

A Facile Method to Prepare Hollow MCM-41 Microspheres via P(St-MPS)/MCM-41 Core/Shell Composite Microspheres

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Hollow MCM-41 microspheres were obtained by removing the templates of poly(styrene- γ -methacrylic propyltrimethoxysilane)/MCM-41 [P(St-MPS)/MCM-41] core/shell composite microspheres prepared using P(St-MPS) microspheres contained in soap-free emulsion and cetyltrimethylammonium bromide as cotemplates. XRD, TEM, and IR measurements show that the pore channels of MCM-41 shell were hexagonally ordered and that the diameter of the hollow microspheres and the thickness of the shells were about 260 and 30 nm, respectively.

Hollow microspheres have found important application in light filler, low dielectric constant materials, controllable transportation, and so on.¹ Mesoporous materials of MCM-41 type have several attractive features such as large surface areas and tunable pore sizes. Apart from catalysis,² recently they have been used for drug delivery^{3,4} and immobilization of cells.⁵ Also, the easy modification of the silica walls helps in encapsulation/adsorption of a variety of guest species.⁶ It is generally accepted that hollow microspheres with mesoporous shells will exhibit more advantages in mass diffusion and transportation compared with conventional hollow microspheres of solid shells.⁷ Therefore, hollow mesoporous microspheres have attracted much attention for their potential applications as catalyst supports and gas/drug/enzyme/semiconductor nanoparticle adsorbents.⁶

Efforts have been made to invent chemically based routes for the preparation of hollow mesoporous microspheres.^{8–11} Core-shell techniques, especially layer-by-layer method (LBL), are probably the most effective approach for this purpose.^{8,12} Earlier reports have shown the use of this approach for the formation of amorphous¹³ and microporous¹⁴ hollow silica shells. Up to now, reports about preparing hollow mesoporous microspheres are still rare, so it is necessary to develop more efficient routes for the preparation of hollow mesoporous microspheres.

Tissot and co-workers made poly(styrene- γ -methacrylic propyltrimethoxysilane) [P(St-MPS)] latex particles by emulsion polymerization.¹² However, the post-processing of the latex particles was complex. Generally, it needs 2–3 days^{7,9} or more^{15,16} to prepare core-shell composite microspheres.

In this paper, we report a facile method to prepare hollow MCM-41 microspheres by removing the templates of P(St-MPS)/MCM-41 core/shell composite microspheres prepared using P(St-MPS) microspheres contained in soap-free emulsion and cetyltrimethylammonium bromide (CTAB) as cotemplates. P(St-MPS) was synthesized by soap-free emulsion copolymerization using styrene and MPS as monomers because the soap-free emulsion systems gave very clean polymer microspheres. The P(St-MPS) microspheres were used directly as core template, and CTAB was used as a template for mesopore structure. The siloxane on the surface of P(St-MPS) hydrolyzed and con-

densed onto CTAB, playing the role of silica source together with tetraethylorthosilicate (TEOS). Poly(ethylene glycol) (PEG) was used as dispersant to prepare monodispersed microspheres. Application of co-silica sources strengthened the chemical affinity of core and shell, thus forming the core-shell composite microspheres in 4 h and greatly shortened the preparation time of hollow mesoporous microspheres.

P(St-MPS) microspheres contained in soap-free emulsion were produced by soap-free emulsion polymerization. The molar composition of the preparation system was H₂O:St:MPS:NaOH:NaHCO₃:K₂S₂O₈ = 100:1:0.1:0.01:0.005:0.009. P(St-MPS)/MCM-41 core-shell composite microspheres were obtained in a typical preparation procedure. First, 1.0 g of CTAB and 0.28 g of NaOH were dissolved into 300 mL of H₂O with stirring at 80 °C. After the solution turned clear, 0.05 g of PEG was added. Half an hour later, 100 mL of soap-free emulsion containing P(St-MPS) microspheres was added. Subsequently, 4.0 mL of TEOS was added dropwise into the above emulsion within 10 min, and the mixture was stirred for 4 h. Finally, the dried powder of core-shell composite microspheres was calcined in air at 550 °C for 6 h to remove the cotemplates and gave hollow MCM-41 microspheres.

The powder XRD patterns were recorded on a Rigaku D/MAX-2500 at 40 kV and 100 mA (Cu K α radiation). TEM observation was performed using a JEOL JEM-100CX electron microscope. Infrared spectra were taken on an FTIR (BIO-RAD FTS165, BIO-RAD) with samples pressed into KBr pellets.

Figure 1a is the FTIR spectra of P(St-MPS), which shows absorption bands at 1602, 1494, and 1454 cm⁻¹ characteristic of the aromatic ring of polystyrene and bands at 1724, 1214, and 1085 cm⁻¹ corresponding to the C=O, Si-C, and Si-O-C bonds of the methacrylate side chains. The band at 1637 cm⁻¹ assigned to the MPS double bond (C=C) disappeared,¹² indicat-

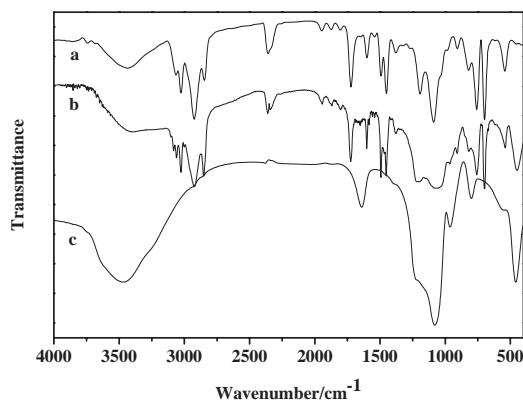


Figure 1. FTIR spectra of P(St-MPS) (a), P(St-MPS)/MCM-41 composite microspheres (b), and hollow MCM-41 microspheres (c).

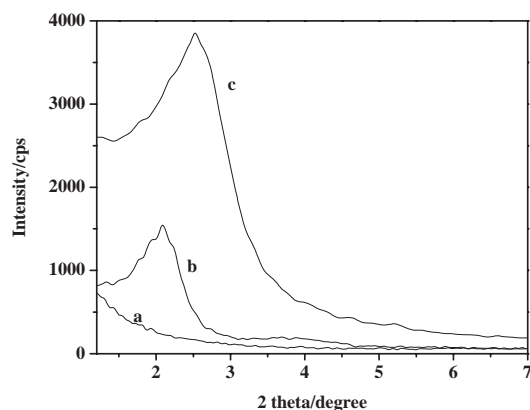


Figure 2. XRD patterns of P(St-MPS) microspheres (a), P(St-MPS)/MCM-41 composite microspheres (b), and hollow MCM-41 microspheres (c).

ing the incorporation of MPS units in the copolymer chain by free-radical polymerization. Figure 1b is the FTIR spectra of P(St-MPS)/MCM-41 composite microspheres. Absorption bands are similar with those in Figure 1a except for the bands at 452 and 964 cm^{-1} characteristic of Si–O–Si bonds.⁸ Figure 1c is the FTIR spectrum of hollow MCM-41 microspheres, which shows absorption bands at 452 , 964 , and 1085 cm^{-1} characteristic of the Si–O–Si bonds of MCM-41.⁸ It illustrates that the complete removal of cotemplates.

The mesoporous structure of microspheres was characterized by XRD. P(St-MPS) microspheres (Figure 2a) show no diffraction peaks, but the XRD pattern of the core–shell composite microspheres (Figure 2b) shows a well-resolved diffraction peak, which can be assigned to the (100) reflection of a hexagonal symmetry structure for typical MCM-41.⁷ Higher order Bragg reflection was not resolved in the patterns, which can be attributed to the small sizes of crystal particles of samples according to Corma.¹⁷ These results reveal that MCM-41 has a shell structure. In Figure 2, both patterns b and c show diffraction peaks which can be assigned to the (100) reflections of hexagonal symmetry structure for typical MCM-41. The peak intensity of c was much higher than that of b, showing the promotion of calcination for the formation of MCM-41 structure and increase of ordering degree. The reason for the shift of (100) peak to higher degree was suggested to be the contraction of pore structure during calcinations.¹⁸ The unit cell parameters calculated from the XRD data were 4.95 and 4.02 nm for P(St-MPS)/MCM-41 core/shell structure microspheres and hollow MCM-41 microspheres, respectively.

Figure 3 shows TEM images of P(St-MPS), P(St-MPS)/MCM-41 core–shell composite microspheres, and hollow MCM-41 microspheres. The P(St-MPS) microspheres were of smooth surface, but the P(St-MPS)/MCM-41 microspheres showed rougher surface. The core–shell composite microspheres were changed into hollow microspheres by losing their core. The size of the hollow microspheres was smaller than core–shell composite microspheres, which can be explained by the contraction of pore structure upon calcination. This is consistent with the result of XRD measurement. It can be clearly seen from Figure 3d that the ordered pore channels of MCM-41 shell are perpendicular to the microspheres surface. The diameters of the hollow MCM-41 microspheres and the thicknesses of the

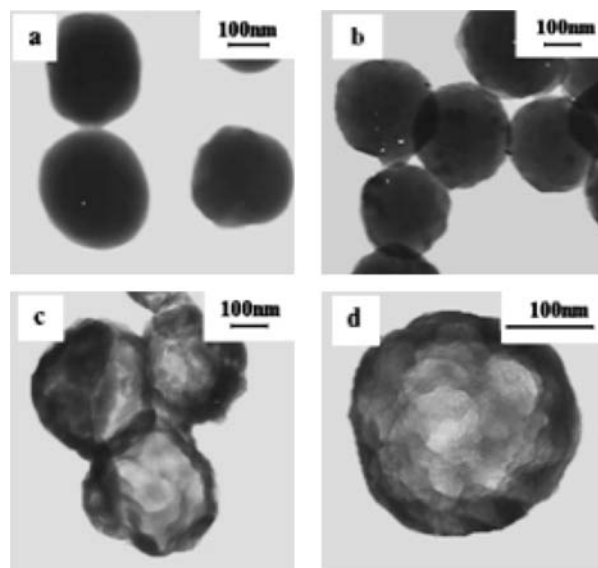


Figure 3. TEM images of P(St-MPS) (a), P(St-MPS)/MCM-41 composite microspheres (b), and hollow MCM-41 microspheres (c, d).

shell that were estimated from the TEM images are about 260 and 30 nm , respectively.

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