A Role of Template Surface Charge in the Preparation of Porous and Hollow Particles Using Spray-drying

Nobuhiro Hagura, Asep Bayu Dani Nandiyanto, Ferry Iskandar, and Kikuo Okuyama*
Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University,
1-4-1 Kagamiyama, Higashi Hiroshima 739-8527

(Received May 11, 2009; CL-090452; E-mail: okuyama@hiroshima-u.ac.jp)

In this paper, the effect of template charge and morphology of particles was studied. Silica nanoparticles (as a model of an inorganic nanoparticle) and differently charged polystyrene (as a model of organic template) were used and self-assembled using a spray-drying method. As a result, particles with porous or hollow structure could be produced when negative or positive zeta-potential template were employed, respectively.

Recently, considerable effort has been devoted to design materials with porous and hollow structure using organic templates. This method was interesting because of its potential advantages: (i) Pore shape is a reflection of template shape and (ii) material morphology, porosity, and pore/core size are depended on template types and concentration.[1] The mechanism of this method is well understood; however, the definition of electrostatic effect in this preparation is not fully agreed. Although a number of attraction–repulsion studies[2] have been reported, surfactants or coating polymers were added to bridge template/shell formation.

In our previous work, we successfully prepared porous particles using either liquid-[3] or gas-phase[1,4–6] synthesis. The controllable outer diameter and pore size (from meso- to macropore structures) were also reported. Herein, we reported a study of particle template charge in controlling particle morphology. Similar to our previous work, the principle of organic template-driven self-assembly was used. A combination of silica nanoparticles (as a model of an inorganic nanoparticle) and two different charges of monodispersed polystyrene (PS) spheres (as models of the template) were employed and self-assembled using spray-drying. In order to minimize other attraction–interaction effects during self-assembly, no additional chemicals, excluding silica and PS, were used. Spray drying using a two-fluid nozzle was used as a model of self-assembly due to rapid synthesis and feasibility toward production of particles in several micrometer sizes.

In the experimental procedure, fabrication of silica with porous or hollow structure involves three major steps: (i) preparation of surfactant-free monodispersed PS, (ii) organic template driven self-assembly using spray drying, and (iii) template removal using heat treatment. First, surfactant-free monodispersed PS particles were prepared as follows: 10 mL of styrene monomer and 240 mL of deionized water were placed into a polymerization reactor system. The reactor system consisted of a 300-mL four-neck flask, a magnetic stirrer, a thermometer with a temperature controller, a N_2 inlet, a condenser, and a heating mantle. The styrene–water solution was heated at 80 °C, stirred (800 rpm), and under N_2 atmosphere. The process was maintained for 30 min to ensure that the solution was oxygen-free and homogenized well. As initiator, different chemicals were used to obtain different charges of PS particles: (i) 0.25 g of potassium persulphate (KPS, Sigma-Aldrich, USA) and (ii) 0.1 g of 2,2′-azobis(isobutyramidine) dihydrochloride (AIBA, Aldrich, USA). In addition, before the reaction, styrene was purified by treating with aqueous NaOH (4 M) to remove inhibitor.[7] The reaction was then performed for 12 h.

In the second step, the PS suspension product from the initial step was cooled to room temperature. Silica nanoparticles (Nissan Chem. Ind., 5 nm, in aqueous solution; $\zeta_{\mathrm{pot}} = -37.2$ mV (at pH 3.95, and 0.5 wt %)) were then added to PS suspension at a mass ratio of silica/PS of 2/7.[6] The suspension of silica/PS was then placed in an ultrasonic bath for several minutes. After a homogenous suspension was obtained, the mixed solution was sprayed using a two-fluid nozzle spray-dryer (SD-1000, Eyela, Tokyo Rikakikai, Japan).[5] In the final step, the spray-dried particles were collected and calcined (450 °C) to remove PS.

Figure 1 shows scanning electron microscopy (SEM, Hitachi S-5000, 20 kV) images of prepared PS particles. Monodispersed and completely spherical PS particles was observed in all cases. Particles with a diameter of 250 and 270 nm could be produced well, as shown in Figures 1a and 1c, respectively. In order to verify the role of initiator, we analyzed the prepared PS particle using a zeta-potential measurement (Malvern Zetasizer, Nano ZS, UK). When AIBA was used, a positive zeta potential of PS ($\zeta_{\mathrm{pot}} = +40$ mV; at pH 7.2 and 0.5 wt %) were produced (Figure 1b). Conversely, a negative value ($\zeta_{\mathrm{pot}} = -39$ mV; at pH 3.95, and 0.5 wt %) was measured when KPS was employed (Figure 1d). After silica was added, the pH was

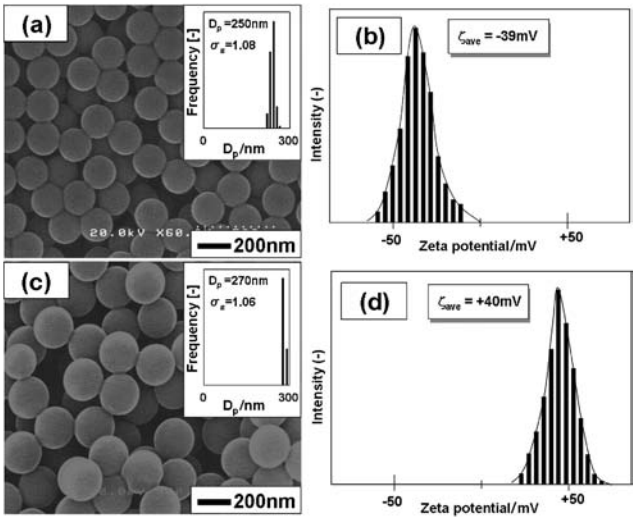

Figure 1. Analysis of PS particles using KPS (a) and (b) and AIBA (c) and (d). (a) and (c) are SEM analysis results, while (b) and (d) are the zeta-potential analysis results.

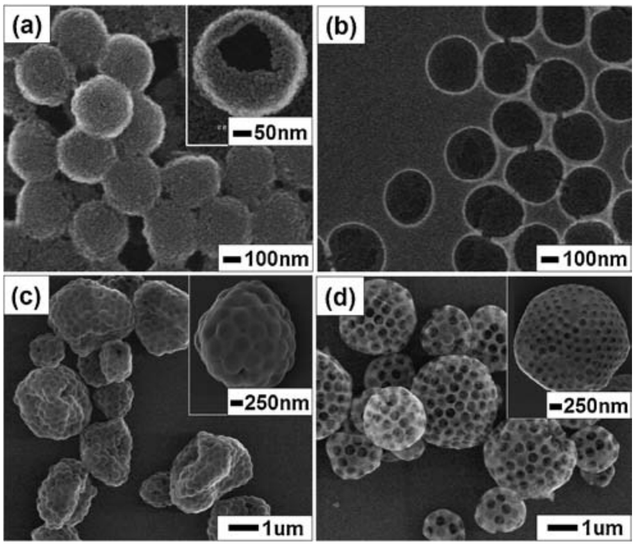

Figure 2. SEM images of initial precursors (a), (b) and spray-dried particles (c), (d) as a function of different PS surface charge (positive (a), (c) and negative (b), (d) zeta-potential value).

9.69 and 9.81, which were corresponded to the KPS- and AIBA-initiated PS solution, respectively. We also confirmed that by changing pH (up to 10, by adding NaOHaq), no changing zeta potential into an opposite value was obtained. PS with a negative value was still in the negative condition ($\zeta_{\rm pot} = -22.94\,{\rm mV}$). Similarly, the PS with a positive was still in the positive zeta-potential value range ($\zeta_{\rm pot} = +27.25\,{\rm mV}$).

Figure 2 shows particle morphology before and after spray-drying process. Before spray-drying, we investigate the effect of PS particle charge on the precursor condition (Figures 2a and 2b). The investigation was performed by placing of the initial mixed PS/silica solution onto the SEM grid, and then the sample was calcined at 450 °C to remove PS. When a PS with positive zeta-potential value (using AIBA) was used, hollow silica particles with outer diameter of about 300 nm were observed (Figure 2a), which to the best of our knowledge, is the first synthesis of self-organized silica hollow particles with no additional surfactant or chemicals. From the SEM image, homogenously hollow particles were observed, and the size of the hollow particles was similar to the size of the initial PS particles. In order to confirm that the particles were hollow, we show a broken particle with a high magnification inserted in Figure 2a. In another investigation, a mixed solution of silica and a negative zeta potential of PS (using KPS) was also analyzed (Figure 2b). The results showed porous film, of which the pore sizes were similar to the initial PS diameter. This results verified that no attraction between silica/PS was occurred in the initial precursor because silica and PS were not in opposite charge value. Thus, silica and PS were dispersed freely; when PS was removed, the holes was formed in the film.

Figures 2c and 2d show spray-dried particle as a function of PS surface charge. When PS particles with a positive zeta potential (using AIBA) were used, raspberry-like particles were produced (Figure 2c). Instead, a porous particle was generated when negative zeta-potential PS particles (using KPS) were employed (Figure 2d). From these results, it is concluded that the different particle morphology was strongly effected by use of different surface charge PS particles.

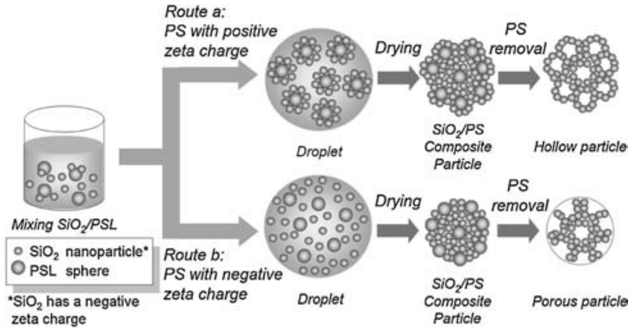

Figure 3. Mechanism illustration of template-driven self-assembly using different charge of organic particle templates.

Based on these results, a possible formation mechanism of the porous and hollow silica particles can be described as follows (Figure 3): When a PS with negative zeta-potential value is used, porous particles are obtained (Figure 3, route a). This is because the charge of silica and PS particles are the same.[8] Thus, the PS was difficult to be covered completely. However, when a PS with positive zeta-potential value is employed, hollow particles are produced (Figure 3, route b). Because the PS particles and the silica nanoparticles have a different charge, the PS particle was easily attached by silica nanoparticles, and aggregation of silica/PS forms in the precursor. After this mixed solution is spray-dried followed by heat treatment, hollow particles are produced.

The main focus in the present study was to investigate the effect of PS surface charge on particle morphology. In addition, the PS size affected only on pore size and no effect on changing particle morphology;[1,5,6] however, in order to make sure that no other effect on hollow or porous particle morphology, PS with almost similar size but have opposite charge, was used. Then, further performance analysis (e.g., PS size, surface area, density, and surface charge density) will be performed in the future work.

In summary, the effect of template surface charge on particle morphology was studied clearly. Silica particles with porous or hollow structure could be produced when different template charge was utilized, respectively.

We acknowledged the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan for supporting this research (Grant-in-Aid Young Scientists B, No. 20760516, 2008) and providing a scholarship for A.B.D.N.

References

1 F. Iskandar, A. B. D. Nandiyanto, K. M. Yun, C. J. Hogan, K. Okuyama, P. Biswas, *Adv. Mater.* **2007**, *19*, 1408.
2 F. Caruso, H. Lichtenfeld, E. Donath, H. Möhwald, *Macromolecules* **1999**, *32*, 2317.
3 A. B. D. Nandiyanto, S.-G. Kim, F. Iskandar, K. Okuyama, *Microporous Mesoporous Mater.* **2009**, *120*, 447.
4 F. Iskandar, Mikrajuddin, K. Okuyama, *Nano Lett.* **2002**, *2*, 389.
5 F. Iskandar, A. B. D. Nandiyanto, W. Widiyastuti, L. S. Young, K. Okuyama, L. Gradon, *Acta Biomater.* **2009**, *5*, 1027.
6 A. B. D. Nandiyanto, F. Iskandar, K. Okuyama, *Chem. Lett.* **2008**, *37*, 1040.
7 J. W. Goodwin, J. Hearn, C. C. Ho, R. H. Ottewil, *Colloid Polym. Sci.* **1974**, *252*, 464.
8 D. Lee, Z. Gemici, M. F. Rubner, R. E. Cohen, *Langmuir* **2007**, *23*, 8833.

Published on the web (Advance View) October 17, 2009; doi:10.1246/cl.2009.1076