The Importance of Salt-Enhanced Electrostatic Repulsion in Colloidal Crystal Engineering with DNA

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ABSTRACT: Realizing functional colloidal single crystals requires precise control over nanoparticles in three dimensions across multiple size regimes. In this regard, colloidal crystallization with programmable atom equivalents (PAEs) composed of DNA-modified nanoparticles allows one to program in a sequence-specific manner crystal symmetry, lattice parameter, and, in certain cases, crystal habit. Here, we explore how salt and the electrostatic properties of DNA regulate the attachment kinetics between PAEs. Counter-intuitively, simulations and theory show that at high salt concentrations (1 M NaCl), the energy barrier for crystal growth increases by over an order of magnitude compared to low concentration (0.3 M), resulting in a transition from interface-limited to diffusion-limited crystal growth at larger crystal sizes. Remarkably, at elevated salt concentrations, well-formed rhombic dodecahedron-shaped microcrystals up to 21 μm in size grow, whereas at low salt concentration, the crystal size typically does not exceed 2 μm. Simulations show an increased barrier to hybridization between complementary PAEs at elevated salt concentrations. Therefore, although one might intuitively conclude that higher salt concentration would lead to less electrostatic repulsion and faster PAE-to-PAE hybridization kinetics, the opposite is the case, especially at larger inter-PAE distances. These observations provide important insight into how solution ionic strength can be used to control the attachment kinetics of nanoparticles coated with charged polymeric materials in general and DNA in particular.

Colloidal crystals composed of nanoparticles are structures that can be designed to have interesting optical and electronic properties, based upon nanoparticle composition, crystal lattice symmetry and spacing, and mesoscopic crystal habit and size.‡,‖ Because of their chemical programmability and sequence-specific interactions, oligonucleotides have emerged as versatile ligands to direct the assembly of nanoparticles into higher order crystalline architectures.§,‖ Indeed, nanoparticles functionalized with a dense shell of upright and oriented DNA behave as "programmable atom equivalents" (PAEs) that can be assembled into a diverse set of crystalline structures following well-established design rules.†,§,‖,15

The size of colloidal crystals is an important design parameter for the preparation of device architectures, particularly those requiring control over the optical path length (i.e., the distance that light travels across the crystal in the orientation of interest).†,‡,‖,16 However, methods for realizing single crystals with tunable sizes have yet to be developed. Single crystals generated by the slow cooling of PAEs typically fall in the 2 μm or less range when synthesized in solutions with monovalent salt concentrations between 50 and 500 mM.‡ Silver ion § and molecular intercalators ‖ have been used to postsynthetically strengthen DNA bonds within such crystals, which have subsequently been utilized as seeds for controlling the extended growth of crystals.‖

In atomic systems, large crystals can be realized by kinetically impeding the formation of critical nuclei. This can occur by either: (i) suppressing the formation of new nuclei, or (ii) expediting the growth of existing crystals to deplete the solution of the atom source (e.g., heterogeneous nucleation and growth).20 In the context of colloidal crystal engineering with DNA, salt concentration can be used to control the kinetics of DNA bond formation.21 At moderate monovalent salt concentrations (below 0.5 M), the kinetics of PAE interactions cannot be explained solely by charge screening as the association of ions becomes favorable via ionic correlations, resulting in the formation of ion clusters.22,23 This has been explored experimentally where high salt concentration causes long-range repulsion between nanoparticle surfaces26 and stabilizes dispersions of charged
colloids in molten salts.27 Furthermore, simulations have shown that the strength of interparticle interactions depends on the surface charge density of nanoparticles; at high salt concentration, weakly charged nanoparticles have a depletion-type attraction, whereas nanoparticles with moderate to high surface charge densities experience long-range repulsion attributed to ionic correlations.25 In particular, for DNA-mediated colloidal assemblies, high salt concentration has been shown to induce phase transitions28 and nanoparticle aggregation in the absence of hybridization interactions.29 However, it is difficult with the current tools to gain a full understanding of the mechanism of how surface grafting densities and electrostatic energies cause salting out.25,29 For nanoparticles grafted with strongly charged polymer chains at similar grafting densities (e.g., PAEs), the effective screening length was measured to be between 2 and 5 nm as opposed to the sub-nanometer length predicted by DLVO.25 Consistently, above certain salt concentrations, simulations that include hybridization interactions show short-range attraction from hybridization interactions at distances where the DNA coronae overlap and longer range repulsion extending to distances where they do not overlap (Figure 1B). This results in an energetic barrier greater than the thermal energy (kBT) (i.e., the thermal fluctuation of the system must cross over the nucleation barrier to initiate crystallization), which slows the attachment kinetics between complementary PAEs. Thus, we hypothesize that the PAEs assemble to form larger crystals at higher solution ionic strengths due to this nucleation barrier (Figures 1C, S1–S2).

To investigate whether PAE assembly at elevated salt concentrations leads to the growth of larger microcrystals, two sets of 15 nm spherical PAEs with complementary DNA sequences were prepared. Each sample was assembled in solution at three different salt concentrations (0.3, 0.5, and 1 M NaCl) and experimental results (DNA melting temperature increases with increasing salt concentration. (C) Mean crystal size obtained without coarsening as a function of the attachment rate to the surface.}

**RESULTS AND DISCUSSION**

To explore the free-energy landscape across which nucleation takes place with varying salt concentrations, molecular dynamics (MD) simulations were used to calculate PAE interaction potential energies (Figure 1A). These simulations used a PAE design consisting of two 15 nm spherical gold nanoparticles, each functionalized with one of two DNA sequences bound to linker strands with complementary “sticky ends” (Figure 1). These PAEs assemble into bcc superlattices. The foundation for these simulations is based on the assumptions that (i) the interaction between the complementary PAEs is the main driving force for crystallization, (ii) the interaction with the second nearest neighbors (i.e., noncomplementary PAEs) is negligible, and (iii) similar trends in the free energy are observed at room temperature (25 °C) and elevated temperature. Effective pair potential energies were calculated by modeling two complementary PAEs at 25 °C with the 3SPN force-field, which included DNA-hybridization attraction, stacking interactions, excluded volume repulsion, and electrostatic interactions between phosphate groups and explicit ions.30,31 The strong parallels between the modeled and experimental results (DNA melting temperature increases with increasing salt concentration) indicate that the binding energy between the PAEs increases with increasing salt concentration (Figures 1B, S4).

The impact of salt concentration on the interaction potential between a pair of PAEs was studied by calculating the potential energies as a function of interparticle distance (i.e., core-to-core distance) ranging from 30 to 40 nm. Previous studies on nanoparticles with noncomplementary DNA strands exhibit repulsion forces between nanoparticles that are longer range than the repulsion predicted by DLVO theory when the salt concentration increases above 0.3 M.25 which is in agreement with experiments on repulsion between charged surfaces at high monovalent salt concentrations.16,27 This electrostatic interaction depends on multiple factors, including grafting density, temperature, and ionic strength, and can even lead to salting out.25,29 For nanoparticles grafted with strongly charged polymer chains at similar grafting densities (e.g., PAEs), the effective screening length was measured to be between 2 and 5 Å, the attachment barrier peaks; this increases with increasing salt concentration (Figures 1C, S1–S2).
M NaCl) and then slowly cooled. This process enables DNA-driven crystallization that favors the formation of single-crystalline rhombic dodecahedra with the gold nanoparticles in a bcc crystallographic symmetry (over a polycrystalline assembly). The effect of salt concentration on PAE assembly above 1 M NaCl was not probed in this study because the PAEs no longer crystallize into rhombic dodecahedron single crystals. Single crystals were chosen as the subject of this study because the crystal domain size is easier to identify and compare between samples. Superlattices were then characterized by small-angle X-ray scattering (SAXS), electron microscopy (EM), and selected area diffraction (SAD).

First, SAXS line shape analysis was used to deconvolute peak broadening arising from grain size and microstrain (Figure S6), and the grain sizes were compared using Williamson-Hall analysis (Figures 2A, S7). Stokes-Wilson strain broadening can be combined with Scherrer size broadening in scattering peaks to extract information about grain size (eqs S12–13). Consistent with both the hypotheses and the calculations of interaction potentials, a significant increase in average grain size is observed when the salt concentration was increased from 0.5 to 1 M for nanoparticle assemblies using both six- and seven-base pair sticky ends (Figures 2A, S7). This further confirms the assumption that similar trends in the free energy are observed at different temperatures. Although the grain size generally increases with increasing salt concentration, it decreases with increasing particle concentration (Figure S8). A decrease in mean crystal size with increasing particle concentration can be attributed to the increase in chemical potential (eq S2). Since the nucleation rate is strongly dependent on the chemical potential of the system, increasing the chemical potential leads to a faster nucleation rate (i.e., a greater number of nuclei forms), and thus, the formation of smaller microcrystals is expected. Note that the chemical

Figure 2. (A) Williamson-Hall analysis of SAXS data (Figures S5–S6) can be used to deconvolute peak broadening arising from grain size (intercept) and microstrain (slope). (B) Scheme (top) showing the dimension that was measured for the statistical analysis of crystal size distribution using SEM images. (i), (ii), and (iii) are schematic representations of three different orientations of the microcrystals commonly observed on the substrate. The length “a” (edge length) was measured and mathematically converted to convey the length shown in the top drawing. Size analyses of approximately 150 microcrystals, assembled at (C) 0.3, (D) 0.5, and (E) 1 M NaCl, show an increase in average crystal size with increasing salt concentration. SEM images of silica-encapsulated bcc gold nanoparticle microcrystals, interlinked with DNA and assembled at (F) 0.3, (G) 0.5, and (H) 1 M NaCl confirm faceted rhombic dodecahedra. For this set of data, nanoparticle assemblies were done using complementary seven-base pair sticky ends. Scale bars are 2 μm.
potential difference is a thermodynamic driving force for crystallization.

To further examine the effect of salt concentration on crystal size along with crystal habit (e.g., facet), we used SEM to determine the size distribution of approximately 150 microcrystals for each salt concentration. Since the formation of microcrystals mediated by the slow cooling approach is similar to conventional homogeneous nucleation (i.e., the crystallization starts from dispersed precursors), a broad range of crystal sizes is expected from classical theory. To prepare samples for SEM imaging, slow-cooled samples were encapsulated in silica using a sol–gel process,\(^{33}\) dispersed in 50% EtOH in water, and slowly dried on a silicon substrate. Although microcrystals generated in solution with different salt concentrations are all rhombic dodecahedra (Figure 2F–H, S9–S10), the overall crystal size increases with increasing salt concentration (Figure 2C–E). Because the microcrystals dried on a substrate lie in different orientations on the substrate, mathematical corrections on each measurement of “a” (edge length) were performed (Figures 2B, S11, Table S2). SEM results show similar size distributions for the 0.3 and 0.5 M salt concentration samples with mean sizes of 3.6 ± 1.6 and 3.5 ± 1.3 \(\mu m\), respectively (Figure 2D, E). However, similar to the conclusions drawn based on the SAXS data, a noticeable increase in the crystal size distribution is observed for the 1 M NaCl sample with a calculated mean size of 4.9 ± 2.6 \(\mu m\) (Figure 2F). As noted earlier, a wide distribution of crystal sizes is predicted for crystal growth via homogeneous nucleation and growth. However, it is worthwhile to note that in addition to the average crystal size analyzed from both SEM and SAXS (Figures 2A, 2C–E, S7), the number of crystals that are smaller than 2 \(\mu m\) decreases drastically with increasing salt concentration; i.e., there were no crystals below 2 \(\mu m\) in the 1 M NaCl sample (Figure 2C–E). Remarkably, these crystals can grow up to 21 \(\mu m\) (the length shown in Figure 2B, top) when the PAEs are assembled at high solution ionic strength (Figure 2H).

The crystallization process is usually described by the formation of critical nuclei (i.e., nucleation) followed by subsequent growth. Generally, the nucleation rate is dependent on both the energy barrier of nanoparticle cluster formation and the attachment rate of the interacting nanoparticles. An emergence of long-range repulsion at high salt concentration (Figure 1B) results in a reduction of the attachment rate, which can be understood from the following relationship:

\[
j = v_0 \exp(-\Delta G^*/k_BT)
\]  

(1)

where \(j\) is the frequency at which two nanoparticles come together, \(v_0\) is the trial rate (a constant, units in 1/time), and \(\Delta G^*\) is the repulsion barrier that nanoparticles must overcome to initiate crystallization (see Simulation section in the Supporting Information for detailed discussion). Thus, from this equation, one can extract that the frequency of nanoparticle attachment events decreases exponentially with an increasing energy barrier. In the case where the long-range diffusion is required, two rate-limiting processes, interface- and diffusion-limited growth, affect the growth rate. The initial stage of crystal growth is limited by interfacial attachment barriers. In this regime, crystal size increases linearly with time (crystal size \(\approx At\), where \(A\) is the growth rate proportional to \(j\) and \(t\) is the time).\(^{34}\) In the case where the nanoparticle attachment occurs extremely fast (i.e., nanoparticle interactions are extremely favorable and \(j\) is large), no interface-limited regime is present, and crystals with irregular shapes and disordered nanoparticles form.\(^{35}\) However, in the case of slow attachment rates (i.e., \(j\) is small), faceted microcrystals form. When most of the nanoparticles are consumed, diffusion can no longer sufficiently transport materials to the crystal–solution interface. Beyond this regime, crystal growth is limited by diffusion, where the growth rate is significantly slowed (crystal size \(\approx t^{1/2}\)).\(^{36}\) The growth rate in this regime is entirely determined by the diffusion constant and the supersaturation, given by \(\epsilon = \epsilon_0\), where \(\epsilon\) and \(\epsilon_0\) are the current and equilibrium concentrations of the free nanoparticles in solution, respectively. The transition between interface-limited to diffusion-limited regimes has been reported for colloidal crystals using MD simulations.\(^{37}\)

The combination of MD simulations and experiments suggests that the reduction in the PAE attachment rate at 1 M NaCl likely impedes the formation of stable clusters/critical nuclei and drastically slows the interface-limited regime, meaning the system at high salt conditions enters the diffusion-limited regime much later than the other two systems. Thus, by suppressing nuclei formation, large single crystals are realized. Since this phenomenon occurs at a large interparticle distance (i.e., before the particles are fully locked into a particular structure) and solely depends on the interactions between salt ions and the DNA corona, this approach can be generalized for different particle cores and lattice symmetries. We presume that a similar trend will be observed when the rate of cooling is changed. It is worth noting that there is a possibility of large crystal growth occurring through coalescence and restructuring processes, where two or more stable crystals merge to form a single crystal. In atomic systems, coarsening typically occurs by Ostwald-like ripening processes;\(^{38}\) however, this process is very slow and unlikely to occur in colloidal systems. On the other hand, it has been shown that the coarsening in colloidal systems could happen by grain-rotation induced coalescence.\(^{39}\)

Similar coarsening has been observed for PAE systems in MD simulations (see Simulation section in the Supporting Information for further discussion).\(^{37}\)

Because defects and inhomogeneity in the superlattice can affect the optical response of these materials, it is crucial to produce high-quality crystals.\(^{40}\) Each SAXS pattern shows, regardless of the solution ionic strength, a high degree of single-crystalline ordering of nanoparticles arranged into a bcc crystallographic symmetry (Figure S5). The crystallinity was further characterized by performing SAD using a transmission electron microscope (TEM) (Figure 3). This characterization

**Figure 3.** (A) and (B) Transmission electron microscopy (TEM) images of a thin (~100 nm) section of silica-encapsulated microcrystals, initially crystallized in 1 M NaCl. (C) Well-defined SAD patterns were obtained by subjecting a parallel beam of high-energy electrons to a thin section of one of the large microcrystals shown in (B). Scale bars are 5 \(\mu m\), 200 nm, and 100 \(\mu m\) for (A), (B), and (C), respectively.
technique provides a diffraction pattern of a thin crystalline specimen within a selected area, which can be used to identify local crystal structures and examine defects, such as twinning and dislocations. Here, we used SAD to qualitatively evaluate the crystallinity of local areas within these microcrystals. Indeed, the appearance of distinct spots in the diffraction patterns of a large single crystal indicates high-quality crystals and that the microstrain is mostly isotropic without random defects (Figure 3C).

Furthermore, it is important to have independent control over the interparticle distance, while retaining crystallinity and habit, because each structural control can be used to influence material properties. A uniform shift in peak position, however, indicates that there is a 5% decrease in the DNA bond length as the salt concentration is raised from 0.3 to 1 M (Figure 4A).

![Figure 4](image-url)

**Figure 4.** (A) The bcc unit cell lattice parameter at different salt concentrations. (B) The change in lattice parameters induced by salt is reversible. The arrows from (i) to (ii) and (iii) to (iv) show the changes in lattice parameters after 1 to 0.3 M and 0.3 to 1 M salt exchange, respectively.

However, since the interactions between the DNA bonds and ions are electrostatic in nature, the lattice parameters of these superlattices can be altered simply by salt exchange (Figure 4B). By changing the salt concentration after the crystals are grown, the salt-induced transition in interparticle spacing is fully reversible, and SAXS patterns collected before and after salt exchange do not show noticeable changes in the SAXS peak widths (Figures 4, S13).

Taken together, the conclusions presented here reveal the properties of polyelectrolyte brushes of nanoparticle-based DNA bonds and provide a powerful way to alter the attachment kinetics of PAEs to control mesoscale crystal size. Importantly, PAE crystallization at elevated salt concentrations can be used to synthesize colloidal single crystals over a significantly larger length scale. Furthermore, through postsynthetic salt exchange process, the salt-induced transition is fully reversible. The extension of this work to different annealing conditions, multivalent cations, and DNA loading should enhance our fundamental understanding of tuning kinetics to control materials properties and lead to new possibilities for the realization of kinetically controlled superlattice structures. The high-level of structural control over colloidal single crystals will enable researchers to probe the effect of crystal size on the optoelectronic and mechanical properties of these materials.1−5

**Safety Statement.** No unexpected or unusually high safety hazards were encountered.

■ ASSOCIATED CONTENT

> Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.8b00826.

Experimental procedures, including simulation details, oligonucleotide sequences, nanoparticle functionalization and assembly, and characterization/analysis techniques (SAXS, SEM, and TEM), and additional figures (PDF)

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**Notes**

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