

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23182240>

# Solvent-Free Synthesis of Janus Colloidal Particles

ARTICLE *in* LANGMUIR · OCTOBER 2008

Impact Factor: 4.46 · DOI: 10.1021/la800895g · Source: PubMed

---

CITATIONS

70

---

READS

48

5 AUTHORS, INCLUDING:



Jeffrey S Moore

University of Illinois, Urbana-Champaign

428 PUBLICATIONS 27,137 CITATIONS

SEE PROFILE

# Solvent-Free Synthesis of Janus Colloidal Particles

Shan Jiang,<sup>†</sup> Mitchell J. Schultz,<sup>‡</sup> Qian Chen,<sup>†</sup> Jeffrey S. Moore,<sup>\*,†,‡</sup> and Steve Granick<sup>\*,†,‡</sup>

Department of Materials Science and Engineering and Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

Received March 21, 2008

Taking advantage of the quick and efficient access of vapor to surfaces, a simple, solvent-free method is demonstrated to synthesize Janus colloidal particles in large quantity and with high efficiency. First, at the liquid–liquid interface of emulsified molten wax and water, untreated silica particles adsorb and are frozen in place when the wax solidifies. The exposed surfaces of the immobilized particles are modified chemically by exposure to silane vapor and, in principle, subsequent dissolution of the wax opens up the inner particle surface for further chemical modification. Applying this scheme, this paper describes the production of amphiphilic Janus particles (hydrophobic on one side, hydrophilic on the other) and dipolar Janus particles (positively charged on one side, negatively charged on the other). Janus geometry is confirmed by fluorescence microscopy and flow cytometry. Amphiphilic Janus particles are found to adsorb strongly to the water–oil interface, whereas dipolar particles assemble into chains in the aqueous phase.

## Introduction

Janus particles, whose surface chemical composition differs on two sides (“Janus” as suggested by de Gennes<sup>1</sup>), are of emerging interest from various scientific and applications standpoints. It has been demonstrated that Janus particles can introduce asymmetric interactions that induce particles to self-assemble.<sup>2</sup> These self-assembled structures differ from the structures formed by homogeneous particles and can be used as potential building blocks for novel three-dimensional structures.<sup>3</sup> Indeed, the assembly of larger (non-Brownian) objects has already been implemented.<sup>4</sup> It has also been predicted that Janus particles with well-defined geometry will better stabilize water–oil emulsions than homogeneous particles.<sup>5</sup>

The novelty of this paper, to produce Janus particles efficiently and in large quantity, improves upon solvent-based methods reported recently in this laboratory.<sup>6</sup> In the current state of the art, the most common method to synthesize Janus particles is to selectively modify homogeneous precursor particles through a protect-and-release process.<sup>7</sup> 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 substrate is protected from modification, and the other side is modified chemically. Sputtering<sup>8</sup> and stamp coating<sup>9</sup> have been used to modify the unprotected side of these monolayer surfaces. These approaches offer good control over the surface area that sustains chemical modification, but only a

few milligrams of Janus particles are produced in one batch. To produce larger quantities, elegant microfluidic approaches have been used; however, the particle size at present is limited to 10  $\mu\text{m}$  or larger in diameter.<sup>10</sup> In another recent development, Janus particles in the micron to submicron size range were successfully synthesized by electrodynamic jetting; however, the size distribution was relatively broad.<sup>11</sup>

To overcome these limitations, chemical modification of particles at liquid–liquid interfaces has been reported.<sup>12</sup> In order to prohibit rotation of particles during chemical modification, a Langmuir–Blodgett (LB) trough has been used to compress particles adsorbed at an interface into a close-packed monolayer; Janus particles of nanometer size were successfully synthesized using this method. However, the use of a monolayer that is confined by an LB trough limited the quantity. One way to generate a large amount of interface within a small volume is emulsification, given the fact that particles generally adsorb tightly to water–oil interfaces.<sup>13</sup> Recent attempts<sup>14</sup> to take this strategy have had to contend with rotation and wobbling of particles at the interface during chemical modification, which can smear the geometry of the Janus particles. Also, we note that selective surface modification using solvent-based methods is a delicate matter for two reasons. First, in order to ensure a Janus geometry, the reactants must remain in one sole phase. Second, because the areas of the particle exposed into the respective water and oil phases depend on the contact angle with these liquid phases, it is imperative that the contact angle does not change during the process of chemical modification. For these reasons, Janus particles with well defined geometry can only be obtained with very special chemical reactions.

A recently reported strategy to overcome these issues is to work with *solidified* emulsions.<sup>6</sup> First, silica particles are adsorbed to the liquid–liquid interface of an emulsion, molten paraffin wax having been selected as the oil phase. Then the emulsions

\* Corresponding author.

<sup>†</sup> Department of Materials Science and Engineering.

<sup>‡</sup> Department of Chemistry.

(1) de Gennes, P. G. *Rev. Mod. Phys.* **1992**, *64*, 645–648.

(2) Hong, L.; Cacciuto, A.; Luijten, E.; Granick, S. *Nano Lett.* **2006**, *6*, 2510–2514.

(3) Zhang, Z. L.; Glotzer, S. C. *Nano Lett.* **2004**, *4*, 1407–1413. (a) van Blaaderen, A. *Nature* **2006**, *439*, 545–546. (b) Van Workum, K.; Douglas, J. F. *Phys. Rev. E* **2006**, *73*, 031502. (c) Glotzer, S. C.; Solomon, M. J. *Nat. Mater.* **2007**, *6*, 557–562.

(4) Terfort, A.; Bowden, N.; Whitesides, G. M. *Nature* **1997**, *386*, 162–164.

(5) Onoe, H.; Matsumoto, K.; Shimoyama, I. *Small* **2007**, *3*, 1383–1389.

(6) Binks, B. P.; Fletcher, P. D. I. *Langmuir* **2001**, *17*, 4708–4710. (a) Jiang, S.; Granick, S. *J. Chem. Phys.* **2007**, *127*, 161102.

(7) Hong, L.; Jiang, S.; Granick, S. *Langmuir* **2006**, *22*, 9495–9499.

(8) Perro, A.; Reculusa, S.; Ravaine, S.; Bourgeat-Lami, E. B.; Duguet, E. *J. Mater. Chem.* **2005**, *15*, 3745–3760.

(9) Takei, H.; Shimizu, N. *Langmuir* **1997**, *13*, 1865–1868.

(10) Cayre, O.; Paunov, V. N.; Velev, O. D. *J. Mater. Chem.* **2003**, *13*, 2445–2450.

(10) Nie, Z. H.; Li, W.; Seo, M.; Xu, S. Q.; Kumacheva, E. *J. Am. Chem. Soc.* **2006**, *128*, 9408–9412. (a) Dendukuri, D.; Hatton, T. A.; Doyle, P. S. *Langmuir* **2007**, *23*, 4669–4674.

(11) Roh, K. H.; Martin, D. C.; Lahann, J. *Nat. Mater.* **2005**, *4*, 759–763.

(12) Pradhan, S.; Xu, L. P.; Chen, S. W. *Adv. Funct. Mater.* **2007**, *17*, 2385–2392.

(13) Binks, B. P. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21–41.

(14) Suzuki, D.; Tsuji, S.; Kawaguchi, H. *J. Am. Chem. Soc.* **2007**, *129*, 8088–8089.

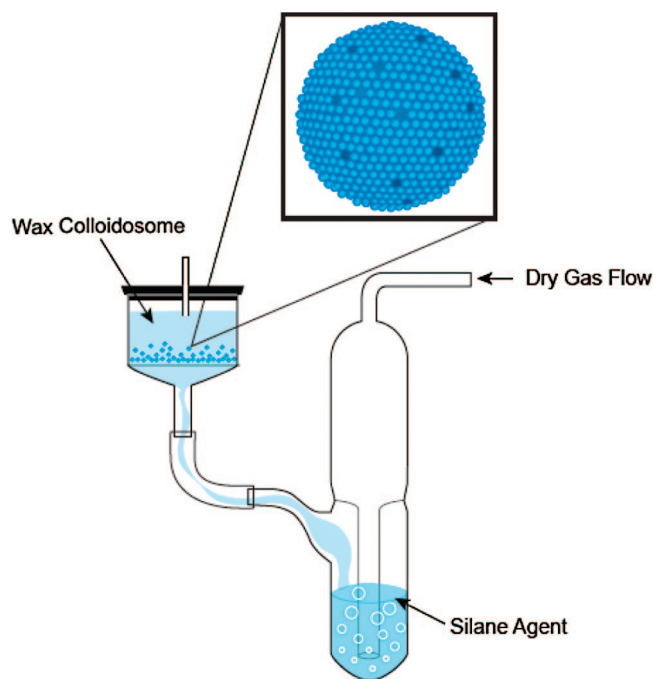
are cooled to room temperature to “lock” particles at frozen wax–water interfaces, preventing particle rotation. The resulting colloidosomes are sufficiently stable, mechanically and chemically, to be washed and modified chemically by reaction in solution. After chemical modification of the exposed side of the adsorbed particles, the wax can be dissolved in organic solvent, and the resulting particles can be further modified chemically. The final geometry of the Janus particles is determined by the contact angle of particle at the emulsion interface. The contact angle can be varied systematically by adding a cationic surfactant,<sup>15</sup> since the surfactants will adsorb onto the negative silica particle surface, changing the effective surface hydrophobicity. However, these methods suffer from two limitations. First, it is found that the chemical modification of particles at the water–wax interface can cause a significant number of weakly attached particles to fall off the colloidosome, thereby lowering yield and potentially causing the product to be a mixture of Janus particles and unfunctionalized particles. Second, the experience of a generation of work with self-assembled monolayers (SAMs) on flat surfaces shows that using solvent-based methods to produce hydrophobic SAMs of high quality is a delicate matter, requiring strict attention to chemical protocol, and not easy to implement.

Seeking to overcome these limitations, we have turned to chemical surface modification from the vapor phase. On physical grounds, we anticipated vapor deposition to have quick and efficient access to surfaces when solid spheres are packed close together, even though most previous use of vapor surface chemical modification involves monolithic flat surfaces.<sup>16</sup> In this paper, we describe methods to implement this strategy, and present characterization of the resulting Janus particles.

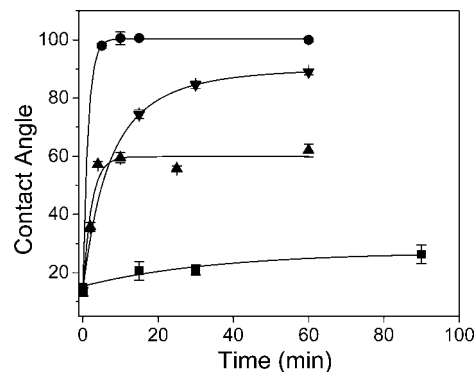
## Results and Discussion

**Vapor-Phase Deposition.** In order for this strategy to succeed, it must be implemented at ambient temperature since heat would melt the solidified wax. To test what types of monomers can be deposited effectively at room temperature, we began by forming monolayers on Si(100) surfaces. A simple, homemade setup was designed as shown in Figure 1. Dry nitrogen or argon gas was bubbled through liquid silane reagent at room temperature. The outlet of the bubbler was attached to a glass frit fitted with a small outlet needle to allow the gas to escape. A freshly cleaned and dried Si(100) wafer was placed facing down on the frit and exposed to the silane vapor. The contact angle change of oxidized Si(100) was monitored at various times to monitor the quality of the resulting self-assembled monolayer.

Results from these screening experiments are summarized in Figure 2. Contact angle is plotted against reaction time. For silanes with low boiling point—dichlorodimethylsilane (DCDMS,  $T_b = 70\text{ }^\circ\text{C}$ ) and aminopropyltrimethylethoxysilane (APDMES,  $T_b = 78\text{ }^\circ\text{C}$ )—the SAM formation occurred rapidly, within 10 min. Silane APDMES was used instead of the more common (3-aminopropyl)triethoxysilane (APS), because it is reported that APDMES forms the more perfect SAM on silicon wafers.<sup>17</sup> However, deposition was slower for silanes with higher boiling point, presumably owing to a combination of lower vapor pressure and lower surface mobility after adsorption to the silicon wafer. For octyltrichlorosilane ( $T_b = 233\text{ }^\circ\text{C}$  at 731 mmHg), the deposition required approximately 1 h to saturate, and for octadecyltrichlorosilane (OTS,  $T_b = 223\text{ }^\circ\text{C}$  at 10 mmHg), the



**Figure 1.** Schematic plot of the setup for vapor deposition of reagent to closely packed silica spheres attached to wax colloidosomes. The flow of dry argon or nitrogen brings the silane vapor in contact with the colloidosome, which is placed over a glass frit and gently rolled every 5–10 min. In this way the exposed surface of particles is modified chemically without the use of solvent.



**Figure 2.** Contact angle change versus vapor deposition time for four different silanes exposed to oxidized silicon wafers using the scheme summarized in Figure 1. From top to the bottom, the silanes are DCDMS (circles), octyltrichlorosilane (down-triangles), APDMES (up-triangles), and OTS (squares). Note that DCDMS (methyl-terminated) and APDMES (amine-terminated) are successful at rapid chemical surface modification. The lines are guides to the eye.

deposition proceeded even more slowly. Among the methyl-terminated silane reagents, only SAMs formed from DCDMS produced the contact angle of  $100^\circ$ , which agrees well with the contact angle of surface modified by the solvent-based method.<sup>18</sup> When these modified silicon wafers were ultrasonicated in acetone for 30 min, no change in the contact angle was observed, thus confirming that the silanes were chemically bonded to the surface.

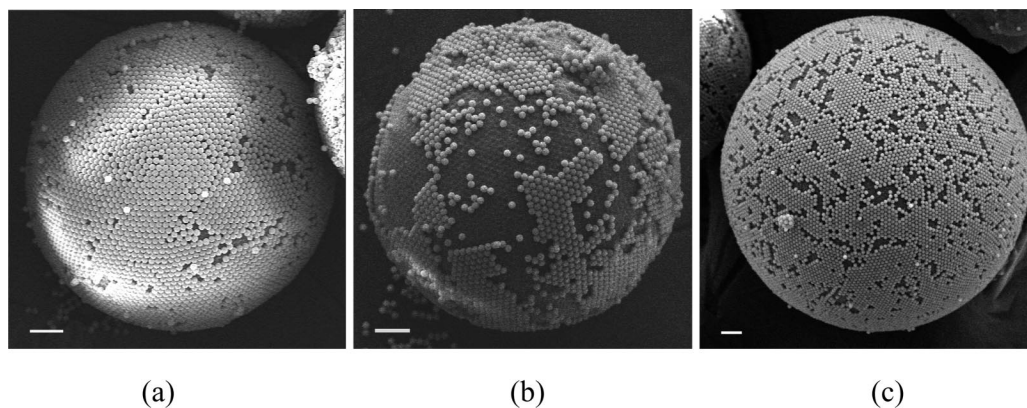
Extending these experiments to the chemical surface modification of silica spheres embedded within wax colloidosomes, we focused on those silanes that were most effective in the screening experiments in Figure 2: DCDMS and APDMES. Performing this same deposition on the colloidosome is envisioned to result in the formation of a Janus particle that should act as a colloidal surfactant: hydrophilic on the wax side owing to native silanol groups, and hydrophobic on the other side owing

(15) Jiang, S.; Granick, S. *Langmuir* **2008**, *24*, 2438–2445.

(16) Pavlovic, E.; Quist, A. P.; Gelius, U.; Oscarsson, S. *J. Colloid Interface Sci.* **2002**, *254*, 200–203.

(17) White, L. D.; Tripp, C. P. *J. Colloid Interface Sci.* **2000**, *232*, 400–407.

(18) Trau, M.; Murray, B. S.; Grant, K.; Grieser, F. *J. Colloid Interface Sci.* **1992**, *148*, 182–189.



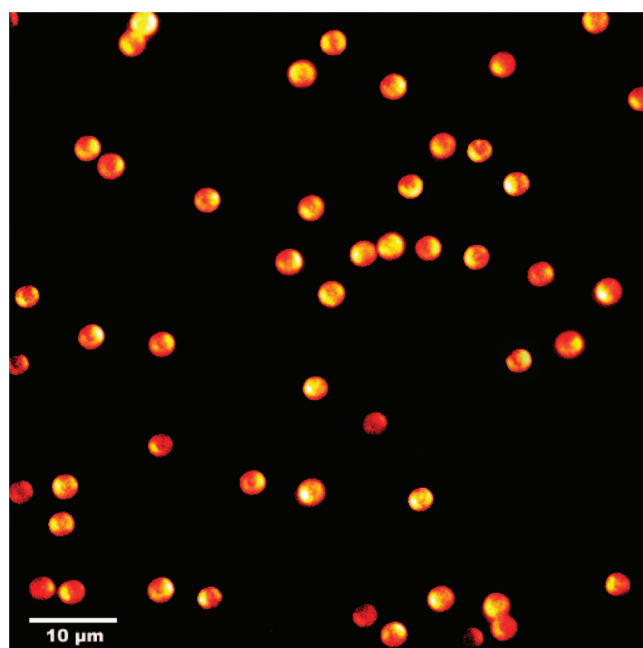
**Figure 3.** SEM images of colloidosomes: (a) before chemical modification; (b) modified to be hydrophobic using solvent-based methods described elsewhere;<sup>15</sup> (c) modified to be hydrophobic using vapor-phase deposition using the method described in Figure 1. Surface modifications were performed at room temperature using wax whose melting point (see Experimental Section) was 53–57 °C. Particle diameter is 2  $\mu\text{m}$ . Scale bar is 10  $\mu\text{m}$ .

to deposition of the hydrophobic SAM. On the other hand, the deposition of APDMES would result in a Janus particle that is dipolar: anionic on the wax side owing to native silanol groups on the silica, cationic on the other side owing to deposition of the amine-terminated SAM. These types of particles could have interesting self-assembly behavior.<sup>2</sup>

The improved findings from vapor-phase deposition, as compared to the solvent-based deposition reported earlier from this laboratory,<sup>15</sup> became clear from comparisons of scanning electron microscopy (SEM) images. In Figure 3, the close-packed coverage of particles on the wax colloidosome surface before surface chemical modification (panel a) was severely disturbed by solvent-based surface chemical modification, which caused many particles to be swept off the colloidosome (panel b). It is possible to remove these detached particles, but to do so requires multiple filtration and further rinsing, which further lowers the efficiency of this method. In contrast, after vapor-phase deposition, nearly all particles remain on the wax colloidosome surface (panel c).

In fairness, we note that efficacy of the solvent-based chemical modification can be improved in two ways. First, the escape of particles can be alleviated by using wax with a higher melting point than the relatively low wax melting point (53–57 °C) selected for these experiments to highlight the versatility of the vapor-phase approach. Second, we find that the escape of particles can be alleviated by performing procedures at lower temperatures, as low as 0 °C, rather than ambient temperature. Nonetheless, under the optimal conditions, it is estimated that only 50% or less of particles originally on the wax colloidosome surface can survive solvent-based surface chemical modification.

**Testing the Efficacy of Janus Surface Chemical Modification to Produce Amphiphilic Particles.** In order to use single-particle fluorescence microscopy to determine whether Janus particles were successfully obtained, fluorescent dyes were attached to the native silanol groups of these silica particles following vapor-phase deposition after dissolving away the wax, using methods described in the Experimental Section. Silane APS was used as the linker instead of APDMES, since high surface density and other measures of monolayer quality are not relevant for the efficacy of fluorescence labeling. To the extent that selective chemical surface modification had been successful, fluorescent dyes in these experiments should selectively bind only to the limited portion of the particle, previously embedded within the wax, which had been protected from vapor-phase surface chemical modification. A typical epifluorescence image



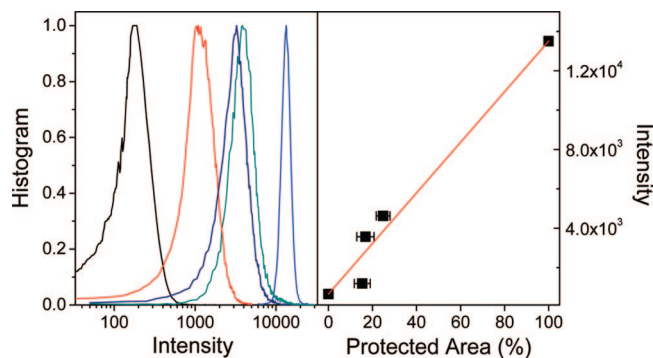
**Figure 4.** An illustrative epifluorescence image of silica particles that, following vapor-phase surface chemical modification with DCDMS, were removed from the wax by dissolving the wax, and to whose native silanol groups a fluorescent dye was attached. To the extent that selective chemical surface modification had been successful, fluorescence should come from the portion of the particle, previously embedded within the wax, which had been protected from vapor-phase surface chemical modification. The image contrast has been tuned to highlight the Janus geometry. Particle diameter is 3  $\mu\text{m}$ .

of the resulting particles is illustrated in Figure 4; statistical analysis of this and other images shows that more than 90% of the particles possessed the desired Janus geometry. While it is true that, in Figure 4, some of the particles appear to display high fluorescence at more than the expected single location on a given bead, this is believed to be an artifact resulting from the internal reflection of light from the backside of these beads, since silica particles are translucent at the green (532 nm) laser wavelength used to acquire these images.

Flow cytometry, a high-throughput technique commonly used in biology to analyze cells,<sup>19</sup> is readily adapted to test the purity of Janus particles whose diameter exceeds 1  $\mu\text{m}$ . In this

(19) Givan, A. L. *Flow Cytometry: First Principles*; Wiley-Liss: New York, 2001.





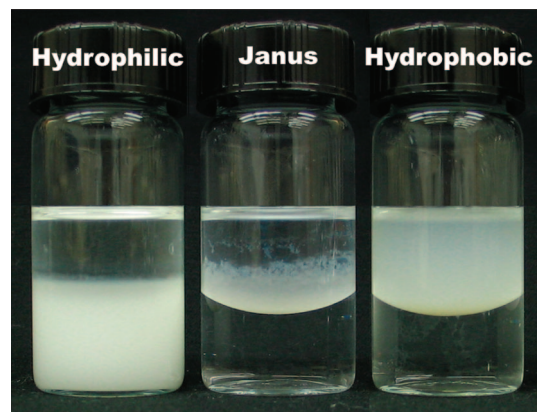
**Figure 5.** Histogram of fluorescent intensity measured by flow cytometry when the area coated by fluorescent dye was varied. Left panel: peaks from left to right show relative fluorescence intensity for homogeneously hydrophobic particles (black), Janus particles with 15% protected area (red), Janus particles with 17% protected (navy), Janus particles with 25% protected area (green) and homogeneously hydrophilic particles (blue). Right panel: testing linearity between fluorescence intensity and the protected area.

characterization approach, using hydrodynamic flow in the usual flow cytometry manner, the particles traverse a laser focus one-by-one, and the histogram of fluorescence intensity is recorded automatically. As shown in Figure 5 (left panel), a single peak was obtained when putative amphiphilic particles were tested. This indicates that nearly all particles indeed possessed a uniform Janus geometry since a mixture with unfunctionalized particles or particles with different Janus geometry would have produced additional fluorescence peaks.

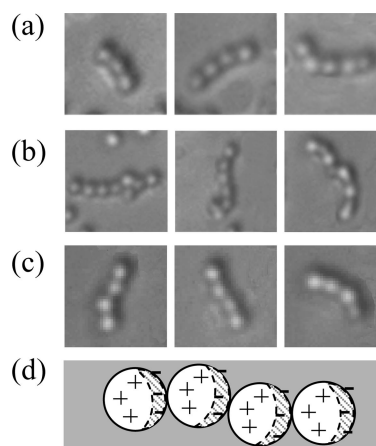
It is natural to expect that the larger the area of the particle protected by wax, the higher should be the average fluorescence intensity, but the flow cytometry technique proved to be insufficiently quantitative to test this directly. In investigating this question, first the wax-protected area was calculated from the depth at which the particles were embedded within the wax colloidosomes. This is readily calculated, as described in detail elsewhere,<sup>15</sup> from examining in SEM images the size of holes in the wax left by escaped particles. In Figure 5 (right panel), the fluorescence intensity is plotted against protected area, which is the area available to be coated by fluorescent dye. One sees that the relationship is not strictly linear in spite of a general trend toward higher fluorescence intensity, the higher the area available to be coated by dye. The fluorescence intensity can be affected by many additional factors, such as rotation of the particles during data acquisition, photo bleaching of the dye molecules, and especially the labeling efficiency, but a quantitative analysis is not offered at this time.

For smaller particles, too small to resolve optically using epifluorescence imaging or flow cytometry, we resorted to the less direct approach of simply observing where they segregated after being dispersed in a mixture of water and toluene. It was found that unmodified silica particles dispersed well only in the water phase, as expected since their surface silanol groups render them hydrophilic (Figure 6, left vial). Particles modified using DCDMS were found to disperse well only into the toluene phase (Figure 6, right vial), as expected if chemical surface modification had rendered them to be hydrophobic. However, DCDMS-coated Janus particles adsorbed strongly along the water/toluene interface (Figure 6, middle vial). This provides evidence that Janus geometry were achieved by vapor phase deposition for particles as small as 500 nm.

**Testing the Efficacy of Janus Surface Chemical Modification to Produce Dipolar Particles.** Dipolar particles, positively charged on one side and negatively charged on the other, self-



**Figure 6.** Unmodified, Janus, and fully modified silica particles dispersed in a mixture of water and toluene. The unmodified particles partitioned into the water phase (left panel), and the homogeneously hydrophobic particles partitioned into the toluene phase (right panel). Amphiphilic Janus particles quickly adsorbed at the water–toluene interface and would not disperse well into either water or toluene phase (middle panel). Particle diameter is 500 nm.



**Figure 7.** Phase contrast microscope images of dipolar particles self-assembled in deionized water and sedimented to the bottom of a hydrophobic sample cell. (a) Particles self-assemble into chains, commonly consisting of three to five particles. (b) Occasionally, particles assemble into longer chains consisting of 6–8 particles. (c) These chain structures, although sedimented to the bottom of the sample cell, change conformations by Brownian motion. (d) Cartoon showing the probable mechanism of self-assembly by head-to-tail aggregation of positive and negative charged regions. Particle diameter: 1  $\mu\text{m}$ .

assemble into clusters when they are dispersed in aqueous medium. This laboratory had reported an earlier experimental study of this phenomenon but, as it was limited in scope by the small quantity of particles that could be prepared using the monolayer-based synthesis, used in that study, of the needed Janus geometry.<sup>2</sup> To synthesize large quantities of samples is of evident interest.

The emulsion-based methods presented in this paper were adapted to this purpose. The synthesis was accomplished using APDMES in the setup described in Figure 1. After dissolving the wax and washing it away, the resulting Janus particles, dispersed in deionized water, were observed to self-assemble into chains (Figure 7). The chain length varies from three to eight particles. Interestingly, although these chain structures sedimented to the bottom of the hydrophobic sample cell, they were not fixed to it, but instead were observed to swim and change their conformation under the microscope, as illustrated in Figure 7c. The probable mechanism of self-assembly, sketched in Figure 7d, is head-to-tail assembly of positively and negatively

charged regions of the particles, but quantitative analysis of self-assembly behavior is not the focus of this paper. Whether clusters form as we reported previously, or strings form as found in the present experiments, appears to depend on the Janus balance, in this instance on the relative charge on the two sides of the particles.

### Conclusions

A simple and effective method to synthesize Janus colloidal particles with different geometry in large quantity has been demonstrated. The key step is to modify the exposed area of silica particles on wax colloidosome surface by silane vapor deposition. Looking to the future, this method can be easily adapted to versatile chemistry. More specific interaction can be introduced to the Janus particles, i.e., DNA chains can be grafted via the amino group on the positive charged side on the dipolar Janus particles. The method also provides the essential preparation for the systematical study of the self-assembly of Janus particles in the bulk and interface and emulsions stabilized by Janus particles.

### Experimental Section

**Chemicals.** Monodisperse silica spheres from different vendors were used. Particles larger than 1  $\mu\text{m}$  in diameter were purchased from Tokuyama, Japan and used as received. Since these particles were synthesized by the Stöber method, their surfaces were fully covered by silanol groups. Particles 500 nm in diameter were purchased from Fiber Optic Center, Inc., U.S.A. These particles were pretreated by Piranha solution in order to fully clean and activate the particle surface. Paraffin wax with melting point ranging from 53 to 57  $^{\circ}\text{C}$  was purchased from Aldrich. OTS (90%), didodecyltrimethylammonium bromide (DDAB, 98%), (3-aminopropyl)dimethylethoxysilane (APMES), APS (99%), DCDMS (99.5%), and octyltrichlorosilane (97%) were purchased from Aldrich and used without further purification.

To produce fluorescent-labeled APS, rhodamine B isothiocyanate (RITC) or fluorescein isothiocyanate isomer (FITC) was attached to APS using a procedure described in the literature.<sup>20</sup>

**Synthesis of the Wax Colloidosome.** First, 1.5 g of silica spheres 3  $\mu\text{m}$  in diameter (0.3 g for silica particles 500 nm in diameter) were dispersed in 9 g of paraffin wax at 75  $^{\circ}\text{C}$  by stirring. The wax suspension was then mixed with 22.5 mL of DDAB water solution with concentration varying from 0.01 to 0.1 mg/mL. The mixture was stirred at 1500 rpm for 15 min to produce an emulsion and then cooled to room temperature, at which time the paraffin wax became solidified. The resulting solidified emulsions were then washed with a 0.1 M solution of  $\text{NaCl}_{(\text{aq})}$  followed by deionized water to remove unattached or weakly attached particles. The colloidosomes were then dried under vacuum (1 mmHg) for 2 days.

**Vapor Deposition.** The setup of the vapor deposition is shown in Figure 1. Dry nitrogen or argon was bubbled through ca. 5 mL of silane for 30 min. This results in the silane vapor being carried through the frit that supports the colloidosome. In order to encourage homogeneous surface chemical modification, the funnel was gently

rolled every 5–10 min to move colloidosomes around. The bubble speed was chosen as ca. 2–3 bubbles/s. After exposure to the silane vapor for the needed time, a dry nitrogen flow was passed through the frit colloidosome for ca. 30 min to blow away any residual silane vapor.

After the reaction, to release the modified silica particles from the colloidosomes, the wax was dissolved in chloroform at room temperature. Particles were then washed with 300 mL of ethanol by 10 cycles of centrifuging and redispersing.

**Characterization.** SEM (JEOL6060 LV) was used to image the colloidosome in the Center for Microanalysis of Materials in the Seitz Materials Research Laboratory at the University of Illinois. Prior to imaging, a thin layer (15 nm) of gold was evaporated onto the colloidosomes to render them electrically conductive, thus avoiding surface charging under the electron beam. By measuring the size of voids left by particles that escaped from the wax surface during the processing steps, the three-phase contact angle was determined using methods described previously.<sup>15</sup>

To label particles for fluorescence imaging,  $\sim 10^8$  particles were dispersed in 5 mL of ethanol solution containing 1 mM APS–FITC or APS–RITC. The reaction proceeded for 30 min under ultrasonication.

For epifluorescence imaging, the home-built optics employed a Zeiss Axiovert 200 microscope. A Nd:YAG laser (532 nm) was focused at the back focal point of a 63 $\times$  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 0.05 s for 800 frames. APS–RITC-labeled particles were used in this experiment.

Flow cytometry measurement was used to measure the histograms of the fluorescence intensity, using the commercial BD LSR II system located in the Carver Biotechnology Center at the University of Illinois. In a typical experiment, particles were dispersed in aqueous solution at the concentration of ca. 10 mg/mL. The small fraction of dimers formed by self-assembly was filtered out by the software provided with the equipment and was not included in the analysis. APS–FITC labeled particles were used in this experiment to give fluorescence under laser excitation at 488 nm.

In the observation of self-assembly of dipolar particles, dipolar particles immediately adsorb tightly onto untreated glass because of the electrostatic attraction between opposite charges. To avoid this, the glass sample cell was rendered hydrophobic using DCDMS.

**Acknowledgment.** This work was supported by the U.S. Department of Energy, Division of Materials Science, under Award No. DE-FG02-07ER46471 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana–Champaign. Q.C. acknowledges the Donors of the Petroleum Research Fund, administered by the American Chemical Society, #45523-AC7. This material is based upon work (partially) supported by the Center of Advanced Materials for the Purification of Water with Systems, a National Science Foundation Science and Technology Center, under Award No. CTS-0120978.

LA800895G

(20) Verhaegh, N. A. M.; Vanblaaderen, A *Langmuir* **1994**, *10*, 1427–1438.