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Citation	Vasquez, Yolanda, Mathias Kolle, Lidiya Mishchenko, Benjamin D. Hatton, and Joanna Aizenberg. 2014. Three-Phase Co-Assembly: In Situ Incorporation of Nanoparticles into Tunable, Highly Ordered, Porous Silica Films. ACS Photonics 1, no. 1: 53-60. doi:10.1021/ph400067z.
Published Version	doi:10.1021/ph400067z
Citable link	http://nrs.harvard.edu/urn-3:HUL.InstRepos:33204051
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Three-Phase Co-Assembly: *In-situ* Incorporation of Nanoparticles into Tunable, Highly-Ordered, Porous Silica Films**

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Supporting Information Placeholder

ABSTRACT: We present a reproducible, one-pot colloidal co-assembly approach that results in large-scale, highly-ordered porous silica films with embedded, uniformly-distributed, accessible gold nanoparticles. The unique coloration of these inverse opal films combines iridescence with plasmonic effects. The coupled optical properties are easily tunable either by changing the concentration of added nanoparticles to the solution before assembly or by localized growth of the embedded Au nanoparticles upon exposure to tetrachloroauric acid solution, after colloidal template removal. The presence of the selectively absorbing particles furthermore enhances the hue and saturation of the inverse opals color by suppressing incoherent diffuse scattering. The composition and optical properties of these films are demonstrated to be locally tunable using selective functionalization of the doped opals.

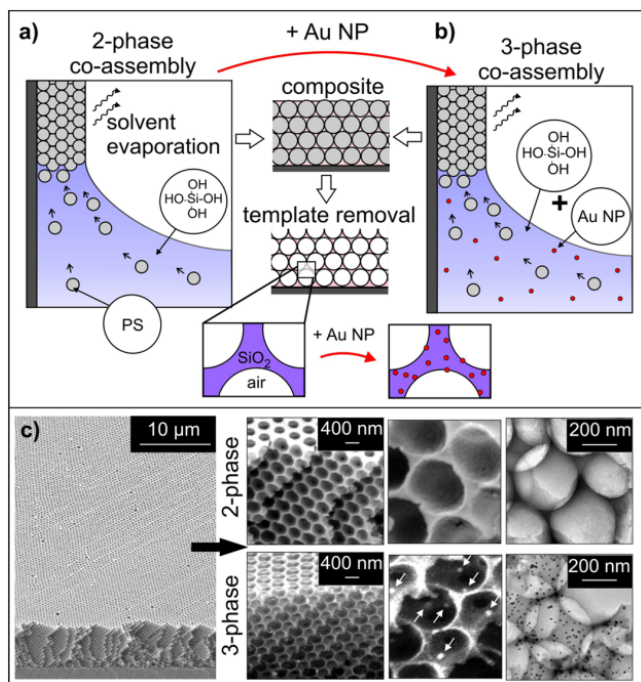
INTRODUCTION

Self-assembly of multi-functional 3D nanoporous structures is gaining considerable interest as a cost-effective alternative to conventional top-down fabrication processes. In particular, the interconnected periodic array of pores in the inverse opal structure, synthesized from a sacrificial colloidal crystal template, has made it a viable bottom-up materials candidate for applications in photonics,¹⁻⁴ tissue engineering,⁵ sensing,^{6, 7} and catalysis.^{8, 9} However, in order to utilize these structures as functional materials, tuning the inverse opal composition is extremely important. The incorporation of metal nanoparticles into inverse opals has recently attracted particular attention in the literature.^{8, 10-21} The high surface area and photonic properties of inverse opals coupled with the plasmonic^{22, 23} or catalytic²⁴ properties of metal nanoparticles greatly expand the possible applications of

these materials as catalysts,⁸ sensors,^{14, 15} photonic structures,¹⁵⁻¹⁸ and in Surface-Enhanced Raman Spectroscopy (SERS).²⁰

In most prior investigations, however, inverse opal structures were fabricated by multi-step processes involving assembly of colloidal crystals as sacrificial templates, then infiltrating the structure with a matrix material, such as an appropriate hydrolyzable alkoxide sol-gel precursor, allowing gelation to take place, and, subsequently, removing the colloidal template by dissolution or thermal decomposition.²⁵⁻²⁷ This technique yields a range of porous inverse opal structures with various chemical compositions including SiO₂, TiO₂, and Al₂O₃.^{4, 28-30} Inverse opal matrix materials such as polymer precursors,^{31, 32} nanoparticles,^{33, 34} and vapor phase precursors³⁵⁻³⁹ have also been deposited by infiltration. These types of synthetic approaches, by their very nature, not only result in fragile, cracked films, but do not allow for precise control of metal nanoparticle content or distribution, yielding non-uniformity in both composition and ensuing properties, and therefore limit their technological potential.

We have recently demonstrated that multi-layered, nanocomposite colloidal crystal films can be generated via co-assembly of polymeric colloidal spheres together with a silica sol-gel precursor solution, thus avoiding the infiltration stage of the process and the associated cracking of the structures (Figure 1a).⁴⁰ Removal of the colloidal template (i.e. thermal decomposition) produces mechanically robust inverse opal films with minimal defects and large, centimeter-scale crystal domains. Herein, we develop a novel, three-phase co-assembly method by incorporating gold (Au) nanoparticles *in-situ* into assembling centimeter-scale inverse opal films, which allows us to manipulate and control their composition. Using this new one-pot three-phase co-assembly method, we are able to reproducibly create robust, high-



ly-ordered gold-loaded inverse opal films with uniform composition, unique optical properties, accessible functionality, and tunability for a wide range of applications.

Figure 1. Schematics of two-phase (a) and three-phase (b) co-assembly methods. Both methods involved evaporative deposition of colloidal particles (340 nm, PMMA) and a hydrolyzed silica sol-gel precursor (TEOS) onto a vertical substrate to create a composite thin film. The organic colloidal template was then removed via calcination to create an inverse opal structure. In three-phase co-assembly, gold nanoparticles assemble along with the colloids and TEOS to result in an inverse opal structure with embedded nanoparticles in the walls ("gold-loaded" opals). (c) SEM and TEM images show the large-scale, ordered, crack-free thin films that result from two- and three-phase co-assembly. SEM and TEM images of gold-loaded inverse opals (bottom) show that three-phase co-assembly leads to films with uniformly distributed nanoparticles in the walls. White arrows point to the brighter contrast gold nanoparticles in the SEM image. The gold nanoparticles in the TEM image appear as dark spots.

RESULTS AND DISCUSSION

To prepare Au-containing inverse opal films, first, gold nanoparticles having a diameter of 10-15 nm were synthesized,^{41, 42} isolated by centrifugation (from 15 mL of original solution), and added to an aqueous mixture containing 340 nm poly-methyl methacrylate (PMMA) colloids and a hydrolyzed silica sol-gel precursor, tetraethyl orthosilicate (TEOS) (Figure 1b). Then a glass substrate was vertically suspended in a vial containing this mixture, and a thin colloidal film was allowed to evaporatively deposit on the substrate. The resulting composite film was then calcined to remove the sacrificial PMMA template, producing a large-scale, crack-free inverse opal structure with embedded gold nanoparticles.

This one-pot synthesis of inverse opals offers a highly uniform distribution of gold nanoparticles inside the porous opal structure (Figure 1c). Note that with the use of moderate nanoparticle concentrations during

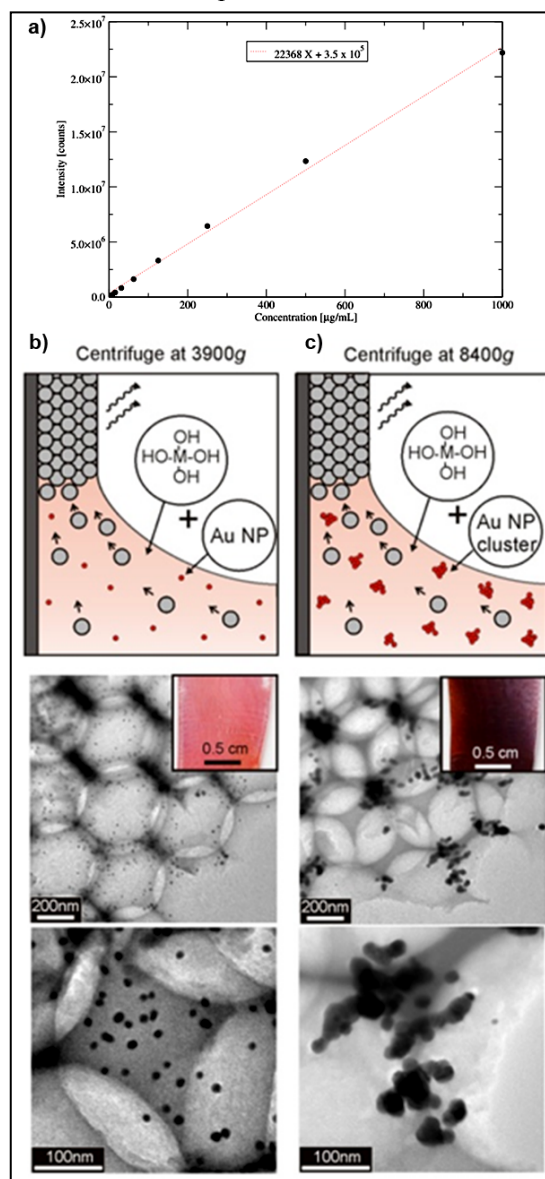


Figure 2. a) Calibration curve of Au standard generated using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Based on the standard curve and digested Au nanoparticle samples used in the inverse opals, it was determined that the $[Au] = 630 \mu\text{g/mL}$. Taking the average size of the nanoparticles to be 10 nm, the concentration used to make most Au inverse opals was $\sim 1.2 \times 10^{14}$ Au NPs/mL. b) Schematic and TEM images of typical Au-loaded film evaporation with nanoparticles prepared via centrifugation of the as synthesized gold solution at 3900g to remove the solvent and isolate the Au NPs. The three-phase assembly results in structures with uniform Au NPs distribution. c) If the centrifugation is performed at 8400g, the Au NPs irreversibly cluster together (schematic) and subsequently assemble into only the larger voids of the inverse opal structure, coarsening during calcination (see TEM images below). Using a higher centrifugation speed for nanoparticle isolation results in a different gold concentration and degree of nanoparticle clustering as compared to lower centrifugation speeds, leading to altered optical properties in the films (see insets).

assembly (approximately 6.0×10^{14} Au NPs/mL, See Figure 2a), the embedded particles in the resulting films did not have physical contact with one another. Consequently, most of the nanoparticles did not coarsen during calcination (maintaining their diameter of 10-15 nm) and remained uniformly dispersed and tightly bound in the silica matrix as determined by TEM images. The uniformity of particle incorporation was also ensured by using negatively charge-stabilized gold nanoparticles in the assembling solution with similarly-charged species (colloids and silica), and low centrifugation speeds during nanoparticle isolation to prevent particle agglomeration⁴³⁻⁴⁴ (Figure 2b,c).

Importantly, the highly-ordered periodic silica structure of a co-assembled inverse opal, combined with the uniform distribution of gold nanoparticles in its walls, led to interesting optical properties that reflect optical signatures of both components. The periodic silica structure is itself a photonic crystal and has an angle-dependent Bragg reflection peak in the visible range (~ 700 nm at normal incidence), which lent an iridescent quality to the films. Gold nanoparticles of this size have plasmonic properties that led to selective absorption of light in the green-blue part of the spectrum (~ 520 nm), lending a reddish tint to the films at all incidence angles. Optical measurements confirmed that an Au-loaded inverse opal possesses a combination of an angle-tunable reflection band of the film with an angle-independent plasmonic absorbance peak as seen in Figure 3a. The gold absorbance peak can also be easily tuned in these films by changing the concentration of gold nanoparticles added to the colloidal solution *prior* to film co-assembly (Figure 3b), which leads to distinct differences in the color intensity depending on the amount of Au loaded.

Though the combination of a plasmonic peak and a Bragg reflection peak has been noted in other studies of inverse opal structures with metal nanoparticles,^{10-12, 15, 18, 20} the precise control over nanoparticle concentration and uniformity in distribution is difficult, if not impossi-

ble, with these previously demonstrated synthetic methods because they rely on homogeneous liquid infiltration into densely-packed colloidal crystals. However, with the three-phase co-assembly method, the uniformity in particle distribution can be easily maintained for a range of concentrations, as seen in the TEM images in Figure 3c. The versatility of our three-phase co-assembly methodology is further demonstrated by taking advantage of the chemical accessibility of the embedded Au NPs. We show that one can tune the optical properties of the inverse opal, not only *during*, but also *after* assembly by selectively growing the NPs in the walls of the structure. This alternative tunability route has been demonstrated in the following set of experiments. Inverse opals with and without embedded gold nanoparticles were immersed in gold growth solution, containing hydroxylamine and tetrachloroauric acid (HAuCl_4), and stirred until the color of the opal began to visibly change due to nanoparticle growth (Figure 4a-c). It has been shown previously⁴⁵ that although hydroxylamine can reduce Au^{3+} ions (from HAuCl_4) into bulk gold (Au), this reduction is dramatically accelerated if the solution is exposed to gold surfaces. We capitalized on this phenomenon and optimized the Au deposition conditions in our system, such that no new particle nucleation occurred in the growth solution, while almost all of the added Au contributed to the growth of existing nanoparticles within the opal.

Under optimized conditions, when all-silica and Au-loaded inverse opals were immersed in this selective growth solution, the all-silica structures (control) remained almost unchanged, with the exception of a few randomly nucleated nanoparticles, due to a lack of nucleating sites (Figure 4d). The gold-loaded opals, on the other hand, changed color due to nanoparticle growth (Figure 4a). As seen from the SEM and TEM images, the size of the nanoparticles in the inverse opal increased (Figures 4b and 4c). Thus, at the very least, the nanoparticles located at the surfaces of the inverse opal walls were accessible to the aqueous growth solution. It is

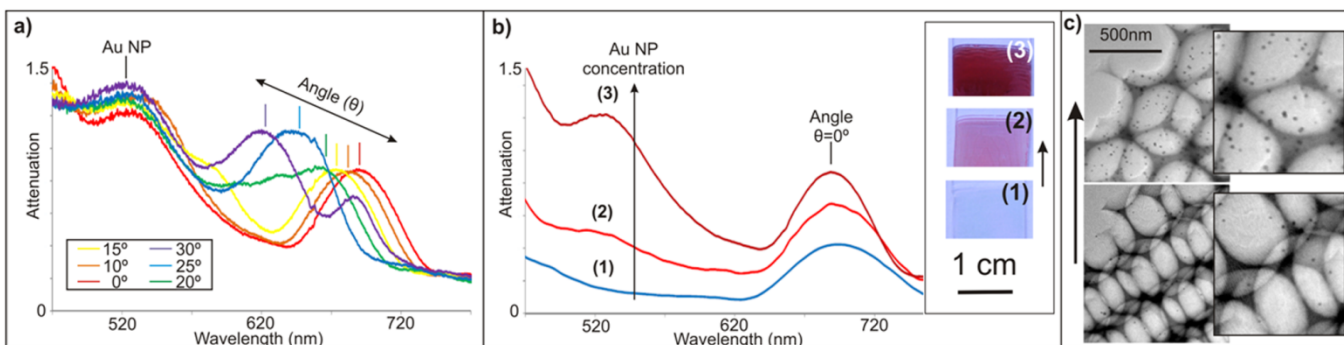


Figure 3. a) Gold-loaded inverse opals combine the angle-dependent Bragg peak of inverse opals (~ 700 nm at normal incidence) with the angle-independent absorption peak of gold nanoparticles (~ 520 nm). b) The gold absorbance peak can be tuned prior to opal assembly by adding higher amounts of gold nanoparticles to the colloidal solution. The optical images and plots correspond to three different concentrations of gold nanoparticles added to the colloidal suspension: 0 Au Np/mL (1), 1.2×10^{15} Au NPs/mL (2), and 7.2×10^{15} Au NPs/mL (3). c) TEM images correspond to inverse opals assembled with Au 6.0×10^{14} Np/mL (bottom) and 1.2×10^{15} Au NPs/mL (top).

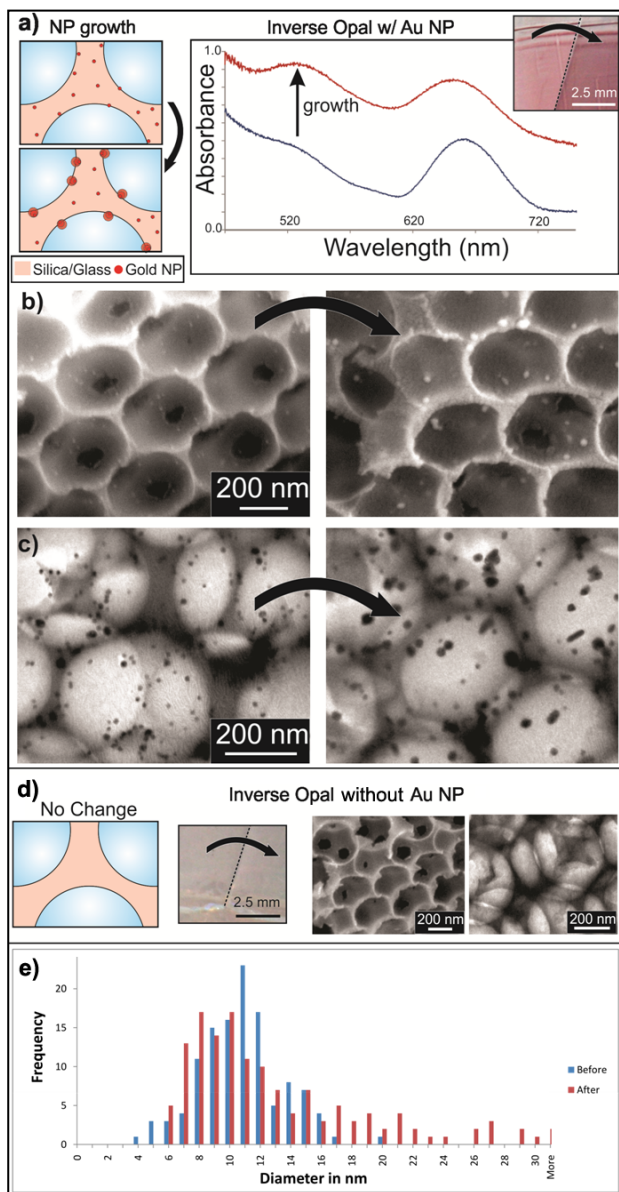


Figure 4. Inverse opals with embedded gold nanoparticles immersed in gold growth solution selectively increased the size of the pre-existing gold nanoparticles. a) Gold-loaded opals changed color (optical images) due to gold nanoparticle growth, as seen in the increase of the absorption peak in the optical spectrum, b) SEM images and c) TEM images of the inverse opals with gold nanoparticles before and after growth. d) Control inverse opal structure without Au NPs shows no growth of Au NPs before and after the film was exposed to the HAuCl_4 growth solution. The optical images (center) shows no change in optical properties and SEM (left) and TEM (right) images of inverse opals also confirm no growth of Au particles in the inverse opal. e) Diameters of Au NPs before and after exposure to the growth solution estimated using TEM images show a clear size increase and availability of embedded Au NPs.

important to note that the size effects of the larger particles may dominate the properties of these materials when the nanoparticles are not uniformly located on the surfaces and, therefore, inaccessible to growth solution. The size distribution of the particles changed, before and after re-growth, as determined by the analysis of TEM

images (Figure 4e). Using a simplified “steady state” diffusion model we have also performed the modeling of the post-assembly growth of the Au nanoparticles in the inverse opal matrix and compared it to the experimental distribution observed in Figure 4e.

Our model was based on four assumptions: (i) Prior to the growth experiment, Au particles of $d = (11 \pm 3)\text{nm}$ (mean \pm standard deviation, deduced from the histogram in Figure 4e) are distributed homogeneously in the solid phase of the inverse opal. (ii) The growth rate $R(x)$ depends on the distance x of each particle from the inverse opal void surface, due to diffusion of precursor into the interstitial volume. (iii) $\Delta A/A = R(x)$ for the overall growth of each individual particle depends on its initial surface A . This means, larger particles grow faster than smaller ones. (iv) The growth rate at the surface of the inverse opal voids is constant, i.e. $R(x = 0) = R_0$, due to an “unlimited” amount of available precursor. At a certain depth $x = x_0$, the growth rate vanishes, i.e. $R(x = x_0) = 0$, due to a complete depletion of precursor by the growing particles in a shell of thickness $x = 0$. This yields a linear relation of the growth rate R as a function of depth x , given by

$$R(x) = \begin{cases} R_0(1 - x/x_0), & x \leq x_0 \\ 0, & x > x_0 \end{cases}$$

With these assumptions, the relevant parameters in our model are the inverse opal surface reaction rate R_0 and the depth x_0 in the interstitial matrix, at which the precursor is depleted.

The experimentally determined particle size distribution (Figure 4e) is well approximated by the model with the parameterization, $R_0 = 5$ and $x_0 = 11$ nm. While the choice for R_0 is somewhat arbitrary, the value of x_0 allows for two possible interpretations of the observed particle distribution after re-growth: (1) the precursor only penetrates to a depth comparable to the average Au particle diameter before being depleted, and (2) only partially exposed particles grow. The deeper the center of the particle lies within the matrix, the smaller the area exposed and the smaller the growth rate. The theoretical formulation of this problem is identical to the linear dependency found in the steady state diffusion model since the exposed area of a particle scales linearly with the depth of the particle in the matrix.

For both cases, such modeling of the particle growth based on diffusion suggests that only surface-bound particles grow as implied by the experimental results (Figure 5). Analogous template-directed growth of crystal nanoparticles from solution has been demonstrated in other systems.⁴⁶⁻⁴⁸ Interestingly, the sol-gel derived silica walls in our system are predicted to have a porosity of $\sim 2\text{-}3\text{ nm}$ ⁴⁹⁻⁵⁰ which seems to be insufficient to allow the growth solution to access nanoparticles that are completely embedded within the inverse opal. The surface-bound growth of nanoparticles that can be controlled by the exposure of the inverse opal to the Au solution fol-

lowing the initial assembly provides a means of fine-tuning the size of the particles at the surface and the associated optical properties of the films.

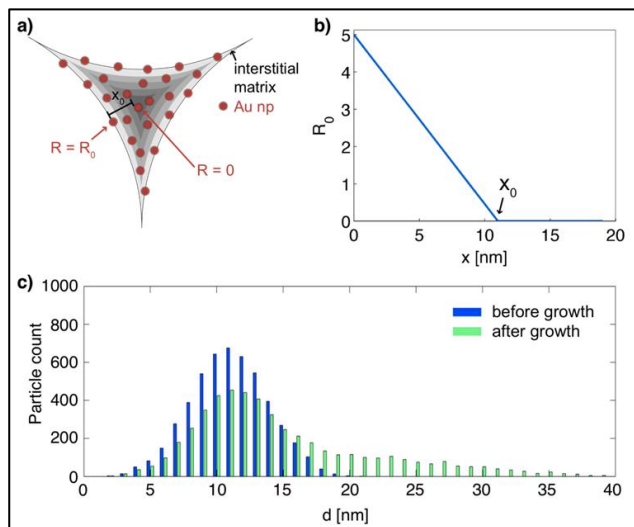


Figure 5. a) Schematic of the modeling volume with Au NPs homogeneously distributed in the inverse opal interstitial matrix. The growth rate is R_0 at the surface and 0 at a depth x_0 (gradient in gray scale in schematic). b) Growth rate as a function of depth in the interstitial volume for a steady state diffusion model. c) Calculated Au particle size distribution before (blue) and after (green) growth.

In addition to the spectral tuning achieved by tailoring the overall initial particle size during assembly, the surface-bound post-assembly growth can be exploited to modify the size-dependent spectrally selective absorption characteristics of the Au NPs at the surface only, providing further control in the engineering of the spectral composition of the inverse opal's reflection. Such surface-selective chemical accessibility of the nanoparticles significantly expands the functionality and possible applications of these large-scale inverse opals and opens a range of additional possibilities to tune the optical and catalytic properties of these films after synthesis.

Since growth of Au particles relies on the ability of the reactant solution to penetrate (i.e., wet) the inverse opal framework, we combined the aforementioned growth solution method with macro-scale chemical patterning to spatially control the wetting properties and color change in our films as another demonstration of this system's versatility. Due to the uniform, large-scale porosity and optical characteristics of co-assembled opals, we were able to use a selective functionalization technique⁷ to pattern the wettability of gold-loaded inverse opals on the macroscopic scale. The opal was first rendered hydrophobic by treating it with vapor of a fluorinated silane. Then, an "M"-shaped PDMS mask was used to cover the film, and the system was exposed to oxygen plasma to render the unprotected area of the film hydrophilic (Figure 6a). Finally, the chemically

patterned film was immersed in aqueous gold growth solution. Because the growth solution could only infiltrate the hydrophilic parts of the porous film (Figure 6b), a color change due to nanoparticle growth occurred only on the outside of the "M" pattern (Figure 6c). Thus, gold-loaded opals can be combined in a straightforward fashion with a selective functionalization technique to locally tune the composition and resulting properties of the inverse opal films.

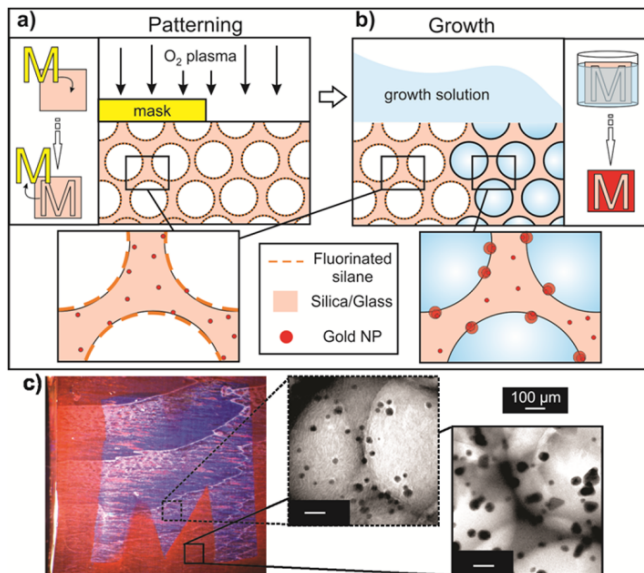


Figure 6. a) A selective functionalization technique^{3,4,23} was used to spatially pattern the wetting properties of a gold-loaded inverse opal. The opal was first rendered hydrophobic via exposure to vapor of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane (not shown). Part of the opal was masked with a PDMS shape ("M") and then exposed to oxygen plasma. The film remained hydrophobic in the masked region, and the rest of the film was rendered hydrophilic by oxygen plasma. b) The inverse opal with patterned wettability was then exposed to aqueous gold growth solution. The growth solution was only able to enter the hydrophilic parts of the opal, where the embedded gold nanoparticles grew in size. The hydrophobic parts of the opal remained unchanged. c) An optical image shows the patterned optical properties of an inverse opal after exposure to growth solution. TEM images (100 nm scale bars) verify that the optical contrast between the unexposed (center) and the exposed (right) regions is due to a localized growth of nanoparticles outside of the "M" shape.

CONCLUSIONS

In conclusion, we have shown that our three-phase co-assembly platform provides a versatile, one-pot approach to create highly-ordered functional inverse opal films with embedded, uniformly-distributed, accessible gold nanoparticles. The high surface area, interconnected porosity, superior compositional and structural uniformity, and accessibility of both pores and embedded nanoparticles of these films makes them a viable bottom-up materials candidate for various applications including optics and sensing. Such level of control over

materials properties is not achievable by typical inverse opal synthesis methods. This bottom-up technique is also substantially less demanding than top-down fabrication techniques, both in terms of the equipment required and the time needed. We have shown that the coupled optical properties of the highly uniform Au-doped inverse opal films, resulting from superposition of the angle-dependent Bragg peak of inverse opals and the angle-independent absorption peak of gold nanoparticles, are easily tunable either by changing the concentration of added nanoparticles to the solution *before* assembly or by selectively growing the embedded nanoparticles *after* colloidal template removal. This is a unique aspect of our work compared to other *co-assembly methods*.²¹

The presence of the selectively absorbing particles furthermore enhances the hue and saturation of the inverse opals color by enhancing resonant scattering while suppressing incoherent diffuse scattering.⁵¹ In particular, for thin inverse opal films on reflecting surfaces (where thin film interference often results in non-negligible reflected intensity in the blue or green spectral range) this allows to create strong red hues, which are difficult to achieve without the Au NP absorption. We have also successfully demonstrated that, by using selective functionalization⁷ of our doped opals, local changes in the composition and optical properties of these films can be induced. This synthetic methodology can be extended to other types of nanoparticles, such as silver,⁵² platinum,⁵³ and palladium,⁵⁴ which are easily synthesized and stabilized in aqueous solutions and can lend other important properties to these hybrid 3D nanoporous materials that are beneficial for antimicrobial activity,⁵² 3D scaffold structures for SERS sensing,⁵⁵⁻⁵⁶ colorimetric fluid analysis,⁵⁷ and catalytic activity.²⁴ We believe that the robust, large-scale, nanoparticle-doped inverse opals of uniform, tunable and accessible composition synthesized via three-phase co-assembly can find use in a whole range of applications in the fields of photonics, sensing, and catalysis.

EXPERIMENTAL SECTION

Gold nanoparticle synthesis.⁴² All glassware used in the gold nanoparticle synthesis was thoroughly cleaned in aqua regia (3 parts HCl, 1 part HNO₃) (Caution: Highly Corrosive), rinsed in triply-distilled H₂O, and oven-dried prior to use. The following stock solutions were prepared from triply-distilled H₂O: 1.0 mM HAuCl₄ (Sigma Aldrich, HAuCl₄•3H₂O salt), 38.8 mM sodium citrate (Sigma Aldrich). In a 250 mL round-bottom flask equipped with a condenser, 150 mL of 1 mM HAuCl₄ was brought to a rolling boil with vigorous stirring (300 rpm, egg-shaped magnetic stir bar) in an oil bath. Rapid addition of 15 mL of 38.8 mM sodium citrate to the vortex of the solution resulted in a color change from pale yellow to burgundy. Boiling was continued for 10 min; the solution was removed from the oil bath, and stirring was continued for an additional 15 min. The solution was then allowed to reach room tempera-

ture prior to use. TEM images were used to determine approximate nanoparticle size.

Film deposition. The as synthesized nanoparticle solution was centrifuged (3900g for 60 min, Beckman-Coulter Allegra X-22R) in 15 mL batches, the supernatant was removed, and varying amounts of Au Nps (6.0×10^{14} - 7.2×10^{15} Au Nps/mL) were re-dispersed into a 20 mL aqueous mixture of a 0.16% vol. monodisperse colloidal suspension of sacrificial template particles (~ 340 nm poly (methyl methacrylate) (PMMA) spheres) and 210 μ L of silica sol-gel precursor solution (prepared from the acid-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS)). (Details on the preparation of substrates, sol-gel solutions, and colloidal particles are described elsewhere.⁴⁰) Glass substrates were suspended vertically in vials containing the colloid/TEOS/Au mixture. The solvent was evaporated slowly over a period of 1–2 d in a 65 °C oven (Memmert UFE 500) on a pneumatic vibration-free table, to allow the deposition of a thin film onto the suspended substrate (growing approximately 2 cm/day). Thereafter, the colloidal template particles were removed (by calcination for 5 h at 500 °C) to result in a porous inverse opal structure. The synthetic conditions were identical for the all-silica films, except no gold nanoparticles were added to the mixture.

The appropriate choice of the centrifugation speed is critical: if higher centrifugation speeds (8400 g for 30 min) were used to remove the solvent from the original gold nanoparticle solution, the nanoparticles permanently clumped together,⁴³ assembling only into the largest voids of the inverse opal structure in localized clusters (Figure 2b,c). These nanoparticles then coarsened during calcination. Using a higher centrifugation speed resulted in different gold concentrations and degrees of nanoparticle clustering, leading to films with different compositions and optical properties than those prepared at lower speeds.

Selective functionalization. To pattern the wettability of inverse opals on the macroscopic scale, we used a selective functionalization technique.^{7, 57} The opal was first rendered hydrophobic with a fluorinated silane (tridecafluoro-1,1,2,2-tetrahydrooctyl)- trichlorosilane (Gelest Inc.) by vapor exposure in a desiccator under vacuum overnight. An “M” shaped PDMS mask was then used to cover the film, and the system was exposed to anisotropic oxygen plasma (Diener Electric GmbH Femto-A plasma cleaner, 5 min at full power) to render the unprotected area of the film hydrophilic.

Post-assembly gold growth experiments. For gold-growth experiments, the gold-loaded opal (either uniformly hydrophilic or patterned using selective functionalization) was suspended vertically in a vial containing 30 mL of 0.5 mM HAuCl₄ (Aldrich). The solution was magnetically stirred as a 400 μ L of 1.8 mM aqueous hydroxylamine (NH₂OH) (Aldrich) solution was rapidly injected. The resulting “growth solution” (with the immersed opal) was stirred until the color of the opal began to visibly change due to nanoparticle growth. The control sample (all-silica opal) was subjected to the same conditions as the gold-loaded opal, resulting in no significant NP nucleation or

visible color change at the same reaction time. (Note: increasing the time of immersion resulted in the increased random nucleation of nanoparticles in the all-silica (control) inverse opal.)

Optical analysis. Absorbance/attenuation spectra were collected at various angles of incidence from sample areas of 1 mm in diameter using a variable-angle spectroscope. A collimated beam of white light was sent through the sample and the transmitted light was collected collinear to the light incidence direction in a solid angle of 1° and coupled into a fiber before being spectrally analyzed using a Maya2000Pro spectrometer (Ocean Optics). By rotating the sample, the transmission for varying angles of light incidence was measured allowing us to calculate the attenuation (losses due to absorption and scattering) as a function of incidence angle. Attenuation is defined here as $\log_{10}(I_0/I)$, where I_0 is the incident light intensity, and I is the transmitted light intensity.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the AFOSR under Award # FA9550-09-1-0669-DOD35CAP. L.M. acknowledges fellowship support from the Department of Homeland Security (DHS). M.K. acknowledges funding from the Alexander von Humboldt-Foundation.

Key Words: colloids · nanoparticles · photonics · self-assembly · structural color

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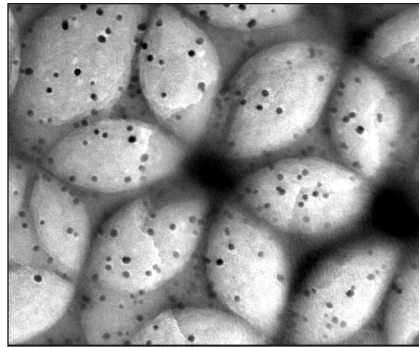
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Three-Phase Co-Assembly: In-situ Incorporation of Nanoparticles into Tunable, Highly-Ordered, Porous Silica Films

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A reproducible one-pot colloidal co-assembly approach results in large-scale, highly-ordered porous silica films with embedded, uniformly-distributed, accessible gold nanoparticles. The combination of iridescence with plasmonic effects in these inverse opals gives rise to a unique coloration that can be locally tuned by post-manufacture modification of their composition and optical properties. The films' high surface area, interconnected porosity, superior compositional and structural uniformity, and accessibility of both pores and embedded nanoparticles makes them a viable self-assembly-based, bottom-up material platform for various applications in optics and sensing.



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