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Transformation of randomly aggregated gold nanoparticles into dendritic structures by square wave potential pulses

Chen Guo [a], Yue Xia [b], Yan-Zhen Xu [a], Ju-Fang Zheng [a], Ze-Lin Li [b],*

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China
[b] Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), Department of Chemistry, Hunan Normal University, Changsha 410081, China

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ABSTRACT

Dendritic gold was facilely fabricated here via a simple two-step method by treating a pure gold electrode sequentially in two blank solutions for very short periods of time. The electrode surface was firstly roughened in 2 M HCl by a step potential for 50 s to form a three-dimensional (3D) nanoporous film consisting of randomly aggregated gold nanoparticles, and was then treated with square wave potential pulses for 500 s in 2 M H_2SO_4 to fulfill the transformation of the aggregated nanoparticles into dendritic structures. The influence of potential range, square wave frequency, electrolyte, and potential waves on the dendrite formation was investigated. A one-step method was also explored for mechanism comparison by treating the polished gold instead in the presence or absence of $HAuCl_4$.

1. Introduction

Gold dendrites have attracted a great deal of attention because of their wide applications in superhydrophobicity [1], surface-enhanced Raman scattering [2], electrocatalysis [3] and so on. Dendritic gold can be prepared by chemical reduction of $AuCl_4^-$ under various conditions. Templates like block copolymers [4], ionic polymers [5], graphene oxide sheets [6], zinc plates [7], and water-oil interfaces [8,9] were employed to conduct the dendrite growth, accompanying diffusion-limited aggregation (DLA) [6] or oriented attachment of gold nanoparticles [7]. In a hydrothermal reduction of $AuCl_4^-$ [10], two capping reagents are believed to be the origin for the formation of dendritic gold.

Electrochemical reduction of $AuCl_4^-$ is an alternative method to make dendritic gold [11,12]. The electrical field distribution between electrodes and the DLA process were responsible for the dendritic formation. Carbon tubes in the bath were supposed to guide the perpendicular growth of gold shrubs in electrodeposition of gold on TiO_2 nanotube arrays [13]. Besides potentials, the concentration of $AuCl_4^-$ also affected the dendritic structures [14]. Flowerlike gold microstructures were prepared by an electrochemically produced seed-mediated growth approach [16] or by electrodeposition either at a constant potential [15] or using square wave potentials (SWPPs) [17]. We previously fabricated dendritic gold by treating AuSn alloys with SWPPs [3], which involved selective removal of Sn, oxidation–reduction cycles (ORCs) of gold and hydrogen evolution.

We report here another novel method to fabricate gold dendrites using a pure gold electrode instead of AuSn alloys. We found that a nanoporous gold film, comprising of randomly aggregated gold nanoparticles obtained by pre-roughening a pure gold electrode in 2 M HCl, can be facilely transformed into compact and uniform dendrites in a blank solution of 2 M H_2SO_4. By this new strategy, neither the processes of dealloying and gas evolution nor the presence of $AuCl_4^-$ is needed. A detailed description of this method is presented here.

2. Experimental section

Fabrication was carried out with a CHI 440A electrochemical station (Chenhua Instruments, Shanghai, China) in a self-made spectroscopic cell [18], where a gold disk (1 mm diameter), a circular platinum wire, and a saturated mercurous sulfate electrode were employed as the working, counter and reference electrode, respectively. The polished gold disk was first roughened in 2 M HCl by applying a step potential of 0.9 V for 50 s, resulting a 3D nanoporous film of randomly aggregated gold nanoparticles [19]. The pre-roughened electrode was then treated by SWPPs in 2 M H_2SO_4 with variation of potential range (1.1/0.6 to −0.3 V), frequency (0.5–50 Hz) and time (100–500 s), as well as medium (2 M NaOH or 1.35 M Na_2SO_4), or treated by cyclic voltammetry (CV) (1.1 to −0.3 V, 14 V/s,

* Corresponding author. Tel.: +86 731 88871533; fax: +86 731 88872531.
E-mail address: lizelin@hunnu.edu.cn (Z.-L. Li).

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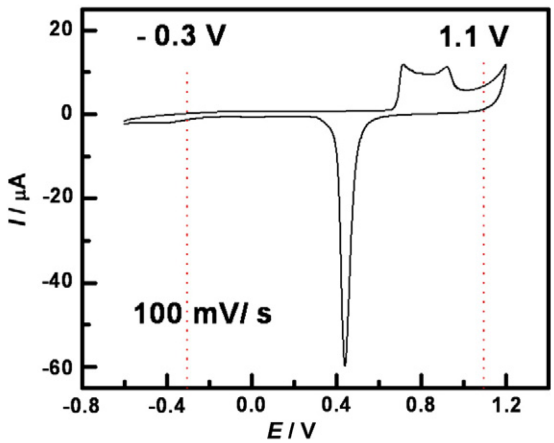

Fig. 1. A cyclic voltammogram of the polished gold electrode in 2 M H_2SO_4.

2500 cycles). For comparison, a polished gold disk was also employed subjecting the above treatments in the absence and presence of 5 mM $HAuCl_4$. Surface morphology was characterized by a Hitachi S-4800 Field-emission scanning electron microscope (SEM).

3. Results and discussion

The typical oxidation–reduction behavior of gold electrodes in sulfuric acid solution is shown in Fig. 1. As evidenced by electrochemical quartz crystal microgravimetry [20], gold oxidation began at 0.65 V forming AuOH first, and then a monolayer film of gold oxide (AuO) formed while the potential reached to about 1.1 V, which can be completely reduced to Au while the potential was reversed to less than 0.2 V.

Fig. 2 shows the morphological evolution of the nanoporous film (about 1 μm thick [19]) consisting of gold nanoparticles. The randomly aggregated nanoparticles (Fig. 2A) from the pre-roughening can be transformed into dendritic structures (Fig. 2D) completely in 500 s by the SWPP (1.1 to −0.3 V, 5 Hz) treatment in 2 M H_2SO_4. Clearly, the nanoparticles at the surface underwent position rearrangement, coalescence, and sintering during the SWPP treatment. We found that the repeated gold redox by the SWPPs plays a key role in the dendrite formation. At 1.1 V, gold oxide monolayer was formed surrounding the nanoparticles and it was then reduced into gold atoms at −0.3 V. The model of DLA for metal electrodeposition [21] and for random metal nanoparticles [22] can be used to explain this structural transformation because both of the newly produced Au atoms and the Au nanoparticles with freshened unprotected surface by the redox of gold under SWPPs are movable at the surface. Note also that the processes of rearrangement, coalescence and sintering for the freshened unprotected Au nanoparticles by the redox could proceed favorably toward the formation of dendrites to decrease the surface energy effectively. However, the exact mechanism needs further investigation.

More influencing factors were investigated on the above structural transformation. As shown in Fig. 3A, the nanoporous structure remained almost unchanged while the upper potential of SWPPs was set at 0.6 V lower than that for the gold oxidation, confirming that gold ORCs are indispensable for the structural transformation via the newly-produced Au atoms and the surface-freshened Au nanoparticles. The conclusion is strengthened by the fact that the structural change by SWPPs could be speeded up at a higher frequency. At 0.5 Hz (Fig. 3B), only a few stems sprouted, while dendrite structures were fully developed at 50 Hz with a more seriously sintered appearance (Fig. 3C and the inset). Wave forms of potential also have an important influence. Instead of the spread dendrites as in Fig. 2D obtained by SWPPs, corn cob like structures appeared (Fig. 3D) using triangular waves, confirming that SWPPs favor the DLA at the surface

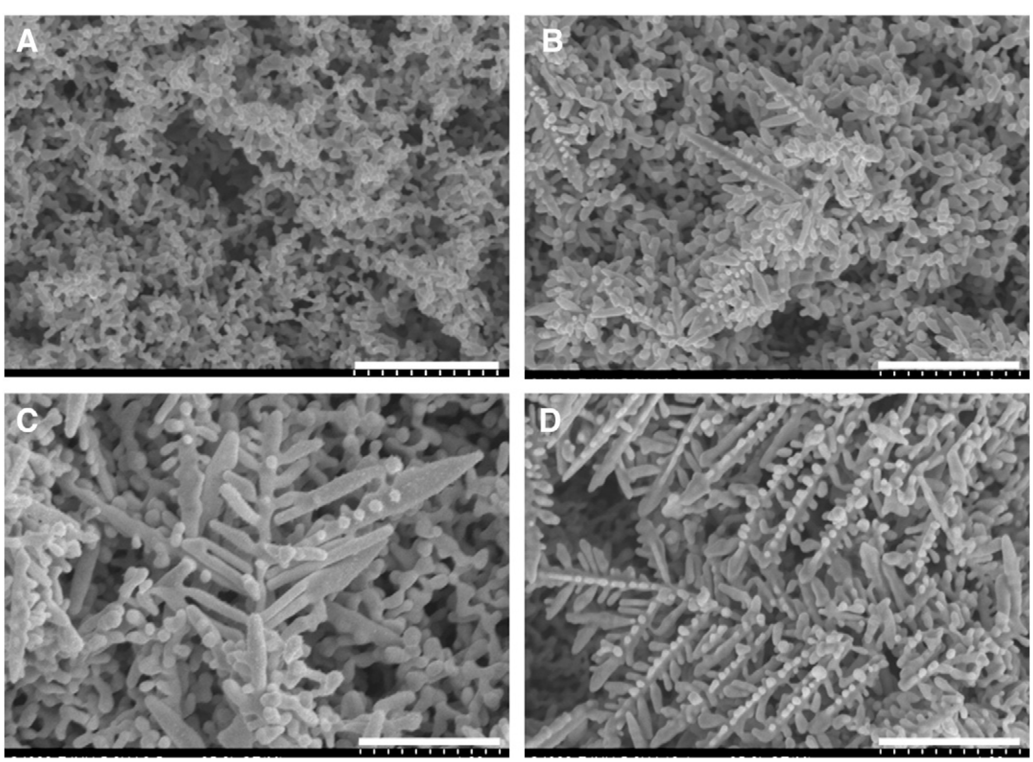

Fig. 2. SEM images of the gold electrode. (A) Roughened in 2 M HCl at 0.9 V for 50 s, and then treated in 2 M H_2SO_4 with SWPPs (1.1 to −0.3 V, 5 Hz) for (B) 100 s, (C) 300 s, and (D) 500 s. The scale bars are 1 μm.