



Nanoparticle self-assemblies with modern complexity

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Thanks to decades of tireless efforts, nanoparticle assemblies have reached an extremely high level of controllability, sophistication, and complexity, with new insights provided by integration with graph theory, cutting-edge characterization, and machine learning (ML)-based computation and modeling, as well as with ever-diversifying applications in energy, catalysis, biomedicine, optics, electronics, magnetics, organic biosynthesis, and quantum technology. Nanoparticle assemblies can be crystalline, known as superlattices or supracrystals. Their assembly entails a transition from disorder—dispersed nanoparticles—to order, which can be achieved through classical nucleation pathways or nonclassical pathways via prenucleation precursors or particle aggregation. The periodic lattices allow facile manipulations of electrons, phonons, photons, and even spins, leading to advanced device components and metamaterials. Meanwhile, aperiodic assemblies out of nanoparticles, such as gels, networks, and amorphous solids, also start to attract attention. Despite the loss of periodicity, symmetry-lowering or symmetry-breaking three-dimensional (3D) structures emerge with unique properties, such as chiroptical activity, topological mechanical strength, and quantum entanglement. Real-space imaging such as electron microscopy and x-ray-based tomography methods are utilized to characterize these complex structures, whereas mathematical tools such as graph theories are in need to describe such complex structures. This issue aims to provide a timely review of the efforts in this greatly broadened materials design space, including experiment, simulation, theory, and applications. Nine top experts (and their teams) from four countries deliver six articles summarizing fundamental mechanistic understandings of nanoparticle assemblies, highlighted with the developments of state-of-the-art *in situ* characterization tools and ML-assisted reverse engineering, and newly emergent applications of nanoarchitectures.

Self-assembly and nanoparticles: The past

The seminal paper “Self-assembly at all scales” by Whitesides and Grzybowski was published in 2002,¹ around the time when the Mars Odyssey found signs of huge water ice deposits on the planet of Mars—both with the intellectual vigor investing into the basic components of materials, and of life. This paper included a long list of building blocks that can achieve “autonomous organization” “into patterns or structures without human intervention,” with sizes ranging from the finest atoms and molecules to weather patterns and galaxies. However, colloidal nanoparticles (NPs) were missing in this list as building blocks, partially because the efforts on their synthetic control and self-assembly were burgeoning. About five years later, Glotzer and Solomon discussed the potential of utilizing anisotropic building blocks for self-assembly into complex structures,² where NPs stood out as advantageous building

blocks due to their substantially improved synthetic control in the shape, size, composition, surface chemistry, and interaction potentials. A bursting flux of literature and needle-shifting experimental efforts were present to push the boundaries of NP synthesis and self-assembly. Some notable examples include the theory and experiments on the growth mechanism of NPs (such as the quantum dot synthesis awarded by the 2023 Nobel Prize in Chemistry), the use of solvent evaporation or liquid–air/liquid interface to assemble dried superlattices from NPs coated with organic ligands (**Figure 1a–b**),^{3–6} and the “Golden handshake”⁷ to link water-soluble NPs into various arbitrary structures using DNA hybridization.^{8,9} Talapin reviewed this exciting progress with extensive discussions on the fundamentals and applications of ordered assemblies of NPs in electronics, catalysis, photonics, plasmonics, and magnetics in 2016.¹⁰ By then, the field of NP self-assembly

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doi:10.1557/s43577-024-00700-1

remained largely an area for chemists, involving inorganic chemists (e.g., synthesis, ligands), physical chemists (e.g., exciton kinetics, charge transport), and materials chemists. It was remarkably interdisciplinary.

Yet the wheel of time continues to turn. Several other areas of research started to prosper and to orchestrate with efforts of NP self-assembly, pushing its progress into those of modern complexity—the focus of this themed issue. Here, complexity does not defy order, which was the traditional holy grail of NP self-assembly to achieve uniformity and periodic patterning, but goes beyond order. Historically, an ordered or periodic superlattice has made the characterization and quantification convenient—ensemble spectroscopy methods such as small-angle x-ray scattering (SAXS) are sufficient to measure lattice spacings and index lattice symmetry. Property prediction of superlattices has been straightforward due to their structural periodicity. A decently small, computationally efficient model containing a few unit cells can be enough to predict the properties of a bulk NP superlattice, a common practice in the calculation of plasmonic properties using finite-difference time-domain (FDTD) simulations. The conventions will not hold once NP self-assemblies deviate from being perfectly ordered, requiring new concepts and toolkits in how to characterize, quantify, and predict the structure–property relationship of complex self-assemblies. The time is right to consider such complexity and its relationship to functionality. Toolkits such as NP building blocks, self-assembly strategies, and *in situ* imaging tools to observe the pathways are well developed, and as new applications are associated with complex, disordered structures (Figure 1c).^{11,12}

Complexity in the generic shape of NPs

Complexity in self-assemblies can originate from the geometric shape of NPs. In their article in this issue, Schneider et al.¹³ discussed nanoscale tetrahedra—the simplest platonic shape yet has numerous geometric variations when it comes to its superstructures, from networks or fractals such as the Sierpiński tetrahedron, Da Vinci’s tetrahedron star, and mechanically robust truss structures in bridges and towers to diverse symmetry-breaking tetrahelix, quasicrystalline phases, and chiral lattices. As NPs, tetrahedra have demonstrated amazing opportunities in synthesis, self-assembly, and mathematical interpretation. Highlighted by “God is in the details,” this article presents meticulously the authors’ first-hand experience and anecdotes on tetrahedral NPs. The first detail to note, which applies to other polyhedral shapes, is that tetrahedra are an extended family. Advancements in colloidal NP synthesis of tetrahedron have enabled fine control over the extent of truncation at the edges and vertices as well as the curvature of facets in the tetrahedra shape family, including related shapes such as tetrapods and tetrahedral frames. Using graph theory (GT), the basic perfect (with sharp corners and flat facets) tetrahedron is represented as an equilateral triangle divided into three smaller triangles. Vertex or edge truncation and twisting are then realized by “ambo,” “chamfer2,” and “snub” operations, whose graph representations are immediately complex. These graph models suggest the minimal geometric features needed to consider in modeling their inter-NP interactions and packing structures.

The level of synthetic control on these shape details was shown to link directly with their self-assembly. Large-scale assemblies from tetrahedra only emerged as the monodispersities of tetrahedral NPs and their analogues are significantly

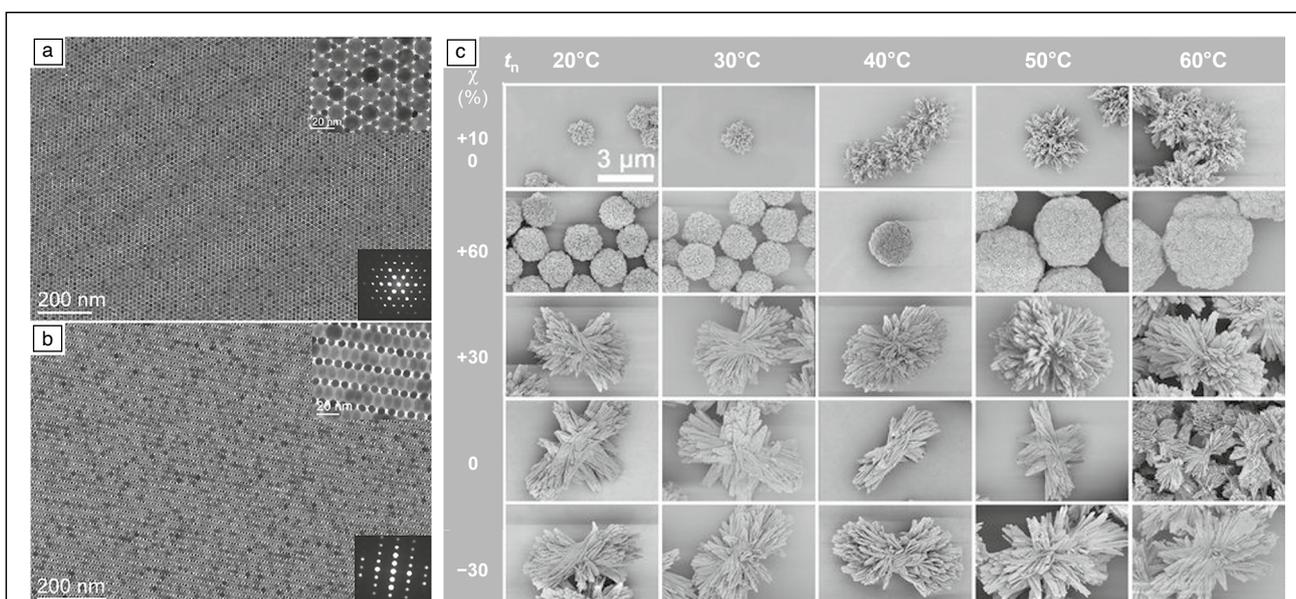


Figure 1. (a, b) Transmission electron microscopy images of ordered nanoparticle (NP) superlattices assembled from binary mixtures of 15 nm Fe₃O₄ and 6 nm FePt NPs using the liquid–air interfacial assembly process.⁸ Reproduced with permission from Springer Nature. (c) Hedgehog supraparticles assembled from chiral Au–S nanoplatelets.¹² From Reference 12. Reprinted and adapted with permission from AAAS.

improved,^{14–19} which involves the help of post-synthesis size selection using depletion attraction. The early stage of progress has focused mostly on two-dimensional (2D) of tetrahedral NPs on a substrate, often the TEM grid.¹⁴ The self-assembly (triangular lattice versus clove structure) largely depends on what facets or edges sit on the substrate, which are modulated by ligand chemistry. Such assemblies due to solvent evaporation on a TEM grid can extend to three dimensions (3D), inducing multilayered assemblies and even supracrystals. In 3D, the bonding motif, such as face-to-face versus vertex-to-vertex attachment, can lead to drastic difference, whose competition depends on asymmetric surface ligand attractive forces. Recent synthetic efforts have led to anisotropically coated NPs with complex facets (more than just {111} facets in earlier studies), which generate a great family of complex crystalline and quasicrystalline lattices due to the possible enumeration of face-to-face attachments (Figure 2a–c).¹⁹ Substrates are found important in guiding the self-assembly into cubic diamond or hexagonal diamond phases. The ultimate level of complexity in tetrahedral assemblies is embodied by the formation of chiral structures, the helical chains,²⁰ and chiroptically active superlattices (Figure 2e).¹⁵ The hallmark of assembly strategies here is the utilization of geometric frustration, where the regular bonding motifs cannot span continuously, leading to local twisting that is amplified as a symmetry-breaking effect as visualized by liquid-phase TEM and simulation. Note that chirality in particular emerges as a fascinating aspect of complexity for more studies, for their applications in optics, mechanics, and electronics, and also for the emergence of synthetic efforts on NPs with chiral/symmetry-breaking morphologies.

The details and lessons learned for nanoscale tetrahedron can be translated to other shapes and broaden the spectrum of applications for nanostructures. The details of corner truncation, for example, have been shown to be the key to control of the shape of supracrystals assembled from tetrahedron.¹⁶ Similarly, Glotzter has shown computationally the precise corner and edge truncation can be used as phase coordinate for hard colloids (Figure 2d), for example, in cubes (the extent of corner truncation leading to cuboctahedron and octahedron) and tetrahedra (the extreme of corner truncation being octahedron), to induce systematic variations in the assembled structures.^{21,22}

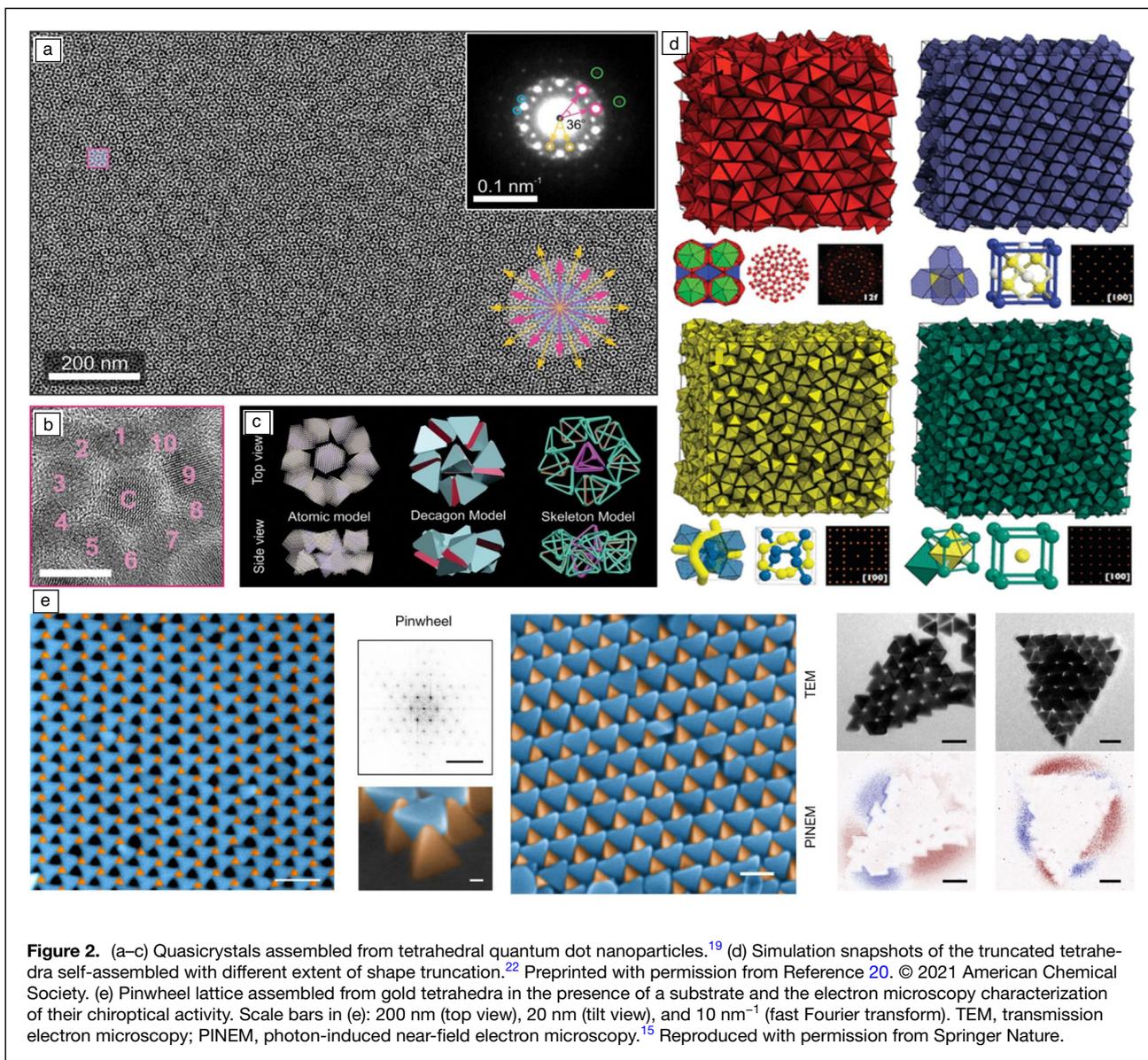
Complexity from symmetry-lowered patchy or heterogeneous NPs

NP building blocks can be symmetry-lowered with a patchy surface, namely covered by different domains of ligand chemistry or composition, leading to NP orientation-dependent interactions. This concept of patchy NPs originated from an even older concept of Janus colloids, where Janus is a Roman god with one face to the past and the other to the future.²³ This surface complexity in patchy NPs plays important roles in directed self-assembly. Compared with non-patchy NPs where ligand coating is continuous and uniform, the hallmark

of patchy NPs is their potential to pack into nonclosely packed structures, such as chains, loops, and networks due to directional interactions (Figure 3).^{24–27} The immediate consequence of directional interactions is that NPs only link with each other through preferred bond geometries, thereby generating structures of low coordination symmetry. This breaking of high coordination symmetry (e.g., the coordination number of 12 in *fcc* and *bcc* lattices) has been demonstrated for patchy NPs by simulation and theories (Figure 3a), which promise to exhibit exotic properties unique to open lattices, such as photonic and phononic bandgaps useful for waveguides, optical computing, sensors, and telecommunications, or reconfigurable and tunable pores for encapsulation and separation technologies. However, despite computational efforts and the demonstration of such open lattices in metal–organic frameworks (MOFs), the design principle of open lattices has been much harder to achieve experimentally from self-assembled patchy NPs. The challenges were multifold: (1) synthesis of patchy NPs in large quantity and high precision; (2) theoretical models that are well integrated with experimentally attainable patchy NPs and inter-NP potentials, to allow for reverse design; and (3) efficient self-assembly strategies to bypass intermediates or kinetic traps for patchy NPs, whose assembly-free energy landscape can be significantly more complicated than non-patchy NPs.

In their article in this issue, Vo²⁸ highlighted the most recent advancements in overcoming the above-mentioned challenges. The article started with discussions on the promises of directed self-assembly, followed by a review of different types of patchy NPs—the soft ones (Figure 3a–b) consisting of synthetic amphiphiles or biomolecules (e.g., proteins, DNA, or RNA origamis),^{25,26} the hard ones of inorganic NPs (such as satellite NPs formed due to dealloying),²⁹ and the hybrid ones with inorganic NPs coated with organic ligands (Figure 3c).^{27,30,31} Then in addition to highlighting existing tools for modeling patchy NPs, the article takes a forward-looking perspective to review recent tools and theories of reverse engineering, to achieve computational design and optimization of patchy NPs' multitude of parameters (e.g., patch location, size, interaction strength, patch geometry). The reverse design approaches can simply aim to connect a final structure with the potential of mean force (PMF). The more data-driven/algorithm-centric approach such as landscape engineering, on the other hand, concerns the practical kinetic pathways.

Great advancements have been made in the integration of experiments and theory in each type of patchy NPs, to understand their synthesis, self-assembly, and stimuli responsiveness. For example, in the case of polymer-coated patchy NPs, the spatial distribution of patches can impose one additional dimension of (a) symmetry on top of the generic shape symmetry of the NPs. As shown in Figure 3c, gold triangular prisms have a symmetry group of D_3 , where the three tips are chemically and geometrically identical. Coating them with polymeric patches in the presence of strong polymer–polymer attraction, however, can lower the symmetry



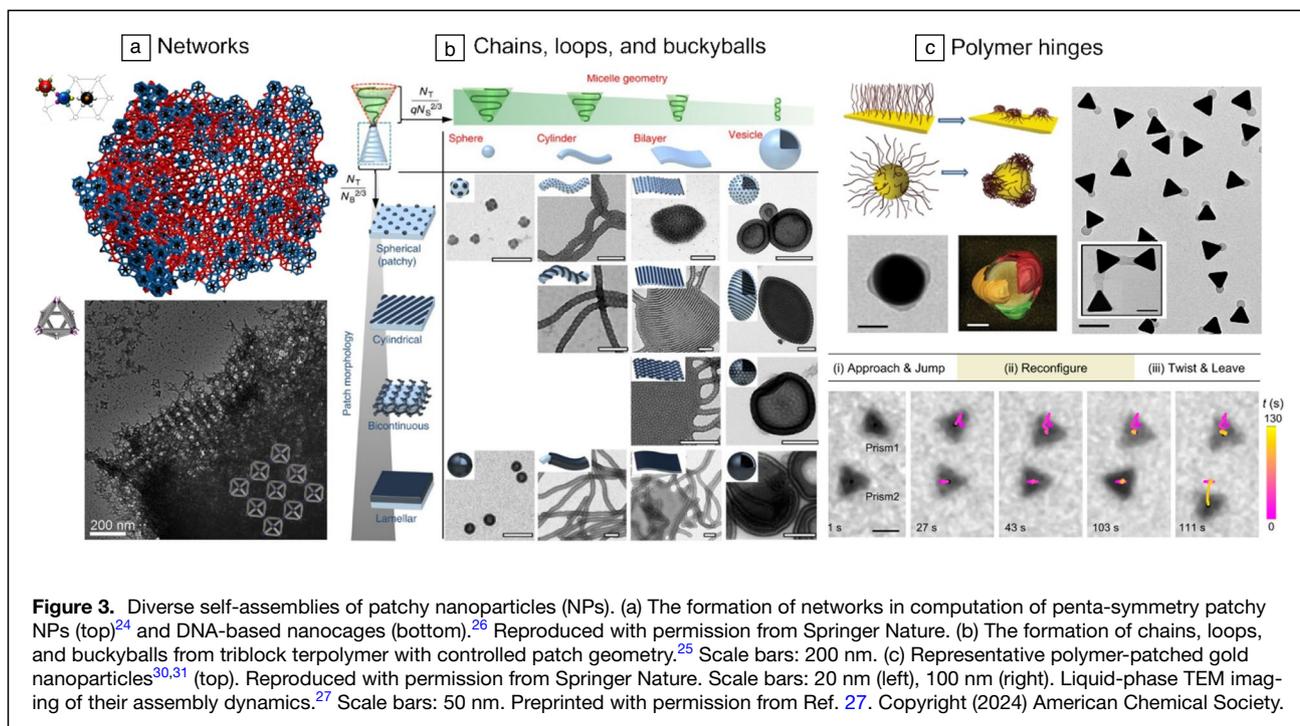
to only one line symmetry, which have been both experimentally achieved and predicted by the scaling theory in polymer physics.³¹ In addition to the patch shape and size, interpenetration of polymer patches and the resulted rotationally flexible bonds are both imaged and predicted by polymer physics theory and MD simulation (Figure 3c).²⁷ Here, high-resolution liquid-phase transmission electron microscopy (TEM) provides the otherwise inaccessible data set of relaxing dynamics of patch particle assemblies. This work also presents networks and branches with low-energy vibration modes. As to the future of patchy NPs, great advances are expected in theory or computation to guide experimental design, and the need to develop more comprehensive models for complex hybrid patchy NPs, where soft meets hard, flexibility meets rigidity, and polymer physics meets solid state.

Importantly, going beyond the laboratory idealization of building blocks of perfect size and shape uniformity,

large-scale manufactured NPs or natural NPs (ubiquitously existing in biominerals) are often heterogeneous in size, shape, and inter-NP interactions. This complexity in building blocks can immediately be magnified into their self-assembly, for example, into irregular gels and networks, which have intriguing optical and mechanical properties.

Generation of complexity due to constraints

One common and successful strategy to generate symmetry-breaking complexity in NP assemblies is to use geometric constraints. The constraint can originate from the special geometric shapes of NPs. For example, tetrahedron as a shape is well known for its difficulty in tessellate space in 3D. As a result, they assemble with different extents of local distortion and strain due to geometric frustration. This frustration can lead to the formation of helices, where the NPs twist as they assemble, into ropes.²⁰



This frustration can lead to the formation of quasicrystals, where no one unit cell can be found but a diversity of 13-fold symmetry tilings is generated. This frustration, in the presence of additional constraints, such as a planar substrate, can lead to the formation of a chiral superlattice.¹⁵ The constraint can come from physical confinements, such as the famous series of columnar structures of spheres packed in a tube,^{32,33} where the tube diameter is on the same order of the sphere diameter; at certain ratios of the diameters, the tubular structures are helical, which have been realized by polystyrene spheres in a tube and colloids pushed by focused flows in a rotating lathe.³⁴ The constraint can emerge from interaction potentials. For example, the Derjaguin, Landau, Verwey, and Overbeek (DLVO) interactions, most commonly considered for colloidal assembly, can have one interesting variation, that is long-range electrostatic repulsion and short-range van der Waals attraction. This separation in length scales can lead to the self-assembly of structures self-limited in size, which are amorphous yet still exhibiting characteristic sizes, such as in the form of supraparticles (particles composed of particles)³⁵ and chiral hedgehogs.³⁶

As highlighted in the previously discussed examples, chirality is one prominent example of structural complexity. Chirality, a fundamental phenomenon in Nature, plays a crucial role in biological systems, spanning from marine to terrestrial environments. Examples include coccolithophore exhibiting hybrid-chirality coexistence in plankton and the complex 3D hierarchical chiral structure of the human skeleton. Organisms, through natural selection and evolution, have developed the ability to create intricate chiral suprastructures using inorganic NPs, providing

biominerals with specific functions for reproduction and survival. Inspired by nature, researchers employ inorganic NP assembly to fabricate chiral suprastructure materials with remarkable chemical, catalytic, optical, plasmonic, electronic, magnetic, and mechanical properties for applications in mechanical performance optimization, molecular recognition, biomedicine, optical materials, and catalysis. In addition to the utilization of geometric constraints, other strategies to achieve chirality include chirality transfer, templated-directed orientation, and induction of chiral external fields. Chirality transfer involves interactions between chiral functional molecules and inorganic NPs, allowing for precise control over the assembly process. Templates, classified into soft and hard templates, provide a chiral configuration for NPs, leading to a variety of chiral suprastructures. External chiral environments, such as circularly polarized light, magnetic field, and mechanical forces, can induce chirality in the assembly process. In their article in this issue, Xing et al.³⁷ has highlighted these insights and highlighted the need for attention to exploring chiral assembly processes *in vivo* at different biological levels, understanding the relationships between assembly structures and functions, and addressing issues of low synthesis efficiency, weak stability, and high preparation costs for practical applications.

Quantification and mathematics of complexity

The article by Mao and Kotov³⁸ in this issue provides a contemporary review and highlights the emergent attention and opportunities on “complexity, disorder, and functionality of

nanoscale materials.” This article has made a heroic effort in putting the current studies on complex materials, numerous but a bit scattered, under a concise, generalizable framework. The emphasis includes how to define complexity in the context of nanomaterials, which can go beyond simple mathematical notions, how to establish methods to image and quantify complexity, and how to link structural complexity, ideally in a predictive and quantitative manner, with their functionalities.

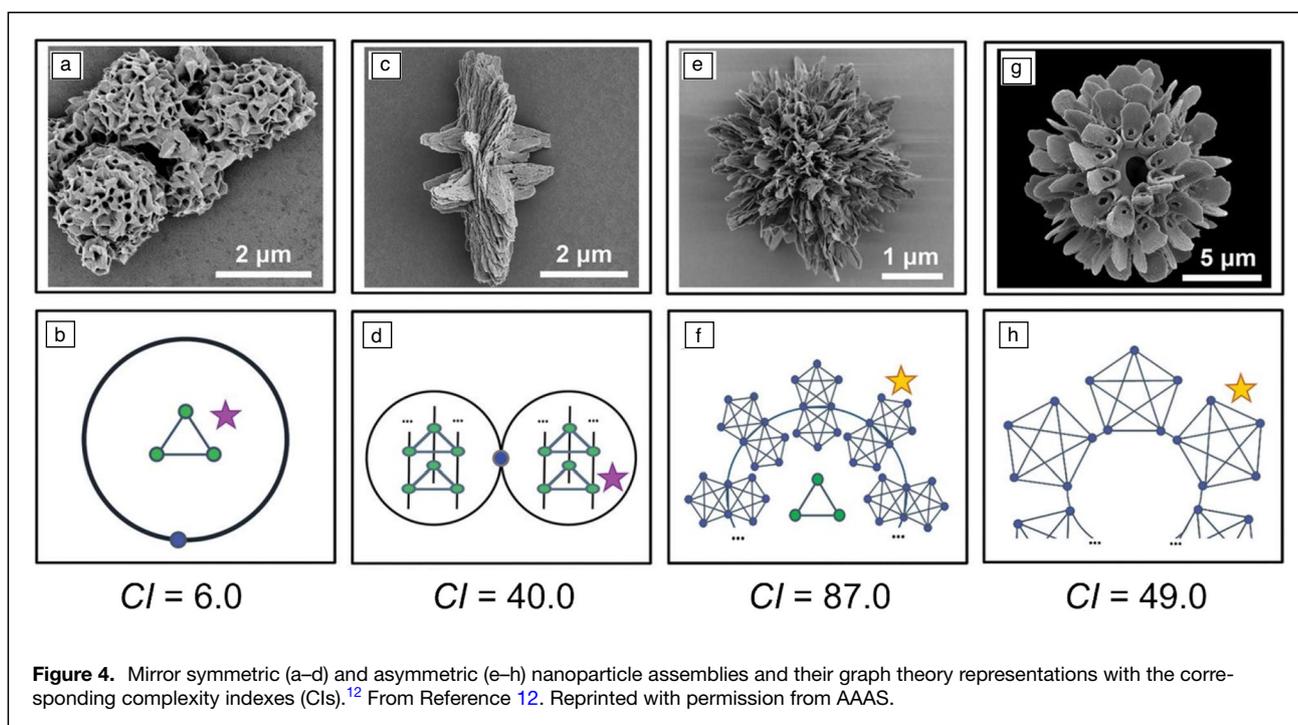
The article is highly interdisciplinary and an intellectually stimulating read. It started with a review of the historical perspective on complexity, which has been ubiquitous but vague. Algorithmic and information complexity (AIC) originated from Kolmogorov³⁹ was first highlighted to measure the complexity by defining the minimal rules needed to describe the structure. The more recent concept of a combination of order and disorder (COD) and self-organized criticality (SOC) focuses more on practical materials systems, is not bound to computational algorithms, and considers the context of the free energy landscape in equilibrium. It is noteworthy that complexity measures depend on the question we seek to answer behind complexity. If functionality, “functionality-based complexity” becomes important, which has been thoroughly reviewed with concrete examples. Coexistence of order and disorder can be important for the hierarchical organization of different building blocks. Reconfigurability or topologically determined mechanical response can also be engineered with certain aspects of complexity more important than others. Notably, the utilization of graph theory (GT), pioneered by the authors of this article,^{40,41} has shown great potential in describing such functionality-related complexities, especially for NP

assemblies (Figure 4). The key advantages of GT characterization are its capability to accommodate polydispersity (each node can be different) and arbitrary structure (no order or non-randomness of disorder is needed) and to invite a huge class of mathematical parameters to quantify the structures, from which one can delineate those that are especially important for the functionalities of interest. Examples are shown on how to measure such complexity by GT elicited from advanced imaging methods. The article ended with a discussion on the pathways toward complexity, including chirality, spatiotemporal chaos, geometric frustration, far-from-equilibrium assembly, and self-organization criticality, all of which cover both fundamentals of kinetic pathways of self-assembly and applications of pathway engineering for advanced materials.

High-resolution *in situ* characterization of assembly pathways toward complexity

A breakthrough on understanding the pathways toward complexity is the development of liquid-phase TEM techniques for imaging and understanding NP self-assembly pathways, namely how NPs interact with each other while undergoing motions upon thermal fluctuation in solutions.^{42–49} Such kinetic pathways were hard to probe even using simulation methods, because the practical complications of NP shape, inter-NP interaction, and entropic effects are all important,⁴² requiring validation and modifications based on direct experimental imaging.

These formation pathways can be complex, even if the final structures are periodic crystals. Classical one-step nucleation means direct transitions from dispersed, disordered individual NPs to the final crystal phase, while



nonclassical nucleation suggests the formation of prenucleation precursors.^{50–52} Great advances have been made for crystallization theory. In their article in this issue, Sushko⁵³ conducted a comprehensive review on the driving forces behind particle-based crystallization, exploring both experimental and theoretical aspects. NP assembly in solution is influenced by a complex interplay of entropic and enthalpic interactions, impacting particle–particle and interfacial solvent-mediated behaviors during attachment. In the first part of the review, Sushko delves into the current status of the oriented attachment (OA) theory. The interparticle interactions during OA are examined across different stages: approach, capture minimum, adhesion barrier, and adhesion. The approach involves the dominance of van der Waals forces and dipolar interactions, while the capture minimum sees attractive forces overcoming repulsive electrostatic forces. The adhesion barrier introduces steric hydration forces, and the adhesion stage, occurring upon physical contact, involves chemical forces like hydrogen bonding. The intricate details of solvent expulsion, defect elimination, and the role of crystal faces are all important in the context of OA, especially for face-specific forces and interactions such as hydration to drive the alignment of OA. Surface chemistry plays a crucial role, and simulations predict that particles align and attach along faces with a close-packed arrangement of charged species. The arrangement of charged groups on crystal faces is identified as a predictor for the likely mode of OA. In addition to OA, such facet-dependent interaction can also impact near-surface nucleation and assembly, as illustrated in the example of colloidal gold in citrate-containing solutions, where nucleation couples with assembly, leading to nonclassical growth processes.

Despite significant progress in understanding mesoscopic and macroscopic forces driving particle dynamics, many questions remain. Challenges include elucidating the elimination of ions and solvents during particle coalescence and developing a predictive theoretical framework that accounts for atomic polarization, interfacial solvent dynamics, and particle material properties. There remains still a need for a comprehensive approach that combines accurate quantum mechanical descriptions with mesoscopic correlation interactions for predictive modeling of the multiscale complexity in particle-based crystallization.

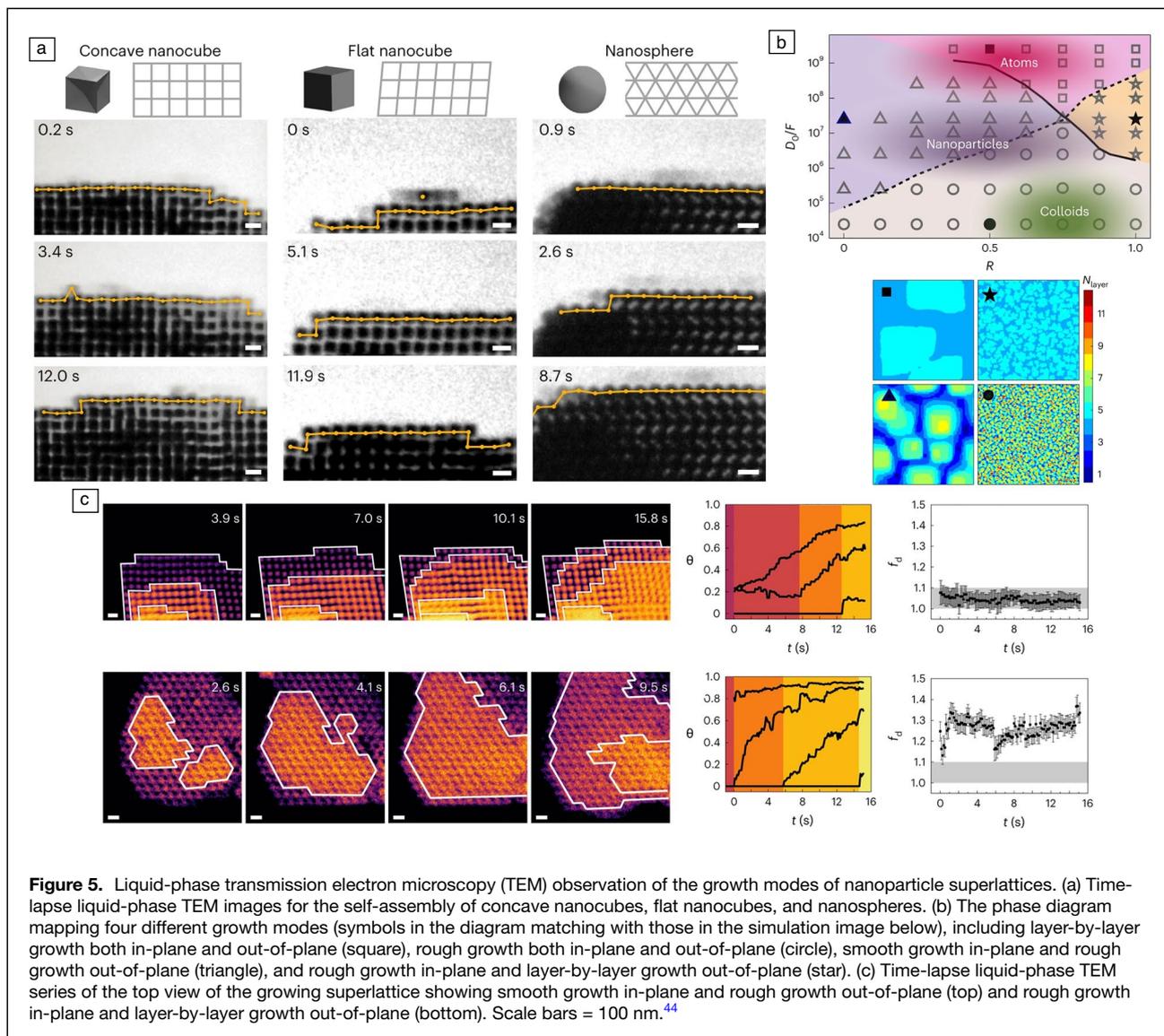
In this context, liquid-phase TEM possesses the unique advantage to image the NP interaction and self-assembly trajectories in real-time and real space. Liquid-phase TEM can accommodate tens to thousands of NPs with the single NP resolution when using SiN_x chambers. In comparison, the graphene-based liquid cells have too small a volume to observe the collective interaction and assembly dynamics of NPs.^{43,44,54–56} Over the last few years, the community has collectively resolved a few key issues, such as beam effects, NP–substrate interaction, and the control of NP concentration in the liquid chamber (i.e., level of supersaturation) to enable liquid-phase TEM a robust experimental tool to map

the NP assembly pathways on the otherwise inaccessible single NP level with nanometer resolution.^{57,58} Park pioneered the study of NP superlattice formation using emergent liquid-phase TEM where the solvent evaporation process was implemented.⁵⁵ Later work was able to retrieve large-scale in solution assembly pathways showing two-step nucleation as well as the formation of prenucleation motifs that are dense and amorphous. The two-step nucleation seems quite universal for carboxylate acid-coated NPs dispersed in water⁴³ and for polystyrene-coated NPs⁵⁴ dispersed in organic solvent. Moreover, liquid-phase TEM studies of even larger-sized crystal formation show that the pathways can be heterogeneous (**Figure 5**). Four growth modes can exist considering the in-plane and out-of-plane growth directions with smooth (layer-by-layer) and rough (steps and terraces) permutated.⁴⁴ The factors of energy barriers for diffusion and NP flux were shown to determine the kinetic growth modes and ultimately the surface morphology as well as bulk density of the superlattices. This aspect of progress synchronizes with the advancements of modern crystallization theory discussed by Sushko.⁵³ Thermodynamically and kinetically, multistep nucleation is favored in various atomic, molecular, and protein crystallization, which in turn provides a theoretical foundation considering the crystallization pathways. In their article in this issue, Kim et al.⁵⁹ have discussed in great detail the current and future liquid-phase TEM studies on NPs.

Liquid-phase TEM is not ensemble-based but resolves single NPs and is compatible with heterogeneity and disorder. Nucleation is a stochastic process with local fluctuations in structural order and packing density. Looking forward, liquid-phase TEM can also be utilized for understanding the formation of noncrystalline structures with broken symmetry. Reprinted and adapted with permission from Springer Nature.

Outlook

The unveiling and engineering of complexities will be enabled by modern characterization methods that are no longer ensemble-averaged and by ML-aided structural analysis that does not rely on just a few manually chosen descriptors. In addition to the liquid-phase TEM studies of NP self-assemblies discussed above, x-ray diffraction imaging-based tomography has been used to achieve 3D imaging of NP positions in a superlattice, mapping not only the overall structural order but also the extensive existence of 1D, 2D, and 3D defects.⁶⁰ This is an important discovery as most assemblies that were seen as crystalline under SAXS are not that perfectly crystalline after all. The existence of defects affects the mechanical structures, sometimes as the weakest point of the material. Furthermore, new analysis or quantification is needed. For example, in the description of patchy NPs, the NP edge length is no longer sufficient, and patches can be of various shapes determining the nature of their bonds. As a result, ML-based methods, such as shape fingerprints to convert the shape contours of patches into a 1D function,



are extremely important for quantification.⁶¹ Similarly, ML-based grouping methods are important in finding similarities out of a complex collection of self-assemblies. Of course, sometimes, the structures can be overwhelmingly complex, much like the chaotic patterns in weather, as awarded by the 2021 Nobel Prize in physics. That is where new mathematical tools that were traditionally foreign to NP self-assemblies, such as graph theory and network science, can initiate a foundational advancement for quantifying the complexity, thereby allowing for the establishment of a constitutive relationship linking the complex structure with synthesis or manufacturing routes and bulk materials performance.

Author contributions

Q.C. wrote the first draft of the article. X.Z. wrote the discussions on the Jiang and Sushko articles in this themed issue. Q.C. and X.Z. finalized the manuscript.

Funding

Q.C. acknowledges the support by National Science Foundation under Award No. 2243104. X.Z. acknowledges the support from IDREAM (Interfacial Dynamics in Radioactive Environments and Materials), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under FWP 68932.

Conflict of interest

The authors claim no conflict of interest for this study.

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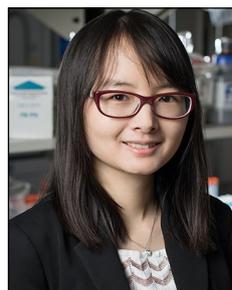
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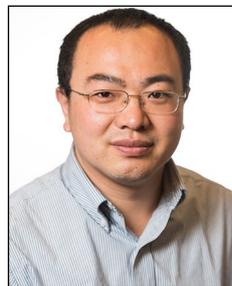
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