Highly Porous Organic Nanoparticles Formed from Supercritical Carbon Dioxide Mediated Sol–Emulsion–Gel Method

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(Received January 20, 2004; CL-040070)

Highly porous organic nanoparticles have been prepared by adapting a novel method, *sol–emulsion–gel process*, through stable dispersion of nanometer-scaled emulsion droplets into continuous phase of supercritical carbon dioxide ($ScCO_2$), sol–gel chemistry in emulsion droplets, and then supercritical drying. This principle offers faithful preparation of nanoparticles (35–90 nm in diameter) having pores of 1–3 nm in radius and high specific surface area (over 2000 m^2/g).

Sol–gel chemistry is the most common method to prepare highly porous nanostructure, referred to as 'aerogel.'[1] The interesting properties of aerogel such as high specific surface area,[2] low density, low thermal conductivity, and low dielectric permittivity, which can be improved significantly by the formation of nanometer-scaled spherical structure of aerogel, have technologically important aspects for heat insulation, optical and electronic applications, and sensors.[3,4] In particular, the use of organic materials allows the flexibility in mechanical processing or application caused by the inherent elastic property and lightness of organic polymeric materials.

Here, we synthesized the highly porous structure of organic nanoparticles (Figure 1) which have been prepared by a novel approach, *sol–emulsion–gel method*, based on emulsion droplets of phenolic novolac/furfural (P/F, 1:1) dispersed in the continuous phase of supercritical carbon dioxide ($ScCO_2$, Figure 2). Transmission electron microscope (TEM) image of nanoparticles shown in Figure 1A clearly demonstrates the formation of subhundred nanometer-sized spheres. We can also observe that each nanosphere itself has a highly porous structure of aerogel from high-resolution electron-microscope (HREM) image shown in Figure 1B, which can be explained by the formation of inner network of interconnected small clusters, so-called as 'string of pears' structure.[5] The porous structure present in nanoparticles could be defined qualitatively by white holes behind the black-shadowed silhouette of clusters (Figure 1B). The quantitative analysis of porosity by using Brunauer–Emmett–Teller (BET) method also indicates that well-defined mesopores have been formed in the range of 1–3 nm in radius (Figure 1C). Nitrogen adsorption method at 78 K was used to determine the surface area and the pore size distribution (PSD) of highly porous nanoparticles by using BET equation and the Dollimore–Heal method.[6] PSD is presented as differential volume (dV/dR) so that the integrated area under the plot directly corresponds to the pore volume. In addition, we can expect that this kind of network induces the high specific surface area caused by rough surface of individual particle, and the BET data represent its high specific surface area of $\approx$2300 m^2/g.

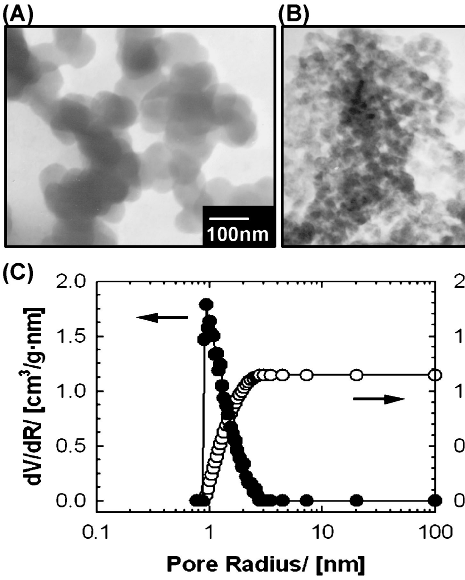

Figure 1. Highly porous structure of P/F (1:1) nanoparticles by sol–emulsion–gel method using $ScCO_2$; (A) TEM image, (B) HREM image and (C) BET measurement. The synthesized nanoparticle was prepared from 30 wt% of solid content of P/F (1:1) and the ratio of phenolic novolac (or furfural) to acid catalyst (P/C ratio) was 5.

The sol–emulsion–gel method used in this study is schematically illustrated in Figure 2. The droplets of heptyl alcohol solution of P/F (1:1) containing acid catalyst (*p*-toluenesulfonic acid) are dispersed in the continuous medium of $ScCO_2$ by forming the stable emulsion that serves as a nanoreactor for gelation.[7] In case of adapting $ScCO_2$ to continuous phase, homopolymers, or block/graft copolymers, as a surfactant, can give steric stabilization effect to form a nanometer-scaled emulsion in nonpolar media. Here we have used triblock copolymer (PPO-*b*-PEO-*b*-PPO), which has CO_2-philic and CO_2-phobic segments that can offer a well-defined and stable structure of emulsion.[8,9] Our synthetic system starts as heterogeneous system of two-phases such that the heptyl alcohol solution of P/F (1:1) containing acid catalyst is insoluble in the $ScCO_2$ at the condition of 1200 psi and 120 °C (point A in Figure 2) which is enough for nucleation to form clusters and their network in a nanoreactor. After gelation, the pressure and temperature of system are changed into 4000 psi and 40 °C, respectively (point B in Figure 2). As heptyl alcohol is completely dissolved into $ScCO_2$ by changing the solvent strength of supercritical fluid, the heptyl alcohol in emulsion droplets starts to be extracted into continuous phase of $ScCO_2$ at this condition. The heptyl alcohol solution in emulsion droplet, therefore, without additional rigorous steps of solvent exchange for drying, can be easily extracted by simple control of solvent strength of $ScCO_2$ through repeated pressure swing between 1200 (point B in Figure 2) and 2400 psi (point C in Figure 2) at 40 °C. In particular, continuous medium of $ScCO_2$ having all of reaction components, when the semicontinuous production is adapted, can be also recycled for another batch of reaction. Finally, as all of $ScCO_2$ in high-pressure reactor are vented (point D in Figure 2) and the temperature is quenched to room temperature (point E in Figure 2), highly porous nanoparticles of powder-form can be obtained.

The physical and chemical properties of synthesized nanoparticles can be adjusted by changing the process conditions. These nanoparticles were prepared by starting the synthesis with different solid content of P/F (1:1) at same ratio of phenolic novolac (or furfural)/acid catalyst (P/C ratio, 5) or with different P/C ratio at the same solid content of P/F (1:1, 30 wt %). Here, we demonstrate the effect of solid content of P/F (1:1), as one of examples, on the structure of highly porous nanoparticles. As shown in Figures 1A and 3, the size of nanoparticles is increased linearly from ≈35 to ≈90 nm by increasing the solid content of P/F (1:1) from 10 to 30 wt %. The variation of the solid content of P/F (1:1) results in change of relative amount of the stabilizer, because we have fixed the total content of stabilizer to 20 wt % for all cases used in this study. Therefore, this result can be explained by emulsion polymerization, in which by decreasing the amount of stabilizer, the particle size becomes larger to decrease the surface area of total emulsion droplets. In contrast, the specific surface areas of nanoparticles are almost the same regardless of the increase of their sizes from ≈35 to ≈90 nm (slightly decreased from ≈2300 to ≈2100 m^2/g), and the average radius of mesopores is 1–3 nm for all cases. These results indicate that the control of particle size, without any significant changes in the porous structure of nanoparticle such as porosity, can be achieved by simple change of solid content of P/F. Comparing with the specific surface area of nanoparticle prepared when P/C ratio was 5 (filled circles in Figure 3D), we have obtained relatively small value of surface area (1600–1800 m^2/g) in case of 10 of P/C ratio. These results can be explained in terms of the increased cluster connections. That is under high catalyst conditions (i.e., P/C = 5), the interconnected clusters are joined together with broad cluster necks (polymeric gels). If the P/C ratio is increased (i.e., P/C = 10), however, the clusters become large in diameter and crosslink (colloidal gels).[10]

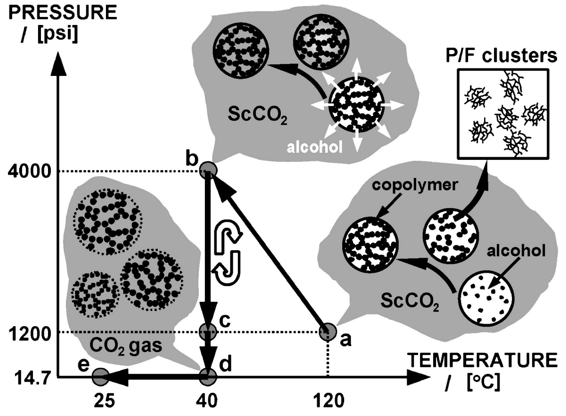

Figure 2. Schematic representation of sol–gel–emulsion method using $ScCO_2$; (A) sol–emulsion–gel polymerization, (B) solvent exchange, (C) supercritical drying, (D) vent of CO_2 and (E) temperature quenching. The reaction medium was exchanged by repeated-pressure swing process between B and C. Critical pressure and temperature of CO_2 are 1070 psi and 31.1 °C, respectively.

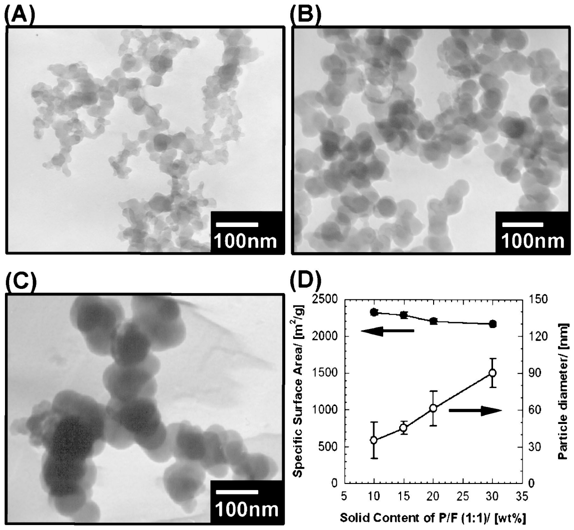

Figure 3. TEM images of highly porous nanoparticles at different solid content of P/F (1:1); (A) 10 wt %, (B) 15 wt %, (C) 20 wt % and (D) Relationship between solid content of P/F (1:1) and size (or specific surface area) of highly porous nanoparticle. P/C ratios used to prepare the nanoparticles were fixed to 5 for all cases.

In conclusion, we report the highly porous structure of organic nanoparticles which are generated by the introduction of sol–emulsion–gel method and the manipulation of inherent nature of supercritical fluid. In particular, when inorganic or organic–inorganic hybrid materials as well as organic materials are applied to the synthesis based on sol–emulsion–gel method, this principle can form the basis in fabrication and is now in progress.

This work was supported by NRL Program of KISTEP and Post-doctoral Fellowship Program of KOSEF, Korea.

References and Notes

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