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Nanoporous and wrinkled electrodes enhance the sensitivity of glucose biosensors

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ABSTRACT

Three-dimensional electrodes improve the performance of biosensors by increasing their surface area to volume ratio, decreasing the analyte diffusion time, and/or improving analyte access or capture at the electrode. We demonstrate a rapid and facile method based on electroless deposition and polymer-induced wrinkling for creating three-dimensional multi-lengthscale electrodes. This all solution-processing method enables the structure of the electrodes to be tuned by inducing continuous or nanoporous wrinkled surfaces. The surface area and analytical sensitivity of the electrodes are tuned by varying the electroless deposition duration, with the nanoporous and wrinkled electrodes demonstrating the highest surface area and analytical sensitivity compared to their wrinkled and planar counterparts. The nanoporous and wrinkled electrodes developed here combine critical lengthscales ranging from the nanoscale to the macroscale by including nanoscale pores, microscale wrinkles and sub-millimetre-scale electrode footprints, and demonstrate a surface area enhancement of more than 5 times compared to the all-solution-processed planar electrodes. These electrodes were applied to glucose sensing, and their response was measured using three classes of electrochemical techniques: cyclic voltammetry, chronoamperometry, and pulsed amperometric detection. When using cyclic voltammetry, these electrodes enable enzyme-free glucose sensing with a sensitivity of 591 $\mu A/mM.cm^2$ in alkaline solutions. This sensitivity is preserved when analysing solutions having a physiologically-relevant concentration of Cl^- ions, and is reduced to 38 $\mu A/mM.cm^2$ when analysing solutions having a neutral pH.

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1. Introduction

Three-dimensional electrodes with micro/nanoscale features are of tremendous interest in the field of electrochemistry, primarily due to their high surface area and the resultant increase in analytical sensitivity. These electrodes have proven to be particularly important for analysing species, such as glucose that undergo kinetically-controlled reactions.[1] For diffusion-limited electrochemical events, the overall geometric surface area of the electrode is responsible for the magnitude of the measured Faradaic current for most experimental timescales. However, in electrochemical events with slow surface reaction kinetics, the electrode's micro/nanoscale features contribute to the magnitude of the Faradaic current, which is leveraged towards increasing the sensor's analytical sensitivity. [2,3]

Enzyme-free glucose detection is desirable due to the instabilities associated with enzymes[4], especially for in-situ and in-vivo monitoring applications. The electrocatalytic nature of three-dimensional micro/nanostructured electrodes has been used for developing sensitive enzyme-free glucose biosensors. Mesoporous platinum fabricated through templated electrodeposition [1], nanoporous Au or Au-Ag created by dealloying Au-Ag alloys [5,6] or anodic polarization[7], Ni microflowers created by electroless deposition, and Co_3O_4 nanostructured films developed using the hydrothermal method[8] or templated calcination[9] are among the structures previously developed for enzyme-free glucose detection.

Polymer-induced wrinkling of conductive thin films has been developed as a method for creating three-dimensional electrodes with micro/nanoscale features[10–13]. In this method, wrinkled films are obtained when compressive stress is applied to a

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compliant polymer substrate modified with a stiff overlying thin film. Wrinkling has been combined with other rapid prototyping methods, such as xurography, to develop a facile and benchtop process for creating multi-lengthscale electrodes. In xurography, a CAD-driven cutting blade is used to pattern a material for masks by removing specific regions of an adhesive film. Xurography with sub-millimetre resolution has been used to define the electrode configuration, while wrinkling has been used to create features with critical dimensions in the micron and sub-micron lengthscale [14]. Furthermore, it is possible to wrinkle porous films created by selective dealloying[15], electroless disposition[16], and self-assembly of nanoparticles[17] on shrinkable polymer substrates.

Wrinkled electrodes are structurally tunable and their wavelength, porosity and height are tuned by varying the film thickness and continuity, or the ratio of the Young's moduli of the thin film and the compliant substrate [10,16,18]. This structural tunability can be leveraged towards controlling the electrode's functional parameters such as sheet resistance, electroactive surface area, and the density and arrangement of self-assembled monolayers. [10,16,19,20] While wrinkled electrodes have been used in electrochemistry experiments[10,19,21], their role in kinetically-controlled electrochemical reactions has not been previously investigated.

Our vision was to investigate the electrochemical properties of wrinkled, as well as nanoporous and wrinkled electrodes to determine their suitability for enzyme-free glucose detection. For this purpose, we created planar, wrinkled, and nanoporous and wrinkled electrodes by combining xurography with an all-solution-processing method based on nanoparticle self-assembly and electroless deposition on polymer substrates. We measured and compared the sensitivity of the three classes of electrodes created here, and found that the rapidly prototyped nanoporous and wrinkled electrodes developed here demonstrated the highest sensitivity compared to their wrinkled and planar counterparts. [22]

2. Experimental

2.1. Chemicals

Potassium chloride (KCl, $\geq$ 99.0%), hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$, > 99.9%), phosphate buffer solution (PBS, 1.0 M, pH 7.4), hydrochloric acid (HCl ACS reagent, 37%) were purchased from Sigma-Aldrich (St. Louis, Missouri). Sulfuric acid (H_2SO_4, 98%), 2- propanol (99.5%), methanol ($\geq$99.8%), dextrose ($CH_2OH(CHOH)_4CHO$, >99%), ascorbic acid ($C_6H_8O_6$) and sodium chloride (NaCl, $\geq$99.0%) were purchased from Caledon (Georgetown, Ontario). Ethanol was purchased from Commercial Alcohols (Brampton, ON). Tris(hydroxymethyl)aminomethane ($(HOCH_2)_2CNH_2$, $\geq$99.9%) was purchased from BioShop Canada (Burlington, ON). Sodium hydroxide (NaOH, 1.0 M) was purchased from LabChem (Zelienople, PA). All reagents were of analytical grade and were used without further purification. Milli-Q grade water (18.2 M Ω) was used to prepare all solutions.

2.2. Polystyrene Substrate Preparation

Pre-stressed polystyrene (PS) substrates (Graphix Shrink Film, Graphix, Maple Heights, Ohio) were cut into the designed shape using the Robo Pro CE5000- 40-CRP cutter (Graphtec America Inc., Irvine, CA). The PS substrates were cleaned with ethanol, DI water, and then dried with air. Following the solvent cleaning step, the substrates were placed in an Expanded Plasma Cleaner (Harrick Plasma) and were treated on HIGH RF power setting for 60 seconds. Following the plasma treatment, the substrates were immersed in an aminosilane bath (10% APTES) in an Incubating Mini Shaker (VWR International) for 16 hours at 120 rpm and at room temperature. Following silanization, the substrates were sonicated in DI H_2O for 10 minutes, rinsed and dried. The desired electrode pattern was designed in Adobe Illustrator and cut into the vinyl mask (FDC 4304, FDC graphic films, South Bend, Indiana) using the Robo Pro CE5000- 40-CRP vinyl cutter. The masks were applied to the silanized PS substrates.

2.3. Gold nanoparticle synthesis and deposition

Gold nanoparticles (Au NPs) were synthesized using previously described methods (Preparation 1)[23] and were kept at 4 °C until used. The PS substrates covered with a vinyl mask were fixed in petri dishes using double sided tape. These substrates were then covered with a solution of Au NPs for 16 hours.

2.4. Electroless Deposition

The PS substrates covered by an AuNP seed layer were placed in an electroless deposition bath containing 5 mL of 0.1% $HAuCl_4$. The bath was placed on the incubation mini shaker at 250 RPM and at room temperature, and 250 μL of 30% H_2O_2 was added to the solution to initiate the Au deposition. Bubbles forming on the edges of the vinyl mask were eliminated using a pipette tip. After removing the vinyl masks, the devices were placed in an oven (ED56, Binder, Tuttlingen, Germany) at 150°C for 3 minutes for shrinking the pre-stressed polystyrene.

2.5. Electrochemistry

The electrochemistry experiments were performed using Gamry reference 600 potentiostat (Gamry Instruments, Warminister, PA, USA) in a standard three-electrode cell. The electrochemical system consisted of an Ag/AgCl reference electrode, a platinum wire counter electrode, and the all-solution-processed Au electrode as the working electrode. All fabricated electrodes were electrochemically polished prior to use for surface area measurements and enzyme-free glucose sensing, by performing cyclic voltammetry (CV) between 0 and 1.5 V for 80 cycles at 0.1 V/s in 0.05 M H_2SO_4.

2.6. Surface Area Measurements

Electrochemical surface area measurements were performed by running another 3 cycles of cyclic voltammetry (in addition to the CVs performed for cleaning) using the same parameters used for electrode cleaning but at 0.05 V/s. The peaks for the reduction portion of the resulting cyclic voltammograms were integrated to obtain the electric charge involved in the redox process and divided by the surface charge density involved in forming a monolayer of oxide on Au (386 $\mu C/cm^2$)[2] to acquire the values of surface area.

2.7. Enzyme-free Glucose Sensing

Enzyme-free glucose sensing was carried out by performing CV in 0, 2.5, 5, 7.5, 10, 15, and 20 mM solutions of dextrose dissolved in 0.1 M NaOH, 0.1 M NaOH and 0.1 M KCl, or 0.1 M PBS. CV was performed with the voltage cycled between -0.8 and 0.8 V or -0.2 and 0.7 V at a scan rate of 0.1 V/s. To determine the signal generated by oxidation of glucose, the maximum point of the oxidation segment of the scan, which occurred at voltages between 0.2 and 0.3 V, was extracted. In the absence of glucose, the current was sampled in the voltage range for glucose oxidation. Selectivity of the glucose sensor was measured using chronoamperometry. Glucose concentrations from 1 to 10 mM were measured in a

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