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TOPICAL REVIEW

Recent progress on patchy colloids and their self-assembly

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Abstract

‘Patchy colloids’ is a term that has been recently introduced to indicate specially engineered particles with directional interactions. Based on this concept, a ‘bottom-up’ process for fabricating functional materials and devices has been envisioned, which employs colloidal building blocks and mimics molecular bonding. This article reviews recent progress which has been made in the synthesis and self-assembly of patchy colloids and discusses future directions as well as unresolved challenges.

(Some figures may appear in colour only in the online journal)

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1. Introduction

- 1 The spontaneous self-assembly of certain proteins leads to
- 2 complex but highly regular icosahedral capsid shells that
- 3 protect the viral genome they envelop (figure 1(a)) [1].
- 4 Molecular simulations, seeking to elucidate how viral proteins
- 5 self-assemble into such complex structures, model proteins
- 6 as spherical beads with highly directional bonds, that is, as
- 7 patchy particles [2–5]. Inspired in part by such molecular
- 8 assembly, colloidal particles with patches have been discussed
- 9 for over two decades [6–9]. Recently, patchy colloids have
- 10 been synthesized and assembled into complex structures using
- 11 both hydrophobic–hydrophobic attraction as well as DNA
- hybridization between patches [10–12].
- Modeling particles with only one type of patch is
- sufficient to realize the diverse configurations observed in
- single-layer viral capsids (figure 1(b)). However, to model
- complex multi-shell capsids, several types of patches are
- required, as illustrated in figure 1(c). While patchy colloids
- are certainly useful for modeling protein–protein interactions
- and their assembly, they may be much more useful for creating
- complex three-dimensional architectures of self-assembled

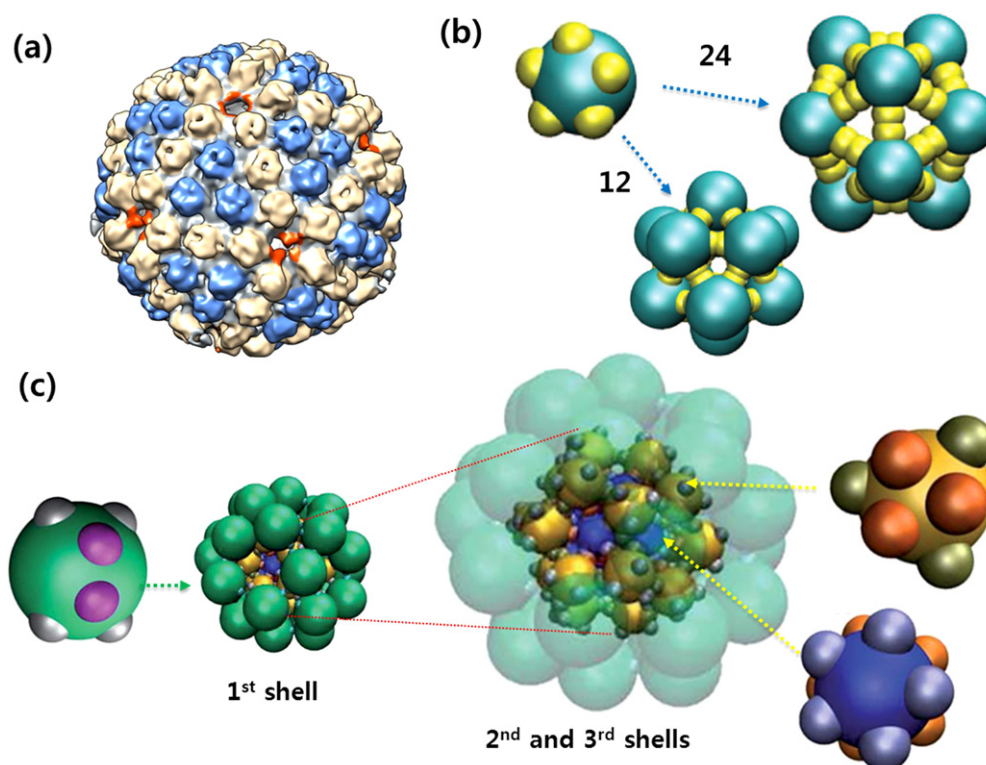


Figure 1. (a) Representative viral capsid structure (Herpes Simplex Virus). (b) Particles with one type of patch form an icosahedral shell structure with either 12 or 24 particles. (Reprinted with permission from [3]. Copyright 2007 American Institute of Physics.) (c) Particles with two types of patches form multi-shell structures. (Reprinted with permission from [4]. Copyright 2011 Royal Society of Chemistry.)

photonic or plasmonic materials [13–15]. For instance, it has been suggested that patchy colloids [10] could provide a route to assemble a diamond lattice of colloidal particles, which is predicted to have a larger photonic band gap than many other structures [16], and thus may be very useful in optoelectronic devices or display applications [15]. Indeed, the lessons we learn from proteins and atoms is that directional interactions are a key component for assembling almost any structure more complex than fcc or bcc crystals. Patchy particles hold the promise of opening up colloidal self-assembly for building not only the diamond lattice but even more complex and useful structures.

In this review, we summarize recent progress on different methods for synthesizing patchy particles. In addition, we discuss methods for selective surface modification of patches, after which we discuss progress on programmed assembly of patchy particles, including potential applications. Microfluidic production of patchy particles and deposition of metallic components on colloidal monolayers is discussed briefly, and then recent developments on the bulk synthesis of patchy particles, including seeded growth, swelling, and phase separation. Relatively less work has been done on self-assembly of patchy particles, but reports of unusual and interesting structures are starting to emerge. Structures can be tuned, of course, by changing the size and configuration of patches on particles.

2. Synthesis of patchy particles

2.1. Angle-dependent physical deposition on monolayered colloids

One of the simplest methods for making patchy particles is site-selective deposition of metal or metal oxide on colloidal monolayers. Colloidal particles can be assembled into two-dimensional crystalline films by various coating techniques, including vertical dip-coating [17], spin-coating [18, 19], and interfacial coating [20, 21]. By controlling coating conditions, bilayer crystalline films of colloidal silica can be formed on substrates and then coated with an organo-silane such as (octadecyltrimethoxysilane, OTMOS). Since the areas on the particles that touch each other cannot be coated with OTMOS, those become hydrophilic patches when silica particles at top layer are removed. Subsequently, those patches could be coated with titania, thereby producing patchy colloids that can be redispersed in suitable solvents (figure 2) [22].

Similarly, Kretzschmar and her colleagues have applied glancing angle deposition (GLAD) to colloidal monolayers, in which the colloids function as a shadow mask for making Janus (2-patch) or multiple metallic patches on colloidal spheres [23–25]. The shape and size of the metallic patches can be precisely controlled by varying the crystalline orientation and deposition angle (figure 3). Interestingly, crystalline arrays of colloidal particles are not strictly required as the colloidal particles themselves work as a shadowing

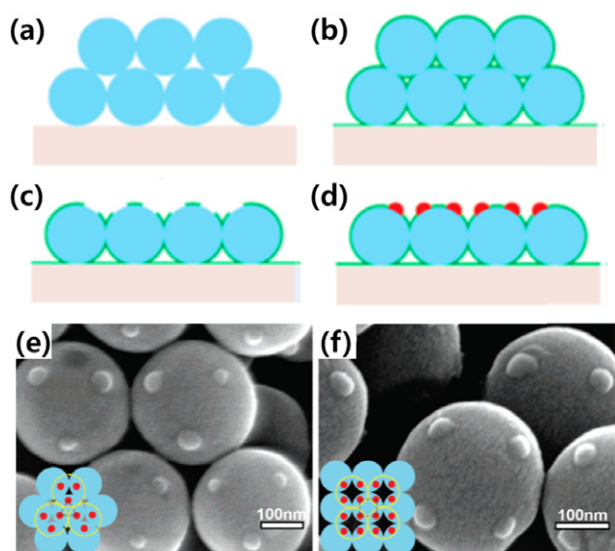


Figure 2. (a)–(d) Schematics for making patches on polymer beads. (e) and (f) SEM images of patchy particles in (e) hexagonal or (f) square lattice. (Reprinted with permission from [22]. Copyright 2007 American Chemical Society.)

mask. However, for uniform patches, particles should be either separated or closed packed perfectly. More recently, particles in grooves were coated with metal using the GLAD technique, which produced more complex patches and in a more controlled manner [26]. However, it still requires a single layer of particles in each groove for a uniform patch. By repeating the GLAD process at different angles, multiple-patch particles or patterned single-patch particles with metallic patches were produced [27, 28].

Anisotropic particles have also been selectively coated using evaporation methods. For example, rod-shaped particles have been selectively coated at one end with a gold thin film by aligning the rods vertically with an electric field assisted and the depositing gold in an electron-beam evaporator (figure 4(a)). Since alignment is not perfect, mis-aligned particles must be removed; some particles at the edges are overcoated with gold, which requires additional etching [29]. Similar structures were demonstrated by Li *et al* as shown in [30–32]. Two-dimensional array of colloidal particles were prepared and then titanium dioxide was grown by pulsed laser deposition (PLD), leaving rod-like Janus particles (figure 4(b)). They could be subsequently dispersed in solvent and were quite versatile in terms of length. On the other hand, rod-like colloidal particles can be produced via lithography [33] and Moon *et al* prepared a two-dimensional array of polymer rods by optical interference lithography and then deposited in place a metal layer on their surface at the exposed end [34]. This process produced rod-like particles with a metal cap (figure 4(c)). The cross-linked rods could be released as they were formed on an uncross-linked sacrificial layer, which was soluble in a suitable solvent.

Janus particles can also be produced with a kind of colloidal lithography, as shown in figure 5. Particles are formed in a two-dimensional colloidal array on a metallic thin film (typically gold or nickel) and etched by reactive ion

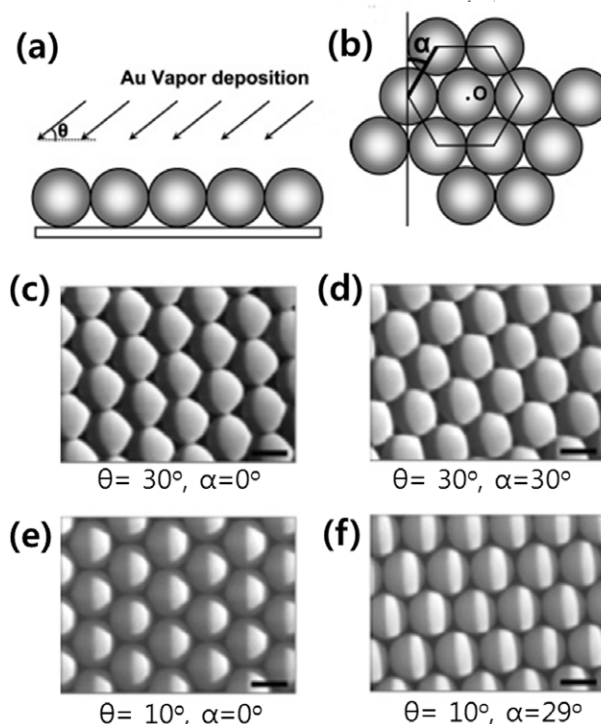


Figure 3. (a) and (b) Schematics of glancing angle deposition of gold on polymer beads. θ and α are the angles between the substrate or monolayer orientation and the incident vapor beam, respectively. (c)–(f) SEM images of different shapes of patches on particles depending on α and θ . (Reprinted with permission from [23]. Copyright 2008 American Chemical Society.)

etching which produces isolated smaller particles. Particles are then deformed thermally and bonded with the metal thin film. Reactive ion or chemical etching is used to remove the metal film between particles. The particles are then released from the substrate by dissolving a sacrificial layer beneath the metal film leaving metal-capped particles that can be dispersed in solution [35]. On the other hand, instead of depositing particles on a film, colloids can be incorporated into electrospun fibers. Anisotropic plasma etching of the fibers leaves behind opposing patches of the fiber material on the colloid surface [36].

2.2. A microfluidic production of multi-phasic particles

Selective deposition of metals and other materials on colloidal particles can generate various patchy particles, as discussed above, but such approaches are batch processes and thus produce relatively small quantities of material. Moreover, it can be very difficult to maintain uniformity from batch-to-batch.

By contrast, the microfluidic devices introduced by the Whitesides group makes a continuous stream of colloidal particles [37]. Lahann and his colleagues demonstrated a continuous generation of biphasic Janus particles using electrospraying techniques [38]. Following their report, Kumacheva reported microfluidic generation of Janus of multi-phasic particles from a photocurable oil-in-water

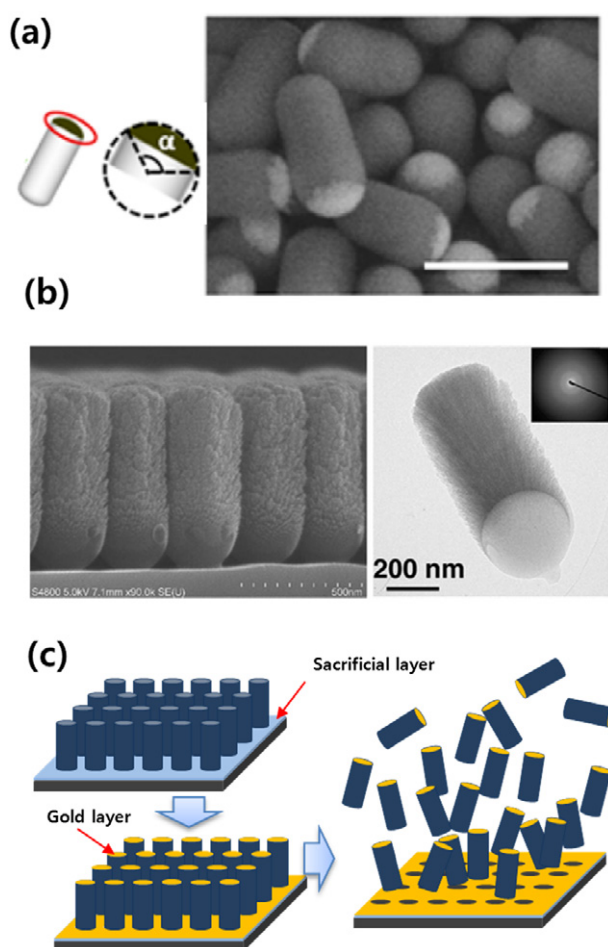


Figure 4. Janus colloidal matchsticks. (a) Gold was deposited on one tip of perpendicularly assembled silica rods. (Reprinted with permission from [29]. Copyright 2012 American Chemical Society.) (b) Titania rods were grown on polystyrene monolayers by pulse laser deposition. (Reprinted with permission from [30]. Copyright 2008 American Chemical Society.) (c) Polymer rods were prepared by holographic lithography and metal deposition. Then, rod-like particles with gold tip were released by removing the sacrificial layer [34].

emulsion [39, 40]. Depending on the channel shape and size, various types of particles can be produced, including rods, spheres, disks, and ellipsoids. Furthermore, other materials such as liquid crystals can be encapsulated inside micron-sized particles while maintaining consistent internal and interfacial structure [41]. Recently, Yuet *et al* demonstrated the fabrication of Janus particles with magnetic nanoparticles in one phase using microfluidic devices [42]. Prasad *et al* have also reported a microfluidic method for making inorganic–organic hybrid Janus particles that are composed of allylhydridopolycarbosilane and perfluoropolyether [43]. Through heat treatment, they could be transformed into asymmetric dimers of SiC and carbon.

On the other hand, Weitz and his colleagues have used simple capillary microfluidic devices for making multiple emulsions which were transformed into particles by solidification [44]. Recently, bowl-like particles were produced by using inert silicone oil as one of the phases [45].

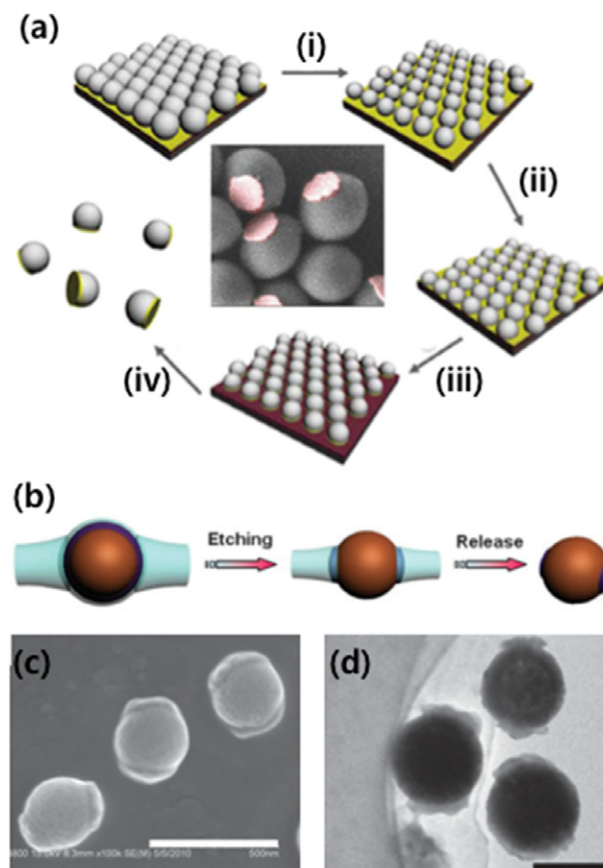


Figure 5. (a) Steps involved in the preparation of patchy particles by colloidal lithography. (i) Formation of a monolayer of polystyrene beads on metallic films (yellow color). (ii) Heat treatment to promote adhesion between the particles and the metal film. (iii) Selective metal etching over the particle-free areas. (iv) Release of the particles by dissolving the sacrificial layer (brown color). (Reprinted with permission from [35]. Copyright 2012 American Chemical Society.) (b)–(d) (b) Schematics, (c) SEM and (d) TEM images of patchy particles prepared by selective etching electrospun core–shell particles. (Reprinted with permission from [36]. Copyright 2011 Royal Society of Chemistry.)

Similarly, by adding nanoparticles either inside or outside emulsion, patchy moon-shaped particles were produced as shown in figure 6(c) [46].

The greatest drawback to these methods is that the total amount of material produced in one chip is not large and is too small generally for measuring bulk properties. Therefore, a good deal of recent work has focused on parallel production in microfluidic devices, or on making high-value specialty particles for niche markets such as pharmaceuticals [47].

2.3. Swelling and de-swelling colloidal particles

Making patchy colloids, either by angle-dependent deposition of metals or by microfluidic generation, is limited in the total quantity of particles that can be produced. Parallelized microfluidic chips can be utilized [48] but the yield is still not sufficient for many practical applications. By contrast, uniform spherical colloidal particles can be synthesized in bulk using scalable conventional processes. Modification

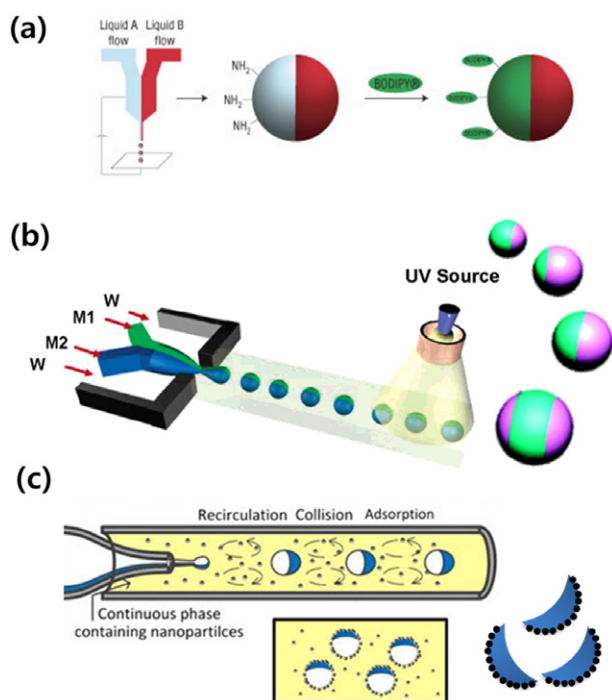


Figure 6. Microfluidic fabrication of biphasic Janus particles in (a) an aerosol generator, (b) a microfluidic emulsion generator, and (c) a capillary emulsion generator. ((a) reprinted with permission from [38]. Copyright 2005 Nature Publishing Group.) ((b) reprinted with permission from [42]. Copyright 2006 American Chemical Society.) ((c) reprinted with permission from [46]. Copyright 2012 Springer.)

of these scalable methods to make patchy colloids would therefore be most desirable. Recently, it was reported that polymeric particles can be swollen with a similar monomer and then separated into two phases during polymerization, thus forming a variety of biphasic particles [48–50].

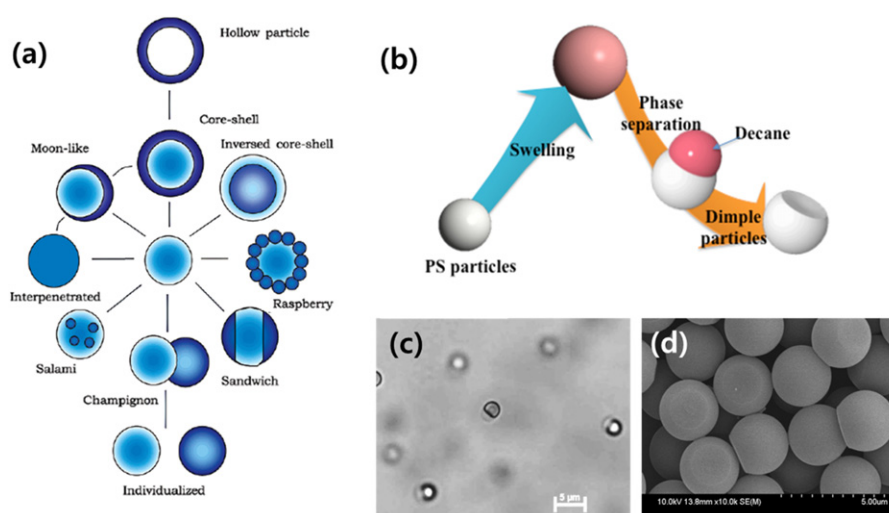


Figure 7. (a) Diagram showing the morphological change of biphasic particles caused by a variation of the relative volume fraction and surface tension between the phases. (Reprinted with permission from [51]. Copyright 2005 American Chemical Society.) (b)–(d) (b) Schematic diagram of a temperature-controlled synthesis of dimpled particles. (c) Optical micrograph of biphasic particles and (d) scanning electron micrograph of dimpled particles. (Reprinted with permission from [52]. Copyright 2012 American Chemical Society.)

Figure 7(a) shows various morphologies of biphasic particles which can be synthesized in a reproducible and predictable manner [51]. Similarly, it has also been shown that particles can be swollen with oil at relatively high temperatures. When cooled down below glass transition temperature, T_g , the oil swelling the particles can spontaneously separate to form two phases. The oil can then be removed by extraction or evaporation to produce a variety of dimpled or multi-dimpled particles, depending on the oil to polymer ratio, interfacial tension, cooling time, temperature, and other parameters as shown in figure 7(b) [52]. This process was shown to simultaneously reshape the particles and introduce well-defined hydrophobic surface patches. During the oil phase extraction, in fact, the surfactant adsorbed at the oil–water interface is also removed, thus leaving a hydrophobic surface exposed.

2.4. Magnetic patchy particles

Anisotropic distributions of magnetic components in and on colloidal particles have been employed in several recent studies to control and manipulate colloidal assembly. At least two different approaches have been reported for large-quantity preparations of magnetic patchy particles. The first involves an emulsion encapsulation and shrinkage method with magnetic nanoparticles and larger micrometer silica beads. Zerrouki *et al* were able to make fairly uniform magnetic Janus particles and dumbbells (figures 8(a) and (b)), as well as a variety of dynamic structures assembled under a magnetic field [53]. To make the composite particles, micrometer-scale silica particles and magnetic nanoparticles were dispersed in an oil phase and then emulsified into quasi-monodisperse emulsions. The oil phase was then extracted leaving behind patches of magnetic nanoparticles on either single silica particles or silica particle dumbbells. On

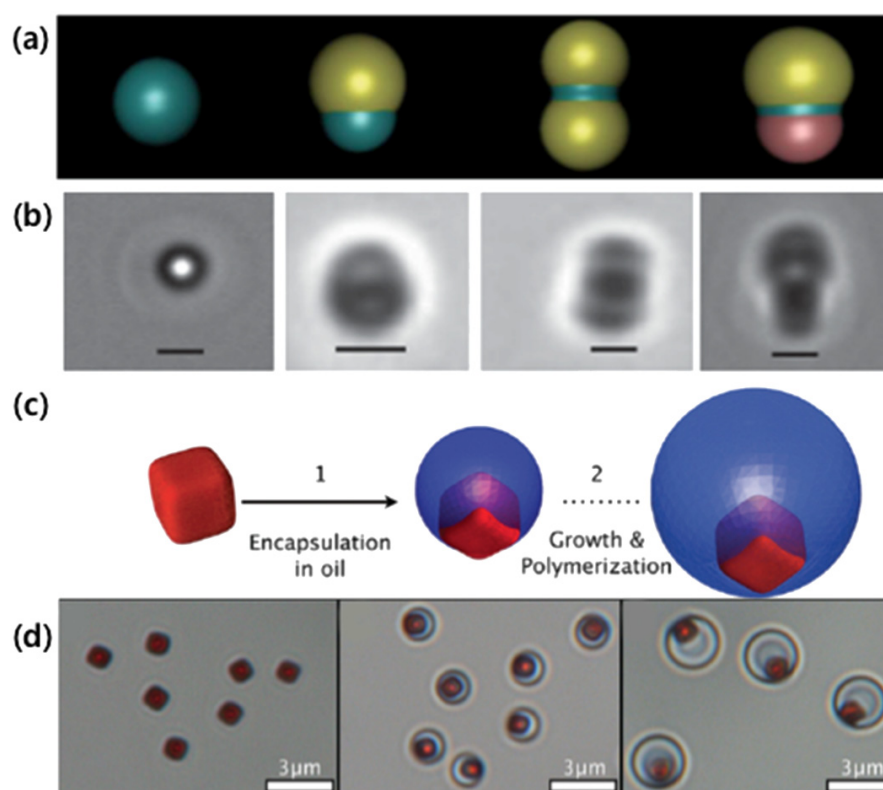


Figure 8. (a) and (b) Schematic diagram and optical micrographs of magnetic patchy particles from emulsion droplets containing magnetic nanoparticles and micron-sized silica beads. (Reprinted with permission from [53]. Copyright 2008 Nature Publishing Group.) (c) and (d) Schematic diagram and optical micrographs showing hematite cubes before and after their encapsulation into a polymer matrix. (Reprinted with permission from [54]. Copyright 2012 American Chemical Society.)

single silica particles, a single magnetic patch was formed. On silica dumbbells, the magnetic nanoparticles formed a belt around the point where the silica particles touched. Depending on their shape, they were assembled into unusual configurations under a magnetic field. Of particular note, were the assemblies of silica dumbbells with a magnetic belt. Upon application of a magnetic field, in fact, the dumbbells assembled into a novel chiral corkscrew structure.

Another example is the eccentric encapsulation of magnetic cubes inside droplets of a reactive silane [54]. First, micrometer-sized hematite cubes are synthesized [55]. Then, an alkoxy silane with an acrylic group (3-(trimethoxysilyl) propyl methacrylate, TPM) is hydrolyzed and condensed using a conventional sol–gel reaction in the presence of the hematite cubes. The cubes serve as nucleation sites for the condensation of the hydrolyzed TPM. Spherical TPM droplets grow around the magnetic cubes as shown in figures 8(c) and (d). Eventually, the TPM droplets grow to be about twice the size of the hematite cubes with one hematite cube per droplet in the vast majority of cases. Surface tension between the liquid TPM and the magnetic cubes causes one face of the hematite to protrude from the droplet. Finally, the TPM is polymerized by adding a radical initiator and heating for several hours.

As discussed in the previous section, magnetic patchy particles can be also prepared using e-beam deposition of nickel on colloidal monolayers [56].

2.5. Seeded polymerization on colloidal clusters

Using an emulsion encapsulation technique, Manoharan *et al* developed a method to prepare various clusters of colloidal particles consisting of $N = 2$ to about 15 particles. Interestingly, for $N < 13$, all clusters of a given N have the same configuration of particles [57–60]. The clusters can be fractionated to obtain pure samples of a given N using density gradient centrifugation. Using colloidal clusters as building blocks, Hynninen *et al* proposed strategies for assembling various new colloidal architectures, which consisted of assemblies of clusters and spheres [60]. However, experimental demonstration of these strategies has not yet been reported. Formation of crystalline structures from a monodispersed suspension of dumbbells using an external electric field was recently reported [61]. In another study, mixtures of clusters and spheres were used to explore the slowing down of translational and rotational diffusion in colloidal suspensions as they approach the glass transition [62].

The emulsion technique that was used to prepare clusters from suspensions of monodisperse microspheres was also used in combination with binary mixtures of large micron-sized colloids and small nanoparticles. This revealed a simple way of making patchy colloids. A common drawback, however, has been the intrinsic polydispersity of the original emulsion droplets which prevents an accurate

control on the number of encapsulated particles, thus hampering the formation of a single type of cluster or patchy particle [64–68]. To attenuate this problem, Zerrouki *et al* took extra care to produce quasi-monodisperse emulsion droplets. This resulted in fewer types of clusters that were successfully fractionated into the monodisperse patchy particles shown in figures 8(a) and (b) [53].

More recently, Wang *et al* synthesized uniform patchy particles with 1–7 (or more) patches as shown in figure 9(a), where the patches were functionalized with DNA with single-stranded (ssDNA) sticky ends [10]. The patchy particles were made by partially encapsulating colloidal clusters of amidinated polystyrene spheres with styrene monomers such that only the extremities of the clusters protruded from the liquid styrene monomers. The styrene was then polymerized around the clusters, with patches formed where the amidinated spheres protruded from the styrene droplets (figure 9(b), (c)) [10]. The amidinated patches could then be functionalized with DNA with sticky ends. The patches could then be programmed such that the particles could be assembled into a variety of structures, which is discussed in the next section.

2.6. Seeded growth of rod-like silica particles

Building on the work of Zhang *et al* and Kuijk *et al* [68, 69], amphiphilic ‘diblock’ rods were synthesized by a wet two-step method [70, 71]. First, hydrophilic silica seeds were nucleated from TEOS at the surface of emulsion droplets and anisotropically grown into rods. Next, this anisotropic growth was continued with an organically modified silane to obtain a hydrophobic block. By controlling the relative length of these two growing segments, rods with various hydrophilic-to-hydrophobic block ratios were successfully fabricated. As discussed in the next section, this ratio determines the self-assembly behavior of such colloids.

3. Assembly of patchy particles

3.1. Cluster formations from single patchy particles

Janus particles and particles with a single patch are relatively easy to fabricate, and thus their self-assembly has been more intensively studied than other systems. Commonly used synthetic methods include microfluidic fabrication and metal deposition on particle monolayers followed by selective functionalization of the deposited metal with hydrophobic ligands such as alkanethiols [11, 39, 72]. Due to their amphiphilicity, Janus particles can be easily anchored at the interface of water and oil or gas and liquid, thus stabilizing emulsions or foams [73, 74]. By adjusting the shape and size of the patch, various types of clusters can be made, including extended structures such as wires and films that were predicted in computer simulations and observed in experimental studies [11, 75].

Amphiphilic Janus colloids featuring a hydrophobic flat or a dimple (figure 7(b)) were also assembled into clusters by gradually changing the solvent polarity. In particular, particles with a hydrophobic flat readily pair up to form dumbbells

while particles with a hydrophobic dimple form clusters only in the presence of hydrophobic spheres that match the dimple size. Because of the particle shape, in fact, these surfaces cannot directly come into contact, but can form trimers by docking to a central hydrophobic sphere. These non-spherical Janus particles also interact with hydrophobic walls, thus allowing for the assembly of micro- and nano-scale lens arrays [52].

As the anisotropy of the particle shape increases, more complex clusters were assembled. For example, rod-like Janus colloids with a tunable hydrophobic-to-hydrophilic block ratio were assembled into diverse cluster morphologies by adjusting the solvent composition. This includes planar monolayers and micelle-like structures [70].

3.2. Colloidal assembly of multi-patchy particles by hydrophobic interactions

The metal evaporation technique for making Janus particles can be extended to make particles with more than one patch by sequential deposition of metal (2 nm Ti/25 nm Au layers) on colloidal monolayers [12, 29, 76, 77]. After the first vapor deposition, described in the previous section, the particle monolayer is lifted up using a polydimethylsiloxane (PDMS) stamp so that patches from the first vapor deposition are facing down. Then, a second deposition is performed, which produces patches on the other pole of the colloids. By modifying the metal with alkanethiol, the patches became hydrophobic while the uncoated middle region around the equator remained hydrophilic. By tuning the polarity of the solvent, the particles can be made to assemble or disassemble in a controlled manner. By creating two symmetric polar patches, the particles can either form a linear chain or assemble into a hexagonal structure. This depends on the ratio of the patchy poles area to sphere (or belt) size.

Triblock particles with two symmetric patches can form a monolayer Kagome lattice, as shown in figure 10. Crystals of octahedral clusters can also form, which correspond to a bilayer Kagome lattice. Changing the patch shape or size ratio can lead to a variety of structures. For asymmetric particles with asymmetric patches, various motifs could be formed with mixed open colloidal structures, as shown in figures 10(c) and (d). Patch size and geometry thus allow the design of more complex architectures. To create such open structures, the interactions between the building blocks must be sufficiently strong to overcome translational entropy still allowing for a relatively high rotational and vibrational entropy [78].

Stein *et al* recently reported the fabrication of tetrapods with carboxylate-modified tips from silica inverse opals, as shown in figures 11(a)–(c) [79]. Two different motifs were obtained from the inverse opals: octahedral and tetrapod particles. The tetrapod particles could be collected by density gradient centrifugation using an ethylene glycol gradient. The tips were then modified with a carboxylate group and bound with amidinated silica using a peptide bonding reaction (figures 11(c) and (d)).

In another report, a stretching process followed by a wet chemical treatment fabricated elongated patchy colloids

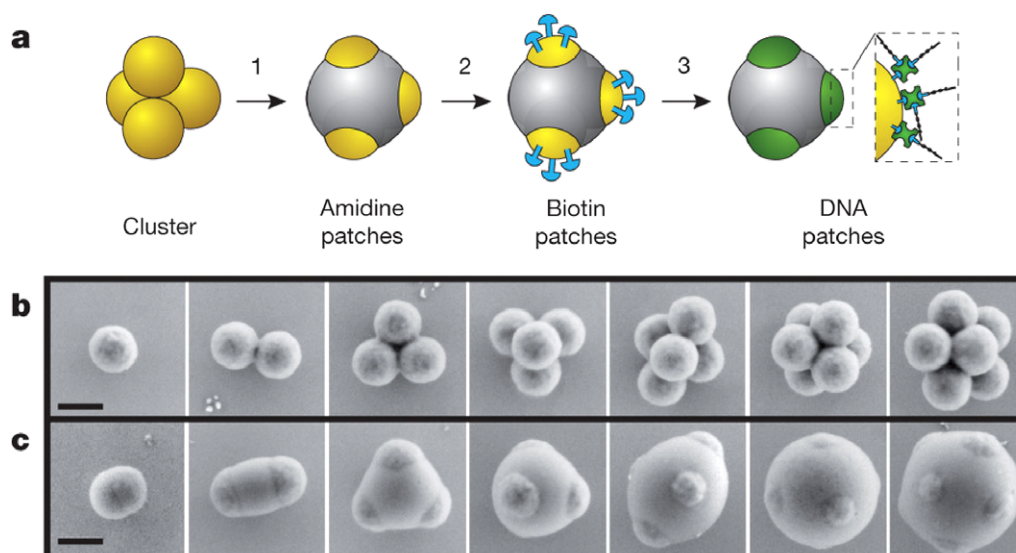


Figure 9. (a) Schematic diagram of seeded polymerization on tetrahedral colloidal clusters. (b) and (c) SEM image of colloidal clusters ($N = 1-7$) and their patchy particles. (Reprinted with permission from [10]. Copyright 2012 Nature Publishing Group.)

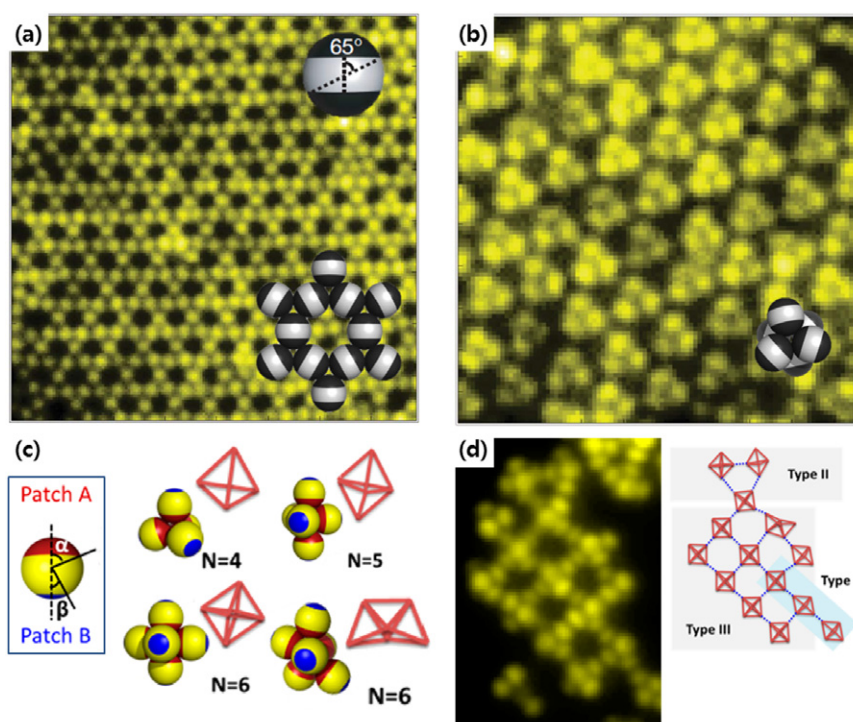


Figure 10. (a) Fluorescent images of triblock spheres assembled in a kagome lattice and (b) a bilayer of parallel kagome lattices. (Reprinted with permission from [11]. Copyright 2011 Nature Publishing Group.) (c) Asymmetric triblock patchy particles formed four different clusters due to the bonding between large red patches. (d) Fluorescent image and schematics of a network of clusters comprising different types of connectivity. (Reprinted with permission from [78]. Copyright 2012 American Chemical Society.)

with sticky attractive tips. First, sterically stabilized PMMA spheres were heated above their glass transition temperature and stretched into prolate ellipsoids. Next, a treatment with sodium methoxide caused a curvature-dependent degradation of the particle's stabilize layer which occurs faster at the particle tips. This resulted in ellipsoidal patchy colloids which were shown to controllably self-assemble into chains or smectic-like 2D structures [80].

Structures linked by hydrophobic interactions are not permanently bonded and thus are flexible with a bonding strength that can be adjusted by controlling solvent conditions. The flexibility of the bonds means that structures can anneal and thus reduce structural defects. On the other hand, control over the positions of patches is still fairly limited, which in turn, hamper our ability to build full three-dimensional structures.

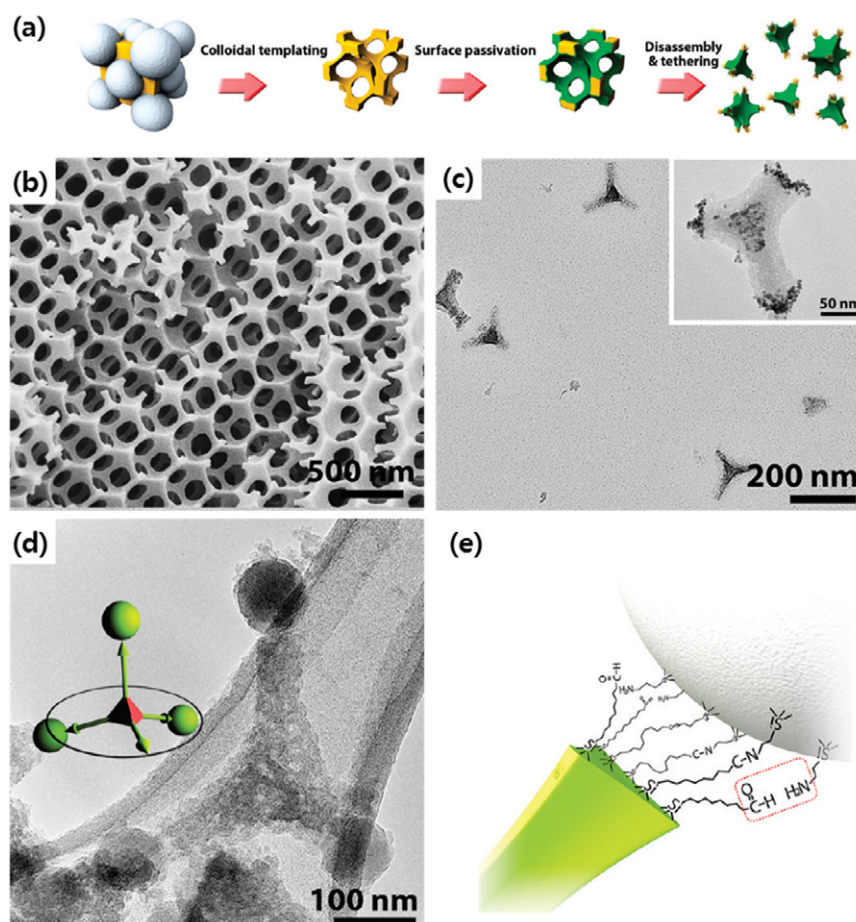


Figure 11. (a) Schematics of patchy tetrapods prepared from inverse opals. (b) SEM image of inverse silica opals and (c) silica tetrapods (inset shown high magnification image). (d) and (e) Amide bonding between carboxylated tips of tetrapods and silica nanoparticles. (Reprinted with permission from [79]. Copyright 2009 American Chemical Society.)

3.3. Dynamic assembly of magnetic patchy particles

Magnetic patchy particles provide a new and dynamic means of assembling colloidal particles. Zerrouki *et al* demonstrated that asymmetric colloidal dumbbells with a paramagnetic belt could form chiral structures when a magnetic field is applied. They also demonstrated a number of other interesting string-like structures could form using colloidal particles with various magnetic patches, as shown in figure 12(a) [51]. Sacanna *et al* have also reported field-assisted structures formed from hematite-cube-containing microspheres [54]. All the structures are formed under a magnetic field, which means the structures are dynamic.

Another example of dynamic self-assembly was recently demonstrated by Yan *et al*, who exposed magnetic Janus colloids to an oscillating magnetic field and observed how the synchronization of their motion would lead to the formation of well-defined tubular structures. In this work, magnetic Janus colloids were first prepared by e-beam deposition of nickel on colloidal monolayers of silica microspheres [56]. Then, a precessing magnetic field (figure 12(c)) was applied to the particle's suspension, producing, on each sphere, a torque with two orthogonal components: one driving the particles to spin around the precessing axis with an angle ϕ , and the other one

driving the particles to oscillate perpendicular to the rotating plane with angle α . Both rotation and oscillation frequencies were controlled by changing the precession angle θ of the applied magnetic field or its frequency. At low values of θ , the magnetic Janus colloids were observed to synchronize their motion and self-organize into well-defined and defect-free tubular structures. Using paramagnetic particles with a nickel patch, chiral chain structures were also observed.

Recently, Palacci *et al* reported that organosilica particles with a protruding hematite cube could be propelled along a glass surface by diffusiophoresis in a chemical gradient created by the light-activated decomposition reaction of hydrogen peroxide in water [81]. Under illumination with blue light, the particles also assembled into two-dimensional crystals which would move, grow, merge together with other crystals, explode and reform. Turning off the light caused the particles to rapidly disassemble and return the suspension to its homogeneous state driven only by thermal fluctuations.

3.4. DNA-mediated assembly of patchy particles

Particles with multiple DNA-functionalized patches open up a new spectrum of programmable self-assembled architectures [82]. In a recent report by Wang *et al* [10],

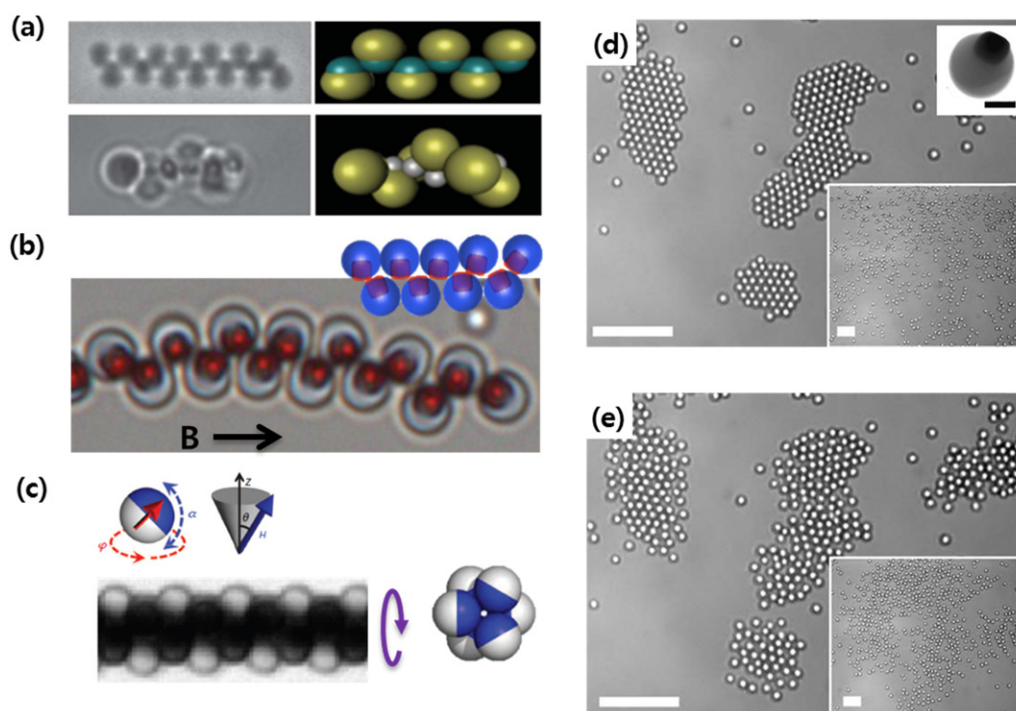


Figure 12. (a) Achiral and chiral chains of magnetic patchy particles. (Reprinted with permission from [53]. Copyright 2008 Nature Publishing Group.) (b) Dynamic formation of clusters of magnetic patchy particles without (left) or with external magnetic field (right). (Reprinted with permission from [54]. Copyright 2012 American Chemical Society.) (c) The director (red) of the magnetic Janus particles rotates around precession axis z (angle φ) while oscillating perpendicularly (angle α), in a precessing field H with precession angle θ . Observed images (left) and corresponding models (right, end views) of microtubes parallel to the precession axis, which have polygonal configurations at triangle end view. (Reprinted with permission from [56]. Copyright 2012 Nature Publishing Group.) (d) Homogeneous suspensions of particles carrying a photo-catalytic patch of hematite were crystallized by irradiation with blue light. The inserts show the suspension before irradiation (bottom) and a TEM image of a single particle (top, scale bar $1\ \mu\text{m}$) and (e) The crystals melt by thermal diffusion when the light is turned off. The main figure and the inset show the melting crystals after 10 and 100 s, respectively. (Reprinted with permission from [81]. Copyright 2013 American Association for the Advancement of Science.)

amidinated patches on polystyrene spheres were modified with biotin and then bound with a streptavidin-DNA complex. Different patchy particles, functionalized with complementary DNA, could then hybridize and bind patches of two different particles together. The patchy particles were fabricated using the emulsion encapsulation technique described above. Particles with 1–7 patches could be produced, with well-defined symmetries similar to those found in atoms, for example, triangular, tetrahedral and octahedral symmetries. Various basic colloidal molecules were produced using this programmed self-assembly approach.

For example, by adding tetravalent–valent particles, that is, particles with four DNA patches, (green in figure 13(a)) to a suspension of monovalent particles with a complementary DNA sequence (red in figure 13(a)), AB_4 -type colloidal molecules were formed. Because the motion of colloidal atoms is sufficiently slow to monitor under an optical microscope, the reaction kinetics occur over many minutes and can be followed in some detail. The monovalent colloids bonded sequentially to the four patches of each tetra-valent patchy particle, with the time between binding events increasing as the binding sites filled up. All reactions took place in bulk so that fully three-dimensional structures were formed, as shown in figure 13(c). Several colloidal ‘molecules’ were demonstrated, including AB , AB_2 , and

AB_3 molecules, as well as alternating $(-\text{AB}-)_n$ alternating copolymer structures.

4. Concluding remarks

In this review, we have summarized the recent progress made in the synthesis of patchy particles and their assembly. Since the realization of synthetic opal and inverse opal structures from monodispersed particles in the early 1990s, new colloidal architectures have been explored, which aim at reaching new or improved optical properties. In particular, the self-assembly of colloidal building blocks into metallo-dielectric nanostructures is stimulating a great deal of interdisciplinary research efforts. Through the use of colloidal self-assembly, in fact, meta-materials with tailored properties and even three-dimensional electronic devices could be fabricated by doing nothing more than mixing their constituent pieces together. To this end, the development of colloidal particles with directional and programmable interactions is crucial. So far, only the assembly of very simple structures has been demonstrated; however, the novel systems of multi-valent patchy colloids that we have reviewed in this paper, are opening new pathways toward limitless colloid-based architectures.

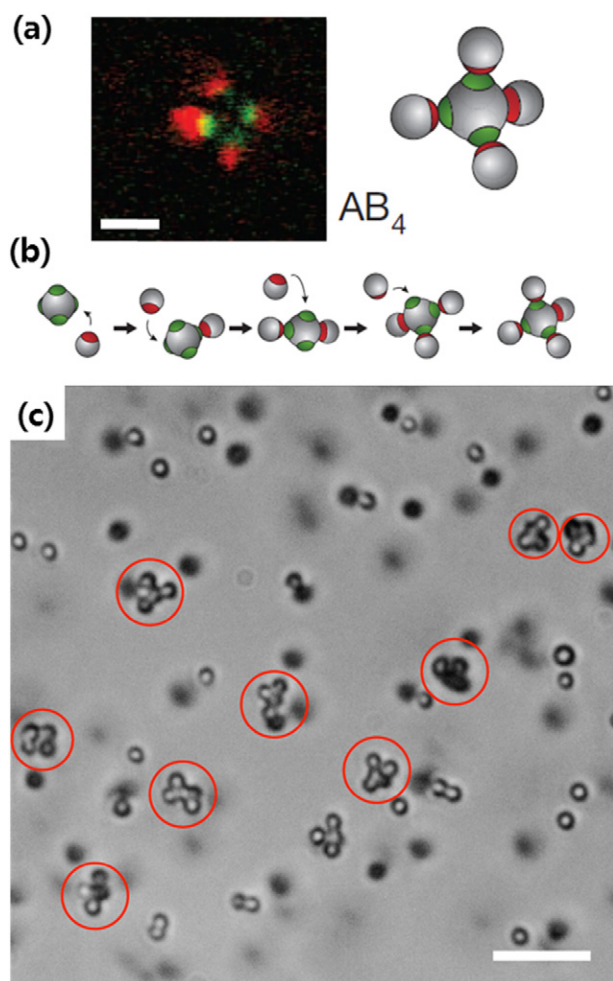


Figure 13. (a) Fluorescent image (left) and schematic (right) of a tetra-valent patchy particle linked to four monovalent particles (AB_4). Scale bar is $2\ \mu\text{m}$. (b) Schematic showing a step-by-step 'reaction' between colloidal atoms. (c) Wide field-of-view optical microscopy image of AB_4 -type colloidal molecules. Scale bar is $10\ \mu\text{m}$. (Reprinted with permission from [10]. Copyright 2012 Nature Publishing Group.)

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