



AFRL-AFOSR-VA-TR-2022-0306

DNA-Programmed Epitaxy of Nanoparticle Superlattices

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06/22/2022
Final Technical Report

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Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
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REPORT DOCUMENTATION PAGE

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1. REPORT DATE 20220622		2. REPORT TYPE Final		3. DATES COVERED <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">START DATE 20170701</td> <td style="width: 50%; border: none;">END DATE 20210630</td> </tr> </table>		START DATE 20170701	END DATE 20210630	
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4. TITLE AND SUBTITLE DNA-Programmed Epitaxy of Nanoparticle Superlattices								
5a. CONTRACT NUMBER		5b. GRANT NUMBER FA9550-17-1-0288		5c. PROGRAM ELEMENT NUMBER 61102F				
5d. PROJECT NUMBER		5e. TASK NUMBER		5f. WORK UNIT NUMBER				
6. AUTHOR(S) Robert MacFarlane								
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) MASSACHUSETTS INSTITUTE OF TECHNOLOGY 77 MASSACHUSETTS AVE CAMBRIDGE, MA 02139 USA					8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB2	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2022-0306			
12. DISTRIBUTION/AVAILABILITY STATEMENT A Distribution Unlimited: PB Public Release								
13. SUPPLEMENTARY NOTES								
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15. SUBJECT TERMS								
16. SECURITY CLASSIFICATION OF: <table style="width: 100%; border: none;"> <tr> <td style="width: 33%; border: none;">a. REPORT U</td> <td style="width: 33%; border: none;">b. ABSTRACT U</td> <td style="width: 33%; border: none;">c. THIS PAGE U</td> </tr> </table>				a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	17. LIMITATION OF ABSTRACT UU	
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19a. NAME OF RESPONSIBLE PERSON BENNETT IBEY				18. NUMBER OF PAGES 78				
19b. PHONE NUMBER (Include area code) 000-0000								

AFOSR Final Progress Report

DNA-Programmed Epitaxy of Nanoparticle Superlattices

Grant Number: FA9550-17-1-0288

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Reporting Period Covered:

7/1/2017-6/30/2021

Report Submitted 9/28/2021

DNA-Programmed Epitaxy of Nanoparticle Superlattices

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Abstract

This AFOSR YIP will investigate methods to combine biomolecule directed self-assembly and lithographic patterning to generate nanoparticle-based materials with simultaneous and independent control over atomic composition, nanoscale structure, and macroscopic shape. These designer materials will consist of nanoparticle superlattices that are epitaxially grown in a layer-by-layer approach from a patterned substrate, using DNA-grafted nanoparticles as building blocks. The crystallographic arrangement of particles will be dictated as a function of DNA design, while the lattice size, shape, and orientation will be determined by the lithographically-patterned surface. Pairing these two methodologies offers the opportunity to completely dictate *all* aspects of structure from the atomic to millimeter length scales, presenting a transformative method for discovering and synthesizing new materials.

Our research plan comprises a fundamental exploration of the unique types of structures that can be generated with this “top-down” meets “bottom-up” approach to material synthesis, followed by two target applications that will exploit the exemplary structural control it enables: (1) We will determine how lithographic pattern design, DNA sequence, and nanoparticle composition affect lattice size, shape, and defect positions in 3D. (2) We will utilize noble metal nanoparticles to construct plasmonically active materials where manipulation of lattice structure is used to dictate lattice reflectivity and absorption. (3) We will fabricate 3D photonic crystals consisting of 100-300 nm particles and microcontact printed substrates, allowing us to precisely mold the flow of visible light.

This unique combination of “top-down” lithography and biomolecule-directed “bottom-up” self-assembly will enable the synthesis of designer materials with independent control over material structure at all length scales: atomic composition, nanoparticle shape, mesoscale ordering, and macroscale form factor. As a result, these target aims present a revolutionary method for tuning a material’s physical properties to achieve designer structures for a variety of applications.

1. Statement of Objectives

In this work, we will assemble DNA-grafted nanoparticles on lithographically defined substrates to simultaneously control material structure at the nanometer, micron, and millimeter length scales. The proposed method uses the adventitious aspects of two well-established materials fabrication techniques to overcome their respective limitations: DNA-directed assembly allows for the formation of nanoparticle superlattices with nanometer-scale precision of particle placement in three dimensions, and lithography enables the fabrication of lattices of arbitrary macroscale shapes. To explore and demonstrate the versatility of this methodology, we plan the following three tasks:

1. Synthesis of multi-layer nanoparticle superlattices of defined size, shape, orientation, and defect structure. Specifically, we will target how mesoscale lattice structure (as defined by the lithographic pattern) affects the crystal growth process. We will also explore methods of using thermodynamic control in the absence of patterns to assemble these structures, allowing for better scalability in the fabrication process.
2. Fabrication of plasmonically active structures. We will use the information gained from task #1 to construct plasmonic thin films whose absorption and scattering profiles in the visible regime will be tailored as a function of their assembled structure.
3. Assembly of photonic band gap materials. By assembling particles at the 100-300 nm length scale, we will take advantage of the precise structural control enabled by this method to generate waveguiding structures that can precisely manipulate the flow of light. We will also develop methods to embed our materials in flexible polymer solids that will allow the materials' use as direction-dependent force sensors.
4. *Additional goal for 4th year extension of proposed work:* In the extension of this grant, we will translate the information gained from the aims above into a wider class of bio-inspired and biomimetic materials in order to develop a more comprehensive understanding of how natural systems generate mechanically resilient protective coatings. We will also synthesize hierarchically ordered, self-healing composites for mechanical protection, and translate our prior successes into a broader class of materials to support a wider range of Air Force operations.

This proposal will establish a new methodology for discovering, synthesizing, and targeting novel materials with desirable physical properties by exerting structural control at several different length regimes concurrently. Our new method for materials design is applicable to a wide variety of nanoparticle sizes and compositions, and thus this YIP will lay the foundation for a transformative approach to generating materials for multiple future applications.

2. Major Accomplishments for Objectives in Reporting Period:

Objective 1: Interfacial assembly of multilayer DNA-directed nanoparticle superlattices with defined macroscale structures

A. Measurement of DNA-directed Crystallization Kinetics and Pathways Controlled by Interfaces

Fundamental Information Developed:

- i. Correlation of thermal annealing conditions and crystallographic symmetry; enables more systematic control over the nano and microstructure of the nanoparticle arrays
- ii. Developed mechanisms by which DNA-programmed particle arrays reorganize from disordered structures to ordered lattices with controlled orientations; allows for significant increase fabrication rate and yield of multilayer nanoparticle arrays with controlled plasmonic properties

Technological Development and Applications:

- i. Oriented, well-ordered thin films of plasmonically active nanoparticles; control over crystal quality and orientation enables reproducibility of optical properties for sensing applications

B. Synthesis of faceted single crystal superlattices via thermodynamic control

Fundamental Information Developed:

- i. Correlation of DNA and nanoparticle design principles to thermodynamically preferred lattice sizes and shapes; enables *a priori* prediction of crystal shape
- ii. New computational model and techniques to use basic concepts of crystal nucleation and growth to explain and control crystallization at interfaces; potentially allows these nanoparticle superlattices to be used as models to explore fundamentals of crystal formation

Technological Development and Applications:

- i. Faceted single crystal superlattices with well-defined shapes enable their integration with technological devices
- ii. Single crystals with predetermined facet angles relative to the substrate enable control over angular dependence of light reflection (see accomplishments in objective 2)

C. Assembly of dynamic, temperature responsive superlattices and measurements of their thermal expansion coefficients

Fundamental Information Developed:

- i. Correlation of DNA and nanoparticle design principles to the coefficients of thermal expansion (CTE) of DNA-assembled nanoparticle superlattices
- ii. Methods to tune the CTE of materials to ultralarge positive and negative values, as well as the establishment of design principles for near-zero expansion materials

Technological Development and Applications:

- i. The ability to tune interparticle distances as a function of temperature enables alteration to plasmon coupling between particles, potentially enabling highly sensitive materials to report on localized temperatures

D. Fully measured and quantified material modulus of DNA-assembled superlattices (in progress 2019-2020, completed 2020-2021 cycle)

Fundamental Information Developed:

- i. Relationship between DNA design, nanoparticle lattice structure, and mechanical properties
- ii. Ability to tune lattice response to mechanical strain; allows for controlled manipulation of lattice structure in a dynamic manner

Technological Development and Applications:

- i. Soft, deformable lattices enable development of plasmonic sensors to measure ultrasoft (pN) mechanical forces
- ii. Ability to control deformation mechanism of lattices to either self-heal or dissipate mechanical force on command

Objective 2: Development of plasmonically active superlattice structures

A. Developed Programmed Assembly Method that Uses Plasmonic Thermalization to Simultaneously Pattern and Crystallize DNA-grafted Nanoparticles

Fundamental Information Developed:

- i. Ability to use localized plasmon thermalization as a means of patterning a material and crystallizing the particles; simultaneous control over material nanoscale ordering and micro- to macroscopic structure allows for complex hierarchical materials with tailored optical response
- ii. Established mechanism of particle reorganization with spatially anisotropic thermal annealing conditions; enables much more complex but still well-controlled particle organizations

Technological Development and Applications:

- i. Hierarchically structured nanoparticle-based materials that can be used as optical coatings and waveguides, with the potential for dynamic and tunable response and/or self-healing

B. Developed optical micromirrors based on DNA-assembled single crystal nanoparticle superlattices

Fundamental Information Developed:

- i. Correlation of superlattice microstructure with optical reflectivity
- ii. Measurement of the amount of specular vs. diffuse reflection from plasmonically active nanoparticle arrays

Technological Development and Applications:

- i. Single crystal superlattices with well-defined facet angles allow for their use as microscale mirrors to couple out of plane light sources

Objective 3: Assembly of dynamic photonic band gap structures embedded in polymer materials

A. Developed protocols to embed PAE lattices in deformable hydrogels

Fundamental Information Developed:

- i. Stability of DNA-directed constructs in different solvent, pH conditions
- ii. Protocols to polymerize a hydrogel network around and within lattices
- iii. Ability to dynamically alter interparticle distance in lattices both isotropically and anisotropically using chemical or mechanical stimuli

Technological Development and Applications:

- i. Hydrogel networks protect nanoparticle superlattices without fixing their structures in place, allowing them to be stable under potential operating conditions but still be accessible to their environment (e.g. able to interact with target molecules in sensing applications)
- ii. Dynamic modulation of lattice structure alters plasmon coupling between particles, allowing for their use in sensing technologies to detect small molecules, biomolecules, mechanical force, temperature, etc.

Objective 4: Development of bio-inspired, scalable, plasmonically active superlattice structures

A. Established design principles to recreate previous DNA-based materials using scalable polymer and supramolecular chemistry functionalities

Fundamental Information Developed:

- i. New synthetic protocols to assemble highly ordered arrays of nanoparticles using biomimetic, DNA-like hydrogen bonding to drive nanoparticle crystallization
- ii. Methods to control molecular, nano, micro, and macroscopic material structure simultaneously
- iii. Correlation of polymer and supramolecular chemistry design handles to processability and microstructure of assembled materials

Technological Development and Applications:

- i. Macroscopic solids assembled using these biomimetic approaches provide designer materials whose optical and mechanical properties can be precisely tailored for use as coatings, structural materials, and sensors.

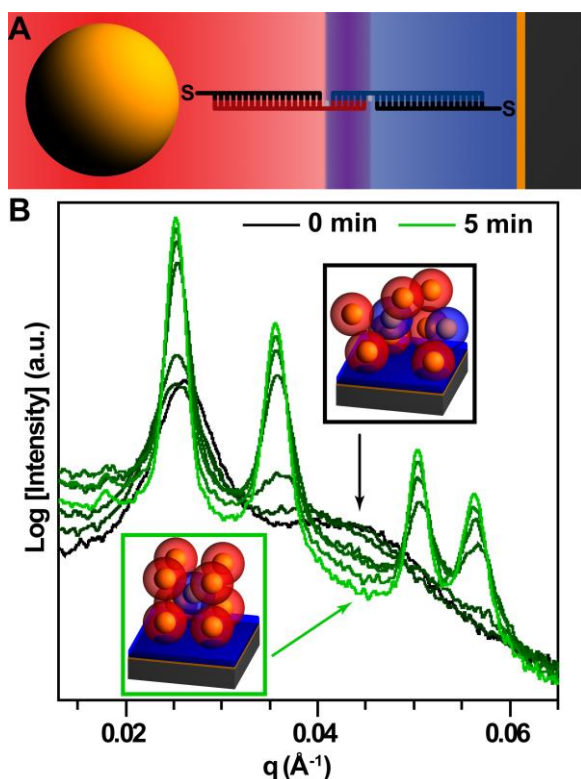
3. Scientific Progress:

In this AFOSR Young Investigator Program award, the Macfarlane lab has developed methods to assemble nanoparticle building blocks called “Programmable Atom Equivalents” (PAEs) on patterned surfaces using DNA as a guiding ligand, specifically examining the physical properties of the superlattices that are generated. In the prior funding year, we have established methods to assemble single crystalline and polycrystalline architectures, and examined both their mechanical and thermal properties.

3.1 Measurement of DNA-directed Crystallization Kinetics and Pathways Controlled by Interfaces

Prior work in this grant (and the works upon which it is based) have demonstrated that DNA-directed nanoparticle (NP) assembly is a promising tool for materials synthesis, as the multitude of accessible particle sizes,^{1,2} shapes,³⁻⁵ and compositions⁶⁻⁸ that can be made provide a large toolbox of material components,⁹ and the programmability of DNA base pairing affords precise control over interparticle interactions.¹⁰⁻¹³ Moreover, the assembly behavior of these building blocks in many ways mimics atomic and molecular crystallization, meaning that these “programmable atom equivalents” (PAEs) can draw on a wealth of established chemistry knowledge to both tailor and explain their assembly behavior.^{2,9,14-16} As a result, PAE assembly has an incredible level of control over the coordination environment of each particle within a lattice. In order to enable the structure-property investigations proposed for tasks 2 and 3 of this grant, the next challenge is developing methods to control aspects of material structure at length scales beyond just the crystallographic unit cell, such as crystallite size, shape, and orientation. Initial investigations into precise thermal annealing procedures have produced single-crystal structures with well-defined surface facets,^{17,18} and earlier work on lithographic patterning (funded under this proposal and separate AFOSR-enabled efforts by the Macfarlane lab) has been used to direct PAE superlattice shape using templated deposition.¹⁹ However, these methods are typically limited to small-scale structures, and additional research is still required to make lattices with complete control over lattice macroscopic geometry. For example, there is still only a limited understanding of how to control crystal texture (orientation of crystal grains) within a bulk PAE material. In multiple proposed applications of PAE-based materials,^{9,20-22} lattice orientation is a crucial determinant of structure-property relationships, and thus it is important to develop an understanding of how texture in bulk PAE superlattices arises during the crystallization process.

Nevertheless, manipulating lattice texture poses a challenging task, as fixing the orientation of a crystallite by definition necessitates controlling the overall meso- and macroscopic symmetry of the NP superlattice, resulting in a more anisotropic system. A common, and often the simplest, method of reducing the symmetry of both atomic and colloidal crystals is the introduction of an interface.^{19,23-30} In atomic systems, interfaces have the ability to energetically stabilize specific crystalline orientations relative to the surface plane, causing aligned grains to nucleate and grow more readily and dominate the final structure.^{23,31,32} This results in a preferential orientation for the crystals, effectively locking one degree of rotational freedom. However, the surface energies in atomic crystals are intrinsic to the elemental composition of the crystal and substrate and thus cannot be arbitrarily modulated.²⁴ In contrast, the interaction potential of a PAE lattice with a DNA-functionalized substrate can use the tailorability of DNA binding to precisely program the binding specificity, functionality, and coverage of deposited PAEs,^{29,30} and changes in the resulting thin film microstructure can be directly observed using various *in situ* techniques.^{33,34} A preliminary study in PAE thin film growth demonstrated a simple example of DNA’s programmability, where a body-centered



Scheme 1. Observing the PAE Thin Film Rearrangement Process. A) The DNA binding scheme utilizes complementary “sticky ends” to control binding. B) Time-resolved structural rearrangement of the thin film is determined through the SAXS pattern transforming from an amorphous structure (black curve and top inset) to an oriented, crystalline structure (green curve and bottom inset) upon annealing.

function of this ability to control crystal texture was examined, demonstrating the notable ability to dynamically alter the symmetry of a crystalline lattice when it is locked to an interface. The results presented in this report of our work during the prior funding period provide significant insight into the energetic interplay between nano- and meso-scale structural control of self-assembled NPs and broaden the ability to dictate material structure across several length scales.

PAE superlattice thin films were assembled using established synthesis protocols.^{29,35} Briefly, gold NPs were densely functionalized with oligonucleotides that each contained a short, unhybridized “sticky end.” PAEs were functionalized with one of two complementary sticky ends, such that when the two complementary sets of particles were mixed together, sticky end hybridization between particles caused the PAEs to aggregate. It has been shown that these PAEs can be thermally annealed near their melting temperature (T_m , the temperature at which assembled PAEs dissociate), inducing their rearrangement into a crystalline lattice where the number of complementary nearest neighbors is maximized.^{2,11,36} Gold-coated silicon wafers were functionalized with one set of oligonucleotide sticky ends and subsequently incubated in a solution of the complementary PAEs, resulting in the deposition of an amorphous monolayer (Scheme 1A). Incubating the monolayer-coated substrate in a solution containing complementary particles resulted

cubic (bcc) lattice was grown with either the {001} or {011} planes parallel to the surface as a function of which DNA strands were used to bind PAEs to the substrate.²⁹

While this prior result showed potential for using a substrate to control crystal growth, only one of the multiple accessible PAE superlattice crystallographic symmetries was examined. Moreover, only the thermodynamic end structure was investigated, and the rearrangement pathway to forming these crystals remains a mystery, despite the fact that this control is critical to understanding the influence of an interface on crystal formation. The work conducted in this reporting period has explored this unknown PAE design space where the implications of reorganization at a tailorable interface can be investigated and ultimately controlled. Specifically, we examined the *in situ* pathway of rearrangement that results in preferentially aligned thin films. Additionally, we explored the effects of reduced symmetry in PAE crystallization beyond just the introduction of an interface, specifically by altering unit cell crystallographic symmetry and using binary systems of PAEs with different interparticle and surface binding affinities. Finally, the asymmetric thermal expansion and contraction behavior exhibited by substrate-bound crystallites as a

in a second layer of NPs binding to the first; this process was repeated step-wise to generate films of the desired thicknesses. It is important to note that, because these depositions were performed at $\sim 23^\circ\text{C}$ (well below their T_m), the resulting films were kinetically trapped, yielding amorphous lattices containing no long-range ordering.

Once these amorphous films were deposited, their rearrangement into ordered superlattices was examined *in situ* by placing them in a temperature-controlled, solvent filled chamber in the path of a synchrotron x-ray beam, yielding high precision structural data. Small angle x-ray scattering (SAXS) patterns were subsequently collected as a function of annealing time and temperature (Scheme 1B). In nearly all cases, the SAXS data revealed a complete transformation from amorphous (as-deposited) to fully crystalline within minutes when annealed near T_m . Importantly, the thin films were placed with the substrate normal to the x-ray beam direction such that any orientational alignment parallel to the superlattice-substrate interface was observed and characterized. Lattice alignment results in the suppression of specific scattering peaks, and the identities of the suppressed peaks are dictated by lattice orientation, which enables characterization of overall lattice texture. Finally, after the thin films reached equilibrium (determined by time-stable SAXS pattern), the samples were embedded in silica³⁷ for visual characterization with scanning electron microscopy (SEM). Additionally, some thin films were annealed for shorter amounts of time, quickly quenched, embedded, and imaged to observe changes in morphology throughout the annealing process.

Morphological Evolution of Lattice Orientation During Crystallization

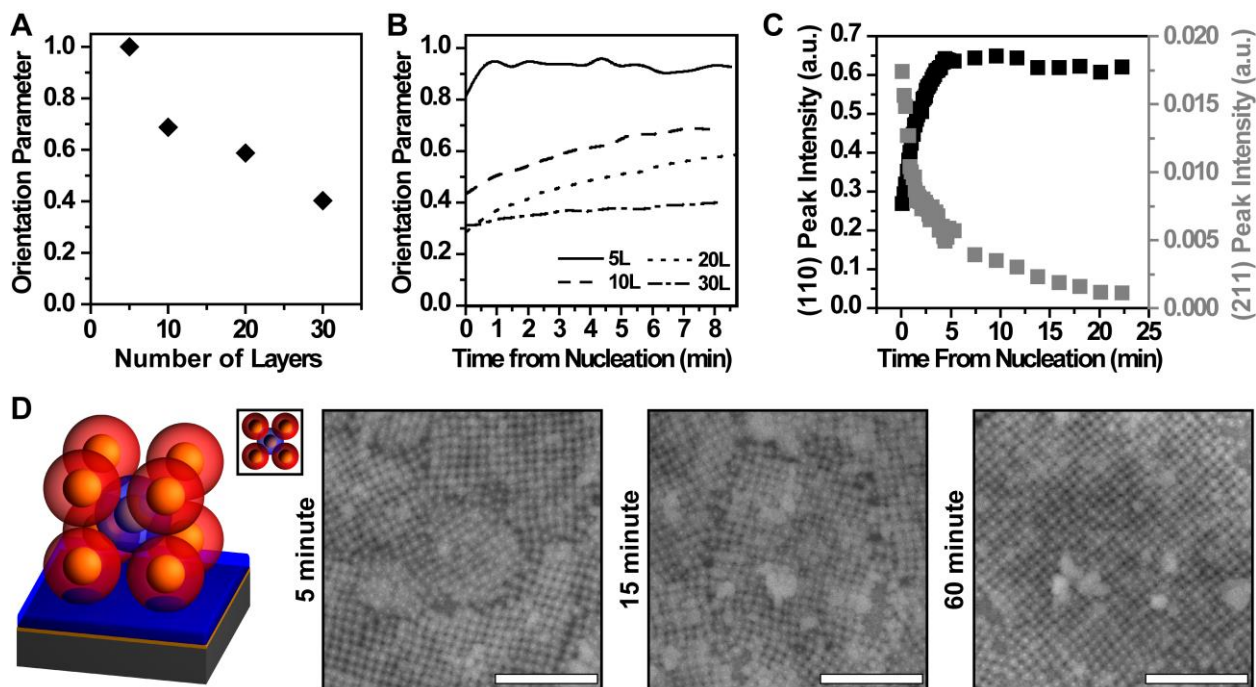


Figure 1. Morphological evolution of PAE thin films with “preferred alignment.” A) Decreasing orientation parameter as a function of layer number reveals waning effects of interface as thickness of film increases and a critical film thickness of 5-10 layers for preferential alignment. B) Differing kinetics to final structure for films of 5, 10, 20, and 30 layers. C) Time evolution of (110) and (211) peak intensities for a 5-layer film. While the PAE rearrangement pathway is well understood for 3D superlattices in solution,³⁶ introducing an interface imposes an anisotropic constraint on crystal reorganization, meaning that PAEs may exhibit different kinetics of reorganization at the substrate interface compared to the bulk material. To examine this

hypothesis, two sets of structurally identical PAEs were synthesized containing identical NP core sizes and DNA lengths, but complementary sticky end sequences. Previous work has shown that this type of binary PAE system rearranges into a bcc superlattice upon annealing, as this structure maximizes the total number of DNA connections between particles.^{1,11,29}

Initially, substrates were functionalized with only one type of sticky end before depositing the PAEs, meaning that only one of the sets of PAEs in this binary system would be able to favorably bind to the substrate. Thus, after rearrangement, the {001} planes would be expected to align parallel to the interface, as the {001} arrangement is the densest-packed plane containing PAEs of only a single sticky end type. Indeed, post-rearrangement, a 5-layer thin film of PAEs was dominated by crystalline domains with the {001} planes parallel to the substrate (Scheme 1B), as evidenced by the suppression of the (211) scattering peak; this superlattice orientation noted by the SAXS data was confirmed by real-space SEM imaging. This observed alignment was consistent with previously reported thermodynamic structures when depositions were done at elevated temperatures.²⁹

Intriguingly, however, this 2D rearrangement process did not follow the same pathway as the previously characterized rearrangement in 3D aggregates. Due to the presence of the substrate interface, the processes of crystal nucleation, grain growth, and melting all occurred at different rates for different crystal orientations. The percentage of grains that are {001} aligned within the thin film were quantified by comparing the relative intensity of the (211) scattering peak to the others, where an order parameter value of 1 indicated full alignment with {001} and an order parameter of 0 indicated no favored orientations. This analysis clearly showed that the stabilizing impact of the substrate on {001} orientations strengthened with decreasing film thickness (Figure 1A). Tracking the order parameter throughout the rearrangement process elucidated the kinetic pathway of arriving at this preferential alignment (Figure 1B).

In PAE films with fewer than 10 layers, where the critical nucleus size was hypothesized to be on the order of the film thickness, aligned grains at the interface were energetically stabilized to such a degree that unaligned grains were never observed. However, above this critical thickness, grains of all orientations nucleated at the top surface of the thin film and began to grow toward the substrate. Grains in contact with the DNA-coated gold surface with the preferred {001} grain aligned parallel to the substrate were thermodynamically more stable due to the larger number of DNA connections between the (001) plane of the bcc lattices and the substrate. Thus, their net growth quickly outpaced that of the unaligned grains. In fact, given enough thermal energy, the aligned grains absorbed neighboring grains of other misaligned orientations (Figures 1C,1D). The introduction of an interface greatly stabilizes grains with preferentially aligned orientations, creating a significant difference in energies between these thermodynamically preferred grains and neighboring ones that are not aligned with substrate. Therefore, the result is a strong driving force for grain coarsening in this 2D system not previously observed in 3D systems devoid of substrate interfacial energies.

Introducing Non-equivalent Substrate Binding Strength via Alterations to Lattice Symmetry

Prior work has shown that PAEs with identical hydrodynamic radii exhibited the same preferred thermodynamic crystal structure when assembled.¹¹ However, the use of two different NP core sizes alters the symmetry of the resulting unit cell, meaning that sets of complementary PAEs with identical hydrodynamic radii but different nanoparticle core sizes produce a cesium chloride-type (CsCl-type) lattice (Figure 2A). Because the particle positions, number of nearest neighbors, and overall DNA connectivity were the same for these bcc and CsCl lattices, it was not surprising that CsCl thin films exhibited the same

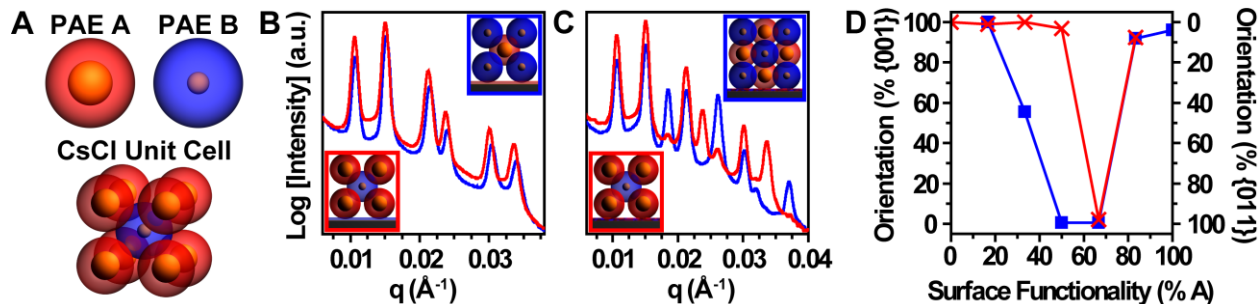


Figure 2. Effects of reducing unit cell symmetry to investigate non-equivalent substrate binding strengths. A) Schematic representation of A (red) vs B (blue) PAEs resulting in a CsCl unit cell structure. Final SAXS patterns of the reorganized CsCl thin films are (B) independent of deposition order (red, A first; blue, B first) when the substrates are functionalized with 100% B or 100% A DNA sticky ends, but are (C) order dependent when functionalized with 50% A, 50% B. Insets: representative cross-sections of each corresponding thin film lattice structure. D) The overall percentage of grains aligned with either {001} (left axis) or {011} (right axis) oriented to the substrate differ as a function of surface functionalization ratio of A to B DNA sticky ends.

{001} alignment to the substrate as the previous bcc lattices (Figure 2B). While the absolute binding strength of PAEs attached to a complementary DNA-functionalized surface may vary as a function of particle diameter (due to the different number of DNA strands attached to PAEs with different NP core sizes), the {001} planes of the CsCl lattice should always represent the densest packed arrangement of particles that can form a DNA connection to substrates functionalized with only one type of DNA linker.

Conversely, it was previously demonstrated that a bi-functionalized substrate with both sticky end types present at the interface would allow both PAE types to bind to the surface, thereby generating bcc lattices with the denser {011} orientation parallel to the substrate.²⁹ Since {011} is also the closest packed plane in CsCl, a bifunctionalized substrate may also be predicted to yield {011} preferential alignment for CsCl lattices. However, because the binding strength of the different PAEs in a CsCl lattice are not equivalent, the deposition order of PAEs in this binary system had significant impact on the final texture of the superlattices. When amorphous films were deposited and the PAE with the smaller NP core (PAE B) was deposited first, the expected {011} orientation was observed after thermal annealing (Figure 2C, blue). However, when amorphous films were deposited and the PAE with the larger NP core (PAE A) was deposited first, the lattices still exhibited the {001} preferential alignment observed in the monofunctionalized substrates after annealing (Figure 2C, red).

This result confirms that the two, non-identical sets of PAEs in these CsCl lattices interact differently with the interface and drive the thin film reorganization towards different end products. Because each layer of PAEs was deposited sequentially, the initial amorphous film should only have one type of particle at the interface—the PAE type that was used in the first round of deposition. The {011} plane would therefore only be expected to form if the second particle type being deposited were able to displace some of the initial monolayer of the opposite type of PAE. The differing interfacial rearrangement behavior for A and B particles was hypothesized to be caused by a stark difference in the sticky end density of the two PAE types in the CsCl structure.¹ Since the DNA on PAE B must be longer to match the overall radius of the PAE A, it will splay out to a greater degree at the PAE periphery, making the density of binding groups less than half that of the PAEs with a larger core (0.010 sticky ends per nm² vs 0.024 sticky ends per nm²). A lower sticky end density resulted in PAE B binding more weakly to the substrate and thus they should have increased mobility during crystal annealing compared to PAE A.^{30,33} Altering the assembly behavior of

PAEs with different substrate affinities therefore necessitated altering the surface chemistry of the substrate to control the relative binding strengths of the two PAE types. To examine this hypothesis, several substrates were functionalized with a breadth of surface functionalities ranging from 100% A sticky ends to 100% B sticky ends. It was previously shown in bcc lattices that as the surface functionalization was modulated from 100:0 to 50:50 mixtures of complementary ligands, the thin films formed grains that were {001}- and {011}-aligned, respectively, with a mixture of the two orientations at intermediate ligand mixtures.²⁹ In contrast, the CsCl system explored here displayed distinctly different distributions of {001} and {011} alignment based on the nanoparticle deposition order (Figure 2D).

Specifically, when the low-sticky-end-density PAE B was deposited first, it was more readily displaced, resulting in a fairly symmetric distribution of orientations as a function of surface functionality. Conversely, when the strongly-bound PAE A was deposited first, the final structure only contained {011} aligned lattices when the relative density of A-complementary sticky ends was approximately half the density of B-complementary sticky ends. In other words, the increased sticky end density on PAE A resulted in an increased affinity to the substrate, meaning that it could only be displaced when the number of sticky ends at the interface to which PAE A could bind was radically reduced. Therefore, in this lower symmetry CsCl system, the deposition order of the non-equivalent PAE A and B had a strong impact on the overall lattice texture, and lattice alignment could be tuned by controlling the relative PAE-substrate binding potentials.

Introducing Variations in Stoichiometry via Utilizing a Hexagonal Unit Cell

The programmability of the PAE building block allows the superlattice unit cell symmetry to be tailored to lower symmetry arrangements than the cubic bcc or CsCl type lattices, including a lattice with a hexagonal unit cell that is isostructural with aluminum diboride (AlB_2).^{2,11} In this hexagonal lattice, the PAEs have both different numbers of DNA strands attached to their surfaces, as well as different overall hydrodynamic radii (Figure 3A). As a result, the two particles in an AlB_2 lattice have different coordination environments, relative binding strengths to the substrate, and number of particles per unit cell. Moreover, the hexagonal unit cell is less symmetric than the cubic unit cells examined above, with an overall unit cell c/a ratio that is typically $\sim 0.7 - 0.85$.¹¹ It could therefore be expected that the reorganization of an AlB_2 -type lattice at a surface would show even stronger anisotropy in its

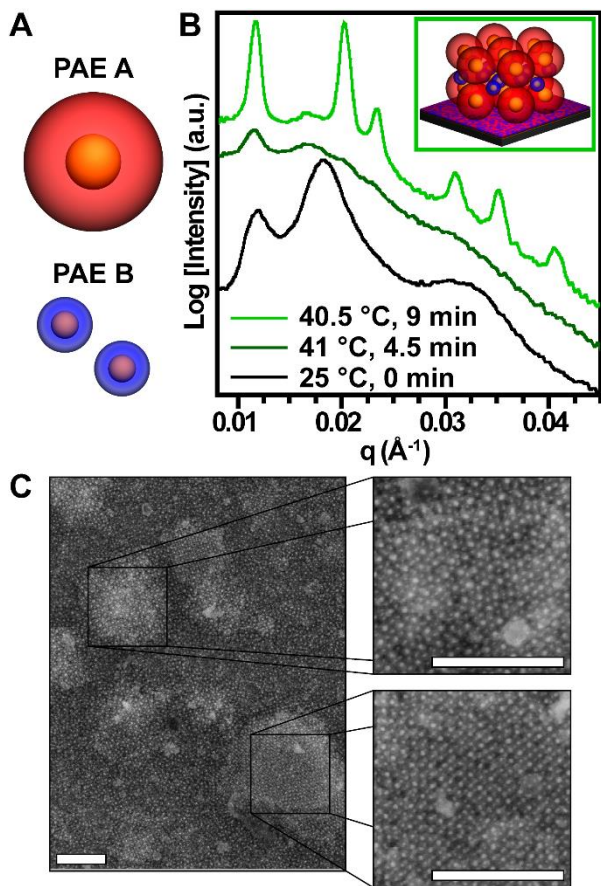


Figure 3. Effects of local stoichiometry and PAEs of different hydrodynamic sizes. A) Schematic representation of PAEs capable of creating a hexagonal, AlB_2 lattice. B) These PAEs exhibit a distinctive ‘fluidic’ (dark green curve) state characterized by very little presence of structural peaks in SAXS during their reorganization to AlB_2 grains with {001} alignment

crystallization compared with cubic lattices examined previously.

In the case of a mono-functionalized surface, the PAE lattice was hypothesized to preferentially align with the hexagonal close-packed {001} plane parallel to the interface, given that it is the most densely-packed single-particle-type plane in the unit cell; this alignment was indeed observed using SAXS (Figure 3B). In fact, the SAXS data indicated that {001}-oriented AlB₂ grains were exclusively observed in the thin films, even when the surface was functionalized with DNA linkers complementary to both types of particles, irrespective of particle deposition order. This result was likely due to both the increased binding strength of the larger PAE, as well as the fact that the hexagonal close-packed arrangement of larger PAEs (PAE A) in the {001} plane represented a significantly denser packing than any other potential lattice plane, even when considering the possibility of both particles binding to the substrate.

Interestingly, despite their significant differences in PAE design, the precursor structures to CsCl and AlB₂ lattices were strikingly similar prior to thermal annealing (Figure S5). However, the reorganization process for this AlB₂ PAE system exhibited several notable differences to the previous bcc and CsCl systems. In both the bcc and CsCl cases, the broad peaks corresponding to the initial short-range ordering were observed to gradually sharpen into the long-range ordered, crystalline peaks without significant alteration to the peak positions (Scheme 1B), and reorganization was induced at temperatures relatively low compared to T_m . This indicated that the particle coordination environment in the initial, short-range ordered structures was similar enough to the final long-range ordered bcc or CsCl lattices that particles could easily rearrange into the thermodynamically preferred crystal state.¹⁵ Conversely, in the AlB₂ cases, nearly all the short-range order was lost before crystalline, long-range order appeared (*i.e.* the broad amorphous peaks disappeared nearly completely before sharp crystalline peaks arose) (Figure 3B), and the AlB₂ reorganization into crystalline order only occurred in a very narrow temperature window immediately below T_m . Moreover, during this reorganization process, the macroscopic thin film appeared “molten” by visual inspection, as the mass of PAEs at the surface slowly flowed down a vertically aligned substrate under the influence of gravity, without fully breaking up the lattice and releasing large quantities of PAEs into solution. Together, these observations implied that the local ordering of PAEs in the initial amorphous sample was significantly different than the AlB₂ lattice and required greater amounts of reorganization to achieve an ordered state. Thus, AlB₂ reorganization was more challenging compared to bcc or CsCl systems, explaining the narrow thermal window in which crystallization was observed. At temperatures immediately below the lattice T_m , PAEs were able to crystallize because in the initial stages of reorganization they were essentially behaving as a viscous fluid where individual particles were only weakly tethered to their neighbors. This fluidic state allowed for significantly increased PAE mobility, enabling the large amount of restructuring needed to form the AlB₂ lattices.

Although only AlB₂ lattices with the {001} planes parallel to the substrate were observed at the end of the annealing process, when the films were subsequently cooled to room temperature, a new SAXS peak clearly arose at a new scattering angle that did not correlate to an AlB₂ structure. However, this peak was consistent with the {110} peak for a CsCl crystal of 53nm lattice parameter, which would be the expected lattice spacing for a CsCl lattice made with these PAEs. Morphological inspection of the reorganized thin films using SEM confirmed an unanticipated combination of {001}-aligned AlB₂ crystalline regions, as well as both {011}-oriented CsCl crystals and large disordered regions (Figure 3C). It is important to note that the PAE design used here was close to the phase boundary for CsCl and AlB₂ lattices.^{11,38} The ability for a binary PAE design that exists near a phase boundary to simultaneously exhibit two stable crystallographic symmetries has been demonstrated previously in non-surface-bound PAE crystallites by changing the

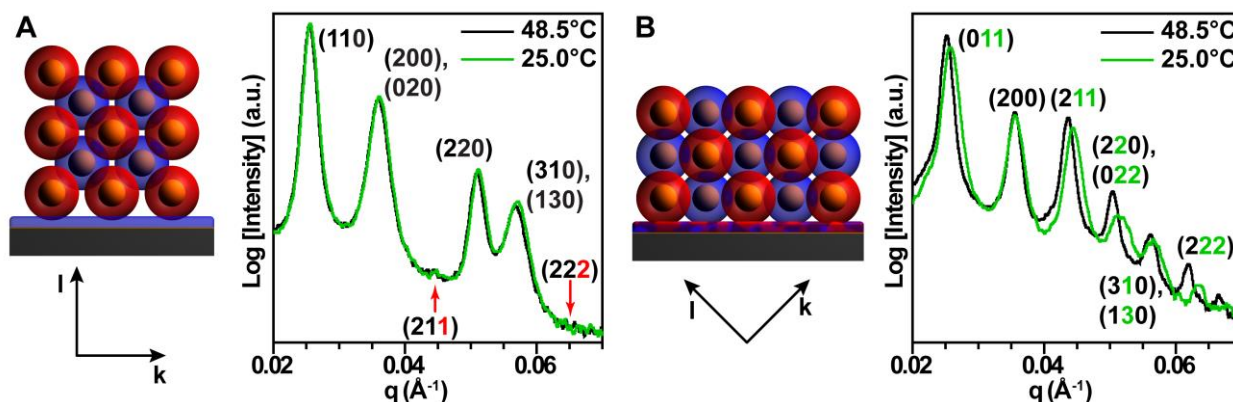


Figure 4. Schematic representations of (A) {001}-oriented and (B) {011}-oriented bcc crystals bound to a substrate with defined *h*, *k*, and *l* directions and correspondingly indexed SAXS patterns reveal asymmetric shrinkage upon cooling. (A) Peaks with *l*-character (red index numbers) are suppressed because the *l* direction is parallel to the x-ray beam direction. (B) Peaks with *k*- and/or *l*-character (green index numbers) shift or broaden dependent upon the amount of *k*- and *l*-character because the compression occurs in the combined *k* and *l* direction.

relative stoichiometric ratios between the A and B particles.^{11,13,38} As the ratio neared 1:1, CsCl was favored, while AlB₂ was favored as the relative amount of B PAEs was increased. This was previously explained as a result of the energetic penalties of vacancies in the AlB₂ lattice making the CsCl lattice more favored when using close to a 1:1 ratio of A- and B-type PAEs. Thus, the presence of these CsCl and amorphous regions that were only observed after cooling the system can be explained as a function of local differences in particle stoichiometry induced by the reorganization process.

Given the nature of layer-by-layer PAE deposition, there was no inherent control over the stoichiometric ratio between A and B PAEs in the initial amorphous films. SAXS data of these initial structures can be used to confirm that the A and B particle types existed in a 1:0.96 ratio, not the ideal 1:2 ratio for an AlB₂ structure. Therefore, in order to form an AlB₂ lattice, localized exclusion of the excess A-type PAEs was required to achieve the ideal 1:2 stoichiometric ratio. This PAE positional reorganization was significantly enhanced in a molten, fluidic state, resulting in the localized accumulation or depletion of PAE types. Once the superlattice is cooled, regions of the substrate that are near a 1:1 ratio began to form CsCl-type lattices. As a result, while the {001} oriented AlB₂ lattice was the thermodynamically preferred state for these thin films, the inherent non-uniform stoichiometry of the final structure meant that different symmetries were stabilized in localized regions on the surface. The ability of the surface to stabilize the less-thermodynamically stable {011} CsCl lattices can be enhanced as a function of which DNA linker strands were attached to the substrate. Specifically, bi-functionalized substrates were observed to contain a higher prevalence of CsCl regions than mono-functionalized ones. This observation was consistent with the hypothesis that such a surface energetically stabilized the more densely packed {011}-plane of CsCl as opposed to any bi-particle plane in AlB₂, further making CsCl symmetries more thermodynamically accessible when limited amounts of B-type PAEs were present. Finally, even with the same particle designs, the AlB₂ and CsCl arrangements would be expected to have different unit cell energies^{11,38} and thus slightly different crystallization temperatures, accounting for the observation that CsCl only crystallized in this system upon cooling. Overall, the AlB₂ system further expounds upon the concept that asymmetry in PAE design can dictate the millimeter scale crystal texture of an entire thin film of PAE crystallites.

Asymmetric Thermal Contraction of Surface-Bound PAE Crystallites

Previous work on solution-dispersed PAE superlattices has demonstrated that PAE crystallites exhibited temperature-dependent lattice parameters, with larger interparticle distances at higher temperatures. The soft, deformable DNA corona around each PAE swelled and contracted as a function of solution temperature, leading to up to 10% shrinkage in unit cell dimensions for certain PAE designs when cooling from ~ 45 to ~ 22 °C.¹ When PAEs were not bound to a substrate, this lattice contraction was isotropic, as the spherical PAEs decreased in diameter uniformly due to their highly symmetric shape and the ability of all DNA strands to expand or condense equally. However, the introduction of a boundary condition like a DNA-functionalized surface changes these interactions, as the DNA strands tethered to the substrate are significantly less mobile, and contraction of the lattice parameters for the plane of particles bound to the substrate would require a significant number of PAE-substrate DNA connections to be broken.^{30,33} This reduced mobility of the first layer of PAEs bound to a substrate would be predicted to prevent (or at least limit) lattice compression in the directions parallel to the DNA-functionalized surface, meaning that the contraction of the DNA brush around each PAE would generate a significant amount of strain that could only be alleviated by expansion or contraction in the direction perpendicular to the surface.

To test this hypothesis, a bcc thin film with all crystallites $\{001\}$ oriented was cooled from its rearrangement temperature (48.5°C) to room temperature (25°C) over several minutes while monitoring the SAXS pattern (Figure 4A). Strikingly, this SAXS pattern showed no change in either the positions or quality of the peaks during cooling. While the lack of change in observed PAE superlattice structure could indicate that there is no change in the interparticle spacing of the superlattice, previous work^{33,39} suggested that it would be unlikely that the PAEs would store $\sim 10\%$ strain within the crystal without some disruption of crystal structure. However, since the x-ray beam used to scan these samples was perpendicular to the substrate, the SAXS pattern was only reflective of structure in the planes parallel to the interface. In other words, every peak that has any l-character (*e.g.* the (211) peak) was suppressed. Therefore, it was possible that the $\sim 10\%$ strain in this system was alleviated by breaking lattice symmetry and compressing the lattice *only* in the direction perpendicular to the substrate. Because none of the peaks observed in superlattices with the $\{001\}$ orientation parallel to the surface (*e.g.* (110), (200), (220), *etc.*) have any l-character, any expansion or contraction that occurred strictly normal to the substrate would be unobservable. However, these SAXS data did confirm that the in-plane lattice parameters of these crystallites remained unchanged during cooling, indicating that the introduction of a boundary condition *via* the DNA-functionalized surface did indeed pin the bottom layer of the PAE superlattice in place when cooling for these samples.

To further explore the hypothesized anisotropic compression, a bi-functionalized interface that enforces a $\{011\}$ orientation was used. Aligning the PAE lattices in this orientation meant that any changes in the direction perpendicular to the substrate were now a combination of the l and k crystal directions, while only the h-direction remained in-plane. Monitoring substrate-bound $\{011\}$ -oriented crystallites during cooling yielded a SAXS pattern that was altered with temperature (Figure 4B). Every peak with k- and/or l-character shifted in the expected *q*-direction with temperature-driven compression, while the (200) peak that has only h-character remained constant. This further corroborates the notion that the interface held the PAEs in the lattice direction parallel to the substrate stable, driving the crystallites to asymmetrically densify in the other lattice planes when the temperature was lowered, thereby breaking lattice symmetry to create a tetragonal unit cell shape in the $\{001\}$ -oriented case and a monoclinic shape in the $\{011\}$ case.³⁹ The morphological results of this phenomena can be directly observed in the SEM micrographs of the final thin film structure. Importantly, this finding highlights that the interface remains an important (and anisotropic) driving force

not just during reorganization, but during all processing of the PAE crystallites while they are still bound to the substrate. This anisotropic compression phenomena warrants deeper exploration in the future.

This work conducted as part of this AFOSR grant has revealed the powerful influence the introduction of an interface can have on PAE superlattices. A substrate, based on its functionalization, will energetically stabilize some crystal orientations over others, allowing them to nucleate and grow more readily and result in a mesoscale structure containing a preferred crystal texture. Additionally, in binary systems where each PAE has differing interfacial binding affinities, the entire mesoscale orientation can be controlled as a function of processing conditions. Finally, substrate-bound PAE crystallites will exhibit unusual, asymmetric behavior due to the anisotropic directing force an interface provides. Ultimately, better understanding how orientation control is programmable through interfacial interactions and how nanoscale and mesoscale structure are interconnected in these systems moves the field one step toward realizing total structural control across many length scales with colloidal materials. This level of control will ultimately enable better manipulation of the plasmonic and optical responses of these materials, as outline in tasks 2 and 3.

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3.2 Plasmon Thermalization based control of PAE Assembly and Patterning

The local control over PAE coordination at the unit cell level afforded by DNA programmability and demonstrated in the above-discussed efforts does not easily translate into control of the aggregate morphology at longer length scales, and dictating the meso to macroscale structuring of PAE materials remains challenging. However, such control is important for the proposed applications of this AFOSR-supported work (specifically in the areas of sensing and waveguiding), as reproducibility and structure control at these length scales is crucial for integrating these materials into device architectures.

Given the challenges associated with existing techniques for controlling PAE processing into ordered crystals, it would be ideal to develop a method that could deliver heat locally and process an amorphous PAE material into a crystalline superlattice with spatial resolution. In other words, by finely controlling the temperature profile along an amorphous PAE lattice, the overall shape of a crystallite could be controlled by inducing crystal reorganization in some regions and crystal melting in others, enabling the formation of an arbitrarily shaped, hierarchically structured material without the need for pre-patterned substrates. The first fundamental challenge in realizing this goal is developing a method to deliver heat in a manner that is both localized and non-damaging. Importantly, the particle cores of PAEs provide such an opportunity, as they are commonly made of noble metals that support a strong plasmon resonance;^{2,17} irradiating them with light can result in plasmon thermalization, which generates heat locally around the NP.^{18–22} Previous work has demonstrated that exposing DNA-functionalized gold NPs to a focused light source results in thermally-driven DNA dehybridization without irreversibly damaging the construct,^{23,24} as may occur when irradiating soft matter.²⁵ Therefore, in principle, a focused laser beam could locally heat and reorganize an amorphous PAE-based material with spatial resolution up to the diffraction-limit.

In this prior reporting period, we explored how heat is locally generated and dissipated in a PAE aggregate upon laser irradiation and examined the resulting behaviors and morphologies of the PAE materials due to the introduction of a local thermal source. We demonstrated that the use of optical processing allows for novel rearrangement mechanisms enabled by fluid-like behavior of the PAE film, in which particles are only transiently bound by dynamic DNA binding interactions. These particle reorganization pathways involve concurrent nanoscale PAE crystallization and mesoscale thermophoretic motion, where the high local temperature at the irradiation site first reversibly breaks the DNA connections holding particles together, and the resulting PAE “fluid” at these local high temperatures is driven out of the path of the laser beam, resulting in nucleation and growth of crystalline grains as the PAEs enter cooler regions further from the heat source. We also utilized the temporal resolution of optical processing to “lock” the PAE film into these fluid-like morphologies *via* short irradiation times following by rapid thermal quenching and explored the implications of this behavior on structural control. Ultimately, combining the goals of task 1 and 2 of this proposal to develop a new material patterning method will enable better application of these materials to AFOSR-relevant sensing and optical device technologies.

To investigate these optically-driven PAE crystallization phenomena in detail, amorphous PAE thin films were deposited on quartz slides following the same protocols outlined in section 3.1 above. A key difference here is the use of optically transparent quartz substrates, which were coated with ~ 8 nm of gold (a thin enough layer to remain optically transparent) and functionalized with thiol-modified oligonucleotide sequences; all other steps to deposit the PAEs remained identical. The substrates with amorphous PAE films were then placed in a chamber filled with 0.5 M phosphate-buffered saline and aligned perpendicular to the beam of a 532 nm laser (near the plasmonic resonant frequency of the gold NP cores) focused to a 60 μm radius. On the opposite side of the film, a Si photodiode sensor was positioned to measure the amount of transmitted light during the experiments. The film was then locally irradiated at different laser powers and exposure times, and the resulting samples were embedded in silica and examined with helium ion microscopy.

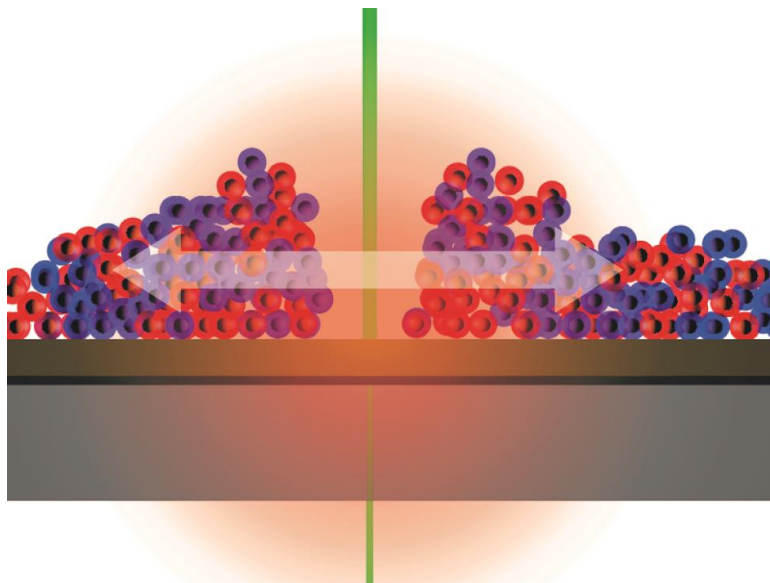


Figure 5. Illustration of optically-induced heat generation driving reorganization and motion in DNA-grafted nanoparticles deposited onto a DNA-functionalized substrate. Plasmon thermalization of incident laser light by particles in the path of illumination simultaneously drives PAE rearrangement into ordered superlattices and pushes particles out of the path of the laser beam *via* thermophoresis (white arrows).

Localized Processing of PAE Thin Film

Each PAE within an aggregate is bound to its neighbors through several, individual DNA hybridizations. A consequence of these polyvalent weak binding interactions is that PAEs can be brought to a temperature slightly below T_m (annealed) where individual DNA hybridizations are in flux, giving PAEs the ability to shift their locations relative to their neighbors without dissociating completely.^{4,9} Thus, when sufficient light impinges on the sample and is converted to local thermal energy *via* plasmon thermalization, these DNA connections between PAEs should undergo dynamic unbinding and rebinding events. At lower temperatures ($T \leq T_m$) PAEs are able to reorganize and adopt more thermodynamically favored arrangements, ultimately forming ordered crystals at different rates that depend on the processing temperature. At temperatures above T_m , the PAEs can actually fully dissociate from one another, resulting in the aggregate breaking apart into individual PAEs in solution.

If the PAE film can indeed be locally heated by laser irradiation, the development of three, distinct regions is would be expected: (1) a hole near the heat source where $T > T_m$ and PAEs melt away from the substrate, (2) a crystalline region surrounding the hole where $T \sim T_m$ and PAEs are mobile enough to reorganize but not melt away, and (3) an under-processed region where $T < T_m$ and PAEs remain in their kinetically-trapped, disordered state. Therefore, the size of the hole may be simply estimated from a model of the temperature profile surrounding the heat source, dependent on the incident power (I_0), the absorptivity of

the film (α), the thermal conductivities of the substrate and solution (k_1, k_2), and the ambient temperature (T_0):

$$T(r) \approx \frac{(1-10^{-\alpha})}{2\pi(k_1+k_2)} \frac{I_0}{r} + T_0 \leftrightarrow r(T) \approx \frac{(1-10^{-\alpha})}{2\pi(k_1+k_2)} \frac{I_0}{T-T_0} \quad (1)$$

Indeed, when processed at 65 mW, the PAE thin film developed a macroscopic hole as expected (Figure 6A and 6B). Morphological inspection of the processed thin film using helium ion microscopy confirmed the presence of the hypothesized three regions with distinct differences in structure surrounding the location of laser beam incidence (Figure 6C). Near the center, very few PAEs remained, generally restricted to a monolayer of particles as would be expected for the portions of the film that reached the highest local temperatures. At intermediate distances from the center, the PAEs had rearranged into NP superlattice structures. Far from the irradiated region and the influence of the resulting thermal energy, the thin film remained structurally amorphous as-deposited. Importantly, assuming the absorptivity of the film remains comparable to its initial value, the above model (Equation 1) predicts that $T = T_m$ at $\sim 170 \mu\text{m}$ from the center which is roughly consistent to the observed hole size. However, when the region around the laser spot was characterized *via* profilometry, a “rim” was observed where the film was thicker than either the irradiated hole or the surrounding areas of the film (Figure 6B). Therefore, rather than simply melting off the surface when the local temperature exceeds T_m as was expected initially, this suggests that the PAEs are subjected to lateral forces that push the “heated” region into the surrounding film. This is attributed to the presence of a thermal gradient inducing directional diffusion from high to low temperature, known as thermophoresis.

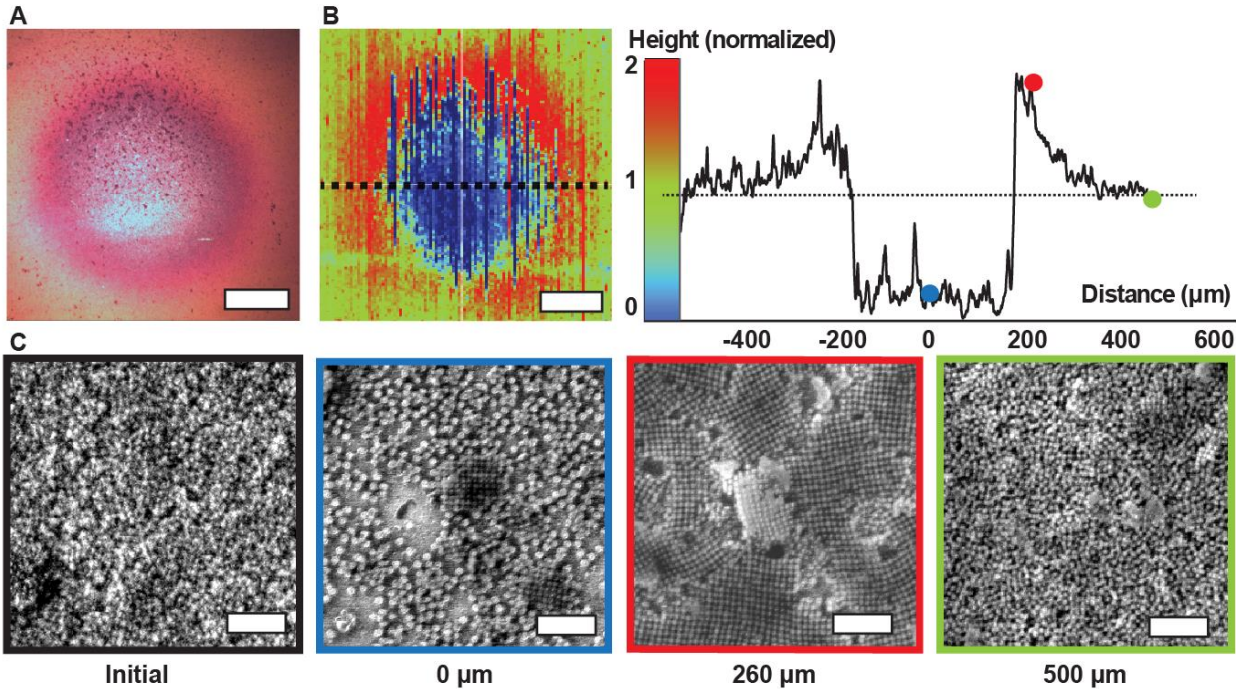


Figure 6. Photograph of a hole resulting from laser-processing of a PAE thin film (A) and corresponding profilometry data (B). Helium ion images taken at varying radial distances at the hole (C) reveal PAE reorganization, with maximum crystallinity occurring at the rim of the resultant hole. Scale bars: A and B - 200 μm ; C - 500 nm.

Previous work has demonstrated that thermophoresis can direct the motion of nanoscale particles away from a heat source; an obvious expectation for PAEs that are no longer permanently bound to the substrate *via* DNA connections would be for the particles to diffuse outwards into solution.^{27,28} The presence of the observed pile-up of particles at the “rim” of the hole indicates that the irradiated PAEs were not forced upward into solution, but rather outward along the substrate surface. While some PAEs likely did dissociate from the surface entirely, the PAEs which relocated from the heated region to the rim must have necessarily retained their PAE-PAE connections while in their mobile state. In other words, a PAE “fluid” consisting of PAEs that were weakly bound to either the substrate or adjacent PAEs receded *collectively* from the hot region at the center of the irradiated beam to the adjacent cold region due to gradients in surface tension, rather than as individually driven particles.²⁹ Again, it is important to note that PAE reorganization is caused by multiple rapid ($\sim$ ms time scale) DNA hybridization and dehybridization events.³⁰ This PAE fluid state is therefore found at temperatures where any DNA bonds between PAEs that are broken *via* heating reform quickly enough to prevent PAEs from immediately breaking away from the aggregate. Previous work has postulated such “fluid” states in similar PAE systems, where *in-situ* measurements found that short-range ordering was disrupted during global heating of a binary superlattice where an initial amorphous state possessed different stoichiometry than the thermodynamically preferred product, requiring significant interparticle diffusion to reorganize.⁷ In bulk heating, PAEs in this fluid state at temperatures near T_m have no directional driving force, and are observed by macroscopic visual inspection to simply diffuse away from the aggregate into solution given enough time at this elevated temperature (typically seconds to minutes).^{31,32} In this system, however, it is hypothesized that the lateral thermophoresis moves the fluid into a cooler region prior to the particles fully dissociating from the surface, essentially “locking” the evidence of fluid-state flow in the film microstructure. The mobile PAEs are pushed away from the irradiation source, maintaining collective cohesion, as they move into regions with lower local temperatures where the dynamic DNA bonds between particles increasingly favor the hybridized state. As a result, fluid PAEs ultimately “solidify” into fully bound lattices that no longer flow once they have been laterally pushed far enough from the irradiation site. Such a phenomenon is consistent with the observed rim feature occurring near the calculated radial distance with local temperature T_m .

Ultimately, these observations indicate that both temperature-induced reorganization (nanoscale structure change) and movement along the surface (mesoscale structure change) contribute in appreciable amounts to the steady-state microstructure of laser-processed PAE thin films, indicating a potentially complex processing pathway for these materials under laser irradiation.

Steady-State Optical Processing vs Incident Power

To further investigate the coupled effects of macroscopic thermophoresis and nanoscale reorganization that are induced by this local heating creating a PAE “fluid,” thin films were processed at various incident laser powers, and their steady-state microstructures were characterized with profilometry and microscopy as above. Additionally, to quantitatively describe the effect of incident power on the processing region, the crystalline ordering as a function of radial distance from the center of the hole was imaged and assessed. From this analysis, the location (distance from center) and quality (correlation length) of the highest ordered region for each of the laser powers was identified (Figure 7A and 7B).

For all studied laser powers, the region of highest crystallinity was observed within the rim surrounding the depleted zone at the center of the irradiated region. Using the distance from the center of the hole to the maximum height of this rim as a measurement of hole size (Figure 7A), it was found that the area of effect for optical processing increased linearly with input power. This is consistent with the proposed model of

the hole forming at a radial distance with local temperature comparable to the melting temperature (Equation 1), as determined by the heat generation of the initial absorptivity of the film.

However, it is important to note that heat generation in this system is a complex function of both incident laser power (held constant) and film absorptivity (which changes as the PAEs are pushed out of the irradiated region). Increased processing power also increases the temperature gradient in the system and, therefore, the thermophoretic driving force. This drives the fluid PAE film to move more quickly from the hotter region with $T \sim T_m$ (where PAE rearrangement occurs) into the cooler region with $T < T_m$ (where PAE rearrangement does not occur). Additionally, since the film absorptivity drops as the PAEs are pushed out of the irradiated region, heat generation within the film decreases more quickly. Thus, the

“goldilocks” zone for rearrangement (where $T \sim T_m$) does not remain at a fixed distance from the laser center, but instead moves towards the center as the film microstructure evolves. With increased power simultaneously driving faster PAE motion outward and the goldilocks temperature region inward, it was observed that the increased processing power actually caused the PAE aggregates to cool at a faster rate than compared to lower laser powers, resulting in smaller crystal grains (smaller correlation length).

Above a threshold power of 65 mW necessary to generate observable amounts of the PAE fluid, the crystallinity of the maximally ordered region decreased with increasing power as hypothesized (Figure 7B). Below this power, there was presumably insufficient driving force for the PAEs to rearrange; this was only measured with a 0mW (unprocessed) sample due to the difficulty of finding and analyzing an irradiated region without a macroscopic feature for reference. Ultimately, this experiment highlights the necessity to explore the complex interplay between temperature-induced rearrangement and thermophoresis, not just at steady-state equilibrium but also during this transient regime.

Transient Nanoscale Rearrangement During Optical Processing

In order to investigate the transient film structures in between the initially disordered state and the processed, steady-state end points examined in the previous sections, films were exposed to powers from 65 mW to 123 mW for 1 to 16 seconds, embedded in silica, and imaged using the same techniques discussed previously. Because the predicted time scale for thermal dissipation of laser-induced heating is calculated

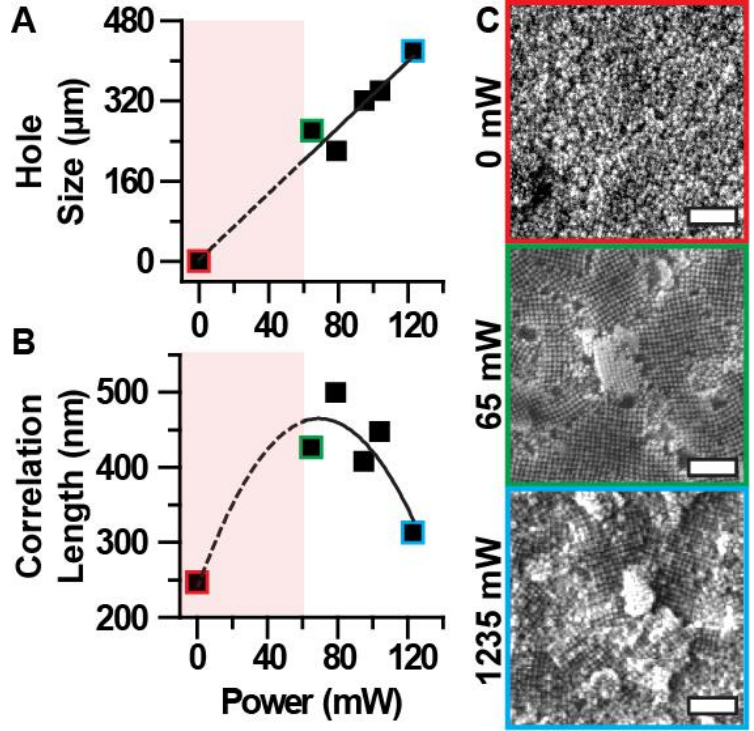


Figure 7. Hole size (A) and maximum correlation length (B) for PAE films processed at various laser power. Helium ion images (C) of the films reveal that correlation length correlates to ordering of the sample. Scale bars are 500nm. Lines are drawn as guides for the eye. The red regions in A and B correlate to power which exhibited no observed macroscopic hole in the experimental timeframe.

to be ~1 second, these short irradiation times were expected to give accurate snapshots of the evolution of the film structure during the plasmon thermalization induced reorganization process.

Consistent with the above results, high-power processing resulted in the removal of PAEs from the surface, either *via* film dewetting or PAE dissociation entirely due to high thermophoretic forces driving lateral motion of the particles. Additionally, several stray PAE aggregates that protruded from the film were observed in these samples; while the exact mechanism of formation of these PAE aggregate “debris” could not be easily ascertained in these

ex-situ experiments, the observed morphology does appear to indicate that these aggregates were either caused by film dewetting, or that the particles released from the substrate and redeposited during processing. Similar “debris” was observed in the steady-state samples discussed above, though not nearly in as much abundance, presumably because these loosely bound aggregates would be expected to be pushed clear after hours of processing. Conversely, lower-power processing yielded nucleation of crystalline hillocks near the beam center prior to significant hole formation (Figure 7C). It should be noted that even at this lower processing power, this central irradiated region would be expected to reach temperatures well above the PAE’s T_m . It is intriguing that the transient morphologies appeared distinctly dissimilar for the high and low power cases, yet the steady-state morphologies generally converged. This is attributed to the rapid development of similar steady-state heat generation and temperature profiles once PAEs are removed from the irradiated region, regardless of the method of removal.

Focusing on the low-power regime where crystallization occurred most robustly, the mechanism and kinetics of both nanoscale rearrangement and microscale thermophoresis were investigated by determining the location (relative to beam center) and correlation length of the region with highest crystallinity for each time point (Figure 8A and 8B). As processing time increased, the location of the maximum ordered region moved farther away from the laser center, while the correlation length of the maximum ordered region increased with time as the size of the crystalline domains grew (Figure 8B). This data suggests that crystal nucleation occurs in the heated material nearer the center of the irradiated region, and these crystalline regions grow as they are pushed into cooler regions further from the center. Importantly, this provides

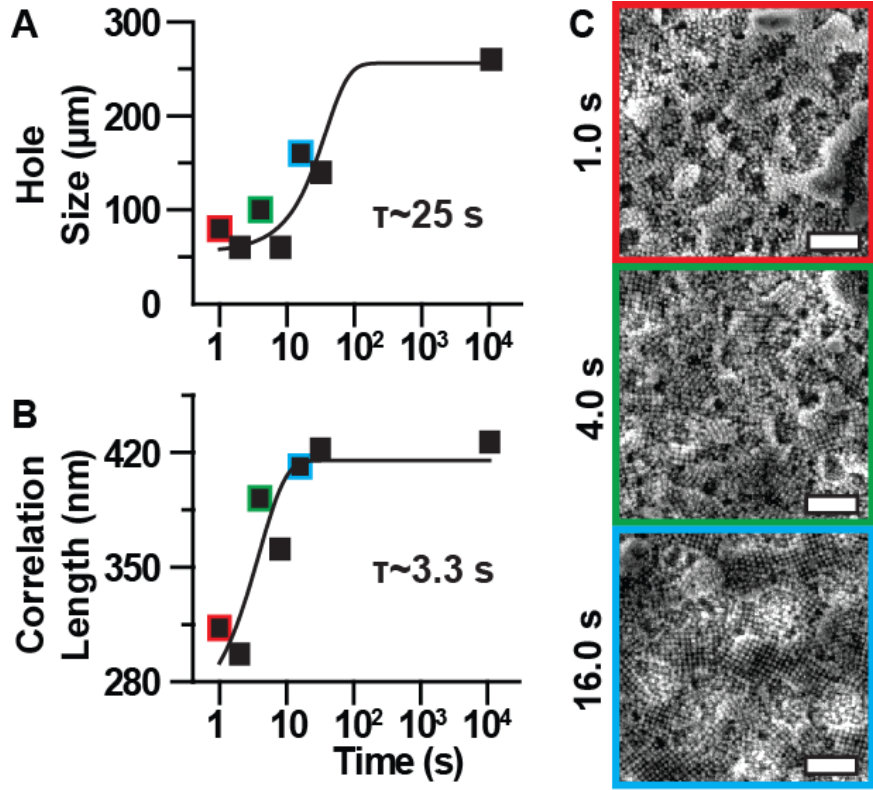


Figure 8. Development of hole size (A) and maximum correlation length (B) for PAE films processed as a function of time. Helium ion images (C) of the films illustrate nucleation and growth of ordered regions. Scale bars in C are 500 nm.

further evidence for the proposed “fluid-like” PAE state in these high-temperature regions, where particles can easily and quickly nucleate crystalline grains but are also susceptible to thermocapillary flow in the presence of thermophoretic forces. In other words, the melting and crystallization behaviors are inherently linked in this optical processing method and happen concurrently.

To estimate the relevant timescales associated with the microscale thermophoresis, the distance from center vs processing time data was fit to a Gompertz curve of the form:

$$f(t) = Ae^{e^{-\frac{t-t_c}{\tau}}} \quad (2)$$

Where $f(t)$ is the time-dependent parameter (either size of hole, or correlation length), A is final amplitude, t_c is the inflection point, and τ is the timescale of the process. Using this analysis, the timescale for NP motion to reach a steady-state hole size was estimated to be $\tau \sim 25$ s (Figure 8A). Similarly, fitting the maximum correlation length vs processing time to an equivalent Gompertz function, the timescale was determined to be $\tau \sim 3.3$ s (Figure 8B). The similarity of the two timescales is consistent with the fact that both mesoscale thermophoretic motion and nanoscale PAE reorganization are a function of PAE mobility. As PAEs are heated, the rates of DNA binding and unbinding events associated with PAE reorganization increase. A sufficiently heated PAE (T approaching T_m) is therefore capable of moving relative to its neighbors to reach a thermodynamically stable unit cell in the nanoscale, but its increased mobility and loosened connections to the bulk make the PAE aggregates more susceptible to collective motion on the mesoscale as well.

Optical Processing Prior to Quasistatic Thermal Profile

Due to the similar timescales of mesoscale restructuring of the PAE film and nanoscale reorganization of PAEs into crystals due to localized heating, using plasmon thermalization to induce crystal formation without also removing PAEs from the processed region is potentially challenging. However, using sufficiently short laser pulses, it should in principle be possible to locally heat the PAE film into the observed fluid state and quickly quench the region’s temperature by removing the laser stimulus, effectively “locking” this fluid structure in the thin film morphology, prior to thermophoresis driving the PAEs to cooler regions of the film.

To explore this potential processing methodology, PAE thin films were exposed for 125-1000 ms at a power of 65 mW; no PAE melting was observed for these laser irradiation conditions. When the PAE thin films were irradiated with laser light for less than 1 s (below the characteristic time scale of thermal diffusion in the system),³³ heat was only able to diffuse minimally, and the solution never reached a quasistatic temperature profile. One immediate consequence of this reduced heat “tail” compared to the thermal steady state was that local heating was more confined to the illuminated region, dramatically reducing the area of effect (compared to the previously observed 500 μm). Additionally, as expected, thermophoretic motion and resulting hole formation was substantially suppressed, since PAE diffusion did not have enough time to occur before the area cooled to ambient temperature, locking the PAEs in place.

Samples processed at low power (65 mW) and for short times (500 ms) appeared to be a highly amorphous glassy structure, attributed to the structure of the fluid PAE phase locked in place (Figure 9A). This glassy structure would be expected to exhibit even lower ordering than the initial kinetically trapped structure, which may exhibit paracrystalline features as particles rearrange during the deposition process. When the PAE film is deposited at room temperature, far below the melting temperature, the thermodynamically stable structure is an ordered superlattice state. Therefore, even though the association of the particles the

surface during the LbL process is stochastic, there is a bias for the particles to initially attach in the superlattice configuration. The effective result is the formation of very small “grains” in the film. The low deposition temperature prevents particle rearrangement after deposition, these “grains” are able to neither join together to form larger grains, nor pull apart to form discernible grain boundaries, resulting in the disordered appearance known as a paracrystalline state.³⁴ Conversely, the PAE fluid is thermodynamically disordered, lacking the stochastic bias of the LbL deposited sample. While this distinction is difficult to determine visually using microscopy, Fourier analysis quantitatively demonstrates a decrease in order parameter relative to the initial film (Figure 9B).

For samples processed at higher power (123 mW) at sufficiently low times (125 ms), the system was locked into a microporous structure. This is consistent with the fluid PAE film beginning to dewet from the surface, but freezing midway through the dewetting process. In general, thin films are unstable due to the large surface area of the configuration, compared to a configuration of droplets on the surface. Classical models of thin film breakup indicate that the capillary instability mechanism, facilitated by thermal fluctuations, allows periodic perturbations to form in an initially flat thin film.³⁵ When the film is sufficiently heated, the combination of decreased viscosity of the PAE fluid and the reduced adhesion to the substrate allows the fastest-growing periodic perturbations to dominate the structure, resulting in the observed finger-like microstructure with well-defined thickness (characteristic of spinodal processes).

Isolation of these unique, fluid PAE phases through conventional, global heating methods is challenging for two reasons. First, heating a PAE film to high temperature (near T_m) can result in significant dissociation of particles from the film into solution, destroying the film. This occurs even prior to the PAE film achieving fluid-like behavior, analogous to the sublimation of a solid. Secondly, the bulk cooling rate of PAE films is limited by the addition of the thermal mass of the entire medium, allowing the fluid morphology to rearrange into a paracrystal or crystal upon

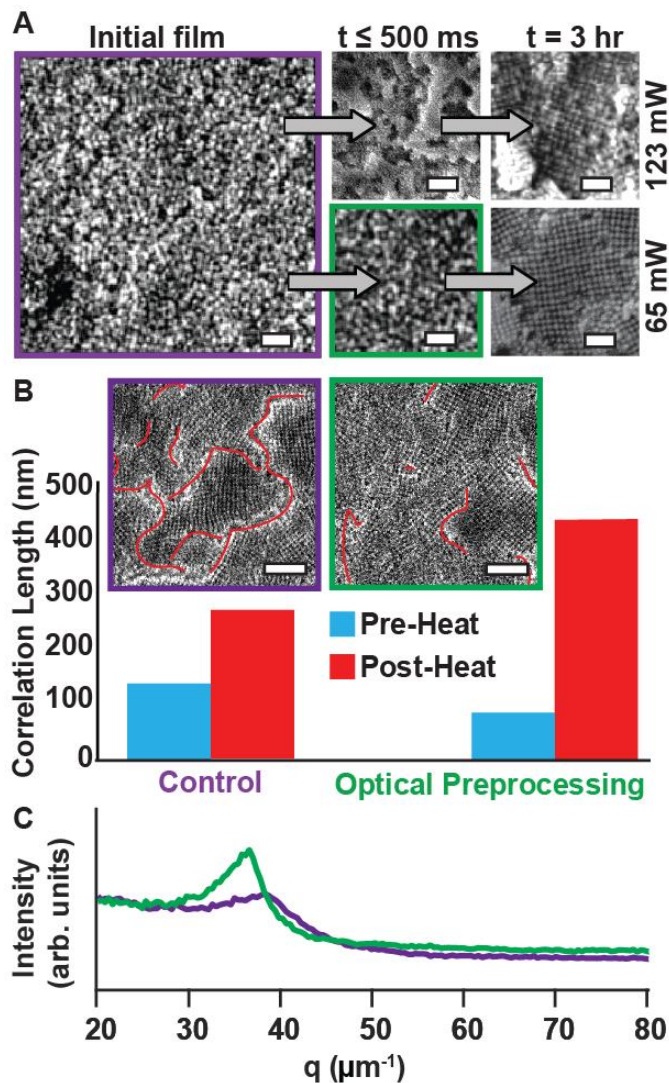


Figure 9. Helium ion micrographs (A) of PAE films processed at varying time and power give microporous, glassy, or crystalline morphologies. Fourier analysis of optically pre-processed samples (B) indicates increased crystallinity after thermal processing, as determined from the 1D Fourier Transform of the images (C).

cooling, rather than being locked into a glass morphology. Optical processing circumvents both of these issues by rapid heating and rapid cooling, enabled by local processing. First, the PAE film may be rapidly heated due to the small thermal mass of the localized processed region, reaching the PAE melting temperature prior to PAEs dissociating away from the substrate. Second, the PAE fluid region may be rapidly cooled because of the high surface-area to volume ratio of the localized processed region, allowing for efficient convective cooling.

While this processing into a glassy morphology marks a novel method for reducing long-range ordering of the PAE system, it may also be used to produce PAE lattices with enhanced ordering. Since the glassy configuration contains fewer pre-nucleation sites compared to the initial, partially-ordered paracrystalline state, it is hypothesized that the film microstructure will be influenced by the number of these sites in subsequent annealing steps. Indeed, while no crystals were observed for samples that received these short annealing times alone, subsequent bulk heating of the entire sample resulted in significantly different crystal qualities for the optically processed regions compared with the rest of the film. Specifically, the regions of the substrate that had been irradiated exhibited remarkably increased correlation lengths compared to the non-irradiated regions, increasing from 270 nm to 450 nm (Figure 9B and 9C). Importantly, the sophisticated control over spatial and temporal heating profile afforded by this laser processing enables a drastic improvement in the quality of PAE-based structures compared with conventional bulk heating of the material.

The results described above explore the behavior of PAE thin films under localized thermal processing. It was demonstrated that the PAE system can be induced to reorganize into a crystalline structure, analogous to established thermal processing techniques but with the addition of spatial control. Furthermore, the spatial confinement provided an additional means of manipulating PAE morphology, including thermophoretic motion and quenching of a previously elusive “fluid” state. This spatially-resolved particle reorganization and thermophoresis enables the future development of a wide range of processing techniques, including the fabrication of patterns *via* direct-write optical lithography by selectively melting, crystallizing, amorphizing, or inducing pileup of PAEs in processed regions. Spatially-resolved particle reorganization could also allow for the development of sophisticated crystallization protocols such as zone-refinement, in order to generate large crystals *via* selective growth of a single domain. The experimental realization of PAEs with locked-in fluid morphology has the potential to improve crystallization protocols *via* pre-nucleation site reduction, as demonstrated, but also allows the exploration of high-disorder phenomena in PAE systems, including strong Anderson localization of photons or phonons for optical or thermal applications. The use of plasmon thermalization as a means of localized heat generation to induce PAE crystallization is therefore a promising method for dictating the meso to macroscale structure of PAE superlattices through multiple novel mechanisms and design handles.

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3.3 Synthesis of Epitaxial Single Crystals

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 In this area of research under the AFOSR program, we demonstrated how programmable DNA hybridization enables the formation of single-crystal Winterbottom constructions¹¹ of substrate-bound nanoparticle superlattices with defined sizes, shapes, orientations, and degrees of anisotropy. Additionally, we discovered that some crystals exhibit deviations from the predicted structure due to an additional growth pathway that would not be predicted in atomic crystals, providing insight into the differences between this model PAE crystallization system and other atomic or molecular crystals. By precisely tailoring both interparticle and particle-surface potentials, we used this model to both understand and rationally control the complex process of interfacial crystallization.

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 10).¹² When appropriately designed and processed, these PAEs can therefore form many different crystal structures with controlled lattice parameters and crystallographic symmetries,^{13,14} where the favored crystalline arrangement typically maximizes the number of DNA connections between particles.¹⁵ For example, in a binary system consisting of two PAEs with

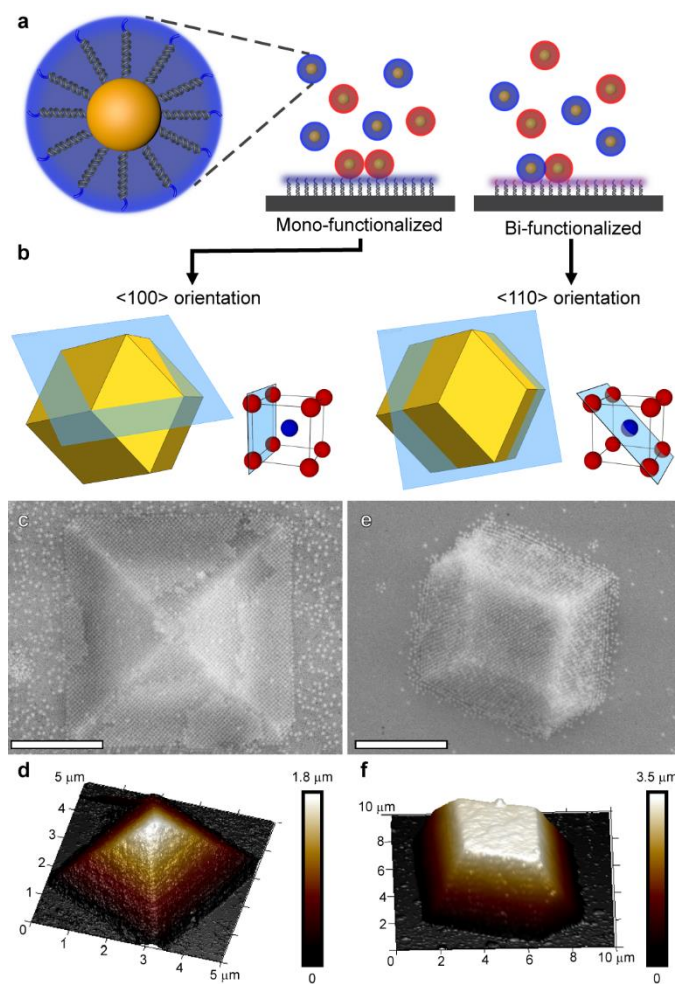


Figure 10: Substrate Growth of Crystals into Winterbottom Shapes. Nanoparticles functionalized with complementary DNA (a) slow-cooled in the presence of a DNA-functionalized substrate will grow single crystal Winterbottom shapes that are truncated Wulff polyhedra (b). Depending on the substrate functionalization, $\langle 100 \rangle$ or $\langle 110 \rangle$ oriented crystals can form, producing pyramidal (c, d) or diamond (e, f) shaped PAE single crystals on the surface. Scale bars are 1 μm.

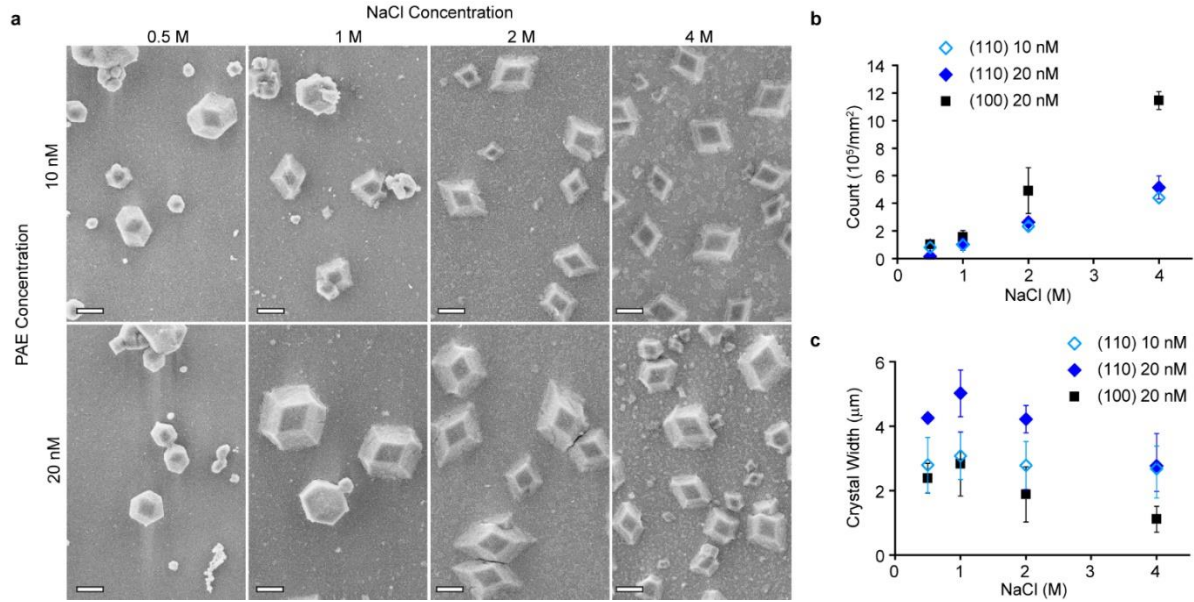


Figure 11: Salt Concentration Effects on Crystal Growth. a) SEM images of <110> oriented crystal growth in different salt concentrations and PAE concentrations, showing increased crystal density with increasing salt concentration, and increased size with increased PAE concentration. Scale bars are 2 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.

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.¹⁶

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.^{5,6,12} 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.¹⁷ In the presence of an interface, the thermodynamically preferred crystal shapes are polyhedra referred to as Winterbottom constructions.^{11,18} 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 10b). 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 10). 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), 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. 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:

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

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 screening²²⁻²⁴, meaning that fully understanding the complexity of this effect may require significant modeling of PAE assembly. However, prior work with the PAE design used here²⁰ 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.

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. 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 9b). 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 9c). 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 NaCl⁹; 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 area⁹. 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

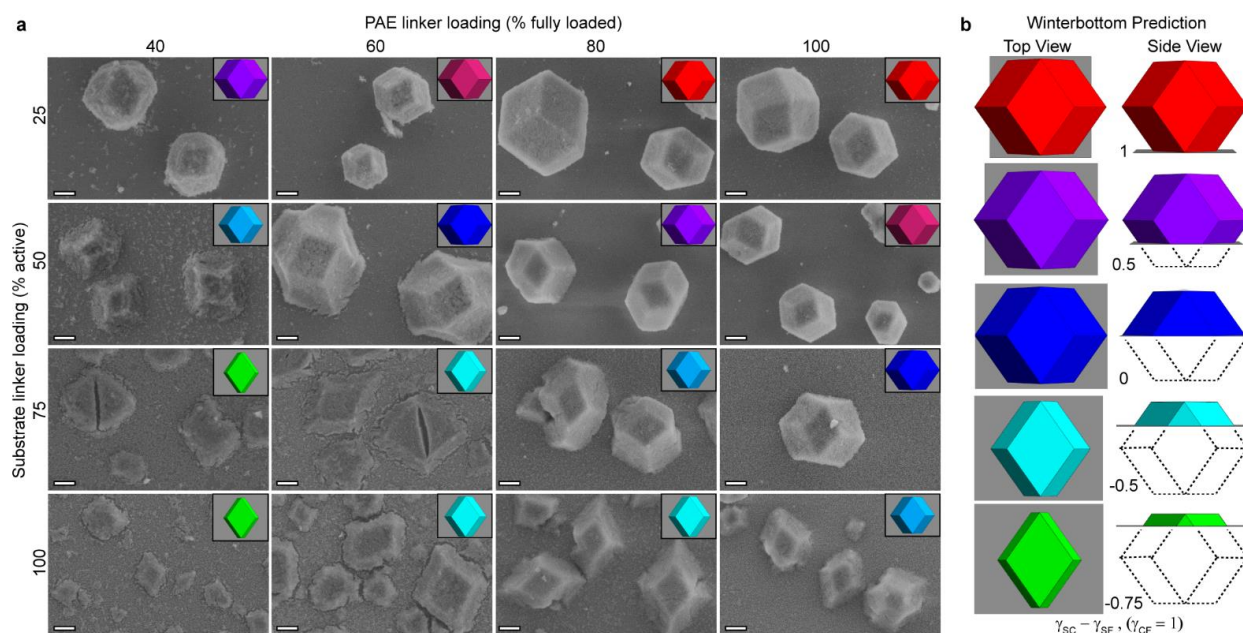


Figure 12: DNA Loading Effects on Winterbottom Shape. a) Increasing DNA loading on the nanoparticles (images from left to right) increases the crystal surface energy, resulting in a less recessed crystal. Increasing the percentage of active DNA strands on the substrate (images from top to bottom) decreases 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%;²³ 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).

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

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

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.

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.¹⁵ 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 12).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 $\langle 110 \rangle$ 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 13). 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 10a and 13a). Calculation of the relative energy difference between these “diamond” shapes and the true Winterbottom constructions (Figure 13c) 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.

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.¹³ 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.¹⁷ Additionally, while AlB₂-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 AlB₂ lattice.²⁶

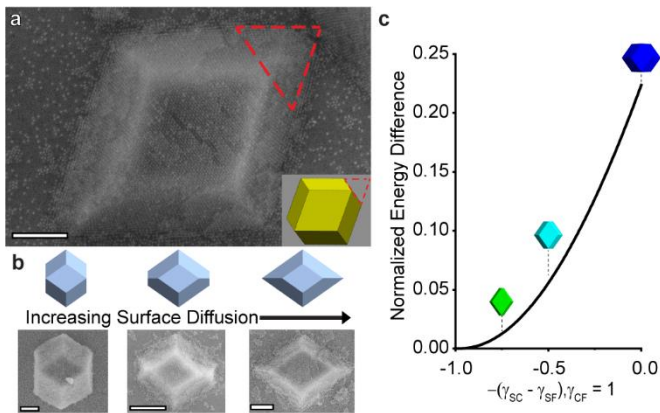


Figure 13: Deviations from Winterbottom Construction. a) Crystals on substrates with high PAE-substrate affinities deviate from the predicted Winterbottom shape (inset). b) These deviations are likely due to PAEs adding to the growing crystals by diffusing to the crystal from the substrate. c) With lower interfacial energies of the crystals, the energy difference between the initial kinetically formed shape and the thermodynamically preferred Winterbottom shape decreases,

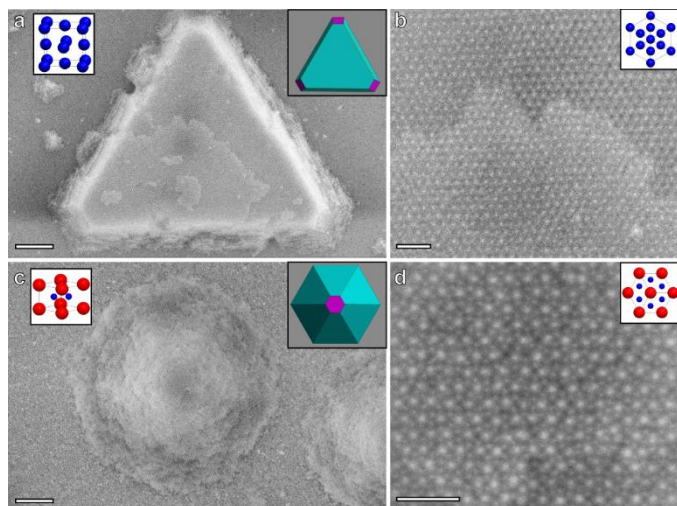


Figure 14: FCC and AlB₂ Crystal Growth on Substrates. a) FCC crystal, conforming to the predicted Winterbottom construction (inset), with confirmed $\langle 111 \rangle$ orientation (b). c) AlB₂ crystal, conforming to predicted Winterbottom construction (inset) with the $\langle 100 \rangle$ orientation (d). Scale bars are 1 μm for a) and c), 200 nm for b) and d).

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, single crystal FCC structures were readily observed with the (111) plane parallel to the substrate (Figure 24a and b). Similar to the FCC lattice, the (001) planes of AlB₂ 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 14c and d), as predicted by the Winterbottom construction (right insets, Figure 14 a and c). 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 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 growth²⁷ 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 resonators⁵, 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.

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3.4 Stabilization of PAE Lattices in Dynamic Hydrogels

Self-assembly is a powerful tool for the bottom up synthesis of materials and devices from small components, enabling precise control over material structure at the nanoscale.^{1,2} By tailoring interactions between particles,³⁻⁵ interactions of particles with a predefined template,^{6,7} or interactions of particles with external forces,⁸⁻¹¹ ordered one-,^{12,13} two-,^{14,15} or three-dimensional^{3,16} nanostructures can be generated with characteristic lengths across the nano and microscales.^{4,11,17} As shown in this AFOSR work, of the methods that have been developed to generate these particle assemblies, the use of DNA strands as programmable directing ligands has emerged as one of the most versatile, allowing for the synthesis of colloidal crystals with a variety of lattice structures, sizes, and compositions.¹⁸⁻²⁰ These DNA grafted particles, or “Programmable Atom Equivalents” (PAEs), consist of a nanoparticle core functionalized with a dense layer of duplexed DNA chains that terminate in short, single-stranded ‘sticky ends’, where duplexation of complementary sticky ends on different PAEs directs the assembly of ordered superlattices in aqueous solution. Although PAEs are an extremely versatile tool for studying self-assembly, the resulting crystals are fragile and can be degraded or destroyed by changes in environmental conditions (such as changes in salinity or the presence of impurities in solution).²¹ Furthermore, to preserve ordering during dehydration, the solvent must be removed slowly at ambient conditions to avoid cracking and maintain order,^{22,23} and the ability to partially dry the lattices to fine tune structure has not been shown.²⁴

Previous work has demonstrated that crystallinity can be preserved by embedding the assemblies inside of amorphous silica.²⁵ While this protocol has allowed for the direct imaging of PAE lattices to study their assembly behavior, the resulting materials are rigid and lose many of the benefits associated with assembling colloidal crystals in solution (e.g. reconfigurability of the structure and dynamicity of the DNA binding interactions). PAE lattices can be stabilized and expanded or contracted by the addition of intercalating agents^{26,27} or stabilizing cations,^{28,29} which may also make the assemblies more resilient to heat and other external forces. However, these methods of stabilization leave the PAEs as individual crystallites in solution, making it difficult to handle and manipulate the lattices, and some loss of crystal quality after stabilization can also be observed via X-ray scattering. Significant benefit could therefore be obtained from the development of a superlattice embedding protocol that retains the open and hydrated nature of the PAE superlattices while also providing a handle by which to more easily manipulate the lattices, as this would allow for greater dynamic modulation of the lattices post-assembly. Here, we present a major step towards this goal by developing a strategy to embed colloidal crystals inside of a deformable hydrogel that is electrostatically associated to the DNA ligands of PAEs.

Electrostatic interactions between the negatively charged sugar-phosphate backbone of DNA strands and cationic polymers (such as poly(ethyleneimine) and poly(dimethylaminoethyl methacrylate)) have been used to encapsulate DNA in the form of ‘polyplexes’; these DNA-polymer assemblies are commonly used to deliver DNA into cells for therapeutic treatment.³⁰⁻³² We therefore hypothesized that the formation of a polymer gel consisting of a network of crosslinked polyelectrolytes that are attracted to the negatively charged PAEs could be used to bind to and stabilize PAE superlattices without the need to embed the assembled particles in a rigid material or collapse the lattices. These gels were prepared by dispersing PAE crystallites in a solution of polymerizable dimethylaminoethyl acrylate (DMAEA) and methylene bis-acrylamide (MBAAm) monomers and then adding a radical initiator to rapidly embed the crystallites within the gel. The lattices exhibited little change in crystallinity upon embedding (as confirmed with small angle X-ray scattering, SAXS) or upon handling of the gels. However, both chemical and mechanical stimuli

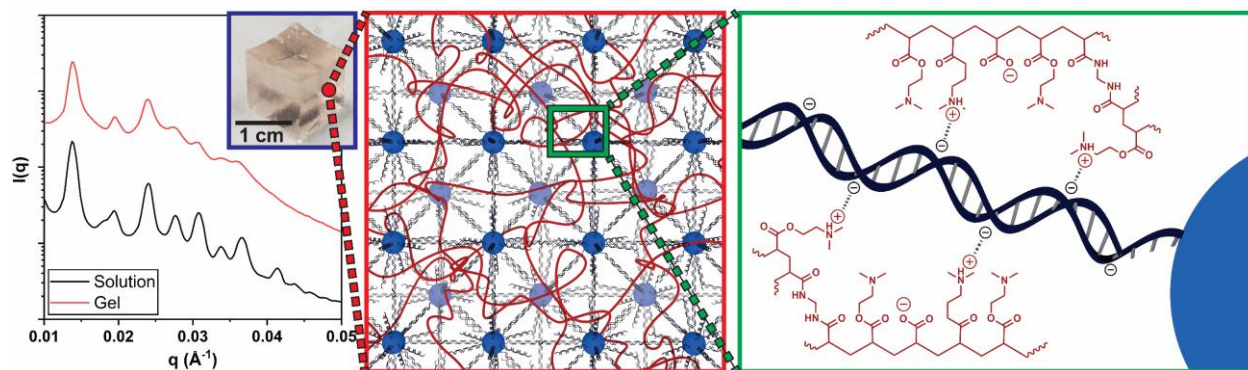


Figure 15. (Left) SAXS showing preservation of structure in LSE PAE crystals after gelation. Inset: Image of P(DMAEA-MBAAm) hydrogel with embedded PAE crystals. (Center) Illustration of PDMAEA chains infiltrating an ordered array of PAEs. (Right) Illustration of crosslinked hydrogel and positive ionic charge that is attracted to the negative charge of the sugar-phosphate groups composing the DNA backbone.

could be used to expand or contract the macroscopic gels, resulting in reversible changes to the particle organization within the lattice.

In order to construct these hydrogels with embedded colloidal crystals, PAEs were first assembled into body centered cubic (bcc) arrays inside of phosphate buffered saline (PBS) solution according to established protocols. The assembled lattices were then exposed to a solution of DMAEA and MBAAm diluted with additional buffer. DMAEA is highly soluble in PBS with a near neutral pKa (~ 8.4 in monomer form and ~ 7.5 as a polymer) and is therefore partially protonated and electrostatically attracted to the DNA strands in solution;³³ MBAAm is a difunctional monomer that was used to decrease the mesh size of the resulting gels to aid in PAE encapsulation.

In water, DMAEA acts as a base and also rapidly hydrolyzes into acrylic acid and dimethylaminoethanol. Therefore, experimental protocols needed to be developed to ensure PAE lattice stability and minimize hydrolysis prior to gelation. The solution pH at the moment of gelation was ~ 11 as measured with litmus paper. After polymerization, the gradual hydrolysis of DMAEA residues consumed hydroxide ions, resulting in a decrease in pH to $\sim 8-9$ over several hours. As the pH decreased, the fraction of protonated DMAEA residues in the polymer increased from approximately 0.2% to 20% allowing for strong electrostatic attraction between the hydrogel and the PAE lattices. Under these conditions, virtually all acrylic acid residues (pKa ~ 4.5)³⁴ resulting from DMAEA hydrolysis were deprotonated, such that the gel was in a zwitterionic state. The polymeric form of DMAEA is significantly more stable than the monomer towards hydrolysis, with a reported half-life of several months at room temperature and near neutral pH.^{33,35–37}

The observed jump in pH upon addition of the hydrogel monomers to a solution containing PAEs could denature DNA complexes and disrupt the nanoparticle assemblies.³⁸ However, the subsequent slow decrease in pH results in conditions much more amenable to DNA hybridization and thus PAE lattice stability. To prevent the transitory pH spike from negatively affecting the organization of nanoparticles within a crystal, two distinct strategies were investigated. First, DNA strands with longer sticky ends (LSE, 10 unpaired bases) were used to form the lattices, as these 10-base duplexes remained stable even when subjected to the initially elevated pH. However, prior efforts have shown that weaker sticky end connections between PAEs often result in higher quality lattices.²¹ Thus, separate experiments were also performed to

demonstrate that a strong acid could be used to neutralize the DMAEA solution before addition to the DNA materials to avoid denaturation. This was shown by embedding PAEs crystals with shorter sticky ends (SSE, 6 unpaired bases) in gels using monomer solutions that were acidified to a pH of ~ 8 prior to use. In all cases, the monomer solutions were kept chilled prior to addition to further aid in maintaining lattice stability and to limit monomer hydrolysis before gelation. Polymerization was initiated by the addition of sodium persulfate, which generated

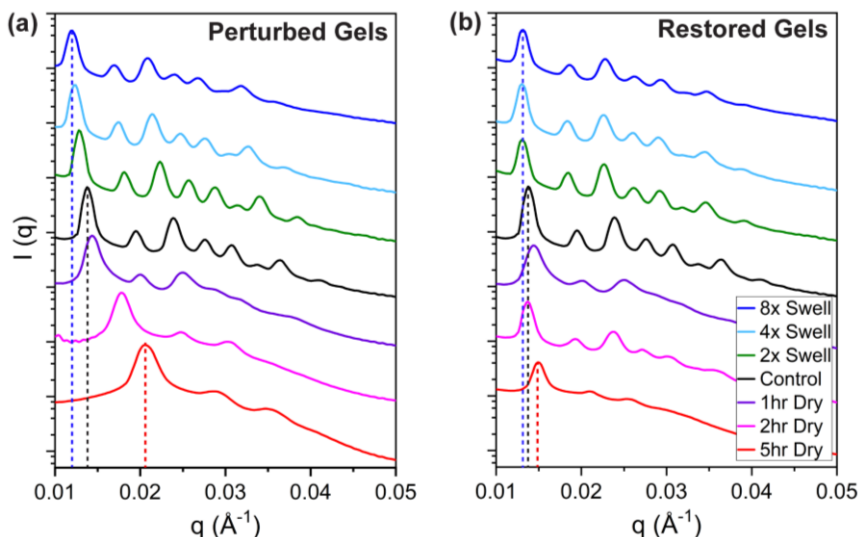


Figure 16. (a) 1D SAXS traces for PAE crystal embedded hydrogels which were swollen by dilution or dried for a specified period of time under vacuum. Dotted lines emphasize the shift to smaller q after swelling and larger q after drying. (b) 1D SAXS of the same samples after being restored by washing with PBS. Dotted lines show a return towards the initial q value.

radical species when reduced by DMAEA, resulting in gelation within a few seconds.³⁹ Both of these strategies were able to maintain the integrity of the PAE lattices during and after hydrogel formation; these two approaches therefore provide useful protocols for future experiments involving the encapsulation of DNA-based materials in hydrogels, including both PAEs and potentially other DNA-nanotechnology constructs. Small angle X-ray scattering (SAXS) experiments were performed both before and after gelation, and no perturbation of the crystal lattice parameters, nor significant degradation of crystallite size were observed in the embedded samples when using either method (Figure 16).

A significant potential advantage of soft encapsulation would be the ability to reversibly manipulate the structure of the embedded microscopic crystalline lattices by manipulating the macroscopic gel. As an example, changes in solute concentrations lead to changes in swelling pressure and thus the expansion or contraction of many hydrogels.⁴⁰ It is possible to induce swelling of the P(DMAEA-MBAAm) gel by adding pure water to dilute the initial solution used to form the gel (which contained 0.5 M NaCl) and to subsequently de-swell the gel by exposing it to saline solution. In addition, the gel can be shrunk from its initial state by simply reducing the water content in a controlled manner under vacuum. This dehydration can also be reversed by adding water back to the gel. For all of these manipulations, it was hypothesized that the ionic interactions between the gel and PAE DNA strands would promote the concomitant deformation of the PAE superlattices within the hydrogel.

To test this hypothesis, several PAE embedded gels were prepared and subjected to swelling and drying treatments, and SAXS was used to evaluate any changes in the structure of the embedded lattices. For swelling, gels were immersed in filtered, de-ionized water (to a total volume of 2, 4, or 8 times the initial volume of the gel), while drying was accomplished by placing gels in a vacuum oven at room temperature for a specified time period (1, 2, or 5 hours) (Figure 6a). The swollen and dehydrated gels were subsequently restored by washing twice with 0.5 M NaCl PBS (Figure 16b).

The PAE lattices remained ordered and were observed to progressively expand with increasing dilution and to progressively contract with increasing drying time. To quantify the extent of deformation of the embedded crystals, the change in lattice parameter (the edge length of the bcc unit cell) was estimated from the location of the first peak (without form factor correction). The lattice parameters increased to 107%, 112%, and 115% of the control value after 2x, 4x, and 8x dilution, respectively, and contracted to 96%, 78%, and 67% of the control value after drying for 1hr, 2 hrs, and 5 hrs, respectively (see Table S1). Remarkably, after washing the gels with 0.5 M NaCl PBS, all of the perturbed lattices returned to within 5% of their original lattice parameters with the exception of the sample that was dried for 5 hours (which remained ordered but only returned to 92% of its initial parameter). A potential reason for the small deviations of the restored lattices from the control is the dilution of any aqueous species in the original gel that are not contained in the PBS (such as any unreacted monomer or dimethylethanolamine resulting from monomer hydrolysis). The embedded superlattices demonstrated remarkable fidelity in the swelling experiments with little loss of lattice quality before or after swelling. While it was possible to achieve greater changes in the lattice parameter by drying, the lattices appeared to be partially degraded and remained so after rehydration. The comparative difficulty of compressing the lattice while maintaining order is attributed to steric and electrostatic repulsion between the dense grafts of DNA on neighboring particles. Furthermore, we hypothesize that the sample that was dried for 5 hrs was unable to fully return to its initial state because the extreme degree of compaction may have significantly disrupted duplexation between the DNA grafts. However, in general, the embedded superlattices showed a remarkable capacity for reversible change in lattice spacing in response to changes in the gel environment.

Importantly, inducing the level of dynamic adjustment observed here previously required the addition of specific ions or intercalating agents, the use of a more complex and pH responsive DNA strand motif,⁴¹ or a transition to organic solvent,⁴² and many of these methods only allowed for either contraction or expansion, not both. Since the size of the gold NP cores of the PAEs are not changed during these experiments, the strain in the bonded DNA grafts between particles can be determined by calculating the surface-to-surface spacing (d_{ss}) (i.e. the length of the bonded DNA grafts) in each state to allow for a more direct comparison to existing methods of manipulating PAE lattices (see Table S1). Previous work showed that the reversible addition of an intercalating agent could increase d_{ss} by up to 24% which is similar to largest increase of 22% observed in the swelling experiments presented here.²⁶ Independently, the use of silver ions as a lattice stabilizer has been shown to result in up to a 25% lattice contraction, corresponding to a d_{ss} strain of -34%, while the maximum strain observed in the partial dehydration experiments shown here was -48% (a further compression of d_{ss} in the Ag^+ stabilized lattices to -77% was observed after complete drying due to collapse of the poly(ethylene glycol) (PEG) segment of the DNA grafts).²⁸ During careful slow drying of solution based PAE crystallites without PEG spacers or any further stabilization, a contraction of 45% was observed in interparticle spacing. While the dried lattices could be rehydrated into ordered lattices, long range order was not observed via SAXS in the dehydrated state.²⁴ Thus, the use of hydrogel embedding allows for a similar range of PAE lattice manipulation to those previously demonstrated by multiple stabilization techniques in a single convenient method.

In addition to providing the ability to modify the structures of these lattices via chemical stimulation, embedding the PAE lattices in gels should also enable direct and precise deformation of the lattices by mechanical manipulation, which potentially offers the opportunity to deform the gels (and thus the lattices) anisotropically. To examine this hypothesis, a linear compression stage was used to partially compress larger gels to various levels of strain while monitoring changes to PAE lattice structure with SAXS (Figure

17). By dividing the 2D SAXS pattern into narrow sectors, the extent to which the lattices were strained along orthogonal axes during mechanical compression could be measured for both an as-made, hydrated gel and a gel which was partially dried under vacuum for 6 hours to reduce its water content by approximately 40%. When the samples were compressed, the initially circular SAXS patterns expanded to larger q values in the 90° sector (aligned with the axis of deformation) indicating lattice compression and contracted to smaller q values in the 0° sector (perpendicular to the direction of compression) indicating lattice expansion. As a result, the 1D sector

averages for 0° and 90° orientations (Figure 18a and 18c) progressively diverged with increasing compression of the gels. For the hydrated gel, up to 35% compression was achieved before the hydrogel burst, whereas the partially dried gel remained intact at up to 50% compression. As with the previously discussed swelling and drying experiments, the lattices exhibited a higher structural fidelity during expansion compared to compression. In fact, the lattice quality of the dried gel seemingly improved in the 0° orientation (in which the lattice was stretched) while the 2D pattern shows much less evidence of order in the 90° orientation (in which the lattice was compressed), further indicating that lattice compression is limited by strong interparticle repulsion but that interactions between the PAEs and the gel network can preserve relative particle positioning during expansion (Figure 17 and 18c).

Lattice parameters were estimated from the location of the first peak in both the 0° and 90° directions as the samples were deformed (Figure 18b and d). During compression, a delay in the onset of change in the embedded crystallites' lattice parameters was observed for the hydrated gel, followed by roughly linear increases in the lattice strain in both directions as sample compression increased. The observed delay is ascribed to the crystallites reinforcing the surrounding hydrogel. Within a PAE superlattice, double stranded DNA segments span between rigid nanoparticle cores. The behavior of B-form DNA is well captured by a worm-like-chain model with a persistence length of ~ 50 nm (depending on specific base pair sequence), which is greater than the d_{ss} of the bcc lattices in this work.⁴³ However, the specific strands used in this work also contain short, flexible poly(ethylene glycol) (PEG) segments near the particle surfaces. As such,

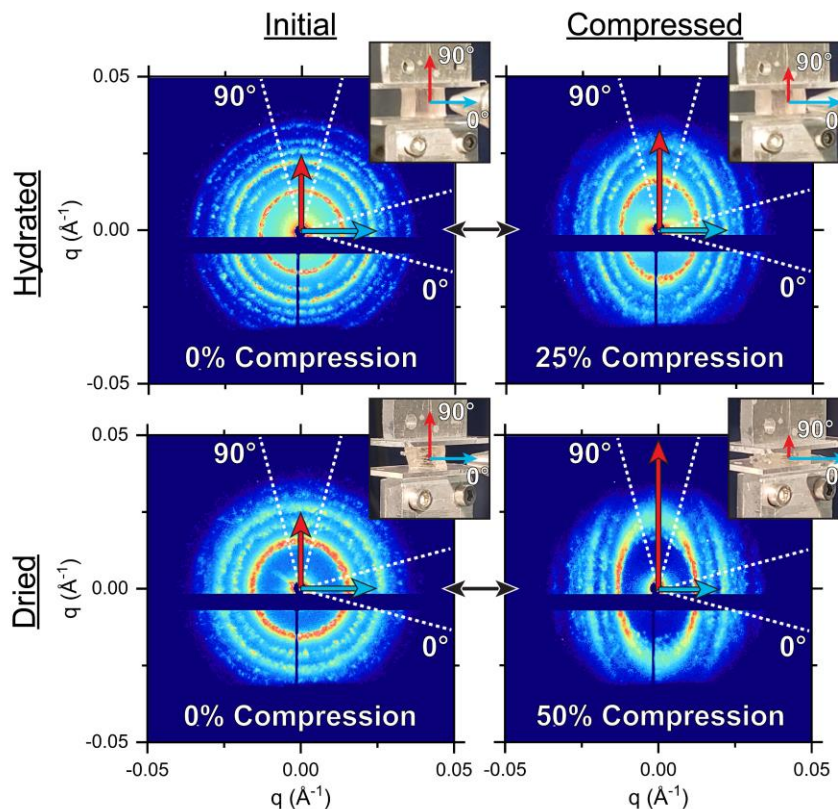


Figure 17. 2D SAXS pattern for an as-made, hydrated gel (top) and a gel which was partially dried under vacuum (bottom). The left column shows the patterns for unstrained gels, while the right column shows the patterns that results when the gels are compressed. Inset images show gels in the in-situ SAXS compression stage.

it is reasonable to hypothesize that the interparticle linkages contribute only a small reinforcing effect at small strains to the flexible hydrogel matrix that interpenetrates the lattices, which (considering the limits of instrument precision) leads to the brief delay observed in the onset of lattice strain. In contrast, for the partially dried (and densified) gel, there was an immediate linear relationship between the strain of the embedded lattices and the gel compression. Given the changes in PAE lattice parameters determined from SAXS, a Poisson's ratio for the deformation of the embedded lattices could be calculated as the negative fraction of strain in the 0° direction relative to the 90° direction. Interestingly, between 10% and 25% compression, a linear fit between strain in the 90° and 0° directions yields a Poisson's ratio of 0.48 (see Table S3) which is close to the 0.5 limit expected

for an incompressible isotropic material such as a fluid or hydrated gel.⁴⁴ A Poisson's ratio of 0.5 is reasonable in this experiment given that the PAE superlattices were randomly oriented within the hydrogel, such that any anisotropy attributed to a particular orientation of a crystal relative to the testing apparatus was statistically eliminated. Beyond 25% strain, the Poisson's ratio between measurement orientations for PAE crystals in the hydrated gel increased above 0.5, which is atypical of most materials. However, this ratio refers only to the PAE superlattice inclusions, not the macroscopic gel. Furthermore, the Poisson's ratio between the 90° and 0° directions in the dehydrated gel was 0.74 as determined by linear fit over the entire experimental range (see Table S4). These larger values of Poisson's ratio are again attributed to the relative ease of lattice expansion in the 0° direction compared to the difficulty of continued compression in the 90° direction. In fact, the Poisson's ratio of the embedded crystallites in the 0° orientation (expanding) relative to the macroscopic sample compression of the partially dried gel was 0.45, which again is close to the value expected for an incompressible material, indicating that the lattices continued to expand readily as the gel was compacted while compression of the lattices themselves was restricted. The strong linear correlations between the lattice strains and the compression of the overall hydrogel show that this method of embedding PAE assemblies allows for precise manipulation of the microscopic colloidal crystals.

Importantly, the ability to alter PAE lattice parameters by deforming the gel in which they are embedded is also reversible and repeatable. PAE lattices in both the hydrated and dried gels were able to be transitioned between the strained (25% and 50% gel compression for the hydrated and dried gels, respectively) and unstrained states over multiple cycles, and the lattice parameters determined in both directions for the hydrated gel consistently returned to their original values after mechanical perturbation (Figure 19a).

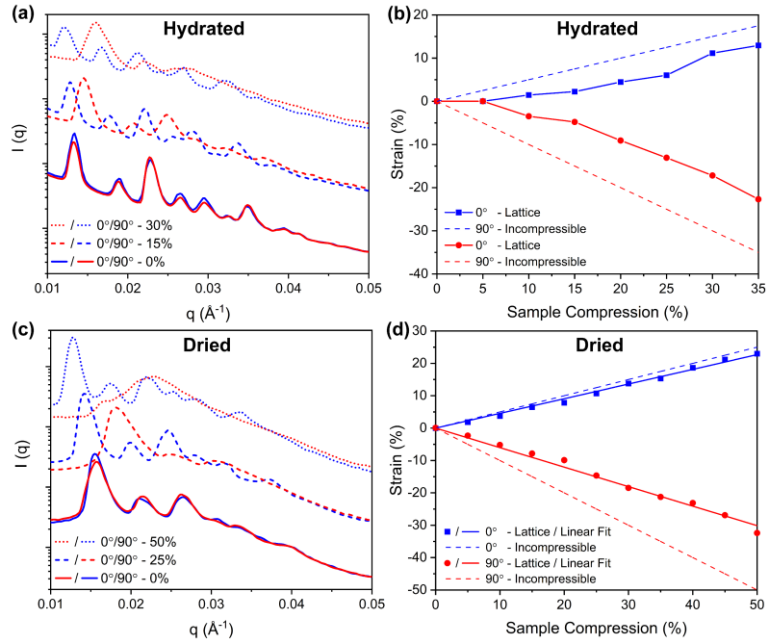


Figure 18. (Left) 1D SAXS traces for superlattices embedded in (a) hydrated and (c) partially dried gels averaged along orthogonal axes during various states of compression. (Right) Strain in lattice parameter in orthogonal directions based on the location of the first peak as a function of gel compression for the (b) hydrated and (d) partially dried gels. Dotted lines show expected values for an incompressible isotropic material relative to the macroscopic gel compression.

However, there was slight creep evident in the values of the lattice parameters when the gel was in the compressed state. This irreversible change in lattice structure may have been caused by the dissociation of a portion of the sticky ends between PAEs during deformation without perfect rehybridization. To evaluate the effect of repeated perturbation on the quality of the lattices, the circularly averaged 1D SAXS patterns before and after five deformation cycles were compared (Figure 19b); some loss of definition of the peaks was observable after cycling, which is consistent with partial disruption of the lattices. For the dried gel (Figures 19c and d), significant hysteresis was observed in the return of the lattice parameters after the third cycle, and the quality of the 1D SAXS pattern is lower after cycling. However, it should be noted that both gels were cycled to large strains near their points of failure, and it is likely that a larger number of cycles could be performed with less effect on the superlattices at lower strains. In all, these results demonstrate that embedding PAE lattices within a hydrogel allows for the lattices to be reversibly deformed in a controlled manner by direct manipulation of the macroscopic gel. As a result, mechanical compression of these materials can break the symmetry of the embedded PAE lattices, opening an interesting and unique possibility to design and intentionally manipulate more complex structures.

Taking inspiration from DNA-polymer polyplexes, we have developed a method for quickly encapsulating and electrostatically binding crystalline nanoparticle assemblies inside of a flexible hydrogel matrix. These macroscopic gels are stable under ambient conditions for months and allow for facile, dynamic manipulation of the lattices contained within them. As shown through swelling and drying tests, it is possible to translate the responses of the hydrogel to environmental stimuli into changes in the structure of the embedded crystallites. Future investigation is warranted to examine the responsiveness and stability of these materials to changes in temperature, pH, and solvent composition. Because the optical response of gold NPs to light depends on how close neighboring particles are to one another, it may be possible to observe these changes in structure with visible light, which could increase the utility of these lattices in applications such as colorimetric sensing. This strategy could be extended to tune or exploit the optical, magnetic, or electronic interactions between a variety of particle types in colloidal assemblies.^{2,45,46} Additionally, we have also shown that it is possible to directly manipulate the self-assembled superlattices in a controlled and reversible manner by physical actuation. Mechanical deformation of embedded lattices may also be

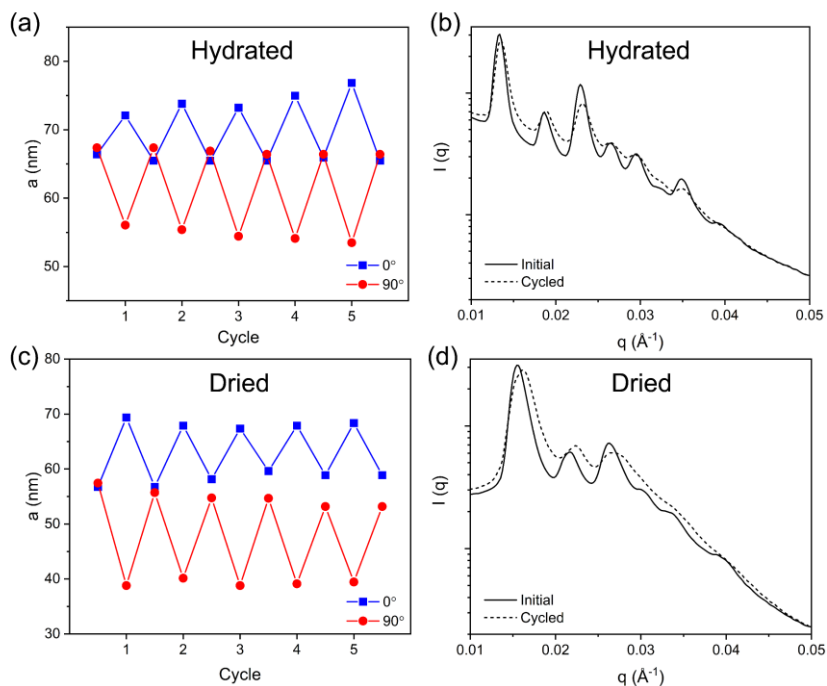


Figure 19. (Left) Lattice parameter measured in orthogonal directions for lattices embedded in a (a) hydrated and a (c) partially dried gel being cyclically compressed. (Right) Circularly averaged 1D SAXS spectra of the (b) hydrated and (d) partially dried gels initially and after 5 cycles of compression.

a simple method of generating lower-symmetry lattices without the need for specific particle core shapes or complex particle functionalization schemes allowing facile synthesis of ordered assemblies with directionally dependent properties. Embedding DNA-based nanostructures inside of a gel also suggests a route towards spatially confining the interacting components of complicated assemblies such as for DNA based computing.⁴⁷ The ability to convert DNA-grafted materials from fragile particles in solution to easily manipulatable macroscopic composites that are responsive to a number of stimuli is a step towards using this well-researched self-assembly system to create new materials for sensors and other devices.

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3.5 Tunable Mechanical Response in PAE Winterbottom Constructions

As noted above and detailed in our prior work with the AFOSR NMS program, DNA-programmed assembly is a powerful method to control nanoscale structure and thereby modulate a material's chemical and physical properties.¹⁻⁶ Most of the work done to date on PAE lattice properties has focused primarily on structure-property relationships in the context of superlattice optical response, resulting in evidence that this level of structure control can indeed impart unique characteristics to an assembled material.⁸⁻¹⁰ Other material properties could also result in equally interesting phenomena and characteristics, but investigations into such behavior have remained limited.¹¹ It would be highly advantageous to know how different PAE design variables can be used to tune a material's response to the mechanical forces they may be subjected to in these applications. While computational work has shown that different PAE designs could potentially be used to tailor a lattice's mechanical properties as a function of the chemical interactions between DNA strands, significant experimental effort still needs to be put forth to understand how the hierarchical organization of PAE lattices can be used to manipulate their response to mechanical stimuli.¹¹ During this reporting period, we examined how the supramolecular connections between DNA duplexes that guide PAE assembly can be used to modulate PAE lattice mechanical behavior in ways that would be unachievable with bulk, unstructured materials.

For the purposes of the experiments conducted here, particles used the standard DNA motif established above, where a brush of oligonucleotides is first directly grafted to the nanoparticles and subsequently functionalized with DNA "linkers" that drive PAE assembly via duplex formation (Figure 20a).¹⁶ This

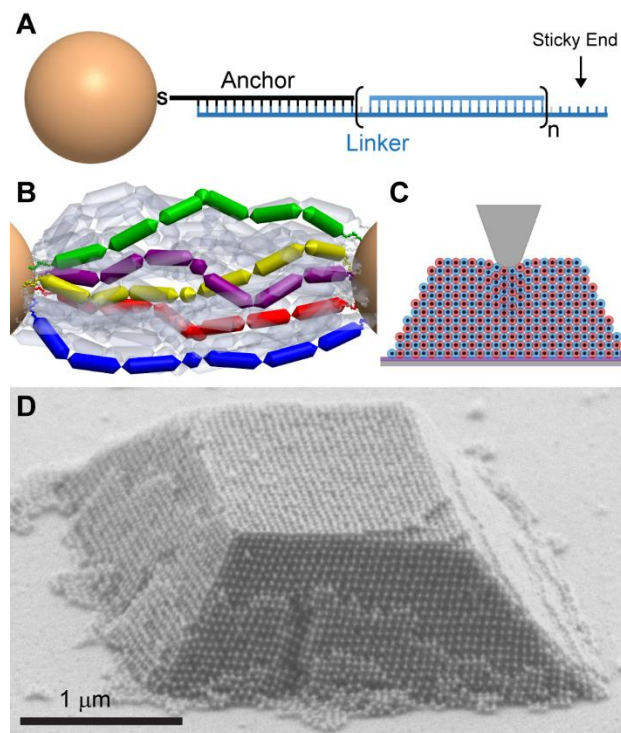


Figure 20. (a) DNA functionalization schematic: a short 'anchor' strand (black) is attached to the gold nanoparticle via a gold-sulfur bond. A second 'linker' strand (blue) is attached to the first, containing three regions; a section complementary to the first, a duplexed (light blue) variable length region sandwiched between single-stranded bases, and a sticky end that hybridizes with other particles. (b) Scaled depiction of DNA conformation between particles for $n=2$ linkers at 50% loading. The single-stranded regions act as hinges, providing flexibility to allow many DNA strands to bind together. Some strands colored for clarity. (c) Cartoon showing nanoindentation of a BCC crystal assembled from two complementary particle types, probe approximately scaled to PAEs. (d) SEM image of a PAE crystal.

modular design can systematically alter the overall DNA length and thus interparticle distance within a lattice without altering the strength of the individual DNA sticky end duplexes linking particles together.³ Each nanoparticle is functionalized with hundreds of these DNA strands, and thus each PAE-PAE bond consists of a large number of DNA connections (Figure 20b).¹⁷

As we previously determined under this AFOSR grant, when PAE BCC lattices are generated by slow-cooling the PAEs from above their melting temperature in the presence of a DNA-functionalized substrate, they will adopt single crystalline structures with well-defined crystal habits.¹⁸ Importantly, these structures can be assembled such that they possess a flat top parallel to the substrate, and this uniform, several μm^2 surface significantly aids in mechanical characterization (Figure 20c and 20d). While no mechanical testing had been performed on PAE superlattices prior to our work here,^{19,20} previous experimental methods to measure the moduli of thin films^{21–25} and soft materials^{26,27} provided guides in the development of protocols to readily measure PAE superlattice mechanical behavior.

The mechanical properties of the DNA-NP superlattices were hypothesized to be dominated by the mechanical response of the DNA, due to the fact that the DNA chains are significantly softer than the inorganic nanoparticle cores; breaking supramolecular connections holding a DNA duplex together should be significantly easier than deforming a lattice of metal atoms²⁸ or breaking covalent bonds within the oligonucleotides. DNA has previously been measured to have a modulus of 100–400 MPa.^{29,30} However, these tests were done on single DNA strands in tension, while the nanoindentation experiments performed here measure the compression of multiple DNA strands between PAEs. Thus, while the exact mechanical response of the PAE superlattices can be assumed to correlate to these prior measurements on individual DNA strands, it is still nontrivial to predict. To determine how different PAE lattice structures affected their mechanical response, BCC crystals were created from 10 – 50 nm diameter nanoparticles and DNA with variable linker lengths, resulting in a range of crystals with ~55 – 114 nm lattice parameters and varying gold and DNA fill fractions. Once the lattices were assembled, nanoindentation was performed on large crystals (1–4 μm tall) immersed in 1.5 M phosphate buffered saline (PBS) at 20 °C.

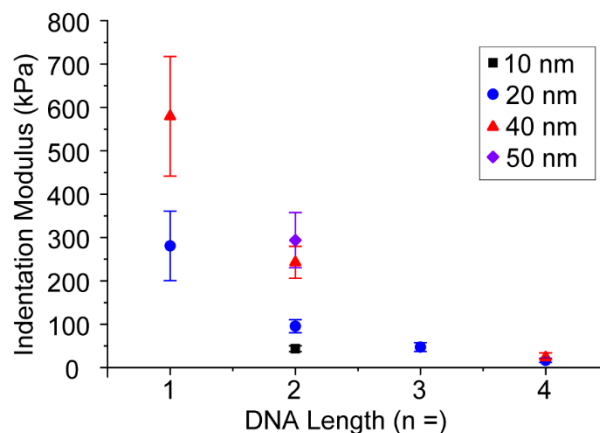


Figure 21. Indentation modulus for different lengths of DNA on different nanoparticle sizes. The indentation modulus is seen to decrease with increasing DNA length and decreasing NP diameter.

Because the superlattices are composites that consist of isolated gold nanoparticles connected via DNA duplex bonds, their moduli could be

expected to scale with the inverse rule of mixtures (i.e. springs in series) given in eq 1, where E_{tot} , E_{cor} and E_{gold} are the Young's modulus of the system, DNA corona, and gold, and F_{cor} and F_{gold} are the volume fractions of the DNA corona and gold, respectively. Note that the calculated volume fractions (see SI, Table S4) ignore empty space in the lattice; this space is filled with PBS media in the experimental measurements, and E_{cor} is calculated by multiplying the volume fraction of DNA in the corona by the modulus of DNA. Because $E_{gold} \gg E_{cor}$, the overall Young's modulus for this composite material should be proportional to $1/F_{cor}$ for a given nanoparticle size.

$$\frac{1}{E_{tot}} = \frac{F_{cor}}{E_{cor}} + \frac{F_{gold}}{E_{gold}} \cong \frac{F_{cor}}{E_{cor}} \quad (\text{eq 1})$$

While this model does not ultimately work to fit the data, it is useful to obtain an intuition for how each of the lattice components will affect the modulus of the composite. Increasing DNA length should decrease the lattice's modulus, as increasing DNA bond length at a fixed nanoparticle size results in a larger portion of the lattice's unit cells being occupied by the DNA corona (i.e. larger F_{DNA} at constant E_{DNA}). Notably, the indentation modulus should also increase with increasing nanoparticle size, due to indirect effects on F_{DNA} and E_{DNA} . In other words, for a constant DNA length, the volume fraction of DNA within the lattice decreases as NP size (and thus NP volume fraction) increases. Further, the density of DNA in the corona also increases at larger nanoparticle sizes due to reduced radius curvature. Although decreasing NP surface curvature has a minor effect on DNA grafting density, with larger radii, the DNA strands spread out to a lesser degree as they extend off of the particle surface resulting in a net increase in DNA density and therefore E_{cor} .^{3,31}

Nanoindentation of the crystals demonstrated that, as predicted, increasing DNA length decreased PAE lattice modulus, and increasing nanoparticle size increased lattice modulus (Figure 21). By using these two design handles in conjunction, the modulus can be scaled over an order of magnitude, from ~20 to ~600 kPa within the range of parameters studied. However, it is important to note here that while the inverse rule of mixtures model can indeed provide qualitative insight into the experimental data, neither the exact values nor the slopes match the measured values. Specifically, the model consistently under-predicts the effects of both DNA length and nanoparticle size. Thus, while the inverse rule of mixtures has some value in providing a framework to predict general trends in these materials, it does not provide any valuable quantitative information and thus a more rigorous model is required (*vide infra*). Developing such a model requires additional analysis of the mechanical structure-property relationships in this system, and therefore a more systematic investigation of the multiple design handles available to PAE assembly was explored.

For example, when the number of DNA linkers attached to a particle was reduced, the PAE lattices also had a proportional reduction in the indentation modulus; this trend was observed for lattices made with both

20 nm and 40 nm nanoparticles (Figure 22a). These reduced moduli could in principle be caused by there being fewer DNA duplex connections between bonded particles (i.e. fewer DNA bonds to break), or they could simply arise from a reduction in the overall volume of DNA that needs to be compressed when performing the indentations. The former would imply that breaking DNA bonds between particles governs the mechanical response of the lattices, while the latter would imply that the modulus is a function of the force required to bend or compress the mass of DNA strands in the lattice. In order to decouple these effects, an additional PAE design was tested in which half of the active DNA strands were replaced with ‘dummy’ strands that did not have sticky ends; these DNA strands occupy the same volume as the linkers with sticky ends, but would not contribute to bonding interactions between particles (Figure 22b). If PAE lattice modulus is dictated predominantly by the breaking of the

sticky end connections between PAEs, the measured value should decrease with this new design in the same manner as the experiments performed with reduced number of linkers and no dummy strands. Conversely, if the modulus is dictated by the deformation of a mass of DNA duplexes between particles, the modulus should remain the same as the modulus of the original sample. When the moduli of these samples were measured, the fraction of DNA linkers that have sticky ends was not observed to significantly affect the modulus. Therefore, the modulus arises from the force required to deform the DNA corona as a whole and is not dependent on the force required to break the DNA duplex bonds between particles. This result is perhaps counterintuitive, as deforming the lattice would inherently require breaking some of the DNA connections between particles as they are pushed away from one another. However, prior work has shown that the dissociation constants of the individual sticky end duplexes between particles are on the order of $\sim 10^4 \text{ sec}^{-1}$ at the temperatures used in the experiments performed here.^{3,32} Thus, the dynamic nature of the supramolecular connections between DNA linkers means that, during lattice deformation, DNA sticky end duplexes are constantly breaking and reforming on a timescale significantly faster than the AFM

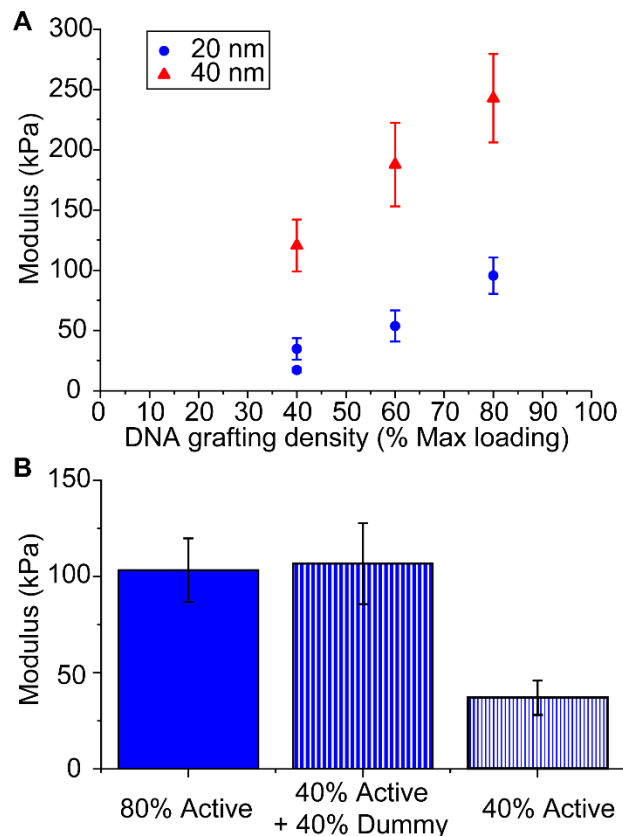


Figure 22. (A) DNA grafting density effect on the indentation modulus. (B) Decoupling the effect of sticky ends from DNA density. Reducing the number of active sticky ends has no effect on the modulus, while decreasing the density has a large effect.

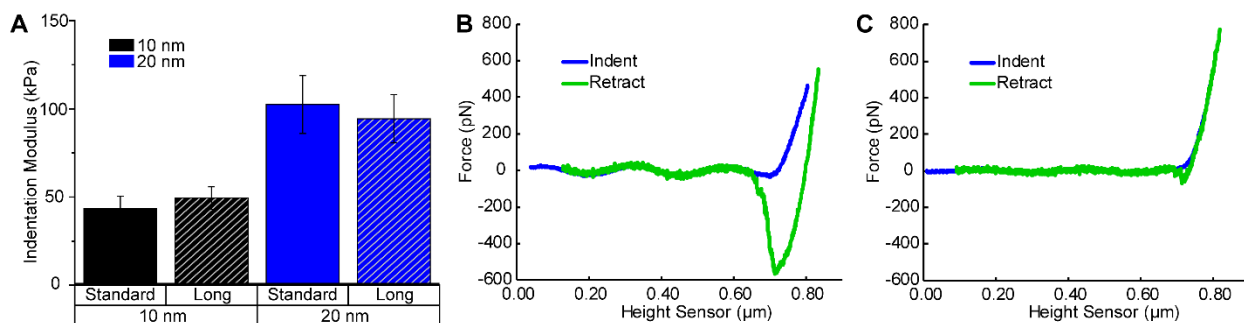


Figure 23. Sticky end strength effect on modulus. (A) For both 10 nm and 20 nm nanoparticles, the sticky end strength had no effect on the modulus. (B) Standard sticky end, showing hysteresis indicative of plastic deformation. (C) Long sticky end, showing entirely elastic response, and much smaller adhesion, with the same 20 nm, $n=2$ PAE design. Blue curve is the loading curve, green is retract curve.

tip indentation rate. PAEs should therefore be able to freely reorganize in response to mechanical stimulus as a means of dissipating mechanical force.

Importantly, this result implies that the overall mechanical behavior of these lattices could be modified if these sticky end duplexes were made more permanent. If the sticky end dissociation constants were reduced such that they were effectively permanent under measurement conditions, breaking these stronger connections could significantly alter the manner in which the PAE lattices deformed under mechanical stress, potentially allowing for the manner in which the lattice dissipates this mechanical energy to be altered. To test this hypothesis, the sticky ends were changed from the standard 6-base design to one with 10 bases (all other parameters were kept constant; samples used had particle diameter = 10 and 20 nm, $n=2$ linker length). Unexpectedly, the longer sticky end had no statistically significant effect on the indentation modulus (Figure 23), indicating that even when the DNA connections between particles were effectively permanent, the modulus was still dominated by the deformation of the DNA corona and not the breaking of DNA bonds between particles.

Surprisingly, however, despite the lack of change in system modulus, the increase in sticky end strength did in fact have a distinct effect on the elastic behavior of the PAE system. For the dynamic 6-base sticky end PAEs, the lattices were observed to deform in a plastic or viscoplastic manner (i.e. particles were readily displaced from their lattice positions upon indentation, and did not return to their original positions post-indentation) (Figure 23b). With the long sticky end connections, however, the deformation was observed to be *entirely* elastic within the range tested (i.e. particle positions were altered during indentation, but the DNA bonds provided a restoring force that caused the lattices to return to their original shapes once the force was removed). These differences are consistent with the above-mentioned kinetics of DNA duplex dissociation and reformation in these two systems. The shorter 6-base sticky end PAEs have transient connections between particles that are constantly being made and broken. Thus, as the particle positions are altered via indentation, the sticky ends rapidly reform duplexes with the new complementary sticky

ends that are nearby after deformation. There is therefore no restoring force for PAEs to return to their initial positions and the resulting deformation is entirely plastic. However, when the 10-base sticky end duplexes are used, the DNA duplex connections are essentially permanent under these experimental conditions, meaning that deformation of the lattice causes strain on the DNA bonds; this strain drives the restoration of particles to their initial positions once the force is removed. Importantly, this change in PAE response to mechanical deformation indicates that the yield strength of the PAE lattices can be tuned independently of the Young's modulus by adjusting different aspects of PAE design that affect DNA bond strength and hybridization kinetics (e.g. sticky end length, overall DNA length, DNA density, etc.).^{3,11,17} As a result, these data provide evidence that the use of supramolecular connections between the particles can be used to tune the manner in which the lattices respond to mechanical stimuli; such a behavior would be difficult or impossible to achieve in non-structured bulk materials.

From these experimental results, it can be concluded that DNA length, density, and nanoparticle size all have significant influence on PAE lattice modulus. The initial attempts at creating an analytical model (*vide supra*) that focused on using an average value for the DNA density with an inverse rule of mixtures generated the expected trends for modulus as a function of these variables, but also underpredicted the effects of DNA length and particle size (see inset of Figure 21). In order to better understand and properly model these interactions, it is therefore important to develop more complex models that account for the hierarchical organization and structure of these PAEs and the supramolecular DNA connections driving their assembly.

SEM images of silica embedded BCC lattices³³ show that there are distinct DNA connections between the nanoparticles, with significant space around each connection; as a result, the PAE lattices loosely resemble a truss structure (Figure 24). It is important to note that the silica embedding process selectively coats the DNA strands, implying that oligonucleotide connections between PAEs are likely to be largely concentrated along the bond axis between adjacent PAEs. This insight allowed for a modified model to be developed that better predicts and explains the mechanical properties of these materials as a function of this truss-like

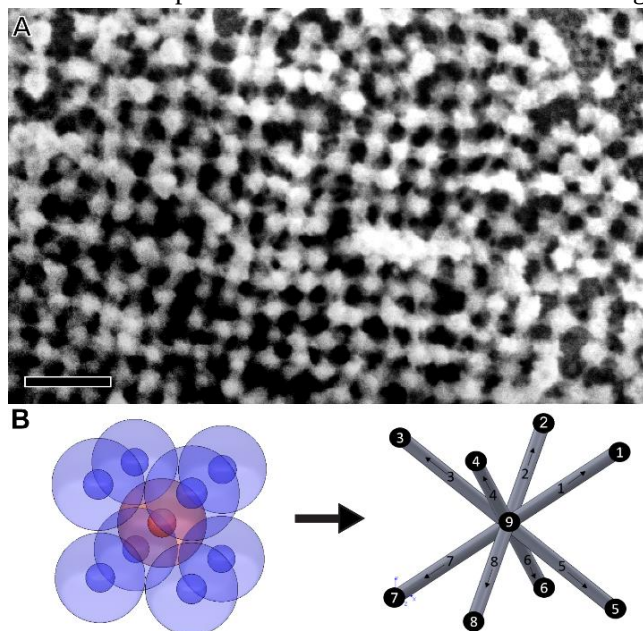


Figure 24. Truss structure approximation. A) SEM image of silica embedded structure showing clear, distinct connections between the nanoparticles. B) Truss approximation of the BCC unit cell. Scale bar 100 nm.

structure. This model was based on idealizing the DNA-linked particles as a series of a DNA “rods” connected at nanoparticle “nodes” with pin joints, and assuming linear elasticity. The spring constant of the lattice is thus the spring constant of the individual components in series, i.e.

$$\frac{1}{k_{tot}} = \sum_i \frac{1}{k_i} \quad (\text{eq 2})$$

where k_{tot} has two components: the spring constant of the gold nanoparticles and the spring constant of the DNA. The spring constant of the gold nanoparticle portion was determined by $k_g = E_g A_g / L_g$, where E_g is the modulus of the gold nanoparticle (50 GPa), L_g is the radius of the nanoparticle, and A_g was assumed to be the same as the sum of the cross-sectional area of all the DNA strands (this assumption is insignificant as the modulus of gold is three orders of magnitude higher than the modulus of DNA). Determination of the DNA spring constant was less straightforward, but a reasonable approximation based on experimental observations and literature values was established and subsequently incorporated (complete details of this analysis can be found in the SI).

The resulting collective moduli of different PAE lattice designs with varied particle sizes and DNA lengths was then compared against the obtained indentation modulus from experiments. This initial model was found to have a scalar offset with respect to particle size; for example, for all particle sizes with $n=2$ DNA length, the calculated modulus needed to be multiplied by 0.59 to obtain the experimental indentation modulus. It is assumed that the majority of the discrepancy is due to the fact that not all DNA strands in the PAE corona are involved in the interparticle bonds¹⁷, as well as the fact that the Poisson’s ratio and anisotropy factor corrections are not known and therefore not included in this model; establishing these two additional correction factors will be the subject of future work.

Interestingly, while the model provided a good fit to the changes in modulus as a function of nanoparticle diameter, the model did not predict the dependence on DNA length (L_{dna}) accurately, missing an exact L_{dna}^2 dependence. Adding in this dependence (normalized to the $n=2$ standard length) causes the model to scale neatly with both nanoparticle diameter and DNA bond length (Figure 25).

The fact that the model deviates from the data by almost an exact L_{dna}^2 dependence implies that this correction factor may have a physical interpretation. From a mechanics standpoint, a length squared dependence is often indicative of Euler buckling behavior (i.e. buckling of rigid rods above a critical load). From a chemistry standpoint, this buckling would be representative of the force required to bend or distort the DNA duplexes that comprised the connections between PAEs. Given that the linker design includes several unpaired “flexor” bases that can act as joints to accommodate buckling, it was not expected that the L^2 dependence arose from changes to the force required to bend the DNA strands, but rather arises from a different aspect of PAE structure. Nevertheless, to test this hypothesis, PAE lattices were synthesized using

DNA strands of equal length to those studied here, but with DNA linker designs that removed some of the unpaired bases, thereby increasing the overall rigidity of the DNA strands. Increased linker rigidity was observed to have no effect on the modulus, indicating that, as predicted, DNA buckling is likely not the origin of the L_{dna}^2 dependence. An alternative hypothesis is that this dependence arises as a function of the density of DNA strands at the periphery of each PAE, which would also vary as a function of DNA length squared (Figure 25C). The areal density of DNA strands at the periphery of the particles would be related to the probability of the DNA strands forming supramolecular connections and/or interacting with neighboring PAEs' DNA strands. This hypothesis is supported by prior experiments with a system that has a similar morphology, where collective post-buckling behavior of carbon nanotube forests have been modeled to have a linear dependence on line density (number of strands per cross-sectional area).³⁴

Incorporating this L_{dna}^2 dependence into the model produces a near perfect fit to the data with a simple scalar modification that is likely due to the overprediction of the number of DNA strands participating in the connections between PAEs.¹⁷ Because the PAE assembly process has been demonstrated to be remarkably predictable and programmable as a function of DNA and particle design, the development of this model therefore potentially allows for the mechanical properties of a PAE lattice to be rationally designed. As a result, the work here further indicates the potential for using DNA-programmed assembly to not only control material structure, but to also control the resulting material properties in a predictable manner.

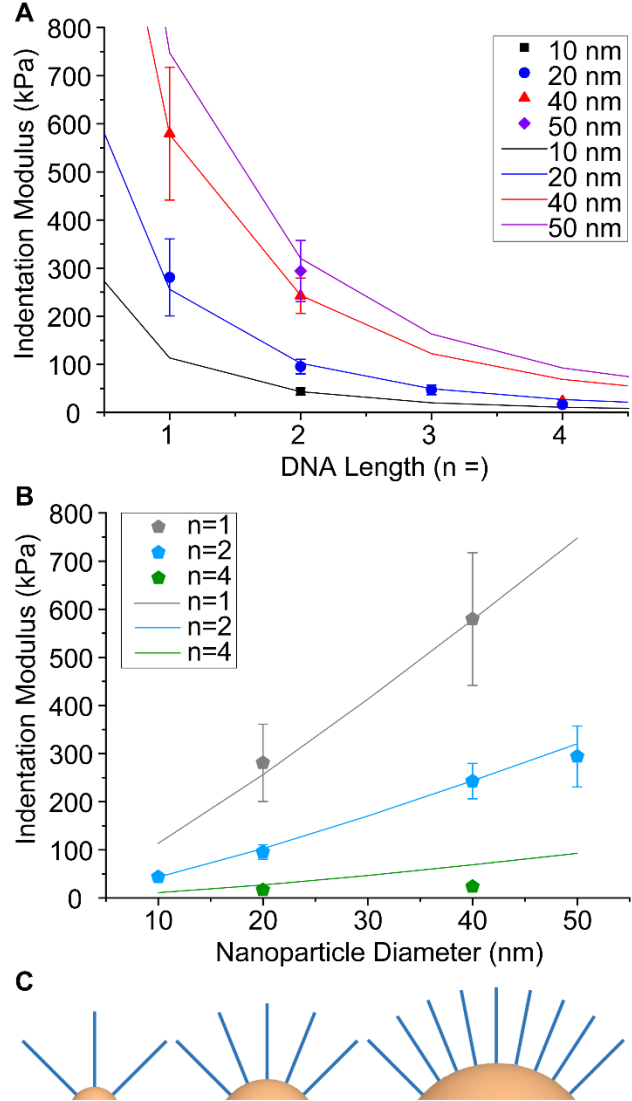


Figure 25. Truss structure model (lines) comparison to data (symbols); (A) Indentation modulus vs. DNA length at different nanoparticle sizes. (B) Indentation modulus vs. NP diameter, at different DNA lengths. (C) Nanoparticle size effect on DNA density, leading to increased modulus. As nanoparticle size increases, the same surface loading will create an overall denser brush of DNA.

For our work in this reporting period, we have demonstrated that the predictable supramolecular interactions between DNA strands allow for control over the mechanical response of a nanoparticle superlattice. We have also shown that these mechanical properties can be readily explained as a function of both DNA and nanoparticle design, and have developed a straight-forward model that can be used to correlate PAE design to lattice mechanical response. We have even demonstrated the ability to independently tune two mechanical behaviors that are typically inherently linked (yield strength and modulus), and shown that this control arises from modulations to the supramolecular duplexation behavior that governs the assembly process. The knowledge of the modulus and the predictive capabilities of the generated model can in principle be used in future work to produce sensors that respond to difficult to detect weak mechanical forces (e.g. pN-nN), to precisely tailor the mechanical properties of biomaterial-scaffolds, or aid in future design of complicated multicomponent assemblies in which shape changes due to fluidic assembly forces need to be taken into account.

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3.6 DNA-Directed Assembly of Optical Micromirrors

Recent advances in the field of self-assembly have given rise to the ability to control the assembly of nanoparticles into a variety of shapes, structures, and crystallographic symmetries. Advances in the composition and structure of individual nanoparticles with increasingly sophisticated individual responses, combined with novel methods of assembling these individual subunits together, have enabled the development of exquisite control of the collective response of the assembly to mechanical, optical, or magnetic stimuli- often referred to the “effective properties” of the self-assembled “metamaterial”. These metamaterial properties, particularly exotic properties that are not found in nature, are often desirable for their use in next-generation devices. In order to make a device, however, it is also crucial to consider the macroscopic geometry of the device. When compared to lithographic nanotechnologies capable of precisely defining the position of each individual subunit, the macroscopic geometry of a self-assembled is often limited due to the absence of externally-imposed structure.

In this regard, our lab’s recent demonstration of DNA-functionalized nanoparticle assembly into Winterbottom structures supported by this program is potentially a useful step in enabling such technologies. In this reporting period, we have utilized the PAE Winterbottom structures’ consistent facet angles relative to the substrate to investigate their potential use as an out-of-plane coupling device, a tilted micromirror. Out-of-plane coupling devices are used to route incident light onto a substrate into planar optical devices. There are many designs for such devices, such as prism couplers which utilize refraction, or grating couplers which utilize diffraction, or resonant couplers which capture light prior to extraction into the device. One challenge with these methods, however, is that they are wavelength-dependent, and accept different wavelengths of light at different incident angles. Tilted micromirrors, on the other hand, utilize reflection to redirect light at the geometrically defined specular angle independent of wavelength, allowing for use in broadband applications. The three-dimensional nature of tilted micromirrors, however, complicates their fabrication by lithographic methods compared to gratings or resonant structures, which may be fabricated using conventional 2D lithography methods.

In order to utilize the Winterbottom crystallites as micromirrors, it was first required to determine if they can function as mirrors at all. In this context, a “mirror” refers not to the surfaces reflectivity, but rather the ability for light reflected off of the surface to retain its angular intensity profile, beamshape, relative phase, or polarization. The reflection profile of light off of a surface can be fully described by the surface’s bidirectional reflectance distribution function (BRDF) $f_R(\theta_i, \phi_i, \theta_r, \phi_r)$, which describes the intensity of light reflected off of a surface for given input azimuth and zenith angles θ_i, ϕ_i and output azimuth and zenith angles θ_r, ϕ_r . This is typically simplified into a categorization that is either specular or diffuse. An ideal specular surface corresponds to a perfect mirror, and will reflect all incoming light at the specular

angle, corresponding to a BRDF of $f_{\text{Specular}}(\theta_i, \phi_i, \theta_r, \phi_r) = R * \delta(\theta_i - \theta_r) * \delta(\phi_i + \pi - \phi_r)$. For incident light with a varying angular profile, such as a focused beam, the specularly reflected light will match the incident angular profile. In contrast, an ideal diffuse surface will reflect light in all directions, corresponding to a uniform BRDF of $f_{\text{Diffuse}}(\theta_i, \phi_i, \theta_r, \phi_r) = \frac{R}{\pi}$, regardless of the orientation, relative phase, or beamshape of the incident light.

At the macroscale, BRDF may be measured using a gonireflectometry setup to directly alter the incident angle of a collimated beam aimed at the surface, and the reflected signal may be directly measured via an angular sweep. At the microscale, however, it is infeasible to aim collimated light, and it is instead necessary to use focusing light. Furthermore, conventional microscopy setups cannot independently alter the incident angle from the measured angle, but will instead be limited to

incident light focusing through the microscope objective, and is limited to measuring light reflected back into the objective, a setup referred to as retroreflection. To overcome these limitations, we introduced a eucentric stage into a microscopy setup capable of tilting the sample, allowing for retroreflection measurements across a range of incident angles relative to the surface normal. The intensity of the retroreflected light as a function of angle may then be fit to a simple model, such as a gaussian beam, in order to parameterize the reflected beam even without a full BRDF. The specularity of a non-ideal surface, which is neither fully specular nor fully diffuse, may be investigated by measuring the change an incident focusing beam with an initial beam divergence of Θ_0 will reflect off of a flat surface to produce an outgoing beam with a larger beam divergence Θ . If $\Theta \sim \Theta_0$, then the surface is qualitatively specular, whereas if $\Theta \gg \Theta_0$, then the surface is qualitatively diffuse.

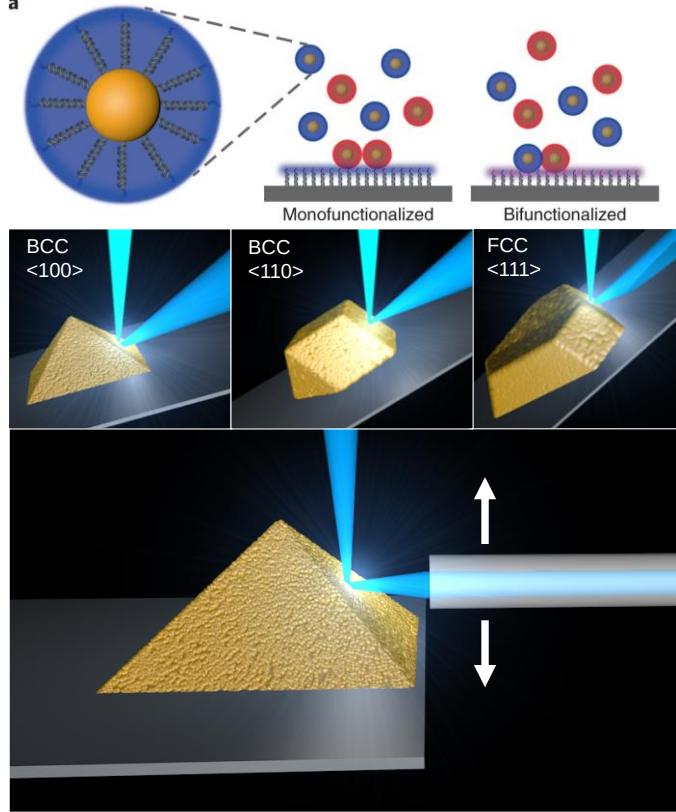


Figure 26. Illustration of various self-assembled faceted structures functioning as isolated micromirrors. The faceted structures are described by the Winterbottom structure motif for self-assembly on a surface (a). Winterbottom crystallites behave as micromirrors with tilt angles determined by their crystallographic symmetry and orientation (b). These self-assembled micromirrors may be used to reroute incident light into the substrate plane, coupling into other elements of a planar device, such as an optical fiber (c).

Retroreflection measurements were initially conducted on FCC and BCC(100) Winterbottom samples, corresponding to crystallites with flat top facets that are co-planar with the surface of the substrate, and were compared to bare Si wafer substrates as a specular control and white repro paper as a diffuse control. The reflected beam intensities were fit to a gaussian profile parameterized by their power, background power, beam divergence, and offset angle. The beam divergence after reflection from the Si surface was measured to be 62° , approximately matches the expected value of 64° for a beam focused by a 0.9NA microscope setup. In contrast, the beam divergence after reflection from the white reprop paper surface increased to 73° , consisted with the expected broadening due to diffuse reflections. The reflections from the FCC and BCC(100) Winterbottom structures exhibited beam divergences of 58° and 57° respectively, roughly equivalent to the beam divergence of the specular control. The slight decrease in beam divergence could be attributed to instrument error, or the presence of slight curvature of the Winterbottom surfaces from the embedding process. However, qualitatively, it appears that the faceted structures are predominantly specular in character.

Retroreflection measurements were subsequently conducted on the side facets of BCC(110), AB_2 , BCC(100), and FCC Winterbottom structures using a eucentric stage with an expanded tilt range, after orienting the facet edge to be colinear with the substrate axis of rotation. As before, the reflected beam intensities were fit to a gaussian profile parameterized by their power, background power, beam divergence, and offset angle. The beam divergence after reflection for all samples also appear similar to the specular

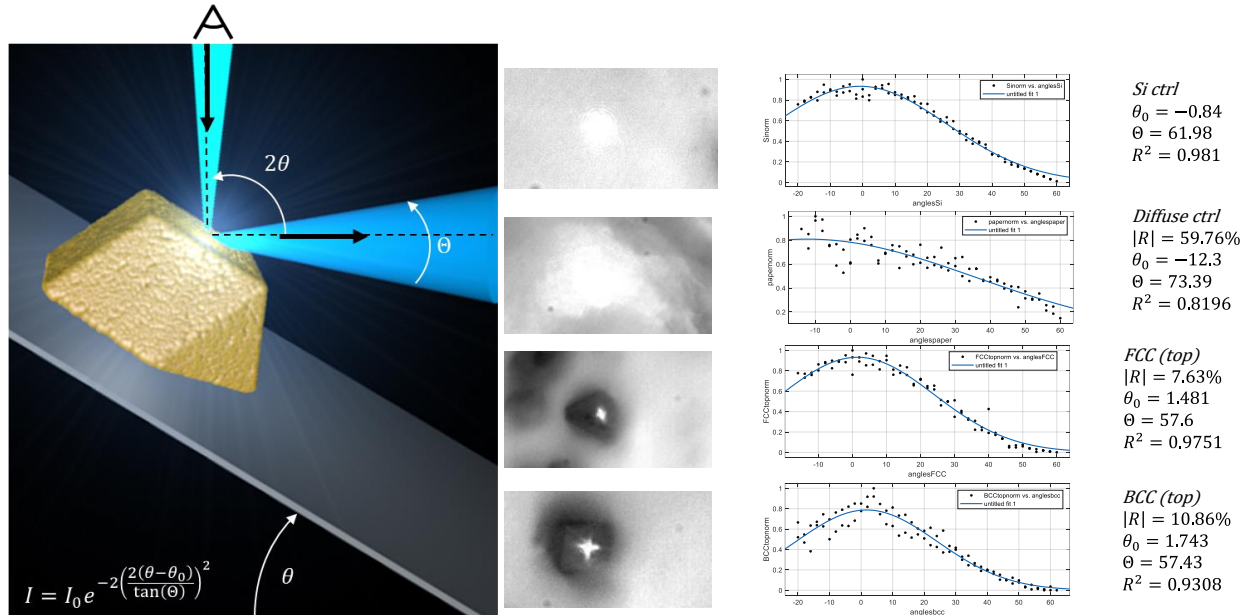


Figure 27. Retroreflection measurements of Winterbottom crystallite top facets, compared to specular (Si) and diffuse (paper) controls. Beam divergence of the specular control is attributed to focusing light through the 0.9 NA lens used in the microscopy setup. Increased beam divergence of the diffuse control is attributed to loss of specularity after reflection. Both FCC and BCC structures retain specular retroreflection profiles, indicating high-quality mirror surfaces.

value, confirming that the side facets of the Winterbottom structure are predominantly specular. Unlike prior measurements, however, the offset angles determined by the gaussian fit not only correct for minor deviations from the substrate tilt, but instead correspond to the dihedral angle of the facet relative to the substrate plane. From fitting, the offset angle of the BCC(110), AB₂, BCC(100), and FCC Winterbottom crystallites were measured to be 33°, 44°, 49°, and 54° respectively. This matches the expected trends dictated by the Winterbottom construction, which predicts dihedral angles of 45°, 54°, 60°, and 71° respectively. The discrepancy between the optically measured dihedral angles and the expected values (confirmed via AFM) is attributed to obfuscation due to secondary reflections from the side plane onto the substrate, which skew reflected light away from the substrate. This experiment concludes that, despite slight deviations, the optical response of Winterbottom crystallites is largely determined by their geometry, consistent with their description as micromirrors with controllably tunable tilt angle relative to the surface.

In order to directly confirm the out-of-plane coupling functionality of the Winterbottom crystallites as tilted micromirrors, we first polished up to the edge of a Winterbottom crystallite using 1µm polishing paper. An

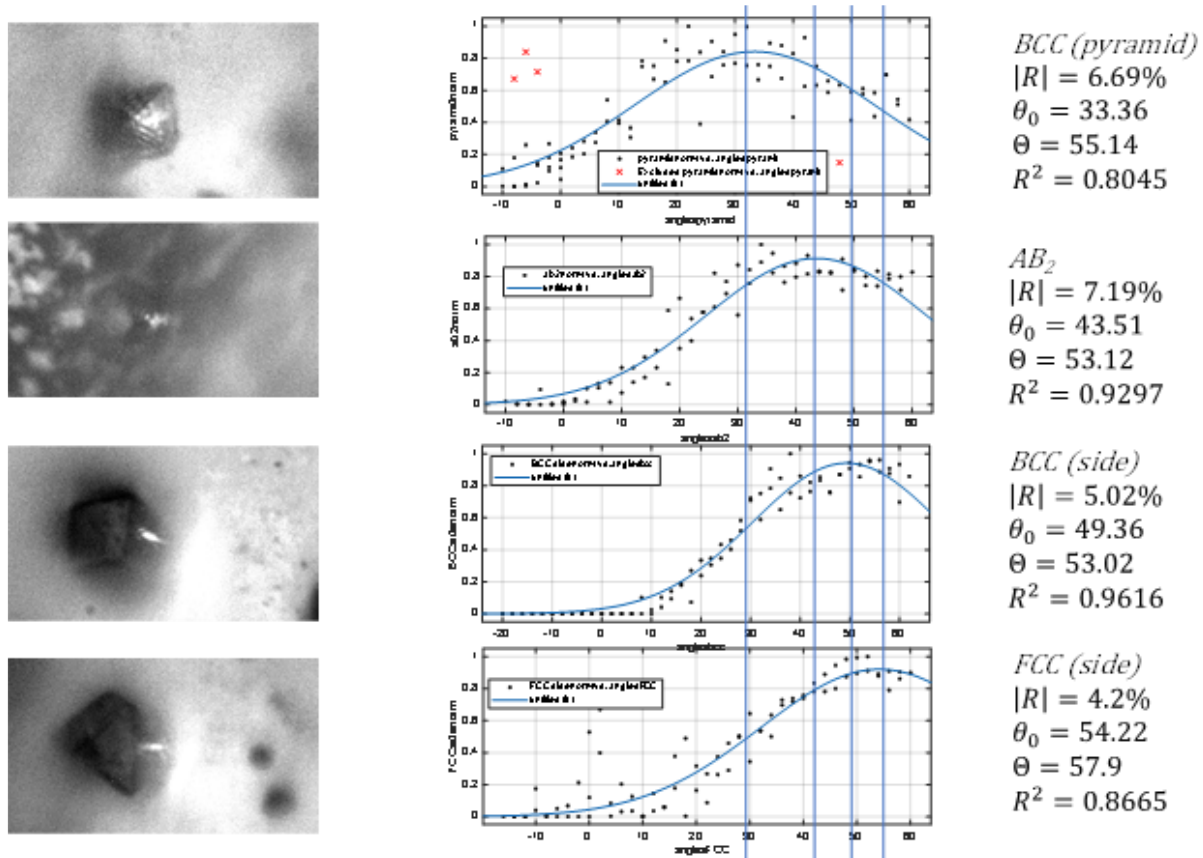


Figure 28. Retroreflection measurements of Winterbottom crystallite side facets. Facet angle of the Winterbottom geometry is determined by the crystallographic symmetry and orientation relative to the substrate. Beam divergence after reflection remain comparable to the specular control, indicating that the side facets of the Winterbottom structure behave as specular mirrors. The maximum retroreflection angle, corresponding to the specular angle of the structure, match the trends of facet angle predicted by the Winterbottom analysis.

optical fiber was then placed in the substrate plane using a micrometer-controlled crane setup. Incident light was focused onto the Winterbottom crystallite using the microscope objective normal to the substrate, and the power of light coupling into the planar fiber was measured. Optical power was observed to reflect into the optical fiber when the objective is aimed at the appropriate facet on the Winterbottom crystal, directly confirming that the facets of the Winterbottom structures behave as micromirrors capable of coupling light from normal incidence into the plane. The reflected power, and the

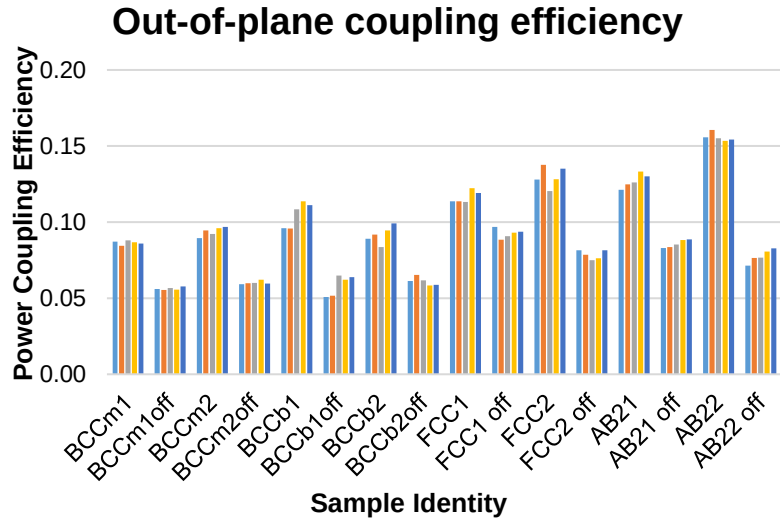


Figure 29. Out-of-plane coupling efficiency measurement for self-assembled faceted structures. The out-of-plane coupling power was measured by comparing the intensity of light reflected from the microscope objective into a perpendicular optical fiber. The power reflected by the crystal facets was compared to a macroscopically polished 45° mirror sample coated with Ag (which perfectly couples light into the fiber). In the untreated samples, light may be measurable reflected from the side facets, as determined by comparing against the power reflected when aimed at other facets of the crystal, but out-of-plane coupling efficiency is low due to the poor reflectivity of the samples.

corresponding calculated out-of-plane coupling efficiency, are low (~10%), which is consistent with the measured reflectivities of the surfaces have been low (~10%). This is because the self-assembly system utilizes gold nanoparticle cores, which have convenient surface chemistry for self-assembly, but exhibit strong absorption at the wavelength (470nm).

However, due to the geometric mechanism for out-of-plane coupling via micromirrors, it is possible to alter the reflectivity of the surface with a reflective coating, without altering the geometry of the micromirror. To demonstrate this, we may modify the Winterbottom crystallite samples with a coating of Ag, which is highly reflective at visible wavelengths, and repeat the direct measurement of out-of-plane coupling. For sufficiently thick, smooth films, the specularity and angle-dependence of the Winterbottom micromirrors is preserved, while the reflectivity is increased dramatically, allowing for a dramatic increase in the out-of-plane coupling efficiency. This may be further generalized to reflectivity at other wavelengths (e.g. telecom wavelengths) or for reflectivity with narrow reflection windows (e.g. wavelength filters) by depositing a reflective coating with the desired reflectivity profile in a sufficiently conformal manner.

The results of this work demonstrate that the thermodynamically determined features of self-assembled systems are sufficient to fabricate functional optical devices that are robust to changes in the inconsistent

features of the self-assembled structures. Specifically, we have demonstrated that self-assembling Winterbottom structures, with thermodynamically determined facet angles relative to the surface, can function as out-of-plane coupling micromirrors. This serves as an example for a practical self-assembled optical device, since the functionality of the device is determined by the consistent features of the self-assembled geometry, as well as the surface reflectivity determined by subsequent material deposition. Thus, this work marks the first such example in which an optical device

may be fabricated via self-assembly where stochastic features of the assembly, such as variable crystal size, are not integral to the functionality of the device, enabling future integration into existing integrated photonic architectures. Future work required to integrate the inclusion of these devices into existing architectures include the development of nucleation and orientation control of the Winterbottom crystallites, so that they may be selectively grown in the region of interest and aligned to the input of the rest of the planar architecture.

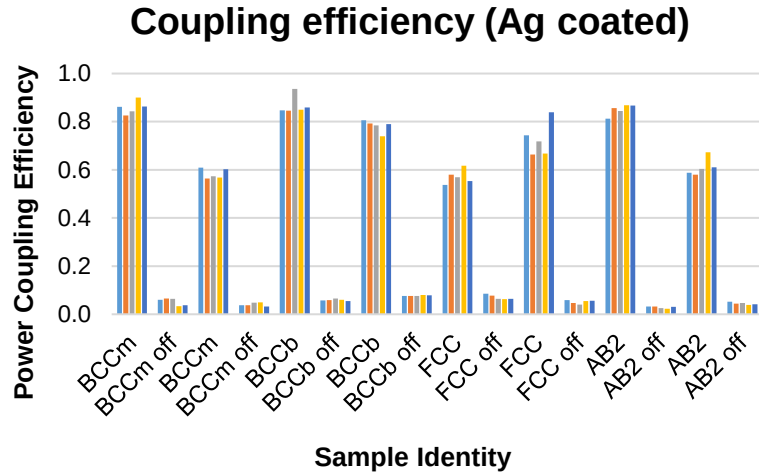


Figure 30. Out-of-plane coupling efficiency measurement for self-assembled faceted structures with reflective Ag coating. The out-of-plane coupling power was measured by comparing the intensity of light reflected from the microscope objective into a perpendicular optical fiber. The power reflected by the crystal facets was compared to a macroscopically polished 45° mirror sample coated with Ag (which perfectly couples light into the fiber). The measured out-of-plane coupling efficiencies are appreciably larger than that of the untreated samples (Figure 4). The large variability between samples is attributed to inconsistencies between the size of the distance between the crystallite edge and the fiber probe and the alignment of the crystallite edge and the fiber probe, which are determined by the

3.7 Macroscopic Assembly of Materials from Nanoparticle Superlattices

Nanoparticle assembly is typically governed by chemical interactions between small molecule ligands grafted to the surface of each particle^{3,4}. In this AFOSR work, we have primarily used DNA to direct such crystal formation processes, but prior efforts have used different ligands to create one-dimensional ribbons^{9,10}, thin films^{11–13}, and micron-scale single crystals^{14–20} with precise nanoscale organization of individual particles. To use these assemblies as components of bulk macroscopic solids, however, it is also necessary to control material organization at larger length scales. Microstructure and macroscopic form remain underexplored design parameters, indicating that the development of processing techniques that can coalesce individual self-assembled structures into macroscopic solids would be an important step in the development of nanoparticle-based bulk solids with complete structure control at all size regimes.

In this regard, the use of biomolecules like DNA are actually a hindrance, as their precision in controlling material structure comes at the cost of significantly reduced scalability compared with other types of materials. Thus, in the one-year extension of this project, we aimed to develop more biomimetic approaches to fabricating complex hierarchical structures. The building block for these efforts, the Nanocomposite Tecton (NCT)²¹ was recently developed by our group and is inspired by the DNA-direct particle assemblies examined in the AFOSR NMS program. NCTs are well-suited for producing large-scale, hierarchical materials, as they consist of inherently scalable components and use dynamic binding interactions to dictate how nanoparticles arrange themselves into ordered arrays in a manner directly analogous to DNA and other types of biomolecular structures (Fig. 31). Each NCT consists of an inorganic nanoparticle core covered with a polymer brush, where every polymer chain terminates in a supramolecular binding group (Fig. 31b). Upon mixing solvent-dispersed NCTs with complementary binding groups, supramolecular interactions guide the assembly of particles into larger structures. Because the supramolecular bonds linking NCTs together are dynamic, cooling a set of NCTs through their dissociation temperature (the melting temperature, T_m) allows them to organize into ordered superlattices, *e.g.* body centered cubic (bcc) arrays (Fig. 31c)²². However, previous attempts to remove the lattices from the assembly solvent caused the lattices to disorder, as the polymer chains rapidly contract during drying. Thus, the formation of free-standing macroscopic solids from these NCT assemblies first requires methods to stabilize them against the loss of ordering during solvent removal^{23,24}.

Stabilizing Colloidal Assemblies as Solids

Because the assembly process occurs in a solvent that swells the NCT polymer brush, we hypothesized the lattices could be stabilized against polymer brush collapse by gradually introducing a non-solvent with an unfavorable interaction energy with the polymer; interactions with this non-solvent would cause the chains to adopt denser conformations and shrink the lattice²⁵. A model NCT system was therefore developed using previously established chemistries²⁶: 15.4 nm gold nanoparticle cores (AuNPs), ~14 kDa polystyrene polymer brushes, and DAP-Thy hydrogen bonding pairs to link the NCTs. This NCT design is readily dispersed in toluene, but when a non-solvent for the polymer (*e.g.* n-decane) is added to crystallized NCTs, the interparticle spacing decreases continuously while preserving bcc ordering as determined by small-angle X-ray scattering (SAXS) (Fig. 32a). Interestingly, the polymer brush collapse is reversible, and a lattice can be cycled between good solvents and non-solvents while maintaining crystallinity, representing a dramatic 78 percent volumetric compression and expansion of the lattice. As a result, alterations to particle

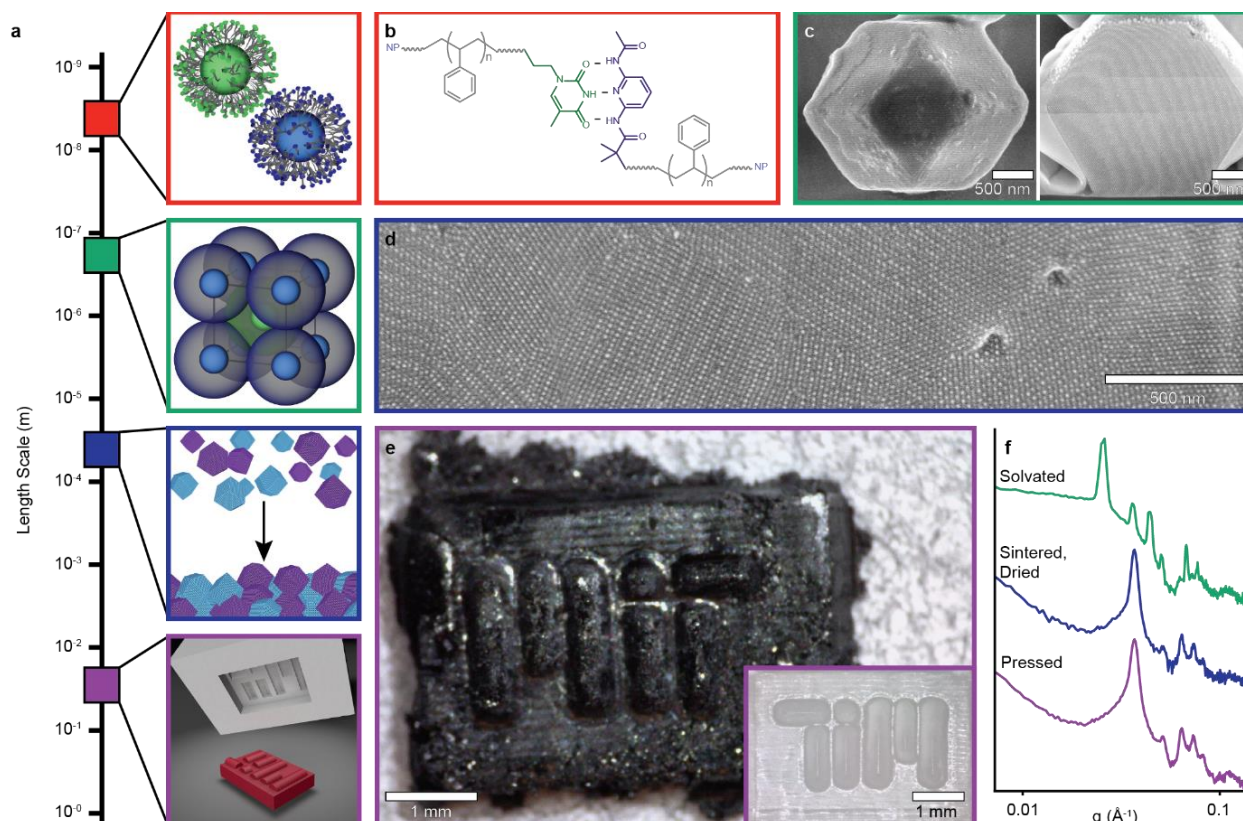


Fig. 31. Nanocomposite Tectons (NCTs) can be processed into bulk solids with simultaneous structural control across 7 orders of magnitude in length scale. (a) (Red) supramolecular interactions assemble nanoparticles into (green) ordered superlattices which form micron-sized crystallites; (blue) these crystallites are ‘sintered’ via centrifugation into a macroscopic material, (purple) which is dried and pressed with a mold. (b) The chemical structure of NCT ligand coatings - a polymer brush which terminates in one-half of a supramolecular binding group, where hydrogen bonding allows for NCT-NCT bonds to be formed. (c) Scanning electron microscope (SEM) micrographs of the surface morphology (left) and cross-section (right) of an NCT crystallite. (d) Cross-sectional SEM micrograph of a sintered NCT solid. (e) Optical image of a sintered NCT solid, pressed using a mold (inset) of the MIT logo. (f) Small angle X-ray scattering (SAXS) data (q vs $I(q)$ (a.u.)) of the sample in (e) demonstrating the body centered cubic (bcc) ordering is preserved throughout the process.

size, polymer brush molecular weight, and solvent content can all be used to tune the distance between particles in a lattice across a broad range (4.1-21 nm).

Because solvent ceases to be a major volumetric component of the NCT lattice after the polymer brushes are condensed, NCT lattices can be subsequently dried without a loss of crystallinity, allowing for characterization of their mesoscopic shapes (Fig. 32a). Scanning electron microscopy (SEM) micrographs of these dried lattices show that under standard assembly conditions, they form faceted rhombic dodecahedral crystallites; rhombic dodecahedra are the thermodynamically favored Wulff constructions for bcc lattices (Fig. 31c)¹⁴. SEM imaging of focused ion-beam (FIB) milled cross-sections further confirms the materials are crystalline throughout the entire polyhedra (Fig. 31c).

Controlling NCT Crystallite Size

Notably, these faceted crystallites form quite rapidly as the assembly process is guided by multiple weak supramolecular interactions that prevent the formation of kinetically trapped states²⁶. Thus, single crystal

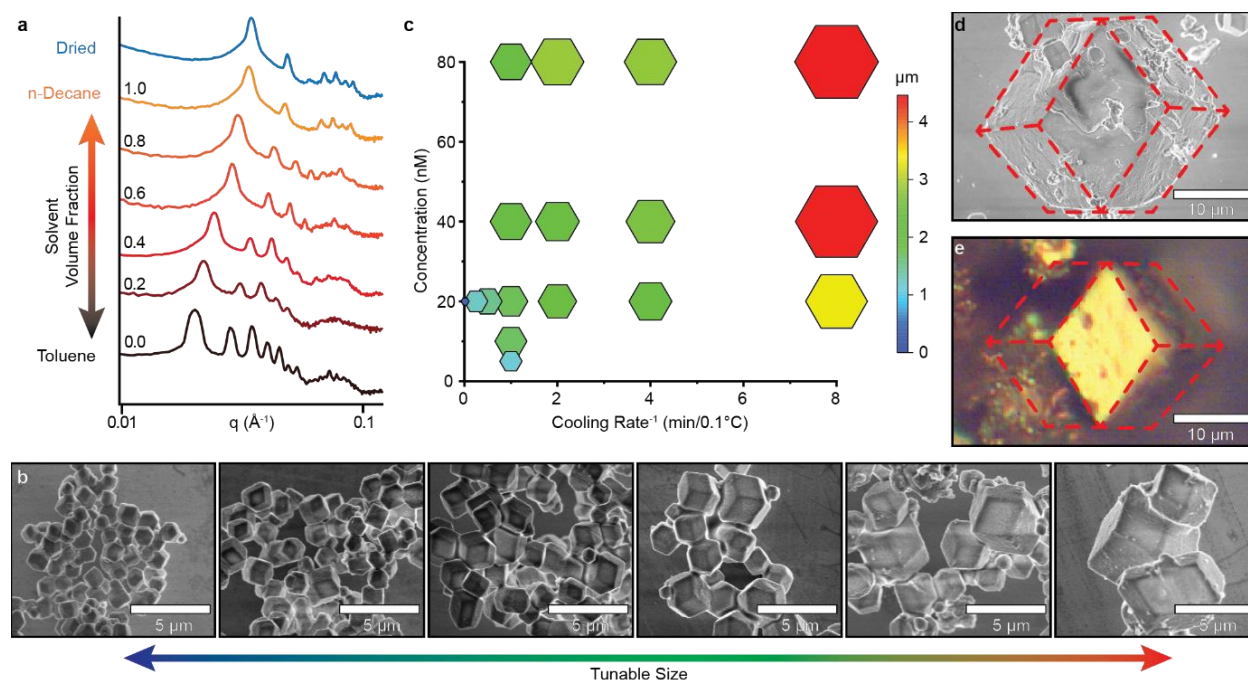


Fig. 32. The formation of solid-state NCT superlattice polyhedra of controlled sizes. (a) SAXS curves (q vs $I(q)$ (a.u.)) of NCT crystallites in varying ratios of solvent (toluene) to non-solvent (n-decane) demonstrating a 40% swelling/deswelling of lattice parameter, confirming bcc ordering is maintained in all solvent conditions, including complete drying of the lattice. (b) SEM micrographs of tunable crystallite size distributions achieved via slow-cooling NCTs (20 nM) at 0.25, 0.5, 1, 2, 4, and 8 min/ 0.1°C (top to bottom). (c) Graph of median characteristic length as a function of cooling rate $^{-1}$ and NCT concentration during crystallization, demonstrating that larger crystallites form at higher concentrations and slower cooling rates. Both data point color and relative size correspond to median crystallite length; full statistical analysis is given in the SI. (d) SEM micrograph and (e) optical images of the largest (> 30 μm) NCT Wulff polyhedra formed at 80 nM and 8 min/ 0.1°C . Lines added for reference.

architectures can be observed even with cooling rates 100x faster than those required in similar nanoparticle assembly methods^{14,15}. Even at the fastest cooling rate that could be controllably measured and achieved (1s/ 0.1°C ; 5 minutes annealing time), NCTs still formed single crystals, and cooling rates of 15s/ 0.1°C (~ 1.25 hour annealing time) were sufficient to generate faceted polyhedra.

Because crystallite grain size is a key aspect of material microstructure, complete structure control in macroscopic solids built from these assemblies requires methods to manipulate crystallite diameter. Given the wide range of assembly conditions that yield single crystals (Fig. 32b), we postulated it would be possible to tailor crystallite size as a function of these variables (Fig. 32b&2c). Indeed, by adjusting the concentration of the NCTs and the rate at which they are cooled, the dried NCT crystallite diameter can be tuned between ~ 500 nm and ~ 30 μm . Additionally, the relationship between NCT concentration, annealing rate, and final crystallite size can be explained by a mathematical model, indicating that the average crystallite size can be reproducibly controlled, even up to sizes large enough to be observed in a low-magnification optical microscope.

Sintering NCT Crystallites into Macroscopic Solids

Inspired by the sintering of nanocrystalline powders to produce macroscopic compacts of conventional metallic, ceramic, and polymeric materials, we hypothesized that an analogous process could create larger

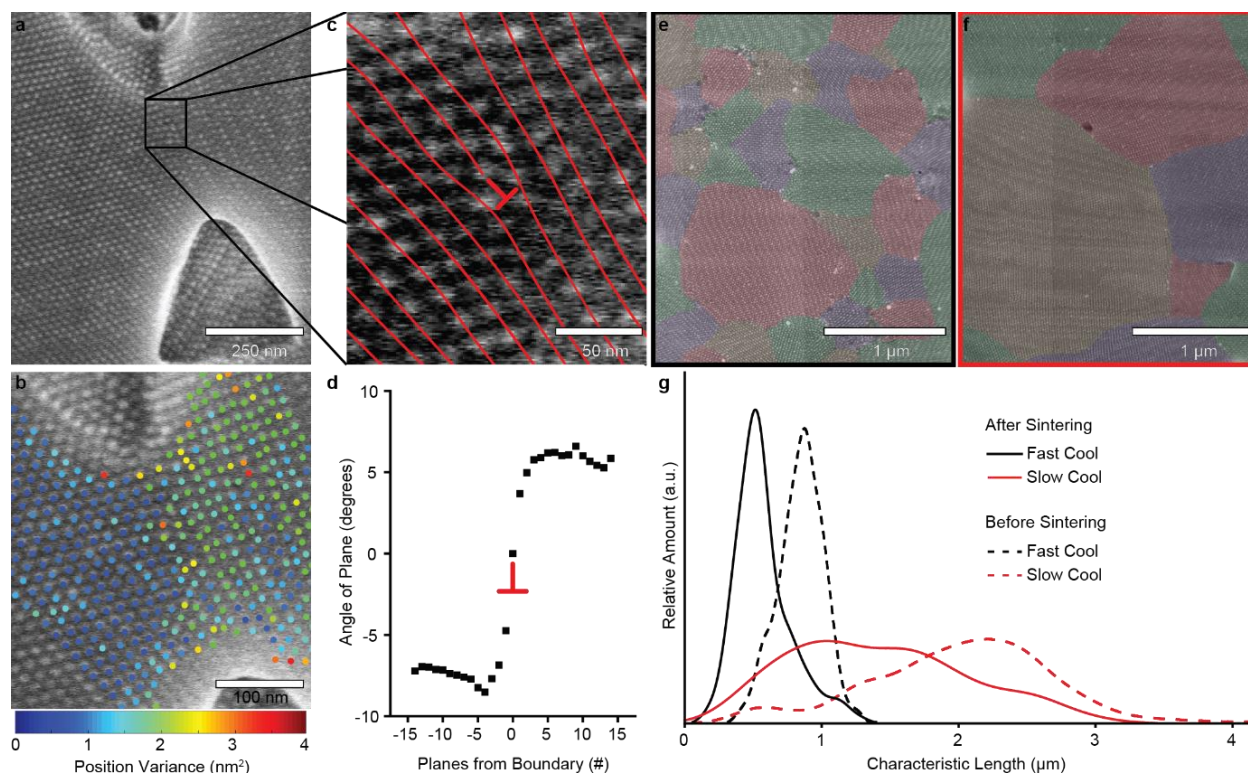


Fig. 33. Control over microstructure in sintered NCT solids. (a) Cross-sectional SEM of a neck between two sintered NCT polyhedra. (b) Positional variance of the particles overlaid onto the neck of (a), confirming the presence of two distinct grains. (c) Close-up of the neck in (a), with the crystallographic planes and a dislocation highlighted. (d) The angle of the planes relative to the grain boundary in the neck region, indicating the offset between crystallites and the strain in the neck. Cross-sectional SEMs of sintered solids made from (e) fast cooled (15 sec/0.1°C) and (f) slow cooled (4 min/0.1°C) NCT crystallites, demonstrating programmable grain size. Each grain colored for reference. (g) Size distribution of NCT crystallites (before sintering) and grains (after sintering) for both cooling conditions demonstrating that grain microstructure is dictated by initial crystallite size.

NCT solids by using these crystallites as higher-order building blocks with inherent microstructural information (i.e. crystallite size). In atomic materials, the application of high heat and pressure weakens bonding interactions, allowing powder particles to plastically flow and densify into a continuous structure^{27,28}. Similar effects can be induced in NCT sintering, but due to the dynamic hydrogen bonds linking NCTs, only mild heating and pressure (centrifuging crystallites at 20,000 RCF for 10 minutes at ~25 °C, collapsing the brush, and drying) are required to produce free-standing monolithic solids.

Importantly, SAXS confirms the NCTs maintain their crystallinity throughout this processing, indicating that the macroscopic deformation and ‘sintering’ was enabled by NCT reorganization as opposed to simply deformation of the polymer brush (Fig. 31f). Additionally, SEM imaging of FIB-milled cross-sections revealed a densified structure with grain boundary-like features (Fig. 31d, Fig. 33a&3b), not unlike the microstructure of polycrystalline bulk solids. Densification is therefore proposed to occur via ordered reorganization of NCTs during sintering and crystallite deformation, which is supported by the observation of necking behavior in the final solids (Fig. 33a). For example, cross-sections show adjacent sintered grains aligned at different angles (Fig. 33b); closer to the interface between these grains, the planes are slightly distorted via lattice strain as they try to make a low energy grain boundary (Fig. 33c&d). At the inflection

point of the change in angle of the planes, several dislocations can be observed, implying that the NCTs participate in energy minimizing reorganization of particle positions during sintering. The lattice strains to allow each NCT to maximize hydrogen bonding interactions with neighboring particles, and dislocations form to accommodate excessive strain. The use of dynamic bonding interactions between NCTs allows for this crystal reorganization, and is the key design feature that gives rise to their ability to “sinter” into bulk materials without loss of crystallinity.

Analogous to methods to control grain sizes in conventional powder sintering, we would predict that the grain size of NCT compacts could also be tuned by an appropriate selection of NCT crystallite precursor diameter (Fig. 33). Two batches of NCT crystallites were thus prepared at different cooling rates (15 sec/0.1°C and 4 min/0.1°C) to generate two distinct populations of Wulff polyhedra sizes, and sintered into separate macroscopic aggregates. SEM cross-sections of the resulting solids reveal that the size distributions of crystallites before sintering indeed correspond to the grain size within a sintered solid (with slight reduction in grain size due to crystallite deformation and measurement artifacts) (Fig. 33). Notably, solids prepared from NCTs with larger size distributions were also qualitatively observed to have an increase in void space, consistent with a sintering mechanism²⁸.

The ability to tune the microstructural features of these solids suggests that these NCT solids may also exhibit similar deformation mechanisms as atomic crystals; observation of these effects would strengthen the analogies drawn between the processing of atomic and NCT macroscopic solids²⁹. To investigate this hypothesis, NCT lattices were sintered and dried, then subjected to 0.4 or 10 tons of mechanical force. Cross-sections reveal short-range ordering is largely preserved after pressing, but SAXS indicates long-range ordering is disturbed with increasing amounts of force. Applying a load of 0.4 tons to these materials notably decreases the amount of void space, and the grain boundaries appear to have a larger number of dislocations than an unpressed sample (Fig. 31d). At 10 tons, defects at the grain boundaries appear even more prominent. Furthermore, within the grains, the lattices appear warped, which we hypothesize is due to plastic deformation of the grains, and is responsible for the loss of ordering in SAXS. Additional features analogous to those observed in mechanically deformed atomic materials (such as fracture planes, twinning, and paracrystalline distortion) are also readily evident.

Control of compositional heterogeneity via NCT assembly and processing

Previous work has demonstrated that NCTs can be synthesized with both gold (Au-NCT) and iron oxide nanoparticle cores (IO-NCTs)³⁰; the assembly of faceted supracrystals and subsequent processing into bulk solids are largely unaffected by nanoparticle core identity (Fig. 34). Therefore, the sintering of solids with more complex hierarchical organization could in principle be achieved by assembling multi-component materials in which gold and iron oxide particles are distributed throughout the solid in either a homogeneous or heterogeneous manner.

Sintered NCT solids with distinct grains containing different nanoparticle compositions were prepared using a mechanically blended combination of bcc IO-NCT crystallites and bcc Au-NCT crystallites (Figs. 34b, 34g). The Au- and IO-NCTs remain phase segregated in this sample, suggesting that minimal grain

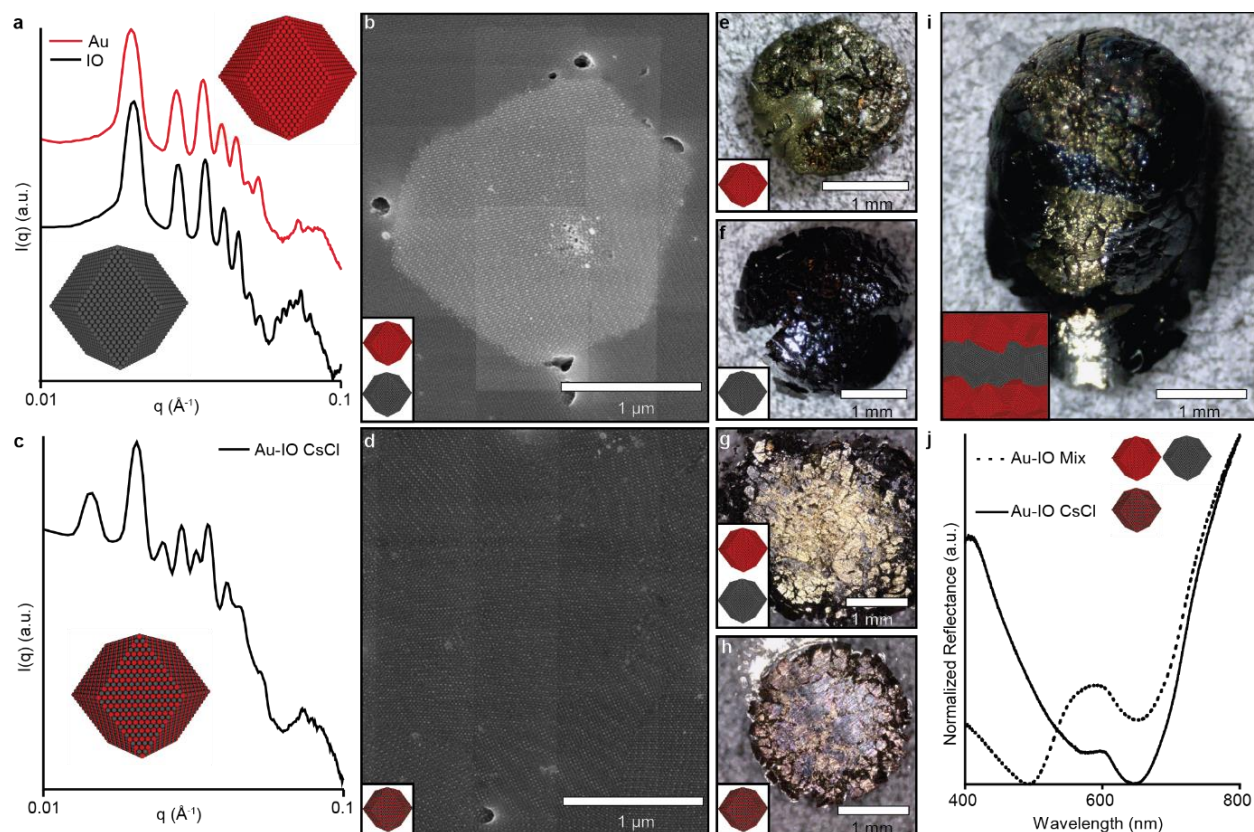


Fig. 34. Independently controlling NCT solid composition, nanoscale ordering, and microstructure. (a) SAXS of Au-NCT and IO-NCT crystallites in solution demonstrating identical bcc ordering regardless of nanoparticle composition. (b) Cross-sectional SEM of a solid sintered from a blend of Au-NCT crystallites and IO-NCT crystallites, demonstrating a heterogeneous microstructure with neighboring grains of distinct composition. (c) SAXS data of co-assembled, complementary Au-NCTs and IO-NCTs demonstrating a CsCl-type lattice (Au and IO NPs were coated with DAP- and Thy-terminated polymers, respectively, ensuring CsCl ordering). (d) Cross-sectional SEM of a bulk solid sintered from CsCl-type NCT crystallites demonstrating a homogeneous microstructure where every alternating nanoparticle is Au or IO. Optical images of the macroscopic, free-standing NCT solids fabricated from (e) Au-NCTs, (f) IO-NCTs, (g) mechanically blended Au/IO-NCTs, and (h) CsCl Au/IO-NCTs, pressed into solids with flat surfaces to enable optical characterization. (i) Heterogeneous structure of successively sintered IO-Au-IO NCTs. (j) Reflectance measurements of NCT solids, demonstrating that material microstructure affects bulk material properties. Au-NCT bcc lattices and the mechanically blended Au/IO NCT sample exhibit a metallic reflection peak at ~550 nm, which is absent in the CsCl sample.

boundary diffusion occurs during sintering; the resulting heterogeneous microstructure is controlled by the relative amounts and sizes of the Au- and IO-NCT crystallites used. Macroscopically observable heterogeneity can also be achieved by sintering together batches of Au- and IO-NCT crystallites in a stepwise manner (Fig. 34i). In contrast, microscopically homogenous composites can be generated by synthesizing CsCl-type NCT crystallites formed from complementary DAP-functionalized Au-NCTs and Thy-functionalized IO-NCTs (Fig. 34C). In these CsCl-type lattices, each unit cell contains exactly one Au-NCT and one IO-NCT, but the overall crystallites form the same Wulff polyhedra as observed when only one particle composition is used. When CsCl-type crystallites are sintered, the result is a continuous macroscopic solid with well-defined, microscale grain sizes where every other nanoparticle consists of a different composition (Figs. 34d, 34h). Taken together, these three types of structures demonstrate the

ability to maintain a constant material composition, but introduce heterogeneity at the nano, micro, and macroscopic length scales.

Controlling structure across these size regimes can tailor the properties of self-assembled nanomaterials by dictating coupled interactions between particles. As an example, striking differences in the optical behavior of these sintered solids can be observed due to different extents of AuNP plasmon coupling. Both the exclusively Au-NCT solid and the solid consisting of blended Au-NCT and IO-NCT bcc crystallites show a metallic reflectance at ~550 nm due to strong plasmon coupling between AuNPs as a result of the small interparticle spacings. However, this peak is suppressed in CsCl lattices due to the presence of the IO-NCT spacers between gold particles, which weakens Au-NCT plasmon coupling (Fig. 34j).

Manipulation of NCT solid macroscopic form

Because IO-NCT components (i.e. iron oxide nanoparticles and polystyrene polymers) can be readily synthesized at gram-scale quantities, and because NCT crystals can be sintered into bulk solids, it should also be possible to manipulate the macroscopic form of these structures with additional processing steps. To demonstrate this additional level of structural control, a sintered solid of IO-NCTs was prepared by the abovementioned centrifugation method (Fig. 34f), and gently pressed (~0.05 tons) into a laser-cut polyoxymethylene mold of the MIT school logo. Removing the continuous NCT solid from the mold yielded a freestanding block with the embossed logo clearly visible (overall block dimensions of 3.9 mm x 2.6 mm x 0.25 mm) (Fig. 31e). SAXS confirmed the NCTs remained ordered (Fig. 31f), and SEM imaging revealed the microstructure is similarly preserved after pressing. NCT-based composites therefore possess the ability to control material structure across 7 orders of magnitude in length scales, including the nanoparticle composition, superlattice ordering, polycrystalline microstructure, and overall macroscopic form of the fabricated object.

Here we have demonstrated a method for manufacturing bulk, solid materials from a nanoparticle-based building block that can be manipulated into arbitrary macroscopic shapes while maintaining nanoscale control over ordering. Because there are many observable analogies between the processing of NCTs and traditional bulk materials, these structures provide an interesting tool for further exploring basic questions in processing science. For example, the nanoscale size of the NCT building blocks enable their *in-situ* characterization (e.g. via electron microscopy) during assembly, sintering, or deformation to allow the visualization of defect formation in a manner that would be challenging or impossible for atomic lattices. Furthermore, since the NCT design concept is agnostic to nanoparticle composition, sintered solids potentially allow for carefully calibrated interactions between nanoparticles like plasmonic coupling, controlled photoluminescence, or magnonic band gaps to be incorporated into bulk solids for application in sensing, display, or energy technologies.^{1,2,5,6} The ability to fabricate hierarchically-ordered, free-standing macroscopic structures with predetermined composition, nanoscale ordering, and microstructure represents a major advancement for the field of nanomaterials synthesis and promises to enable significant further research in both materials synthesis and structure-property relationships.

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4. Personnel Supported and Engaged in Research:

Rob Macfarlane, PI	
Paul Gabrys, graduate student	(also supported by NSF graduate fellowship)
Peter Santos, graduate student	(also supported by NSF graduate fellowship)
Leonardo Zornberg, graduate student	(also supported by NSF graduate fellowship)
Josh Kubiak, graduate student	(supported by NDSEG fellowship)
Diana Lewis, graduate student	(supported by Draper Laboratory fellowship)

5. Publications:

1. P. A. Gabrys, **R. J. Macfarlane**
Controlling Crystal Texture in Programmable Atom Equivalent Thin Films
ACS Nano, 2019, 13, 8452-8460.
2. L. Z. Zornberg, P. A. Gabrys, **R. J. Macfarlane**
Optical Processing of DNA-Programmed Nanoparticle Superlattices
Nano Letters, 2019, 19, 8074-8081.
Highlighted in Science: "Programming Programmable Materials", Science, 366, 703-704.
3. D. J. Lewis, L. Z. Zornberg, David J. Carter, R. J. Macfarlane
Single Crystal Winterbottom Constructions of Nanoparticle Superlattices
Nature Materials 2020, 19, 719-724.
4. T. Pashuck, N. Seeman, R. J. Macfarlane
Self-assembly of Bio-inspired and Biologically Functional Materials
MRS Bulletin 2020, 45, 832-840.
Invited Article; Cover Feature
5. D. J. Lewis, D. J. D. Carter, R. J. Macfarlane
Using DNA to Control the Mechanical Response of Nanoparticle Superlattices
JACS 2020, 142, 19181–19188.
6. P. J. Santos, P. A. Gabrys, L. Z. Zornberg, R. J. Macfarlane
Macroscopic Materials Assembled from Nanoparticle Superlattices
Nature 2021, 591, 586-591.
Highlighted in C&E News: "Nanoparticles lattices stack up in solids", March 29, 2021
Highlighted in Nature Chemistry: "Colloidal metallurgy", vol. 13, pg. 514-515
Highlighted in Matter: "Nanoparticles exploring the macroscopic world", vol. 4, pg. 2661-2663
7. J. M. Kubiak, A. P. Morje, D. J. Lewis, S. L. Wilson, R. J. Macfarlane
Dynamic Manipulation of DNA-Programmed Crystals Embedded in a Polyelectrolyte Hydrogel
ACS Applied Materials and Interfaces 2021, 13, 11215-11223.
8. R. J. Macfarlane
From Nano to Macro: Thinking Bigger in Nanoparticle Assembly
Nano Letters 2021, *in press*.

5. Presentations:

1. “Holistic Control of Structural Hierarchy in Nanocomposites”
2018, **ACS Fall Meeting**, Boston, MA
2. “Systems-Level Control of Molecular Multivalency”
2018, **Ryan Fellows Symposium**, Evanston, IL
3. “Systems-Level Control of Molecular Multivalency”
2018, **MRS Fall Meeting**, Boston, MA
4. “‘Soft’ Epitaxy of Programmable Atom Equivalents”
2018, **MRS Fall Meeting**, Boston, MA
5. “Systems-Level Control of Structural Hierarchy”
2018, **Rutgers University**, New Brunswick, NJ
6. “Systems-level Control of Structural Hierarchy in Nanocomposites”
2018, **University of Connecticut Polymer Program Symposium**, Storrs, CT
7. “Systems-Level Control of Structural Hierarchy”
2019, **84th Annual Meeting of the Israeli Chemical Society**, Tel Aviv, Israel
8. “Systems-Level Control of Structural Hierarchy”
2019, **ACS Spring Meeting**, Orlando, FL
9. “Surface-Directed, DNA-programmed Crystallization of Nanoparticles”
2019, **ACS Spring Meeting**, Orlando, FL
10. “Systems-Level Control of Structural Hierarchy”
2019, **MRS Spring Meeting**, Phoenix, AZ
11. “DNA-Programmed Interfacial Crystallization”
2019, **ACS Fall Meeting**, San Diego, CA
12. “A Systems Approach to Supramolecular Materials”
2019, **Boston University Materials Science and Engineering Colloquium Series**, Boston, MA
13. “Materials Synthesis via Systems Chemistry”
2019, **Northeastern University Chemistry Department Colloquium Series**, Boston, MA
14. “A Systems Approach to Supramolecular Materials”
2019, **Brandeis University**, Waltham, MA
15. “A Systems Approach to Supramolecular Materials”
2019, **City University New York ASRC**, New York, NY
16. “Biokleptic, Biomimetic, and Bioinspired Approaches to Materials Systems”
2020, **DOD Basic Research Forum**, Washington, DC

17. “Systems-Level Control of Structural Hierarchy”
2020, **UC Berkeley**, Berkeley, CA
18. “Systems-Level Control of Structural Hierarchy”
2020, **University of Illinois Urbana Champaign**, Urbana, IL
19. “‘Systems’ Approaches to Hierarchical Materials”
2020, **University of Massachusetts Lowell**, Lowell, MA
20. “Single Crystal Winterbottom Constructions of Nanoparticle Superlattices”
2020, **Goldschmidt Conference**, Honolulu, HI (*Virtual due to COVID-19*)
21. “Macroscopic Materials Assembled from Nanoparticle Superlattices”
2020, **Nanoscience Global Webinar presented by Nano Letters**
22. “Self-assembly of Bioinspired and Biologically Functional Materials”
2020, **MRS Bulletin Webinar**
23. “Macroscopic Materials Assembled from Nanoparticle Superlattices”
2020, **Noble Metal Nanoparticles Gordon Research Conference** (*Delayed, COVID-19*)
24. “Macroscopic Materials Assembled from Nanoparticle Superlattices”
2020, **Systems Chemistry Gordon Research Conference** (*Delayed, COVID-19*)
25. “Single Crystal Winterbottom Constructions of Nanoparticle Superlattices”
2021, **ACS National Meeting**, Atlanta, GA
26. “Single Crystal Winterbottom Constructions of Nanoparticle Superlattices”
2021, **ACS Colloids National Meeting**, Houston, TX (*Virtual due to COVID-19*)
27. “Macroscopic Materials Assembled from Nanoparticle Superlattices”
2020, **Nanoscience Global Webinar presented by Nano Letters**
28. “Macroscopic Materials Assembled from Nanoparticle Superlattices”
2021, **Japan Society for the Promotion of Science**, Tokyo (*Virtual due to COVID-19*)
29. “‘Systems’ Approaches to Hierarchical Materials”
2021, **Merrimack College**, North Andover, MA (*Virtual due to COVID-19*)

6. Awards and Honors:

1. 2019 Paul M. Cook Professorship Chair, MIT
2. 2019 3M Non-Tenured Faculty Award

7. Completed Theses:

1. Diana Lewis, PhD in Aero/Astro Engineering, 2019
Deposition, crystallization and nanoindentation of substrate-bound biomolecule-assembled nanomaterials
2. Paul Gabrys, PhD in Materials Science, 2020
Controlling Structure Across Length Scales with Directed Assembly of Colloidal Nanoparticles
3. Peter Santos, PhD in Materials Science, 2020
Self-Assembling Nanostructures for Ordered Superlattices
4. Joshua Kubiak, PhD in Materials Science, 2021
Polymer Grafted Nanoparticles as Functional and Mechanically Robust Single-Component Composites

8. Student Awards and Honors:

1. NSF Graduate Fellowship, Paul Gabrys
2. NSF Graduate Fellowship, Leonardo Zornberg
3. NSF Graduate Fellowship, Peter Santos
4. NDSEG Graduate Fellowship, Joshua Kubiak
5. Draper Laboratory Graduate Fellowship, Diana Lewis

9. Patents:

N/A

10. Tech Transitions:

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11. Collaborations and Synergistic Activities:

Collaboration with Draper Laboratories, Cambridge MA

Synthesis of single-crystalline PAE superlattices at interfaces

Measurement of PAE superlattice mechanical properties

Development of instrumentation to measure plasmonic properties and reflectivity of PAE superlattices