A combined electrochemical route to fabricate large-area and free-standing inverse opaline film

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A B S T R A C T

A combined electrochemical route involving electrophoresis and electrodeposition is developed to fabricate a large-area unsupported nickel inverse opaline film with thickness less than 10 μm. A vertical electrophoresis allows for the packing of 495 nm polystyrene microspheres on an ITO-coated glass to form a colloidal crystal with significantly reduced defects. Subsequently, a nickel electrodeposition is employed to fill the interstitial voids among the close-packed polystyrene microspheres, followed by the removal of the colloidal template in a two-stage process, leaving a robust nickel skeleton with hexagonally arranged pores and interconnected pore channels. This nickel skeleton is then detached from the ITO-coated glass via a liquid nitrogen treatment, rendering a free-standing nickel inverse opaline film in 2×2 cm^2. Porometer measurements indicate a narrow pore size distribution consistent with images from scanning electron microscope. We determine that the intensity ratio of (111)/(100) diffraction peak is an indicator for the strength of the Ni inverse opals, and thus affects its structural integrity upon detachment from the ITO-coated glass.

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1. Introduction

Fabrication of inverse opals has been of particular interests to researchers in various fields due to their unique periodic nanostructures [1,2]. The inverse opals are also known as three-dimensionally ordered macroporous materials (3DOM) which contain hexagonally arranged sub-micrometer pores with interconnected pore channels. Conventional fabrication schemes for the inverse opals involve the packing of polystyrene (PS) microspheres via sedimentation or solvent evaporation to form a colloidal template, followed by chemical or electrochemical deposition of desirable materials into the interstitial voids among the PS microspheres [3–5]. Afterward, the colloidal template is selectively removed via chemical or physical means, leading to the formation of periodic porous structure that reveals a large surface area for reaction and interconnected pores for facile mass transfer. In general, the diameter for the microspheres is deliberately selected to produce 3DOM with tailored-made pore size. To date, applications including sensors, catalysis and electrocatalysis have been explored with designed 3DOM structures [2,6]. Materials such as metals (Ni, Pt, Cu, Au, Ag, Pd) and compounds (SiO$_2$, TiO$_2$, CdS, ZnO, CeO$_2$) have been prepared in inverse opals [7–16]. A comprehensive review on the morphology control for the inverse opals is provided by Stein et al. [1].

In the literature, the inverse opals were fabricated in both planar and cylindrical forms [17–19]. However, for both cases, a substrate is always necessary to support the inverse opals due to its finite thickness. Earlier, Huang et al. reported a complicated method to produce free-standing Au inverse opals with thickness less than 1 μm [20]. However, a simpler scheme to fabricate large-area and free-standing inverse opals with thicker film has not been reported yet. This severely circumvents possible new applications in membranes and filters. Previously, we demonstrated that a vertical electrophoresis method enabled the construction of SiO$_2$-based colloidal crystals on a Si wafer with negligible defects and impressive surface uniformity, and the colloidal crystals can be used as a template for inverse opals with controlled thickness [9,21]. Because the PS microspheres carry more surface charges than that of SiO$_2$, a more stable suspension of PS microspheres allows for better control in the electrophoresis process. In this work, we demonstrate a combined electrochemical route involving both the electrophoresis of PS microspheres and Ni electrodeposition to fabricate large-area (2×2 cm^2) inverse opals on an ITO-coated glass substrate. We further show that the inverse opals can be detached from the ITO substrate via a simple freezing step, rendering a free-standing Ni inverse opaline film with impressive mechanical strength and flexibility.

2. Experimental

The PS microspheres were synthesized via an emulsifier-free emulsion polymerization process. First, appropriate amounts of styrene (after removing inhibitors) and K$_2$S$_2$O$_8$ were used as the monomer and initiator, respectively. The polymerization was carried out at 70 °C and the average size of the PS microspheres was 495 ± 24 nm. The assembly
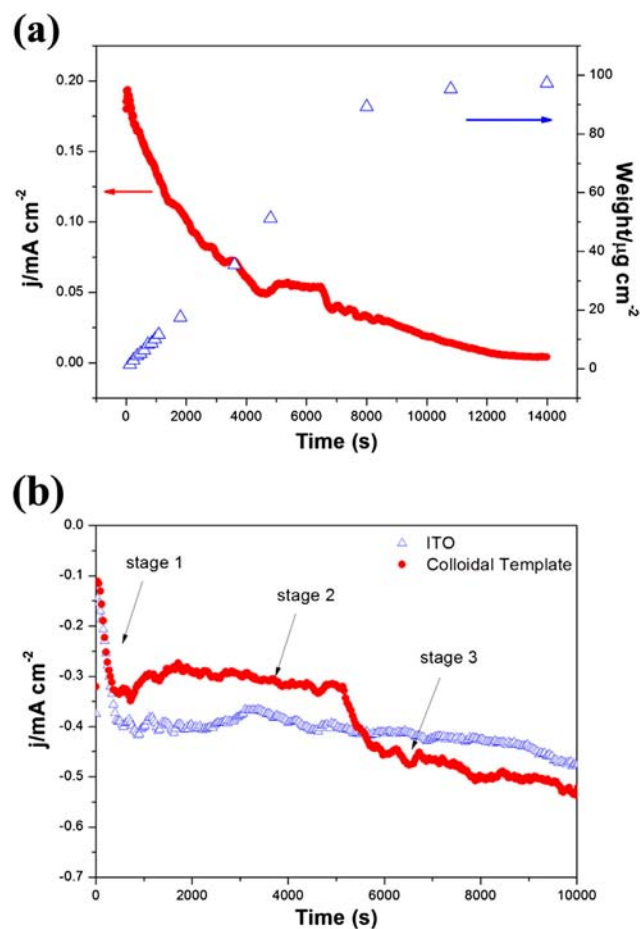
of PS microspheres was conducted via a vertical electrophoresis process at 25 °C. The PS microspheres (1 g) were dispersed in an anhydrous ethanol (100 ml) with pH value adjusted to 9. The electrophoresis was performed at 12 V cm^{-1} for 15 min using ITO-coated glass (4 cm^2) and stainless steel plate (25 cm^2) as the working and counter electrode, respectively. Next, the PS colloidal crystals were removed and dried in air for 60 min. To fabricate Ni inverse opals, a Ni plating bath consisting of NiSO$_4$•6H$_2$O (130 g L^{-1}), NiCl$_2$•6H$_2$O (30 g L^{-1}) and H$_3$BO$_3$ (18 g L^{-1}) was used. The PS colloidal crystals and Ni plate (25 cm^2) were employed as the working and counter electrode, respectively, and their distance was kept at 2 cm. The electroplating was conducted at 1 V for 80 min. The PS colloidal template was removed via a two-stage process: (1) immersed the sample in an ethyl acetate (95 wt%) solution for 1 h at 25 °C, and (2) subjected the sample to a heat treatment in 5% H$_2$-Ar at 330 °C for 2 h. To detach the Ni inverse opals from the ITO substrate, we put a tape atop the inverse opals and immersed it into liquid nitrogen for 30 s. A large difference in the thermal expansion coefficient caused the separation of Ni inverse opals from the ITO substrate underneath. Subsequently, the ethyl acetate was used to dissolve the tape, rendering a free-standing inverse opaline film in 2 × 2 cm^2. Our ITO-coated glass was purchased from UNI-Ward Corporation (UR-ITO007-0.7) with sheet resistance of 7 Ω/□. Its thickness was 0.7 mm.

Scanning electron microscope (SEM; Joel JSM-6700F) was used to observe the morphologies for the PS colloidal crystals and Ni inverse opals. X-ray diffraction patterns (XRD) were obtained using a Bruker D2 Phaser equipped with a Cu Kα radiation source (λ = 1.54 Å) to identify the crystallinity of the electroplated Ni. Electrophoresis and electroplating were conducted by a potentiostat (EG&G 263A). The pore size of the free-standing Ni inverse opals was determined by a capillary flow porometer (PMI-1200 AEX).

3. Results and discussion

The surface uniformity and crystallinity of the colloidal crystals are rather important in preparing a desirable large-area inverse opal structure. This is because even a minor thickness variation in the colloidal crystal leads to uneven Ni plating producing unwanted localized protrusion and voids. This would weaken the mechanical strength and thus compromise the structural integrity of the Ni inverses opals once both the colloidal template and substrate are removed. In our vertical electrophoresis cell, we have determined the optimized parameters (zeta potential, solvent, electrical field, time, etc.) to produce a colloidal crystal with significantly reduced crystallographic defects. Fig. 1a demonstrates the time evolution of electrophoretic current and deposited weight. The deposited weight exhibited a linear increase for 8000 s until it reached a plateau around 25 μg cm^{-2}. In contrast, the electrophoretic current revealed a fast decline for the first 4000 s, followed by a steady decrease as time progressed. These responses are consistent with the screening effect in which the arriving PS microspheres effectively reduces the magnitude of electric field that leads to slower electrophoretic action [22]. In our case, a deliberate control for a defect-less PS colloidal crystal can be achieved in the linear regime where the layer of colloids is directly proportional to the electrophoresis time.

Fig. 1b exhibits the time evolution of current density in the Ni electrodeposition on both colloidal template and ITO substrate. The current profile for the ITO substrate showed a rapid increase indicating a nucleation process was occurring [23,24]. After that, the current was somewhat flattened at 0.4 mA cm^{-2}. In contrast, for the colloidal template, stage 1 was the nucleation process as expected, whereas at stage 2, the current was somewhat subdued, followed by an increased current at stage 3. From SEM observation, we determined that at stage 2, the Ni was filling the interstitial voids so the colloidal template inhibited the Ni growth that engendered a lower current. Once the Ni plating was complete, at stage 3, the overplating atop the colloidal

Fig. 1. (a) Time evolution of current density and deposited weight during the electrophoretic deposition of PS microspheres. The PS microspheres (1 g) were dispersed in an anhydrous ethanol (100 ml) and the electrophoresis was performed at 12 V cm^{-1} for 15 min at pH 9. (b) Time evolution of current density for Ni electrodeposition on colloidal template and ITO substrate, respectively. The Ni plating bath contained NiSO$_4$•6H$_2$O (130 g L^{-1}), NiCl$_2$•6H$_2$O (30 g L^{-1}) and H$_3$BO$_3$ (18 g L^{-1}). The electroplating was conducted at 1 V for 80 min.

template led to a rougher surface as compared to that of ITO substrate. As a result, the plating current became larger. In our case, the plating of Ni was maintained within stage 2 so the plated Ni grew at a similar rate over the entire surface within the colloidal template. In this way, the buildup of residual stress was kept at minimum so the colloidal template was still intact.

According to Sapoletova et al., the formation of metal inverse opals in colloidal templates proceeds in the following stages [25]: (I) nucleation, (II) growth of metal, within the colloidal template, (III) overgrowth of metal atop the colloidal template and (IV) formation of continuous metal film. In some cases, there appeared current oscillations during a potentiostatic plating process in stage II, and this pattern was attributed to the crystallinity of colloidal template and uniform deposit growth. Both characteristics are greatly affected by the surface quality of the substrate. For example, current oscillations were observed on Au substrates but not on ITO substrates [25,26]. A possible cause for this discrepancy is that on ITO substrates, fewer nucleation sites are present so during electroplating there is localized variation in the deposit thickness. Consequently, any periodic oscillation in the plating current becomes unlikely. In contrast, on Au substrates, there are more active nucleation sites which allows for the deposit to grow in a conformal pattern, resulting in current variations reflecting the contour of the close-packed microspheres. Analysis of atomic force microscopy on our ITO substrates indicated an average roughness (Ra) of 2.22 nm and a root mean square roughness (Rq) of 2.81 nm. Therefore, during