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Synthesis and Directed Self-Assembly of Patterned Anisometric Polymeric Particles

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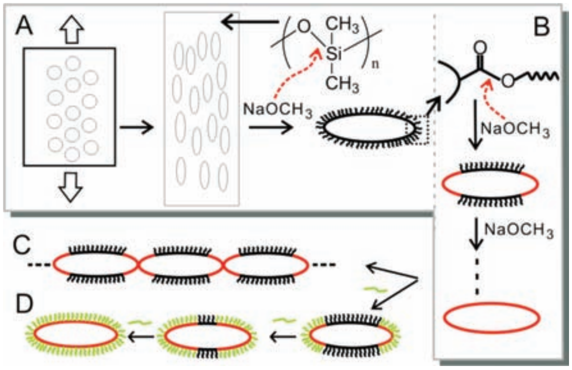
Abstract: A simple and versatile method for making chemically patterned anisotropic colloidal particles is proposed and demonstrated for two different types of patterning. Using a combination of thermo/mechanical stretching followed by a wet chemical treatment of a sterically stabilized latex, both patchy ellipsoidal particles with sticky interactions near the tips as well as particles with tunable fluorescent patterns could be easily produced. The potential of such model colloidal particles is demonstrated, specifically for the case of directed self-assembly.

Controlling particle shape and imparting directionality in interactions have been identified as key concepts for future progress in colloid and nanoparticle materials design,[1] certainly by using principles of directed self-assembly.[2] Recent advances in particle synthesis and functionalization have proven the power of these concepts, but the synthesis methods for suitable anisotropic particles are normally rather cumbersome and the yields are limited.[3] Compared with the relative ease of manipulating spherical particles,[4] introduction of patchiness or patterns onto *anisotropic* particles in a site-specific manner remains challenging and only a few examples, typically limited to metal or semiconductor nanocrystals, have been reported.[5,6] In the present work, a simple strategy for producing anisometric colloidal particles has been developed, typically to be used for, but not limited to, spheroids. The method yields particles which can be chemically patterned to produce a range of materials, going from uniform sterically stabilized hard-core ellipsoidal particles, over fluorescently patterned stable "pom-pom" particles to patchy ellipsoids with sticky attractive interactions near the tips ("inverse pom-pom" particles). The method works for particle sizes ranging from about 100 nm up to several micrometers, provides monodisperse particles with aspect ratios ranging from 3 to 8, and gives yields on the order of grams.

Ellipsoidal particles in the colloidal domain find numerous applications that specifically exploit their shape, for example in photonics, efficient stabilizing of Pickering emulsions and model systems for understanding the shape-effect on the drug delivery, to cite just a few examples.[7] Particle shape also affects fundamental aspects of colloidal behavior such as Brownian motion, maximum packing, crystal structures of anisotropic particles, as well as capillary force-mediated self-assembly at a liquid−liquid interface.[8−10] The ellipsoidal particles used in this work were prepared on the basis of a principle originally developed by Keller and co-workers (Scheme 1A):[11] spherical latex particles were embedded in a polymer film which was then heated above the glass transition temperature (T_g) of the latex and stretched to certain strain. The latex particles deformed into ellipsoids. This method has been extended to many kind of polymeric particles and is not limited to ellipsoids as even more complex shapes have been obtained (e.g., worms, disks, etc.).[12] Here, poly(methyl methacrylate) (PMMA) latex particles were dispersed in a poly(dimethylsiloxane) (PDMS) solution in hexane, which was subsequently cast and cross-linked into a rectangular film.[13] The PMMA particles are grafted with a layer of comblike stabilizers consisting of a linear PMMA as the backbone and poly-12-hydroxystearic acid (PHSA) as the teeth (Scheme S1, Supporting Information (SI)). These particles have been used as model hard spheres and have played a pivotal role in the understanding of colloidal suspensions.[14] The cross-linked PDMS film loaded with PMMA particles was stretched to a given strain and heated to a temperature above T_g of the PMMA (Scheme 1A). The particles deform into prolate ellipsoids and are recovered from the film after solidification by cooling, using sodium methoxide (SM) to degrade the PDMS matrix.[10] Stretching particles that initially carry a fluorescently labeled stabilizer revealed ellipsoids with an essentially constant fluorescent halo, if anything slightly denser near the tips. This suggests the stabilizer redistributes itself during stretching above T_g, in agreement with the earlier observations by Ottewil and co-workers for the charge distribution of polystyrene (PS) ellipsoids prepared from stretching PS particles.[15]

Scheme 1. (A) Thermo/mechanical Stretching of Polymeric Particles in a Film. (B) Curvature-dependent Chemical Wet Etching. (C) Tip-to-tip Assembly of Patchy Ellipsoids. (D) Preparation of Fluorescently Patterned Particles



In the present work, by monitoring the degrading procedure, it was observed that the originally grafted comblike stabilizers were removed from the particle surface by sodium methoxide (SM). This occurs because the stabilizers are linked to the surface by ester bonds which can be attacked by SM via a transesterfication process.[16] More importantly, we observed that the stabilizers near the tips of the ellipsoids are removed faster than those in other areas (Scheme 1B). This may be caused by the higher surface curvature near the tips with several factors possibly contributing. First, the brush consists of densely grafted chains which are restricted in their motion.[17] Recent measurements showed that the

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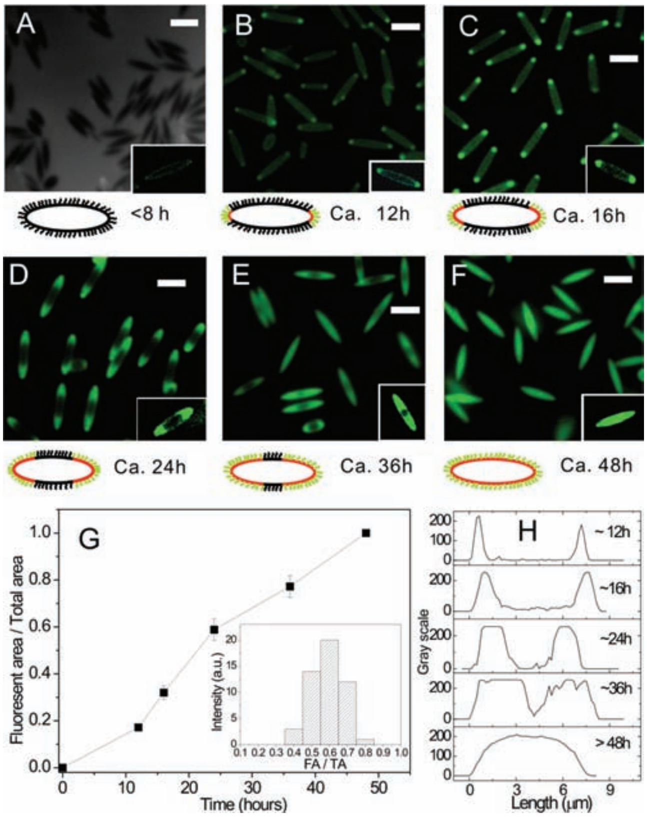

Figure 1. Fluorescently patterned anisotropic particles. (A−F) Fluorescent microscopy images of particles recovered from varying wet etching times and after readsorption with fluorescent stabilizers. The final concentration the sodium methoxide is 0.04% (w/w). The particles were dispersed in decalin. The insets are CLSM images. Under each image, the schematic structure and the degradation time are shown (scale bar: 5 μm). (G) Evolution of the relative fluorescent area (FA) with the etching time. (Inset) distribution of the FA over the total area (TA) for the particles shown in (D) based on 50 particles. (H) Fluorescence intensity profiles along the maximum axis of the particle listed in the insets of (A−F).

maximum size of a molecule that can enter a brush for a spherical particle is 0.65 nm.[18] The stretching of the particles will lead to a decrease of the average grafting density and, enhanced by the curvature, a locally slightly more open and more accessible brush. Second, as recent experiments demonstrate, mass transfer depends on the local curvature, simply because there are more molecules per unit area available for adsorption when the curvature is higher.[19] Hence, the etching of the surface-grafted groups becomes curvature dependent.

Evidence of this localized, surface-curvature-dependent etching of the stabilizer is three-fold: Negative staining TEM reveals that, at the initial stage of the degradation, the surface of the bare PMMA ellipsoids is smooth and that, with increased degradation time, defects appearing first near the tips gradually spread over the whole surface as the protective grafted layer is removed (Figure S2 (SI)). Second, the curvature-dependent etching produces site-specific patchy particles: the structure of inverse pom-pom like anisotropic polymeric particles can be inferred from their self-assembly in bulk via their bare tips (as discussed later on). Finally, following the procedure illustrated in Scheme 1B and D and replacing the original stabilizer with a second fluorescent species, the localized etching can directly be visualized and fluorescently patterned ellipsoids can be prepared. For this purpose, the same comblike stabilizers as those originally grafted onto the PMMA surface, but now with a fluorescent dye (7-nitrobenzo-2-oxa-1,3-diazol (NBD)) randomly distributed along the backbone, were used as the fluorescence marker. This fluorescent stabilizer can physically adsorb onto the PMMA surface and can be chemically grafted when required.[20] The area of the particle from which the initial stabilizer will be removed can be controlled by varying the concentration of the degrading agent (SM) and, more importantly, the degradation time. For short wet etching times, the dominant reaction is the breakage of the siloxane bonds of the PDMS matrix, and the particles recovered for etching times shorter than 8 h do not readsorb significant amounts of fluorescent stabilizer (Figure 1A). For longer wet etching times, the original stabilizers are first removed near the tips of the ellipsoids, where the curvature is highest. When the fluorescent stabilizer is subsequently adsorbed, the resulting particles have two fluorescent tips and a relatively dark middle part (Figure 1B). With increased wet etching time, the area where the original stabilizer is removed increases and progresses from the tips to the equatorial area (Figure 1B−E), giving rise to fully fluorescently labeled particles after etching for 48 h (Figure 1F). Figure 1G depicts the temporal evolution of the fluorescent area, which is representative of the area where the original stabilizer has been etched away, as a function of etching time. The patterns at each specific stage are reasonably uniform in size (inset of Figure 1G). When spheres are subjected to the same procedure as the ellipsoids, particles with homogeneous fluorescent rings are observed (Figure S3 (SI)), confirming that the localized degradation of the stabilizer is due to differences in curvature. The patterned ellipsoidal particles were further characterized by confocal laser scanning microscopy (CLSM) (Figure S4 (SI) and insets in Figure 1B−F). The variation of the fluorescent intensity along the long axes of the ellipsoids obtained from the CLSM images (Figure 1H) confirms the fluorescence distribution. In conclusion, using a simple method spatially modulated patterns are introduced onto otherwise homogeneous anisotropic polymeric particles at the truly colloidal length scale.

These fluorescently patterned particles can aid the visualization of colloidal dynamics and self-assembly processes, for example those controlled by capillary forces occurring at a liquid−liquid interface.[2] In bulk of apolar solvents such as decalin, hexane, etc., the produced particles interact with a well-known relatively hard interaction from the steric repulsion,[21] as can be concluded from the well-dispersed states in all pictures in Figure 1. When the particles were dispersed at the decalin/air interface, the particles self-assembled side-by-side into well-defined stripes images (inset of Figure 2A), due to shape-induced capillary interactions.[9] Figure 2B shows that single stripes formed by particles in Figure 1C can further self-assemble into a 2D-smectic-like structure. In this example there is a clear benefit for in situ visualization of the details of the local structure as fully fluorescent particles would lead to a blurring of the image (inset of Figure 2A). The stripes can also grow a millimeter long and evolve into morphologies of rich, hierarchical structures (Figure 2B). When mixing fluorescently patterned particles (Figure 1D) with fully fluorescent ones (Figure 1F), optical patterns can be introduced into the stripes (inset of Figure 2B).

When no fluorescent stabilizer is readsorbed to the etched ellipsoids, patchy particles with localized sticky interactions are obtained. The patterns of chemical heterogeneity on these particles will mimic those observed for the fluorescent particles in Figure 1, and the etching time required for an amount of bare versus covered areas for these “inverse pom-pom” particles can be directly inferred from the trends of Figure 1G. For etching times shorter than 8 h, the particles expose no bare surface yet, and the suspensions are stable (Figure 3B). After wet etching the film and the particles for slightly more than 8 h, the particles will have two symmetric bare tips and a middle part that is still sterically stabilized by the comblike stabilizer in a good solvent for the latter, such as decalin.[21]The particles will then remain sterically repelling on the sides, while attractive interactions such as the van der Waals forces or attractions between polar groups at the surface will dominate the interaction near the tips. Such directionality in interactions of anisotropic particles has so far only been reported for metallic nanorods by taking advantage of the selectively binding of ligands to certain crystal facets.[5,6] With the proposed method, the size of the bare area at the tips can be easily controlled by varying the degradation time as was shown by the fluorescently tagged counterparts of the present particles in Figure 1.

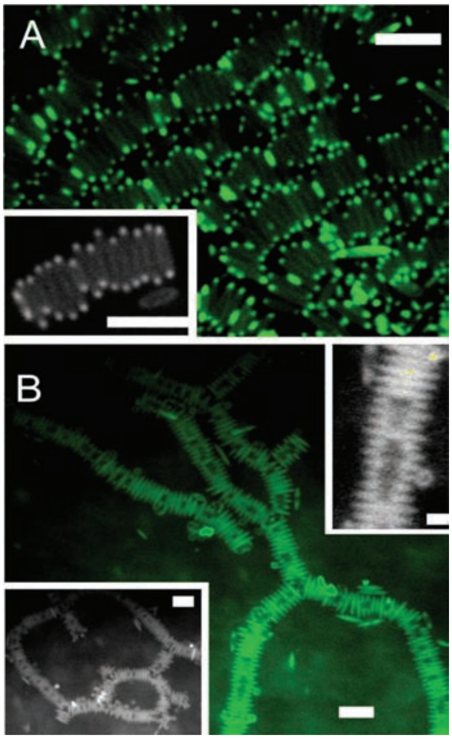

Figure 2. Capillary force-mediated self-assembly of hard-core ellipsoids at an oil/air interface. (A) Smectic-like 2D structure. (Inset) Single stripe observed by CLSM. (B) Hierarchal structure. (Upper-right inset) Magnified image of the side-by-side assembly of mixed fluorescently patterned and fully fluorescent ellipsoids, scale bar: 2 μm. (Bottom-left inset) Structure of more complicated morphology. Scale bar: 10 μm in (A) and 5 μm in (B).

This directional interaction forces the particles to self-assemble into chains by connecting their tips, as shown in the in situ bright-field microscopy image (Figure 3C). Particles with small bare area at the tips will connect with each other with a bond angle α around 180° (inset Figure 3C, corresponding to the sticky counterparts of the particles in Figure 1B and C). With increasing degradation time, the bare areas at the tips increase (corresponding to the sticky counterparts of the particles in Figure 1D and E), which makes a wider range of bond angles possible (inset in Figure 3D) and also allows more than two particle tips in a connection point. The increased connectivity combined with the increase in the strength of attraction per particle leads to the formation of an aggregated network structure (Figure 3D). Further reduction of the area covered by the stabilizer layer at this volume fraction results finally in a collapse of the network and the formation of random dense aggregates (Figure 3E). All aggregated suspensions can be brought back to a stable state by remixing with stabilizers. These qualitative observations demonstrate the potential applications of the inverse pom-pom particles as a model to investigate the emerging topic of polymerization-like self-assembly of nanocolloidal rods with directional interactions.[6]

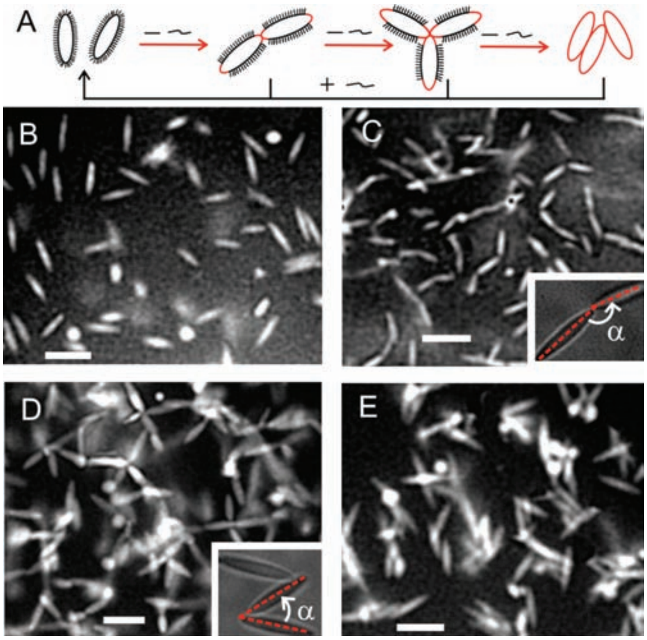

Figure 3. *In situ* visualization of directional self-assembly of inverse pom-pom ellipsoids at varied degradation stages by bright-field optical microscope. (A) Schematic of self-assembly of particles of varied surface properties. (B) Stable suspension of ellipsoids fully covered with stabilizers. (C) Linear chains formed by particles with the same 15% bare area at each tip as in Figure 1C. (D) Aggregated network formed by particles with the same 30% bare area as in Figure 1D. (E) Random aggregates of particles which are fully stripped of stabilizers. Insets in (C) and (D): Typical angular configuration of the ellipsoids in the chains. Scale bar: 10 μm.

In summary, curvature-dependent wet chemical etching provides an easy route to produce patchy nonspherical particles, where the size and shape of the particles and nature and extent of the patchiness can be easily varied. In the present work, colloidal ellipsoids were synthesized with gram-scale yield, possessing tunable interparticle interactions ranging from stable over patchy to fully attractive. We demonstrated this technique by producing patchy, inverse pom-pom ellipsoids which interact directionally and can self-assemble into chains or denser structures in bulk, depending on the etching conditions. Similarly, locally labeled fluorescently patterned ellipsoids are made which offer advantages of visualization in microscopy observation. Since curvature difference exists in any anisotropic shape, the current method may represent a general, cost-effective and scalable way to introduce site-directed properties onto a wide range of model colloids, suitable as model systems for colloid physics, for exploiting directed self-assembly, and to investigate colloidal gels and biomimetic networks.

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Supporting Information Available: Detailed experimental procedures, additional results from each experiment. This material is available free of charge via the Internet at http://pubs.acs.org

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