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Rational design of nanomaterials from assembly and reconfigurability of polymer-tethered nanoparticles

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Abstract

Polymer-based nanomaterials have captured increasing interest over the past decades for their promising use in a wide variety of applications including photovoltaics, catalysis, optics, and energy storage. Bottom-up assembly engineering based on the self- and directed-assembly of polymer-based building blocks has been considered a powerful means to robustly fabricate and efficiently manipulate target nanostructures. Here, we give a brief review of the recent advances in assembly and reconfigurability of polymer-based nanostructures. We also highlight the role of computer simulation in discovering the fundamental principles of assembly science and providing critical design tools for assembly engineering of complex nanostructured materials.

Introduction

We are in the midst of a materials revolution—a revolution in which materials will be designed, optimized, and engineered, rather than merely selected, for targeted properties, behavior, and function. Twenty-first century materials and devices will be made and tailored to target specifications, combining disparate and even competing attributes of multiple materials classes to achieve new functionality. They will be dynamic and responsive, able to reconfigure autonomously or on command, changing their appearance, strength, electronic, and other properties. Examples include reconfigurable automotive "skins" to optimize aerodynamics, smart prosthetics and bionics, shape-shifting robots, and camouflaging coatings with adaptive optical properties that, through biomimicry, match surroundings to avoid detection. This intrinsic tailorability and dynamism will contrast starkly with today's relatively static matter that is largely chosen, rather than designed, for the task at hand.[1]

Since the first studies of hard disks conducted in the late 1950s, computer simulation has evolved into a powerful, and in many cases, indispensable, tool for investigating atomic, molecular, and mesoscopic systems. Revolutionary advances in computer architectures and simulation algorithms over the past two decades have enabled computational scientists to elucidate problems spanning many orders of magnitude greater in time and length scales and from various angles. In particular, open-source molecular dynamics (MD) packages such as

Gromacs,[2] LAMMPS,[3] and HOOMD-Blue[4,5] have facilitated the spread of tools and ideas, as well as set a standard for rigorous and reproducible simulations that the scale from laptops to supercomputing clusters. More interesting, perhaps, is the ability of computational studies to offer predictions that are testable, which prove highly valuable for bottom-up engineering of nanomaterials. Finally, the ability to predictively design new materials is at hand, and available to computational experts and non-experts alike.

The rational design of nanomaterials via computer simulation requires identifying the desired target nanostructures, candidate-building blocks, and efficient assembly pathways. In this regard, computational techniques such as Monte Carlo, MD, and self-consistent field theory have played a vital role in predicting assembled structures obtained with almost arbitrary types of building blocks, including block copolymer and nanoparticle (NP) systems.[6–8] Coupled with today's increasingly powerful computing capacity, these techniques allow simulators to rapidly predict assembled morphologies, screen candidate-building blocks, and search for efficient assembly pathways over a wide range of parameters.

Next generation materials require new types of building blocks, made in large quantities, that can self-assemble into complex, functional, and reconfigurable structures.[9] Bottom-up assembly engineering builds upon the thermodynamic foundations of assembly science to engineer these building blocks in order to optimize the yield (quantity as well as quality) of a desired assembly. This paradigm shift is possible today due to the great strides in synthesis and characterization over the

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past decade. New NP and colloidal building blocks, comprised of organic, inorganic, and/or biological constituents, and with arbitrary shape and interaction patchiness, can now be made nearly to specification.

One interesting class of nanoscale building block is the tethered nanoparticle (TNP):[10] a NP to which a polymer tether (T) is permanently attached, creating a surfactant-like, amphiphilic object with a large (NP) head group and a tail (T). In more complex architectures, multiple tethers, of similar, or different types, attached at different places on the NP, are also possible. The TNP conceptual framework allows for tuning domain properties on nearly every scale.[10] When assembled, NPs make up the functional domains of the material, while polymer tethers form the continuous space between these domains; alternatively, the polymer domains can serve as the functional material, while NP domains can form surfaces or other structural elements. Moreover, TNPs create a spectrum of mesoscopic assemblies, including: (1) pseudo-two-dimensional (2D) assemblies (e.g. lamellae),[11–13] (2) micellar structures adopting body-centered cubic (BCC), Frank–Kasper, quasis-crystalline patterns,[14] and (3) complex gyroid,[15] diamond,[16] or other networks.[17] With such a wide range of assembly behavior, an enormous design space is accessible for the design and discovery of new materials.

We begin with a brief overview of the available toolkit for assembly engineering of TNP systems, which includes current advances in the synthesis of TNPs, as well as how they are being utilized in self-assembly. We then turn our attention to how computer simulation can be applied to rapidly screen candidate TNPs for useful structures, or even to predict the type of TNPs that might assemble a desired structure. Finally, we discuss how reconfigurability can be used as a tool to create more versatile and responsive structures from TNPs, reminiscent of biological systems.

Assembly toolkit for TNPs
Tethered NP building blocks

Tremendous effort in synthesis techniques has been devoted to controlling the shape, size, and composition of nanobuilding blocks for high yield and uniformity. Methods such as seed-mediated growth and redox transmetallation have been widely applied, allowing for a zoo of building blocks in various geometries (e.g. spheres, rods, cubes, plates, and stars) and materials (e.g. semi-conductor, metal and metallic oxides).[18] Other anisotropy dimensions have also been realized via selective surface modification, functionalization, and compart-mentalization.[19] For instance, NPs and colloids can be functionalized with different chemical moieties through the use of appropriate stabilizers and linkers [Fig. 1(a)]. To precisely control the number of the attached functional groups, one can take advantage of techniques based on "click chemistry"[21,27] and DNA conjugation.[22,23,28,29]

In the case of "click chemistry"[21,27] [Fig. 1(b)], multicomponent building blocks, e.g. surfactants and shape amphiphiles, are created through a series of sequential "click reactions",

namely the copper-catalyzed azide-alkyne cycloaddition reaction and the thiolene reaction.[21,27] This technique has recently been used to interchange nearly every portion of the building block.[21,30–32] Examples include the ability to interchange head groups from polyhedral oligomeric silsesquioxane (POSS) cages to gold NPs, as well as to exchange polymer types such as polystyrene or poly(methyl methacrylate) (PMMA); additionally, the size, number, and placement of these chemically distinct domains can be controlled, such as tethering a single corner of a POSS molecule with one or more polymer tethers.[21,27,30–32]

Related methods have been used to create additional types of polymer–NP composite blocks. Protein–polymer conjugates, for example, were created using a covalent binding malei-mide–thiol coupling reaction to create bioconjugates.[33–35] These bioconjugates were also been used in self-assembly experiments, demonstrating the same phase diversity as related building blocks.[35] Other materials, such as polyoxometalate anionic metal–oxygen nanocages, have been successfully attached to polymer tethers via covalent bonds.[36,37] As these studies demonstrate, a wide range of materials are amenable to this type of modification and are experimentally accessible, opening up an enormous design space for new functional materials.

An alternative strategy that has also produced numerous candidate TNPs is to functionalize NPs or colloids with a finite number of DNA oligomers [Figs 1(c) and 1(d)]. The highly specific interactions between complementary strands of DNA induce attraction between specific NP-type pairs. This suggests a robust framework that has already enabled the design of numerous NP superlattices upon tuning the NP size and bond distance using DNA linkers.[22,23,29]

TNP colloidal "molecules" are indeed reminiscent of their molecular counterparts, as their interaction can be made directional and highly specific. For example, coordination polymeric structures exist that link polymeric or molecular subunits using non-covalent interactions, creating adaptive, and responsive polymer-like superstructures. In these building blocks interactions are made highly specific at certain sites via the use of suitable metallic ions and ligands [Fig. 1(e)].[24] Patchy particles and multicompartmentalized particles are realized via selective surface treatment methods[38] and electrohydrody-namic co-jetting [Fig. 1(e)], respectively. Recently, Sacanna and Pine[39] reported a simple, yet generic, route to fabricating colloids with tunable cavity, which enable a host of complex assemblies.

It is interesting to note that techniques now are available to consider the synthesis and fabrication of building blocks whose size and shape can change, in situ, in a controlled manner. For example, colloidal gold nanorods can be shortened or shifted irreversibly to other shapes such as spheres, bent, twisted, or φ-shaped using laser pulses with different wavelengths and widths.[40–42] Kim et al.[43] reported thermally responsive capsule structures with 25 nm diameter pores on shells formed by hierarchical self-assembly of double-tethered rod amphiphiles. Upon heating or cooling, the hydrophilic oligo-(ethylene oxide)
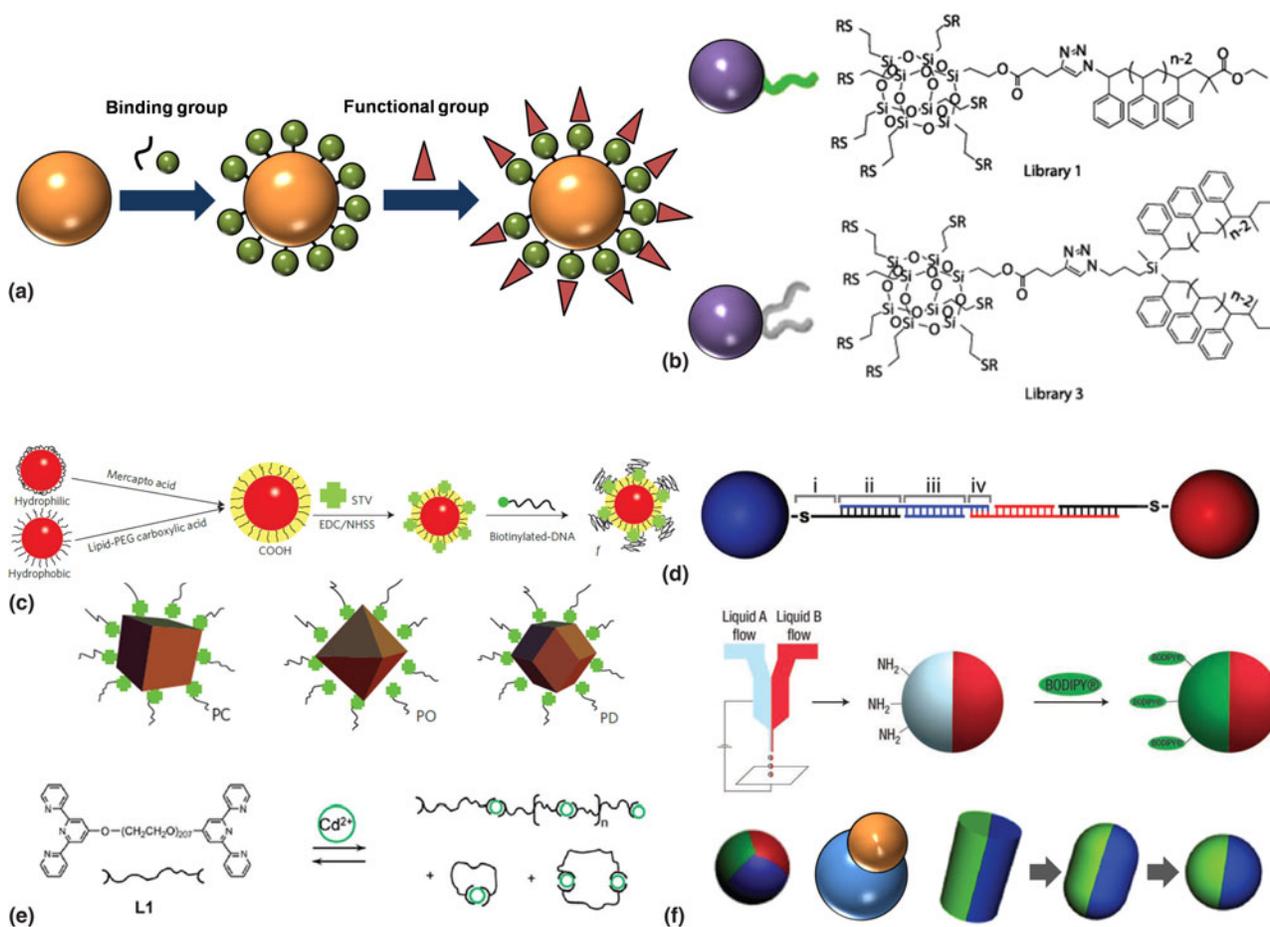
Figure 1. Building blocks synthesized from various techniques: (a) Functionalization (adopted from Ref. 20); (b) click reactions (Ref. 21); DNA conjugation with (c) multiple DNA strands[22] and (d) single DNA strand[23] per building block; (e) coordination with metal ions,[24] and (f) electrohydrodynamic co-jetting methods that are used to produce multicompartmentalized building blocks[19,25,26]. Panel (c) reprinted by permission from Macmillan Publishers Ltd.: *Nature Nanotechnology*[22], copyright 2013. Panel (d) from Ref. 23. Reprinted with permission from AAAS. Panel (e) adapted from Ref. 24 with permission of The Royal Society of Chemistry.

coils at one end of the rods shrink or expand, respectively, resulting in a reversible closed/open gating motion of the nanopores. They also demonstrated a reversible transformation between 2D sheets and tubular structures assembled by laterally grafted rod amphiphiles upon heating via a similar mechanism.[44] Alternatively, polypeptide-based block copolymers can be used as stimuli-responsive building blocks due to the ability of the polypeptide segments to adapt various conformations.[45–47] For instance, Gebhardt et al.[47] demonstrated that the polypeptide rod segment in the poly(butadiene)–poly (L-lysine) block copolymers undergoes an R-helix to coil transition in response to a change in pH and temperature. Yoo et al.[48] synthesized polymeric particles that are able to switch shape in response to changes in temperature, pH, and chemical additives. Multicompartmental particles based on poly-(lactic-co-glycolic acid) are able to morph into various shapes upon heating one of the polymeric compartments above its glass transition temperature.[26]

Assembled nanostructures

While initial experimental efforts were primarily directed at TNP synthesis, attention has increasingly turned to structure assembly. Tethering short polymer segments to NPs produces an enormous design space, comparable with that of copolymers, but with an expanded spectrum of properties and structures beyond the complex phases exhibited by coordination polymers and block copolymers[6,7,24,28,49–53] [Figs 2(a)–2(c)].

As mentioned previously, direct realizations of TNP assembly have come from the use of "click chemistry" to attach tethers to NPs directly, creating gram quantities of material.[21,27,30] TNPs created with this method have been used to self-assemble many of the same structures observed in block copolymers, but with the additional benefit of controlling the specific material composition of each domain of the material. By tuning various portions of the block geometry, different types of structures are accessible. For example, by increasing the length of a polystyrene tether attached to the corner of a POSS cube Cheng
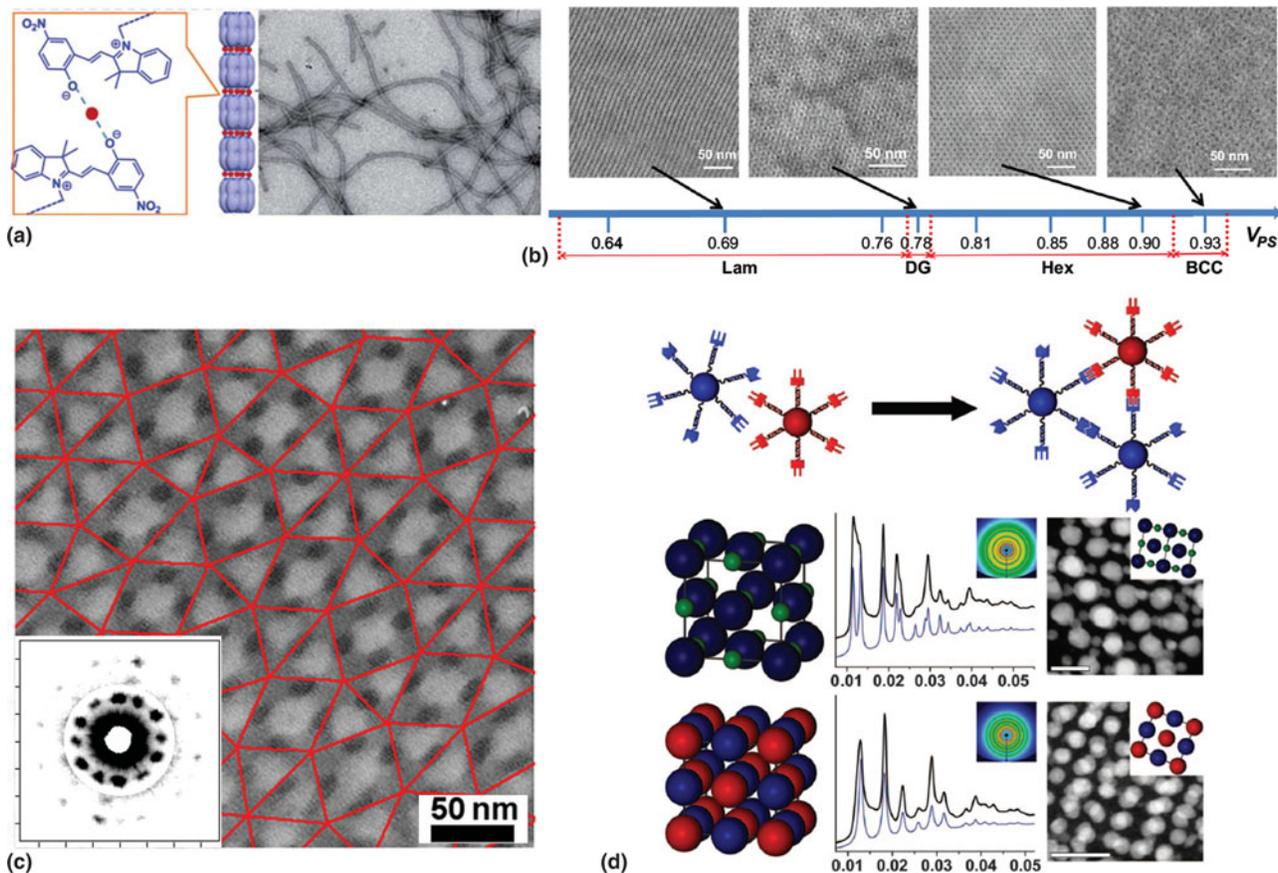
Figure 2. Static assemblies: (a) Nanotubular assemblies from coordination polymers upon addition of divalent metal ions (red circle),[24] (b) assembled structures from shape amphiphiles, including lamellar, gyroid, hexagonal cylinders, and BCC micelle phases, as reported in[21]. (c) Dodecagonal quasicrystal formed in a blend of polyisoprene–polystyrene–poly(2-vinylpyridine) star block copolymers/polystere homopolymer blend.[53] (d) Ordered structures formed by gold NPs functionalized with complementary DNA strands (top): NaCl lattice (middle) and simple cubic lattice (bottom)[22]. Panel (a) adapted from Ref. 24 with permission of The Royal Society of Chemistry. Panel (c) reprinted with permission from Ref. 53. Copyright (2007) by the American Physical Society. Panel (d) from Ref. 23. Reprinted with permission from AAAS.

et al.[31] can tune between lamella, the double-gyroid, hexagonal tubes, and BCC micelles, as seen in Fig. 2(b). Moreover, these structures demonstrated a high degree of sensitivity to the block features; by fixing the volume fraction of each component, but adding additional tethers to one corner of the POSS cube, they could induce a phase inversion in the hexagonal tubes phase, resulting in a matrix of POSS and tubes of polymer. Similarly, by replacing a single tail with two tails of half the length, they could select either the double gyroid for the former or hexagonal tubes for the latter. As we will highlight in the following section, computer simulation has played a large role in predicting the types of morphologies we observe in TNP systems and will continue to help guide work as these materials are integrated into devices. It is important to note that while initial experimental work has demonstrated the feasibility of the synthesis and assembly of these materials, there are still enormous opportunities for the design of new building blocks and structures.

For building blocks with highly specific interactions, it is possible to design nanostructures with a higher degree of complexity. For instance, using self-complementary and non-self-complementary DNA strands, Macfarlane et al.[23] have showed that one can program the multivalent interaction between DNA-functionalized NPs. With such encoded interactions, the resulting structure can be a NaCl or simple cubic lattice, depending on the size ratio of the inorganic NPs [Fig. 2(d)].

Shape-changing TNPs provide additional possibilities for structural complexity in resulting assemblies. For example, Lee et al.[44] showed that a bilayer sheet formed by rod–coil molecules in aqueous solution roll into a tubular structure upon heating and vice versa [Fig. 3(a)]. The driving force for reconfiguration is attributed to the increase or decrease in the excluded volume interaction of the coil segments in response to the change in temperature. As another example, the lattice spacing of the superlattices formed by DNA-grafted gold NPs
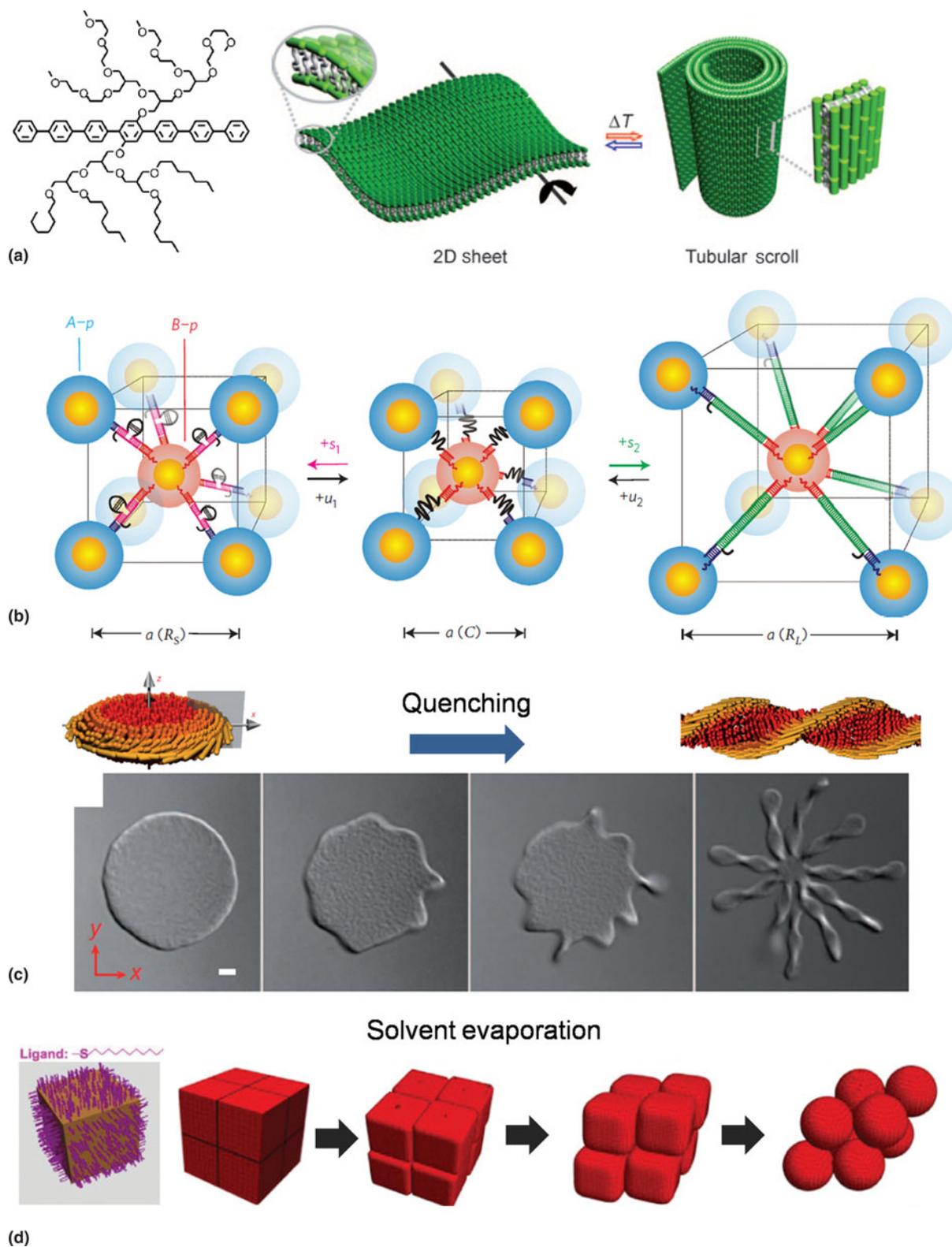
Figure 3. Reconfigurable assemblies: (a) Reversible transformation between flat sheet and tubule formed by rod–coil macromolecules upon heating and cooling[44]; (b) BCC structure with lattice spacings tunable by adding set and unset DNA strands[54]; (c) transition from a disk into twisted ribbons upon quenching[55]; (d) transition from a simple cubic lattice to face-centered cubic lattice assembled by dodecanethiol ligated palladium nanocubes[56]. Panel (a) from E. Lee, J. K. Kim, and M. Lee. "Reversible scrolling of 2D sheets from self-assembly of laterally grafted amphiphilic rods." *Angew. Chem. Int. Ed. Engl.*, John Wiley and Sons Publishing Group. Panels (b) and (c) reprinted with permission from Macmillan Publishers Ltd: *Nat. Nanotechnol.*[54], copyright 2009, and *Nature*[55], copyright 2012. Panel (d) reprinted with permission from Ref. 56. Copyright (2011) by the American Physical Society.

was shown to be tunable upon adding suitable set and unset complementary DNA strands[44] [Fig. 3(b)]. Consequently, one can imagine the application of such dynamic superlattices to responsive photonic band gap materials or automative "skins". By tuning the interfacial tension via temperature, Gibaud et al.[55] reported a novel way to induce morphological transitions in colloidal membranes through changes occurred at microscopic levels [Fig. 3(c)]. Zhang et al.[56] demonstrated that a simple cubic lattice of palladium nanocubes coated by dodecanethiol ligands in toluene, a poor solvent for the ligands, transforms into a rhombohedral lattice upon solvent evaporation [Fig. 3(d)]. Shifting of the NP shape from cuboid to ellipsoid was attributed to the swelling ligands as the solvent concentration decreased during evaporation.

Computational design of functional nanostructures

Given the versatility of the assembly toolkit and the enormity of the design space provided by TNPs, what types of structures are possible? Can we design and assemble domain-specific materials with precisely controlled bulk and nanoscale properties?

This question drove an initial flurry of computational investigation into tethered NPs[10,57] a decade ago. Nanoparticles, it was hypothesized, would offer a truly limitless design platform, provided they could successfully be used to create composite polymer–NP blocks. Initial investigations focused on establishing relationships between existing theory for polymers and surfactants, and TNPs via simulation.[11,58] Toward this end, the focus has been on the phase behavior[10,11,15,57,59] and properties[60–64] of TNPs, as a function of the size of the isotropic NPs. Figure 4 shows examples of interesting assembled structures from our studies, including double gyroids,[17] cylinders and columnar structures,[65] bilayer sheets,[66] and dodecagonal quasicrystals.[14] Key amongst these findings was the realization that the phase behavior of tethered NPs, to a great extent, is consistent with that of surfactants and liquid crystals.[11] Recently, many of these initial findings have also been corroborated with experiments.[31]

Given the close relationship between tethered NPs and liquid crystals,[58] the roles of the shape of the NP head group have also been extensively investigated.[12,13,67–70] In these cases, it was again found that structures and transitions similar to those in liquid crystals were observed, such as lamella, gyroids, cylinders, and micelles. However, the connectivity and coordination of the micelles and networks were altered by the packing of the head groups. Additional types of liquid-crystalline ordering were found within these domains, such as long micelles and lamella,[69] twisted columns and sheets with liquid crystalline order,[12,13,67] honeycombs,[13] and gyroids.[68]

The focus of recent studies has included increasing the architectural complexity of TNP building-blocks, including interactions between blocks and the solvent, as well as tuning their respective block volume fraction, thereby mirroring trends within the copolymer community.[50] Asymmetry within these

domains, for example, can be tuned between single- and double-gyroid morphologies.[17] Moreover, controlling their architecture and interaction has led to open, simple cubic, and diamond networks,[71] which are known to be useful candidates for photonic applications.[72–75] As the spacing and characteristics of individual domains can be tuned in a reliable manner, it is possible to propose new and previously inaccessible structures, as well as create complex and hierarchical morphologies.[76–83] Finally, the solvent selectivity is important to the kinds of morphologies that will assemble, and has been found to dramatically affect the nature of self-assembled structures allowing for a wide variety of tunable micellar structures.[84]

As the complexity of static assemblies has grown over the past decade, so too has the desire to incorporate these assemblies into devices and other applications. Recently, particular interest has grown in tunable, responsive assemblies. Drawing inspiration from nature and biology, researchers aim to create building blocks that can dynamically respond to either internal or external stimuli. Enzymes and proteins, for example, change their conformation and interactions to activate processes within the body as necessary.[85] Similarly, simplistic versions of these building blocks could, for example, suppress the formation of close-packed structures that then lead to other complex structures that would be otherwise inaccessible, such as quasicrystals or Frank–Kasper phases.[14,86,87]

Toward this end, the work has begun on dynamic blocks that can reconfigure during assembly. Early investigations were largely centered on simply introducing anisotropy in a single dimension to building blocks during a simulation. Using computer simulation, for example, Batista et al.[88] studied the crystalline packing of deformable spherical colloids. They modeled the shape change in the colloids by allowing the spherical particles to continuously change shape into prolate or oblate ellipsoids. Interestingly, the system was shown to undergo a second transition to an orientationally ordered crystal upon shape shifting. Nguyen et al.[66] predicted that when the rod segments in polymer-tethered nanorod systems are shortened or lengthened continuously, the assembled structures reconfigure between various mesophases such as square grids, honeycomb, and bilayer sheets. This idea was extended to more complex structural transitions, including transitions between 2D tiles such as rhombi and pentagons, as well as kinked rods, zigzags, and cross structures.[89] Importantly, these studies showed not only reversible transitions between equilibrium assemblies, but also the ability to obtain configurations that would otherwise be inaccessible to static building blocks. Such transitions are exciting because they open up the possibility for obtaining structures that otherwise do not appear in equilibrium self-assembly.[90]

Conclusion and outlook

With powerful tools in hand both to synthesize TNP-building blocks of arbitrary complexity,[30] and to simulate their assembly behavior,[17] it is tempting to begin exploring complex assemblies that could lead to new applications and devices.[91–94]
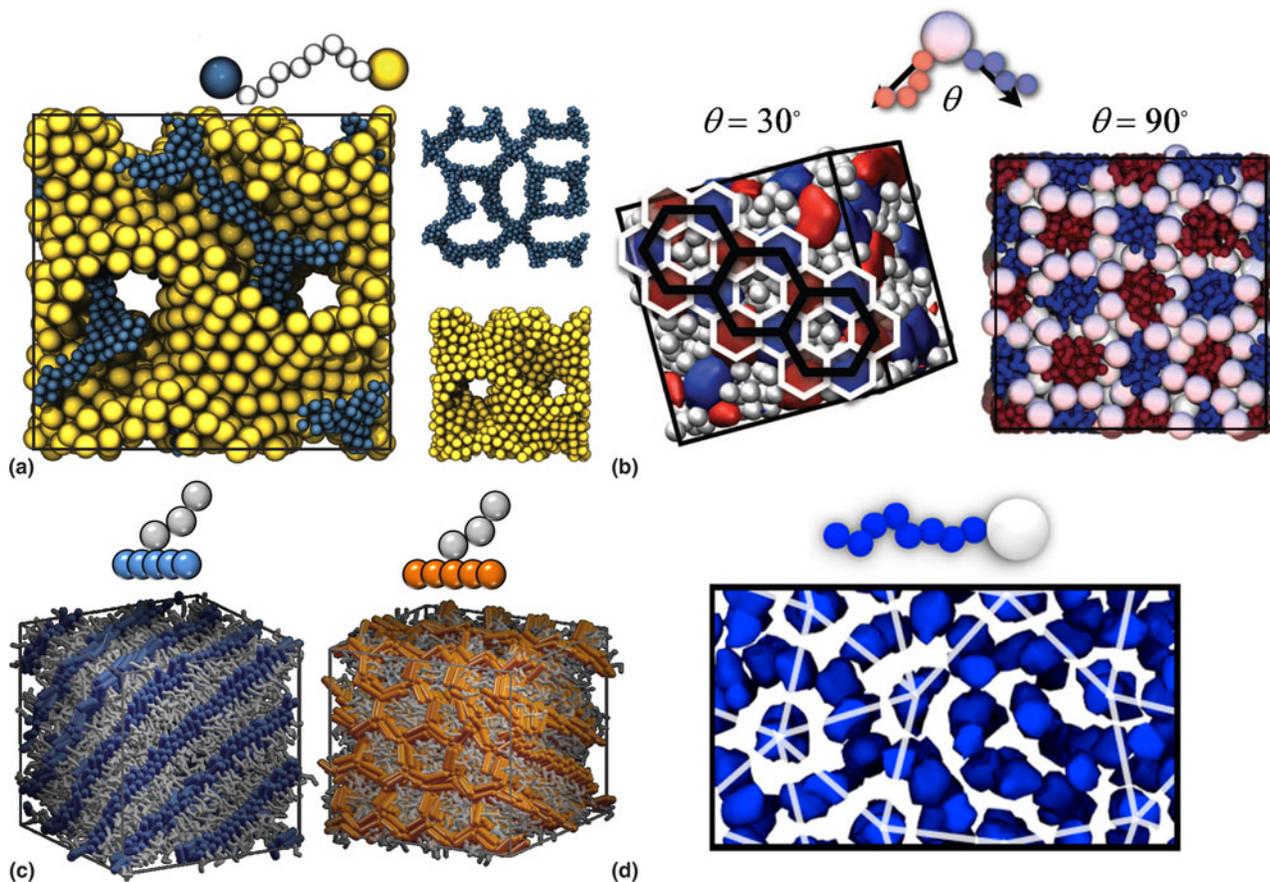
Figure 4. Simulation predictions: (a) Double gyroid formed by TNP telechelics[17]; (b) tetragonally cylinder structure, and [6;6;6] columnar structure assembled by di-tethered nanospheres with different planar angles, θ, between two tethers[65]; (c) bilayer sheets and honeycomb grid formed by laterally tethered nanorods[66]; (d) dodecagonal quasicrystal formed by mono-tethered NPs[14]. Panel (a) reprinted with permission from Ref. 17. Copyright (2014) American Chemical Society." Panel (b) reprinted with permission from Ref. 65. Copyright (2009) American Chemical Society. Panel (b) reprinted with permission from Ref. 66. Copyright (2010) American Chemical Society.

A pressing challenge is unifying these tools before moving into application. We have highlighted just a few of the conceptual design axes, as we highlight in Fig. 5. Despite having already sketched out a framework that encompasses the vast design space,[9] linking structural prediction to properties within a simulation framework would expedite application-specific design. As new building blocks and assemblies continue to emerge, the fundamental question is no longer if we can build targeted structures of exquisite complexity, but how we can design a target structure? What specific building blocks or set of interactions may lead to its formation, and how can the assembled structure be utilized from a technology standpoint?

Knowing the target structure that will suit a particular application is one of the most crucial aspects of the problem. Diamond structures, for example, are known to be excellent candidates for photonics applications.[72–75] The challenge is then to supply a proper set of design conditions to produce the structure. Computation allows us to rapidly screen candidate blocks for targeted assemblies. New data science approaches, coupled with high performance computing-enabled prediction of TNP self-assembly, promise to further expedite material design in this space,[95–97] in the spirit of the Materials Genome Initiative.[98]

Tethered NPs and related structures hold a great deal of promise as candidate-building blocks for next generation materials. Their design flexibility makes them useful for a wide range of potential applications. The theory that drives their assembly is well understood, while computation allows us to quickly make predictions about their assembly behavior. Many realizations of TNP assemblies that were initially predicted via simulation have been realized in the laboratory. Researchers now have the ability to predict, design, and assemble targeted structures for a given application. Importantly, these predictions are not specific to particular material types, and thus can guide the synthesis and assembly of many types of TNPs. Moreover, this design approach provides experimentalists flexibility in their design strategy—the same set of results holds equally for polymer-tethered gold particles, or proteins,
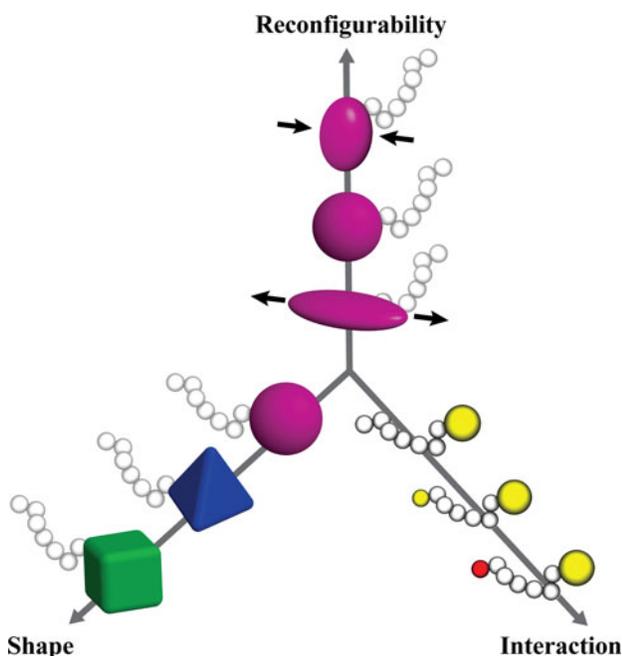
Figure 5. Anisotropy axis for relevant assembly dimensions in TNP systems. By tuning NP shape and interaction, researchers can tune the resultant structure and ordering in TNP systems. Additionally, reconfigurability of these building blocks will allow for tunable and responsive next-generation materials.

as for giant surfactants of ligand functionalized POSS molecules, provided the geometric length scales of particle and tether are commensurate. Any materials that are amenable to surface modification can be incorporated into this scheme, providing a versatile materials design platform.

Acknowledgments

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