# Template Assisted Three-Dimensional Nanolithography via Geometrically Irreversible Processing

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ABSTRACT

An innovative and versatile nanofabrication technique based on template assisted three dimensional nanolithography is presented which takes advantage of the irreversibility of conformal growth and conformal etching at locations with negative surface curvatures in 3D templates. Using colloidal crystals as templates, nano ring particles are generated with quantity much higher than conventional methods. Relying on the same principle, metallodielectric photonic crystals with discrete metal elements are fabricated which show strong absorption in the near-IR and transmission at longer wavelengths.

KEYWORDS

Nano ring particles, metallic photonic crystals, colloidal lithography

MANUSCRIPT TEXT

In recent years, considerable efforts have been put into combining conventional top-down nanofabrication and self-assembly based bottom-up methods to generate a diversity of complex nanostructures.[1-3] For example, through nanosphere lithography, a process that uses a colloidal monolayer as a deposition or etch mask, a variety of innovative 2-D nanostructures including triangles, rings, dots, and honeycomb structures have been generated.[4] However, the resulting patterns are generally limited to two dimensional structures of certain specific symmetries. Here we present a three dimensional template assisted nano fabrication technique that uniformly generates metallic and ceramic nanostructures throughout self-assembled colloidal templates. This method allows us to position the nanostructured objects at specific locations within the template, forming highly periodic multicomponent composite structures. Dissolving the template releases large quantities of unique shaped particles. Because the nanostructures are produced throughout the 3D template, much higher quantities particles are generated than for a 2-D fabrication process. In particular, ring shaped particles have attracted considerable attention because of their unique plasmonic,[5] optical[6] and magnetic properties[7] depending on the choice of materials. 2D based colloidal lithography has been a very popular method to generate particles of this kind.[4] However, each colloid in the colloidal monolayer only generates one ring particle, greatly limiting the quantities of particles generated per unit area. The advantages of a 3D lithographic approach are obvious, since all the colloids in the 3D colloidal crystal are utilized and each colloid generates 6 ring particles. As a result, particle areal density is increased by two orders of magnitude over a monolayer process.

The method proposed here takes advantage of the fact that conformal etching is not the geometric reverse of conformal growth at locations with negative surface curvature. A simple 2D representation illustrating this is shown in Figure 1. When the conformal coating thickness exceeds the minimum radius of the negative curvature, shown at point A in figure 1, the growth front along the normal direction moves faster than the rate of conformal coating. However, conformal etching propagates at the same rate along all directions. As a result, when the etching thickness equals the coating thickness, some coating material is left in the area originally having negative surface curvature.

3D colloidal crystals composed of close packed silica or polymer spheres are good examples of structures abundant of negative curvatures at the contact point of each pair of spheres. Using these as templates, nanoring particles can be fabricated as illustrated in figure 2. First a smooth film of tungsten with uniform thickness is coated onto a 3D silica colloid template through a static chemical vapor deposition (CVD) process (Fig. 2b).[8] Then, the tungsten coated sample is anodized in a sulfuric acid solution, converting roughly 10 nm of the surface of the tungsten to tungsten oxide.[9] The oxide layer is etched away in a potassium hydroxide solution. This process of anodization followed by chemical etching is repeated multiple times until the tungsten coated on the surface of the spheres other than the contact region is completely etched way, resulting in tungsten rings at the contact points between spheres (Fig. 2c). It is worthwhile to point out that for this specific system, the tungsten coating layer functions as the conductive pathway in the anodization step. Once a tungsten ring is electrically disconnected from the substrate, it is no longer etched. This makes the anodization a self-limiting process. As a result, even if the anodization is not completely uniform through the thickness of the template, the resulting tungsten rings are still quite monodispersed. After etching of the colloids in a dilute hydrofluoric acid (HF) solution followed by a washing and centrifugation step, the tungsten nanoring particles can be harvested (Figure 2d). A distinct advantage of this nanoring fabrication process is that it does not require a perfect colloidal crystal template, since the rings are only formed at each colloid pair contact point. So, even a randomly packed colloidal film can be used (supporting information figure S1). Electron diffraction (supporting information figure S2) indicates the rings are amorphous as expected for the CVD process utilized. The same principle can be applied to any material as long as the conformal coating and etching process exist which are compatible with the template being used. Aluminum oxide rings are generated by coating polystyrene colloidal crystal with $Al_2O_3$ through atomic layer deposition (ALD) followed by a slow HF etching (bottom SEM images of figure 2c,d) (details in supporting information).

The dimension of the rings generated can be easily calculated by simple geometry. **R** is the radius of the colloidal spheres; **x** is the thickness of the conformal coating layer and also the conformal etching layer (assuming they are equal); **r** and **h** are the radius and thickness of the ring particle.

$$r = \sqrt{x^2 + 2xR} - x \sim \sqrt{2xR} - x$$
$$h = \frac{2xR}{x + R} \sim 2x$$

The approximation is valid when **x«R** (in real case, x/R is <0.15 due to geometrical constraints). Since both **x** and **R** can be independently selected, the radius and the thickness of the ring particles can be independently controlled as shown in the figure 3a,b, where tungsten films of two different thickness, 60 nm and 40 nm, respectively, are coated on colloidal template grown using 1.58 µm diameter colloids. The thicker coating generates rings of greater thickness, 132 nm vs. 93 nm, and diameter, 640 nm vs. 454 nm. When colloidal templates of different sizes, 1.58 µm vs. 920 nm, are coated with tungsten with the same thickness (40nm), the radii of the final ring particles vary, 454 nm vs. 328 nm, while the thicknesses are kept roughly the same, 93 nm vs. 89 nm (figure 3b,c). By scaling the colloid size and coating thickness together, ring particles of different sizes but similar in aspect ratio are generated (figure 3a,d). Detailed dimensions of tungsten particle in each case are listed in table 1. SEM images of released ring particles fabricated from templates of different colloid sizes are shown in supporting information figure S4. The ability to independently modulate the dimensions of the resulting nanoparticles could be advantageous for numerous applications.

Along with providing a relatively high volume nanostructure fabrication process, this 3D lithography method results in a unique metallodielectric photonic crystal consisting of disconnected metallic elements supported by a dielectric structure. Popular methods for generating 3D metallodielectric photonic crystal involve the use of templates formed by colloidal self-assembly,[10] interference lithography[11, 12] or direct writing[13, 14] which are filled with a metal by conformal coating,[15] nanoparticle infilling,[16, 17] or electrodeposition.[18] The result is a connected metallic structure in which electric fields are conductively coupled. 3D optical metamaterials based on resonant structures require discrete capacitively coupled metal elements to be positioned inside a 3D matrix with accurate control over their position, geometry and orientation.[19, 20] In those cases, conductive coupling of the metallic elements is undesirable. The ability to position disconnected metallic elements in 3D space using a colloidal crystal template and our template assisted three-dimensional nanolithography process is demonstrated for the case of tungsten rings generated in a 3D silica colloidal crystal (figure 4a). Here, the disconnected tungsten rings form a periodic structure corresponding to Wyckoff notation 24d of space group Fm-3m with the ring axis normal to the colloid surface. The reflection and transmission spectra of the template (figure 4b) and the metallodielectric photonic crystal after all processing steps (figure 4c) are measured. Strong absorption is observed around 2.5 μm, while a pass band at long wavelengths is indicative of the discrete nature of the metal elements. Although the structure shown here is not a metamaterial, which requires resonance elements such as split rings[21] and a lower loss metal than CVD tungsten, we believe that by designing and fabricating a proper template with the appropriate curvature distribution using methods such as interference lithography or direct writing[11-14] and by choosing the right low loss materials, such structures may be achievable.

In summary, we describe an innovative fabrication technique: template assisted 3D nanolithography. Using colloidal crystals as templates, nanoring particles and metallodielectric photonic crystals are fabricated. The combination of this approach with more complex templates, with designed negative curvature distribution, for example those formed through optical interference,[11, 23, 24] may provide a path to otherwise unobtainable nanostructures and complex photonic structures.

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**Supporting Information Available:** Tungsten rings formed in random colloidal film, TEM images and electron diffraction pattern from an individual W ring particle, SEM image of large quantities of tungsten rings solvent cast on a Si wafer, reflection and transmission spectra of metallodielectric photonic crystals as a function of number of layers, reflection and transmission spectrum of refractive index matched dielectric template and metallodielectric photonic crystal, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

**Table 1.** Colloid diameter, W coating thickness, and ring particle dimensions for images presented in

| | colloid diameter (nm) | W coating thickness (nm) | ring particle diameter (nm) ± standard deviation (nm) | ring particle thickness (nm) ± standard deviation (nm) |
|---|---|---|---|---|
| (a) | 1580 | 60 | 640±58 | 132±9.4 |
| (b) | 1580 | 40 | 454±93 | 93.1±4.6 |
| (c) | 920 | 40 | 328±37 | 88.8±4.2 |
| (d) | 550 | 20 | 220±12 | 41.9±4.0 |

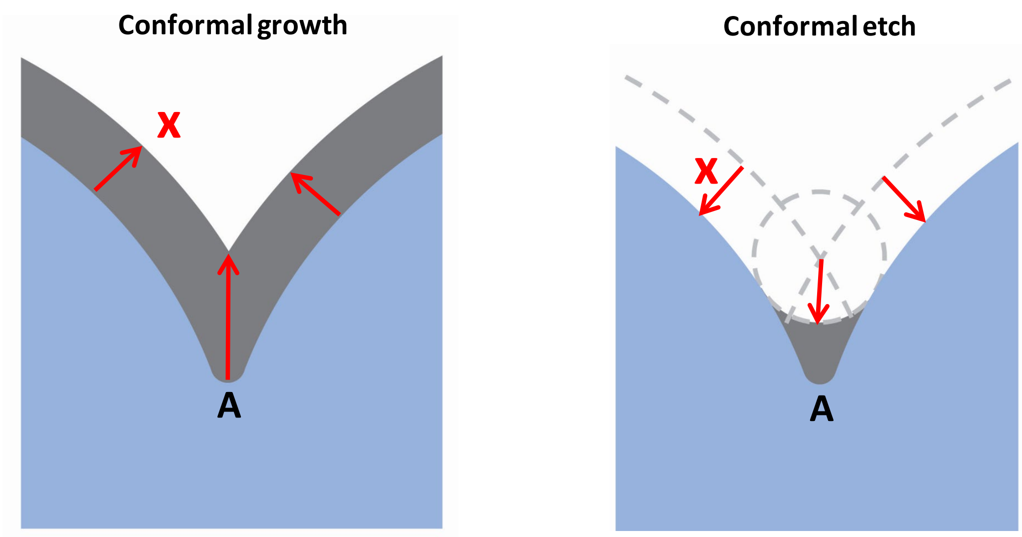


**Figure 1.** Schematic of an irreversible conformal growth (a) and conformal etching (b) process in two dimensions. After deposition and etching of the same thickness of material, some material remains in areas with a small negative radius of curvature.

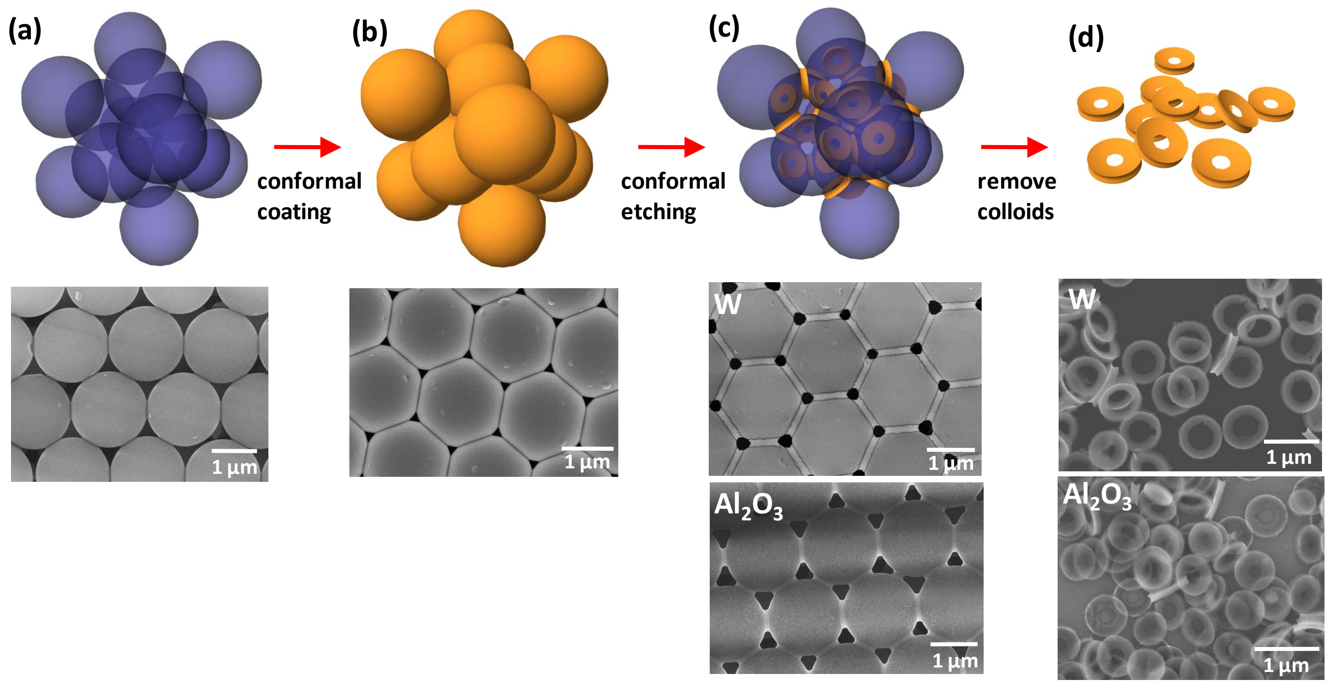


**Figure 2.** Schematic diagram and SEM images of the four stages of the process for synthesizing ring particles: (a) colloidal crystal template formed by self-assembly, SEM image shows a crystalline silica colloidal film; (b) after conformal coating by CVD or ALD, SEM shows a tungsten CVD coated silica colloidal crystal; (c) ring particles formed in between colloids after conformal wet etch, SEM images show tungsten and $Al_2O_3$ ring particles formed at the silica and polystyrene colloid contact points, respectively; (d) released ring particles, SEM images show well dispersed tungsten and $Al_2O_3$ ring particles after etching of the colloidal crystal template.

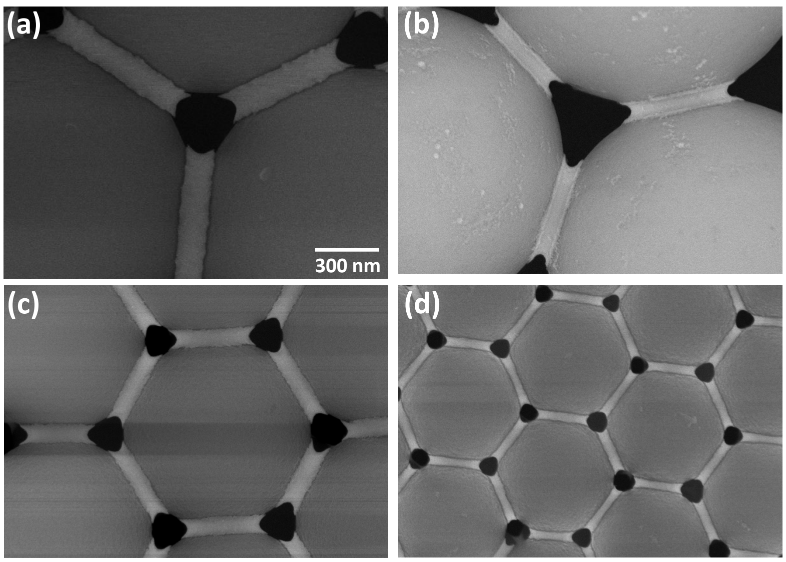


**Figure 3.** (a-d) SEM images of tungsten ring particles before release from the colloidal template. All images are of the same magnification. The diameter and the thickness of the rings can be independently adjusted by using colloids of different sizes as templates and by varying the conformal coating thickness (see table 1 for numerical values).

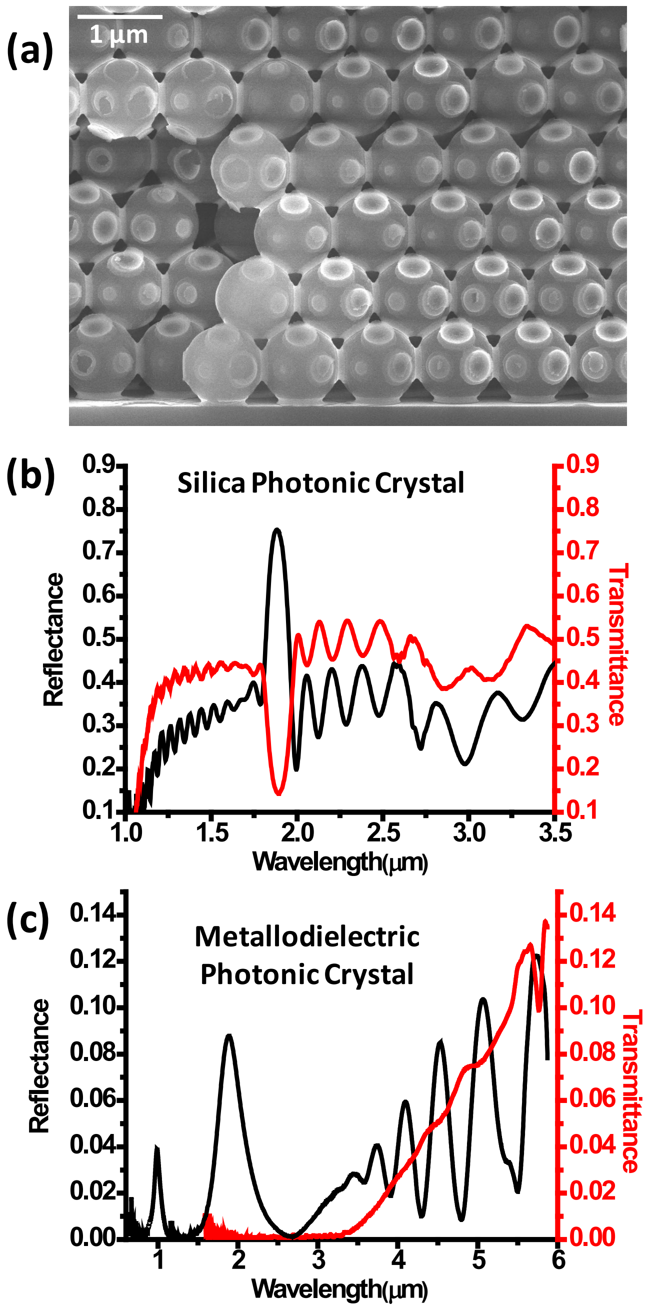


**Figure 4.** Metallodielectric photonic crystal composed of discrete W ring particles formed in-situ using a 920 nm diameter silica colloidal crystal template. (a) Cross-section SEM image of the metallodielectric colloidal crystal. Discrete tungsten ring particles are clearly seen. (b) Reflection (black trace) and transmission (red trace) spectra of silica colloidal crystal template before tungsten deposition. (c) Reflection (black trace) and transmission (red trace) spectra of metallodielectric photonic crystal shown in (a) after W deposition and etching.

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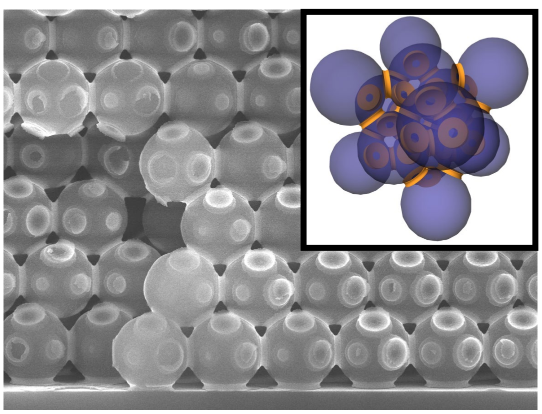
SYNOPSIS TOC

Metallodielectric photonic crystal



Nanoring particles