

Mass-Limited Growth in Zeptoliter Beakers: A General Approach for the Synthesis of Nanocrystals

Jeremy E. Barton and Teri W. Odom*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

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ABSTRACT

Nanoscale fabrication methods provide a unique approach to synthesize nanoscale materials. Laser-assisted embossing was used to generate close-packed arrays of hemispherical nanowells with zeptoliter (zL) volumes. The volumes of the nanowells were controlled by changing the fluence of the laser, by applying variable pressure between the mold and the substrate, and by growing an amorphous oxide on the patterned silicon. Nanowells with diameters as small as 50 nm were used as reaction vessels for the preparation of simple inorganic salts and semiconducting nanocrystals. Under most growth conditions, individual nanocrystals were formed in individual nanowells.

This paper demonstrates an approach to grow well-separated nanocrystals in arrays based on the simple precipitation and reaction of precursors in zeptoliter (zL) volumes. We have used laser-assisted embossing with transparent molds of 100-nm silica spheres to generate hemispherical wells in amorphous silicon. The size and depth of the wells were readily manipulated by changing the fluence of the laser, by applying variable pressure between the nanosphere mold and the substrate, and by growing an amorphous oxide on the patterned silicon. These nanowells functioned as small beakers for the growth of inorganic salts and semiconducting nanocrystals with controlled sizes. This work provides a direct method to apply nanoscale patterning (feature sizes < 100 nm) to the chemical synthesis of nanoscale materials.

Nanocrystals can exhibit new optical and electronic properties when their sizes become smaller than a key physical dimension.^{1,2} High temperature (150–250 °C) solution synthesis is one of the most successful methods to achieve size and shape control of nanocrystalline materials by nucleation and growth kinetics in the presence of selective surfactant molecules.^{3,4} Inhomogeneity in the injection of precursors, mixing of the reactants, and temperature gradients in the reaction flask, however, can contribute to dispersions in the size of nanoparticles. To control the chemical and thermal homogeneity, small volume reaction vessels, such as dendrimers and reverse micelles, provide an appealing alternative. The sizes of the nanoparticles formed within these structures depend on either the number of ions that can be intercalated into the dendritic branches or the interior water

content of the micelles.^{5–7} Drawbacks to growth in these soft structures, however, include the polycrystalline nature of materials because of the low-temperature reaction conditions and the organic template coating the nanoparticles. Small volume (< μm^3) reactors, in which particles could be grown at high temperatures and subsequently removed, are potentially a useful approach for achieving size control of crystalline nanoparticles.

Micro- and nanofabricated structures have been used previously to template and direct the growth of crystalline materials from solution.^{8–13} Templates such as anodized alumina membranes can generate polycrystalline nanorods with critical dimensions that are determined by the pore size (20–300 nm); electrodeposition is used to generate the quasi-ordered arrays of nanorods, which can be removed by etching the membrane. Microfluidic reaction systems have also been employed to synthesize micro- and nanocrystals. Glass microchannel reactors and silicon micromixers were fabricated to grow nanoparticles of CdSe and CdS with well-controlled sizes by changing the reaction temperature, the concentration of precursors, and the flow rates.^{11,12} The microsystem reactors were operated in a continuous flow mode to produce concentrations of nanoparticles comparable to large scale growth. In addition, microcrystals of calcite and apatite were precipitated at the interface of laminar flow streams within PDMS microchannels; in this system, the particles were patterned on the surface.¹⁴

Arrays of microstructures that can prepare arrays of microcrystals from solution include micropatterns of self-assembled monolayers (SAMs) and microwells in soft materials (PDMS and photoresist).^{15–18} Insertion of these

* Corresponding author. E-mail: todom@chem.northwestern.edu.

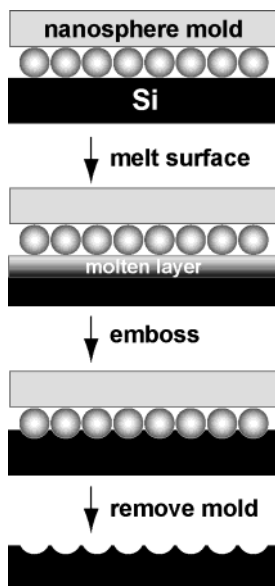


Figure 1. Scheme for fabricating nanoscale wells in silicon by laser-assisted embossing.

patterned substrates into a precursor solution, followed by the slow withdrawal of the substrates (discontinuous dewetting),¹⁰ resulted in the formation of liquid droplets on the patterned areas of SAMs and within the microwells. After the evaporation of the solvent, simple inorganic salts and organic molecular crystals precipitated into ordered arrays. The sizes of the crystals depended on the patterned area or the well volume in addition to the concentration of the reactants. This technique for nanocrystal growth has been demonstrated successfully for 30-nm NaCl crystals in 100-nm wells of photoresist,¹⁹ however, the material properties of the wells limit the types of nanomaterials that can be grown. For example, these organic substrates are not robust at high (>100 °C) temperatures and are not compatible with polar or organic solvents.

The challenges of soft materials can be overcome by using harder, inorganic materials such as silicon and silicon dioxide, which are inert to common solvents and can withstand temperatures up to 900 °C. The use of nanofabricated structures made from these materials enables the growth and assembly of nanocrystals potentially more interesting than inorganic salts and organic molecular crystals. In addition, the growth of nanocrystals in confined volumes has several advantages: (i) simple syntheses based on bulk reactions; (ii) flexible size control achieved using different concentrations of precursor materials; (iii) generation of isolated nanocrystals in ordered arrays; and (iv) the possibility of reusable templates for future reactions.

We prepared silicon nanowells by the laser-assisted embossing of silicon substrates²⁰ using a mold consisting of monolayers or multilayers of 100-nm silica spheres compressed against a fused silica flat (nanosphere mold). Figure 1 outlines the embossing procedure for generating hemispherical wells in silicon with diameters less than 100 nm. Silica spheres (purchased from Polysciences and used as received) of different sizes (50–450 nm) were deposited by drop coating onto silicon substrates cleaned by a piranha and

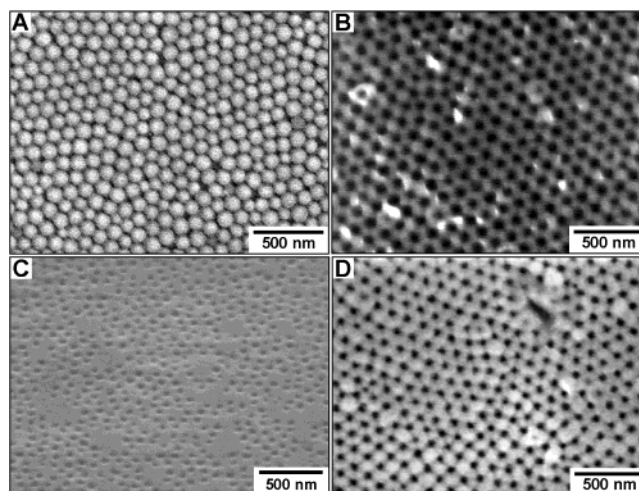


Figure 2. Scanning electron microscopy (SEM) image of (A) slightly disordered monolayer of 100-nm silica spheres. The disorder results from the polydispersity in sphere sizes. (B) Embossed nanowells. (C) Shallow nanowells embossed under low laser energy densities (0.8 J/cm^2). (D) Nanowells from (B) that were thermally oxidized. The diameters of the wells were reduced by 10–20 nm by oxidation.

HF etch. These silica spheres formed well-ordered, close-packed layers at the surface of the silicon (Figure 2A). A fused silica flat was then placed against the spheres, and a slight mechanical pressure was applied between the mold and the silicon substrate. A single pulse (20 ns) from a KrF excimer laser (248 nm) was directed through the silica flat with an energy density of $0.8\text{--}2 \text{ J cm}^{-2}$. This pulse melted the top surface ($\sim 50\text{--}200$ nm) of the silicon substrate.²⁰ Because of the applied pressure, the molten silicon filled the recessed regions of the silica sphere monolayer. After the molten silicon cooled, the surface was embossed into hemispherical nanowells.

Figure 2B shows the patterned silicon surface after removal of the nanosphere mold (and after etching in HF to eliminate residual silica spheres). The sizes of the nanowells were controlled by several factors: (i) the size of the spheres in the mold, (ii) the energy density of the laser pulse, and (iii) the applied mechanical pressure. The widths of the nanowells were primarily determined by the physical size of the silica spheres, while the depth was affected by the energy density and mechanical pressure (Figure 2C). Moreover, thermal oxidation of the patterned silicon substrates at 1000 °C for 7 h resulted in a size reduction in the wells of 10–20 nm in diameter (Figure 2D), which may be attributed to the larger volumes (~ 2 times) occupied by amorphous silicon dioxide compared to silicon.²¹

These nanoscale wells are ideal reaction vessels for the growth of nanocrystals. Because of their small volumes and chemical functionality, low concentrations of precursor materials should enable the growth of different types of nanoparticles with controllable size. We demonstrated how lower concentrations of precursors resulted in smaller nanoparticles by crystallizing NaCl from 1 to 5 M solutions in similarly sized nanowells (Figure 3). The nanowells were filled in a single step by discontinuous dewetting. After the

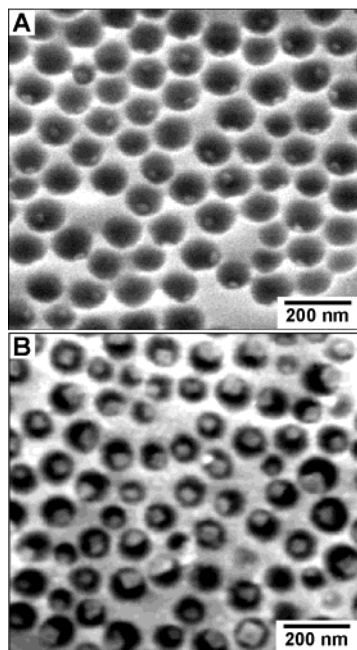


Figure 3. SEM images of individual NaCl nanocrystals grown within (A) 80-nm wells from a 1 M NaCl solution (tilt angle = 30°) and (B) 50–80-nm wells from a 5 M NaCl solution (tilt angle = 0°). The differences among nanocrystal sizes in (B) can be attributed to differences in well volumes and the local surface structure, which affect the amount of solution deposited within each well during the dewetting process.

water evaporated, the precipitates in the wells were recrystallized in a humid atmosphere under short (2 s) exposure times.¹⁸ Nanowells filled with 1 M salt concentrations (Figure 3A) resulted in, qualitatively, smaller crystals than those formed from 5 M solutions (Figure 3B). Square crystals of NaCl grown in 100-nm wells from a 1 M solution have edge lengths as small as 25 nm. Because the SEM images were acquired with a tilt angle of 30°, nanocrystals pinned to the edges of the nanowells that face away from the detector were not visible.

In addition to the precipitation of simple inorganic salts, we have used our nanowells to grow functional nanoscale materials. Also, since the nanowells are patterned in silicon or silicon dioxide, we could easily control the hydrophobicity and hydrophilicity of the surfaces by functionalizing them with silane molecules; this chemical functionality assisted in filling the nanowells. We created nanowells with hydrophobic surfaces for the preparation of CdS nanocrystals.²² The CdS reactions required two separate steps: (i) filling the wells with cadmium acetate (0.1 M) by discontinuous dewetting, and (ii) immersing the substrate into a sodium sulfide solution (1 M) for 5–10 s. Following step (i), cadmium acetate nanocrystals remained in the nanowells; during step (ii), the cadmium acetate reacted immediately with the sodium sulfide solution. The sample was gently washed with water to remove any unreacted precursor materials.

Figure 4 shows uniformly embossed nanowells in which CdS nanoparticles were grown. Moreover, higher resolution images reveal that each nanowell contained only one

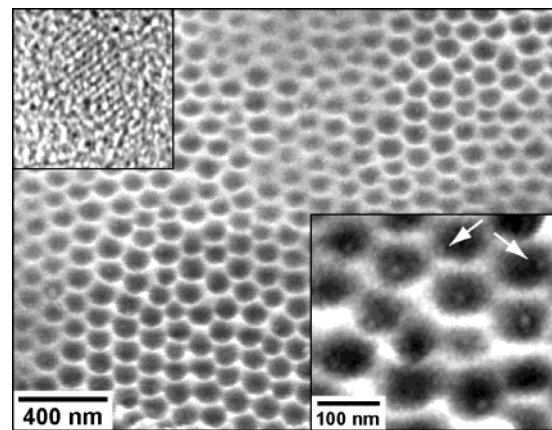


Figure 4. SEM image of an array of nanoscale wells that contain one CdS nanocrystal per well. The lower inset magnifies a small area of the array; the white arrows indicate crystals formed at the edges of the wells. The upper inset is a TEM image of an individual CdS nanocrystal removed from the array of nanowells by sonication. The separation between lattice fringes is 3.36 Å and matches the (111) plane of CdS.

nanoparticle (Figure 4, bottom inset). To characterize their crystallinity, we removed the nanoparticles from the wells by sonication in hexane and analyzed them by transmission electron microscopy (TEM). The top inset of Figure 4 indicates that the small (~5 nm) CdS nanoparticles are crystalline; the lattice fringes correspond to (111) planes of CdS and are separated by 3.36 Å. We have also annealed isolated CdS nanoparticles under argon at 500 °C for 4 h to assist in the crystallization process; in general, the room temperature reaction conditions resulted in crystalline CdS nanoparticles. This simple, two-step process for synthesizing nanoparticles can form arrays of crystals simultaneously over areas up to mm².

In summary, we have developed a technique for the fabrication of nanowells with zL volumes and have demonstrated how these wells provide a general method to confine chemical reactions and to synthesize nanocrystals. Laser-assisted embossing provides a relatively fast and easy method for the patterning of high densities of nanowells in silicon. Limitations of this route to nanocrystals include the relatively low concentrations of synthesized nanoparticles and the rapid evaporation of solvent from the small volumes. The generation of large areas (cm²) of nanowells (e.g., using Langmuir–Blodgett assembly methods) and performing reactions in a controlled environment should overcome these drawbacks. Because our method can produce isolated nanoparticles, detailed studies of the properties (e.g., localized surface plasmon resonance and catalytic activity) of individual particles are now possible. We anticipate that these reactors can also be used to synthesize new types of nanoscale materials at high temperatures. In particular, one exciting prospect is to perform solid state reactions in nanowells that have been filled with the appropriate ratios of molecular precursors. Our combination of top-down nanoscale patterning and bottom-up chemical syntheses shows significant promise for the growth and parallel assembly of individual nanocrystals with complex properties.

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