfer as an electrode. Individual CNTs were coated with a conformal coating of PPy(DBS), retaining the high effective surface area of VACNTs forests and greater concentration of reactions sites towards higher sensitivity. The glucose sensor was exposed to iterative glucose concentrations to demonstrate its use as a flexible glucose sensor. A response time of shorter than 5 seconds is observed, enabling the use of this sensor for continuous monitoring. A linear range of 0.1 mM and up to 12 mM is observed with a highly linear response trend and sensitivity of 10 mA cm^{-2} M^{-1}. Applications of strain were introduced to demonstrate the use of this sensor for stretchable sensing applications up to 75% with stable and reliable sensing. Each strain application shown demonstrated a coefficient of determination greater than 0.976. Stretchable biosensors composed of PDMS/CNT/PPy(DBS) can be used for the flexible sensing of alternative electrochemical species, as demonstrated with this proof of concept with glucose oxidase and glucose. The capability of stretchability with electrochemical sensing may ultimately lead to the sensing of biomarkers in a patient's physiological fluids towards potential wearable electronics applications.

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