

Ultrafine nanoporous gold by low-temperature dealloying and kinetics of nanopore formation

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A low-temperature dealloying technique was developed to tailor the characteristic length scale of nanoporous gold for advanced functional applications. By systematically investigating the kinetics of nanopore formation during free corrosion, the authors experimentally demonstrated that the dealloying process is controlled by the diffusion of gold atoms at alloy/electrolyte interfaces, which strongly relies on the reaction temperatures. Low dealloying temperatures significantly reduce the interfacial diffusivity of gold atoms and result in an ultrafine nanoporous structure that has been proved to be useful with improved chemical and physical properties. © 2007 American Institute of Physics. [DOI: 10.1063/1.2773757]

Porous materials have recently been attracting considerable attention because of a wide range of applications in catalysis, sensing, micro/nanoelectromechanical systems (MEMS/NEMS), and biotechnology. One example is nanoporous gold formed by chemically or electrochemically dealloying silver-gold alloys,^{1–4} which possesses bicontinuous porosity and excellent electrical and thermal conductivities. Nevertheless, conventional nanoporous gold with a nanopore size of about tens of nanometers does not demonstrate too many remarkable functions in physics and chemistry.^{5–10} It has been theoretically predicted and experimentally proved that reducing the size of a nanostructured material in one or more dimensions, the physical and chemical properties can be dramatically altered by controlling the size and the shape at the nanoscale.¹¹ Thus, it is expected that the properties of nanoporous gold may be improved by reducing nanopore sizes. Ultrafine nanoporous gold with a pore size smaller than 10 nm has been reported in the samples prepared by room-temperature dealloying.¹² However, this claim is based on scanning electron microscope observations with a low resolution, and the supporting evidence with a high-resolution image has not been forthcoming. Our systematical studies with a transmission electron microscope (TEM) as the characterization tool demonstrate that it is difficult to control nanopore sizes smaller than 10 nm during room-temperature dealloying because of the fast diffusion of gold atoms at the alloy/electrolyte interfaces.^{13,14} In this study, we systematically investigated the evolution of nanoporous structure at various temperatures and developed a low-temperature dealloying technique to control the nanopore sizes from conventional tens of nanometers down to ~5 nm.

Nanoporous gold films with a thickness of ~100 nm were fabricated by dealloying Ag₆₅Au₃₅ (atomic ratio) leafs. The films were handled by a glass sheet and floated on a 70% (mass ratio) HNO₃ solution. Etching process was performed at three scheduled temperatures (25, 0, and -20 °C) that were controlled by a commercial cooling/heating setup with an accuracy of ±2 °C. The intermediate nanoporous structure was quenched by distilled water and the residual acid within the nanopore channels was removed by water

rinsing. The nanoporous gold films were placed on Cu grids for TEM characterization. The chemical composition of nanoporous gold, in particular the amount of residual silver, was determined by TEM energy dispersive x-ray (EDX) analysis. The average nanopore sizes, defined by the equivalent diameters of nanopores or the gold ligaments, were measured by a rotationally averaged fast Fourier transform (FFT) method, in which the TEM micrographs were transformed into FFT power spectra that contain the scattering peaks corresponding to the characteristic length scales of the bicontinuous nanostructure.¹⁵

The chemical etching process results in selective dissolution of silver atoms and the formation of a nanoporous structure by the self-assembly of gold atoms at alloy/electrolyte interfaces.^{4,16} The pore sizes increase with etching time and temperature, and the coarsening process exhibits significant temperature dependence. However, the bicontinuous morphology of the samples is similar to each other except for the difference in the characteristic length scale. The relationship between the average pore size and the dealloying time at various temperatures was plotted in Fig. 1(a). The analysis of the kinetic data suggests that the coarsening rate of nanopores follows a nonlinear relationship, which is interestingly similar to the isothermal grain growth in polycrystalline materials,¹⁷ i.e.,

$$d(t)^n = k_0 t \exp\left(\frac{-E}{RT}\right) = K t D_s, \quad (1)$$

where diffusivity $D_s = D_0 \exp\left(\frac{-E}{RT}\right)$ and $d(t)$ is pore size at etching time t ; k_0 , K , and D_0 are constants and $k_0 = K D_0$; n is coarsening exponent; R is the gas constant; T is the etching temperature; and E is the activation energy for the nanopore formation and coarsening. The coarsening exponent n can be directly measured by plotting the $\ln[d(t)]$ vs $\ln t$ curves, as shown in Fig. 1(b). The excellent linear relations between $\ln[d(t)]$ and $\ln t$ at various temperatures further verify the logarithmic coarsening mechanism of nanoporous gold. The nearly identical slope, ~0.28, of the fitting lines for different etching temperatures implies an invariable coarsening mechanism at different temperatures. The n value for the coarsening of nanoporous gold is determined to be ~3.4–3.7, which is very close to the kinetic parameter, ~4,

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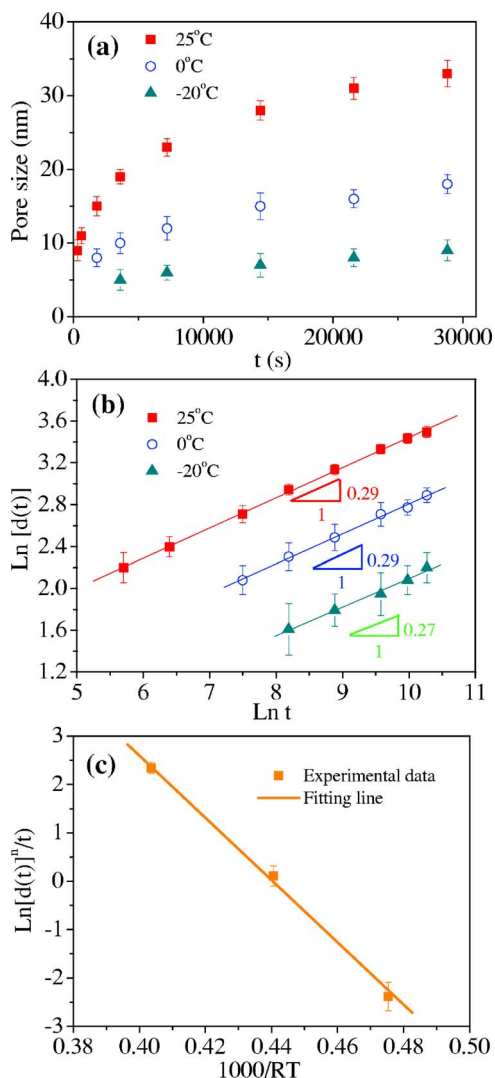


FIG. 1. (Color online) Evolution of nanopore size with etching time and temperature. (a) Correlation between nanopore size and time at various etching temperatures. (b) Measurements of the coarsening exponent by plotting $\ln[d(t)]$ vs $\ln t$ at each etching temperature. (c) Estimation of the activation energy for the nanopore formation.

reflecting surface relaxation of roughened metals in solutions.¹⁸

Because the formation of the nanoporous structure is dependent on the temperature and time, apparently it is a thermal-activation process and the measurement of activation energy will be helpful to understand the underlying mechanisms of the dealloying process. Based on the linear fitting between $\ln(d(t)^n/t)$ and $(RT)^{-1}$ [Fig. 1(c)], the activation energy for the formation and coarsening of nanoporous gold is measured to be ~ 63.4 kJ/mol. This value is close to that of surface diffusion of gold atoms in acids (50–60 kJ/mol),¹⁸ strongly suggesting that the formation and the coarsening of nanoporous gold are controlled by the gold diffusion at the alloy/electrolyte interfaces. The excellent linear relationship spanning the whole etching time scale [Figs. 1(b) and 1(c)] indicates that both dealloying and nanopore coarsening are dominated by one process, i.e., the surface diffusion of gold atoms in electrolyte.

It was found that a low dealloying temperature can effectively delay the coarsening of the nanoporous structure. For example, the average nanopore size is ~ 7 and 15 nm after etching for 4 h at -20 and 0 °C, respectively

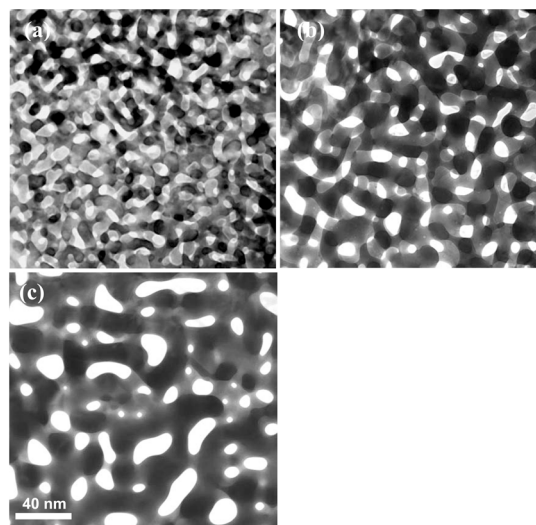


FIG. 2. TEM micrographs of nanoporous gold dealloyed at (a) -20 , (b) 0 , and (c) 25 °C for 4 h.

[Figs. 2(a) and 2(b)]. In contrast, four-hour dealloying at room temperature results in an average pore size up to ~ 28 nm. With the same dealloying time, the nanopore size at 25 °C is about four times larger than that at -20 °C, further verifying the remarkable temperature effect on the characteristic length of nanoporous gold. Based on the surface diffusion controlled coarsening mechanism, the diffusivity (D_s) of gold atoms at each etching temperature can be estimated by the equation¹⁹

$$D_s = \frac{d(t)^4 kT}{32\gamma a^4}, \quad (2)$$

where k is Boltzmann constant, γ is surface energy, t is the etching time, and a is the lattice parameter. According to the parameters compiled in Ref. 14 and measured by this study, the surface diffusivity of gold in electrolyte at -20 , 0 , and 25 °C are estimated to be 9.0×10^{-22} , 1.5×10^{-20} , and 2.0×10^{-19} m²/s, respectively. Therefore, slight temperature changes, for example from 25 to -20 °C, can alter the diffusivity of gold at alloy/electrolyte interfaces up to two orders of magnitude. Thus, the strong temperature dependence of nanopore sizes reported in this study is fairly in accord with the recent kinetic Monte Carlo simulation in which lower diffusivity (D_s) of gold atoms at the solid/electrolyte interfaces leads to a smaller nanoporous size (d).⁴ According to the theoretical study, the characteristic length of nanoporous gold is predicted to be the function of interfacial diffusivity of gold atoms, i.e.,

$$d \propto (D_s/V_0)^\mu, \quad (3)$$

where V_0 is the velocity of a flat alloy surface with no gold accumulated on it, and μ is a constant suggested to be $1/6$ according to the Cahn-Hilliard equation.⁴ Apparently, the theoretical model [Eq. (3)] is equivalent to our empirical kinetic one [Eq. (1)] in principle, except that its coarsening exponent ($\mu=1/6$) is slightly smaller than the experimental value $\mu=1/n \approx 1/4$. Although, in addition to temperature and time, a number of other dealloying parameters have been suggested to affect the characteristic length of nanoporous gold, particularly during electrochemical dealloying,^{4,16} our empirical equation [Eq. (1)] suggests a simple way of tailor-

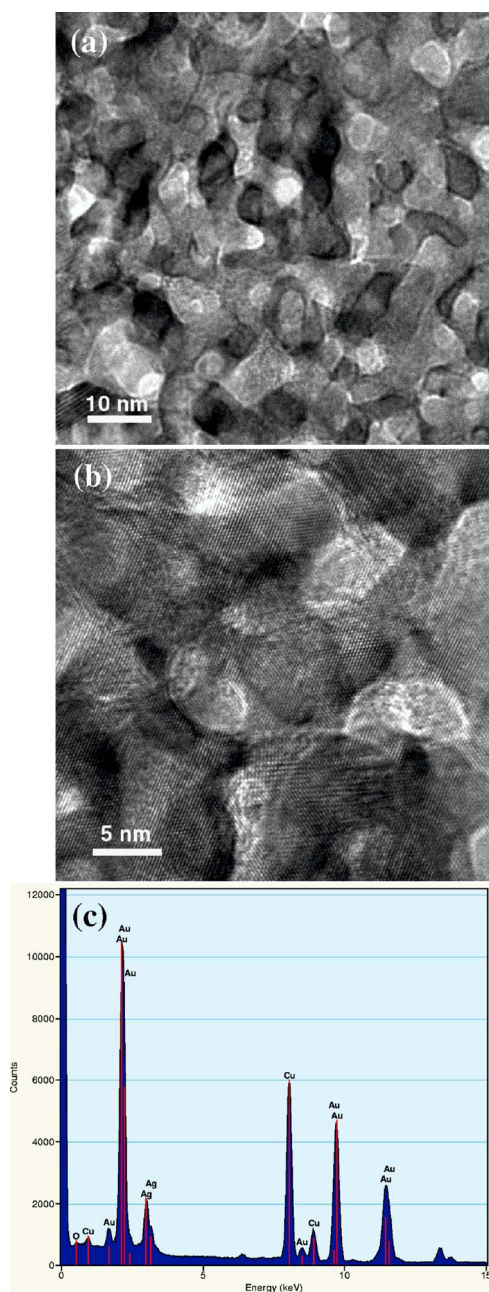


FIG. 3. (Color online) Microstructure and composition of ultrafine nanoporous gold dealloyed at -20°C for 1 h. (a) Bright-field TEM image. (b) HREM micrograph (c) TEM EDX spectrum.

ing the nanopore sizes with nanoscale accuracy by controlling etching time and temperature.

Considering that small nanopores may dramatically alter the properties of nanoporous gold, we systematically characterize the microstructure and composition of ultrafine nanoporous gold developed by low-temperature dealloying. With the 70% HNO_3 aqueous solution, the lowest temperature for dealloying is about -20°C . Below this, the dealloying cannot be performed because the solution freezes. At -20°C , the nanopore sizes can be tailored down to about 2–3 nm with short etching time of 10 min, evidencing that the low dealloying temperature and short time suppress the diffusion of gold atoms and thereby lead to the formation of the ultrafine nanoporous structure. However, the low temperature and short time also limit the dissolution of silver, resulting in about 17 at. % silver remaining in the ligaments. After dealloying at -20°C for 1 h, the characteristic length scale of

the nanoporous structure is still very small, as illustrated in a bright-field TEM image [Fig. 3(a)]. The contrast, mainly from the mass difference between empty nanopore channels and gold ligaments, shows that the ultrafine nanoporous structure is bicontinuous; i.e., both the bright nanopore channels and the dark gold ligaments interconnect across the entire image region. High-resolution electron microscope (HREM) image [Fig. 3(b)] shows that the average nanopore size is about 5 nm with a nearly identical ligament width. The continuous crystal lattices suggest that the gold ligaments surrounding a nanopore remain to be a single crystal. Importantly, TEM EDX spectrum shown in Fig. 3(c) demonstrates that only about 6 at. % silver is left behind in the nanoporous structure, indicating that the dissolution of the residual silver takes place with longer dealloying time at the low temperature. Additionally, detectable crystal defects, such as twins and dislocations, are rarely seen in the ultrafine nanoporous samples.

The ultrafine nanoporous structure shows improved chemical and physical properties. By tuning the nanopore size from ~ 33 nm down to ~ 5 nm, the surface enhanced Raman scattering (SERS) effect of nanoporous gold can be significantly improved. The ultrafine nanoporous gold is expected to be a promising SERS substrate for ultrasensitive instrumentation applications.¹⁰ The electronic transport properties of nanoporous gold also show interesting nanopore size dependence. The ultrafine nanoporous gold with randomly oriented gold ligaments were found to effectively suppress the cyclotron motion of conduction electrons in strong magnetic fields and result in unusual transport properties in high magnetic fields, which make the ultrafine nanoporous an ideal material for applications in noise-free metallic devices in strong magnetic fields.²⁰

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