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Patchy Nanoparticle Synthesis and Self-Assembly

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Abstract

Biological building blocks (i.e., proteins) are encoded with the information of target structure into the chemical and morphological patches, guiding their assembly into the levels of functional structures that are crucial for living organisms. Learning from nature, researchers have been attracted to the artificial analogues, “patchy particles,” which have controlled geometries of patches that serve as directional bonding sites. However, unlike the abundant studies of micron-scale patchy particles, which demonstrated complex assembly structures and unique behaviors attributed to the patches, research on patchy nanoparticles (NPs) has remained challenging. In the present chapter, we discuss the recent understandings on patchy NP design and synthesis strategies, and physical principles of their assembly behaviors, which are the main factors to program patchy NP self-assembly into target structures that cannot be achieved by conventional non-patched NPs. We further summarize the self-assembly of patchy NPs under external fields, in simulation, and in kinetically controlled assembly pathways, to show the structural richness patchy NPs bring. The patchy NP assembly is novel by their structures as well as the multicomponent features, and thus exhibits unique optical, chemical, and mechanical properties, potentially aiding applications in catalysts, photonic crystals, and metamaterials as well as fundamental nanoscience.

Keywords: patchy nanoparticle, colloidal synthesis, self-assembly

1. Introduction

1.1 Definition and types of patchy particles

Anisotropic particles have been one of the fundamental focuses of materials research since their introduction several decades ago [1–4]. In the search for the next breakthrough functional materials, tremendous efforts have been dedicated to surface anisotropic particles. Surface anisotropy has proven to be vital in biological systems; examples include the surface structure of virus capsid, which enables the spread of disease by self-assembly of viral particles in vivo [5], and globular proteins with patches, which act as recognition sites [6].

Starting from Janus particles with two dissimilar hemispheres, anisotropic particles with dual or multiple surface patches [7], i.e., patchy particles, have been

introduced over the past decades. Patchy particles are defined as a class of particles with discrete patches that induce strongly anisotropic and highly directional interactions, which can facilitate their self-assembly into ordered structures [8]. The patches are described as distinct features with limited numbers on the surface of core particles [8], and their properties, location, and numbers can be well controlled during synthesis [9].

The concept of patchy particles has been investigated in the realms of “hard” patchy colloids, hard colloids with “soft” patches, and soft patchy micelles. Hard colloids refer to colloid particles that do not exhibit morphological changes in suspension [10], including metal, metal oxide, and silica particles along with cross-linked polymer particles. Such patchy colloids can be synthesized from the controlled clustering of several individual particles and inorganic patch growth on parent particles [11, 12]. When the patches are soft materials such as polymer or DNA, they give different self-assembly behavior compared with hard counterparts. A recent example of this type of patchy particles is the gold triangular nanoprism with polymer patches on the three tips [13]. Lastly, patchy micelles are made from block copolymers with an insoluble core and soluble patches which can be distinguished chemically or physically [14]. Patchy particles are of interest in self-assembly as they generate unique assembly structures. For example, gold nanorods (AuNRs) with polymer patches were observed to self-assemble into clusters, linear and branched chains [15–17]. Furthermore, triblock copolymers are shown to first assemble into patchy micelles and further into linear and network superstructures [18].

1.2 Applications of patchy particles

Gaining control over the interactions between particles through their patches enables the potential bottom-up fabrication of functional materials for drug delivery, electronics, photonics, and sensors [19, 20]. Colloidal patchy polymers with the ability to self-knot have been proposed as prospective drug delivery vehicles [19]. These colloidal patchy polymers have a lock-unlock mechanism controlled by the end monomers, enabling the transport and release of drug molecules. DNA-patched particles with directional interactions governed by thermal reversibility have also been introduced with potential applications in drug delivery, solid-state electronic devices, and photonic crystals [21]. The self-assembled bidirectional percolated network and lattice structures of patchy metal-dielectric particles under high-frequency alternating current (AC) electric fields have been demonstrated as a promising method to achieve bottom-up fabrication of devices [20]. The self-assembly of these particles can be further guided by quadrupolar and multipolar interactions, and it has potential applications in the fields of photonics and electronics.

Although many self-assembled patchy particles with potential applications are being routinely presented, the current advancement in the field is not enough to meet the complex needs of future technological applications [8]. For synthetic self-assembled patchy particles to serve advantageous purposes in the fields of medicine, electronics, and photonics, structural complexity and hierarchy should be achieved, as those in biological functional structures. However, there are a few challenges in achieving such complex high order structures from synthetic patchy nanoparticles: the difficulty to precisely synthesize particles that are highly monodispersed in patch size and position; to arrange particles into highly ordered large-scale structures by fine-tuning the interaction; and to “position” the kinetic assembly pathways on the single particle level.

1.3 Scope

Nanoparticles are of special interest to the patchy particle community as they serve as versatile building blocks encoded with directional interactions, which enable spontaneous assembly into exotic structures for novel functional nanomaterials [22]. Hence the primary scope of this chapter will be patchy nanoparticles. This chapter covers both the experimental aspect—fabrication and self-assembly of patchy nanoparticles—and the simulation studies of their assembly behavior. We will first discuss controlling the multidimensional design space of patchy nanoparticles, with special considerations on the impact of core and patch design, followed by presenting three routes of patchy nanoparticle synthesis. A review of interactions driving self-assembly, including van der Waals (vdW), electrostatic, hydrophobic, functional group-based, other entropy-related, and field-assisted interactions, is then presented, with simulation of patchy nanoparticle assembly as a complimentary tool to guide and explain experiments. Finally, the rational design of kinetic assembly pathways for achieving three-dimensional (3D) hierarchical lattice is discussed, as well as our vision in the future directions of patchy nanoparticle assembly.

2. Preparation of patchy nanoparticles

2.1 Design rules of core and patch

Patches are distinct domains of surface chemistry (enthalpic patch) or structure (entropic patch) on particles. The regional inhomogeneity of patchy nanoparticles encodes directional interaction between patches, which determines the favorable interparticle alignment. Consequently, although core nanoparticles still matter, “patchiness” can completely alter the interaction dynamics and govern the final superlattice structures. The decades of extensive studies on conventional nanoparticles without patches have revealed the factors determining interaction between nanoparticles and their packing behavior, including shape anisotropy [23, 24], crystal facets [25], and entropy of the system [26, 27]. In recent years, both in experiment and theory, researchers have been trying to identify the design parameters for the patches to direct assembly behaviors of patchy nanoparticles. Some of those parameters are size [28], composition [29], surface chemistry [30, 31], symmetry [32], number of patches per particle [33, 34], as well as the binding energy between the patches [35]. While understanding the key design parameters is complicated because the impact of each is often hard to decouple from one another, some well-established design rules for patchy particles are listed herein. First, unlike the spherical nanoparticles without patches, whose coordination number in lattice is driven by the maximum packing density, in the case of the patchy nanoparticles, the “valency” is determined by the number of the patches. While symmetrically placed 12 patches on nanoparticles leads to the formation of face-centered cubic (*fcc*) superlattice due to the quasi-isotropic net interaction, decreased number of patches can generate lattices with lower structural symmetry and even open lattices that are hard to achieve by conventional nanoparticles [36, 37]. Note that even with the same number of patches and the same core shape, the particles can assemble into different final lattices as the angular symmetry of the patches changes. Second, the relative size of the patches to that of the core nanoparticle alters the valency of the patches. In the simplest case, the particles with one patch can undergo self-limited assembly into dimer, trimer, and tetramer clusters, as the relative patch size decreases. For the particles with multiple patches, optimal patch width is a trade-off

between structural selectivity and kinetic accessibility [38]. Thus, the patches should be small enough to energetically favor the desired clusters. Meanwhile, they also need to be sufficiently large to bypass the kinetic traps, which will prevent the large-scale ordering. One of the successful examples achieving such is Kagome lattice by Chen et al. [36]. Following theoretical studies have revealed that the large-scale Kagome lattice is formed due to the balance in interactions caused by the patch area-dependent coordination number and entropy [39].

2.2 Synthetic routes of patchy nanoparticles

Inhomogeneous surface chemistry or local structure on nanoparticles can be obtained by a range of approaches, including colloidal assembly, phase separation, and site-specific surface modification. Such methods are mostly in solution base, thus can be easily scaled up with proper engineering. A library of patchy nanoparticles with controllable geometry and chemistry achieved herein paves the way to bring unprecedented assembly structures that cannot be realized by conventional nanoparticles with homogeneous surface.

2.2.1 Controlled assembly of nanocolloids

The assembly of conventional nanoparticles without patches into small clusters is a facile way to synthesize patchy nanoparticles. The immediate advantage of this approach is that two or more pre-synthesized nanoparticles with desired qualities (e.g., size, shape, monodispersity, and crystallinity) can be incorporated into a single moiety [40–42]. However, precise control over cluster size and shape requires optimal assembly condition [40]. First, the suspension of colloidal particles is destabilized due to interparticle interactions that are strong enough to assemble nanoparticles into clusters. Then the assembled clusters are prevented from further aggregation aided by surface charge, steric hindrance, or low enough particle concentration causing diffusion-limited assembly process. Such clusterization in a controlled manner can be realized by various types of interactions, including vdW, electrostatic, depletion, chemical bonding, or geometrical confinement.

The morphologies of patchy particles formed by clusterization are often driven by minimization of free energy. Wagner et al. [43] demonstrated the preparation of clusters composed of 2–7 spherical polystyrene (PS) nanoparticles, by combining ultrasonication-induced miniemulsions with dense packing—minimizing the second moment of the mass distribution, originally developed by Manoharan et al. [41]. Ultrasonic emulsification provided large yields of various patchy particles with a narrow size distribution, including line segments, triangles, tetrahedra, and octahedra (**Figure 1a** and **b**). Note that in order to achieve desired geometries, the subtle strength of interaction between nanoparticles is required to avoid rapid assembly and to allow the particles to rearrange within the clusters. When it comes to clusterization of binary composites with opposite charges, the balance of two competing forces, attraction toward the center particle and repulsions between the outer particles, at given feeding ratio assists controllable clusterization [44].

In case of metal or semiconductor nanoparticles with similar lattice constants of the core and the patch materials, oriented attachment can aid the clusterization process. Xiong et al. [45] synthesized heterodimers composed of silver prisms and Ag₂S spheres. Patchy nanoparticles with controllable size and thickness can be easily achieved by varying the dimension of prism and sphere constituting the structure. The as-synthesized patchy nanoparticles have remarkable bactericidal activity under illumination of visible light, attributed to the Ag/Ag₂S junction formed via oriented attachment. Furthermore, nanoparticles without the lattice

Figure 1.
(a) Schematics demonstrating cluster preparation. First, ultrasonication makes miniemulsion with toluene droplets ($<2\ \mu\text{m}$ in diameter) containing PS particles bound to the surface. Then the clusterization of the particles is driven during the evaporation of toluene. (b) The background photo shows a test tube containing a fractionized suspension of clusters differentiated by size after centrifugation in a density gradient. Inset scanning electron microscope (SEM) images show clusters obtained from six distinct bands: single particles (1), doublets (2), triplets (3), tetrahedrons (4), triangular dipyramids (5), and octahedrons (6). Fraction 7 contains clusters consisting of seven or more PS particles. Scale bars: 200 nm. Adapted from Ref. 44. Copyright 2008 American Chemical Society. (c) Mechanism of a two-step clustering and subsequent welding process making Au/Ag₂S patchy nanoparticles. Adapted from Ref. 46. Copyright 2019 Springer Nature.

match can cluster into well-defined composition by coulombic attraction. For example, using oppositely charged gold and chalcogenide nanoparticles, Huang et al. [46] demonstrated a method to synthesize patchy nanoparticles (Figure 1c). Their process involves a two-step mechanism of clustering and subsequent welding process, during which ligand desorption-induced conformational contact between nanoparticles allows atomic diffusion at the interface. Therefore, nanoparticles can assemble into patchy particles with desired composition, despite different capping agents, different solvent media, or large lattice mismatch between core and patch materials. Likewise, nanoparticle assembly via clusterization can provide a library of patchy nanoparticles with various patch composition and shape. However, the major drawback of this method is that patchy particles have low monodispersity in terms of the size and geometry of the clusters due to angular degeneracy. In order to improve the size dispersity, centrifugation or filtration can be used to separate the clusters of desired size among other types. Moreover, to achieve patchy nanoparticles with desired geometry, directional bonds of DNA wireframes can be used to guide tailored polyhedral shape, expanding the library of controlled assembly-derived patchy nanoparticles [47].

2.2.2 Phase separation-derived method

Phase separation is driven by the thermodynamic instability of a homogeneous mixture to lower the free energy of system upon the creation of two or more distinct phases. These mechanisms have been applied to polymer blends [48] and metallic glasses having components with different miscibility [49], in order to fabricate well-ordered or porous films that cannot be easily achieved by “top-down” nanolithography.

On the nanoparticle level, phase separation has also shown its value in preparing a variety of patchy nanoparticles with distinct surface chemistry, compositions, and shapes. For example, using the self-assembly induced phase separation of triblock terpolymer of polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate), Muller

and co-workers reported Janus, hamburger, clover, and football patchy nanoparticles [50, 51]. The different morphologies are attributed to the variations in the length of polymer blocks that selectively segregate upon reducing the solvent quality. Similarly, raspberry-like patchy nanoparticles have been demonstrated by using the emulsion solvent-evaporation process of polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) solution. From these initially prepared patchy nanoparticles, Janus nanoparticles can be further derived by cross-linking the P4VP patches [52], followed by dissociating PS cores in good solvent. In addition, the composition and functionality of the particles are further extended, as metallic and oxide nanoparticles are preferentially grown within the P4VP domains upon precursor addition during phase separation. The same group also showed that patchy nanoparticles can possess hierarchical internal structures, by exploiting the phase separation of incompatible binary blends of amphiphilic block copolymer, PS-*b*-P4VP and homopolymer, poly(methyl methacrylate) (PMMA), in a confined 3D geometry (**Figure 2a and b**) [53]. Moreover, not only polymeric but also metallic patchy nanoparticles with internal hierarchy structure have been achieved by utilizing the alloy and phase-separated state of five metallic elements (Au, Ag, Co, Cu, and Ni) via polymer nanoreactor-mediated synthesis [54].

Phase separation can also be extended to the self-organization of ligands mixture on inorganic nanoparticle surface, to make chemically and topologically distinct patterns. For example, ligand layers composed of two types of thiol with different molecular lengths were observed to self-organize into striped patterns on gold nanospheres [55]. Chen and co-workers also reported polymer-patched gold nanospheres with controllable patch area and eccentricity from the core, as a function of ratio between two immiscible ligands (**Figure 2c–e**) [56, 57]. The controllable patch dimension is ascribed to the competition between hydrophilic and hydrophobic ligands attaching on the gold surface, followed by the adsorption of amphiphilic polymer only onto hydrophobic ligand-coated area. The phase separation of polymer solution into two phases, collapsed polymer and pure solvent, as reducing solvent quality has also been demonstrated on nanoparticles.

Figure 2.

(a and b) Transmission electron microscopy (TEM) images and schematics (insets) of PS-*b*-P4VP/PMMA patchy nanoparticles with hierarchical structure synthesized by emulsion solvent-evaporation process. Yellow, red, and green represent PMMA, PS, and P4VP, respectively. Adapted from Ref. 53. Copyright 2014 American Chemical Society. (c–e) Homocentric and eccentric Au@PSPAA nanoparticles depending on the hydrophobic and hydrophilic ligand ratio at 1:132 (c), 1:22 (d), and 1:0 (e). Adapted from Ref. 56. Copyright 2008 American Chemical Society. (f–h) Schematics of gold nanocube patterning with polymer patches and the corresponding TEM images. Surface-pinned micelle-like patches are formed upon reduction in solvent quality to homogeneously coated PS brushes on Au nanocube. (g) Nanocubes factionalized with PS forming a uniform polymer ligand shell in good solvent. (h) Patches formed on the vertices of nanocubes in poor solvent condition. Adapted from Ref. 59. Copyright 2017 American Chemical Society. Scale bars: 50 nm in (c–e, g and h).

Choueiri et al. [58] showed that in poor solvent, uniformly grafted PS brushes on nanoparticles can undergo thermodynamically driven segregation, forming surface-pinned micelle-like patches. The dimension, spatial distribution, and the number of patches are determined by the grafting density, solvent quality, relative size, and local surface curvature of the core particle (**Figure 2f–h**) [59]. Similarly, AuNRs with helicoidal PS patches are also achieved [60], by precisely controlling the molar ratio between two immiscible polymer brushes grafted on AuNRs. These polymer patches can be cross-linked to preserve the structure, or can go back to corona shell by increasing the solvent quality. Therefore, segregation-derived patch formation is a promising route to synthesize stimuli-responsive patchy nanoparticles, with morphological reversibility upon change of temperature, pH, salt concentration, etc.

2.2.3 Inhomogeneous surface modification-derived method

Surface modification is a powerful set of tools to tailor physical, chemical, or biological surface properties of nanoparticles required for a range of applications, such as abrasive resistance, biocompatibility, and colloidal stability in suspension. Surface engineering at the nanoscale is commonly done via bottom-up approach (e.g., overgrowth and ligand exchange), relying on chemical reaction of individual atoms and molecules to the nanoparticle surface. Thus, homogeneity of the modified nanoparticle surfaces depends on the thermodynamics and kinetics of the reactions, which are often challenging to be controlled site-specifically. In recent years, however, new knowledge acquired in heterogeneous nucleation and overgrowth, site-selective ligand exchange, and template-assisted materials deposition on nanoparticles, is paving ways to introduce patchiness on nanoparticles.

Seed-mediated nucleation and growth is a facile approach to synthesize multicomponent inorganic nanoparticles [61]. Among the possible morphologies of heterostructure nanoparticles, if the lattice strain induced by the mismatch is negligible, precursors form a shell that completely encapsulates the core. However, if the lattice strain is sufficiently high, the lattice relaxation induces the patchy crystal that partially deposited on nanoparticles [62–64], similar to the two dimensional (2D)-to-three dimensional transition in the Stranski-Krastanov model [65]. Utilizing this mechanism, various shapes of nanoparticles with crystal patches have been achieved, including rods, dumbbells and tetrapods [62, 66–69]. For example, Peng et al. demonstrated iron oxide nanoparticles with one to eight number of silver patches, via heterogeneous nucleation and growth approach [70]. In the synthetic process, first, the surface of iron nanoparticles is oxidized to generate amorphous iron oxide shells. Then silver patches overgrow on the shell, facilitated by the low enough interfacial energy between the amorphous iron oxide and crystalline silver. A similar mechanism has been adopted to synthesize gold-patched $\text{MnO}@SiO_2$ (**Figure 3a and b**) [71], and gold-patched anisotropic CdSe, PbSe, FePt, Cu_2O , and FePt–CdS nanocrystals [72]. Although the range of number and size of the patches can often be tuned by the reaction time or the concentration of precursor forming the patches [70], orthogonal control of such is not easy. It is because the event of heterogeneous nucleation and growth cannot be sharply separated by their nature. As a result, achieving highly monodisperse patchy nanoparticles in terms of the patch number (controlled by the number of heterogeneous nucleation events on one particle) and the size (controlled by growth) remains as a challenge. Moreover, if particles have multiple patches, controlling angular symmetry of the patches is not easy. Especially when the core particles are spherical, the position of patch-nucleation can be easily randomized, due to the lack of site-selectivity on homogeneous spherical nanoparticle surface.

Figure 3.

(a) TEM image of gold patched MnO@SiO₂ nanoparticles. (b) TEM micrograph of a single gold patch MnO@SiO₂ nanoparticle showing a silica shell of ~3 nm thickness. Adapted from Ref. 71. Copyright 2014 American Chemical Society. (c) Representation of the less compact areas of CTAB layer on the AuNR, which facilitates the growth of TiO₂ to the tips of the AuNR. (d) SEM image of AuNR-TiO₂ dumbbells synthesized using CTAB capped AuNRs as a template. Adapted from Ref. 74. Copyright 2016 American Chemical Society. (e and f) Schematics of metal or metal oxide patch growth on (d) rod and (e) spherical nanoparticles using collapsed polymer shells to protect selected domains, making multicomponent colloidal nanostructures (MCNs). Adapted from Ref. 85. Copyright 2016 Springer Nature.

Anisotropic nanoparticles have intrinsic surface inhomogeneity, which can guide the site-selective ligand exchange and materials deposition. As an example, AuNRs have distinct surface curvature and crystal facets at the tip compared to the side. Due to this inhomogeneity, the common stabilizing surfactant, cetyltrimethylammonium bromide (CTAB), binds less densely at the tip of AuNRs, exposing the tip area to be more susceptible for modification [73]. Tip-patched AuNRs with inorganic (e.g., TiO₂, SiO₂, etc.) and organic (e.g., PS, cysteine, etc.) patches have been achieved by site-selective overgrowth and ligand exchange at the tip (**Figure 3c** and **d**) [74–76]. Similarly, Kim et al. also reported nanoprisms tip-patched with polymer brushes, by exploiting the preferential chemisorption of 2-naphthalenethiol (2-NAT) on nanoprism tips, followed by polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) physisorption on ligands “island” via hydrophobic attraction [13]. The patch area and height can be orthogonally controlled as a function of 2-NAT and PS-*b*-PAA concentration, respectively. Various shapes of patchy prisms, including trefoil, T-shaped, and reuleaux triangle are demonstrated as a result of gradual patch expansion [13]. Likewise, patchy nanoparticle synthesis exploiting surface inhomogeneity provides site-selectively grown patches with decent monodispersity. However, this approach can be applicable only to the anisotropic nanoparticles with spatially distinct curvature or ligand distribution. Moreover, as the patch formation is governed by the local surface inhomogeneity,

most of the patchy nanoparticles achieved herein have symmetric shapes as guided by the core particles' symmetry, posing difficulty in realizing asymmetrically patched anisotropic nanoparticles.

Template-assisted surface modification exploits immobilization of nanoparticles on solid surfaces, liquid-liquid interfaces, or liquid-gas interfaces [77–80], to expose only the part of nanoparticle surfaces to be accessible to the precursors dissolved in one phase. Using this approach, Janus nanoparticles with a library of compositions have been achieved, including metal-metal (e.g., FePt-Ag, Au-Ag), metal-oxide (e.g., Fe₃O₄-Ag), and polymer-metal [81–84]. Size of the patches can be kinetically tuned as a function of the precursor to seed-particle ratio and reaction time [80]. However, nanoparticles at the interfaces tend to tumble due to thermal and interfacial fluctuations, resulting in imprecise surface modification in terms of patch geometry and size. Another way to utilize template-assisted surface modification has been reported by Huang et al. (**Figure 3e and f**) [85]. In this method, selected domains of gold nanoparticle surface are protected by collapsed polymer shells, followed by the deposition of inorganic precursors on unprotected area into tubular metal or metal oxide patches. Similar concept has been used for silica-protected AuNRs to overgrow Ag, Pd and Pt metal patches on the exposed area [73], expanding the library of patchy nanoparticles with unprecedented shapes and properties.

3. Self-assembly of patchy nanoparticles

3.1 Experimental studies of patchy nanoparticle assembly

The bottom-up approach, exploiting the interactions between primary building units to assemble superstructures, has advantages of high throughput and energy efficiency, and low cost for nanofabrication [51, 86]. Beyond the conventional nanoscopic building blocks commonly making closely packed lattices, patchy nanoparticles have advantages in bringing an exotic library of programmable structures with tailored physicochemical properties ascribed to the directional interactions encoded via patchiness. As extensively studied in micron-scale patchy colloids systems [87], vdW and electrostatic interaction, hydrophobic attraction, chemical bonding, entropy-originated interactions, and field-assisted assemblies can all be utilized to induce patchy nanoparticle self-assembly. Nonetheless, due to two to three orders of magnitude difference in scale, nanoscopic self-assembly compared to that at micron-scale has intrinsic differences worth our attention. To list some, interaction between nanoparticles is long-range relative to their size, allowing recognition and specific alignment of nanoparticles even when they are physically apart [88, 89]. Moreover, unlike those of micron-scale particles, nanoparticle interactions are more drastically controlled by particles' local morphology details (e.g., truncation at the nanoprism tip), possibly due to the long-range effect and facet-dependent density of capping ligands. Lastly, quantitative understanding of nanoparticle interaction is still in its infancy, as often the interaction is non-additive, and theories developed for micron-scale colloids is not applicable, or difficult to be tested in situ [90]. Despite such complexity, the listed distinctive features of nanoscale self-assembly bring huge opportunities in designing self-assembly structures and understanding self-organization phenomena found in nature and biology. Acknowledging such opportunities, here we summarize self-assembly strategies stemmed from different types of interactions that have been successfully exploited for patchy nanoparticle.

3.1.1 DLVO interaction

vdW force, originated from the instantaneous interaction of permanent or transient dipoles between the atoms and molecules, is one of the major forces causing random aggregation of nanoparticles and uncontrolled assembly. To prevent such instability of nanocolloids, electrostatic repulsion is often introduced by grafting charged ligands onto the surface of nanoparticles. This electrostatic repulsion can be easily tuned by varying the ligand density and the charge screening effect, which are determined by the ionic strength of the nanoparticle suspension [91]. The interplay between vdW attraction and screened electrostatic forces can collapse into a Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction energy profile [92], which controls the overall interaction of nanoparticles and final self-assembly structures [87]. Although such interaction is nondirectional in general, in case of patchy nanoparticles, the distinct domains of patched and non-patched regions with different physicochemical properties introduce site-specific DLVO interactions, allowing direction-dependent attraction or repulsion over the surface.

As an example, the gold patched organosilica nanoparticles covered with CTAB molecules can reversibly assemble into well-controlled clusters with “hot-spots” consisting of gold patches in physical contact [29], by controlling the DLVO interaction between gold patches (**Figure 4a–c**). The reversible patch-to-patch assembly is ascribed to the dominating gold-gold vdW attraction as the positively charged CTAB molecules on gold patches are washed out in ethanol. Dimers and trimers are obtained by tuning the steric hindrance as a function of the relative patch size. Compared to the self-assembly driven by covalent bonds of chemical linkers, exploiting DLVO interaction has advantages in that it is fast, reversible, often low cost, and requires less intensive synthesis efforts [29]. Triangular gold nanoprisms tip-patched with negatively charged polymers also show controlled self-assembly into twisted dimers, star and slanting-diamond (**Figure 4d and e**) [13]. By increasing the ionic strength of the patchy nanoprism suspension, the electrostatic repulsion between the particles is screened, and the exposed vdW force between the non-patched gold prism surfaces causes assembly into dimers. The tip-patched nanoprisms could assemble into large-scale 2D lattice if the directional repulsion introduced by patches is controlled to render specific angle between the particles. Zhu et al. [93] achieved the *fcc* superlattices from near-spherical quantum dots patched with gold satellites (**Figure 4f and j**), in which the orientations of individual nanoparticles are aligned. Using both small-angle X-ray scattering (SAXS, **Figure 4g and k**) and wide-angle electron diffraction (**Figure 4h, i, l and m**), they showed that by varying the ligand thickness; the degree of alignment can be controlled through the distance-dependent vdW attraction. It is expected that upon decreasing the number of gold patches, the particles could form into the 3D structures with lower coordination numbers, including body-centered-cubic and diamond lattices. Achieving these exotic self-assembly structures by controlling directional DLVO interactions of patchy particles can be universal, and thus many research interests are focused on experimental efforts to improve the purity of nanoparticles and to precisely control the interaction [94].

3.1.2 Hydrophobic attraction

Hydrophobic attraction originates from the entropy gain of the system when hydrophobes in aqueous solution aggregate to minimize their contact with water molecules, which otherwise make ordered cage-like structure on hydrophobic surfaces [95]. As already exploited by nature during protein folding into functional

Figure 4. (a–c) TEM characterization of assembled Au patched organosilica nanoparticles with different steric hindrance. The size of Au patches is (a) 24, (b) 44, and (c) 62 nm, respectively. The size of organosilica nanoparticle is about 120 nm. Adapted from Ref. [29]. Copyright 2016 American Chemical Society. (d and e) Self-assembly of tip-patched Au nanoprisms into twisted star (d) and slanting diamond (e) structures. Adapted from Ref. [13]. Copyright 2019 American Chemical Society. (f–m) Control of patchy nanoparticle orientations via ligand layer thickness. (f and j) TEM images of the nanoparticle superlattice (SL) viewed along the close-packed $(111)_{SL}$ zone axis, assembled from nanoparticle with different surface ligand density. Insets: Zoomed-in TEM images of the superlattice. (g and k) SAXS patterns of the corresponding superlattices. (h, i, l, and m) Wide-angle electron diffraction patterns along $(111)_{SL}$ (h and l) and $(001)_{SL}$ (i and m) of the assembled superlattices. Adapted from Ref. [93]. Copyright 2019 American Chemical Society. Scale bars: 50 nm in (d and e); 5 nm in (f and j insets); 2 nm^{-1} in (h, i, l, and m).

structures and phospholipid assembly into bilayer membranes, hydrophobic attraction can also be utilized to achieve controlled assembly structure by introducing the hydrophobic patches on nanoparticles with hydrophilic surface, or vice versa. By grafting PS on both ends of the AuNRs, Nie et al. achieved tip-to-tip, linear, or ring self-assembly structures ascribed to the directional hydrophobic attraction between the PS on AuNR tips [15]. The following study further shows that the solvent quality and the molecular weight of PS play an important role in controlling the strength of hydrophobic attraction, and thus provide diverse structures, including short bundles and bundled chains (**Figure 5a–d**) [96]. The linear assembly of PS-grafted AuNRs resembles step growth polymerization. The kinetic study of the system shows that the aggregation number of the chains increases linearly with reaction time, which is a characteristic of reaction-controlled step growth polymerization [97]. Other studies also report that concepts adapted from conventional polymerization, such as copolymerization and chain stoppers can be implemented to make a library of assembly structures with controllable composition and dimension [98, 99]. Similar to the polymer-patched inorganic particles, soft micelle nanoparticles prepared from diblock or triblock copolymers also show the controllable assembly

Figure 5.

(a) Left column: Schematics of PS with varying molecular weight on AuNRs. Central column: Schematics of different self-assembled structures of AuNRs. (b–d) SEM images of different self-assembled structures of AuNRs. Adapted from Ref. [96]. Copyright 2008 American Chemical Society. (e) Spherical micelles of polystyrene-poly(4-vinylpyridine) (PS-P4VP). (f) Patchy nanoparticle monomers of PS-P4VP. (g) A self-assembled polymer chain of PS-P4VP patchy nanoparticles. Adapted from Ref. [100] with permission from the Royal Society of Chemistry. Scale bars: 100 nm.

induced by solvophobic attraction between the patches (**Figure 5e–g**) [100, 101]. For example, upon gradual decrease of the solvent quality, polystyrene-block-polybutadiene-block-poly(methyl methacrylate) molecules undergo staged assemblies: micelle formation, dimerization of micelles into double-patched particles, followed by further assembly of patchy nanoparticles via step-growth polymerization and branching [51]. As a result, the intrinsically self-assembled soft patchy nanoparticles exhibit a complicated final assembly structures in 1D (chain) or 2D (network) [18]. Such hierarchical complexity induced by patchiness is promising for achieving abundant and sophisticated structures and yet to be further explored at nanoscale (further discussion in Section 3.3).

3.1.3 Formation of specific bonds between functional groups

Specific bonds between functional groups, including covalent bond and hydrogen bond (i.e., DNA base-pairing) on the site-selectively modified nanoparticles, can trigger programmable self-assembly, as encoded by functional groups [102]. A well-known example of the specific bond directed self-assembly is the biotin-streptavidin pair [103]. Herein, both tips of the AuNR are first patched with biotin disulfide. Then the tip-modified AuNRs gradually assemble into linear chain-like structures when streptavidins are added to covalently “link” two disulfide groups (**Figure 6a and b**). Another recent example utilizes the chemical reaction between amine group and carboxyl group, inducing the self-assembly between concavely patched silica nanoparticles and spherical silica nanoparticles [104]. The self-assembled structures are clusters with sp , sp^2 , and sp^3 hybridized molecular structures (**Figure 6c–h**), which can be potentially used as building blocks for hierarchical self-assembly. Nanoparticle assemblies through DNA linkage have gained extensive research interests to encode directional bonding between the nanoparticles, after first reported by Mirkin and Alivisatos groups [105, 106]. Especially, the patch formation by regioselectively coated DNA linkers on the nanoparticle surface is a promising strategy to form programmable, unprecedented structures [30, 31, 107]. Xu et al. [30] synthesized gold nanospheres asymmetrically grafted with oligonucleotide DNA linkers, by utilizing magnetic microparticles as templates for the nanospheres to attach upon and undergo partial surface modification on the exposed region. These patchy nanospheres are co-assembled with nanoparticles

Figure 6.

(a) Schematics showing the assembly of AuNRs (golden ovals) by surface functionalization with the biotin disulfide (red), and subsequent addition of streptavidin (blue), to produce aggregates of AuNRs. (b) TEM image of assembled AuNRs, surface-derivatized with either biotin disulfide, after addition of streptavidin. Adapted from Ref. [103]. Copyright 2003 American Chemical Society. (c-f) TEM images of the colloid molecules assembled from mixing particles with four aminated dimples with 100 nm silica nanospheres and 90 nm core-shell nanoparticles in different ratio. (g and h) TEM images of the colloid molecules assembled from mixing particles with two aminated dimples with 100 nm silica nanospheres and 90 nm core-shell nanoparticles in different ratio. Adapted from Ref. [104]. Copyright 2018 Beilstein-Institut. (i-n) Self-assembly of partially functionalized gold nanoparticles into (i and l) cat paw, (j and m) satellite, and (k and n) dendrimer-like structures. Adapted from Ref. [30]. Copyright 2006 American Chemical Society. Scale bars: 100 nm in (c-h); 20 nm in insets of (l and m).

uniformly coated with DNAs into cat paw-, satellite-, and dendrimer-like structures (**Figure 6i–n**). Others also use isotropic gold nanoparticles embedded in highly anisotropic DNA origami to achieve self-assembly structures controllable from zero dimensional clusters to 3D diamond family superlattices [31, 107]. Chen and co-workers [56, 57] and Chen et al. [108] explore the self-assembly of a variety of gold nanoparticles (e.g., nanorods, nanoprisms, and nanocubes) site-specifically patched with single-stranded DNA (ssDNA) molecules. The nanoparticles are selectively covered by polymer shells, and ssDNAs are attached onto remnant area of nanoparticle surface (e.g., tip, edge, and face). As the ssDNAs on patches hybridize, the nanoparticles self-assemble into various structures, including dumbbell-, exclamation mark-, pearl necklace-, starfish-, and snowman-like clusters. The self-assembly of DNA-patched nanoparticles into large-scale lattices are yet to be achieved, aided by developing strategies: site-specifically functionalizing nanoparticles and assembling nanoparticles homogeneously coated by DNAs.

3.1.4 Other interactions of an entropic origin

Entropy effects other than hydrophobic interactions on nanoparticle self-assembly are commonly originated from depletion attraction or from the densest packing of particles in suspension of maximum translational entropy [87]. The depletion attraction is triggered when depletants of small sizes exist in the colloidal suspension [109], which has excluded volume in the vicinity of the colloids. The total entropy of the system increases as the particles come into contact and cause the overlapped excluded volume to increase and allow the depletants to explore more space [110]. The phenomenon can be interpreted as when depletants are absent in the space between two particles, the lower osmotic pressure of the pure solvent in this volume pushes particles toward each other [94]. Depletion attraction has been successfully exploited to trigger self-assembly of micro-sized concave patchy colloids as “lock-and-key” and non-patchy anisotropic nanoparticles with large flat facets (**Figure 7a–d**), in the presence of surfactant micelles or non-adsorbing water-soluble polymers [111–114]. The entropy-induced packing of shape-anisotropic

Figure 7.

(a–d) Schematics and SEM images of different depletion attraction-driven nanoprism self-assembly structures: (a) single-layer *p*-honeycomb, (b) multilayer *p*-honeycomb, (c) single-layer *i*-honeycomb, and (d) multilayer *i*-honeycomb. Adapted from Ref. [114]. Copyright 2017 American Chemical Society. (e–p) Potential wells by taking slices of the potential of mean force and torque (computed from the frequency histogram of the relative Cartesian coordinates of pairs of particles in Monte Carlo simulations of monodisperse hard particles) parallel to the faces of a (e–h) tetrahedron, (i–l) tetrahedrally faceted sphere, and (m–p) cube at various packing fractions $\phi = 0.2, 0.3, 0.4$, and 0.5 as indicated at the head of each column. Adapted from Ref. [115]. Copyright 2014 National Academy of Sciences. Scale bars: 100 nm in (a–d).

nanoparticles has been extensively studied on a theoretical level [115–117]. The driving force of assembly, herein, is often referred as “entropic patchiness” [118, 119] due to the preferential interaction between the planar face over curved surface regions (**Figure 7e–p**). This preference has been rationalized as the emergence of “directional entropic forces” [24, 120]. In experimental systems, entropic patchiness is frequently employed to achieve the self-assembled superlattice from shape-anisotropic nanoparticles. Murray and co-workers demonstrated that NaYF_4 nanoparticles with different geometries, including spheres, rods, hexagonal prisms, and plates, self-assemble into densely packed lattices as entropically-directed [121]. They further showed from experimental and computational investigations that hexagonal nanoplates self-assemble into long-range ordered tiltings, ascribed to the balance between shape-induced entropic and edge-specific enthalpic interactions [122]. Moreover, entropic patchiness-driven self-assembly strategy is not only limited to single-component but can be extended to binary-components with compatibility in size and shape [123, 124]. For example, Ye et al. [123, 124] demonstrated that the relative size of AuNRs and gold nanospheres affects the entropy of the system and triggers the co-assembly of nanoparticles into three different types of phases, including lamellar structure with disordered spheres and AB_2 -type binary superlattice. Optimum design rules for entropic patchy nanoparticle combinations are yet to be further explored both in experiment and computation, and promise a richer library of superlattices and phase behaviors beyond those from a single component.

3.1.5 Field-driven assembly

Patchy particles, when appropriately designed, have programmable direction and magnitude of interparticle interaction controlled by types of external field (e.g., electric and magnetic), field properties [125], as well as the composition and shape of the particles. As a result, patchy particles can align to the field, or transform the input energy into mechanical energy to exhibit out-of-equilibrium dynamic behaviors such as self-propulsion or rotation. Moreover, the magnitude of interparticle interaction can be altered from one to three orders of $k_B T$, as a function

of the strength of field and frequency, providing an effective “switch” to reversibly control the interaction and assembly.

AC electric field is commonly used to alter the particle interactions while effectively suppressing the electrolysis of the liquid in comparison to the use of direct current electric field. Compared to non-patchy particles, patchy particles could exhibit richer assembly structures due to their unique shapes and special arrangements of induced dipole moments. For example, under AC electric field, spherical or ellipsoidal colloids with homogeneous surface charge assemble into a face-centered ABC layer packing [126]. By contrast, patchy particles with negatively charged patches under AC electric field can form 1D, 2D, 3D, and even double-helix structures (**Figure 8a**) [127]. Such helical structure stems from the charge redistribution on patchy particle surface where patches align to maximize the attraction along the structural axis. Another example shows that particles with a protruding patch assemble into various chiral clusters under AC electric field (**Figure 8b**) [128]. The diverse structures where patches point toward the chiral center are attributed to the induced dipolar interactions tunable by field frequency and patch size. The chirality of clusters induces imbalanced hydrodynamic flow, leading to the rotation of clusters in the direction opposite to their handedness. Chiral clusters with similar behavior are also co-assembled from self-propelling metal-dielectric patchy particles in combination with non-patchy particles, under AC electric field [129]. Likewise, if the patchy particles have compositions with distinct dielectric permittivity (e.g., titanium/silica), the anisotropy in the magnitude and in frequency-dependent responses trigger various modes of self-propelled behaviors [130]. For metal-dielectric patchy particles subjected to the AC electric field of different frequencies, dynamic collective structures of swarms, chains, and clusters have been achieved. Moreover, if triangular Au-patches are formed on PS particles, the particles were aligned and propelled following helical trajectories under AC (**Figure 8c–e**) [131]. The structural and behavioral similarity in these studies suggests the existence of governing rules when it comes to assemble patchy particles under electric fields, possibly due to the overwhelmingly large dipole interactions relative to thermal fluctuations.

Magnetic responses of patchy particles usually require paramagnetic or ferromagnetic compositions. Permanent magnetic moment in ferromagnetic patchy particles often allows the assembled structures to be preserved even after the external magnetic field is turned off. Granick group and the others have investigated the rich superstructures with distinct crystalline symmetries formed by ferromagnetic patchy particles [132, 133]. For example, under the high-frequency magnetic field, nickel-deposited silica patchy particles pair into dimers that subsequently assemble into reconfigurable hierarchical structures, including zigzag chains, square, and hexagonal lattices [125]. Other structures, such as chains and layered structures (**Figure 8f–i**), and microtubes have been achieved by applying static or precessing magnetic fields [134–136]. At nanoscale, under static magnetic field, Fe₃O₄-Ag heterodimeric, ferromagnetic patchy nanoparticles can be assembled into densely packed helical superstructures [137]. As the size of silver patch increases, gradual structural transition from helix to belt is observed, resulting from the balance among magnetic dipole-dipole interactions, vdW attraction, Zeeman coupling, and entropic forces.

Comparing to the phenomenal amount of in-depth studies on dynamic assembly of micron-scale particles, there are only a few studies on the field-driven assembly of patchy nanoparticles. It is mainly caused by the technical difficulties posed in lack of imaging tools for nanoscale structures in situ [138]. Nonetheless, dynamic assembly of patchy nanoparticles has a huge potential in offering unanticipated structures and exotic properties for the future nanomaterials. The recent technical

Figure 8.

(a) Optical microscopy (OM) image and schematics of double helix regions formed from tripatch particles under AC electric field. The double helix regions in the two paired chains are denoted by red and blue dots. Adapted from Ref. [127]. Copyright 2015 American Chemical Society. (b) OM images and schematics of chiral tetramers assembled from spherical particles with protruding patch under AC electric fields. Adapted from Ref. [128]. Copyright 2015 National Academy of Sciences. (c) Schematic and (d and e) OM images of Au-patched PS particles alignment following helical trajectories under AC-electric field, denoted as E . The arrows represent the direction of helical motion of patchy particles. L and R denote left and right-handed helical trajectories. Adapted from Ref. [131]. Copyright 2019 Springer Nature. (f) Schematic and OM snapshots of spherical particles with a magnetic patch assembling into linear chains and layered structures under external magnetic field, denoted as B . Adapted from Ref. [135]. Copyright 2012 American Chemical Society. (g and h) SEM images of particle assemblies into (g) staggered chain and (h) double chain after drying the particle suspension under static magnetic field. Brighter areas on the particles are iron oxide caps, and darker regions are unmodified PS surface. (i) Assembly behavior diagram as a function of iron oxide deposition thickness and time indicating regions of staggered chain, double chain, and no assembly behavior. Regimes denoted as I and II refer to transition behavior, where deposition parameters lead to particles exhibiting either of the adjacent assembly behaviors. Adapted from Ref. [134]. Copyright 2012 American Chemical Society. Scale bars: $5\ \mu\text{m}$ in (a, b, d, e, g, and h).

development in liquid-phase transmission electron microscopy [139], which enables the in situ imaging of the nanoparticle suspension in real time and real space at the single particle level, is a promising and powerful tool to overcome the current difficulties. Applying the electric fields and decoupling the electron beam effect from the generic behavior of the particles [88, 140], or utilizing electron beam itself as a handle to manipulate the behavior of nanoparticles [141] is gaining increasing research interest. Assembly mechanism and various structures observed both from

in situ micron-scale patchy particles and ex situ patchy nanoparticles can be important guidelines for the in situ studies at nanoscale in the future.

3.2 Simulation of self-assembly behaviors of patchy nanoparticles

For the past two decades, simulation of patchy particles has been extensively developed using simplified models to understand complicated assembly systems [142], including protein folding [143], viral capsid formation [144, 145], and even phase transition of atoms and molecules [146]. In the field of synthetic patchy nanoparticles, simulation aids understanding of experimental observations. For example, Lu et al. [147] experimentally showed nanocubes whose corners have ssDNA patches pack into unique lattices with zigzag arrangement. By adapting a scaling theory and Monte Carlo simulation for the ssDNA grafting on cubes, they predicted the shape of the corona morphology transforming from face-preferred to corner-preferred, as ssDNA length increases. They further developed the perturbation theory and potential mean force calculation for the set of patchy nanocubes to reveal the crucial role of concave or convex patches in controlling the angular arrangement of particles in the lattice. The fidelity of the simulation is further confirmed by comparing to the SAXS measurement of the lattices. Walker et al. [148] experimentally showed 3D open-lattices assembled from gold nanodumbbells with chemical patches on the neck of the particles. From finite-element calculations, they confirmed the most favorable alignment of two nanodumbbells is the cross-stack of the particles by their patches, consistent with the unit structure of the lattice. Zhu et al. [93] reported quantum dots decorated with gold patches and assembled them into close-packed structures. The molecular dynamics simulation not only reproduced their superlattices but also suggested a means of tuning the orientational alignment of the building blocks in the superlattice by varying distance-dependent vdW force between the gold patches. Complementarily, in their experiments, the interparticle distance is controlled by the ligand thickness, and the orientational alignment change is confirmed by wide-angle electron diffraction.

Moreover, simulation often has been regarded as the only method to systematically study impacts of each geometric and interaction parameter constituting patchy particles, especially at the nanoscale where direct imaging of assembly behaviors has remained as a challenge. Systematic variation and decoupling of geometric factors and interactions can be achieved by simulation to guide experiments. Smallenburg and Sciortino showed patchy particles can have stable liquid phase that does not transform to gel structures even at the zero-temperature limit [146]. Their study suggests the flexibility of bonds and limited valence, which can be controlled by the patch number and size are the crucial factors in designing stable amorphous structures and glass-forming molecular networks. The same group also suggests through rational design of patch shape and symmetry that triblock patchy particles can selectively crystallize into tetrastack lattice with unique photonic properties, and even a colloidal clathrate-like structure [149]. Other structures including icosahedra, tetrahedra, square pyramids [8], helical structures [150], quasicrystals of dodecagonal symmetry [35, 151], and open lattices [152, 143] (**Figure 9a** and **b**) with high structural selectivity over other polymorphs are studied (**Figure 9c**) [153]. Together with recent studies in mechanical and functional properties of the exotic structures formed as bottom-up [154, 155], these theoretical studies have been paving ways to experimentally achieve novel functional nanostructures.

Lastly, simulation helps the experimental design of patchy nanoparticles to achieve targeted assemblies with desired properties via “inverse design” [117]. Inverse design is a powerful strategy to find crucial geometric parameters and physical interactions for patchy nanoparticles, especially to realize unprecedented

Figure 9.

(a and b) Molecular dynamics simulation snapshots of triblock patchy particles. (a) Model spherical particle has two attractive patches (blue shell). (b) Simulation snapshots of crystalline structure from triblock patchy particles (patches in blue). Particles are colored according to the local lattice environment: green and red particles are in a cubic and hexagonal structure, respectively, while yellow particles are in a mixed local environment. Adapted from Ref. [152]. Copyright 2016 American Chemical Society. (c) Schematics of close packed tilting to open lattice structure obtained from simulation of rhombi particles with differently located four patches. Adapted from Ref. [153]. Copyright 2019 American Chemical Society. (d) Flowchart of the landscape engineering inverse design procedure. Adapted from Ref. [156]. Copyright 2019 Royal Society of Chemistry.

3D structures. By engineering the free energy landscape via evolutionary algorithms, Ma and Ferguson discovered patchy particles that can hierarchically assemble into pyrochlore and cubic diamond lattices with complete photonic bandgaps (**Figure 9d**) [156]. Moreover, a generalizable inverse statistical mechanism approach is developed by Chen et al. [157] to provide a set of design rules for a collection of 2D crystals, including square, honeycomb, kagome, and parallelogrammic lattices. Along the similar direction, Whitlam reported a strategy of minimal positive design and identified distinct types of interaction between patchy particles required for achieving eight kinds of Archimedean tilting plane structures [158].

3.3 Design of kinetic pathways: To achieve 3D lattice via hierarchical assembly

Designing 3D open lattices with complicated structural details and low coordination number presents a challenge because conventional non-patchy particles tend to pack closely, instead of allowing for periodic arrays of holes [107]. Open and highly ordered structures have tailorable properties, including light weight, high porosity, low thermal conductivity, tailored stress–strain response, and photonic bandgap [159], and benefiting applications in catalyst [160], photonics [149], and metamaterials [161]. One of the promising strategies to realize such open lattice in an energy efficient way is by hierarchical assembly of patchy building blocks, which has also been exploited in polyhedral DNA scaffolds [162], collagen fibrils [163], and microscale particles [164]. The hierarchical assembly often requires two or more types of interparticle interactions that can be orthogonally triggered at different stages of assembly, which can be acquired by introducing patchiness. Both experimental and simulation efforts have been made to find the rules for achieving such high-level sophistication in superlattice. Muller and co-workers reported two types of polymeric patchy nanoparticles co-assemble into triangular clusters, which then further assemble into micron-scale compartmentalized chain or network structures, as dictated by the balance of interactions between attractive

and repulsive patches [18, 51]. Chen and co-workers reported three types of hierarchically assembled structures: two different types of quasicrystals and body-centered-cubic supracrystals from patchy CdSe tetrahedral quantum dots, which are undergoing primary assembly into clusters attributed to specific facet-to-facet interaction between the patched surfaces [165, 166]. At an extremely small scale, the hierarchical construction of molecular films with honeycomb structure from fan-shaped molecular building blocks is achieved by Hou et al. (**Figure 10a–c**) [167]. The building units can be regarded as patchy as they are composed of polyoxometalate at the corner and polyhedral oligomeric silsesquioxanes on the one hand. On the other hand, using Monte Carlo simulations, rhombic platelets with two patches are triggered to assemble into several types of uniform clusters and into various lattices [168]. The structures were systematically explored as the simulation samples of the parameter space of attraction strength and patch position. Morphew et al. [169] used cluster-move Monte Carlo algorithm to understand how to encode hierarchy in interaction strength of triblock patchy particles. They further showed that hierarchy is essential for achieving final assembly of cubic diamond crystals via tetrahedral clusters (**Figure 10d**), as also consistent to the earlier experimental observation by Chen et al. (**Figure 10f**) [170]. When the patch width is expanded, the increasing patch-to-patch interaction range leads to the formation of body-centered cubic structure via octahedral clusters (**Figure 10e**), suggesting the generalizability of the design rules. The cooperative and iterative feedbacks shown in between this joint experiment and theory set a valuable example of how patchy nanoparticles assembly can effectively advance to introduce the novel hierarchical nanostructures.

Figure 10.

(a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images showing honeycomb lattice composed of polyoxometalate (POM) cluster and four polyhedral oligomeric silsesquioxane (POSS) clusters (POM-4POSS). (b) Hierarchical structure of a honeycomb cell. Truncated triangle and the pentagon in red highlight the structural units at multilevels. (c) Snapshot of coarse-grained model simulation of honeycomb superstructure self-assembled from POM-4POSS. Adapted from Ref. [167]. Copyright 2018 American Chemical Society. (d and e) Two-level structural hierarchy in assembly structures from triblock patchy particle with varied patch size. Structural motifs (insets) and snapshot of typical crystal configuration assembled via (d) tetrahedral and (e) octahedral clusters. Adapted from Ref. [169]. Copyright 2018 American Chemical Society. (f) Fluorescence microscopy images of illustrative network structure assembled from triblock patchy particles. Adapted from Ref. [170]. Copyright 2012 American Chemical Society.

4. Conclusion and outlook

Diverse synthetic routes lead to different patchy nanoparticles with various patch size, number, morphology, and composition. To mention a few representative examples in terms of the composition, inorganic patchy particles can be obtained by controlled self-assembly of nanocrystals, the phase separation of polymer micelles leads to polymeric patchy particles, and the surface modification of inorganic nanoparticles can provide hybrid patchy nanoparticles with inorganic core and organic patches. In terms of self-assembly of patchy nanoparticles, different driving forces, including vdW, electrostatic, chemical and entropic interactions, have been explored. However, at current stage, most of the self-assembled structures are still limited to 0D cluster [30, 104] and 1D chain structures [15, 100, 101, 103]. Large-scale 2D planar structure [18] or 3D lattices [148] have only been realized in a few examples with limited domain size, causing a delay in realizing potential applications in medicine, electronic devices, and photonic crystals. Dispersity and impurity of the patchy nanoparticles are a few of main causes of this challenge. Thus, we expect patchy nanoparticles with polymeric patches could help, as the squish “soft” patches can easily adopt in the large-scale assembly structure and tolerate the differences in the shape and size of individual patchy particles.

On the other hand, direct imaging of patchy nanoparticle self-assembly in liquid can help advancing large scale assembly with low defects and long-range order. First of all, direct observation of assembly process provides quantitative “picture” of interparticle interaction governing dynamic assembly process. For example, from velocity and diffusivity of tracked nanoparticles forming chains and clusters, the magnitude and the range of forces can be experimentally investigated [171]. Moreover, as it also has been extensively demonstrated in micron-scale patchy particles under OM, real-time imaging provides a deep understanding in kinetic pathways of self-assembly process. For example, transient assembly structures before particles rearrange into final structures elucidates favored structures before equilibrium and the time scale of such events, providing the full assembly kinetic coordinates [172]. Thus the understanding of the kinetic coordinates in assembly can provide insights into generating highly ordered and desired assembly structures, by facilitating the specific assembly routes, among all other possible pathways upon differing assembly kinetics. Moreover, interference in transient assembly stages before the rearrangements, or restriction in assembly conditions can even “freeze” particles as they are trapped in nonequilibrium metastable structures, further opening future directions in achieving “kinetically-trapped” assembly structures by design [173]. Although OM has been routinely used to observe dynamics of micron-scale particles, it is not the case for the nanoparticles because of the diffraction limit of visible light disable single particle-level resolution at nanoscale. In order to circumvent such obstacle in terms of the imaging tool, recent progresses in liquid-phase transmission electron microscopy (LPTEM) have been gaining increasing attention, as it provides self-assembly pathways of nanoparticles in real time and space [88, 89, 174]. In order to push the limit of current status of LPTEM to fully resolve nanoparticle interactions within the time scale of assembly events, K3 cameras with a frame rate up to 1500 frames per second and machine learning algorithms to automatically extract out meaningful physical information from overwhelming amount of data have also been developed [175]. We see that with a proper handling of liquid confinement effect in chamber and the electron beam effect (e.g., the low image contrast and beam sensitivity of the organic patches), liquid-phase TEM technique can serve as a powerful tool to realize and experimentally guide patchy nanoparticle self-assembly for novel functional structures.

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