

Electrodeposition of Three-Dimensionally Periodic Metal Meshes and Spheres

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ABSTRACT

Electrochemical methods have been used to produce three-dimensionally periodic metal meshes and spheres. Nickel is initially deposited into porous opal sheets. The opals themselves consist of close-packed silica spheres, which serve as a template for the growth of the nickel arrays within the void space between SiO₂ spheres. Dissolution of the SiO₂ spheres results in open, three-dimensionally periodic nickel mesh structures. The metal meshes can then be oxidized in air to produce nonconducting NiO meshes. This results in an inverse template that can be used for the growth of three-dimensionally periodic metal sphere arrays. Details on the preparation and characterization of these materials are presented.

INTRODUCTION

Three-dimensionally ordered arrays of nanospheres and their replicas (porous networks) are of great interest for applications in a variety of areas, including catalysis, separations, photonics, magnetics, and thermoelectrics. Opal nanosphere arrays (colloidal crystals) [1] of silica or latex spheres have been used as templates for the formation of inverse mesh replicas of a variety of materials by metal alkoxide hydrolysis [2, 3], particle infusion [4, 5], polymerization [6], chemical vapor deposition (CVD) [7, 8], melt infiltration [9], salt precipitation [10], electroless deposition [11] and electrodeposition [12-15]. Dissolution of the templates then produces open three-dimensional mesh structures. More recently, ordered nanosphere arrays have also been acquired by the subsequent use of the fabricated mesh materials as templates [16, 17]. Herein we describe the production of metal meshes and spheres by the electrochemical deposition approach. In this method, by the use of poorly conducting oxide sphere or mesh arrays as molds, well-defined metal meshes and spheres can be readily obtained.

EXPERIMENTAL

Electrode Fabrication. Synthetic opals were prepared by the methods described previously [18]. The opal used here was composed of 290 nm silica spheres. Figure 1 shows the fabrication procedure for the opal sheet electrode. We first sputtered a Au film (*ca.* 1 μm thick) onto one side of an opal piece (typically 7 \times 10 \times 1.5 mm), then Ag paste (Ted Pella, Inc.) was used to attach a length of Cu wire to the Au film, and finally the Au/wire side of the electrode, as well as the edges, were covered with an insulating glue (3M).

Sample Preparation. Using the opal membrane as the working electrode, versus a Pt wire counter electrode, Ni was deposited galvanostatically into the opal template [13] at a current density of 0.12 mA/cm². The Ni electroplating solution was obtained commercially (Technic,

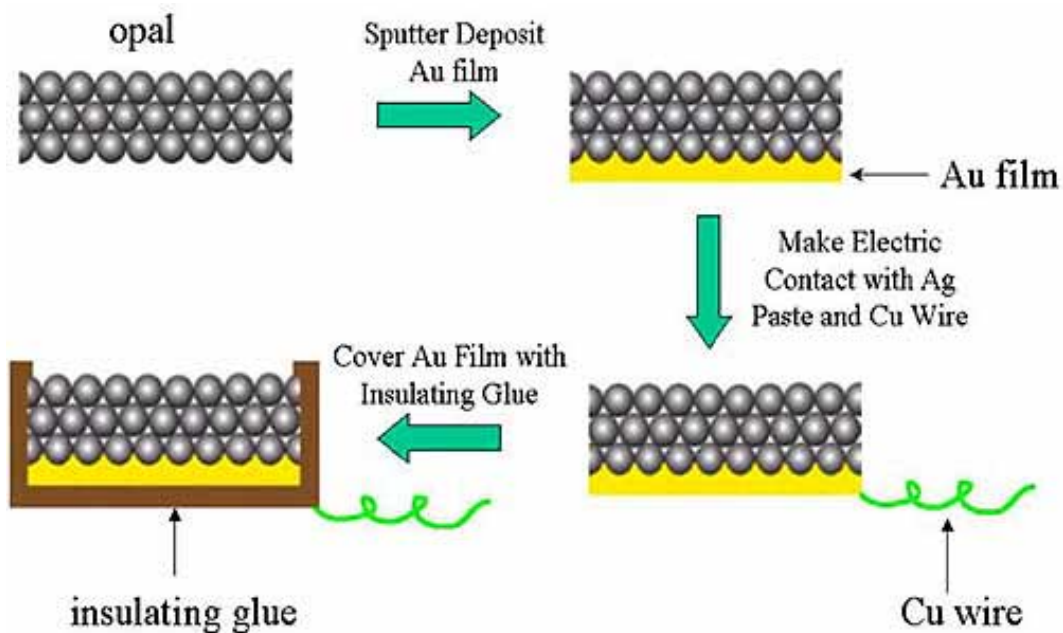


Figure 1. Schematic of opal electrode fabrication.

Inc.). The deposition time was 144 hours (*ca.* 80 μm thick nickel deposited). After the deposition, freestanding porous Ni mesh could be obtained by etching away the opal template with a 2% (v/v) HF solution.

Poorly conducting NiO mesh was obtained by slowly oxidizing the Ni mesh (the gold backing still in place) in open air to 550°C at 1°C/min., followed by an 8-hour isotherm. The NiO mesh was then used as an electrode after the copper wire and glue were reapplied. Au was electrodeposited within the NiO mesh over a 12 h period at constant current (0.5 mA/cm²) from a commercial gold plating solution (Technic, Inc., 15 - 20 ml of *ca.* 0.04 M) with a platinum wire counter electrode. After the deposition, the NiO mesh was removed in a boiling dilute sulfuric acid solution (20% v/v, 15 min.), resulting in ordered Au sphere arrays.

Characterization. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were performed on a JEOL JSM 5410 SEM. Transmission electron micrographs (TEM) were obtained by using a JEOL 2010 TEM operating at 200 kV. For TEM, a small piece of the sample was mounted directly on the Formvar carbon film grid.

RESULTS AND DISCUSSION

In the preparation of Ni mesh (inverse Ni opal), a low plating current density (0.12 mA/cm²) was used for the even growth of nickel within the opal membrane. The thickness of the Ni mesh film can be controlled by simply adjusting the deposition time. Figure 2 shows typical SEM images of the macroporous Ni mesh after removal of the silica spheres. Figure 2a reveals a highly ordered (100) orientation of the Ni mesh and Figure 2b shows the Ni mesh in predominately a (111) orientation. TEM was also used to examine the Ni mesh. Figure 3a shows a TEM image of silica spheres filled with Ni. A (100) monolayer and multiple silica layers, as well as (111) stacking faults can be seen. Figure 3b shows the TEM image of the silica-free Ni mesh in the (111) orientation. NiO mesh can be readily obtained by annealing the

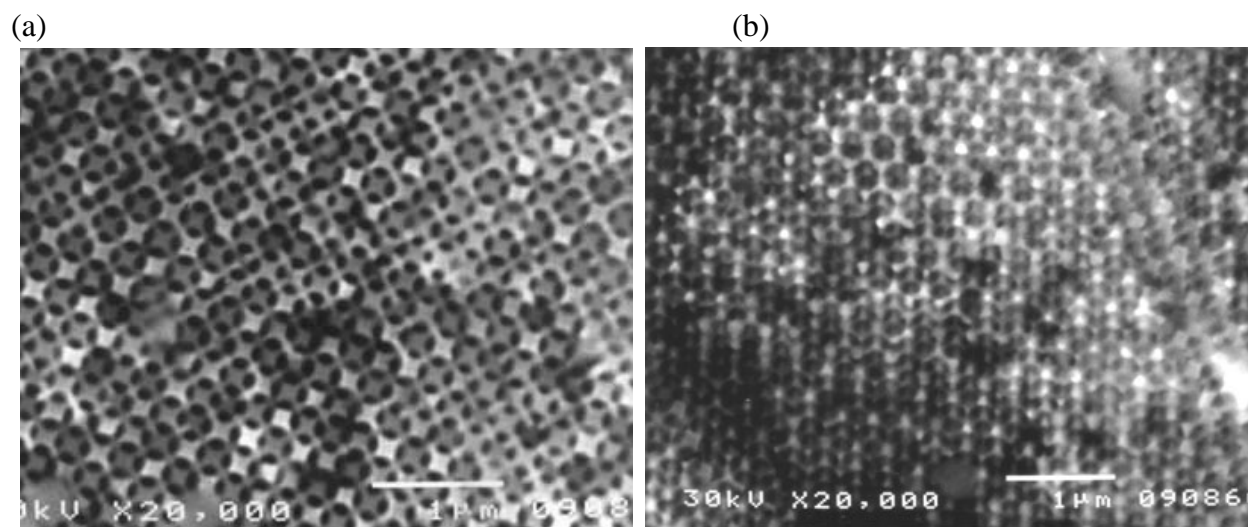


Figure 2. SEM images of (a) nickel metal mesh along (100) direction, (b) nickel mesh predominately along (111) direction.

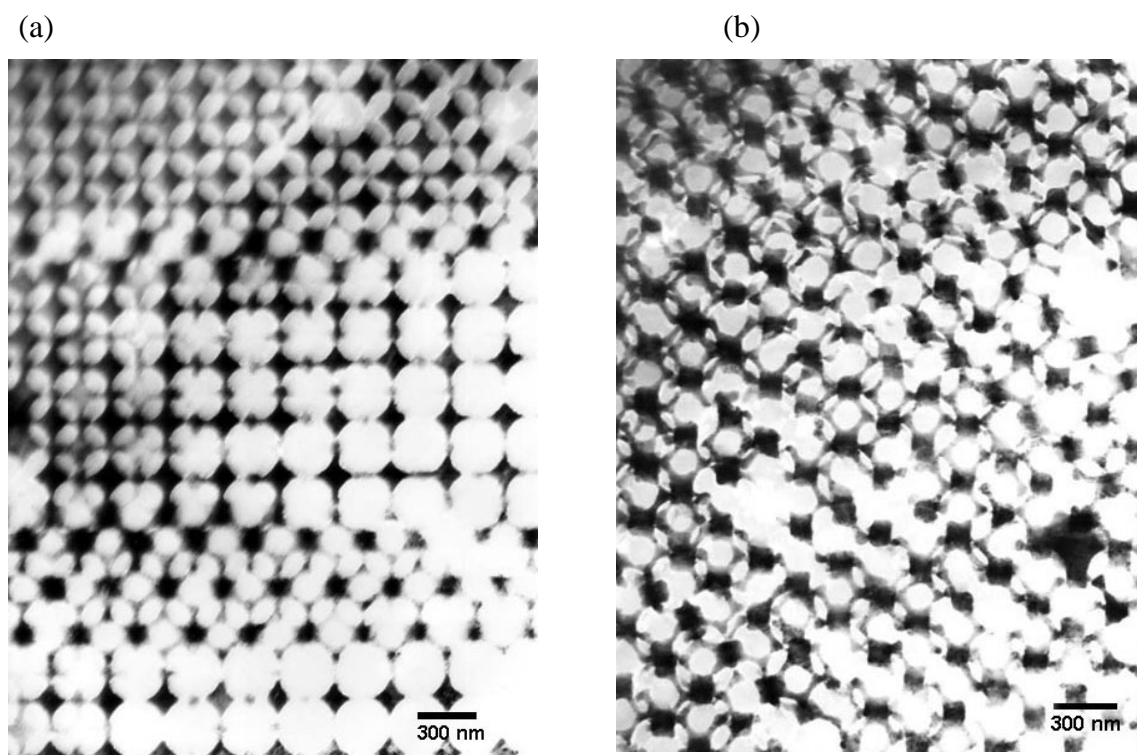


Figure 3. TEM images of (a) silica colloids with Ni infiltration, (b) macroporous Ni mesh.

Ni mesh in open air. Semiquantitative analysis with EDX shows a stoichiometry of approximately 1:1 (Ni:O) for the NiO mesh. After annealing, the mesh could not be attracted by a strong magnet, which indicated that the Ni was well oxidized. Figure 4 shows the SEM image of NiO mesh (10,000× magnification).

Using the NiO mesh as a template, well-defined metal-sphere arrays were obtained. Figure 5 shows cross-sectional SEM images of the gold spheres that were electrochemically deposited within the NiO mesh. EDX analysis reveals the presence of only Au in the sphere arrays after complete dissolution of the NiO template by acid. The extended three-dimensional sphere network can be seen in Figure 5a. The spheres can be seen linked to each other by narrow interconnects. Cross-sections for SEM studies were prepared simply by physically separating segments with small tweezers, the clumps and large hollows seen in Figure 5a therefore likely result from this process. Figure 5b shows a higher-magnification image of Au sphere arrays in the (111) orientation.

Interestingly, the gold spheres are slightly smaller in diameter (*ca.* 270 nm) relative to those of the starting opal membrane (290 nm). This likely relates to volume changes that occur on oxidation of the Ni mesh to NiO. If one assumes that the overall dimensions of the mesh piece do not vary with oxidation and that the volume changes that do occur only go to reduce the internal void volume of the mesh, then one can estimate the expected change in the internal void space by considering the formula weights and densities of Ni and NiO. Based on these values, the fraction of space occupied by the Ni mesh (~ 0.26) would be expected to increase to *ca.* 0.44 for the NiO mesh. This would correspond to a reduction in the diameter from that of the opal spheres to approximately 260 nm, similar to what is observed. Further studies on the nickel mesh arrays are needed to better understand the effect of oxidation on the void volume of these materials.

We are currently working on the application of these techniques to a variety of other materials. It will be straightforward to apply the electrodeposition methods to other metals. More challenging, however, will be the use of this approach for the formation of binary and ternary compounds with desired crystal structure and precise composition.

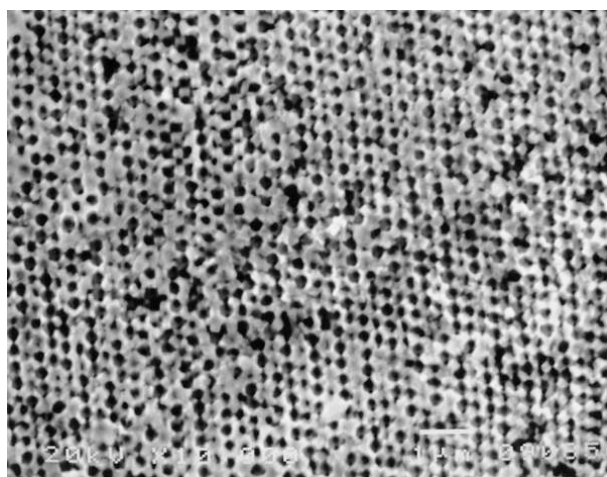
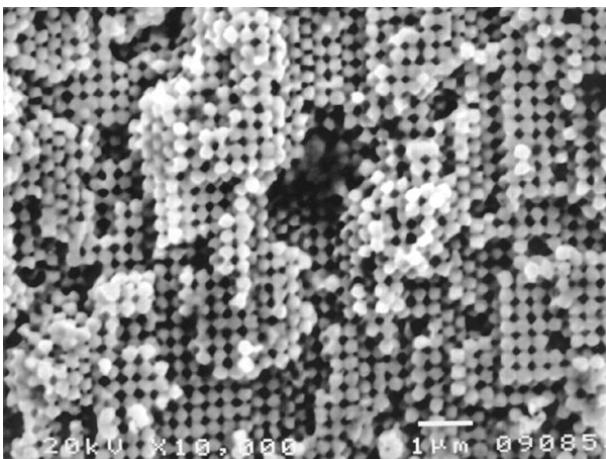


Figure 4. SEM image of porous NiO mesh.

(a)



(b)

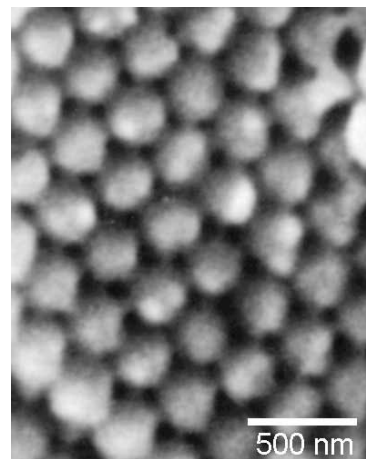


Figure 5. SEM images of (a) nanoscale Au sphere arrays at 10,000 \times magnification, (b) Au sphere arrays along (111) direction.

CONCLUSIONS

Electrochemical methods offer an effective route for the preparation of both metal mesh and metal sphere arrays. It is expected that this approach, possibly in combination with other techniques like melt infiltration, will allow access to new materials with technologically important properties.

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