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Colloidal Clusters of Microspheres from Water-in-Oil Emulsions

Young-Sang Cho,[†] Gi-Ra Yi,[‡] Shin-Hyun Kim,[†] David J. Pine,[§] and Seung-Man Yang*,[†]

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea, Corporate R&D Center, LG Chem Research Park, 104-1 Moonji-dong, Yuseong-gu, Daejeon 305-380, Korea, and Department of Physics, New York University, 4 Washington Place, New York, New York 10003

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We report a general method for small aggregates (or clusters) of water-borne colloids inside water-in-oil (W/O) emulsions. First, an aqueous suspension of monodisperse polystyrene or silica (SiO_2) microspheres was emulsified into polydisperse water droplets on micrometer scales in oil phase and colloidal aggregates were produced spontaneously during slow evaporation of water. Then, the colloidal clusters consolidated by complete removal of water were separated from the oil phase and re-dispersed in water for the subsequent fractionation according to the number (n) of the constituent spheres by a density gradient ultracentrifugation. Each cluster of n particles possessed a unique configuration except for a few particular cases of $n = 7$, 8, and 11, in which we observed some isomeric structures, depending on their surface properties of colloidal microspheres. These isomers have not been reported in the preceding studies for colloidal clusters fabricated from the phase-inverted oil-in-water emulsions.

Introduction

Dense packings of identical spheres have been studied theoretically to elucidate the microscopic phenomena of crystallization of atoms or ions.[1−3] Colloidal particles have been used for experimental demonstrations of such packing problems because their size and interparticle potentials could be controlled precisely. Similarly, small clusters of colloidal microspheres have been proposed as model systems for nanocrystals which are essentially aggregates of a few particles. Recently, encapsulation and shrinkage method of colloidal particles was reported in the literature, which showed that the packing structures were unique depending mainly on the number of the constituent particles.[4] These clusters have attracted much attention due to their potential for exploring novel and new complex phenomena caused by nonisotropic shapes.[4−6] More importantly, it is potentially possible to build up novel photonic crystals using dimeric or tetrahedral clusters as building blocks with further surface modification for directional assembly of diamond lattices.[7] Also, the colloidal clusters can be used as photonic molecules for tight binding photon devices and sensors, and mirrorless microlasing.[8]

Several groups have also recently proposed other clever schemes for nonisotropic colloidal aggregates. Xia et al. have reported that a well-defined small number (∼2−8) of uniform colloidal particles could be organized into clusters by geometrical confinement in cylindrical holes patterned into a film of photoresist.[9] In this case, the cluster structures could be controlled by varying the geometrical aspects of the cylindrical holes, but they were limited to those built up in a layer-by-layer fashion. Meanwhile, a few other groups have tried to seek out a chemical synthetic route and proposed that nonisotropic particles could be synthesized by controlled precipitation which produced dimers, tetramers, or daisy-like structures.[10] However, their configurations were limited also and it is still challenging to control precisely the shape of clusters and the subsequent fractionations.

Aforementioned encapsulation and shrinkage approach was shown efficient to create clusters containing a small number of spheres ($n = \sim 2-15$) and was capable of producing a massively large number of clusters, approximately 10^8-10^{10} in lab-scale experiments.[4,6] The process was based on emulsifying a dispersion of lightly cross-linked polystyrene (PS) microspheres in toluene into an aqueous surfactant solution. This yielded a toluene-in-water emulsion with the PS microspheres bound by surface tension to the droplet interfaces. When the toluene was removed by evaporation, the PS beads formed stable clusters of colloidal particles dispersed in water. Subsequently, clusters of different aggregation numbers were readily fractionated using a density gradient centrifugation. More recently, we expanded the oil-in-water emulsion-based process to a wide range of colloidal materials for the production of colloidal molecules with

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* Corresponding author. E-mail: smyang@kaist.ac.kr.
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[‡] LG Chem Research Park.
[§] New York University.

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various material properties.[5] In our recent attempt, inorganic particles or polymer latexes, which generally were not stable in water but sterically stabilized in oil, were clustered and subsequently encapsulated by sol−gel reaction on the surface of the clusters.

Here, we described a simple and facile method for making colloidal clusters of PS or silica microspheres using *phase-inverted* water-in-oil (W/O) emulsions. Unlike the previous reports based on O/W emulsions that always required stable colloids in oil, the present method based on W/O emulsions is practically versatile since most of the commercially available colloids are suspended in aqueous media with much better phase stability. Obviously, when dispersed in aqueous phase, the PS or silica microspheres exhibit soft electrostatic repulsions due to the chargeable surface moieties in contact with water. In addition, the hydrophilic silica spheres in aqueous emulsion droplets tend to reside in the interior of the aqueous phase rather than migrating toward the interface between aqueous and oil phases. These situations are quite different from the oil-in-water emulsions, which have been considered by the previous studies.[4−6] In this study, we thus investigated how the surface properties of the colloidal particles in water-in-oil emulsion droplets affected the cluster structures, which was in fact significant when the number of constituting particles in a cluster was greater than six. In particular, we observed some isomeric structures for a few cases of $n = 7$, 8, and 11, depending on their surface properties of colloidal microspheres. These isomers have not been reported in the preceding studies for colloidal clusters fabricated from the phase inverted oil-in-water emulsions.

Experimental Section

Materials. Styrene (99%), potassium persulfate (initiator, 98%), and sodium hydrogen carbonate (buffer, 99%) were purchased from Kanto Chemicals and divinylbenzene monomer (80%) for seeded polymerization was obtained from Aldrich. Milli-Q water (18.2 MΩcm^{-1}) was used as the reaction medium for the polymerization. Tetraethyl orthosilicate (TEOS, 99.999%, Aldrich) and ammonia (28−30%, Junsei) were used as a sol−gel precursor and a catalyst, respectively. Ethanol (99.9%) and hexane (98%) were obtained from Merck and toluene (99.8%) and hexadecane (99%) from Sigma-Aldrich. Emulsifier, Span 80 (sorbithan monooleate), and Hypermer 2296 were obtained from Aldrich and Uniquema, respectively. Gradient maker, Ficoll 400, and glycerol (99%) were purchased from Sigma and Showa Chemicals, respectively.

Instrumentation. Optical microscopy was performed on a Nikon TE 2000 microscope and scanning electron microscopy was carried out on a field emission scanning electron microscope (FE-SEM, XL305FEG, Philips). Emulsification of the water in oil medium was performed by a homogenizer (DIAX 900, Heidolph). A vortex mixer was used to re-disperse PS and silica clusters in water (Maxi Mix II, Type 37600 mixer, Thermolyne).

Synthesis of Monodisperse Colloids. Cross-linked PS spheres of 230 nm in diameter were prepared by emulsifier-free emulsion polymerization following the procedures in the previous reports.[11] PS particles were cross-linked by copolymerization of styrene and divinylbenzene (DVB) at 70 °C with vigorous stirring for 10 h in which potassium persulfate was used as initiator. Since clusters of the PS spheres were dispersed subsequently in an oil phase of toluene, the polymer particles were cross-linked by (DVB) to prevent the PS particles from being dissolved. PS particles of 830 nm in diameter were synthesized by the method of seeded growth using 230-nm particles as seed particles. Uniform silica particles with a mean diameter of 800 nm were prepared via controlled hydrolysis and condensation of TEOS in ethanol in the presence of water and ammonia following the modified seeded-growth method.[12] Detailed procedures were reported in our previous reports.[5]

Cluster Formation. Colloidal clusters of PS particles were prepared from W/O emulsion droplets. Three milliliters of aqueous PS suspension (0.9% w/w) was added to the mixture of 1% w/w Span 80 surfactant and 17 mL of toluene. To prepare water droplets in toluene, aqueous PS suspension was emulsified in toluene with a homogenizer for 60 s at 12000 rpm. Then, the PS particles were aggregated with slow evaporation of water from droplets at 100 °C for 1 h. During evaporation of water, a small amount of toluene was added to the vessel to keep toluene from being dried up. After being cooled to room temperature, clusters of the PS spheres were diluted with ethanol and solvent was replaced with water by centrifugation at 3000 rpm for 15 min and re-dispersion with a vortex mixer.

Colloidal clusters of 800-nm silica particles were formed by a similar process. Two milliliters of aqueous silica suspension (0.9% w/w) was added to 16 mL of hexadecane with 0.3% w/w. An amphiphilic block copolymer (Hypermer 2296: Uniquema) was used as a stabilizer. To obtain water droplets in hexadecane, the aqueous silica suspension was emulsified in hexadecane at 8000 rpm for 40 s and 9500 rpm for 20 s. By slow evaporation at 100 °C for 1 h, silica clusters were formed. Then, the sediment of colloidal clusters was collected with residual hexadecane, which was removed carefully from the sediment of clusters by washing with hexane and re-dispersion several times. Hexane was also evaporated from the sediments at room temperature and colloidal clusters were re-dispersed in water by gentle mixing.

Density Gradient Centrifugation. For colloidal clusters of PS microspheres of 830 nm in diameter, fractionation was performed by using a linear density gradient of polysaccharide (Ficoll 400). A two-jar type gradient forming device was used to make 3−9 wt % linear gradient inside a glass tube; 0.3 mL of the cluster suspension was carefully loaded on top of 11 mL of the gradient solution. Then, ultracentrifugation using a swing-bucket rotor at an acceleration of 3700*g* for 20 min fractionated the clusters into isolated bands, each of which contained clusters of an equal number of the constituent PS microspheres. The fractionated clusters were taken out from each band by a syringe in blunt needle. For fractionation of silica clusters, gentle centrifugation was performed using 24−85 wt % linear density gradient of glycerol, at 500*g* for 15 min. The clusters were also separated from the individual band with a syringe. These fractionated uniform clusters were washed by repeated centrifugation and redispersion several times to remove the gradient maker of polysaccharide or glycerol for clear SEM imaging without any contaminants.

Sample Characterization. PS and silica microspheres captured by water droplets in oil phase were observed by using an optical microscope. FE-SEM was performed to observe the configurations of PS and silica clusters. Before the SEM observation, the aqueous suspension of clusters was dried completely at room temperature and gold-coated to avoid electric charging.

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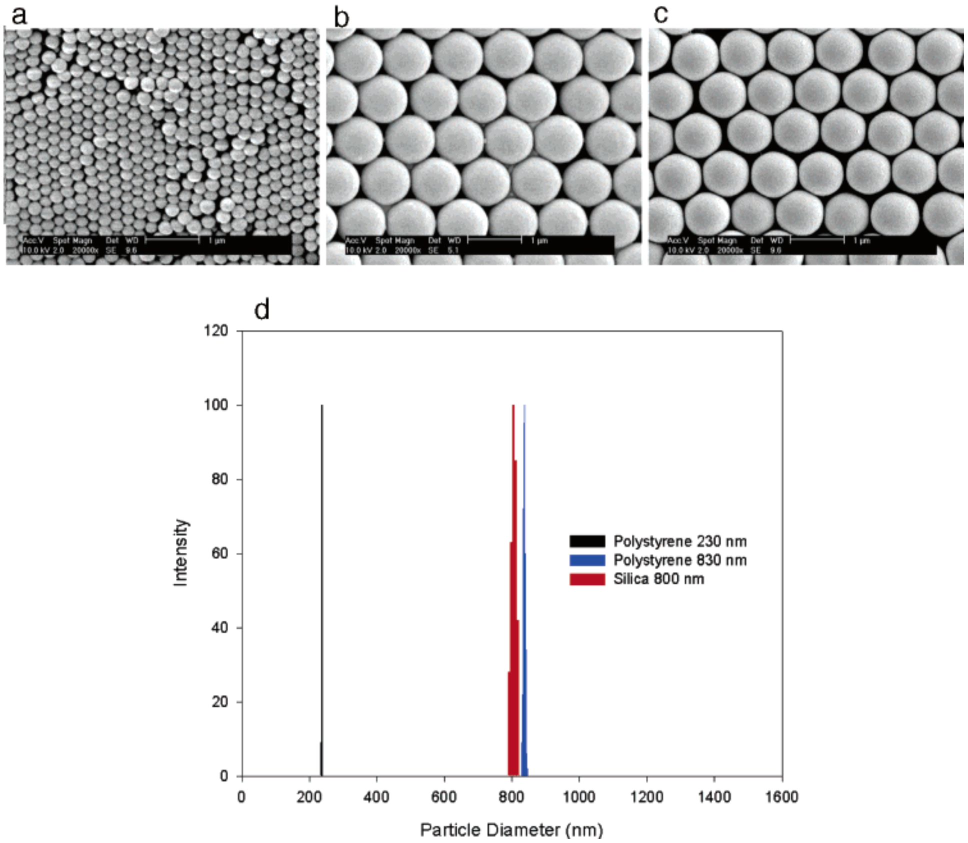

Figure 1. Scanning electron micrographs of monodisperse microspheres: (a) 230-nm PS, (b) 830-nm PS, and (c) 800-nm silica. (d) Particle size distribution measured by dynamic light scattering. Scale bars are 1 μm.

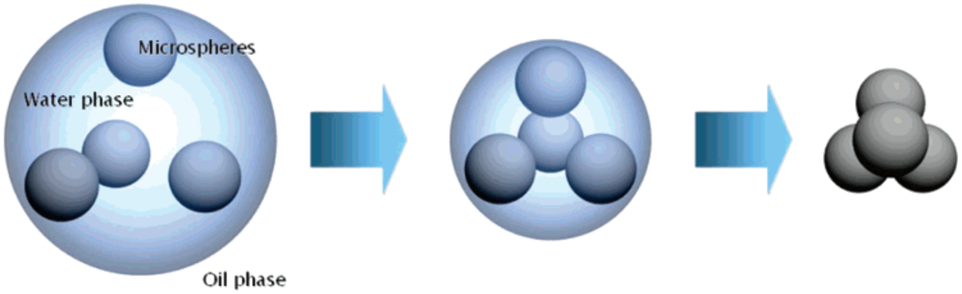

Figure 2. Schematic diagram for the fabrication of colloidal clusters of microspheres from water-in-oil emulsions.

Results and Discussion

Figure 1 shows the SEM images of PS or silica (SiO_2) microspheres, which were synthesized by emulsifier-free emulsion polymerization and modified Stöber method, respectively. As can be seen in the SEM images, monodisperse microspheres of PS and SiO_2 were successfully prepared and the size distributions of microspheres obtained from dynamic light scattering coincided well with the SEM observation.

The procedure for the fabrication of colloidal clusters from the W/O emulsion is described schematically in Figure 2. Monodisperse microspheres inside droplets were slowly aggregated as the aqueous droplet was shrunk with slow diffusion of water into the oil phase. To observe the behavior of PS microspheres in aqueous emulsion droplets in toluene through an optical microscope, we used rather large PS spheres of 830 nm in diameter. Preceding studies using a phase-inverted toluene-in-water emulsions revealed that partially cross-linked PS microspheres resided near the interface of toluene and water.[4] During evaporation of toluene, the PS microspheres on the interface approached each other and the adjacent microspheres began to contact, closely forming the so-called critical packings. Further evaporation of toluene induced the rearrangement and final dense packings of microspheres.[13] Likewise, our PS particles in water-in-toluene emulsions were also positioned near the interfaces as shown in optical micrographs in Figure 3.

Our colloidal clusters from the W/O emulsions consisted of several types of regular polyhedral aggregates with various numbers (*n*) of the constituent PS microspheres. This is because the number of PS spheres captured in different water droplets were not uniform at all. Thus, polydisperse colloidal clusters were fractionated according to the number of constituent PS beads by density gradient centrifugation. To do this, we followed the procedure reported by Manoharan

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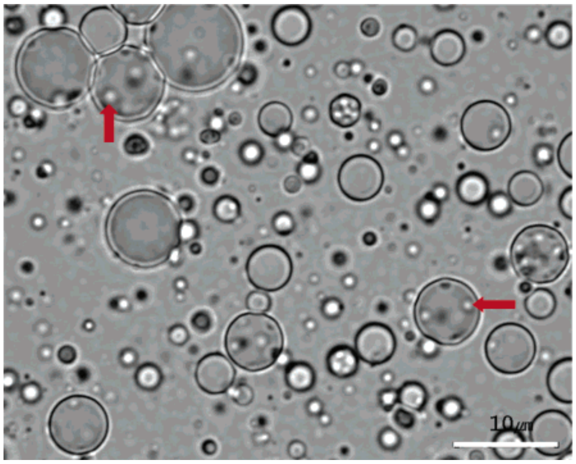

Figure 3. Optical microscope of 830-nm PS microspheres encapsulated in water droplets in toluene. Arrows indicate the PS microspheres near the interfaces of water-in-toluene emulsions.

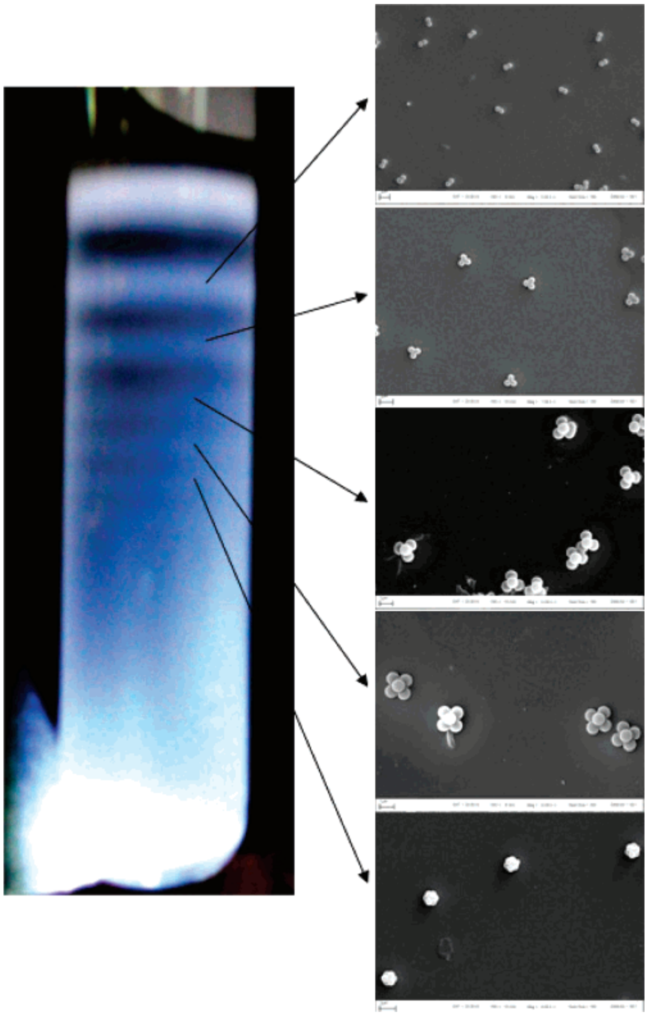

Figure 4. Test tube containing a cluster suspension of 830-nm PS microspheres separated by density gradient centrifugation and scanning electron micrograph image of colloidal clusters extracted from each band.

et al. Figure 4 shows that PS clusters redispersed in water were separated successfully into several isolated bands in linear density gradient of polysaccharide (Ficoll type 400) by centrifugation at 4000*g* for 30 min. From optical and SEM images, we observed that each band had all-identical clusters. The slight structural deviation of the fractionated $n = 5$ clusters from the original triangular dipyramid was caused by the repeated centrifugation and redispersion steps for the removal of density gradient maker, polysaccharide, to obtain clear SEM images without any contaminants.

Packings of microspheres were induced by capillary force acting on the particles. Since Kepler's conjecture on the optimal infinite packing of spheres, the theoretical studies on the sphere packings have been performed to predict the geometrical structure of clusters as a function of the number of constituent particles. Up to now, three typical optimal sphere packings or cluster structures have been proposed by optimizing their respective object functions, namely, Lennard-Jones (L−J) potential, second moment of the mass distribution, and Coulomb potential.[1,2,14,15] First, the geometries of L−J clusters which minimize L−J potential between spheres were predicted using global optimization algorithm by Floudas. A few lower order L−J clusters are touching two particles for $n = 2$, triangles for $n = 3$, tetrahedrons for $n = 4$, triangular dipyramids for $n = 5$, octahedrons for $n = 6$, and pentagonal dipyramids for $n = 7$.[1] Second, the structures of clusters for the minimal second moment are the same as the L−J clusters for $n \leq 7$. However, for $n \geq 8$, the two model clusters do not have identical structures. For example, the second-moment clusters of snub disphenoids ($n = 8$), triaugmented triangular prisms ($n = 9$), and gyroelongated square dipyrarmids ($n = 10$) do not minimize the L−J potential. Third, the minimum Coulomb potential determines the configurations of repulsive point charges or so-called Coulomb clusters.[2,15] Interestingly, the geometries of Coulomb clusters are also the same as L−J clusters for $n \leq 7$. For higher order clusters ($n \geq 8$), the structures are quite different from either L−J clusters or second-moment clusters. For instance, for $n = 8$, the 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. In the present study, we have investigated our PS and silica clusters obtained from the W/O emulsions and classified them according to the models outline above.

The SEM images of clusters of 230-nm PS microspheres formed inside aqueous emulsion droplets are reproduced in Figure 5. As noted, the configurations were unique depending on the number of constituent particles ($n = 2-13$). Their configurations for $n \leq 11$ corresponded to the theoretically predicted second-moment clusters except for $n = 8$. In this particular case, $n = 8$, we observed two isomers; one was a second-moment cluster of snub disphenoid and the other a Coulomb cluster of twisted squares.[2,15] Twisted squares were less popular than snub disphenoids as observed through the scanning electron microscope. However, the fraction of twisted squares was high enough to be observed in every sample. We believe that electrostatic repulsion between the PS beads in water droplets caused formation of the Coulomb clusters for $n = 8$. In particular, Manoharan et al. prepared colloidal clusters of PS microspheres from phase-inverted toluene-in-water emulsions, and they could not observe the

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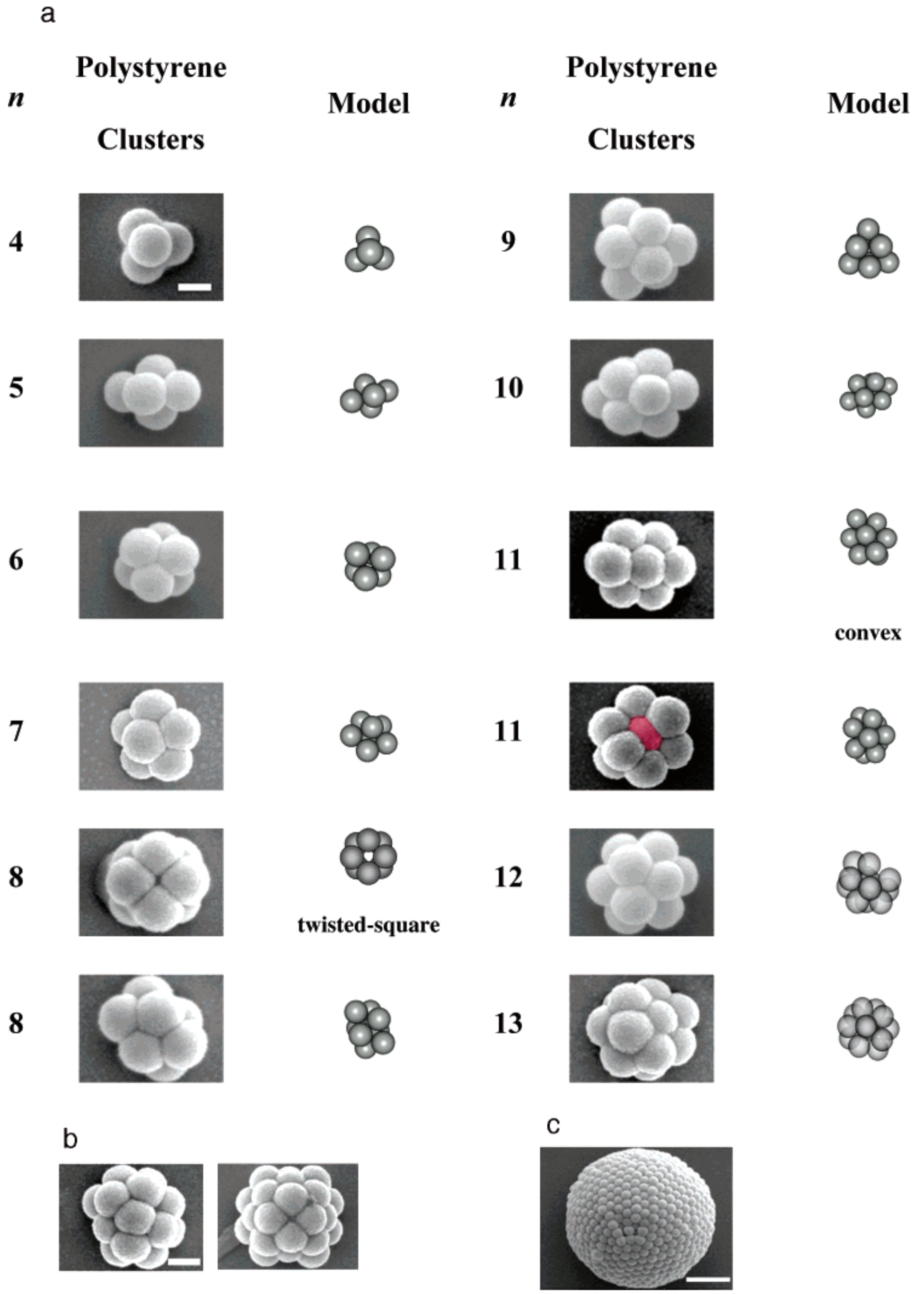

Figure 5. Scanning electron micrographs of (a) colloidal clusters of 230-nm PS for $n = 4-12$, (b) colloidal clusters of 230-nm PS for $n > 13$, in which the scale bar is 200 nm, and (c) supraballs: scale bar is 1 μm. All model clusters correspond to the minimal second-moment configurations except for the isomeric clusters of $n = 8$ (twisted-square) and 11 (convex).

Coulomb clusters for $n = 8$.[4] This was because the PS microspheres in their case were dispersed in toluene, and consequently the electrostatic repulsion between the PS beads was negligibly small. Another isomeric structure was also found for $n = 11$. Both convex and nonconvex types of clusters were found together as shown in Figure 5. The nonconvex configuration corresponds to the eleventh order minimal second-moment cluster. In the eleventh order clusters of nonconvex shape, one sphere colored in red of the SEM image could not pop out in the rearrangement process. In their previous study, Manoharan et al. observed only a *nonconvex* structure for $n = 11$ colloidal clusters of PS microspheres prepared from toluene in water emulsions.[4] Meanwhile, in our recent study, we found that *convex* clusters of poly(methyl methacrylate) (PMMA) microspheres were produced from hexane in water emulsions.[5] In our case, the PMMA spheres were covered with a steric barrier of poly(dimethylsiloxane) (PDMS) and they had soft repulsive potentials. Therefore, the PMMA spheres in hexane behaved like soft spheres, which was responsible for the formation of convex structure. In the present case, the PS beads acted as soft spheres inside water droplets due to their negative surface charges, which possibly led to the formation of convex structure for the eleventh order clusters. Thus, we have observed isomeric clusters of order $n = 8$ and 11 when the constituting PS beads exhibited soft repulsive interactions.

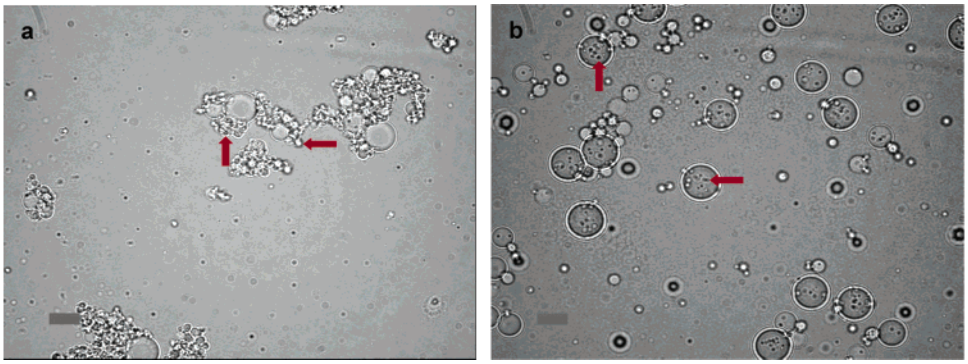

Figure 6. Optical micrographs of 800-nm silica microspheres encapsulated in water-in-oil emulsions: (a) water droplets in mineral oil stabilized with Span 80; (b) water droplets in hexadecane stabilized with Hypermer 2296. Scale bars are 5 μm. Arrows indicate the locations of silica microspheres.

Besides the cluster configurations, an interesting feature was observed in the morphology of the constituent PS particles. Since the evaporation of water droplets proceeded at 100 °C, which was around the glass transition temperature of PS, thermal annealing of touching microspheres could lead to the formation of polygonal interfaces between the PS particles after the formation of aggregates. In Figure 5, the interfacial facing area between particles turned out to be polygonal and in close contact with neighbors. Such morphological change was because of the viscoelastic deformation of PS microspheres which was similar to the space-filling shape of colloidal crystals by heating.[16,17] Thermal annealing of the PS clusters and swelling in toluene resulted in such unusual morphologies as shown in Figure 5.

In general, the probability that a specific number (n) of spheres are captured in a single droplet is governed by Poisson distribution when the size of emulsion droplets is monodisperse.[18] In our group, we reported a series of novel emulsification strategies which can generate monodisperse emulsion droplets using microfluidic devices,[19a,19b] micropipet injection,[20c] and electrospray.[21] In these cases, therefore, the relative amount of clusters with an identical configuration will exhibit a Poisson distribution. For the present case, however, the situation is more complicated since the size distribution of emulsion droplets is polydisperse, and consequently the fluctuation in the number of microspheres encapsulated in a droplet is not exactly governed by Poisson distribution. In fact, a broad spectrum of small clusters for $n \leq 12$ was found as reproduced in Figure 5a. Nevertheless, we can adjust somehow the relative amount of clusters with an identical morphology type by changing the loadings of microspheres in colloidal suspension before emulsification or by changing the size of emulsion droplets under various shearing conditions.

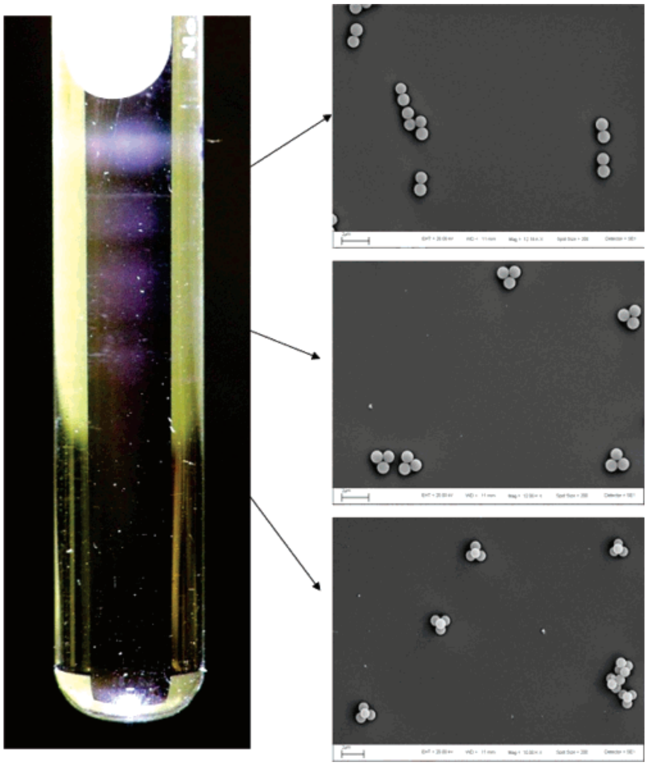

Figure 7. Test tube containing a cluster suspension of 800-nm silica microspheres separated by density gradient centrifugation and scanning electron micrograph of colloidal clusters extracted from each band.

It is noteworthy that the configurations of clusters belong to the subset of face-centered cubic (fcc) symmetry only for $n \leq 6$. We found also several types of higher order clusters ($n \geq 13$), but it was not easy to figure out their exact internal configurations from the SEM images in Figure 5b. Evidently, for large n, PS microspheres were hexagonally packed into a supraball of Figure 5c, as previously reported by Mauaziz et al.[22] These supraballs have a face-centered cubic (fcc) symmetry in a finite spherical domain with a few inevitable defects as reported by Bausch et al.[23] As noted, the (111) direction of fcc packing was normal to the supraball surface. It is a simple matter to estimate the number of PS microspheres of radius r constituting a supraball of radius

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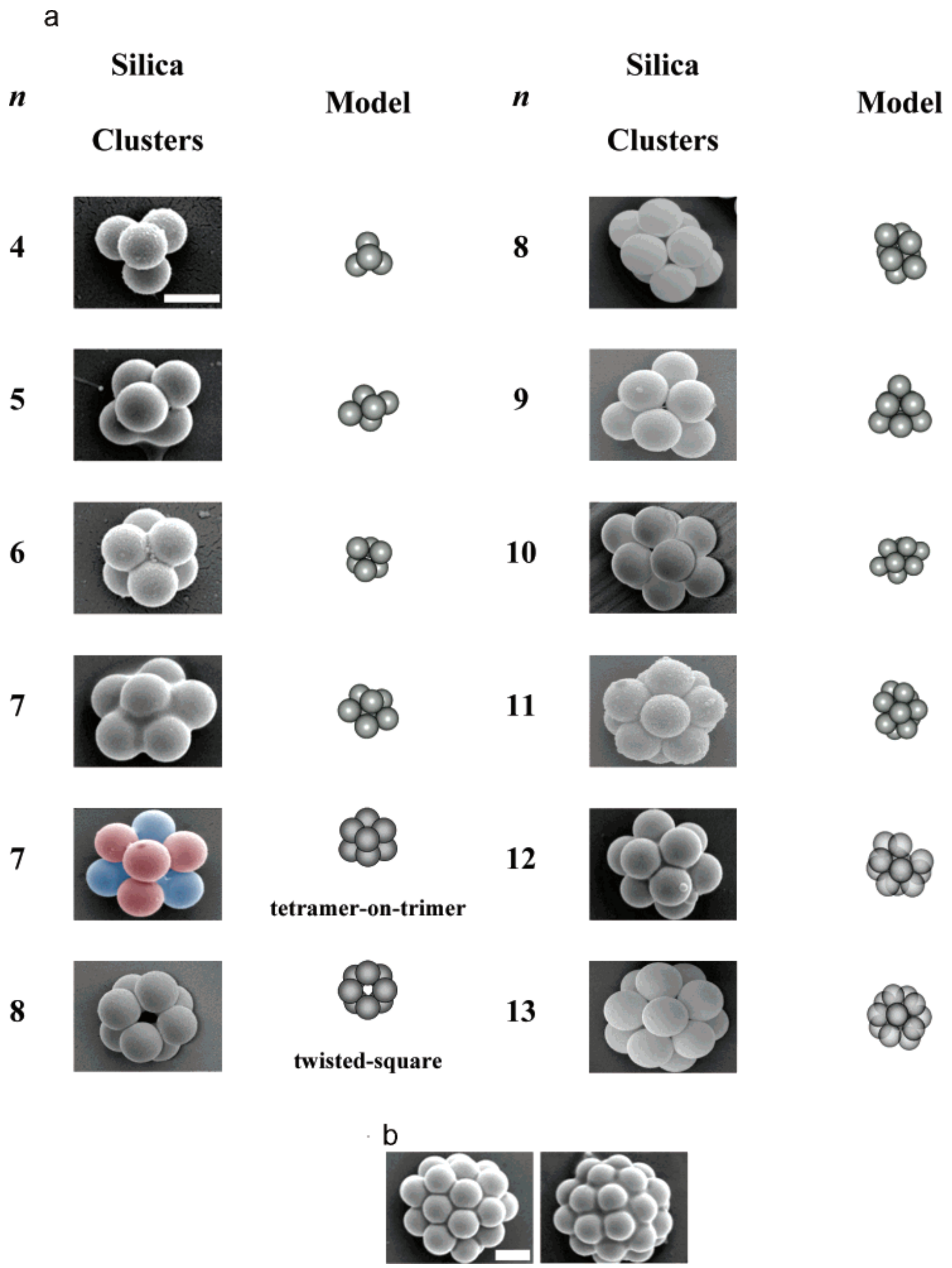

Figure 8. Scanning electron micrographs of (a) colloidal clusters for $n = 4-12$ and (b) higher order clusters of silica. Scale bars are 1 μm. All model clusters correspond to the minimal second-moment configurations except for the isomeric clusters of $n = 7$ (tetramer-on-trimer) and 8 (twisted-square).

R from the simple relationship,

$$n = f\cdot\left(\frac{R}{r}\right)^3$$

in which f is the packing density of the fcc lattice. For the spherical aggregate of 3.2 μm in diameter as shown in Figure 5c, the number of 230-nm PS microspheres can be estimated as $n = 1993$, assuming that the inside of the supraball is completely packed in fcc symmetry.

Our strategy for the fabrication of colloidal clusters from W/O emulsions was not limited to the polymeric building blocks. With use of inorganic silica particles that were stable in water, small clusters could also be prepared with carefully selected oil and stabilizer for stable emulsions containing particles. In particular, when we used mineral oil as a continuous medium with nonionic surfactant of Span 80, silica particles in aqueous emulsion drops escaped into the mineral oil phase as water evaporated. This can be clearly seen from the optical microscope image in Figure 6a. Such migration of the silica particles from water droplets to oil phase was due to the fact that the nonionic surfactant, Span 80, diffused into water droplets and adsorbed on the silica particles, which rendered them hydrophobic and stable in oil.[19]

To address this problem, we used hexadecane as the oil phase and nonionic polymeric surfactant (Hypermer 2296) which was insoluble in water. In addition, the mobility of the polymeric surfactant was negligibly small. The optical micrograph in Figure 6b shows that no migration of silica particles toward the oily hexadecane phases occurred in this particular case. In addition, unlike PS beads in aqueous emulsions in toluene, silica particles were not trapped at the interface but resided inside the water droplets because of strong hydrophilicity of silica particles. After performing the same procedures as described previously, we obtained clusters of the silica microspheres. It is worth commenting that, for silica clusters, a glycerol−water mixture was used as a density gradient medium for the ultracentrifugal fractionation since silica spheres had a higher specific gravity than PS beads. As shown in Figure 7, the silica clusters were separated into about four bands inside a glass tube and each band has uniform clusters with the same size and configuration.

As noted from Figure 8, the configurations of silica clusters were almost the same as those observed in the PS clusters in Figure 5. For $n = 7$, we observed an isomeric structure of “tetramer-on-trimer” configuration, which was different from the minimal second moment cluster of the pentagonal dipyramid. However, even though the majority of the seventh order clusters was the minimal second moment, it was not that difficult to find out the former type cluster under a scanning electron microscope. As noted previously, the silica spheres resided in the interior of the water droplets rather than gathering near the interface. Under this situation, the silica spheres were able to form this compact isomeric cluster for $n = 7$ by the compressive capillary forces. As before, the silica clusters for $n = 8$ have two isomeric structures, namely, minimal second moment and Coulomb clusters. This is again due to the fact that the silica microspheres were highly negatively charged due to the hydroxyl group, which induced Coulombic twisted-square clusters. When the number of silica microspheres encapsulated inside aqueous emulsion droplets in hexadecane were large enough, higher order clusters were also obtained as shown in Figure 8b.

Conclusions

A simple and facile method for small colloidal clusters of microspheres was proposed based on evaporation-induced assembly of water-borne colloids in water-in-oil (W/O) emulsions. With use of an aqueous suspension of monodisperse cross-linked PS microspheres, colloidal clusters were produced from slow evaporation of water droplets in toluene and fractionated according to the number of constituent particles in each cluster by density gradient centrifugation. The clusters that we produced were unique configurations, but we have observed some isomeric clusters for $n = 8$ and 11 depending on the electro-kinetic surface properties of the colloidal particles. The same procedures have been applied to aqueous silica suspension droplets in hexadecane with nonionic polymeric stabilizer and also produced some isomeric structures. The isomers of PS and silica spheres formed in our water-in-oil emulsions have not been reported in the preceding studies for colloidal clusters fabricated from the phase-inverted oil-in-water emulsions. The colloidal clusters have diverse applications including photonic crystals with novel and promising structures, photonic molecules, additives for latex paints, and so forth.[24] In particular, dimeric ($n = 2$) or tetragonal ($n = 4$) clusters can be used as building blocks of diamond lattices which possess complete, full photonic band gaps.

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