Nanoporous Metals with Controlled Multimodal Pore Size Distribution

Yi Ding, and Jonah Erlebacher

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 20 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Nanoporous Metals with Controlled Multimodal Pore Size Distribution

Yi Ding and Jonah Erlebacher*

Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218

Received March 25, 2003; E-mail: jonah.erlebacher@jhu.edu

Porous noble metals are of interest in a wide variety of applications including catalysis,[1] sensing,[2] microfluidic flow control,[3] etc. Each of these applications is optimized when the metal has a particular pore size. For instance, larger sized pores (100s of nm) are useful in microfluidic flow control, whereas very small pores (10s of nm) are useful for increasing device surface area as required for sensor applications. For microfluidic-based sensors, a bimodal pore size distribution composed of large porosity channels with highly porous channel walls is desirable in order to achieve fast response time and high sensitivity. We report here a simple strategy to make free-standing noble metal membranes with this kind of hierarchical porous architecture.

Typically, methods to fabricate porous metals with controlled pore size result in materials with unimodal pore size distributions. We are thinking here of methods that are based on filling pre-prepared templates such as electroplating into the hexagonally packed cylindrical pores of certain self-assembled liquid crystal surfactants to make mesoporous metals with a typical pore size less than 50 nm[4] or electroplating into larger scale structures such as colloidal fcc crystals,[5,6] porous block copolymers,[7,8] or anodic porous alumina to make macroporous metals with pore size larger than 100 nm;[9] after plating, the nonmetallic scaffold is dissolved or burned away. These fabrication techniques have the advantages of precise control over the size and structure of the final porous structure but are generally difficult and time-consuming to implement.

We have been investigating metallic corrosion phenomena in electrochemical systems, in particular the selective dissolution (an etching process also called *dealloying*) of silver from silver/gold alloys. A simple method to dealloy these silver/gold alloys is to immerse them in nitric acid, in which silver is soluble but gold is not. For alloy compositions between approximately 15−40 atom % Au, dealloying of silver/gold alloys exhibits an unusual three-dimensional (3-D) pattern-forming instability, a kind of self-assembly that results in the formation of an open, bicontinuous highly porous network of pure gold with ligament and channel width tunable between 5 nm to many microns by varying the starting alloy composition, varying the electrochemical potential driving dissolution, or employing thermal anneals after dealloying.[10,11] We call this material nanoporous gold (NPG). Recently we have found that commercially available 12-carat white gold leaf (Ag/Au alloy, 50:50 wt %) either 100 nm or 1 μm in thickness may be dealloyed to create free-standing NPG membranes that are inexpensive and crack-free over 80 cm[2]. Figure 1a shows the microstructure of dealloyed 1 μm thick NPG leaf. For this sample, the pore size is uniform and approximately 15 nm. Etching was carried out under free corrosion, i.e., simply floating the leaf on concentrated nitric acid surface for 1 h. During etching, silver atoms were selectively dissolved, and the gold atoms left behind assembled into the 3D porous structure shown in Figure 1a. This material can be coarsened to yield a self-similar structure but with much larger pore sizes by annealing at an elevated temperature.[11]
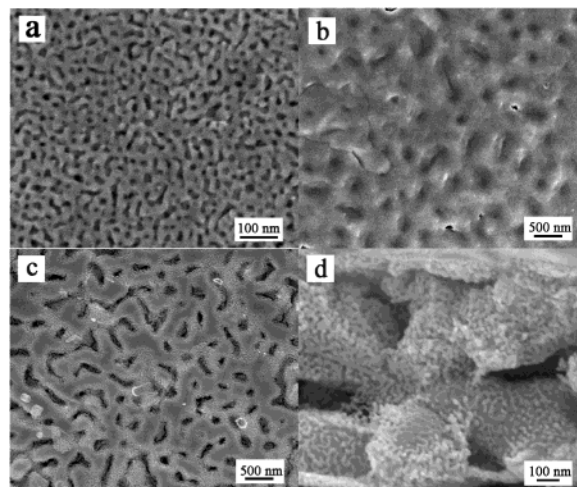
Figure 1. SEM images of NPG structures. All SEM images were acquired on a JEOL JSM-6700F. (a) A 1 μm thick NPG membrane made by dealloying a piece of 12-carat white gold leaf in nitric acid for 1 h.[16] (b) Large pore NPG membrane made by annealing sample (a) at 400 °C for 8 h and filled with silver. Plating proceeded in a dilute N_2H_4 atmosphere for about 10 min, as described in the text.[17] (c) Hierarchical porous membrane (plan view) made by annealing the sample shown in (b) at 400 °C for 4 h, and performing a second dealloying etch in nitric acid for 5 min. (d) Cross-section micrograph of sample (c).

The general idea of our method to make NPG architectures with two pores sizes is to anneal a membrane of porous gold to increase its pore size, fill the pores of the annealed membrane with silver, perform a second anneal, and then re-dealloy. The initial anneal sets the scale for the larger of the two pore sizes that ultimately form, and the second anneal serves to partially rehomogenize the buried gold/silver interface. The second dealloying step dissolves away the plated silver, at the same time dealloying the rehomogenized gold/silver interface. The final result is a porous membrane with large pores, but highly porous channel walls. The extent of rehomogenization allows independent control over the scale of the smaller of the two pores sizes. Trimodal and higher order architectures are in principle possible to engineer by repeating the process more times.

Although it may be thought that standard electrochemical or electroless plating methods might be used to uniformly fill the surface of NPG leaf, there are peculiar difficulties in filling 3-D porous gold membranes when their pore size is on the order of 10 or 100 nm. Primarily, NPG has an intrinsically catalytic surface, so conventional diffusion-limited electro(less)-plating processes (in which the object to be plated is submersed into a plating bath) will initiate and proceed preferentially on the top and bottom surfaces of the membrane and interior pore surfaces will remain uncoated. A more mundane difficulty is that NPG membranes always float on the surface of any aqueous solution in which one attempts to immerse them.

The observation that NPG leaf always floats on water, however, inspired us to develop a new gas-phase electroless plating technique. Our method is to float an NPG membrane on the surface of an electroless plating solution containing only a suspension of metal ions and not any reducing agent. Metals ions in the solution are pulled into the nanopores but do not plate because of the absence of reducing agent. We supply the reducing agent as a vapor that we flow over the surface of the floating leaf. Because metal ions are supplied to the pores of the leaf from below, and the reducing agent is supplied from above, plating is confined to occur only within the porous structure and not preferentially on either side. Furthermore, the reaction is self-limiting because as the pores fill with plated metal, the reaction shuts down. For the work presented here, the reducing agent was hydrazine (N_2H_4), and the plated metal was silver.

Figure 1b shows an annealed NPG membrane with 150 nm pores filled with silver using our method. That is, we have allowed the plating reaction to go to completion and completely fill the pores with silver. This is clearly shown in Figure 1b, which also shows the underlying coarsened NPG structure. The structure is essentially a dense film composed of intertwining skeletons, one of pure gold and the other of pure silver. Intermixing of the alloy constituents is kinetically restricted because plating proceeded at room temperature.

The next step in making the bimodal porous architecture is to rehomogenize the buried gold/silver interface so that over an appreciable width the interface has a composition that results in nanoporosity evolution upon dealloying. The proper temperature and annealing time for this step are informed by some simple theoretical guidance. Silver and gold form a nearly ideal solid solution. Therefore, upon annealing, silver-plated NPG should not only coarsen but also homogenize in composition. The rate at which such homogenization occurs is governed by the interdiffusion coefficient D. For Ag/Au bilayer interfaces, we have used literature measurements to estimate D to be on the order of 10^{-19} m^2/s at 400 °C.[12−14] Upon annealing, the composition profile of the Ag/Au interface evolves with time according to Fick's Second Law. The relevant solution for the interdiffusing interface with mutually soluble components is:[15]

$$C(x,t) = 0.5 + 0.5 erf(x/(2(Dt)^{1/2})) \quad (1)$$

Here, C is the atom fraction of gold as a function of time t and distance x from the bilayer interface. Equation 1 predicts that annealing the Ag-filled NPG sample at 400 °C for 4 h would result in a 50 nm thick interfacial region with gold fraction between 15 and 50% that conformally coats the original large pore gold structure made after the first anneal. This composition is typical of alloy compositions that result in nanoporous morphologies upon dealloying; compositions with higher gold content are unaffected by (electro)chemical etching.[10]

Upon performing this annealing cycle on Ag-filled NPG, and then performing a second etch in nitric acid for 5 min, we obtained the desired architecture—an NPG membrane with a bimodal pore size distribution. The large pore structure remained (with its lengthscale intact; compare Figure 1b and Figure 1c), and we successfully added to it a nanoporous skin. Visually, the depth of the porous layer on the channel walls is a few tens of nanometers as predicted from the interdiffusion model. Micrographs of our hierarchical porous gold architecture are illustrated in Figures 1c,d. Cross-section micrographs of the membrane (Figure 1d) show the
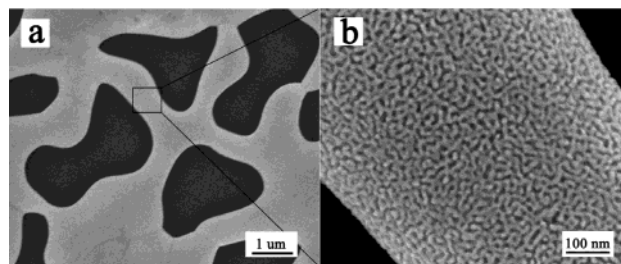
Figure 2. A 2-D/3-D hybrid NPG structure, where the dimension of unit structure in 2-D ($1−2$ μm) is 2 orders of magnitude larger than that in 3-D substructure (∼8 nm). Here, 100 nm thick gold leaf was used, and the second stage annealing was carried out at 500 °C for 8 h.

two porous lengthscales particularly well. The pore size of the backbone structure is slightly larger than 150 nm, whereas the skin of the backbone has a fine pore size of approximately 15 nm.

Our two-step dealloying strategy to create multimodal pore size distributions is quite versatile. Some of the general characteristics of the method that are worthy of immediate exploration include (1) applicability to any system that exhibits porosity evolution upon dealloying (not just Au/Ag alloys), (2) fabrication of trimodal and higher order porous architectures by additional annealing/plating/redealloying cycles, and (3) independent tunability of pore sizes, and even pore topology. This last characteristic we have begun exploring by performing the same kind of plating/redealloying experiments on a 100 nm thick NPG membrane and subsequently annealing at 500 °C for 8 h. Upon re-dealloying for just 2 min in nitric acid under free corrosion, we produced a *two*-dimensional (electrically conductive) network with highly porous ligaments. Figure 2 shows representative micrographs of this sample, in which $1−2$ μm sized pores (holes) and 8 nm sized small pores coexist.

References

(1) He, X.; Antonelli, D. *Angew. Chem., Intl. Ed.* **2001**, *41*, 214.
(2) Tierney, M. J.; Kim, H. O. L. *Anal. Chem.* **1993**, *65*, 3435.
(3) Rintoul, M. D.; Torquato, S.; Yeong, C.; Keane, D. T.; Erramilli, S.; Jun, Y. N.; Dabbs, D. M.; Aksay, I. A. *Phys. Rev. E* **1996**, *54*, 2663.
(4) Attard, G. S.; Bartlett, P. N.; Coleman, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. *Science* **1997**, *278*, 838.
(5) Velev, O. D.; Tessier, P. M.; Lenhoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548.
(6) Jiang, P.; Bertone, J. F.; Colvin, V. L. *Science* **2001**, *291*, 453.
(7) Prost, J.; Rondelez, F. *Nature* **1991**, *350*, 11.
(8) Breulmann, M.; Davis, S. A.; Mann, S.; Hentze, H. P.; Antonietti, M. *Adv. Mater.* **2000**, *12*, 502.
(9) Masuda, H.; Fukuda, K. *Science* **1995**, *268*, 1466.
(10) Erlebacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450.
(11) Li, R.; Sieradzki, K. *Phys. Rev. Lett.* **1992**, *68*, 1168.
(12) Wonnell, S. K.; Delaye, J. M.; Bibole, M.; Limoge, Y. *J. Appl. Phys.* **1992**, *72*, 5195.
(13) Janot, C.; Roth, M.; Marchal, G.; Piecuch, M.; Bruson, A. *J. Noncryst. Solids* **1986**, *81*, 41.
(14) Bukaluk, A. *Appl. Surf. Sci.* **2001**, *175−176*, 790.
(15) Porter, D. A.; Easterling, K. E. *Phase transformations in metals and alloys*, 2nd ed.; Chapman & Hall, London 1992.
(16) Gold leaves with thickness of 1 μm were obtained from Wehrung & Billmeier Co. (Chicago) and 100 nm thick gold leaves were purchased from Sepp Leaf Products Inc. (New York).
(17) Our silver plating solution contained 0.05 M AgNO$_3$, 2 M ammonium hydroxide, and 0.1 M Na$_2$EDTA·2H$_2$O. All chemicals were purchased from Alfa-Aesar, and the water used was Nanopure grade from a Millipore system.

JA035318G