Simple fabrication of snowman-like colloids

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ARTICLE INFO	ABSTRACT
	Anisotropic colloidal particles consisting of different compositions and geometry are useful for various applications. These include optical biosensing, antireflective coatings and electronic displays. In this work we demonstrate a simple and cost-effective method for fabricating anisotropic colloidal particles bearing a snowman-like shape. This is achieved by first settling the positively-charged polystyrene latex (PSL) colloids and negatively-charged silica colloids in deionized water onto a glass substrate, forming hetero-doublets. The temperature is then raised above the glass transition temperature of the polymer. As a result, the silica particle spontaneously rises to the top of the PSL particle forming a snowman like structure. We have extended this method to different sizes and shown that the structure of the hybrid particles can be tuned by adjusting the size ratio between the silica and the PSL colloids. The surface coverage of the PSL, and hence of the snowman particles, on the glass substrate can also be varied by changing the ionic strength of the solution during the adhesion of PSL to the glass. © 2012 Elsevier Inc. All rights reserved.

1. Introduction

In the field of colloidal science, much attention has recently been devoted to the synthesis and characterization of anisotropic particles (colloidal particles with anisotropy in shape or chemical composition) owing to their special properties that are different from isotropic particles [1–8]. These anisotropic colloidal particles are not only interesting for a fundamental understanding of colloidal particles in general, but also for various potential applications in material science and bioengineering [9,10]. In particular, there is a growing interest in the field of advanced materials science to synthesize anisotropic particles that combine organic and inorganic parts, for applications in the areas of optics, electronics, protective coatings, catalysis, and sensors [9,11,12].

Towards this direction, the fabrication of snowman-like colloidal particles emerging upward from a surface has been of particular interest [13]. Snowman-like colloidal particles are generally fabricated on a substrate and consist of one particle sitting on top of another. The two constituent particles of a snowman-like assembly are generally of different size and chemical composition. Such structures have been fabricated using seeded emulsion [14–17] or dynamic swelling [18–20] methods. More recently, advanced techniques like layer-by-layer self assembly [13] and asymmetric wet-etching [21] have been reported. Based on the application, snowman particles were made either from single organic constituents such as polystyrene or PMMA (polymethyl-

methacrylate), or made from both organic (polystyrene) and inorganic (silica) parts.

Some of these fabrication techniques require complicated fabrication steps, while others cannot produce the particles in large quantities. In this paper we describe a method for fabricating snowman-like colloids with anisotropy in shape and chemical composition. The process involves adhering polystyrene latex (PSL) particles to glass and then attaching silica microspheres to the PSL particles, forming heterodoublets. The assembly is then heated above the glass transition temperature of polystyrene (~95 °C). The silica particle spontaneously rises to the top of the PSL particle and forms a snowman-like structure. The proposed technique for fabricating snowman-like colloids offers several advantages: (1) The technique is simple and reproducible, (2) is able to assemble two different materials, (3) has high fractional yield, with approximately 85% of the total particles on the glass substrate being snowman-like, (4) is scalable to large areas, (5) has a tunable structure by adjusting the size ratio between the silica and the PSL colloids, and (6) is adjustable in surface coverage of the substrate by changing the ionic strength of the solution. This paper provides the techniques we used to fabricate and characterize the snowmen, and discusses variations that allow one to change the structure of the assemblies on the substrate.
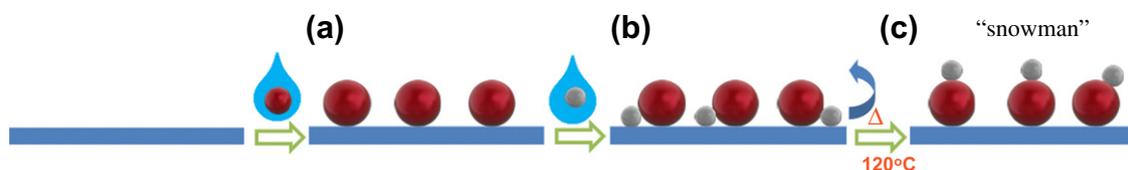
2. Materials and methods

2.1. Materials

Several types of particles were used in this work. Monodisperse, surfactant-free, amine-functionalized polystyrene latex (PSL)

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Fig. 1. Schematic showing the fabrication of snowman-like colloids. (a) Positively-charged PSL particles are adhered to the negatively-charged glass coverslip. (b) Negatively-charged silica particles are adhered to larger PSL particles to form heterodoublets. (c) Heterodoublets are heated in an autoclave at 120 °C for 15 min, forming snowman-like colloids. Upon cooling, the structures are mechanically stable.

microspheres were purchased from Invitrogen. Specifically, 100 nm and 200 nm amine-functionalized PSL microspheres (2% w/v) were used in the experiments described in the paper. Mono-disperse, surfactant-free, 520 nm amidine-functionalized polystyrene latex microspheres (4.2% w/v) were purchased from Interfacial Dynamics Corporation. Monodisperse 35 nm (5.9% w/v), 100 nm (5.6% w/v) and 110 nm (10.0% w/v) silica microspheres were purchased from Bang's Laboratories. Potassium chloride (KCl, MW 74.55) was purchased from Aldrich Chemicals. The plain glass microscope slides, glass coverslips, and the Pyrex Petri dishes were obtained from VWR International. The deionized (DI) water that was used for all experiments and washing steps (Millipore Corp. Milli-Q system) had a specific resistance of 18.1 MΩ cm.

2.2. Instrumentation

Heat treatments were carried out in a consolidated stills and sterilizers steam autoclave (model Steromaster MKII) at 120 °C and 18 psig. The ultrasonicator was from VWR International (model 550T). Field emission electron microscopy images were obtained on a Zeiss SMT 1530 with an accelerating voltage of 1 keV at the Penn State Nanofabrication Facility. A thin film of gold was deposited using the semi core e-gun evaporator at the Penn State Nanofabrication Facility.

2.3. Zeta potentials

The particle zeta (ζ) potentials were measured on a Brookhaven Instruments ZetaPALS (phase analysis light scattering) ζ potential analyzer. The ζ potential of 520 nm amidine functionalized PSL microspheres was 65 ± 0.4 mV. For the 200 nm amine functionalized PSL microspheres, ζ = 36 ± 0.5 mV; for the 100 nm amine functionalized PSL microspheres, ζ = 48 ± 0.8 mV; for the 110 nm silica microspheres, ζ = −37 ± 0.9 mV; for the 100 nm silica microspheres, ζ = −53 ± 0.7 mV; and for the 35 nm silica microspheres, ζ = −45 ± 0.8 mV. All these ζ potential measurements were taken in DI water, which was used in our experiments.

2.4. Fabrication of snowman-like colloidal doublets

Positively-charged amine PSL spheres were first adhered to a glass substrate. 10 mL of DI water was added to a Petri dish that contained a glass coverslip. To this Petri dish, 3.5 µL of 200 nm amine functionalized PSL microspheres were added and the particles were allowed to settle for 12 h. The positively-charged particles adhered to the negatively-charged coverslip due to electrostatic attraction (Fig. 1a). As the particles settled from the bulk to the surface of the glass coverslip, the concentration of the particles increased. Thus the surface concentration of particles was much higher (roughly 50–100 times) than the bulk concentration due to settling. The excess liquid and unsettled particles were decanted off, and the dish was washed 8–10 times with de-ionized (DI) water to remove any unadhered particles. The result was a monolayer of amine PSL particles that were electrostatically

adhered to the glass coverslip surface, with a fractional surface coverage (area covered by the particles on the substrate/area of the substrate) of roughly 0.05.

Next the negatively-charged silica was introduced into the system. 10 mL of DI water and 5 µL of 110 nm silica microspheres were added. The negatively-charged silica was allowed to settle in solution with the amine PSL particles for 12 h, and the result was that we formed silica–amine PSL heterodoublets (Fig. 1b). Addition of excess silica was avoided in this step, since it gives the formation of higher order aggregates. The excess solution was then poured out of the Petri dish, and the adhered particles were washed with DI water to remove any excess silica.

The dish containing the adhered particles in DI water was placed in an autoclave oven at 120 °C for 15 min to heat the particle construction above the glass transition temperature (T_g) of the polystyrene (T_g = 90–95 °C). This step spontaneously raised the silica colloids from the bottom to the top of the PSL microsphere, forming snowman like colloids (Fig. 1c). The resulting structures were characterized using FE-SEM.

2.5. Snowman-like colloids of different sizes

Different sizes of snowman-like colloids were fabricated, using different size combinations of PSL and silica colloids. Heterodoublets with particle concentrations as specified in Table 1 were formed, by first settling the positively-charged PSL colloids on a glass coverslip, followed by adhering the silica colloids to the PSL particles. They were then heated in an autoclave at 120 °C for 15 min to fabricate snowman colloids.
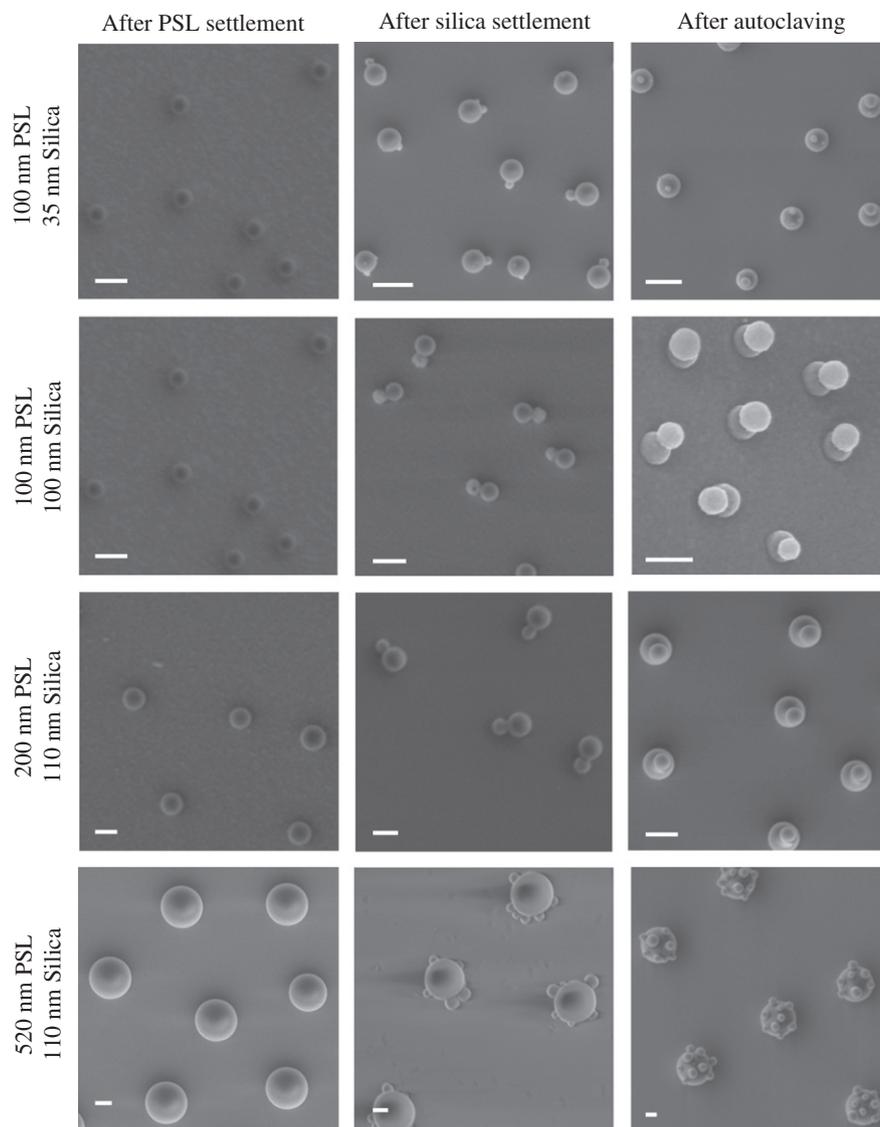
2.6. Surface coverage dependence on ionic strength

Changing the surface coverage of snowmen is possible by adjusting the ionic strength of the solution. The adhesion of positively-charged PSL colloids on negatively-charged glass substrate depends on the electrostatic attraction between PSL and glass, and the spacing depends on the electrostatic repulsion between the PSL particles. The packing density of the PSL colloids on the glass substrate governs the packing density of the final snowman assemblies. Parameters such as pH and ionic strength can be used as 'tuning knobs' to modify the degree of adhesion and packing density of charged particles on glass substrate [22]. In order to investigate experimentally how the ionic strength of the solution affects the packing density of the snowman colloids, monolayers of positively charged PSL microspheres were formed on the substrate at different ionic strengths. 100 nm amine-functionalized and 520 nm amidine-functionalized PSL microspheres were settled on glass coverslips in 10 mL of three different ionic strength solutions (DI water, 0.1 mM KCl, and 1 mM KCl).

2.7. Mechanical stability of snowman-like colloids

The snowman-like colloids are initially somewhat stable, but were made more mechanically stable by coating them with a thin

Table 1
Size combinations and volumes of PSL and silica particle solution used for fabricating different sizes of snowman colloids, as shown in Figs. 2 and 4. Note that the volume percents are indeed usually less than 0.01%.

|	Positively charged PSL particle diameter (nm)	Negatively charged silica particle diameter (nm)	Volume (vol.%) of PSL particle solution in 10 mL DI water	Volume (vol.%) of silica particle solution in 10 mL DI water
(a)	100	35	3 μL (0.0006%)	100 μL (0.022%)
(b)	100	100	3 μL (0.0006%)	75 μL (0.016%)
(c)	200	110	3.5 μL (0.0006%)	5 μL (0.019%)
(d)	520	110	5 μL (0.002%)	10 μL (0.004%)

Fig. 2. Progression showing different steps involved in the fabrication of snowman-like colloidal particles. Column 1: positively-charged PSL particles adhered to the negatively-charged glass coverslip forming a monolayer of the PSL colloids on the glass substrate; column 2: negatively-charged silica particles adhered to PSL particles forming heterodoublets; and column 3: snowman assemblies formed after 15 min of pressurized heating. (a) 100 nm PSL with 35 nm silica, (b) 100 nm PSL with 100 nm silica, (c) 200 nm PSL with 110 nm silica, and (d) 520 nm PSL with 110 nm silica. Scale bar = 200 nm.

gold film. A 20 nm thick gold layer was evaporated on the 200 nm PSL with 110 nm silica snowman sample using conformal coating in an e-beam evaporator (semi core evaporator). The gold covers the entire snowman assembly, except for the region where the colloid is in contact with the glass substrate. In order to confirm the mechanical stability of the final construction, sonication of the snowman sample before and after gold evaporation were performed for 15 min in DI water.

3. Results and discussions

3.1. Fabrication of snowman-like colloidal particles

Snowman-like colloidal doublets were fabricated with the various sizes of particles, as shown in Fig. 2. The first column of Fig. 2 shows the FE-SEM images of the monolayer of the PSL colloids formed on the glass substrate; the second column shows the het-
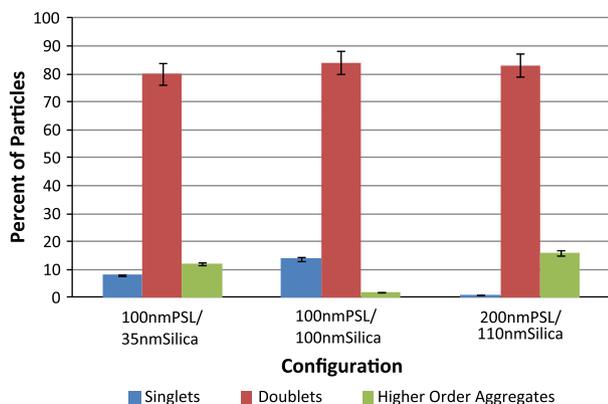
Fig. 3. Fractional yields of singlets, doublets, and larger particle aggregates in the final PSL and silica particle solution. The data was obtained by counting approximately 1000 particles in 10 SEM images. The first set of bars gives the percentages of single PSL particles, the second set gives the percentages of PSL particles that formed doublets with silica, and the third set gives the percentages of PSL particles that formed higher order aggregates with silica particles.

erodoublets formed from PSL and silica nanoparticles before autoclave heating; and the third column shows the FE-SEM images of the snowman-like colloids formed after autoclave heating of the heterodoublets.

Surface charge groups (e.g. sulfate, carboxyl, amine and amidine) are often used to provide electrostatic repulsion, thus stabilizing colloidal particles in solution. In our case, we first used positively-charged amine and amidine functionalized PSL particles to form a monolayer on the glass substrate, since the positively-charged PSL particles are attracted electrostatically to the negatively-charged glass substrate. When negatively charged silica particles are added to the system, they settle toward the substrate. Furthermore, the silica particles are attracted to the positively-charged PSL particle [23], but repelled from the negatively-charged glass substrate. Thus, in the usual case when a silica particle does not land on a positively-charged particle, but rather lands on the negatively-charged substrate, the silica does not adhere to the substrate, but rather diffuses laterally above the substrate until it approaches a PSL particle.

When a silica particle contacts a positively charged PSL particle, they adhere electrostatically. As expected, the contact usually occurs such that the silica adheres to the side of the PSL. When the system is heated above the glass transition temperature (T_g) of the PSL particle, surface tension holds the PSL and silica together, however, at the same time the silica tries to move as far from the glass substrate as possible due to the repulsive electrostatic forces. Our Debye lengths are comparable to our particle diameters, and so this electrostatic repulsion acts over distances of several particle diameters. The fluid state of the PSL particle above its T_g allows mobility of silica over its surface. The resultant of these forces leaves the silica particle on top of the PSL particle. The silica is adhered to the PSL particle by surface tension, but moves far from the glass substrate due to electrostatic repulsive forces. There might be other factors that contribute to the upward movement, such as an upward convective flux due to the heating of the substrate by the steam heat [24], or even Marongoni effects due to temperature gradients [25] but we expect such factors to be secondary.

We have used our process to produce a consistent 85% yield of snowman heterodoublets on a glass substrate, with 10% of singlets and 5% of larger particle aggregates. Fig. 3 shows the yield of doublets and other entities, for different size combinations, produced using this method.

In addition to the high fractional yield, the structure of the hybrid particles can also be tuned by adjusting the size ratio be-

tween the silica and the PSL colloids. For example, 100 nm PSL with 35 nm silica, and 200 nm PSL with 110 nm silica form snowman-like colloids; 100 nm PSL with 100 nm silica form dumbbell-like particles; and 520 nm PSL with 110 nm silica form raspberry-like colloids, as shown in Fig. 4. Note that the "sinking into the substrate" effect in Fig. 4b (and in the TOC graphic) is an artifact. This image was taken after a 20 nm thick gold layer was deposited on the snowman colloids using the conformal deposition by an e-beam evaporator. Due to the conformal coating, gold deposition near the periphery of the particle was less than rest of the glass substrate, which gave the particle "sinking into the substrate" effect.

3.2. Surface coverage dependence on ionic strength

Different applications require different surface coverage of the assemblies on the substrate. In our system the inter-particle spacing between the snowman-like colloids can be adjusted using the ionic strength of the solution while settling the first layer of colloidal particles. Amine/amidine functionalized PSL particles are positively-charged in solution with a thin layer of counter ions around the particles called the "electrical double layer". The repulsive lateral electrostatic interactions keep the particles well-separated when they are settled on a substrate. However, if salt is added to the suspension during the settling, the electrostatic repulsion between the particles is reduced, which allows them to pack more closely [26,27]. Thus, the surface coverage of the substrate by PSL colloids can be tuned by controlling the ionic strength of the solution.

To test this hypothesis, monolayers of 100 nm and 520 nm PSL particles were formed on the glass coverslips in different ionic strength solutions (DI water, 0.1 mM KCl solution and 1 mM KCl solution). Fig. 5 shows FESEM images of PSL particles settled on glass substrate in DI water and 0.1 mM KCl solution, which suggests increased surface coverage with increased ionic strength. The adhered PSL particles were counted for many images and the data showed that the fractional surface coverage increased from
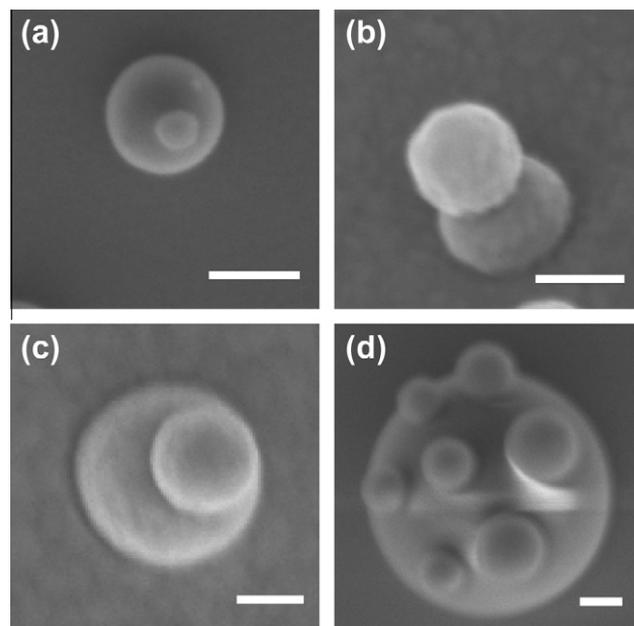
Fig. 4. Snowman-like structures fabricated using the experimental conditions given in Table 1. The close up FESEM images are of (a) 100 nm PSL with 35 nm silica (snowman), (b) 100 nm PSL with 100 nm silica (dumbbell), (c) 200 nm PSL with 110 nm silica (snowman), and (d) 520 nm PSL with 110 nm silica (raspberry). Scale bar = 100 nm.

DI water   0.1 mM KCl
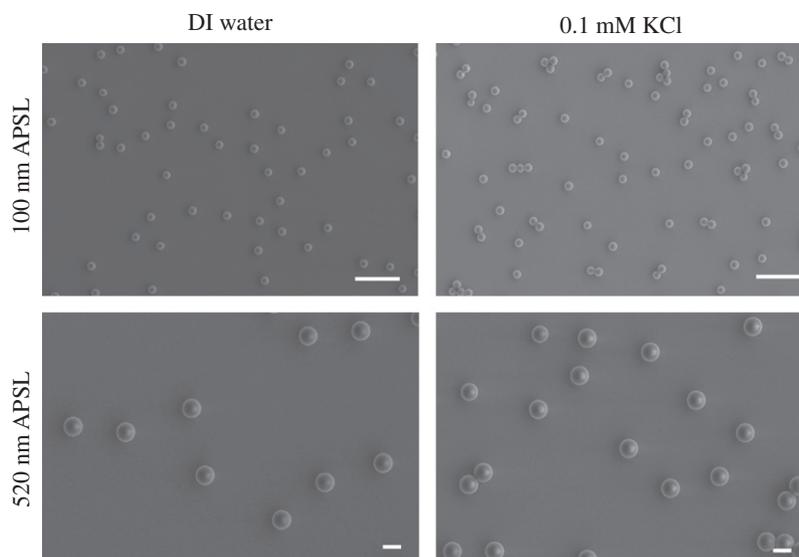
Fig. 5. FESEM images of the monolayer of positively charged colloids formed on glass substrate, at different ionic strengths of the solution. Scale bar = 1 μm.

0.05 to 0.075, resulting in ∼50% increase in the surface coverage when going from DI water to 0.1 mM KCl solution. The same trend was not observed for 1 mM KCl solution, where larger particle aggregates were formed. This is because ionic strength can be increased only to a certain point, until the particles start to aggregate. At higher salt concentrations, the electrostatic repulsion between the particles becomes too small, allowing the attractive van der Waals forces to cause aggregation of particles.

3.3. Mechanical stability of snowman-like colloids

Assembled particles that rely only on van der Waals or electrostatic attractive forces to hold them together are not generally stable and will break up under stresses such as bath sonication [26]. Fusing of polymeric components is an easy and reliable way to enhance the mechanical stability of the assemblies, although here we have only one polymer particle with one silica particle. An additional way to hold the assembled particles together is to coat the entire structure with a thin layer of metal/polymer. In this work the snowman colloids were coated with a 20 nm thick gold film, which protected them from breakup in a bath sonicator. The snowman colloids with a 20 nm thick gold film were ultrasonicated in DI water for 15 min. The number of stable snowman structures were counted in many SEM images. The data suggests that ∼70% of the total snowman structures were stable and did not break apart under sonication, making this technique more mechanically stable. The FE-SEM image of Fig. 6 shows the snowman-like colloids with 20 nm thick gold coating after 15 min of ultrasonication in DI water. The two constituents of the snowman-like colloids did not come apart due to gold film. However, if the snowman colloids were not coated with a layer of gold, they broke up easily under sonication.

3.4. Potential applications of snowman-like colloidal particles

The proposed fabrication technique will enable the practical realization of applications based on snowman-like structures. An array of dense anisotropic snowman-like colloidal particles on a target substrate emulates surface relief structures [28–31] and can provide anti-reflection behavior [13], that are of importance in many optical applications [28,29,31,32]. In the case of gold-coated snowman structures, the edge of the contact region be-
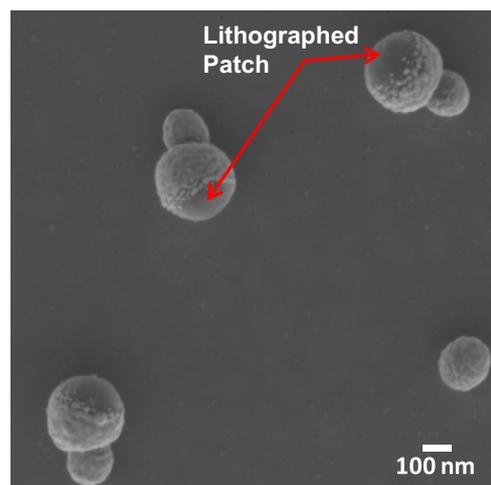
Fig. 6. Mechanical stability of snowman-like colloids. The FESEM image is of snowman having 200 nm APSL with 110 nm silica, with a gold coating. The particles remain mechanically stable as snowmen, even after 15 min of sonication. Note that where the PSL particle had been adhered to the substrate, the gold does not cover, thus forming a lithographed patch.

tween PSL and silica particle provides a sharp metallic region, which can provide large enhancements of electric field due to the resonance of electron sea excitations [33–36]. Such enhancements in electric field are very important, as they have the ability to enhance various non-linear processes, such as surface enhanced Raman scattering (SERS) [37,38].

If the snowman structures are coated with gold or polymer nanoparticles and then released in solution, a lithographed patch is formed on them (Fig. 6). The lithographed patch has the same chemical functionality as the underlying PSL particle, which makes it a useful starting material for fabricating more complex colloidal structures [8]. In addition, if snowman structures are coated with polymer nanoparticles, and fused and sonicated for appropriate times such that silica is removed but the nanoparticle coating is intact, then two lithographed patches can be formed on the core polystyrene latex particle. The size and placement of the lithographed patches can be controlled by altering the size or the placement of the constituent particles, providing an easy route for the

fabrication of complex colloidal assemblies like colloidal trimers and colloidal water [7,39,40].

4. Conclusion

We have developed a simple and cost-effective method for the fabrication of snowman-like particles. This was achieved by first forming the heterodoublets from PSL and silica colloids on a glass substrate, and then heating the doublet assemblies in DI water above the T_g of the polymer. The silica particles spontaneously rise to the top of the PSL particles, forming snowman structures. We have extended this method to different sizes and shown that the structure of the hybrid particles can be tuned by adjusting the size ratio between the silica and the PSL colloids. The structures thus formed may find further applications in antireflective coatings and surface enhanced Raman spectroscopy (SERS) and for directed assembly of other colloidal structures, such as colloidal trimers. The technique provides a new high fractional yield technique for growing both structurally and chemically anisotropic particles for various applications as well as for the study of the controlled self assembly of colloidal particles.

Acknowledgments

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