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Surface-anisotropic spherical colloids in geometric and field confinement

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ABSTRACT

The development of novel approaches to assemble colloids into hierarchical structures, in which every colloidal particle is taking a predetermined position, is at the core of modern applied colloids technology. Current assembly techniques for isotropic spherical colloids often include the application of either templates such as patterned surfaces and geometrical confinement or external forces such as electric and/or magnetic fields. More recently, researchers have begun to modify the surfaces of colloids in such a way that their natural assembly process is changed giving access to new colloids-based materials and applications. In this review, the fabrication methods for these surface-modified colloids, i.e., Janus and patchy colloids, are briefly introduced followed by a review of work from the past five years dealing with the assembly of such surface-anisotropic spherical colloids under geometric and field confinement. The observed differences in the assembly of plain and modified colloids are highlighted and the review concludes in a discussion of potential applications of these colloids and the resulting materials.

1. Introduction

The study of colloidal interactions has been of great interest to many researchers owing to the ability of colloids to mimic most phases of condensed matter [1]. The thermodynamic assembly of surface-isotropic spherical colloids is largely understood experimentally and theoretically and researchers of the colloidal domain have moved on to the study of dynamic colloidal systems.

More recently, researchers have begun to address the need to engineer the interactions between colloids by modifying the surface of colloids with patches of varying interaction strength. These patches can cause attractive and repulsive interactions between colloids during assembly or allow the direction of colloids by external fields leading to assembly behavior in confined geometries and external fields different from that of surface-isotropic colloids. The interesting aspect of these patchy colloids is that they combine both external (addressability) and internal (patch–patch interaction) control of assembly interactions. A thorough review by Grzelczak et al. [2] on directed self-assembly of nanoparticles ranging from particles with stimuli responsive interactions, morphological, and functional features to particles with specific physical properties susceptible to field interactions is recommended for introductory reading.

In the following, preparation methods for Janus and patchy colloids from the past 5 years are introduced followed by a brief summary of the current knowledge regarding the assembly behavior of surface-isotropic colloids in confined geometries, on patterned surfaces, and in external fields. The short section on isotropic spherical colloids is followed by a review of the literature with respect to the assembly of surface-anisotropic spherical colloids in confined geometries and external fields. Next, the perceived similarities and differences between surface-isotropic and anisotropic spherical colloids with respect to their assembly behavior in confined geometries and external fields are summarized. Last but not least, a range of proposed and realized applications of Janus and patchy colloids is given to alert researchers in this field to the potential of surface-anisotropic spherical colloids. Note, we have excluded from our review the vast amount of literature available on self-assembly [2] (i.e., assembly in the absence of fields and geometric confinement) of plain, Janus, and patchy colloids as well as fabrication and assembly of non-spherical surface-anisotropic particles [3].

2. Preparation of surface-anisotropic spherical colloids

A surface-anisotropic spherical colloid is a spherical particle that has non-uniform, but well-defined surface properties, often also referred to as a patchy particle [4]. Janus colloids are a special class of surface-anisotropic spherical colloids with two well-defined regions of equal size. There are five distinct routes to the preparation of surface-anisotropic spherical particles; (i) shadowing, (ii) templating, (iii) field induction, (iv) phase separation, and (v) nucleation. In the following, Janus and patchy particle fabrication methods from the past 5 years are briefly introduced. The interested reader is directed to two

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recent reviews focused on Janus [5] and patchy particle synthesis [4] for more details.

2.1. Shadowing

The shadowing approach involves physical vapor deposition (PVD) during which part of the particle is shadowed from a directional flow of material by itself or other particles. The simplest approach to prepare a Janus particle is by PVD onto a monolayer of particles [6–8]. The Kretzschmar group has expanded the use of PVD to the glancing angle deposition (GLAD) technique for the preparation of patchy particles with (i) one patch ranging in size from 50% to 3.7% of the particle surface [9], (ii) with two overlapping patches creating a new patch as small as 1.7% of the particle surface, or two patches on opposite poles ranging from 25% to 3.7% of the particle surface [10]. Zhang et al. [11] used a combination of etching and PVD to decorate micronspheres in the 3rd layer of colloidal crystals of varying stacking order with gold patches yielding bi-, tri-, tetra-, and penta-patch particles. The fabrication of bimetallic Janus particles has been attempted using a two-step PVD approach involving an inversion of the particle layer, but dewetting around the particle equator leads to an exposed "belt" area [12]. Bimetallic patchy particles with overlapping patches covering more than 50% of the particle surface have been produced by application of PVD to a monolayer of convectively assembled Janus particles [13]. Another approach to patchy particles with a patch smaller than 50% is via line-of-sight PVD followed by time-dependent etching of the metal cap.

2.2. Templating

Generation of surface-anisotropic spherical colloids via the templating route requires partial templating of the colloid surface followed by exposure of the uncoated part to chemical or physical modification. Templates used for patchy and Janus particle fabrication range from polymers such as polydimethylsiloxane (PDMS) [14] and photoresist [15] into which a particle monolayer is pressed to particle monolayers spin-coated with polymethylmetacrylate (PMMA) followed by chemical etching [16]. Researchers have also reported about particle monolayers deposited onto a polymer film which are then sunk into the polymer film through heat treatment [17] and pressure application [18] as well as the use of surfaces as templates [19,20] and transfer agents [21]. The most promising route to large-scale synthesis of Janus colloids has been developed by Hong and Granick [22] and involves the embedding of particles in the surface of solidified emulsion droplets.

2.3. Field-induced patchiness

In contrast to surface modification of spherical colloids, surface-anisotropic spherical colloids can also be obtained using liquid, photocurable mixtures of two components of which one can be addressed by a magnetic field thereby causing the localization of the magnetic component in patches upon photopolymerization of spherical droplets. Velev's [23] and Paunov's groups [24] have pioneered this technique and achieved both Janus particles and mono-, bi-, and tri-patch particles.

2.4. Phase separation

A high-yield approach to Janus and patchy particles is based on phase separation using immiscible fluids in a microfluidic set up as demonstrated, for example, by Weitz [25–27] and Doyle [28] and recently reviewed by Walther et al. [29] for Janus-type particles and more generally by Doyle [30]. In addition, microfluidic emulsification immediately followed by surfactant stabilization and photocuring has been used to prepare electrically addressable bi-color Janus particles [31]. Electrojetting of immiscible fluids [32], salt-induced domain formation in polymer droplets [33,34] and drying-induced phase separation [35] are other approaches making use of phase separation and leading to particles with a patchy surface. While the microfluidic, electrojetting, and drying-induced phase separation approaches yield uniform spherical Janus and patchy particles, the salt-induced domain formation results in particles with random patchiness.

2.5. Heterogeneous nucleation

More recently, an approach that may lead to the large-scale synthesis of patchy particles has been reported by Taylor et al. [36]. They show that pretreatment of submicron silica spheres with a mixture of alkanoamine and silver nitrate can lead to a high patch yield. They present a phase diagram showing that a low monoethanolamine-to-silver ratio (~6) results in a larger number of particles with three patches, whereas a higher ratio (~42) results mainly in particles with two patches.

Despite ongoing efforts of researchers around the world, a facile method that would enable the production of large quantities of patchy colloids is still at large. The lack of such a method is what is currently hampering the extended study of Janus and patchy colloid assembly.

3. Assembly of surface-isotropic spheres—plain colloids

Surface-isotropic colloids left to their own devices assemble into face-centered cubic (FCC), hexagonal close-packed (HCP), and random-stacked crystals [37]. If the assembly process is directed by patterned surfaces, geometric confinement, or external fields, other colloidal assemblies may result. These colloidal assemblies are of importance in photonics [38], microchip high performance liquid chromatography (HPLC) [39], and fabrication of porous materials [40]. In the following, the current state-of-the-art in the assembly of spherical isotropic colloids in confined geometries, on patterned surfaces, and in external fields is summarized briefly. A recent review article focused on the self-assembly of nanoparticles can be found in reference [41].

3.1. Template-directed colloidal assembly

A comprehensive review of template-directed colloidal assembly before the year 2004 can be found in the article written by Wang and Möhwald [37]. In the following, we will discuss assembly methods for isotropic colloids in confined geometries and on patterned surfaces developed since 2004 to illustrate the general behavior of isotropic spherical colloids.

3.1.1. Colloidal assembly in confined geometries

Xia's group has pushed the development of template-assisted self-assembly (TASA) for colloids ranging in size from several microns to a few nanometers [42]. The experimental set up for TASA is shown schematically in Fig. 1A. A fluidic cell with a lithographically patterned bottom surface is tilted at an angle and filled with a colloidal solution (1–2 wt.%). As the liquid dewets across the cell during TASA, three forces act on the particles; gravitational (F_g), electrostatic (F_e), and capillary forces (F_c). The capillary force dominates the assembly process if the particle density is chosen similar to that of the assembling liquid and the electrostatic forces are reduced by chemical modification of the particle surface. The assembly process is further directed by tuning the ratio of particle diameter to template hole. Fig. 1B and C shows an example for a 2.22 ratio and other ratios and the type of clusters produced, respectively. TASA has been used to generate polygonal and polyhedral clusters; linear, zigzag, or helical chains; and circular rings and hybrid aggregates with HF and H_2O structures that consisted of colloids with varying composition. One limitation of TASA is the achievable line width