Electrodeposition of gold nanorods with a uni-directional crystal growth and lower Au(111) facets area

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Stable Au nanorods with a uni-directional pin-like morphology have been prepared on the surface of glassy carbon (GC) electrodes via a potential-step electrodeposition method from H₂SO₄ solution containing Na[AuCl₄] in the presence of cysteine as an additive. The Au nanorods are characterized by a relatively low Au(111) facets area because of a continuous uni-directional growth of the crystal along the (111) orientation leading to a pin-like morphology of the crystals. In other words, there is a significant enrichment of Au(100) and Au(110) facets in contrast to the spherical Au nanoparticles prepared in the absence of cysteine. The peak potential of the oxygen reduction reaction, measured in O₂-saturated 0.5 M H₂SO₄, at the thus-prepared Au nanorods electrodeposited onto glassy carbon (nano-Au/GC) electrodes shows a significant positive shift compared to that obtained at the nano Au/GC electrode prepared in the absence of cysteine, demonstrating a higher electrocatalytic activity of these Au nanorods.

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Introduction

Nowadays, synthesis and application of metallic nanocrystals with controllable morphology and shapes are of great interest. Gold nanoparticles are one of the most stable metal nanoparticles and have been studied for many years due to their quantum size-related electronic, optical and magnetic properties, and wide applications in catalytic, electrochemical, biochemical and materials sciences. For example, rods, cubes, and mixtures of triangular, hexagonal and spherical gold nanoparticles have been successfully prepared. Additionally, the particle size and crystallographic morphology of gold particles are important factors in their electrocatalytic behavior, design of nanoelectrode, investigation of catalytic mechanism and the structure sensitivity of some important electrochemical reactions, e.g., oxygen reduction⁴,⁶, etc. Synthesis and optical properties of “branched” gold nanocrystals in high yield (over 90%) via a wet-chemical route have been reported⁶. Gold nanoparticles have been dispersed on supports of α-Fe₂O₃, Co₂O₄, or NiO oxides by coprecipitation method⁸, and utilized not only for the catalytic hydrogenation of unsaturated alcohols and aldehydes, but also for oxygen reduction because of their remarkable electrocatalytic activity⁹,¹⁴. Recently, Daniel and Astruc¹⁵ presented a review on the assembly, supramolecular chemistry, quantum-size-related properties, and applications in biology, catalysis, and nanotechnology. A notable point is that most of the Au crystals have a larger area of Au(111) facets than Au(100) facets since the crystal structure of gold is close-packed face-center cubic (fcc) and has cuboctahedral equilibrium shape with (111) facets normally presenting lower surface energy than (100) facets. Facet area is inversely related to the surface energy of its facet; facets of lower surface energy forming larger facets area¹⁶.

At the same time, most of these gold nanocrystals are prepared in solutions but not fixed on a substrate, since the gathering of such nanocrystals into large clusters or domains would change or cause the disappearance of the advanced properties of nanosize. It is well known that several applications of nanocrystals in the fields of electrocatalysis, bioelectrochemistry, functional materials and electric devices are based on their conducting and attaching or binding properties with substrate surfaces. Although specific binding molecules have been used to connect gold nanoparticles and the substrates, such as molecules with -SH or -NH₂ groups to bond with...
gold particles and silanol or 4-mercaptophenyl groups bonded to the substrates of glass or carbon, gold nanoparticles formed on the conducting substrate without using binder molecules are of great interest, in view of the fact that the surrounding environment of the nanoparticles strongly influences their catalytic activity and conductivity.

In the present work, pin-like Au nanorods with obviously lower Au(111) facets area have been obtained directly and stably on the surface of GC electrode. Potential-step electrolysis has been performed to prepare Au nanocrystals in the presence of cysteine as an additive. Such Au nanorods possess a significant enrichment of areas of (100) and (110) facets at the expense of (111) facets, leading to considerable electrocatalytic activity for the oxygen reduction reaction in 0.5 M H_2SO_4 solution.

**Materials and Methods**

Au nanorods were deposited on GC electrode (φ = 3 mm) by electrodeposition from N_2-saturated 0.5 M H_2SO_4 solution containing 1.0 mM Na[AuCl_4] (Wako Pure Chemical Co., Japan) in the presence of 0.1 mM cysteine (Wako Pure Chemical Co., Japan) by applying potential step electrolysis from 1.1 to 0 V for different deposition time (t_d). Self-assembled monolayer (SAM) of cysteine was prepared on the thus-prepared nano-Au/GC electrodes (obtained at t_d = 1000 s in the presence and absence of cysteine, respectively) by immersing into 1.0 mM cysteine (aqueous solution) for 20 min.

A computer-controlled electrochemical analyzer (ALS/CHI 630A) and a standard two-compartment three-electrode electrochemical cell were used for the electrochemical measurements, with a platinum wire auxiliary electrode and a potassium chloride-saturated silver|silver chloride (Ag|AgCl, KCl-sat.) reference electrode. Prior to use, GC electrodes were polished with emery paper, and aqueous slurries of successively finer alumina powder (down to 0.06 μm) on a polishing microcloth, wet with Milli-Q water and then carefully rinsed with Milli-Q water in an ultrasonic bath for 10 min. Au electrodes (φ = 1 mm) were polished in the same way, and then electrochemically pretreated in 0.05 M H_2SO_4 solution (N_2-saturated) by cycling the electrode potential between −0.2 and 1.5 V at 100 mV s\(^{-1}\) for 10 min, or until the characteristic I-V curve of a clean Au electrode was obtained. All the electrochemical measurements were performed at room temperature (25 ± 1°C), and current densities were calculated on the basis of the geometric surface areas of the GC and Au electrodes.

The morphology of the different Au particles electrodeposited onto GC electrode was studied by scanning electron microscopy (SEM) measurements, conducted with a JSM-T220 scanning electron microscope (JEOL, Japan) at an acceleration voltage of 15 kV and a working distance of 4-5 mm. The X-ray diffraction (XRD) measurements were performed on a Philips PW1700 Power X-ray diffractometer, using Cu Kα1 radiation (λ = 1.54056 Å) with a Ni filter working at 40 kV and 30 mA.

**Results and Discussion**

SEM photographs of the Au nanorods prepared at different t_d's, 1000 and 2000 s, in the presence of cysteine are shown in Fig. 1 (a & b), while those of Au nanoparticles obtained under the same experimental conditions but in the absence of cysteine are presented in Fig. 1 (c & d) for comparison. Au nanoparticles deposited at t_d = 2000 s were much larger in size than those at t_d = 1000 s irrespective of the presence or absence of the additive cysteine, which suggests that the size of Au particles increases with increasing t_d. A noticeable image of the Au particles electrodeposited in the presence of cysteine [shown in Fig. 1 (a & b)] is that they are pin-like crystals (i.e., uni-directionally grown nanorods) and do not possess spherical domains such as those prepared in the absence of cysteine (shown in Fig. 1 (c & d)). This implies that such a preferential crystallization of Au particles occurs on a certain crystalline facet, which might be caused by the existence of cysteine that favors an electrodeposition and growth of Au crystals in a particular crystalline orientation.

To study the influence of cysteine on the preferential crystallographic orientation of the electrodeposited Au nanoparticles, SAMs of cysteine on the nano-Au/GC electrodes were prepared. Figure 2 shows the cyclic voltammograms obtained at two successive potential scans for the reductive desorption of cysteine SAMs formed on the Au/GC electrode, which were prepared in the presence (curve a) and absence (curve b) of cysteine. It is clearly observed that the peak currents for the nano-Au/GC electrodes prepared in the presence of cysteine are higher than those prepared in its absence, which will lead to a higher total faradaic charge consumed during the reductive desorption process at curve (a) than that at curve (b). That is because the pin-like Au crystals,
Fig. 1—SEM photographs of Au particles electrodeposited on GC electrode from N₂-saturated 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in the presence (a and b) and absence (c and d) of 0.1 mM cysteine by applying a potential step electrolysis from 1.1 to 0 V for 1000 s (a and c) and 2000 s (b and d). Each division of the gauge in the photographs is 500 nm.

Deposited on the GC electrode with cysteine, contribute more crystalline facets and in turn higher surface area binding with cysteine SAMs, which were desorbed during the two successive potential scans. The reduction peak at ca. -0.78 V in the first scan (corresponding to the reductive desorption of cysteine from (111) facets of the Au crystals) disappeared completely in the second scan, which means that the binding between cysteine and (111) facets was easily broken during the potential scans, and therefore no reductive peak appeared at (111) facets in the second scan. Meanwhile, the current response at ca. -1.0 V and -1.1 V (ascribed to that from the (100) and (110) facets of Au crystals respectively) could be observed clearly in the second scan although considerably decreased. The above results prove that Au(111) is the most favorable facet of Au crystals from which the reductive desorption of cysteine occurs, and that cysteine adsorbs more strongly on the Au(100) and Au(110) facets than on the Au(111) facets. Thus, the presence of cysteine enriches Au(100) and Au(110) facets by strongly binding with these facets and preventing more Au particles from depositing on these facets during the process of deposition. Consequently, a preferential electrodeposition of Au particles would occur on Au(111) facet, ultimately leading to a growth of the pin-like Au nanorods along the (111) orientation.

The electrodeposition behavior of Au particles was characterized by CV responses on bare GC electrode in N₂-saturated 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in the presence and absence of 0.1 mM cysteine, and the results are presented in Fig. 3 (A and B). Gradual increase of the reduction peak (at ca. 1 V vs. Ag/AgCl, KCl-sat.) in curve (a) indicates an increased amount of the Au particles deposited on
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Fig. 2—Cyclic voltammograms for the reductive desorption of cysteine SAMs on the Au/GC electrodes (d = 3 mm) in N₂-saturated 0.5 M KOH solution. Potential scan rate: 100 mV s⁻¹. The Au/GC electrodes were prepared by applying a potential step electrolysis from 1.1 to 0 V for 1000 s in 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in the presence (a) and absence (b) of 0.1 mM cysteine. The numbers 1 and 2 refer to the first and the second potential cycles, respectively.

Fig. 3—Cyclic voltammograms of ten successive potential scans on bare GC electrodes in N₂-saturated 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in the presence (A) and absence (B) of 0.1 mM cysteine. In both cases, the cyclic voltammograms (dotted lines (curve b)) were obtained at bare GC electrode in N₂-saturated 0.5 M H₂SO₄ solution. Potential scan rate: 50 mV s⁻¹.

XRD patterns shown in Fig. 4, the strong peaks at ca. 26, 43 and 78° were assigned as C(111), C(010) and C(110), respectively, due to the substrate of GC on which Au nanoparticles were electrodeposited, and the peak at ca. 38° was ascribed to the Au(111) facets of the Au nanoparticles. On the basis of the XRD data shown in Fig. 4, we can see that the presence of cysteine as an additive in the electrodeposition of the Au crystals decreases the Au(111) domains, and that contrary to the expectation from the reductive desorption patterns (shown in Fig. 2), the XRD peaks...
corresponding to the Au(100) and Au(110) domains are not observed. This is due to the fact that according to the extinction rule of diffraction in the XRD measurements of a face-centered lattice crystal, for a given facet of $hkl$ orientation to have a significantly observed XRD peak, it should have all-odd or all-even $h$, $k$ and $l$ numbers. Facets with mixed odd and even $h$, $k$ and $l$ values have a structure factor $F_{hkl}$ of zero. Thus, the XRD peaks assigned to the Au(111) and Au(100) domains could not be observed, and the intensity of the peak corresponding to the Au(111) facet was taken as the probing parameter to evaluate the effect of cysteine. In our recent work we have shown that the presence of cysteine (as an additive) during the electrodeposition of Au nanoparticles onto Au(111) substrate results in a significant increase in the peak intensity located at 20 of $ca. 44^\circ$ [corresponding to Au(200)], but we could not observe this peak in the present case owing to the high background intensity of the GC substrate used in this study. Figure 4 shows that the XRD peak intensity located at 20 of $ca. 38^\circ$ corresponding to the Au(111) facets of the samples obtained in the presence of cysteine (curve a) is weaker than that in its absence (curve b), indicating that Au(111) crystalline facets are less favorably formed on the GC surface in the presence of cysteine. This is in agreement with the fact that the Au electrodeposition in the presence of cysteine would more easily get the larger Au(100) and Au(110) facets area at the expense of Au(111) facets, in addition to the unique directional growth of the Au nanorods.

**Electrocatalytic activity for oxygen reduction**
The electrochemical application of such Au nanorods was achieved by their electrocatalytic activity for oxygen reduction. The CV responses for oxygen reduction reaction were measured at bare GC and polycrystalline Au electrodes and nano-Au/GC electrodes prepared in the absence and presence of cysteine in O$_2$-saturated 0.5 M H$_2$SO$_4$ solution (Fig. 5). A 2-step 4-electron reduction of oxygen was observed on both nano-Au/GC electrodes (curves c and d). Compared with those at the bare GC and polycrystalline Au electrodes (curves a and b respectively), the oxygen reduction potential at both nano-Au/GC electrodes shifted positively, indicating that the Au nanoparticles possess a more effective catalytic ability for oxygen reduction. In addition, from the comparison of curves (c) and (d), we can see that the nano-Au/GC electrode prepared in the presence of cysteine is superior in its electrocatalytic activity for oxygen reduction to that prepared in the absence of cysteine.

All the electrochemical measurements as well as the SEM and XRD studies were directly carried out on the Au nanocrystals on the GC electrode surface.
demonstrating that such Au pin-like nanorods were directly and stably electrodeposited on the electrode surface with their conducting property and electrocatalytic activity.

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