# Epitaxial growth of DNA-assembled nanoparticle superlattices on patterned substrates

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**1) DNA Design**

The DNA attached to the gold nanoparticles, and to the template sites, is as follows:

Thiol ‘A’: TCA ACT ATT CCT ACC TAC (/iSP18/)10-SH

Thiol ‘B’: TCC ACT CAT ACT CAG CAA /iSP18/10-SH

Linker ‘A’: GTA GGT AGG AAT AGT TGA /iSP18/ TTT CCT T

Linker ‘B’: TTG CTG AGT ATG AGT GGA /iSP18/ AAG GAA A

/iSP18/ is an 18-atom hexa-ethyleneglycol spacer. (/iSP18/)10 implies the addition of 10 of these spacers at the designated location. The –SH before attachment is a dithiol which is cleaved before use.

**2) Experimental Methods**

Substrates were silicon with native oxide, cleaned for 60 minutes in Nanostrip (Cyantek), rinsed, dried under nitrogen, and baked for 2 minutes at 180 degrees C. 950-A2 PMMA photoresist was spun onto these wafers at 3500 RPM for 60 seconds, and the resist was post-baked for 5 minutes at 180 degrees C. After lithography, chips were developed in cold MIBK:IPA in a 1:3 ratio for 60 seconds. Metals were deposited in an electron-beam evaporator, followed by liftoff in warm (80-90 degrees C) PG Remover (Microchem).

Before liftoff, 5 OD lyophilized thiol ‘A’ and 250 μL of 100 mM ditihiotreitol in 170 mM phosphate buffer were combined for 2 hours to deprotect the thiol, after which the DNA was purified in water by running through a NAP-5 column. Immediately after liftoff, chips were immersed in a solution containing 1 μM deprotected thiol ‘A’ in 5 mM phosphate buffer with 1M $Na^+$ and left to sit at room temperature.

After 24 hours, chips were removed from the thiol solution, rinsed thoroughly in 10 mM phosphate buffer with 0.5M $Na^+$, and added to 0.5 μM linker 'A' in the same solution. Chips in the linker solution were then heated to 60 degrees C and let cool back to room temperature over the course of three hours, to ensure hybridization of the linker and thiol DNA. Following this step chips were again rinsed thoroughly in 0.5M $Na^+$ 10 mM phosphate buffer.

Nanoparticles were prepared similarly. 20 OD of freshly cleaved thiol 'B' and 20 ml of 30 nm citrate-capped gold nanoparticles (Pella) were combined and left to sit for 2 hours. After this, they were centrifuged at 11500 RPM for 20 minutes at room temperature, and the supernatant was removed and discarded. The nanoparticles were redispersed in 0.01% w/v sodium dodecyl sulfate (SDS), vortexed, centrifuged again, and the supernatant discarded again. This process was repeated twice. After the final rinse, particles were dispersed at 0.0005 μM concentration with 5 μM linker DNA in 0.5M $Na^+$ 10 mM phosphate buffer. Particles and linkers were heated together at 45 degrees C for 1 hour and let cool for 30 minutes.

Lastly, substrates were immersed in the nanoparticle solution either at room temperature or at 37 degrees C overnight, after which substrates were rinsed and stored in 0.5M $Na^+$ 10 mM phosphate buffer. For imaging, substrates were then treated with 2 uL *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride and 4 uL triethoxysilane in 1 mL buffer, and shaken at 700 RPM at room temperature for 24 hours. Chips were then removed from solution, rinsed in water, dried with nitrogen, and imaged with an FEI Sirion scanning electron microscope.

### 3) BCC Lattices

To better visualize the results of the nanoparticle adlayer growth as a function of template orientation, we include here plots of ideal (calculated) few-layer BCC (100), (110), and (111) crystals, shown from the side and in the x-y direction. 'A' and 'B' DNA functionalization are alternately shown in red and blue.

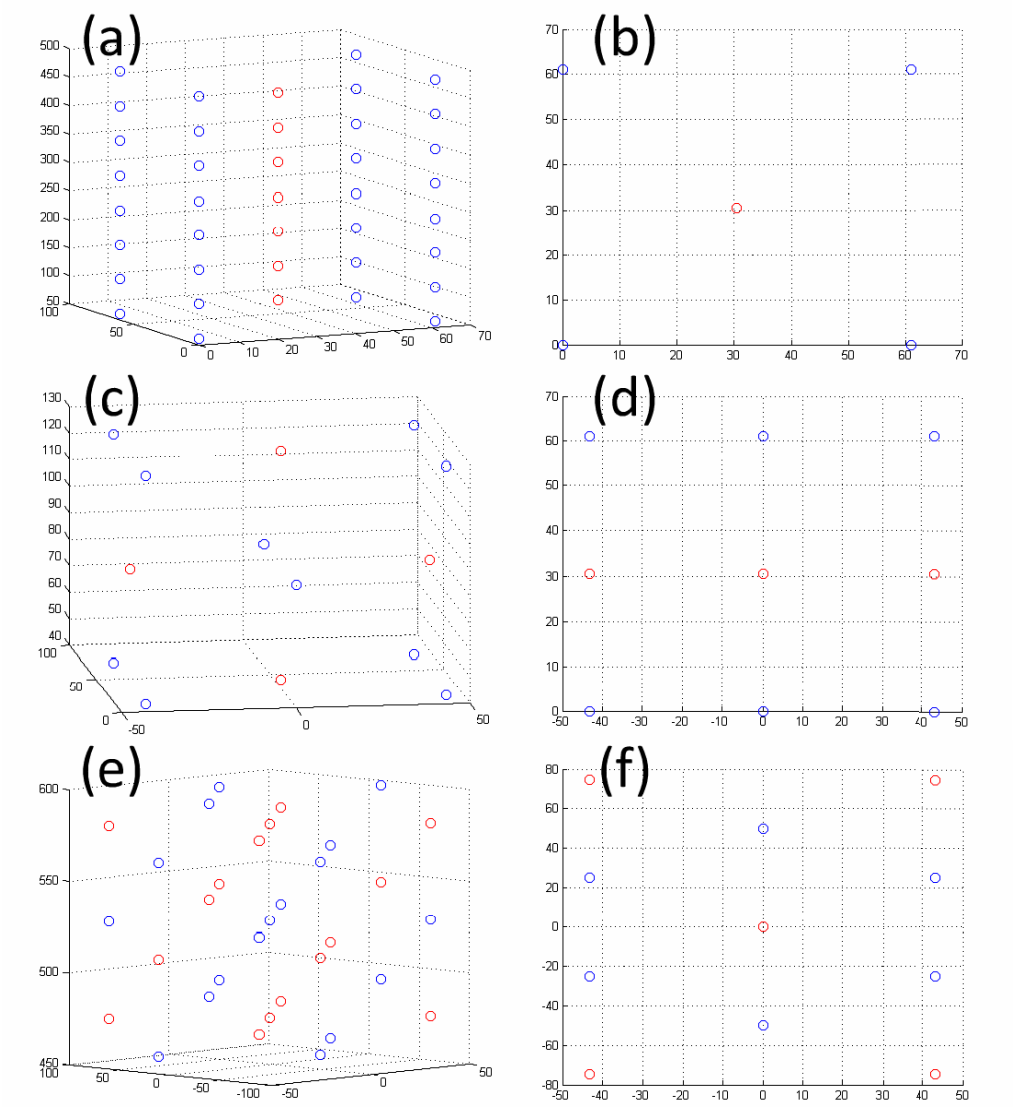


**Figure S1.** a) BCC (100) bulk lattice, side view. b) BCC (100) bulk lattice, top view. c) BCC (110) bulk lattice, side view. d) BCC (110) bulk lattice, top view. e) BCC (111) bulk lattice, side view. f) BCC (111) bulk lattice, top view.

**4) Additional Microscopy**

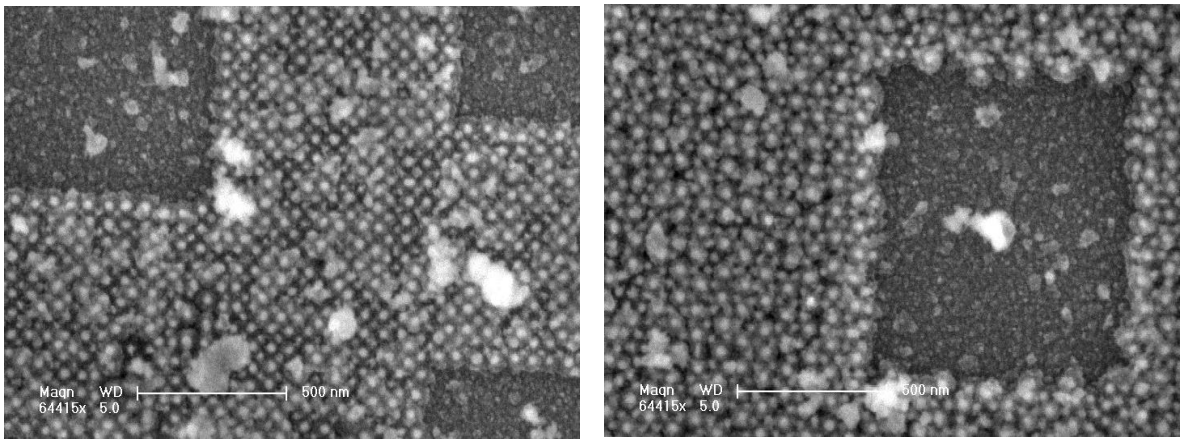


**Figure S2.** Monolayers grown on BCC (100, left) and (111, right) templates with square defects fabricated into the template lattice. The nanoparticle adlayer follows the template defect with high fidelity. All scale bars are 500 nm.

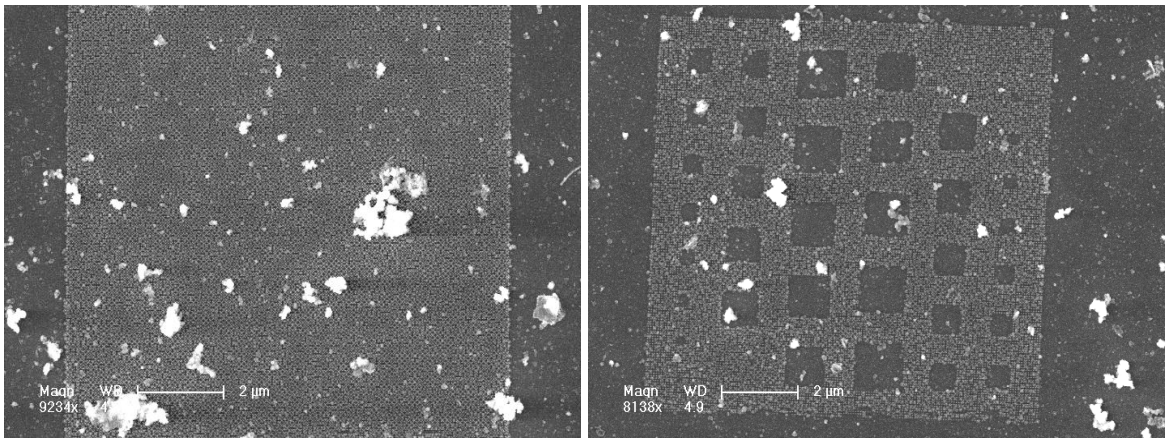


**Figure S3:** Low magnification images of BCC (100) templates with particles attached, to demonstrate the size scale of single grains accessible by the epitaxial growth technique. White residue is excess silica from the sol-gel embedding process. The right image has a series of prefabricated defects in the template. Both scale bars are 2µm.

**5) Sample Spread**

To illustrate the reproducibility of the data presented in manuscript Figure 2, we tabulate here the counted number of occupied corner, edge, and center sites for every BCC (100) lattice-matched crystal we have prepared to date.

| ID# | Site # | occupied corners | occupied edges | occupied centers |
|---|---|---|---|---|
| 1 | 1 | 0 | 68 | 339 |
| 1 | 2 | 2 | 22 | 88 |
| 2 | 1 | 1 | 44 | 253 |
| 2 | 2 | 1 | 48 | 268 |
| 2 | 3 | 1 | 23 | 164 |
| 2 | 4 | 0 | 16 | 166 |
| 3 | 1 | 6 | 72 | 354 |
| 3 | 2 | 7 | 40 | 417 |
| 3 | 3 | 3 | 16 | 138 |
| 3 | 4 | 1 | 31 | 199 |
| 4 | 1 | 8 | 80 | 212 |
| 4 | 2 | 11 | 42 | 124 |
| 5 | 1 | 58 | 180 | 16 |
| 5 | 2 | 29 | 89 | 4 |
| 6 | 1 | 3 | 14 | 547 |
| 6 | 2 | 1 | 2 | 571 |
| 6 | 3 | 1 | 5 | 560 |
| 6 | 4 | 4 | 12 | 586 |
| 6 | 5 | 0 | 5 | 210 |
| 6 | 6 | 0 | 0 | 266 |
| 7 | 1 | 0 | 30 | 298 |
| 7 | 2 | 0 | 35 | 283 |
| 7 | 3 | 4 | 29 | 321 |
| **Sums** | | 141 | 903 | 6384 |
| **%s** | | **1.90%** | **12.16%** | **85.95%** |

**Figure S4:** Number of occupied corner, edge, and center sites for BCC (100) lattice-matched crystals, including the total sum and percentage calculation as tabulated in manuscript Figure 2.

Importantly, over the >7000 attached particles, 23 crystal sites and 7 substrates that we prepared and characterized, only one substrate (#5) presented aberrational data. Data spread for alternate orientations and for strained samples are comparable.

**6) Grazing Incidence Small Angle X-ray Scattering (GISAXS)**

All GISAXS experiments were conducted at the 12ID-B station at the Advanced Photon Source (APS) at Argonne National Laboratory. The samples were probed using 12 keV (1.033 Å) x-rays at a sample-to-detector distance of approximately 3.5 m, calibrated using a silver behenate standard. Scattered radiation was detected using a Pilatus2M detector. The samples were kept in 0.5 M PBS buffer at all times to maintain the saline environment necessary for preserving Watson-Crick base-pairing.

Grazing Incidence Small Angle X-ray Scattering (GISAXS) was used to confirm the crystallinity of DNA nanoparticle superlattice thin-films. Here, superlattices were grown on an unpatterned DNA-modified Au coated Si substrate in order to provide the square mm sized area necessary for obtaining enough signal. The lattice parameter was determined from the position of the first order q* (110) peak. For a BCC crystal, the nearest neighbor interparticle distance, d, is

$$d = \mathrm{sqrt}(6)\, \pi / q^*$$

and the lattice parameter, a, is

$$a = 2\, d / \mathrm{sqrt}(3)\ .$$

From the GISAXS scattering pattern of DNA nanoparticle superlattice thin-films grown as described above, the $q_x^*$ peak at 0.0142 $Å^{-1}$ corresponds to a lattice parameter a = 62.5 nm.

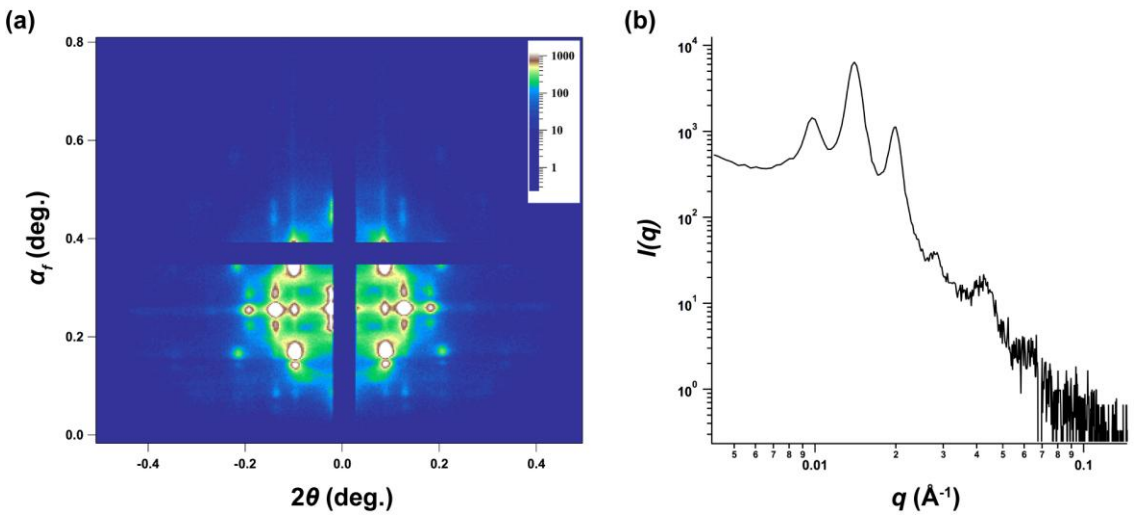


**Figure S5.** a) 2D GISAXS scattering pattern of thin-film DNA nanoparticle superlattices grown on unpatterned DNA functionalized Au coated Si substrates. b) A horizontal linecut of (a) taken at $\alpha_i = \alpha_f$. The peak at 0.01 Å$^{-1}$ comes from diffuse scattering, and the others correspond to various order reflections: 0.0142 Å$^{-1}$ (110), 0.022 Å$^{-1}$ (200), 0.03 Å$^{-1}$ (211), 0.04 Å$^{-1}$ (220), 0.042 Å$^{-1}$ (310).