HAL
open science

Particles with magnetic patches: synthesis, morphology control, and assembly

Elham Yammine, Eddy Souaid, Sami Youssef, Maher Abboud, Stéphane Mornet, Michel Nakhl, Etienne Duguet

To cite this version:

Elham Yammine, Eddy Souaid, Sami Youssef, Maher Abboud, Stéphane Mornet, et al.. Particles with magnetic patches: synthesis, morphology control, and assembly. Particle & Particle Systems Characterization, 2020, 37 (7), 2000111 (12 p.). 10.1002/ppsc.202000111 . hal-02906254

HAL Id: hal-02906254
https://hal.science/hal-02906254v1

Submitted on 24 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DOI: 10.1002/ ((please add manuscript number))
Article type: Review

Particles with Magnetic Patches: Synthesis, Morphology Control, and Assembly.

*Elham Yammine, Eddy Souaid, Sami Youssef, Maher Abboud, Stéphane Mornet, Michel Nakhl and Etienne Duguet**

Dr. E. Yammine, Dr. S. Mornet, Prof. E. Duguet
Univ. Bordeaux, CNRS, ICMCB, UMR 5026, 33600 Pessac, France
E-mail: etienne.duguet@icmcb.cnrs.fr
Dr. E. Yammine, Dr. E. Souaid, Prof. M. Nakhl
LCPM/PR_2N (EDST), Lebanese University, Faculty of Sciences II, 90656 Jdeidet El Metn, Lebanon
Dr. S. Youssef
Ecole supérieure d'ingénieurs de Beyrouth, Université Saint-Joseph, Campus des Sciences et Technologies Mar Roukos – B.P. 1514, Riad El Solh, Beirut 1107 2050, Lebanon
Prof. M. Abboud
Unité Environnement Génomique et Protéomique, U-EGP, Faculté des Sciences, Université Saint-Joseph, Campus des Sciences et Technologies Mar Roukos – B.P. 1514, Riad El Solh, Beirut 1107 2050, Lebanon

Keywords: patchy particles, magnetic patches, synthesis, self-assembly, magnetic-driven assembly

The concept of patchy particle is revolutionizing the research field of colloidal assembly, by the design of particles whose surface is purposely patterned to promote with their neighbors attractive interactions in limited number, and in privileged and programmed directions. The idea of magnetic patches makes it possible to imagine assemblies not only spontaneous by simple magnetic coupling but also triggered and canceled at will thanks to external magnetic fields. This review shows the studies published until then mainly dealt with particles with a single magnetic patch, often called Janus particles. The very diverse synthetic routes have been brought together into four main strategies, covering the size range from 100 nm to 100 μm. Their assembly capacity is described both from an experimental and simulation viewpoints. The orientation of the magnetic moment of the patch and its decentering extent with respect to the particle are the key parameters for controlling the morphology of clusters, loops, staggered chains, double chains, helices, microtubes, etc. The review then offers some perspectives to generalize these studies to multipatch particles, examples of which are still too

rare, and to make assemblies sustainable, especially after the removal of the structuring magnetic fields.

1. Introduction

"Bottom-up" approaches are unmissable for building hierarchical structures with unique properties for both fundamental studies and technological applications.[1] That is why the preparation of particles serving as building blocks for controlled assembly is currently one of the most active research areas in nanotechnology. In contrast to conventional spherical particles, anisotropic particles are able to order into many novel colloidal structures (crystalline or non-crystalline).[2] In particular, this aroused a great interest in envisioning patchy particles as valence-endowed colloidal building blocks for diversifying the attainable structures.[3] These surface-patterned particles can indeed experience specific directional interactions with the neighboring particles. Notably, magnetic anisotropic colloids are a research topic that received attention over the past fifteen years.[4–9] The anisotropy may arise from their non-spherical shape and/or their chemical composition mainly by shifting the dipole moment out of the particle center. Thereby, magnetic manipulation of these particles allows their magnetophoretic mobility in a liquid carrier medium to promote their orientation along the magnetic field lines as well as their assembly into well-defined structures depending on their morphology, size, and physicochemical properties. Remote manipulation of the particles by a magnetic field makes them ideal to build functional devices for a wide range of applications such as micro- or nanomotors,[10] electric paper pixels,[11] targeted drug delivery,[12] surfactants for Pickering emulsions,[13] microstirrers,[14] water treatment,[15] etc. They can also be assembled into complex structures like non close-packed lattices and low-coordination architectures.

In this review, we first introduce the concept of patchy particles, and then discuss the preparation of magnetic patchy particles and their different assembly pathways. We assume

the bias of having organized the plan of the review such that the magnetic Janus particles, already known for several decades, appear as the subcategory of the particles with a patch and not conversely the historical reference of which the multipatch particles would only be a subcategory or an intellectual extension.

2. The Recent Concept of Patchy Particles Encompassing much Older Objects

The concept was envisioned for the first time by Glotzer and coll. for simulation experiments in order to force spheres to crystallize in a diamond lattice.[3] Patches are surface discontinuities which encode directional particle-particle interactions.[16,17] The nature of these surface discontinuities are either topological, *e.g.* dimples, or chemical, *i.e.* small areas with chemical groups different from those on the surface remainder. Sometimes, they are called entropic and enthalpic patches, respectively.[17] Patches are of great interest when they are attractive, *i.e.* sticky by lowering the coordination number of the particle to the number of surface patches and tuning the interactions between the neighboring particles. The overall shape, size, position and patch number are critical parameters.[18–21] Among the most wanted patchy particles, those bearing four patches arranged according to a tetrahedral repulsion figure are being of special interest because they could help self-assembly in a diamond-like structure. The latter is the Holy Grail of researchers in photonics since it could serve as precursor for photonic full band-gap crystals.[22] From a more general point of view, the field of patchy particles must be considered as that of an enabling technology and its applicability will depend on our ability to control the number and position of the patches, to prepare pure and large batches, and soon combine within the same particle patches of different chemical nature to sequence the assembly process through different forces and better control the hierarchy and reconfiguration of the assemblies.

Nevertheless, when magnetic patches are considered, one-patch particles have essentially been reported so far. To a certain extent, Janus particles can be considered as one-patch

particles. These are named after the two-faced Roman god and exhibit a dissymmetric chemical composition.[7,8] One side is indeed considered as a single patch and the other one as the remainder of a conventional particle. **Figure 1** gives an overview of already-described Janus particles combining chemical dissymmetry and possibly shape anisotropy.[7] In order to preserve the original concept of patchy particles, only Janus particles deriving from spheres are considered in this review, *i.e.* original Janus spheres as defined by De Gennes[23] (a), acorn-like (b), dumbbell-like (c) and snowman-like (d) morphologies, where the blue component represents the magnetic part while the red one the nonmagnetic.

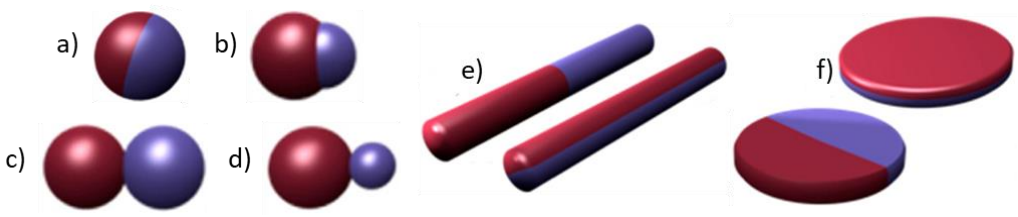


Figure 1. Drawing showing the diversity of Janus particles combining chemical dissymmetry and possibly shape anisotropy: a) original Janus spherical particle as defined by De Gennes, b) acorn-like particle, c) dumbbell-like particle, d) snowman-like particle, e) Janus disk-like particle, and f) Janus rod-like particle. Those considered as one-patch particle in this review are a) to d). Adapted with permission.[7] Copyright 2013, American Chemical Society.

3. Fabrication of Particles with One Magnetic Patch

An overview of the literature has taught us that magnetic patchy particles are essentially made of a single patch and can be classified in four categories (**Figure 2**). The magnetic component on a nonmagnetic sphere can indeed result from the side-specific deposition of a thin magnetic film or the adsorption of preformed tiny magnetic nanoparticles. It can also be a magnetic particle or an aggregate of tiny magnetic particles (also named colloidal supraparticle[24]) more or less inlaid on the nonmagnetic sphere, even fully embedded just below its surface.

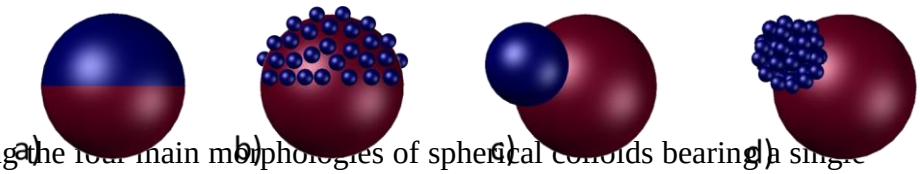


Figure 2. Drawing showing the four main morphologies of spherical colloids bearing a single magnetic patch, colored in blue, which can be a) a thin film, b) a collection of tiny particles, c) a quite large single particle or d) a colloidal supraparticule. For these two last cases, the magnetic component can be more or less embedded in the nonmagnetic sphere (colored in red).

The fabrication routes involve chemical surface modification methods, phase separation processes or templating strategies using 2D substrates or particles. The main synthesis strategies that have been reported so far are:

i) the site-specific decoration of a nonmagnetic one-patch particle with magnetic nanoparticles;

ii) the symmetry breaking of a nonmagnetic particle by the addition of a magnetic component;

iii) the symmetry breaking of a magnetic particle or colloidal supraparticle by the addition of a nonmagnetic component;

iv) the one-pot synthesis where both magnetic and nonmagnetic components are simultaneously synthesized, assembled or reshaped.

Since they are out of the scope, the review doesn't deal with shape-anisotropy particles like triangles,[25] cubes,[26] or cylinders[27] synthesized for instance by photolithography and side-specifically coated by a metallic magnetic film.[28–30]

3.1 Site-specific Decoration of a Nonmagnetic One-patch Particle with Magnetic Nanoparticles

The method involves using preformed one-patch particle and taking advantage of the differentiated surface properties to adsorb/graft selectively tiny magnetic particles. According to this strategy, Kim *et al.* prepared first ellipsoidal bicompartmentalized poly(styrene-*co*-(vinyl alcohol)/poly(tetradecyl acrylate) microparticles by seeded monomer swelling and subsequent photopolymerization.[31] Then they achieved the site-specific patching of magnetic nanoparticles using the electrostatic interaction between the polyethylenimine-coated surface and polyvinylpyrrolidone-stabilized maghemite (γ-Fe_2O_3) nanoparticles (**Figure 3**).

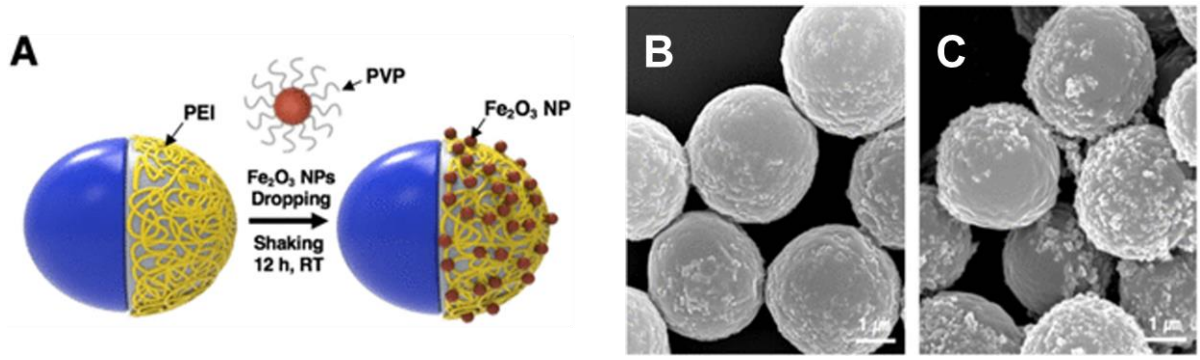


Figure 3. Side-specific adsorption of magnetic nanoparticles on amphiphilic polymeric microspheres: (A) drawing illustrating the selective adsorption process; SEM images of the magnetic one-patch microspheres obtained with a weight ratio of maghemite nanoparticles of (B) 0.25 and (C) 0.5. Scale bars: 1 μm. Adapted with permission.[31] Copyright 2018, American Chemical Society.

In other reports, it was sometimes necessary to activate the surface chemical functions of the nonmagnetic patch. This was the case for polyacrylonitrile/polystyrene nanoparticles obtained by Tang *et al.* through seed-growth emulsion polymerization.[32] The polyacrylonitrile component was selectively hydrolyzed to reveal carboxylic functional groups. Subsequently, superparamagnetic magnetite (Fe_3O_4) nanoparticles coated with

chitosan, *i.e.* positively charged macromolecules, were adsorbed on the surface of the hydrolyzed region by electrostatic interactions with the carboxylate groups.

3.2 Symmetry Breaking of a Nonmagnetic Isotropic Particle by a Thin Magnetic Film

A monolayer of the particles to be made dissymmetrical are first immobilized on a planar substrate by various techniques, *e.g.* spin-coating or dip-coating. Then a metal or metal oxide is evaporated on the particles monolayer. The process is quite simple and practically applicable to any type of particles regardless of their size or shape. Nevertheless, it necessitates a close packing of the particles while managing the risk to see them stuck together by the deposited thin film.

For instance, polystyrene microparticles were made patchy by evaporation of iron[33] or nickel under reducing atmosphere.[34] In the latter case, it was shown that the particle behavior was tuned from ferromagnetic to superparamagnetic by reducing the film thickness. The evaporation method also allows the successive deposition of several coatings, for example, cobalt/platinum[35] or cobalt/palladium[36] on silica microparticles or cobalt/palladium on polystyrene nanoparticles.[37] The deposited metallic film is mainly thick at the center of the hemisphere therefore magnetic dipole can be off-centered and oriented along with a specific directionality.

Moreover, Ren *et al.* showed that the variation of the deposition rate of iron by physical vapor deposition in an oxidizing atmosphere leads to particles with an iron oxide patch where the oxidation state of the iron atoms may be tuned.[38] Furthermore, they demonstrated that the patch-to-particle surface area can be decreased from 50 to 20 % by embedding 80 % of the particle surface in a coating of controlled thickness of a protective photoresist (**Figure 4**).[39] Unfortunately, this technique cannot be used for nanoparticles because the thickness of the photoresist coating would be too tricky to control.

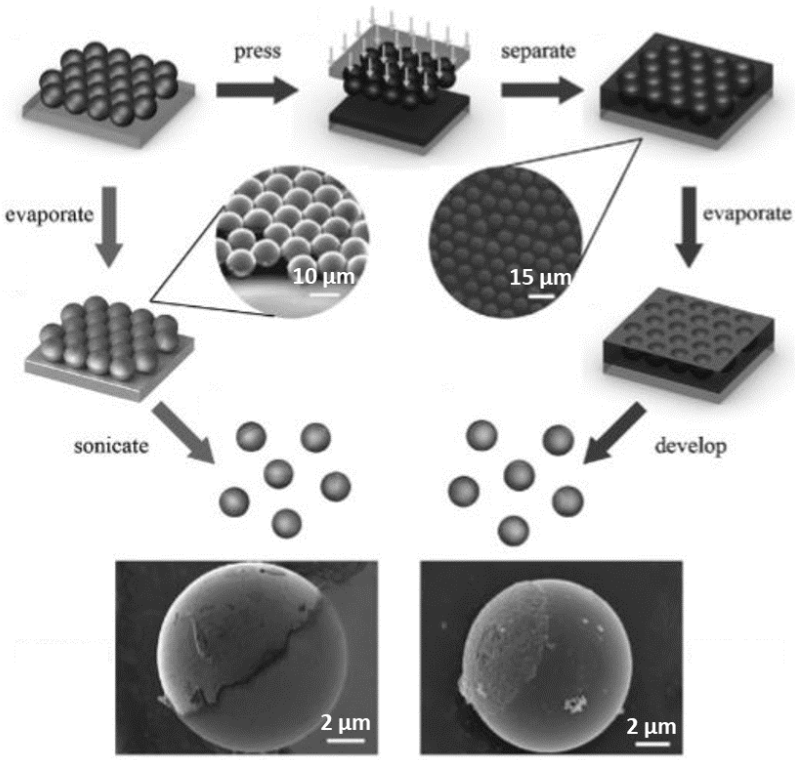


Figure 4. Side-specific evapc polystyrene particles on a gla supplementary step where the substrate to be partially embedc are shown on SEM images. Adapted with permission.[39] Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Although relatively simple to implement, the physical deposition technique is limited in yield and cost, because only low amounts of particles can be made patchy during the same experiment, even in continuous processes.

3.3. Symmetry Breaking of a Magnetic Isotropic Particle or Colloidal Supraparticle by a Nonmagnetic Component

Sacanna *et al.* partially encapsulated a micron-sized cube of hematite (α-Fe_2O_3) in a spherical organosilica particle.[40] Among magnetic microparticles, hematite is of special interest because its magnetic properties originate from a canted antiferromagnetism at room temperature making its spontaneous magnetization much lower than that of other iron oxides but its domain size is of the order of a few micrometers.[6] Consequently, it still has a permanent dipole moment (single domain regime) up to a micrometric size, while the others

become multidomain and lost their magnetization most of the time. Synthesized following the protocol of Sugimoto,[41] the size-monodisperse cubes were dispersed in an aqueous emulsion of an alkoxysilane carrying a methacrylate group. They spontaneously positioned at the water/oil interface and they were progressively trapped in the oil droplets as far as the progress of the hydrolysis-condensation of the silane and the subsequent crosslinking by free-radical polymerization of the methacrylate groups. Thus, well-calibrated spherical microparticles were obtained with a magnetic cubic patch with only one of its faces emerging from the surface of the particle (**Figure 5**). More recently, the same authors showed that a preliminary subtle surface modification of the cubes allows controlling the extent of its encapsulation in the oil droplets.[42]

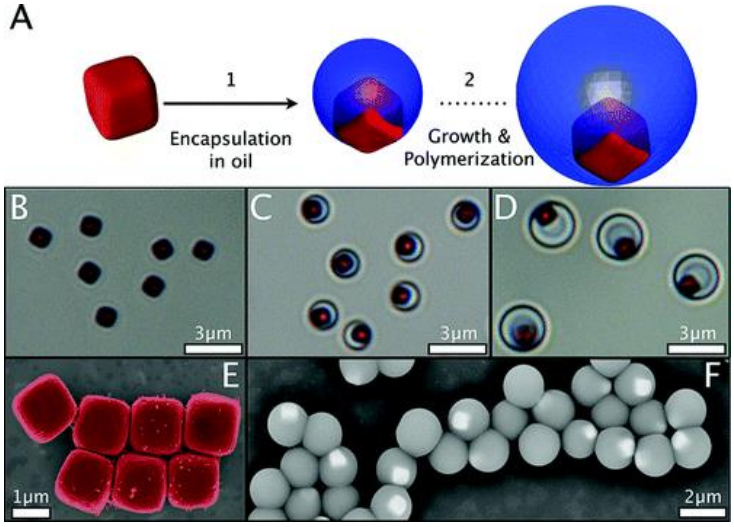


Figure 5. Partial encapsulation of hematite cubes in organosilica microspheres: A) drawing showing the synthesis strategy; (B-D) optical images showing the encapsulation progress; (E) SEM image of the hematite cubes in false color and (F) SEM image of the one-patch particles. Reproduced with permission.[40] Copyright 2012, American Chemical Society.

Zhang *et al.* reported the growth of mesoporous silica nanowires from magnetite colloidal supraparticles according to a sol-gel reaction performed in the presence of

cetyltrimethylammonium bromide as structuring agent (**Figure 6**).[43] The aspect ratio was controlled by playing with the tetraethoxysilane/magnetite molar ratio.

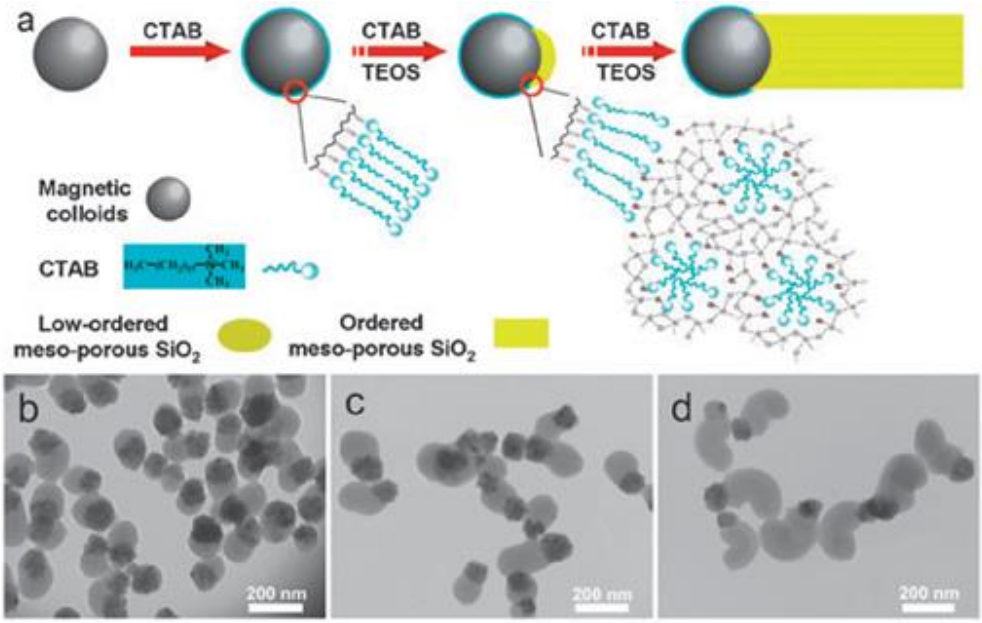


Figure 6. Growth of mesoporous silica nanowires from magnetite colloidal supraparticles: (a) Drawing showing the growth mechanism in the presence of cetyltrimethylammonium bromide (CTAB) and tetraethoxysilane (TEOS); TEM images of one-patch particles obtained with different aspect ratios thanks to varying TEOS/magnetite molar ratio: (b) 2:1, (c) 3:1 and (d) 4:1. Reproduced with permission.[43] Copyright 2011, The Royal Society of Chemistry.

Seed-growth emulsion polymerization is a well-known method for obtaining biphasic particles of complex shapes such as dumbbell-like, snowman-like, multipod-like morphologies with high yield.[44] According to this strategy, Elaissari and coll. prepared magnetic polystyrene particles by using azobisisobutyronitrile as an organosoluble initiator (**Figure 7** ***Left***).[45] Quite similar morphologies were obtained by varying the crosslinking density with the use of divinylbenzene as comonomer.[46] Assuming that a patch can also be positioned just below the surface of the particle, some other reports deserve to be cited. Indeed, Ge *et al.* produced particles with an off-centered magnetic core by emulsion

polymerization of styrene in the presence of silica-coated magnetite supraparticles functionalized by γ-methacryloxypropyl groups and sodium dodecyl sulfate as surfactant (**Figure 7** ***Center***).[47] Xu *et al.* obtained very similar structures without surfactant (**Figure 7** ***Right***).[48] The surface tension, the styrene/supraparticle mass ratio and the degree of crosslinking are the critical parameters allowing the morphology control. The seed-growth emulsion polymerization strategy was recently rationalized by Wang, He and coll., who studied in particular the growth of one polystyrene latex particle on hematite ellipsoids (length: 230 nm and width: 125 nm).[21]

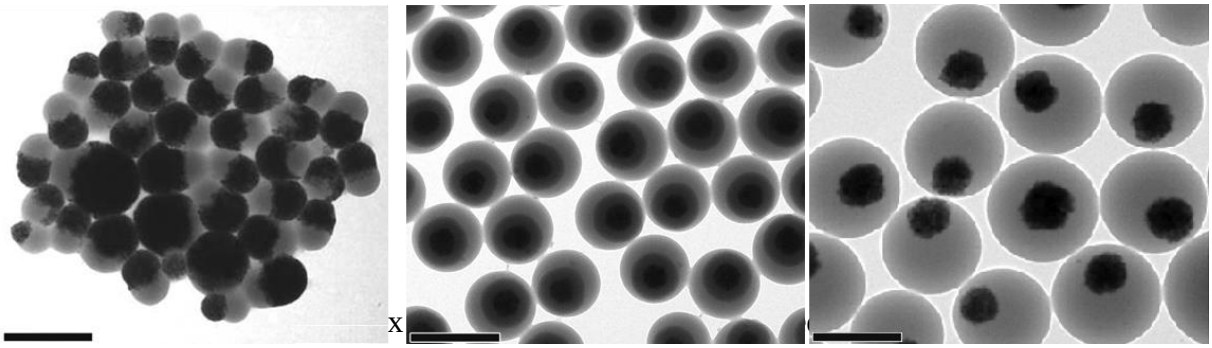


Figure 7. x

polymerization. *Left:* TEM images of one-patch of polystyrene/maghemite particles with a styrene-to-azobisisobutyronitrile molar ratio of 100. Reproduced with permission.[45] Copyright 2011, The Royal Society of Chemistry. *Center:* TEM image of magnetite colloidal supraparticles embedded in silica and then in polystyrene. Reproduced with permission.[47] Copyright 2007, American Chemical Society. *Right:* TEM image of magnetite supraparticles embedded in polystyrene. Reproduced with permission.[48] Copyright 2012, American Chemical Society. Scale bars: 400 nm.

3.4. Simultaneous Synthesis, Assembly or Reshaping of Magnetic and Nonmagnetic Components

The assembly of microparticles by emulsion confinement was originally described by Manoharan *et al.*[49] Oil droplets containing polystyrene particles are stabilized in water by

surfactants. Then, the evaporation of the organic solvent induces the particle assembly into clusters whose geometry depends on their number. Zerrouki *et al.* showed that the method can be applied to more complex systems for instance by combining silica microparticles and ferrofluid droplets.[50] In particular, they obtained well-calibrated magnetic one-patch particles and studied their assembly behavior (see section 4.2.1). Other methods involving dispersed media have been also investigated. For instance, asymmetric magnetic polystyrene particles were obtained by emulsion solvent evaporation.[51,52] The macromolecules are first solubilized in an organic phase containing maghemite nanoparticles and then the mixture is emulsified in water in the presence of a surfactant. In specific conditions, the subsequent evaporation of the organic phase results in the precipitation of the polymer and phase separation of the magnetic nanoparticles that accumulate in one or several layers on one side of the polystyrene particle as a function of the magnetic nanoparticles/polymer ratio.

The sol-gel reactions carried out in dispersed media such as miniemulsions allowed also Wang, Shi and coll. producing magnetic one-patch polystyrene particles with a snowman shape where the magnetic nanoparticles are dispersed inside the organosilica head attached to a polystyrene body (**Figure 8**).[53] Teo *et al.* achieved reverse morphologies with a magnetic polystyrene body and a pure silica head, when the magnetic nanoparticles were previously made hydrophobic by surface modification with γ-methacryloxypropyl groups.[54]

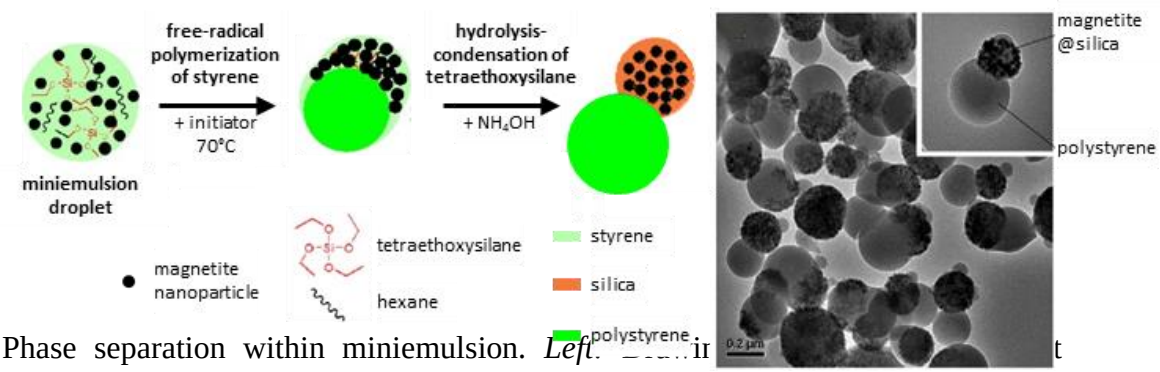


Figure 8. Phase separation within miniemulsion. *Left:* [illegible] in [illegible] t process combining sol-gel reaction and styrene polymerization. *Right:* TEM images of the as-

obtained one-patch particles. Scale bars: 200 nm. Adapted with permission.[53] Copyright 2011, American Chemical Society.

When the patch is expected to be made of a collection of tiny magnetic nanoparticles, it can be further achieved thanks to the application of an external magnetic field. Paunov and coll. used a magnetic emulsion formed from a polymerisable oil containing magnetite nanoparticles and stabilized with an anionic surfactant.[55] In order to make the droplets immobile during the application of the magnetic field gradient, the aqueous phase was gelled with agarose. Then, the polymerization of the droplets was initiated by heating while the nanoparticles were concentrated in one hemisphere of the particle, depending on the direction of the external magnetic field gradient. Finally, the gel was liquefied by heating and the obtained one-patch microparticles were recovered. Because of the "arrested" orientation of the magnetite nanoparticles in the polymer matrix, the microparticles retained remnant magnetization with coercivity values as high as 700 Oe indicative of a ferromagnetic behavior. Nevertheless, they appeared to be highly size-polydisperse (**Figure 9** ***Left***), probably because of the large size distribution of the initial emulsion droplets.

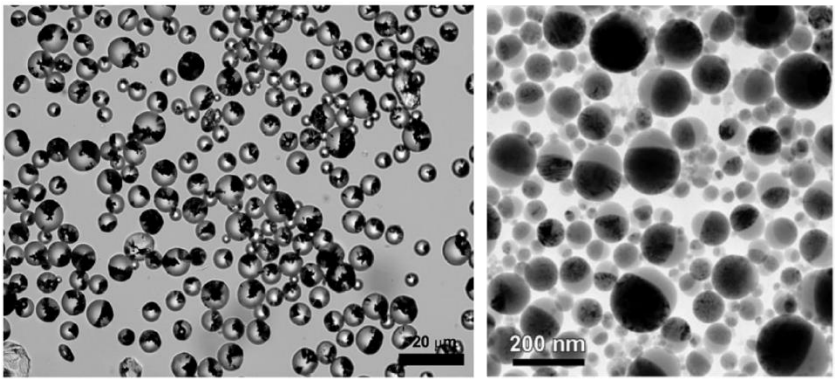


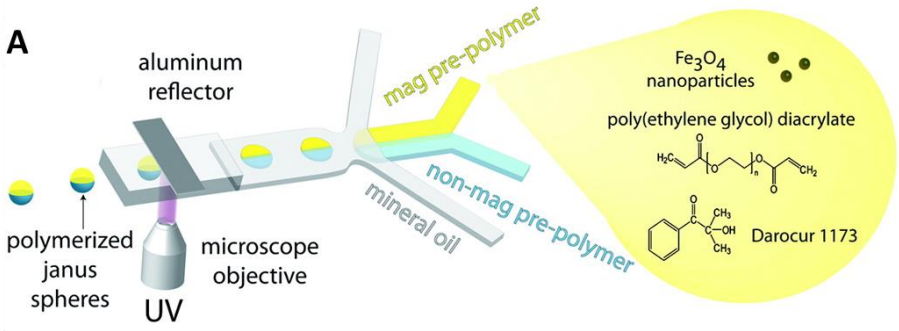
Figure 9. *Left:* Optical image of one-patch polymer/magnetite microparticles obtained by application of magnetic field gradient on a polymerizing magnetic emulsion. Reproduced with permission.[55] Copyright 2009, The Royal Society of Chemistry. *Right:* TEM image of one-

patch silica/maghemite particles obtained by flame synthesis. Reproduced with permission.[56] Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

The flame synthesis route has also been investigated by Zhao and Gao to get dissymmetrical maghemite/silica particles. Precursors were mixed with a solvent and sprayed without the help of a gas.[56] Near the flame, the evaporation and combustion of the organic solvent led to a solid mixture, which underwent phase separation when the temperature reached 1100 °C (**Figure 9** ***Right***).

The microfluidic technique has been also used to produce in one-step in a T-junction magnetic polymeric particles in the size range of 20-100 μm.[57,58] Particle morphology was locked-in via UV-initiated photopolymerization. There exist several strategies to control phase separation and hence generate one-patch particles. Weitz and coll. used a microfluidic device with a flow focusing geometry by combining in every droplets at the polymerization time the microgel shrinkage and the clustering of positively-charged magnetic nanoparticles thanks to negative polyelectrolytes.[59] With a quite similar device, Abate and coll. entrapped one droplet, filled with a styrene/divinylbenzene mixture and a commercial ferrofluid, within a larger droplet made of acrylamide monomers dispersed in water.[60] The subsequent polymerization/crosslinking stage was begun under UV irradiation and completed at 60°C to get very monodisperse batches of 55-nm hydrogel particles where the magnetic patch is a 20-μm fully off-centered sphere. Alternatively, Zhao, Gu and coll. used a permanent magnet to force the segregation of the magnetic nanoparticles.[61] Doyle and coll. used a Y-shaped channel where two streams of mineral oil sheared off droplets of two coflowing polymeric streams, one containing UV-curable monomer and magnetic nanoparticles and one not containing magnetic material (**Figure 10**).[62] They obtained 50 μm-sized bicompartment hydrogel spheres, where the magnetic patch represents half of the particle volume. Lastly, Onoe and coll. used a centrifuge-based microfluidic device for obtaining 100-μm alginate

hydrogel particles with superparamagnetic magnetite nanoparticles concentrated in one hemisphere.[63] The cross-linking step was carried out just after capillary ejection by reaction with calcium cation solution at the bottom of the centrifugation tube.



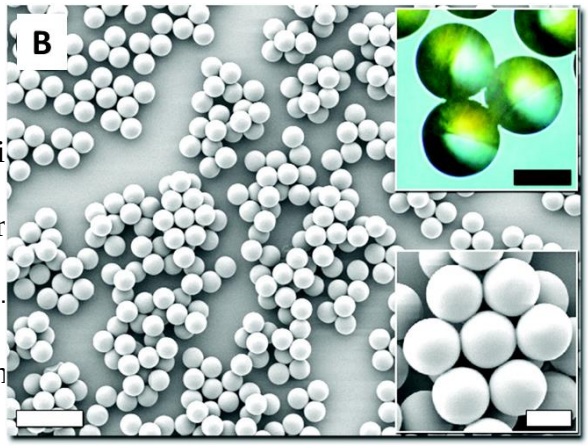


Figure 10. Application of the microflui ne-patch microparticles: (A) drawing of the micr erference contrast (upper insert) images of the as 5 μm for the inserts. Reproduced with permission iety.

4. Assembly of Particles with Magnetic Patches

It is important to distinguish between superparamagnetic particles that require an external field to be magnetized and therefore to efficiently interact and ferro/ferrimagnetic particles, *i.e.* with a permanent magnetic moment, allowing also for spontaneous self-assembly by magnetostatic interactions. This feature, which offers the possibility for the magnetic dipole to be permanently embedded into particles, is very different from electric dipoles, which require the application of an external electric field to be created and exploited. It should be noted that the total interaction potential between magnetic anisotropic colloids is not mathematically described in this review. Interested readers will refer to more specific works such as those describing either magnetic interactions,[64,65] or combining magnetic and electrostatic dipolar interactions.[66]

4.1 Spontaneous Self-assembly

Ferro/ferrimagnetic particles undergo magnetostatic interaction phenomena as soon as the distance between them is sufficiently short. If the viscosity of the medium and the thermal fluctuations are low enough, then the particles self-assemble to minimize their overall magnetic moment. In order to avoid irreversible flocculation, magnetic attractive forces are therefore coupled with electric double-layer or steric repulsions.

Isotropic magnetic particles can form spontaneously dipolar chains or rings through flux-closure in order to minimize the overall magnetic moment. When the particles are made magnetically anisotropic by decentering the magnetic moment, there is a competition between magnetic coupling and steric constraints leading to new structures. Baraban *et al.* studied the spontaneous self-assembly of 5-µm silica particles surface-coated with a single cobalt/platinum multilayer patch.[67] Their magnetic dipole moment is off-centered and points perpendicularly to the patch surface, *i.e.* the so-called radially shifted dipole configuration. Initially confined between two glass plates where they can freely rotate, the particles were individually manipulated with optical laser tweezers to grow 2D clusters by adding the particles one by one. The observed magnetically-compensated structures correspond to planar clusters with 3, 12 or 27 particles, as confirmed by simulation studies.[68,69] Sacanna *et al.* observed also the spontaneous assembly of the microparticles patched with a micron-sized cube of hematite.[40] Indeed the patchy particles are purely repulsive in deionized water where they stay as Brownian singlets. But when the surface charges are partially screened by means of added salt (1.5 mM NaCl allowing to reduce the Debye screening length below 6 nm), the patches become attractive by magnetostatic interactions and clusters are observed with aggregation numbers up to 3 (**Figure 11**). This is due to steric constraints and can be tuned by the patch-to-particle size ratio. These clusters unbind either by decreasing the ionic strength or, when they diffuse on the observation glass side, by applying quickly a perpendicular 3-mT

field which forces the magnetic dipoles to change their direction and therefore to generate dipole-dipole repulsion. Linse and coll. tried to correlate these experimental results to those of Monte Carlo simulations.[70] They observed similar behaviors, but they were not able to conclude about the orientation of the off-centered magnetic moment with regard to the patch surface. The system made of particle with an off-centered magnetic moment was recently reinvestigated by Cordova-Figueroa and coll. using Brownian dynamics simulations.[65] Considering laterally oriented magnetic moment, they confirmed that not only chain-like structures are expected when the dipolar shift is close to zero, but also that clusters of three patchy particles are predominant when the shift is higher than 0.6. But, for intermediary values, they obtained rings, *i.e.* large flux-closure structures, whose size decreases when the shift increases.

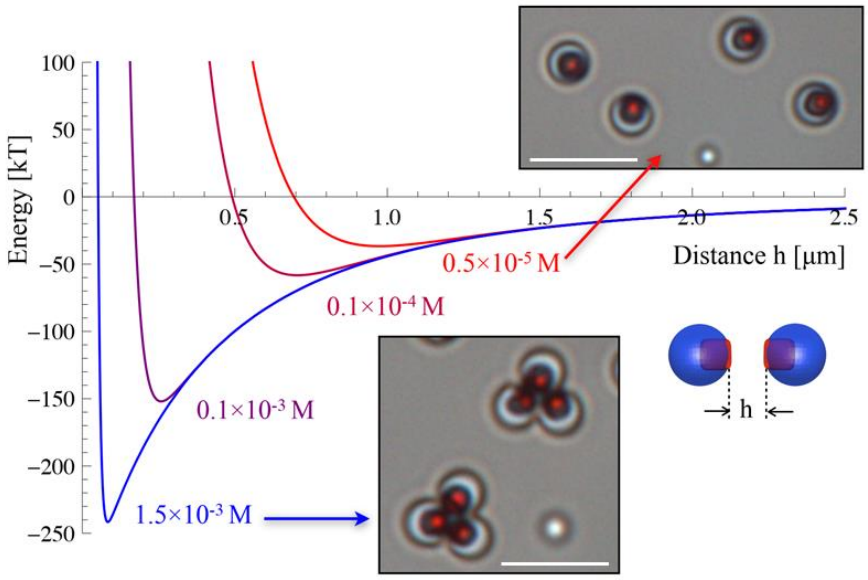


Figure 11. Total potential strengths (1-1 electrolyte), modelling electrostatic int between dipoles oriented in a head-to-tail configuration. The resulting behaviors are illustrated by optical microscopy images. Scale bars: 5 µm. Reproduced with permission.[40] Copyright 2012, American Chemical Society.

4.2 Magnetic Field-Driven Assembly of Particles with Magnetic Patches

Exploiting external electromagnetic fields, *i.e.* electric or magnetic fields, is a way to enlarge the range of achievable assembled structures with regard to the static self-assembly routes, which take advantage of van der Waals forces, electrostatic interaction, hydrogen bonding, solvophobic interaction, covalent coupling, *etc*. External electromagnetic fields typically induce particle polarization, alignment of dipoles, and dipolar chain formation.[71] Despite the magnetic dipolar interaction between particles shares similar formula with its electric counterpart, there exist a number of noteworthy differences between magnetophoresis and dielectrophoresis conditions. First, interactions between magnetic particles are not screened by mobile ions in solution, unlike the electrostatic systems, allowing applying magnetic fields over a large volume remotely. Second, conventional liquid dispersing media and nonmagnetic particles have negligible response to magnetic field, *i.e*. high magnetic susceptibility contrast with the magnetic particles. On the contrary, all kinds of particles and liquids can be polarized by electric fields. They contribute, in conjunction to mobile ions, to complex electrohydrodynamic flows while in magnetophoresis hydrodynamics arises only from the motion of the magnetic colloids themselves. Because its intensity can be finely tuned, magnetic field can be used to counterbalance other static interactions and study the phenomena that occur when two driving forces for self-assembly are competing.[71]

4.2.1 Application of a Uniaxial Static Magnetic Field

Magnetic field guided colloidal assembly is now a mature technology and for instance 1D, 2D and 3D assemblies of isotropic superparamagnetic nanoparticles are now well described and controlled.[72] The magnetic colloids experience generally two types of magnetic interactions in external magnetic fields, originating from their permanent or induced dipole moments. The interparticle dipole–dipole force describes the interaction of a dipole with the magnetic field induced by another dipole, while the packing force results from the gradient of the external magnetic field. When the external magnetic field is adequately strong, the magnetic moment of the particle reaches a saturated value creating an induced magnetic field (**Figure 12a**) felt

by the other particles. When the interaction energy is large enough to overcome thermal fluctuations, the dipole-dipole interaction between two particles is attractive or repulsive depending on their relative orientation (**Figure 12b,c**). That is why 1D chain-like structures aligned along the magnetic fields represent the simplest ordered state when transitioning from random Brownian fluids (**Figure 12d**). The distance between the particles can be tuned by adjusting the balance between the magnetic dipolar forces and the electrostatic repulsive forces. At high chain concentration, the system become thermodynamically unstable and the chains aggregate into zig-zag multichains, 2D labyrinth structures or even 3D structures to minimize the repulsive potentials.

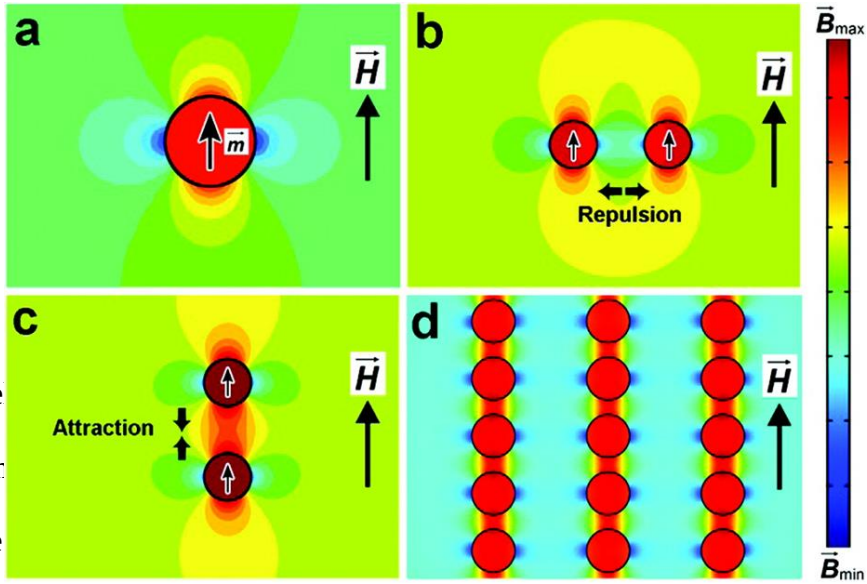


Figure 12. (a) Magnetic fie
a dipole moment in the sar
attractive (c) dipole–dipole
particle chains along the magnetic field (d). The color bar on the right shows the relative strength of the local magnetic field. Reproduced with permission.[73] Copyright 2012, American Chemical Society.

In similar conditions, particles with a single magnetic patch align also to minimize the magnetic energy, but into staggered chains[33,43,47,50,51,55,62] or double chains[33,38] with magnetic poles facing each other. These specific structures result from the steric hindrance promoted by the nonmagnetic counterpart of the particles. The magnetic flux density or

strength of the applied fields vary from 3 to 200 mT and their direction is usually perpendicular to the observation direction.

A first example was reported by Ge *et al.* who observed the chain staggering effect as soon as the magnetic core of core-shell sub-microparticles is slightly off-centered.[47] Zerrouki *et al.* observed also staggered chains of silica microspheres bearing a protruding patch made of a colloidal magnetic supraparticle (**Figure 13A**)[50]. Smoukov *et al.* reported that when the thickness of the evaporated iron ferromagnetic patch on 4-µm polystyrene spheres was decreased from 34 to 8 nm, the assemblies upon the application of a magnetic field of ~150 mT is no longer staggered chains but double chains, *i.e.* two single chains of particles with metal parts facing the same way.[33] It is consistent with the fact that the thinner the patch, the more shifted away the lateral dipole and therefore the more close packed the staggered chain. Nevertheless, the authors observed also staggered chains with the thinnest patches, but at the expense of higher applied fields. They showed also that the staggered chains are strong and rigid enough to withstand drag forces and, in particular, to remain intact in rotating magnetic fields up to 60 rpm. When two chains came close enough, they connected to form a single long chain continuing to rotate around its new mass center. Lastly, the chains remain assembled even after the removal of the magnetic field, due to the remnant magnetization in the metal patches. Nevertheless, they spontaneously disassemble after demagnetization with an AC coil. Ren *et al.* observed also staggered or double chains with evaporated iron oxide patch on 2.4-µm polystyrene spheres as a function of the oxidation number of iron atoms which was controlled by varying the deposition rate of iron in a Ar/O_2 atmosphere during the physical vapor deposition process (**Figure 13B**).[38] Quite fragile staggered chains were observed for nonstoichiometric $Fe_{1-x}O$ patch obtained at high rate, while double chains were observed with magnetite patches obtained at lower rate. This is consistent with the weak ferromagnetism of $Fe_{1-x}O$ when produced in thin films (<300 nm) and the ferrimagnetism of magnetite. These two previous studies correspond to systems whose magnetic dipole moment

is off-centered and align alongside the patch surface, *i.e.* the so-called laterally shifted dipole configuration. Lastly, Sacanna *et al.* observed similar structures and their ability to achieve layered packings at high volume fractions of the microparticles equipped with a cube-shaped hematite patch (**Figure 13C**).[40] Linse *et al*. confirmed these observations using Monte Carlo simulations.[70]

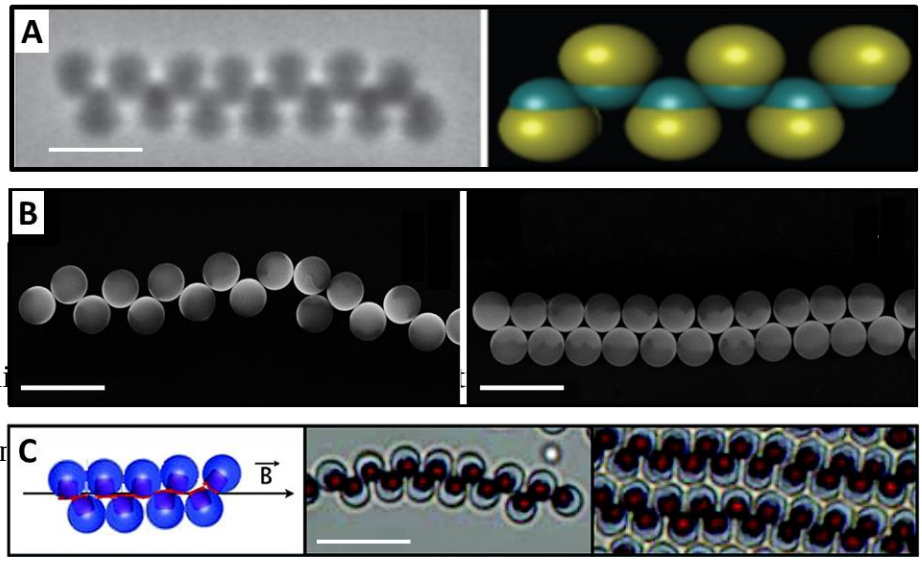


Figure 13. Linear assembli

(A) Optical microscopy i

under a 10-mT magnetic

Nature. (B) High-resolution SEM images of particle assemblies obtained after complete drying of the solution under continuous exposure to a 80-mT magnetic field: staggered chain structure (left) and double chain structure (right). The lighter area on the particles is the iron oxide patch. Adapted with permission.[38] Copyright 2012, American Chemical Society. (C) Scheme and optical microscopy images of more or less close-packed staggered chains obtained in a 3-mT magnetic field leading to layered packings at high particle volume fraction. Reproduced with permission.[40] Copyright 2012, American Chemical Society. All scale bars: 5 µm.

More unexpectedly, Fejer and coll. have simulated the possibility of organizing one-patch particles with dumbbell-like morphology in helical superstructures.[66] For this purpose, they designed dumbbells with a off-centered magnetic dipole pointing perpendicularly to the main

particle axis, and combined screened electrostatic as well as magnetic dipolar interactions. The pitch of the helix was tuned around 30 % by modulating the Debye screening length over an experimentally accessible range.

4.2.2 Application of Time-dependent Magnetic Fields

Rotating or precessing fields are also used to manipulate magnetic colloids and give rise to self-assembled structures of unusual symmetry. They are generated conveniently by orthogonal arrangement of solenoids in a bi- or triaxial way, respectively.[9] They allow greater freedom in selecting magnetic structures thanks to extra parameters such as frequency and relative strength between the field intensity in various directions.

In-plane rotating magnetic fields are obtained by two orthogonal pairs of solenoids and applying sinusoidal currents with the same frequency but 90 degrees phase lag. By superimposing a *z*-directional magnetic field on a *x*-*y* rotating field, the as-created triaxial magnetic field precesses on a cone with an angle θ with respect to the *z*-axis.

The assembly of microparticles with magnetic patch was first reported in precessing fields by Granick and coll..[74] They studied the collective behavior of 3-μm silica particles with a surface magnetic patch made of nickel (~20 nm in thickness). While isotropic magnetic particles in such conditions experience chaining, branching and expansion into 2D membranes and even 3D structures at high concentration,[9] one-patch particles behave like magnetic discs endorsing the particles a crucial phase freedom. Thus, individual particles exhibit rotation around the precessing axis and oscillation perpendicular to the rotating plane. The rotation and oscillation frequencies can be controlled by tuning the precession angle θ of the applied magnetic field or its frequency. By synchronizing their motion, they self-assemble into unconventional achiral microtubes that can be described as staggered stacks of regular colloidal triangles, squares or pentagons where the magnetic patches face inward (**Figure 14 *Right***). This offers a new method of controlling colloidal structures using dynamic

synchronization rather than static energy minimization. By using 100-µm hydrogel particles whose one hemisphere is filled with superparamagnetic magnetite nanoparticles in similar precessing fields, Onoe and coll. observed staggered chains, double chains and 2D close-packed clusters that transit to each other by tuning the θ angle.[63]

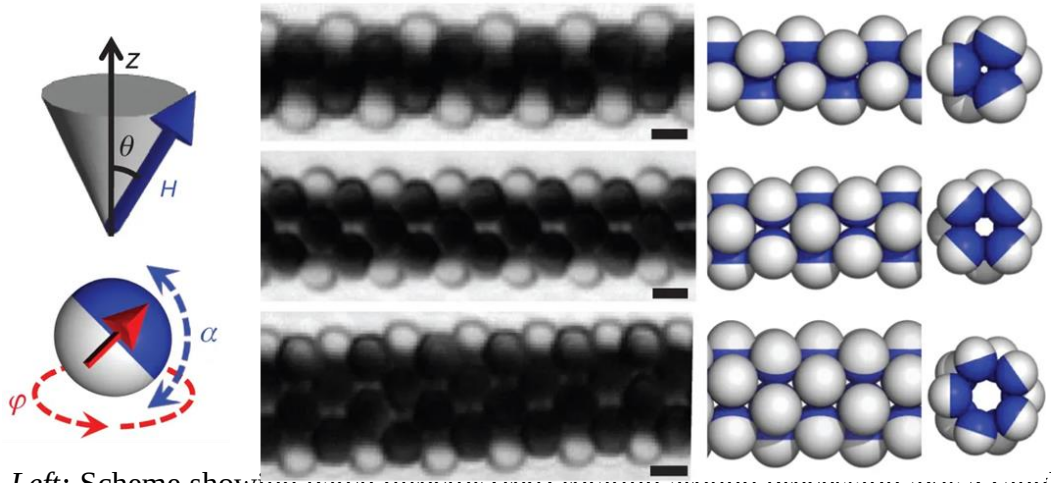


Figure 14. *Left:* Scheme showing patch director (red) rotating around precession axis z (angle φ) while oscillating perpendicularly (angle α), in a precessing field H with precession angle θ. *Right:* Optical microscopy images and corresponding models of the microtubes formed parallel to the precession axis. Scale bars: 3 µm. Adapted with permission.[74] Copyright 2012, Springer Nature.

More recently, Granick and coll. used rotating fields.[75,76] Until then, it was known that in concentrated dispersions of isotropic magnetic particles, the magnetic dipolar interaction remains anisotropic at low frequency leading to linear chains that rotate synchronously. At higher frequency, the viscous torque is stronger slowing down the chain rotation and breaking up them into shorter ones. Above a critical frequency, the rotation stops and the time-averaged dipolar interaction between particles becomes isotropic and attractive within the rotation plane. For instance, using commercial superparamagnetic polystyrene microparticles, Biswal and coll. observed various 2D thermodynamic assemblies transiting with the field

strength variation.[77] With silica microparticles bearing a nickel-based magnetic patch in rotating fields (20 Hz ; 2 mT), Granick and coll. observed hexagonally ordered crystal in which the particles rotate synchronously with the external field, as previously predicted by Brownian dynamics simulation.[78] They observed also the rotation of the whole crystal with a lower angular velocity (a few Hz) thanks to the unbalanced hydrodynamic shear force exerted by the spinning particles placed at the crystal boundary.[76] In specific patch thickness conditions, original bilayer crystals with a square symmetry were also observed.[75] Interestingly, for larger field strength, *e.g.* 30 mT, when the response regime becomes nonlinear, particles form dimers sharing their patch and lead to a plethora of new structures induced by shape anisotropy.

5. Perspectives

5.1 Towards Multipatchy Particles

The literature presented above shows that all studies have been focused on particles having a single magnetic patch. The researchers apparently overlooked the option of particles carrying multiple patches. The difficulty of manufacturing such objects is not the only problem, since to our knowledge the simulators have not published such studies either, while studies of particle assembly having several nonmagnetic patches abound.[21]

However, two studies mention the possibility of making particles with two magnetic patches. The microfluidic route using double emulsion templates reported by Abate and coll. allowed encapsulating not only one but also two droplets of magnetic particles in hydrogel microparticles by increasing the inner flow (**Figure 15** ***Top***).[60] Sacanna *et al.* have actually observed two-patch particles as by-products when manufacturing organosilica microparticles carrying one hematite cube. They even verified that they have the same assembly ability as the one-patch particles (**Figure 15** ***Bottom***). In both cases, the relative position of the two patches was not finely tuned and there is therefore a need to find robust and tunable synthesis

routes for custom manufacturing of large quantities of particles having 2, 3, 4, *etc.* magnetic patches, if possible positioned according to predefined geometric figures. The synthesis of multipatch particles was recently reviewed[21] and probably some of the reported routes could be applied to generate magnetic patches. Nevertheless, a probably promising way could also consist in taking advantage of the synthesis expertise acquired with the particles with one magnetic patch to assemble them together by their nonmagnetic components. It should preferentially concern polymer-based particles, drawing inspiration from the following works, even if these have concerned nonmagnetic colloids up to now. These works indeed allowed obtaining well-defined clusters with quite well controlled aggregation numbers. This is of particular interest for controlling the number and position of the patches. For instance, Bon and coll. prepared micron-sized asymmetric dumbbells made of a polystyrene sphere and a poly(n-butylacrylate) lobe and showed their ability to form well defined clusters when dispersed in aqueous media.[79] The assembly process is induced by the desorption of the poly(vinylpyrrolidone) stabilizer from the particles and the merging of the soft poly(n-butylacrylate) lobes upon contact through collision. More recently, Xu and coll. exploited the drying of Pickering-like water droplets made from 200 mm hydrophilic poly(ethylene glycol) diacrylate sphere with 160 mm ethoxylated trimethylolpropane tri-acrylate lobe prepared by a microfluidic technology.[80] They obtained quite regular submillimeter-sized clusters with aggregation number up to eight. Lastly, Duguet and coll. reported that dumbbell-shaped silica/polystyrene nanoparticles can be assembled in regular clusters in mixtures of good/bad solvents for polystyrene.[81] These three strategies could be adapted for clustering one-patch magnetic particles and therefore lead to colloids with multiple magnetic patches. This adaptation could consist in pre-encapsulating the magnetic component in the polymer particle for the two first strategies or in the silica particle for the last one. While there are great similarities in the behavior of colloids under magnetic fields and under electric fields, it

should nevertheless be noted that in the latter case, there is at least one example of assembling particles with two, three and four patches.[82]

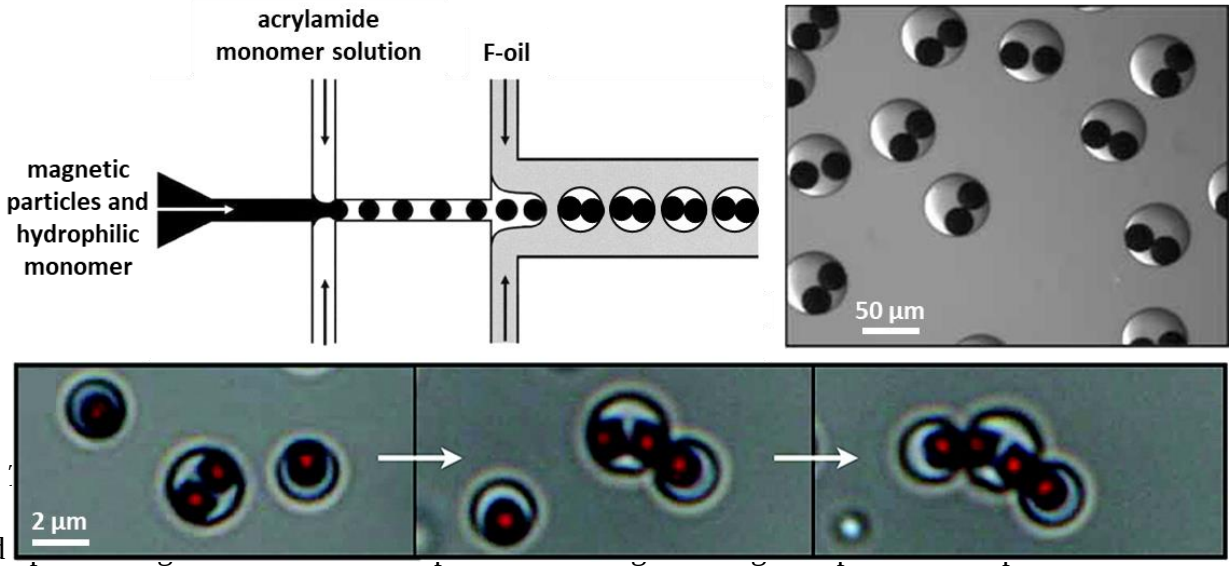


Figure 15. [illegible] droplets and [illegible] with permission. [60] Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. *Bottom:* Optical images showing the self-assembly of two one-patch microparticles and one two-patch microparticle where the magnetic patch is a hematite cube. Reproduced with permission.[40] Copyright 2012, American Chemical Society.

5.2 Towards Sustainable Assemblies

Unlike the assemblies made under electric fields that dissociate quickly as soon as the field is removed, the assemblies obtained under magnetic field can in certain cases remain stable over time due to the remnant magnetization of the patches.[7] This is obviously true for ferro- and ferrimagnetic patches depending on the nature of the compound as well as the size/thickness of the patch. In order to dissociate the assembly and for example to develop reconfigurable systems, it is then necessary to use antagonistic forces which can be electrostatic repulsions by reducing the ionic force of the liquid medium[40] or apply an alternating magnetic field oriented perpendicularly.[33] In the case of superparamagnetic patches which spontaneously

lose their magnetization as soon as the magnetic field ceases, it is possible in the meantime to develop physico-chemical consolidation strategies, such as that developed by Bharti *et al.* using capillary interactions.[83] Specifically adsorbed on the maghemite patch deposited on 4-µm polystyrene spheres, fatty acid salts form lipid shells that bind the particles together as soon as the magnetic field pulls them into contact. This bonding is also flexible and sensitive to the phase transition temperature of the lipid layer allowing reconfiguration of the colloidal assemblies.

6. Conclusion

In this literature review, we have highlighted the potential of magnetic dipolar interactions to drive the assembly of colloids through their magnetic patch. We intentionally focused on globally spherical colloids whose surface or volume just below the surface includes one or more magnetic components. We have shown that the examples in the literature mainly relate to one-patch particles. There are indeed very many access routes to these particles on a wide range of scales from a few hundreds of nm to a few millimeters. The physical deposition of magnetic material on colloidal monolayers is quite simple but its yield is intrinsically low. Nevertheless, there exist several other routes for large-scale synthesis. The microfluidic route makes it possible to prepare micrometric particles with excellent reproducibility thus ensuring the morphological purity of the batches obtained and it is possible to increase greatly the quantities produced by parallelizing the chips. The seed-growth synthetic routes using solutions or emulsions remain the most productive and the purity of the batches is generally good.

When the patch has a remnant magnetization, the assembly is spontaneous on the possible condition of partial screening of the electrostatic repulsion forces. The structures obtained depend on the mode and extent of decentering of the magnetic moment and results from the competition between magnetic interactions and geometric constraints. By using external

magnetic fields, it is possible to force the assembly out of equilibrium and thus to diversify the assemblies obtained. Manipulation by a magnetic field has the advantage over the electric field of being insensitive to the chemical nature of the other components of the system, *e.g.* carrier liquid, nonmagnetic components of the colloid, *etc.* Work is probably still lacking to establish an effective correlation between the decentering extent and the orientation of the magnetic dipole within the patches, and the diversity of the structures accessible by assembly.

The assembly of particles with a magnetic patch is still in its infancy, especially if we compare to the other assembly routes that have already seized the potential of the co-existence of several patches.[21] This is very probably one of the most exciting perspectives, which requires both the development of robust synthetic routes and simulation studies to determine in advance the most probable structures as well as the experimental conditions to reach them. Indeed, the coexistence of several superparamagnetic patches on the same particle is entirely possible, including with the objective of controlling their position. On the other hand, it will undoubtedly be more challenging for patches having a remnant magnetization, such as the hematite cubes, for which it will be a question of finding the means of disadvantaging the intracolloid magnetic couplings for the benefit of intercolloid ones. This problem will become all the more acute as the size of the targeted building blocks will be smaller. In fact, most of the assembly studies reported so far relate to micron-sized patchy colloids, which are more readily observable by optical microscopy. The challenges related to downsizing will therefore mainly concern the relative range of the different interaction forces, but also the observation, which will require heavy and expensive techniques such as transmission electron microscopy in liquid cells.

It is thanks to these new developments that the enabling technology of colloidal assembly through magnetic patches will become both mature and versatile enough to consider applications.

Acknowledgements

Mikel Azour is acknowledged for some of the scheme drawings.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References

[1] M.A. Boles, M. Engel, D. V. Talapin, *Chem. Rev.* **2016**, *116*, 11220.

[2] N. Wu, D. Lee, A. Striolo, Anisotropic Particle Assemblies, Elsevier, Amsterdam, The Netherlands **2018**.

[3] Z. Zhang, S.C. Glotzer, *Nano Lett.* **2004**, *4*, 1407.

[4] P. Tierno, *Phys. Chem. Chem. Phys.* **2014**, *16*, 23515.

[5] B.M. Teo, D.J. Young, X.J. Loh, *Part. Part. Syst. Charact.* **2016**, *33*, 709.

[6] L. Rossi, in Self-Assembly of Nano- and Micro-structured Materials using Colloidal Engineering (Eds: D. Chakrabarti, S. Sacanna), Frontiers of Nanoscience Series, Vol. 13 (Eds: R.E. Palmer, R. L. Johnston), Elsevier Ltd., 2019: Ch. 1.

[7] A. Walther, A.H.E. Müller, *Chem. Rev.* **2013**, *113*, 5194.

[8] J. Zhang, B.A. Grzybowski, S. Granick, *Langmuir* **2017**, *33*, 6964.

[9] F. Ma, X. Yang, N. Wu, in Anisotropic Particle Assemblies: Synthesis, Assembly, Modeling, and Applications (Eds: N. Wu, D. Lee, A. Striolo), Elsevier, 2018, Ch. 5.

[10] M. Guix, S.M. Weiz, O.G. Schmidt, M. Medina-Sánchez, *Part. Part. Syst. Charact.* **2018**, *35*, 1700382.

[11] T. Arita, M. Kanahara, K. Motoyoshi, K. Koike, T. Higuchi, H. Yabu, *J. Mater. Chem. C* **2013**, *1*, 207.

[12] F. Wang, G.M. Pauletti, J. Wang, J. Zhang, R.C. Ewing, Y. Wang, D. Shi, *Adv. Mater.* **2013**, *25*, 3485.

[13] E. Passas-Lagos, F. Schüth, *Langmuir* **2015**, *31*, 7749.

[14] M. Xia, K.H. Kim, J. Lee, E.M. Go, B. Park, T. Yu, S.K. Kwak, H. Bin Na, B.J. Park, *Chem. Eng. J.* **2018**, *339*, 125.

[15] D. Pan, F. Mou, X. Li, Z. Deng, J. Sun, L. Xu, J. Guan, *J. Mater. Chem. A* **2016**, *4*, 11768.

[16] Zhang, A.S. Keys, T. Chen, S.C. Glotzer, *Langmuir* **2005**, *21*, 11547.

[17] G. van Anders, D. Klotsa, A.S. Karas, P.M. Dodd, S.C. Glotzer, *ACS Nano* **2015**, *9*, 9542.

[18] D. Rodríguez-Fernández, L.M. Liz-Marzán, *Part. Part. Syst. Charact.* **2013**, *30*, 46.

[19] G.-R. Yi, D.J. Pine, S. Sacanna, *J. Phys. Condens. Matter*. **2013**, *25*, 193101.

[20] S. Ravaine, E. Duguet, *Curr. Opin. Colloid Interface Sci.* **2017**, *30*, 45.

[21] W. Li, H. Palis, R. Mérindol, J. Majimel, S. Ravaine, E. Duguet, *Chem. Soc. Rev.* **2020**, *49*, 1955.

[22] K.M. Ho, C.T. Chan, C.M. Soukoulis, *Phys. Rev. Lett.* **1990**, *65*, 3152.

[23] P.-G. de Gennes, *Angew. Chemie Int. Ed. English* **1992**, *31*, 842.

[24] S. Wintzheimer, T. Granath, M. Oppmann, T. Kister, T. Thai, T. Kraus, N. Vogel, K. Mandel, *ACS Nano* **2018**, *12*, 5093.

[25] S.Q. Choi, S.G. Jang, A.J. Pascall, M.D. Dimitriou, T. Kang, C.J. Hawker, T.M. Squires, *Adv. Mater.* **2011**, *23*, 2348.

[26] K. Han, C.W. Shields, N.M. Diwakar, B. Bharti, G.P. López, O.D. Velev, *Sci. Adv.* **2017**, *3*, 1.

[27] C. Wyatt Shields Iv, S. Zhu, Y. Yang, B. Bharti, J. Liu, B.B. Yellen, O.D. Velev, G.P. López, *Soft Matter* **2013**, *9*, 9219.

[28] J. Yan, K. Chaudhary, S. Chul Bae, J.A. Lewis, S. Granick, *Nat. Commun.* **2013**, *4*, 1516.

[29] R.M. Erb, H.S. Son, B. Samanta, V.M. Rotello, B.B. Yellen, *Nature* **2009**, *457*, 999.

[30] A. Joseph, S. Mathew, *Chempluschem* **2014**, *79*, 1382.

[31] H. Kim, J. Cho, J. Cho, B.J. Park, J.W. Kim, *ACS Appl. Mater. Interfaces* **2018**, *10*, 1408.

[32] C. Tang, C. Zhang, J. Liu, X. Qu, J. Li, Z. Yang, *Macromolecules* **2010**, *43*, 5114.

[33] S.K. Smoukov, S. Gangwal, M. Marquez, O.D. Velev, *Soft Matter* **2009**, *5*, 1285.

[34] I. Sinn, P. Kinnunen, S.N. Pei, R. Clarke, B.H. McNaughton, R. Kopelman, *Appl. Phys. Lett.* **2011**, *98*, 024101.

[35] L.F. Valadares, Y.-G. Tao, N.S. Zacharia, V. Kitaev, F. Galembeck, R. Kapral, G.A. Ozin, *Small* **2010**, *6*, 565.

[36] G. Steinbach, S. Gemming, A. Erbe, *Eur. Phys. J. E* **2016**, *39*,.

[37] M. Albrecht, G. Hu, I.L. Guhr, T.C. Ulbrich, J. Boneberg, P. Leiderer, G. Schatz, *Nat. Mater.* **2005**, *4*, 203.

[38] B. Ren, A. Ruditskiy, J.H. Song, I. Kretzschmar, *Langmuir* **2012**, *28*, 1149.

[39] R.M. Erb, N.J. Jenness, R.L. Clark, B.B. Yellen, *Adv. Mater.* **2009**, *21*, 4825.

[40] S. Sacanna, L. Rossi, D.J. Pine, *J. Am. Chem. Soc.* **2012**, *134*, 6112.

[41] T. Sugimoto, M.M. Khan, A. Muramatsu, H. Itoh, *Colloids Surfaces A Physicochem. Eng. Asp.* **1993**, *79*, 233.

[42] M. Youssef, T. Hueckel, G.-R. Yi, S. Sacanna, *Nat. Commun.* **2016**, *7*, 12216.

[43] L. Zhang, F. Zhang, W.F. Dong, J.F. Song, Q.S. Huo, H.B. Sun, *Chem. Commun.* **2011**, *47*, 1225.

[44] E. Duguet, A. Désert, A. Perro, S. Ravaine, *Chem. Soc. Rev.* **2011**, *40*, 941.

[45] M.M. Rahman, F. Montagne, H. Fessi, A. Elaissari, *Soft Matter* **2011**, *7*, 1483.

[46] S. Braconnot, M.M. Eissa, A. Elaissari, *Colloid Polym. Sci.* **2013**, *291*, 193.

[47] J. Ge, Y. Hu, T. Zhang, Y. Yin, *J. Am. Chem. Soc.* **2007**, *129*, 8974.

[48] S. Xu, W.-F. Ma, L.-J. You, J.-M. Li, J. Guo, J.J. Hu, C.-C. Wang, *Langmuir* **2012**, *28*, 3271.

[49] V.N. Manoharan, M.T. Elsesser, D.J. Pine, *Science* **2003**, *301*, 483.

[50] D. Zerrouki, J. Baudry, D. Pine, P. Chaikin, J. Bibette, *Nature* **2008**, *455*, 380.

[51] T. Isojima, S.K. Suh, J.B. Vander Sande, T.A. Hatton, *Langmuir* **2009**, *25*, 8292.

[52] C. Kaewsaneha, P. Tangboriboonrat, D. Polpanich, M. Eissa, A. Elaissari, *J. Colloid Interface Sci.* **2013**, *409*, 66.

[53] Y. Wang, H. Xu, Y. Ma, F. Guo, F. Wang, D. Shi, *Langmuir* **2011**, *27*, 7207.

[54] B.M. Teo, S.K. Suh, T.A. Hatton, M. Ashokkumar, F. Grieser, *Langmuir* **2011**, *27*, 30.

[55] A.K.F. Dyab, M. Ozmen, M. Ersoz, V.N. Paunov, *J. Mater. Chem.* **2009**, *19*, 3475.

[56] N. Zhao, M. Gao, *Adv. Mater.* **2009**, *21*, 184.

[57] C.A. Serra, Z. Chang, *Chem. Eng. Technol.* **2008**, *31*, 1099.

[58] D.K. Hwang, D. Dendukuri, P.S. Doyle, *Lab Chip*. **2008**, *8*, 1640.

[59] R.K. Shah, J.-W. Kim, D.A. Weitz, *Adv. Mater.* **2009**, *21*, 1949.

[60] C.-H. Chen, A.R. Abate, D. Lee, E.M. Terentjev, D.A. Weitz, *Adv. Mater.* **2009**, *21*, 3201.

[61] L. Shang, F. Shangguan, Y. Cheng, J. Lu, Z. Xie, Y. Zhao, Z. Gu, *Nanoscale* **2013**, *5*, 9553.

[62] K.P. Yuet, D.K. Hwang, R. Haghgooie, P.S. Doyle, *Langmuir* **2010**, *26*, 4281.

[63] S. Yoshida, M. Takinoue, E. Iwase, H. Onoe, *J. Appl. Phys.* **2016**, *120*, 084905.

[64] J. Hernández-Rojas, D. Chakrabarti, D.J. Wales, *Phys. Chem. Chem. Phys.* **2016**, *18*, 26579.

[65] G.I. Vega-Bellido, R.A. DeLaCruz-Araujo, I. Kretzschmar, U.M. Córdova-Figueroa, *Soft Matter* **2019**, *15*, 4078.

[66] S.N. Fejer, D. Chakrabarti, H. Kusumaatmaja, D.J. Wales, *Nanoscale* **2014**, *6*, 9448.

[67] L. Baraban, D. Makarov, M. Albrecht, N. Rivier, P. Leiderer, A. Erbe, *Phys. Rev. E* **2008**, *77*, 031407.

[68] N. Mikuszeit, L. Baraban, E.Y. Vedmedenko, A. Erbe, P. Leiderer, R. Wiesendanger, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2009**, *80*, 1.

[69] M. Klinkigt, R. Weeber, S. Kantorovich, C. Holm, *Soft Matter* **2013**, *9*, 3535.

[70] A.I. Abrikosov, S. Sacanna, A.P. Philipse, P. Linse, *Soft Matter* **2013**, *9*, 8904.

[71] V. Liljeström, C. Chen, P. Dommersnes, J.O. Fossum, A.H. Gröschel, *Curr. Opin. Colloid Interface Sci.* **2019**, *40*, 25.

[72] M. Wang, L. He, Y. Yin, *Mater. Today* **2013**, *16*, 110.

[73] L. He, M. Wang, J. Ge, Y. Yin, *Acc. Chem. Res.* **2012**, *45*, 1431.

[74] J. Yan, M. Bloom, S.C. Bae, E. Luijten, S. Granick, *Nature* **2012**, *491*, 578.

[75] J. Yan, S.C. Bae, S. Granick, *Adv. Mater.* **2015**, *27*, 874.

[76] J. Yan, S.C. Bae, S. Granick, *Soft Matter* **2015**, *11*, 147.

[77] D. Du, D. Li, M. Thakur, S.L. Biswal, *Soft Matter* **2013**, *9*, 6867.

[78] S. Jäger, S.H.L. Klapp, *Soft Matter* **2011**, *7*, 6606.

[79] T.S. Skelhon, Y. Chen, S.A.F. Bon, *Soft Matter* **2014**, *10*, 7730.

[80] X.-H. Ge, Y.-H. Geng, J. Chen, J.-H. Xu, *ChemPhysChem* **2018**, *19*, 2009.

[81] W. Li, S. Ravaine, E. Duguet, *J. Colloid Interface Sci.* **2020**, *560*, 639.

[82] P. Song, Y. Wang, Y. Wang, A.D. Hollingsworth, M. Weck, D.J. Pine, M.D. Ward, *J. Am. Chem. Soc.* **2015**, *137*, 3069.

[83] B. Bharti, D. Rutkowski, K. Han, A.U. Kumar, C.K. Hall, O.D. Velev, *J. Am. Chem. Soc.* **2016**, *138*, 14948.