



# Synthesis and assembly of patchy particles: Recent progress and future prospects



Serge Ravaine <sup>a,\*</sup>, Etienne Duguet <sup>b</sup>

<sup>a</sup> CNRS, Univ. Bordeaux, CRPP, UPR 8641, 115 avenue du Dr Albert Schweitzer, F-33600 Pessac, France

<sup>b</sup> CNRS, Univ. Bordeaux, ICMCB, UPR 9048, 87 avenue du Dr Albert Schweitzer, F-33600, Pessac, France

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## ABSTRACT

The burgeoning need to fabricate new functional materials through the assembly of colloidal building blocks has motivated an intensive research focused on patchy particles. A large variety of efficient strategies to synthesize and assemble such colloids have been investigated in the last few years. Here we attempt to give an overview of these latest developments. The major limitations of current methods as well as unresolved challenges are also discussed.

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## 1. Introduction

With the intention of indicating a few of the perspectives that actual trends in chemistry open up, Jean-Marie Lehn has recently splendidly emphasized that chemistry has a key role in the understanding and implementation of the self-organization processes which are the driving force behind the evolution towards more and more complex forms of matter [1]. Indeed, intensive research in molecular and supramolecular chemistry has been conducted for many decades with the motivation of reproducing the hierarchical assembly of biomolecular building units into living systems [2,3]. One of the most striking recent examples of molecular assembly is the one-step construction of two-dimensional (2D) and three-dimensional (3D) structures with sophisticated shapes using hundreds of DNA single strands as bricks [4]. The key feature of the developed modular-assembly method is that each brick carries a particular sequence that directs it to fit only to its predesigned position, as during the self-assembly of proteins into the form of complex icosahedral capsid shells. Inspired by these examples at the molecular level, and motivated by the burgeoning need to fabricate next-generation functional materials without human intervention, attention has increasingly focused on the encoding of the information needed for assembling target structures into micro- and nano-sized particles through the design of their interactions and interaction rules. The first key property that scientists working with colloids have to consider is specificity, since colloidal entities are usually highly symmetric and interact through nonspecific forces. The simplest way to address this lack of specificity is to work with oppositely charged particles, which attract

together thanks to electrostatic interactions while like-charged particles stay apart [5]. Another popular way is to attach molecules that recognize one another onto the particle surface, such as complementary DNA strands for instance [6–8]. The second –even more challenging– property to address is the directionality of the interactions. An efficient strategy to induce directional interactions between colloidal particles consists in dispersing them into an anisotropic medium such as liquid crystals [9]. Alternatively, the particles can be exposed to an external electric or magnetic field [10], which also allows one to tune the dynamics of the interactions between colloids [11]. It is also possible to take benefit of the large panel of anisotropic shape of particles such as cubes, ellipsoids, rods, triangles,.... that can be synthesized nowadays [12–13]. Finally, a fourth strategy relies on the regioselective modification of the surface of colloids in order to form the so-called patchy particles. A patchy particle is a surface-patterned particle with a controlled number of favored interaction areas [14]. These symmetry-breaking zones are indeed chemical or topographic discontinuities recently classified as enthalpic or entropic patches, respectively. Patchy Janus particles, named in allusion to the Roman god with two faces, are particles with two distinct surface areas, ideally of equal amounts, and can be considered as a subclass of patchy particles.

The purposes of this review are to give an overview of the advances made in the last three years in the emerging field of patchy particles from an experimental point of view and to outline perspectives for future research. Indeed, over the past three years there has been a tremendous effort to design, synthesize new patchy particles with a high purity in shape and with a smaller and smaller size, down to a few tens of nanometers [15–16]. A lot of progresses have also been made in the study of spatially selectively patching functional zones on particles and directionality of their interactions. Finally, a large number of

\* Corresponding author.

E-mail address: [ravaine@crpp-bordeaux.cnrs.fr](mailto:ravaine@crpp-bordeaux.cnrs.fr) (S. Ravaine).

works have been devoted to the assembly of patchy particles under an external stimulus, resulting in self-propelled motion and reconfigurable materials. In the following, we present the most recent progress on the synthesis of patchy colloids, followed by a section on their self-assembly and their assembly under external fields. Last, the current limitations and future potential are discussed.

## 2. Synthesis of patchy particles

A large arsenal of methods for fabricating patchy particles has been developed for the last two decades. We direct the reader to recent excellent reviews [17–22] to have a complete overview of all of them, as this paper only concerns the latest developments made in this field since 2013.

### 2.1. Heterogeneous nucleation

A very simple, one-pot and template-free approach to patchy particles is based on the heterogeneous nucleation of silver onto the bare surface of silica particles followed by surface diffusion dominated growth [23]. This method was extended to the formation of gold patches onto cationic polystyrene (PS) nanospheres using ascorbic acid to reduce the auric ion [24]. It was shown that the gold patches morphology is dependent on the ascorbic acid concentration, pH and temperature. In particular dendritic patches were obtained at high concentration of ascorbic acid, while non-dendritic ones were formed when this concentration was reduced.

### 2.2. Masking

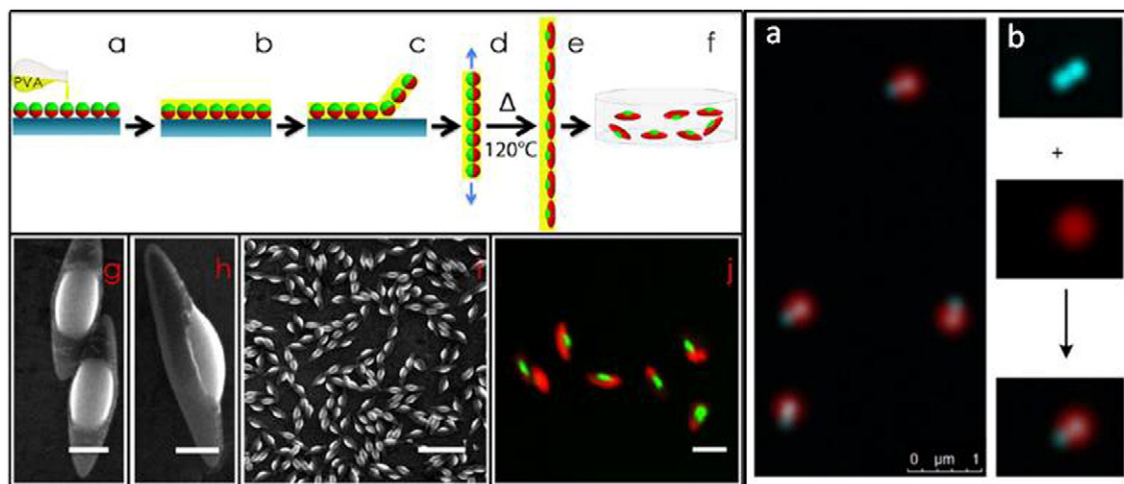
Partial protection of the particles surface by organizing them onto a flat or curved surface, along an interface, or into a crystalline lattice, followed by modification of the exposed part is another route that has been widely employed to synthesize patchy particles [25].

Motivated by their interesting assembly behavior both in the bulk [26] and under confinement [27], van Oostrum et al. have recently adapted the gel trapping technique to synthesize inverse patchy particles [28], that consist of charged, repulsive particles with polar patches with charges of the opposite sign that repel each other and that are attracted by the rest of the particles. The first step is the injection of a colloidal dispersion of silica microparticles at the surface of an agarose gel, where they form a crystalline monolayer upon evaporation of the dispersing liquid. The subsequent deposition of a controlled amount of

a PS solution and the evaporation of the solvent leads to the formation of a PS membrane around the silica particle equatorial plane. The PS thin film serves as a mask during the regioselective functionalization of the unprotected regions of the particles with a charged dye. After dissolution of the PS membrane, silica particles with a negatively charged equatorial region and fluorescently labeled cationic patches are obtained and characterized by fluorescent microscopy. Direction dependent attractions and repulsions between the positively charged poles and the negatively charged equatorial regions were indirectly observed under the microscope.

Another popular way to synthesize patchy particles involves metal deposition [29–31]. Recent works in this area have been focused on the control of patch size, shape and anisotropy. By combining elongational stretching under heating with chrome and gold deposition using an e-beam evaporator, Shah et al. have reported the synthesis of Janus spheroid patchy particles that combine both shape and interaction anisotropy [32]. They also showed that original “kayak” shaped patchy particles (Fig. 1 Left) can be obtained when the stretching process is performed after the metal deposition. This stretching method seems to be highly versatile as a variation of the elongational strain or the use of another metal deposition technique should allow one to vary the aspect ratio of patchy particles and the patch size, respectively. The Kretschmar group has pursued its use of the template-assisted glancing deposition technique for the fabrication of a large variety of patchy particles with patches of controlled anisotropic shape and chemical nature [33]. In particular, gold patches with a triangular shape, which had been envisioned by Romano and Sciortino to be an efficient way to drive the patchy particles to crystallize into a single cubic tetrastack lattice by eliminating the undesired polymorphs [34], have been obtained. The subsequent evaporation of iron has also been used to add a second patch of a different metal, which partially overlaps the first patch. The overlapping part was varied by changing the rotational angle and angle of incidence and was predicted using a computational model.

One of the main drawbacks of the strategies based on the use of a two-dimensional template is the low amount of produced particles per batch, which is a severe limitation for further applications. Alternatively, the use of 3D colloidal crystals, emulsion droplets or larger particles as scaffolds, which provide a higher amount of surface area per unit volume, allowed one to fabricate patchy particles in a higher yield. Following previous works published by them [35] and others [36], Bae et al. have regioselectively functionalized the exposed surfaces of silica spheres previously assembled into a face-centered-cubic crystal with



**Fig. 1.** Left: (a–f) Schematic of kayak particle synthesis. SEM: (g) top view, (h) side view, and (i) zoomed-out view. (j) Two-channel confocal laser scanning microscopy image. Scale bar: (g, h) 0.5  $\mu\text{m}$ , (i) 5  $\mu\text{m}$ , and (j) 3  $\mu\text{m}$ . Adapted with permission from [32]. Copyright 2013 American Chemical Society. Right: Confocal images of anisotropic particles after functionalization of the chlorinated patch with fluoresceinamine. (a): Image captured by combining two imaging channels, with one recording in reflection mode (cyan) and the other in fluorescence mode (red). (b) enlargement of the two separate imaging channels. Adapted with permission from [40]. Copyright 2013 American Chemical Society.

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