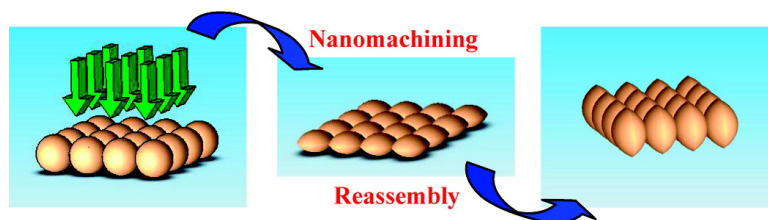


Generation and Assembly of Spheroid-like Particles

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Generation and Assembly of Spheroid-like Particles

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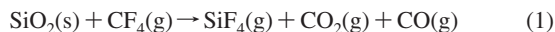
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This communication presents a straightforward approach in generating spheroid-like particles through a unidirectional chemical etching process. Manipulation of the etching profile can also generate nonspherical particles with other geometries. The spheroid-like particles generated are uniform in size and shape so it is feasible to use them in the evaporation assisted assembly process.¹ The initial observation of the self-assembly structure of these particles showed a counterintuitive orientational order in the monolayer with their long axis perpendicular to the substrate.

Research in the biological systems frequently involves the use of particles.^{2a,b} The study of particle assembly with different packing geometry is also critical for the understanding of the bulk properties of various materials, such as optical^{2c} and composite materials.^{2d} Most of such studies, however, involve only spherical particles. The challenges in the synthesis of nonspherical particles limit the widespread use of these particles in both fundamental studies and industrial applications. The rising interests in nonspherical particles motivate the increased effort in developing processes to synthesize these particles.^{3,4} Whitesides,^{3a} Lahann,^{3b} Weitz,^{3c} Velev,^{3d} Xia,^{3e} Pine,^{3f} and others^{3g,h} reported various approaches of generating nonspherical particles in liquid matrixes or at the liquid interface. The Xia^{4a} and Mitragotri^{4b} groups also demonstrated the generation of nonspherical particles in stretched or compressed solid matrixes. The nonspherical particles generated in most of these approaches are limited either to a certain size range or to specific materials.

This communication reports a general approach that is applicable to generate nonspherical particles of a wide range of materials, including organic and inorganic materials. Using spherical particles as the starting material, the approach transfers the spherical geometry into a nonspherical geometry through an anisotropic chemical etching reaction. The reaction occurs in a reactive ion plasma-etching chamber, with a unidirectional electric field to guide the direction of the reaction. Figure 1a,b describe the generation of a layer of spheroid-like silica particles using directional CF₄ etching chemistry. Equation 1 gives the simplified version of the overall etching reaction in such a process:⁵



In the plasma field, CF₄ molecules are broken down to various ionic species that move vertically to the silica surface in the unidirectional electric field. As the reactive species reach the silica surface, the reaction between these species and silica generates SiF₄, which is volatile and diffuses away from the surface to expose new silica sites for the further etching reaction.

A pure geometry analysis can predict the final dimension of the resulting particles. Figure 1c shows the cross section (blue circle) of the starting particle placed in the Cartesian coordination plane with the origin (O) at the center of the blue circle and y-axis as the etching direction. Equation 2 describes the cross section of the outer surface of the starting particle:

$$x^2 + y^2 = r_0^2 \quad (2)$$

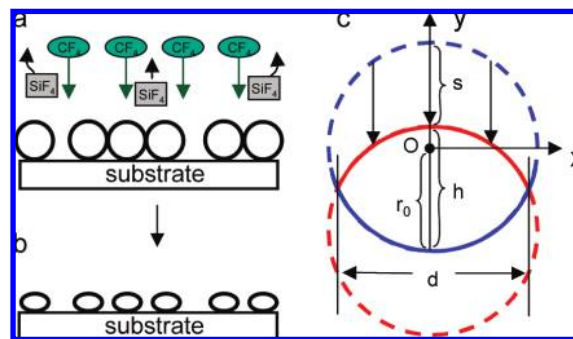


Figure 1. (a) Schematic of the unidirectional etching reaction; (b) nonspherical particle after etching; (c) schematic of the cross section of the resulting particle within the Cartesian plane.

In the equation r_0 is the radius of the starting particle. As the etching starts, reaction 1 occurs at equal speed at all locations of the top surface. There is a negligible reaction at the bottom surface due to the masking effect by the top surface in the unidirectional etching field. After a certain reaction time, the top surface moves down a distance of s and rests on the red circle (eq 3):

$$x^2 + (y + S)^2 = r_0^2 \quad (3)$$

The cross section of the resulting particle is the intersection of the two circles and forms a shape similar to an ellipse. The schematic showed so far is the cross section along the etching direction. Rotating the intersection along its short axis (y -axis) will result in the schematic of the final particle in three dimensions, which is a spheroid-like particle (close to an oblated spheroid). To generate particles with uniform size and shape in this approach, the starting particles should be a mono- (or submono-) layer, with no order or close-packing needed. If more than one layer of particles are used, the masking effect from the overlapping will introduce variance in the final particle geometry. Yang et al. used close-packed particles for size tunable nanopatterning and tried to apply the masking effect to generate particles with pores on their surfaces using ordered close-packed double layers of particles as the starting material.⁶ The multidomain and the inherent imperfection of the double-layer structure make it difficult to generate particles with pores of uniform sizes and location. Their approach also required a separation step to collect the resulting particles. The collection of the resulting particles in this approach only involves a single release step and makes the scale-up process feasible.

Figure 2 shows the change of the height (h) of the silica particles with time during the directional CF₄ etching in the experiment. The starting materials were spherical silica particles with a diameter of ~510 nm, synthesized using the standard Stober process.⁷ Dip coating of a solution containing ~20 wt% silica particles in ethanol deposited a monolayer of these particles onto the silica substrate. The directional CF₄ etching occurred in Anelva-5 (Anelva Corporation, Japan) with

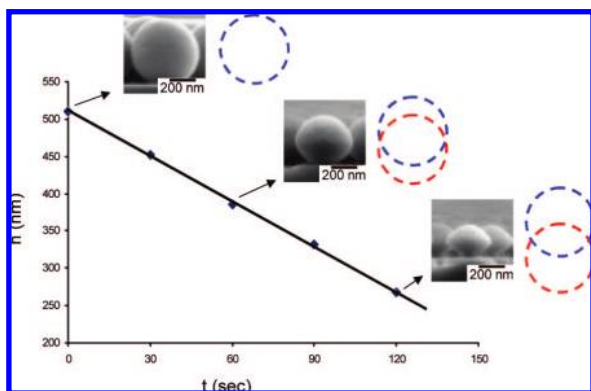


Figure 2. Plot of the height of the silica particles during the etching process. The inserts show the profile of the starting particle and the particle after 1-min and 2-min etching.

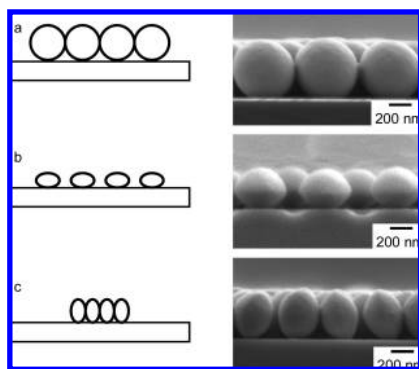


Figure 3. Monolayer of particles (a) before etching, (b) after etching, and (c) after release and reassembly.

the RF power at ~ 500 W. The inserts of Figure 2 are SEM pictures of the particles after 0, 1, and 2 min of etching. The schematic on the right side of the SEM pictures shows the predicted downward movement of the cross-sectional top surface of the particle (red circle). The dimension and shape of these particles matched well with the pure geometry analysis, with the aspect ratio of h/d (d is the width of the particle in the x direction, Figure 1c) reaching ~ 0.6 after 2-min etching. Analysis based in Figure 1c shows theoretically the aspect ratio can become infinitely small, while in the experiment the smallest aspect ratio that can be reached will depend on the spatial resolution of the etching process.

After release and collection, these spheroid-like particles were redispersed in ethanol to make a solution of ~ 0.5 wt%. Through an evaporation-assisted assembly, these particles formed a monolayer on the silicon substrate. Figure 3 shows the schematic and the images of monolayer of the particles at different processing stages. For the starting particles, there was no orientational order due to the spherical symmetry (Figure 3a). After the unidirectional etching, the particles had an orientational order with their long axis parallel to the substrate (Figure 3b) due to the vertical etching direction. An etching direction other than vertical will generate orientational order with tilted axis.

After release and reassembly of these spheroid-like particles, there are several possibilities for the orientational order in the monolayer. The directionality of their long axis (parallel, tilted, or perpendicular to the substrate) defines these orientational orders. In the gravity field, the energy of the states increases as the long axis moves from the parallel state, to the tilted state, and to the perpendicular state. In the experiment, however, most of the time

the state observed was the perpendicular state (Figure 3c), with the tilted state observed at the edge of the monolayer. The parallel state was observed where there were isolated particles. In an evaporation-assisted assembly, capillary force plays a dominant role in forming the structure. As the meniscus of the solution withdraws, the capillary force tends to rotate the spheroid-like particles at the air–ethanol–silicon interface. For isolated particles on the silicon substrate, eventually the meniscus will sweep past the particles and leave some residue liquid around the particles. As the residue liquid evaporates, capillary force diminishes and eventually the gravity force dominates so the particle takes the parallel state, the lowest energy state in the gravity field. For the multiple particles in the meniscus, we speculate that the rotating facilitates the jamming of the particles, which somehow helps align the particles with their long axis perpendicular to the substrate. Further detailed study of the assembly of these particles, such as the effect of the aspect ratio and particle size, is needed to understand the orientational order and also to explore other possible packing geometries.

In conclusion, this report presents a general approach in generating spheroid-like particles. Directional chemical etching has the capability to generate structures with sizes ~ 10 nm⁸ and can be applicable to various materials.⁹ It is thus possible to extend the current approach to generate nonspherical particles of a broad range of materials (Supporting Information: images of spheroid-like polystyrene particles), with the dimension of the particles as small as tens of nanometers. This process will help further open the door for the fundamental studies of these nonspherical particles and will facilitate the understanding of the impact of the geometry to the bulk properties.

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Supporting Information Available: Images of polystyrene spheroid-like particles generated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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