



Porous carbon and Prussian blue composite: A highly sensitive electrochemical platform for glucose biosensing



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ABSTRACT

Porous carbon (PC) has attracted considerable attention for various applications including sensing due to its accessible specific surface area, tunable surface chemistry, and short diffusion pathways for rapid mass transfer. This report details fabrication of a highly sensitive enzymatic glucose biosensor that uses a composite of PC and Prussian blue (PB). Melamine foam, a low-cost material was used as a precursor for the synthesis of PC that acted as an excellent matrix for efficient loading of glucose oxidase (GOx). The high specific surface area and efficient electrical wiring in the PB embedded tetrapod architecture of PC composite improved the catalytic activity of this device for glucose sensing. When glucose contacts this biosensor, alterations occur in both cathodic (due to consumption of O₂) and anodic (due to release of H₂O₂) currents during cyclic voltammetry measurements. Due to the synergistic effect between PC and PB, the cathodic region (−0.05 V) had the highest sensitivity (218.78 μAmM^{−1}cm^{−2}) among all PC-based biosensors for glucose detection with a lower detection limit of 0.03 mM. The anodic region (+0.7 V) had a good sensitivity of 50.63 μAmM^{−1}cm^{−2} and a lower detection limit of 0.2 mM which is comparable to most of the enzymatic glucose biosensors that involve complex fabrication procedures. The high selectivity of this biosensor enabled accurate glucose level detection in serum samples. The PCPB composite-based sensing platform uses inexpensive precursors, is simple to fabricate, and displays excellent performance, suggesting potential for construction of sensors that release or consume oxygen during the analyte recognition process.

1. Introduction

Regular monitoring of glucose levels in physiological fluids is critically important for the management of both type I and type II diabetes mellitus. Glucose concentrations in human blood vary from the normal fasting value of 3.9 mM–6.2 mM to 3.9 mM–7.8 mM post prandially and both higher and lower values are associated with numerous clinically significant diseases. Glucose has been a common analyte of interest in the field of biosensor research because there is still considerable need for development of highly reliable, low-cost, and rapid self-monitoring glucose sensors [1–3]. In addition to the applications in medical diagnostics, glucose biosensors have found application in numerous important fields such as bioprocess monitoring, beverage industry, the textile industry, and environmental monitoring [4,5]. Optical and electrochemical techniques are more popular amongst several other techniques for the development of glucose biosensors [6–11]. Due to its precision and wide linear range of detection, colorimetry is considered to be the most reliable method in clinical assays of glucose. However, limitations of colorimetric methods

for in-home usage include the need for appropriate training and complex reagents to perform the assay protocol. Therefore, electrochemical techniques that have high reproducibility and portability are being studied actively for measurements of glucose [1,2] and several other important analytes in physiological fluids for point-of-care diagnostics [12–14].

Various electrochemical techniques including cyclic voltammetry and amperometry have been used for glucose sensing. The sensing procedure usually involves modification of an electrode with a material of choice to obtain sensors with superior performance. Both enzymatic and non-enzymatic electrochemical sensors have been reported for glucose sensing [4,8,9,11,15,16]. Non-enzymatic glucose sensors can offer high sensitivity, long shelf life, and low cost compared to enzymatic sensors. However, lower selectivity and constraint to operate in basic pH conditions make non-enzymatic sensors less favorable than enzymatic sensors. Initial reports for enzymatic glucose sensing were based on immobilization of enzyme glucose oxidase on the surface of bare metal (platinum, gold, nickel) or carbon-based electrodes (glassy carbon, graphite) [17–19]. To improve the sensing performance of the

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biosensor, combinations of two or more materials such as metal/metal oxide nanoparticles, conducting polymers, hexacyanoferrates, magnetic nanoparticles, graphene, and carbon nanotubes, were used to modify the electrode surface [20–23]. Introduction of these novel materials greatly enhanced the sensitivity, selectivity, reproducibility, and shelf life of the biosensor. Carbon-based materials, such as carbon nanotubes, graphene, graphene oxide, and graphite, in particular have shown advantages when used for electrode modification. These advantages include low cost, ease of mass production, very good chemical and electrochemical stability, high available surface areas in nanoscale dimension, acceptable biocompatibility, and good electrical conductivity which facilitates efficient electron transfer during biorecognition events [24–27]. Integration of these materials with metal/metal oxide nanoparticles, hexacyanoferrates, conducting polymers, and quantum dots has been shown to enhance the electron transfer and electrocatalytic efficiency of the resulting composite [28–33].

In the present work, we report a new composite of porous carbon (PC) and Prussian blue (PB) that was synthesized and explored for its glucose biosensing properties. PC has found application in electrocatalysis, energy storage, electrochemical sensing, and capacitor devices due to notable properties such as a large accessible specific surface area, tunable surface chemistry, and short diffusion pathway for rapid mass transfer [34–37]. PC has not been extensively studied in biosensing applications [5,38–41]. The usual route for synthesis of PC employs materials such as zeolites, mesoporous silicas, or supramolecule aggregates with homogeneous channel network, which are used as templates to form pores of the desired size [42,43]. In this work, we report the use of an inexpensive and template-free pathway based on commercially available melamine foam as the precursor for the synthesis of PC. There is a recent report wherein nitrogen-doped PC made from melamine foam was used for fabrication of a glucose biosensor; however, the electrode fabrication procedure involved elaborate steps [39]. PB on the other hand has been extensively explored for sensing owing to its electrocatalytic property for reduction of H_2O_2 [13,44–46]. In addition, PB has been reported to exhibit electrocatalytic properties for the reduction of oxygen [47,48]. PB along with carbon materials and metal supports has been explored previously for the fabrication of oxygen reduction reaction (ORR) catalysts [48–50]. In our present work we use PC to perform the dual functions of protecting both PB and enzyme glucose oxidase (GOx) within its matrix and improving the conductivity of the composite material. The choice of materials used for the synthesis of PCPB composite and the synergistic effects between them increase the catalytic activity of our biosensor for glucose sensing. This new PCPB-GOx biosensor reported herein has the highest sensitivity amongst all PC-based glucose biosensors reported until now. The resulting PCPB composite demonstrates promising features for biosensors that can detect various analytes important in medical diagnostics.

2. Experimental

2.1. Chemicals

Melamine foam was purchased from Basotect as a commercial product. D-(+)-glucose, chitosan, glucose oxidase (EC 1.1.3.4, 17.3 units per mg, from *Aspergillus niger*), KOH, urea, uric acid, dopamine, ascorbic acid, hexamine ruthenium chloride, KCl, and phosphate buffer solution (PBS) were obtained from Sigma-Aldrich. Aqueous solutions were prepared in deionized water (DI).

2.2. Instruments

The morphology of the PC and composite was characterized by a Hitachi S4800 field-emission scanning electron microscope (SEM). Fourier transform infrared (FT-IR) spectroscopy was recorded using Bruker Vector. Electrochemical measurements were performed using CH Instruments 760D electrochemical workstation. The electrochemi-

cal setup comprised of a three-electrode system with Ag/AgCl (saturated KCl) as the reference electrode and platinum (Pt) wire counter electrode. The working electrode was Pt (CHI102, 2 mm diameter), which was modified with the composite (PCPB-GOx) for the sensing studies. The cyclic voltammetry measurements were carried out in 0.1 MPBS (pH 6.5) between potential window of -0.2 V to 0.8 V with a scan rate of 50 mV/s. The performance of the biosensor for selectivity and estimation of glucose in human blood serum samples was evaluated using cyclic voltammetry. All the experiments were carried out at room temperature.

2.3. Synthesis of PC and PB

For the synthesis of PC, melamine foam was first soaked in 1 M KOH solution and dried overnight at room temperature. The KOH treated foam was gradually heated to 850°C at a rate of $3^\circ\text{C}/\text{min}$ under 0.5 LPM argon flow protection. After annealing for 1 h, the system was allowed to cool down to room temperature. The resultant PC foam was then soaked in water overnight and dried.

For the synthesis of PB, to a 19 mL solution of 2 mM $K_3Fe(CN)_6$ in 0.3% H_2O_2 , 1 mL of 20 mM $FeCl_3$ was added dropwise under ultrasonication followed by magnetic stirring for 30 min at room temperature. During this process, the color of solution changes rapidly from yellowish orange to dark cyan. After stirring, the obtained colloidal solution was centrifuged and re-dispersed in DI water to obtain a final concentration of 5 mg/mL.

2.4. Preparation of PCPB composite

Composites with various ratios of PC and PB (1:1, 2:1, 1:2, 3:1, and 1:3) were made. To allow homogeneous distribution of PB within the matrix of PC, appropriate amount of PC was weighed and soaked in desired volume of PB dispersion followed by ultrasonication for 30 min. After sonication, the PB-loaded PC was dried at 100°C and grounded mechanically to obtain a fine powder. For electrode modification, 2 mg of PCPB composite was dispersed in 100 μL of PBS (phosphate buffer, pH 6.5). To this evenly dispersed composite suspension, 5 mg of GOx was added. 10 μL of the GOx-composite mixture was dropcasted on a pre-cleaned Pt electrode and allowed to dry in air. To prevent enzyme leaching for improved stability of biosensor, 10 μL chitosan solution (1% chitosan in 1% acetic acid solution) was dropcasted on the GOx composite electrode. The biosensor was stored at 4°C in dry condition when not in use. The step-wise fabrication of the biosensor is shown in the schematic (Fig. 1).

3. Results and discussion

3.1. Characterization of biosensor electrode

SEM images of carbonized melamine foam, PCPB composite (with PC: PB as 2:1), and PCPB-GOx are shown in Fig. 2. The carbonized melamine foam (i.e., PC) shows the knitted network type of morphology, which is commonly observed when melamine foams are used as the synthetic precursors [39]. This type of structure imparts good electrical conductivity and provides a large surface area for adsorption of the biomolecules. The PCPB composite has a distinct morphology compared to the PC. Post pyrolysis, the carbonized PC loses its elasticity and incorporation of PB within the matrix of PC makes it more brittle, enabling the grinding of the composite into finer pieces. The broken pieces resemble the tetrapod architecture, similar to the work reported by Lee et al., wherein N-doped Ketjenblack incorporated into Fe/Fe₃C-functionalized melamine foam was utilized for oxygen reduction reaction (ORR) [51]. Although the macropores originally present in PC are destroyed during the grinding process, the stacking of these tetrapod-like pieces of PCPB composite over each other leads to the formation of a porous structure, which facilitates mass transfer and

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