Electrochemical Growth of Gold Pyramidal Nanostructures: Toward Super-Amphiphobic Surfaces

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In this communication, we report electrochemical deposition of gold pyramidal nanostructures, leading to super-amphiphobic surfaces. Super-amphiphobic surfaces, i.e., surfaces that exhibit both water-repellent and oil-repellent properties, have attracted considerable interest because of their great importance in daily life as well as in many industrial and biological applications.[1,2] Because of the small contact area with liquid, chemical reactions or bond formation through liquid would be limited for super-amphiphobic surfaces. So, various phenomena are expected to be inhibited on such surfaces, for example, snow sticking, contamination, corrosion, oxidation, and current conduction. Up until now, a large number of efforts from various fields have been focused on fabricating super-hydrophobic or super-lipophobic surfaces.[3−6] These surfaces have been commonly prepared through the combination of a suitable chemical structure (surface energy) and a topographical structure (surface roughness). However, there are only a few reports on both super-hydrophobic and -lipophobic surfaces. Jiang and his co-workers have realized a super-amphiphobic surface on aligned carbon nanotube films.[7] More recently, a super-hydrophobic and -lipophobic coating surface has been prepared with polymer materials.[8] Nakajima and his co-workers have realized a super-amphiphobic surface using a combination of boehmite nanoparticles and fluoroalkylsilane and found that a super-lipophobic surface requires a larger surface roughness than a super-hydrophobic one.[1,9]

Recently, nanostructured metal particles have attracted more and more attention from various fields because of their unique physical and chemical properties that are different from those of bulk metals. Synthesis of metal nanostructured particles, ranging from nanorods,[10] nanowires,[11] nanorings,[12] and nanobelts[13] to nanocubes,[14] nanoprisms,[15] and nanoplates,[16] have been reported on the basis of their potential applications in electronic, optical, thermal, catalytic, or magnetic functional[17−21] materials and devices. These broad applications motivate the exploration and development in assembling metal nanoparticles onto solid substrates. Up until now, nontemplated and templated self-assembly techniques, electron-beam lithography (EBL), and other methods have been employed to fabricate metal nanostructures. Besides these routes, electrochemical deposition is another effective means. Various morphologies including rodlike[22] and dendritic[23a] gold nanostructures have been obtained in a one-step process without templates, typically in the presence of an additive such as Pb^{4+},[23−26] cysteine,[23] or I^-.[23b] However, those nanostructures have not necessarily been well-defined.

Here, nanopyramidal, nanorodlike, and nanospherical gold nanostructures were fabricated onto sputtered gold substrates by electrochemical deposition for the sake of unique functional surface preparation. It is interesting that among the as-prepared nanostructured gold films, the nanopyramidal surface shows both super-hydrophobic and super-lipophobic

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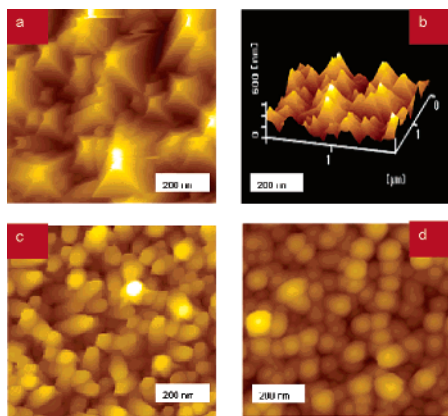
Figure 1. AFM images of the electrodeposited pyramidal ((a) plan and (b) cross), (c) rodlike, and (d) spherical gold nanostructures. Similar images were obtained when different spots were scanned.

Figure 2. CA of (a–c) water drops and (d–f) oil drops on (a, d) nanopyramidal gold film, (b, e) nanorodlike gold film, and (c, f) nanospherical gold film, after the modification of perfluorodecanethiol for 3 h. Drop volume for both water and oil is 4 μL.

properties; it does so only after being immersed into perfluorodecanethiol (low surface energy) methanolic solution for 3 h to reduce its surface free energy, not only due to the rough surface but also due to the very large fraction of air and the very small fraction of pyramidal gold particles on the sputtered gold film. A large-area super-amphiphobic surface was created in an ambient atmosphere with gold pyramidal nanostructures.

Pyramidal, rodlike, and spherical gold nanostructures were electrodeposited for 2 min onto Au sputtered ITO films (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 the thickness of about 50 nm estimated by AFM was sputtered on the clean ITO glass plate.) 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 vs Ag/AgCl, respectively. The morphology of gold nanostructures with various shapes, such as nanopyramidal (images a and b of Figure 1), nanorodlike (Figure 1c), and nanospherical structures (Figure 1d), were characterized by atomic force microscopy (AFM). In the case of nanopyramids, the edge length of the bottom was 50−200 nm and the height observed from the cross-section shown in the inset of Figure 1b was several hundred nanometers. Nanorods grew out to about 100 nm wide and up to 200−300 nm long, or more. On the other hand, the diameters of the nanospheres ranged from 70 to 100 nm. The preliminary elucidation on the growth mechanisms of gold nanostructures was studied by electrochemical methods (see the Supporting Information). The experimental results indicated that nanopyramidal structures grew at the early stage by diffusion-controlled step, followed by intananeous 3D nuclei growth on the gold substrate, whereas nanospherical structures closely followed the response predicted for 3D progressive nucleation controlled by the diffusion of Au(III) ions. The growth of nanorodlike structures could be defined as instantaneous, followed by 3D growth limited by adatom incorporation into the substrate lattice. The different growth mechanisms determine the shape and morphology of gold nanostructures electrodeposited onto gold substrates. The roughness factors for nanopyramidal, nanorodlike, and nanospherical surfaces estimated from AFM
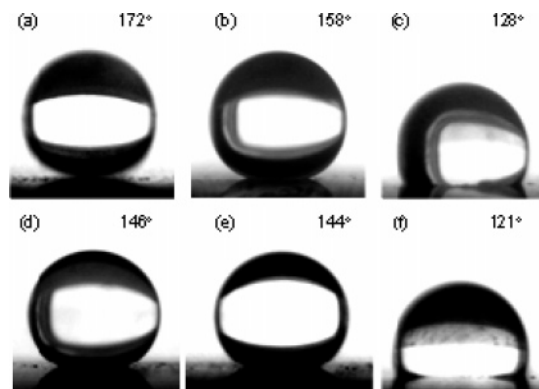
images are 3.26 ± 0.05, 2.43 ± 0.07, and 1.21 ± 0.11 (average ± standard error of 3 samples), respectively.

The CAs of the as-grown nanostructured, i.e., nanopyramidal, nanorodlike, nanospherical, gold films for water are about 5, 8, and 27°, whereas the CAs for rapeseed oil (the primary composition of this kind of rapeseed employed in our experiments was oleic acid ($CH_3(CH_2)_7(CH)_2(CH_2)_7$-COOH)) were about 7, 15, and 43°, respectively. The CAs of gold substrates for water and oil are 32 and 48°, respectively. However, after the modification of 1H,1H,2H,-2H-perfluorodecanethiol, which repels both water and oil, the CAs for both water and oil remarkably increased at all nanostructured gold surfaces. We optimized the modified time and found that the CAs exhibited the maximum value at an immersion time of about 3 h. The shape of a water or oil droplet on the surfaces after modification of perfluorodecanethiol for 3 h are demonstrated in Figure 2. We can see that the CAs of nanostructured gold surfaces both for water and oil increase with the increasing roughness factor, in the order nanopyramids > nanorods > nanospheres. The surface topographic structure is an important factor that strongly affects the wettability. As described in Wenzel's equation,[27]

$$\cos \theta_r = r \cos \theta$$

in which θ_r is the apparent CA on a rough surface and θ is the intrinsic CA on a flat surface, the surface roughness can enhance both the hydrophilicity and the hydrophobicity of the surfaces. So, among the three kinds of nanostructured gold surfaces, the nanopyramidal surface shows the most amphiphilic and the most amphiphobic properties before and after the modification, respectively, because it has the greatest roughness.

From the X-ray diffraction (XRD) patterns of gold nanostructures as shown in Figure 3, we can determine that the diffraction peaks of nanopyramidal, nanorodlike, and nanospherical gold structures electrodeposited on gold substrates correspond to (111), (200), (220), (311), and (222) diffraction peaks of metallic Au, demonstrating that as-prepared nanostructured gold films are composed of pure

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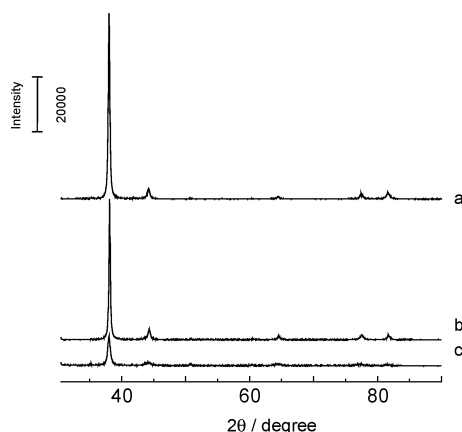
Figure 3. X-ray diffraction patterns of the electrodeposited (a) pyramidal, (b) rodlike, and (c) spherical gold nanostructures.

crystalline Au with face-centered cubic (fcc) structures. So, 1H,1H,2H,2H-perfluorodecanethiol strongly assembles onto the nanostructured gold surfaces through Au−S chemical bonds, as reported previously,[28] and the modified nanostructured gold surfaces were fluorinated. The chemical composition was also confirmed by X-ray photoelectron spectroscope (XPS). The C and F concentrations at the modified nanostructured gold surfaces are more than 80 at %, thus indicating that these surfaces are mainly composed of fluorocarbon. The CAs of the nanopyramidal surface for water and oil were found to be $172.1 \pm 1.6°$ (Figure 2a) and $150 \pm 2.1°$ (Figure 2d), showing both super-hydrophobic and -lipophobic properties, although the CAs of the gold substrate were only $136.5 \pm 1.1°$ and $115 \pm 1.2°$ for water and oil after modification, respectively. We also use sliding angle (SA) as a criterion for the evaluation of hydrophobicity of a solid surface, which is considered to be an important factor in deciding the super-hydrophobicity. In our experiments, even with a small tilt angle of the surface ($<3°$), the water droplets will roll off the surface, confirming again that this nanopyramid surface is super-hydrophobic.

To further understand the characteristic of such nanostructured gold surfaces, we introduce Cassie's equation[29]

$$\cos \theta_r = f_1 \cos \theta - f_2$$

in which f_1 and f_2 are the fractions of nanostructured gold particles and air on the gold films, respectively (i.e., $f_1 + f_2 = 1$). This equation indicates that θ_r increases with an increasing fraction of air (f_2). We can roughly estimate f_1 and f_2 from known contact angles. Taking the raised nanopyramidal gold surface as an example, we found that

the water contact angle θ_r on the nanopyramidal gold surface after perfluorodecanethiol modification was $172.1 \pm 1.6°$ and the contact angle θ on the perfluorodecanethiol-modified gold substrate was $136.5 \pm 1.1°$. Using these values, we calculated f_1 and f_2 to be 0.03 and 0.97, respectively. These values reveal that there is a very large fraction of air and a very small fraction of nanopyramidal gold particles on the sputtered gold film, thus resulting in super-hydrophobic and -lipophobic properties. This result is comparable to that obtained at super-amphiphobic aligned carbon nanotube films.[8] On the other hand, in the case of nanorods and nanospheres gold films, f_1 and f_2 are similarly calculated to be 0.16 and 0.84 ($\theta_r = 158°$, $\theta = 120°$), 0.41 and 0.59 ($\theta_r = 129°$, $\theta = 87°$), respectively. So, we can deduce that the most super-amphiphobic properties of the nanopyramidal gold surface are not only attributed to the roughest surface but also ascribed to the largest fraction of air. The air trapped within the interstices of the nanopyramidal surface greatly increases the air/liquid interface, effectively preventing the penetration of water or oil droplets into the grooves. These results demonstrate that the surface morphology plays a highly important role in the creation of a super-hydrophobic and super-lipophobic surface. The as-prepared nanostructured gold surfaces showed good reproducibility. We also investigated the stability of the nanostructured gold films, and the CAs showed no obvious changes after 50 days of being exposed to an ambient atmosphere, indicating that as-prepared gold nanostructures have a relatively long stable period.

In summary, gold pyramidal nanostructures were prepared by a one-step, nontemplated, low-cost electrochemical method and were compared with electrochemically prepared rodlike and spherical gold nanostructures. The rough gold nanopyramidal surface, combined with a perfluorodecanethiol coating and very large fraction of air on the film, determines the super-hydrophobic and super-lipophobic properties. This study provided a methodology for fabricating diverse nanostructured metal films and subsequently creating super-amphiphobic surfaces for resistance to corrosion, self-cleaning, and other practical applications. Further investigation on the growth mechanism of the gold nanostructures is underway.

Supporting Information Available: Preliminary elucidation on the growth mechanism of gold nanostructures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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