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Self-assembly of particles—The regulatory role of particle flexibility

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ABSTRACT

Aspects of the self-assembly of particles, which uses nanometer or micrometer sized building blocks to bridge the gap between microscopic and macroscopic scales, are reviewed. Particle self-assembly has been the focus of considerable research in recent years because it can lead to superstructures with a complexity inaccessible by molecular self-assembly, and functionalities entirely different from or superior to those of the primary particles. Examples in molecular self-assembly suggests that anisotropic interactions could be useful in promoting particle self-assembly, with the exception of colloidal crystallization, which requires particles of uniform size and shape. Anisotropic particles prepared by surface modification of precursor particles are often rigid and submicron or micron sized, and thus relatively strong isotropic van der Waals interactions tend to resist self-assembly into regular superstructures. In addition, the relatively large contact area between particles needed for a sufficient binding enthalpy to stabilize a superstructure is difficult for rigid spherical particles. In contrast, flexible anisotropic polymeric particles dispersed in solvents have been shown to self-assemble into various superstructures. The flexibility of primary anisotropic particles enables them to fuse and stabilize into a superstructure. Some flexible and multicomponent particles that are isotropic in common solvents can undergo deformation and sufficient material redistribution to anisotropically self-assemble into regular superstructures in selective solvents. The self-assembly is also driven by anisotropic interactions, which is induced during self-assembly rather than in the particles as synthesized. This review focuses on recent achievements in soft particle self-assembly and describes briefly the advancements in rigid particle self-assembly. The presentation is divided into discussion of self-assembly by the colloidal crystallization of isotropic rigid particles, anisotropic rigid particles, anisotropic soft particles and isotropic soft particles, in that order.

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1. Introduction

Self-assembly is a topic of intense scientific interest, as demonstrated by the inclusion of "How far can we push chemical self-assembly" in the Top 25 big questions discussed in the special 125th anniversary issue of Science magazine [1]. The past three decades have seen an explosive development in molecular self-assembly. Various strategies for molecular self-assembly have been developed for the construction of molecular aggregates with designed properties, geometries and dimensions. These promise to address or provide solutions to both theoretical and practical problems in many areas, such as drug delivery, catalysis, medical diagnostics and sensors [2-23]. In recent years, self-assembly using particles as building blocks, has drawn attention as a newly emerging scientific area. Self-assembly of particles controls the distribution of particles on the entire assembly by modulating inter-particle interactions on the nanoscale and focuses on constructing ordered and complex structures that are inaccessible to molecular self-assembly. Selfassembled superstructures can have functionalities that are different from or superior to those of the primary particles. For example, mono-dispersed silica and polymer latex were used as building blocks in colloidal crystallization to build photonic crystals with a tunable band gap by varying the stacking symmetry and inter-particle distance [24,25]. Gold nanoparticles decorated with linkers can be used for the detection of a variety of substances based on plasmon coupling by different nanoparticle aggregation mechanisms [26]. Silica spheres with a low polystyrene grafting density can self-assemble into string or sheet-like aggregates in a polystyrene matrix, which are superior mechanical enhancers for the matrix [27]. Multi-compartment nanostructures, fabricated from the self-assembly of polymeric nanoparticles with delicately designed inter-particle interactions, can serve as templates for decoration of functional species on specific compartments [4,28].

Apart from helping us design and prepare novel superstructures and functional materials, studying particle self-assembly can help us understand more about how life works because particle self-assembly is an essential process carried out within organisms. Proteins self-assemble intra-molecularly into particles, and particle–particle or particle–biomolecule self-assembly leads to hierarchical structures such as the cell membrane [29], chromatin [30,31], and microtubules [32].

This review describes recent scientific efforts toward understanding the self-assembly of particles and is divided into four parts according to the types of building blocks used. We begin by briefly surveying colloidal crystallization of isotropic rigid particles such as mono-dispersed silica spheres, polymer latex, semiconductor nanoparticles and metal nanoparticles with designed surface functionality, and charged inorganic nanoparticles. Colloidal crystallization of silica or polymer latex on the order of hundreds of nanometers is usually driven by entropy, while colloidal crystallization of smaller nanoparticles (approximately 10 nm in size) is mainly driven by isotropic inter-particle attractions such as van der Waals interactions, DNA base pair interactions and electrostatic interactions. In the second part of our review, we briefly discuss the preparation and self-assembly of anisotropic rigid particles. Much effort has been devoted to the preparation of anisotropic rigid particles with designed features, and a variety of these particles have been reported in the literature. In most cases, anisotropic rigid particles are submicron or micron sized, and it is difficult for them to self-assemble into regular superstructures. Strong van der Waals interactions caused by the relatively large mass counteract the anisotropic interactions, and this rigidity makes anisotropic rigid particles difficult to stabilize into superstructures. For the third part of our review, we summarize the self-assembly of anisotropic soft particles that are usually polymeric or have polymeric components and can be dispersed in solvent. This solvent dispersibility makes anisotropic soft particles able to self-assemble in solution, where the isotropic inter-particle van der Waals attraction is overcome by solvation of the polymeric component; the solvated polymer chains are repulsed by one another due to their exclusive volume. Spherical, cylindrical, tubular and sheet-like superstructures can thus be obtained. During self-assembly, anisotropic soft particles are able to adjust their shape and anisotropy due to their flexibility, which should be necessary for the formation

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and stabilization of superstructures. In the last part of our review, we focus particularly on the self-assembly of isotropic soft particles. Isotropic soft particles, which are usually core-shell structured particles with hair-like shells and have great flexibility, can undergo deformation and sufficient material redistribution and behave like anisotropic particles during the self-assembly process. These isotropic soft particles may actually become anisotropic in the resultant superstructures, resulting in a wealth of intricate hierarchies. Delicate thermodynamics and kinetics are always involved in the self-assembly of isotropic soft particles; the deformation of isotropic soft particles facilitates inter-particle coupling, and the entropy loss of deformation is compensated for by a gain in enthalpy from coupling. This entropy loss and enthalpy gain varies and covers a relatively large range, and the balance between them provides a diversity of superstructures.

2. Crystallization of isotropic rigid particles

Isotropic particles are spherical particles with uniform surface chemistry. Isotropic particles with a narrow size distribution can crystallize into colloidal crystals in a process driven by either entropy or enthalpy. Colloidal suspensions of mono-dispersed isotropic particles hundreds of nanometers in size that are sterically stabilized by organic molecules in a solvent with a refractive index comparable to that of the particles are classified as hard sphere repulsion systems, where the van der Waals attraction between particles is small [33,34]. Colloidal crystallization of the hard sphere system is an entropy-driven process. The entropy of the entire system consists of configurational and free volume entropy. At low suspension concentrations, the configurational entropy dominates, and the fluid state is stable. At high suspension concentrations, the free volume entropy dominates, and the colloidal crystal state is favored [35]. In earlier studies, colloidal crystallization was performed by incubation of concentrated colloidal suspensions [33] or by sedimentation of dilute colloidal suspensions (after sedimentation, the colloidal suspensions were concentrated) [36]. Both methods required a relatively long time for the disorder-to-order transition to allow for particle diffusion and sufficient rearrangement during crystallization, which is due to the slow relaxation of large colloidal spheres and the high viscosity of the concentrated suspension. Face-centered-cubic and hexagonal-close-packed structures are thermodynamically favored, as they can gain more free volume entropy than other packing symmetries.

Entropy-driven colloidal crystallization is a lowcost and low-energy consumption pathway to threedimensional photonic structures. However, colloidal crystals produced from concentration suspensions and sedimentation methods have defects, including vacancies, macroscopic cracks, polycrystalline domains, and stacking faults. Through further intensive research in this field, large-scale fabrication of colloidal crystals with fewer defects and good mechanical stabilities as well as binary superstructures with different superlattices has been successfully realized [24,37–39]. In addition, superparticles of colloidal crystals have also been reported [37,40], which were prepared by using droplets dispersed in a liquid medium as a template. One of the more elegant examples was reported by Wittemann et al. By using relatively small droplets as a template and density gradient centrifugation for separation, they prepared superparticles composed of a specific number of primary particles, and this proved to be an ideal model for investigating Brownian motion of anisotropic particles [40].

Crystallization of inorganic nanoparticles with optical, electronic or magnetic properties into well-defined structures that maintain and enhance the functions of nanomaterials or that exhibit new physical properties is particularly interesting. These functional particles are usually approximately 10 nm in size, and their crystallization is driven by inter-particle attraction. By introducing the inter-particle van der Waals attraction and destabilizing the quantum dot dispersion, Bawendi et al. demonstrated that the crystallization of CdSe nanocrystallites stabilized by trialkylphosphine chalcogenide into three-dimensional superlattices [41]. DNA base pair interactions and electrostatic interactions were also introduced to drive the crystallization of small functional particles. Compared with van der Waals interactions, DNA base pair interactions and electrostatic interactions are tunable over a large range and thus versatile in their ability to control the crystal structure of small-sized particles. Through tailoring the interactions between building blocks, single- and binary-component colloidal crystals with various superlattices have been fabricated [42-45].

Whether colloidal crystallization belongs to the field of particle self-assembly is debatable. Particle self-assembly produces superparticles with specific shapes and sizes, like molecular assemblies, while colloidal crystallization usually leads to bulky colloidal crystals, except for the case of templated colloidal crystallization. However, the principles and techniques used for tailoring non-covalent interactions between isotropic particles can be used to guide the design of particle self-assembly.

3. Self-assembly of anisotropic rigid particles

Except for colloidal crystallization where isotropic particles are used, anisotropic interactions between particles are thought to be necessary for particle self-assembly, which is analogous to molecular self-assembly where anisotropic interactions between molecules are required; each anisotropic particle consists of stable and unstable regions (or repulsive and attractive regions). Self-assembly of anisotropic rigid particles is induced by the attractive interaction between the unstable regions, and the resultant assemblies are stabilized by the stable (or repulsive) regions. In this section, we briefly describe the preparation and self-assembly of anisotropic rigid particles. We define rigid particles as particles whose shape and distribution of components on the surface does not change during self-assembly.

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Fig. 1. Predicted complex structures from self-assembly of patchy particles. (Left) Twisted wire of tethered triangular nanoparticles; (middle) tetrahedon, icosahedron, and ring self-assembled from spherical patchy particles; (right) micelles of tethered nanospheres. To fabricate rings from patchy particles, selective sticky patches are placed anisotropically on the equatorial plane at a relative angle of <180°. The diameter of the rings is controlled by the angle between the patches. Tetrahedra and icosahedra form from particles with selective, ring-like patches shifted off the equatorial plane. Reproduced with permission from [46].

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3.1. Preparation and self-assembly of rigid patchy particles

Glotzer et al. predicted various patchy particles by computer simulation and anticipated that their selfassembly would lead to a variety of intricate assemblies such as chains, sheets, rings, icosahedra, square pyramids, tetrahedra, and twisted and staircase structures, which provides for a unique way of constructing complex and ordered superstructures (Fig. 1) [46,47]. Experimentally, synthesis of these anisotropic particles is still challenging. Thermodynamically, isotropic decoration or random decoration is favored over patchy decoration due to entropy. Dynamically, each point on the surface of the precursor spheres should have the same probability to be decorated when a common solution reaction is used for the surface modification. Therefore, deliberately designed processes are required for patchy particle preparation.

Patchy particles with a distribution of patches similar to atomic hybridized orbits were prepared by downward Au vapor deposition on the third layer of a four- or five-layered polystyrene colloidal crystal on a substrate (PS spheres, 270 and 920 nm were used as the diameters); the upper bilayers of the PS colloidal crystals were used as masks for Au deposition on the spheres in the third layer (Fig. 2A) [48]. The spheres of the upper bilayers were etched by O₂ plasma to different extents to provide different shielding for the third layer. By varying the stacking symmetry of the PS crystal (ABCABC or ABAB), controlling the interstice between the PS spheres and adjusting the incident angle between the Au vapor flow and the normal direction of the crystal films, Wang et al. fabricated colloidal particles decorated with Au nanodots exhibiting sp-, sp²-, sp³- or even sp³d-like distributions (Fig. 2); the lower half of each of the spheres in the third layer has a round Au nanodot on the apex deposited by the upward Au vapor flow that forms due to reflection by the substrate (Fig. 2D). Further self-assembly of such well-defined patchy particles has not yet been reported.

3.2. Preparation of rigid Janus particles and their self-assembly

Janus particles, named after the double-faced Roman God Janus, have two sides of different chemistry [49]. As one kind of anisotropic particles, Janus particles are most accessible experimentally. These particles are analogous to surfactant or block copolymers. Therefore, their preparation and self-assembly has attracted much attention in the particle self-assembly field.

Janus particles can be prepared by two-dimensional techniques, where particle arrays or layers on the surface of a flat substrate or another two-dimensional interface are protected on one side and decorated with metals or other materials on the other side [50,51]. Microfluidic methods have also been used for preparing Janus particles with welldefined shapes and structures [52,53]. However, both the two-dimensional methods and the microfluidic methods suffer from low preparation efficiency. To circumvent this problem, Granick et al. developed a method for preparing Janus particles on a gram scale [54]. First, a Pickering emulsion of wax in water was created using silica spheres as a stabilizer and by heating above the melting temperature of the wax. After cooling to room temperature, the wax droplet solidified, and the silica spheres were frozen at the solid wax/water interface to allow for solution-based modification of the hemisphere exposed to the water phase. The increased interface area on the wax particle surface is responsible for the high production efficiency.

Solution-based synthetic strategies, such as seeded emulsion polymerization [55–57], seeded epitaxial growth [58] and phase-separation in emulsion droplets [59,60], have also been used for the large-scale synthesis of Janus particles. Of note, Yang et al. proposed a facile method based on seeded emulsion polymerization for the preparation of submicron-sized Janus colloids with a tunable morphology [56,57]. This is the first report on the large-scale preparation of Janus colloids with distinctly compartmentalized components. Typically, silica spheres modified with vinyl groups functioned as seeds to direct

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Fig. 2. (A) Scheme for the construction of Au nanodot patterns on PS spheres. The orange areas represent the Au domains that remained on the spheres after the removal of the upper two layers. (B–E) Preparation of PS spheres (920 nm in diameter) with sp-like Au nanodot patterns (ABCABC stacking symmetry, 10 min of O_2 plasma etching and Au vapor with an incidence angle of 0°). (D) SEM image of the Au patterns obtained on the lower halves of the 920 nm spheres. (F–K) Preparation of sp³ – and sp² – like Au nanodot patterns on 270 nm PS spheres ((F, H, J) ABAB stacking symmetry, 3 min of O_2 plasma with an incidence angle of 0° ; (G, I, K) ABAB stacking symmetry, 3 min of O_2 plasma and Au vapor with an incidence angle of 0°). (L–N) Preparation of sp³d-like Au nanodot patterns on 920 nm PS spheres (ABAB stacking symmetry, 10 min of O_2 plasma and Au vapor with incidence angle of 0°). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced with permission from [48].

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the polymerization of styrene and divinylbenzene (DVB) in the oil-in-water emulsion system (Fig. 3). Growth occurred in an anisotropic fashion, as opposed to conventional core-shell growth, due to the incompatibility between PS-DVB and the silica spheres. Furthermore, the organic thin layer on the silica hemisphere was removed by slight etching with diluted HF. The as-prepared particles were truly Janus colloids in terms of not only the structural asymmetry but also the compositional asymmetry.

Janus particles prepared using colloidal spheres as precursor particles are usually submicron or micron sized and rigid. Due to their relatively large size and mass, the isotropic van der Waals attraction between the Janus particles is relatively large and dominant; their aggregation can lead to irregular clusters with fractal structures. To overcome this strong isotropic van der Waals interaction, charged or steric stabilizers can be introduced on Janus particles. For example, Granick et al. prepared zwitterionic polystyrene colloids with two oppositely charged hemispheres [61]. Self-assembly of the Janus colloids was conducted in phosphate-buffered saline (PBS, pH 6) at 1 mM ionic strength, where the Debye screening length is approximately 10nm, much smaller than the particle diameter. It was demonstrated by epifluorescence microscopy that clusters of charged Janus particles formed in dilute suspension (the maximum volume fraction was approximately 10^{-3}). It was noted from images (not shown here) that the superstructures were somewhat irregular. In another paper by the same group [62], self-assembly of rigid Janus particles was investigated by using amphiphilic colloidal particles with one hydrophobic hemisphere and one hydrophilic negatively-charged hemisphere, which was used to strengthen the anisotropic interaction that could be adjusted by varying the ionic strength of the suspension. In deionized water, the particles repelled each other and were individually dispersed in the system (Fig. 4A). Small compact clusters of amphiphilic particles formed due to hydrophobic interactions in a suspension with an ionic strength of 1 mM (Fig. 4B), and these clusters linked up into extended worm-like strings when the ionic strength was increased (Fig. 4C). These results were consistent with Monte Carlo computer simulations. However, one can still see from the image that there is considerable irregularity in the superstructures.

As we can see from the aforementioned results, it is difficult to obtain uniform and regular particle assemblies from the self-assembly of rigid Janus particles. Due to the relatively large mass of each of the rigid Janus particles, isotropic van der Waals interactions are strong and can counteract or weaken the anisotropic interactions between rigid Janus particles. In addition, the lack of structural flexibility indicates that rigid particles are incapable of adjusting their anisotropy and their shape to meet the requirements for forming stable and regular superstructures. We can imagine that the contact area between rigid spheres is very small such that the binding energy between primary particles in the superstructure may be small; introducing strong anisotropic interactions between anisotropic particles or providing the particles with enough flexibility may resolve this problem.

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Fig. 3. (a) [3-(Methacryloyloxy) propyl] trimethoxysilane-modified silica colloids. (b–d) Silica/polymer anisotropic composite colloids prepared at increasing monomer: silica weight ratios (0.1:1, 0.5:1 and 6:1 for b, c and d, respectively). In the monomer mixture, the St:DVB weight ratio is fixed at 1:1. (e) Schematic synthesis of Janus colloids by the wet etching of anisotropic composite colloids formed by polymerization induced dewetting. Reproduced with permission from [57]. © 2010 Royal Society of Chemistry.

3.3. Strong interaction-induced "self-assembly" of anisotropic rigid particles

As mentioned above, when the primary particles are rigid and relatively large or have a very small ratio of attractive to repulsive components, the adhesion energy between the primary particles is insufficient to stabilize any superstructures. For these cases, strong interactions are introduced to form stable superstructures.

Nanoparticles with ripple-like patches can be prepared from the synthesis of gold nanoparticles (AuNPs) in the presence of a mixture of protective ligands (specifically, a 2:1 molar ratio of octanethiol to mercaptopropionic acid) [63]. Spontaneous phase-separation between the ligands driven by surface curvature occurs on the surface of the AuNPs, and the ligands align into parallel ripples that encircle the AuNPs (Fig. 5a–d). Other types of *n*-alkane thiols (n=5, 7, 9, and 11) were used in place of octanethiol to control the height difference between the peaks and valleys of the ripples. The peak-to-peak distance decreased as the nanoparticle diameter increased due to the curvature effect. By changing the ligand ratio, the domain morphology can be varied from perfect ripples to defect-rich ripples and discrete domains. The rippled particles were effective in avoiding non-specific adsorption of a variety of proteins due to the unique alternative distribution of hydrophobic and hydrophilic regions on the surface on a sub-nanometer scale. Remarkably, the authors found that the two diametrically opposed singularities at the particle poles, where the ripples collapse into points, were defect points and could be replaced first in ligand-exchange reactions [64]. In this way, divalent AuNPs with two reactive points at two particle poles can be synthesized in a high-throughput manner. The divalent AuNPs can be used as "artificial monomers" that

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Fig. 4. Self-assembly of amphiphilic particles (1 µm in diameter) into clusters of various sizes and shapes formed by varying the salt concentration. The images with a green background represent epifluorescence experiments. The blue and yellow colors in the Monte Carlo simulations represent charged and hydrophobic hemispheres, respectively. (A) Discrete particles in deionized water. (B) Small clusters in 1 mM aqueous KNO₃ solution. (C) Long, branched, wormlike strings in 5 mM aqueous KNO₃ solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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can be connected covalently by complementary divalent molecules into nanoparticular chains (Fig. 5e and f).

Some anisotropic particles were prepared by modifying each precursor particle with an exact number of functional groups. One, two or three functional groups were introduced on the surface of each particle. These particles can be considered as patchy particles, which are analogous to atoms with an exact valence. Because each patch is composed of one functional group, weak interactions between the functional groups do not stabilize the resultant superstructures. Strong interactions such as DNA base pair interactions and covalent bonds were introduced. For example, single ssDNA chain tethered AuNPs can be isolated by gel electrophoresis or anion-exchange HPLC [65,66] from mixed conjugates of ssDNA-SH and AuNPs (Fig. 6). In fact, AuNPs decorated with more than one ssDNA chain each have some portion of mixed conjugates, which can also be separated (Fig. 6). However, for the multi-chain tethered AuNPs, the tethering positions are randomly distributed on the surface. Suzuki et al. controlled the number and position of ssDNAs on a AuNP at the same time (Fig. 7) [67]. A geometrical template was utilized for the controlled immobilization of ssDNA-SH onto a AuNP. The template consisted of three blocks, with a dsDNA middle block and two ssDNA end blocks (Fig. 7). Hybridization of the two end blocks with the other two –SH end-capped ssDNA chains led to a complex with two –SH groups located at the two ends of the middle block; the distance between

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Fig. 5. (a) STM image of octanethiol:mercaptopropionic acid (2:1 molar ratio) AuNPs showing phase-separated ripples in their ligand shell. The scale bar is 10 nm. (b) STM image of one rippled nanoparticle. (c) Schematic drawing of a single rippled nanoparticle in which the yellow lobes represent octanethiol and the red lobes represent mercaptopropionic acid. (d) Surface plot of the ligand shell contour showing the order that is present there (scales are in nm). The surface plot was obtained from the nanoparticle shown in (b) over the white line. The distance between the two red arrows indicates the ripple spacing. (e, f) Schematic depiction of the chain formation reaction and TEM images of the nanoparticle chains. Scale bars are 200 nm for the main image and 50 nm for the inset. Parts (a–d) reproduced with permission from [63]. © 2004 Nature Publishing Group; part (e–f) reproduced with permission from [64]. © 2007 American Association for the Advancement of Science. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the two –SH groups was controlled by the length of the middle block. Then, the template was conjugated with AuNPs via Au–S bonding, and the one-to-one hybrid template/AuNP complex was separated by gel electrophoresis. After dehybridization and centrifugation, the AuNPs

with two ssDNAs and controlled spacing were obtained (Fig. 7).

Anisotropic particles with an exact number of ssDNA chains can be used for fabrication of a variety of discrete AuNP assemblies with controlled geometry via strong

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Fig. 6. (A) Electrophoretic mobility of 5 nm Au particle/100-base ssDNA-SH conjugates (3% gel). The first lane (left to the right) corresponds to 5 nm particles (single band). When \sim 1 equiv. of DNA is added to the Au particles (second lane), discrete bands appear (namely 0, 1, 2, 3, . . .). When the DNA amount is doubled (third lane), the intensity of the discrete bands change and additional retarded bands appear (4, 5). (B) Anion-exchange HPLC elution profiles of varying lengths of polythymine DNA conjugated to 20 nm Au particle. Leftmost peak is unconjugated gold. Monoconjugate peak migrates to longer retention times as DNA length is increased, with near-baseline separation achieved for monoconjugates of 15-base ssDNA-SH. Part (A) reproduced with permission from [66]. © 2001 American Chemical Society; (B) reproduced with permission from [65]. © 2008 American Chemical Society.

Waston–Crick base pairing directed by designed DNA scaffolds. Using this technique, linear, branched, triangular, quadrangular, parallel, and tetrahedron morphologies of the assemblies were obtained (Fig. 8) [68–72].

4. Self-assembly of anisotropic soft particles

Particles that can change either their shape or component distribution or both are defined as soft particles. Typical soft particles are slightly swollen polymeric particles stabilized by linear polymer chains in solvents. Component redistribution on the surface can be realized by phase separation of the components on the surface or a conformational change of the shell-forming polymer chains or both.

Anisotropic soft particles are capable of self-assembling into various regular superstructures and are dispersible in solvents. Isotropic van der Waals interactions between particles can thus be overcome by solvation of polymer chains. Additionally, the flexibility of these soft particles allows the attractive part of different particles to fuse together in superstructures; in this way, the superstructure can be stabilized.

We outline in Fig. 9 the building blocks and the resultant superstructures to give an overview of soft anisotropic particle self-assembly. For soft Janus particles (Section 4.1), superstructures ranging from clusters to spheres and strings to tubes and sheets were obtained by varying the structural parameters or the solvophilic/solvophobic component ratios (Fig. 9A). To emphasize the capability of self-assembly of soft Janus particles, we classify the content based on the morphologies of the superstructures. Although most of the superstructures obtained have a spherical morphology, other morphologies such as strings, sheets and tubes were also produced by delicately balancing the attractive and repulsive interactions. For soft patchy particles (Section 4.2), two-dimensional freestanding films, multi-compartment superstructures, rod chains and bundles were reported to form via self-assembly (Fig. 9B-D). However, examples of the preparation and

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Fig. 8. Discrete assemblies of ssDNA-decorated patchy particles. (A) Head-to-tail, head-to-head and parallel trimer configurations resulted from selfassembly onto the ssDNA template. (B) Tetrahedral assemblies from four ssDNA-decorated particles with designed sequences. (C) TEM image of the tetrahedral assemblies. Part (A) reproduced with permission from [71]. 1996 Nature Publishing Group. Parts (B) and (C) reproduced with permission from [72]. © 2009 American Chemical Society.

self-assembly of patchy particles are quite limited. In addition, the patchy particles that are reported in the literature are different in both their geometry and anisotropy. Indeed, the studies reporting on the preparation and selfassembly of patchy particles are not systematic. Therefore, we describe the preparation and self-assembly of soft patchy particles on a case by case basis.

Similar to block copolymer self-assembly in selective solvents, soft anisotropic particles can self-assemble in selective solvents into superstructures with various morphologies. There are also differences between molecular and particle self-assembly. Some of the morphologies of the superstructures are difficult to obtain by molecular selfassembly. For example, two-dimensional free-standing films were produced from particle self-assembly, but are seldom obtained from molecular self-assembly because two-dimensional molecular assemblies may experience simultaneous curvature due to their insufficient rigidity, resulting in the formation of vesicles or tubes. Compared with the preparation of molecular amphiphiles, the preparation of anisotropic particles requires more complicated techniques. In addition, the preparation methods differ greatly for each kind of anisotropic soft particle and always involve delicate polymer phase-separation processes, such as the microphase separation of a triblock copolymer and intramicellar phase separation. Therefore, both the preparation and self-assembly of anisotropic soft particles will be presented in this review. As indicated by our

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A Soft Janus particles, the increment of solvophobic/solvophilic ratios

Fig. 9. An overview of the self-assembly of anisotropic soft particles. (A) Soft Janus particles and their self-assembly into clustered, spherical, fibrous, sheet-like and tubular superstructures by varying the solvophobic/solvophilic component ratios. (B) Self-assembly of toroidal patchy particles into twodimensional superparticle monolayers. (C) Self-assembly of patchy micelles into segmented cylinders. (D) Self-assembly of rod- or fiber-like amphiphiles with two end patches into chains and bundle chains. The red and blue parts represent the solvophobic and solvophilic components, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

upcoming discussion, anisotropic soft particles adjust their shape and even anisotropy during self-assembly to meet the requirements for organizing into regular and stable superstructures (Fig. 9); mismatches that inevitably exist between the anisotropic particles if they were rigid can thus be compensated for when the particles have sufficient flexibility.

4.1. Self-assembly of soft Janus particles

Among both rigid and soft anisotropic particles, Janus particles are the most accessible experimentally. Rigid Janus particles have a limited capability for self-assembly into regular superstructures, as mentioned earlier. Selfassembly of soft Janus particles actually makes up the majority of the cases of particle self-assembly into regular superstructures. As we will see, most of the superstructures are spherical, comparable to core–shell block copolymer micelles. Superstructures such as vesicles and tubes can also be produced, but this requires a delicate balance between attractive and repulsive interactions, whereas spherical superstructures can form in a kinetically controlled fashion [73].

4.1.1. Preparation of soft Janus particles and their self-assembly into spherical superstructures

Block copolymers are promising precursors of soft Janus particles. For example, ABC triblock copolymers have two end blocks of different chemistry and can be used as precursors in Janus particle synthesis. ABC triblock copolymers can self-assemble in bulk to form many phase-separated nanostructures. For the case of a nanostructure where a B domain is sandwiched between an A domain and a C domain, fixing the B domain and then dissolving the A and C domains will lead to Janus particles (Fig. 10). This has been fully explored by Muller and coworkers [74–78]. For example, the triblock copolymer polystyrene-b-polybutadiene-bpoly(methyl methacrylate) (PS₅₁-b-PB₆-b-PMMA₄₃, the subscripts represent the degree of polymerization of the

Fig. 10. Schematic representation of the preparation of Janus micelles, cylinders and disks based on the crosslinking of the polybutadiene segments of various bulk triblock copolymers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced with permission from [51]. © 2008 Royal Society of Chemistry.

respective blocks) can phase-separate into a structure where PB spheres are sandwiched between PS and PMMA lamellas. By crosslinking the PB spheres in the phaseseparated state and subsequently dissolving the PS and PMMA in the common solvent THF, Janus micelles with PS and PMMA shells on opposite sides and a PB core were obtained (Fig. 10). When the morphology is that of a PB cylinder or lamella sandwiched between an A lamella and a Clamella, the same procedure results in Janus cylinders or Janus disks (Fig. 10). The prepared Janus particles maintain their chain distribution in the bulk state and are well-defined, with two sides of entirely different chemistry. Janus micelles below a critical concentration of approximately 7 mg/mL in THF are individually dissolved in solvent, as indicated by the Rh value of approximately 10 nm determined by fluorescent correlation spectroscopy (the Rh value is consistent with the size of the Janus micelles estimated from the size of the PB domain in the bulk state). The Janus micelles have unusual solution properties compared to precursor chains and can

aggregate into supermicelles with an Rh value 53 nm above the critical concentration, possibly due to the amplified difference in solubility between the PS and PMMA shells or the loss in conformational entropy after crosslinking of PB; the Janus particles self-assemble in the solvent that is a good solvent for both PS and PMMA. Janus micelles can be further modified into amphiphilic Janus particles through PMMA ester hydrolysis (Fig. 11A). In an aqueous suspension containing 0.17 M NaCl, amphiphilic Janus particles have a critical aggregation concentration of approximately 0.03 mg/mL, which is much higher than that of the precursor triblock copolymers in selective solvents. This is explained by the fact that the hydrophobic PS hemisphere can be partially protected by the hydrophilic PMAA chains stretching from the opposite hemisphere due to the overall flexibility of the particles (Fig. 11A). Above a critical aggregation concentration, they can self-assemble into spherical supermicelles with uniform size and a smooth profile, and some very large spheres were inferred to consist of multilayers of Janus micelles (Fig. 11B-E). Self-assembly of the

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Fig. 11. (A) The hydrolysis of Janus micelles into amphiphilic Janus micelles and their self-assembly in water. (B–E) Tapping mode AFM images of spherical supermicelles (B, C) and very large spheres (D, E) from the self-assembly of amphiphilic Janus micelles (B, D, topography, 0–100 nm; C, E, phase 0–25°). Reproduced with permission from [78].

as-prepared Janus cylinders and Janus disks has also been investigated. Janus cylinders with one side covered by PS chains and the other side covered by PMMA chains can aggregate into fiber-like nanoobjects in acetone (the selective solvent for PMMA). It is interesting that, in an aqueous suspension at pH 10 at a concentration of 1 mg/mL, small amphiphilic Janus disks sized below approximately 100 nm can mostly be individually dispersed in water with a significant hydrophobic face exposed to water. In water at pH 10 and at a polymer concentration of 0.1 mg/mL, large amphiphilic Janus disks of several microns, much larger than the persistent length of the disks, bend into wrinkled structures where hydrophobic PS planes undergo backto-back stacking and hydrophilic PMAA planes face the outside medium. Janus micelles are predicted to have much higher adsorption energy at a liquid-liquid interface than isotropic particles. Muller et al. conducted Pickering emulsion polymerization using amphiphilic Janus particles as a stabilizer [79]. Mono-dispersed polymer latex from different monomers can be prepared, and the latex size can be controlled by changing the concentration of the stabilizer.

In addition to the aforementioned method with phaseseparated structures as precursors, simple intra-molecular crosslinking of the middle block of an ABC triblock copolymer in its common solvent can lead to the smallest Janus particles or single chain Janus particles [80]. Specifically, we developed efficient pathways toward single chain polymeric Janus particles by crosslinking the

Fig. 12. (A) Schematic representation of the synthesis of single chain polymeric Janus particles and their concentration-dependent self-assembly in common solvent DMF. (B) TEM images of single chain Janus particles from PS-b-P2VP-b-PEO intramolecularly crosslinked by 1.4-dibromobutane (stained by RuO₄). (C) Supermicelles self-assembled from Janus particles. Magnified images are shown as insets with 50 nm scale bars. Reproduced with permission from [80]. © 2008 American Chemical Society.

middle block of the molecularly-dispersed triblock copolymer polystyrene-b-poly(2-vinylpyridine)-b-poly(ethylene oxide) (PS₁₃₀₈-b-P2VP₄₅₂-b-PEO₁₈₃₀, the subscripts represent the degree of polymerization of the respective blocks) in its common solvent DMF by 1,4-dibromobutane (Fig. 12A). Using this method, single-chain Janus particles are prepared with cross-linked P2VP as the particle and one PS and PEO chain tethered. The preparation concentration of the triblock copolymer can be up to 20 mg/mL due to the successful prohibition of inter-chain crosslinking that takes advantage of the shielding effects of the two relatively long end blocks PS1308 and PEO452. The single-chain Janus particles prepared display a concentration-dependent selfassembly behavior in DMF into spherical supermicelles. It is interesting to note the morphology of dried single chain Janus particles by TEM. In the inset of Fig. 12B, individual PS and PEO block chains and the crosslinked P2VP single-chain spheres can be seen distinctly (stained by RuO₄). Additionally, in the superstructures, the outline of each individual Janus particle is clearly apparent (Fig. 12C). This method can be extended to other triblock copolymers with a crosslinkable middle block, which makes further modification of single-chain Janus particles possible.

Soft Janus particles can be obtained from intramicellar phase separation between the hydrophobic and hydrophilic components in the shell [81]. For example, the

di-block copolymer [Ru]-PEO₁₀₂-PPO₁₅ ([Ru] represents the Grubbs catalyst, which is the end-capping group of the PEO block; the subscripts represent the degree of polymerization of the respective blocks) in THF self-assembles into micelles with PPO as the core and PEO-[Ru] as the shell after the fast addition of water into a THF solution. The hydrophobic [Ru] groups (less hydrophobic than PPO) on the corona of each of the micelles gather together to form single hydrophobic domains, leading to a snowman-like structure that is seen when the highly flexible PEO block chains are of sufficient length (Fig. 13a and b). The resultant Janus particles cannot be thermodynamically stabilized in a uniparticle fashion and tend to spontaneously assemble into ill-defined clusters or well-defined spherical aggregates for short and extended equilibrium times due to the secondary aggregation of the [Ru] domains between the Janus particles (Fig. 13a, c, d). This is another good example of soft anisotropic particles self-assembling into stable and uniform superstructures.

Our group also developed an efficient one-pot pathway to amphiphilic polymeric Janus particles using a water-dispersible diblock copolymer/inorganic nanotube hybrid as an asymmetric template [82]. By an interaction between yttrium hydroxide nanotubes [83,84] and P4VP block chains of poly(ethylene oxide)-b-poly(4vinylpyridine) (PEO-b-P4VP), hybrid nanotubes composed

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Fig. 13. (a) Scheme for the formation of Janus-type micelles from the two-step micellization of a diblock copolymer end-capped with a Grubbs catalyst group, [Ru]-PEO-PPO, and their assembly into larger aggregates, which depends on the equilibration time. (b) TEM images of Janus micelles. (c) Ill-defined aggregates of Janus micelles are observed after 0.5 h of equilibration time. (d) After a 3 h equilibration, large, well-defined assemblies (supermicelles) of the Janus micelles can be observed. Reproduced with permission from [81].

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of an inorganic nanotube surrounded by a hydrophobic polymer inner layer (P4VP) and hydrophilic outer layer (PEO) were prepared (Fig. 14A and B). In the aqueous suspension, the hydrophobic monomer divinylbenzene (DVB) and hydrophobic initiator azobisisobutyronitrile (AIBN) were solubilized in the hydrophobic layer and hydrophilic monomer N-isopropyl acrylamide (NIPAM) in the water phase. At 80 °C, polymerization took place in the inner hydrophobic layer, and PDVB grew into spheres due to the phase separation between the PDVB and P4VP hydrophobic

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Fig. 14. (A) A diagram illustrating the formation of a water-dispersible hybrid nanotube, the synthesis of Janus particles using the hybrid nanotubes as an asymmetric tool, the self-assembly of these Janus particles into a supermicelle and the dissociation of the supermicelle; (B) TEM image of a hybrid nanotube with a larger magnification in the insert to show the polymer layer surrounding the yttrium hydroxide nanotube; (C) TEM image of the supermicelles; (D) TEM image of the supermicelles at a larger magnification; (E) AFM image of the petal-like Janus particles that result from the dissociation of the supermicelles on mica; (F) TEM image of the Janus particles stained with RuO₄; (G) the distribution of the hydrodynamic diameters of the supermicelles (\bigcirc) and the Janus particles (\triangle) .

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polymeric layers. When the diameter of the PDVB spheres was larger than the layer thickness, one side of the PDVB spheres is exposed to water and initiates grafting polymerization of NIPAM. The other side of the PDVB spheres is still embedded in the hydrophobic layer and thus protected (Fig. 14A). Thus, Janus particles with PDVB spheres as the hydrophobic part and PNIPAM grafts as the hydrophilic part were prepared. In an aqueous suspension, the obtained amphiphilic PDVB-PNIPAM polymeric Janus particles spontaneously self-assemble into uniform flower-like superstructures with a narrow size distribution (Fig. 14C and D). The hydrophobic side formed by PDVB was actually a highly flexible structure, as evidenced by a large size difference between superparticles in the dried state and in water suspensions (Fig. 14D and G). These structural features should be responsible for the capability of as-prepared Janus particles to self-assemble into uniform and regular superstructures. The superstructure can be dissociated into single Janus particles in a common solvent for both PDVB (PDVB should be a network with a relatively low crosslinking density) and PNIPAM or with a polar substrate, where the Janus particles exhibit a corn-like morphology (Fig. 14E and F). This approach should allow for the production of a series of amphiphilic Janus particles by varying the hydrophobic and hydrophilic monomer. The size and structural features of the Janus particles can be adjusted by varying the thickness of the hydrophobic layer.

4.1.2. Self-assembly of soft Janus particles into clusters, fibers, tubes and sheets

Similar to block copolymer self-assembly, one can obtain spherical, cylindrical and vesicular aggregates by varying the structural parameters of the building blocks. Starting from Janus particles that can form spherical superstructures, lowering the component ratio leads to clusters that consist of a small number of Janus building blocks. By increasing the solvophobic/solvophilic ratio, we can obtain fiber-like, tube-like and sheet-like superstructures (Fig. 9A).

Self-assembly of Janus particles with a small solvophobic/solvophilic ratio into dimers was reported by Chen et al. [85]. The Janus particles were prepared by eccentric encapsulation of 15 nm AuNPs by amphiphilic PS₁₅₄-b-PAA₆₀ block copolymers (Fig. 15a). The authors encapsulated hydrophobic AuNPs (coated by 2-dipalmitoyl-sn-glycero-3-phosphothioethanol (sodium salt)) in the presence of the second competing hydrophilic ligand diethylamine (without the presence of hydrophilic ligand, homocentric hybrid particles were prepared as shown in Fig. 15b and e). The amphiphilic AuNPs can undergo surface ligand de-mixing and localize at the micellar core-shell boundary with their hydrophilic domains exposed to water and hydrophobic domains embedded in the micellar core (Fig. 15c, d, f and g). The resulting snowman-like hybrid Janus particles with a small attractive patch can self-assemble into dimers via a head-to-head coupling when the hydrophilic domains are destabilized by increasing the pH and ionic strength of the medium (Fig. 15h).

In the aforementioned example, complete de-mixing of the two stabilizers on the AuNP surface is a key step for the formation of Janus particles. Lipid de-mixing on the mixed membranes, driven by incompatibility between saturated and unsaturated lipid tails, can result in Janus vesicles [86]. The Janus vesicles can be further selectively decorated by insertion of cholestervl-ssDNA into the saturated lipid domains [87]. In the presence of cardiolipin in particular, which increases the free energy cost of the insertion of cholesterol into unsaturated lipid domains, the surface concentration of ssDNA in the saturated hemispheres was at least an order of magnitude greater than that for unsaturated hemispheres. By mixing two populations of Janus vesicles with complementary ssDNA, they can adhere and self-assemble into clusters. The soft vesicles can deform into flat planes in the contact areas to allow for multiple DNA bonding. This work provides an intuitive example for demonstrating the regulatory role of particle flexibility in letting the attractive regions interact as much as possible at the expense of a small amount of entropy.

Li et al. used sheet-like HS-PEO (thiol end-capped poly (ethylene oxide)) single crystals several microns in size as masks to prepare Janus AuNPs with PEO chains on one side and poly(methyl methacrylate) (PMMA) or poly(tert-butyl acrylate) (PtBA) chains on the other side [88.89]. The end -SH groups were mostly located on the surface of the PEO crystals (the -SH end groups are excluded onto the crystal surface during crystallization of the PEO) and can capture ammonium-ligand-protected 6 nm AuNPs in pentyl acetate/toluene (5:1, v/v). The crystal templates protect the underlying surface of captured AuNPs from subsequent polymer grafting and can be dissolved after modification (Fig. 16). The prepared Janus AuNPs with 6 nm gold cores and compartmentalized PEO₁₁₄/PMMA₂₀₈ shells with a PEO/PMMA chain mass ratio of approximately 1/3.2 can be dissolved in acetone (a common solvent for both PEO and PMMA) and self-assemble into fiber-like superstructures in dioxane (the selective solvent for PMMA) [90].

Hatton et al. developed a method of preparing polymerdecorated Janus magnetic nanoparticles (MagNPs) with silica spheres of 700 nm in size as masks [91]. Tennanometer-diameter PAA-coated MagNPs were prepared and then allowed to interact with positively charged amine-coated silica spheres approximately 700 nm in diameter; one side of the MagNPs was adsorbed onto the surface of the silica spheres and was thus protected (Fig. 17). Polymer grafting on the exposed side of the MagNPs is based on an amidation reaction between PAA on the MagNPs and -NH₂ on the end of the polymer chains used for modification (PSSNa, PDMAEMA and PNIPAM can be grafted, which represent polystyrene sodium sulfonate, polydimethylamino ethylmethacrylate and poly(N-isopropyl acrylamide), respectively). Janus MagNPs were produced after removing the masks by increasing the pH value of the medium. The PSSNa/PAA Janus MagNPs can self-assemble when the pH of the medium is decreased, and the PAA can undergo protonation and associate. The prepared Janus MagNPs with compartmentalized PSSNa/PAA, PDMAEMA/PAA or PNI-PAM/PAA were pH or temperature responsive and can reversibly self-assemble into stable particle clusters or fiber-like superstructures.

It is expected that flexible Janus particles with a higher solvophobic/solvophilic ratio may self-assemble

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Fig. 15. Schematic diagram showing the formation of homocentric (a and b) and eccentric (a, c and d) AuNP/polymer hybrids. TEM images of the hybrid particles when the hydrophobic:hydrophilic ligand ratios = 1:0 (e), 1:22 (f), and 1:132 (g), which corresponds to (b), (c), and (d), respectively. (h) Aggregates of the eccentric hybrid particles after incubation with a basic NaCl solution (0.1 M NaCl and 0.04 M NaOH). The insert is the image with larger magnification. The scale bars are 50 nm for (e), (f), and (g) and 100 nm for (h). Reproduced with permission from [85].

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Fig. 16. Schematic illustration of the formation of polymer-functionalized Janus AuNPs by combining "solid-state grafting-to" and "grafting-from" methods. Reproduced with permission from [89].

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into superstructures with low curvatures. Such polymeric Janus particles were prepared in our laboratory via an intra-micellar phase separation of mixed-shellmicelles (MSMs) [92]. The MSMs were prepared by non-covalent crosslinking of the PAA blocks by the addition of 1,2-propanediamine into a mixture of poly(ethylene oxide)-b-poly(acrylic acid) (PEO-b-PAA) and poly(2-vinyl naphthalene)-b-poly(acrylic acid) (P2VN-b-PAA) in DMF, where the mixed shell was formed by PEO and P2VN and the core by the PAA/1,2-propanediamine complex (Fig. 18A). After switching the solvent to neat water, P2VN collapsed into small hydrophobic domains on the surface of the core, which were stabilized and protected by the PEO chains (Fig. 18A and C). These MSMs were highly flexible because the core was of a swollen structure; this was evident by the large size difference observed between the size of the micelles in water and in the dried state (Fig. 18B and C). By decreasing the pH value to 3.1, the PEO chains collapsed into the PAA core due to complexation between PAA and PEO. Without the protection of the PEO chains, small P2VN domains aggregated together into a single hydrophobic domain (Fig. 18A), which was facilitated by the great flexibility of the MSMs. Both of these processes occurred in an intra-micellar way and resulted in a Janus particle with

Fig. 17. Scheme of the masking procedure for the asymmetric functionalization of PAA-coated magnetic nanoparticles. Reproduced with permission from [91]. © 2007 American Chemical Society.

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Fig. 18. (A) A schematic illustration of the processes involved in preparing MSMs in DMF (a) and water (b) as well as their intramicellar complexation (c) to form Janus nanoparticles (d). Note that one MSM transforms into one Janus nanoparticle, and the black P2VN domain in the Janus nanoparticle formed through the aggregation of all of the P2VN small domains in the MSM. (B) The hydrodynamic radius distributions of the MSMs in DMF and water. (C) TEM images of the MSMs cast from water (stained with RuO₄). (D, E) TEM images of aggregates observed at different magnifications immediately after their pH reached 3.1. (F–I) TEM images of nanosheets of the nanotubules in aqueous solution (pH 3.1) with trapezoidal (F) and semicircular (G and I) shapes after ultrasonicating for both 20 s (F) and 30 min or more (G and I). A schematic representation of a nanosheet is shown in the inset of (G). The microdomains of P2VN are black, PAA are red, and PEO are blue. The inset in the AFM image (H) shows the thickness profile of the nanosheet. The scale bars are 100 nm for (C), 500 nm for (D), 100 nm for (E), 1000 nm for (G), 200 nm for (H), and 200 nm for (I). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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P2VN on one side and a PEO/PAA complex on the other side (Fig. 18A). These Janus particles can spontaneously self-assemble into tubular superstructures (Fig. 18D and E) and the tubular superstructures converted to sheet-like superstructures after ultrasonication (Fig. 18F–I). By regulating the structural parameters and the particle geometry and composition of the MSMs, we are hoping to adjust the structural parameters of the Janus particles to obtain other kinds of superstructures through particle self-assembly.

4.2. Preparation of soft patchy particles and their self-assembly

Patchy particles are much more complicated than Janus particles in their structural geometry and anisotropy (Janus particles are the simplest anisotropic particles). Due to difficulty with their preparation, examples concerning selfassembly of soft patchy particles are quite limited; the studies of soft patchy particles are far from systematic. Therefore, we review the studies case by case.

4.2.1. Anisotropic particles with toroidal patches and their two-dimensional self-assembly

Based on computer simulations, particles with toroidal patches are anisotropic particles that can self-assemble along the plane defined by the toroidal region into two-dimensional superstructures [46,47]. Recently, our group developed a method for preparing anisotropic particles with toroidal attractive patches via one-to-one ssDNA/micelle complexation [93]. These micelles, prepared from micellization of guaternized poly(ethylene oxide)-b-poly(2-vinylpyridine)-b-polystyrene (PEO₇₁-P2VP₁₂-PS₂₉, the subscripts represent the degree of polymerization of the respective blocks) in water, displayed a core-shell-corona structure with an average diameter of 20 nm and a perimeter of 63 nm (Fig. 19a and i). Complexation between the micelles and ssDNA chains was driven by electrostatic interactions between the positively charged quaternized P2VP shell and the negatively charged ssDNA phosphate backbone. ssDNA chains with an average of 200 nucleotides (68 nm in contour length) were selected, and these chains formed one cycle around a micelle. One-to-one complexation was ensured when the solution was highly diluted and the molar ratio of micelles to ssDNA chains was nearly 1:1 (Fig. 19b). The ssDNA/micelle complex had an unstable toroidal DNA-bound region due to charge neutralization and stable upper and lower hemispheres and thus can spontaneously self-assemble along the plane of unstable toroidal region into free-suspending films with a rather smooth surface via fusion of the polymeric components due to high chain mobility (Fig. 19c-h). As far as we know, this represents the first example of template-free two-dimensional assembly of soft anisotropic polymeric nanoparticles into highly ordered two-dimensional superstructures.

4.2.2. Preparation and self-assembly of patchy micelles

An elegant example of preparing patchy particles as well as their self-assembly was reported by Muller et al. [94]. The patchy micelles were obtained from phase separation between two incompatible components of the mixed shell block copolymer micelles. The authors designed and prepared mixed shell micelles from the self-assembly of the triblock copolymer, poly(4-tert-butoxystyrene)-bpolybutadiene-b-poly(tert-butyl methacrylate) (PtBS₄₅₂b-PB₅₁₃-b-PtBMA₄₆₃), where the middle PB block was modified with a fluorinated side group (Fig. 20). In organic fluorophobic media (e.g., dioxane, a good solvent for both the PtBS and PtBMA end blocks), the fluorinated block acted as a micellar core, and PtBS and PtBMA were uniformly mixed in the shell. At a temperature higher than the glass transition temperature of the middle block (the core of the micelles), the flexibility of the micelle core in the rubber state during thermal annealing allowed for sufficient dynamics and redistribution of the arms, forming a patchy surface due to the incompatibility between PtBS and PtBMA. The patchy surface can be further fixed after cooling the system to room temperature (Fig. 20). The patchy micelles can self-assemble into branched, undulated cylinders in a solvent (ethanol) selective for the PtBMA block, and this self-assembly is driven by the attractive interaction between the PtBS patches. It should be noted that without annealing and phase separation into the patchy surface, the isotropic mixed shell micelles aggregated into ill-defined structures in the selective solvent. The transition from original isotropic micelles to micelles with a patchy surface is necessary for the self-assembly into regular superstructures.

4.2.3. Self-assembly of nanofibers or nanorods with two end patches

Rubinstein et al. reported the self-assembly of ABA type rod amphiphiles, which were prepared via selective binding of thiol-terminated polystyrene to the two ends of CTAB-coated gold nanorods 8 nm in diameter and 42 nm in length; such hybrid particles are considered patchy because they have two hydrophobic patches on the ends [95]. By adding water (a selective solvent for the CTAB bilayer) to the suspension in DMF (DMF is the common solvent), rod amphiphiles self-assembled into intricate superstructures. The morphologies of the resultant superstructures can be adjusted by varying the structural parameters of the rod amphiphiles or the water content of the medium (Fig. 21). By increasing the length of the PS chains on the ends, the resulting assemblies can vary from single rods to rod chains to bundled rod chains. One can imagine that shorter PS chains are localized near the rod ends and can only undergo end-to-end coupling, whereas longer PS chains can stretch to the side of the nanorods and thus allow for side-by-side coupling (Fig. 21a-d). When the water content was increased, rod bundles, bundle chains or rod chains were obtained. In low amounts of water, the PS chains were able to stretch to the side of the nanorods to allow side-by-side coupling. When higher amounts of water are used, the chains collapse, and the PS is localized near the ends so that only end-to-end coupling can occur (Fig. 21e-h).

Recently, Wooley et al. reported the dynamic self-assembly of polymer brushes into cylindrical superstructures via end-to-end coupling [96]. The amphiphilic brushes were synthesized by a ring-opening

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Fig. 19. TEM images of (a) the micelles (stained with RuO_4), (b) the ssDNA/micelle complex (unstained), (c) the aggregates formed during the intermediate assembly stage of the toroidal complex (unstained) and (d) the free-suspending films (FSFs) formed during the final assembly stage of the toroidal complex (unstained), which wrinkled while drying on the carbon-coated copper grids. (e) The SAXS profile of the FSFs. (f–h) The thickness profiles and AFM images of the FSFs (on silicon wafer substrates). The red and green lines in (f) are the height profiles obtained along the straight lines in (g) and (h), respectively. As indicated in the two insets in (c) and (d), a network superstructure with an average spacing of 8–10 nm is visible. (i) The proposed mechanism for the formation of the FSFs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced with permission from [93].

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Fig. 20. The formation of micelles with a compartmentalized corona by annealing their fluorinated micellar cores in dioxane, and the preparation of undulated multicompartment cylinders by the directed stacking of these micelles in ethanol. Reproduced with permission from [94]. © 2009 Wiley-Blackwell.

metathesis polymerization of a triblock macromonomer α -norbornenyl polystyrene-b-poly(methyl acrylate)-b-poly(tert-butyl acrylate) (NB-PS₂₈-b-PMA₂₈-b-PtBA₇₆) and subsequent hydrolysis of the PtBA into PAA (Fig. 22A and B). The brushes were characterized by a high side chain density, while the two ends had a much lower chain density; the brushes are actually patchy particles with

hydrophobic patches on the two ends, which is similar to the aforementioned ABA rod amphiphiles. When the selective solvent water was added to a solution of the brushes in DMF, the brushes tended to aggregate into cylindrical assemblies via end-to-end coupling (Fig. 22 D and E). The hydrophobic interaction between the PMA and PS acts as the driving force and stabilizes the superstructure. When

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Fig. 21. (a) A schematic representation of the relative locations of PS molecules of varying molecular weight with respect to the central gold block and the self-assembled, triblock structures formed when water is added to the solution of gold nanorods in DMF. These schematics are not to scale. (b, c, d) Scanning electron microscopy (SEM) images of the self-assembled triblock structures carrying PS-5K (b), PS-12K (c), and PS-30K (d) in a water/DMF mixture with 6 wt% in water. The scale bar is 100 nm. (e) Schematic of the relative locations of PS molecules with respect to the central gold block in water/DMF mixtures with varying water content, and the self-assembled triblock structure of 50K-PS. These schematics are not to scale. (f, g, h) SEM images of the assembled triblock structure of 50K-PS. These schematics are not to scale. (f, g, h) SEM images of the assembled triblock structures with 4 wt% water (f), 10 wt% water (g), and 20 wt% water (h). The scale bar is 100 nm. (e) 2008 American Chemical Society.

a solution of these assemblies was heated to $70 \,^{\circ}$ C, the hydrophobic interaction became weak, and the cylinders dissociated into individual building blocks. Interestingly, when the solution cooled down, the individual brushes were not able to reassemble into cylinders because the

ends of the brushes were kinetically stabilized by the PAA chains (Fig. 22F). The brushes lacked the flexibility to redistribute their chains and to couple with each other. When some amount of THF was added to this solution, the mobility of the PS and PMA chains increased remarkably

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Fig. 22. (A) The synthesis and self-assembly of concentrically amphiphilic molecular brushes, which have triblock PS-b-PMA-b-PAA side chains, and linear amphiphilic PS-b-PMA-b-PAA triblock copolymers. (B) Gel permeation chromatography profiles for NB-PS, NB-PS-b-PMA, NB-PS-b-PMA, and PNB-g-(PS-b-PMA-b-PtBA). (C) TEM image of the nanostructures self-assembled from linear NB-PS-b-PMA-b-PAA triblock copolymers in solution and then cast onto a carbon-coated copper grid. (D) TEM image of the hierarchical PNB-g-(PS-b-PMA-b-PAA) cylindrical nanostructures self-assembled in solution and then cast onto a carbon-coated copper grid. (E) AFM image of the hierarchical PNB-g-(PS-b-PMA-b-PAA) cylindrical nanostructures self-assembled in solution and then cast onto a mica substrate. The scale bar is 100 nm. (F) TEM images of the disassembled nanostructures after heating an aqueous solution of PNB-g-(PS-b-PMA-b-PAA) at 70 °C for 3 h. (G) TEM images of partially reassembled nanostructures after adding an equivalent volume of THF to the heated PNB-g-(PS-b-PMA-b-PAA) aqueous solution. The scale bar is 100 nm. Reproduced with permission from [96].

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to the point where they were able to reassemble into cylindrical superstructures (Fig. 22G).

In a common solvent, anisotropic soft particles can be solubilized, and the interaction between particles and solvent molecules can overcome the interaction between particles. When the solvent is switched to a selective one, the insoluble component tends to aggregate, while the soluble component may stabilize to form regular

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superstructures. For soft anisotropic particles, the flexibility allows the primary building blocks in the superstructure to adjust their shape to fuse together during self-assembly, which leads to a large enthalpy gain at the cost of a relatively small entropy loss. As a result, stable superstructures with different morphologies can be prepared. To obtain superstructures with much more complexity, synthetic techniques are desired that can not only prepare but also tailor the structural parameters of the soft anisotropic particles.

5. Self-assembly of isotropic soft particles

As shown by the aforementioned examples, soft Janus particles, compared with rigid Janus particles, are much more capable of further self-assembly into regular superstructures. The flexibility of these soft particles allows them to adjust their shape as well as their anisotropy during selfassembly. The former is necessary because most primary particles are spherical. By adjustment of their shape during self-assembly, the contact area between these primary particles in the final superstructures can be enlarged, which provides more adhesion between building blocks to stabilize the superstructure. The latter is also indispensable; when the attractive regions change their position, shape and size, which should be accompanied by a change in anisotropy, the contact area between the attractive regions can be maximized, and the area of the attractive regions exposed to the solvent can be minimized. As a result, stable superstructures can be obtained. In term of their flexibility, soft particles are intermediate between rigid particles and block copolymer coils. The block copolymer coils, when considered as highly flexible particles, are usually isotropic in the common solvent. During self-assembly of the block copolymer in a selective solvent, due to the great flexibility, the block copolymer chains will change their conformation to adopt the anisotropic morphologies to meet the requirements for forming spherical micelles, worm-like micelles or vesicles. In either the assemblies in solution or the phaseseparated structures in bulk, the block copolymers become entirely anisotropic. It should be inspiring to us that it is also possible for flexible isotropic particles to undergo sufficient particle deformation and material redistribution to self-assemble into stable superstructures where particles adopt an anisotropic morphology. This is significant because the isotropic particles are much easier to prepare than anisotropic particles. The particles should have at least two components that provide for both the repulsive and attractive interactions between particles under the conditions for self-assembly. The attractive interactions drive the self-assembly of the particles, while the repulsive interactions stabilize the superstructures and the balance between the attractive and repulsive interactions, which is regulated by the flexibility of the particles, determines the morphologies of the resultant superstructures. We should point out here the difference between anisotropic particles and isotropic particles that are capable of self-assembling into superparticles; the former are prepared with anisotropy, but the latter are synthesized with isotropy, and the anisotropy of the latter is induced by

self-assembly. This concept has been successfully reported in several recently published papers.

It is known that aggregation of isotropic uniform particles (e.g., isotropic inorganic nanoparticles) is governed by the well-known mechanisms of diffusion-limited aggregation and reaction-limited aggregation, which results in irregular clusters with fractal structures. However, we demonstrate here that the situation is quite different when the particles are core-shell structured with linear or branched polymer chains, as the shell and the attractive interaction occurs between the cores of the core-shell particles (such structured shells are opened, which makes the core accessible). The core-core attractive interaction can be modulated by the shell-shell repulsive interaction to form regular superstructures. In addition, isotropic core-shell particles with a mixed shell composed of two kinds of polymer chains of different affinity can be induced into anisotropic particles and thus self-assemble into various regular superstructures under certain conditions. The shell-forming mixed polymer chains redistribute into anisotropic structures during self-assembly; the original isotropic particles become anisotropic in the resultant superstructure after self-assembly.

In this section, we describe the self-assembly of soft isotropic particles in two parts: core-core couplingdriven self-assembly of core-shell particles with a uniform shell (Section 5.1) and shell-shell attraction-induced selfassembly of particles with a mixed amphiphilic shell (Section 5.2). Before each subsection, we illustrate in figures the primary particles, the resultant superstructures and the anisotropy proposed for the building blocks in the final superstructures. In the superparticles from either the core-core coupling (Section 5.1) or the shell-shell attraction (Section 5.2.1, self-assembly of isotropic soft particles via shell-shell attraction in a patchy fashion), the constituent particles that are originally isotropic adopt patchy-like morphologies. However, we can still see the difference between these superstructures from the core-core coupling and the shell-shell attraction. The former leads to core-shell superstructures, whereas the latter usually produces multi-compartment superparticles, as detailed below.

5.1. Self-assembly via core-core coupling

For isotropic core-shell particles with an attractive core and a repulsive hair-like shell, three consequences are expected when they are mixed together. First, when the repulsion of the shell, which depends on the length and density of the shell-forming chains, provides enough protection for the reactive core, no core-core coupling can occur. Second, when the protection is far from sufficient, irregular aggregates will form. Third, with a moderate protection from the shell-forming chains and enough flexibility of the particles, diverse regular assemblies will be produced (Fig. 23).

We reported in 2005 [97] that the core-core coupling between flexible core-shell spherical nanoparticles could lead to regular core-shell nanofibers; each of the core-shell spherical nanoparticles behaved like a difunctional monomer, and the nanofibers can be thought

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Core-core coupling, the decrease of shell–forming chain density

Morphology of the building blocks in the final superstructures

Two-patch-particles Three-patch-particles

Four-patch-particles

Fig. 23. The core-core coupling of isotropic soft particles with attractive cores and a moderate shell-forming chain density. With a decrease in the shell-forming chain density, cylindrical, branched, sheet-like and vesicular superstructures can be obtained. In the image, the red parts represent the attractive cores, and the blue semitransparent parts represent the hair-like shell of particles with relatively low chain densities (the greater the transparency, the lower the shell-forming chain density). The building blocks in the resultant superstructure adopt a patchy structure with two, three or four patches. It is noted that the density of the shell-forming chains in the uncoupled areas of the core surface increase remarkably after self-assembly, which makes further coupling of the superparticles with either primary particles or other superparticles difficult. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of as an oligomer of the particles (Table 1, Fig. 24). In the example we reported, the core-shell particles were prepared by arm-first anionic polymerization (Fig. 24j). A polystyrene (PS) anionic macroinitiator was used to initiate the polymerization of the mixture of 4-vinylpyridine (4VP) and divinylbenzene (DVB) in THF at -78 °C, resulting in core-shell particles with unreacted carbanions and carbon-carbon double bonds within their core; the core was flexible because it was a loosely crosslinked network in the common solvent. The chain length and density of the PS shell can be adjusted by controlling the molecular weight of the PS macroinitiator and PS/4VP feed ratio (Table 1). Under conditions where the length and density of the PS arms were intermediate, the core-shell nanoparticles coupled with each other into fiber-like or graft-like superstructures (Fig. 24c-i). We pointed out in our study that, when the core-shell nanoparticles were flexible enough, core-core coupling induced a redistribution of the PS arms from the coupling point to the neighboring uncoupled area, resulting in a considerable increase in the density of the PS arms at the neighboring uncoupled area, whereas the area opposite to the coupling point was less affected. Considering

System no.	$M_{ m w,PS}{}^{ m a}$	PDI _{PS} ^b	$N_{4\rm VP}/N_{ m St}^{\rm c}$	$N_{\rm DVB}/N_{\rm 4VP}{}^{\rm d}$	$\langle R_{\rm h} \rangle$ (nm) ^e	PDI _{DLS} ^f
1	90 281	1.12	1.04	1/9	66	0.09
2	114 520	1.23	1.41	1/9	111	0.09
3	80 622	1.03	3.21	1/9	78	1.00
4	84 244	1.10	4.61	1/9	95	1.00
5	8 213	1.18	3.00	1/9	217	1.00

Table 1

Composition, size, and size distribution of the resultant nano-objects.

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^a Molecular weight of the polystyrene macroinitiator.

^b Polydispersity index of the polystyrene macroinitiator.

^c Molar ratio of 4-vinylpyridine (4VP) to the styrene units in the PS macroinitiator.

 $^{\rm d}\,$ Molar ratio of divinylbenzene (DVB) to 4VP.

^e Average hydrodynamic radius of the nano-objects measured by dynamic light scattering (DLS).

 $^{\rm f}\,$ Polydispersity index of the size distribution measured by DLS.

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Fig. 24. (a) SEM and (b) TEM images of the nanospheres produced by system 1; (c) SEM and (d, e) TEM images of the nanofibers produced by system 3; (f) SEM and (g) TEM images of the nanofibers produced by system 4; (h, i) SEM images of the graft-like aggregates produced by system 5. The scale bars are 500 nm in (a), 200 nm in (b), 500 nm in (c), 500 nm in (d), 200 nm in (e), 2000 nm in (f), 200 nm in (g), 10,000 nm in (h), and 2000 nm in (i). (j) Schematic representation of the core-core coupling between polymeric core-shell nanospheres. Detailed information for each system can be found in Table 1. Reproduced with permission from [97].

this, after the two opposite poles of a particle were coupled with two other particles, the density of the arms on the side of the particle increased remarkably, and further coupling from the side became much more difficult (Fig. 24j). As a result, during this process, the isotropic core-shell particles behaved like a di-functional monomer (particles on the fiber-like structure) or a tri-functional monomer (a particle on the graft-point of the graft-like structure) in condensation polymerizations. In this case, the "attractive interaction" was the interparticle reaction between carbanions and carbon–carbon double bonds within the core. The repulsive interaction between the solvated PS shell and the high flexibility of the core modulated the aggregation driven by the core–core coupling; the flexibility enabled the PS arms to redistribute to the side by adopting a conformation that directed away from the coupling point. To our knowledge, this is the first study on the mechanism and possibility of the anisotropic

assembly of flexible isotropic particles into regular superstructures.

We also reported that polymerization of water-soluble spherical polydivinylbenzene (PDVB) nanoparticles bearing vinyl groups resulted in two-dimensional particle films in water [98]. The PDVB nanoparticles are very small, with a size below 10 nm, and are prepared via an azobisisobutyronitrile (AIBN)-initiated polymerization of DVB in the glassy polymer matrix poly(4-vinylpyridine), where particle size growth by particle-particle aggregation can be successfully prohibited (Fig. 25A and B). Subsequent modification of the -CN groups (residue groups of the initiator AIBN) into hydrophilic -COOH and -NH₂ groups makes the particles hydrophilic. Although crosslinked, the PDVB nanoparticles have loose inner structures resulting from the diffusion-limited process of particle formation (Fig. 25A) and thus have enough flexibility to allow for material redistribution. During further polymerization of the remaining carbon-carbon double bonds between different particles initiated by $(NH_4)_2S_2O_8$, the PDVB nanoparticles undergo side-by-side coupling, and the hydrophilic groups redistribute to uncoupled areas and stabilize the final particle films (Fig. 25C).

Kumar et al. investigated the anisotropic self-assembly of isotropic polystyrene-grafted 14 nm silica nanoparticles (nanoparticle amphiphiles) in a polystyrene matrix [27]. When the graft chain length or density was increased, a variety of superstructures ranging from spherical clusters to thick and thin sheets, strings and finally well-dispersed particles can be produced after thermal annealing, which was consistent with the results from a computer simulation (Fig. 26). The simulation suggested that a delicate balance between inter-particle attraction and the entropy loss of the graft chains when particles approached was responsible for the anisotropic self-assembly. The entropy loss of the graft chains actually provided for a repulsive interaction between the particles. The author's approach indicated a facile route for the creation of nanocomposites with various nanostructures and enhanced mechanical properties. In addition, it was proposed that the self-assembly of these nanoparticle amphiphiles had clear parallels to the behavior of conventional surfactants.

Core-core coupling-induced self-assembly of 3.4 nm CdSe/CdS core-shell nanoparticles with grafted PEO chains in water was studied by Weller and coworkers [99]. The particles with various PEO surface chain densities were prepared via a ligand-exchange reaction between PEO chains with end amino ligands and trioctylphosphine/trioctylphosphine oxide ligands. When the amphiphilic nanocrystals were dissolved in water, a series of superstructures ranging from short cylinders to particle networks and vesicles spontaneously form via core-core coupling, with a decrease in the density of the PEO chains on the quantum dots (Fig. 27). Polymer chain redistribution is also involved in this process of self-assembly, which allows for the quantum dots to have proximity at the cost of a relatively small entropy loss of the polymer chains.

Meijer et al. investigated the self-assembly of isotropic particles with a dynamic view [100]. Flexible isotropic particles were fabricated via host-guest supramolecular chemistry of a hydrophobic dendrimer host molecule and excess hydrophilic guest molecules. The fifth-generation urea-adamantyl poly(propylene imine) dendrimer was the host, and ureido acetic acid molecules were the guest (Fig. 28a). The host-guest complex can be thought of as a core-shell particle with a hydrophobic dendrimer as the core and hydrophilic guest molecules as the shell. The host-guest interaction was first conducted in chloroform (the common solvent), where host-guest complexation was strong. After switching the solvent to water, the complexation was weakened, and a part of guest molecules dissociated from particles into the water phase upon dilution; guest molecules in the water phase and on particles were in a dynamic equilibrium (Fig. 28b). Soft particles with hydrophobic patches were produced by the dissociation of the hydrophilic guest molecules from the hydrophobic surface of the dendrimer and the amount of hydrophobic patches could be adjusted via controlling the dilution factor of the solution. They can self-assemble into worm-like and network-like superstructures (Fig. 28b and c).

5.2. Self-assembly via shell-shell attraction

Similar to core-core coupling, shell-shell attraction between core-shell particles with an amphiphilic mixed shell can also lead to cylindrical, branched and network-like superstructures, and the building blocks exhibit a patchy morphology in the final superstructures as well (Fig. 29A). Interestingly, the superstructures from shell-shell interactions are usually multicompartmentalized, which is promising for delivering different functional species at the same time. When the ratio of the length of the shell-forming chains to the core diameter is large enough, the solvophilic shell-forming polymer chains fully phase separate from solvophobic chains to form amphiphilic Janus-like particles that self-assemble into spherical, cylindrical, sheet-like and vesicular superstructures (Fig. 29B). In the resultant superstructures, the cores of the primary particles locate at the phase boundary of the attractive and the repulsive components. The superparticles can be thought of as multicompartment particles where the core of the primary particles forms one of the compartments and is different from the molecular aggregates produced by block copolymer self-assembly.

5.2.1. Self-assembly of isotropic soft particles via shell-shell attraction in a patchy fashion

In most cases, shell–shell attraction-induced selfassembly occurs with soft core–shell particles with a mixed shell. In selective solvents, the attractive interaction between the insoluble components of the mixed shell drives aggregation of the particles. Meanwhile, the interaction between the soluble components is repulsive, which modulates and balances the attractive interaction. The attractive and repulsive interactions can be regulated by deformation of the soft particles and redistribution of the shell-forming polymer chains, which facilitates the balance between the interactions. Usually, the mixed shell consists of two kinds of mixed linear polymer chains. It should be noted that the volume ratio of the two components of the mixed shell in a common solvent is entirely different

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Fig. 25. (A) A schematic representation of the mechanism that forms loose PDVB nanoparticles. (B) TEM images of the PDVB nanoparticles (RuO₄ staining). (C) TEM image of the nanoparticle films generated by polymerizing the PDVB nanoparticles in the aqueous suspension. Reproduced with permission from [98]. © 2009 Royal Society of Chemistry.

from that in a selective solvent. Therefore, the fraction of the insoluble component should be high enough, and the patches formed by the collapsed insoluble polymer chains can be large enough to induce self-assembly of the primary particles. This has been shown in our study on the selfassembly of heteroarm core-shell polymeric nanoparticles (HCPNs) with PS and P4VP as the mixed shell. It was found that the PS/P4VP length ratio is significant in controlling the self-assembly behavior of the nanoparticles in selective solvent (Fig. 30A) [101]. When the length ratio of PS/P4VP was larger than 1.5:1 (the PS/P4VP molar ratio is 1:1), the HCPNs dispersed in toluene (the selective solvent for the longer PS arm) in a uniparticle fashion, with collapsed P4VP being fully protected by the solvated PS chains (Fig. 30C). However, in acidic water (pH 1), a selective solvent for the short P4VP arm, the HCPNs self-assembled into large spherical superparticles (Fig. 30D and E). During self-assembly, PS chains formed relatively large attractive patches due to the large fraction of the PS arms that drive the aggregation. The high flexibility of HCPNs (due to swelling of the 4VP containing core in acidic water) makes it possible for the core to deform remarkably, in cooperation with the conformational change of the two arms, to realize a delicate balance between the attraction of the PS patches and the repulsion of the protonated P4VP arms, resulting in uniform spherical superparticles. The spherical superparticles had a unique inner structure and could be used as a

versatile template for controlled synthesis of hybrid particles with various architectures, especially for forming dendritic metallic clusters, which are inaccessible by other templates (Fig. 30F–I).

Apart from solid micelles, vesicles can also be used as building blocks for particle self-assembly. An excellent example of polymerization-like self-assembly of polymeric vesicles was reported by Zhou et al. [102]. Hyperbranched multiarm copolymers of HBPO-star-PEO and HBPO-star-PDMAEMA (HBPO represents hyperbranched poly(3-ethyl-3-oxetanemethanol) were used as the precursors for co-assembly into mixed shell vesicles at a pH where the PDMAEMA is soluble. By increasing the pH of the medium, the PDMAEMA was deprotonated and aggregated into hydrophobic domains on the vesicle surface, which served as the binding sites and drove the "polymerization" of the multivalent vesicles into linear, branched and network-like superstructures in a hierarchical way triggered by the solution pH. Such a hierarchical selfassembly resembles the bonding of functional monomers during homopolymerization, graft copolymerization, intramolecular cyclization, and crosslinking.

Most of the building blocks for self-assembly have a spherical morphology. Cylindrical micelles with a mixed shell can also self-assemble into intricate superstructures. Recently, Liu et al. reported a delicately controlled system of self-assembly of ABC triblock

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Fig. 26. Theoretical predictions and comparison of theory to experiments. (a) Simulation snapshots for particles with six uniformly spaced grafts, going from bare particles forming spherical aggregates, to flattened cylinders with N=2; branched cylinders with thinner arms N=5; sheets with N=6 (sheet shown in the detail); long strings with N=8 (only one string shown); short chains with N=10 (not shown); and isolated particles with N=14. (b) Results of simulations and theory at different grafting densities. Lines are predictions of analytical theory; symbols are from simulation. Red symbols: spheres, dark blue: sheets, light blue: strings, magenta: well-dispersed particles. (c) Experimental 'morphology diagram' of polymer-tethered particles mixed with matrix polymers. Red symbols represent spherical aggregates, blue symbols are sheets and interconnected structures, cyan symbols are short strings and purple symbols are dispersed particles. The lines that separate the different regions are merely guides to the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced with permission from [27].

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copolymers into helical superstructures in a marginal mixed solvent [103]. The ABC triblock copolymer was poly(n-butyl methacrylate)-b-poly(2-cinnamoyloxyethyl methacrylate)-b-poly(tert-butyl acrylate) (PBMA₃₅₀-b-PCEMA₁₆₀-b-PtBA₁₆₀, the subscripts represent the degree of polymerization of the respective blocks, Fig. 31A). In 50% CH₃OH/CH₂Cl₂, spherical aggregates formed with a PCEMA micellar core and PBMA and PtBA mixed shells. When the volume fraction of CH₃OH in CH₃OH/CH₂Cl₂ reached 82%, the spherical micelles organized into cylindrical micelles, driven by the interactions between the PCEMA

micellar cores (Fig. 31B), and PBMA became marginally soluble, whereas PtBA remained soluble. The cylindrical micelles cannot stabilize themselves due to the presence of solvophobic PBMA patches on the surface of the cylinder. As a result, the cylindrical micelles bent and twisted into double or triple helical superstructures, the insoluble PBMA patches fused together, and helical superstructures were stabilized by soluble PtBA chains (Fig. 31C–F). The helical superstructures were favored because, in this way, the PBMA patches get as much contact as possible (Fig. 31G). Energy loss from the formation of the twisted

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Fig. 27. A series of TEM (a–e) and cryo-TEM (f–h) images of the structures formed by spontaneous self-assembly of CdSe/CdS nanoparticles with bound PEO chains. The polymer/nanoparticle ratios are given in the top-right corner of (a–e) while the ratio for (f, g and h) is 150. As the polymer/nanoparticle ratio decreases, the formation of short cylinders, networks, and vesicles is observed. Reproduced with permission from [99].

cylinders was compensated for by PBMA chain mixing in a helical fashion. It is noted that, under marginal conditions, the energy gain from PBMA chain mixing was much smaller than that in a poor solvent. In other words, the required energy for twisting the cylindrical aggregates was very small due to their great flexibility. In other marginal PBMA solvents, for example, 83% CH₃OH/CHCl₃ and 77% CH₃OH/THF, helices were also observed, which suggests that the helices were thermodynamic products. Also, the authors demonstrated the formation of helices by using partially or fully hydrolyzed PBMA-b-PCEMA-b-PtBA terpolymer (PtBA transformed into PAA after hydrolysis) under special solvation conditions [104].

As mentioned previously, shell-shell attractioninduced self-assembly usually occurs among soft particles with an amphiphilic mixed shell. However, one special case was reported by Wooley et al., where the building blocks had a single component shell [4]. The shell-shell attraction of spherical micelles with non-covalently cross-linked shells was kinetically controlled, resulting in segmented superstructures. The micelles of poly(acrylic acid)-b-poly(methyl acrylate)-b-polystyrene (PAA94-b- PMA_{103} -b-PS₄₄) were prepared in a 1:4 (v/v) ratio of THF/water mixed solvent (Fig. 32A) in the presence of 2,2'-(ethylenedioxy)diethylamine (EDDA, EDDA/COOH molar ratio of 1:1). After immediately adding THF into the system to a final THF/water ratio of 2:1 (v/v), the micelles aggregated into segmented cylinders with alternate hydrophobic and hydrophilic segments perpendicular to the cylinder axis (Fig. 32B-E). EDDA acted as a crosslinking agent for micelle coupling due to the interaction between the ammonium cations and carboxylic anions.

The high flexibility of PS micellar cores in 2:1 THF/water allowed for a morphology transition from spherical to disk-like micelles (Fig. 32D), in which the block copolymer retained a local lamellar structure. This made face-to-face one-dimensional micellar aggregation more favorable (Fig. 32C). The intra-micellar process of local chain adjustment to form disk-like micelles was much faster than inter-micellar coupling. In other words, the flexibility of the micelles provided sufficient mismatch of the intramicellar and the inter-micellar processes for the forming of regular and complex superstructures. In this case, the shell of the primary micelles is composed of the single component PAA; the surface of the micelles is crosslinkable by the crosslinker EDDA. Therefore, a larger coagulation should be a thermodynamically favorable product of the crosslinking; in the larger coagulation, PAA can be largely cross-linked. However, it is significant that specific kinetic manipulation resulted in programmed cascade self-assembly processes that avoided the aforementioned global equilibrium structure.

Another elegant example of soft isotropic particle selfassembly into segmented cylindrical superstructures was reported by Liu et al. [105]. Self-assembly of poly(tert-butyl acrylate)-block-poly(2-cinnamoyloxyethyl methacrylate)block-poly(sucinnated glyceryl monomethacrylate) (PtBA₁₁₀-b-PCEMA₁₉₅-b-PSGMA₁₁₅) resulted in hamburger-like nanostructures and segmented cylinders in the presence of (-)-sparteinein and a selective solvent for PtBA. The segmented cylinder consisted of alternative PCEMA and noncovalently crosslinked PSGMA domains with a PtBA domain that stretched out from the PCEMA domains to stabilize the whole superstructure

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Fig. 28. The molecular building blocks that make up the patchy particles and their assemblies. (a) The fifth-generation urea-adamantyl poly(propylene imine) dendrimer (host) and the ureido acetic acid guest molecule (guest). Binding is governed by acid-base and hydrogen-bonding interactions. (b) Host and guest are mixed in chloroform (pre-complex) and via the neat state transferred to water. Depending on the ratio of guest molecules and binding sites (*n*/*B*), a small complex with, on average, three host molecules trapped in the core (*n*/*B* < 1) is formed (that is, the trapped core particle) or a stable guest-host complex (*n*/*B* > 1) is obtained in H₂O (that is, the patchy particle). Following the dilution (with H₂O) of the trapped core particle, no gradual change in structure was observed. Diluting a solution of the patchy particles, however, gives rise to a range of reversible equilibrium structures for which the fractal dimension increases upon lowering the concentration. For both the trapped core particle extreme dilution leads to precipitation. (c) Molecular model of the patchy particle. The host molecule forms the core of the particle (red) and the guest molecules (blue), which are partially folded to the side for clarity (cutting plane indicated in yellow), form a protective shell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced with permission from [100].

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Fig. 29. Self-assembly of soft isotropic particles with an amphiphilic mixed shell in fashions like patchy particle self-assembly (A) and Janus particle self-assembly (B). In (A), when the ratio of the shell length to the core diameter is small, with increment in volume ratio of attractive to repulsive component, superstructures with cylindrical (A1), branched (A2) and vesicular (A3) multi-compartment morphologies were obtained. In the superstructures, the originally isotropic soft particles adopt patchy-like structures. In (B), when the ratio of the shell-forming chain length to the core diameter is large, and the solvophilic shell-forming polymer chains could fully phase separate from the solvophobic ones to form amphiphilic, Janus-like particles that self-assemble into spherical (B1), cylindrical (B2), sheet-like (B3) and vesicular (B4) superstructures. The volume ratio between the repulsive and attractive components, adtractive components and particle cores, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 33). During self-assembly, PSGMA associated with (–)-sparteinein first, forming the primary particles. Then, the addition of 1-propanol or 2-propanol induced aggregation of the PCEMA blocks, which are the shell of the primary particles. The cooperation between these two self-assembly processes produced regular kinetically stabilized superstructures.

By increasing the attractive/repulsive component ratio of the mixed-shell particles, vesicular superstructures can be produced, as demonstrated recently by Duan et al. [106]. Amphiphilic AuNPs (14 nm in diameter) with PEO (5 kDa, 88 chains) and PMMA (22 kDa, 176 chains) mixed grafts were used as building blocks, which were prepared from grafting PEG-SH and 2,2'-dithiobis[1-(2-bromo-2methylpropionyloxy)]ethane (an ATRP initiator) to 14 nm AuNPs and subsequent grafting of PMMA from AuNPs via surface-initiated ATRP. By using the film rehydration method, vesicles composed of a monolayer of AuNPs were obtained, as revealed in Fig. 34a and b. The superstructures are connected by PMMA shell-shell attraction and stabilized in water by PEO chains. We believe that, during self-assembly, the PMMA shell chains reorganize to form patchy-like structures to gain more contact areas between neighboring particles, and the PEO shell chains may redistribute to face the aqueous environment (Fig. 34c)

5.2.2. Self-assembly of mixed shell particles in a Janus fashion directed by shell-shell attraction

When the length of the shell-forming mixed chains of the mixed-shell particles are significantly larger than the core size, the two polymeric components of the mixed shell may phase separate into two opposite sides of the particles, and the particles behave like block copolymers during selfassembly. In the final superstructures, they adopt a Janus morphology (Fig. 29B).

For example, Zubarev et al. synthesized amphiphilic AuNPs with V-shaped arms by grafting an amphiphilic polystyrene-b-poly(ethylene oxide) $(PS_{40}-b-PEO_{50})$ diblock copolymer with a reactive group located at its junction point onto 2 nm AuNPs (Fig. 35A) [107]. Welldefined worm-like assemblies with discrete AuNPs at the core-shell interface can be prepared via self-assembly in water (Fig. 35C). In this case, as mentioned previously, the arm lengths were significantly larger than the diameter of the AuNPs. The authors proposed that the two incompatible flexible arms stretched to the two opposite sides to form Janus-like nanoparticles in water at first and then self-assemble into superstructures (Fig. 35B). AuNPs that can be used as a catalytic center were in the boundary of hydrophobic and hydrophilic phases, which made the assemblies a potential catalyst for heterogeneous synthesis or catalytic synthesis of oil-soluble reagents into water-soluble products.

Spherical and vesicular superstructures obtained from the self-assembly of core-shell hybrid particles of CdS quantum dots (QDs) grafted with poly(methacrylic acid)/polystyrene (PMAA/PS) mixed shells in aqueous conditions (a selective solvent for PMAA) was reported by Moffitt et al. [108]. Preparation of the hybrid micelles started from Cd²⁺/PAA complexation-induced micellization of the triblock copolymer PS₁₉₆-b-PAA₄₁-b-PMMA₂₃₆ (PMMA, poly(methyl methacrylate)), forming micelles with PMMA/PS as the mixed shell and PAA/Cd²⁺ complexes as the core in benzene/methanol (9/1, v/v). Further

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Fig. 30. (A) A schematic representation of the formation of superparticles. (B) TEM images of HCPNs cast from a common solvent, DMF, and stained by RuO₄. The scale bar is 100 nm. (C) TEM images of HCPNs cast from toluene and stained with C_4H_9I . The scale bar is 100 nm. (D, E) TEM images of superparticles self-assembled from the HCPNs in 0.1 M HCl solution with different magnifications. (F-I) TEM images and UV–vis spectra of AuNP/superparticle hybrids in 0.1 M HCl (F, G) and a mixture of 0.1 M HCl/DMF (v/v, 9/1) (H, I). The scale bars are 200 nm. Reproduced with permission from [101].

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Fig. 31. (A) The chemical structure of PBMA-b-PCEMA-b-PtBA. (B–F) TEM images of aggregates sprayed from CH_2Cl_2/CH_3OH at $f_M = 82\%$ after aging for (B) 1, (C) 8, (D) 16, (E) 24, and (F) 90 d. The samples were stained by OsO₄. (G) Schematic representation of the chain packing in a double-helix section (a) and two pipe cleaners twisted into a double helix (b). Reproduced with permission from [103]. © 2009 Wiley-Blackwell.

reaction with H₂S produced CdS QDs sized 5.8 nm in the micellar core. Subsequently, the micelles were stabilized by crosslinking the PAA chains and then hydrolyzing PMMA into PMAA to obtain amphiphilic hybrid micelles. Spherical superstructures with PS cores, the PMAA shells and CdS/PAA complexes at the interfaces were prepared by adding water into a 0.5 wt% amphiphilic hybrid micelle solution in THF to a total water content of 75 wt%. Fig. 36A shows the supermicelles with discrete CdS/PAA complexes at the interface of the hydrophobic PS core and the hydrophilic PMAA shell. In the final superstructures, the original building blocks adopted a Janus morphology. In addition, vesicular superstructures with two layers of densely packed CdS/PAA complexes at the PMAA/PS interface can be obtained by adding water to a 1.0 wt% hybrid micelle solution in THF to a total water content of 75 wt% in the presence of NaCl (the molar ratio of NaCl and the methacrylic acid repeat units is 3:1) (Fig. 36B). NaCl decreased the repulsion between PMAA chains and facilitated the formation of the low curvature superparticles.

Recently, we reported on the self-assembly of core-shell micelles with loosely crosslinked cores into regular superparticles in water, a selective solvent for the cores [109]. These core-shell micelles were prepared by crosslinking the P4VP block of polystyrene-b-poly(4-vinylpyridine) (PS₈₉₁-b-P4VP₃₁₁) in a common solvent, DMF, using propargyl bromide (PB) as the crosslinker; PB quaternized the pyridine groups first, followed by reaction of the grafted propargyl groups with each other, resulting in crosslinking of the P4VP block chains. The crosslinking density of the P4VP/PB core was relatively low, but the pyridine units in the core were fully quarternized when excess PB was used. In the common solvent DMF, the nanoparticles had a morphology similar to that of normal core-shell micelles. However, in a dilute aqueous suspension, the primary micelles deformed, and a partial surface of the P4VP/PB core was exposed to water because the core is a largely swollen hydrophilic network and the amount of collapsed PS chains was insufficient to cover the entire core. As a result, the particles in water adopted a Janus-like structure and were amphiphilic and capable of self-assembly into regular spherical superstructures.

From the discussion above, we can see that, in many cases, isotropic particles can self-assemble anisotropically. Isotropic soft particles become anisotropic via deformation and sufficient material redistribution during self-assembly and thus can assemble into intricate superstructures. Isotropic soft particles are different from anisotropic particles in that they can be easily prepared and self-assemble into regular superstructures via thermodynamically or kinetically controlled processes. Clearly, self-assembly of isotropic soft particles provides a new route for building complex and ordered superstructures.

6. Summary and outlook

Self-assembly of particles provide a unique way to prepare materials with complex and ordered structures as a bottom-up technique, demonstrated by recent

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Fig. 32. (A) Spherical micelles of PAA₉₄-b-PMA₁₀₃-b-PS₄₄ formed at the 1:4 ratio of THF to water in the presence of EDDA (molar ratio of amine groups:acid groups = 1:1). (B) TEM image of the one-dimensional aggregation of spherical micelles immediately after introducing THF to the original solution to reach a 2:1 final ratio of THF to water. Further growth of these short structures led to a giant, one-dimensional supra-assembly. (C) The growth mechanism of the spherical micelles. The sphere-disk transition first occurred when THF was introduced, and the anisotropic shape of disk-like micelles allows for preferred growth in one-dimension. The inserted schematic illustrates the proposed chain packing of the spherical micelles, disk-like micelles and one-dimensional packing structures. (D) Separate disk-like micelles are marked with a black arrow. (E, F) Branches appear as a growth defect. The samples were stained with an aqueous solution of uranyl acetate.

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Fig. 33. (A, B) The chemical structures of PtBA-b-PCEMA-b-PSGMA (A) and (-)-sparteine (B); (C, D) TEM images of the dominant hamburger (C) and segmented cylinder (D) structures. The samples were sprayed from THF/(-)-sparteine/1-propanol (C) and THF/(-)-sparteine/2-propanol (D) with f_{POH} = 95% and a (-)-sparteine/SGMA molar ratio of 0.10. The staining agent used was OsO₄. Reproduced with permission from [105]. © 2007 Royal Society of Chemistry.

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Fig. 34. (a) TEM and (b) SEM images of the plasmonic vesicles assembled from 14 nm AuNPs with mixed poly(ethylene glycol) and poly(methyl methacrylate) brushes. (c) A schematic illustration of the self-assembly of amphiphilic particles with mixed polymer brushes into vesicular structures. Reproduced with permission from [106]. © 2011 American Chemical Society.

advancements in this area. Isotropic rigid particles can be organized into either two- or three-dimensional periodic structures through colloidal crystallization driven by entropy, van der Waals interactions, DNA base pair interactions and electrostatic interactions. Nevertheless, superstructures other than colloidal crystals, such as superparticles with cylindrical, vesicular and tubular morphology, can only be obtained through the anisotropic self-assembly of particles. A variety of primary particles with different anisotropic interactions were predicted, and various intricate superstructures were anticipated to form based on their respective anisotropic interactions. Experimentally, a lot of anisotropic particles were prepared and most of them are rigid Janus particles resulted from asymmetric surface modification of either silica or polymer latex. These rigid Janus particles are mostly large in size (usually submicron or micron sized) and thus have limited capability to self-assemble into regular superstructures. Meanwhile, several kinds of soft Janus particles, which usually possess polymeric structures, were also produced and can be solubilized to overcome the isotropic van der Waals attraction through solvation. During selfassembly, the particle flexibility allows them to adjust their shape and anisotropy to organize into uniform and regular superstructures, such as spherical, vesicular, tubular and sheet-like superparticles. Furthermore, isotropic soft particles, which are usually core-shell structures with hair-like shells, can form intricate superstructures through either core-core coupling or shell-shell attraction. A large variety of intricate structures, such as spherical superparticles, core-shell nanowires and nanorods, cylindrical and branched nanofibers, multi-compartmental cylinders, sheet-like aggregates, nanoparticle vesicles and both double and triple helices, can be acquired through the self-assembly of isotropic soft particles. During selfassembly, isotropic soft particles undergo deformation and sufficient material redistribution to behave like anisotropic particles. In the final superstructures, the primary particles that are originally isotropic become anisotropic like Janus or patchy particles. We would like to re-emphasize the difference between the anisotropic and isotropic particles that are capable of self-assembling into superparticles; the former are prepared anisotropic, whereas the latter are synthesized isotropic and the anisotropy is induced during self-assembly. Although anisotropic particles are very promising for the construction of superstructures, facile methods for their preparation are still limited. However, the preparation methods for isotropic soft particles are well-developed, and these particles can adopt anisotropic structures that are regulated by their self-assembly at the cost of a small entropy loss due to their great flexibility. This entropy loss can be compensated for by the enthalpy gain from the enhanced interaction between attractive components in the resultant superstructures. In addition, the shape of the isotropic soft primary particles in the superstructures should be unique after their deformation

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Fig. 35. (A) The chemical structure of V-shaped PS-b-PEO. (B) A schematic representation of the self-assembly of amphiphilic AuNPs with V-shaped PS-b-PEO arms. (C) TEM image of a sample prepared from an aqueous suspension of the amphiphilic AuNPs with V-shaped PS-PEO arms after the dialysis of a THF/H₂O (1/3, v/v) suspension against water. Reproduced with permission from [107]. © 2006 American Chemical Society.

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Fig. 36. (A) A TEM image of the spherical superstructures that self-assembled from amphiphilic CdS QDs/polymer hybrids; the insert shows a microtomed section of the superstructures where the CdS QDs (dark dots) are localized at the surface of the PS core. (B) Self-assembly of the hybrid particles into vesicular superstructures; the insert shows a cartoon containing two densely packed CdS QDs particle layers and the white arrows indicate the CdS QDs particle layers.

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and material redistribution, and such shapes are difficult to design and prepare. Therefore, this method provides a pathway to the construction of unique superstructures that are inaccessible by conventional building block design, preparation and assembly techniques.

Future research should undoubtedly focus on developing methods to efficiently fabricate and then functionalize sophisticated superstructures for different applications. For these purposes, primary particles with designed anisotropic interactions as well as sufficient flexibility are necessary; flexibility can facilitate the self-assembly of anisotropic particles into desired superstructures. Additionally, flexible isotropic particles that can anisotropically self-assemble should be useful because they can be efficiently and conveniently prepared and their self-assembly may lead to unique and unexpected superstructures. Furthermore, biological systems can teach us a great deal about particle self-assembly, including the methods and mechanisms needed to achieve not only intricate superstructures but also superior functionality. In addition, systematic studies of particle self-assembly are necessary to determine the rules for tailoring the structure and function of superparticles. We expect that the superstructures will serve as ideal platforms for controlling multiscale material distribution as well as the collection and cooperation of different functions.

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