Size-controlled Fabrication of Periodic Nanocrystal Arrays by Using the Hemispherical Metal Nanowells

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A periodic array of NaCl nanocrystals is prepared using a nanoreactor array, which consists of hemispherical nanowells of 800 nm in diameter fused side-by-side prepared by sputter deposition of Fe and Au layers over hexagonally close-packed 1-μm polystyrene (PS) beads. The size of the nanocrystals can be controlled simply by changing the concentration of the precursor solution.

Nanometer-scale single crystals have been extensively studied for their unique chemical and physical properties,[1] which are extremely interesting in applications for magnetism,[2] optics,[3] and electronics.[4] Various approaches to preparation of nanocrystalline noble metals and semiconductors have been developed using surfactants,[5] dendrimers,[6] coordination polymers,[7] and microfluidic reactors.[8] Although these methods allow high-efficiency production of relatively monodispersed nanocrystals either in bulk solutions or in matrices, it is very difficult to assemble the resulting nanocrystals into 1D, 2D, and 3D arrays necessary for the development of nanocrystal-based devices.[9] To this end, the use of a nanofabricated reactor array that serves the dual functions of crystal growth and surface positional orientation is relatively easy to use in practice. Recently, several realistic micro- and nanoreactor fabrication techniques have emerged, including laser-assisted embossing of a silicon surface,[10] photolithographic patterning of poly(dimethylsiloxane),[11] polystyrene (PS) bead templated NiO patterning.[12] However, no system is yet to fully satisfy long-range periodicity and nanosize crystal preparation simultaneously.

In this communication we demonstrate the use of a metal well nanoreactor for the size-controlled preparation and periodic assembly of nanocrystals. Previously, we have prepared a thin metallic film that consists of nanosize hemispheres fused at the edges by sputter deposition of Ti and Fe over a monolayer of hexagonally close-packed polystyrene beads 1 μm in diameter.[13,14] The resulting thin films have nanowells with inner diameter of 900 nm, which are capable of catching small objects as we demonstrated by docking 800 nm PS beads in the hollows. If these metal nanowells are equally effective in trapping consistent volumes of fluid, periodic arrays of nanocrystals can be directly grown from various solutions of inorganic salts and organometallic complexes (Figure 1a). In this study, metal nanowells were fabricated by casting a 1.5-nm Au corrosion protection layer deposited by resistance heating and a 50 nm structured Fe layer deposited by magnetron sputtering both at a rate of 1–2 Å s^{-1} over a PS monolayer, which was exposed to heptadecafluoro-1-decanethiol vapor prior to the deposition. Subsequently, PS beads were dissolved by gentle agitation in toluene to release the deposited metal layers from the substrate surface. Then the detouched film was scooped onto a silicon substrate so that the concave sides of the nanowells faced upward (Figure 1b). Nanowell arrays were filled with a freshly prepared solution of twice recrystallized NaCl[15] by discontinuous dewetting, in which a small drop of the solution was dragged across the object surface.[16] The solution-treated substrate was immediately transferred to a dessicator and sealed along with a water-filled petri dish to retard the solvent evaporation.

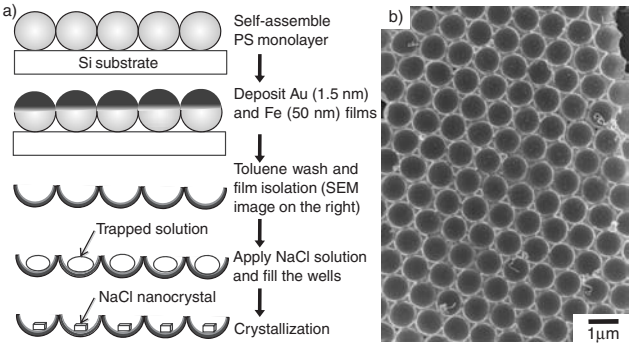

Figure 1. (a) Schematics representation of the nanocrystal preparation procedure. (b) SEM image of empty nanowells.

Figure 2 shows SEM micrographs of the nanowell array with NaCl nanocrystals grown from a 3 M aqueous solution. The nanowell has estimated inner diameter of 800 nm[17] with calculated aspect ratio (depth:width) of 1:4. All the crystals are found in the wells and no crystallization is recognized elsewhere, verifying that the wells are filled with solution as intended (Figure 2a). No substantial size distribution among crystals is recognized, indicating uniformity of the well volume and the amount of solution trapped in it. A higher magnification image shows that substantial number of nanocrystals appears to have regular to slightly distorted square shapes with the edge lengths in the range of 250 ± 20 nm (Figure 2b).

Crystal size could be controlled simply by changing the solution concentration in the above procedure. Figure 3 shows NaCl nanocrystals grown under the same conditions except that the solution is diluted to 0.5 M. Crystal sizes become uniformly smaller with estimated average diameter of 90 nm, suggesting that this method is effectively fulfilling the purpose.

We demonstrated fabrication of periodic NaCl nanocrystal arrays by utilizing hemispehrical nanowells as reaction vessels that can grow crystals from the trapped solution. This method is applicable to assemble a superlattice of nanocrystals directly from the solution.[18] Although this demonstration used NaCl as source material, chemical inertness anticipated in our Au/Fe double layer structured film is applicable to prepare nanosized metal alloys and composites from various sources. In addition, if thermal stability is confirmed, it would be possible to increase crystallinity and to study thermal phase transitions in nanocrystals by repeated annealing without causing particle coalescence.[19]

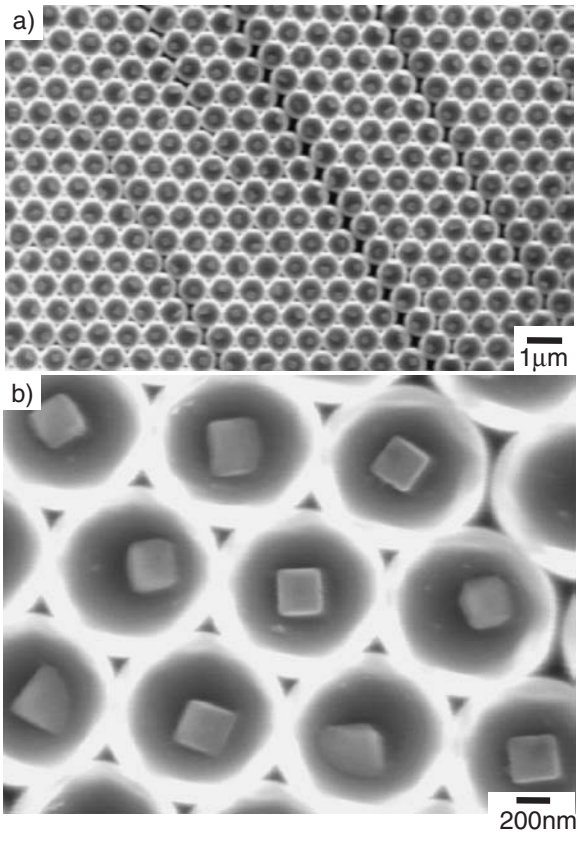

Figure 2. SEM micrographs of a NaCl nanocrystal array grown from a 3 M aqueous solution.

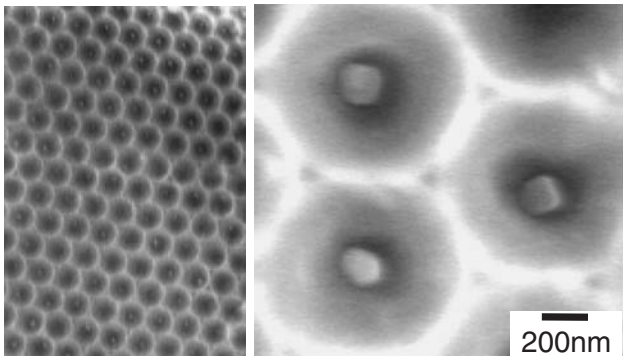

Figure 3. SEM micrographs of NaCl nanocrystal arrays grown from a 0.5 M solution. Low (left) and high (right) magnification images of the same sample are shown.

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