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Fabrication of Carbon Nanocapsules Using PMMA/PDVB Core/Shell Nanoparticles

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Carbon nanocapsules[1] have the unique feature of encapsulating nanometer-sized materials in their cores. They also provide the remarkable properties of high specific surface area, large pore volume, chemical inertness, and good mechanical stability.[2] Therefore, hollow carbon nanospheres are useful for many areas of modern science and technology, including delivery, protection of proteins and enzymes, protection of magnetic particles from oxidation, design of radioactive nanoparticles for radiology, radiation therapy, sensing, and storage.[3]

The growing needs for carbon nanocapsules have motivated the development of various fabrication methods. Techniques for the synthesis of hollow carbon nanostructures include the use of polymer lattices,[4] inorganic spheres,[5,6] vesicles,[7] nonsolvent,[8,9] and metal nanoparticles[10] as the templates. However, removal of the core part to make carbon nanocapsules is unavoidable, and the fabrication procedure is relatively complicated.

Herein, we report the fabrication of carbon nanocapsules with an average diameter of ca. 15 nm using polymer core templating. In this methodology, etching the polymer core part to fabricate ultrafine carbon hollow spheres is unnecessary. When the core/shell polymer nanomaterial is carbonized, the polymer core part is eliminated, and the shell is transformed into a carbon nanocapsule during the carbonization process. This means that carbon nanocapsules can be fabricated without an additional core etching procedure. Moreover, pore size control is also a key factor in the fabrication of tailored carbon nanocapsules. Several parameters such as surfactant type, surfactant concentration, monomer concentration, and initiator amount can be carefully

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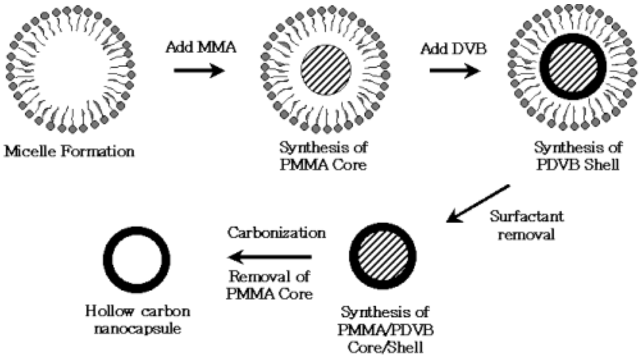

Figure 1. Schematic diagram for carbon nanocapsule fabrication.

manipulated for the fabrication of hollow carbon nanoparticle samples with selective pore sizes, as determined in our previous studies.[6,9,11,12]

Under these experimental conditions, we used the cerium(IV) sulfate and nitrilotriacetic acid (NTA) in place of azobis(isobutyronitrile) (AIBN) as the initiator.[12] The mobility of the surfactant chains decreases as a result of the decreasing of the polymerization temperature.[11] This restricted surfactant molecule mobility produces less free volume inside the micelles and smaller nanoparticles. Nanocapsules that were nearly spherical shape were fabricated compared to those in our previous paper.[12] The spherical polymer nanoparticles can be fabricated from robust micelles using redox polymerization at room temperature.

The procedure for the synthesis of carbon nanocapsules is shown in Figure 1. A variable amount of octyltrimethylammonium bromide[13] (OTAB) was magnetically stirred in 40 mL of distilled water. Precisely 1.0 g of methyl methacrylate (MMA) was added dropwise to the surfactant solution, and the mixture was magnetically stirred to ensure that the MMA penetrated into the micelle by diffusion.

Subsequently, 0.4 g of cerium(IV) sulfate and 0.1 g of NTA as redox initiators and a small amount of sulfuric acid as a catalyst were added to the surfactant/MMA solution, and the polymerization was carried out in the micelle as a nanoreactor at room temperature for 2 h.[14] To fabricate the shell layer, 1.0 g of divinylbenzene (DVB), which was used as a carbon precursor, was incorporated into the solution dropwise. Then, the initiator was added to the monomer/surfactant mixture. Upon completion of the redox microemulsion polymerization, PMMA/poly(divinylbenzene) (PDVB) core/shell nanospheres were obtained. The solution was moved to a separation funnel, and then excess methanol was added to remove the residual surfactants. The PMMA/PDVB core/shell nanoparticles were precipitated for 1 day, and the upper solution containing surfactants was discarded. The core/shell nanosphere products were dried at room temperature. In the reaction using 0.4 mol/L OTAB at room temperature, the product was mainly PMMA/PDVB core/shell nanoparticles.

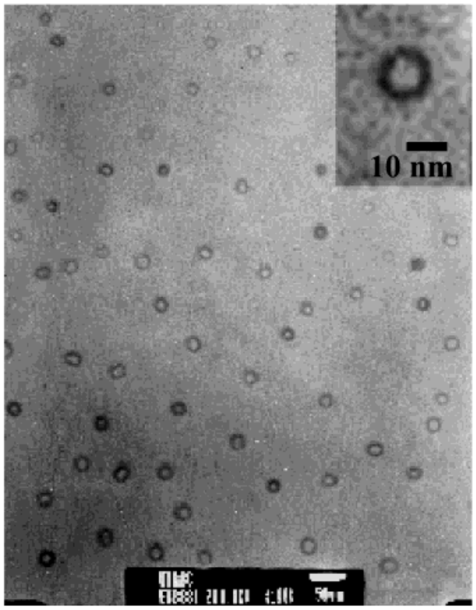

Figure 2. TEM images of hollow carbon nanocapsules fabricated with OTAB as the surfactant.

The FT-IR spectrum of PMMA/PDVB core/shell nanospheres showed the characteristic PMMA peaks at 1277, 1241, 1195, and 1150 cm^{-1}, which were due to the C−O stretching mode. In addition, a band at 1731 cm^{-1} was assigned to the C═O stretching peak of PMMA. After polymerization of DVB, a clear peak appeared at 697 cm^{-1}. This means that PMMA/PDVB core/shell nanospheres were successfully synthesized. The transmission electron microscopy (TEM) image also revealed PMMA/PDVB core/shell nanoparticles.

To obtain ultrafine carbon nanocapsules, PMMA/PDVB core/shell nanospheres were put into a quarz tube and were carbonized in an electric furnace under a N_2 gas flow (0.2 L/min). The sample was heated to 800 °C at a heating rate of 3 °C/min, held at 800 °C for 5 h, and then naturally cooled to room temperature.[6,11]

The formation of carbon nanocapsules was confirmed by elemental analysis (EA), Raman spectroscopy, X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

The XRD experiment showed a broad diffraction band at a low angle of around 24° in 2θ. This peak is the characteristic 002 Bragg reflection of graphenes.[15] Elemental analysis indicated that the carbon content of the sample was over 95%. TGA results on the carbon capsules indicated that the amount of residue was less than 5 wt % under an oxygen flow. In addition, Raman spectroscopy showed peaks at 1580 and 1360 cm^{-1}, which were attributed to the vibration of atoms on the plane of carbons and the disorder and imperfection of the carbon crystallites.[15] Judging from these data, carbon nanocapsules were clearly fabricated.

The structures of the carbon nanocapsules were investigated by gas adsorption and TEM. Figure 2 shows a TEM image of carbon capsules obtained using OTAB as a surfactant after carbonization of PMMA/PDVB core/shell nanoparticles.

This TEM image indicates that the outer carbon shells remained intact during pyrolysis. It was con-

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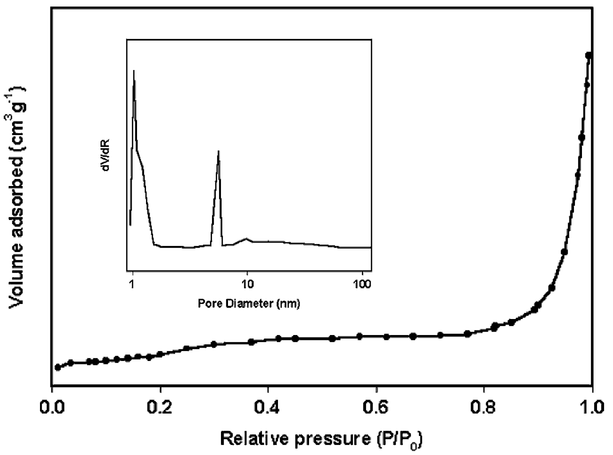

Figure 3. Nitrogen adsorption isotherm and corresponding pore size distribution of carbon nanocapsules.

firmed that the PMMA core parts were removed during the carbonization process. The typical morphology of the carbon nanocapsules is clearly that of hollow spheres, and the average diameter and shell thickness of the hollow nanocapsules are ca. 15 and ca. 3 nm, respectively. The pore structure of carbon nanocapsules was characterized by nitrogen adsorption isotherm at 77 K. The corresponding pore size distribution (PSD) curve of the carbon nanocapsules was derived from the nitrogen adsorption branches by the Barrett−Joyner−Halenda (BJH) method and found to exhibit pore sizes that were uniformly distributed about a center of at 7 nm (Figure 3). In addition, the Brunauer−Emmett−Teller (BET) surface area of the carbon hollow spheres was ca. 600 m^2/g.

To verify the effect of the surfactant type, supplementary experiments were performed with P123 nonionic surfactant instead of the cationic surfactant, and the other parameters for redox emulsion polymerization were fixed. In this case, PMMA/PDVB core/shell nanoparticles were fabricated for a concentration of P123 of 0.02 mol/L between CMC I and CMC II.[16] The average diameter of the carbon nanocapsules was ca. 13 nm, and the shell thickness was ca. 3 nm. From this result, these carbon nanocapsules were determined to be similar to those fabricated using OTAB.

In conclusion, carbon nanocapsules with diameters of less than 15 nm were fabricated by the carbonization of polymeric core/shell nanocomposites. The organic core/shell nanospheres were prepared using a redox microemulsion polymerization. Importantly, the redox microemulsion polymerization is thought to have a novel route to the fabrication of various hollow nanomaterials.

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Supporting Information Available: FT-IR spectrum and peak assignment of PMMA and PDVB nanoparticles. TGA thermogram, XRS result, and RAMAN spectrum of carbon nanocapsules. TEM images of PMMA/PDVB core/shell nanoparticles and TEM image of carbon nanocapsules using P123 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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