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Free-standing Au inverse opals for enhanced glucose sensing

Chen-Hong Liao [a], Yu-Chi Hsieh [b], Bo-Han Huang [a], Chia-Hao Pai [a], Pu-Wei Wu [a], *

[a] *Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan, ROC*
[b] *Tantti Inc., Tao-Yuan 338, Taiwan, ROC*

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ABSTRACT

We successfully fabricate free-standing gold inverse opals (GIO) with a highly ordered porous structure, adjustable pore size, and large geometric size (2.5×2.5 cm^2). The process involves a vertical electrophoresis to assemble polystyrene (PS) microspheres in a closed-packed form, followed by backfilling of Ni and Au into the interstitial voids among the PS microspheres. Subsequently, the PS microspheres and Ni are removed to render free-standing GIO samples with pore size of 300, 405, and 600 nm, respectively. The free-standing GIO structures reveal a hexagonally-arranged pores with impressive mechanical strength and flexibility. Diffraction patterns from the X-ray diffractometer indicate a strong preferred orientation in the (111) plane. Cyclic voltammetric scans show excessive electrochemical surface area for the GIO samples as compared to that of planar Au in identical footprint. In glucose oxidation, the GIO structures demonstrate apparent current densities that are ten times larger over planar Au. Among the GIO structures, the sample with 300 nm pore size demonstrates the highest specific activity and the largest I_a/I_c value. We believe that the relatively smaller 300 nm pores facilitate the confinement of byproduct intermediates, and thus results in more effective oxidation of glucose.

1. Introduction

The construction of colloidal crystals and their inverse opals have attracted considerable attention for many years because these self-assembly based nanostructures demonstrate unique advantages that render them suitable for a variety of applications [1–3]. The colloidal crystals are assembly of microspheres in a close-packed order, and thus exhibit a theoretic packing density of 74%. In contrast, the inverse opals represent the inverse replica of colloidal crystals, resulting in a theoretic packing density of 26% with pores in a honeycomb array. In the literatures, the inverse opals are also known as three-dimensionally ordered macroporous materials (3DOM) which contain hexagonally arranged submicrometer pores with interconnected pore channels [4–6]. Conventional fabrication methods for the inverse opals start with the packing of polystyrene (PS) or SiO_2 microspheres via sedimentation or solvent evaporation to produce a colloidal template, followed by filling of selective materials into the interstitial voids among the close-packed microspheres. Subsequently, the colloidal template is deliberately removed via chemical or physical routes, resulting in a porous skeleton consisting of large pores (left by the microspheres) and pore channels connecting neighboring pores. This unique porous structure enables a large internal surface area for fast reaction and interconnected channels for rapid mass transfer. In general, the diameter for the microspheres can be designed to produce inverse opals with tailored-made pore size for targeted applications. So far, applications including sensors, catalysis, and lithography have been explored with various 3DOM structures [7–10]. Materials such as metals (Ni, Pt, Cu, Au, Ag) and compounds (SiO_2, TiO_2, CdS, ZnO, CeO_2) have been prepared in inverse opals [4,5,8,11–19].

The inverse opals are often produced in both planar and cylindrical forms with a finite thickness of less than 30 μm [10,20,21]. Therefore, a substrate is always necessary for mechanical support. This requirement of substrate hampers many possible applications where free-standing inverse opals become desirable. In addition, a free-standing sample allows for the transfer of inverse opals to different substrates, and thus opens up new processing windows and applications. It is understood that the critical step for fabricating a free-standing inverse opals is the substrate removal process in which the integrity of the entire inverse opaline film needs to be maintained. This is especially challenging once the size for the inverse opals becomes significant. Another hurdle is this field is the formation of inverse opals in practical sizes for industrial purposes.

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* Corresponding author.
E-mail address: ppwu@mail.nctu.edu.tw (P.-W. Wu).

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The successful fabrication of inverse opals in several cm^2 footprint requires high quality colloidal crystals in similar or even larger sizes. Unfortunately, conventional colloidal crystal formation routes are rather limited in producing uniform and defectless samples in such sizes. Earlier, we demonstrated a vertical electrophoresis process that is capable of producing large-area colloidal crystals with significantly reduced crystallographic defects and superb surface uniformity [20]. Our ability to prepare high quality colloidal template with tangible sizes enables us to explore further for large area inverse opals without substrate support. Our efforts have successfully produced free-standing Ni inverse opaline film in 2×2 cm^2 via a combined electrochemical route and liquid nitrogen immersion approach [22].

In this work, we demonstrate our recent progress in fabricating a series of large area (2.5×2.5 cm^2) free-standing Au inverse opals (GIO) with different pore sizes and thickness. Extensive material characterization is performed and electrochemical analysis is carried out for the effect of GIO pore size toward glucose oxidation.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of polystyrene microspheres

We used an emulsification method to fabricate mono-sized PS microspheres. First, a 40 mL styrene monomer solution (99.6 wt%) was added into a 300 mL sodium bicarbonate (12 mM) and sodium styrene sulfonic acid solution. The mixture was stirred at 350 rpm for 1 h, while its temperature was kept at 65 °C. Then, potassium sulfate (0.25 g) was added into the mixture to initiate the polymerization reaction. After 16 h, all the styrene monomers were completely consumed. In this study, we synthesized mono-sized PS microspheres with diameter of 300, 405 and 600 nm, by controlling the concentration of sodium styrene sulfonic acid solution at 0.8, 0.48, and 0.13 mM, respectively.

2.1.2. Formation of colloidal crystal templates

The mono-sized PS microsphere suspension with concentration of 0.01 g mL^{-1} was prepared by suspending the PS microspheres in anhydrous ethanol, and its pH was adjusted to 9 using NH_4OH. Next, we applied a vertical electrophoresis process at 10 V cm^{-1} to deposit the PS microspheres on a 2.5×2.5 cm^2 indium tin oxide (ITO) coated glass substrate. The ITO-coated glass was purchased from UNI-Ward Corporation (UR-ITO007–0.7) with a sheet resistance of 7 Ω/□. Its thickness was 0.7 mm. The electrophoresis lasted for 10–15 min. At this stage, a three-dimensionally ordered colloidal crystal, with thickness above 12 μm was formed. In total, we assembled three kinds of colloidal crystals using mono-sized PS microspheres with diameter of 300, 405, and 600 nm, respectively.

2.1.3. Fabrication of GIO structure

The colloidal crystal was used as the template so Ni and Au were electrodeposited sequentially to backfill the interstitial voids among the close-packed PS microspheres. First, a thin Ni layer was plated at the bottom of the colloidal crystal template as a sacrificial layer. The Ni plating entailed a galvanostatic current of 2.5 mA cm^{-2} for 5–10 min, with the colloidal crystal template used as the working electrode and a 4×4 cm^2 Ni foil employed as the counter electrode in Watt's bath electrolyte. Next, a cyanide-free Au aqueous electroplating solution containing 0.05 M $HAuCl_4$, 0.42 M Na_2SO_3, 0.42 M $Na_2S_2O_3$, and 0.3 M Na_2HPO_4 was prepared. The Au layer was deposited on top of the sacrificial Ni layer by applying a fixed voltage at 0.8 V for 90 min, with a Pt foil (4×4 cm^2) used as the counter electrode. Subsequently, the sample was immersed in ethyl acetate for 24 h at 25 °C to dissolve away the PS microspheres, so a Ni–Au inverse opal film is formed. Finally, the Ni–Au inverse opal film was immersed in HNO_3 solution (0.1 M) at 25 °C to dissolve the Ni, thereby forming a free-standing GIO structure. In this study, three kinds of free-standing GIO samples were prepared, using the colloidal crystal templates composed of PS microspheres with diameter of 300, 405, and 600 nm, and they were designated as GIO-300, GIOT-405, and GIO-600, respectively. The processes involved in the GIO samples fabrication are illustrated in Fig. 1.

2.2. Characterization

2.2.1. Structural and compositional analysis

Scanning electron microscopy (SEM) analyses were carried out on a JEOL LSM-6700 microscope to observe the assembly of PS microspheres and the structure of GIO. Determination of relevant phase and grain size was achieved through X-ray diffraction (XRD) measurements using a X-ray diffractometer with a Cu Kα radiation ($\lambda = 1.54$ Å), and the diffractograms were collected with a scan rate of 0.04° s^{-1} and a 2θ range of 30 to 80°. X-ray photoelectron spectroscopy (XPS: Thermo Microlab 350) was adopted to evaluate the C 1s signal from glucose oxidation.

2.2.2. Electrochemical measurements

Electrochemical experiments were performed at 25 °C in a three-electrode configuration using a Princeton Applied Research STAT4 instrument. A Pt foil (10 cm^2) and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrochemical oxidation of glucose was evaluated in an Ar-saturated 0.05 M glucose and 0.1 M NaOH aqueous solution by cyclic voltammetry (CV) scanned at 50 mV s^{-1} between −0.8 and 0.6 V. The electrochemical surface area (ECSA) of GIOs was determined from the CV curves obtained in an Ar-saturated 0.5 M H_2SO_4 aqueous solution at 50 mV s^{-1} between 0.2 and 1.5 V. For comparison purpose, a solid Au foil was used as a benchmark for ECSA and glucose oxidation measurements.

3. Results and discussion

Fig. 2 exhibits the colloidal crystal templates with PS microspheres of different diameters. The SEM top views are provided in Fig. 2a,b,c, which confirm that the sizes for the as-synthesized PS microspheres were properly controlled within a 3% deviation. This reduced size discrepancy allows us to assemble the PS microspheres with better crystallinity and surface uniformity. Apparently, the assembled PS microspheres revealed a hexagonal pattern without presence of undesirable vacancies and islands. Fig. 2d,e,f exhibit the colloidal crystals templates in cross-sectional views. The thickness for the colloidal crystal template with PS microsphere diameter of 300, 405 and 600 nm can be measured at 14.2, 15.2 and 13 μm, respectively. These cross-sectional images also indicate that the PS microspheres were assembled in an orderly closed-packed face-centered cubic (FCC) arrangement.

The GIO samples were obtained by electroplating a thin Ni at the bottom of the colloidal crystal template (thickness of 1–2 inverse opaline layer), followed by the deposition of Au. After removing the colloidal crystal template by ethyl acetate, the Ni layer was etched so a free-standing GIO was produced. Fig. 3 shows the SEM images for GIO-300, GIO-405, and GIO-600, respectively. Their cross-sectional images (Fig. 3a,b,c) exhibit thickness of 9.3, 9, and 8.5 μm, which correspond to 35, 30, and 19 inverse opaline layers, respectively. It is important that the thickness for the Au layer must be thinner than the thickness of colloid crystal template. Otherwise, the Au would fill up the interstitial voids entirely and form a solid continuous film atop the colloidal crystal template. The high magnification cross-sectional images (insets of Fig. 3a,b,c) confirm