

## Two-Step Template Synthesis of Metallic Colloidal Crystals

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### INTRODUCTION

Two-step template synthesis has been previously applied to prepare one-dimensionally ordered nanohole arrays [1]. Recently, this approach was extended to fabricate three-dimensional nanoscale structures [2-11]. By the use of opal (colloidal crystal with ordered silica or latex spheres) as a template, inverse opal can be fabricated by established methods [12]. Then the inverse opal can be further used as a mold to synthesis diverse colloidal crystals and nanocomposites, such as silica [2,3], metal oxide [4-6], and metallic colloidal crystals [7,8] and carbon/metal [7a], carbon/semiconductor [7a], carbon/polyaniline [9], and ferromagnetic/ferroelectric composites [10]. These new types of materials, which are hard to produce by other techniques, have potential applications in a variety of areas, including photonics [13], gas sensing [5], and magnetics [8]. A number of methods like sol-gel hydrolysis [3-6], electrochemical deposition [7-9] and melt infiltration [7a] have been employed to fabricate colloidal crystals and nanocomposites. Electrodeposition offers an effective method for producing metallic colloidal crystals, due to the nearly complete filling of the channels of porous templates and easy control of the extent of metal growth. In this paper, we describe the two-step template synthesis of metallic colloidal crystals. First, poly(methyl methacrylate) (PMMA) mesh was prepared from an opal template. Then, using the non-conducting PMMA mesh as a mold, highly ordered metal spheres were readily obtained by electrochemical deposition.

### EXPERIMENTAL

Commercial Ni (Nickel Sulfamate RTU) and Pd (Pallaspeed VHS) plating solutions were obtained from Technic, Inc. The prepared Co plating solution contained 200 g/liter  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , 6 g/liter NaCl, and 40 g/liter  $\text{H}_3\text{BO}_3$  (pH ~ 3.5). Synthetic opals consisting of three-dimensionally ordered silica spheres (290 nm or 180 nm diameter) were prepared by the methods described previously [14]. A piece of silica opal (typically  $7 \times 10 \times 1.5$  mm) was immersed in methyl methacrylate (MMA) monomer with 1 wt.% benzoyl peroxide as an initiator. Polymerization was performed at 40°C for 10 hrs, then 60°C for 12 hrs. Excess poly(methyl methacrylate) (PMMA) was removed by wiping the exposed opal surface clean with dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). A Au film (ca. 1  $\mu\text{m}$  thick) was sputtered onto one side of the PMMA/opal, a Cu wire was attached to the Au film with Ag paste (Ted Pella, Inc.), and the Au/wire side of the electrode, as well as the edges, were covered with insulating glue (3M). Silica opal spheres were removed with a 10 wt.% HF solution (12 h) to obtain a freestanding PMMA mesh (inverse opal). The mesh was kept in water before use as working electrode in electrodeposition. The PMMA mesh was filled with metals by galvanostatic electrodeposition using a Pt wire counter electrode and an EG&G Model 263A Potentiostat/ Galvanostat. The

current density is  $0.8 \text{ mA/cm}^2$  for Ni or Co deposition and  $0.6 \text{ mA/cm}^2$  for Pd deposition; the plating times were all 48 hrs. After electrodeposition, freestanding metal sphere arrays were obtained by etching away the PMMA template with warm  $\text{CH}_2\text{Cl}_2$ . The thickness of a typical metal colloidal crystal was about  $60 \mu\text{m}$ . Sonication was carried out in distilled water in a 75 W ultrasonic bath (Branson 1510) to break the metallic colloidal crystal into smaller pieces.

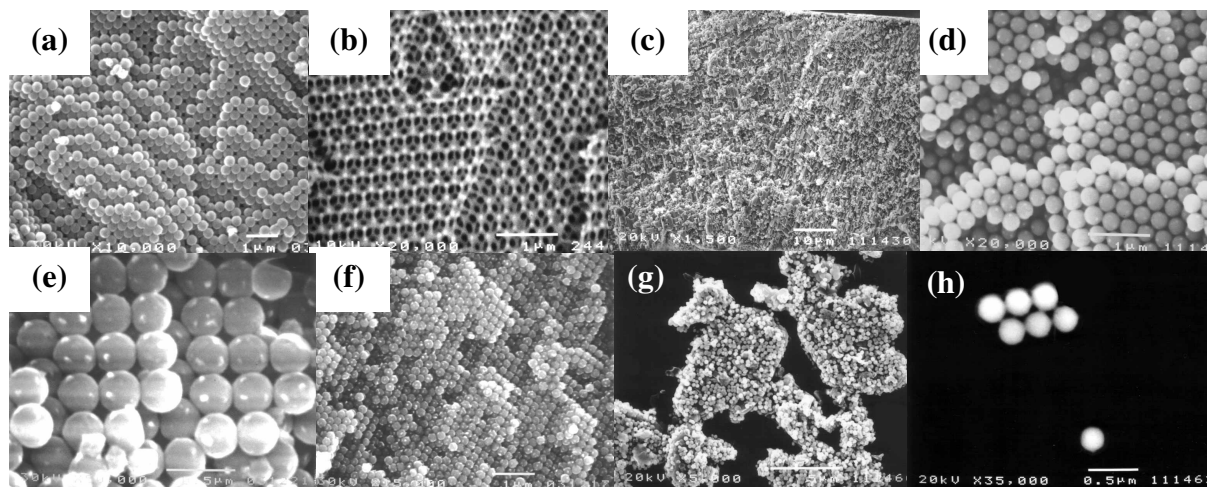
## RESULTS AND DISCUSSION

Figure 1a shows a cross-sectional image of a piece of opal containing 290 nm diameter silica spheres. The SEM image in Figure 1b reveals the uniform porous structure of the PMMA mesh, which contains 290 nm diameter pores. Since the macropores in PMMA mesh are interconnected, the PMMA mesh allows the electroplating solutions to diffuse through the mesh and reach the Au electrode, so that electrochemical growth of the metal spheres can take place, starting from the Au electrode. Because of the hydrophobicity of the PMMA surface, the PMMA mesh had to be kept wet after removal of the silica opal spheres by HF solution, otherwise the aqueous plating solutions could not effectively diffuse into the mesh. Also, the wet PMMA mesh maintains its porous structure, with pore diameters similar to that of the original silica spheres. Figure 1c shows a cross-sectional view of Pd spheres between the Au electrode and the sample surface. The filling is quite complete, and the periodicity extends over the entire area, except when interrupted by defects present largely as stacking faults in the original opal. Figure 1d shows the Pd spheres at larger magnification, and Figure 1e shows Ni spheres made by this type of process. The location of broken nanoscale interconnects (to spheres removed from the sample) can be clearly seen in the Fig. 1d and 1e, as white spots on the sphere surfaces. Based on Figure 1e, the diameter of as-prepared metal spheres is estimated to be  $290 \pm 10 \text{ nm}$ , very close to that of original silica spheres, indicating that electrodeposition produces high-density infiltration through volume templating. On the contrary, a sol-gel process either forms hollow colloidal crystals through surface templating or experiences significant reduction of sphere diameter [3-6]. Opal with 180 nm diameter silica spheres was also used to fabricate metallic colloidal crystals (Figure 1f). Since these metallic colloidal crystals have structures with three-dimensional periodicity on a length scale comparable to that of light, they are metallic photonic crystals [15]. These materials strongly diffract white light and exhibit iridescent colors.

Ultrasonication has been used to disintegrate the colloidal crystals into small arrays of spheres, and even single spheres [4a,16]. Due to the strong interconnection between adjacent metal spheres, it is more difficult to fragment the metallic colloidal crystals than to fragment ceramic colloidal crystals. After 2-hour sonication in a 75 W ultrasonic bath, the metallic colloidal crystal was broken into about 1 mm size pieces of colloidal crystals. Some smaller pieces, several microns in size, (Figure 1g) were detached from the larger pieces and dispersed in water. Continued ultrasonication of the smaller pieces resulted in even smaller sphere arrays, and isolated spheres. Figure 1h shows a segment consisting of six spheres and a single sphere. The six spheres are still connected to each other through the small interconnects.

## ACKNOWLEDGMENTS

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**Figure 1.** SEM images of (a) opal comprising 290 nm diameter silica spheres, (b) PMMA mesh containing 290 nm diameter pores, (c) 290 nm diameter Pd spheres between the Au electrode and the sample surface, (d) 290 nm Pd spheres, (e) 290 nm Ni spheres, and (f) 180 nm Ni spheres. SEM images of (g) small pieces of ordered Pd spheres after 2-hour ultrasonication, (h) an array of six spheres and an isolated Pd sphere after longer ultrasonication.

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