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Hierarchical porous gold electrodes: Preparation, characterization, and electrochemical behavior

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ABSTRACT

Hierarchical porous gold films with a well-defined bimodal architecture have been made by electrodepositing gold at a constant current around a close-packed assembly of raspberry-like latex spheres (1200/60 nm) followed by template removal. Electrodeposition was stopped when the gold was either ½ layer or 1½ layer thick as evident from oscillations in the potential vs time traces. Scanning electron microscopy (SEM) images show the hierarchical pore structure with an ensemble of small ~20 nm openings located in a large ~1200 nm diameter macropore. Prior to electrochemical characterization, the electrodes were cleaned either chemically and/or via UV radiation and X-ray photoelectron spectroscopy (XPS) was used to evaluate the presence of residual polystyrene. Of the three cleaning methods investigated, sonication in chloroform–acetone followed by UV radiation proved best. The surface area of the hierarchical porous gold electrodes, determined by integrating the area under the gold oxide peak, was 4× larger than a bare gold electrode and 2× larger than a macroporous gold electrode prepared using unimodal, 1200 nm diameter latex spheres as the template. The electrochemical performance of the electrodes relative to the macroporous gold and flat gold was undertaken using cyclic voltammetry. The results show that the non-Faradaic current scales linearly with electrode area while the Faradaic current of a diffusing electrochemically reversible redox probe (ferrocene methanol) does not. For an adsorbed redox couple (ferrocene hexanethiol), the voltammetric wave shapes and surface coverage were different for the different electrodes.

1. Introduction

High surface area electrodes have received considerable attention in recent years [1–6]. These electrodes provide an effective way to increase the real surface area of an electrode without compromising its physical size. This attribute is especially important for miniaturized devices that require electrodes to be geometrically small but also to have a high surface area to improve sensitivity and lower detection limits. In addition to chemical sensing, such materials are also important in the design of catalytic supports [4,6], batteries, and fuel cells [2,7]. High surface area noble metal electrodes have been fabricated using a number of different approaches that include hard templating of latex spheres or SiO_2 spheres [8–11], chemical dealloying [12–14], electrochemical dealloying [15,16], H_2 bubble formation [17], electrodeposition in the pores of nanopore membranes [18,19] as well as from ensembles of gold nanoparticles, gold microparticles [20], and electrospun gold nanofibers [21]. The electrochemical properties of such macroporous, and nanoporous electrodes have been described in the literature [3,5,6].

Equally important to the need for high surface area is the need for this area to be accessible. One means to do this is to design a hierarchical electrode, one that will have well-defined pores on more than one length scale. A large pore, for example, will facilitate transport to the smaller pores which act to increase the electrode area and provide additional places for electron exchange to take place. However, there have been very few examples of hierarchical porous electrodes with well-defined pores on more than one length scale reported in the literature [17,22–26]. In recent work, we described the fabrication of a hierarchical template formed by coupling two different sized polystyrene latex spheres together [27]. The size and morphology of the hierarchical template was defined by the sizes of both the "core" and the "satellite" spheres, as well as by altering the coverage of "satellites" on the "core" [27]. When these hierarchical latex spheres are used as hard templates, hierarchical, high surface area materials can be easily prepared. The main advantages of such a strategy is that it provides an easy means for template removal since the template is prepared from only one material (polystyrene) and it provides a means to form a hierarchical material with an *interconnected* pore structure.

In this work, the preparation and characterization of hierarchical gold electrodes using a hierarchical raspberry-like template prepared by coupling epoxy/sulfate functionalized polystyrene

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(PS) spheres to a significantly larger amine-functionalized PS sphere is described. Following the electrodeposition of gold around a close-packed layer of the 1200/60 nm hierarchical raspberry-like templates on a gold slide and template removal, a hierarchical gold electrode with well-defined architecture was obtained. The size of the pores in the gold electrode was defined by the size of the "core" and the "satellite" spheres that make up the hierarchical template. The electrochemical properties of the hierarchical gold electrode prepared from 1200/60 nm hierarchical template were examined in detail after a suitable cleaning protocol was obtained. Comparisons of the surface area and the non-Faradaic response of the hierarchical gold electrodes were made to a macroporous gold electrode formed from a 1200 nm diameter sphere and to an electrodeposited flat gold electrode or an as-received flat gold electrode. Likewise the electroactivity of ferrocene methanol in solution and a ferrocene derivative self-assembled on the surface of these electrodes were also examined.

2. Experiment

2.1. Reagents and chemicals

Ferrocene methanol, 97% was purchased from Acros Organics. 2-aminoethanethiol was purchased from Fisher Scientific. 6-Ferrocenyl-1-hexanethiol (FcSH) was purchased from Dojindo Molecular Technologies Inc. All reagents were used as received. Aqueous suspensions of polystyrene (PS) microspheres functionalized with either amine or epoxy/sulfate groups with diameters ranging from 29 nm to 1.2 μm were obtained from Invitrogen (formally Interfacial Dynamics Corporation (IDC), 2.1 wt/v% for PS-NH_2, and 4.1 wt/v% for PS-Epoxy/Sulfate). Gold mirror electrodes (100 nm Au, 10 nm Ti) were purchased from EMF Corporation. The gold plating solution, Gold 25, was purchased from Technic Inc. Water was purified with a Millipore water purification system.

2.2. Synthesis of hierarchical gold electrodes

Hierarchical templates were made via the base-assisted coupling of epoxy groups with NH_2 groups as described in our previous work [27]. Briefly, the amino-spheres latex (1.2 μm) and an excess epoxy-spheres latex (60 nm) were mixed uniformly together by sonication for several minutes, and then a Na_2CO_3 buffer (pH = 10, 0.1 M) was added into the colloidal solution to start the coupling between amine and epoxy groups. After 24 h coupling, the hierarchical templates were separated from the original solution by centrifugation.

To prepare the hierarchical gold electrodes, the gold slides were first sonicated in soap solution and ethanol for 10 min, respectively, followed by plasma cleaning (South Bay) at 10 W for 2 min and immersion in a 10 mM 2-aminoethanethiol hydrochloride/ethanol solution for 2 days. The templates were then packed on the modified gold slides by slow speed spin coating. Specifically, ~50 μL of an aqueous suspension of the templates (~2 wt.%) was spread in a circular area of ~1 cm^2. After sitting for about 1 min, the sample was then dried by slowly rotating the electrode at a spin speed of 450 rpm for about 30–45 min. The electrode area (~0.3 cm^2) was defined by a ¼ in. circle hand punched in a piece of Teflon tape (Hyde) placed over the surface of the densely packed spheres. Electrodeposition was carried out galvanostatically with a current of 0.1 mA in a three-electrode electrochemical cell. After electrodeposition, the Teflon tape was removed and sphere-coated gold slide was rinsed with water and air dried. To remove the polystyrene templates, the sphere-coated gold slide was soaked in a 2:1 ratio chloroform/acetone mixture for several minutes followed by sonication for 5 min. As described in the text, the electrodes were further cleaned by KOH + H_2O_2 (50 mM KOH and 25% H_2O_2 for 2 h) [28], or by irradiation with UV light (254 nm, 20 W) for at least 18 h. A hole punched piece of Teflon tape (1/4 or 1/8 in.) defined the electrode area.

2.3. Instrumentation

Scanning electron microscopy (SEM) was conducted on a Hitachi 70 scanning electron microscope. As necessary, the materials were coated with a thin layer of gold prior to imaging. X-ray photoelectron spectroscopy (XPS) analysis was performed with a ThermoFisher ESCAlab 250 imaging X-ray photoelectron spectrometer (Al Kα (1486.68 eV), 500 μm spot size, 150 eV pass energy, 0.2 eV step size). Spectra were calibrated by taking the C 1s peak as occurring at 284.6 eV. For each sample, three different positions on the electrode surface were analyzed. Electrodeposition and cyclic voltammetry were conducted with a CH Instruments Galvanostat/Potentiostat using an Ag/AgCl (3.5 M KCl) reference electrode and a Pt auxiliary electrode in a one-chamber electrochemical cell.

3. Results and discussion

3.1. Preparation of hierarchical gold electrodes

Hierarchical gold electrodes with well-defined pores of more than one size were prepared by electrodepositing gold around a packed ensemble of hierarchical PS latex spheres followed by their removal. The hierarchical templates were prepared by synthetically joining appropriately functionalized commercially available polystyrene latex spheres together as previously described [27]. The size and morphology of the pores in the gold electrode are defined by the size of the "core" and the "satellite" PS spheres, both of which can be changed. In the present work, the hierarchical template was prepared by coupling the NH_2 groups on a 1200 nm diameter PS latex sphere with the epoxy groups on the 60 nm diameter spheres. In addition to this size, other hierarchical templates with a core/satellite of 710/29 nm and 340/29 nm were also made. SEM images of all three hierarchical templates are shown in Fig. 1. The epoxy spheres (e.g., satellite spheres) have relatively rough surfaces and are more polydisperse, particularly as their size decreases from 60 nm to 29 nm. The irregular shape and the surface roughness of the satellite spheres on the hierarchical template will interfere with how close the latex spheres can pack on the surface and give rise to significantly more defects in the hierarchical electrodes. To minimize this, only the largest size hierarchical template (1200/60 nm) was used to fabricate the hierarchical gold electrodes described herein.

The hierarchical templates were packed in a close-packed arrangement by placing a small drop of a suspension of the hierarchical spheres on a modified gold substrate and slowly rotating it. Under these conditions, a very thick layer of spheres covered the electrode with the bottom few layers being relatively ordered compared to the top few layers. Since electrodeposition of gold begins from the bottom, this method works well for making gold electrodes that have an ordered arrangement of pores. The disordered top layers of the PS spheres are just simply washed away when the template is removed in the chloroform/acetone solution.

To fabricate the hierarchical gold electrode, gold was electrodeposited around the template in a manner similar to what has been described in the literature for the formation of a unimodal macroporous gold electrode [9] with the exception that deposition proceeded galvanostatically vs potentiostatically. A simplified cartoon of the fabrication process is shown in Fig. 2, top. For comparison purposes, a unimodal macroporous gold electrode with a pore size of 1200 nm was also made in a similar fashion. Also