Formation of Thick, Large-area Nanoparticle Superlattices in Lithographically Defined Geometries

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SUPPORTING INFORMATION

Nanoparticle Preparation:

A typical synthesis of CdSe nanoparticles is as follows[1]: 102.8 mg of CdO, 910 mg of stearic acid and 32 mL of octadecene was mixed in a 120 mL three-necked flask. The mixture was heated at 250˚C for 10 min to allow the formation of cadmium stearate. Then 4 g of trioctylphosphine oxide and 4 g of octadecylamine was added followed by degassing. The mixture was then heated to 300˚C, and a 4 mL solution of 1.0 M trioctylphosphine selenide in trioctylphosphine was injected quickly. The growth was carried out at 280˚C. γ-Fe_2O_3 nanoparticles were synthesized as follows[2]: A mixture of 10 mL octyl ether and 2.14 mL oleic acid was degassed at 100 ˚C for 1 hr, followed by injection of 0.2 mL iron pentacarbonyl. The mixture was heated to 280˚C and held at that temperature for 1 hr. Both products were purified with ethanol/toluene as a nonsolvent/solvent pair. Core diameters were determined by TEM, and for CdSe nanoparticles also by luminescence. All particles were monodisperse (5% variation in core diameter) and crystalline, as determined by x-ray and electron diffraction. All chemicals were purchased from Aldrich.

Substrate Preparation:

Si <100> wafers were patterned with chrome etch masks by conventional electron-beam lithography techniques (PMMA resist deposition, followed by exposure to the electron beam, development in methyl isobutyl ketone, thermally-evaporated chrome deposition, and resist liftoff). The wafers were then etched in two steps using an inductively-coupled plasma (Oxford Plasmalab 80 Plus ICP) system, following a technique generally known as an Advanced Silicon Etch. First, the wafers were etched with a mixture of C_4F_8 and O_2 for 30 sec, to remove any native oxides formed during exposure to air. Next, a two-step anisotropic silicon etch was performed. In the first step, a low-power (50 W) plasma of C_4F_8 was applied for 5 sec, producing a passivation layer on the surface of the silicon substrate. Then, a 30 sec, high-power (300 W) plasma of SF_6 was applied to rapidly etch away silicon around the chrome mask pattern. The resulting sample substrate consisted of a 1.2 μm high wall of silicon in the shape of the chrome etch mask. The sample surface was found to be hydrophobic following the etch process; the as-fabricated samples were stored in a dry box to prevent contamination.

Nanoparticle Deposition:

Solutions of 3% (volume) decanol in xylene were prepared, with ~10^{15} NPs/mL. The solution was injected into the reservoir on the substrate using a microinjector (Narishige IM-300) until the reservoir was filled. The sample was then allowed to sit in air for ~20 min while the xylene evaporated. Samples were then placed in a vacuum chamber at ~100 mTorr in most cases and allowed to dry for 12 h.

Small Angle X-ray Scattering:

Reflection mode experiments were performed with 0.35° angle of incidence, which is greater than the critical angle of 0.14° for the silicon substrate.

The data for the transmission mode experiments (performed at normal incidence) are shown in Fig. S1.

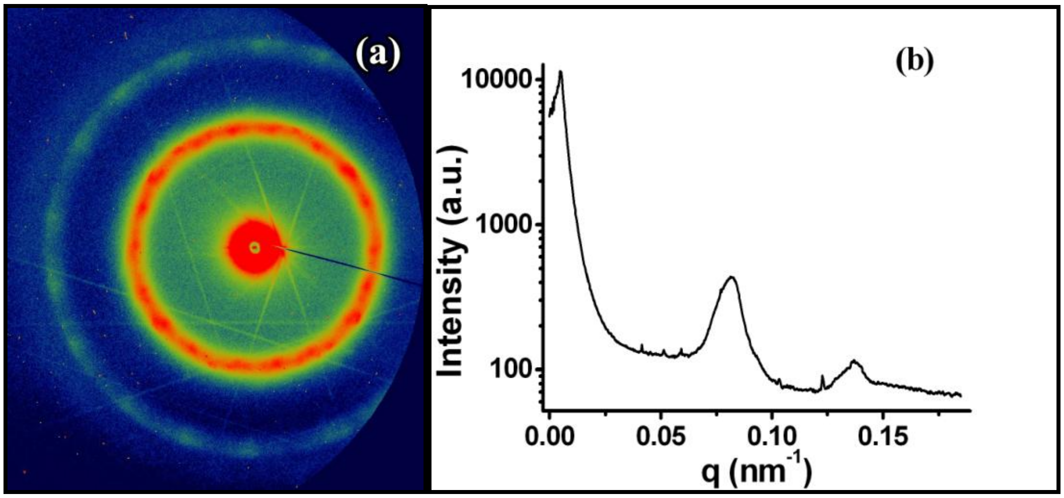

Figure S1: Data from small angle x-ray scattering (SAXS) measurements of superlattices of 8.0 nm Fe_2O_3 nanoparticles, taken in transmission mode. (a) Data, showing rings typical of powder-type diffraction. (b) Graph of a one-dimensional trace across the transmission data. The first peak corresponds to the (100) plane with a lattice parameter of a = 9.7 nm.

Additional Superlattice Characterization:

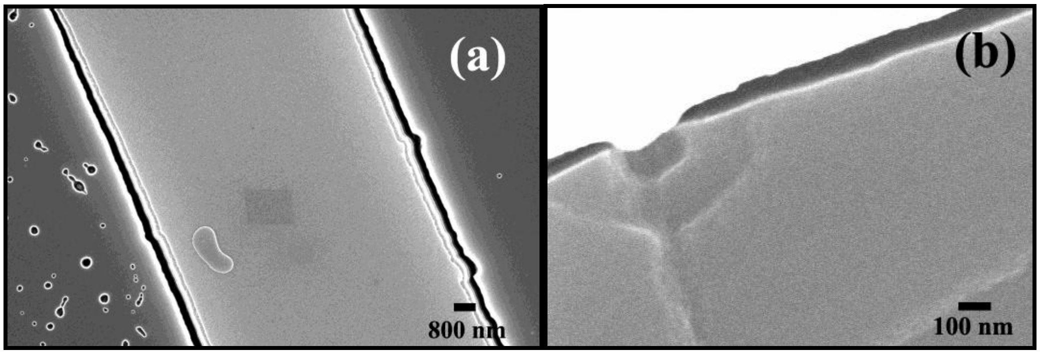

Figure S2: SEM images showing cracks between the walls of the lithographically-defined capillary channel and the supercrystal for a (a) 5.5 nm CdSe nanoparticle supercrystal, (b) 8.0 nm Fe_2O_3 nanoparticle supercrystal. The cracks closely copy the local morphology of the walls and run parallel to the walls.

References:

1. Peng, Z. A.; Peng, X. G. *J. Am. Chem. Soc.* **2001,** 123, (1), 183-184.

2. Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Bin Na, H. *J. Am. Chem. Soc.* **2001,** 123, (51), 12798-12801.