Supporting Information: Ordered Two-Dimensional Superstructures of Colloidal Octapod-Shaped Nanocrystals on Flat Substrates

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DETAILED EXPERIMENTAL DESCRIPTION

The octapod-shaped nanocrystals used in the experiments were synthesized following protocols developed by us and previously published in Refs. [1, 2].

In a typical synthesis, 6 g of trioctylphosphine oxide, 160 mg of hexylphosphonic acid, 580 mg of octadecylphosphonic acid, and 120 mg of cadmium oxide (CdO) were placed in a three-neck flask connected to a Schlenk line. The flask was pumped to vacuum while the mixture was heated to 150 °C for 120 minutes under vigorous stirring, after which the solution was put under a blanket of nitrogen and the temperature was raised to 350 °C. At this point 1.6 g of trioctylphosphine (TOP) were injected with a syringe, and the mixture was allowed to recover to 350 °C. Previously prepared and purified $Cu_{2-x}Se$ nanocrystals were dissolved in TOP inside the glove box. A stock solution for the injection was prepared by dissolving 16 mg of elemental sulfur in 0.5 mg of TOP, and by subsequently adding the previously prepared and purified $Cu_{2-x}Se$ nanocrystals to this solution, such that the stock solution contained $0.3 \cdot 10^{-9}$ mol of $Cu_{2-x}Se$ nanocrystals. This solution was quickly injected in the reaction flask via a syringe, after which the resulting mixture in the flask was allowed to recover at the pre-injection temperature (i.e., 350 °C). The synthesis was stopped by removing the heating mantle, after which the flask was allowed to cool to room temperature. Depending on the reaction time, octapods with different pod length-to-diameter ratio (L/D) were obtained. For example, 6 to 7 minutes of reaction time yielded octapods with L/D ratios generally in a range around 4 to 5, while for reaction times of 10 to 12 minutes octapods with $L/D > 6$ were obtained. The octapods were isolated and purified by repeated precipitations (via slow addition of methanol), followed by centrifugation at 3,000 rpm for 10 minutes and re-dissolution of the precipitate in 5 ml of toluene.

The formation of the assemblies was tested on various substrates, namely: a) $\langle 100 \rangle$ highly polished silicon wafer; b) $\langle 100 \rangle$ highly polished silicon wafer coated with 20 nm of amorphous carbon; c) highly ordered pyrolytic graphite; d) Si_3N_4 membrane (See Fig. 1). In a nitrogen-filled glove box, 0.5 μL of a freshly prepared solution of octapods in toluene (with an octapod concentration of around 10^{-8} M) were drop-cast on the substrate, after which the solvent was allowed to evaporate at room temperature. Evaporation of the solvent varied from sample to sample, but in general did not take more than a few minutes. For example, it took around 5 minutes on silicon. The sample was then annealed to remove excess organics (which could not be entirely removed by the cleaning step). This was done by placing the sample on a hot plate, where it was heated to 200 °C (in about 60 seconds) and kept at this temperature for 30 minutes.

The sample observation was carried out in a high resolution scanning electron microscope (SEM) JEOL JSM 7500FA, equipped with a cold field emission gun which allows a resolution of 1 nm at 15 kV. Images were collected with an in-lens secondary electron detector (SEI) and, to avoid charging effects related to the excess of organics and to the presence of substrates with low conductivity, with a low-angle backscattered electron (LABE) detector.

ADDITIONAL SIMULATION DETAILS

We modeled the octapod-shaped nanocrystals by four hard inter-penetrating spherocylinders, which were constrained to move in a quasi-2D geometry, see Fig. 2a. The four spherocylinders intersect in their respective centers and are oriented along the $(\pm 1, \pm 1, \pm 1)$ directions of a standard Cartesian coordinate frame (the intersection point is located in the origin). The hard-particle model is completely described by the length-to-diameter ratio L/D of the spherocylinders, with L the length (excluding the hemispherical caps) and D the diameter. To emulate the quasi-2D geometry of the monolayers observed in the experimental system, in which the octapods touch the substrate with four tips, we constrained the centers of our octapod models to move in the xy-plane and imposed that the tips of the pods are coplanar with their centers. Effectively the octapods are sandwiched between two frictionless walls, with four tips touching the top and four tips touching the bottom wall (substrate), see Fig. 2a. The simulation box is only periodic in the direction parallel to the plane. Finally, it is important to note that another type of 'interlocking' can occur for the octapods

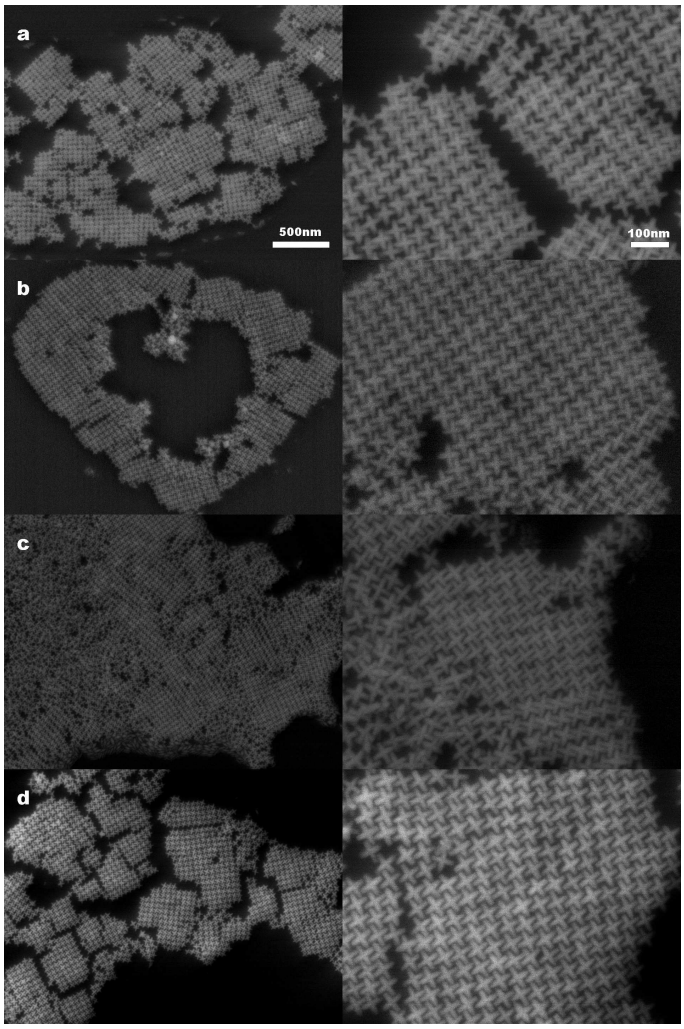

FIG. 1. Scanning electron microscopy (SEM) images of square lattices of octapods formed on four different substrates: a) ⟨100⟩ highly polished silicon wafer; b) ⟨100⟩ highly polished silicon Wafer coated with 20 nm of amorphous carbon; c) highly ordered pyrolytic graphite; d) Si_3N_4 membrane. For each sample, two SEM images (left/right) are reported at different magnifications. The scale bars are 500 nm and 100 nm, respectively.

in the quasi-2D geometry, as is illustrated in Fig. 2b.

In the isothermal-isochoric (NVT) ensemble Monte Carlo simulations (free-energy calculations) we only allowed translations in the xy-plane and rotations around the z-axis. For simulations in the isothermal-isobaric (NPT) ensemble, by which we determined the equations of state (EOSs), we used the same particle moves and only allowed the box to change its size and shape in the xy-plane. We define the reduced pressure as $P^* = PA/k_BT$, where k_B is Boltzmann's constant, T is the temperature, P is the pressure, and A is the planar area enclosed by the box. We express the density in terms of this area as well $\rho = N/A$, with N the number of

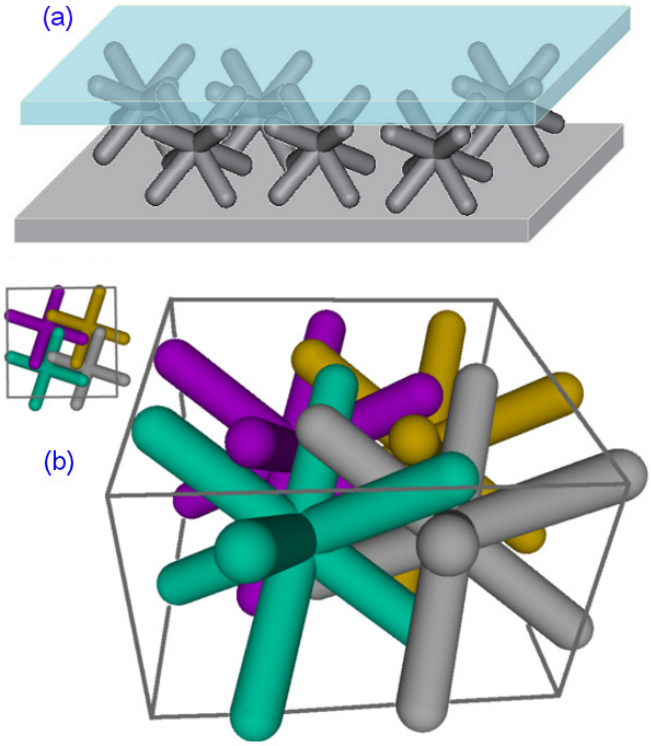

FIG. 2. (a) An illustration of the octapod model in the quasi-2D geometry we used. We constrain the bottom four tips to be in contact with the substrate; the octapods therefore effectively behave as if they are trapped between two frictionless walls. (b) A 3D image showing four model octapods in an interlocking configuration, the octapods have been indicated with different colors for clarity. The inset shows a top view of the 3D image, in which the arms of the interlocking octapods appear to overlap.

particles. The volume fraction occupied by the particles is defined as $\eta = \rho V_c/h$, where h is the height between the two confining walls and V_c is the volume of the octapod. We determined the height $h = L/\sqrt{3} + D$ using simple geometric arguments and V_c using Monte Carlo integration, for which we achieved a numerical precision of 4 decimals.

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[1] S. Deka et al., Nano Lett. **10**, 3770 (2010).
[2] K. Miszta et al., Nat. Mater. **10**, 872 (2011).