Electrochemical Growth of Two-Dimensional Gold Nanostructures on a Thin Polypyrrole Film Modified ITO Electrode

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Two-dimensional gold nanostructures have been fabricated by electrochemical deposition of gold nanoparticles onto indium tin oxide (ITO) glass substrate modified with thin polypyrrole film. By controlling the electrodeposition conditions, gold nanoparticles with dendritic rod, sheet, flower-like (consisting of staggered nanosheets), and pinecone-like structures were generated. The flower-like gold nanoparticles showed high catalytic activity on electrochemical reduction of oxygen, and its activity was measured to be approximately 25 times that of gold pinecones and 10^4 times that of gold nanosheets in terms of gold weight. The pinecone-like nanoparticles can form a compact film with nano-/microscale binary structure like a lotus leaf surface. After modification with *n*-dodecanethiol, the surface showed superhydrophobic properties with a water contact angle of 153.4° and a tilt angle of 4.4° (5 μ L droplet).

Introduction

Nanoparticles of noble metals have attracted steadily growing attention due to their interesting optical,¹ electrochemical,² electronic,³ and photoelectrochemical⁴ properties. Recently, colloid chemistry has been widely applied to synthesize metal nanoparticles with various structures such as triangular prisms,⁵ cubes,6 rods,7 and wires.8 However, metal colloidal nanoparticles dispersed in liquid phase cannot be used directly for some purposes, for example, catalysis, because the separation and recycle of the metal particles should be taken into account. So an additional procedure is required to immobilize nanocatalysts to a solid substrate to form two-dimensional (2-D) nanostructures.9 In the past few years, many studies have investigated the control of gold nanoparticle size, their composition, and their self-assembly or self-organization into two-dimensional (2D) and three-dimensional (3D) structures.^{10,11} A number of onestep techniques including physical vapor deposition,¹² electrochemical plating,¹³ a modified silver reaction,¹⁴ and galvanic replacement¹⁵ have been developed for fabricating 2-D nanostructures. Gold nanoparticles deposited on solid supports exhibit useful catalytic and electrocatalytic properties. Moreover, the catalytic activity of gold nanoparticles exhibits significant size dependence.16

On the other hand, as one of the most studied conducting polymers, polypyrrole (PPY) is an excellent material to be used as a substrate or matrix for deposition of metal nanoparticles (including copper, palladium, and hybrid materials).¹⁷ In this paper, we desire to report electrochemical deposition of gold nanoparticles on a thin dodecylbenzene sulfonate (DBS) doped polypyrrole film coated ITO electrode surface. It was found that gold nanoparticles with dendritic rod, nanosheet, flower-like,

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and pinecone-like structures were generated. Furthermore, the electrocatalysis activity and surface property of the films made of these nanoparticles depend strongly on their morphology.

Experimental Section

Chemicals. KAuCl₄, H_2SO_4 , sodium dodecylbenzene sulfonate (DBS), *n*-dodecanethiol, HClO₄, and LiClO₄ were products of Beijing Chemical Company (Beijing, China) and were used directly. The ITO glass plates were purchased from Asahi Beer Optical, Ltd (Japan) and they were used after being washed in acetone, ethanol, and pure water by sonication and drying with a nitrogen stream. In all the procedures, we used pure water prepared using a Millipore Autopure WR600A apparatus. Pyrrole (Chinese Army Medical Institute, Beijing, China) was distilled under reduced pressure before use.

Instruments. Scanning electron micrographs (SEM) were taken out by the use of a FEI Sirion 200 or a S530 (Hitachi) scanning electron microscope. Water contact angles were measured on a contact angle system model OCA 20 made by Dataphysics Instruments GmbH (Germany); the size of the distilled water droplet was 5 μ L. Electrochemical deposition and examinations were performed in a one-compartment cell by the use of a Model 273A potentiostat (EG&G Princeton Applied Research) under computer control.

Electrochemical Growth of PPY Film. The working electrode was an ITO glass sheet (0.5 cm^2) , and the counter electrode was a platinum sheet (3.0 cm^2) . The two electrodes were placed 1.5 cm apart. All potentials were referred to an Ag/AgCl electrode, which was immersed directly in the electrolyte. The typical electrolyte was a 0.1 or 0.2 M DBS solution containing 0.1 M pyrrole. All the solutions were deaerated by dry nitrogen bubbling for 5 min and a slight nitrogen overpressure was maintained during the experiments. The PPY films were grown



Figure 1. SEM images of the gold nanostructures deposited at 0.6 mA cm⁻² for 200 s each on a bare ITO (a) and the ITOs modified with 10 (b) 14 (c), 20 (d), or 30 nm (e) PPY. The PPY films of panels b-e were grown in the electrolyte containing 0.2 M DBS, while that of panel f was prepared in the electrolyte containing 0.1 M DBS (film thickness = 14 nm).



Figure 2. SEM images of Au nanoparticles deposited on a 14-nm-thick PPY at 0.6 mA cm⁻² for 15 (a), 20 (b), 25 (c), or 2000 s (d). Inset of part b: a magnified view. Insert of part d: a photo of a water droplet (5 μ L) on the surface of part d modified with *n*-dodecanethiol.



Figure 3. SEM images of Au nanoparticles deposited on a 14-nm-thick PPY modified ITO at 0.125 mA cm⁻² for 100 (a), 2000 (c), or 4000 s (e); panels b, d, and f are the magnified views of panels a, c, and e, respectively.

at a constant current density of 2.45 mA cm⁻² and their thickness was calculated from the total charge density passed through the cell during the film growth process (the thickness of a PPY film grown for 500 mC cm⁻² was measured to be 1 μ m).

Electrochemical Growth of Au Nanostructures. The working electrode was an ITO sheet covered with a thin PPY film, the counter electrode was a platinum sheet, and the reference electrode was a saturated calomel electrode (SCE). Au nanostructures were electrodeposited by electrolyzing the aqueous solution of $0.5 \text{ M H}_2\text{SO}_4$ and 0.1 M KAuCl_4 at a constant current density.

Modification of the Two-Dimensional Gold Nanostructures to Superhydrophobic Surface.^{18,19} The ITO electrodes coated with PPY films and Au nanostructures were immersed into the ethanol solution of 0.01 M *n*-dodecanethiol for 24 h, then taken out and washed repeatedly with ethanol, and finally dried in air.

Electrocatalytic Reduction of Oxygen. The working electrode was an ITO sheet coated with a PPY film and Au nanostructures and the counter electrode was a platinum sheet. The two electrodes were placed 1.5 cm apart. All potentials were referred to a saturated calomel electrode (SCE). The electrolyte was an aqueous solution of 0.01 M LiClO₄ and 0.1 M HClO₄. The deoxygenated and oxygen saturated electrolytes were prepared by bubbling the electrolytes with dry N₂ or O₂ for 30 min, respectively.

Results and Discussion

The Effects of PPY Film. The polypyyrole (PPY) film grown from an aqueous or acetonitrile solution of LiClO₄ was found to be brittle and weak. Furthermore, it adhered weakly to the ITO substrate. Thus, we used an organic salt, DBS, as the supporting electrolyte. The PPY film deposited from the 0.2 M aqueous solution of DBS at a constant current density of 2.45 mA cm⁻² coated the electrode surface firmly and uniformly. Figure 1 shows the SEM images of gold nanostructures deposited at 0.6 mA cm⁻² for 200 s each on a bare ITO (a) and a ITO modified with 10 (b), 14 (c), 20 (d), or 30 nm (e) PPY, respectively. As can be seen from this figure, the nanoparticles grown on the bare ITO electrode are roundish and located sparsely on the electrode surface. The particles adhered weakly to the substrate and part of them fell off the substrate during the processes of electrodeposition and sample washing. This is why the number density of gold nanoparicles in Figure 1a is distinctly lower than that shown in Figure 1b. On the PPY modified surfaces, the nanoparticles tend to aggregate into 3-dimensional nanoarchitectures with morphology like pinecones. With the increase of PPY film thickness, gold nanoparticles tend to aggregate into larger pinecones in lower number density. This is possibly due to a thicker PPY film providing fewer pinholes for nucleation and growth of the nanoparticle. Because equal charge density produces a nearly



Figure 4. SEM images of gold nanoparticles deposited on a 14-nm-thick PPY modified ITO at 1.2 mA cm⁻² for 10 (a), 20 (b), 30 (c), 50 (d), 100 (e), and 200 s (f). The insets of panels c, d, and f are the corresponding magnified views.

equal amount of gold in unit area (neglect the charge used for reduction of the PPY film because of its ultrathin thickness), thus larger particles should be generated on a thicker PPY film. The optimum thickness of the PPY film for growing uniform pinecones and other gold nanostructured films was tested to be about 10-15 nm. The increase of DBS concentration in the electrolyte used for PPY growth was found to be helpful for growing a uniform gold nanoparticle film. In comparison, as a 0.1 M aqueous solution of DBS was used, the uniformity of the nanoparticles (Figure 1f) was worse than that deposited on the PPY film formed by using a 0.2 M DBS solution (a saturated solution) as the electrolyte (Figure 1c).

The Effects of Current and Charge Densities. As described above, the nanoparticles grown on a 14 nm PPY modified ITO at a current density of 0.6 mA cm⁻² have morphology like pinecones. Figure 2 illustrates the SEM images of gold nanoparticles grown under this condition for different deposition times (or charge density). It is clear from this figure that the number density of the pinecones increased with the increase of deposition time. Finally, the nanoparticles merged together to form a nano-/microscale binary structured film like a lotus leaf surface (Figure 2d). We modified the surface shown in Figure 2d with the ethanol solution of *n*-dodecanethiol. The water contact angle of the modified surface was measured to be as high as 153.4° and its tilt angle was 4.4° (Insert of Figure 2d). In comparison, the contact angle of a flat gold film modified with *n*-dodecanethiol was measured to be only 110°. This result indicated that the nano-/microscale binary structure of the nanoparticle film surface strongly enhanced its hydrophobicity. In this case, the water contact angle of the rough surface (θ^*) can be explained by Cassie's equation, $\cos\theta^* = -1 + \varphi_s(1 + \cos \theta)$ (φ_s is the fraction of solid in contact with water, θ is the contact angle of a flat surface). Accordingly, the φ_s of the modified nano-/microscale binary structured gold surface was calculated to be approximately 16.1%, indicating about 83.9% of the total surface area was trapped with air.

If the gold nanostructure was grown at a relatively low constant current density of 0.125 mA cm⁻², as shown in Figure 3, the morphology of the nanoparticles was different from that shown in Figure 2. In the initial stage (Figure 3a,b), flower-like gold nanoparticles consisting of staggered nanosheets were generated and located sparsely on the electrode surface. The diameter of the flower was about 4 μ m and the thickness of the nanosheets was about 70 nm. The size of the flowers is much larger than that of the pinecones shown in Figure 2 (<1 μ m).With the increase of deposition time, the nanosheets changed into irregular particles such as pine nuts, just like the particles deposited at 0.6 mA cm⁻². When the deposition time increased up to 4000 s, nanoparticles merged together to form a flat film. After modification with dodecanethiol, the contact



Figure 5. The voltage (V) versus time (t) curves recorded during the electrochemical deposition process. The Au was deposited on a 14-nm-thick PPY modified ITO at 0.125 (a), 0.6 (b), and 1.2 mA cm⁻² (c), respectively.



Figure 6. Cyclic voltammograms of various 2-dimensional gold nanostructures grown on 14-nm PPY modified ITO electrodes in deoxygenated (the blue cycle) or oxygen saturated aqueous solutions (the other cycles) of 0.1 M $HCIO_4 + 0.01$ M $NaCIO_4$ at a potential scan rate of 20 mV s⁻¹: (A) red and blue, pinecones (grown at 0.6 mA cm⁻² for 200 s); green, flowers (grown at 0.125 mA cm⁻² for 100 s); black, a 0.1 mm gold wire; (B) sheets (grown at 1.2 mA cm⁻² for 520 s).

angle of the film was measured to be lower than 120°, indicating the film was flat and compact.

At a high constant current density of 1.2 mA cm^{-2} , in the initial stage of electrochemical deposition (Figure 4a,b), the morphology of the gold nanoparticles is similar to that of the particles formed at 0.6 mA cm⁻² (Figure 1a,b). However, the particle sizes are not uniform and most of them are as small as only several tens nanometers. With the increase of deposition time, nanoparticles with dendritic rod structures were generated and their number density was also increased (Figure 4c-e). Finally, the dendritic rods changed into nanosheets with

thickness of about 20 nm and the nanosheets stand upright with their surfaces vertical to that of the substrate and staggered into a 2-dimensional network (Figure 4f).

Mechanism Considerations. As described above, the morphologies of gold nanostructures depend strongly on the electrochemical deposition conditions. Figure 5 illustrates the typical voltage–time (V-t) curves recorded during the electrochemical deposition process. It is clear from this figure that the deposition voltage decreases sharply in the initial period, then gradually to a stable value. This is the process of nucleation. As we know, in the instantaneous growth mode, once all of the



Figure 7. XRD patterns of the flower-like (a, grown at 0.125 mA cm^{-2} for 100 s), sheet-like (b, grown at 1.2 mA cm^{-2} for 2000 s), and pinecone-like (c, grown at 0.6 mA cm^{-2} for 200 s) nanostructured films on 14-nm-thick PPY modified ITO electrodes.

nucleation sites are occupied, further increase in the deposition time would only increase the size of the nanocrystals and not their number density because no new nucleation sites are created.^{20,21} According to Figure 5 and the SEM results described above, the growth of gold nanostructures described above can be regarded as an instantaneous nucleation process.

On the other hand, it is interesting to find that Figure 5a shows a lowest potential at about -2.5 V and a stable potential at about -2 V. These values are much lower than those shown in Figure 5b. This is possibly due to that at the low current density of 0.125 mA cm⁻², gold nanoparticles nucleated principally on the surface of PPY film because of their large sizes ($\sim 4 \mu m$). Accompanied by the deposition of gold nanoparticles, the PPY film was reduced into the insulating state and the high resistance of the PPY film contributed a large potential drop. With the increase of current density, more and more gold nuclei are formed in the PPY matrix or on the bare ITO surface^{22,23} because of the reducing of nuclei sizes. Thus, the contribution of the PPY film resistance to the potential drop was greatly weakened. The PPY surface induced the formation of relatively flowerlike nuclei, while the nuclei formed in the PPY matrix or on bare ITO are roundish. However, at a very high current density (e.g., 1.2 mA cm⁻²), the edges and corners of the roundish nuclei grow faster than their other regions and finally grow into gold nanosheets with stable crystal phases as confirmed by XRD examinations described below. The quality of the PPY film is crucial for growing high-quality gold nanostructures. For example, polymerization of pyrrole at a high current density (e.g., 10 mA cm⁻²) generated a highly porous PPY coating and gold flowers could not be grown on this surface. In this case, the gold nanostructures were favored to be grown randomly in the pores of the film. This result strongly supports the mechanism described above.

Electrocatalytic Reduction of Oxygen. Gold nanoparticles are known to have catalytic activity on electrochemical reduction of oxygen.^{24,25} We used pinecone-like (grown at 0.6 mA cm⁻² for 200 s), flower-like (grown at 0.125 mA cm⁻² for 100 s), and sheet-like (grown at 1.2 mA cm⁻² for 520 s) 2-dimensional gold nanoarchitectures on a 14 nm PPY modified ITO as a test. In a deoxygenated electrolyte, the cyclic voltammogram of the electrode with pinecone nanostructures showed no reduction waves of oxygen in the potential range of -0.8 to 0 V (Figure 6A, blue cycle). However, in an oxygen-saturated electrolyte, a well-defined broad cathodic wave centered at approximately -370 mV appeared as the potential swept from -1.0 to 0.0 V

(Figure 6A, red cycle). This wave is assigned to catalytic reduction of oxygen.²⁴ In comparison, on the CV of bare gold wire (Figure 6A, black cycle) or the electrode with sheet-like nanostructures (Figure 6B) the catalytic reduction wave is weak. indicating a fairly low catalytic activity. The catalytic oxygen reduction current densities (calculated by minus the peak current densities with their corresponding baseline current densities at the same potentials) of the pinecone-like and flower-like nanostructures were measured to be 6.5 and 20.3 times that of the gold wire in terms of film area, respectively. Furthermore, according to the total charge density used for electrochemical depositions, the gold amount within a given surface area for the flower-like nanostructure was only 12% to that of pineconelike nanostructure and about 0.2% to that of sheet-like nanostructures. Thus, the catalytic activity for the flower-like nanostructure was about 25 times that of pinecone-like nanostructures and about 10⁴ times that of a nano-sheet-like nanostructure in terms of gold weight.

The particle sizes of gold flowers (>4 μ m) are much larger than those of nanosheets or pinecones ($<1 \mu m$), and as a result, their specific surface area is the lowest among these three gold nanostructures. Thus, the high catalytic activity of gold flowers cannot be attributed only to their high specific surface area. The XRD (X-ray diffraction) patterns of the three 2-dimensional nanoarchitectures described above were illustrated in Figure 7. It was clear from this figure that all the patterns have the lines of gold [111] and [200] crystal faces. However, only the pattern of flower-like nanostructures showed the lines of Au [220] and Au [331] faces with medium intensity (Figure 7a). The [220] and [331] lines in parts b and c of Figure 7 are very weak. The catalysis characters were related to the crystal structures of the nanoarchitectures. High-Miller-index crystal faces exposed surface irregularities.²⁶ The gold atoms in Au [220] and Au [331] faces have higher unsaturation than those in Au [111] and Au [200] faces. Thus, they adsorbed oxygen molecules more easily and had relatively higher catalysis activity. This is why the flower-like nanostructures have excellent catalytic behavior.

Conclusions

Gold nanostructures with morphology of pinecone-like, flower-like, dendritic rods, and nanosheets were generated by electrochemical deposition of gold on ITO electrode modified with a thin PPY film. The pinecone-like nanostructures were generated at a high deposition current density of 0.6 mA cm^{-2} and they can be grown into a nano-/microscale binary structure like that of the lotus leaf surface. A superhydrophobic surface with water contact angle of 153.4° and a tilt angle of 4.4° was fabricated by modifying the nano-/microscale binary structured surface with *n*-dodecanethiol. The flower-like nanostructures consisting of staggered nanosheets can be generated at a low deposition current density of about 0.125 mA cm^{-2} for a low deposition charge density ($<30 \text{ mC cm}^{-2}$). They have high contents of [220] and [331] gold crystal faces which provided the nanostructures with higher catalytic activity of oxygen reduction. Gold nanosheets with a thickness of about 20 nm were obtained by deposition of the gold at a current density of 1.2 mA cm⁻² for a large charge density (>60 mC cm⁻²). The pinecones and nanosheets consist of mainly the [111] and [220] crystal faces and had low catalytic activity.

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References and Notes

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