Colloidal Rings by Site-Selective Growth on Patchy Colloidal Disc Templates

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Abstract: Anisotropic colloidal building blocks are quite attractive as they enable the self-assembly towards new materials with designated hierarchical structures. Although many advances have been achieved in colloidal synthetic methodology, synthesis of colloidal rings with low polydispersity and on a large scale remains a challenge. To address this issue we introduce a new site-selective growth strategy, which relies on using patchy particles. For example, by using patchy discs as templates, silica can selectively be grown on only side surfaces, resulting in formation of silica rings. We demonstrate that shape parameters are tunable and find that these silica rings can be used as secondary template to synthesize other types of rings. This method for synthesizing ring-like colloids provides possibilities for studying their self-assembly and associated phase transitions, and this patchy particles template strategy paves a new route for fabricating other new colloidal particles.

Self-assembly towards new materials with desirable structures requires building blocks of colloidal particles more with anisotropic shapes. Shape is an important parameter for tuning colloidal interactions and for controlling self-assembly. Typical examples are rods and platelets that form liquid crystalline phases or plastic crystals that are in sharp contrast to their spherical counterparts. In past years, advances in synthetic methodologies have resulted in an emerging family of anisotropic colloidal building blocks, such as dumbbells, rods, ellipsoids, cubes, triangles, discs, bowls, rings etc. Among these, ring-like colloids are of particularly interest because they have a ring cavity, which gives them either in single or collective states new electromagnetic or optical properties. It is also reported by recent computer simulations that ring-like colloids can form highly open liquid crystalline smectic phases which are unique compared to smectic phases of more conventional particles. Experimental studies of ring-like colloidal self-assembly are rare because of a paucity of suitable model systems. However, several methods to synthesize ring-like colloids have been reported, including lithography, controlled wetting, protective etching, and hydrothermal processing.

Template synthesis is an effective strategy to prepare certain colloids with special structural properties. Syntheses of many kinds of hollow spheres are good examples. Resulting spherical structures duplicate the respective template surfaces. Patchy particles usually exhibit two or more kinds of surface chemistries. In principle, it is possible to control templating chemistry so that only specific types of patches are templated, resulting in new structures inaccessible by other imprinting methods.

Herein, we present a synthesis of colloidal rings by employing patchy colloidal particles as templates via an effective site-selective growth strategy. To illustrate this concept, patchy colloidal discs were used. As shown in Scheme 1, our template discs exhibit two types of surfaces, where the top- and bottom-surfaces have the same chemical composition, but different from the outer side surface. If a coating reaction is controlled to only coat the side surface, subsequent removal of the template, if done without damaging the side coating, yields colloidal rings. Some specific interactions can be employed to facilitate this site-selective coating. Our method shows good control of diameter \((D)\), aspect ratio (length/diameter, \(L/D\)), and polydispersity, and it can be used for preparation on a large scale. Furthermore, we illustrate that the obtained colloidal rings have a Janus character, where the inner and the outer surfaces exhibit different surface energies, and hence, different wettabilities.

In a typical experiment, polystyrene (PS) microspheres with a diameter of 1.73 µm (measured by TEM, polydispersity 1.3 %: the mean value divided by standard deviation) were synthesized and the stabilizer is polyvinylpyrrolidone (PVP). To deformathe PS microspheres to discs, a phase-separation technique was employed following Fujibayashi and Okubo. Briefly, PS microspheres were swelled by decane in a mixed solvent of methanol/water, accompanied by polymerization of the author(s) of this article can be found under: https://doi.org/10.1002/anie.201704541. [8] Y. Wu, Z. Luo, Prof. Dr. B. Liu, Prof. Dr. Z. Yang
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2-ethylhexyl methacrylate (EHMA). Poly(EHMA) is not soluble in this mixed solvent so it stays on the surface of PS. When phase separation takes place spherical PS was extruded into disc shapes inside the decane droplets due to a competition of interfacial tensions. Interestingly, we found that these PS discs have patchy surfaces, and conjectured that the original stabilizer PVP remained on the side surface while the top- and bottom-surfaces were covered by poly(EHMA). The existence of poly(EHMA) was confirmed by Fourier transform infrared spectroscopy (FTIR) characterization and atomic force microscopy (AFM) (see Figures S1 and S2 in the Supporting Information). Though extensive washing was done, FTIR spectra indicated residual poly(EHMA) remained on the top- and bottom-surfaces. To further verify if the poly(EHMA) was on the top- and bottom-surfaces, we did adhesion force scanning by AFM. The adhesion diagrams indicated two phases, which correspond to PS and poly(EHMA) (Figure S2).

We tested the selectivity of our PS discs by adsorbing Stöber silica nanoparticles (NPs). Silica is known to be able to form hydrogen bonds with PVP between silica surface hydroxyl groups and PVP carbonyl groups. It was hypothesized that silica NPs can adsorb onto only the sides of PS discs. Neither PS nor poly(EHMA) is a good host for attachment of silica NPs. Selectivity was clearly confirmed by adsorption experiments. As shown in Figures 1a and b, no matter how concentrated a silica NP suspension was used, we saw essentially no attachment to the top- and bottom-surfaces. Such selectivity was also examined for adsorption of citrate-stabilized gold NPs due to the replacement of citrate ion by PVP (Figures 1c and S3). Similar selectivity was found for laponite clay sheets, which can be modified only on their edges.[10]

We further tested selectivity by dispersing our patchy PS discs into a Stöber reaction system that contained ethanol, water, ammonia and tetraethyl orthosilicate (TEOS). In this system we tried coating PS disc with SiO₂. Indeed the coating reaction was found to take place predominantly on the sides of PS discs. By observing these samples with the time, growing silica layers became more and more obvious, as indicated by arrows in Figures 1d–f. It was noticeable that such site-selectivity was found not only for PS discs, but also for other patchy PS particles prepared by a similar synthetic route (Figure S4).

In the following we describe results where we synthesized D and L/D variations for our colloidal SiO₂ rings. Three different routes were adopted. Our first route used PS discs with given values of D and L as templates, which were obtained from PS microspheres of various diameters. The diameter of a PS microsphere determines a disc resulting D and L/D value. As an illustration, three kinds of PS microspheres were synthesized, and their diameters were 0.84 ± 0.02 μm, 1.10 ± 0.05 μm and 1.73 ± 0.05 μm, respectively. The diameters of the resulting PS discs were 1.23 ± 0.06 μm, 1.5 ± 0.05 μm, and 2.54 ± 0.06 μm, respectively (Figure 2). It is clear

Figure 1. SEM images showing the site-selectivity of patchy PS discs. a, b) Silica NPs selectively adsorbed on the sides of PS discs, and c) gold NPs selectively attached onto the sides of PS discs. d–f) Silica growth took place only on the sides of PS discs in a Stöber system with the increasing reaction time: 20 minutes (d), 1 h (e) and 8 h (f). All the scale bars represent 1.0 μm.

Figure 2. SiO₂ colloidal rings obtained from PS discs with given diameters, which were synthesized from PS microspheres with various diameters. The diameters of PS discs are 1.23 ± 0.06 μm in (a), 1.55 ± 0.05 μm in (b) and 2.54 ± 0.06 μm in (c). The inset in (c) shows the sides of rings. Scale bars in (a) and (b) are 2.0 μm, in (c) is 5.0 μm, and in the inset of (c) is 1.0 μm.
that the resulting SiO₂ rings have almost the same diameter as their respective PS templates. The ring thicknesses, ΔD (here refer to the difference of the outer and the inner diameter), was usually about 50 nm. These synthesized SiO₂ rings exhibit monodispersity that matches their templates.

Our second route used PS disc templates with tunable sizes from PS microspheres but with a fixed diameter. In this case, the reaction time is an efficient control parameter. By following the whole reaction, it was found that the deformation process is a function of time and that the diameters of PS discs increase with reaction time. As shown in Figure 3a–c, when reaction time was for 9 h, 12 h, and 24 h, PS discs with diameters of 2.64 ± 0.07 μm, 2.78 ± 0.07 μm, and 3.22 ± 0.04 μm, respectively, were obtained (Figure 3d–f). Obviously, PS discs having larger diameters must have smaller thicknesses. As a result, the D/L values of the resultant SiO₂ rings can be tuned by adjusting reaction time. For the PS discs mentioned above, the D/L values of SiO₂ rings were about 3.6, 6.5, and 15.9, respectively. Interestingly, some SiO₂ rings show even some flexibility, possibly because their lengths (L) are only 200 ± 30 nm, and their thicknesses are about 50 nm (Figure 3f).

A third route uses seeded growth of silica rings by growing an extra silica layer. It is a practical approach to tuning the aspect ratio L/D, although it should not impact diameter as long as growth is isotropic. To implement this route, (initial) SiO₂ rings were dispersed into a standard Stöber system and TEOS was added in an amount to control the thickness of the growing layer. This coating process can be done repeatedly until the desired size is reached. With more times of this coating process, both L and ΔD obviously increased as shown in Figure 4a. By this method a large amount of silica rings can be prepared (Figure 4b). To quantitatively follow this growing process, we use AFM to measure L and D concurrently. However, it is difficult to get ΔD due to a strong smear effect of AFM for our ring-shaped samples. Therefore, we estimated ΔD from SEM images. These data are summarized in Figure 4c. As expected, the ΔD values of colloidal rings almost remain the same; however, L and ΔD increase with added TEOS amount. Certainly, it is possible to replace this batch process by a continuous growth process.[11] In addition, SiO₂ allows for covalent incorporation of fluorescent dye molecules, which makes these rings visible under fluorescent light as can be seen using a fluorescent microscope or a laser confocal scanning microscope. Labeling was done by following a reported procedure.[12] As shown in Figure 4d, these labeled colloidal rings show strong fluorescent emission.

Interestingly, it was found that SiO₂ rings obtained by this template route have a Janus character, where the outer surface is hydrophilic and the inner surface is slightly hydrophobic. To demonstrate this effect, a seeded emulsion polymerization of St was done in the presence of sodium dodecyl sulfate (SDS) by using SiO₂ colloidal rings as seeds. Notice that, in this case the surfaces of these rings were not subjected to any pretreatment. Generally, the hydrophilic SiO₂ surface is difficult to coat with PS without further surface treatment according to previous studies.[13] Indeed, PS attached only onto the hydrophobic inner surface of SiO₂ rings (Figure 5a–c). In principle, our silica ring synthesis is based on a standard Stöber procedure. Therefore, both the outer and the inner surfaces should be hydrophilic. To explore the origin of this hydrophobicity, we analyzed the obtained SiO₂ rings by FTIR. As shown in Figure S5, a characteristic peak at 1737 cm⁻¹ corresponding to the carbonyl group appeared in the FTIR spectra of SiO₂ rings, which sits almost the same position of wavenumber with the carbonyl group of pure poly(EHMA), implying the obtained SiO₂ rings contain the residues of poly(EHMA), which cannot be washed out with tetrahydrofuran (THF) for ten times.

By modifying the whole surface of SiO₂ rings, it is possible to result in many kinds of core–shell SiO₂/polymer composite rings (Figure 5d). For example, we obtained SiO₂/PS core–shell rings by the introduction of double bonds onto the surface of SiO₂ rings and following with seeded emulsion polymerization of St. As shown in Figure S6, a PS shell
uniformly grew on the ring surface. Interestingly, without the use of SDS, an eccentric structure formed where PS grew more on one region of rings (Figure 5e) than on others. The formation of this structure might originate from the competition of interfacial tensions and kinetic factors, and the mechanism for this effect needs further investigation. After removing silica cores, hollow PS rings were obtained (Figure S6b and S7a). A similar synthesis was extended to prepare SiO$_2$/polymer core–shell rings and hollow PMMA rings (Figures 5f and S7b). These polymer rings could be cross-linked when cross-linking agent was used (Figure S8). In principle, this method is general and can be used to synthesize polymer rings on a large scale, which cannot be easily realized by other synthetic procedures of colloidal rings.

Finally, an extra benefit from this template route is that, the outer surface of SiO$_2$ rings can be selectively modified by, for instance, atomic transfer radical polymerization (ATRP) initiator while the inner surface remains unmodified due to protection afforded by the templating PS discs. This modification was done in mixed ethanol/water solvent; these mixtures are bad for PS. Three types of polymer brushes, poly(isopropyl acrylamide) (poly(NIPAM)), poly(sodium styrene sulphonate) (poly(NaSS)), and poly(lauryl methacrylate) (poly(LMA)) were grown via ATRP (Figure 5g). Poly(NIPAM) is known to provide a thermoresponsive interaction between rings due to the switch behavior of hydrogen bond among poly(NIPAM) molecules and between poly(NIPAM) and water. In Figure 5h, the TEM image of SiO$_2$ rings with poly(NIPAM) brushes is shown. Though these polymer brushes are difficult to see under regular TEM imaging, they indeed show a thermoresponsive aggregation behavior (Figure 5i). Clearly, at 25°C, poly(NIPAM)-grafted SiO$_2$ rings disperse well in water and they form irregular clusters at 50°C, a higher temperature than LCST of poly(NIPAM). Poly(NaSS) is a strong polyelectrolyte in water and thus provides stable charges for the outer surface of the rings (Figure S9). Poly(LMA) makes the rings well dispersed in nonpolar solvents such as cyclohexane (Figure S10), which provides an index of refraction matching system for light scattering studies of concentrated colloidal rings. The success of this brush growth was also confirmed by FTIR analysis (Figure S11). These polymer brushes will provide extra tunable parameters for future studies of ring assembly. Moreover, such selectivity of the anchoring sites, only on the outer surface or the inner surface, can strengthen corresponding Janus effects of such colloidal ring systems.

In summary, we have demonstrated an effective strategy to synthesize monodisperse colloidal rings by employing patchy colloidal discs as templates. These rings have Janus character, in that the outer surface is hydrophilic and the inner surface is hydrophobic. The diameters, the lengths, and aspect ratios are tunable. This tuning was illustrated by three different routes. Our rings can be selectively decorated on the inner surface or the outer surface by diversified polymerization technique, or fully coated to form core–shell rings and hollow rings. This study points to the direction of engineering new kinds of colloidal suprastructures. Such structures include liquid crystalline or crystalline phases by self-assembly of ring-like colloids, which have hardly studied so far and recently were reported in computer simulation studies.[5] Our synthetic strategy enables preparation of colloidal rings with high monodispersity and on a large scale, which is necessary for experimental studies of self-assembly and for other practical applications. Furthermore, the ability to incorporate fluorescent dyes into these rings allows one to study such colloidal rings at the single particle level by using confocal microscopy.

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Conflict of interest

The authors declare no conflict of interest.

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