Article

Self-Organization of Bidisperse Colloids in Water Droplets

Young-Sang Cho, Gi-Ra Yi, Jong-Min Lim, Shin-Hyun Kim,
Vinothan N. Manoharan, David J. Pine, and Seung-Man Yang

J. Am. Chem. Soc., **2005**, 127 (45), 15968-15975• DOI: 10.1021/ja0550632 • Publication Date (Web): 19 October 2005

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

Self-Organization of Bidisperse Colloids in Water Droplets

Young-Sang Cho,[†] Gi-Ra Yi,[‡] Jong-Min Lim,[†] Shin-Hyun Kim,[†]
Vinothan N. Manoharan,[⊥] David J. Pine,[§] and Seung-Man Yang*[,†]

Contribution from the Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701 Korea, Corporate R&D Center, LG Chem Research Park, Daejeon 305-380 Korea, Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, and Department of Physics, New York University, New York 10003

Received July 26, 2005; E-mail: smyang@kaist.ac.kr

Abstract: Most of the colloidal clusters have been produced from oil-in-water emulsions with identical microspheres dispersed in oil droplets. Here, we present new types of binary colloidal clusters from phase-inverted water-in-oil emulsions using various combinations of two different colloids with several size ratios: monodisperse silica or polystyrene microspheres for larger particles and silica or titania nanoparticles for smaller particles. Obviously, a better understanding of how finite groups of different colloids self-organize in a confined geometry may help us control the structure of matter at multiple length scales. In addition, since aqueous dispersions have much better phase stability, we could produce much more diverse colloidal materials from water-in-oil emulsions rather than from oil-in-water emulsions. Interestingly, the configurations of the large microspheres were not changed by the presence of the small particles. However, the arrangement of the smaller particles was strongly dependent on the nature of the interparticle interactions. The experimentally observed structural evolutions were consistent with the numerical simulations calculated using Surface Evolver. These clusters with nonisotropic structures can be used as building blocks for novel colloidal structures with unusual properties or by themselves as light scatterers, diffusers, and complex adaptive matter exhibiting emergent behavior.

Introduction

Nanoparticles can take several nonspherical morphologies such as truncated cubes, multi-pod structures, and tetrahedrons.[1−5] These special nanoparticles, which have been prepared from reducing precursors with shape-controlling agents, possess unusual optical and catalytic properties, depending on their structures.[6] Similarly, at micrometer scales, colloidal particles with complex shapes are also of interest since they would have unique optical, electrical, magnetic, or rheological properties.[7,8] However, the above approaches based on crystalline growth in a solvent cannot be extended to micrometer scales.

Recently, several experimental schemes have been proposed to produce microparticles with complex shapes. For instance, ellipsoidal microspheres with various aspect ratios were produced by stretching of spherical particles in a polymeric matrix, ion beam irradiation of silica microspheres, photoinduced deformation of polymeric microspheres, and reaction of an inorganic precursor in a stretched macroporous film.[9−16] For other shapes, controlled precipitation of sol−gel precursors in the solution phase has been studied in an effort to generate ellipsoidal, polyhedral, disklike, or lancelike inorganic particles.[17−20] A practical method to prepare small clusters of equal-sized microspheres was also recently disclosed by Mano-

---

[†] Korea Advanced Institute of Science and Technology.
[‡] Corporate R&D Center, LG Chem Research Park.
[⊥] Harvard University.
[§] New York University.

(1) Wiley, B.; Herricks, T.; Sun, Y.; Xia, Y. *Nano Lett*. **2004**, *4*, 1733.
(2) Im, S. H.; Lee, Y. T.; Wiley, B.; Xia, Y. *Angew. Chem., Int. Ed*. **2005**, *44*, 2.
(3) Kuo, C.-H.; Huang, M. H. *Langmuir* **2005**, *21*, 2012.
(4) Leung, Y. H.; Djurisic, A. B.; Choy, W. C. H.; Xie, M. H.; Gao, J.; Cheah, K. W.; Man, K. Y. K.; Chan, W. K. *J. Crystal Growth* **2005**, *274*, 430.
(5) Djurisic, A. B.; Leung, Y. H.; Choy, W. C. H.; Cheah, K. W.; Chan, W. K. *Appl. Phys. Lett.* **2004**, *84*, 2635.
(6) Herricks, T.; Chen, J.; Xia, Y. *Nano Lett.* **2004**, *4*, 2367.
(7) (a) Manoharan, V. N.; Elsesser, M. T.; Pine, D. J. *Science* **2003**, *301*, 483. (b) Manoharan, V. N.; Pine, D. J. *MRS Bull.* **2004**, February, 91.
(8) (a) Velev, O. D.; Lenhoff, A. M.; Kaler, E. W. *Science* **2000**, *287*, 2240. (b) Velev, O. D.; Nagayama, K. *Langmuir* **1997**, *13*, 1856. (c) Yi, G.-R.; Moon, J. H.; Yang, S.-M. *Chem. Mater.* **2001**, *13*, 2613. (d) Cho, Y.-S.; Yi, G.-R.; Kim, S.-H.; Pine, D. J.; Yang, S.-M. *Chem. Mater.* **2005**, *17*, 5006.
(9) Ho, C. C.; Keller, A.; Odell, J. A.; Ottewill, R. H. *Colloids Polym. Sci.* **1993**, *271*, 469.
(10) Jiang, P.; Bertone, J. F.; Colvin, V. L. *Science* **2001**, *291*, 453.
(11) Ruhl, T.; Spahn, P.; Hellmann, G. P. *Polymer* **2003**, *44*, 7625.
(12) Ji, L.; Rong, J.; Yang, Z. *Chem. Commun.* **2003**, 1080.
(13) Snoeks, E.; van Blaaderen, A.; Dillen, T.; Kats, C. M.; Brongersma, M. L.; Polman, A. *Adv. Mater.* **2000**, *12*, 1511.
(14) Xu, S.; Nie, Z.; Seo, M.; Lewis, P.; Kumacheva, E.; Stone, H. A.; Garstecki, P.; Weibel, D. B.; Gitlin, I.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 724.
(15) Li, Y.; He, Y.; Tong, X.; Wang, X. *J. Am. Chem. Soc.* **2005**, *127*, 2402.
(16) Skjeltorp, A. T.; Ugelstad, J.; Ellingsen, T. *J. Colloid Interface Sci.* **1986**, *113*, 577.
(17) Ozaki, M.; Kratohvil, S.; Matijevic, E. *J. Colloid Interface Sci.* **1984**, *102*, 146.
(18) Matijevic, E. *J. Colloid Interface Sci.* **1981**, *14*, 22.
(19) Janekovic, A.; Matijevic, E. *J. Colloid Interface Sci.* **1985**, *103*, 436.
(20) Sugimoto, T.; Itoh, H.; Miyake, H. *J. Colloid Interface Sci.* **1997**, *188*, 101.

10.1021/ja0550632 CCC: $30.25

haran et al.[7] The clusters were fabricated by drying the oil out of an oil-in-water emulsion in which polystyrene microspheres were bound to the surface of the oil droplets. Subsequent density gradient centrifugation yielded an intriguing sequence of colloidal clusters consisting of 2 to 15 spheres. One of the salient features is that the configuration of all equal microspheres arranged in a cluster is identical for a given number of the constituting spheres. However, colloidal clusters of all identical spheres have no configurational degree of freedom, and there is limited flexibility in controlling the structure of matter at many different length scales. Moreover, it is practically impossible to construct novel colloidal crystals using colloidal clusters of all identical spheres as building blocks unless the clusters are somehow endowed with a selective directional interaction on the surfaces.[21]

In this study, we developed a facile method for producing new types of colloidal aggregates by self-organization of bimodal or hybrid particles confined in water droplets of a phase-inverted water-in-oil emulsion. To do this, we used various combinations of bimodal or hybrid colloids with different size ratios: monodisperse silica or polystyrene (PS) microspheres for larger particles and silica or titania nanoparticles for smaller particles. Recently, core−shell particles have been produced from a bimodal dispersion of PS nanospheres and silica microspheres using specific chemical or biological interactions,[22] and hybrid clusters of daisylike multipod structures have also been created with silica and PS particles via surface emulsion polymerization.[23] Also, the self-assembly of bidisperse nanoparticles has been studied in two-dimensional scales by computer simulation.[24] Despite these advances, a better understanding of how finite groups of bimodal or hybrid colloids self-organize in a confined geometry may help us control the structure of matter at multiple length scales. In addition, since aqueous dispersions have much better phase stability, we could produce much more diverse colloidal materials.[8] More importantly, the use of bimodal or hybrid particles with different sizes and properties provides more flexibility in controlling material properties and configurational degrees of freedom, which are essential for practical applications. For example, the silica microsphere clusters prepared here were not fully covered with nanoparticles, and the noses (or parts of the exterior surface) of each cluster were exposed completely. This special feature may induce a selective directional interaction which is required for constructing a large colloidal structure with these nonisotropic clusters. As such, colloidal clusters made of bimodal or hybrid particles can serve as complex adaptive matter exhibiting emergent behavior. This behavior arises from interactions between many subunits, but its existence cannot be deduced from individual properties of the subunits.[25]

Experimental Section

Materials. All solvents and chemicals were of reagent grade and were used without further purification. Tetraethyl orthosilicate (TEOS, 99.999%, Aldrich) and ammonia (28−30%, Junsei) were used as a sol−gel precursor (silicon alkoxide) and catalyst, respectively. Ethanol (99.9%) and hexane (98%) were obtained from Merck. (Caution: Hexane is extremely toxic and should be handled with care.) Hexadecane (99%) was purchased from Sigma-Aldrich and the emulsion stabilizer, Hypermer 2296, from Uniquema. Since the melting point of hexadecane is 18 °C, it is a liquid at room temperature. Therefore, we could produce water-in-hexadecane emulsions with a homogenizer. Meanwhile, the boiling point of hexadecane is 151 °C, and the rate of evaporation of hexadecane is negligibly slow during the removal of water from the aqueous emulsion droplets at 100 °C. An aqueous dispersion of silica nanoparticles was purchased from Aldrich (Ludox HS-40, 12 nm) and an aqueous suspension of 2.3-μm silica microspheres from Bangs Laboratory Co. ltd. Amidine PS microspheres 1 μm in diameter were purchased from Interfacial Dynamics Co. ltd and titania nanoparticles dispersed in methanol (DH-40, 30 nm) from Nissan Chemical Industries.

Synthesis of Monodisperse Silica Microspheres. Uniform-sized silica microspheres with mean diameters of 230 nm were synthesized by a modified Stöber method. Monodisperse 800-nm silica microspheres were prepared via controlled hydrolysis and condensation of TEOS in ethanol in the presence of water and ammonia following the seeded-growth method proposed by Zhang and co-workers.[26,27]

Formation of Silica Binary Clusters from W/O Emulsions. Binary clusters of silica were produced from water-in-oil emulsions with two different size ratios of 67 and 10. For a binary colloid with a size ratio of 67, 1 mL of an aqueous dispersion of 800-nm silica microspheres (1.8% w/w) was mixed with 1 mL of an aqueous dispersion of 12-nm silica nanoparticles (0.4% w/w, Ludox HS-40). The mixture was poured into 16 mL of hexadecane with a stabilizer (0.3% w/w, Hypermer 2296) and emulsified by shearing at 8000 rpm for 40 s and subsequently at 9500 rpm for 20 s. Silica binary clusters were formed by self-organization of bimodal silica particles during the slow evaporation of water at 100 °C for 1 h. The sediment of the composite clusters was then collected from hexadecane. The remaining hexadecane in the sediment was carefully washed out with hexane several times. Finally, silica binary clusters were redispersed in water by gentle mixing. For a smaller size ratio of 10, we used silica microspheres of 2.3-μm and 230-nm diameter. A 1-mL portion of an aqueous bimodal dispersion composed of 2.3-μm silica microspheres (5 wt %) and 230-nm silica nanoparticles (1.35% w/w) was emulsified in 8 mL of hexadecane with an emulsifier, Hypermer 2296.

Composite Clusters of Amidine PS and Silica. Composite clusters of amidine PS microspheres and silica microparticles were obtained by similar procedures. A 1-mL portion of an aqueous dispersion of amidine PS microspheres (1% w/w) was mixed with 1 mL of an aqueous dispersion of silica nanoparticles (0.4% w/w, Ludox HS-40). The mixture was added to 16 mL of hexadecane with a stabilizer (0.3% w/w, Hypermer 2296). Hollow clusters of silica nanoparticles were produced from the composite clusters by burning the PS microspheres at 500 °C for 3 h in an electric furnace.

Binary Clusters of Titania Nanoparticles and Silica or PS Microspheres. A 0.1-mL volume of titania nanocrystals dispersed initially in methanol was diluted with 10 mL of water. To remove the residual methanol, the dispersion of titania was evaporated in a hood at room temperature for several days. Then, 1 mL of an aqueous dispersion of silica microspheres (1.8% w/w) was mixed with 1 mL of an aqueous dispersion of titania nanoparticles (0.3% w/w). The mixture was added to 16 mL of hexadecane and emulsified with 0.3% w/w stabilizer (Hypermer 2296). Composite clusters of titania and amidine PS were also produced using 1% w/w of amidine PS microspheres instead of silica. The clusters were then calcined at 500 °C for 3 h for hollow titania clusters.

Instruments. SEM was carried out on a field emission scanning electron microscope (FE-SEM, XL305FEG, Philips). TEM was carried

---

[21] Xia, Y.; Gates, B.; Li, Z.-Y. *Adv. Mater.* **2001**, *13*, 409.

[22] Fleming, M. S.; Mandal, T. K.; Walt, D. R. *Chem. Mater.* **2001**, *13*, 2210.

[23] Reculusa, S.; Mingotaud, C.; Bourgeat-Lami, E.; Duguet, E.; Ravaine, S. *Nano Lett.* **2004**, *4* (9), 1677.

[24] Rabideau, B. D.; Bonnecaze, R. T. *Langmuir* **2004**, *20*, 9408.

[25] Cox, D. L.; Pines, D. *MRS Bull.* **2005**, *30*, 425.

[26] Zhang, J. H.; Zhan, P.; Wang, Z. L.; Zhang, W. Y.; Ming, N. B. *J. Mater. Res.* **2003**, *18*, 649.

[27] Yi, G.-R.; Manoharan, V. N.; Micheal, E.; Elsesser, M. T.; Yang, S.-M.; Pine, D.-J. *Adv. Mater.* **2004**, *16*, 1205.

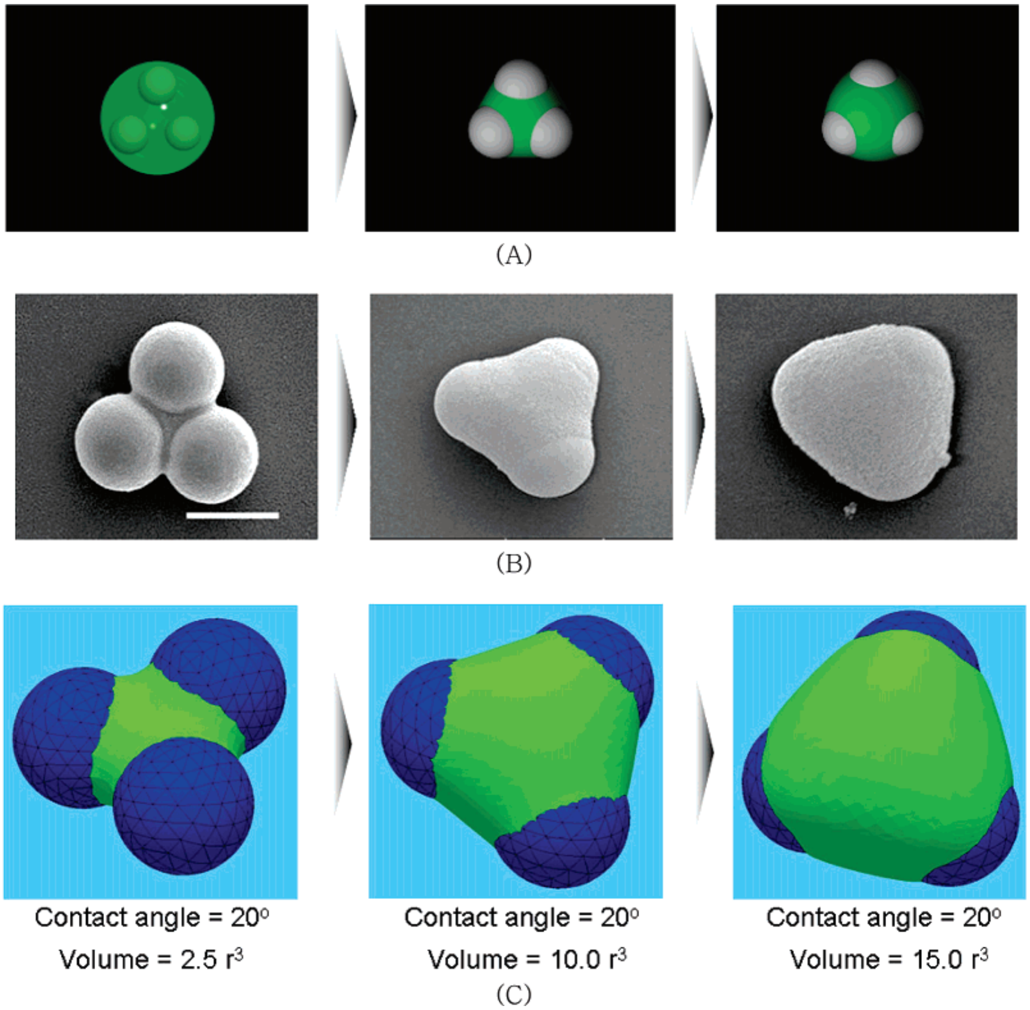

Figure 1. (A) Schematic of the formation of a trimer cluster of silica microparticles with silica nanoparticles from water-in-oil emulsions. (B) SEM images for the structural evolution of binary colloidal clusters of silica microspheres and nanoparticles for $n = 3$. Scale bar is 1 μm. (C) Surface Evolver simulated structural evolution for $n = 3$ as a function of the amount of silica nanoparticles. The quantity $10r^3$ or $15r^3$ is the superficial volume of nanoparticles packed in the bimodal clusters. Since r is the radius of silica microspheres, the superficial volume of packed nanoparticles is increased from $2.5(3/4\pi) = 0.597$ in the left to $15(3/4\pi) = 3.581$ in the right.

out on a transmission electron microscope (F20 Tecnai). Powder X-ray diffraction was performed using Cu Kα radiation on a Rigaku D/MAX-RC for titania nanoparticles. The incident wavelength was 0.154056 nm and the detector was moved between $2\theta = 15°$ and 75°. The scan speed was 3°/min. Emulsification of aqueous bidisperse colloids in hexadecane was performed using a homogenizer (DIAX 900, Heidolph). A vortex mixer was used to redisperse nonspherical microparticles and composite clusters in water (Maxi Mix II, Type 37600 mixer, Thermolyne). A muffle furnace (Isuzu, PK9712150030-9) was used to burn out PS microspheres from the composite clusters.

Results and Discussions

As shown in the schematic of Figure 1A, an aqueous suspension of microspheres and nanoparticles was emulsified into an oil phase. The two types of colloidal particles were subsequently self-organized into nonspherical colloidal clusters inside the aqueous emulsion droplets as the water was removed slowly by heating at 100 °C. Vital to the formation of colloidal clusters is the use of stable, well-dispersed colloids that are kept stable inside the aqueous emulsion droplets during evaporation. To this end, we have used highly hydrophilic microspheres and nanoparticles, or, in some cases, modified the surface of the microspheres with more hydrophilic functional groups.

Table 1. Binary Colloidal Systems Made of Polystyrene, Silica, and Titania with Various Size Ratios

system	large particles: diameter, charge	small particles: diameter, charge	size ratio
A	silica: 800 nm, negative	silica: 12 nm, negative	67
B	silica: 2300 nm, negative	silica: 230 nm, negative	10
C	amidine PS: 1000 nm, positive	silica: 12 nm, negative	83
D	silica: 800 nm, negative	titania: 30 nm, negative	27
E	amidine PS: 1000 nm, positive	titania: 30 nm, negative	33

To investigate the final morphology of the binary colloidal clusters, which were confined into the aqueous phase by capillary forces, we used five different types of binary colloidal systems, as summarized in Table 1. The PS spheres were terminated with amine groups, which were dissociated in an aqueous medium, and positive surface charges were induced on the PS spheres. Meanwhile, the silica and titania particles have surface moieties which gain negative surface charges in contact with water. For system “A”, an aqueous suspension of silica microspheres (800 nm) and silica nanoparticles (12 nm) was emulsified into hexadecane in the presence of a dissolving emulsifier (Hypermer 2296) and clustered by preferentially evaporating the water from the aqueous emulsion droplet, as illustrated in Figure 1A. For example, consider an aqueous emulsion droplet that initially contains three large silica microspheres. As the water is removed slowly, the large particles are packed into a trimer cluster in a triangular configuration, as shown in the SEM images of Figure 1B. Therefore, the triangular configuration of the large microspheres is not changed by the presence of the small particles. This is because in binary colloids with large size ratios, the presence of small particles induces an attractive depletion interaction between large particles, and the depletion interaction and compressive interfacial tension force the microspheres to form triangular clusters during the evaporation of water. As the layer of water on the surfaces of the silica microspheres outside of the cluster is drained out, the silica nanoparticles are not left behind on the surfaces that are exposed to hexadecane at the intermediate stage of evaporation. This is due to the repulsive electrostatic interaction between the silica microspheres and nanoparticles with co-charges. In the final stage of the evaporation-induced clustering, the aqueous phase forms menisci around the valleys between the large microspheres of the trimer cluster, and capillary forces pull the small particles into the valleys. For a given number (n) of larger microspheres captured in an aqueous emulsion droplet, the morphology of the cluster made of colloids is changed by the amount of nanoparticles.

As mentioned previously, we used a homogenizer to generate water-in-hexadecane emulsions by emulsifying the aqueous suspension of bidisperse colloids. Consequently, the size of the emulsion droplets was polydisperse. Thus, many different-sized emulsion droplets were produced, which contained even an identical number (n) of silica microspheres. Since the amount of small silica particles was approximately proportional to the size of the emulsion droplets, the number of silica nanoparticles contained in each emulsion droplet differed among others. Indeed, we could observe a number of different types of binary clusters for $n = 3$, depending on the relative amount of silica nanoparticles. In Figure 1B, the SEM images of three types of representative trimer clusters were reproduced according to the amount of small particles. As expected, the small silica particles did not coat the entire surfaces of the trimer clusters but aggregated in the valleys between the large microspheres.

The structural evolution for a timer ($n = 3$) cluster can be simulated theoretically by using the so-called Surface Evolver,[28] and the result is reproduced in Figure 1C. The Surface Evolver has been used for the interfaces shaped by surface tension and other energies by minimizing the total energy of the surface subject to various constraints. In the present study, we used the Surface Evolver keeping the original triangular configuration of a trimer cluster of the large silica microspheres with the adjustable parameters such as interfacial contact angle and occupied volume of nanoparticles. In this particular case, we assumed that the contact angle of the water−hexadecane interface on the silica microsphere cluster was fixed at 20°, which is typical of water and hydrophilic silica. As the occupied volume of the small silica nanoparticles increased from $2.5r^3$ to $15r^3$, where r is the radius of the large silica microspheres, the morphology of the trimer was changed as shown in Figure 1C. As noted, the simulated morphology is quite similar to that observed experimentally in Figure 1B.

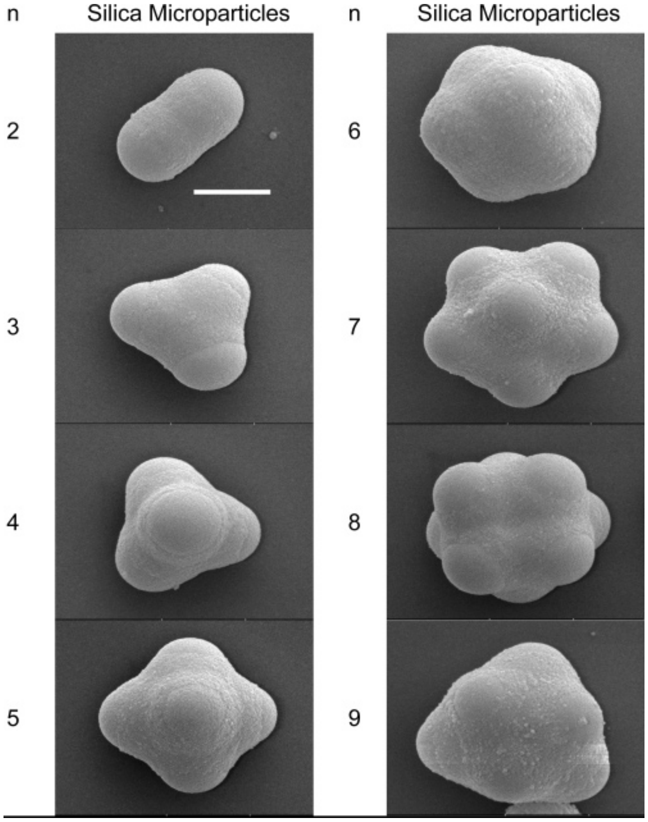

Figure 2. SEM images of silica−silica composite clusters for $n = 2-9$. Scale bar is 1 μm. The size ratio of silica microspheres to silica nanoparticles was fixed at 67.

Due to the emulsion polydispersity, various binary colloidal clusters of silica micro- and nanoparticles were prepared with the size ratio fixed at about 67. The resulting SEM images are reproduced in Figure 2. Interestingly, the configurations of silica microspheres in the binary colloidal clusters were not affected by the presence of silica nanoparticles but the same as the minimal second-moment clusters for $n \leq 10$, except $n = 8$.[7] Incidentally, aside from the morphology of the silica nanoparticles, the sequence of silica microsphere packings for $n \leq 7$ was also similar to that of Coulomb clusters, which minimize the electrostatic Coulomb potential.[29,30] In particular, the Coulomb clusters are also the same as Lennard-Jones clusters for $n \leq 7$ which minimize the Lennard-Jones potential by maximizing the number of contacts between the silica microspheres.[31] Manoharan et al. made colloidal clusters of pure PS latex microspheres by drying toluene out of toluene-in-water emulsion droplets and found that the sequence of sphere packings $n \leq 10$ minimized the second moment of the mass distribution.[7] In our case, for $n = 8$, the silica microspheres were packed into a Coulomb cluster instead of a minimal second-moment snub disphenoid. The eighth-order Coulomb cluster is composed of two regular tetramers lying in parallel planes with one twisted relative to the other by 45°, forming a twisted-square structure. We believe that electrostatic repulsion between the silica microspheres in water droplets caused the formation of the Coulomb clusters for $n = 8$. The eighth-order Coulomb cluster was not observed by Manoharan et al. from PS clusters produced in phase-inverted toluene-in-water emul-

---

(28) http://www.susqu.edu/facstaff/b/brakke/evolver/evolver.html.

(29) Wille, L. T. *Nature* **1986**, *324*, 46.

(30) Livshits, A. M.; Lozovik, Yu. E. *Chem. Phys. Lett.* **1999**, *314*, 577.

(31) Maranas, C. D.; Floudas, C. A. *J. Chem. Phys.* **1992**, *97* (10), 7667.

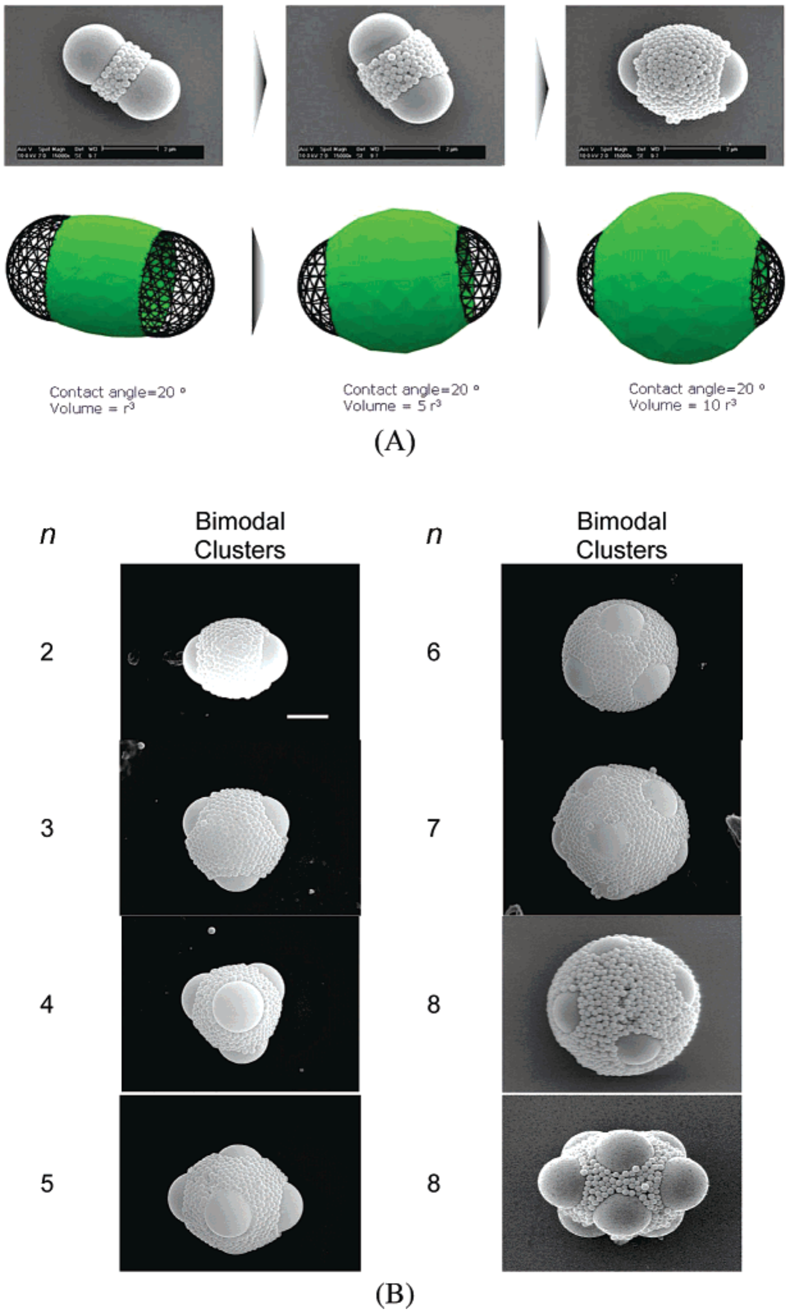

Figure 3. (A) Top: SEM images for the structural evolution of bimodal colloidal clusters of silica microspheres and nanospheres for $n = 2$. Bottom: Surface Evolver simulated structural evolution for $n = 2$ as a function of the amount of silica nanospheres. (B) SEM images of silica−silica composite clusters for $n = 2-8$. Scale bar is 2 μm. The size ratio of large and small silica particles was fixed at 10.

sions. In their study, the PS microspheres were dispersed in toluene, and consequently the electrostatic repulsion between the PS beads was negligibly small.

One of the other notable features is that the silica microspheres were not fully covered with nanoparticles, and the noses (or parts of the exterior surface) of each microsphere cluster were exposed completely. This special feature may induce a selective directional interaction which is required for constructing a large colloidal structure with these nonisotropic clusters, if the surfaces of large or small particles are selectively modified.

It is expected that the configuration of microspheres will not be modified by the presence of much smaller particles as in the previous case. However, if the size ratio of larger to smaller particles is decreased, smaller particles may affect the sequence of larger sphere packings. To assess this hypothesis, we used bimodal colloids of system “B” in Table 1 with a much smaller size ratio of 10; silica microspheres and nanoparticles were 2.3 μm and 230 nm in diameter, respectively. In the SEM images of Figure 3A, the configurational evolution of bimodal colloidal clusters for $n = 2$ is shown with an increased amount of small silica particles. As noted, the morphology evolved in the same fashion as in the previous case in which the size ratio was 67. This structure evolution was also confirmed by using Surface Evolver, assuming that the contact angle of the water−hexadecane interface on the silica dimer cluster was fixed at 20°. As the volume of the nanoparticles increased, the morphology of the bimodal cluster for $n = 2$ changed similarly, as shown in the SEM images in Figure 3A.

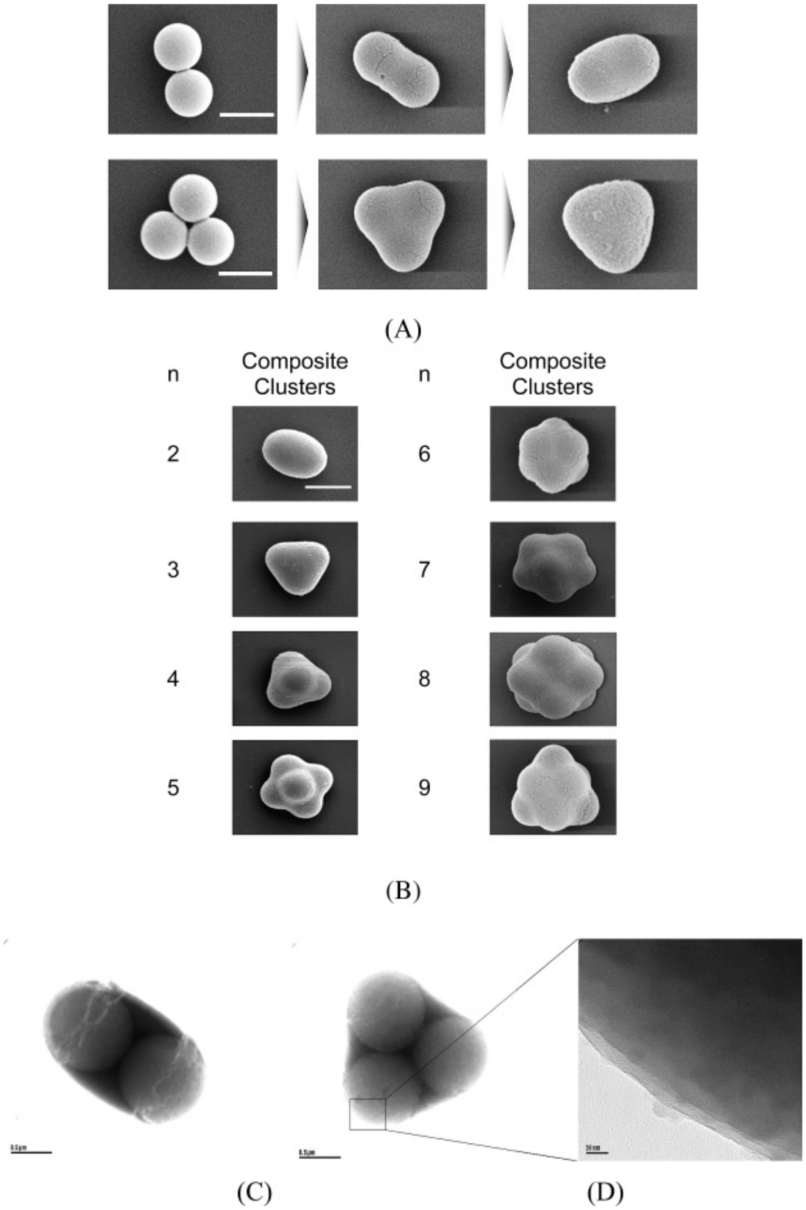

Figure 4. (A) SEM images for the structural evolution of hybrid colloidal clusters of PS microspheres and silica nanoparticles for $n = 2$ and 3. (B) SEM images of PS−silica composite clusters for $n = 2-9$. Scale bars are 1 μm. (C) and (D) TEM images of PS−silica composite clusters for $n = 2$ and 3, respectively.

Also shown in Figure 3B are the SEM images of higher-order clusters of bimodal colloids. For $n \leq 10$, the sequence of silica microsphere packings is identical to the minimal second moment clusters, except for $n = 8$. Interestingly, we observed two isomers of the eighth-order clusters; one was a second-moment cluster of a snub disphenoid and the other a Coulomb cluster of a twisted square. Snub disphenoids were less common than twisted square.

Thus far, we have considered bimodal colloids with the same surface charges, for which the noses of large microspheres outside of each cluster were exposed with no coverage of nanoparticles and the clusters exhibited nonisotropic, directional interactions. In many cases, however, hybrid colloids possess different surface charges, which may change the cluster configuration. To investigate this further, we used a hybrid colloid of positively charged large microspheres of amidine PS and negatively charged small silica or titania nanoparticles (systems “C” or “E” in Table 1), which were confined in water droplets in a water-in-hexadecane emulsion. In Figure 4A, the SEM images show the structural evolutions of dimer and trimer clusters of hybrid colloids as a function of the amount of silica nanoparticles. It can be noted from the SEM images in Figure 4B that the configurations of the PS microspheres in the clusters of the hybrid colloid with counter-charges are identical to those in Figure 2 for the bimodal colloid of silica microspheres and nanoparticles with co-charges. However, as noted from the TEM images in Figure 4C and Figure 4D, all clusters are completely covered with silica nanoparticles, and the silica shells in the outer edges of each cluster are almost uniform and monolayered. Therefore, the morphologies of the surface coverage of the smaller particles are strongly dependent on the interactions between the microspheres and nanoparticles. Specifically, the nanoparticles were partially coated on the clusters, as shown in Figure 2, when the bimodal colloids possessed co-charges and the interactions were repulsive. Meanwhile, for a hybrid cluster of PS microspheres and silica nanoparticles with counter-

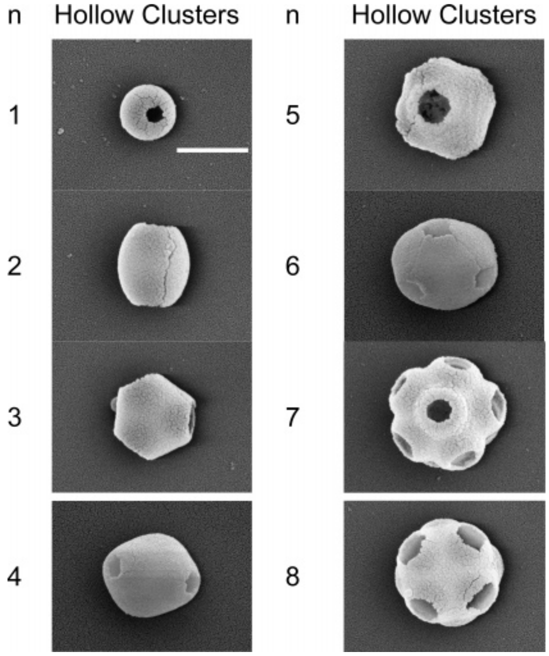

Figure 5. SEM images of hollow silica shells produced from PS−silica composite clusters for $n = 1-8$.

charges, the silica nanoparticles adsorbed and formed a monolayer on the entire surface of each PS microsphere before the mixture colloid was emulsified. When the aqueous hybrid colloid was emulsified into hexadecane, excess silica nanoparticles coexisted with the silica-coated amidine PS microspheres in aqueous emulsion droplets. During evaporation of water, they organized themselves into clusters, which were fully coated with the silica nanoparticles.

By heat treatment at 500 °C for 3 h, the PS microspheres were removed from silica−PS core−shell microclusters, and hollow silica clusters were left behind, as shown in Figure 5. Clearly, thin layers of silica particle shells at the outer edges of the clusters were destroyed during heat treatment due to the insufficient mechanical strength. Also, the SEM image of the silica shell for $n = 8$ confirms that the configuration of the PS microspheres in the eighth-order cluster was a Coulomb cluster of twisted squares, which is less clearly seen from the SEM image in Figure 4B.

Our strategy for binary clusters from water-in-oil emulsions is not limited to PS and silica but can also be extended to other materials. In this work, we also used titania nanoparticles with silica or PS microspheres for the self-assembly of hybrid colloids (systems “D” and “E” in Table 1), and the results are reproduced in Figures 6 and 7. The TEM image in Figure 6A and the XRD spectra in Figure 6B show that the titania nanoparticles are approximately 30 nm in diameter and have a dominant anatase crystallinity. The isoelectric points of silica and anatase titania are pH = 2 and 4, respectively. Since the water emulsion droplets at very dilute low particle loadings were almost pH-neutral or weakly acidic, both the surfaces of silica and titania nanoparticles were negatively charged. Furthermore, the amidine PS microspheres gained positive surface charges in contact with a pH-neutral aqueous medium right from the start for both the silica and titania nanoparticles.

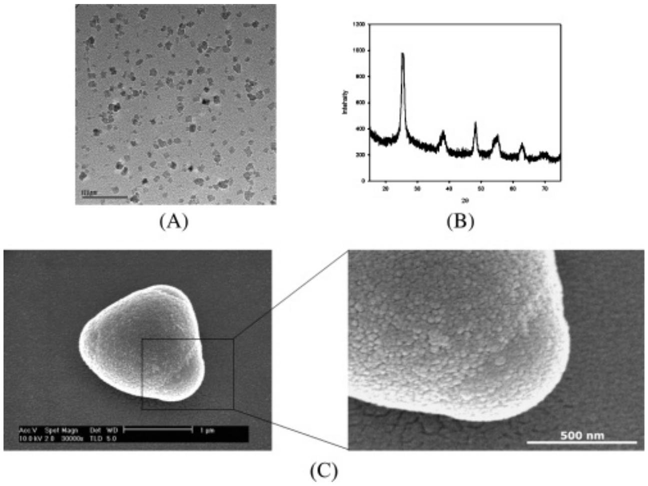

Figure 6. (A) TEM images of titania nanocolloid. Scale bar is 100 nm. (B) Powder X-ray diffraction peaks of titania nanocolloid. (C) SEM image of titania-coated silica microclusters for $n = 3$, and a magnified view near an outer edge of a trimer cluster.

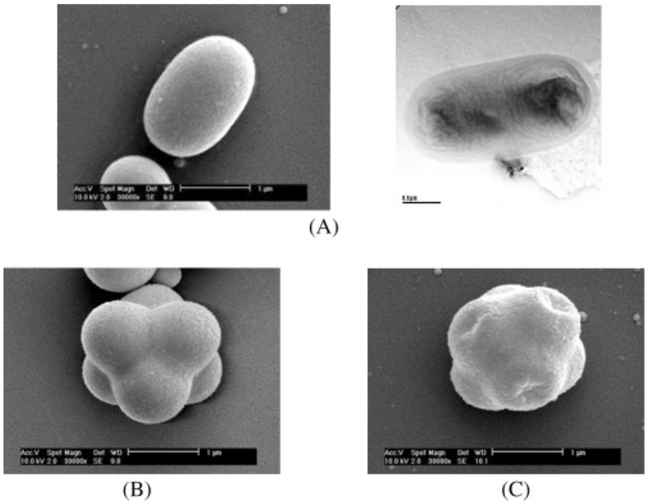

Figure 7. (A) SEM and TEM images of a titania/polystyrene composite cluster for $n = 2$. Scale bars are 1 μm and 0.5 μm, respectively. (B) SEM image of a titania/ polystyrene composite cluster for $n = 6$. (C) SEM image of a titania hollow cluster for $n = 6$. Scale bars in (B) and (C) are 1 μm.

For an illustrative purpose, we included in Figure 6C the SEM image of the surface coverage of the titania nanoparticles over a trimer cluster of silica microspheres. Indeed, the surface coverage of titania nanoparticles was similar to that of silica nanoparticles over the silica microspheres shown in Figure 1B. Meanwhile, when amidine PS microspheres were used instead of silica microspheres, titania nanoparticles with counter-charges completely covered the clusters of PS microspheres, as shown in Figure 7, parts A and B, for dimer and hexamer clusters of PS microspheres, respectively. The complete coverage of titania nanoparticles over PS microspheres was also confirmed from the TEM image in Figure 7A. Therefore, when titania nanoparticles were used instead of silica nanoparticles, the general feature in the final morphology of binary clusters remained unchanged because the electrokinetic interactions between silica and PS particles were identical to those between titania and PS particles.

Finally, we reproduced in Figure 7C the SEM image of hollow shell architecture of titania nanoparticles that was left behind after thermal decomposition of the PS microspheres. Dimpled edges on the hollow shells indicate that titania shells were not mechanically strong enough for heat treatment.

Thus far, we have demonstrated a simple method for producing various types of bidisperse clusters for *n* ranging from 1 to 15 in a single emusification. In this experimental scheme, we could observe most effectively the structural evolution of bidisperse colloidal clusters as a function of the interaction between large and small particles, the number (*n*) of large microspheres, and the amount of small particles relative to that of large spheres. For practical applications, however, we have to engineer the emulsification system for uniform and pure clusters. In our group, we have developed a number of novel systems to generate monodisperse emulsion droplets, including microfluidic devices, micropipet injection devices, and electrospray.[32] Nevertheless, the number of large microspheres will fluctuate even in these engineered systems following the Poisson distribution.[33] However, the morphology of bimodal clusters will be uniform for a fixed number of large microspheres, *n*. This is because the amount of small particles is proportional mainly to the volume of the emulsion droplet for a given *n*. Then, the clusters can be fractionated subsequently according to *n* by the well-known techniques, that is, density gradient centrifugation or flow cytometry.[7,34]

Conclusions

In this work, we fabricated new types of colloidal aggregates by self-organization of two types of particles in geometrically confining water-in-oil (W/O) emulsion droplets. Interestingly, the configurations of the large microspheres were not changed by the presence of the small particles. However, the morphologies of the surface coverage of the smaller particles were strongly dependent on the nature of the interparticle and interphase interactions. Specifically, the nanoparticles were partially or completely coated depending on the electrostatic interactions of the microspheres and nanoparticles and the wetting properties of the water phase on the microspheres. In particular, binary colloids of silica microspheres and silica (or titania) nanoparticles with co-charges organized themselves into composite clusters with elaborate structures in which silica (or titania) nanoparticles partially coated the clusters of silica microspheres, leaving uncovered, exposed outer edges. Meanwhile, when hybrid clusters of PS microspheres and silica (or titania) nanoparticles with counter-charges were considered, the nanoparticles formed fully covered shells over the clusters of the large PS microspheres. These composite clusters have a wide range of potential applications because the use of particles with different sizes and properties lends more flexibility in controlling the structure of matter at multiple length scales and material properties. These clusters can be used as building blocks for novel colloidal structures with unusual properties or by themselves as light scatterers, diffusers, and complex adaptive matter exhibiting emergent behavior.[25,35]

Acknowledgment. We express our gratitude for the financial support by the International Joint Research Project of Korea and USA and partial support from the BK21 Program, the CUPS-ERC, the National R&D Project of Nano Science and Technology of Korea, and the Center for Nanoscale Mechatronics & Manufacturing of the 21st Century Frontier Research Program (M102KN010001-02K1401-00212). The Korea Basic Science Institute is also acknowledged for the SEM images.

JA0550632

---

(32) (a) Yi, G.-R.; Thorsen, T.; Manoharan, V. N.; Hwang, M.-J.; Jeon, S.-J.; Pine, D. J.; Quake, S. R.; Yang, S.-M. *Adv. Mater.* **2003**, *15*, 1300. (b) Yi, G.-R.; Manoharan, V. N.; Klein, S.; Brzezinska, K. R.; Pine, D. J.; Lange, F. F.; Yang, S.-M. *Adv. Mater.* **2002**, *14*, 1137. (c) Moon, J. H.; Yi, G.-R.; Yang, S.-M.; Pine, D. J.; Park, S.-B. *Adv. Mater.* **2004**, *16*, 605.

(33) Hinds, W. C. *Aerosol Technology*, 2nd ed.; John Wiley & Sons: New York, 1998.

(34) Liddel, C. M.; Summers, C. J. *Adv. Mater.* **2003**, *15*, 1715.

(35) Wriedt, T. *Part. Part. Syst. Charact.* **2002**, *19*, 256.