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Rapid Fabrication of Hollow SiO_2 Spheres with Novel Morphology

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Abstract: The hydrolysis of tetraethoxysilane (TEOS) occurred on the surface of poly(methyl methacrylate) (PMMA) microshperes immediately after these microshperes were prepared in TEOS. Micron-sized hollow SiO_2 spheres were obtained by calcination of the coated PMMA microshperes. It was found that the final hollow spheres were constituted by small SiO_2 particles.

Keywords: Hollow SiO_2 spheres, PMMA microshperes, rapid fabrication.

Hollow spheres have recently attracted much attention because their unusual properties may find wide potential applications in chemistry, biotechnology, and materials science[1, 2]. The production of hollow spheres of inorganic materials can be achieved using a number of methods, including vaporphase transport treatment[3], layer-by-layer self-assembly[4], and functionalized polymer core method[5]. However, it is not easy to fabricate micron-sized hollow silica using the above methods, because of the difficulties in preparing modified cores and slow rate of the hydrolysis reaction of silica precursors. Herein, we suggest a succinct path for fabrication of silica hollow spheres, in which PMMA microspheres were directly obtained in TEOS without emulsifier or stabilizer, therefore, the procedures of purification and modification were omitted. On the other hand, the silica hollow spheres prepared by this method were found to be constituted by small silica particles, which structure had not been reported previously.

PMMA microspheres were prepared in TEOS using the self-assembly method which we reported previously[6]. After separation of these polymer particles from TEOS medium, they were immediately dispersed in ammonia solution under magnetic stirring. The hydrolysis and condensation of TEOS occurred on the surface of PMMA microspheres to form silica shell at room temperature for 5 days. Finally, hollow silica spheres were achieved after removal PMMA cores by calcination at 500°C for 5 hr.

A typical SEM (taken on a JSM35CF SEM instrument) image of core-shell particles was shown in **Figure 1** after the hydrolysis reaction of TEOS, in which the template of PMMA microspheres in the size of 7 μ m were adopted. The silica hollow spheres with average wall thickness of about 150 nm can be preserved after calcination

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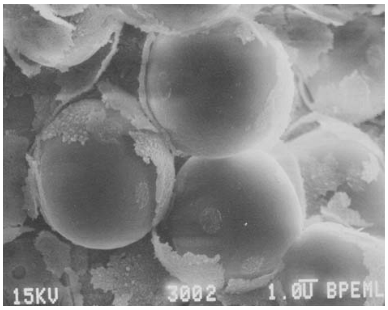

Figure 1 SEM image of the broken microspheres indicates the core-shell structure

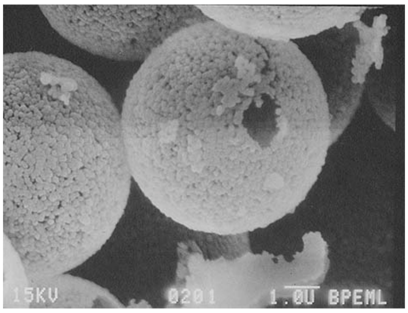

Figure 2 SEM image of the obtained hollow silica spheres

(**Figure 2**). Both SEM and TEM (**Figure 3)** revealed that these silica hollow spheres were formed by one layer of silica particles, in which SiO_2 particles with size of about 150 nm connecting each other. Furthermore, it should be noted that there were gaps between SiO_2 particles in the range from 50 nm to 150 nm, and this phenomenon revealed that the obtained hollow silica microspheres may be used as special micronsized reactor.

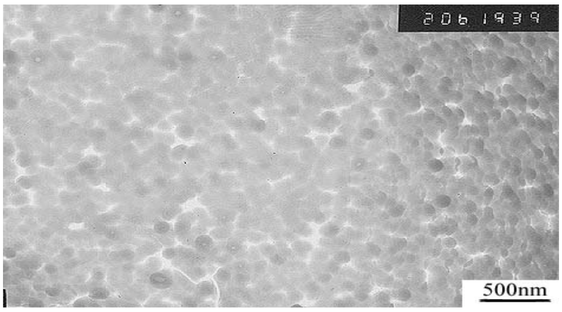

Figure 3 TEM image of fragment of a hollow silica sphere (taken with JEM 100-CX)

The size of obtained silica hollow spheres could be controlled by changing the size of PMMA templates[6]. We have found that the hydrolysis and condensation conditions significantly influence the wall morphology of these silica hollow microspheres, the related works are still under investigation. This convenient and rapid method to fabricate silica hollow spheres will find its applications in micronsized reactor, filtration, catalysis, *etc*.

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