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Anodic Fabrication of Nanoporous Gold Films from Pure Gold in Oxalic Acid Solution and Their Applications in Electrocatalysis and SERS

Shili Xu[1], *Yuan Yao*[1], *Pengshu Wang*[1], *Yingchang Yang*[2], *Yue Xia*[1], *Jun Liu*[1], *Zelin Li*[1], *Wei Huang*[1,*]

[1] Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research, Ministry of Education of China, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China
[2] Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China
[*]E-mail: hjhw9513@163.com

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Nanoporous gold films (NPGFs) with high roughness have been fabricated by strong anodization of pure gold substrates in an aqueous solution of oxalic acid (OA), a facile method similar to the recent work of Nishio and Masuda (Angew. Chem. Int. Ed., 50 (2011) 1). The influence of anodic step potential, anodic polarization time and OA concentration on the roughness factor (R) of NPGFs has been investigated. The fabrication might be mainly related to the formation of multilayer gold oxide and chemical reduction of gold oxide by OA. The as–prepared NPGF exhibits a high electrocatalytic activity toward the oxidation of ethanol, glucose and ascorbic acid as well as the reduction of hydrogen peroxide. Furthermore, the NPGF also shows strong surface enhanced Raman spectroscopy (SERS) effect.

Keywords: Nanoporous gold film, oxalic acid, highly anodic polarization, electrocatalysis, SERS

1. INTRODUCTION

Nanoporous gold film (NPGF) has received more attention due to its intensive applications in electrocatalysis [1], SERS [2], electroanalysis [3], etc.

To date, many methods have been employed to fabricate the materials with porous nanostructures [1–2,4–6]. Among them, templating [4–6] and dealloying [1–2,7] are the most conventional approaches. The former involves multistep procedures including template assisted deposition and template removal [4–6]. The latter is usually used to prepare nanoporous metal films, where nanopores of noble component leave behind by selectively dissolving the active component of the alloy [1–2]. Furthermore, researchers have devoted to develop some novel and facile synthesis strategies. For example, three–dimensional (3D) porous foams of metals and alloys have been electrodeposited directly with gas bubble dynamic template [8–10]. 3D nanoporous gold film has been prepared from a pure gold substrate by applying a potential step for about 1 min, involving electrodissolution, disproportion and re–deposition processes [11]. 3D micro–nano porous gold film has been fabricated from smooth gold substrate in a blank NaOH solution under square wave potential pulses, where the hydrogen bubble dynamic template shapes the assembly of the gold nanoparticles from the oxidation–reduction [12]. 3D porous films of Pb or Sn have been made by a highly cathodic polarization of pure metals in NaOH solution, relating to decomposition of unstable metal hydrides and assembly of in situ–produced nanoparticles with hydrogen bubble template [13].

Recently, Nishio et al. firstly reported a facile one–step approach to prepare NPGFs by anodization of gold in an oxalate–containing solution [14]. By this method, the smooth gold surface was rebuilt into a 3D porous film without any Au(III) precursors, surfactants or post–treatments. The nanopore generation was explained by the formation of a carbonaceous passivation film and the subsequent breakdown of the film on the nanoscopic scale [14]. In the present work, we further investigate the influence of anodization potential, anodization time and OA concentration on the roughness factor of NPGFs. Besides, some new explanations on the NPGF formation are presented. Both electrocatalytic activities for some small organic/inorganic molecules and SERS activity are tested.

2. EXPERIMENTAL PART

Electrochemical experiments were carried out in a conventional H–type glass cell with a CHI 660C electrochemical station (Chenhua Instruments, Shanghai, China). A gold disk (1 mm in diameter, purity ≥ 99.99%), a large Pt foil, and a saturated mercurous sulfate electrode (SMSE) were employed as the working, counter and reference electrode, respectively. Prior to use the Au disk was polished with 1200 grit Carbimet paper, followed by rinsing in Millipore water with ultrasonic waves. Then, the gold electrode was electrochemically cleaned in 0.5 M (M = mol dm^{-3}) H_2SO_4 by cyclic voltammetry (CV) at 100 mV s^{-1} between –0.7 and 1 V until a stable voltammogram was observed. The clean gold electrode was then oxidized potentiostatically in oxalic acid (OA) solutions to prepare the NPGFs. To prove that the multilayer gold oxide can be reduced to gold atoms by OA, a thick gold oxide film was first prepared by anodizing the smooth gold at 4 V for 100 s in 0.5 M H_2SO_4, followed with rinsing by ultrapure water, and then transferred to 0.1 M OA solution quickly and the open circuit potential (OCP) –time curve was recorded at once. The preparation conditions of NPGFs were optimized by varying the anodic potential (2, 4 and 8 V), polarization time (50, 100, 200, 400, 800, 1000, 1500, 2000, 3000 and 6000 s) and OA concentration (0.1 and 0.5 M). The roughness factor (*R*) for the NPGFs was characterized by cyclic voltammetry (CV) in 0.5 M H_2SO_4 [15].

The electrocatalytical activity of NPGF was tested in 1 M NaOH + 1 M ethanol, 1 M NaOH + 1 M glucose, 1 M NaOH + 0.1 M ascorbic acid, and 0.5 M H_2SO_4 + 0.1 M H_2O_2. The in situ SERS was taken in a solution including 0.1 M KCl + 0.01 M pyridine with a Renishaw RM1000 microscopy confocal Raman spectrometer (Gloucestershire, U.K.). A detailed description of the Raman measurements with a spectroelectrochemical cell can be found elsewhere [16]. The exciting wavelength was 785 nm laser with a power of ca. 4.4 mW on the NPGF surface and a collection time of 10 s. The morphologies of the NPGFs were characterized by a field emission scanning electron microscope (FESEM, Nova NanoSEM 230).

All solutions were freshly prepared with Millipore water and analytical grade chemicals. All experiments were performed at room temperature (about 20 ^oC).

3. RESULTS AND DISCUSSION

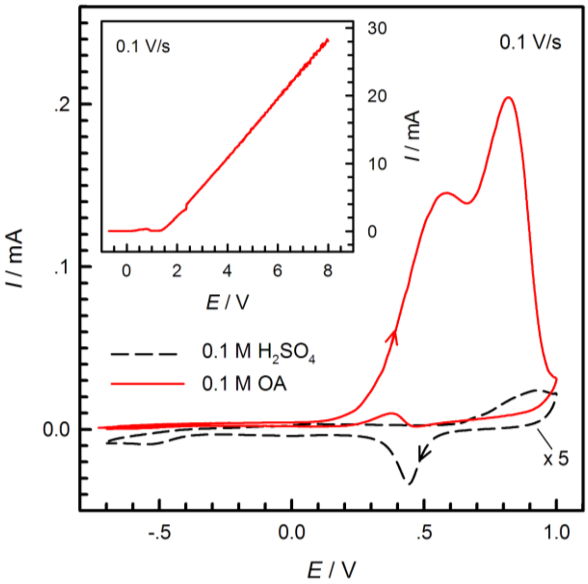

Figure 1. CVs with an upper potential limit of 1 V on the smooth gold electrode in 0.1 M H_2SO_4 (the dashed line) and 0.1 M OA (the solid line) respectively. Note that the data of dashed line have been magnified by 5 times. The inset shows the linear sweep voltammetry with an upper potential limit of 8 V.

The dashed line in Fig. 1 shows a typical CV behavior of the smooth gold electrode in a 0.1 M H_2SO_4 solution, where the broad anodic peak (0.6 ~ 1 V) is attributed to the formation of gold oxide monolayer and the cathodic peak at about 0.44 V is corresponding to its reduction [17]. While in 0.1 M OA solution, the CV (the solid line in Fig. 1) shows lower onset potential and enhanced anodic current (forward potential scan) but no cathodic current for gold oxide reduction (backward potential scan), indicating that gold has an obvious electrocatalytic activity toward the oxidation of OA [18]. When the upper potential limit is shifted more positively (above 1.5 V), as shown in the inset of Fig.1, the oxidation current increases linearly with applied potential. Meanwhile, the gold surface became dark with gas release, and the blackening potential (~ 1.5 V) was lower than the value of 1.8 V described by Nishio [14], mainly due to the easier polarization on smaller–area Au disc than on larger–area Au foil. NPGFs thus form when the smooth gold surface is treated under high anodic potentials [14]. These potentials are so high that the gold surface should undergo electrooxidization, generating gold oxide multilayer [17]. Noteworthy, this oxide is easily reduced to gold atoms by OA, as evidenced by the

OCP–time behavior (Fig .2) for the thick gold oxide film in OA solution. As shown in Fig. 2, the OCP decay happens rapidly at first, then slows down, and finally stabilizes near −0.1 V with time increasing. Meantime, we observed a marked color change of gold surface from red (thick oxide film) to black (NPGF). These facts show that the generation of gold oxide multilayer and its reduction by OA probably play an important role in fabricating NPGFs.

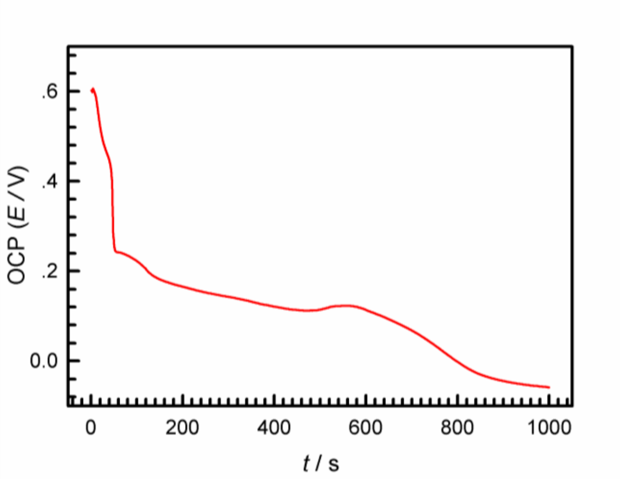

Figure 2. Open circuit potential (OCP)–time curve for the thick film of gold oxide in 0.1 M OA solution. The oxide film used here is prepared ex situ by oxidizing the smooth gold electrode at 4 V for 100 s in 0.5 M H_2SO_4 solution.

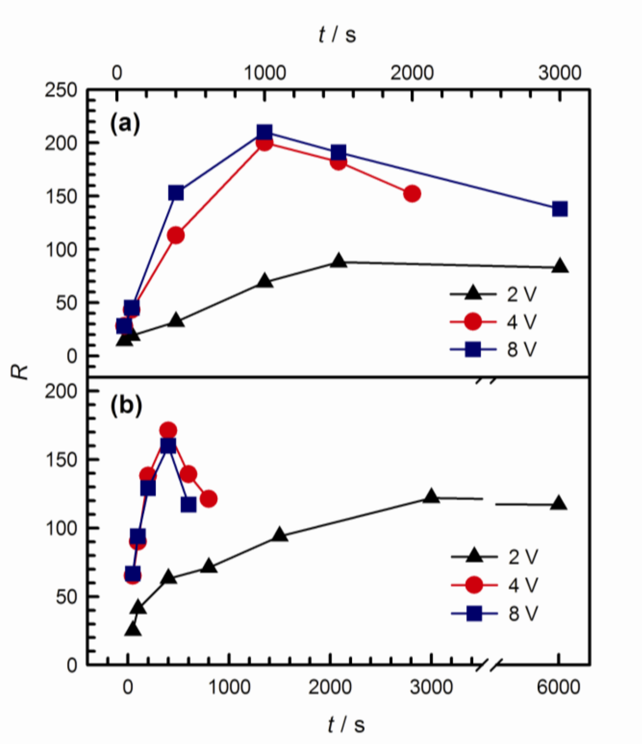

Figure 3. The dependence of roughness factor (*R*) on step time at different anodic potentials on the smooth Au electrode in an aqueous solution of (a) 0.1 M and (b) 0.5 M OA.

The dependences of roughness factor (*R*) on step time, step potential and OA concentration are exhibited in Fig. 3. At 2 V, being close to that used in literature [14], the *R* rises firstly and then stabilizes (~90) at 1500 s when the step time prolongs in 0.1 M OA (Fig. 3a). At higher anodic potential of 4 or 8 V, *R* increases rapidly and reaches to a maximum ~ 200 at 1000 s, and then decreases with the increase of step time. Both longer time and higher potential should be in favor of thickening the porous gold layer and thus resulting in high *R*. However, the porous film will collapse and fall off obviously under continuous, strong gas evolution while stepping to higher potentials (4 or 8 V) too long. The *R* changes in 0.5 M OA are somewhat similar to those in 0.1 M OA, except for that in Fig. 3b a slight smaller maximum *R* (~170) can be obtained with an obvious shorter time of 400 s at 4 or 8 V. This indicates that higher concentration of OA is helpful in fast formation of NPGFs. One explanation for this might be that, at high concentration, electrogenerated gold oxide is reduced rapidly by OA and thus the NPGF with high *R* forms at short time.

The surface morphology of smooth Au treated at 8 V in 0.1 M OA with different step time is shown in Fig. 4. In 10 s, as viewed by the naked eye, the gold surface starts darkening. But there are no obvious nanopores on the surface (Fig. 4a). Instead, many aggregates sizing from several to dozens of nanometers show up. As the step time prolongs (for example, 1000 s), obvious 3D nanoporous structure forms (Fig. 4b). Besides, the surface looks loose, curly and comprises microscopic flakes with 3D nanoporous structure (Fig. 4c–d). Such an uneven surface should be resulted from the strong impact of gas evolution.

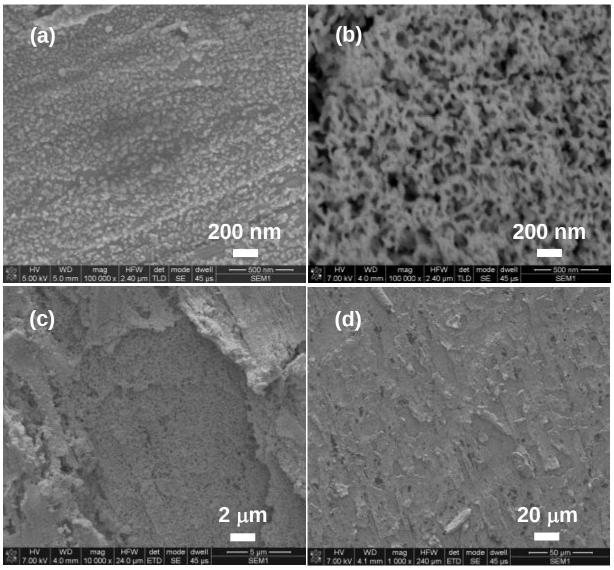

Figure 4. SEM images of NPGFs prepared by anodization of gold at 8 V for (a) 10 s and (b–d) 1000 s in 0.1 M OA.

Based on above results, we can try to give some new explanations on the formation mechanism of NPGFs. Overall, at high anodic potentials, complex electrode processes might occur simultaneously and/or subsequently, mainly involving the formation of multilayer gold oxide [17] and chemical reduction of gold oxide by OA. Once a high anodic potential is imposed, the smooth gold surface is oxidized immediately and forms a thick gold oxide layer. The oxide is then reduced chemically to gold atoms by OA. These newly–born atoms easily aggregate to gold nanoparticles. Increasing the anodic polarization time, above processes repeat and more and more nanoparticles produce, and finally they assemble into a 3D nanoporous gold film. The thickness of NPGFs no longer increases with the anodic polarization time prolonged further, as the reactants can hardly enter deep sites through the as–formed thick nanoporous layer. The strong reducing ability of high concentration of OA might accelerate the conversion of gold oxide to gold atoms and thus the formation of NPGF. A very thin carbonaceous film [14] is helpful in enhancing the stability of NPGFs. Note that gas evolution at high anodic potentials might result in several influences on the preparation. In situ generation, growth and departure of gas bubbles can produce a force to promote the diffusion of newly–produced gold atoms/nanoparticles from substrate to surface layer. The agitation of gas evolution can also replenish the surface concentration of reducer OA and so avoid the depletion of surface OA due to the electrocatalytic oxidation. However, the NPGFs become non–uninform by strong impact force of gas evolution (see Fig 4c–d).

As shown in Fig 5, the as–fabricated NPGF exhibits good catalytic activities toward electrooxidation of ethanol (a), glucose (b), ascorbic acid (c) and electroreduction of H_2O_2 (d). The enhanced peak current is due to the large surface area of the NPGF, and the negative (for electrooxidation) or positive (for electroreduction) shift of the onset potentials is attributed to the high reactivity of the gold nanoparticles.

The NPGF also exhibit considerable SERS activity (Fig. 6), as evidenced by the characteristic band at 1015 and 1039 cm^{-1} for the adsorbed pyridine [19]. Note that the SERS intensity of the strongest peak 1015 cm^{-1} reaches about 2000 counts per second (cps).

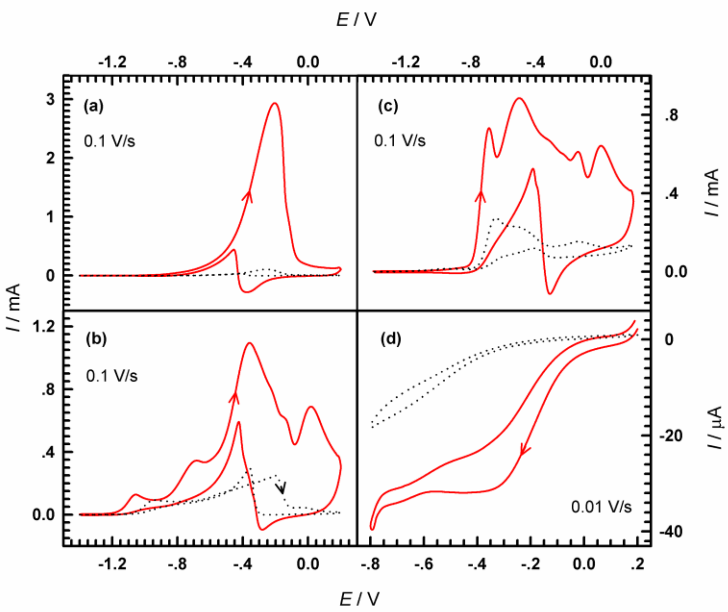

Figure 5. CVs on smooth Au (the dotted lines) and NPGF (the solid lines) electrodes in (a) 1 M NaOH + 1 M ethanol, (b) 1 M NaOH + 1 M glucose, (c) 1 M NaOH + 0.1 M ascorbic acid, and (d) 0.5 M H_2SO_4 + 0.1 M H_2O_2. The NPGF electrodes were prepared by anodic oxidation at 8 V for 1000 s.

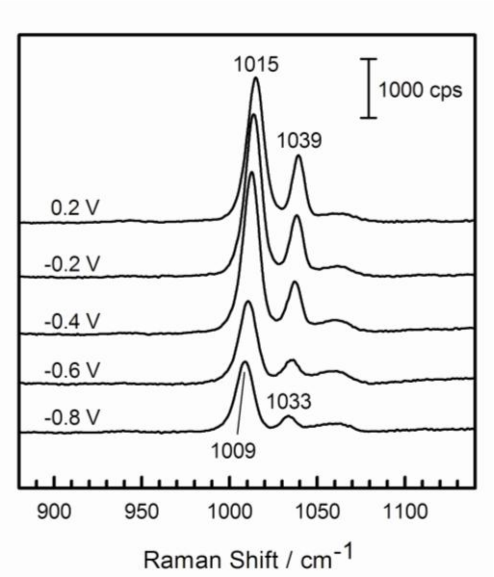

Figure 6. SERS spectra of pyridine (Py) on the NPGF electrode in a solution of 0.01 M Py + 0.1 M KCl. The NPGF was prepared under the same condition as shown in Fig. 5.

4. CONCLUSIONS

In summary, NPGFs were fabricated from a smooth gold substrate under highly anodic polarization in an aqueous solution of OA. Several interfacial processes, such as electrooxidation of pure gold and chemical reduction of multilayer oxide, might be responsible for the formation of such structure. The as–prepared NPGF exhibited high electrocatalytic activities toward the oxidation of ethanol, glucose and ascorbic acid as well as the reduction of hydrogen peroxide. The film also showed considerable SERS activity.

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References

1. Y. Ding, M. W. Chen, and J. Erlebacher, *J. Am. Chem. Soc.*, 126 (2004) 6876.
2. J. Biener, G. W. Nyce, A. M. Hodge, M. M. Biener, A. V. Hamza, and S. A. Maier, *Adv. Mater.*, 20 (2008) 1211.
3. Y. Xia, W. Huang, J. F. Zheng, Z. J. Niu, and Z. L. Li, *Biosens. Bioelectron.*, 26 (2011) 3555.
4. F. C. Meldrum, and R. Seshadri, *Chem. Commun.*, (2000) 29.
5. F. Lufrano, and P. Staiti, *Int. J. Electrochem. Sci.*, 5 (2010) 903.
6. P. N. Bartlett, P. R. Birkin, and M. A. Ghanem, *Chem. Commun.*, (2000) 1671.
7. J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, and K. Sieradzki, *Nature*, 410 (2001) 450.
8. H. C. Shin, J. Dong, and M. L. Liu, *Adv. Mater.*, 15 (2003) 1610.

9. H. C. Shin, and M. L. Liu, *Adv. Funct. Mater.*, 15 (2005) 582.
10. J. Liu, L. Cao, W. Huang, and Z. L. Li, *ACS Appl. Mater. Interfaces*, 3 (2011**)** 3552.
11. Y. P. Deng, W. Huang, X. Chen, and Z. L. Li, *Electrochem. Commun.*, 10 (2008) 810.
12. W. Huang, M. H. Wang, J. F. Zheng, and Z. L. Li, *J. Phys. Chem. C*, 113 (2009) 1800.
13. W. Huang, L. Fu, Y. C. Yang, S. Hu, C. Li, and Z. L. Li, *Electrochem. Solid-State Lett.*, 13 (2010) K46.
14. K. Nishio, and H. Masuda, *Angew. Chem. Int. Ed.*, 50 (2011) 1.
15. S. Trasatti, and O. A. Petrii, *Pure & Appl. Chem.*, 63 (1991) 711.
16. Y. D. Peng, Z. J. Niu, W. Huang, S. Chen, and Z. L. Li, *J. Phys. Chem. B*, 109 (2005) 10880.
17. L. D. Burke, and P. F. Nugent, *Gold Bull.*, 30 (1997) 43.
18. B. Beden, I. Çetin, A. Kahyaoglu, D. Takky, and C. Lamy, *J. Catal.*, 104 (1987) 37.
19. D. Y. Wu, J. F. Li, B. Ren, and Z. Q. Tian, *Chem. Soc. Rev.*, 37 (2008) 1025.

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