Supporting Information

Preliminary elucidation on the growth mechanism of gold nanostructures

The electrodepositon processes are heterogeneous reactions and quite complex because of the possible influence of many factors, such as the structure and crystallographic orientation of the substrate, deposition-substrate interaction, deposited potential and current density, mass transport and temperature, electrolyte composition, the characteristic of the adsorbate, and etc. So, it is a challenging work to predict the final state and properties of deposited metal nanostructures. We paid our efforts on the preliminary elucidation of the growth mechanisms by electrochemical methods, such as cyclic voltammetry and chronoamperometry. Electrochemical deposition methods usually divide into two kinds based on their deposited potentials: one is underpotential deposition (UPD), which forms two-dimensional (2D) films; the other is overpotential deposition (OPD) employed in our case, which grows 3D structures. From CVs obtained at gold substrates in an aqueous solution of HAuCl₄ with concentrations of 40 mM and 4 mM, at both concentrations, some overcrossings on the cathodic branches were noticed. Such characteristic indicates the existence of a nucleation process on the Au substrate surface. For the sake of further elucidation of growth mechanism and kinetics, we characterized the nucleation process in more detail using chronoamperometric method. Different shapes of potentiostatic current-time curves were observed for different concentrations as depicted in Fig. S1, implying that the nanostructured gold electrocrystallization process proceeded by different mechanisms. The shape of current-time curves obtained at the deposited potentials of -0.08 V (a) and -0.2 V (c) in 40 mM HAuCl₄ solution (enlarge in the inset) indicates that kinetics at the early stages is diffusion-controlled step, followed by 3D nuclei growth, which is divided into instantaneous and progressive type as the following equations (1) and (2): 1,2

$$j_{\text{(instantaneous)}} = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-N_0\pi kDt)]$$

$$k = \left(\frac{8\pi cM}{\rho}\right)^{1/2}$$
(1)

$$j_{\text{(progessive)}} = \frac{nFD^{1/2}c}{\pi^{1/2}t^{1/2}} [1 - \exp(-\frac{AN_0\pi k'Dt^2}{2})]$$

$$k = \frac{4}{3} \left(\frac{8\pi cM}{\rho}\right)^{1/2}$$
(2)

Where N_0 is the number density of active sites, k is the growth rate constant of a nucleus, A corresponds to the nucleation rate constant, M is the molar mass, ρ is density of the doposited material, nF is the molar charge transferred during electrodeposition, D is the diffusion coefficient, c is the bulk concentration of the gold species. We compared the theoretical non-dimensional plots for instantaneous and progressive nucleation with our experimental data, and found that nanopyramids formed at deposited potential of -0.08 V in 40 mM HAuCl₄ solution grew at the early stage by diffusion-controlled step, followed by intananeous 3D nuclei growth on the gold substrate, whereas, nanospheres obtained at different deposited potential of -0.2 V in the same 40 mM HAuCl₄ solution followed closely the response predicted for 3D-progressive nucleation controlled by diffusion of Au(III) ions. We calculated the parameters such as N_0 and A. The density of active sites increases from 2×10^7 to $4 \times$ 10^9 cm⁻², as well as the nucleation rate constant changes from 0.56 to 2.33 s⁻¹, as the deposition potential is negatively shifted from -0.08 V to -0.2 V. The lower density of active sites and slower nucleation rate may lead to intananeous 3D nuclei growth. On the contrary, progress 3D nuclei growth possibly results in the formation of nanoshperes.

On the other hand, the wave of current-time for nanostructured gold deposition from 4 mM HAuCl₄ solution shown in Fig. S1(b) was completely distinguished from those observed at higher concentration. Again, it means that the mechanism of nanostructured gold films growth at low concentration is different from that at higher concentration. At the deposited potential of -0.08 V, in the initial stage the deposition current rise as a function of the deposited time, and at longer times, the current reached a steady state condition. This behavior means that nuclei grew in a direction parallel to the surface with a rate constant k_1 , and with a different rate constant defined as k_2 in the perpendicular direction, as demonstrated in Equations (3) and (4).

$$j_{\text{(instantaneous)}} = nFk_2 \left[1 - \exp\left(\frac{-\pi M^2 k_1^2 N_0 t^2}{\rho^2}\right) \right]$$
(3)

$$j_{\text{(progressive)}} = nFk_2 \left[1 - \exp\left(\frac{-\pi M^2 k_1^2 A N_0 t^3}{3\rho^2}\right) \right]$$
(4)

All parameters mentioned in these equations are same as described in equation (1) and (2). Compared to calculated sets for instantaneous and progressive nucleation, our experimental data showed *j* was linear with t^2 , thus suggesting that the growth of nanorods obtained at deposited potential of -0.08 V in 4 mM HAuCl₄ solution could be defined as instantaneous, furthermore, the nucleation was followed by 3D growth limited by adatom incorporation into the substrate lattice. The rate constant in the perpendicular direction k_2 was estimated to be about 4.6×10^7 mol cm⁻² s⁻¹, and the rate constant in the parallel direction k_1 might be smaller than k_2 , thus resulting in the formation of nanorods. It is hard to calculate the rate constant in the parallel direction k_1 at the present stage.

On the basis of the preliminary mechanisms analysis of nanostructured gold growth, it is clear that various shape of electrochemical fabricated gold nanostrutures, such as nanopyramids, nanorods, and nanospheres are formed by different growth mechanisms, originated from different electrodeposited potentials and the concentration of Au (III) ions in solution. So, the mechanism studies provided us a methodology for shape-controlled fabrication of metal nanostructures on various substrates by manipulating the deposited potentials, concentration of growth species,



Figure S1. Current-time curves obtained at (a) sputtered gold substrate, at deposited potential of -0.08 V vs. Ag/AgCl in 0.1 M HClO₄ solutions containing 40 mM HAuCl₄, (b) at deposited potential of -0.08 V vs. Ag/AgCl in 0.1 M HClO₄ solutions containing 4 mM HAuCl₄, (c) at deposited potential of -0.2 V vs. Ag/AgCl in 0.1 M HClO₄ solutions containing 40 mM HAuCl₄.

even the morphology of substrate surfaces. Further progress and better understanding of an electrocrystallization process should be improved by in situ microscopic techniques.

References:

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