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Gold particles growth on carbon felt for efficient micropower generation in a hybrid biofuel cell

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ABSTRACT

In this study, homogeneously dispersed gold particles growth onto carbon felt were fabricated by electrodeposition method followed by a thermal treatment at 1000 °C under nitrogen. The thermal treatment induced the dewetting of gold and the formation of well-crystallized gold particles that exhibited large surface area. The structural properties of the resulted Au@CF material were evaluated by SEM, XRD and TGA. We studied the electrocatalytic properties of this new gold material through the abiotic glucose oxidation in alkaline medium and the enzymatic dioxygen electroreduction by the enzyme bilirubin oxidase. Finally, we showed the potentiality of the resulting Au@CF material to build a 3-dimensional glucose hybrid biofuel cell by assemblying an abiotic anode with an enzymatic cathode. The system exhibited high electrochemical performance with an open circuit voltage of 0.71 V and a maximum power density of 310 $\mu W\ cm^{-2}$ at 352 mV (by taking into account the projected surface area), in spite of a low gold loading (0.2 wt%). The advance presented in this work is the efficiency of the synthesis technique to get a new free-standing material for electrocatalysis based on gold particles with high reactive surface area for electron transfer and macropores for diffusion transport.

1. Introduction

Gold nanoparticles (AuNPs) and nanoporous gold, as well as metallic nanostructured films are becoming popular as electrode materials for electrocatalysis. These electrodes are attractive due to their large electrochemical surface area, excellent chemical stability, high conductivity and biocompatibility [1,2]. Several techniques are used to prepare three-dimensional gold electrodes mainly based on (i) the immobilization of already synthesized nanoparticles by drop-casting, layer-by-layer methods and entrapment in a sol gel matrix [3–8], or (ii) the direct preparation of nanoparticles on electrode surface by electrochemical deposition, sputtering followed by dealloying, chemical reduction, seed-mediated growth and ion implantation [9–13]. These techniques use high metal loading (20–40 wt.%) [3], and since gold is an expensive material, they are mostly adapted for small electrode areas, and require strong reducing agents (boron hydride) and thiol groups for nanoparticles stabilization [7,8].

Thanks to their catalytic efficiency and biocompatibility, AuNPs can be used either co-immobilized with redox enzymes or as the main catalyst. Three-dimensional gold nanoparticles electrodes have been widely applied to direct electron transfer reactions of redox enzymes [14–19], which can afford higher enzyme loading, better orientation by chemical modification and more efficient electrical contact. From examples found in the literature, AuNPs electrodes have shown to improve biofuel cells performance [20,21] and glucose biosensors detection [17,22] compared to planar electrodes. Additionally, AuNPs exhibit good activity toward glucose oxidation (with typical current values ranging from some hundreds of μA to a few mA) due to their large surface area, high number of active sites and resistance to surface poisoning during electrochemical processes [7,23,24].

Hybrid biofuel cells, unlike fully enzymatic ones, present only one enzymatic electrode (bioanode or biocathode), while the other is catalyzed by nanometallic catalysts. In enzymatic BFCs, the enzymes offer high reactant specificity and high reaction rate. Glucose oxidase has been widely studied in glucose biofuel cells through MET-type catalysis (Mediated Electron Transfer) with the use of mediators such as ferrocene [25] or osmium complexes [26,27] or through DET-type catalysis (Direct Electron Transfer)

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with the introduction of nanomaterials including carbon nanotubes, graphene or gold NPs [19]. However, the limited stability and regeneration of the enzymes hinder the potential use of enzymatic glucose BFC for long-term operation. An alternative option is thus the use of abiotic catalysts with high catalytic activity toward glucose oxidation and efficient stability that makes them more suitable for long-term applications. The non-selectivity of abiotic glucose catalysts can be easily overcome by the addition of a separation membrane. In our previous studies, we reported the construction of hybrid biofuel cells involving an abiotic anode and an enzymatic cathode that can potentially convert chemical energy into electricity [28,29]. The devices were made of self-standing electrospun carbon electrodes modified by Au NPs at the anode for the electrocatalytic oxidation of glucose and by the enzyme bilirubin oxidase (BOD) at the cathode for the electrocatalytic reduction of dioxygen. The abiotic anodes were obtained either by the direct synthesis of the nanoparticles supported on carbon Vulcan® and deposited on the electrode surface [28], or by the formation *in situ* of the nanoparticles embedded in electrospun carbon fibers [29]. The electrodes were characterized by gold loadings of 21 and 12.2 wt.%, respectively, determined by thermogravimetric analysis. These results clearly showed the advantage to prepare *in situ* the nanoparticles to form very stable carbon-gold bonding with well dispersed AuNPs on the electrode surface to enhance the long-term stability of our devices.

Considering the importance of the bonding stability between the NPs and the electrode material, the aim of this work is to propose a new simple method to prepare gold particles attached on a commercial porous carbon template that affords conformal coating and homogeneous dispersion of the gold onto the electrode surface. The technique is applied to prepare Au@CF material with the objective of using a very low gold loading (0.2 wt %). Besides, compared to our previous studies, the bioelectrode is prepared by connecting AuNPs directly to the enzymes instead of using MWCNTs to establish electrical contact. The Au@CF material is obtained from the electrodeposition of gold salts on a porous carbon felt followed by a subsequent thermal treatment at 1000 °C under nitrogen gas flow to induce the dewetting of gold [30], and the formation of well-crystallized gold particles that exhibit large surface area. The benefits of this synthetic route is achieving a free-standing material with (i) increased reactive surface area induced by the Au nanoparticles for high enzyme loadings, and (ii) high mass transport of reactants thanks to the porous carbon template.

To our knowledge, this is the first time that this synthesis approach is used to confine gold particles in a three-dimensional electrode applied to the development of hybrid biofuel cells. Structural properties of the new Au@CF material are characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA). We focus on the electrocatalyic properties of this new material regarding both the abiotic glucose oxidation in alkaline medium and the enzymatic dioxygen electroreduction. The enzyme BOD, known to promote the four-electron reduction of oxygen directly to water [31], was chosen to perform DET. DET allows avoiding the problems associated with the use of redox mediators like limited stability, potential toxicity and lower electrode potential. As DET depends significantly on the distance between the redox active center of the enzyme and the electrode surface, we expect that the gold nanoparticles will promote DET between the BOD and the porous carbon electrode. BOD is entrapped within chitosan matrix which provides favorable microenvironment and high stability for multicopper oxidases [32], and further immobilized within the porous Au@CF by simple immersion in solutions. Finally, the potentiality of the resulting Au@CF electrodes to assemble a glucose hybrid biofuel cell is shown by using bare CF@Au at the anode, and BOD-modified CF@Au at the cathode. In spite of low gold loading (0.2 wt%), this hybrid device exhibits higher electrochemical performance than the previous hybrid glucose biofuel cells, proving the efficiency of the synthesis technique to form gold electrodes with high active surface for electrocatalysis.

2. Experimental

2.1. Materials

The carbon felt was purchased from A Johnson Matthey Co., Germany. Chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.99%) was obtained from Sigma Aldrich. Potassium hexacyanoferrate ($\geq$ 99%) and potassium nitrate ($\geq$ 99%) were bought from Fluka, enzyme bilirubin oxidase (BOD, 2.51 U mg^{-1} solid) from Amano Enzyme Inc., Japan; potassium hydroxide (KOH pellets pure) from Merck; D-(+)-glucose monohydrate, chitosan and acid sulfuric (98%) from Sigma-Aldrich, and used without further purification. Dihydrogen phosphate monohydrate ($NaH_2PO_4.H_2O$) and di-sodium hydrogen phosphate (Na_2HPO_4) salts from Merck were employed for preparation of the buffer phosphate (0.1 M) pH 7.0 (PBS). The aqueous solutions were prepared using 18.2 MΩ cm MilliQ water (Millipore). Glucose solution was stirred for 24 h prior to use.

2.2. Preparation of gold nanoparticles-modified carbon felt (CF@Au)

The commercial carbon felt was firstly cleaned in an ultrasonic bath with acetone for 2 h to remove adsorbed contaminations, followed by thorough rinse with deionized water and drying at 60 °C for 24 h. This pretreated carbon felt was denoted as raw CF. After that, the gold layer was deposited on the surface of the porous carbon by cyclic voltammetry (CV) technique running 70 scans from -0.9 to 0 V versus SCE (Saturated Calomel Electrode) at a scan rate of 10 mV s^{-1} in a N_2-saturated solution containing 0.05 mg mL^{-1} chloroauric acid. The process was recorded on a μ3AUT70466 Autolab system (Eco Chemie BV, Netherlands) using a three-electrode system with the CF as working electrode, a SCE as reference electrode and platinum foil as counter electrode. Aiming to form the gold particles by dewetting, an additional thermal treatment was realized in a tubular furnace (Vecstar Ltd) fed by nitrogen gas at the flow rate of 200 mL min^{-1} with heating rate of 5 °C min^{-1} and temperature ranging from 20 to 1200 °C. The parameters affecting the deposition of gold nanoparticles on the surface of the carbon felt were investigated, such as the concentration of chloroauric acid and treatment temperature. One electrode was prepared for each chloroauric acid trihydrate concentrations and for each treatment temperature from 600 to 1000 °C. The sample at the best state was noted as gold carbon felt (CF@Au).

2.3. Preparation of enzyme-immobilized electrode

The biocathode consisted of an Au@CF electrode modified with BOD enzyme entrapped in a chitosan film. First the Au@CF material was immersed in a solution (300 μL) of BOD (19.5 mg mL^{-1}) in PBS (0.1 M) pH 7 until complete absorption of the liquid inside the porous electrode. More concentrated solutions of BOD did not yield higher catalytic currents. After drying, the modified electrode was covered by a chitosan solution, also by immersion. The solution was prepared by dissolving 1 wt.% of chitosan in 1 mL of acetic acid solution (1 vol.%) until complete dissolution, followed by the addition of 50 μL glutaraldehyde. The resulting electrode was let to dry at 5 °C for 48 h. The enzyme concentration was estimated at 5.8 mg for a projected surface area of 1 cm^2 for an electrode of 1 cm thickness.