Synthesis of Cagelike Polymer Microspheres with Hollow Core/Porous Shell Structures by Self-Assembly of Latex Particles at the Emulsion Droplet Interface

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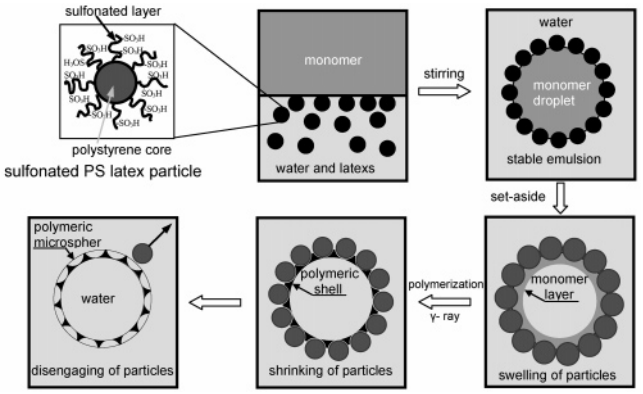
The design and fabrication of hollow spherical materials have attracted a considerable amount of attention in recent years because of their potential applications in drug storage and controlled release, selective separation, catalytic supports, electronics, optics, chromatography, and so on.[1−5] A variety of hollow particles comprised of metals, ceramics, polymers, or composites with various diameters and wall thicknesses have been fabricated, mostly on the basis of template-assisted processes involving either the replication of organized reaction fields such as emulsion vesicles,[6,7] emulsion droplets, and bicontinuous microemulsions[8−10] or the overlay of colloidal crystals such as silica or latex polymer spheres,[11,12] followed by the removal of the template materials using calcination or solvent etching.

More recently, this research was further extended to hollow spherical materials with porous shells. Because of their low density and high specific surface, such materials are very useful in surface-related applications, such as sensors,[13,14] electrorheological properties,[15] solar cells,[16] mimicking photosynthesis,[17] catalyst,[18] and optical applications.[19,20] Several interesting materials, especially inorganic silica material, have been reported, in which both macropores and micro- or mesopores are incorporated into the structure.[21] Since the synthesis of mesoporous MCM-41 in 1992,[22] many methods for the preparation of porous hollow silica microspheres have been reported by hundreds of groups worldwide.[23−25] However, only a few reports on porous microcapsules of organic materials have been published. Dinsmore et al. described the porous microcapsules prepared by sintering the particulate emulsifiers around the droplet phase.[26]

Scheme 1. Schematic Illustration of Polymer Microsphere Formation with a Hollow Core/Porous Shell Structure



In this communication, we report a novel approach to synthesize cagelike polymer microspheres with a hollow core/porous shell structure. The overall synthetic procedure is shown in Scheme 1. The first step was to prepare a stable emulsion from surface-sulfonated polystyrene (PS) particles by self-assembly of PS particles at the water−monomer (methyl methacrylate or vinyl acetate) droplet interface. The hydrophilicity of PS particles was adjusted by controlling the sulfonation time and, therefore, the density of chemigrafted SO_3H group on the particle surfaces. From our previous work,[27] we found that PS particles sulfonated for 21 h gave the most stable emulsion system. Following the preparation of the emulsion system, it is important that the emulsion was set aside for a certain amount of time. During this reserving period, monomers tended to diffuse into the

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adsorbed latex particles, resulting in the swelling of the adsorbed latex particles. Along with the swelling of the adsorbed latex particles, the size of the particle-packed droplets would change accordingly. Compared with the initial value, experiments found that all samples exhibited an increase of droplet diameter of about one-third and volume of about one and one-half after being reserved for 48−72 h. With the gradual decrease of the internal monomer, a hollow core formed. After polymerization of the monomer induced by γ-ray irradiation, a microsphere with a polymeric shell and hollow core was formed. At the same time, the polymerization of the monomer led to the shrinkage of the polymeric shell and the swelled PS particles which propelled the PS latex particles to disengage themselves automatically from the polymeric shell, leaving behind a porous polymer shell.

The methyl methacrylate and vinyl acetate emulsion systems were polymerized using γ-ray irradiation at a dose rate of 80 Gy/min and absorbed dose of 9.6 kGy. Both emulsion systems were prepared using PS particles sulfonated for 21 h and set aside for 72 h before polymerization. The scanning electron microscopy (SEM) images showed that the microspheres possessed porous shell structure and neither agglomeration nor collapse occurred after polymerization. Under the same conditions, the average pore size of the polymeric shell is around 1.92 μm for poly(methyl methacrylate) (PMMA) particles and 450 nm for poly(vinyl acetate) (PVA) particles (Figure 1a,d). The porous shell structures of both samples were more evidently shown in Figure 1b,e. With a decreased pore diameter, the porous shell structure became more compact and the surface became more uniform. The arrowhead in Figure 1b indicates that a bowl-like thin wall inside the pore can be clearly observed, of which the formation was attributed to the separation of the adsorbed latex particles from the microspheres after polymerization. The transmission electron microscopy (TEM) images shown in Figure 1c,f further confirmed that both polymer microspheres have hollow core/porous shell structure. Compared to PMMA microspheres, PVA microspheres possess a more compact and uniform porous shell, as evidenced from the contrast of dark- and bright-field TEM images. The thicknesses of the porous shell were approximately 172 and 38 nm for PMMA and PVA, respectively (estimated from the dark framework around the perimeter of the hollow spheres). Moreover, a few solid particles of PS also appeared in the TEM image (see the arrowhead in Figure 1c), suggesting that not all of the PS particles disengaged from the shell. When the size of sulfonated PS latex particles changed from 2.13 to 2.94 μm, with the other conditions remaining the same, the average diameter of the microspheres increased from 9.3 to 19 μm. (Figure 1a,g). Besides, no hollow core was observed for microspheres fabricated from emulsions without a reserving period (Figure 1h).

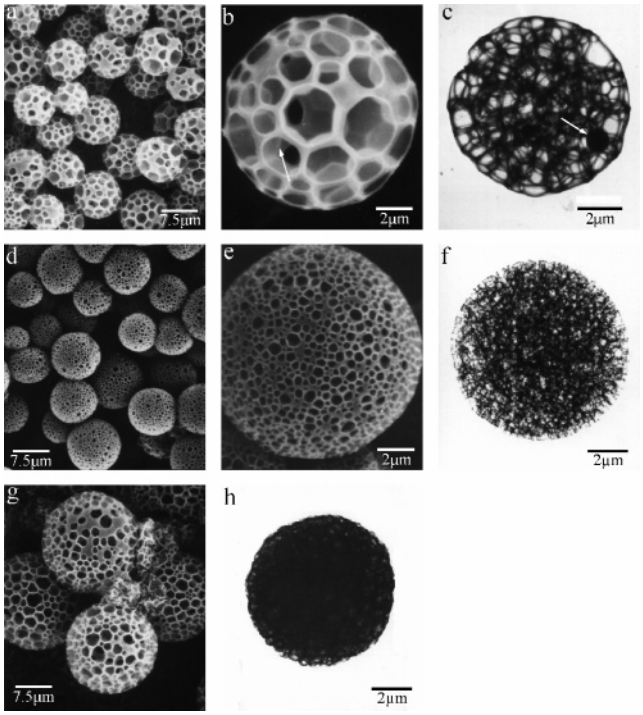

Figure 1. Morphological characterizations of the polymer microspheres. SEM (a and b) and TEM (c) micrographs of PMMA microspheres; SEM (d and e) and TEM (f) micrographs of PVA microspheres prepared under the same conditions; (g) SEM micrograph of PMMA microspheres using 2.94 μm PS latex particles as emulsion stabilizers; (h) TEM micrograph of PMMA microspheres from emulsion without being reserved for a certain time.

In summary, we report a novel and efficient approach to synthesize cagelike polymer microsphere materials with hollow core/porous shell structures by self-assembly of sulfonated PS latex particles at the monomer droplet interface. The swelling of the PS latex particles by the oil phase provide a driving force to develop a hollow core. The latex particles also serve as a porogen that will disengage automatically during polymerization, leaving behind a uniform porous shell. The size of the microspheres and the pore size of the shell can be easily adjusted. Moreover, this technique is suitable for different vinyl monomers. The obtained microspheres may find potential applications in the fabrication of functionalized composites for controlled release systems and catalytic applications.

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Supporting Information Available: Experimental details for the microspheres and figure of the average droplet diameter varying with the reserving time (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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