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Supporting Information

Hollow Hybrid Spheres with Silica Inner Shell for Non-Deformable, Core Exchangeable Properties

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Experimental

Preparation of melamine-formaldehyde hybrid capsules with silica inner shell

In a beaker, 6.6 g of poly(styrene-alt-maleic acid), sodium salt (Mw 120000, 30 wt% aqueous solution), 24 g of octadecane and 6.0 g of TEOS were added in 45 g deionized water, and then emulsified with homogenizer, 24000 rpm tip speed (Ika, T25 basic homogenizer) in 70 ^{o}C heating bath for 10 min. Just after adding a few drops of aq. NaOH and aq. H_2SO_4 to adjust the solution pH to 4.5, the emulsion solution was added into melaminetrimethylol solution which was prepared through the reaction of 3.96 g of melamine powder with 7.68 g of 37 wt% aqueous formaldehyde solution in 12 g of deionized water at 70 ^{o}C for 10 min. After that, the mixture was stirred for 3 h at 70 ^{o}C. The resulting capsules formed in solution were isolated and purified through repeated centrifugation and washing with water, ethanol, and hexane, respectively.

To form silica inner shell, 300 mg of isolated capsules containing octadecane and TEOS core were dispersed in 10ml of aq. ammonium hydroxide solution (28%) for 24 h at 70 ^{o}C, and then resulting capsules were washed with ethanol and deionized water, centrifuged to isolation, and dried in freeze dryer to yield 220 mg of white powder.

Preparation of melamine-formaldehyde capsules with polymer single layer

6.6 g of poly(styrene-alt-maleic acid), sodium salt (Mw 120000, 30 wt% aqueous solution,), and 30 g of octadecane were added in 45 g deionized water, and then emulsified with homogenizer, 24000 rpm tip speed (Ika, T25 homogenizer) in 70 ^{o}C heating bath for 10 min. Just after adding a few drops of aq. NaOH and aq. H_2SO_4 to adjust the solution pH to 4.5, the emulsion solution was added into melaminetrimethylol solution which was prepared through the reaction of 3.96 g of melamine powder with 7.68 g of 37 wt% aqueous formaldehyde solution in 12 g of deionized water at 70 ^{o}C for 10 min.

After that, the mixture was stirred for 3 h at 70 ^{o}C. The resulting microcapsules formed in solution were isolated and purified through repeated centrifugation and washing with water, ethanol, and hexane, respectively.

Core substances exchange experiment

To investigate the core substances removal and to form the hollow capsules, capsules with silica inner shell and octadecane core were dispersed into chloroform for 1 h with ultrasonication (Branson, Bransonic 2210). This treatment was repeated three times after washing with chloroform and centrifugation, and then dried under vacuum.

The resulting hollow capsules were dispersed again into chloroform/dodecane, 1:1 volume ratio solution. After ultrasonication for 1h, chloroform in solution was gradually removed under reduced pressure for 30 min. The resulting capsules with dodecane core were washed with hexane and centrifuged off to give the capsules with dodecane core.

To determine the core substance contents in capsule, analysis with differential scanning calorimetry (DSC) was performed for octadecane-containing capsules, hollow capsules, and dodecane-containing capsules, respectively, on TA Instrument, DSC Q100, where the phase changes of octadecane and dodecane were detected during temperature variation from -100 ^{o}C to 100 ^{o}C with 10 ^{o}C/min increment.

Elemental analysis for the hollow capsule was performed on CE Instruments, EA-1110 Elemental Analyzer: N 39.28; C 33.85; H 4.92

Formation of polystyrene core

The hollow capsules obtained from the same procedures in core exchange experiment were dispersed in styrene containing 0.1 wt% azobisisobutyronitrile, and then ultrasonicated for 30 min at room temperature. The capsules were isolated from styrene solution by centrifugation and washed with hexane. The resulting styrene-containing capsules were dispersed in water and maintained at 80 ^{o}C for 8 h. Throughout washing with water and ehtanol and centrifugation, polystyrene-containing capsules were obtained as white powder.

T_g of polystyrene was confirmed through differential scanning calorimetry (Figure s1).

Scanning electron microscopy and transmission electron microscopy of the capsules

The scanning electron micrographs were taken on a SEM, Jeol, JSM-6700F. The samples were prepared on glass plate through placing a drop of capsule-dispersed water solution on plate and drying. The

samples were coated with Au to improve the conductivity. Transmission electron microscopy analysis were performed on a FEI Tecnai G^2 20 electron microscope operating at 200 kV. For sample preparation, a drop of capsule-dispersed water solution was placed on a carbon coated copper grid and dried.

Elimination of polymer shell for direct microscopic observation of inner shell

The hollow capsules with silica inner shell were dispersed in water, and then a few drops were placed on glass plate and dried. The sample plate was put into a UV-ozone chamber (UV Lamp power10mW/cm^2, Yuil Ultra violet system Co. YUC-1001) for 5 min and then sample plate was immersed into 3M aq. HCl solution for 30 min and dried. These treatments were repeated three times and the sample plate was washed through immersing into deionized water.

Figure s1. DSC thermogram of microcapsules with polystyrene core