Simple Method to Produce Janus Colloidal Particles in Large Quantity

Liang Hong,[†] Shan Jiang,[†] and Steve Granick*

Departments of Materials Science and Engineering, Chemistry, and Physics, University of Illinois, Urbana, Illinois 61801

Received September 16, 2006. In Final Form: September 30, 2006

A simple, generalizable, inexpensive method is demonstrated to synthesize Janus colloidal particles in large quantity. At the liquid−liquid interface of emulsified molten wax and water, untreated particles adsorb and are frozen in place when the wax solidifies. The exposed surfaces of the immobilized particles are modified chemically. Finally, wax is dissolved, and the inner surfaces are modified chemically. Gram-sized quantities or more of Janus particles can be synthesized by taking this approach.

Introduction

Colloidal particles—larger than molecules but small enough to sustain Brownian motion—are fundamental in nature and technology. A traditional goal in colloid and nanoparticle science was to obtain particles that are homogeneous in their chemical composition, and applications of this kind continue to have value in applications such as painting, ceramics, and photonic materials.[1] Of emerging interest is the alternative idea of obtaining particles whose surface chemical composition differs on two sides of the particle (Janus as suggested by de Gennes[2]). How could it be used? Anisotropic surface chemical composition, superposed on a homogeneous shape, could introduce asymmetric interactions that induce particles to self-assemble.[3] Janus-type spherical particles can be used as microrheological probes.[4] With magnetic fields being used to exert force on one side of the particle, Janus-type spherical particles can be used to manipulate particles with controlled magnetic fields.[5] Janus particles can also be used as potential building blocks for new 3D self-assembled structures, but this purpose requires a method to produce large quantities of material.

How can Janus particles be produced? The methods to produce Janus particles of colloidal size ($\leq 1\ \mu$m in dimension) are severely limited in the amount of product.[6] Microfluidic methods can be used to produce larger quantities, but the particle size at present is limited to ∼10−100 μm diameter.[7] One current approach to produce Janus-type Brownian particles is to join two different materials.[8] However, the shape and monodisperity of the resulting particles are difficult to control. Another way is to modify homogeneous precursor particles selectively by a protect-and-release process. Most endeavors of this kind have employed planar solid substrates as protecting surfaces onto which particles

are first placed as a monolayer. The side of the particle that faces the solid is protected from modification, and the other side is modified chemically. Sputtering,[9] stamp coating,[10] and Langmuir−Blodgett-based methods[11] have been used to modify the unprotected side of these monolayer surfaces chemically. These approaches offer good control over the surface area that sustains chemical modification, but only a few milligrams of particles are produced in one batch because the approach relies on 2D modification of a monolayer. Discrete particles can also be joined from two phases at the liquid−liquid interface to form heterodimers, for example.[12] The experimental challenges of producing large quantities of colloidal-sized Janus particles have limited their use in technological applications and scientific studies.

To overcome these limitations, it has been suggested to add a small amount of water to a particle-in-oil dispersion, causing silica particles to aggregate by capillary forces to form clusters whose exterior is chemically modified.[13] This interesting approach can produce gram-sized quantities of chemically modified sample. Here, alternatively, we describe a simple and efficient method to fabricate large amount of Janus particles under conditions where thermodynamically controlled surface coverage control has been achieved.

The method in this study is based on using oil−water emulsions. However, it is advantageous to select molten paraffin wax as the oil phase. The emulsion is made at a temperature where wax is molten, and then it is cooled to room temperature to "lock" particles at frozen wax−aqueous surfaces, preventing particle rotation and facilitating subsequent chemical modification and purification. These emulsions are sufficiently stable, mechanically and chemically, to be washed and modified chemically by reaction in solution. After surface chemical modification on the aqueous side of the emulsion interface, wax can be dissolved in organic solvent, and the resulting particles can be further modified chemically.

To test the generality of this synthesis approach, in the study described below we produced and characterized two varieties of

---

[†] These authors contributed equally.

(1) Qi, M. H.; Lidorikis, E.; Rakich P. T.; Johnson S. G.; Joannopoulos, J. D.; Ippen, E. P.; Smith, H. I. *Nature (London)* **2004,** *429,* 538.

(2) de Gennes, P. G. *Rev. Mod. Phys.* **1992,** *64,* 645.

(3) Hong, L.; Cacciuto, A.; Luijten, E.; Granick, S. *Nano Lett.*, in press, 2006.

(4) Behrend, C. J.; Anker, J. N.; McNaughton, B. H.; Roberts, T. G.; Brasuel, M.; Philbert, M. A.; Kopelman, R. *J. Phys. Chem. B* **2004,** *108,* 10408.

(5) Behrend, C. J.; Anker, J. N.; McNaughton, B. H.; Kopelman, R. *J. Magn. Magn. Mater.* **2005,** *293,* 663.

(6) Perro, A.; Reculusa, S.; Ravaine, S.; Bourgeat-Lami, E.; Duguet, E. *J. Mater. Chem.* **2005,** *15,* 3745.

(7) Nie, Z.; Li, W.; Seo, Minseok.; Xu, S.; Kumacheva, E. *J. Am. Chem. Soc.* **2006,** *128,* 9408. Nisisako, T.; Torii, T.; Takahashi, T.; Takizawa, Y. *Adv. Mater.* **2006,** *18,* 1152. Dendukuri, D.; Pregibon, D. C.; Collins, J.; Hattan, T. A.; Doyle, P. S. *Nat. Mater.* **2006,** *5,* 365.

(8) Erhardt, R.; Böker, A.; Zettl, H.; Kaya, H.; Pyckhout-Hintzen, W.; Krausch, G.; Abetz, V.; Müller, A. H. E. *Macromolecules* **2001,** *34,* 1069. Roh, K.; Martin, D. C.; Lahann, J. *Nat. Mater.* **2005,** *4,* 759.

(9) Takei, H.; Shimizu, N. *Langmuir* **1997,** *13,* 1865. Lu, Y.; Xiong, H.; Jiang, X.; Xia, Y.; Prentiss, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003,** *125,* 12724.

(10) Cayre, O.; Paunov, V. N.; Velev, O. D. *J. Mater. Chem.* **2003,** *13,* 2445. Paunov, V. N.; Cayre, O. J. *Adv. Mater.* **2004,** *16,* 788.

(11) Fujimoto, K.; Nakahama, K.; Shidara, M.; Kawaguchi, H. *Langmuir* **1999,** *15,* 4630.

(12) Gu, H. W.; Yang, Z. M.; Gao, J. H.; Chang, C. K.; Xu, B. *J. Am. Chem. Soc.* **2005,** *127,* 34.

(13) Takahara, Y. K.; Ikeda, S.; Ishino, S.; Tachi, K.; Ikeue, K.; Sakata, T.; Hasegawa, T.; Mori, H.; Matsumura, M.; Ohtani, B. *J. Am. Chem. Soc.* **2005,** *127,* 6271.
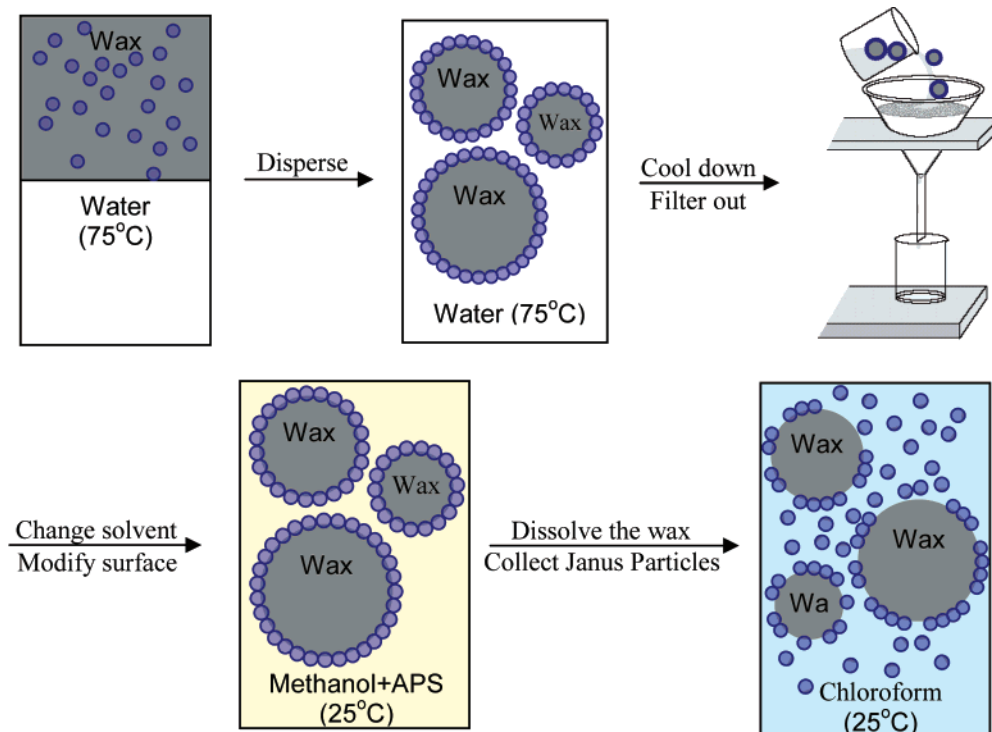
Figure 1. Schematic procedure to create Janus particles by functionalizing particles adsorbed onto an emulsion of water and oil and then cooling the sample so that the oil crystallizes to form a wax.

Janus particles. The first kind was bipolar: cationic on one side and anionic on the other side. The second kind was the colloid analogue of a surfactant: charged on one side and hydrophobic on the other side.

Experimental Section

Chemicals. Fused silica particles used in these experiments were 800 nm and 1.5 μm in diameter, obtained from Alfa Aesa and Tokuyama, respectively. To prepare the particle surfaces for subsequent chemical modification, first the particles were treated with pirahna solution, then they were centrifuged, and finally they were dried at 80 °C under vacuum. The paraffin wax used in these experiments had a melting point of roughly 55 °C. Both (amino-propyl)triethoxysilane (APS) (99%) and *n*-octadecanetrichlorosilane (OTS) were purchased from Aldrich. To produce fluorescent-labeled APS, rhodamine B isothiocyanate was attached to APS using a procedure described in the literature.[14] Before OTS was used in these experiments, it was freshly purified by distilling it under vacuum.

Fabrication of Janus Particles. First, 0.2 g of fused silica particles was dispersed homogeneously in 1 g of paraffin wax at 75 °C and then mixed with 10 g of Millipore water. The emulsions were produced using magnetic stirring at 1600 rpm for 1 h and then were cooled to room temperature, at which paraffin wax is solid.

Deionized water was used to wash the wax emulsions multiple times to remove particles in the aqueous solution as well as weakly attached particles. The resulting exposed surfaces of particles attached to the emulsions were allowed to react chemically with 2 mM labeled APS in methanol solution for 30 min. The reaction solutions were washed with pure methanol to remove excess silane. To release these modified silica particles from wax, the wax was dissolved in chloroform at room temperature. Then, the resulting particles were further modified chemically. For example, those particles that had been allowed to react with APS on one hemisphere could be further allowed to react with OTS (on the second hemisphere), producing particles that were cationic on the APS side and hydrophobic on the OTS side.

Characterization. Scanning electron microscopy, SEM (JEOL 6060 LV), was used to image the emulsions. Prior to imaging, a thin layer of gold was evaporated onto them to render them electrically conductive, avoiding surface charging in the electron beam.

To determine chemical composition, we used a combination of optical imaging and epifluorescence imaging. Optical imaging employed a Zeiss Axiovert 200 microscope with a 40× objective. For epifluorescence imaging, we employed 532 nm illumination (a Nd:YAG laser) and focused the laser beam at the back focal point of a 63× air objective. The fluorescence images were collected using this same objective and recorded using an electron multiplying CCD camera (Andor Ixon) after filtering out light from the excitation laser. Images of particle rotation were recorded with an exposure time of 0.1 s for 800 frames.

Results and Discussion

A schematic representation of the main idea is summarized in Figure 1. It is known that at a liquid−liquid interface (here, an emulsion) particles whose surface energy is between that of the two will adsorb, lowering the total free energy.[15] In the case of our wax−water system, hydrophilic fused silica particles adsorbed to oil-in-water emulsions. Chemical modification at temperatures where the oil phase is solid is desirable for several reasons. First, it fixes the particles into fixed positions during the chemical modification step, avoiding the possibility that adsorbed particles might wobble or rotate at a liquid−liquid interface. Indeed, particle rotation at the liquid−air interface has been inferred by others.[11] Second, the presence of a waxy phase presents advantages at the stage of separation and purification of the particles. Third, when two stages of chemical modification are intended, this eliminates the need to find a liquid−liquid pair where the reactant is soluble in only one liquid.

Figure 2 shows SEM images of illustrative emulsions. First, as is known from prior work by many others, we found that silica

(14) Verhaegh, N. A. M.; van Blaaderen, A. *Langmuir* **1994**, *10*, 1427.

(15) Aveyard, R.; Binks, B. P.; Clint, J. H. *Adv. Colloid Interfaces Sci.* **2003**, *100*, 503.
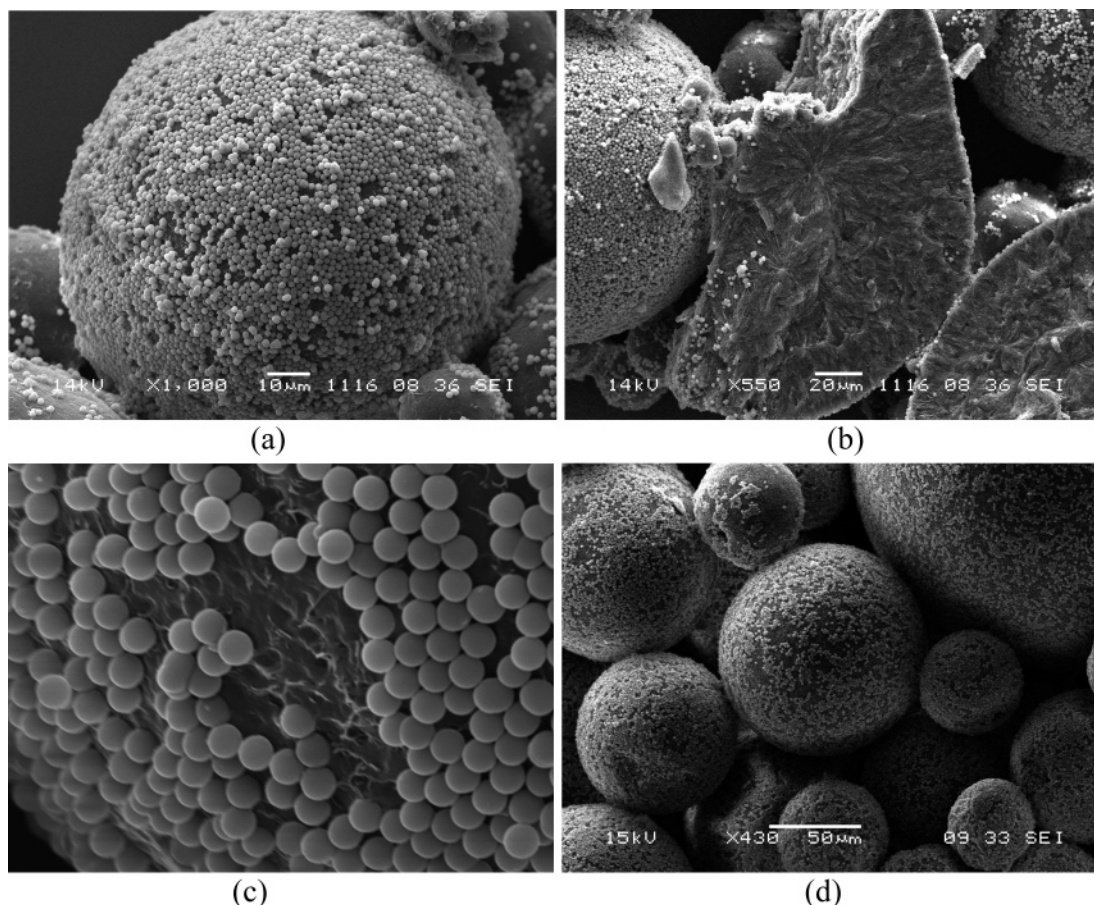
Figure 2. SEM (scanning electron micrograph) images illustrating that silica particles formed a monolayer on the surface of the colloidosome and that the interior colloidosome was free of particles. Specifically, SEM images are shown of (a) a colloidosome filtered from water, (b) a broken colloidosome with a view of its inside, (c) particles adsorbed onto the wax surface of this colloidosome, and (d) the colloidosome modified by aminopropylsilane (APS). The particle diameter was 1.5 μm.

particles adsorbed to form colloidosomes[16] (i.e., close-packed monolayers). Even after cooling to room temperature, which involved some disruptive volume shrinkage of the wax phase, the monolayer surface coverage remained high (Figure 2a). When the oil phase solidified to a wax, particles were locked in place and ceased to rotate. An examination of broken wax emulsions showed that >99% of the particles were located at the emulsion surface (Figure 2b), having been adsorbed to this surface from prior dispersion in the wax phase. This behavior left nearly all particles accessible for the chemical reactions described below. For the particles shown in Figure 2c, quantitative analyis of the average fraction of covered particle surface showed that the contact angle against water was approximately 40° at room temperature, which agrees well with the literature value of 37°.[15]

The solidified emulsions survived multiple washings, suggesting good mechanical stability. SEM images, after chemical modification of the outside surfaces by aminopropylsilane (APS) in methanol, showed reproducible shape and contact angles (Figure 2d). Most importantly, nearly all particles continued to remain at the interface, indicating fairly strong adsorption between silica particles and the wax surface. This is what enabled sequential chemical modifications on these adsorbed particle surfaces.

To produce bipolar particles (cationic on one side and anionic on the other side), first the outer surface was modified by labeled APS to create amino-terminated self-assembled monolayers, leaving a positive charge on this side and a negative electrical

charge on the other side of the sphere, because silica is negatively charged at neutral pH.

To produce the colloidal analogue of a surfactant (charged on one side and hydrophobic on the other), after APS chemical modification of the outer surface, the inner surface was allowed to react with OTS to create a methyl-terminated self-assembled monolayer.

Figure 3 summarizes tests showing that the asymmetric surface modification was successful. First, we compared unmodified and treated silica particles with respect to surfactant behavior. Unmodified silica particles failed to adsorb to a planar hydrophobic surface (OTS on quartz), as shown in Figure 3a, yet considerable adsorption was observed when particles treated to be hydrophobic on the second side were exposed to these same hydrophobic surfaces (Figure 3b). This not only confirmed the Janus geometry of the particles but also showed that silica surfaces originally protected by wax were still active for further chemical reaction.

Other tests were performed to investigate what fraction of particles were actually successfully modified in Janus fashion as opposed to the alternative possibility that, in principle, they might have been located in the wax or water phase rather than at the liquid−liquid interface of the emulsion. To this end, we compared optical images (Figure 3c) and fluorescence images (Figure 3d) of the spatial position of particles adsorbed to this planar hydrophobic surface. One observes that the same particles show up in both images, the only exception being one particle at the bottom left corner of Figure 3c. We conclude that this anomalous particle failed to be labeled as fluorescent because

(16) Noble, P. F.; Cayre, O. L.; Alargova, R. G.; Velev, O. D.; Paunov, V. N *J. Am. Chem. Soc.* **2005**, *127*, 6271. Dinsmore, A.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006.
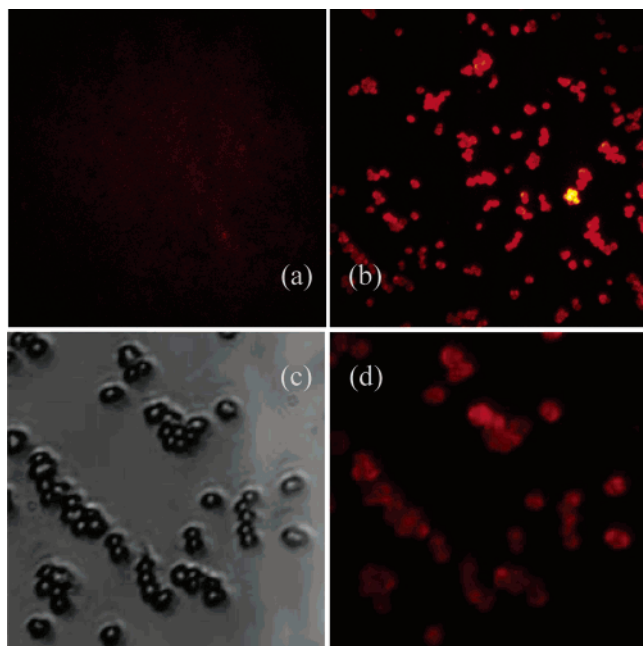
Figure 3. Tests showing that Janus chemical modification was achieved efficiently. (a) Epifluorescence image of chemically unmodified silica particles exposed to a hydrophobic, methyl-terminated (OTE) planar surface. No fluorescence is observed, denoting that particles did not adsorb. (b) Epifluorescence image of Janus chemically modified particles exposed to this same surface. Note that the intensity scales in panels a and b are the same. (c) Phase contrast microscope image of a section of a hydrophobic surface to which chemically modified particles have been allowed to adsorb. (d) Epifluorescence image of the same surface area as in panel c. One sole particle (bottom left corner of the phase contrast image) appears in panel c but not in panel d. It is located in the interior of the colloidosome rather than at the liquid−liquid interface, but quantification shows that it comprised approximately 1% of the total particles. The particle diameter was 1.5 μm.

in the original emulsion it was located within the waxy phase. In this location, it could not be modified by APS but could be modified by OTS, resulting in a uniformly hydrophobic particle that adsorbed to the hydrophobic surface without fluorescence emission. We emphasize that anomalous behavior of this kind was rare. Examples of this kind comprised approximately 1% of the particles that we observed.

Additional tests to check the efficacy of Janus surface chemical modification were based on the idea that if one sole side of the particles was truly fluorescent then this should be observed in a fluorescence image. Figure 4 shows a time sequence of epifluorescence images demonstrating that the bipolar particles rotated in an aqueous suspension. The context is work by Kopelman and co-workers showing that a Janus particle, if coated on one hemisphere with a thin metal coating, displays high fluorescence when the metal coating is oriented away from the illuminating light and low fluorescence when it faces the illuminating light.[4] Because the occluding hemispheres are not metal in the present experiments, they block fluorescence less efficiently, yet nonetheless we observed asymmetric fluorescence emission profiles according to which side of the colloidal particle faced the excitation laser. Figure 4a shows a fluorescence image illustrating this. The silica particles are opaque, and because of the asymmetric coating by the dye, the particles display fluorescence whose intensity differs according to their orientation with respect to the illumination direction, in expected Janus fashion. Going beyond this by tracking how the fluorescence emission of individual particles changed with elapsed time, we
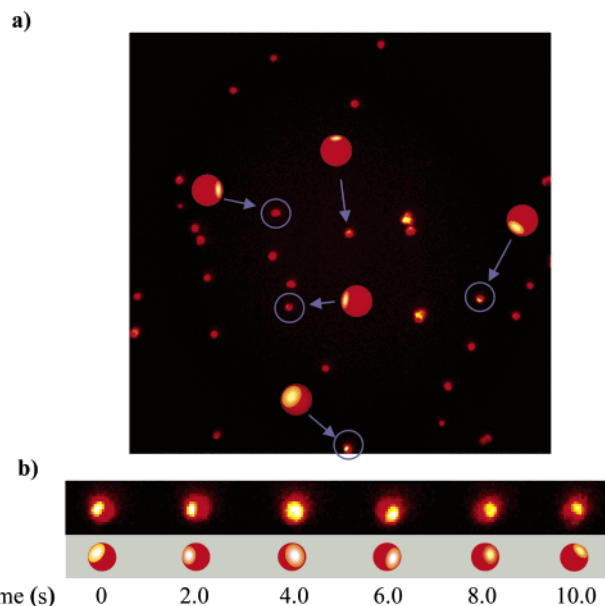

Figure 4. Epifluorescence images that demonstrate the rotation of Janus-modified particles in an aqueous suspension. They are positively charged around the sphere but fluorescent on one hemisphere only. (a) In an image of an ensemble of particles in a Brownian suspension, some are highly fluorescent, and others are less fluorescent, showing that their fluorescent hemispheres have different angles of orientation with respect to illumination and the camera. (b) Time-dependent rotation in an aqueous suspension of a single particle. Images of fluorescence intensity (red) are shown at several values of elapsed time, demonstrating the rotation of the particle. The particle diameter was 1.5 μm.

observed a time-dependent modulation of fluorescence emission. Figure 4b illustrates a sequence of snapshots for one typical particle. At different times, the particle rotated, by Brownian motion, to different orientations. In this situation, a tracking algorithm can be used to quantify the rotational diffusion coefficient.[17]

Exploring the robustness of these colloidosome-based methods, we confirmed these findings using two sizes of silica particles, 800 nm and 1.5 μm diameters, obtained from two different providers. Methods to generalize this approach to smaller particles are under development and will be reported subsequently.

Outlook

A simple, generalizable, and inexpensive strategy to produce large quantities of Janus particles has been described. The advantages of this fabrication approach are threefold. First, the process is solution-based with ~50% yield. The benchtop experiments performed to date have allowed 0.1 g of particles to be made in one batch. This is 2 orders of magnitude larger than the traditional approach to form Janus particles using the chemical modification of particles localized on monolayer surfaces.

Second, the emulsion process that forms the basis of this synthesis strategy is achieved simply by mechanical mixing for a short time. The resulting emulsions are mechanically rigid and stable in moderately aggressive chemical environments. The scale-up ease and low cost of production show how to make particles produced by this method, such as bipolar particles (positive charge on one side, negative charge on the other side) and surfactant particles (electrically charged on one side, hydrophobic on the other side), available in large quantities for various applications.

(17) Anthony, S. M.; Hong, L.; Kim, M.; Granick, S. *Langmuir*, in press, 2006. Hong, L.; Anthony, S. M.; Granick, S. *Langmuir* **2006**, *22*, 7128.

Third, the surface coverage of modified chemical makeup is controlled thermodynamically. Compared to alternative methods where the surface coverage of modified chemical makeup is controlled kinetically, this is easier to achieve, and the mono-dispersity of surface coverage is better from batch to batch because the area coated depends thermodynamically on the contact angle between the particle surface and the liquids used in the emulsion. Though we do not yet have a reliable way to quantify the monodispersity of the resulting surface chemical modification, we believe it to be reasonably monodisperse on the basis of observing the three-phase contact angles from SEM measurements.

Looking to the future, this fabrication approach can be extended to much smaller particles. Also, it can be extended to particles other than the silica particles described here because theory predicts[15] that particles as small as 100 nm in diameter also stabilize emulsions. By judicious adjustment of the choice of liquids used to form the emulsion, especially their surface tension, and by employing this choice with judiciously selected particles of different surface energy, theoretical considerations show that different three-phase contact angles will result.[15] These considerations show how, in the future, to vary systematically the relative sizes of the surface chemical patches created by this approach to fabricate Janus particles.