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Perspective

Nanoparticle Assembly as a Materials Development Tool

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ABSTRACT: Nanoparticle assembly is a complex and versatile method of generating new materials, capable of using thousands of different combinations of particle size, shape, composition, and ligand chemistry to generate a library of unique structures. Here, a history of particle self-assembly as a strategy for materials discovery is presented, focusing on key advances in both synthesis and measurement of emergent properties to describe the current state of the field. Several key challenges for further advancement of nanoparticle assembly are also outlined, establishing a roadmap of critical research areas to enable the next generation of nanoparticle-based materials synthesis.

INTRODUCTION

The concept of nanoparticles (NPs) as "artificial atoms" has been a valuable framework for both interrogating and understanding the unique chemical and physical properties that arise from matter confined to the ∼1−100 nm length scale.[1,2] Initial comparisons to atoms were drawn when it was observed that these tiny bits of nanoscale matter exhibited discrete optical and electrical characteristics, and that those characteristics could be easily analogized to the properties of atoms that are governed by the filling of their electron orbitals.[3−5] Thus, well-understood topics from general chemistry provided a useful common language to describe the properties of nanoparticles as chemists, physicists, and materials scientists began to explore this emerging field. As colloidal synthesis methods advanced and nanoparticles of various sizes, shapes, compositions, and ligand coatings propagated through the community, the "NPs as atoms" analogy expanded to encompass materials synthesis as well (Figure 1).[6−13] Ligand interactions between NPs became "bonds", and both discrete clusters (i.e., "molecules") and extended superlattices ("crystals") could be generated by controlling nanoscale bonding. This analogy allows decades of chemical research to inform our intuition on how NPs might assemble, and also permits the nomenclature and terms used in conventional chemistry to facilitate our description of NP-based materials. In many ways, however, using NPs as fundamental units of materials synthesis provides several advantages not found when starting with individual atomic species, the most obvious of which lie in their compositional variation. At the time of writing, there are only 118 named elements that can be selected as building blocks for materials synthesis; practically, this number is even smaller, as many elements are either too rare or too unstable to be commonly used. Conversely, NPs have significantly greater variety in terms of their elemental makeup, size, shape, and surface coatings, leading to potentially thousands of unique material synthons. Nevertheless, our understanding of the use of NP "artificial atoms" to build materials is still in its infancy compared with conventional chemical synthesis, and it remains a daunting challenge to establish basic scientific principles in NP assembly that are as well-understood as chemical bond formation. The previous decades have built up an impressive (and still expanding) library of NP tools and assembly methods for materials synthesis that has benefitted from analogizing their behavior to textbook-level chemical knowledge—the next challenges for this field lie in writing our own textbooks and design rules.

In this perspective, we will highlight key advancements in NP materials synthesis of the past decades, noting specific milestones in their development and the new functionality or structures they have enabled. We will also describe the properties that have been induced in these NP assemblies, and note current or potential applications that enable novel functionality not achievable in traditional bulk materials. These advancements will allow us to draw a roadmap of future work for NP assembly, and highlight challenges and limitations that must be addressed to both increase our scientific understanding of the assembly process and provide utility for NP materials in functional devices.

HISTORY AND CURRENT METHODS OF NANOPARTICLE ASSEMBLY

Multiple strategies have been established for building structures out of NPs. Here we highlight the history of materials containing NPs, ranging from the formation of random aggregates to advances in directly controlling NP organization within an extended structure.

Aggregation and Uncontrolled Precipitation. The most basic category of nanoparticle assembly is uncontrolled

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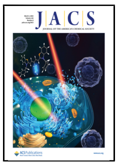

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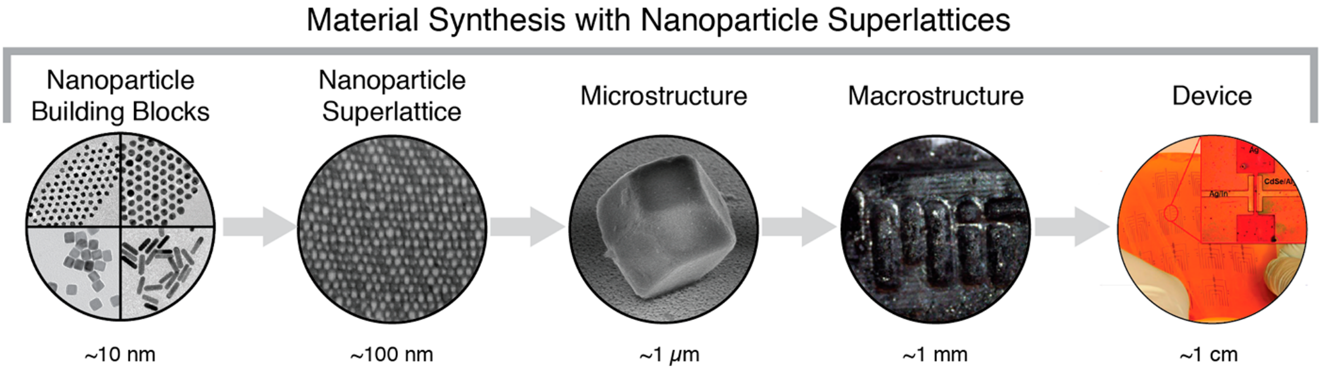

Figure 1. Material synthesis with nanoparticle superlattices allows for hierarchical structural control across multiple length scales. Nanoparticle building blocks (∼10 nm) can be assembled into microscopic nanoparticle superlattices (∼100 nm−1 μm), which can be processed into macroscopic structures (∼1 mm) and ultimately devices (≥1 cm). Adapted from refs 71, 145. Reprinted by permission from Springer Nature: Nature Portfolio, Nature, ref 71. Macroscopic materials assembled from nanoparticle superlattices, Santos et al, copyright (2021). Reference 145 republished with permission of Science, from Exploiting the colloidal nanocrystal library to construct electronic devices, Choi et al, 362, 6282, 2016; permission conveyed through Copyright Clearance Center, Inc.

aggregation, which occurs when dispersed particles in solution assemble into disordered clusters or films. For example, the aggregation of noble metal nanoparticles, particularly gold, is of interest both as a model system for understanding nanoparticle aggregation, more broadly, and as a practical system with applications in optical sensing.[14] These nanoparticles are typically synthesized with a capping ligand such as citrate or cetyltrimethylammonium bromide (CTAB) to achieve stable colloidal dispersions via a balance of van der Waals attraction and electrostatic repulsion.[15−17] The stabilizing effect of the charged capping ligand can be disrupted either by replacing the surface ligand to lower the surface potential or by screening or neutralizing the surface charge,[18,19] allowing surface ligands to induce assembly upon introduction of a specific external stimulus like light, heat, solution ionic strength, or solution pH.[20,21] Nanoparticles can also be deposited on surfaces to form films, which are useful in situations where functional surfaces with a high surface-area-to-volume ratio are desired, such as solar cells and hydrophobic coatings.[22,23] Common wet deposition methods for generating nanoparticle films include the Langmuir−Blodgett technique, dip coating, spin coating, and layer-by-layer deposition.[24−27] Each of these techniques offers some degree of control over the quality of the deposited film (e.g., particle density, particle distribution, particle coverage, film thickness, etc.) using assembly handles such as solution viscosity, nanoparticle concentration, substrate withdrawal rate, or substrate pretreatment.

The main advantage of uncontrolled nanoparticle aggregation and deposition techniques lies in their simplicity. Since long-range order is often not a goal for these rapid material syntheses, uncontrolled aggregation and deposition methods are tolerant of high nanoparticle size and shape dispersity, allowing for almost any kind of nanoparticle to be used. These aggregation and deposition methods are also amenable to large-scale production, making them attractive for industrially relevant coatings. However, the inability to manipulate NP ordering means that the emergent properties that often arise from precisely dictated interparticle distances and coordination environments either are not seen in these simple materials or exhibit limited ability to be controlled.

Drop Casting and Evaporation-Driven Assembly. Evaporation-based self-assembly relies on solvent drying to direct the assembly of nanoparticles into nominally 2-D arrays.[28−30] The most basic of these superlattices, ordered hexagonal arrays of close-packed spheres, can be simply made by drop casting a small volume of hydrocarbon-capped nanoparticles in an organic solvent onto a substrate and letting the solvent gradually evaporate.[31] More complex unary particle close-packed patterns can be obtained by using anisotropic particles such as rods, rectangular prisms, and cubes, which introduce a shape-direction element into the evaporation-driven assembly process, as ligand interactions between particles depend on the degree of interfacial alignment between NPs.[32] For example, while CTAB prevents particle aggregation in solution via electrostatic repulsion, upon drying, CTAB ligands assist close-packing by pulling particles closer together to facilitate counterion sharing or alkyl tail interdigitation between adjacent particles.[32,33]

Some of the most impressive advances in the development of evaporation-based assembly relate to the synthesis of binary nanocrystal superlattices (BNSLs), complex ordered arrays composed of two types of nanoparticles. A large library of BNSLs have been demonstrated using various small-molecule-capped inorganic nanoparticles evaporated onto either a canted surface or a liquid interface (Figure 2A).[30,34,35] Upon gradual solvent evaporation under reduced pressure, ordered BNSL films are formed at the receding solvent−substrate interface. Assembly of BNSLs is governed by a combination of competing short-range Coulombic, dipolar, and van der Waals interactions dictated by the various ligands on the particles' surfaces; this competition allows for a broad range of crystal symmetries. These ligand interactions have been studied extensively, and the enthalpic and entropic contributions arising from both ligand packing and ligand−ligand binding are now well-understood enough to enable highly reproducible and large-area crystalline features, and to explain the fundamental nature of the interparticle bonding interactions driving assembly (Figure 2A).[36,37] Recently, this BNSL approach has been expanded to the use of polymer ligands, which provides a much broader design space to explore, at the cost of typically more complicated and technically demanding assembly protocols.[38] Ternary NPSLs have also been made, but the number of examples remains limited due to the technical challenge of forming a ternary NPSL in a reproducible manner; such syntheses are often prone to forming different BNSLs containing only two of the three

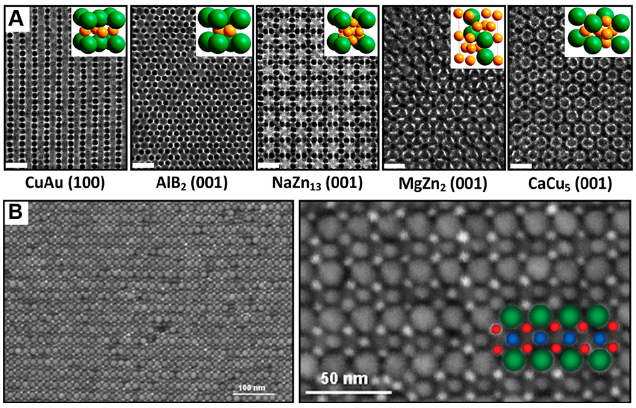

Figure 2. Evaporation-driven assembly of ordered nanoparticle arrays presents a simple means of generating complex nanoscale architectures. (A) Binary nanoparticle superlattices assembled with different crystal symmetries based on variations in particle sizes and ligand chemistries. Scale bars are 20 nm. (B) Ternary nanoparticle superlattices assembled using cocrystallization of three particle types. Adapted from refs 36, 39. Reprinted with permission from ref 36. Copyright 2015 American Chemical Society. Reprinted with permission from ref 39. Copyright 2011 American Chemical Society.

nanoparticle components on different regions of the substrate (Figure 2B).[39,40]

The main advantages of evaporation-based techniques lie in their low cost and ability to generate highly ordered 2-D films of varying composition with different kinds of nanoparticles. These films are potentially of interest for applications like optical coatings or devices (see section on emergent properties below). Drawbacks to these techniques include a limited ability to accommodate particle dispersity and the difficulty of achieving nonclose-packed structures. Specifically, BNSLs require nanoparticles with very low dispersity in shape and size to achieve good long-range ordering, which restricts their composition to nanomaterials that can be synthesized with typically <5% size dispersity.[41] Lastly, while evaporation-based assembly is an excellent method for generating ordered 2-D superlattices, it is not as robust in generating materials with NPSLs of arbitrary 3-D geometries.

Biomolecule Assembly. Biomolecules represent a complex ligand for nanoparticle assembly, as their macromolecular structures enable sophisticated interactions that can be significantly more complicated than those of a small molecule ligand, or even a synthetic polymer. DNA is arguably the most versatile biomolecule for particle assembly, capable of producing structures ranging from simple aggregates to intricate 3-D lattices with an unprecedented degree of control over particle arrangement and spacing (Figure 3A).[10,42,43] Watson−Crick base-pairing interactions between complementary DNA strands are capable of producing a virtually infinite number of pairwise DNA interactions, making it possible to utilize both strand length and nucleobase sequence to program the formation of different crystallographic symmetries and lattice parameters using a wide range of NP compositions. Importantly, in all of these syntheses, the NP assembly process shows remarkable similarity to atomic crystallization, leading to the description of these DNA-grafted NPs as "Programmable Atom Equivalents" (PAEs).[42] A series of design rules (analogized to Pauling's design rules for ionic lattices) has even been established for these PAEs, using the overarching hypothesis that the most stable particle lattice is the organization that maximizes the number of DNA duplexes formed.[43] Moreover, assembling PAEs at equilibrium enables the synthesis of faceted single crystals with the same well-defined microscale shapes predicted for atomic crystals of the same symmetry.[44,45] While most PAE lattices form highly symmetric, close-packed structures, anisotropy in crystal unit cells can be introduced by either heterogeneously functionalizing the particle surface,[46] using nonspherical nanoparticle cores,[47] or encapsulating particles in DNA origami cages.[48] PAEs can also be assembled at DNA coated interfaces, enabling the use of this surface-derived boundary for crystal growth to control the size, shape, and orientation of the crystallites.[49,50] For additional information on DNA-mediated self-assembly, we refer the reader to other sources dedicated to the topic.[10,51]

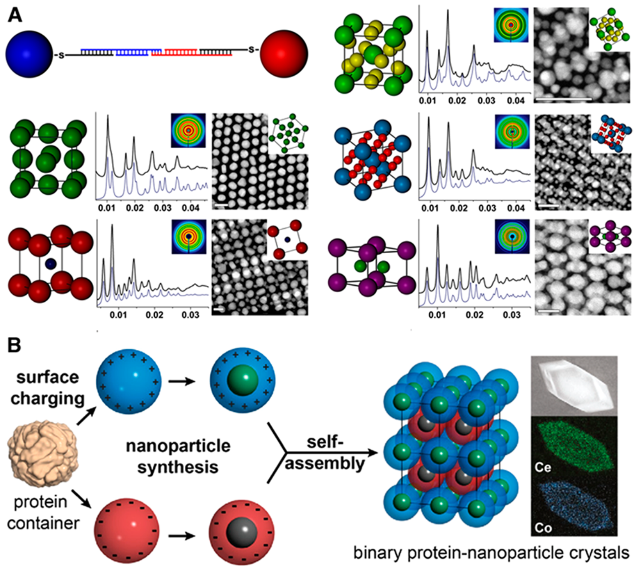

Figure 3. Biomolecule complexity can be used to precisely tune the organization of nanoparticles in 3-D arrays. (A) DNA-mediated self-assembly provides a means to both predict and program superlattice crystal structure as a function of nucleobase sequence. X-ray scattering plots show the superlattice structure factor (y axis, arbitrary units) versus scattering vector q (x axis, Å^{-1}) for each crystal structure. Scale bars are 50 nm. (B) Protein cages with encapsulated nanoparticles can assemble into BNSLs via electrostatic attraction. Adapted from refs 43, 63. Reference 43 republished with permission of Science, from Nanoparticle Superlattice Engineering with DNA, Macfarlane et al, 334, 6053, 2011; permission conveyed through Copyright Clearance Center, Inc. Reprinted with permission from ref 63. Copyright 2016 American Chemical Society.

Proteins can also drive NP assembly, though their more complex structures mean that they form a distinct set of lattice or cluster types compared to DNA-driven assembly.[52] For example, patchy protein cages formed from native cowpea chlorotic mottle virus and recombinant ferritin can encapsulate RNA or iron oxide nanoparticles, respectively. These protein cages with negatively charged directional patches can then be assembled into binary superlattices with positively charged gold nanoparticles by tuning their electrostatic interactions.[53] Peptides and proteins can also be engineered with supramolecular binding groups to drive assembly into 2-D and 3-D nanostructures using noncovalent interactions such as disulfide bridging, metal-coordination, and pi stacking.[54,55] Furthermore, natural proteins can be extracted from bacteria to be used as biotemplates for the adsorption and assembly of gold nanoparticles and CdSe/ZnS core/shell quantum dots into 2-D arrays.[56] Protein templates can also be engineered to covalently bind to nanoparticles, for instance by modifying arrays of chaperonins with cysteine to create binding sites for metal nanoparticles.[57]

The main advantage of biomolecule assembly is the ability to exploit the natural structural organization of these molecules, which is typically far more complex than simple small molecules. DNA-mediated programmable nanoscale self-assembly can achieve a level of structural control that is essentially unmatched by any other assembly method, particularly in the fabrication of nonclose-packed ordered arrays. In addition, biomolecular coatings on the NPs could make these assemblies more suited to use in applications that require biocompatibility. However, a significant drawback to biomolecule assembly is its high cost compared to non-biological molecules or macromolecules, making such assemblies difficult to scale-up or produce in macroscopic quantities.

Supramolecular Assembly. Reversible noncovalent interactions (e.g., hydrogen bonding, pi−pi stacking, hydrophobic interactions, host−guest binding) are ideal means to drive the assembly of ordered NP materials.[58] Although weaker than permanent covalent bonds, the transient nature of noncovalent intermolecular forces allows particles to rearrange their organization during the assembly process and avoid kinetic traps.

While electrostatic interactions can be used to maintain colloidal stability when all particles are functionalized with like charges, ordered patterns can be generated from sets of NPs grafted with oppositely charged ligands.[59,60] BNSLs can use NP size, surface ligand length, and solution salt concentration to modulate the screening length, surface charge, and degree of electrostatic attraction between particles in solution, thereby regulating the formation of different NPSL structures.[60−62] Electrostatic interactions can also be engineered on particle surfaces using protein shells (Figure 3B).[63]

Hydrogen bonding is a common means of supramolecular-driven NP assembly, as these bonds are typically thermally addressable, and are easily incorporated into ligands with polar functional groups.[64] Polymer-grafted nanoparticles with hydrogen-bonding groups can be assembled into robust nanocomposites with high filler content, and both crystallization and self-healing in these materials can be triggered simply by heating up the material to allow hydrogen bonds to dynamically exchange with one another.[65] For example, nanocomposite tectons (NCTs), a nanocomposite building block composed of an inorganic core functionalized with a dense brush of polymers terminated with supramolecular binding groups (Figure 4A), use hydrogen bonding between complementary particles to form body-centered cubic (BCC) NPSLs, where crystal lattice parameters are dictated by both the NP diameter and the polymer length (Figure 4B).[66,67] By using polymers rather than short alkyl chains, a much higher dispersity in polymer length and core size can be accommodated without negatively affecting lattice ordering, unlike assembly systems that require highly monodisperse particles to achieve ordered structures.[68] By using different nanoparticle core materials or introducing additional binding chemistries with coloading, it is possible to combine hydrogen bonding with other assembly stimuli to further direct the organization and stability of the final structure.[69−72]

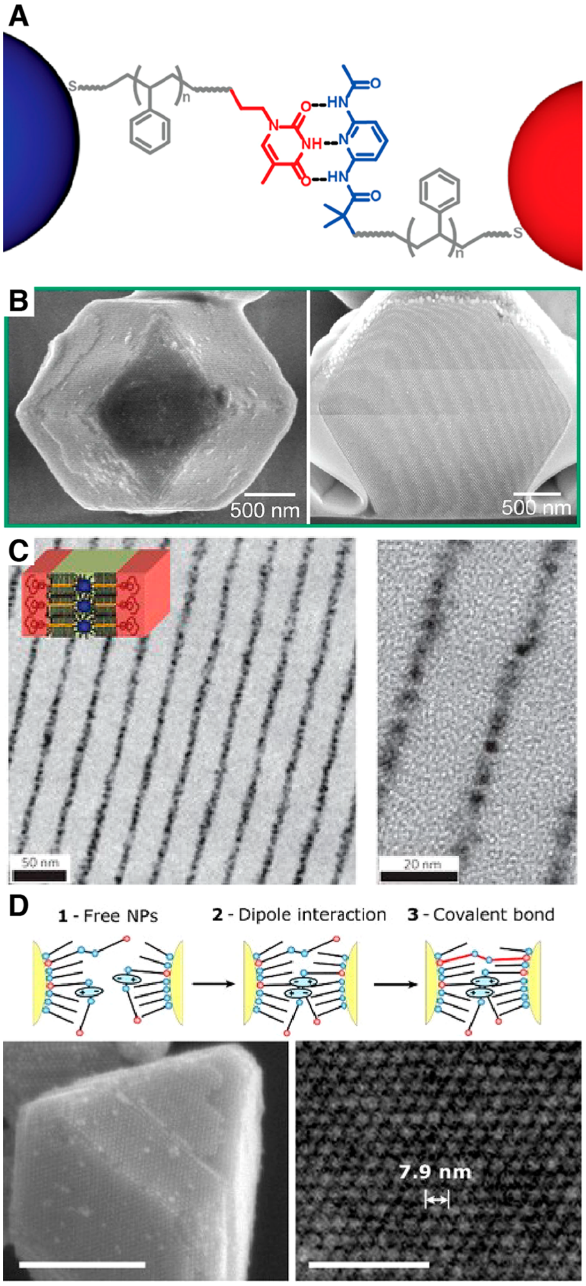

Figure 4. Reversible supramolecular interactions via nanoparticle surface ligands provide multiple means of tuning particle assembly as a function of different stimuli. (A) Hydrogen bonding interactions between polymer-grafted nanoparticles (so-called Nanocomposite Tectons) rapidly assemble nanoparticles into both polycrystalline and (B) single crystal superlattices with well-defined, faceted microscale shapes. (C) BCPs form lamellar domain structures in which nanoparticles can organize using reversible supramolecular bonding. (D) Light irradiation modulates both covalent and noncovalent interactions between photoresponsive ligands. Scale bars are 200 nm (left) and 50 nm (right). Adapted from refs 68, 71, 74, 82. Reprinted with permission from ref 68. Copyright 2019 American Chemical Society. Reprinted by permission from Springer Nature: Nature Portfolio, Nature, ref 71. Macroscopic materials assembled from nanoparticle superlattices, Santos et al, copyright (2021). Reprinted by permission from Springer Nature: Nature Portfolio, Nature Materials, ref 74. Small-molecule-directed nanoparticle assembly toward stimuli-responsive nanocomposites, Zhao et al, copyright (2009). Reference 82 copyright (2007) National Academy of Sciences, U.S.A.

The main advantage of supramolecular assembly methods lies in their customizability. Since supramolecular interactions can be incorporated into materials ranging from proteins to short alkyl chains, there exists a large design space to tailor both the composition and binding chemistry of the final nanoparticle assembly for the desired application. Multiple stimuli can be used to trigger assembly in supramolecular assembly systems, while the reversible nature of noncovalent interactions makes it possible to synthesize materials with self-healing and dynamic responses. Although supramolecular assembly techniques cannot match the level of structural control exhibited by biomolecule assembly methods or some evaporation-driven BNSLs, they are typically more amenable to both large-scale and 3-D material fabrication. While future advances in supramolecular chemistry may enable the same level of sophistication in intermolecular interactions that is currently found in complex biomacromolecules, research in this area requires additional effort (see "future challenges" section below).

Additional Assembly Methods. The diversity of available NP and ligand chemistries also enables opportunities for assembly methods that do not easily fit into the categories above. For example, block copolymers (BCPs) can self-assemble into periodic structures that serve as a matrix to encapsulate aggregates of NPs; functionalizing NPs with ligands that have favorable interactions with one or both blocks of the BCP can control how they organize within the polymer array (Figure 4C).[73,74] NPs functionalized with block copolymers are typically used for the self-assembly of vesicles, micelles, and other discrete structures rather than ordered arrays, but can be dried to produce NP thin films with interparticle spacing determined by the molecular weight of the BCP ligand.[75−77]

Templated self-assembly is particularly well-suited for generating ordered 2-D nanoparticle arrays of interest in the largescale fabrication of nanodevices. One such example is chemical electron-beam lithography, which combines top-down lithography to generate arbitrarily shaped surface patterns of different functional groups, creating preferential regions for nanoparticles to bind during the assembly process.[78] Precise patterns can also be obtained with DNA-directed NP assembly by placing single-stranded DNA on the patterned features.[79,80] Protein lattices can also be used as templates for NP arrays by directly synthesizing particles from a precursor added to protein cavities arrayed in an ordered 2-D pattern.[81]

External stimuli such as light and magnetic fields can be used either on their own to drive nanoparticle self-assembly or in conjunction with another self-assembly technique to add additional structural complexity or responsiveness to the nanostructure. For instance, nanoparticles functionalized with light-responsive ligands and covalent cross-linkers can be either reversibly or irreversibly assembled into superlattices via light-induced dipole−dipole interactions followed by covalent cross-linking (Figure 4D).[82] Evaporation-driven assembly of maghemite nanocubes in the absence of a magnetic field generates monolayers with no long-range order, but applying a field perpendicular to the surface results in highly ordered, defect-free superlattices.[83] It has also been shown that an applied magnetic field can affect both the crystal symmetry and micro- to macroscopic shape of the assembled lattice, generating complex superlattice crystal habits like elongated rods or twisted ribbons.[84,85]

EMERGENT PROPERTIES OF NANOPARTICLE ASSEMBLIES

Materials development is often driven by the desire to generate and understand new emergent properties, as well as applications that benefit from these new characteristics. In NPSLs, such properties can include those that stem from the inherent large surface-area-to-volume ratios possessed by nanoscale objects, such as a larger number of catalytic active sites, or specific surface facets that expose low-coordination number atomic species. NP properties also inherently include emergent phenomena that arise when matter is confined to the nanometer length scale, such as the size- and shape-dependent plasmonic absorption of noble metal NPs or quantum confinement effects in luminescent semiconductor particles. Self-assembly of ordered arrays offers the possibility to control the coupling of particles' individual properties to generate exotic metamaterial behaviors based on the hierarchical organization of the NPs. Here we will note multiple different properties and potential applications enabled by recent advances in controlling the organization of NPs in multiple dimensions.

Plasmonic Properties of NPSLs. A quintessential example of how nanostructure can generate or tune an emergent physical property is localized surface plasmon resonance (LSPR), in which an incident photon is in resonance with coherently oscillating surface electrons of metallic NPs, leading to strong absorption and scattering of the incident light.[86] As the LSPR spectrum is sensitive to multiple factors including the composition of the surrounding environment, plasmonic nanoparticles have found significant application as ultrasensitive sensors.[87] One well-known application of this is in surface-enhanced Raman scattering (SERS), where the enhanced electromagnetic field around plasmonic particles amplifies the Raman scattering signal of adsorbed molecules.[88]

The organization of plasmonic nanoparticles into clusters or arrays can also be used to further control their optical responses, as bringing plasmonic particles in close proximity to each other allows their surface plasmons to couple, generating hybridized plasmon modes that change their extinction spectra. For example, when spherical nanoparticles are coupled into 1-D chains, their LSPR frequency splits into a transverse and a longitudinal plasmon mode; such splitting can even be used to further the "artificial atoms" analogy, as this splitting can be described in a manner similar to the splitting of orbitals in molecular orbital theory.[89,90] NPSL films of silver cuboctahedra nanocrystals have also shown that the coupling between nanoparticles can be controlled by changing the interparticle spacing, density, and packing symmetry to tune their optical response over the entire visible range (Figure 5A).[91] Similarly, the collective plasmonic response of BNSLs can be tuned across the entire visible spectrum by varying the composition and symmetry of the superlattice.[92] Macroscopic solids of NPSLs also exhibit composition and symmetry dependent plasmonic properties. For example, a blend of gold BCC NPSLs and iron oxide BCC NPSLs exhibits a plasmonic response, whereas CsCl-type BNSLs of gold and iron oxide nanoparticles do not, as the iron oxide particles act as spacers that suppress plasmonic coupling between gold NPs (Figure 5B).[71]

Coupling between plasmonic nanoparticles also results in significant enhancements of the electromagnetic field in the regions between the nanoparticles. These regions, commonly

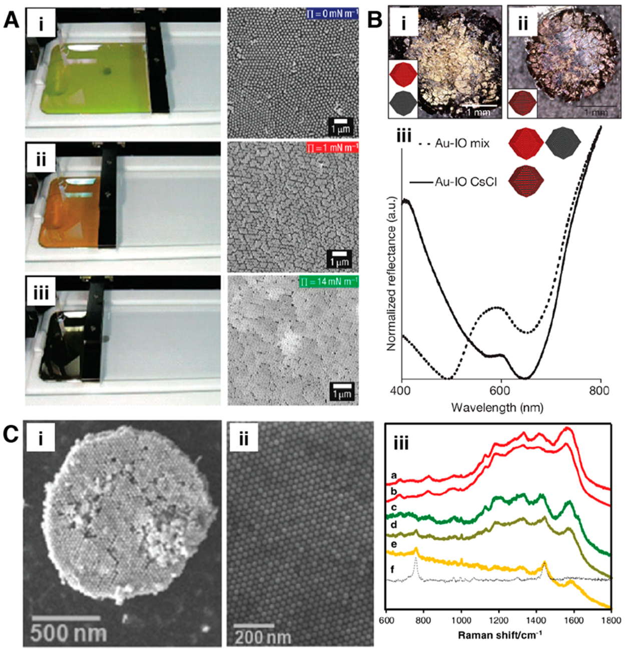

Figure 5. Emergent plasmonic properties in NPSLs. (A) Changes to surface pressure (increasing from images (i) to (iii)) in Langmuir–Blodgett assembly of NPs changes the plasmon response via reduction of interparticle spacing. (B) Macroscopic solids made from (i) a blend of gold NPSLs and iron oxide NPSLs and (ii) BNSLs of gold and iron oxide nanoparticles exhibit significantly different optical responses (iii). (C) (i,ii) Gold nanorod superlattices as SERS substrates for the detection of prions in blood. (iii) SERS spectra of (a) blood, (b) prion spiked blood, (c) plasma, (d) prion spiked plasma, (e) prion spiked plasma with plasma background subtracted, and (f) the scrambled prion. Adapted from refs 71, 91, 97. Reprinted by permission from Springer Nature: Nature Portfolio, Nature, ref 71. Macroscopic materials assembled from nanoparticle superlattices, Santos et al, copyright (2021). Reprinted by permission from Springer Nature: Nature Portfolio, Nature Nanotechnology, ref 91. Tunable plasmonic lattices of silver nanocrystals, Tao et al, copyright (2007). Reference 97. Copyright (2007) National Academy of Sciences, U.S.A.

referred to as "hot spots", have fields that are of 10 orders of magnitude stronger than those of isolated nanoparticles,[93] which enable a variety of plasmon-enhanced molecular spectroscopy techniques.[94] For example, in plasmon-enhanced Raman spectroscopy, the enhanced electric fields in the "hot spots" allow samples there to produce Raman signals that are 10^6–10^{12} times stronger than when in the free state.[95,96] In one example, gold nanorod superlattices were used as SERS substrates for the rapid detection of prions at concentrations even as low as 10^{-10} M (Figure 5C).[97] Similarly, gold nanorod superlattices coated with SiO_2 could be used to detect bacteria-produced pyocyanin at 10^{-14} M,[98] and Au/Ag bimetallic nanocuboid superlattice-based SERS substrates, have been used to detect water treatment chemicals at 10^{-12} M.[99]

Photonic Properties of NPSLs. One of the most common photonic applications of particle assembly is the formation of photonic band gaps via periodic alteration of the refractive index throughout a lattice.[100] However, because most demonstrations of this type of self-assembled photonic crystal use particles that are >200 nm, such structures are outside the scope of this perspective; we refer the reader to recent reviews for additional details.[11,101]

Nevertheless, plasmonic NPs are able to open a photonic band gap via strong coupling between surface plasmons and photonic modes of a microscale crystallite of defined shape. DNA-functionalized gold nanoparticles assembled into BCC rhombic dodecahedra single crystals exhibited a band gap in the visible range despite having interparticle distances that were <50 nm. The strong coupling between the surface plasmons of the gold nanoparticles and the photonic modes enabled by the size and geometry of the crystal led to the creation of plasmon polaritons with anticrossing behavior in the dispersion diagram, prohibiting the propagation of certain photonic modes.[102] Additionally, the effective refractive index of a plasmonic assembly can be tuned by controlling the interparticle distance of the constituent nanoparticles. In thin films (∼150 nm) that are unable to accommodate significant phase shifts in the transmitted light, extinction is primarily due to plasmon absorption. However, when light travels through NPSLs with 3-D geometries (∼1 μm), sufficient phase interference between light on the interior and exterior of the structure results in light scattering (Figure 6A).[103] A set of design guidelines for the fabrication of intentionally designed plasmonic photonic crystals with designer stopband locations has even been developed by using the fundamental principles developed from these observations.[104]

The assembly of anisotropic ellipsoid nanoparticles into NPSLs has been computationally predicted to produce dichromatic crystals that exhibit birefringence. In addition, when assembled into NPSLs with anisotropic crystal habits, depending on their orientation, the crystals displayed a skin depth approaching that of pure metals or were able to directionally confine waves.[105] NPSLs with cubic symmetry, assembled using gold nanocubes, have exhibited multipolar Mie resonances and refractive indices as high as 8 in the mid-infrared (Figure 6B); rationally designed arrays of these NPSLs crystals could exhibit negative refractive indices due to their overlapping Mie resonances.[106]

While NPs are typically too small on their own to produce photonic crystals, coating NPs in thick polymer shells can be used to produce spacings large enough to assemble with visible photonic band gaps. Assemblies of ∼70 nm SiO_2 NPs produced structural coloration, where the wavelength of reflected light scaled with the thickness of the polymer coating.[107] In 2-D arrays of plasmonic nanoparticles, hybridization of plasmonic and photonic modes can produce hybrid modes termed surface lattice resonances (SLRs). These SLRs are delocalized over large distances and exhibit narrow resonance widths and enhanced electric fields.[108] Plasmonic arrays fabricated via lithography processes can exhibit SLRs with high quality factors of order 100 (resonance wavelength/width of resonance),[109] although they are challenging to fabricate. Self-assembly approaches have been able to generate SLRs by encapsulating 100 nm plasmonic nanoparticles in a soft hydrogel shell, and assembling them into hexagonally ordered NPSL films with an interparticle spacing of ∼500 nm (similar to the LSPR wavelengths of the plasmonic NP cores). Once the films were coated with an index-matched polymer, SLRs with quality factors of 25.7 were observed.[110] Similar methods using gold NPSL films demonstrated SLRs with quality factors ∼20.[111]

Magnetic Properties of NPSLs. Magnetically responsive NPs below a critical size typically prefer a single-magnetic-domain structure, as domain formation is not energetically favorable in these small particles. These monodomain

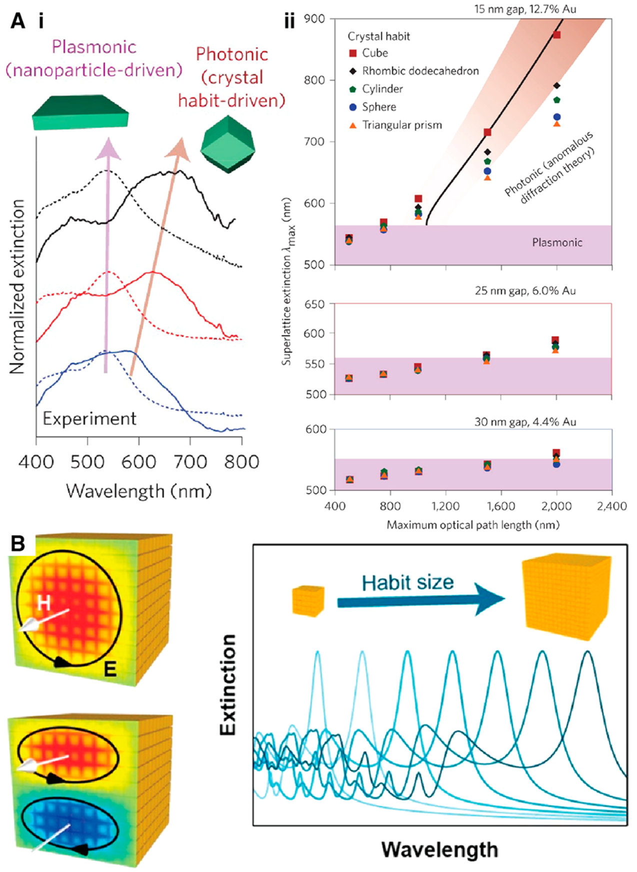

Figure 6. Emergent photonic properties in NPSLs. (A) Photonic band gaps can be realized via strong coupling between surface plasmons and photonic modes in 3-D NPSL crystals. (i) Extinction spectra for NPSL thin films (dashed) and 3-D crystals (solid) of similar composition differ significantly due to the presence of coupled photonic modes in the 3-D crystals. (ii) The extinction wavelength of a 3-D NPSL crystal can be plasmonic or photonic in nature depending on its interparticle spacing, size, and crystal habit. (B) Gold nanocubes assembled into NPSLs with cubic symmetry can exhibit multipolar Mie resonances which can be tuned by increasing the habit size of the crystal. Adapted from refs 103, 106. Reprinted by permission from Springer Nature: Nature Portfolio, Nature Nanotechnology, ref 103. Nanoscale form dictates mesoscale function in plasmonic DNA–nanoparticle superlattices, Ross et al, copyright (2015). Reprinted with permission from ref 106. Copyright 2020 American Chemical Society.

nanoparticles can be considered "superspins" with magnetic moments of ~10^3–10^5 μ_B.[112] Assembly of such NPs offers significant potential to tune the collective magnetic response of NP arrays as the structural organization of the NPSL can control the strength of dipole coupling between particles as a function of interparticle distance and coordination environment.

For example, in well-ordered NPSLs, each nanoparticle has the same spatial distribution of NP neighbors, and consequently experiences the same dipole–dipole interactions, leading to a narrower distribution of blocking temperatures. Furthermore, long-range order enhances the magnetic anisotropy of the whole assembly. As a result, NPSLs exhibit narrower magnetization peaks during zero-field cooling, a more gradual approach to saturation, and higher coercivity compared to their disordered counterparts (Figure 7A).[113]

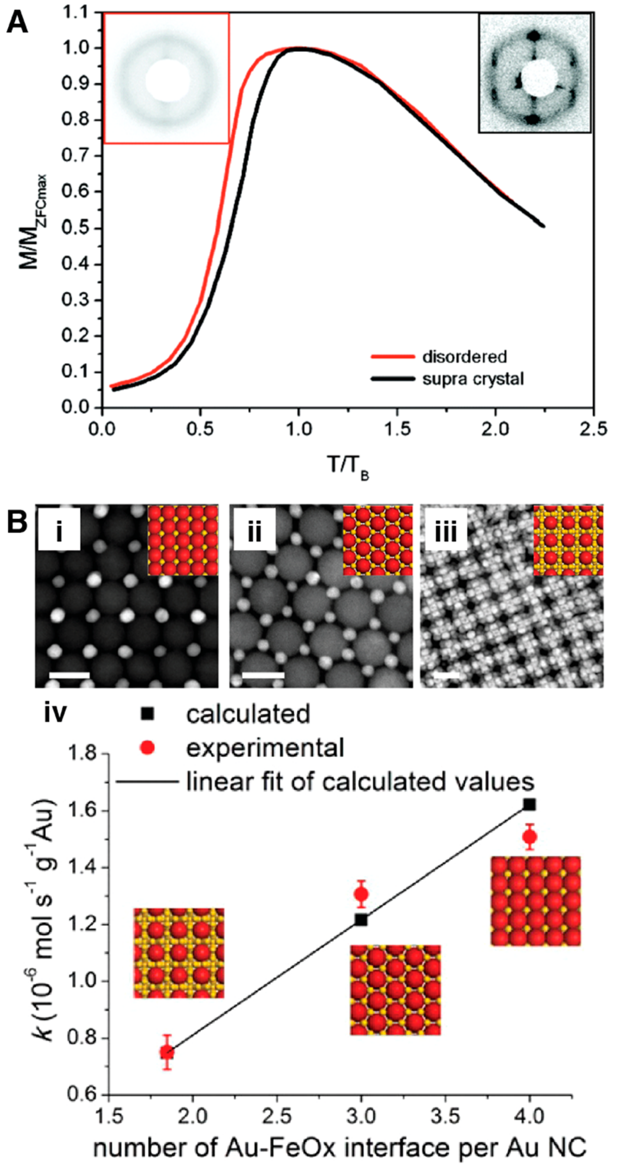

Figure 7. Emergent magnetic and catalytic properties in NPSLs. (A) Structural ordering of Co NPs causes a narrowing of the zero-field cooled magnetization peak compared to disordered aggregates. (B) BNSLs of gold and iron oxide nanoparticles with (i) AB, (ii) AB_2, and (iii) AB_{13} Au-FeO_x symmetries exhibited (iv) catalytic activities toward CO oxidation proportional to the number of Au-FeO_x contacts per gold nanoparticle. Scale bars are 20 nm (i), (iii) and 10 nm (ii). Adapted from refs 113, 125. Reprinted with permission from ref 113. Copyright 2007 American Chemical Society. Reprinted with permission from ref 125. Copyright 2013 American Chemical Society.

Depending on the strength of dipolar correlations, superspin ensembles can exist in superparamagnetic (SPM), superspin glass (SSG), or superferromagnetic (SFM) phases, the study of which collectively comprise the field of "supermagnetism".[112] Monte Carlo simulations have been used to examine these different material properties by constructing a phase diagram for face-centered cubic (FCC) NPSLs in the temperature-anisotropy plane.[114] In the SPM phase, the dipoles are uncorrelated or only weakly correlated, so each nanoparticle has an independently fluctuating moment and the whole ensemble follows the same relaxation dynamics as its constituents.[115] In the SSG phase, moments are randomly oriented but frozen. Even without structural disorder, magnetic disorder in SSG NPSLs is still possible due to frustration from the random distribution of easy axis orientations.[114] Co NPs assembled into 3-D FCC multilayers, for instance, have shown characteristic features of the SSG phase, including aging and memory effects. However, significant contributions of mesoscopic structural order to the SSG behavior have yet to be observed.[116]

In contrast to the SPM and SSG states, the superspins in the SFM state are strongly correlated and exhibit long-range magnetic order, which indicates that lattice organization should have significant effects on collective magnetic behavior. An illustration of predicted order-induced effects is that, in the strongly coupled regime, the ground state of an NPSL material has been predicted to be antiferromagnetic in simple cubic arrays, but ferromagnetic in FCC and BCC arrays.[117] However, directly measuring such a result experimentally is challenging, as there are many additional factors that influence the dipole configuration in NPSLs, including the dimensionality of the superlattice, finite-size effects, and temperature. Thus, evidence of SFM ordering has been limited to 2-D close-packed arrays[118] and the exact relationship between structural ordering and magnetic ordering remains an open question.[119] Significantly more effort in NP-based materials is required to elucidate the scope of opportunities for NPSLs in this area.

Catalytic Properties of NPSLs. Nanomaterials often exhibit size-dependent catalytic properties that arise due to increased surface-area-to-volume ratios and an increased number of high energy active sites.[120,121] NPs can also be used in photocatalytic applications by using their optical properties (e.g., plasmon resonances) as a means of injecting energy into a system.[122] Many catalytic nanomaterials are often used in tandem with other (nano)materials because the formation of an interface between distinct compositions both enables new catalytic properties and provides a design handle to control catalytic behavior as a function of factors like distances between different materials.[123] As NPSLs are able to precisely structure shaped-nanomaterials together, they provide a unique platform to engineer these interfacial contacts in a deterministic and predictable manner to control emergent catalytic properties. It is important to note that while surface ligands are critical for the assembly of NPs into NPSLs, their presence passivates the NP surface and prevents the formation of interfacial contacts between NPs. As such, the ligands generally need to be removed before any emergent catalytic properties can be observed.[124]

One instance of these emergent catalytic properties has been observed in Pt octahedra bound by (111) facets coassembled with Pd nanospheres to form binary NPSL films with ico-AB_{13} symmetry; these arrays exhibit four times more catalytic activity in reducing oxygen to water than either the pure Pt NPs or random arrangements of the Pt and Pd NPs.[124] This dramatic increase was attributed to combining the high catalytic activities of the Pt(111) planes with the synergistic catalytic effects of Pd and Pt. In a subsequent study, the well-known synergistic effects of Au and Fe_3O_4 in catalyzing CO oxidation were exploited by synthesizing Au−Fe_3O_4 binary NPSLs. The crystal symmetry of the NPSLs controlled the number of interfacial contacts between the two nanoparticle types and thus could be used as a design handle to tune catalytic activity (Figure 7B).[125]

NPSLs are also unique in that they can be used to design multifunctional catalytic materials by integrating different types of catalysts together. In one instance, carbon coated Co−Mn oxide (CoMnO) NPSLs were used as efficient bifunctional water splitting electrocatalysts, with the CoMnO nanoparticles and their nitrogen-doped carbon coating acting as oxygen evolution reaction and hydrogen evolution reaction catalysts, respectively. Importantly, the NPSLs had significantly better catalytic activities than their disordered counterparts, confirming that ordering of the nanoparticles resulted in emergent catalytic properties.[126] Tandem catalysts have also been developed by first assembling a monolayer of Pt nanocubes onto a silicon substrate and then assembling CeO_2 nanocubes on top of the Pt structures. In doing so, two different interfaces were generated that catalyzed sequential reactions to allow for the formation of propanal from ethylene and methanol. When the reaction was conducted using physical mixtures of Pt-CeO_2 and Pt-SiO_2 catalysts instead, no propanal was formed, which indicated that the precise interfacial contact afforded by the NPSLs was key to enabling the tandem catalysis. In addition, when surface ligands were left on the nanocube bilayers, no reaction was observed as well, indicating that the removal of the ligands was indeed necessary for the formation of the CeO_2−Pt and Pt-SiO_2 interfaces.[127] Additional research has also shown that ordering in NPSLs can improve both mass activity and charge transfer properties.[128,129] Collectively, NPSLs therefore offer significant potential for generating new catalytic materials based not only on the composition of the NP building blocks, but also how they are organized in 3-D space.

Mechanical Properties of NPSLs. Because there are multiple methods and ligand interactions that can be used to govern their assembly, different NPSLs have been found to exhibit a wide range of mechanical properties depending on their composition and processing conditions:[130] Young's moduli can range from 100 kPa for hydrated PAE lattices,[131] to 100 MPa for dried hydrogen-bonded polymer-grafted nanoparticles,[65] to 64 GPa for dried NPSLs with cross-linked molecular ligands.[132] In general, however, the mechanical properties of most NPSLs to date have been determined to be comparable to that of glassy polymers, with Young's moduli between 1−10 GPa and hardness on the order of 100 MPa. However, they are typically brittle, with fracture toughness values around 40 $kPa/m^{1/2}$.[130]

Considering that most NPSLs are held together by weak van der Waals interactions between molecular ligands, the large Young's modulus and hardness values observed suggests that there are some collective emergent mechanical properties that arise from their ordering. Indeed, when compared to amorphous nanoparticle assemblies, the mechanical properties of ordered NPSLs were found to be at least 2-fold greater.[133]

Multiple hypotheses have been put forth to account for this behavior. One possible factor is that the ligands interdigitate and interact strongly with each other when confined to the nanoparticle surfaces and the interstitial spaces, which increases their modulus significantly.[134] On the other hand, recent computational work suggests that it is the deflection of the ligands rather than their interdigitation during compression that is primarily responsible for the high stiffness values observed.[135] The presence of residual compressive stress in the NPSL has also been suggested to play a role, as ligands that are kinetically trapped in nonequilibrium conformations induce a compressive stress in the superlattice, which resists bulk compression and artificially inflates the elastic modulus.[136] However, because multiple factors may influence both the packing of surface ligands and the strength of their interactions with one another, it is difficult to definitively state how they govern the observed mechanical behaviors.[137−140]

Aside from exhibiting exceptional mechanical properties, NPSLs have also been able to demonstrate other unusual mechanical behaviors. In DNA-based NPSLs, the yield strength and Young's modulus can be decoupled and independently tuned, which is difficult to achieve in conventional bulk materials;[131] this decoupling means that the stiffness and mode of deformation (i.e., elastic vs plastic) can be independently dictated (Figure 8A). NPSLs assembled via hydrogen bonding have been shown in computational studies to exhibit an anomalous pressure softening due to the compression-induced buckling of the ligands.[141] Additionally, interparticle spacing-dependent photonic properties of NPSLs have been used to introduce mechanochromic properties (Figure 8B).[65] Collectively, these unique properties indicate that a wealth of new properties and structure−property relationships could be obtained via NP assembly, and thus this emerging area of research should be thoroughly explored in the near future.

FUTURE CHALLENGES IN NANOPARTICLE-BASED MATERIALS

Given the wide design space afforded by materials synthesis via NP assembly, it is likely that new technologies and applications will continue to emerge that exploit the properties described in the previous section.[8,51,101] In addition to making new NP-based materials and investigating their structure−property relationships, however, there are multiple additional challenges that are just beginning to become apparent (Figure 9). Here, we will explicitly note the areas of research we believe to be critical to enabling such technological transitions, and provide examples that provide preliminary insight on how these advancements might be accomplished (Figure 10).

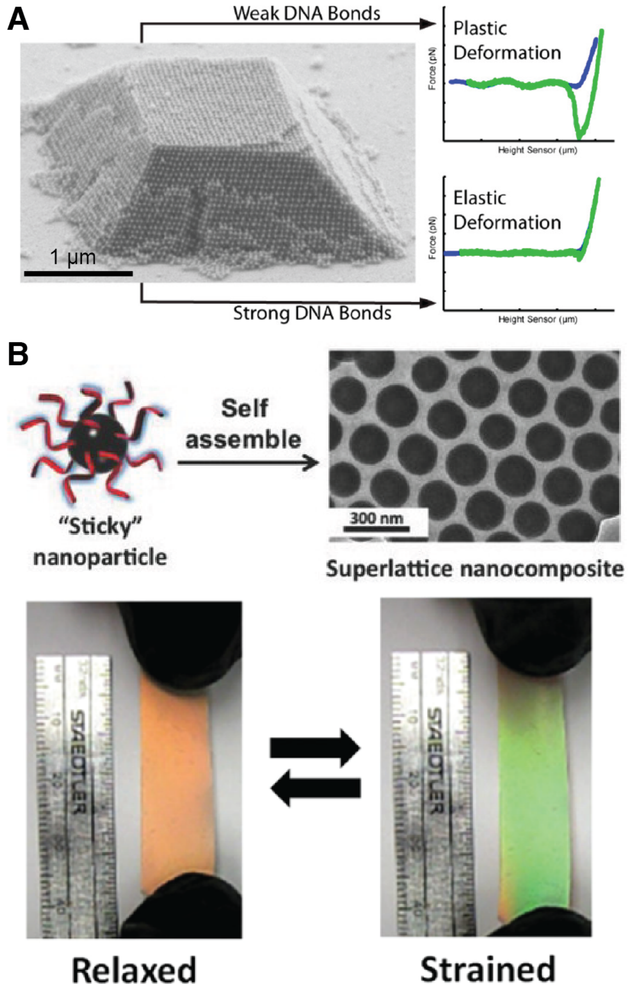

Figure 8. Emergent mechanical properties in NPSLs. (A) The Young's modulus and yield strength of DNA-based NPSLs can be decoupled and independently tuned by varying the type of DNA used to drive assembly. (B) Interparticle spacing-dependent photonic properties can be used to imbue mechanochromic properties to the material, such as reversible color changes upon mechanical strain. Adapted from refs 65, 131. Reprinted with permission from ref 65. Copyright 2015 John Wiley and Sons. Reprinted with permission from ref 131. Copyright 2020 American Chemical Society.

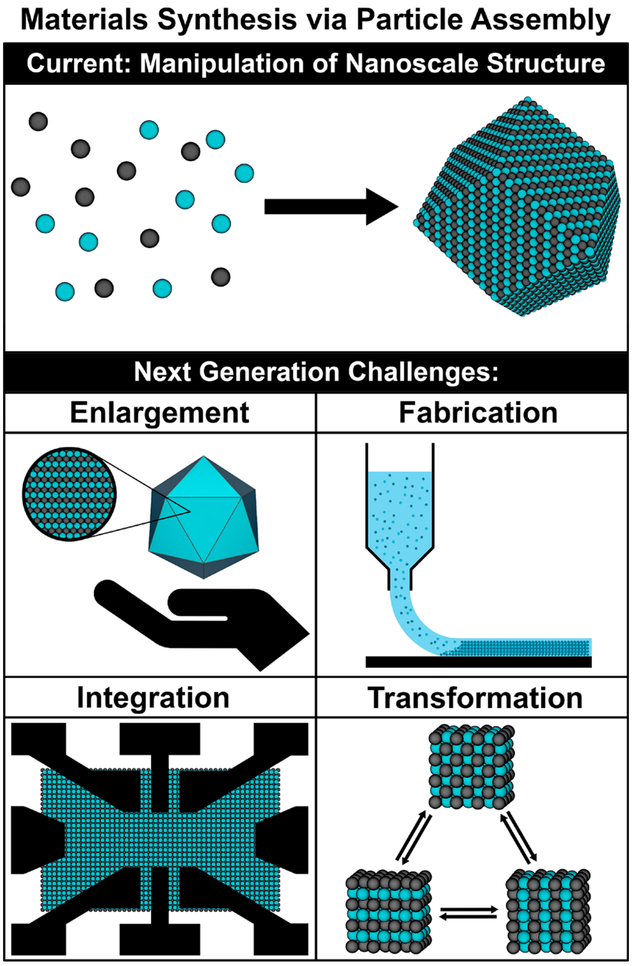

Figure 9. Advancements in nanoparticle assembly have provided a wealth of unique materials for study. Now that numerous assembly techniques have been developed, new challenges are beginning to emerge. Significant opportunities exist for both basic scientific investigation of structure−property relationships and functional device fabrication for NP assembly methods capable of being produced at macroscopic scales, patterned into arbitrary shapes, integrated with traditional bulk materials and devices, or intentionally toggled between different organization states.

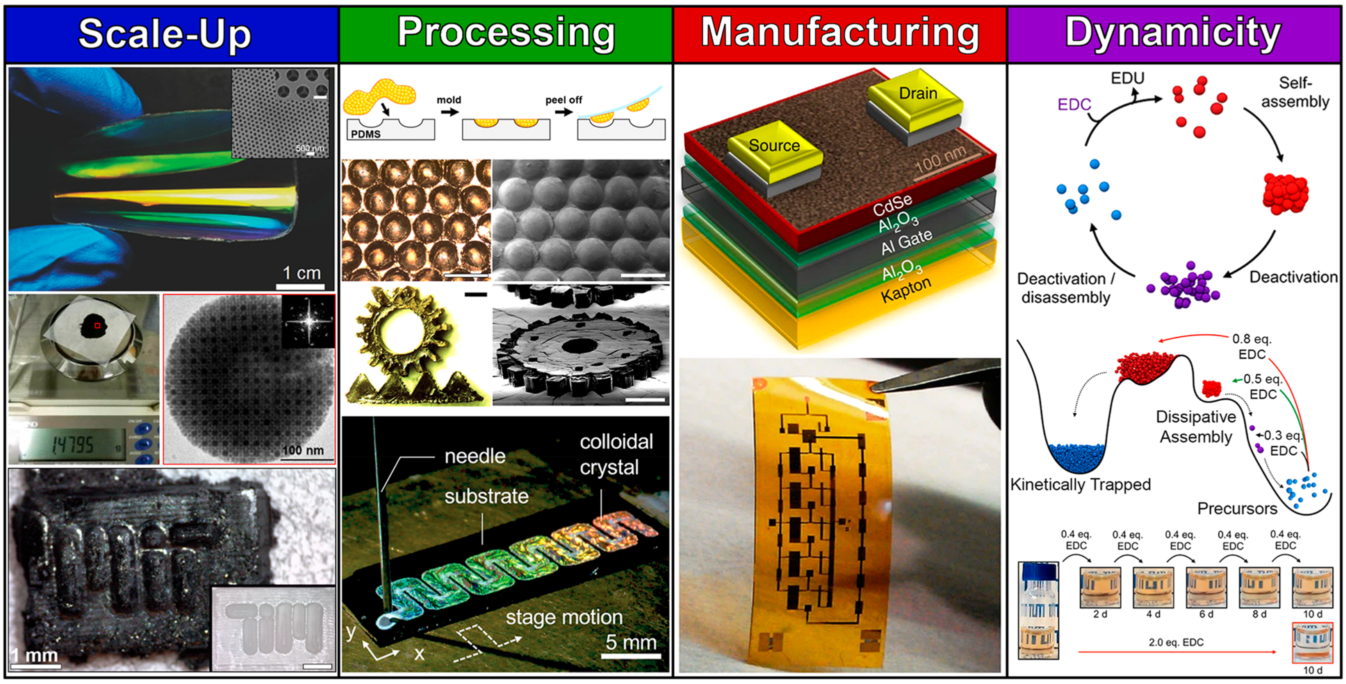

Figure 10. In order to address the challenges outlined in Figure 9, four key areas of research in NP assembly must be undertaken. Successful advancements in these areas will lead to the establishment of NP assembly as a materials synthesis method that is potentially as well-understood and useful as traditional chemical syntheses. These include: scale-up of NP assembly methods, development of processing techniques to control micro- and macrostructural features, integration of NP-based materials with conventional bulk structures, and introduction of design handles to make dynamic or stimuli responsive assemblies. Initial research results in each of these areas indicate that the field is rapidly progressing toward accomplishing this goal. Adapted from refs 71, 142, 144, 155, 170, 174, 185. Reprinted by permission from Springer Nature: Nature Portfolio, Nature, ref 71. Macroscopic materials assembled from nanoparticle superlattices, Santos et al, copyright (2021). Reprinted with permission from ref 142. Copyright 2018 American Chemical Society. Reprinted by permission from Springer Nature: Nature Portfolio, Nature Communications, ref 144. Flexible and low-voltage integrated circuits constructed from high-performance nanocrystal transistors, Kim et al, copyright (2012). Reprinted with permission from ref 155. Copyright 2017 John Wiley and Sons. Reference 170 republished with permission of Science, from Plastic and Moldable Metals by Self-Assembly of Sticky Nanoparticle Aggregates, Klajn et al, 316, 5822, 2007; permission conveyed through Copyright Clearance Center, Inc. Reprinted with permission from ref 174. Copyright 2020 John Wiley and Sons. Reprinted with permission from ref 185. Copyright 2019 American Chemical Society.

Scale Up and Macroscopic Fabrication. If we define the term "device" as a specific structure tailored to take advantage of a material's properties for a desired effect, then devices can constitute a wide array of functional forms. Because most NPSL synthetic methods currently produce predominantly microscopic structures[44,60,142] or nominally 2-D films,[34,38,91] the most immediate applications for NPSLs involve devices with either small or planar form factors. For example, the size- and shape-dependent plasmonic and photonic phenomena of DNA-programmed NP assemblies discussed above would make them suitable for waveguiding in microelectronics due to their micron-scale assembly sizes and precise nanoscale structure control.[45,143] Conversely, the 2-D films generated in evaporation-driven BNSL assembly are well-suited for the synthesis of large-scale coatings for mechanical protection or for modification of the properties of an underlying substrate.[31,144−146] Technologies are also emerging for the use of NPSL films in light absorption and emission, applications for which the planar shape of these BNSL arrays is ideal.[147,148]

These types of microscale or planar geometries are likely to continue to be the main devices in the near future, as one of the predominant remaining challenges for NPSLs is their scale up to larger quantities. Compared with bulk atomic, molecular, or macromolecular materials, NPSLs can only be made in limited amounts, primarily due to the challenges of producing large volumes of low-dispersity NPs via colloidal synthesis, and in precisely regulating assembly conditions across large volumes to produce uniform materials.[149−151] However, as synthetic procedures continue to improve, methods to produce large quantities of particles suitable for NPSL assembly are becoming more common, making multiple NP compositions (e.g., noble metals, oxides, semiconductors) readily available for purchase and enabling their use by researchers in a variety of disciplines outside just chemistry and materials science. Additional efforts to expand both the variety and quantity of nanoparticles available could also be improved by researching higher throughput batch processing or flow chemistry methods for continuous NP synthesis.[152−154]

It is important to note, though, that the process of scaling up a material's synthesis constitutes a bigger challenge than simply "making more" of it. Once enough material can be produced that the structures exist at the micron, centimeter, or larger size regimes, those length scales also become relevant for dictating material properties and behavior, and must be considered as part of the synthetic process.[71,155] For example, as chemists, we often view the formation of perfect crystals as the ultimate in material structure control. However, we also know from traditional atomic materials that defects and microstructural deviations are often key for generating or controlling material performance.[156] Substitutional defects or vacancies can be used to dope semiconductors and control their band gaps,[157] dislocations and grain boundaries affect mechanical properties by enabling or limiting slip planes,[156] and surface defects are often the most active sites of a catalyst.[158] Point defects, line defects, and grain boundaries are already commonly observed in NPSLs, though our ability to intentionally generate them is still in its infancy.[159,160] Nevertheless, the fact that NPs can be assembled independently of their composition allows for intentional programming of point defects like vacancies (e.g., "hollow" PAEs that graft DNA brushes to an empty polymer nanoparticle shell[161]) or substitutional defects by assembling NPSLs using a batch of NPs that incorporates small amounts of NPs with the same size and ligand chemistry, but different composition.[71,162] Methods to control 2-D and 3-D defects are more difficult to envision, but still potentially possible. Templated assembly is one potential path to generating these more complex microstructural features, by patterning a specific defect into an underlying substrate that propagates as the material is assembled on top of the pattern. Other methods such as postassembly treatment of the assemblies with an external force (e.g., thermal gradients, solvent flow, or optical energy) that induce reorganization of NPs are also a potential route to controlling 2-D and 3-D microstructure.[163,164] Significantly greater effort needs to be put into techniques to induce these defects in a controlled manner, and also to determine if such defects and microstructuring affect the collective properties of NPSLs in the same manner as their atomic analogues. In this regard, computational efforts will be critical both to guide the development of these new techniques, and to help understand the emergent properties as they arise. Computational efforts for hierarchical materials that span multiple length scales will undoubtedly be increasingly difficult as the scale of these assemblies increases, as coarse-grained models are required to make large systems or long timeframes computationally tractable. As such, methods must be developed to coordinate simulations or calculations and interpolate data across the wide range of time and length scales associated with molecular bonding, nanoscale assembly, and macroscopic shaping.[37,165]

Processing of NPSLs into Functional Forms. A key step in synthesizing materials for both fundamental structure–property measurements and device fabrication is the ability to shape the material into the correct functional form. For example, optical interrogation of a film can be hampered if factors like surface roughness, film thickness, or uniformity across the light source's cross-sectional diameter are not properly controlled. Similarly, mechanical measurements can be significantly affected by the shape of the object being compressed or extended. For advancing both our understanding of NP material synthesis and use of these materials in different applications, it is important to consider how we process the as-synthesized material into the appropriate shape for examination and use. However, the types of conventional materials processing strategies that can be employed with NPSLs are currently limited. Some NPSLs are only stable in solution,[43,166,167] others are mechanically brittle once assembled and dried,[168,169] and many are easily disrupted at elevated temperatures;[10,66] processing techniques that require high temperatures or application of mechanical force are therefore likely to ruin the ordering generated by self-assembly. Thus, advancement of NPSL synthesis to generate materials with controlled micro- or macroscopic forms requires that we develop compatible processing steps that do not disturb their ordering, or develop protection methods that stabilize the lattice structure postassembly.

For example, drop casting is a simple processing method to generate coatings, and sedimentation of NPSL via solvent evaporation can be thought of as a simultaneous assembly and processing step, for 2-D structures.[9] Also in the context of films and substrate-bound assemblies, it is possible to use plasmon thermalization as a means of simultaneously crystallizing and macroscopically shaping a material by irradiating plasmonic nanoparticle superlattices with a laser and allowing the local thermal gradient to induce NPSL reorganization and diffusion.[163] For macroscopic 3-D NPSL structures, appropriate control over the thermodynamics of interparticle interactions can allow for bulk quantities of NPSL crystallites to be "sintered" into free-standing structures of arbitrary shapes via compression molding.[71,170] Shear alignment during solvent flow has also been shown to control particle organization in colloidal structures,[171−173] meaning that extrusion or compression could be fruitful avenues for exploration,[169,174] provided that we can fully understand and manipulate the chemical interactions between the NPs and the surrounding fluid; computation is certainly a key factor to enabling such understanding.[175] To enable these methods, assembly within different solvents must be investigated, including the use of more viscous alternatives than small molecule liquids, such as homopolymer or block copolymer melts.[72,74] With regards to protection of the superlattice postassembly, methods to sinter NPSLs into covalently connected solids via chemical, thermal, or optical stimulus have been developed, where weak intermolecular forces between NP ligands are replaced or reinforced with permanent chemical bonds.[146,176−178] It is also possible to embed NPSLs into different materials like metals, oxides, or cross-linked polymers and gels, where the superlattices act as a scaffold around which these other materials can be grown.[179−181]

Another area of NPSL processing research that remains underinvestigated is the establishment of methods to use NPSLs as additives in other bulk materials. By using the NPSLs as components of a material (as opposed to the entirety of a macroscopic structure), the physical properties induced by NP assembly can be exploited while minimizing the amount of NPSLs that must be synthesized. Examples of block copolymers with embedded, isolated NPs have already been demonstrated,[73,74,182] but encapsulation of fully formed NPSLs is less common. New chemical strategies to stabilize these assemblies so that they can be mixed with bulk polymers or other materials should be a key focus of our community's research efforts. In this regard, it will be important to research both the stability of lattices (pre- and post-protected) during macroscopic processing methods, and to understand how the interfaces between NPSLs and bulk material around them affect the emergent properties of the lattices, such as optical refraction or phonon transport.

Integration with Other Devices. Although great examples have been shown of devices made solely from NPSLs,[143,145] most technological applications of these materials will require them to be properly integrated with other types of materials.[144,183] The ability both to interrogate the properties enabled by NPSL assembly and to use those properties in a given application therefore requires that we can either deposit assembled lattices at the site of interest, or that we can directly assemble them at a desired location within a preformed device. This research advancement also requires that the sizes, shapes, and orientations of the structure be controlled so that the other instrument or device components can properly interact with the NPSL. Thus, key areas of investigation must include means to break the symmetry of assembled materials to induce the formation of complex microscale and macroscale geometries. Given that the forces governing interparticle interactions often provide limited means of controlling structure beyond each NP's nearest neighbors, advancement in this area will require multidisciplinary approaches that combine chemical synthesis and NP assembly with top-down fabrication.

As an example, assembly on patterned substrates is a well-explored method to achieve the goal of macroscopic positioning, as lithography can easily create arbitrarily shaped and oriented patterns in an intentional manner.[50,78] Some examples are discussed in the earlier sections of this perspective, such as DNA-programmed assembly on patterned and DNA-grafted substrates, or deposition of particles into specifically shaped wells. However, many of these methods are either tedious in their preparation or limited in their ability to fully control NPSL structure, requiring further study and advancement. The next stages for NPSL assembly therefore include developing a better understanding of how such confined assembly techniques affect assembly thermodynamics and kinetics, as well as how the underlying pattern affects the stability of different NPSL lattice types; it may even be possible to use these larger patterns as a way to "frustrate" crystallization to specifically manipulate crystal symmetry or microstructure.[184] More research is needed to fully understand how top-down patterning at the micro- to macroscopic scale affects the behavior of NPs as they form ordered arrays with nanoscale repeat structures.

Dynamic/Living Systems. The majority of NPSLs that have been synthesized to date are intentionally targeted thermodynamic products. The key advantage of assembling particles into their thermodynamically favored arrangement is that it simplifies the synthetic process—if the desired crystallographic symmetry represents the thermodynamic minimum for the selected set of NP building blocks, then assembly is just a matter of applying enough time and energy to allow the NPs to reorganize into the appropriate state. Kinetically driven or out-of-equilibrium structures are thus more rare,[166,185] as both the NP building blocks and the assembly conditions must be more tightly controlled in order to reproducibly generate, isolate, and stabilize these inherently transient or intermediate species. Nevertheless, such structures offer the possibility of generating more complex organizations with broken or lower symmetry than thermodynamic products often provide, as well as specific microstructural features or nonequilibrium properties that would open up new applications like energy storage or harvesting.

In order to induce such kinetic structures, design principles for NP assembly must be more refined to describe all relevant parameters (including factors like rates of assembly or relative stability of intermediate species) and the assembly pathways need to be better characterized and modeled. Properly controlling such kinetic products requires significantly more fundamental research. Important avenues of exploration are the establishment of new computational techniques to simulate dynamic colloids as they reorganize, coupled with methods to extrapolate the thermodynamic stability of different points in this complex phase space.[186] Additionally, experimental methods would be aided by the development of tools from traditional materials science to describe and explain crystallization phenomena (e.g., time−temperature-transition diagrams).[187] New instrumentation and technologies to track these formation processes in real time must also be established, such as in situ TEM or X-ray based techniques.[188,189] In situ TEM is particularly attractive for monitoring and understanding dynamic assembly processes, as NP crystallization occurs on a much slower time scale than traditional atomic or molecular crystal formation, and thus NPSLs could be used as model systems to directly monitor crystallization phenomena in a manner not accessible to lattices built from atomic species.

An additional goal for dynamic systems is the development of NPSLs that can reprogram their structures upon application of an external stimulus, as this offers the opportunity to toggle properties on the fly.[67,82,167,185,190,191] Additionally, because self-assembly is inherently based on the concept of designing building blocks that spontaneously form a predetermined structure upon application of a stimulus, dynamic NPSLs would in principle permit materials to reorganize and self-heal any mechanical damage by simply reapplying the initial assembly conditions (e.g., thermally reannealing the disrupted structure). However, many current reorganization methods require excessive amounts of time to reorganize upon introduction of a stimulus as they are limited by the rates of diffusion of either the molecule stimuli or the NPs themselves. Additionally, many reorganization processes are order−disorder−order transitions, where an initial stimulus changes the thermodynamically preferred state of a lattice and causes a loss of ordering that requires reassembling the structure to generate the new ordered array. The next challenges for dynamic NPSLs therefore lie in improving the switching rates for these materials by employing processes not driven by a chemical stimulus (e.g., lattices that switch with the use of thermal, magnetic, optical, or electrical stimuli), or developing methods to generate order-to-order transitions that do not require an intermediate annealing or reorganization step. The difficulty of establishing such processes lies in determining methods to force NP reorganization without the need for long-range mass transport, as diffusion of either the stimulus or of the NPs themselves would inherently result in a significantly slower process than one guided by solely local reorganization of individual NPs.

■ OUTLOOK AND FUTURE IMPACT

NPSLs are an exciting class of material, with significant potential for enabling both basic scientific research into understanding the chemistry of crystallization, and the exploration and use of new emergent properties controlled by NP organization in 3-D space. These nanoscale "artificial atoms" can use principles that have been quantified and explored in atomic systems as a guide, but they are not bound by the same limitations imposed by the limited palette of available atomic species selectable from the periodic table. This opportunity comes with significant challenges, though, as their assembly is in many ways far more complex than atomic crystallization. Nevertheless, the multitude of available NP building blocks and assembly methods, combined with our continually growing knowledge of the fundamental principles governing NP assembly, make it not unreasonable to predict that in the foreseeable future we will be able to explain, predict, and control the formation of a host of new materials by design.

The impact of these NPSLs on the future of chemistry and materials science is dependent upon our ability to both use the structures and properties we have already generated and invent new ways of scaling up, integrating, and controlling the larger-scale structures of these NPSLs to enable advances in both fundamental science and engineering applications. Ultimately, the extent to which NPSLs affect the chemistry and materials science communities will be defined by our ability to identify key properties that can be best (or only) produced with NPSLs, as well as our ability to control NPSL structure from the molecular to macroscopic scale simultaneously. Scientific insight is necessary to define design principles for controlling and explaining NP assembly to the same levels of complexity and precision as the atomic precursors chemistry has studied for decades, and pairing these scientific insights with engineering research into integrating and using NP structures will enable multiple applications in a wide range of disciplines.

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Notes

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■ ABBREVIATIONS

NP, nanoparticle; NPSL, nanoparticle superlattice; BNSL, binary nanoparticle superlattice; PAE, programmable atom equivalent

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