Shape-Controlled Electrodeposition of Gold Nanostructures

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A one-step, nontemplated, low-cost electrochemical method for the growth of gold nanostructures with different shapes is reported here. It is the first time that nanopyramidal, nanorod-like, and spherical gold nanostructures were fabricated on polycrystalline gold substrates through electrochemical overpotential deposition (OPD) by easily manipulating the deposited potentials and concentrations of $HAuCl_4$. X-ray diffraction and electrochemical analyses revealed that the pyramidal structures are more extensively dominated by (111) facets in comparison with the other nanostructures. The nanopyramids, which have anisotropic structures, exhibited broad extinction over the visible region, most likely due to plasmon resonance. Oxygen reduction activity of a gold electrode with the pyramidal structures was lower than those of the electrodes with the other nanostructures since the activity at the gold (111) surface is lower than that at the (100) and (110) surfaces.

Introduction

In the past couple of decades, there has been a burst of research activity on nanostructured metal particles, particularly noble metal nanoparticles with controlled size, morphology, and crystal orientation, because of their unique physical and chemical properties different from bulk metals.[1,2] The synthesis of noble metal nanorods,[3] nanowires,[4] nanorings,[5] nanobelts,[6] and nanopolyhedrons,[7,8] including nanocubes,[9] nanoprisms,[10] and nanoplates,[11] has been reported on the basis of their potential applications to materials and devices with a special electronic, optical, thermal, catalytic, or magnetic function.[1,2,12-14] Among the noble metals, gold is of importance for its stability and unique optical properties.

In fabrication of such functional materials and devices, it is sometimes important to assemble the metal nanoparticles onto solid substrates. Charged polymers and other functional polymers have been employed to anchor the noble metal nanoparticles as a monolayer onto various substrates,[15,16] including glasses, semiconductors, metals, and carbons. This self-assembly technique could also fabricate robust multilayers by layer-bylayer (LBL) assembly.[17,18] Besides polymers, proteins[19] and DNA[20] have also been exploited as anchoring agents. More recently, a templated self-assembly technique has been developed to fabricate three-dimensional nanoparticle arrays by using a nanoporous alumina template.[21] In addition to these two-step methods, there have been reported methods for fabricating metal nanoparticle arrays on the basis of electron-beam lithography (EBL)[22] or nanotemplating.[23,24] However, these methods require expensive equipment or special templates.

Another useful method is electrochemical deposition.[25-29] Various morphologies including rod-like[28] and dendritic[29a] gold nanostructures have been obtained in a one-step process without templates, typically in the presence of an additive such as Pb^{4+},[25-28] cysteine,[29] or I^-.[29b] However, those nanostructures were not necessarily well-defined. In this paper, we demonstrate one-step, inexpensive, nontemplated electrochemical fabrication of pyramidal, rod-like, and spherical gold nanostructures on a sputtered gold film. The structures are characterized by atomic force microscopy (AFM), visible spectroscopy, X-ray diffraction (XRD), and electrochemical methods. Their electrochemical activities for oxygen reduction are also examined.

Experimental Procedures

Chemicals and Materials. Hydrogen tetrachloroaurate(III) ($HAuCl_4$) trihydrate was purchased from Aldrich (St. Louis, MO) and used as supplied. Sodium hydroxide and perchloric acid were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The solution used in this work was freshly prepared Milli-Q water. ITO-coated glass plates with a square resistance of 10-20 ¿ cm^{-2} were obtained from Asahi Glass (Japan).

Preparation of Gold Nanostructures. ITO-coated glass plates were thoroughly cleaned by sonication for 30 min in the following solvents successively: soapy water, water, neat acetone, and 1 M NaOH. Then, a gold film with a thickness of about 50 nm estimated by AFM was sputtered on the clean ITO glass plate. Pyramidal, rod-like, and spherical gold nanostructures were electrodeposited from aqueous solutions of 0.1 M $HClO_4$ containing 40, 4, and 40 mM $HAuCl_4$, respectively, at -0.08, -0.08, and -0.2 V versus AgjAgCl, respectively, for 2 min.

Instruments and Measurements. An atomic force microscope SPA-300HV (Seiko Instruments Inc., Japan) was employed to record the images of the nanostructured gold surfaces. The XRD pattern was obtained by a D/max2550VB3+/PC X-ray diffractometer using Cu (40 kV, 100 mA). The visible reflectance spectra of the nanostructured surfaces were collected by a UV-vis spectrophotometer MCPD-3000 (Otsuka Electronics, Japan). A CHI 660 electrochemical work station (CH instruments, Austin, TX) was employed in all electrochemical

measurements, which were carried out with a conventional twocompartment three-electrode electrochemical cell. The reference electrode was a KCl-saturated AgjAgCl electrode, while the auxiliary electrode was a platinum wire. The real surface area of gold nanostructures was determined by calculating the charge consumed during the formation of the surface oxide monolayer in H_2SO_4 solution.[30]

Results and Discussion

Morphology of Gold Nanostructures. Gold nanostructures with various shapes were prepared by one-step and nontemplated electrochemical deposition under different experimental conditions. In the present work, we applied sufficiently negative potentials, -0.08 and -0.2 V versus AgjAgCl, to the electrode, to obtain three-dimensional structures.

The morphology of the nanostructured gold films was characterized by AFM (Figure 1). As Figure 1a shows, deposition at -0.08 V versus AgjAgCl in a 40 mM $HAuCl_4$ solution gave nanopyramidal structures. On the other hand, at a lower $HAuCl_4$ concentration (4 mM), rod-like nanostructures were obtained, as Figure 1b shows. At a more negative potential, -0.2 V, rather featureless spherical nanostructures formed in the 40 mM $HAuCl_4$ solution (Figure 1c). In the case of the nanopyramids, the edge length of the bottom was 50-200 nm, and the height was several hundreds of nanometers. The nanorods grew out to about 100 nm wide and up to 200-300 nm long, or more. The diameters of the nanospheres ranged from 70 to 100 nm. For comparison, an AFM image of the sputtered gold substrate is also shown in Figure 1d. Its spherical morphology with diameter of 25-50 nm is clearly different from the electrochemically deposited nanostructures, either in size or in shape.

Crystallographic Characterization. The crystalline orientation of the gold nanostructures was investigated by XRD. The diffraction peaks of the electrodeposited pyramidal, rod-like, and spherical gold nanostructures are shown in Figure 2a-c, respectively. The observed peaks corresponding to the (111), (200), (220), (311), and (222) facets demonstrate that the electrodeposited gold is composed of pure crystalline gold with the face-centered cubic (fcc) structure. The intensity ratios of the (200) peak to the (111) peak obtained for the pyramidal (0.059), rod-like (0.078), and spherical (0.13) structures were much lower than that reported in the standard file (JCPDS, 0.33),[11] indicating that the gold nanostructures, nanopyramids in particular, were preferentially dominated by (111) facets. In contrast, the sputtered gold film exhibited a less prominent (111) peak (Figure 2d), in comparison with those for the electrochemically deposited nanostructures, indicating that the (100) and (110) facets constitute a considerable portion of the sputtered gold surface. Incidentally, the (222), (441), and (622) peaks of the ITO substrate are also seen in Figure 2d.

An electrochemical method was also employed for characterization. It is known that different gold facets show different cyclic voltammograms (CVs) in acidic solutions.[31] Figure 3 depicts the CVs collected at the nanostructured gold electrodes in 0.01 M aqueous H_2SO_4. It is noteworthy that the CV for the pyramidal nanostructure (Figure 3a), characterized by the oxidation peak at around +1.3 V versus AgjAgCl, is characteristic of the gold (111) surface.[31] In the case of the CVs for the rod-like and spherical nanostructures (Figure 3b,c, respectively), a small oxidation peak at around +1.1 V, which is indicative of the presence of the gold (100) and/or (110) facets,[31] was observed, although there still was the large peak for the (111) surface. On the other hand, in the case of the CV for the sputtered gold, the peak for the (111) facets was much less significant. These results are qualitatively in agreement with the conclusions drawn from the XRD data.

Thus, it is reasonable to consider, on the basis of these results, that each nanopyramid is a gold single crystal with (111) facets. The nanopyramid can be recognized as a part of an octahedral gold nanocrystal, and octahedral gold crystals are noramally enclosed by (111) facets. It is known that the (111) facet is the thermodynamically most stable among the possible facets of the fcc crystals. Therefore, it is rational that the crystal with the (111) facet is preferentially grown at a mild electrode potential, which enables relatively slow crystal growth, in a solution enriched with Au^{3+}.

Conclusions

Pyramidal, rod-like, and spherical gold nanostructures were electrochemically prepared at different potentials and different $HAuCl_4$ concentrations. The nanopyramids were primarily dominated by (111) facets. The pyramidal nanostructures exhibited a unique plasmon-based color due to their anisotropic morphology and a low oxygen reduction activity owing to a lack of (100) and (110) facets, which are more active for the reaction than (111). The shape-controlled deposition of gold nanostructures would be useful in the development of gold films that are potentially applicable to electrocatalysis, surfaceenhanced Raman scattering (SERS), surface plasmon sensors (SPR), and so on.