Strictly Biphasic Janus Structures

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Strictly Biphasic Soft and Hard Janus Structures: Synthesis, Properties, and Applications

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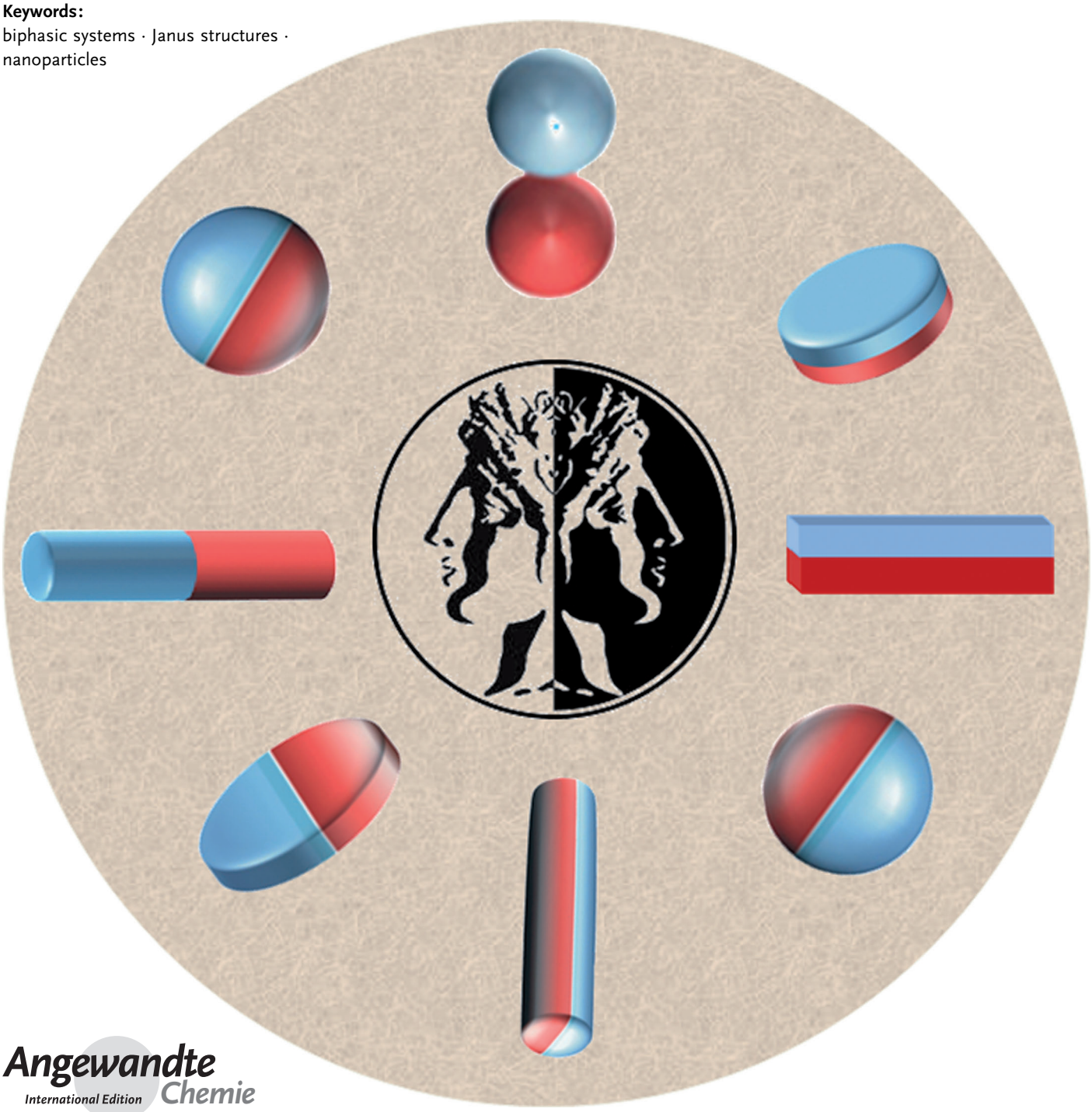

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Janus structures, named after the ancient two-faced Roman god Janus, comprise two hemistructures (e.g. hemispheres) with different compositions and functionalities. Much research has been carried out over the past few years on Janus structures because of the intriguing properties and promising potential applications of these unusually shaped materials. This Review discusses recent progress made in the synthesis, properties, and applications of strictly biphasic Janus structures possessing symmetrical structures but made of disparate materials. Depending on the chemical compositions, such biphasic structures can be categorized into soft, hard, and hybrid soft/hard Janus structures of different architectures, including spheres, rodlike, disclike, or any other shape. The main synthetic routes to soft, hard, and hybrid soft/hard Janus structures are summarized and their unique properties and applications are introduced. The perspectives for future research and development are also described.

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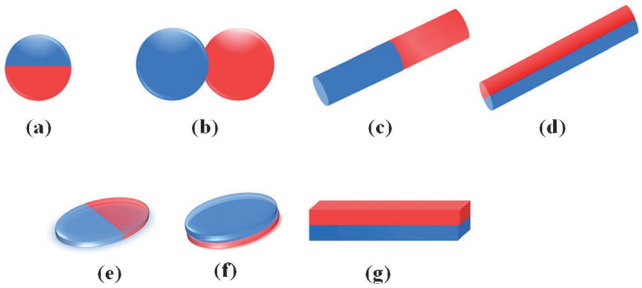
1. Introduction

Janus structures are objects on a micro- or nanometer scale that possess non-centrosymmetric architectures. The concept of Janus was coined by de Gennes in his Nobel Lecture in 1991.[1] In Roman mythology, Janus is usually represented as a god with two faces placed back to back so he can look in opposite directions at the same time.[2] Janus structures possess similar behaviors as certain molecules, such as surfactants, which bear opposite functionalities.[3–7] They have attracted increasing attention in recent years because of their unique properties and potential use in a range of applications, including interfacial stabilizers, biosensors, drug delivery, electronic paper displays, nanoengines, optical imaging, and catalysis.[8,9] For example, uniform bifunctional Janus supraballs with excellent fluorescent and magneto-responsive capabilities composed of magnetic Fe_3O_4 and fluorescent CdS hemispheres have recently been prepared in a simple microfluidic device.[10] A magneto-driven fluorescent switch based on such Janus supraballs enables free writing under a magnetic field.[10] This study provides insight into fabricating intriguing flexible displays with Janus supraballs. Recently, biphasic TiO_2/Au Janus nanoparticles have been shown to exhibit catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride, with 99% conversion achieved in 6 min.[11]

Many synthetic approaches have been developed for the fabrication of Janus structures, including self-assembly,[12–17] microfluidics,[18–20] biphasic electrified jetting,[21–23] olefin metathesis,[24] protonation-deprotonation cycling,[25] etc.[26–29] Notably, several reviews describing synthetic procedures, properties, and applications of Janus structures from different viewpoints have been reported.[8,26,30–36] These concentrated on the fabrication methods and self-assembly of polymeric Janus particles,[35,37,38] the synthetic strategies and self-assembly of both polymeric and inorganic Janus particles,[2,8,26,30] or the design and preparation of Janus structures with different morphologies (e.g. patchy, multicompartmental, ellipsoidal, snowman-like). It is noteworthy that none of them concentrated on perfectly biphasic Janus structures consisting of two completely dissimilar materials.[26,30–34]

Strictly biphasic Janus structures can be divided into three categories depending on the composition: soft (i.e. polymeric), hard (i.e. inorganic), and hybrid soft/hard. In addition, they can also be classified according to their architecture and dimensionality into spherical Janus particles (i.e. J-1, Scheme 1a), dumbbell-like (J-2, Scheme 1b), rodlike (J-3, Scheme 1c, and J-4, Scheme 1d), disclike (J-5, Scheme 1e, and J-6, Scheme 1f), and sheetlike (or ribbon-like; J-7, Scheme 1g). This Review seeks to summarize the preparation strategies for strictly biphasic Janus structures, highlight their unique



Scheme 1. Overview of strictly biphasic Janus architectures. a) Sphere (J-1), b) dumbbell-like (J-2), c, d) cylinders (J-3 (left/right) and J-4 (up/down)), e, f) disclike (J-5 (left/right) and J-6 (up/down)), and g) sheetlike or ribbonlike (J-7).

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properties and applications, and finally provide an outlook on where research in this fascinating area may lead.

2. Synthesis of Strictly Biphasic Janus Structures

This section highlights recent studies on a variety of synthetic strategies for the fabrication of three types of strictly biphasic Janus structures, that is, soft, hard, and soft/hard hybrids, composed of chemically dissimilar materials.

2.1. Soft Janus Structures

Soft (i.e. polymeric) Janus structures have garnered much attention during recent years because of their potential applications in chemical and biological sensors, colloidal surfactants, display materials on electronic paper, staged drug delivery, and controlled release systems.[8] Many ingenious approaches have been available to prepare soft Janus particles, including phase separation,[48,49] microfluidics,[39–42] and electrodynamic cojetting.[34,92–96]

The most practical method for synthesizing polymeric Janus structures is based on phase separation, which can be explained by three mechanisms: a) the interaction between polymers and other monomers differed from polymers (i.e. dissimilar monomers), depending on the polymer swelling volume fraction and the polymer/monomer interaction parameter;[43–46] b) the interaction between different polymers;[47] c) the interfacial tension between polymeric particles and water.[15,48,49] The phase-separation strategy includes three interesting approaches. The first approach involves the use of emulsion polymerization based on a growth-seeded step.[43–46] Studies on the formation of Janus structures have been performed under growth-seeded conditions in the presence of a prefabricated polymer.[43,50,51] The complex growth process of strictly biphasic polymeric Janus structures has been elucidated theoretically by both geometric and thermodynamic studies.[52,53] For example, a convenient method for the preparation of anisotropic nonspherical particles consisting of polystyrene (PS) and poly(butyl methacrylate) (PBMA; dumbbell-like; J-2, Scheme 1b) with well-controlled shapes has recently been reported (Figure 1).[47] Specifically, spherical cross-linked PSs (CPSs) were first synthesized as seed particles by seeded polymerization, with divinylbenzene (DVB) used as the cross-linking agent. The seeded polymerization was carried out again using

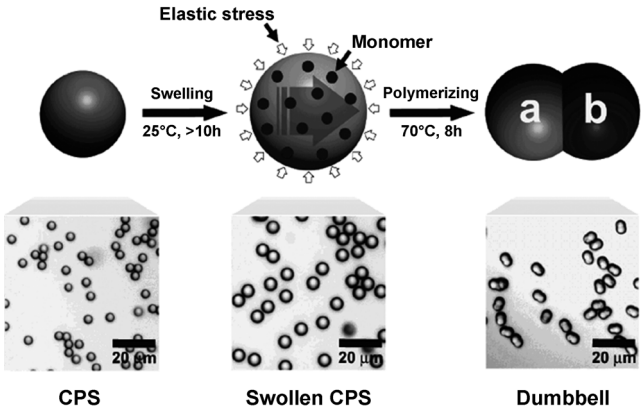

Figure 1. Synthesis of anisotropic dumbbell-like particles through the seeded polymerization technique. Bright-field micrographs show the PS/PBMA dumbbell particles. Reprinted from Ref. [47] with permission.

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CPS particles as the seed and BMA as the monomer to produce PS/PBMA dumbbell-like Janus particles. Heating the CPS particles swollen with the BMA monomer led to the phase separation as a result of the elastic stress driven by the entropy change of the swollen networks. Eventually, BMA monomers formed a bulb attached to the CPS seed particles. The conversion of BMA monomers into PBMA yielded dumbbell-like PS/PBMA Janus particles. Consequently, the final dumbbell-like Janus particles consisted of two bulbs: one containing the original PS seed particles and the other containing the polymerized materials.

It is worth noting that other dumbbell-like Janus particles (e.g. PS/PMMA) can also be made by this method.[47] During the fabrication of two-phase nonspherical particles, the elastic contraction of the swollen polymer particles induced by increasing the polymerization temperature was critical to the phase-separation process. Zukoski and co-workers expanded this approach to fabricate colloids with charge anisotropy.[54,55] Landfester and co-workers invented a simple route to two-component particles by using a miniemulsion.[56] The miniemulsions formed from a fluorescent homopolymer blend of poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) and a poly(*para*-phenylene) ladder polymer (m-LPPP) yielded spherical particles. Photoluminescence spectra clearly indicated that each particle contained a symmetric biphasic blend of both polymers (Figure 2).

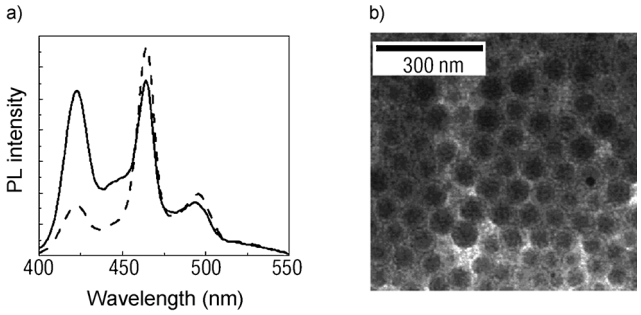

Figure 2. Energy transfer in two-component blend nanoparticles. a) Photoluminescence spectra of nanospheres containing both m-LPPP (dashed curve) and poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (solid curve) at a 1:1 weight ratio. b) TEM image of two-component nanoparticles. Reprinted from Ref. [56] with permission.

The second phase-separation approach is based on utilizing the phase separation of different homopolymers in the polymer blend to produce soft Janus structures. Recently, PS/PMMA Janus structures have been prepared by dispersing toluene solutions of PMMA and PS in an aqueous surfactant (polyoxyethylene nonylphenyl ether, E911) solution (J-1, Scheme 1a).[57] As the toluene evaporates, spherical droplets consisting of PS and PMMA homopolymers phase separate to form polymeric Janus particles with different hemispheres (Figure 3). Importantly, the morphology can be tuned by changing the molecular weights (MWs) of the polymers. As the MWs of PS and PMMA increases, the PS/PMMA interfacial tension increases; thus the morphology of the resulting PS/PMMA composite particles is thermodynamically controlled.[57] The main disadvantages of this strategy are the broad size distribution of Janus particles and the existence of surfactant molecules on Janus particles, thus limiting some potential applications.

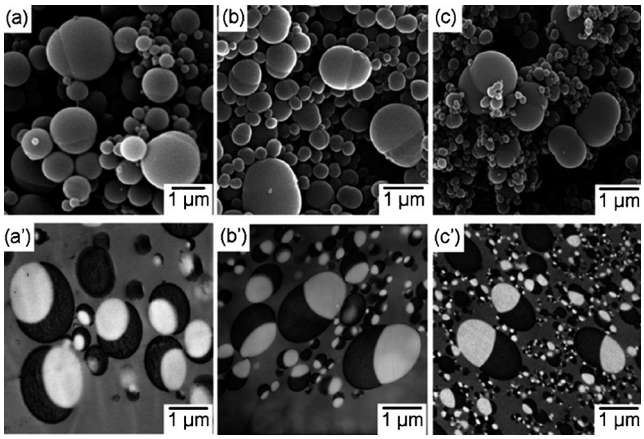

Figure 3. a–c) SEM images of PS/PMMA composite particles prepared by the release of toluene from polymer/toluene (1:12, w/w) droplets. a′–c′) TEM images of ultrathin cross-sections of polymer particles. Reprinted from Ref. [57] with permission.

Virgilio and Favis investigated the morphological development of model quaternary homopolymer blend systems consisting of two major phases of high-density polyethylene (HDPE) and polypropylene (PP) and two minor phases of PS and PMMA (Figure 4).[58] Axially symmetric Janus composite droplets comprising PS and PMMA hemispheres (J-1, Scheme 1a) have been fabricated by melt processing quaternary HDPE/PP/PS/PMMA homopolymer blends (45:45:5:5 by vol%). The formation of microstructures resulted from the combination of partial and complete wetting regimes occurring between different phases.[58] In the unmodified blend, Janus droplets composed of PS and PMMA hemispheres are interfacially active and located at the HDPE/PP interface. The PS hemisphere is in contact with all other three phases, while the PMMA phase is only in contact with the PP and PS phases. As a result, these particles have a Janus-like architecture but behave like homogeneous particles because of the stronger affinity of PS and PMMA to PP.[58] After modifying the HDPE/PP/PS/PMMA blend by the addition of PE-*b*-PMMA diblock copolymer, the PMMA hemisphere is located exclusively in the HDPE phase as a result of the interfacial activity of the block copolymers. In contrast, the PS hemisphere is only in contact with the PP phase.[58] Thus, more strictly biphasic PS/PMMA Janus structures can be produced. This strategy has also been employed to successfully fabricate other polymeric Janus structures, such as polystyrene/polyisoprene (PS/PI), PS/PMMA, and polystyrene/poly(propylene carbonate).[59–61]

The self-assembly of block copolymers in the solution or the bulk phase is the third method based on phase separation to yield Janus nanostructures. Block copolymers are spontaneously phase segregated into distinct domains in the bulk phase or in selective solvents.[62–66] ABC-type triblock copolymers are the most widely used block copolymers to craft

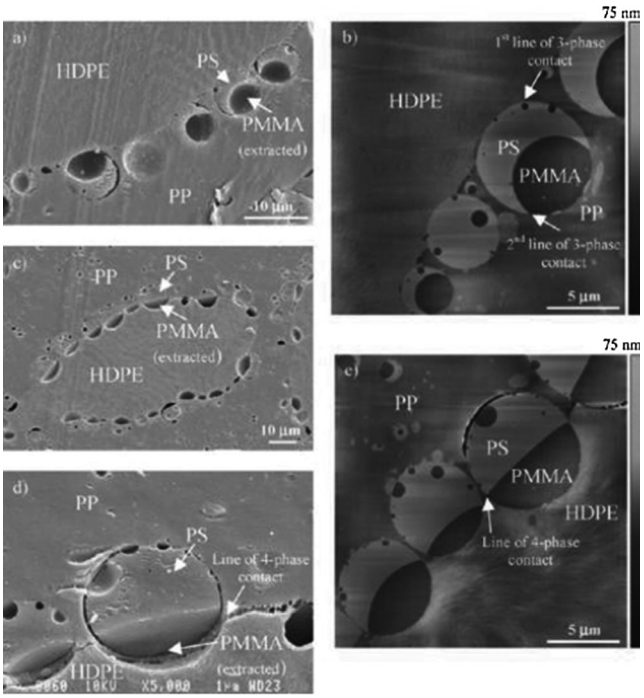

Figure 4. a) SEM micrograph and b) a FIB-AFM image of an unmodified HDPE/PP/PS/PMMA (45:45:5:5) blend after annealing for 30 min. Asymmetric composite Janus PS/PMMA droplets are observed at the HDPE/PP interface, but they do not display an amphiphilic behavior. Two three-phase lines of contact are also seen. c–e) Quaternary blend modified with 2% PE-*b*-PMMA (according to the PMMA content) and annealed for 30 min. PS/PMMA composite droplets have a Janus structure and display an amphiphilic behavior, with the PS adjacent to the PP phase and the PMMA to the HDPE phase. Reprinted from Ref. [58] with permission.

perfectly biphasic polymeric Janus structures. The general procedure can be summarized as follows: the middle B block is solidified by covalent or noncovalent cross-linking, while the mutually incompatible A and C blocks aggregate in different directions to form Janus structures.[8,26,35] Figure 5 shows a schematic representation of the preparation strategy.[67] The use of the self-assembly of triblock copolymers to prepare cross-linked Janus polymeric nanoparticles was pioneered by Müller and co-workers in 2001.[68,69] A variety of morphologies with a high degree of spatial control can be obtained spontaneously by the self-organization of triblock copolymers during film casting.[8] For example, PS/PMMA Janus particles (J-1, Scheme 1 a) were prepared by the self-assembly of polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) (PS-*b*-PB-*b*-PMMA) triblock copolymers in the bulk phase. First, PS-*b*-PB-*b*-PMMA with a very narrow polydispersity index formed alternating lamellae of PS and PMMA, with PB spheres located between the lamellae.[68] The PB block was then cross-linked either by vulcanization or using azobisisobutyronitrile (AIBN) with a polythiol.[70] Dissolution of the films by means of a suitable solvent (e.g. chloroform) led to J-1-type PS/PMMA Janus particles. Lamellae cylinders and fully lamellar structures can also be achieved by altering the molecular weight of the different blocks (Figure 5).[71–73] Similarly, cylindrical (J-4, Scheme 1 d) and disc-shaped (J-6, Scheme 1 d) polymeric Janus structures were obtained upon dissolution of the films. This approach was later extended to the fabrication of amphiphilic, spherical Janus micelles (J-1 type).[14] Furthermore, the same process was also used to produce perfectly biphasic polymeric Janus sheets and ribbons (J-7, Scheme 1 f) from one specific triblock copolymer, poly(*tert*-butoxystyrene)-*b*-poly(butadiene)-*b*-poly(*tert*-butyl methacrylate) (P*t*BSt-*b*-PB-*b*-P*t*BMA) by controlling phase transitions.[74] The use of S_2Cl_2 as a cross-linking agent led to two-dimensional Janus sheets through a cold vulcanization process. The use of a mixture of decane and acetonitrile (1:1 by vol%) as cosolvents for the dissolution of the cross-linked phase-separated structures afforded Janus ribbons through the joining of two different cylinders (i.e. P*t*BSt and P*t*BMA) along their major axis via a thin cross-linked PB layer (Figure 6).[74]

The block copolymer self-assembly strategy has also been investigated by other research groups to prepare soft and strictly biphasic Janus structures. Sfika et al. synthesized biphasic polymeric Janus micelles from poly(2-vinylpyridine)-*b*-poly(methyl methacrylate)-*b*-poly(acrylic acid) (P2VP-*b*-PMMA-*b*-PAA) triblock copolymers dissolved in water at a low pH value. The PMMA block formed the core while the two hydrophilic blocks (i.e. P2VP and PAA) phase-separated on the surface to yield two symmetrical phases (J-1-type).[48] Voets et al. prepared polymeric Janus micelles (J-6 type) by mixing two different diblock copolymers, poly(2-methylvinylpyridinium iodide)-*b*-poly(ethylene oxide) (P2MVP-*b*-PEO) and poly(acrylic acid)-*b*-poly(acryl amide) (PAA-*b*-PAAm).[15,49] As a consequence of the electrostatic interaction between the negatively charged PAA blocks and

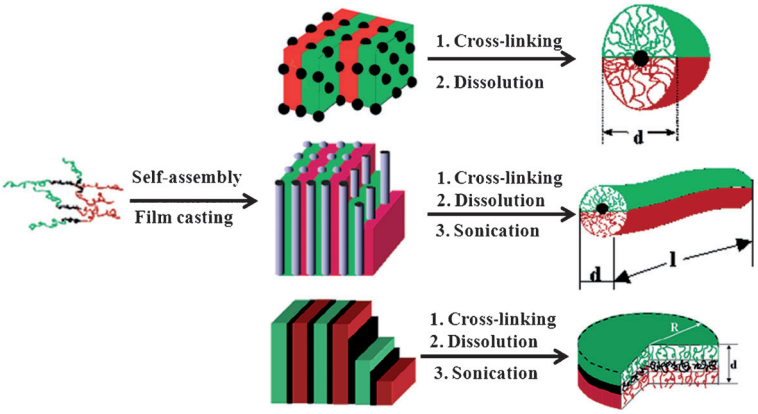

Figure 5. Preparation of Janus nanostructures from a triblock copolymer. The process starts with the film casting of the triblock copolymer, followed by the cross-linking of the intermediate block, and finally by the dissolution using a suitable solvent and sonication of the phase-separated film. Depending on the structure and molecular weight of the triblock copolymer, film casting produces a matrix with different morphologies that forms Janus nanostructures with different shapes upon dissolution: spherical, cylindrical, and disclike. Reprinted from Refs. [67, 71, 114] with permission.

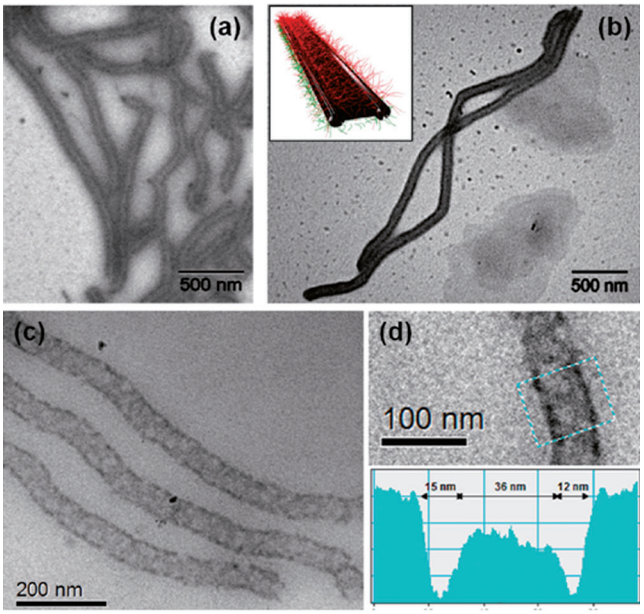

Figure 6. a,b) TEM images of dried Janus ribbons. The inset in (b) shows one Janus ribbon. c, d) Cryo-TEM images in vitrified toluene. The inset in (d) shows a cross-section analysis. Reprinted from Ref. [74] with permission.

positively charged P2MVP blocks, a complex coacervate core (PAA and P2MVP) was formed first, and the PEO and PAAm blocks were then phase-separated on the core to form disclike Janus structures composed of PEO and PAAm hemispheres (J-6 type). Moreover, perfectly biphasic polymeric Janus micelles PEO-PNIPAm can also be achieved by mixing two different diblock copolymers (i.e. P2VP-*b*-PEO and P2VP-*b*-PNIPAm).[75] In addition to the polymeric Janus structures noted above, biphasic soft Janus structures have also been obtained using other materials, such as the PEO/poly(2-aminoethyl methacrylate) (PAMA) system (J-1 type).[76]

The phase-separation strategy is advantageous, as the whole process is simple and convenient. It allows for the fabrication of many strictly biphasic polymeric Janus structures with different morphologies over a large length scale (from hundreds of nanometers to several micrometers). However, the three methods based on phase separation discussed above still have some limitations: 1) The size of the perfectly biphasic Janus structures formed by emulsion polymerization techniques is difficult to control, and Janus structures produced by blending different homopolymers usually possess a broad size distribution.[37] 2) The concentration of Janus particles formed by the self-assembly of block copolymers in solution is often too dilute to yield large amounts of Janus structures.

In addition to phase separation, microfluidic synthesis has become a prevalent strategy for the fabrication of strictly biphasic polymeric Janus structures. It works by using a Y-shaped channel to make a two-phase monomer stream with a planar sheath-flow geometry. The monomer stream is either cross-linked by a masked flashlight or combined with an aqueous stream to produce biphasic droplets.[39–42] Recently, a 2D microfluidic technique was developed to generate precursor Janus droplets (J-1 type) that were subsequently cured into strictly biphasic polymeric Janus particles (Figure 7).[77] These monodisperse bicolored spheres with an asymmetric charge distribution exhibited electrical actuation. The scaled-up production by the integration of multiple channels was also presented.[77] In addition, ternary particles (i.e. symmetrical spherical A/B/A types) with two sharp interfaces between the A and B phases generated from largely immiscible liquids were also successfully prepared by using the microfluidic technique.[78] The geometry of the microfluidic devices was varied in different studies, and ranged from a single flow tube to up to 128 flow tubes.[35]

Apart from Janus particles, other morphologies such as Janus rods (J-3 type) have been reported by a photolithography-based microfluidic technique.[79] The advantage of this technique over traditional lithography[80,81] lies in the continuous nature of the process, which permits high-throughput generation of polymeric particles (400000 particles h^{-1}; Figure 8).[79] Interestingly, novel Janus structures comprising different polymer/inorganic nanoparticle composites located

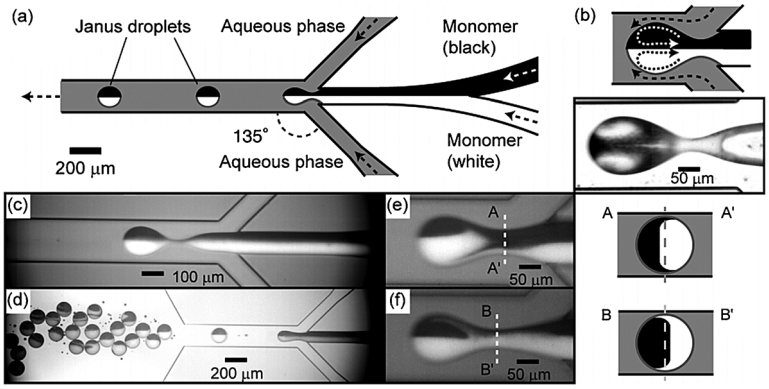

Figure 7. Formation of two-color Janus droplets in a microfluidic device. a) The setup, b) convection in the head of an organic fluid cylinder, c) detachment of a two-phase droplet upon contacting with the aqueous stream, d) collection of Janus droplets, and e, f) formation of Janus particles at different relative velocities of the black and the white monomers. Reprinted from Ref. [77] with permission.

at different hemistructures could also be obtained when polymer/inorganic nanoparticle composites were used instead of pure polymers during the fabrication of Janus structures. For example, as previously described, Janus supraballs (J-1 type) with superparamagnetic nanoparticles (Fe_3O_4) confined in one hemisphere and quantum dots (QDs, CdS) localized in the other were formed by using a simple microfluidic device.[10] Such Janus particles in which magnetic and fluorescent materials were constrained in two different hemispheres resulted in a fluorescence and magnetic response within one anisotropic structure.[10]

Soft Janus structures can also be fabricated by electrodynamic cojetting of polymer solutions.[21,82–86] Lahann and coworkers studied the formation mechanism of biphasic Janus

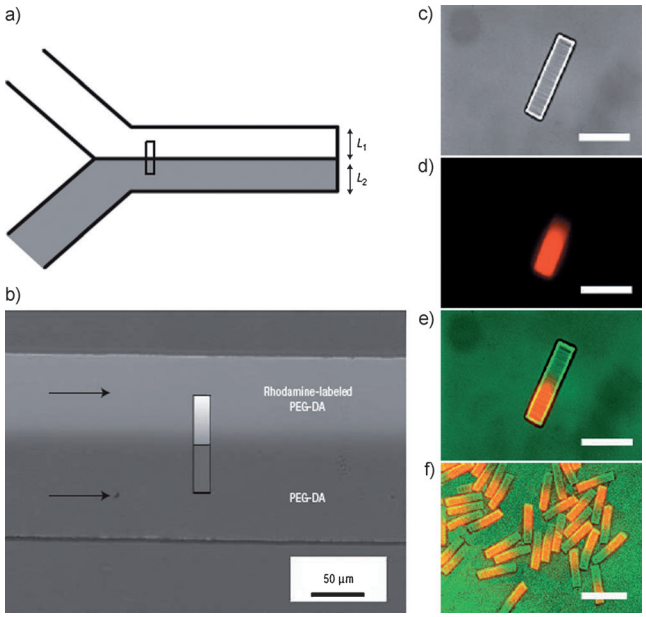

Figure 8. Synthesis of Janus structures. a) A schematic diagram showing the synthesis of two-phased Janus structures. b) Two streams containing PEG-DA (gray) and PEG-DA with rhodamine-labeled cross-linker (white) are coflowed through a channel. Schematic representation of the formation of a bar-shaped particle 130 μm long and 20 μm wide. c) DIC image of a Janus particle. d) Fluorescence image of the particle in (c). The rhodamine-labeled portion is seen in red. e) An overlaid image of the entire particle to show both the fluorescently labeled (orange) and the nonlabeled (green) sections. The scale bars in (c)–(e) are 50 μm. f) Multiple Janus particles with the fluorescent portion shown in orange. Scale bar = 100 μm. Reprinted from Ref. [79] with permission.

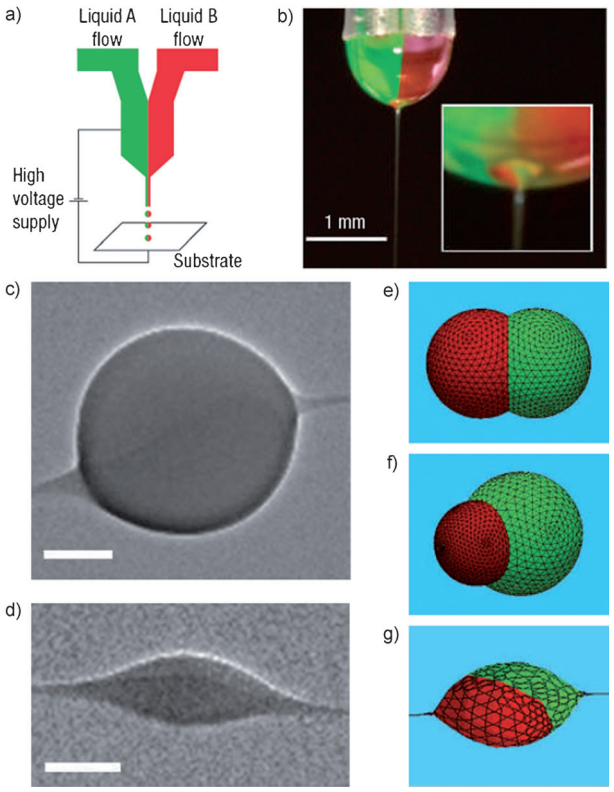

Figure 9. a, b) Biphasic electrified jetting using side-by-side dual capillaries. Biphasic anisotropy examined by TEM (c, d) and modeling (e–g). Scale bar = 100 nm. Reprinted from Ref. [21] with permission.

particles with tunable anisotropy through electrodynamic jetting of two liquid solutions of immiscible polymers.[21] The primary shape of the obtained particles is spherical (J-1 type). Several polymer pairs can be used in this method, and Janus particles were created with different dyes encapsulated inside to prove their segregation (Figure 9). Importantly, a model was also built to predict the shape and size of the resulting Janus structures. Biphasic polymeric particles can be formed by delicately controlling two competing factors, that is, the diffusion rate of two polymer solutions and the solidification rate during solvent evaporation.[21] Sub-micrometer polymeric Janus particles were also prepared by the same research group by electrohydrodynamic cojetting of two very similar polymer solutions in water, one containing a dye and the other with gold nanoparticles, followed by thermal cross-linking.[87] Interestingly, Janus nanoparticles (J-1 type) with spatially controlled affinity for cells have also recently been prepared by cojetting two different solutions of PAAm-*b*-PAA.[88] We note that in addition to the three main strategies for the production of strictly biphasic polymeric Janus structures, other approaches include lithography, templating, and surface-controlled nucleation techniques.[89–95] However, these latter approaches suffer from many limitations, for example, the need for complicated equipment, difficulty in preparing nanoscale structures, uncontrollable sizes and architectures, only suitable for certain materials, etc., and are, therefore, difficult to generalize.

Clearly, the phase-separation strategy can be exploited to conveniently design and fabricate soft biphasic Janus structures, while microfluidic approaches and electrohydrodynamic cojetting techniques can be readily scaled up to produce larger amounts of Janus structures in a continuous process. However, the size of the soft Janus structures prepared by the microfluidics method is often limited to approximately 5–100 μm; moreover, the loss of pressure and the closing of the pipeline during the production process usually lead to different ratios of the two immiscible phases in Janus structures. On the other hand, the electrohydrodynamic cojetting technique seems to be suitable only for conductive polymers.

2.2. Hard Janus Structures

Combining the disparate properties provided by two dissimilar hard materials for a wide range of applications (e.g., electronics, catalysis, diagnostics, etc.) has generated tremendous interest in this field.[31] A hard (i.e. inorganic) Janus structure composed of two different inorganic materials is a promising architecture for combining disparate properties (e.g. magnetic, electric, semiconducting, optical, optoelectronic, and catalytic properties) in proximity.[26] Figure 10 summarizes the formation mechanisms of inorganic Janus structures, including direct heterogeneous nucleation, non-

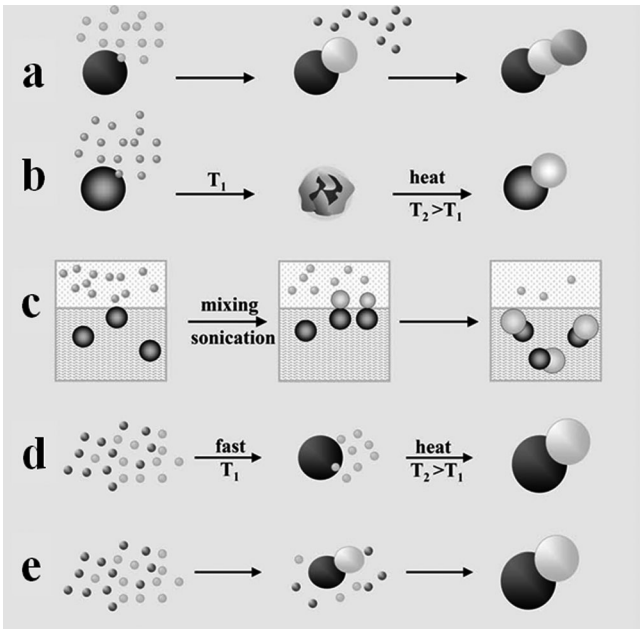

Figure 10. Mechanisms underlying the formation of oligomer-type hybrid nanocrystals: a) direct heterogeneous nucleation; b) non-epitaxial deposition followed by thermally driven coalescence/crystallization and/or solid-state atomic diffusion; c) reactions at liquid/liquid interfaces; and d, e) self-regulated homogeneous/heterogeneous nucleation. Reprinted from Ref. [97] with permission.

epitaxial deposition followed by coalescence/crystallization, reactions at liquid/liquid interfaces, and self-regulated homogeneous as well as heterogeneous nucleation.[96,97] Despite the fact that substantial inorganic Janus structures have been synthesized through the reaction mechanisms noted above, few studies have been reported on the preparation of strictly biphasic inorganic Janus structures.

One successful study is the Au-Fe_3O_4 Janus system (J-2 type) based on the epitaxial growth of Fe_3O_4 particles from the surface of an Au particle, a process that can be controlled by tuning the nucleation and growth conditions of the second particle.[98] Symmetric dumbbell-like Au-Fe_3O_4 Janus nanoparticles were generated by the decomposition of $[Fe(CO)_5]$ on Au nanoparticles followed by oxidation in 1-octadecene.[98] These Au/Fe_3O_4 dumbbells were obtained by the epitaxial growth of Fe_3O_4 on Au seeds (Figure 11), where the growth

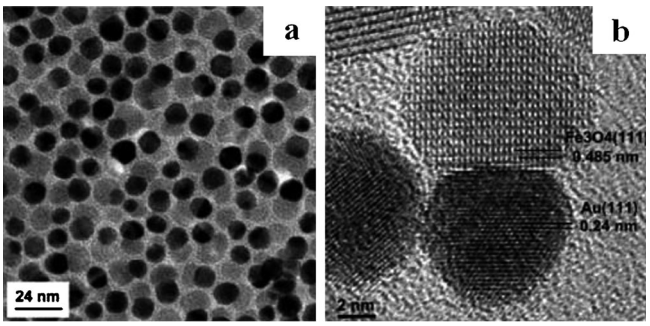

Figure 11. a) TEM image, and b) high-resolution TEM image of dumbbell-like Au/Fe_3O_4 nanoparticles. Reprinted from Ref. [98] with permission.

can be affected by the solvent polarity. The resulting Janus structures simultaneously displayed the characteristic surface plasmon absorption of Au and magnetic properties of Fe_3O_4, thus making them suitable as magnetic imaging probes for tracking drug delivery. These properties are influenced by the interaction between Au and Fe_3O_4. For example, in the case of Au nanoparticles, the electrons are trapped in a small Au metal box and exhibit a characteristic collective oscillation frequency of plasmon resonance, which gives rise to a plasmon resonance band at 520 nm.[99] However, the attachment of the Fe_3O_4 results in the Au nanoparticles showing a plasmon absorption at 538 nm (i.e. a 18 nm red-shift). This results from the charge variation of the Au particles within the dumbbell structure.[98] Previous studies have demonstrated that excess electrons on Au nanoparticles can shift the plasmon absorption to shorter wavelengths, while an electron deficiency would cause the absorption to shift toward longer wavelengths.[99] The red shift in the surface plasmon spectra of the dumbbell structure indicated that the interfacial communication between Au and Fe_3O_4 resulted in a deficient electron population on the surface of the Au nanoparticles.[98] The formation of these strictly biphasic inorganic Janus structures (J-2 type) is facilitated by the intrinsic incompatibility of the crystal lattices of these two inorganic materials. In general, when the first particle acts as the seed, the lattice incompatibility makes it difficult for the second material to form a stable core/shell structure, and thus the formation of a biphasic inorganic Janus structure is energetically favored.[98,100,101] The reaction conditions leading to homogeneous nucleation can be avoided by reducing the temperature at which the second particle is nucleated, since homogenous nucleation becomes dominant at sufficiently high temperature.[102]

Similarly, other strictly biphasic inorganic Janus structures can also be prepared from two different materials.[101] For example, dumbbell-like Janus particles (J-2 type) of FePt/Ag and Au/Ag have been synthesized.[101] FePt and Au nanoparticles were used as seed particles, which were dispersed in an organic solvent (e.g. dichlorobenzene, dichloromethane, hexane, or dioctyl ether) prior to their addition into an aqueous solution of silver nitrate. The Ag cations were reduced rapidly and essentially on the seed particle surface, thereby leading to the nucleation and growth of one Ag particle on the surface of each seed particle (Figure 12). It is noteworthy that, regardless of the inorganic Janus structures that can also be fabricated based on other formation mechanisms (i.e. non-epitaxial deposition, reactions at liquid/liquid interfaces, and homogeneous and heterogeneous nucleation),[96,97] except for the dumbbell-like Janus particles (J-2 type) described above, no successful examples of the fabrication of strictly biphasic inorganic Janus structures have been reported in the literature.

A novel and interesting approach, that is, the flame synthesis technique, has been developed for the preparation of strictly biphasic inorganic Janus structures (SiO_2/Fe_2O_3 Janus magnetic nanoparticles, J-1 type; Figure 13).[103] This one-step fabrication was initiated by the ignition of a mixture of an iron precursor and a silicon precursor in methanol, which acted not only as a solvent but also a fuel. During the

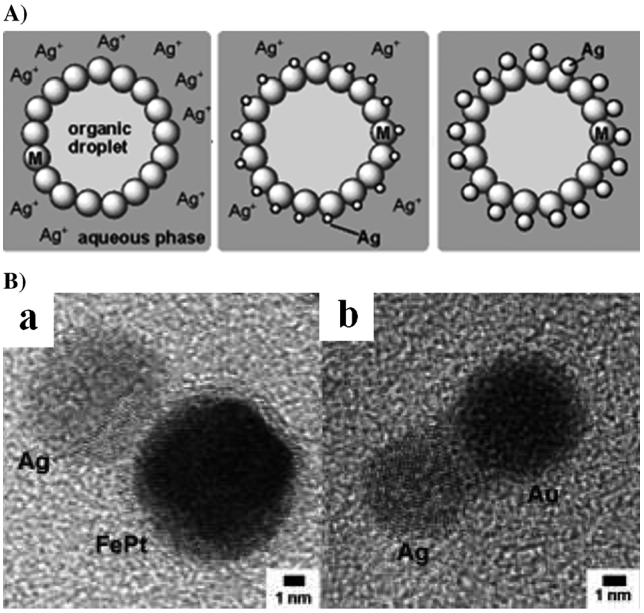

Figure 12. A) Schematic representation of the nucleation and growth of Ag colloids onto particle M on the surface of oil droplets; M = FePt or Au nanoparticles. B) TEM images of a) FePt/Ag and b) Au/Ag. Reprinted from Ref. [101] with permission.

combustion, a phase separation between the iron oxide and silica occurred, thereby leading to the formation of Janus nanoparticles while the two substances were still in their liquid phases. These Janus particles have well-defined morphology, but the size distribution was broad.

2.3. Hybrid Soft/Hard Janus Structures

Strictly biphasic soft/hard Janus structures combine the properties from both the soft (i.e. polymer) and hard (i.e. inorganic) constituents. They may be used in functional coatings or films and biomedical applications, as well as serve as building blocks for novel devices and materials.

A series of strictly biphasic polymeric/inorganic hybrid Janus structures have been successfully prepared through the controlled surface nucleation of latex particles onto inorganic nanoparticles. This process is derived from the growth-seeded emulsion polymerization technique, with inorganic particles used as seeds. Only surface interaction with organic monomers is possible (i.e. latex surface nucleation) because the inorganic seeds cannot be deformed and swelled by monomers.[2,104] To promote favorable interactions, the modification of the seed surface with molecular agents by polymer coating through an emulsion polymerization technique is necessary for the encapsulation of inorganic particles.[2] If the surface of the inorganic seed particles is only moderately modified, the capture of organic monomers or oligomeric radical species by the inorganic surface is possible, but the latex particles would grow independently. For example, strictly biphasic polymeric/inorganic hybrid Janus structures (J-2 type) made of silica and PS particles were obtained by hydrophobically modifying silica particles with a polymerizable moiety, followed by performing seeded polymerization of styrene monomer (Figure 14).[104]

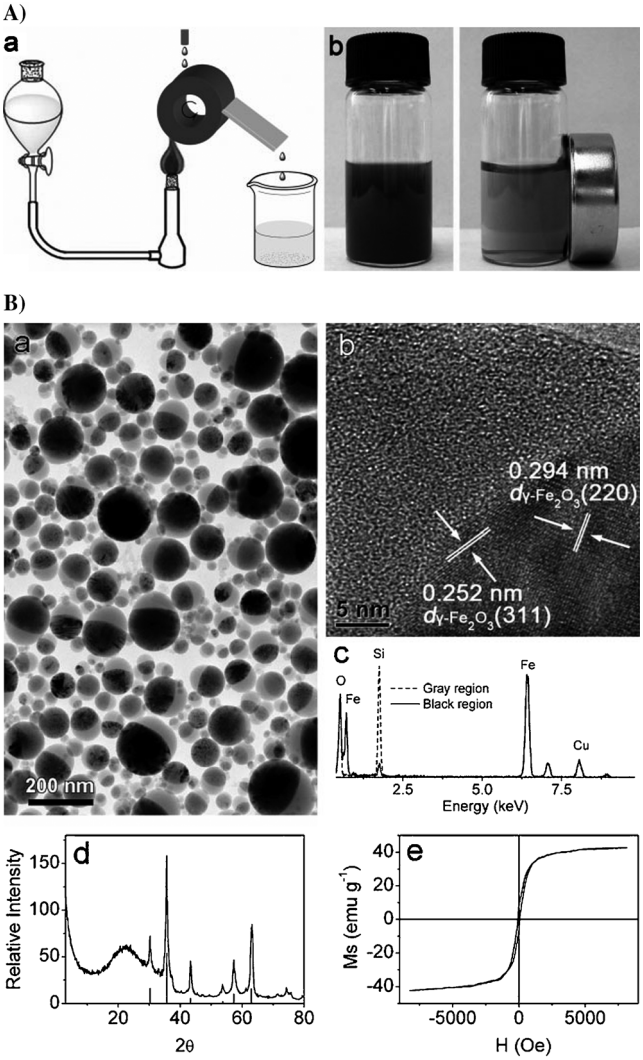

Figure 13. A-a) A schematic drawing of the setup for preparing γ-Fe_2O_3/SiO_2 Janus particles. A-b) Photographs of an aqueous dispersion of Janus particles taken before (left) and 4 h after (right) it was exposed to a permanent magnet (0.2 T). B-a) TEM, B-b) HRTEM, B-c) EDS, B-d) powder X-ray diffraction, and B-e) M_s-H characteristic. Reprinted from Ref. [103] with permission.

Similarly, by taking full advantage of the phase separation between the growing PS particles and tetraethoxysilane (TEOS), polymeric/inorganic biphasic Janus particles (i.e. PS/SiO_2, J-1 type) were obtained with silica constituting one hemisphere by hydrolysis condensation and PS forming the other hemisphere after polymerization of styrene monomers.[105] The Janus microspheres showed amphiphilicity as a result of the different chemical composition of each hemisphere.[105] Recently, magnetite/PS-silica Janus nanoparticles (J-2 type) were synthesized by forming a miniemulsion of the styrene monomer in the presence of magnetite and TEOS, with sodium dodecylsulfate (SDS) used as the surfactant. The magnetite/PS composites formed as one hemisphere, while the silica nanoparticles constituted the other hemisphere.[106] The polymerization was initiated by

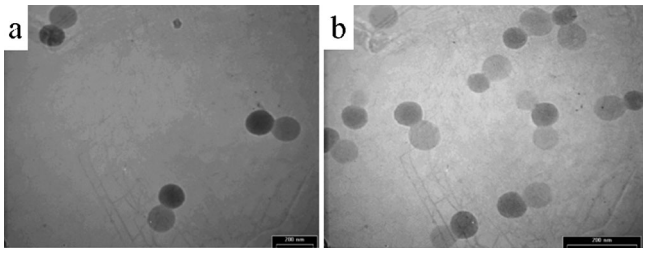

Figure 14. TEM images of dumbbell-like SiO_2/PS Janus particles (J-2) obtained by latex surface nucleation on the SiO_2 particle surface (light gray: PS particles; dark gray: SiO_2 particles). The polymerization time of styrene monomer is a) 60 min, and b) 120 min. Reprinted from Ref. [104] with permission.

ultrasonication, which resulted in the phase separation of TEOS and PS. The addition of ammonia during the sonication afforded magnetic PS/silica Janus particles (Figure 15). Magnetic polymeric/inorganic hybrid Janus particles have also been reported,[107] in which ferrofluid oil nanodroplets were swelled with styrene monomer and the polymerization induced the phase separation of magnetite from PS.

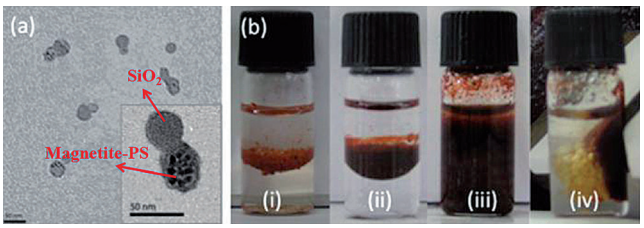

Figure 15. a) TEM image of magnetite-PS/SiO_2 Janus particles. Scale bar: 50 nm (inset: 50 nm). b) Photographs of various forms of toluene/water/Janus particle systems: i) interfacial behavior at low loading of magnetic Janus particles; ii) interfacial behavior at high loading of magnetite Janus particles in the water/toluene dual-phase system; iii) an oil/water emulsion from (ii) with asymmetric magnetite Janus particles; and iv) the magnetic Janus particle system in (iii) exposed to an external magnetic field. Reprinted from Ref. [106] with permission.

Interestingly, a simple method for the preparation of polymer particles named self-organized precipitation (SORP) has recently been developed.[108] In this method, a good solvent evaporates from a polymer solution containing a poor solvent for the dissolved polymer. Polymers are then precipitated as spherical particles after complete evaporation of the good solvent. A wide variety of polymeric particles including conjugated polymers, engineering plastics, and biodegradable polymers can be prepared by this simple process.[109] The size of the particles can be controlled from tens of nanometers to several micrometers by changing the preparation conditions, including the solution concentration and the mixing ratio of the good solvent to poor solvent. A perfectly biphasic polymeric/inorganic hybrid Janus particle composed of PI on one hemisphere and PS/γ-Fe_2O_3 on the other hemisphere (J-1 type) was successfully formed by using this simple route.[110] Evaporation of tetrahydrofuran (THF) from the solution of PS-*b*-PAA-stabilized γ-Fe_2O_3 nanoparticles, PS, PI, and water led to an aqueous dispersion of Janus microparticles, in which the γ-Fe_2O_3 nanoparticles were selectively segregated in the PS phase (Figure 16).[110]

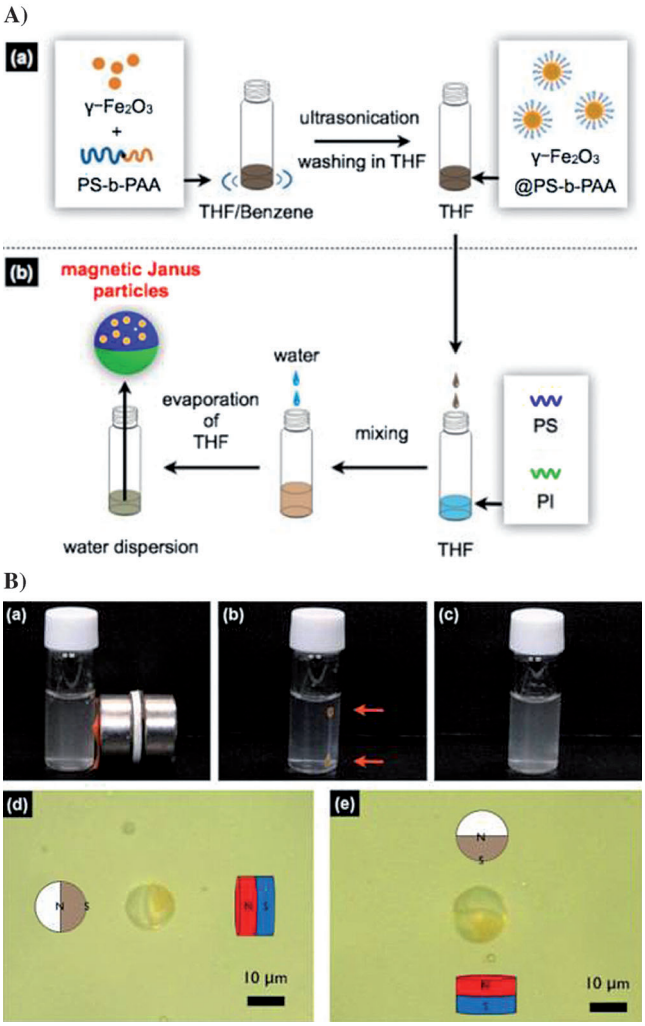

Figure 16. A) Schematic illustrations of a) stabilization of γ-Fe_2O_3 NPs with PS-b-PAA and b) preparation of magnetic Janus particles. B) Images of an aqueous dispersion of magnetic Janus particles: a) before and b) after accumulation with a neodymium magnet, and c) of a redispersed dispersion. d, e) Optical micrographs of the alignment of a magnetic Janus particle along the magnetic field. Reprinted from Ref. [110] with permission.

3. Properties and Applications of Strictly Biphasic Janus Structures

The distinct shape, composition, and functionality render Janus nanostructures with interesting and unique properties. In particular, the amphiphilicity as well as the optical, magnetic, and catalytic properties of strictly biphasic Janus structures and the associated applications have been explored in recent years.

3.1. Janus Structures as Surfactants

Janus structures can be exploited as an emulsion stabilizing agent. de Gennes envisioned Janus particles would adsorb at a liquid/liquid or liquid/air interface to form a monolayer.[111] A homogeneous particle with suitable surface chemistry can also adsorb at the interface. However, when the particle size is very small (< 10 nm), the adsorption energy for homogeneous particles at a liquid/liquid interface becomes comparable to the thermal energy and the particles can be easily detached from the interface.[111,112] In stark contrast, Janus structures can stabilize emulsions as they adsorb much more strongly at the liquid/liquid interface. Theoretical calculations show that Janus structures with the correct surface chemistry can improve the adsorption energy up to three times compared to homogeneous structures.[112] The effect of the Janus composition on the hydrophilic and lipophilic properties has also been investigated.[113]

Compared to common stabilizers, the surface area stabilized by a Janus particle exceeds its cross-section several times, thus suggesting a superior performance of Janus particles during emulsion polymerization.[114] Strictly biphasic polymeric PS/PMMA Janus particles have been applied in an industrially relevant setting, that is, the emulsion polymerization of different monomers.[114] The emulsion polymerization can be carried out with no need for surfactants.[115] The resulting latex dispersions have well-controlled particle size with extremely low polydispersity (Figure 17), thereby enabling their use in fundamental research and future industrial applications.[114] The particle size decreases as the amount of Janus stabilizer increases. A detailed analysis of the surface coverage of latex particles revealed a loose coverage by the Janus particles.[115]

In addition, the amphiphilic properties of strictly biphasic Janus structures show great promise for their use as size-dependent semipermeable membranes at the interface between two immiscible fluids. Such membranes can be utilized as buoys for water-floating micromachines, superhydrophobic coatings, etc.[116] Janus particles with superhydrophobic and hydrophilic hemispheres can act as a highly flexible superhydrophobic barrier (Figure 18).[116] Janus particles can also be used to form liquid marbles that can be controlled by magnets.[117]

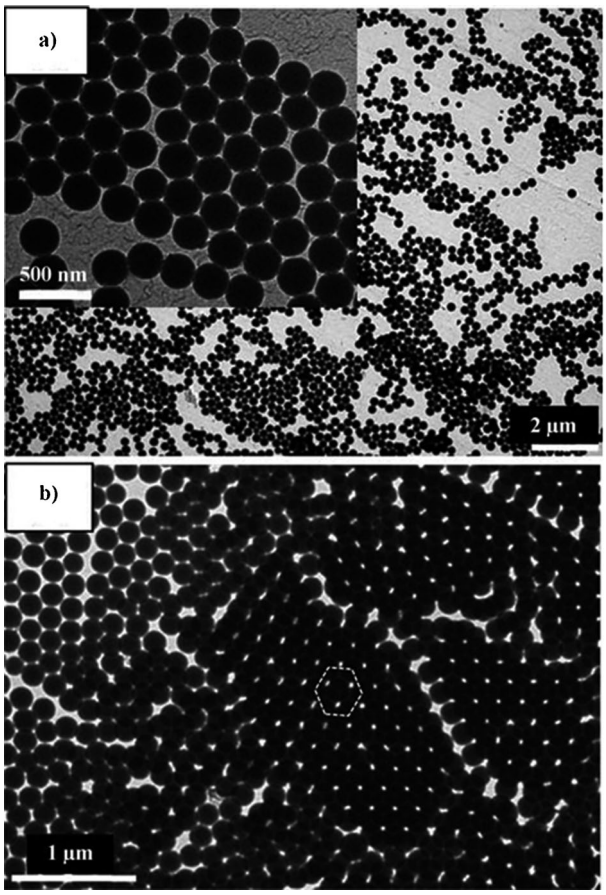

Figure 17. TEM images of PS latexes with a stabilizer content of a) 0.5 and b) 4 wt%. A double layer of particles can be seen in (b). Reprinted from Ref. [114] with permission.

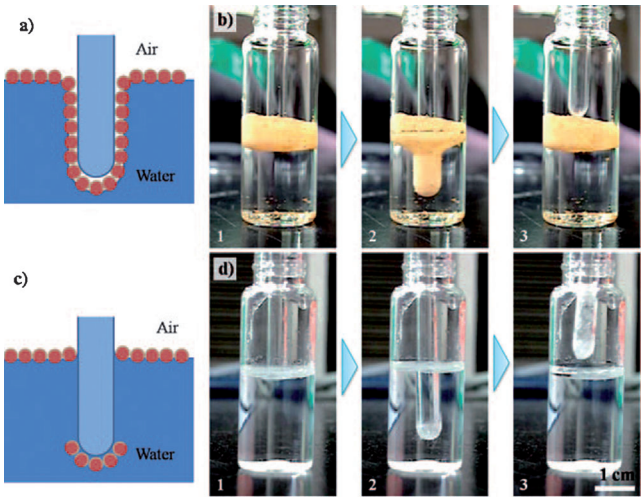

Figure 18. a) Response of a Janus microsphere monolayer to the intrusion of a hydrophilic stick, demonstrating the monolayer can act as a flexible barrier at the air/water interface. b) Sequential images of an air/water interface protected with a monolayer of Janus microspheres with porous surfaces. c) The monolayer of Janus microspheres fails when subjected to poking by a non-hydrophilic stick. d) Digital images showing the breakdown of a protective layer composed of Janus microspheres. Reprinted from Ref. [117] with permission.

3.2. Optical Properties

Janus structures may exhibit unique optical properties as a result of the proximity of two disparate materials.[118] A potential application based on the optical properties of Janus structures is to utilize them to probe local rheological properties of the environment of interest (i.e. serving as rheological probes). The optical properties of biphasic metal/metal oxide Janus particles are dependent on the surface plasmon resonance of the metal nanoparticles that absorb radiation in the visible region. Such Janus particles containing optically active species are suitable for use as sensors. For example, the UV/Vis absorption of Au/Fe_3O_4 biphasic Janus

particles (J-2 type) is red-shifted by approximately 18 nm compared to Au nanoparticles alone.[99,98]

3.3. Magnetic Properties

Janus particles made up of magnetic components enable magnetic manipulation for use as magnetic imaging probes and magnetically recyclable catalysts, as well as in drug delivery and high-throughput immunoassays.[26] Superparamagnetic Janus particles can be aligned and assembled to show eccentric rotational motion under an external magnetic field.[119–122] For example, complex magnetic Janus particles comprising γ-$Fe_2O_3$and SiO_2 have recently been used for remote manipulation.[123]

As noted in Section 1, strictly biphasic Janus particles composed of fluorescent CdS QDs and magnetic Fe_3O_4 can be utilized for magnet-driven fluorescent switches and flexible bead displays.[10] Janus particles were inserted in the highly ordered hole arrays in the panel (Figure 19). When the direction of the external magnetic field was changed, the alternation of the upward orientation of the hemispheres of Fe_3O_4 nanoparticles (OFF state) and CdS QD hemispheres (ON state) can be exploited as a typical fluorescent switch (Figure 19a). When the Fe_3O_4 nanoparticle hemispheres faced upward, the panel showed a reddish-brown color under daylight (Figure 19b) and black color under UV light. Similarly, when the QD hemispheres were directed upward, the panel displayed a white color under daylight and a bright blue emission under UV irradiation (Figure 19c,d). As a result, the magnet-responsive rotation of Janus particles can allow free writing on the flat panel by using a magnetic needle.

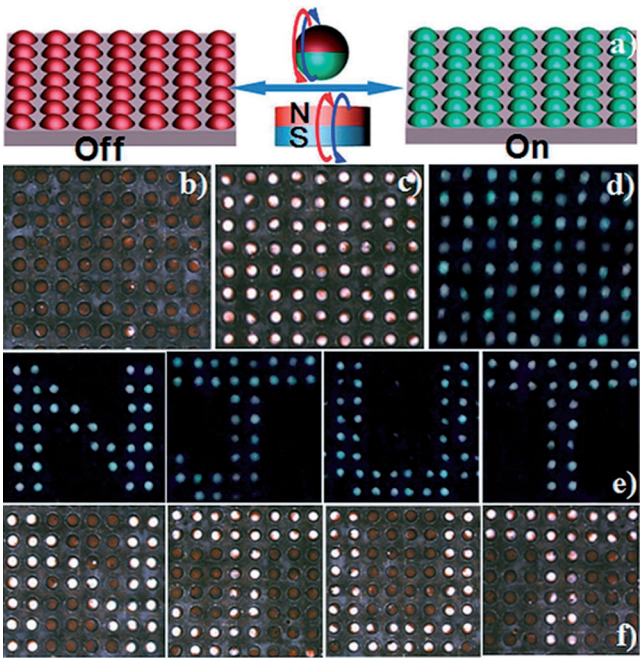

Figure 19. a) Principle of a fluorescent switch of Janus particles controlled by varying the direction of an external magnetic field. b–f) Optical images of a magnetoresponsive bead display prepared from Janus particles: b, c, f) under daylight and d, e) under UV irradiation. Reprinted from Ref. [10] with permission.

3.4. Catalysis

Catalytic biphasic Janus structures can be employed in the degradation of organic pollutants, synthesis of organic functional compounds, fuel-cell electrochemistry, antibacterial protection, etc.[124,125] For example, as noted in Section 1, TiO_2/Au biphasic Janus nanoparticles exhibited catalytic activity in the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride, with 99% conversion in 6 min.[11] Janus nanostructures were found to catalyze the reaction at the same rate as bare spherical Au nanoparticles during the first cycle of use. This can be ascribed to the fact that the exposed Au core on one side of the Janus catalysts provided direct access to 4-nitrophenol. In addition, Janus catalysts can be reused over five cycles without any apparent decrease in activity.

4. Summary and Outlook

Since the concept of "Janus grains" was highlighted by de Gennes in 1991, research into this field has developed rapidly, especially in recent years. However, despite much work being carried out on Janus structures of different size, shape, composition, and properties, little work has been implemented on strictly biphasic Janus structures. The focus of this Review is on highlighting recent developments in synthetic strategies, properties, and applications of strictly biphasic Janus structures. Three strictly biphasic Janus structures are discussed: soft (i.e. polymeric), hard (i.e. inorganic), and hybrid soft/hard (i.e. polymeric/inorganic). They can be crafted by a variety of techniques, including phase separation, microfluidics, and controlled surface nucleation. The unique properties and applications of these intriguing Janus structures are also presented. Among all the techniques reported to date, the phase-separation approach has several advantages, such as easy fabrication process and controllable size range (nm to μm) can be achieved. However, it is mainly used to produce polymeric and strictly biphasic polymeric/inorganic Janus structures. Moreover, this approach cannot be easily scaled up to large amounts because of either the use of dilute solution or a broad particle size distribution. In sharp contrast, the microfluidic method allows the production of large quantities of polymeric and polymeric/inorganic Janus structures (sometimes with unconventional morphologies) in a continuous fashion. However, as a result of the relatively large size of the microfluidic channels, the resulting Janus particles are typically rather large, and it is difficult to obtain nanosized colloids (10–100 nm). The channels often require special designs. Furthermore, the choice of available materials is limited.

As Janus structures are composed of two (or more) components with distinct chemistry and morphology, they possess many intriguing properties such as amphiphilic, optical, magnetic, and catalytic properties, as well as the possibility for self-assembly, which in turn makes them suitable for applications as surface modifiers and interfacial stabilizers, water-repellent coatings, optical probes, switchable display devices, and nanomotors as well as in chemical catalysis and drug delivery.

Future work on the rational design and synthesis of strictly biphasic Janus structures and subsequent exploration of their intriguing properties and applications will likely include, but not limited to, the following directions: 1) Current preparative strategies are not sufficient for producing different Janus structures, particularly since most of the strategies are not suitable for large-scale production. Clearly, further effort should be made in the development of simple, general, robust, and reliable strategies that impart the formation of a large variety of high-quality perfectly biphasic Janus structures over large scales. We note that achieving strict biphasic Janus character is still challenging for chemists and materials scientists. 2) As the two constituents in hybrid soft/hard (i.e. polymeric/inorganic) Janus structures possess totally different chemical properties, they allow the combination of properties from the substantially dissimilar soft and hard constituents. Janus structures of this kind could have potential use in functional coatings or films and biomedical applications. 3) Most Janus particles reported to date are regarded as prototypes for the development of novel synthesis methods. Looking to the future, a greater diversity of Janus structures with more practical applicability may be crafted and accessed by judicious combination (and coupling that yields additional functionality) of intriguing functionalities from two constituents, including superparamagnetic, fluorescent, biocompatible, photocatalytic, mechanical, electrical, stimulus-responsive proberties. 4) Despite a multitude of potential applications having been mentioned, most of them stay as concepts and have not yet been realized. Clearly, this offers new opportunities to further explore the relationship between the structure, property, and application of Janus structures.

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