Complex Colloidal Microclusters from Aerosol Droplets

Young-Sang Cho,[†] Gi-Ra Yi,[‡] Yun Seup Chung,[§] Seung Bin Park,[†] and Seung-Man Yang*,[†]

National Creative Research Initiative Center for Integrated Optofluidic Systems and Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea, Nano-Bio System Research Team, Seoul Center, Korea Basic Science Institute, Seoul 136-713, Korea, and Small Business Corporation, 24-3, Yoido-dong, Youngdungpo-gu, Seoul 150-718, Korea

In this Article, we report on a packing scheme of monodisperse colloidal nanospheres by aerosol-assisted clustering. When an aqueous suspension of colloidal nanospheres was sprayed into aerosol droplets by an ultrasonic nebulizer, the nanospheres were encapsulated in the aerosol droplets and the evaporation of water from the droplets at high temperatures led to the packings of nanospheres. The configurations of the colloidal nanospheres minimized the interparticle potential energy or the second moment of mass distribution depending on the number of the constituting nanospheres. Other types of nonspherical microparticles or hollow microclusters were also produced by self-organizing organic–inorganic binary colloids of different sizes in an aerosol spray pyrolysis reactor. The aerosol-assisted fabrication of colloidal clusters was very effective as compared to the method based on oil-in-water or water-in-oil emulsions, in which the removal of residual oil was not easy and time-consuming.

1. Introduction

Dense packings of monodisperse colloidal particles with specific interparticle interactions have attracted great interest in various areas of materials chemistry and soft condensed matter physics such as nucleation and growth of atoms or molecules, optimization of potential functions between colloidal particles, and novel complex building blocks for self-assembled photonic crystals.[1–4] In particular, self-assembly of monodisperse microspheres for photonic band gap materials has received growing attention since photonic crystals were produced successfully from self-assembled emulsion droplets in 1997.[4a] Thus far, a number of methods for fabricating colloidal crystals of monodisperse microspheres have been developed by self-organization with controllable defects and lattice orientations.

Although colloidal crystals of spherical building blocks have a few stop bands, they do not have a robust full photonic band gap due to the spherical symmetry of photonic crystal lattices. To address this problem, theoretical calculations have been conducted for designing asymmetric lattices of photonic crystal. Also, nonspherical building blocks such as ellipsoidal particles (prolates or oblates) and two-sphere clusters (dimers) have been prepared experimentally by deforming spherical particle into ellipsoid or self-organizing two spheres into a dimer.[5–13] Usually,

dimers or other polygonal clusters have been prepared by dewetting colloidal suspensions on patterned surfaces.[14,15] However, the pattern-assisted approach has drawbacks in that only two-dimensional microclusters are prepared and the production yield of asymmetric building blocks is not enough to fabricate photonic crystals. To overcome these problems, dense packing of monodisperse or bidisperse colloidal microspheres has been studied by self-organizing colloidal particles inside oil-in-water emulsion droplets into three-dimensional colloidal clusters with various polyhedral structures.[3,16] However, the preparation of monodisperse emulsion droplets and the subsequent removal of residual oil are not easy and are time-consuming, and a more convenient and practical method is necessary to obtain complex colloidal clusters. Some methods for the solution-phase synthesis of colloidal clusters such as DNA-assisted fabrication of polystyrene clusters or reversible cluster formation of nanoparticles by interparticle photodimerization may provide alternative ways, but the high yield of cluster formation and precise control of cluster structures cannot be accomplished by these methods.[17,18]

Aerosol-assisted technology has been widely adopted for compacting and sintering nanoparticles or nanospheres by transforming a particle suspension to agglomerated particles for use in electronic, chemical, and mechanical industries.[19] For example, polystyrene latex spheres have been aggregated to spherical supraball assemblies by spraying colloidal dispersion into aerosol droplets and drying the solvent from droplets to induce the packing of the microspheres inside the aerosol

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* Corresponding author. E-mail: smyang@kaist.ac.kr.
† Korea Advanced Institute of Science and Technology.
‡ Korea Basic Science Institute.
§ Small Business Corp.

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droplets.[20] Also, chain-like triplet aggregate or quadruplets in the form of branched chains have been produced by nebulizing aqueous latex spheres, and the size of aggregated latex spheres has been measured and theoretically predicted.[21,22] Despite these advances, it still remains challenging in the area of colloidal and aerosol science to fabricate three-dimensional nonspherical clusters and control the configuration of the clusters.

In the present Article, we report a method for preparing colloidal clusters of silica nanospheres by aerosol-assisted technology. In particular, silica nanosphere clusters with various polyhedral structures have been fabricated in a furnace under drying conditions at 100−700 °C without employing the emulsification process and prefabrication of patterned substrates. By using aerosol droplets as confined geometry, a bimodal colloidal dispersion of large silica nanospheres and small nanoparticles was also self-assembled for the generation of nonspherical or anisotropic microparticles. Moreover, hollow silica microclusters were also fabricated by self-assembling binary colloids of polystyrene nanospheres and silica nanoparticles followed by burning out the organic cores of the silica-coated binary clusters. Our strategy for the generation of microclusters by using aerosol droplets has unique advantages. First, aerosol-assisted fabrication of colloidal clusters is applicable to various types of solvents including water. Second, the aerosol process does not need emulsifiers, which requires a tedious oil removal process. Third, the generation of aerosol droplets encapsulating colloidal nanospheres and the self-organized consolidation of the nanospheres in aerosol droplets proceed very fast and almost simultaneously in a single experimental system. The airborne colloidal clusters can be used as novel complex colloidal building blocks for the preparation of lower symmetry photonic crystals with complete band gaps.

2. Experimental Section

Materials. All solvents and chemicals were of reagent grade and used without further purification. Tetraethylorthosilicate (TEOS, 99.999%, Aldrich) and ammonia (28−30%, Junsei) were used as sol−gel precursor (silicon alkoxide) and catalyst, respectively. Ethanol (99.9%) was obtained from Merck. Styrene (99%), potassium persulfate (99%), and sodium hydrogen carbonate (99%) were purchased from Kanto Chemicals. Sodium styrene sulfonate (90%) was bought from Aldrich. An aqueous dispersion of silica nanoparticles of 12 nm in primary particle size and amine-coated polystyrene (PS) nanospheres of 410 nm in diameter were purchased from Aldrich (Ludox HS-40) and Interfacial Dynamics, respectively.

Instrumentation. Scanning electron microscopy was carried out on a field emission scanning electron microscope (FE-SEM, XL305FEG, Philips).

Synthesis of Monodisperse Silica and Polystyrene Colloids. Monodisperse silica nanospheres with mean diameters ranging from 230 to 300 nm were prepared by the modified Stöber method.[23] Hydrolysis and condensation of TEOS in ethanol in the presence of water and ammonia produced spherical silica particles with narrow size distribution. After the reaction completed, unreacted precursors were removed through solvent exchange twice by centrifugation and redispersion of the particles in fresh water under ultrasonication for 30 min.

Monodisperse PS nanospheres with mean diameters of 230 nm were prepared by emulsifier-free emulsion polymerization using styrene as monomer, potassium persulfate as initiator, and sodium hydrogen carbonate as buffer.[24] The size of PS particles could be

controlled by varying the amount of the comonomer, sodium styrene sulfonate. During polymerization, the temperature was maintained at 70 °C under vigorous agitation at 300 rpm. After the particle syntheses, the PS nanospheres were washed through solvent exchange twice by centrifugation and redispersion in water under ultrasonication.

Formation of Silica Microclusters from Aerosol Droplets. Colloidal microclusters of silica nanospheres were prepared by aerosol process. The apparatus was divided into three parts: droplet generator, drying part, and collecting part. The aerosol droplet generator consisted of an ultrasonic nebulizer (1.67 MHz vibration frequency) and a water circulator to remove excessive heat from vibrating nebulizer. The drying part was made by putting a quartz glass tube (3.5 cm in outer diameter and 1.5 m long) into a vertical electric furnace, of which the temperature was controlled by a temperature controller. A dilute aqueous suspension of silica (0.01−0.08 wt %) was atomized by the ultrasonic nebulizer to generate aerosol droplets that contained a small number of the silica nanospheres. Nitrogen (N_2) gas was introduced as carrier gas at 2 L/min to transport the atomized droplets into the drying furnace. The water of aerosol droplets was evaporated in the drying furnace at 100−700 °C. After the drying process, the resulted silica clusters were collected directly into distilled water in a flask.

Formation of Asymmetric Silica Microclusters from Aerosol Droplets. Asymmetric silica microclusters were produced by nebulizing 0.01 wt % of aqueous binary colloid of silica and PS particles (3:2 weight ratio) with the same particle size (230 nm) in an aerosol reactor. N_2 gas was introduced to the furnace at 2 L/min as carrier gas. The binary microclusters of silica and PS nanospheres were burnt out in the furnace, which was maintained at 700 °C to obtain asymmetric silica microclusters by removing the PS nanospheres.

Formation of Nonspherical Silica Microparticles from Aerosol Droplets. Nonspherical silica microparticles were fabricated by the same procedures for the formation of silica microclusters from aerosol droplets containing bidispersed charged silica particles of two quite different sizes. In doing this, a dilute suspension of silica nanospheres (230 nm, 0.01 wt %) and silica nanoparticles (12 nm, 0.001 wt %) was atomized by ultrasonic nebulizer to generate aerosol droplets. Nitrogen gas was introduced at 1 L/min as carrier gas to transport the atomized droplets into the drying furnace. The water from the aerosol droplets was evaporated in the drying furnace at 500 °C. After the drying process, the resulted silica clusters were collected directly into distilled water in a flask.

Formation of Hollow Silica Microclusters from Aerosol Droplets. Hollow silica microclusters were produced by atomizing an aqueous binary suspension of 0.025 wt % amine-coated PS nanospheres (410 nm) and 0.01 wt % silica nanoparticles (12 nm) into aerosol droplets. After the consolidation was completed, the sacrificial PS nanosphere templates were burnt out in the furnace at 600 °C. The feed rate of N_2 carrier gas was adjusted at 1 L/min.

Sample Characterization. A field emission scanning electron microscope was used to observe the configurations and morphologies of silica microclusters, nonspherical silica microparticles, and hollow silica clusters. Samples for FE-SEM images were prepared by drying the clusters dispersed in water at room temperature and coating with gold to avoid possible charging effects.

3. Results and Discussion

Silica and PS nanospheres were synthesized by the modified Stöber method and emulsifier-free emulsion polymerization, respectively, in which size distributions were very narrow (see Figure S1 in Supporting Information). As seen from the images in Figure S1, monodisperse nanospheres of silica and PS were prepared successfully.

The procedure for the fabrication of colloidal clusters from aerosol droplets is described schematically in Figure 1. First, an aqueous suspension containing silica nanospheres was sprayed into air by using an ultrasonic nebulizer, which was connected

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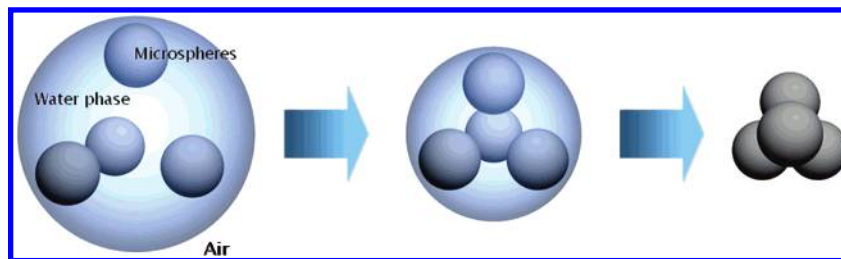(24) Yi, G.-R.; Moon, J. H.; Yang, S.-M. *Chem. Mater.* **2001**, *13*, 2613.

Figure 1. Schematic diagram for the cluster formation of silica nanospheres from aerosol droplets.
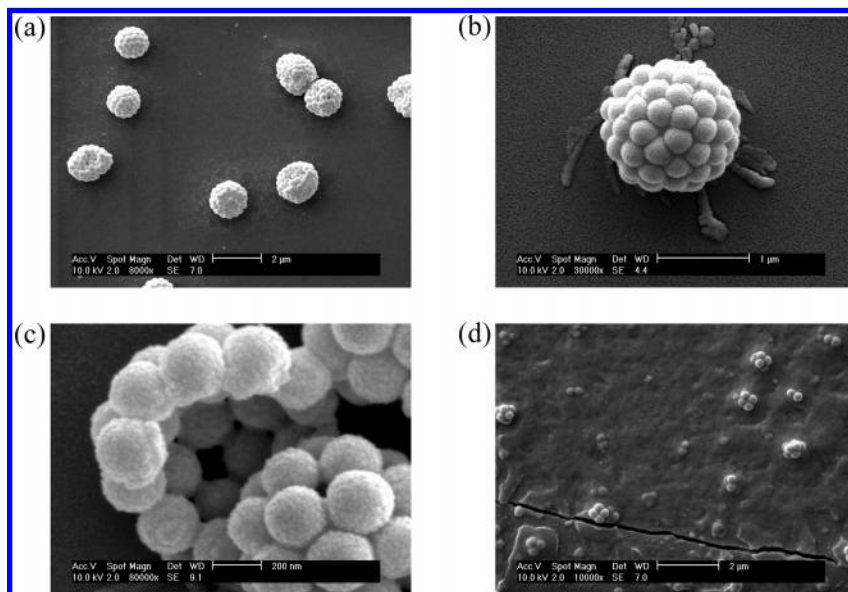

Figure 2. Scanning electron micrographs of spherical aggregates of silica spheres (atomized 0.08 wt % of 230 nm silica suspension, dried at 700 °C): (a) Scale bar is 2 μm. (b) Scale bar is 1 μm. (c) Scanning electron micrographs of broken spherical aggregates of silica nanospheres. Scale bar is 200 nm. (d) Small colloidal clusters separated from the same sample for (a)−(c). Scale bar is 2 μm.

to a high-temperature furnace tube. Monodisperse nanospheres inside aerosol droplets were rapidly aggregated as the water in aerosol droplets was evaporated in the furnace. Packings of the nanospheres were induced by compressive capillary force acting on the particles.

The size of aerosol droplets produced by an ultrasonic nebulizer can be predicted by the following empirical expression for the count mean diameter (CMD) of aerosol droplets.[25]

$$\text{CMD} = \left(\frac{\gamma}{\rho_L f^2}\right)$$

in which γ and ρ_L are the surface tension and density of the liquid, respectively, and f is the excitation frequency of nebulizer. According to this formula, aerosol droplets of about 3 μm in diameter can be produced when pure water is sprayed by nebulizer at the excitation frequency of 1.67 MHz. For the atomization of an aqueous dilute suspension of silica, the average size of droplets will not deviate substantially from that of pure water droplets because the surface tension of dilute particulate suspension is almost the same as that of pure water. In this study, monodisperse silica particles of 230 or 300 nm in size were captured inside aerosol droplets by using a nebulizer operating at the frequency of 1.67 MHz to generate the colloidal clusters. It was impossible to produce colloidal clusters composed of silica particles larger than 600 nm in diameter because of increased gravitational effects, which inhibited the particles from being captured inside aerosol droplets.

To obtain the proper experimental conditions for fabricating colloidal clusters, we examined the effect on the morphology of the final aggregates by changing the concentration of the silica suspension. Figure 2a and b shows the SEM images of colloidal aggregates of the silica nanospheres prepared by atomizing a 0.08 wt % suspension of 230 nm silica nanospheres and drying at 700 °C. As shown in the SEM images, nearly spherical aggregates or supraballs in micrometer scale were produced, indicating that the concentration of the silica suspension was quite high to prepare colloidal clusters of the silica nanospheres. The supraballs were 1−2 μm in diameter, and the size distribution was quite monodisperse. The small polydispersity of the size was due to the nonuniform size of aerosol droplets generated by an ultrasonic nebulizer. In fact, the sizes of aerosol droplets were nearly monodisperse and the polydispersity was as small as 1.2−1.3, unlike the polydisperse nature of emulsion droplets generated by conventional homogenizer. Figure 2c shows the SEM image of the broken silica supraballs by sonication, which reveals the hollow structure of the particle assembly. The possible explanation for this hollow structure of supraball has been proposed by Edwards et al. by using two characteristic times: the drying time of a droplet, t_d, and the diffusion time of spheres from the edge of the droplet to its center, R^2/D, where R is the radius of the aerosol droplet and D is the diffusion coefficient of the colloidal spheres.[26] When the ratio of these two characteristic times, the effective Peclet number, is large, that is, for the case of rapid drying, the spheres accumulate near the drying front of the aerosol

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drop, yielding the hollow structures due to the insufficient migration time of the nanospheres.

For the same sample, small colloidal clusters were also observed together with silica supraballs as shown in Figure 2d, although the population of these clusters was quite small. This implies the encapsulation of silica spheres inside aerosol droplet is a stochastic process rather than a deterministic phenomena. It was possible to separate these clusters from the silica supraballs by centrifugation of the sample at 1500 rpm for 1 h and isolating the supernatant for SEM imaging.

The colloidal clusters of 230 nm silica nanospheres were prepared by atomizing 0.01 wt % of aqueous silica suspension, followed by drying at 700 °C (see SEM images of Figure S2 in Supporting Information). Unlike the previous case of 0.08 wt % silica suspension, colloidal clusters composed of a small number of silica nanospheres were produced as shown in the SEM images. Although the aerosol drops were highly monodisperse in size, the number of the constituent silica nanospheres was not uniform. This is because the encapsulation of colloidal particles inside aerosol droplets by ultrasonic nebulization is stochastic and the number of colloidal particles captured inside aerosol droplets follows Poisson distribution.[25] This is important especially when the particle volume fraction is low in the mother suspension. When the particle concentration is high enough, the spherical supraparticles can be generated as shown in Figure 2a. In this case, the numbers of particles encapsulated in aerosol droplets are not deviated appreciably, and the resulting supraballs are almost identical in size. However, when the suspension is sufficiently dilute, the stochastic nature becomes pronounced and the numbers of particles captured in aerosol droplets will deviate and follow the Poisson distribution. Consequently, various cluster structures formed from aerosol droplets in low particle concentrations.

Each cluster had a unique configuration depending on the number of nanospheres such as dimers, triangular trimers, tetrahedral tetramers, and others. Although we can find some singlets, there are many three-dimensional clusters from $n = 2$ to 10 or higher order clusters as shown in Figure S2. We have examined the yield of each type of clusters according to the number n of the constituent silica nanospheres by counting the number of the silica clusters through a scanning electron microscope. The resulting yield is plotted as a function of n in Figure S3. The yield of doublets from aerosol-assisted clustering was the highest and 35.4% for 0.01 wt % of 230 nm silica suspension that was atomized and dried at 700 °C. The yield can be controlled by changing the size of aerosol droplets or the concentration of silica suspension before atomization. Because aerosol-assisted clustering forms various types of clusters with different numbers of the constituent nanospheres (n) in a batch, we need to separate the clusters to obtain pure clusters according to n by using density gradient centrifugation or flow cytometry.[3,9,16b] These fractionation methods have been shown very useful to separate colloidal clusters and coagulated particles.

Since Kepler's conjecture on the optimal packing of an infinite number of spheres, much theoretical research on the geometry of dense packed spheres or point charges has been conducted to predict the structure of clusters as a function of the number (n) of the constituent spheres. At the present time, there are four categories of sphere packing structures that can be obtained by optimization theories.[1,2,27,28] First, the structures of Lennard-Jones (LJ) clusters have been obtained by adopting Lennard-

Jones potential between monodisperse spheres as the objective function. The geometries of LJ clusters calculated by using global optimization algorithm by Floudas and his co-workers are touching two spheres ($n = 2$), triangle ($n = 3$), tetrahedron ($n = 4$), trigonal dipyramid ($n = 5$), octahedron ($n = 6$), and pentagonal dipyramid ($n = 7$).[1] For higher order clusters ($n \geq 8$), it has been reported that LJ clusters minimize the potential energy by maximizing the number of contacts between particles, which leads to the polytetrahedral packing of spheres.[3] The second moment of mass distribution of the constituting spheres has been adopted also as the objective function to study the dense packed structures of spheres.[27] The configurations of these minimal second-moment clusters are the same as those of LJ clusters only for $2 \leq n \leq 7$. For $n \geq 8$, however, snub disphenoid for $n = 8$, triaugmented triangular prism for $n = 9$, and gyroelongated square dipyramid for $n = 10$ were reported as the minimal second-moment clusters. As the third category of sphere packings, the configurations of repulsive point charges have been obtained by using Coulomb potential as the objective function, which leads to so-called Coulomb clusters.[2,28] The structures of Coulomb clusters are also identical to those of LJ and minimal second-moment clusters only for $2 \leq n \leq 7$. However, for more complex clusters ($n \geq 8$), the configurations are quite different from those of LJ or minimal second-moment clusters. For example, for $n = 8$, the structure of the Coulomb cluster is two touching regular tetramers that lie in parallel planes with a relative rotation angle of 45°, a twisted-square structure. The last category of sphere packings is the sausage packing, which minimizes the volume of the convex hull that encapsulates the cluster.[29] The geometries of our aerosol clusters were similar to LJ, minimal second moment, and Coulomb clusters, but clusters with unusual structures were observed depending on the number of the constituent spheres and experimental conditions.

The SEM images of Figure 3 show the configurations of silica microclusters prepared by atomizing a 230 nm silica suspension. As shown in the SEM images, the structures of some clusters were very exotic, and they have not been reported yet. The formation of such weird three-dimensional clusters as shown in the SEM images is because at sufficiently high drying temperatures the colloidal particles inside aerosol droplets will touch each other and can be sintered before they reach the minimal energy configurations. Also, some unusually structured clusters may form due to the cluster−cluster aggregation that occurs inside of a long furnace tube. As the aerosol droplets evaporate to form clusters inside the furnace, the resultant clusters may collide with nearby neighbors before they reach the collection part of the aerosol reactor, which leads to cluster−cluster aggregation. The configurations of clusters composed of two and three spheres were line segment ($n = 2$) and triangle ($n = 3$), respectively. These structures were the same as those of LJ and minimal second-moment clusters. However, higher order clusters ($n \geq 4$) had different configurations for a given number of the constituent nanospheres except for $n = 6, 8, 10, 11, 12$, and 13. For the fourth order clusters, we found an unusual isomer of square configuration of four spheres in addition to the minimal second-moment clusters of tetrahedral coordination. The square configuration of four sphere cluster was reported earlier for the self-organization of microspheres inside of cylindrical holes or on tops of cylindrical pillars using geometric confinement effect.[5,30] For $n = 5$, both triangular dipyramid and square pyramid structure were found. The former structure was the LJ (or minimal second moment or Coulombic) clusters, but the latter did not

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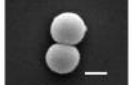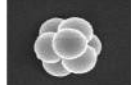(30) Xia, Y.; Yin, Y.; Lu, Y.; McLellan, J. *Adv. Funct. Mater.* **2003**, *13*, 907.
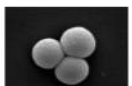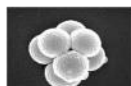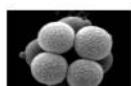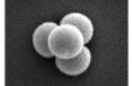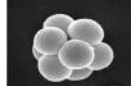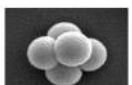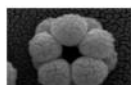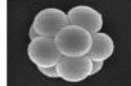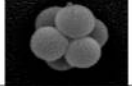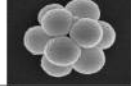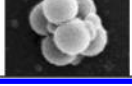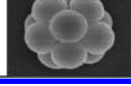
n	Silica Clusters	Model	n	Silica Clusters	Model
2			7		Tetramer-on-trimer
3			7		Trimer-on-regular square
4		Regular square	8		Twisted square
4			9		
5			10		Twisted pentagon
5		Square pyramid	11		
6			12		
6		Trimer-on-trimer	13		

Figure 3. Scanning electron micrographs of colloidal clusters of silica spheres (atomized 0.01 wt % of 230 nm silica suspension, dried at 700 °C). Scale bar is 200 nm.

correspond to the global minimal structure. It has been reported that patterned substrate with reverse pyramidal pits could produce the square pyramidal clusters by dewetting colloidal suspension on the patterned substrate.[30] It is very advantageous that these aerosol-assisted clusters can be prepared without the tedious fabrication of solid substrate. For $n = 6$, octahedral clusters were found, which matched the LJ or minimal second-moment clusters. Additionally, for $n = 6$, trimer-on-trimer structures were also found together with octahedral clusters, although their population was very low as shown in the SEM image in Figure 3.

For $n = 7$ clusters, the usual second-moment clusters of pentagonal dipyramid were not produced in aerosol droplets. Instead, we found two types of isomers: tetramer-on-trimer and trimer-on-square. Unlike PS microspheres that were bound to the interfaces of toluene droplets in water,[3] the silica particles were located inside of the aerosol droplets. Thus, more compactly packed isomers could be generated for silica nanospheres as shown in Figure 3. For $n = 8$, silica nanospheres were self-organized into Coulombic twisted-square instead of the minimal second-moment snub disphenoid due to the negative surface charges of silica nanospheres. This twisted square structure was also found from the cluster sample prepared from water-in-oil emulsion droplets in our previous report.[16b] For $n = 9$, the silica spheres formed the minimal second-moment triaugmented triangular prism structure. Finally, for $n = 10$, we found twisted pentagonal clusters. The reason why these types of isomeric clusters were formed instead of the minimal second-moment clusters is still unclear. However, fast evaporation of water droplets may lead to the formation of unfamiliar structure because the

migration time of the particles into the central part of aerosol droplet is relatively short as compared to the fast shrinking rate of aerosol droplets.

To investigate the effect of the drying temperature on the structure of silica microclusters, we prepared colloidal clusters of silica nanospheres under different drying conditions. In doing this, aerosol droplets were atomized and collected directly into fresh water at room temperature without heating in the furnace. It can be expected that the silica nanosphere structures, which might form inside aerosol droplets without thermal consolidation, would be disengaged and redispersed in water (see Figure S4 in Supporting Information). Indeed, as shown in the SEM image in Figure S4, the clusters that were dried at room temperature have one or two-dimensional shapes such as dimers, triangles, and chainlike trimers. No complex three-dimensional polyhedral clusters were observed for this sample.

The colloidal clusters were also prepared by spraying an aqueous suspension of 300 nm silica particles at 100 °C. Unlike the aerosol-assisted clustering at 700 °C, the minimal second-moment clusters were formed for $n = 2-13$ under a moderate heating rate (see Figure S5 in Supporting Information). In particular, for $n = 8$, the minimal second-moment snub disphenoid clusters were formed together with Coulombic twisted-square clusters. This implies that the evaporation rate of aerosol droplets is a crucial factor in determining the structure of the final configuration of silica nanospheres. Because the evaporation rate of aerosol droplets at 100 °C was much slower than the rate at 700 °C, enough packing time of silica nanospheres yielded the minimal second-moment clusters. For eighth order ($n = 8$)
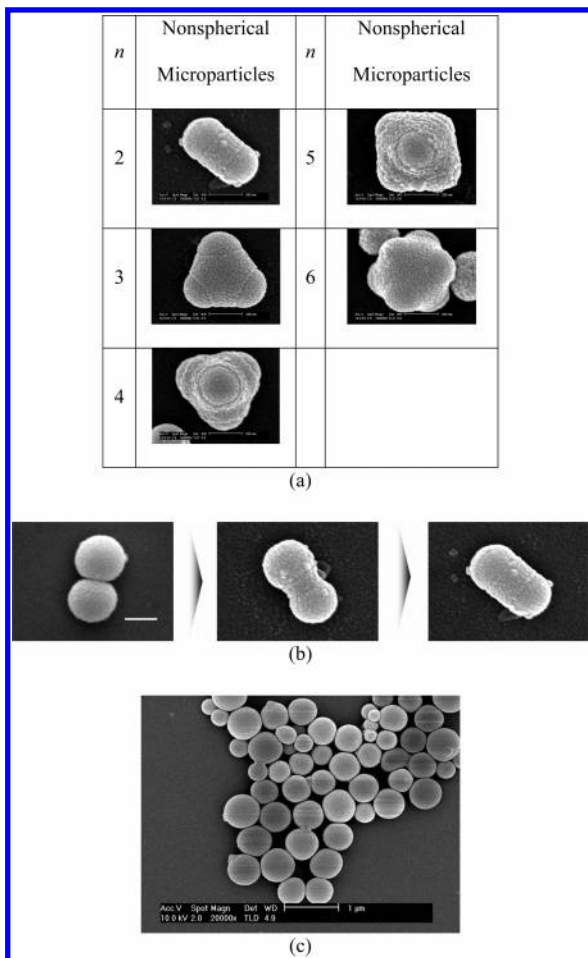
Figure 4. (a) Scanning electron micrographs of nonspherical silica microparticles produced from aerosol droplets containing bimodal silica colloids. Scale bars are 200 nm. (b) Structure evolution of nonspherical silica microparticles for $n = 2$. Scale bar is 200 nm. (c) Scanning electron micrograph of spherical silica microparticles produced from aerosol droplets. Scale bar is 1 μm.

clusters, the electrostatic repulsive interactions were responsible for the formation of Coulombic twisted-square cluster. The higher order colloidal clusters ($n > 13$) were also formed as noted from the SEM images in Figure S5. However, it is very difficult to figure out the exact structure of these higher order clusters from these SEM images.

It is possible to use our colloidal clusters as novel building blocks for assembling ordered arrays of particles, which are different from the usual colloidal crystals of face center cubic (fcc) lattices. For instance, the face centered cubic structure of dimers in Figure 3 and Figure S5 can form colloidal crystals of tetrahedrally coordinated diamond structure if the line segment of dimer is parallel to the (111) direction of fcc lattices.[31] Moreover, the square tetramers in Figure 3 can serve as building blocks for the fabrication of face centered cubic colloidal crystals with (100) planes parallel to the surface of the substrate as reported by Xia et al.[14] Tetrahedral clusters in Figure 3 or Figure S5 can be used also as building blocks for colloidal crystals with diamond lattices, which have a complete photonic band gap.[4] Fractionation of these clusters according to the configuration and number of the constituent particles can be done by using various methods such as density gradient centrifugation and flow cytometry.[3,9,16b] The clusters generated from aerosol droplets are not sufficiently sturdy under severe sonication. However, the airborne clusters

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(31) Xia, Y.; Gates, B.; Li, Z. Y. *Adv. Mater.* **2001**, *13*, 409.
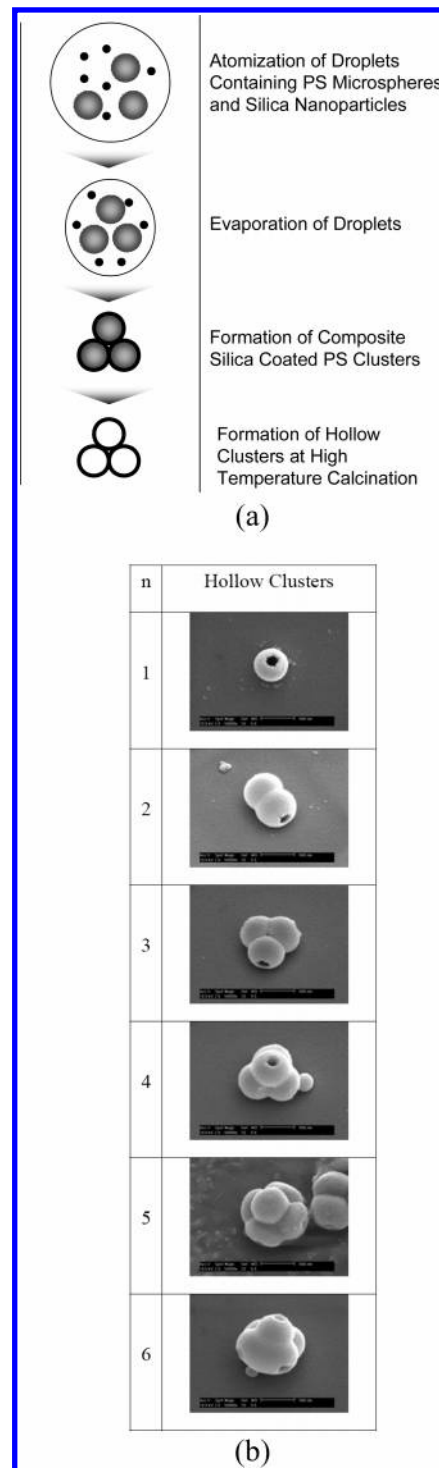

Figure 5. (a) Schematic diagram for producing hollow silica microclusters from bimodal dispersion of amine-coated polystyrene nanospheres and silica nanoparticles inside an aerosol droplet. (b) Scanning electron micrographs of hollow silica microclusters produced from aerosol droplets. Scale bars are 500 nm.

have enough durability during fractionation, which is especially true when aerosol droplets are dried at sufficiently high temperatures. In fact, it is not easy to find "broken" supraparticles (such as an open hollow cluster in Figure 2c) even after strong sonication. The sturdiness of airborne clusters arises from the fact that aerosol-assisted self-assembly involves high temperature heat treatment to dry aerosol droplets. Our results show that drying at 700 °C is high enough for a mild sintering of silica particles.

Aerosol-assisted method also enabled us to prepare asymmetric clusters by nebulizing the binary colloidal suspension of 230 nm PS and 230 nm silica particles. Heat treatment of the aerosol droplets at 700 °C led to the removal of organic PS parts from the composite clusters (see the SEM images and corresponding model illustrations in Figure S6 in Supporting Information). As illustrated, these highly asymmetric silica clusters were formed from square pyramidal clusters of PS and silica nanospheres, and the structures were dependent on the number of the PS beads.

Colloidal clusters of bimodal particles were assembled by atomizing aqueous suspensions of 12 nm silica nanoparticles and 230 nm silica nanospheres. It can be expected that if a proper amount of silica nanoparticles is self-assembled with silica nanospheres, anisotropic nonspherical microparticles can be produced. Figure 4a contains the SEM images of the nonspherical silica microparticles such as ellipsoidal, peanut-like, and triangular microclusters in which the silica microclusters were covered partially with the silica nanoparticles. As noted, the shape of the microclusters was dependent on the number of the silica nanospheres and the encapsulated amount of the silica nanoparticles. When the concentration of the silica nanoparticles was less than 0.001 wt %, the microclusters had patches which were uncovered with the silica nanoparticles. In Figure 4b, the SEM images show the shape evolution for $n = 2$ from dimers to peanut-like and ellipsoidal microclusters with the loading of the silica nanoparticles. However, when the loading of the silica nanoparticles was increased to 0.008 wt %, the silica microclusters became spherical because the silica nanoparticles formed a spherical hull encompassing the silica nanospheres as shown in SEM image in Figure 4c. The nonspherical microparticles in Figure 4a are of practical importance for novel building blocks of self-assembled structures and light scatterers. This kind of shape-anisotropic particles can be also fractionated by using density gradient centrifugation.[16c]

Finally, the aerosol-assisted fabrication of colloidal clusters was used to produce hollow silica architectures by atomizing an aqueous binary colloid of amine-coated PS nanospheres of 410 nm in diameter and 12 nm silica nanoparticles in a furnace. Figure 5a shows the fabrication process schematically. As the atomized aerosol droplets were evaporated in the furnace, the composite clusters of the PS nanospheres and the silica nanoparticles were produced. In this process, the PS nanospheres formed the organic core, which was completely covered with the silica nanoparticles due to electrostatic attraction between the negatively charged silica nanoparticles and the positively charged amine-coated PS nanospheres. Next, burning out the PS core at the furnace left behind hollow silica structures, as shown in the SEM images in Figure 5b. It can be seen from the SEM images that small holes were formed on the surfaces of the hollow architectures. Thin silica films around the edges of the composite clusters could not sustain their structures during the sudden removal of the PS latexes from the silica-coated composite clusters, resulting in the formation of small holes or dimples on their surfaces. These hollow structures can be utilized as catalytic supports.

4. Conclusion

A strategy for the fabrication of colloidal clusters was demonstrated using aerosol-assisted self-organization. The colloidal clusters were produced by drying aerosol droplets, which were generated from aqueous colloidal suspensions. Silica or PS nanospheres or their binary colloids were used for fabricating various types of microclusters. The configurations of the colloidal clusters were polyhedral, which were dependent on the interparticle interactions and the rate of evaporation. From the binary colloidal clusters, the organic PS nanospheres could be removed selectively at high temperatures to produce silica clusters of unusual configurations. These microclusters can find diverse applications for the preparation of three-dimensional photonic crystals with lattice structures such as tetrahedrally coordinated diamond lattices, which cannot be obtained by self-assembling spherical building blocks. Nonspherical or anisotropic microparticles were also generated by self-assembling bimodal dispersion of large silica or PS nanospheres and small silica nanoparticles inside aerosol droplets. The silica nanoparticles covered the composite clusters either fully or partly depending on the sense of electrostatic interactions. Specifically, when the electrostatic interaction was repulsive between the nanospheres and the nanoparticles, the composite cluster had uncovered patches on the surface. Meanwhile, for attractive interactions, the silica nanoparticles fully covered the composite clusters. Additionally, various types of hollow silica architectures were produced by removing the PS latexes from the composite clusters of PS nanospheres and silica nanoparticles. The present aerosol-assisted process followed by density gradient centrifugation can produce all identical "pure" clusters in macroscopic quantities, which is essential for practical applications. Overall, the productivity of silica clusters from simple aerosol-assisted process is as high as that from the rather complicated emulsion-templated process.

Supporting Information Available: SEM images of silica and PS nanospheres, colloidal clusters of silica spheres generated by atomizing 0.01 wt % of 230 nm silica suspension followed by drying at 700 °C, yield of silica clusters, SEM images of colloidal silica clusters at different drying conditions, and asymmetric silica clusters generated by atomizing 230 nm silica and PS spheres followed by drying at 700 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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