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Single-crystal Winterbottom constructions of nanoparticle superlattices

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Single Crystal Winterbottom Constructions of Nanoparticle Superlattices

AUTHOR NAMES.

Diana J. Lewis†‡, Leonardo Z. Zornberg†, David J.D. Carter‡ and Robert J. Macfarlane*,†

AUTHOR ADDRESS.

†Department of Materials Science and Engineering, Massachusetts Institute of Technology (MIT), 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States; ‡The Charles Stark Draper Laboratory, Inc., 555 Technology Square, Cambridge, Massachusetts 02139

*Address correspondence to rmacfarl@mit.edu

Abstract

Colloidal nanoparticle assembly methods can serve as ideal models to explore the fundamentals of homogeneous crystallization phenomena, as interparticle interactions can be readily tuned in order to modify crystal nucleation and growth. However, heterogeneous crystallization at interfaces is often more challenging to control, as it requires that both interparticle and particle-surface interactions be manipulated simultaneously. Here we demonstrate how programmable DNA hybridization enables the formation of single-crystal Winterbottom constructions of substrate-bound nanoparticle superlattices with defined sizes, shapes, orientations, and degrees of anisotropy. Additionally, we show that some crystals exhibit deviations from their predicted Winterbottom structures due to an additional growth pathway that is not typically observed in atomic crystals, providing insight into the differences between this model system and other atomic or molecular crystals. By precisely tailoring both interparticle and particle-surface potentials, we therefore can use this model to both understand and rationally control the complex process of interfacial crystallization.

Text

Crystallization is a complex process where multiple building blocks spontaneously form an ordered arrangement that reduces the free energy of the system. Because the time, length and energy scales associated with the synthesis of atomic crystals make studying their intricate formation pathways challenging, colloid-based models have often been employed to study crystallization behavior.[1–3] However, many of these models only examine crystal growth in solution, even though important technological processes often require the more complicated task of growing crystals at interfaces in order to allow for property measurement or integration into device architectures.[4–6] While models based on colloid sedimentation can provide interesting analogues for interfacial crystal growth, it remains difficult to fully tune the interparticle and particle-surface interactions that dictate crystal growth on surfaces.[7–10] As such, additional methods to study interfacial crystallization that can appropriately tune all interparticle and particle-surface chemical potentials must be developed to more readily use colloidal models to study crystal growth occurring on a surface.

DNA-grafted nanoparticles provide an ideal building block for studying crystal nucleation and growth on substrates, as previous investigations have shown that their crystallization behaviors in many ways accurately mimic traditional atomic crystal formation, earning them the moniker of "programmable atom equivalents" (PAEs) (Figure 1).[11] When appropriately designed and processed, these PAEs can therefore form many different crystal structures with controlled lattice parameters and crystallographic symmetries,[12,13] where the favored crystalline arrangement typically maximizes the number of DNA connections between particles.[14] For example, in a binary system consisting of two PAEs with complementary DNA sequences and identical PAE sizes, BCC lattices are formed upon thermal annealing. Additionally, by functionalizing a substrate with DNA complementary to the DNA strands on either one particle type or both, BCC crystal grains can be grown layer-by-layer from the substrate with (100) (densest plane consisting of a single particle type) or (110) (densest plane consisting of both particle types) planes bound to the substrate, respectively.[15]

These prior works indicate that PAE assembly can indeed be conducted at an interface, although they only were able to generate limited thickness polycrystalline films without control over crystallite size or shape; control over such factors may be desirable for manipulating various structure-property relationships.[5,6,11] However, in both atomic and PAE systems, slow-cooling of a material through its melting transition can result in single crystalline superlattices with surface facets that represent the lowest energy crystal planes.[16] In the presence of an interface, the thermodynamically preferred crystal shapes are polyhedra referred to as Winterbottom constructions.[17,18] These single crystal architectures are essentially Wulff polyhedra that are truncated at a plane and depth that depend on the crystals' orientation and the relative surface energies of crystal and substrate (Figure 1b). Assembling PAEs at an interface via slow-cooling through their melting transition therefore potentially allows for the synthesis of complex, single crystal superlattices that can be tailored as a function of both PAE and substrate design.

For a BCC system, the Wulff shape is a rhombic dodecahedron bound by {110} planes. When BCC-forming PAEs were slowly cooled through their melting transition in the presence of "mono-functionalized" substrates (i.e. coated with DNA linkers complementary to just one of the PAEs), the substrate-bound crystals adopted a square pyramid shape consistent with the truncation of a BCC rhombic dodecahedron along a (100) plane. Conversely, when the crystals were

formed in the presence of a "bi-functionalized" substrate (i.e. coated with two types of DNA strands, each one complementary to one of the PAE types in solution), flat-topped diamond structures were formed, consistent with truncation of a BCC rhombic dodecahedron along a (110) plane (Figure 1). In other words, the most favored single crystal architecture maximized the number of DNA connections between particles by forming a BCC lattice bound by {110} planes, and maximized the number of DNA connections to the substrate by orienting the single crystal so that the appropriate plane was parallel to the surface. Thus, DNA interactions between PAEs determines the nanoscale crystal unit cell, while DNA interactions between PAEs and the substrate determines the mesoscale crystal habit. Importantly, the introduction of an interface introduces design handles not present in solution-phase crystallization, and also alters the manner in which other parameters affect substrate-grown crystals compared with their solution phase counterparts. For instance, all interface-growth systems studied here showed a monotonic increase in crystal size with increasing PAE concentration (Figure 2 and Supplementary Figures 11-12), without altering the number of crystals on the surface. This unexpected trend contrasts prior solution phase work, which showed that crystal size decreases with increasing concentration of PAEs.[19] In principle, the nucleation rate should increase with increasing PAE concentration, resulting in an increased number of crystals and overall lower crystal size. The observed lack of increase in nucleation rate for substrate-bound crystals is hypothesized to arise because the concentration of PAEs in solution vastly exceeds the concentration that has been demonstrated to saturate the substrate[20,21]; this result was also corroborated using a two-dimensional Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach (see Supplementary Note 1 for calculations). There is therefore an equilibrium nucleation site density (N*) for these saturated surfaces that is dependent on the energy barrier associated with nucleation (ΔG*), but has no dependence on PAE concentration:

$$N^* = \theta^{n^*-1} n_s \exp\left(-\frac{\Delta G^*}{k_B T}\right) \tag{1}$$

where θ is the surface coverage (assumed to be constant in this system), n* is the critical cluster size for nucleation, n_s is the total density of surface sites.

While alterations to PAE concentration are therefore not expected to alter the number of substrate grown crystals, increasing the ionic strength of the solution should conversely have a large impact on crystal nucleation rate as it will

affect ΔG*. Because DNA is negatively charged, increasing the amount of counterions in solution strongly modifies the interactions between individual PAEs and between PAEs and the substrate. These interactions have been shown to be more complex than simple charge screening [22–24], meaning that fully understanding the complexity of this effect may require significant modeling of PAE assembly. However, prior work with the PAE design used here[20] has shown that at [NaCl] below 1.5 M, the combined result of these complex interactions resulted in increased surface coverage with increasing salt concentration. From this prior work, increasing the counterion concentration would be predicted to decrease the electrostatic repulsion both between individual PAEs and between PAEs and the substrate, increasing N*.[4] Further increases in [NaCl] beyond 1.5 M could result in the more complex phenomena noted above having significant effects on the interparticle and particle substrate interactions, but the model used here provides a beneficial simplification from which basic conclusions can be drawn (see Supplementary Note 1 and Supplementary Figure 3 for additional discussion).

As predicted, very few substrate-grown crystals were positively identified for crystals grown in solutions with only 0.5 M NaCl; the majority of observed crystals appeared to have formed in solution and subsequently adhered to the substrate (see Supplementary Figure 10 for details). An increase in buffer [NaCl], however, resulted in a proportional increase in the number of crystals grown on both the mono- and bi-functionalized surfaces (Figure 2b, Supplementary Figures 13-14). Interestingly, increasing [NaCl] also initially increased crystal size up to 1 M, but actually decreased crystallite size beyond this concentration (up to 4 M NaCl, Figure 2c). The initial increase is attributed to increased screening of charge between PAEs and the substrate, resulting in a higher probability of attachment. At 2 M and 4 M NaCl, the total volume of PAEs on the surface is larger than at 1 M NaCl (see Supplementary Figure 15); the decrease in crystal size at these concentrations is hypothesized to be partially due to the nanoparticles being distributed between a significantly higher number of crystals (and in patches of monolayers/bilayers surrounding the crystals). Additionally, as noted above, these higher salt concentrations could result in more complex interactions between particles, the net result being the observed decrease in crystal size.

Crystal growth can also be affected by providing a defect site at the surface from which crystals can nucleate and subsequently grow. On substrates with microscopic scratches, crystal nucleation rate was noticed to be significantly

increased, often resulting in large arrays of crystallites deposited across the entire scratched area (Supplementary Figure 19). Moreover, when the nucleation rate was high enough, these crystals grew into each other, resulting in anisotropic extension of the Winterbottom shapes; programmed deformation of the substrate could therefore potentially be used to grow faceted anisotropic single crystals.

In addition to controlling the size and orientation of single crystals, interfacial crystallization allows for manipulation of the degree of anisotropy in crystal shape. The Winterbottom construction determines the geometry of a fixed volume of material through minimization of surface energies, including both the crystal-fluid and substrate-fluid interfaces. The resulting shape therefore equates to a Wulff polyhedron that "wets" the substrate, where the wetting angle, α, follows Young's equation:[25]

$$\alpha = \cos^{-1}((\gamma_{sc} - \gamma_{sf})/ \gamma_{cf}) \qquad (2)$$

where γ_{sc}, γ_{sf}, and γ_{cf} are the relative surface energies between the crystal and substrate, the substrate and fluid, and the crystal and fluid, respectively. Thus, the more negative γ_{sc} becomes relative to γ_{cf} (i.e. the higher the PAE affinity for the surface), the more recessed and less isotropic the thermodynamically preferred shape becomes (see SI for additional calculations).

Importantly, the PAE model system presents a unique opportunity to explore interfacial crystallization using building blocks where these relative surface energies can be controlled independently from the crystal unit cell geometry. Again, for most PAE designs (including those examined here), the most favored crystallographic symmetry for a set of PAEs is typically the one that maximizes the number of DNA connections formed. Therefore, changes to the absolute number of DNA strands on each particle in a binary system do not significantly change the lattice parameters or favored crystal symmetry so long as the ratio of DNA strands on the complementary particles remains the same.[14] By using the DNA grafting densities on the particles and the substrates as independently tunable design handles, the relative PAE-PAE and PAE-substrate interaction potentials can be controlled separately from one another. Specifically, reducing the number of DNA strands on the nanoparticles decreases the number of dangling bonds at a crystal surface, resulting in a less positive surface energy of the crystal without altering the substrate-fluid interaction. Additionally, the substrate can be

loaded with a percentage of dummy strands (DNA strands that are identical in length but lack complementary binding), thereby altering the interfacial energy between the crystal and the substrate without changing the substrate-fluid or crystal-fluid surface energies. Loading the substrate with a higher percentage of dummy strands results in fewer bonds between PAEs and the surface while maintaining the repulsion from negatively charged DNA. By lowering the number of DNA connections but maintaining the amount of electrostatic repulsion, PAEs have less affinity for the surface, which should result in the crystals favoring a crystallite shape that protrudes further from the substrate.

The resulting crystal formations for various combinations of 25-100% substrate loadings (i.e. 75-0% dummy strands) and PAE loadings of 40-100% of the maximum DNA grafting density were therefore compared to computationally predicted Winterbottom shapes (Figure 3, additionally see Supplementary Figure 6 for quantification and Supplementary Figure 16 for mono-functionalized data).[25] As expected, decreasing the linker density on the nanoparticles resulted in the crystals becoming more recessed into the surface. Additionally, increasing active linker loading on the substrate also caused an increase in surface wetting, and again resulted in "flatter" crystals.

Interestingly, as the number of DNA strands on the PAEs was decreased and/or substrate active linker loading was increased, it was observed that individual particles, then partial bilayers, and finally full multilayers surrounded the base of each crystal. Additionally, as the number of PAEs in these mono- and multilayers increased, the <110> oriented single crystals exhibited increasing deviation from the predicted Winterbottom constructions. While the crystals on these bi-functionalized substrates remained faceted by (110) planes, the narrow ends of the diamond were not truncated at the vertical (110) planes. Instead, the (110) edge facets of the diamond extended, eventually fully eliminating the vertical (110) plane altogether (Figure 4). Because this deviation from the Winterbottom construction is not commonly observed in atomic or molecular surface-grown crystals[11, 25], it potentially offers insight into the crystallization pathway for this model colloidal system.

The discrepancy is hypothesized to arise due to a particular crystal growth pathway that leads to the formation of kinetic traps. Based on prior work, it is known that substrate-bound PAEs at elevated temperatures can readily diffuse across the surface without fully dissociating from it.[20] This allows the PAEs to migrate to the edges of the crystals, providing the growing crystals with an additional source of particles to those impinging from the solution. A simple geometric

argument shows that when crystals grow via this surface diffusion mechanism, the tip grows faster than the rest of the sides given the same impingement rate along the line between the crystal and the substrate. This diffusion-mediated crystal growth is supported by the incomplete layers of PAEs observed around the sides of the crystals (e.g. Figure 1c and 4a). Calculation of the relative energy difference between these "diamond" shapes and the true Winterbottom constructions (Figure 4c, Supplementary Figures 7-9) show that as the height of the crystal decreases, the difference in surface energies between the kinetic "diamond" shape and the thermodynamically preferred Winterbottom construction becomes smaller, explaining why the kinetic structure does not have the driving force to rearrange in systems where PAE-PAE binding is weaker relative to PAE-substrate binding. Further evidence for the surface diffusion mechanism arises from observations of crystals that formed in solution and subsequently landed on the substrate and started to rearrange. When this rearrangement occurred via surface diffusion, the kinetic tips formed, while bulk rearrangement showed the Winterbottom shape (Supplementary Figure 20).

Notably, while PAEs can produce many different crystallographic symmetries beyond the simple BCC lattice, only BCC and CsCl-type crystals have been shown to form single crystal thermodynamic end products via slow cooling in solution.[12] For example, FCC-type PAE lattices (generated from PAEs with self-complementary DNA sequences) formed via slow cooling are typically polycrystalline structures with a significant number of stacking faults along {111} planes oriented along many different angles.[16] Additionally, while AlB$_2$-type systems (created using two sets of complementary PAEs that are slightly different in their overall particle radii) do produce highly ordered single crystals, they do not form true Wulff polyhedra due to the complicated growth kinetics for different facets of the AlB$_2$ lattice.[26]

Importantly, PAEs assembled at a substrate tend to form 2D hexagonally-close-packed (HCP) monolayers when thermally annealed.[20] In the FCC system, it was therefore hypothesized that using a substrate would stabilize the (111) plane, as particles in this plane form a 2D HCP arrangement. Making one particular crystal orientation significantly favored should limit the possibility for the formation of non-parallel stacking faults between HCP layers that would be difficult to anneal out of the system. Indeed, by appropriately tuning the interparticle and particle-surface energies as discussed above (see Supplementary Figure 17 for linker experiments with FCC), single crystal FCC structures were readily observed with the (111) plane parallel to the substrate (Figure 5a and b, full description of PAE designs in

Supplementary Materials). Similar to the FCC lattice, the (001) planes of AlB_2 lattices also consist of a 2D HCP layer of one of the particle types. When substrates were functionalized with DNA complementary to only the particle type that forms these HCP layers, the PAEs formed hexagonal pyramids (Figure 5c and 5d, Supplementary Figure 18), as predicted by the Winterbottom construction (right insets, Figure 5a and c, and Supplementary Figures 4-5). Therefore, by using the surface as a design handle to preferentially stabilize particular crystal facets, single crystal architectures previously unachievable to solution-phase crystal growth can readily be obtained, highlighting the unique tunability of interfacial-drive crystal formation.

Here we have shown that crystallization of multiple PAE crystal habits can occur on substrates in a manner analogous to atomic systems, and the morphology and density of the crystals can be controlled as a function of multiple orthogonally addressable design handles, ultimately forming lattice shapes that can be explained via the Winterbottom construction. The ability to grow nanoparticle crystals of controlled shapes, dimensions, and surface densities at an interface enables future studies to better understand how interfacial crystal growth occurs, examining processes like nucleation, grain growth[27] and surface dewetting.[28] PAE crystals have been demonstrated to be effective models for crystal growth, and extending our understanding to more heterogeneous growth conditions, as well as noting and explaining ways in which PAE crystal growth deviates from prediction based on atomic crystallization is crucial for advancing the field. Moreover, the ability to generate these surface-bound Winterbottom constructions potentially allows for use of these PAE crystals in a wider range of applications where both nanoscale and mesoscale architecture are important in dictating material properties, such as optical resonators[5], chemical or biological sensors,[29] or soft structural materials.[30] Thus, the ability to tune single crystal interfacial growth via programmable DNA hybridization should enable significant future studies in the field of crystal growth.

Methods

Oligonucleotide design and sequences (Supplementary Figure 1 and Supplementary Table 1), gold nanoparticle production (Supplementary Figure 2), functionalization procedures and silica embedding procedures are detailed in Supplementary Methods. Briefly, two sets of 20 nm gold nanoparticles were functionalized with different anchor-strand DNA through a salt aging procedure.[31] Substrates were functionalized with a third type of anchor strand by immersing

in a concentrated 5 µM oligonucleotide, 0.5 M NaCl solution overnight. The use of three anchor strands prevented cross-contamination of the linker strands at elevated temperatures. 6 M and 0.5 M phosphate buffered saline, both types of nanoparticles, and duplexed linker strands complementary to the particle anchor strands were added to a microcentrifuge tube in ratios that achieved the desired salt and nanoparticle concentrations, as well as appropriate linker loadings, at a total volume of 50 µL. The addition of the linker strands caused the aggregation and precipitation of the PAEs. Then 3.5 mm x 3.5mm gold-coated quartz substrates were wedged vertically into the tubes (fully immersed), and duplexed linkers complementary to the substrate (both active and dummy strands at the appropriate ratios) were added to achieve a ~10-fold excess of substrate linkers in solution. (Heating above the melting temperature caused the linkers to diffuse away from the substrate; without an excess, the resulting dilute solution of linkers did not re-attach in sufficient quantity to initiate crystallization.) All tubes were vortexed to disperse the aggregates into solution immediately prior to placement in a thermal cycler (Techne 5Prime/05) and slow-cooled from 65 °C to 25 °C at 0.1 °C/10 min. After crystal formation, all substrates were placed in 0.5 M PBS and underwent the silica embedding procedure described in the Supplementary Information. Once silica embedded, the substrates were rinsed in DI water and allowed to air dry before SEM imaging (Zeiss Supra 35VP). ImageJ was used for all image analysis.

Data Availability

The data supporting the findings of this study are available within this article and its Supplementary Information, or from the corresponding author on reasonable request.

Supporting Information. Experimental procedures, including oligonucleotide sequences, nanoparticle functionalization and assembly, substrate preparation, and characterization/analysis techniques (SEM and AFM) are available in Supplementary Methods. Additional calculations and experiments are provided in Supplementary Note 1 and 2, respectively.

Author Contributions

Experiments were designed by DJL, DJDC and RJM. DJL conducted experiments. DJL and LZZ performed data analysis. DJL, LZZ, DJDC and RJM wrote the manuscript.

Notes

The authors declare no competing financial interest.

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Figure Captions:

Figure 1: Substrate Growth of Crystals into Winterbottom Shapes

Nanoparticles functionalized with complementary DNA (a) slow-cooled in the presence of a DNA-functionalized substrate will grow single crystal Winterbottom shapes that are truncated Wulff polyhedra (b). Depending on the substrate functionalization, <100> or <110> oriented crystals can form, producing pyramidal (c, d) or diamond (e, f) shaped PAE single crystals on the surface. Scale bars are 1µm.

Figure 2: Salt Concentration Effects on Crystal Growth

a) SEM images of <110> oriented crystal growth in different salt concentrations and PAE concentrations, showing increased crystal density with increasing salt concentration, and increased size with increased PAE concentration. Scale bars are 2 µm. b) Quantification of increased crystal density with increasing salt concentration for both <100> and <110> crystal growth. c) Crystal size as a function of salt concentration, which initially increases between 0.5 M and 1 M [NaCl], then decreases with further salt addition, likely due in part to the same quantity of PAEs being distributed between an increased number of crystals. Irregularly shaped particles in 0.5 and 1 M images are excess silica particles generated during the embedding process; these silica particles do not contain PAE crystallites. Error bars in b) and c) are standard deviations computed from at least 7 measurements.

Figure 3: DNA Loading Effects on Winterbottom Shape

a) Increasing DNA loading on the nanoparticles (images from left to right) increases the crystal surface energy, resulting in a less recessed crystal. Increasing the percentage of active DNA strands on the substrate (images from top to bottom) decreases the crystal-substrate interfacial energy, resulting in a more recessed crystal. Low substrate linker loadings coupled with high PAE loadings (upper right images) did not result in identifiable crystal formation on the substrate – crystals shown were likely deposited from solution, as evidenced by the random orientations of the observed crystals.

Scale bars are 1 μm. Note that the silica embedding process used to solidify the crystals for imaging causes DNA lattices to shrink by about 5%; on a substrate, the positions of PAEs at the bottom of the crystal are fixed, causing the top of the crystal to shrink more than the bottom. The resulting strain causes cracking of some of the crystals, particularly visible on some of the large, shallow crystals (75% substrate loading, 40 and 60% PAE loading). Insets show relation to b), the predicted Winterbottom shapes for various surface energy ratios, colored as a function of the difference between the surface energy of the substrate-to-crystal interface and the substrate surface energy (normalized to a crystal surface energy value of one).

Figure 4: Deviations from Winterbottom Construction

a) Crystals on substrates with high PAE-substrate affinities deviate from the predicted Winterbottom shape (inset). b) These deviations are likely due to PAEs adding to the growing crystals by diffusing to the crystal from the substrate. c) With lower interfacial energies of the crystals, the energy difference between the initial kinetically formed shape and the thermodynamically preferred Winterbottom shape decreases, removing the driving force to rearrange. Inset shapes show shapes corresponding to the relative surface energies as in Figure 3b. Scale bars are 1 μm.

Figure 5: FCC and AlB2 Crystal Growth on Substrates

a) FCC crystal, conforming to the predicted Winterbottom construction (inset), with confirmed <111> orientation (b).

c) AlB2 crystal, conforming to predicted Winterbottom construction (inset) with the <100> orientation (d). Scale bars are 1 μm for a) and c), 200 nm for b) and d).