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# Fabrication of Au(111) single-crystal nanoisland-arrayed electrode ensembles by template-directed seeding growth†

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**A new and simple approach for preparation of Au(111) *single-crystal* nanoisland-arrayed electrode *ensembles*, based on fine colloidal Au monolayer-directed seeding growth, is reported.**

Nanoelectrode ensembles (NEEs) are important in electrochemistry and electroanalysis due to interesting and unusual electrochemical phenomena that are predicted to occur.[1,2] These properties have been put to applications ranging from *in vivo* sensors to 'smart' electronic noses, and have potential applications in the creation of organized nanodevices such as sensor arrays, data storage systems, and electrochemically controlled drug delivery systems.[1] To date, NEEs are typically prepared in three ways, *i.e.* the 'template synthesis' approach,[1,2] the self-assembled monolayer (SAM)[1,3] and block copolymer self-assembly[1] based approaches. While these approaches are quite effective, NEEs made from these methods are *polycrystalline* in nature. As a result, the crystallinity of the electrode and therefore its double-layer properties can vary from electrode to electrode. This fact prevents assessment of the role of interfacial properties in the kinetics of very fast electron transfer processes.[4] Herein we report a new and simple approach for preparing Au(111) *single-crystal* nanoisland-arrayed electrode *ensembles*, based on self-assembly of gold nanoparticles from solution onto silanized indium-tin-oxide (ITO) electrodes and have followed colloidal gold surface-catalyzed reduction of $Au^{3+}$ by $NH_2OH$.[5]

Hydroxylamine seeding of surface-confined colloidal Au nanoparticles has been proven to be a valuable tool in the controlled formation of conductive Au films[6] and has led to the successful preparation of SPR substrates.[7] Recently, we also found that both the crystallinity and conductivity of films prepared by $NH_2OH$ seeding of surface-confined colloidal Au are highly dependent on mass transfer process and the size of colloid used. For example, although the same 2.5 nm-diameter colloidal Au monolayer templates on surface of glass slides were used, minor variation in preparation (agitation or not) can effectively lead to yield continuous polycrystalline thin Au films that are SPR-active[7] or well-arranged two-dimensional (2D) arrays of electrically isolated Au(111) single-crystal nanoislands with relatively uniform size, respectively. Fig. 1 shows the X-ray diffractometry (XRD) patterns of (a) a SPR-active Au film on a glass slide plated from a 2.5-nm-diameter monolayer template under agitation, (b) an island film statically plated from 18-nm diameter colloid Au monolayers, and (c) an island film statically plated from 2.5-nm diameter colloid Au monolayers. The seeding solution comprises 6 ml of aqueous 0.4 mM hydroxylamine hydrochloride and 0.1% $HAuCl_4 \cdot 3H_2O$. For more valid comparison, 10 min of plating time was used for all specimens. Although (111) is the predominant surface orientation, the other crystallographic planes are also pronounced on the surface of the SPR-active Au film (Fig. 1(a)), which in good agreement with the previous data of electroless plated gold on glass substrates.[8] The XRD patterns of statically prepared island films are different from that of SPR-active Au film. The XRD pattern of the island film statically plated from 18-nm diameter colloid Au monolayers (Fig. 1(b)) shows a stronger (111) peak and a weaker (200) peak. Significantly, the XRD pattern of the island film statically plated from 2.5-nm diameter colloid Au monolayers (Fig. 1(c)) shows only one (111) reflection, suggesting that the island-like crystallites are indeed Au (111) single crystals. The transverse resistances of the above-mentioned Au films are different from each other. The typical resistances are below 1 Ω and *ca*. 280 Ω for specimen a and b, respectively, while specimen c is insulating, with a resistance in excess of $10^7$ Ω (the highest value measured is 200 MΩ at present),[9] indicative of a discontinuous and almost electrically separated, though close packed, inter-island nature of the Au island arrays.

The nanoelectrode ensembles of Au(111) single-crystal nanoisland arrays were fabricated on (3-aminopropyl)trimethoxysilane (APTMS)-modified ITO electrode using a 2.5-nm diameter colloid Au monolayer as template. In a typical preparation, a carefully cleaned ITO electrode was placed in a dilute solution of APTMS (0.3 ml of APTMS in 3 ml of $CH_3OH$) for 12 h and rinsed with copious amounts of $CH_3OH$ upon removal. The APTMS-modified electrode was subsequently immersed in colloidal Au solution (*ca*. 2.5 nm in diameter) for 12–18 h for Au nanoparticles assembling. Then the Au monolayers were rinsed with water and were immediately immersed in 6 ml of aqueous 0.4 mM hydroxylamine hydrochloride and 0.1% $HAuCl_4 \cdot 3H_2O$. The solution was kept seeding statically for 10 ± 0.5 min. After plating, the substrate was rinsed thoroughly with water, dried under a nitrogen stream, and was ready for characterizations and electrochemical applications.

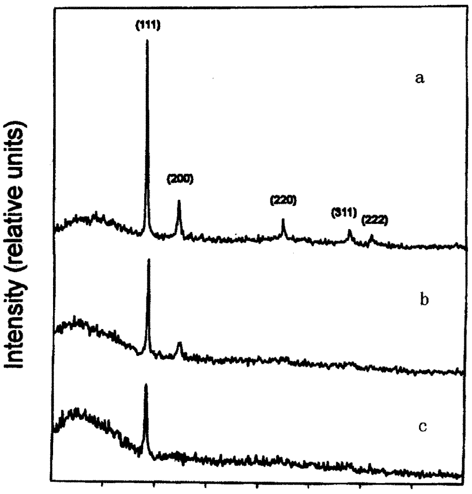

**Fig. 1** XRD patterns of (a) a SPR-active Au film on a glass slide plated for 10 min from 2.5-nm diameter colloid Au monolayers, (b) an island film statically plated for 10 min from 18-nm diameter colloid Au monolayers, and (c) an island film statically plated for 10 min from 2.5-nm diameter colloid Au monolayers.

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† Electronic supplementary information (ESI) available: cyclic voltammograms. See http://www.rsc.org/suppdata/cc/b2/b204231m/

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Fig. 2 shows representative AFM image of the resulting island films prepared by 10 min of static $Au^{3+}/NH_2OH$ seeding of 2.5-nm colloid Au monolayers, which shows well-arranged and close packed 2D arrays of nanoislands with comparatively uniform size (grain size on the order of ~100 nm) and shape. An AFM image zoomed onto a few islands (inset of Fig. 2) reveals the relatively smooth and round-shaped geometry of the structure. Fig. 3 shows the XRD patterns of a bare ITO electrode and the as-prepared ITO/APTMS/Au islands electrode. Subtracting XRD patterns from that of the ITO electrode, the as-prepared Au nanoislands also show one (111) reflection. The peak corresponding to Au(222) results from the second-order diffraction of Au(111).

The electrochemical behavior of the ITO/APTMS/Au islands electrode measured in 0.10 M $H_2SO_4$ is shown in Fig. 4. The current–voltage curve has a characteristic shape in the positive region which is used to identify the orientation of the surface and confirm that single-crystal quality has been maintained during the electrochemical experiments. In the case of a (111) crystal face three anodic peaks are observed in the positive-going sweep, and a large reduction peak corresponding to reduction of gold oxide is observed on the negative sweep.[4] In present case, three oxide formation peaks were observed at +0.99, +1.05 and +1.25 V, similar to previous result of the anneal-quenched Au(111) single-crystal electrode.[10] It is important to note that the current value (bar: 0.1 μA) is about 1–2 orders of magnitude lower than that of the SPR-active Au electrode (bar: 0.1 mA) we reported previously,[7] thus confirming that we have produced here for the first time the nanoelectrode ensembles of well-arranged Au(111) single-crystal nanoisland arrays *via* a simple solution-based step-by-step assembly protocol.

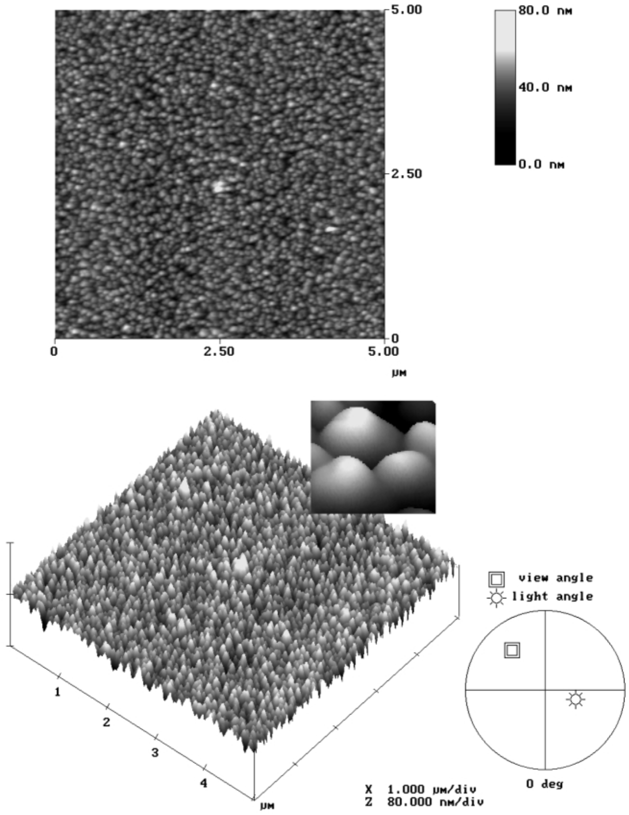

**Fig. 2** AFM images of an Au island film prepared on a APTMS-modified ITO surface by 10 min of static $Au^{3+}/NH_2OH$ seeding of 2.5-nm diameter colloid Au monolayers. An AFM image zoomed onto a few islands illustrates the geometry of the structure.

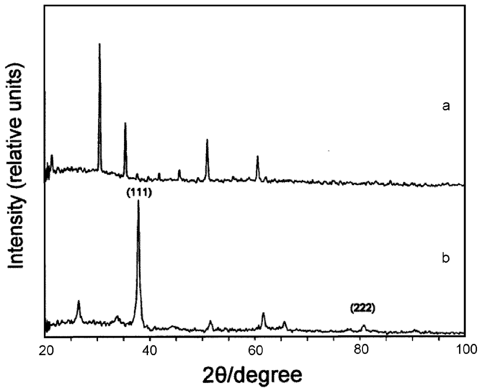

**Fig. 3** XRD patterns of (a) ITO electrode and (b) ITO/APTMS/Au islands electrode.

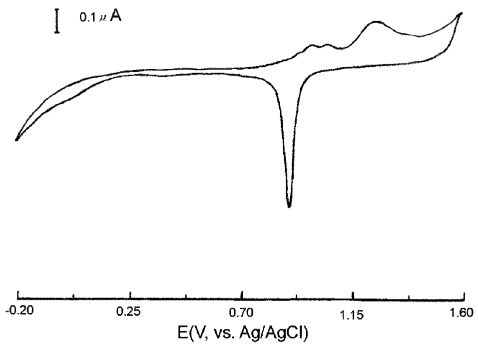

**Fig. 4** Cyclic voltammogram at an ITO/APTMS/Au(111) single-crystal array electrode with an area of ~0.40 $cm^2$ recorded in 0.10 M $H_2SO_4$ at 10 mV $s^{-1}$.

In conclusion, a new and effective strategy for preparing Au(111) single-crystal nanoisland-arrayed electrode ensembles has been reported. In principle, this protocol is also suitable to silicon substrates. Although detailed mechanisms—of which both the size-dependent catalysis nature of the seed nanoparticles and surface-nanoconfined quasi-one dimensional mass transfer fashion may play a important role—are not yet clear, the Au(111) single-crystal nanoisland arrays and its electrode ensembles should find many applications, especially in array-based sensors or optoelectric nanodevices.

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