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Fabrication of palladium nanowire array electrode for biofuel cell application

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ABSTRACT

Bioelectrocatalysis was demonstrated with palladium (Pd) nanowire array electrode via nonenzymatic and enzymatic methods for glucose, which was validated by the generation of anodic current in the presence of glucose. The vertically standing Pd nanowires used for the fabrication of the electrodes were on average 5.6 μm in length and 64 nm in diameter. In comparison, the nonenzymatic bioanode exhibited lower current densities and required the application of larger overpotential which resulted in a large cell voltage drop (V_{oc} = 13.5 mV) and limited power production when assembled as a biofuel cell under physiological conditions (pH 7, 0.1 M phosphate buffer saline) with laccase covalently bounded to Pd nanowires as the biocathode. The glucose/O_2 biofuel cell was studied in phosphate buffer saline using the enzymatic bioanode that was developed with the co-immobilization of catalase and glucose oxidase on Pd nanowires and the laccase-Pd as the biocathode. The biofuel cell exhibited an open-circuit voltage of 0.506 V, delivered a maximum power density of 72 μW cm^{-2} at a cell voltage of 0.25 V and a short-circuit current density of 411 μA cm^{-2} when operating in 10 mM glucose. Such low-cost lightweight glucose/O_2 biofuel cells have a great promise to be optimized, miniaturized to power bio-implantable devices.

1. Introduction

The resurgent development of biofuel cell devices has been driven by the mass-market acceptance of conventional fuel cell technologies, in which many efforts have been devoted to biocatalytically modified electrode materials, specifically for sensor applications [1–8]. These research activities in biocatalytically modified metal electrodes have provided a significant technological foundation for current biofuel cell development. Enzymatic biofuel cells employ biocatalysts to convert the chemical free energy stored in biofuels, such as glucose directly into bioelectricity. The generation of electricity is a product of the oxidation of the biofuel and the reduction of molecular oxygen by inexpensive biocatalysts. Researched biofuel cells employ direct electron transfer, as well as employ mediator electron transfer [9–15]. Katz et al. [12] studied the immobilization of a biocatalyst and a mediator at both the anode and cathode of an enzymatic fuel cell and showed that a maximal power density of 4 μW/cm^2 at a cell potential of 40 mV can be obtained by operating in 1 mM glucose (pH 7). Tsujimura et al. [13] demonstrated anodic oxidation of glucose in a compartmentless glucose-oxygen fuel cell using glucose dehydrogenase, and a power density of 58 μW/cm^2 was achieved at a pH of 7. To date, the development of stable and continuous enzymatic biofuel cells designed to catalyze the oxidation of fuel has been limited by low power densities [16–18].

Although Pd has been demonstrated to exhibit high degree of selectivity for glucose in nonenzymatic amperometric glucose sensing under high pH (0.1 M NaOH) conditions [19–20], there are no reports of Pd being used in nonenzymatic glucose-based biofuel cell application due to the large overpotential of Pd. In this study, we describe the fabrication of the first glucose biofuel cell bioanode based on the combination of glucose oxidase and Pd nanowire array to reduce the overpotential in order to maximize electron transfer processes for glucose/O_2 biofuel cell applications. The Pd nanowire array electrodes realized from anodized aluminum oxide (AAO) template electrodeposition method [21–22] exhibit a large surface area, which results in an increased number of adsorption sites for the immobilization of glucose oxidase. This further enables the electron generated during the biocatalysis to be directly transferred to the Pd electrode from the active center of glucose oxidase, thereby compensating for the large overpotential of bare Pd electrode. We also present the fabrication and electrochemical characterization of the enzymatic glucose biofuel cell based on Pd nanowires by combining the advantageous features of non-toxic biocatalytic systems to enhance the biofuel cell performance for application in miniaturized systems. The palladium nanowires maximize the surface area of the cells and may serve as an alternative nanostructured electrode material to CNTs that can help sustain the voltage generated, and thus increase the power densities of the cells.

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2. Experimental section

2.1. Chemicals

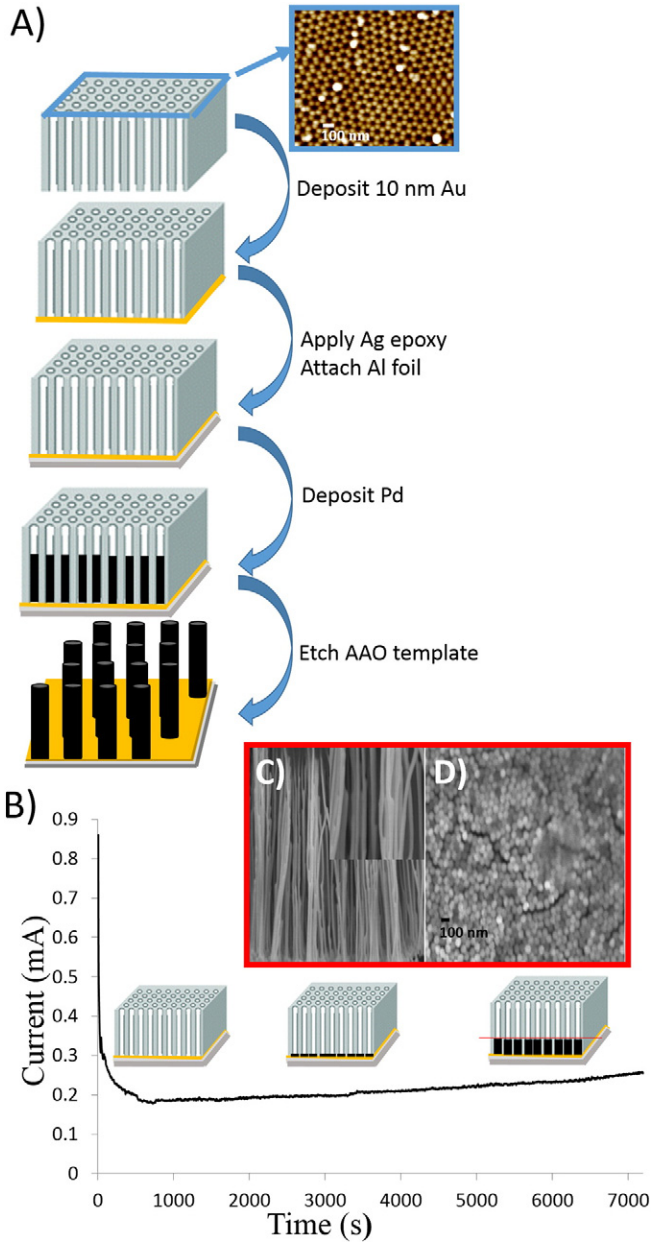
Aluminum foils (99.9999% purity, 0.25 mm thickness) were purchased from Alfa Aesar. Anodized Aluminum Oxide (AAO) templates with estimated porosity 15%, were purchased from Synkera Technologies, Inc. Tetraamminepalladium(II) chloride monohydrate, ammonium chloride, glucose oxidase (GOx, EC 1.1.3.4 from Aspergillus niger), D-(+)-glucose, catalase (EC 1.11.1.6 from bovine liver), laccase (EC 1.10.3.2 from Trametes versicolor), hydroxyethylmethacrylate (HEMA), tetraethyleneglycol diacrylate (TEGDA), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), 3-aminopropyltrimethoxysilane (γ-APS, 97%), glutaraldehyde, ethyldimethyl-aminopropyl carbodiimide (EDC) and poly(ethylene glycol) methacrylate (PEGMA) were purchased from Sigma-Aldrich. The diacrylate and methacrylate reagents were passed through an inhibitor removal column in order to remove the hydroquinone and monomethyl ether hydroquinone polymerization inhibitors before use. Acryloyl(polyethyleneglycol)-N-hydroxysuccinamide (MW 3500), was purchased from Jenkem Technology. All supplementary chemicals were of analytical grades and solutions were prepared with 18.2 MΩ cm Milli-Q water.

2.2. Electrochemical deposition of Pd nanowires

Prior to electrodeposition, the anodized aluminum oxide (AAO, 3 × 3 mm) templates were degreased in acetone followed by drying under nitrogen flow. A thin film of Au (100 Å) was sputtered onto one side of the AAO templates to provide an electrical conduction path for the electrodeposition of the Pd nanowires by exposing the pores of the AAO template to the underlying Au film. To create an electrical connection to the AAO electrodes, 4 × 10 mm strips of aluminum foil were degreased in acetone, and then dried in vacuum at 450 °C for 3 h and were attached to the Au sputtered side of the AAO substrate using silver epoxy (SEC 1233 ResinLab). Silicone epoxy was used for bioelectrode passivation and to define the electroactive area of the bioelectrodes. The passivation method employed also serves to seal the sides of the AAO templates. Furthermore, it prevents any breaking or swelling of the electrode material in contact with the electrolyte. The AAO template affixed to the aluminum foil (Al-AAO) was dried overnight at room temperature. Scheme 1 illustrates the process flow for preparing Pd nanowires. The Al-AAO template served as the working electrode in a three-electrode electrochemical cell setup with a platinum wire and a $Ag/AgCl_{(sat)}$ electrode as the counter and reference electrodes, respectively in a water jacketed electrochemical cell. The Al-AAO template was immersed in the electrodeposition solution containing 1 g/L $Pd(NH_3)_4Cl_2$ (99.99%) and 10 g/L NH_4Cl (99.99%) for ~15 min prior to electrochemically depositing Pd from the aqueous solution at a pH of 8. The electrodeposition was conducted at −600 mV versus Ag/AgCl at a temperature of 30 °C for 2 h using BASi potentiostat/galvanostats EC Epsilon. After electrodeposition, the substrate was rinsed in deionized water and the AAO template was etched away in 2 M NaOH for 6 min at room temperature with mild agitation. The resulting free standing Pd nanowire array electrodes were then rinsed three times with ethanol followed by deionized water.

2.3. Functionalization of palladium nanowires

The surface of the as-prepared Pd nanowire bioelectrodes was subsequently functionalized by treatment with γ-APS, 0.1 vol% in ethanol at 40 °C for 30 min in order to introduce silane surface functionalities as previously reported [3]. After silanization, the Pd nanowire array bioelectrodes were rinsed by sequential washing for 1 min in ethanol, and then in ethanol/water mixture (1:1, *v*/*v*). Finally, the γ-APS coated Pd nanowire array bioelectrodes were cured at 110 °C for 20 min in a convection oven. And then, incubated in 6% glutaraldehyde at room temperature for 30 min. The surfaces of the Pd nanowires were thoroughly rinsed and placed in 0.1 M phosphate buffer, pH 7. This was followed by a derivatization step to create a continuous path of covalent bonding between the Pd nanowire bioelectrode surfaces and the biocatalysts.



Scheme 1. A) Schematic representation of the electrodeposition of Pd nanowire using AAO template. Top right: AFM top-view micrograph of the AAO template with pore diameter ranging from 62 to 70 nm. B) Current transient curve for the electrochemical deposition of the Pd into the AAO template. C) SEM cross-sectional view and D) top-view micrographs of free standing Pd nanowires after etching away the AAO template in 2 mM NaOH.

2.4. Preparation of bioelectrodes

The biocatalyst immobilizations were achieved by incubating the γ-APS-aldehyde functionalized Pd nanowire bioelectrodes in the appropriate enzyme solution (bioanode: 1 mg/ml glucose oxidase and 0.5 mg/ml catalase or biocathode: 1 mg/ml laccase in 0.05 M phosphate buffer with 0.15 M NaCl (PBS), pH 7) for 30 min. The surfaces were thoroughly rinsed in PBS and incubated for an additional 30 min in HEPES