



Pore-size tuning and optical performances of nanoporous gold films



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ABSTRACT

Through pulse electrochemical dealloying (PED) and chemical dealloying (CD), a variety of nanoporous gold (NPG) films of 100 nm thickness with a wide range of pore size (4–140 nm) were prepared. The coarsening mechanism of pore and the effect of residual Ag on optical performances were investigated. The pore size was tuned by controlling the dissolution rate of active Ag atoms and surface diffusion rate of noble Au atoms along the alloy/solution interfaces. The maximum pore size of 140 nm was obtained by surfactant-assisted chemical dealloying (SA-CD) and the minimum pore size of 4 nm was achieved by PED. It is found that the surface diffusivity of gold in PED is about $0.4\text{--}2 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$, four orders of magnitude smaller than that in SA-CD ($2.4 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$). Finally, optical performances of the NPG films were investigated by UV-vis and surface-enhanced Raman scattering (SERS) spectra. The results reveal that the NPG film with a pore size of 8 nm fabricated by PED exhibits higher surface-plasmon absorption and the strongest SERS effect.

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1. Introduction

Nanoporous gold (NPG) fabricated by dealloying has attracted a considerable attention due to the intriguing optical [1,2], electrochemical [3–6], and biocatalytic [7] performances. These performances arise from the large surface area of nanoscale pores, which are therefore significantly affected by the pore size. For instance, Lang et al. [8] studied the surface-enhanced Raman scattering (SERS) of NPG films with pore dimensions ranging from 15 to 41 nm and showed that the SERS intensity increased as pore size decreased. The process parameters that can change the length scale of ligaments/channels involve the concentration of electrolyte, etching time and temperature [9], etc. At present, the small pores with sizes of 5–41 nm can be formed in NPG films of around 100 nm thick through short-time dealloying or at a low temperature [8–10]. These NPG films usually contain a larger amount of residual silver [11]. For pores larger than 90 nm (90–700 nm), an alloy belt of several or tens of micrometers must be used, which is annealed for various durations after free dealloying [12]. It should be noted that the prominent performances of NPG film, such as the catalytic reaction, SERS and biosensing, only occur at the surface. A thick film of several or tens of micrometers induces

not only a significant waste of noble metal, since over 90% of material is unused, but also interferences [13], since the light transmittance and surface-plasmon resonance are attenuated. Both residual Ag atoms and the micrometer scale thick film abate the performance [11,13]. Thus, it is critical to achieve a wide range of pore size in ultrathin (say 100 nm) NPG films.

It is well known that the formation of porous structure during dealloying does not simply excavate one active component off a binary alloy [14,15]. It involves both removal of less noble element by etching and rearrangement of noble element by surface diffusion [14]. Although the kinetic Monte-Carlo simulation, conducted by Erlebacher et al. [16], has indicated that Ag atoms are dissolved into solution layer-by-layer and Au atoms rearranged on the crystal lattice to form a three-dimensional (3D) network, the formation and coarsening of pores are not well understood experimentally.

In this study, a variety of ultrathin NPG films (~100 nm) with a wide range of pore size (4–140 nm) were prepared by two methods: pulse electrochemical dealloying (PED) for the pore size of 4–8 nm and chemical dealloying (CD) for 7–140 nm. The latter method was conducted at a low temperature (LT-CD) for 7–40 nm pores, room temperature (RT-CD) for 20–45 nm pores, low concentration of electrolyte (LC-CD) for 9–40 nm pores and with surfactant-assistance (SA-CD) for 12–140 nm pores, respectively. With the continuous variation of pore size in the NPG films of the same thickness, we can then systematically investigate the

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coarsening mechanism, surface diffusion and the influence of pore size on optical performances.

2. Experimental details

White gold films ($\text{Au}_{35}\text{Ag}_{65}$ in at.%) of 100 nm thick were used in this study. The NPG films with different pore sizes were prepared by five processes, e.g. PED, LT-CD, RT-CD, LC-CD, and SA-CD. The PED was carried out using a square-wave voltage of 0.6 V with a successive cycle of 50 ms on-time and 10 ms off-time. The two-electrode system was employed, in which a platinum wire and the $\text{Au}_{35}\text{Ag}_{65}$ film were used as the counter and working electrodes, respectively. All CD processes were performed by floating the films in HNO_3 solution. In SA-CD, the NPG films were immersed into 8 M HNO_3 containing 0.1% (wt.%) hexadecyl trimethyl ammonium bromide (CTAB), and washed by 1% (wt.%) NH_3 solution. The detailed parameters were listed in Table 1.

The surface topography was observed using an FEI Quanta 450 field-emission scanning electron microscopy (SEM), equipped with an energy dispersive X-ray spectrometer (EDX) to determine the chemical compositions. The average pore size was measured by a rotationally fast Fourier transform (FFT) method combined with the conventional linear intercept (LI) method from SEM images. FFT measurement was used for the close length scale of pore channels and gold ligaments. A commercial software package, Digital-Micrograph™, was used to obtain the FFT power spectrum, which provided a scattering peak from contrast changes in SEM micrographs. The scattering peak corresponds to the characteristic length scale of the bicontinuous structure [17]. The LI method was suitable for all kinds of NPG samples, but the estimated value exhibited a relative larger discrepancy due to the irregular shape of both channels and ligaments. Specifically, the pore size was firstly estimated by the LI method, and then the FFT method to achieve an accurate value on the condition of the close length of ligament (l) and pore (d). The pore size, marked by LI, was calculated by conventional linear intercept method, and the others unmarked were from FFT method, as shown in Table 1. The NPG films were referred to as NPG- d with different pore sizes. The surface morphology was observed using an atomic force microscopy (AFM, Shimadzu, N9500) operated in semi-contact (tapping) mode. The root mean square roughness (Rms) was measured over a scan area of $1 \times 1 \mu\text{m}$. The X-ray photoelectron spectrometry (XPS, Phi

V5000) with an Al K_{α} X-ray source was used to determine the residual Ag content in NPG films.

UV–vis absorption spectra and SERS of NPG films were investigated. The NPG was placed onto a glass slide for the measurement of UV–vis extinction (Lambda 750S UV–vis Spectrometer). Prior to SERS measurement, the NPG films were immersed into 10^{-5} M crystal violet aqueous solution for 6 h to allow sufficient adsorption. The films were then taken out by glass slides, rapidly rinsed with distilled water to remove the residual droplets on the surfaces, and finally air dried. SERS was collected with a Renishaw Raman microscopy operating with a 632.8 nm He-Ne ion laser (beam size of 1 μm).

3. Results

3.1. Surface morphology

Fig. 1 shows the typical top-view SEM images of NPG films with various pore sizes prepared under different conditions. Fig. 1(a) and (b) display the surface morphologies of NPG-4 and NPG-8 films prepared by PED, where the average pore size is 4 (LI) and 8 nm, respectively. The magnification inset in Fig. 1(b) clearly displays the bicontinuous porous structure. It should be pointed out that the maximum pore size achieved by PED is 8 nm, irrespective of the etching time after 20 min. Fig. 1(c)–(f) are the typical morphologies of NPG films prepared by CD at different conditions. The smallest pore size is about 7 (LI) nm by LT-CD at 0 °C for 10 min (Fig. 1(c)). The morphologies of NPG-20 by RT-CD for 10 min and NPG-40 by LC-CD for 600 min exhibit similar bicontinuous nanoporosity, as shown in Fig. 1(d) and (e), respectively. The average pore size is obviously increased to 140 nm by SA-CD containing 0.1% CTAB for 60 min, as shown in Fig. 1(f). The further increase of pore size results in the fragmentation of 100 nm NPG film. It is worth noting that the structural imperfections, characterized by some unreacted zones, as indicated by arrows in the magnification insets of Fig. 1(a) and (c), are observed in NPG-4 by PED and NPG-7 by LT-CD. However, continuous pores homogeneously distributed on the surface are also observed in the NPG films, including NPG-8 by PED, NPG-20 by RT-CD, NPG-40 by LC-CD and NPG-140 by SA-CD, as shown in Fig. 1(b) and (d)–(f).

The detailed microstructural characteristics of the NPG films prepared by different methods are shown in Table 1, including pore size, pore/ligament ratio, residual Ag content, structural

Table 1
Processing parameters and structural characteristics of nanoporous gold by dealloying.

Method	Processing			Microstructure					
	T (°C)	C_{HNO_3} (M)	Agent (wt.%)	d (nm)	Ratio d/l	t (min)	C_{Ag} (at.%)	Rms (nm)	Morphology
LT-CD	0	16	/	7 ± 4 (LI)	0.78	10	44 ± 5	6.3	Heterogeneous pores
				12 ± 3 (LI)	0.80	20	34 ± 4	/	Heterogeneous pores
				18 ± 1	0.95	60	21 ± 4	/	Bicontinuous pores
				40 ± 1	1.05	600	12 ± 3	/	Bicontinuous pores
RT-CD	23	16	/	20 ± 1	0.98	10	35 ± 3	9.6	Bicontinuous pores
				35 ± 1	1.05	60	12 ± 2	/	Bicontinuous pores
				40 ± 1	0.98	120	11 ± 3	/	Bicontinuous pores
				9 ± 4 (LI)	0.78	10	62 ± 5	/	Heterogeneous pores
LC-CD	23	8	/	26 ± 1 (LI)	1.05	300	37 ± 4	/	Heterogeneous pores
				40 ± 1	0.98	600	15 ± 3	10.4	Bicontinuous pores
				12 ± 4 (LI)	0.89	10	54 ± 5	/	Heterogeneous pores
				25 ± 3 (LI)	0.91	30	45 ± 4	/	Heterogeneous pores
SA-CD	23	8	CTAB 0.1	140 ± 7	1.15	60	15 ± 4	19	Bicontinuous pores
				4 ± 2 (LI)	0.85	5	35 ± 4	/	Heterogeneous pores
PED	23	8	/	8 ± 1	0.93	20	3 ± 2	2.4	Bicontinuous pores

Note: LT-CD: chemical dealloying at low temperature; RT-CD: chemical dealloying at room temperature; LC-CD: chemical dealloying at low concentration; SA-CD: surfactant-assisted chemical dealloying; PED: pulse electrochemical dealloying; CTAB: hexadecyl trimethyl ammonium bromide; T : etching temperature; C_{HNO_3} : concentration of HNO_3 ; ratio (d/l) is the rate of pore size to ligament length; t : etching time; C_{Ag} : concentration of residual Ag atoms; Rms: root mean square roughness; the LI, means pore size, d , was calculated by conventional linear intercept method, and the others unmarked were from FFT methods.

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