Synthesis of Highly Monodispersed Core/Shell Mesoporous Silica Spheres

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Highly monodispersed core/shell mesoporous silica spheres with radially aligned pore structure have been successfully obtained by adding different type of silica precursor to the existed particles in the preparation.

Recent development in the synthesis of mesoporous silica has opened up the door for the applications in the new types of catalysis,[1] adsorbents,[2] and host materials.[3] Morphological control of these materials has been one of the main objectives toward the industrial use. Among various shapes, spheres are of great interest for applications in chromatography,[4] cosmetics,[5] and colloidal crystals. Recently, we have successfully synthesized monodispersed mesoporous silica spheres (MMSS) possessing highly ordered hexagonal regularity from tetramethoxysilane (TMOS) and alkyltrimethylammonium halide in a methanol/water mixture.[6] Furthermore, we have fabricated colloidal crystal films from MMSS and investigated their optical properties.[7] In the process of investigation of the formation mechanism of MMSS, it was found that primary generated small particles grew to larger particles homogeneously, leading to the formation of monodispersed spherical particles.[8] On the basis of the data, it is speculated that the addition of silica precursors after the completion of the reaction enlarges particles of MMSS. Furthermore, by changing the type of additional silica precursors to the original one, core/shell MMSS can be obtained.

There have been many reports conducting on the synthesis of core/shell particles. The objectives of the researches are classified into the following three categories: 1. Protection of cores. Magnetic particles were coated with silica shell to prevent from coaggulation.[9] 2. Enhancing the properties of shell. Carbon core increased the oxidation current of metal shell. This material was expected for the methanol oxidation catalyst of direct methanol fuel cell.[10] By coating on Stöber silica spheres, plasmon peak of Au was shifted.[11] 3. Preparation of core/shell particles from materials with different properties. The combinations of particles with magnetic and optical properties were widely carried out. Increase of fluorescence radiation decay was observed for Co/CdSe core/shell particles.[12] Plasmon peak red-shifted and coercivity increased for magnetite/Au core/shell nanoparticles.[13]

Incorporation of guest materials like metal,[14] metal oxides,[15] and chromophores,[16] into mesoporous silica has been conducted by many researchers. If core/shell mesoporous silica spheres are obtained, different types of guests can be incorporated into their core and shell, selectively, by designing the combination of core and shell properties. Here, we report the synthesis of MMSS with core/shell structure.

In a typical synthesis, 3.52 g of hexadecyltrimethylammonium chloride and 2.28 mL of 1 M sodium hydroxide solution were dissolved in 800 g of methanol/water (50/50 = w/w) solution. Then 1.32 g of TMOS was added to the solution with vigorous stirring at 298 K. After the addition of TMOS, the clear solution turned opaque in three min and resulted in white precipitate. After 30 min the experiment started, 1.32 g of TMOS was added again. This procedure was repeated. Then, the mixture was stirred for 6 h and aged overnight. The white powder was filtered off, washed with distilled water at least three times, and dried at 318 K for 72 h. The powder obtained was calcined in air at 823 K for 6 h to remove the surfactant. In case an organically modified silane was used, surfactants were extracted by acidic ethanol at 333 K for 3 h instead of calcination.

Figure 1 shows SEM images of particles obtained by different number of TMOS addition times and its schematic illustration of the particle growth. The diameter of the particles became larger upon the addition of TMOS while retaining its monodispersion characteristic (standard deviation in parenthesis). This result indicates that added TMOS preferred to react with the surface silanol of existing particles rather than generated new particles by reacting between TMOS.

The above results support the assumption that core/shell MMSS can be obtained by changing the type of additive silica precursor from the original one as illustrated in Scheme 1.

Synthesis was conducted in which double the molar amounts of mercaptopropyltrimethoxysilane (MPTMS)/TMOS (= 20/80 mol/mol) mixture instead of TMOS was added to the solution. Because the synthesis was conducted under a large molar ratio of a surfactant (sur/Si = 1.27), the amount of surfactant in the solution was sufficient for further mesoporous silica

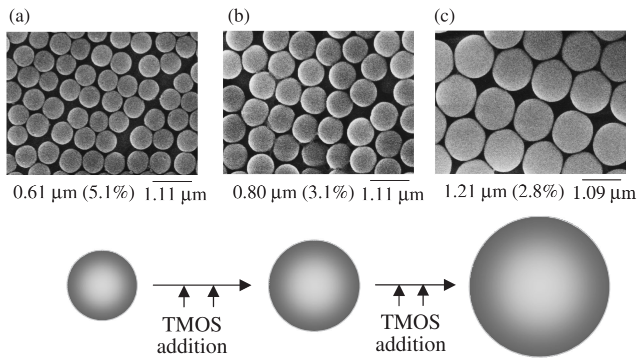
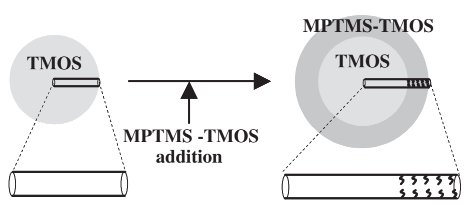


Figure 1. SEM images of particles obtained by the different TMOS addition times: (a) 0, (b) 2, and (c) 4, and schematic illustration of the particle growth.



Scheme 1.

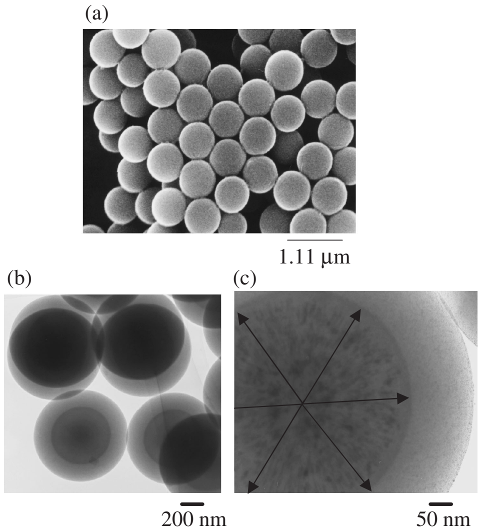


Figure 2. (a) SEM image of the core/shell MMSS. (b) and (c) TEM images of the platinum-introduced silica/mercaptopropyl-modified silica core/shell MMSS. Pore directions are shown by arrows.

formation. Figure 2a shows the SEM image of the obtained particles. The average diameter was 0.73 μm, and the standard deviation was 4.3%, indicating that the particles were highly monodispersed. It is expected that the obtained particles possess silica/mercaptopropyl-modified silica core/shell structure, more specifically, hydrophilic/hydrophobic core/shell structure. To confirm this, tetraammineplatinum chloride solution was introduced into mesopores and heated 673 K for 2 h at a reduced atmosphere.[17] An egg-type structure is clearly seen in Figures 2b and 2c. Platinum (dark portion) is concentrated in the hydrophilic core part. Because platinum was incorporated into mesopores using an aqueous solution as a precursor, platinum particles were selectively introduced into the hydrophilic core part. Radial alignment of mesopores is confirmed by the distribution of platinum particles in the core. From these results it is obvious that MMSS with core/shell structure was successfully obtained by changing the type of additive silica precursor.

To investigate the effect of core/shell structure on the adsorption behavior of mesoporous silica, water adsorption–desorption measurements were carried out for three kinds of MMSSs obtained from TMOS (TMOS-MMSS), propyltrimethoxysilane (PTMS)/TMOS (= 30/70 mol/mol) mixture (propyl-modified MMSS), and TMOS followed by equimolar of PTMS/TMOS mixture (silica/propyl-modified silica core/shell MMSS) at 298 K by using a Belsorp18 (Bel Japan). The propyl-modified MMSS adsorbed water vapor at a higher relative pressure region than the TMOS-MMSS even though the pore diameter of the propyl-modified MMSS is the smallest. This is explained by the hydrophobic property of the propyl-modified MMSS. Interestingly, the silica/propyl-modified silica core/shell MMSS adsorbed water vapor at the median relative pressure of the TMOS-MMSS and the propyl-modified MMSS. If particles are the mixture of the TMOS-MMSS and the propyl-modified MMSS, amount of adsorbed water vapor should be increased stepwise at the corresponding relative pressures to the TMOS-MMSS and the propyl-modified MMSS, respectively. This result also supports that core/shell structure was successfully prepared. This unique adsorption behavior was observed for the first time for the core/shell mesoporous silicas.

In conclusion, core/shell monodispersed mesoporous silica spheres with radially aligned pore structure have successfully obtained for the first time by adding different type of silica precursor to the existed particles in the synthesis. Work is underway to explore new potential applications of these unique materials which possess both core/shell structure and radially aligned hexagonal mesopores.

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