

## Potential-controlled electrodeposition of gold dendrites in the presence of cysteine

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### Experimental

**1. Materials** Hydrogen tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , Acros, for analysis ACS) and cysteine, (Acros, >99 %) were used without further purification. Two types of GC electrodes were employed as deposition substrates in this study: a GC rod electrode (diameter: 3 mm) for electrochemical measurements and a GC plate electrode for surface characterization of the electrodeposited Au. Before use, the GC surface was polished on a nanocloth with alumina slurries (0.3 and 0.05  $\mu\text{m}$ ) in sequence. The polished GC was further cleaned in an ultrasonic bath of water and ethanol for 15 min and was thoroughly rinsed with Milli-Q water.

**2. Preparation and characterization of Au dendrites.** The electrodeposition of Au was performed on the GC electrode in an aqueous solution of 1.0 mM  $\text{HAuCl}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$  in the presence of 0.1 mM cysteine. The Au dendrites were formed at concentrations of cysteine less than  $\sim 1.0$  mM because the growth of Au is severely inhibited on all crystallographic faces with cysteine at larger concentrations. A conventional three-electrode system in an electrochemical workstation (CHI 614B) was employed for the electrodeposition. A platinum wire served as counter electrode; the reference electrode was a saturated calomel electrode (SCE). Square-wave potential

pulses were applied to the GC electrode at a frequency of  $5\text{ s}^{-1}$ . The pulsed potential form was used to reduce the effect of diffusion limitation on the rate of electrodeposition. The lower and higher potentials of the square-wave pulse were set at  $-0.8$  and  $+0.2$  V, respectively, with respect to the SCE.

A monolayer of cysteine was formed after immersing an Au dendrite-deposited GC electrode into a solution of  $1.0\text{ mM}$  cysteine for  $15\text{ min}$ . The electrode was then rinsed with de-ionized water to remove the non-chemisorbed cysteine. Reductive desorption of the cysteine monolayer, which was used to determine the surface facets of the Au dendrite, was subsequently performed in a  $0.5\text{ M}$  KOH solution saturated with  $\text{N}_2$ .

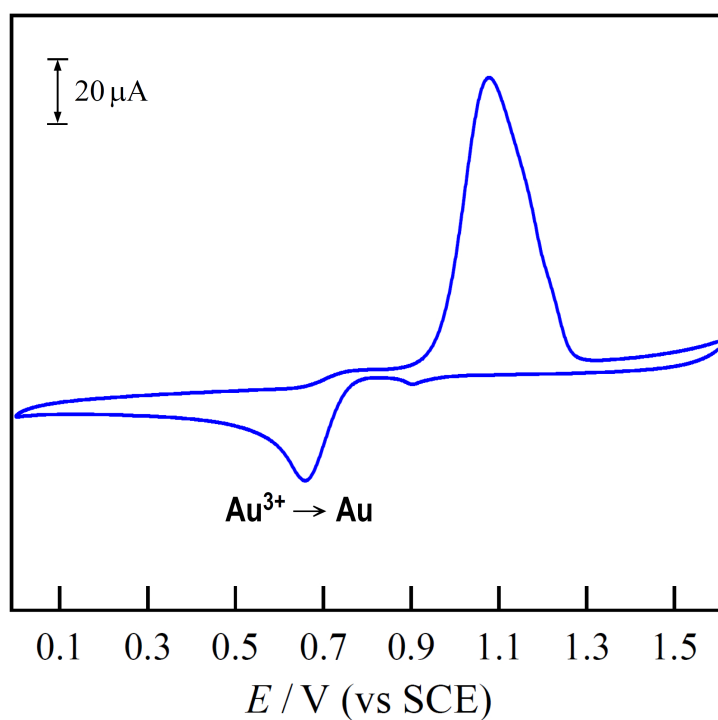
Electrochemical measurements on the Au dendrites were performed also at the electrochemical workstation used for electrodeposition. The chemical compositions and morphologies of the Au deposits were characterized using energy dispersive X-ray (EDX) spectra and a scanning electron microscope (SEM; LEO 1530 FE). The crystallinity of the Au dendrites was analyzed through X-ray diffraction (XRD; Nonius Kappa). The deposited Au dendrites were removable from the GC surface under sonication in water for the TEM measurement (Philips FEI Tecnai G2).

In order to study the electrocatalytic activity, the oxidation of  $\text{CH}_3\text{OH}$  on the Au dendrite deposited the GC electrode was examined in an aqueous solution (saturated with  $\text{N}_2$ ) of  $1.0\text{ M}$  KOH and  $2.0\text{ M}$   $\text{CH}_3\text{OH}$ . The current density was used to a measure of electrocatalytic activity, which was calculated from the ratio of the peak current and the surface area of Au dendrites. In order to determine the surface area, the CV scans of the Au dendrite-deposited GC electrode was recorded in  $\text{H}_2\text{SO}_4$  solution ( $0.5\text{ M}$ , saturated with  $\text{N}_2$ ). The surface area was estimated by calculating the amount charge consumed

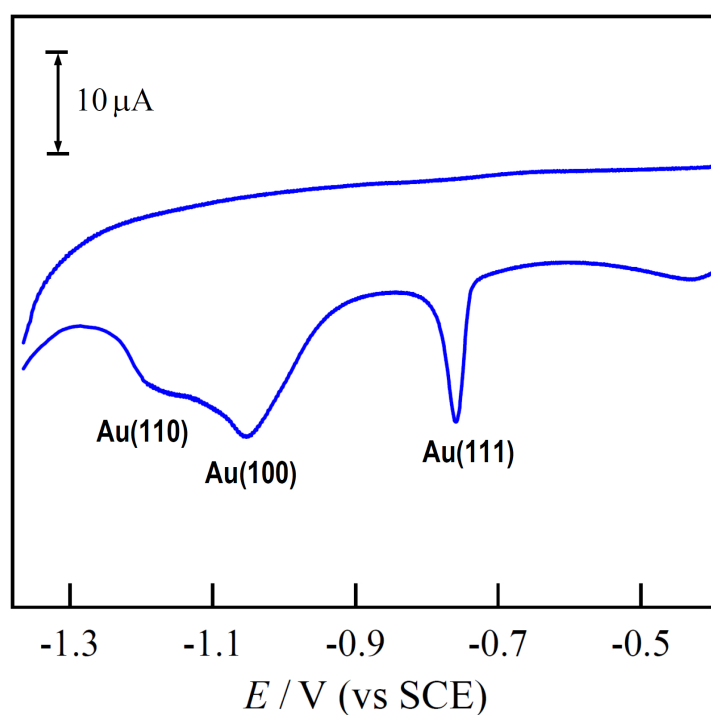
during the reduction of Au surface oxide monolayer using a reported value of  $400 \mu\text{C cm}^{-1}$ .

**References:**

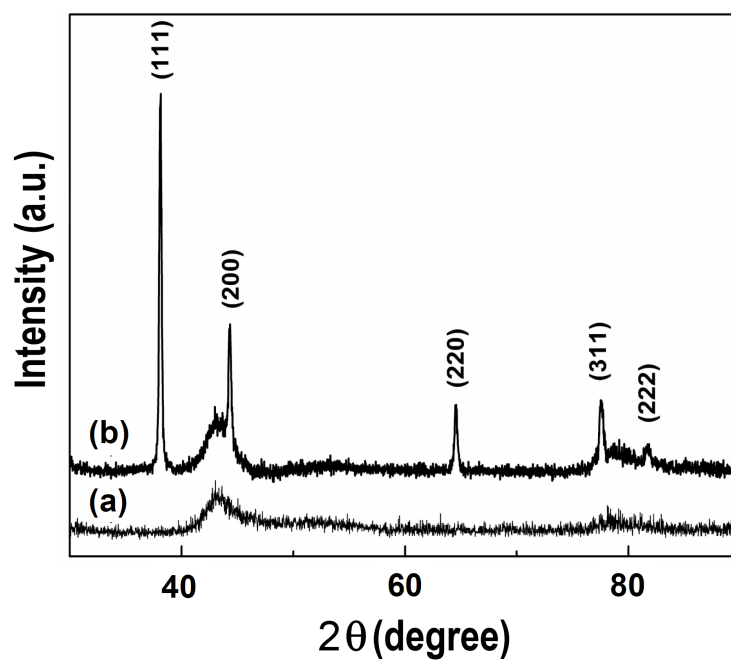
1. (a) H. A. Kozłowska, B. E. Conway, H. Hamelin and L. Stoicoviciu, *J. electroanal. Chem.*, 1987, **228**, 429; (b) S. Trasatti, O. A. Petrii, *J. electroanal. Chem.*, 1992, **327**, 353.



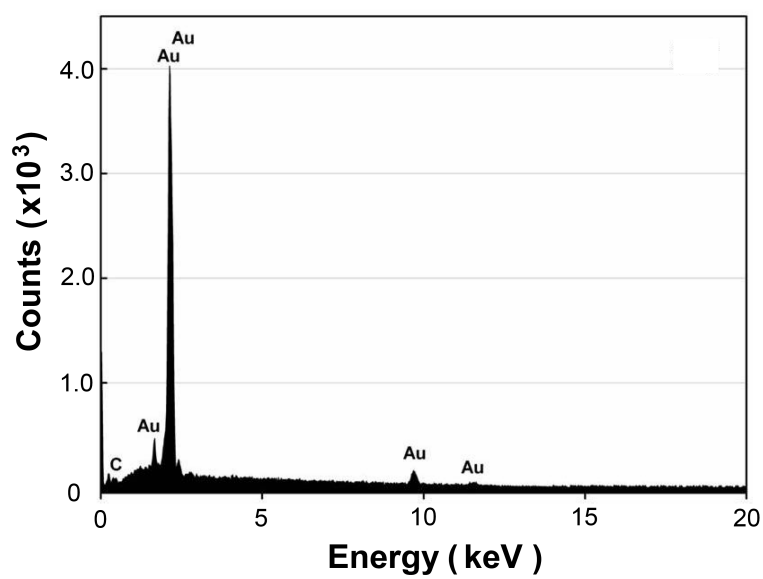
**Fig. S1** CV scans of a GC electrode in a solution of 1.0 mM HAuCl<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub>. Potential scan rate: 50 mV s<sup>-1</sup>. The cathodic peak at 0.67 V is due to the reduction of Au<sup>3+</sup> to form Au and the anodic broad feature at 1.08 V is attributed to quasi-reversible oxidation of Au and the formation of surface Au oxides. The CV scan thus indicates that a potential less than ~0.8 V applied to a GC electrode causes the deposition of Au metal.



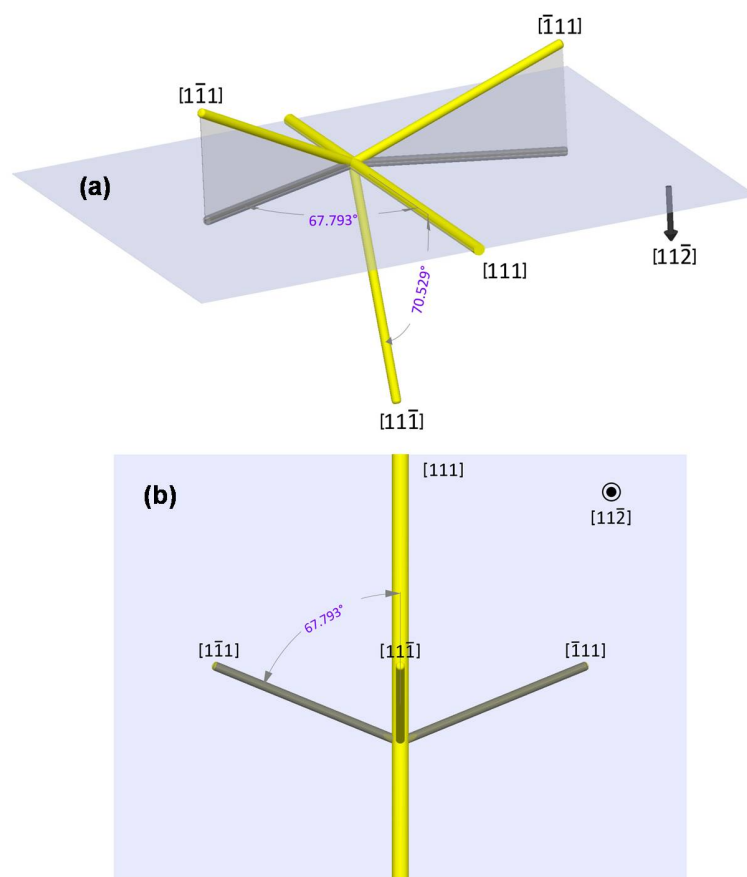
**Fig. S2** CV scans of cysteine adsorbed on a poly-Au electrode in 0.5 M KOH solution. Potential scan rate: 50 mV s<sup>-1</sup>. The poly-Au electrode was pretreated in a solution of cysteine (1.0 mM) for 15 min. As shown in the curve, two cathodic peaks and one shoulder are apparent at 0.76, 1.05, and ca. 1.15 V, respectively. These CV features correspond to the reductive desorption of cysteine from the Au(111), Au(100), and Au(110) domains on a poly-Au surface, respectively.



**Fig. S3** XRD patterns of (a) a bare GC electrode and (b) an Au dendrite-deposited GC electrode.

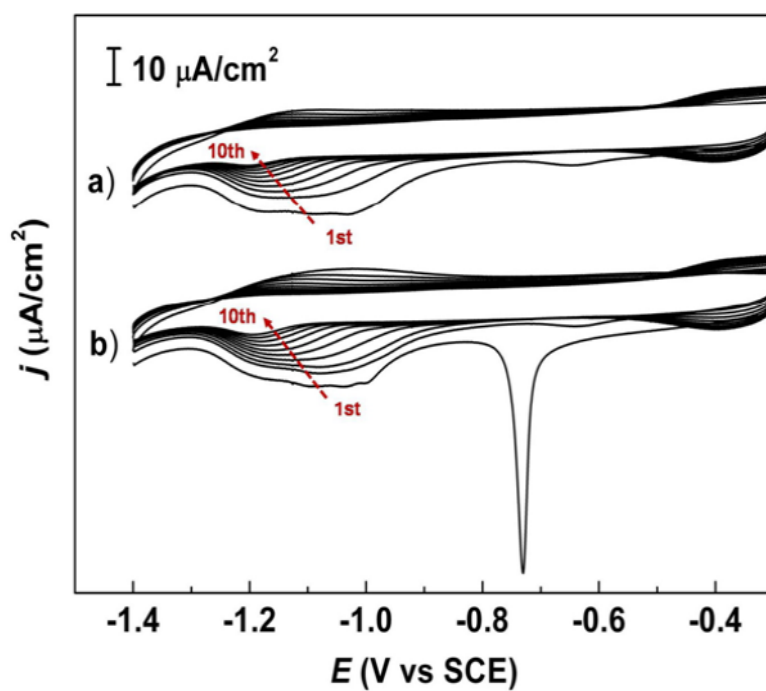


**Fig. S4** EDX spectrum of an Au dendrite-deposited GC electrode.

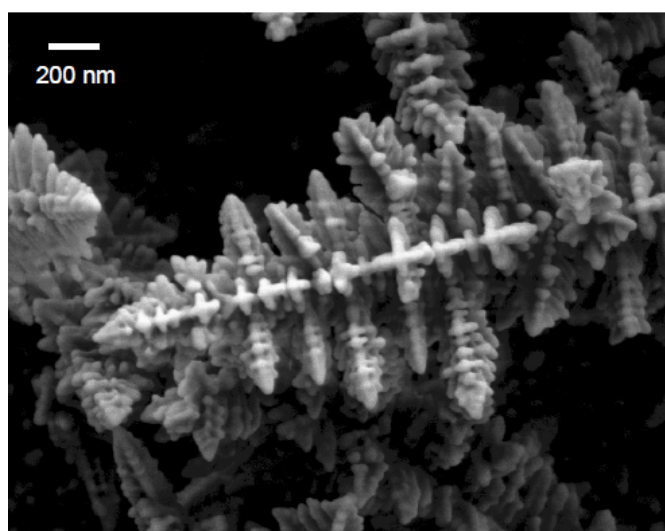


**Fig. S5** Schematic diagrams of  $\langle 111 \rangle$  directions in a fcc Au structure on the  $(11\bar{2})$  projection plane. (a) side view and (b) top view of the  $(11\bar{2})$  plane. The angle between  $[111]$  and  $[\bar{1}\bar{1}1]$  (or  $[\bar{1}\bar{1}1]$ ) projected on the  $(11\bar{2})$  plane is  $67.8^\circ$ .

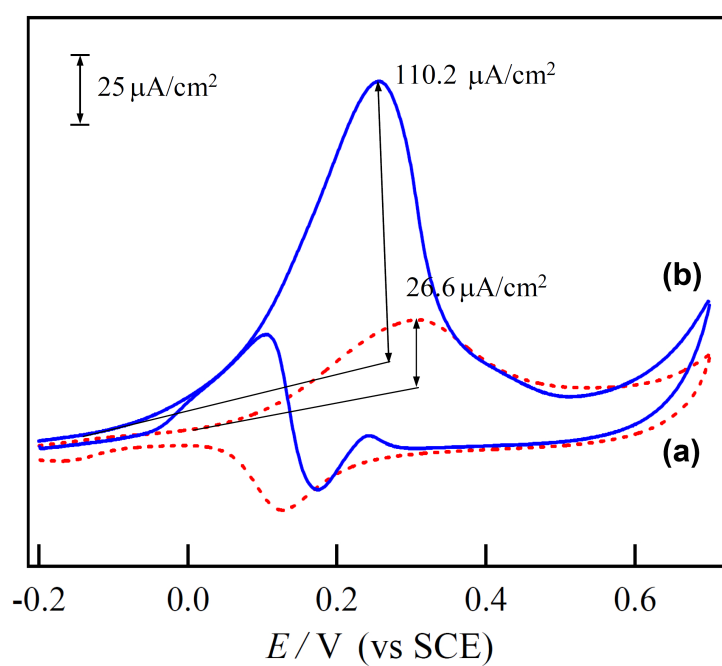




**Fig. S6.** Consecutive CV scans of (a) the as-grown Au dendrite and (b) the cysteine-treated Au dendrite on the GC electrode in 0.5 M KOH solution. Potential scan rate:  $50 \text{ mV s}^{-1}$ . The electrode in (b) was pretreated in a solution of 1.0 mM cysteine for 15 min.



**Fig. S7** SEM image of Au electrodeposited on a GC electrode at a fixed potential of  $-0.8$  V for 3000 s in a solution of  $\text{HAuCl}_4$  (1.0 mM) and  $\text{H}_2\text{SO}_4$  (0.5 M) containing 4-MBA (0.1 mM).



**Fig. S8** CV scans of (a) a poly-Au electrode (dash line, ---) and (b) an Au dendrite-electrodeposited GC electrode (solid line, —) in a solution of 0.1 M KOH and 2.0 M  $\text{CH}_3\text{OH}$  (2.0 M). Potential scan rate:  $10 \text{ mV s}^{-1}$ .

