

Hierarchically Structured Nanocomposites via a “Systems Materials Science” Approach

Rebecca L. Li, Carl J. Thrasher, Theodore Hueckel, and Robert J. Macfarlane*



Cite This: *Acc. Mater. Res.* 2022, 3, 1248–1259



Read Online

ACCESS |

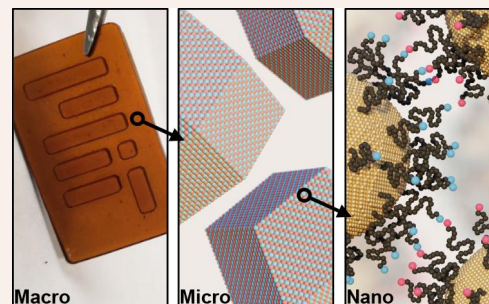
Metrics & More

Article Recommendations

CONSPECTUS: Nanocomposite materials can achieve desirable characteristics otherwise unavailable to single component systems, making them attractive platforms to precisely modulate a material's mechanical, electromagnetic, thermal, and optical properties. Because these properties are often dependent on the organization of constituent materials just as much as their relative composition, intentionally programming composite properties requires hierarchical structural control across many length scales. However, the fundamental forces governing the atomic, molecular, nanoscale, microscale, and macroscale composition and structure of a material are all interlinked, and thus must be manipulated simultaneously to properly create ideal designer materials. This fundamental interdependency indicates the need for a “systems materials science” approach to rational nanocomposite design. Much like the fields of “systems biology” and “systems chemistry”, a “systems materials science” approach would emphasize emergent connections arising from complex networks of interactions between individual components. In the context of materials synthesis, a systems-level approach would need to consider how structural changes across multiple length scales (chemical bonding, nano- and microstructural evolution, macroscopic geometry) influence one another during all steps of material synthesis and processing.

In this account, we highlight our recent work exploring pathways to “systems materials science” inspired design via the development of versatile, programmable, and scalable nanocomposite building blocks. Our group has established a suite of polymer-grafted nanoparticle designs that are inherently composite architectures, containing rigid inorganic cores with dynamic polymer ligand brushes. These building blocks provide molecular and nanoscale handles to dictate particle assembly into higher-order structures by exploiting biomolecular recognition, supramolecular chemistry, nanoparticle synthesis, and an array of different processing conditions. Moreover, they also enable systems-level approaches to material design, as they provide a means of using nano- to macroscale modifications to material structure as a means of altering molecular to nanoscale behaviors. We outline the advancements that have guided our thinking about composite synthesis, underscore key design motifs, and detail how feedback and feedforward mechanisms can govern structure formation at multiple length scales.

The contents of this account are organized by length scale, starting with an examination of molecular interactions capable of guiding assembly. This section considers the trade-offs between precision and scalability, culminating in a discussion of strategies which provide a balance of programmability, compositional versatility, and accessibility. We proceed to describe the thermodynamic principles of building block assembly, showing how the resulting nanostructures can be dictated via both composition and assembly environment. Further, we connect molecular and nanoscale design considerations to higher order mesoscale structures (with principal dimensions ranging from hundreds of nanometers to hundreds of microns). We discuss the kinetic factors controlling long-range ordering and the additional variables they overlay on design and assembly techniques. Following this, we discuss macroscale structural features where we emphasize the difficulty in processing and manipulating these materials while maintaining or programmatically modulating their nano- and microscale order. We end with an examination of relevant application areas for these hierarchical composites, the implications of recent advances, and key challenges for future research. From this work, we conclude that “systems materials science” will be a critical guiding philosophy to advancing nanocomposite design and development.



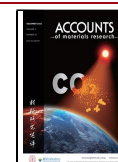
■ INTRODUCTION

Composites integrate multiple components to achieve properties that cannot be exhibited by one component alone, and therefore represent an important class of materials for advancing many biomedical, energy, structural, and transportation-related technologies.^{1–3} Polymer nanocomposites (consisting of nanoscale filler particles embedded within a macromolecule matrix)

Received: August 7, 2022

Revised: November 6, 2022

Published: November 22, 2022



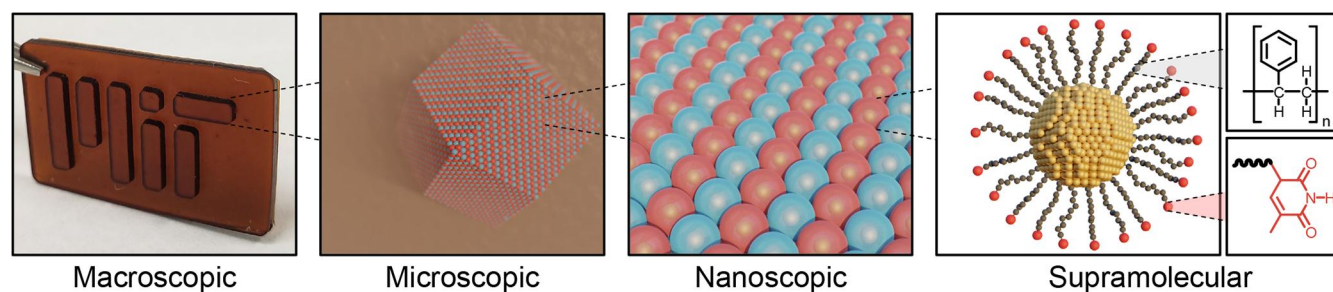


Figure 1. Hierarchical construction of nanocomposite materials with structural organization bridging various length scales. This design concept emphasizes a “systems materials science” approach, where structural features at all of these length scales must be considered to fully control and understand material properties, processing, and performance.

are a quintessential example of the potential of this materials design strategy, as polymers often possess desirable mechanical properties and processability, but exhibit narrower ranges of thermal, magnetic, and electrical properties compared with inorganic substances. Blending these two disparate material types thus enables far greater versatility in tailoring structure–property relationships. However, the properties of these materials are dictated by more than just the composition of the constituent pieces, as filler organization can heavily influence material behavior.^{1–3} Examples include the formation of percolating particle networks that break the “rule of mixtures” in dictating thermal or electrical transport properties, or emergent phenomena arising from interactions between adjacent particles (for example, optical or magnetic coupling). Thus, to intentionally program composite properties for use in functional applications, it is critical to manipulate material architecture hierarchically across multiple length scales via simultaneous control of atomic and molecular composition, nanoscale organization, microstructural features, and final macroscopic geometry.

The enormity of this task (controlling material ordering across $\sim 10^9$ length scales simultaneously) inherently demands a system-level perspective. A “systems materials science” approach to design would need to emphasize the connections between chemical bonding, microstructural evolution, and macroscopic shape changes during all steps of material synthesis and processing. By understanding how structure changes at each length scale affects the organization of motifs at both larger and smaller size regimes, the final structures, properties, and performance of a hierarchical material could be intentionally and rationally programmed (Figure 1). Moreover, particular attention should focus on the *interdependency* of these behaviors—that is, understanding how small building blocks collectively interact to generate specific meso- or macroscale motifs, and how these larger forms can feed back to influence the individual bonding interactions governing the assembly process.

One of the first steps toward a systems materials design concept for hierarchical composites is therefore to elucidate appropriate building blocks that have structural features that can be intentionally programmed at these different length scales. Our group has tackled this challenge by developing a suite of polymer-grafted nanoparticles that are inherently composite architectures, containing both rigid inorganic cores and soft polymeric brushes.^{4–9} These designs provide a major advantage in the investigation of “systems” approaches to materials synthesis by using molecular and nanoscale handles to manipulate assembly during the formation of higher-order structures, and also allowing nanoscale design features to alter supramolecular behavior. By exploiting biomolecular recog-

nition, supramolecular chemistry, nanoparticle synthesis, and processing methods, we have begun to outline a potential pathway toward a “systems materials science” approach to developing new polymer composites. Here, the influence of different length scale structures (from molecular to macroscopic) will be discussed, culminating in examples of how hierarchical systems affect composite properties and performance. We outline the steps that have led to this means of thinking about composite synthesis, as well as key challenges for future advancement of the field.

■ BUILDING BLOCKS FOR SELF-ASSEMBLY

To synthesize targeted materials with hierarchical structure from the bottom up, proper design of the fundamental building blocks is crucial. Because polymer nanocomposites can consist of many different types of polymers or nanoparticles, developing general principles for tailoring the interactions between these components would enable more versatility in materials development. As such, a key starting point for investigating systems-level approaches to hierarchical composites is the judicious selection of molecular and supramolecular interactions that enable control over particle–particle and particle–matrix bonding to permit the directed assembly of complex structural features (Figure 2).

The well understood and highly specific interactions of Watson–Crick base pairing therefore makes DNA an ideal tool for establishing generalizable principles that can be used to rationally program composite hierarchy. For example, synthetic oligonucleotides grafted to nanoparticle surfaces can drive particle assembly into a myriad of different superlattices as a function of both nucleotide sequence, particle size, and shape (Figure 2C).^{10,11} These building blocks have been thus dubbed “programmable atom equivalents” (PAEs), as they tend to form crystalline arrangements structurally analogous to atomic crystals, but with significantly greater control and predictability in lattice design.¹² Moreover, unique nanoscale-derived properties have been observed (for example, enhanced stability or binding constants compared to isolated DNA strands), indicating that the organization of multiple macromolecules on a nanoparticle scaffold can influence the behavior of collections of biomacromolecules.^{13,14} Because the scientific principles governing the DNA interactions between nanoparticle-based systems have been extensively covered in prior work, we direct the reader to previous literature on the topic;^{15–17} subsequent sections will discuss how these supramolecular interactions control larger length scale features in PAE nanocomposites. However, it is important to note here that synthetic oligonucleotides are unfortunately synthesized at

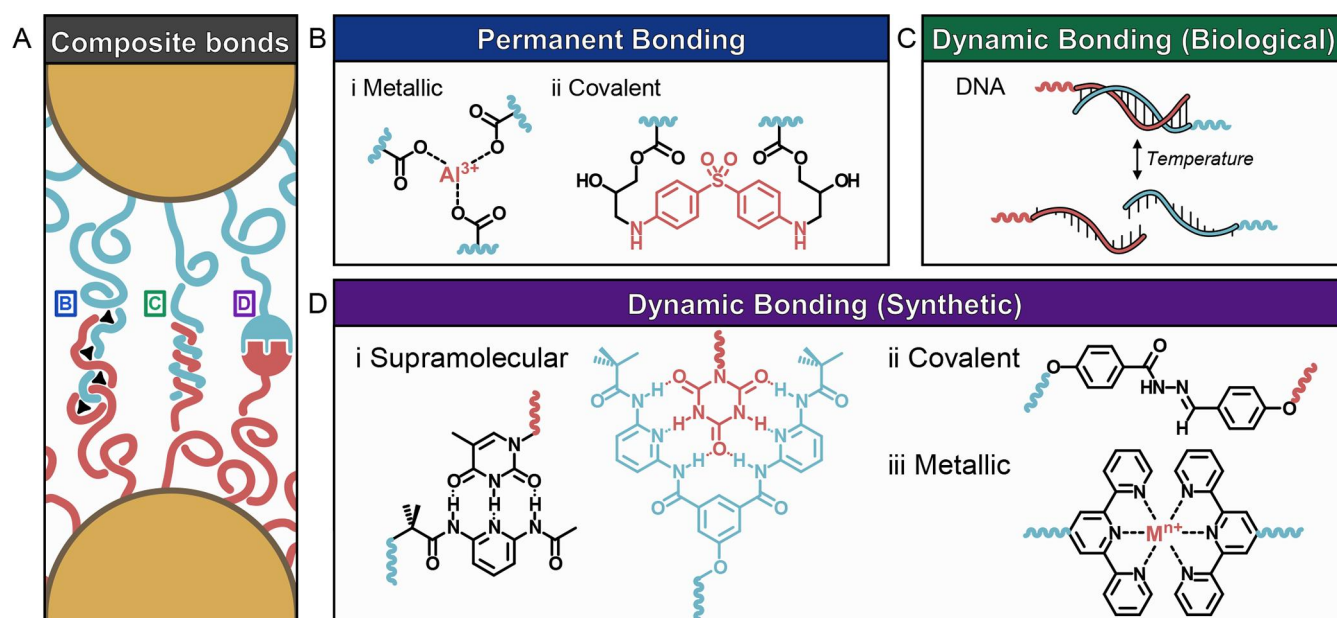


Figure 2. Bonding interactions that can be used to control brush particle building block assembly. (A) Composite bonding can be either permanent or dynamic with a tunable range of interaction strength. (B) Polymer chains can be permanently cross-linked through chain-end or side-chain reactions. (C, D) Dynamic binding can be tuned through a range of supramolecular, dynamic covalent, or metallic interactions (synthetic), and also by programmable DNA hybridization (biological).

significantly lower scales than typical commodity polymers, limiting the sizes of objects that can ultimately be fabricated. Additionally, although minor modifications to DNA's molecular structure can alter its assembly, the programmability of DNA relies on a rigid set of supramolecular interactions that prevent significant variation in its composition, properties, or assembly conditions. Thus, while DNA provides a valuable blueprint to outline design considerations for using supramolecular assembly to synthesize hierarchical composites, additional building blocks that expand upon these principles are needed to fully develop composites via a “systems-level” approach.

In contrast to DNA, synthetic polymers possess greater compositional variation, scalability, and processability. Polymer nanocomposites containing brush-coated particles typically graft ligands of the same composition as the matrix polymer onto the nanoscale fillers.¹⁸ These brushes overcome unfavorable interfacial interactions between filler and matrix, thereby improving filler dispersion. However, polymer brushes only fully entangle with the surrounding matrix chains when they are of sufficient length—below this length, integration is hindered and mechanical performance suffers. While the entanglement length can vary, it is almost always long enough that the polymer brush volume greatly inhibits nanocomposite filler density within a composite, thereby limiting the tunability of material properties.

To circumvent this limitation, we have developed polymer grafted nanoparticles (PGNPs) that possess short brushes that can be cross-linked postprocessing (Figure 2B).^{7–9,19} The use of cross-links instead of chain entanglement to impart mechanical strength enables filler loadings as high as 57 vol % without sacrificing mechanical properties.⁷ These PGNPs can use different types of cross-linking moieties (for example, anhydrides and amides), and can be processed into conformal films and arbitrarily shaped 3D objects through hot pressing, compression molding, extrusion, or vacuum forming.^{7,8,19}

Nevertheless, while these cross-linked PGNPs possess homogeneously distributed fillers, they lack long-range organization.

To bridge the gap between these opposing types of macromolecule-grafted particles (PAEs that are precise but not versatile or scalable, and PGNPs that are the opposite), we hypothesized that modifying PGNP brushes with programmable supramolecular groups could guide the formation of ordered architectures without sacrificing compositional variety or scalability of the resulting composites. To this end, we reported a new type of nanoscale building block, termed the nanocomposite tecton (NCT), capable of using rationally selected molecular interactions to form hierarchically ordered structures (Figure 2D).^{4,5,20–23}

NCTs' key advancement is that the polymer backbone and nanoparticle core composition can be modified independently from the motifs that drive particle self-assembly, which allows for greater modification of composition and assembly conditions.⁴ In the first iteration of the NCT concept, programmable molecular recognition was enabled by diaminopyridine (DAP) and thymine (THY) complexes that form complementary hydrogen bonding pairs. The types of supramolecular interactions that could be used to direct NCT assembly were later expanded to include other types of hydrogen bonding motifs, metal ion coordination, and reversible covalent bonding.²⁰ Separately, other groups have expanded on this concept to induce assembly through interactions such as stereochemistry-driven polymer complexation.²⁴

The reversible association (solidification) and disassociation (melting) of colloiddally suspended NCTs can be monitored through changes in their optical characteristics. For NCTs assembled using hydrogen bonds, thermal energy is the simplest method of breaking these supramolecular interactions, and a “melting temperature” can be determined for any given NCT assembly. This characteristic melting temperature can be increased by increasing particle diameter and decreased by increasing the length of the grafted polymer brush.^{4,21} These

trends in thermal properties can broadly be explained by variations in the local density of hydrogen bonding groups around the NCTs. However, more complex effects are observed when considering hierarchical design parameters and the influence of larger scale features on supramolecular behaviors; these effects are further detailed in the subsequent section.

NCTs can also be modified to achieve sophisticated assembly behaviors triggered by external environmental stimuli (Figure 2D).²⁰ NCTs functionalized with terpyridine (Tpy) ligands, for instance, assemble in the presence of metal ions based on coordination between the ions and the lone pairs on the nitrogen atoms of the Tpy units. As a result, these NCTs can be triggered to disassemble with the addition of acids via the protonation of Tpy nitrogen atoms. By pairing this pH-driven response with an external molecule that changes its protonation state in response to light, optical stimuli can also be used to modify solution pH and thereby control complexation. NCTs containing both hydrogen bonding and metal ion coordination groups exhibited pathway dependent structures contingent on the order in which heat and metal ions were applied. In addition, NCTs that expressed both supramolecular complexes and moieties capable of dynamic covalent chemistry could use the weak supramolecular interactions to assemble the particles, then lock these structures in place via rapid covalent bond formation accelerated by the high local concentration of the corresponding moieties around the assembled particles.

Collectively, this suite of nanocomposite building blocks (PAEs, PGNPs, and NCTs) highlights the value of using controlled molecular interactions to guide hierarchical organization within a composite. While brush-coated particles conventionally use chain entanglement to manipulate interactions between particles and surrounding matrix, both permanent covalent bonds and reversible supramolecular connections provide additional handles to tune composite structure and composition. Future efforts to expand the scope of different particle, polymer, and supramolecular chemistries are projected to have significant benefit in modulating structure property relationships.

■ NANOSCALE STRUCTURES FROM SELF-ASSEMBLY

The interplay between polymer ligands, recognition complexes, nanoparticle coupling, particle environment, and processing conditions determines the types of nanoscale structures that can arise from the assembly of NCT, PGNP, or PAE building blocks. By independently tuning composition and assembly conditions, principles that govern assembly and resulting structure have been elucidated, resulting in a library of reported crystal structures.^{2,11}

When colloidal assembly is primarily driven by enthalpic attraction, the building blocks tend to adopt structures that maximize the number of connections between complementary particles. The use of weak, reversible interactions permits thermal annealing to induce particle reorganization into these thermodynamically preferred arrangements (Figure 3). For example, PAEs possessing self-complementary DNA ends (generating a unary system where all particles can bond to all other particles in solution) will adopt close packed face centered cubic (FCC) lattice structures at thermodynamic equilibrium, as FCC lattices represent the densest packing of spheres and thus maximize the number of DNA duplexes that can form.¹⁰ In contrast, binary sets of equally sized PAEs possessing complementary DNA binding groups typically form body centered cubic (BCC) lattices to maximize the number of

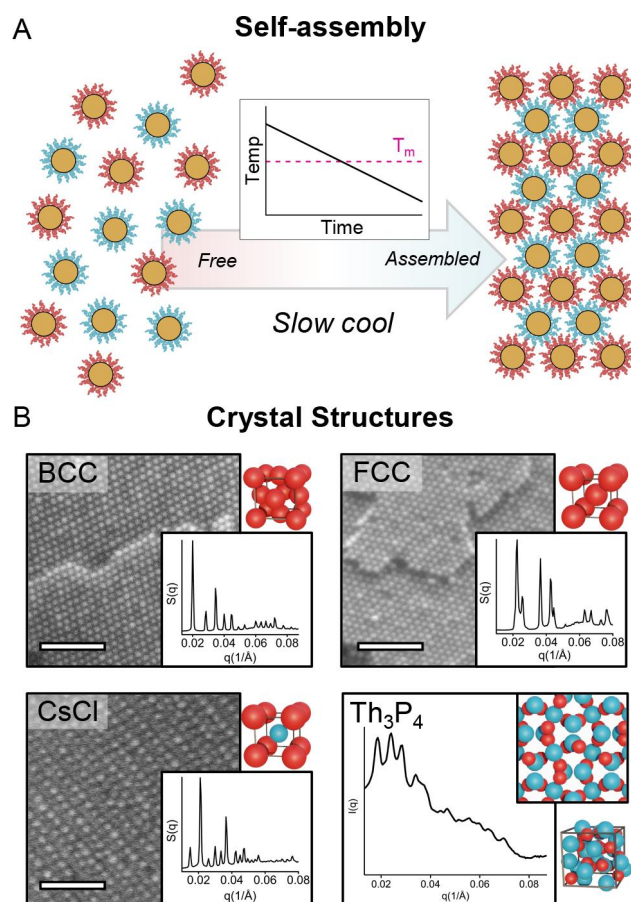


Figure 3. (A) Thermodynamic control of building block self-assembly directs nanoscale structural organization. Slowly cooling nanoparticles with dynamic binding interactions below their melting temperature produces ordered nanoscale structures. (B) Example lattice types include BCC, CsCl, FCC, and Th_3P_4 depending on nanoparticle composition and assembly conditions. Scale bars 200 nm.

complementary nearest neighbors (and thus maximize DNA connections). NCTs assembled from nanoparticles separately grafted with DAP and THY recognition units form BCC lattices for analogous reasons.^{4,10} Symmetrically altering the nanoparticle size or polymer length in these systems generally changes the relative spacing of the formed lattice without altering lattice structure. However, more diverse lattice structures can be attained by introducing asymmetric changes to binary particle systems. For example, pairing different core compositions with complementary binding groups leads to the formation of CsCl lattices for both PAE and NCT systems.²² PAEs can further produce AlB_2 , Cr_3Si , and Cs_6C_{60} lattices from binary sets of particles with large disparities in hydrodynamic radius, metastable HCP lattices by kinetic trapping, and NaCl, simple cubic, and even three-component lattices (for example, perovskites, ABC_3 -type lattices) using particles that express multiple orthogonal DNA sequences.^{10,11,25}

A crucial factor for engineering nanoscale organization within a composite is understanding the role of dispersity. Homogeneous building blocks are often required to achieve high quality colloidal crystals, which limits usable materials to those with reported low dispersity syntheses.²⁶ However, “softening” nanoparticles by adding polymeric shells allows for variations in inorganic particle diameter to be tolerated. Early work showed that PAEs would form ordered crystals with up to ~10%

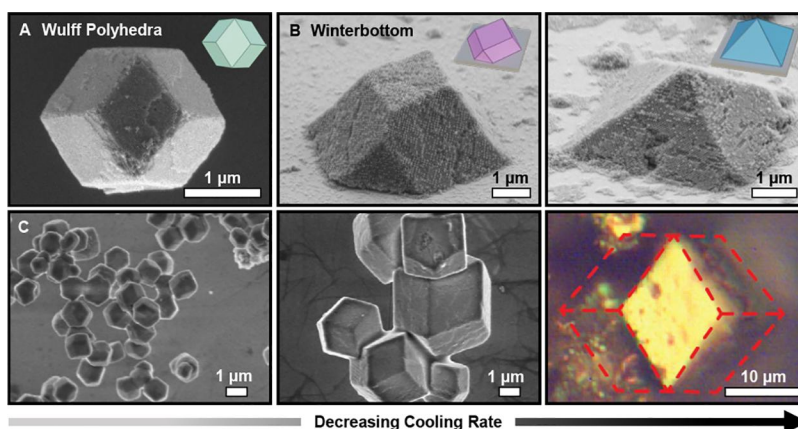


Figure 4. Emergent mesoscale crystallites. (A) Rhombic dodecahedron-shaped Wulff polyhedra of NCTs with BCC unit cell symmetry. (B) Flat topped diamond and square pyramid Winterbottom structures made from binary PAE systems with one or both particle types complementary to the substrate, respectively. (C) Size tunability of NCT crystallites is enabled via cooling rate control. Images reproduced with permission from ref 5. Copyright 2021 Springer Nature.

variation in spherical nanoparticle core size.^{10,27} Counter-intuitively, despite having multiple sources of dispersity (both particle size and polymer length), NCTs extend this effect even further, and represent one of the most tolerant methods to obtain ordered nanoparticle superlattices developed to date. We found that NCTs will tolerate polymer $\bar{D}$ values as high as 1.44 or core diameters with 23% relative standard deviation while still forming highly ordered structures.²³ The high degree of accepted variation in building block uniformity is hypothesized to arise from the ability of polymer chains to compress or stretch in order to maintain the maximum number of interparticle connections that is achieved from an ordered lattice. This tolerance of dispersity greatly broadens the range of applicable materials and synthetic methods, making NCTs an excellent choice for scalable materials development.

The assemblies described above use the organization of multiple supramolecular interactions around a nanoscale scaffold to induce the formation of nano- to mesoscale ordering. Interestingly, we have discovered that such organization can also enforce hierarchical effects in the opposite direction—in other words, the nanoscale scaffolds can be used as a design handle to modulate molecular thermodynamics. This is a key aspect of “systems” approaches to material design, as the integration of composite structural motifs across different size regimes should inherently allow for hierarchy to be induced both up and down length scales. We have observed this unique phenomenon of larger scale motifs manipulating smaller scale organization through NCT-NCT bonds forming “bundles” of supramolecular recognition complexes, where both the size and number of supramolecular bundles in each NCT-NCT interaction are dictated by the size and shape of the nanoscale scaffold.²¹ This odd and complex behavior can be explained by examining the balance of thermodynamic factors associated with NCT-NCT bond formation—namely, the enthalpy benefit of forming a supramolecular complex between two brush chain ends, and the entropy penalty of “tethering” those polymer chains together upon complex formation (which limits their configurational freedom). For any supramolecular group in an NCT-NCT bond to participate in a given “bundle” within that bond, the enthalpic gain of forming the complex must outweigh the entropic penalty. By understanding this paradigm, it is possible to use nanoscale morphological control to manipulate supramolecular behavior, as the size and shape of the nanoparticle scaffold dictates the

extent of entropy loss upon tethering two polymer chains from adjacent particles. Indeed, in prior systems, face-to-face and edge-to-edge configuration of brush-coated NPs has been shown to influence both the enthalpy and entropy of these interactions.^{28,29} However, most prior efforts used macro-molecule brushes where either the entropic or the enthalpic effects dominated particle behaviors, potentially explaining why NCTs were the first building block with which this “bundling” phenomenon could be readily observed and quantified. More efforts to examine this effect are required in both NCT and other systems. Importantly, the influence of nanostructuring on supramolecular thermodynamics can also be used to induce counterintuitive effects on particle assembly that can only be understood via examining an entire NCT system at one. As an example, in NCTs grafted with polystyrene brushes terminating in hydrogen bonding groups, the addition of polar solvent will simultaneously weaken individual supramolecular bonds, but also enhance the collective enthalpy of an NCT-NCT bond. Coarse-grained models indicate this increased interaction strength is the result of the polar solvent altering the configuration of polymer chains within the brush in a manner that permits bundles with higher levels of multivalency. Thus, although each supramolecular bond is individually weakened, more of these bonds can participate in any given bundle. Modulating the thermodynamics of NCT assembly in this manner allows a single set of NCTs to either form CsCl or Th₃P₄-type superlattices, as these different packing arrangements require different amounts of polymer confinement to generate an equivalent number of supramolecular bonds. This result is significant because it suggests that hierarchical ordering of these systems cannot be predetermined by summing interactions of individual molecules, but rather that a systems-level design process where the morphology at each length scale is considered both a cause and effect of behavior at each level is needed.

■ MESOSCALE ORGANIZATION OF COMPOSITES

An inherent challenge in using self-assembly to modulate a material's structure across multiple length scales is that ligand interactions typically only affect the local coordination environment around particles. However, when given enough time and energy to reorganize, micron-scale crystalline superlattices will tend to adopt specific polyhedral shapes that possess well-

defined faceted surfaces. The shapes of these polyhedra (that is, their crystal habits) are a reflection of the unit cell crystallographic symmetry, as the most favored structures are often bound by crystal planes that minimize unfavorable surface energies, dubbed Wulff constructions.^{5,30}

For example, both NCT and PAE superlattices with BCC unit cell symmetry adopt rhombic dodecahedron shaped crystals (Figure 4A). This shape represents the lowest energy superlattice habit because it is the smallest surface-area-to-volume ratio shape that is bounded entirely by {110} planes, which minimizes the number of “dangling bonds” present at the surface of the crystallite. Other superlattice crystallites with different unit cell geometries grown at thermodynamic equilibrium also follow the general pattern of minimizing surface energy.^{30–32} Kinetically controlled growth of faceted crystallites remains more challenging, but could potentially be a future route to achieving more complex crystal shapes.

While the requirement of assembly at thermodynamic equilibrium to achieve faceted crystal shapes limits the design handles for tailoring mesostructure, assembling particles while imposing micro- to macroscale boundary conditions can also anisotropically alter crystal growth. The simplest means of restricting superlattice growth to modify crystal habit is to assemble particles at an interface.^{6,27,33–36} When single crystals are grown heterogeneously, they can adopt faceted shapes called Winterbottom structures. The key difference between Wulff and Winterbottom shapes is that the Winterbottom constructions also consider interactions between the growing crystal and the underlying substrate. For instance, when substrates are functionalized with DNA sequences complementary to just one particle in a binary PAE system that adopts BCC unit cells, square pyramid crystal shapes are observed ($\langle 100 \rangle$ orientation perpendicular to the surface). In contrast, if the substrate-grafted DNA strands are complementary to both PAEs, flat-topped diamond shaped crystals are formed ($\langle 110 \rangle$ orientation perpendicular to the surface) (Figure 4B).⁶ The degree of protrusion from the substrate for these Wulff constructions can be modified by changing the relative density of ligands on substrates and particles; increasing PAE-to-surface interactions relative to PAE–PAE interactions results in less protrusion as the crystallites “wet” the surface to enable greater substrate contact area per crystallite volume.

It has also been observed that heterogeneous growth of crystals allows for single crystal superlattices to be formed for other symmetries that have difficulty forming Wulff constructions, such as FCC or AlB₂ type lattices.⁶ In each of these cases, a specific crystallite facet maximizes PAE–substrate interactions; the favorability of having this plane at the interface “pins” crystal growth to a limited subset of orientations, making the growth of single-crystal architectures more readily achievable. Future efforts in this area include the use of patterned surfaces to “frustrate” crystal growth and induce anisotropic crystal habits. We have already shown that patterned surfaces can control crystallite size and shape,³⁴ and even shown that alteration to the micron-scale designs can influence PAE lattice structure.²⁷ though more investigation is needed to explore how such patterns manipulate the thermodynamic Winterbottom shapes of different lattices. The ability to regulate crystallite size is another important tool for mesoscale structure control and is typically accomplished by tuning nucleation and growth processes. Even though unit cell symmetries and crystallite habits of nanoparticle superlattices are structurally identical to atomic crystals, the growth mechanisms are clearly

different and require more investigation.⁵ Our initial efforts mapping the parameters affecting NCT crystal growth show that NCT crystallite size is directly proportional to concentration and inversely related to cooling rates (Figure 4C). The positive dependence of crystallite size with NCT concentration is counterintuitive as classical nucleation theory indicates that higher initial concentrations should form more nuclei and hence smaller crystallites. We hypothesize that this deviation stems from the lower characteristic concentrations and diffusion constants of nanoparticles compared to atoms during crystal nucleation, as well as the multivalent nature of NCT binding interactions. In simple terms, NCTs continuously melt or solidify across a range of temperatures, unlike atomic systems that possess discrete melting points. Between the upper and lower bounds of this range, the equilibrium state is neither solely a crystal nor a dispersion of particles, but a mixture of each. Thus, when nanoparticle superlattice crystallites nucleate, the concentration and diffusion rates of the particles (both of which are significantly lower than atomic systems) dictate a specific volume across which nanoparticles can diffuse to form a nucleus. At a given temperature, particles within this fixed volume will eventually reach a state of dynamic equilibrium with only a fraction of particles as part of the crystal. Thus, increasing particle concentration shifts the equilibrium toward larger crystallites (as there are more particles in a given volume), and slower cooling allows for a larger fixed volume at a given temperature (since the particles have more time to diffuse before equilibrium is shifted). Given the potential of such methods to modulate mesoscale organization in these composites, further investigation of fundamental crystallization mechanisms is essential.

■ MACROSTRUCTURE, SCALABILITY, AND FABRICATION

In traditional bulk materials, microstructure and macroscopic form are generally manipulated during processing to shape the desired object from a material feedstock. For polymer nanocomposites synthesized via self-assembly, particular care must be paid to maintaining the nanoscale order during processing, as the weak, reversible bonds required for forming well-ordered particle arrangements are often incompatible with techniques commonly used to process materials.³⁷ Additionally, considerations of cost, yield, and production volume become relevant to achieving scalability, as the quantity of material that can be produced ultimately dictates the feasible length scales of objects to be made. Nevertheless, the development of composite systems that can be hierarchically organized across macroscopic scales is vital for advancing the field, as unique structural features (and thus opportunities to tune structure–property relationships or use macroscopic processing techniques to influence nanoscale assembly) arise at larger length scales.^{2,38} For instance, in polycrystalline systems, manipulation of features such as grain boundaries and vacancies open new avenues for property control via “defect” engineering. Furthermore, the integration of nanoparticle superlattice composites into other bulk materials requires manipulation of the interfacial energies between the superlattice and surrounding matrix.³⁹ Investigation of methods to compatibilize particle assemblies with other composite feedstocks is therefore warranted.

The formation of films comprising ordered nanoparticles, typically by evaporation driven assembly, has been widely studied and demonstrated for a large variety of materials.⁴⁰ Such films have significant potential for applications requiring 2D

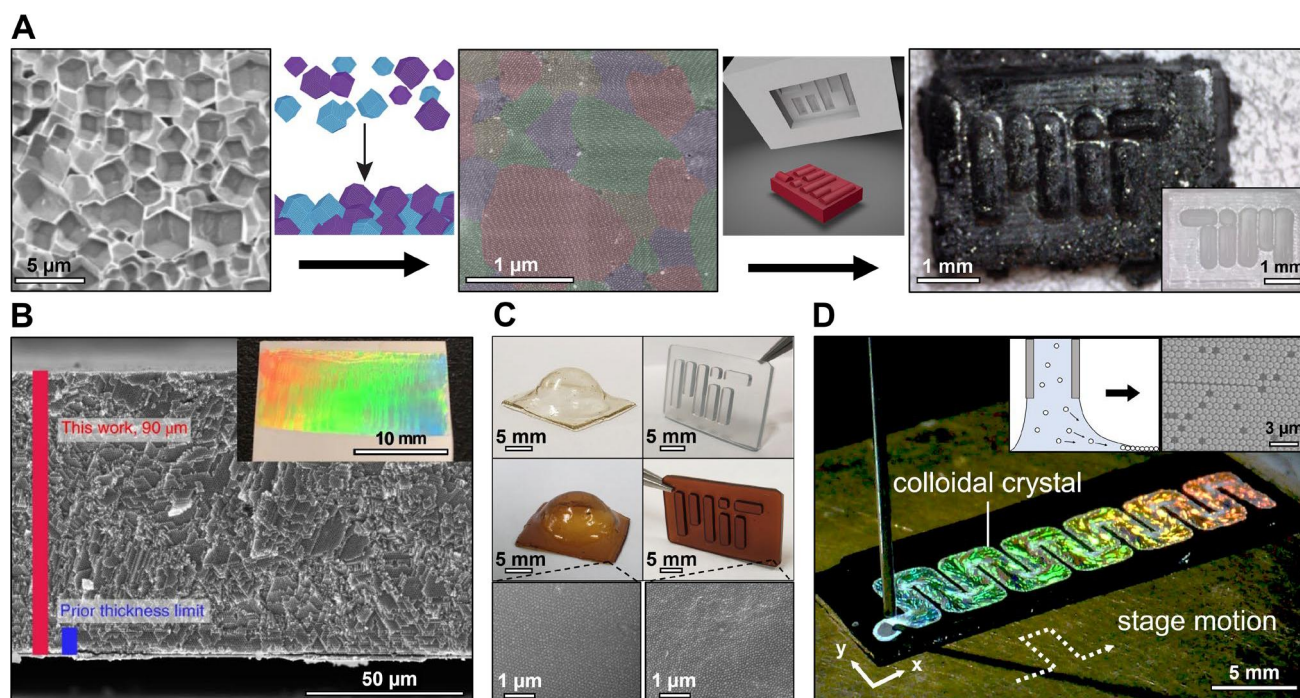


Figure 5. Processing and fabrication of hierarchically structured composites with nanoscale ordering. (A) A collection of micro sized polyhedra composed of crystalline nanoparticle NCT superlattices can be centrifuged into a sintered polycrystalline material, which can then be pressed into a macroscopic shape. (B) Thick film crack-free inverted metal nanolattice made via wet-electrostatic deposition of nickel into a superlattice of charged silica particles. (C) Thermoformable and moldable single component PGNP composites before (top) and after (middle) thermally induced anhydride cross-linking. (D) Direct-write printing of colloidal crystals where assembly occurs simultaneously with deposition. Images reproduced with permission from refs 5, 53, 8, and 41, respectively. Copyrights 2021 Springer Nature, 2021 Springer Nature, 2022 Wiley, and 2020 Wiley, respectively.

form factors (for example, displays, coatings), and have been discussed at length elsewhere.³⁸ However, a major challenge facing the field is the establishment of processing techniques to produce more complex, arbitrary 3D geometries.⁴¹ Our lab has produced one of the first such examples by “sintering” NCT crystallites into free-standing solids. Under mild temperature and pressure ($\sim 22^\circ\text{C}$ and centrifugation at $\sim 20\text{k RCF}$), individual crystallites with well-controlled habits and sizes can be compressed into a monolithic solid.⁵ These compressed solids can even be further molded to generate macroscopic 3D objects of arbitrary shape (Figure 5A), permitting hierarchical structure control across $\sim 10^7$ length scales.⁵

The processing of superlattices into larger solids permits the investigation of microstructural features that arise during solid densification, such as grain boundaries and crystallographic defects like vacancies, dislocations, and twinning.⁴² In bulk materials, these defects typically exhibit an outsized influence on a materials’ behavior, but it remains unclear what effects defects have in composites of ordered nanoparticle arrays. Efforts to control microstructure in nanoparticle superlattices are still nascent, but the polycrystalline NCT solids have shown the ability to control grain sizes as a function of the initial single crystals being compressed.⁵ This work also showed that the processed superlattices can undergo paracrystalline distortion under applied mechanical force, suggesting their mechanical properties likely differ from both other composites with the same composition (but different structural organization), and atomic solids with analogous crystalline organization (but at a notably different length scale). These observations also imply that macroscopic forces can indeed be used to alter nano- or microstructure in a programmable manner. Future efforts focusing on controlling and characterizing the property changes

resulting from superlattice microstructure is therefore an exciting but underdeveloped area of nanocomposite design. As the parameter space for such manipulations is quite large, computational methods will certainly be needed to guide and focus research pathways. It would also be prudent to cross-apply lessons learned in parallel fields, such as powder-based 3D printing, where control of 3D defects such as cracking and voids is critical.⁴³

■ FUTURE DIRECTIONS AND POTENTIAL APPLICATIONS FOR HIERARCHICAL NANOCOMPOSITE ASSEMBLIES

As nanoscale design and assembly becomes more advanced, research into hierarchical nanocomposites is shifting to later stages of the materials development life cycle where synthesis is targeted toward application-specific structures and properties. In some instances, self-assembled composite materials possess emergent properties unique to their particular architecture (for example, photonic band gaps, plasmonic/excitonic coupling).³ Other examples simply perform better than disordered counterparts due to better control over relevant nano- or microscale features that govern material properties or greater homogeneity of hierarchical structure.^{44–46} Here, we briefly discuss how new materials design and processing strategies could impact a few key areas (Figure 6) and offer insight into potential opportunities for future composite systems that use nanoparticle assembly.

One of the most well-studied applications of hierarchical nanocomposites involves tuning electromagnetic interactions of nanoparticle superlattices via controlling lattice spacing and symmetry.⁴⁷ Indeed, much of the early work in applications of such composites is in generating optical phenomena like photonic band gaps, plasmonic coupling, and light emission.⁴⁸

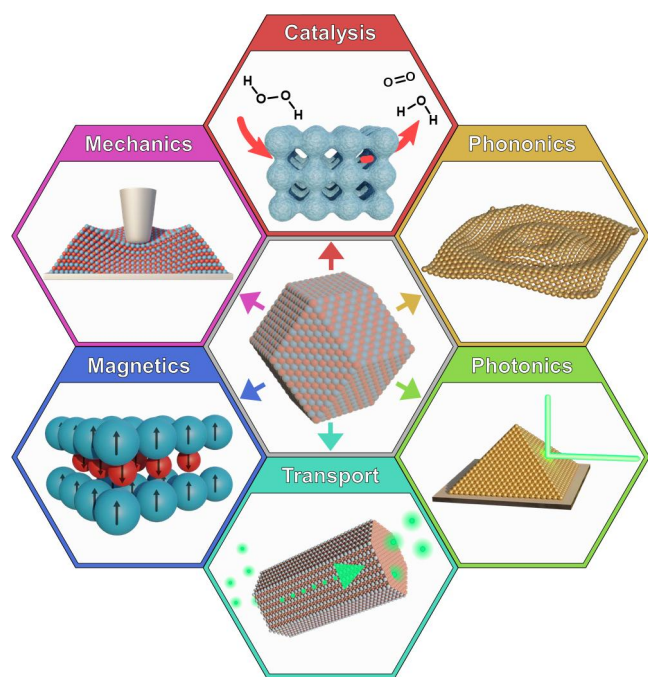


Figure 6. Application areas of hierarchically structured nano-composites. In each proposed application, the properties and performance of the material rely on being able to control structural features of the entire system across multiple length scales.

Such properties have been extensively documented and discussed in the literature, and we refer the reader to prior works to learn more about such behaviors in detail.⁴⁷

While optical properties governed by interparticle coupling have been thoroughly examined in these nanocomposites, an under investigated means of manipulating composite optical response is understanding how electromagnetic interactions can influence and be controlled with larger-scale motifs beyond just the symmetry or density of particles within a superlattice. For example, our work with PAEs showed that plasmon thermalization can be used to locally deliver heat to a material, thereby driving crystallization only at a specific point within a composite.⁴⁹ Unlike assembly methods that deliver thermal energy via bulk heating or chemical changes via solvent evaporation, the ability to spatially deliver energy to induce nanoparticle crystallization promises more sophisticated patterning of composite architectures. Such processes also permit macroscopic design parameters to influence nanoscale assembly, where the directionality and spot size of the delivered energy can alter the local shapes of the nanoparticle crystals. Moreover, such methods could allow for nanocomposite superlattice processing methods analogous to techniques like zone-refining that are critical for making wafer-scale single crystals in bulk materials, but are impossible to achieve in bulk-annealed nanocomposite superlattices.

Nanoparticle assemblies with specific microstructural features also permit new optical applications, such as the use of PAE assemblies to fabricate devices that use crystal habit to control wave-guiding.⁵⁰ Further, PAE Winterbottom constructions could be used as deliberately shaped components of microscale devices where the faceted shape of a crystal habit enables angle-dependent absorption, reflection, or scattering; the ability to anisotropically manipulate light in such a manner would be useful for planar optical devices in sensing and computing technologies. The importance of such efforts cannot be

understated, since the ability to use nanoparticle crystallization to control larger length scale features like crystal habit potentially provides new routes to nano- and microscale material fabrication, even without any exotic emergent properties that are directly correlated to superlattice symmetry.

Because cross-linked PGNP composites with well-dispersed particles remain transparent (even up to ~60 vol % particle loading), they also present opportunities for optical applications, such as highly processable composites with tailored refractive indices well beyond those of typical polymers. Such PGNP composites could be valuable as protective coatings or adhesive layers for lenses or optical devices. More sophisticated processing methods could be used to make layered composites for antireflection coatings or complex metalens structures by varying the density of high refractive index nanoparticle contact at different depths.

The compositional and structural flexibility of nanoparticle superlattices could also benefit the field of heterogeneous catalysis, where unique catalytic activities are enabled at the interface between two distinct materials. These enhanced catalytic effects are partially due to the optimized hetero contact area enabled by ordered particle arrays, but also because well-defined percolation pathways can be controlled by altering lattice parameters.^{51,52} Binary superlattices also maintain spatial separation between particles that would otherwise sinter at typical reaction temperatures, thereby preventing the loss of surface area, restriction of molecular transport, and lowering of catalytic activity which all occur in disordered binary solids.⁵² To make use of macroscopic nanoparticle superlattices for heterogeneous catalysis, however, it will be important to understand the role of grain boundaries and 3D defects such as cracks and voids on molecular transport.

Composites built from nanoparticle assembly have utility for the fabrication of strong and lightweight porous materials. While metal foams, aerogels, and other disordered porous materials can exhibit excellent strength to weight characteristics, ordered networks of hierarchical structure can more efficiently distribute material to better maintain properties such as stiffness, strength, and energy dissipation capacity compared to random cellular architectures.⁴⁶ Nanoparticle superlattices can be exploited as templates, allowing for the deposition of a secondary material into the negative space of the lattice followed by the selective removal of the original nanoparticle lattice material.⁵³ Further innovation in producing strong, lightweight structures from nanoparticle superlattices will require both large quantities of defect free lattices in macroscopic 3D geometries and novel ways of scalably infiltrating lattice materials. Moreover, significant effort must be placed in investigating how hierarchical ordering affects mechanical behavior, and how macroscopic deformation translates to alteration of nanoscale organization in these self-assembled materials.⁵ We have recently demonstrated that PAE superlattices can exhibit mechanical metamaterial behavior as a function of DNA design, indicating promise for using supra-molecular interactions to intentionally alter composite performance.³⁶ Specifically, different PAE lattices can be designed such that their Young's moduli are identical, but the different lattices deform through either plastic or viscoelastic mechanisms; the former would allow for tailored dissipation of mechanical force, the latter would enable self-healing. In a separate effort, bulk polycrystalline NCT lattices subjected to mechanical compression dissipated energy either via mechanisms expected based on traditional metal or ceramic lattices (for example, dislocations), or unexpected behavior predicted to arise from the composite

nature of the building blocks (for example, paracrystalline distortion due to motion of the soft polymer brushes).⁵ Clearly, further examination of how different compositions, nanoscale ordering, and mesoscale structures affect composite performance and how they are affected by the application of macroscopic force are required.

Nanoparticle superlattices are also potentially useful platforms for tailoring mass and energy transport for a diverse array of applications including heat dissipation, energy storage, and nanofiltration.^{54–56} While disordered materials with micro or nanopores have achieved high performance in these areas, they do not permit systematic investigation of structure–property relationships. Further, defect free organized structures can provide more consistent performance, enabling thinner device architectures.⁴⁵ Additionally, the ability to rationally alter both nanoscale structuring and nanoparticle surface chemistry provides a broad range of tunability in these hierarchical composites. Energy transport via electron or ion motion (for example, in battery anode, cathode, and membrane materials) is also an attractive possibility, as the highly ordered particle arrays could enable the fabrication of composites with large quantities of active inorganic filler without creating tortuous pathways for transport or particle aggregates that limit surface area to volume ratios. With their compositional diversity and ability to be molded and pressed into arbitrary shapes, NCTs and PGNPs are well suited for applications seeking tailored control of molecular transport.

Superlattices of magnetic particles can demonstrate unique properties arising from the pairing of disparate magnetic materials. Although progress in this field has been limited, the fabrication of exchange-spring magnets has been demonstrated by the coassembly of FePt and Fe₃O₄ particles.^{57,58} Exchange-spring magnets are the product of coupling between hard (high coercivity) and soft (low coercivity) materials which interact to produce a larger energy product than their individual constituent materials and are a potential route to ultrastrong permanent magnets. For magnetic nanoparticle assemblies to supplant rare-earth based magnets, additional complementary coupling material combinations and methods to produce large 3D arrays of coupled particles need to be identified. In addition, the role of polycrystallinity and defects on magnetic coupling in particle superlattices begs further study to determine at what length scales such devices can be relevant. Thus, the hierarchical composite assemblies generated with PAEs and NCTs provide an attractive route for advancing this field.

One application of polymer nanocomposites where hierarchical 3D control is particularly relevant is that of phonon-engineering. Phonons are quasiparticles representing collective mechanical vibration of atoms running the spectrum from sound (centimeter to meter wavelengths) to heat (nanometer wavelengths); therefore phonon control involves full spectrum size control of features.⁵⁹ More complicated architectures could allow for directional manipulation of phonon propagation, resulting in thermal shielding, concentrating, and rectifying behaviors.⁶⁰ In the related application of thermoelectric materials, efficiency is proportional to electrical conductivity and inversely proportional to thermal conductivity. While electronic and phononic properties are intrinsically linked at the atomic scale, nanoparticle superlattice parameters such as size, shape, spacing, and composition can effectively decouple electronic and thermal conduction.⁶¹ Utilizing NCTs for their compositional flexibility and capacity to sinter into polycrystalline solids could be an attractive path toward phonon-

engineered materials as the composition, nanoparticle size, and grain size could be designed to block short, mid, and large wavelength phonon propagation respectively, leading to ultra-low thermal conductivity.

While there is clearly potential for a “systems” approach to materials design, much needs to be done in multiple areas to fully enable this materials synthesis strategy. In each of these highlighted applications, unmet technical challenges prevent further discovery or exploration. With these application areas in mind, we suggest the following as high potential targets for future efforts using hierarchical nanocomposite assemblies:

- Assembly strategies that are compositionally agnostic to enable more versatile approaches
- Methods to form large volume, defect free assemblies
- High-yield production of mesoscale structures with low dispersity and tailored crystal habits
- Targeted defect engineering, and meso and micro-structural tunability
- Scalable processing methods that retain nanoscale ordering while molding or shaping the macroscopic 3D form of the material
- Postprocessing methods to transform the assemblies (for example pyrolysis, infiltration with secondary material, selective removal of target materials, or others)

Each of these research areas is critical for both understanding and exploiting hierarchical nanocomposite or nanoparticle-based systems, and we encourage the materials community to incorporate such ideas into future research efforts.

■ CONCLUSIONS AND OUTLOOK

On the basis of the research described above, we envision the field of nanocomposite design as operating in a transitory stage. While many building blocks, design principles, and processing strategies have been elucidated, the application of these materials is still largely nascent. This account has detailed an exploration of a “systems materials science” approach toward nanocomposite design, which we believe will be a key guiding philosophy for future maturation of nanocomposite technologies. This systems-level approach to considering and intentionally programming hierarchical complexity in composites emphasizes the dynamic interplay between structure and composition across the full spectrum of length scales responsible for dictating material properties and performance, and will be crucial for developing new methods of processing and fabricating nanocomposite materials at scale. Nanoparticle-based composites are ideal for this approach, as they provide building blocks with rational molecular and nanoscale design handles that can be easily tuned. Interactions between the fields of chemical synthesis, supramolecular chemistry and assembly, and materials processing must continue in order to enable a “systems materials science” approach to hierarchically controlling material structure, properties and performance. Many application areas with specific property requirements suitable for designed nanocomposites have been identified, and we encourage the community to build on both the concepts explicitly discussed above and the exciting work in the fields of nanoparticle assembly and composite synthesis. As such, advancements in defining structure–property relationships, multiscale and multiproperty modeling, and macroscale fabrication methods for architected nanocomposites hold significant potential to engineering disruptive materials innovation.

AUTHOR INFORMATION

Corresponding Author

Robert J. Macfarlane – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;

orcid.org/0000-0001-9449-2680; Email: rmacfarl@mit.edu

Authors

Rebecca L. Li – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Carl J. Thrasher – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Theodore Hueckel – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/accountsmr.2c00153>

Notes

The authors declare no competing financial interest.

Biographies

Rebecca L. Li received her B.S. in Chemistry from University of California, Los Angeles in 2016 and her Ph.D. in Chemistry from Northwestern University in 2021 under the mentorship of Prof. William Dichtel. She is currently an ASEE Engineering Postdoctoral Fellow in the laboratory of Prof. Robert Macfarlane at Massachusetts Institute of Technology. Her research interests include developing new synthesis strategies that control supramolecular material structures and their structure–property relationships.

Carl J. Thrasher received his B.S. in Chemistry from the United States Air Force Academy in 2015, his M.Sc. in Chemistry from University of Washington, Seattle in 2017 and is currently pursuing a Ph.D. in Materials Science and Engineering at Massachusetts Institute of Technology as a National Defense Science and Engineering Graduate Fellow. Prior to this he worked as a research scientist at the Air Force Research Laboratory. His research interests include 3D printing, stretchable electronics, and functional colloidal materials.

Theodore Hueckel is a postdoctoral associate in the laboratory of Prof. Robert J. Macfarlane at MIT. Theodore received his Ph.D. in Chemistry from New York University (2013–2019), where he studied colloidal synthesis and self-assembly with Prof. Stefano Sacanna. Theodore's current research interests focus on nanomaterial assembly on patterned interfaces.

Robert Macfarlane is the Paul M. Cook Associate Professor of Materials Science and Engineering at MIT. He received his Ph.D. in chemistry from Northwestern University, followed by a Kavli Nanoscience Postdoctoral Fellowship at the California Institute of Technology. He is a leading expert in the fields of nanotechnology, soft matter, self-assembly, and materials chemistry. His research efforts focus on developing new strategies to synthesize and process nanoparticle- and polymer-based composites with precisely controlled structures at the molecular, nano, and macroscopic length scales.

ACKNOWLEDGMENTS

This work was supported by the NSF via a CAREER grant, Award Number CHE-1653289, and Award Number DMR-2204222. It was also supported by funding from the Department of the Navy, Office of Naval Research under ONR award number N00014-22-1-2148 and Contract No. FA8650-15-C-7543, the Air Force Office of Scientific Research's (AFOSR) Young Investigator Research Program (FA9550-17-1-0288), and the US Army Research Office under Cooperative Agreement No. W911NF-19-2-0026 for the Institute for Collaborative Biotechnologies. R.L.L. is supported by the National Science Foundation under Grant #EEC-2127509 to the American Society for Engineering Education. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation or the American Society for Engineering Education. C.J.T. is supported through a National Defense Science and Engineering Graduate Fellowship (NDSEG).

REFERENCES

- (1) Wang, Y.; Desroches, G. J.; Macfarlane, R. J. Ordered Polymer Composite Materials: Challenges and Opportunities. *Nanoscale* **2021**, *13* (2), 426–443.
- (2) Gabrys, P. A.; Zornberg, L. Z.; Macfarlane, R. J. Programmable Atom Equivalents: Atomic Crystallization as a Framework for Synthesizing Nanoparticle Superlattices. *Small* **2019**, *15* (26), 1805424.
- (3) Hsu, S.-W.; Rodarte, A. L.; Som, M.; Arya, G.; Tao, A. R. Colloidal Plasmonic Nanocomposites: From Fabrication to Optical Function. *Chem. Rev.* **2018**, *118* (6), 3100–3120.
- (4) Zhang, J.; Santos, P. J.; Gabrys, P. A.; Lee, S.; Liu, C.; Macfarlane, R. J. Self-Assembling Nanocomposite Tectons. *J. Am. Chem. Soc.* **2016**, *138* (50), 16228–16231.
- (5) Santos, P. J.; Gabrys, P. A.; Zornberg, L. Z.; Lee, M. S.; Macfarlane, R. J. Macroscopic Materials Assembled from Nanoparticle Superlattices. *Nature* **2021**, *591* (7851), 586–591.
- (6) Lewis, D. J.; Zornberg, L. Z.; Carter, D. J. D.; Macfarlane, R. J. Single-Crystal Winterbottom Constructions of Nanoparticle Superlattices. *Nat. Mater.* **2020**, *19* (7), 719–724.
- (7) Kubiak, J. M.; Macfarlane, R. J. Forming Covalent Crosslinks between Polymer-Grafted Nanoparticles as a Route to Highly Filled and Mechanically Robust Nanocomposites. *Adv. Funct. Mater.* **2019**, *29* (44), 1905168.
- (8) Kubiak, J. M.; Macfarlane, R. J. Polymer-Grafted Nanoparticles as Single-Component, High Filler Content Composites via Simple Transformative Aging. *Adv. Funct. Mater.* **2022**, *32* (6), 2107139.
- (9) Desroches, G.; Wang, Y.; Kubiak, J.; Macfarlane, R. Crosslinking of Pressure-Sensitive Adhesives with Polymer-Grafted Nanoparticles. *ACS Appl. Mater. Interfaces* **2022**, *14* (7), 9579–9586.
- (10) Park, S. Y.; Lytton-Jean, A. K. R.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A. DNA-Programmable Nanoparticle Crystallization. *Nature* **2008**, *451* (7178), 553–556.
- (11) Macfarlane, R. J.; Lee, B.; Jones, M. R.; Harris, N.; Schatz, G. C.; Mirkin, C. A. Nanoparticle Superlattice Engineering with DNA. *Science* **2011**, *334* (6053), 204–208.
- (12) Macfarlane, R. J.; O'Brien, M. N.; Petrosko, S. H.; Mirkin, C. A. Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New "Table of Elements. *Angew. Chem., Int. Ed.* **2013**, *52* (22), 5688–5698.
- (13) Jin, R.; Wu, G.; Li, Z.; Mirkin, C. A.; Schatz, G. C. What Controls the Melting Properties of DNA-Linked Gold Nanoparticle Assemblies? *J. Am. Chem. Soc.* **2003**, *125* (6), 1643–1654.
- (14) Cutler, J. I.; Auyeung, E.; Mirkin, C. A. Spherical Nucleic Acids. *J. Am. Chem. Soc.* **2012**, *134* (3), 1376–1391.
- (15) Seeman, N. C.; Sleiman, H. F. DNA Nanotechnology. *Nat. Rev. Mater.* **2018**, *3* (1), 17068.

- (16) Rogers, W. B.; Shih, W. M.; Manoharan, V. N. Using DNA to Program the Self-Assembly of Colloidal Nanoparticles and Microparticles. *Nat. Rev. Mater.* **2016**, *1* (3), 16008.
- (17) Samanta, D.; Zhou, W.; Ebrahimi, S. B.; Petrosko, S. H.; Mirkin, C. A. Programmable Matter: The Nanoparticle Atom and DNA Bond. *Adv. Mater.* **2022**, *34* (12), 2107875.
- (18) Hui, C. M.; Pietrasik, J.; Schmitt, M.; Mahoney, C.; Choi, J.; Bockstaller, M. R.; Matyjaszewski, K. Surface-Initiated Polymerization as an Enabling Tool for Multifunctional (Nano-)Engineered Hybrid Materials. *Chem. Mater.* **2014**, *26* (1), 745–762.
- (19) Kubiak, J. M.; Li, B.; Suazo, M.; Macfarlane, R. J. Polymer Grafted Nanoparticle Composites with Enhanced Thermal and Mechanical Properties. *ACS Appl. Mater. Interfaces* **2022**, *14* (18), 21535–21543.
- (20) Wang, Y.; Santos, P. J.; Kubiak, J. M.; Guo, X.; Lee, M. S.; Macfarlane, R. J. Multistimuli Responsive Nanocomposite Tectons for Pathway Dependent Self-Assembly and Acceleration of Covalent Bond Formation. *J. Am. Chem. Soc.* **2019**, *141* (33), 13234–13243.
- (21) Santos, P. J.; Cao, Z.; Zhang, J.; Alexander-Katz, A.; Macfarlane, R. J. Dictating Nanoparticle Assembly via Systems-Level Control of Molecular Multivalency. *J. Am. Chem. Soc.* **2019**, *141* (37), 14624–14632.
- (22) Santos, P. J.; Macfarlane, R. J. Reinforcing Supramolecular Bonding with Magnetic Dipole Interactions to Assemble Dynamic Nanoparticle Superlattices. *J. Am. Chem. Soc.* **2020**, *142* (3), 1170–1174.
- (23) Santos, P. J.; Cheung, T. C.; Macfarlane, R. J. Assembling Ordered Crystals with Disperse Building Blocks. *Nano Lett.* **2019**, *19* (8), 5774–5780.
- (24) Abdilla, A.; Dolinski, N. D.; de Roos, P.; Ren, J. M.; van der Woude, E.; Seo, S. E.; Zayas, M. S.; Lawrence, J.; Read de Alaniz, J.; Hawker, C. J. Polymer Stereocomplexation as a Scalable Platform for Nanoparticle Assembly. *J. Am. Chem. Soc.* **2020**, *142* (4), 1667–1672.
- (25) Macfarlane, R. J.; Jones, M. R.; Lee, B.; Auyeung, E.; Mirkin, C. A. Topotactic Interconversion of Nanoparticle Superlattices. *Science* **2013**, *341* (6151), 1222–1225.
- (26) O'Brien, M. N.; Jones, M. R.; Mirkin, C. A. The Nature and Implications of Uniformity in the Hierarchical Organization of Nanomaterials. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (42), 11717–11725.
- (27) Gabrys, P. A.; Seo, S. E.; Wang, M. X.; Oh, E.; Macfarlane, R. J.; Mirkin, C. A. Lattice Mismatch in Crystalline Nanoparticle Thin Films. *Nano Lett.* **2018**, *18* (1), 579–585.
- (28) Gao, B.; Arya, G.; Tao, A. R. Self-Orienting Nanocubes for the Assembly of Plasmonic Nanojunctions. *Nat. Nanotechnol.* **2012**, *7* (7), 433–437.
- (29) Jones, M. R.; Macfarlane, R. J.; Prigodich, A. E.; Patel, P. C.; Mirkin, C. A. Nanoparticle Shape Anisotropy Dictates the Collective Behavior of Surface-Bound Ligands. *J. Am. Chem. Soc.* **2011**, *133* (46), 18865–18869.
- (30) Auyeung, E.; Li, T. I. N. G.; Senesi, A. J.; Schmucker, A. L.; Pals, B. C.; de la Cruz, M. O.; Mirkin, C. A. DNA-Mediated Nanoparticle Crystallization into Wulff Polyhedra. *Nature* **2014**, *505* (7481), 73–77.
- (31) O'Brien, M. N.; Lin, H.-X.; Girard, M.; Olvera de la Cruz, M.; Mirkin, C. A. Programming Colloidal Crystal Habit with Anisotropic Nanoparticle Building Blocks and DNA Bonds. *J. Am. Chem. Soc.* **2016**, *138* (44), 14562–14565.
- (32) Seo, S. E.; Girard, M.; Olvera de la Cruz, M.; Mirkin, C. A. Non-Equilibrium Anisotropic Colloidal Single Crystal Growth with DNA. *Nat. Commun.* **2018**, *9* (1), 4558.
- (33) Gabrys, P. A.; Macfarlane, R. J. Controlling Crystal Texture in Programmable Atom Equivalent Thin Films. *ACS Nano* **2019**, *13* (7), 8452–8460.
- (34) Wang, M. X.; Seo, S. E.; Gabrys, P. A.; Fleischman, D.; Lee, B.; Kim, Y.; Atwater, H. A.; Macfarlane, R. J.; Mirkin, C. A. Epitaxy: Programmable Atom Equivalents Versus Atoms. *ACS Nano* **2017**, *11* (1), 180–185.
- (35) Lewis, D. J.; Gabrys, P. A.; Macfarlane, R. J. DNA-Directed Non-Langmuir Deposition of Programmable Atom Equivalents. *Langmuir* **2018**, *34* (49), 14842–14850.
- (36) Lewis, D. J.; Carter, D. J. D.; Macfarlane, R. J. Using DNA to Control the Mechanical Response of Nanoparticle Superlattices. *J. Am. Chem. Soc.* **2020**, *142* (45), 19181–19188.
- (37) Lee, M. S.; Alexander-Katz, A.; Macfarlane, R. J. Nanoparticle Assembly in High Polymer Concentration Solutions Increases Superlattice Stability. *Small* **2021**, *17* (36), 2102107.
- (38) Deng, K.; Luo, Z.; Tan, L.; Quan, Z. Self-Assembly of Anisotropic Nanoparticles into Functional Superstructures. *Chem. Soc. Rev.* **2020**, *49* (16), 6002–6038.
- (39) Kubiak, J. M.; Morje, A. P.; Lewis, D. J.; Wilson, S. L.; Macfarlane, R. J. Dynamic Manipulation of DNA-Programmed Crystals Embedded in a Polyelectrolyte Hydrogel. *ACS Appl. Mater. Interfaces* **2021**, *13* (9), 11215–11223.
- (40) Dong, A.; Chen, J.; Vora, P. M.; Kikkawa, J. M.; Murray, C. B. Binary Nanocrystal Superlattice Membranes Self-Assembled at the Liquid–Air Interface. *Nature* **2010**, *466* (7305), 474–477.
- (41) Tan, A. T. L.; Nagelberg, S.; Chang-Davidson, E.; Tan, J.; Yang, J. K. W.; Kolle, M.; Hart, A. J. In-Plane Direct-Write Assembly of Iridescent Colloidal Crystals. *Small* **2020**, *16* (4), 1905519.
- (42) Bodnarchuk, M. I.; Shevchenko, E. V.; Talapin, D. V. Structural Defects in Periodic and Quasicrystalline Binary Nanocrystal Superlattices. *J. Am. Chem. Soc.* **2011**, *133* (51), 20837–20849.
- (43) Chen, Z.; Li, Z.; Li, J.; Liu, C.; Lao, C.; Fu, Y.; Liu, C.; Li, Y.; Wang, P.; He, Y. 3D Printing of Ceramics: A Review. *J. Eur. Ceram. Soc.* **2019**, *39* (4), 661–687.
- (44) Lu, L.; Zou, S.; Fang, B. The Critical Impacts of Ligands on Heterogeneous Nanocatalysis: A Review. *ACS Catal.* **2021**, *11* (10), 6020–6058.
- (45) He, J.; Lin, X.-M.; Chan, H.; Vuković, L.; Král, P.; Jaeger, H. M. Diffusion and Filtration Properties of Self-Assembled Gold Nanocrystal Membranes. *Nano Lett.* **2011**, *11* (6), 2430–2435.
- (46) Schaedler, T. A.; Jacobsen, A. J.; Torrents, A. E.; Sorensen, A. E.; Lian, J.; Greer, J. R.; Valdevit, L.; Carter, W. B. Ultralight Metallic Microlattices. *Science* **2011**, *334* (6058), 962–965.
- (47) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem. Rev.* **2010**, *110* (1), 389–458.
- (48) Vlasov, Y. A.; Bo, X.-Z.; Sturm, J. C.; Norris, D. J. On-Chip Natural Assembly of Silicon Photonic Bandgap Crystals. *Nature* **2001**, *414* (6861), 289–293.
- (49) Zornberg, L. Z.; Gabrys, P. A.; Macfarlane, R. J. Optical Processing of DNA-Programmed Nanoparticle Superlattices. *Nano Lett.* **2019**, *19* (11), 8074–8081.
- (50) Ross, M. B.; Ku, J. C.; Vaccarezza, V. M.; Schatz, G. C.; Mirkin, C. A. Nanoscale Form Dictates Mesoscale Function in Plasmonic DNA–Nanoparticle Superlattices. *Nat. Nanotechnol.* **2015**, *10* (5), 453–458.
- (51) Kang, Y.; Ye, X.; Chen, J.; Cai, Y.; Diaz, R. E.; Adzic, R. R.; Stach, E. A.; Murray, C. B. Design of Pt–Pd Binary Superlattices Exploiting Shape Effects and Synergistic Effects for Oxygen Reduction Reactions. *J. Am. Chem. Soc.* **2013**, *135* (1), 42–45.
- (52) Kang, Y.; Ye, X.; Chen, J.; Qi, L.; Diaz, R. E.; Doan-Nguyen, V.; Xing, G.; Kagan, C. R.; Li, J.; Gorte, R. J.; Stach, E. A.; Murray, C. B. Engineering Catalytic Contacts and Thermal Stability: Gold/Iron Oxide Binary Nanocrystal Superlattices for CO Oxidation. *J. Am. Chem. Soc.* **2013**, *135* (4), 1499–1505.
- (53) Jiang, Z.; Pikul, J. H. Centimetre-Scale Crack-Free Self-Assembly for Ultra-High Tensile Strength Metallic Nanolattices. *Nat. Mater.* **2021**, *20* (11), 1512–1518.
- (54) Green, E.; Fullwood, E.; Selden, J.; Zharov, I. Functional Membranes via Nanoparticle Self-Assembly. *Chem. Commun.* **2015**, *51* (37), 7770–7780.
- (55) Zhang, C.; Palko, J. W.; Barako, M. T.; Asheghi, M.; Santiago, J. G.; Goodson, K. E. Enhanced Capillary-Fed Boiling in Copper Inverse Opals via Template Sintering. *Adv. Funct. Mater.* **2018**, *28* (41), 1803689.
- (56) Pham, Q. N.; Zhang, S.; Hao, S.; Montazeri, K.; Lin, C.-H.; Lee, J.; Mohraz, A.; Won, Y. Boiling Heat Transfer with a Well-Ordered Microporous Architecture. *ACS Appl. Mater. Interfaces* **2020**, *12* (16), 19174–19183.

(57) Zeng, H.; Li, J.; Liu, J. P.; Wang, Z. L.; Sun, S. Exchange-Coupled Nanocomposite Magnets by Nanoparticle Self-Assembly. *Nature* **2002**, *420* (6914), 395–398.

(58) Chen, J.; Ye, X.; Oh, S. J.; Kikkawa, J. M.; Kagan, C. R.; Murray, C. B. Bistable Magnetoresistance Switching in Exchange-Coupled CoFe₂O₄–Fe₃O₄ Binary Nanocrystal Superlattices by Self-Assembly and Thermal Annealing. *ACS Nano* **2013**, *7* (2), 1478–1486.

(59) Cheng, W.; Wang, J.; Jonas, U.; Fytas, G.; Stefanou, N. Observation and Tuning of Hypersonic Bandgaps in Colloidal Crystals. *Nat. Mater.* **2006**, *5* (10), 830–836.

(60) Maldovan, M. Sound and Heat Revolutions in Phononics. *Nature* **2013**, *503* (7475), 209–217.

(61) Yazdani, N.; Jansen, M.; Bozyigit, D.; Lin, W. M. M.; Volk, S.; Yarema, O.; Yarema, M.; Juranyi, F.; Huber, S. D.; Wood, V. Nanocrystal Superlattices as Phonon-Engineered Solids and Acoustic Metamaterials. *Nat. Commun.* **2019**, *10* (1), 4236.

Recommended by ACS

Self-Reporting Joule Heating Modulated Stiffness of Polymeric Nanocomposites for Shape Reconfiguration

Shaobo Ji, Xiaodong Chen, *et al.*

OCTOBER 04, 2022
ACS NANO

READ 

Scalable Nano Building Blocks of Waterborne Polyurethane and Nanocellulose for Tough and Strong Bioinspired Nanocomposites by a Self-Healing and Shape-Retaining St...

Panyi Xi, Yijun Jiang, *et al.*

MAY 21, 2022
ACS APPLIED MATERIALS & INTERFACES

READ 

Well-Ordered Nanonetwork Metamaterials from Block Copolymer Templated Syntheses

Kai-Chieh Yang, Rong-Ming Ho, *et al.*

JULY 18, 2022
ACCOUNTS OF CHEMICAL RESEARCH

READ 

Complex Composites Built through Freezing

Sylvain Deville, Sylvain Meille, *et al.*

MAY 19, 2022
ACCOUNTS OF CHEMICAL RESEARCH

READ 

Get More Suggestions >