Fabrication of Colloidal Clusters of Polymer Microspheres and Nonspherical Hollow Micro-particles from Pickering Emulsions

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We have introduced the Pickering emulsion systems to generate novel confining geometries for the self-organization of monodisperse polymer microspheres using nanoparticle-stabilized emulsion droplets encapsulating the building block particles. Then, through the slow evaporation of emulsion phases by heating, these microspheres were packed into regular polyhedral colloidal clusters covered with nanoparticle-stabilizers made of silica. Furthermore, polymer composite colloidal clusters were burnt out leaving nonspherical hollow micro-particles, in which the configurations of the cluster structure were preserved during calcination. The self-assembled porous architectures in this study will be potentially useful in various applications such as novel building block particles or supporting materials for catalysis or gas adsorption.

Key Words : Colloidal clusters, Self-assembly, Hollow particles, Pickering emulsions

Introduction

The self-organized colloidal structures have attracted lots of attention due to their potential uses in various applications including drug delivery, optoelectronic devices such as photonic crystals, solar cells, or antireflective coatings, and biological diagnosis for DNA detection.[1-7] For more complex and better colloidal architectures, the self-organization of monodisperse microspheres has been recently developed for non-spherical colloidal particles, which are called as *colloidal molecules*.[8-12] Several strategies have been proposed to prepare such colloidal molecules by controlled aggregation of the preformed colloidal particles or modifying a single colloid into an anisotropic particle through the growth of nodules.[13] One of the most efficient schemes for the self-assembly of colloidal particles is the generation of confining geometries for the encapsulation of the particles and evaporation-driven self-organization.[14] In previous reports, emulsion droplets stabilized with conventional surface active agents have been adopted as confining geometries for the small colloidal assemblies,[15-18] or tiny aerosol droplets were also utilized in similar manner.[19,20] The concept of the evaporation-driven self-assembly based on emulsion-assisted technology has been reported in pioneering work by Velev and his colleagues, in which spherical or sessile droplets were used as confining geometries.[21-23]

In colloidal clusters fabricated by controlled aggregation inside evaporating droplets, dense packings of colloidal microspheres were consistent for given number of particles and the resultant micro-structures of the colloidal assemblies were explained as minimal second moment clusters, in which the second moment M of the particle species with central position of r_i, in which M is defined according to the following equation using the position of the center of mass

for the particulate system, r_o.

$$M = \sum_{i=1}^{n} \left\| r_i - r_0 \right\|^2$$

The resultant minimal second moment clusters and their isomers were successfully generated inside confining geometries such as tiny emulsion droplets or aerosols.[14,19] However, the emulsion-assisted approaches have fatal limitations in that it is very difficult to remove the tedious continuous phases such as oils or surfactants on the surface of the self-assembled aggregates which were originally adsorbed on the interfaces of the emulsion droplets. Additionally, the facile generation of the aerosol droplets is also difficult since large-scale nebulizers and furnaces operating at high temperature are required for the atomization and evaporation of the droplets inside aerosol reactor.

Without using conventional surfactants, micron-sized emulsion droplets could be successfully prepared with the aids of the suitable nanoparticle-stabilizers rendering the similar function as the emulsion stabilizers such as surfactants or amphiphilic polymers.[24-27] These nanoparticle-stabilized droplets are called as *Pickering emulsions* named after S. U. Pickering because of his significant contribution for the study of this subject.[28] Those systems could be applied for the synthesis of innovative architectures such as stimuli-responsive core-shell particles.[29]

For stabilizing Pickering emulsions, solid nanoparticles should be chosen for adsorption onto the interface between the two phases-dispersed and continuous phase, by preventing the emulsion droplets from aggregating together. These special emulsion systems may have potential importance as confining geometries for the self-organization of microspheres inside the droplets, if the encapsulation of the additional particle species into the emulsion is possible,
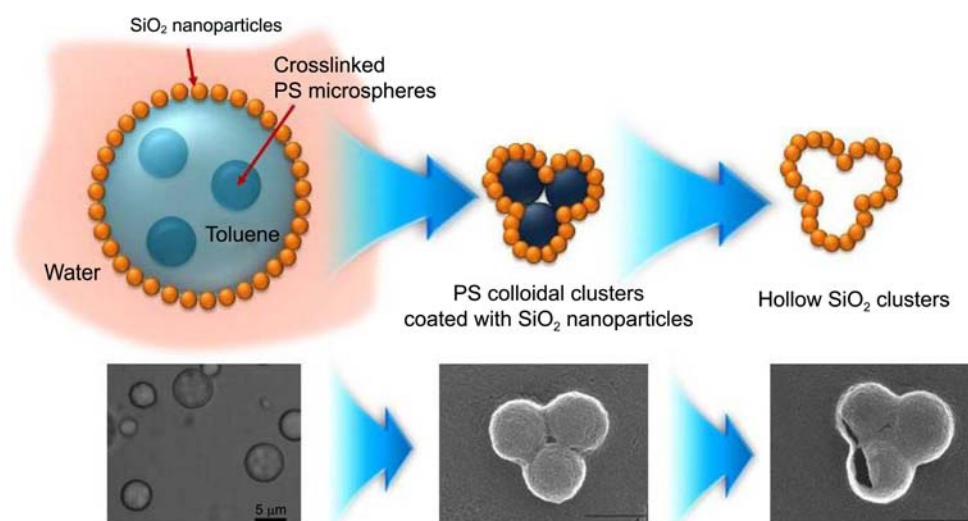
Figure 1. The schematic figure of the Pickering emulsion droplet containing hydrophobic PS microspheres. After evaporation-driven self-assembly, the microspheres can be self-organized into colloidal micro-clusters covered with silica nanoparticles which originally stabilize the emulsion droplets before demulsification. Further calcination results in the generation of hollow micro-clusters.

since the adsorbed nanoparticle-stabilizer on the droplet surface can provide special functionalities on the resultant self-assembled structures. However, the nanoparticle-stabilized emulsions have not been explored yet for assembling microspheres, albeit the final self-organized structure may have various interesting features such as structural or compositional complexities and functionalities.

In this article, we have introduced the combined ideas from polymer, sol-gel, and physical chemistry of the complex fluid system such as Pickering emulsions for the innovative architectures of hollow micro-particles based on the concept of *integrative chemistry* proposed by Backov and his colleagues.[30] Specifically, for the colloidal clusters of polystyrene microspheres, nanoparticle-stabilized Pickering emulsions were prepared by shear-induced emulsification process, in which uniform microspheres were encapsulated. Then, controlled aggregation of microspheres with nanoparticles at interface was induced during slow evaporation of the oil droplets as described in the scheme of Figure 1. Then, nonspherical hollow micro-particles were obtained by burning out the organic microspheres, leaving behind the silica nanoparticles which were utilized as covering layer on the surface of the colloidal clusters. Resultant structures of the colloidal clusters and hollow micro-particles were examined by scanning electron microscopy, and the compositions of the colloidal aggregates were confirmed using FT-IR analysis. The thermogravimetric analysis was also performed to examine the weight loss of the polystyrene micro-clusters covered with silica nanoparticles as a function of temperature.

Experimental

Materials. Styrene (99.5%, Samchun Chemicals) and divinylbenzene (DVB, 95%, Aldrich) were used as monomer and crosslinker, respectively, to synthesize monodisperse

polystyrene (PS) microspheres by emulsifier-free emulsion polymerization. During the synthesis of the microspheres, potassium persulfate (95%, Junsei) as initiator and sodium chloride (EP grade, Burdick & Jackson) as salt were used to prepare sulfate-coated PS particles. For the case of amidine-coated PS microspheres, α,α'-azodiisobutyramidine dihydrochloride (98%, Fluka) was used as an initiator. The commercial silica nanoparticle suspension (30 nm, Ludox CL, 30 wt. % in H_2O, Aldrich) was utilized to obtain nanoparticle-stabilized emulsion droplets made of toluene (Sigma-Aldrich, 99.8%) encapsulating the PS microspheres. The continuous phase of the Pickering emulsion system was made of distilled water which was obtained using Pure Water System (Human Power, Scholar). To prepare the Pickering emulsions, the diluted suspension of the Ludox CL silica nanoparticles was mixed with hydrochloric acid (35-37%, Samchun Chemicals) and potassium hydrogen phthalate (KHP, Sigma-Aldrich, 99.95%) before the emulsification procedure.

The Synthesis of Monodisperse Polymeric Microspheres. Monodisperse PS microspheres were synthesized using the surfactant-free emulsion polymerization by mixing the styrene monomer with distilled water during vigorous stirring under nitrogen atmosphere. DVB was used as crosslinker to prevent the resultant microspheres from being dissolved out in organic solvent such as toluene. For some case, seeded polymerization was performed to synthesize monodisperse PS microspheres. The detailed reaction conditions for the sulfate and amidine-coated PS microspheres are summarized in Table 1 and Table 2, respectively. By using the proper initiator, sulfate or amidine coated PS microspheres with 800 nm or 750 nm in diameter, respectively, could be successfully synthesized with narrow size distribution. The polymerization reaction temperature was maintained at 66 and 77 °C for the sulfate and amidine-coated PS microspheres, respectively. The resultant PS microspheres were washed by centrifugation at 3,900 rpm for 30 minutes and redispersed

Table 1. Detailed emulsion polymerization conditions for the synthesis of sulfate-coated PS microspheres using sodium chloride as salt

Chemicals	Amounts
Deionized water	595 mL
NaCl	1 g
Styrene	45.3 g
Divinylbenzene	0.453 g
Initiator	0.287 g

Table 2. Detailed emulsion polymerization conditions for the synthesis of amidine-coated PS microspheres by using two-step seeded growth method

Chemicals	Seed particles	1st Grown particles
Deionized water	450 mL	350 mL
Styrene	44.9 g	44.9 g
Divinylbenzene	0.57 g	0.57 g
Seed particle suspension	-	100 mL (9.1 wt. %)
Initiator	0.37 g	0.37 g

in ethanol followed by sonication to remove any unreacted precursors. The same centrifugation and redispersion procedures were employed to obtain the PS microspheres dispersed in toluene with proper solid particle concentrations. (*CAUTION*: Toluene is extremely toxic, thus should be handled with care.)

The Evaporation-driven Self-assembly of Polymeric Microspheres Inside Pickering Emulsions. To prepare the aqueous solution containing the nanoparticle-stabilizers composed of commercial silica nanoparticles, 3 mL of Ludox CL suspension was diluted with 42 mL of distilled water, and 0.1136 g of KHP and 20 μL of hydrochloric acid were added under vigorous agitation.[25] Then, 8 mL of the aqueous suspension of the nanoparticle-stabilizer was mixed with 1 mL of toluene dispersion containing polystyrene microspheres (2.7 and 1 wt. % for sulfate and amidine-coated PS microspheres, respectively), followed by the emulsification using homogenizer (PRO200, PRO Scientific Inc.). The optical microscope images of the resultant Pickering emulsion droplets were taken using Nikon TE 2000 microscope. High mechanical shear force was imposed to the mixture of PS suspension in toluene and aqueous nanoparticle stabilizer by using homogenizer at 30,000 rpm for 1 minute. The resultant Pickering emulsion droplets encapsulating the cross-linked PS microspheres were shrunken by heating at 80 °C for 1 hour and successive evaporation of toluene under vacuum, or the elevated temperature such as 100 °C, resulting in the self-organization of the PS particles. The FT-IR analysis of the PS microspheres and PS colloidal clusters covered with silica nanoparticles were performed using FT/IR 6300 equipment (Jasco).

The Fabrication of Nonspherical Hollow Microparticles Made of Silica Nanoparticles by Calcination. The aqueous suspension containing PS colloidal clusters covered with silica nanoparticles was dried on cover glass, followed by

calcination at 500 °C inside box furnace (EM Tech, Korea) for 5 hours to obtain hollow silica micro-clusters.

Characterizations. The size distribution of Pickering emulsion droplets were measured using Malvern Mastersizer 2000 (Malvern Instruments Ltd) by assuming the refractive index of toluene as 1.395. The morphologies of the original PS colloidal clusters and the hollow micro-particles were observed using field emission scanning electron microscope (FE-SEM, Mira II LMH). The BET surface area of the nonspherical hollow micro-particles was obtained by Barrett-Joyner-Halanda (BJH) method. The TGA analysis of the bare PS particles and PS micro-clusters covered with silica nanoparticles were performed using Thermal Analysis System (SDT Q600, Water Corporation). The heating rate was maintained as 10 °C/min under air environment during the TGA analysis.

Results and Discussion

Evaporation-driven self-assembly of the polystyrene microspheres inside Pickering emulsion droplets was depicted in Figure 1. Silica nanoparticles can be adsorbed on the interface between toluene droplets and continuous water phase as nanoparticle-stabilizer to prevent the emulsions from coalescing together, which stabilize emulsions as conventional surfactants do. Inside these nanoparticle-stabilized emulsions, namely Pickering emulsions, small number of the PS microspheres can be encapsulated, and they can be pulled together by inward capillary pressure during slow evpaporation of emulsion droplets by heating. Finally, the PS microspheres can be self-assembled into regular and polyhedral micro-clusters covered with silica nanoparticles, when evaporation was completed. After the formation of the PS colloidal clusters, further calcination process can be performed which produces the hollow micro-particles made of silica, as described schematically in Figure 1.

Figure 2(a) contains the TEM image of the alumina-coated silica nanoparticles (Ludox CL, *ca* 30 nm in average diameter) used for the formation of the Pickering emulsions in this study. We have adopted the positively charged alumina-coated silica nanoparticles as emulsion stabilizers since the facile fabrication of the nanoparticle-stabilizer is possible by adsorbing KHP molecules on their surfaces.[25] Though other synthetic or commercial routes for the nanoparticle-stabilizers such as polystyrene or titania particles are possible, we have utilized 30-nm Ludox CL silica nanoparticles as emulsifier for the formation of nonspherical hollow micro-particles as a model system.[31,32] Figure 2(b) and 2(c) display the SEM images of the sulfate-coated monodisperse cross-linked PS building block particles with 800 nm in diameter before and after the redispersion in toluene, respectively. As shown in the SEM image of Figure 2(c), the spherical morphologies of the PS microspheres are almost maintained even after the drying from the dispersion medium, toluene, implying that the particles are cross-linked well. However, the SEM image in Figure 2(c) reveals that it is difficult to restore the original spherical morphologies of the the swollen
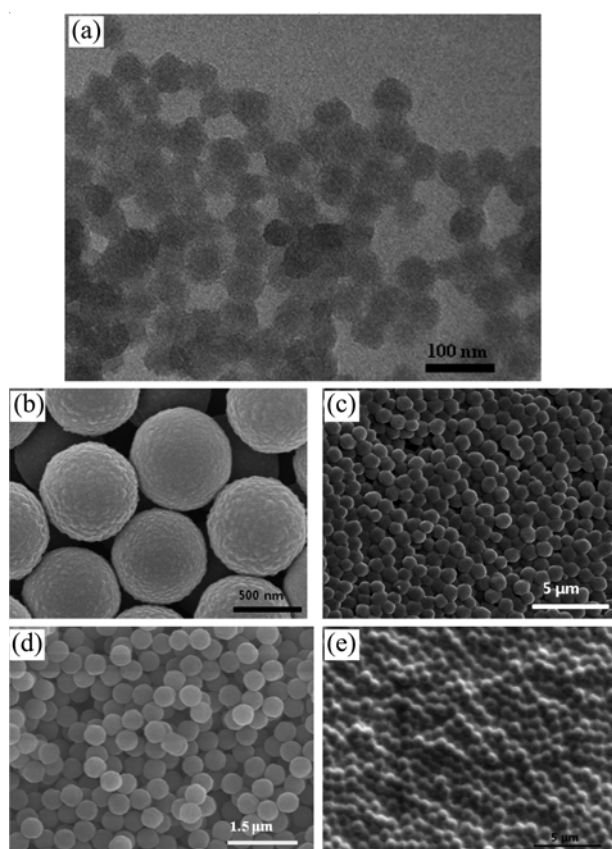
Figure 2. (a) TEM image of silica nanoparticles used as nano-particle-stabilizer (Ludox CL). Scale bar indicates 100 nm. (b) and (c) SEM images of sulfate-coated PS microspheres before and after redispersion in the dispersion medium, toluene. Scale bars are 500 nm and 5 μm, respectively. (d) and (e) SEM images of amidine-coated PS microspheres before and after redispersion in the dispersion medium, toluene. Scale bars are 1.5 μm and 5 μm, respectively.

particles with toluene even after the drying of dispersion medium. Similar results were observed for the amidine-coated cross-linked PS mirospheres with 750 nm in diameter, as displayed in the SEM images of Figure 2(d). When they were re-dispersed in toluene and dried for SEM imaging, we can clearly observe wrinkled surfaces as shown in Figure 2(e), since the spherical PS partilcles are slightly swollen due to the infiltration of the toluene solvent into the interior part of the cross-linked particles.

Figure 3(a) contains the picture and optical miscroscope image of the Pickering emulsions encapsulating polystyrene microspheres which were prepared using homogenizer at 20,000 rpm for 60 seconds in the presence of 2 wt. % of silica nanoparticles. As displyaed in the optical microscope image, micron-sized toluene emulsions were successfully fabricated using Ludox CL silica nanoparticles as nano-particle-stabilizers which are adsorbed between the inter-faces of water as continuous medium and toluene droplets as dispersed phase. The monodispersity of the Pickering emul-sion droplets was improved by decreasing the concentration of the silica nanoparticles in continuous medium as dis-played in the droplet size distribution curves of Figure S1 in
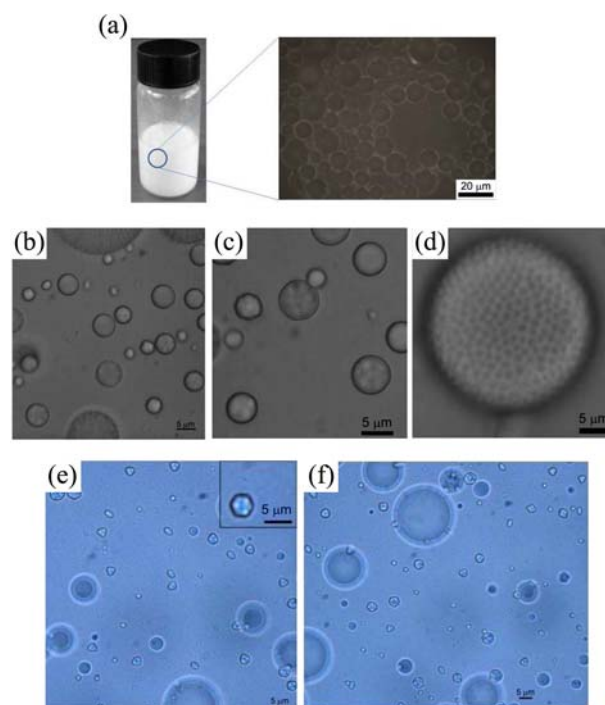
Figure 3. (a) Photograph of complex fluid system consisted of Pickering emulsion droplets without PS microspheres. The optical microscope image contains the Pickering emulsion droplets with polydisperse size distribution generated by homogenizer. Scale bar indicates 20 μm. (b)-(f) Optical microscope images of the Picker-ing emulsions containing cross-linked PS microspheres inside the droplets. Scale bars are 5 μm.

Supporting Information. As the amount of the nanoparticle stabilizer in water phase decreases, the fraction of small droplets begins to disappear, finally reaching almost mono-modal size distribution of the Pickering emulsions for the complex fluid system with 0.33 wt. % of silica nanoparticles in continuous medium. This phenomena may be explained by *limited coalescence scenario*, in which Pickering emul-sion droplets only coalesce to a limited extent, increasing the total droplet surface area until their surfaces are completely covered with solid particles.[33-35] Therefore, when the con-centration of nanoparticle stabilizer is insufficient for the complete coverage of the excess amount of Pickering emul-sions, some partially unprotected droplets can coalesce, resulting in the generation of monodisperse emulsion system. In this study, the Pickering emulsions with relatively narrow size distribution could be also obtained by de-creasing the amount of silica nanoaprticles in continuous medium, as shown in the size distribution curve of Figure S1. To fabricate colloidal clusters with small number of constituent particles, we have adopted the Pickering emul-sions stabilized with 2 wt. % of silica nanoparticles to obtain toluene droplets having relatively small sizes.

To estimate the thickness of adsorbed layers composed of silica nanoparticles on toluene emulsion droplets, we have measured the concentration of the unbound silica nano-particles in continuous phase since it is very difficult to observe the nanoparticles bound onto volatile toluene

emulsions directly under electron microscope such as TEM. The Pickering emulsions with unbound free nanoparticles were filtered using hydrophilic syringe filter (cellulose acetate, 0.2 μm, Advantec) to separate emulsion and obtain the clear solution of continuous phase as proposed by Prestidge and his coworkers.[36] The filtered solution was dried at 100 °C to measure the nanoparticle concentration C_c (1.53 wt. %) to estimate the adsorbed thickness of silica, t, on toluene droplet surface by the following equation.

$$t = \frac{V_W(C_i - C_c)}{V_T A_T \rho_T \rho_S} \quad (1)$$

Here, V_W, V_T, ρ_T, ρ_S, and C_i represent the known values such as the volume of continuous and dispersed phase, the density of toluene and water, and the initial concentration of silica nanoparticles in continuous phase (2 wt. %), respectively. By measuring the specific surface area of toluene droplets, A_T using Malvern Mastersizer as 0.191 m²/g, we could roughly estimate the value of t as 100 nm, indicating the number of layers of adsorbed nanoparticle stabilizers on toluene interface is about 3 to 4 since the primary particle size of the nanoparticles is about 30 nm as displayed in the TEM image of Figure 2(a). Thus, the silica nanoparticles on toluene droplets form multilayer rather than monolayer, which is consistent with previous results on the paraffin oil emulsions stabilized with thick multilayer of positively charged nanoparticles reported by D. Sun and his co-workers.[37]

In the case of the Pickering emulsions encapsulating the sulfate-coated PS microspheres inside the droplets, the optical miscroscope images are contained in Figure 3(b), 3(c), and 3(d). Before emulsification, the PS microspheres were redispersed in toluene with 2.7 wt. % of solid concentration. As shown in the images of Figure 3(b) and 3(c), small number of the PS microspheres are contained inside the toluene droplets after shear-induced emulsification by using homogenizer, indicating that all microspheres are located inside the confining droplets for the partilcle self-assembly. Since the size distribution of emulsion droplets is broad when mechanical shear-induced emulsification was utilized for the complex fluid systems fabricated by homogenizer, large number of the particles could be also encapsulated inside relatively huge toluene droplets, as shown in Figure 3(d). The PS microspheres did not escaped into the continuous phase, water, as displayed in the optical microscope image in Figure 3(d).

In the case of amidine-coated PS microspheres, 1 wt. % of the PS particles were redispersed in toluene by sonication and Pickering emulsions were prepared by using homogenizer. Since the evaporation rate of the toluene solvent is relatively rapid even under at room temperature, some toluene emulsion droplets were shrunken and colloidal clusters were already observed under the optical microscope, as shown in Figure 3(e) and 3(f). Thus, amidine-coated PS microspheres could be self-organized into octahedron structure inside the Pickering emulsion droplets as displayed in the inset picture of Figure 3(e), when 6 particles were

encapsulated.

After the evaporation-driven self-assembly of the PS microspheres encapsulated inside Pickering emulsion droplets shown in Figure 3(b) to 3(d), the sulfate-coated PS colloidal clusters covered with silica nanopartilcles were generated with regular polyhedral structures with the number of the constituent particles, N = 2 to 12, as displayed in the SEM images in Figure 4(a). Higher-order clusters (N > 13) and supraballs were also observed as displayed in the SEM images of Figure 4(b), although the exact configurations of the particles are difficult to figure out due to their complicated structures and large number of the constituent particles. In the case of amidine-coated PS microspheres, various polyhedral structures of self-assembled clusters from Pickering emulsion droplets are also contained in the SEM images of Figure S2 in Supporting Informations. Notably, some isomers such as *square pyramid*, *trimer on tetramer*, or *flower minus one* structures were also found which were not observed in minimal second moment clusters in previous reports by Manoharan *et al.* and Wittemann *et al.*[14,38] However, the isomeric cluster with twisted square structure
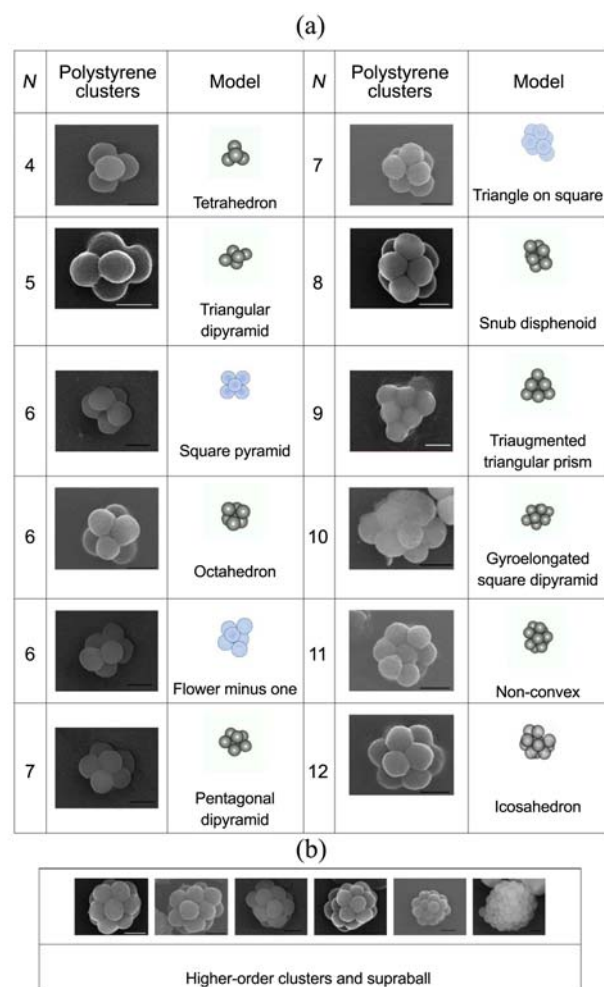
Figure 4. (a) SEM images of colloidal micro-clusters made of sulfate-coated PS microspheres covered with nanoparticle-stabilizer, silica. Scale bars are 1 μm. (b) SEM images of higher-order clusters. Scale bars are 1 μm.
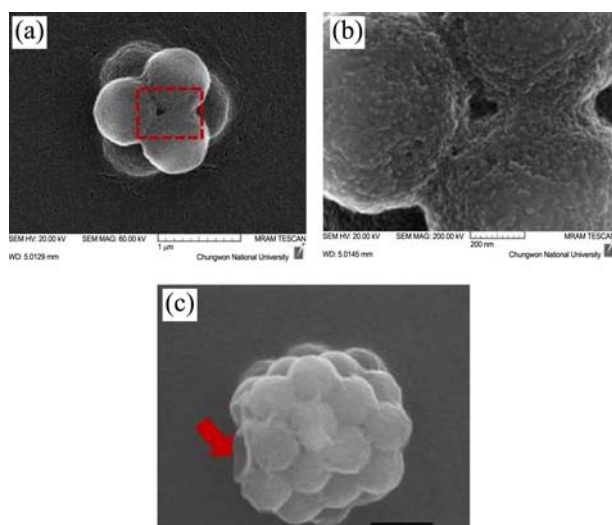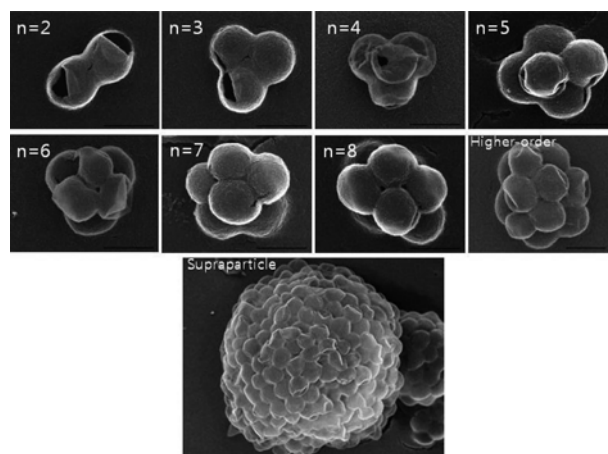
Figure 5. (a) and (b) High magnification SEM images of octahedral structure of PS micro-cluster covered with silica nanoparticles. Scale bars indicate 1 μm and 200 nm, respectively. (c) SEM image of higher-order PS micro-clusters covered with silica nanoparticles having point defect. Scale bar indicates 1 μm.

Figure 6. SEM images of hollow micro-clusters made of silica generated from sulfate-coated PS micro-clusters as sacrificial templates, respectively. Scale bars are 1 μm.

Figure 7. (a) and (b) High-magnification SEM image of hollow silica micro-clusters for $N = 4$. Scare bars are 500 and 200 nm, respectively. (c) and (d) SEM images of hollow silica microclusters from amidine-coated PS microspheres as sacrificial templates. Scare bar is 1 μm. For $N = 2$ and 3, the nonspherical hollow structures were broken by scratching the samples intentionally to observe the internal structures of the complex morphologies.

for $N = 8$ was not found which was observed in colloidal clusters from water-in-oil emulsions or aqueous aerosol droplets, possiblely due to the absecence of the electrostatic repulsive potential between the particles inside the emulsion templates made of oil droplets.[15,16,19,39]
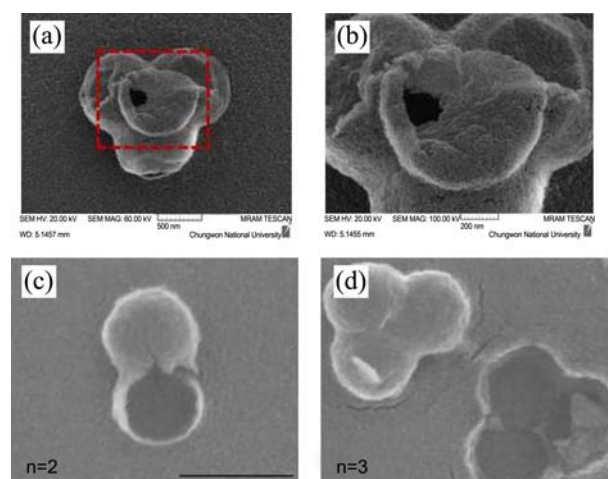
Figure 5(a) and 5(b) contain the SEM image of the PS colloidal clusters with octahedral structure and its high magnification SEM image observed near the cluster surface. As shown in the SEM images, the surface of the PS colloidal clusters is covered with silica nanoparticles which were utilized to stabilize the original Pickering emulsion droplets, and small nano-sized particles can be observed on the cluster surface. In some PS colloidal clusters, point defects were observed since one constituent particle is escaped out, as noted by arrow in the SEM image of Figure 5(c).

After the calcination of these sulfate-coated PS colloidal clusters covered with silica nanoparticles, the hollow nonspherical micro-particles could be fabricated by burning out the organic PS micro-clusters as sacrificial templates, as displayed in the SEM images of Figure 6. During the calcination, the evaporative flux of the PS particles generated some cracks on the surface of the hollow micro-clusters, which can be observed from the SEM images in Figure 6. In the case of more larger aggregates, spherical assembly with hollow structures could be also found from the sample as displayed in the SEM image of Figure 6.

High magnification SEM image of the hollow silica clusters for $N = 4$, in which N indicates the constituent number of the sacrificial PS microspheres before calcination procedure, was also taken to observe the surface microstructure of the nonspherical hollow micro-particles. As shown in the SEM images of Figure 7(a) and 7(b), the hollow particle is composed of small silica nanoparticles with about 30 nm in diameter, which were originally used

for the stabilization of the Pickering emulsion droplets.

The high temperature calcination was also performed for the colloidal clusters of amidine PS microspheres covered with silica nanoparticles, and the resultant hollow microstructures were intentionally destroyed to observe the interior structures, as displayed in the SEM images in Figure 7(c) and 7(d). As shown in the SEM images, the internal parts of the hollow clusters are void due to the removal of the organic PS microspheres during the calcination step.

The thickness of the nonspherical hollow microparticles was also measured by crushing the hollow clusters after calcination step, followed by collecting the powder samples for the SEM observation. Figure S3 contains the SEM images of the destroyed hollow microparticles, indicating the shell thickness of the samples is ranged from 50 to 87 nm. This thickness is slightly smaller than the calculated

value from equation (1), possibly due to the desorption of the nanoparticle stabilizer from the multilayer shell on the cluster surface. The BET surface area of the sample was also measured as 178.68 m^2/g, which is larger value than that of macroporous titania particles fabricated by aerosol reactor.[40]

We have also performed the similar self-asembly experiments using monodisperse silica microspheres with 750 nm in diameter having hydrophobic surface functional groups, as displayed in the SEM image of Figure S4 in Supporting Informations. The seeded growth scheme was adopted to synthesize the monodisperse silica microspheres, and the particle surface was modified using octadecyltrimethoxy-silane (OTMOS) to disperse the microspheres in oil such as toluene as dispersion medium, following the procedures in the literature.[17] By generating the Pickering emulsions encapsulating the hydrophobic silica microspheres, the self-organization of the building block particles were induced by heating and evaporating the toluene droplets, and similar cluster structures were observed as shown in the SEM

(a)
—— PS Microspheres
- - - PS Micro-clusters covered with silica Nanoparticles

(b)
—— Bare PS Microspheres
········· PS Micro-clusters covered with silica Nanoparticles

Figure 8. (a) FT-IR analysis results of sulfate-coated PS microspheres and PS micro-clusters covered with silica nanoparticles. (b) TGA results of sulfate-coated PS microspheres and PS micro-clusters covered with silica nanoparticles.

images of Figure S5 in Supporting Informations. Similarly with the clustering results of the PS microspheres, the isomeric structure such as *flower minus one* was found for $N = 6$.
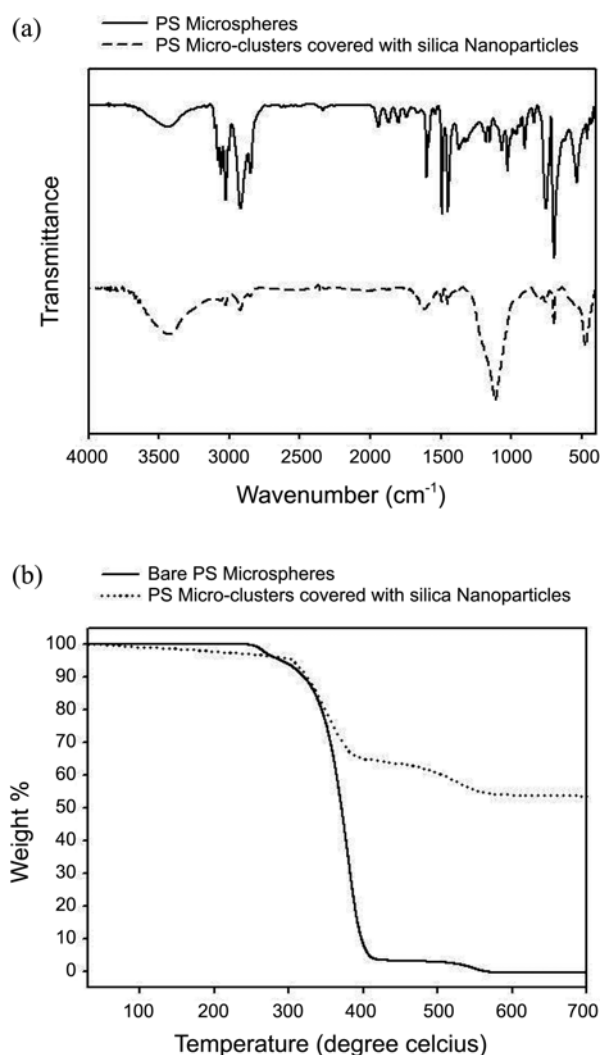
Figure 8(a) contains the FT-IR analysis results of sulfate-coated PS microspheres and their colloidal clusters covered with silica nanoparticles. In the case of PS particles, the stretching vibration of benzene ring at about 1600 cm^{-1} and strecthing band of hydrocarbon such as C=C and C-H in the range from 2,900 to 3,000 cm^{-1} were observed whereas Si stretching at around 1,000 to 1,100 cm^{-1} was occured for PS colloidal clusters covered with silica nanoparticles.[41-44] For the latter case, the inorganic peak due to the silica nanoparticles covering the PS colloidal clusters were so strong that the IR peaks from the organic particles were almost dissappeared.

Figure 8(b) contains the thermogravimetric analysis results of sulfate-coated PS microspheres and their colloidal clusters covered with silica nanoparticles. For the PS microspheres, the sample was burnt out at the temperature higher than 570 °C, appoaching the sample weight of zero percent. However, the sample weight of PS colloidal clusters covered with silica nanoparticles were reduced to 53.72% at the temperature higher than 600 °C, due to the existence of the silica nanoparticles adsorbed on the surface of the clusters and the excess amount of silica nanoparticles used for the emulsification process.

The colloidal clusters and hollow microparticles fabricated in this study will be useful as novel building block particles for the colloidal self-assembly or supporting materials for versitile purposes like porous catalytic supports. As building block particles, the colloidal clusters can be used for the second self-organization to prepare colloidal crystals with diamond lattices other than face centered cubic structures having complete photonic band gap or the researches on the inter-cluster interactions of colloidal cluster fluid.[45-47] In the case of supporting materials, the nonspherical hollow particles can be used as macroporous frameworks with large surface area for the enhanced catalytic properties.[48]

Conclusions

The monodisperse polymeric microspheres were self-organized into colloidal clusters having small number of constituent particles covered with silica nanoparticles by evaporation-driven self-assembly inside Pickering emulsions. During the droplet shrinkage by heating, the polystyrene microspheres encapsulated inside the nanoparticle-stabilized toluene emulsion droplets were self-assembled into regular, polyhedral micro-clusters, leaving the silica nanoparticles which were originally resided at the water-toluene interface on the surface of the resultant polymeric micro-clusters. The Pickering emulsion system used in this study can provide new confining geometries for the self-organization of the polymer microspheres without using the conventional surfactants which would be difficult to remove. The nanoparticle-stabilizer such as silica covering the cluster struc-

tures could be used as inorganic frameworks to generate nonspherical hollow micro-particles by calcination at high temperature.

Supporting Information Available. Size distribution graphes of Pickering emulsion droplets. SEM images of colloidal clusters made of amidine-coated PS microspheres from Pickering emulsion droplets. SEM images of destroyed nonspherical hollow micro-particles for the measurements of shell thickness. SEM image of monodisperse silica microspheres as building block particles for the cluster generation. SEM images of colloidal micro-clusters made of silica microspheres generated by evaporation driven-self-assembly from Pickering emulsions as confining geometries. These materials are available on request from the corresponding author.

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