Fabrication of Hollow Carbon Spheres with Porous Shells by Interfacial Sol–Gel Polymerization

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Hollow resorcinol–formaldehyde (RF) aerogel spheres were synthesized by interfacial polymerization of resorcinol and formaldehyde monomers with NaOH as a catalyst. Commercial hollow polystyrene spheres were used as catalyst storage materials and templates in the synthesis. Hollow carbon aerogel spheres were prepared by carbonization of the RF aerogel spheres at a high temperature under a nitrogen atmosphere. The processing procedures and the conditions of the structures of hollow carbon spheres were studied.

Hollow spheres, especially hollow carbon spheres, have great potential for use in many fields and offer many possibilities for novel applications as electrode materials, nanoreactors for catalyzed reactions, and advanced storage materials.[1–3] In recent years, hollow carbon spheres with tailored pore systems have received a great deal of attention.[4] Herein, we report a novel method for the fabrication of hollow carbon aerogel spheres with tunable porous shell structures.

The overall synthetic procedure of the hollow aerogel spheres is shown in Figure 1. In the synthesis, polystyrene (PS) sphere with hollow structure was applied as template and catalyst storage material. Resorcinol–formaldehyde (RF) was applied as the carbon source. The rod-like particle shown in Figure 1 corresponds to the catalyst (sodium hydroxide). During the reaction, the catalyst and RF precursor will diffuse to form a reactive interface. After that, RF gelation will start at the interface and then coat the cores to form the gel shell. Finally, carbon hollow spheres can be achieved by subsequent carbonization.

In the synthesis, a precursor solution comprised of resorcinol (3.88 g) and formaldehyde (5.2 mL). Ethanol (60 mL) was used as solvent and dispersant. The PS spheres were synthesized by emulsion method and used without any surface modification. Sodium hydroxide was impregnated in the PS cores by immersing the cores in a sodium hydroxide solution with concentration of about 1 mol L^{-1} (Data for inclusion of sodium hydroxide in PS spheres, see Supporting Information).[9] Before adding the PS cores to the RF precursor solution, the templates were washed by rinsing in ethanol several times to remove the remaining catalyst on the surface of the cores. The PS–RF spheres were separated from the RF precursor solution when the RF gel process was no longer observed (about 24 h later). Carbon hollow spheres can be achieved by the following carbonization process: The spheres are heated at 1.5 K min^{-1} to 373 K and held at that temperature for 1 h under flowing nitrogen. The temperature is then ramped at 1.5 K min^{-1} to 1323 K and held at this temperature for 5 h to carbonize the spheres. The morphology of the carbon spheres was studied using field emission scanning electron microscopy (FE-SEM), which was performed using a ZEISS-SUPRA55 microscope, working at a 10 kV accelerating voltage. Simultaneous thermogravimetric and differential thermal analyses (TG-DTA) were performed on a Netzsch STA-409 instrument under flowing nitrogen at a heating rate of 10 K min^{-1}.

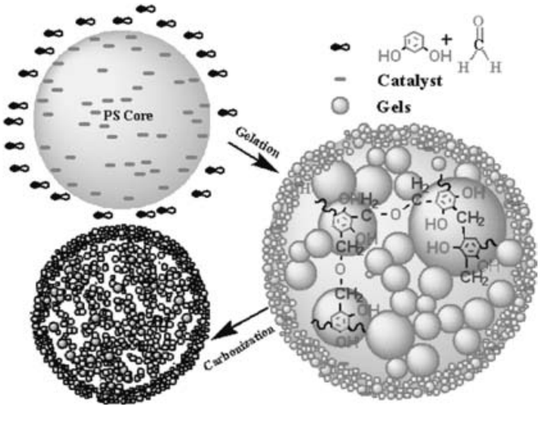

Figure 1. Schematic illustration of the formation process of hollow carbon spheres.

Figure 2 shows optical microscopy images of the gel process, in which the templates were freshly transferred into the mixture (RF, ethanol) (Figure 2a), 33 min later (Figure 2b), 1 h and 47 min later (Figure 2c), and 4 h and 46 min later (Figure 2d). These optical microscopy images clearly show the precursor gels

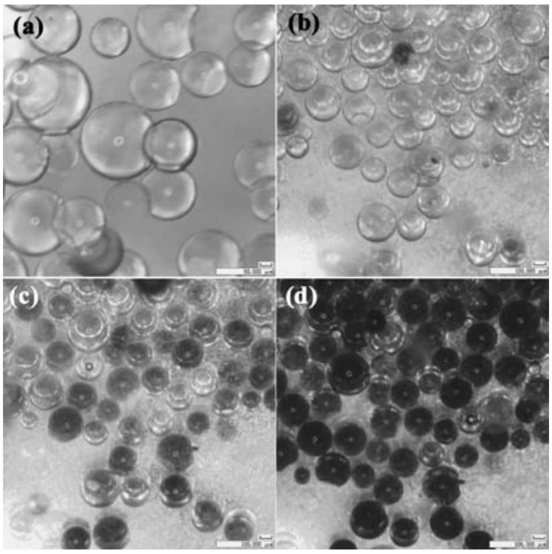

Figure 2. Optical microscopy images of the gel process: (a) the templates were freshly transferred into the solution precursor, (b) 33 min later, (c) 1 h and 47 min later, (d) 4 h and 46 min later.

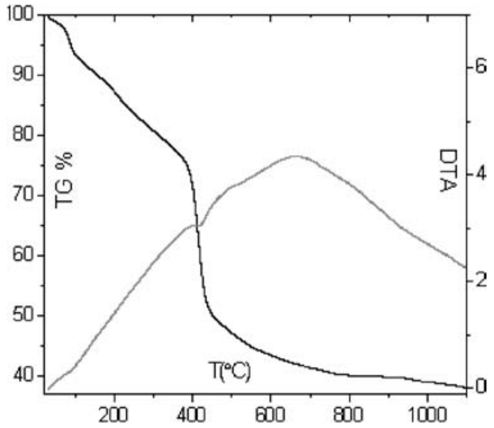

Figure 3. TG-DTA curves for the PS–RF hollow spheres.

on the PS spheres. The sodium hydroxide accelerates the reaction in the interface of the RF precursor and catalyst, and the sol particles further react to form a cross-linked polymer network that constructs the RF shell.

Weight loss behavior corresponds to the results of a typical TG study for the PS–RF spheres (Figure 3). The curves indicate a total weight loss of about 62.78% during pyrolysis in N_2. Thermogravimetric analysis of the PS–RF spheres under nitrogen (Figure 3) shows a large endothermic loss of mass at 397 °C, which is consistent with decomposition of PS. The weight loss is about 22.78% during this stage.

The morphologies and structure of the hollow carbon spheres were investigated by FE-SEM. The hollow structure of the carbon spheres is shown in the FE-SEM image (Figure 4a). It demonstrates that the new method can be used to fabricate the hollow structure. The FE-SEM image (Figure 4b) shows that the porous shell structure of the carbon spheres has been graded. It was fabricated using two layers: the inner and outer layers, which have different porous structure. The outer shell of the carbon spheres consists of well-defined spherical carbon particles with a diameter of about 2–5 µm. These microparticles coalesce through neck-like structures (Figure 4b inset) to form macropore space with a developed pore interconnectivity. The inner shell consists of spherical carbon particles with small diameter (Figure 4b), high cross-link density, and increased nanopore and bulk density with decreased particle size. The porous structure of the carbon gel resulted from the different synthetic conditions.[5–8] The concentration of the catalyst mainly determines the size of the carbon particles and the morphology of the cross-linked structure. With a high concentration of sodium hydroxide, the size of the particles decreases, while with a low concentration of sodium hydroxide the particles are able to increase in size.[7] According to Yamamoto et al.,[7] the difference in the pore structure between the inner shell and outer shell should be determined by the gradient radial concentration of the sodium hydroxide during the process (the concentration of sodium hydroxide is relatively high at the center of the core and reduces along the radial direction). This means that it should be possible to control the pore characteristics of the RF/carbon shell by changing the concentration of catalyst which is stored in the PS templates.

Hollow carbon aerogel spheres were fabricated by interfacial sol–gel polymerization. First, the hollow structure of the carbon spheres could be achieved without additional processing to remove the templates for the depolymerization of the PS templates during the carbonization. Second, the pore characteristics of the RF aerogels varied with different synthetic conditions, and it should be possible to control the pore characteristics of the RF/carbon shell by changing the synthetic conditions. Third, compare to previous interfacial polymerization method, this method need not to use two immiscible solvents, miscible solvents also can be used. These features make the interfacial gelation synthesis an efficient, simple route to form hollow carbon spheres.

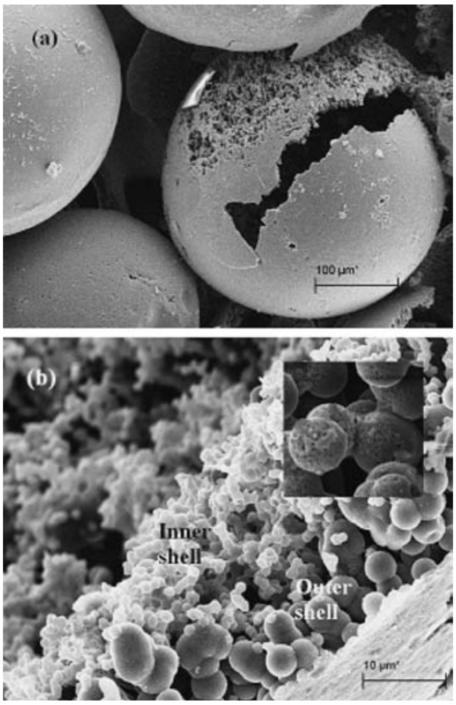

Figure 4. FE-SEM images of (a) the morphology of the hollow spheres, (b) cross section of the hollow sphere shell, morphology of the outer shell and inner shell, inset: microparticles coalesce through the formation of neck-like structures.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) July 11, 2009; doi:10.1246/cl.2009.816