



Surface Modification of PTMS Particles with Organosilanes: TEOS-, VTMS-, and MTMS-Modified Particles

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Abstract. The surface modification of phenyltrimethoxysilane (PTMS) particles was performed in an alcoholic solution with tetraethyl orthosilicate (TEOS) and in an aqueous solution with other organoalkoxysilane monomers such as vinyltrimethoxysilane (VTMS) and methyltrimethoxysilane (MTMS). The surface modification with organoalkoxysilane monomers could lead to the improvement in functionality of PTMS particles. In addition, the surface-modified PTMS particles could be made the channeled hollow particles by core dissolution in organic solvents instead of by chemical etching. This resulted from that PTMS particles serving as cores have the selective solubility in organic solvents.

Keywords: surface modification, organo-silica, hollow particles, template, organosilanes

1. Introduction

Surface-modified silica particles have generated intense interest in a wide range of application fields. The modification of inorganic silica particles with organics leads to the production of organic-inorganic hybrid particles in which the organic components may be chemically bonded to a silica matrix [1]. Somewhat similar to inorganic silicate glasses, the structure of the silica network can be modified by the presence of organic groups. The mechanical, electrical and optical properties of the resulting organic-inorganic hybrid particles are then governed by the type and concentration of the organics used [1, 2]. Furthermore, the utilization of nanosized organic-inorganic hybrid particles for the production of advanced ceramic materials requires high quality with respect to chemical purity, homogeneity, morphology, and a controlled state of agglomeration as well as low production costs. Meanwhile, ceramic hollow particles have also been studied in recent years and their syntheses have been reported on the earlier literature [3, 4]. Among syntheses, the

templating method is composed of a shell coating procedure and a subsequent core removing procedure that is performed via a thermal decomposition or a chemical dissolution [5, 6]. In this study, the surface modification of PTMS particles was performed in an ethanolic solution or in an aqueous solution with silane monomers such as TEOS, VTMS, and MTMS. Using a feature of PTMS particles, selective solubility in organic solvents [7], TEOS-, VTMS-, and MTMS-modified PTMS particles could be made the channeled hollow particles.

2. Experimental

2.1. TEOS-Modified PTMS Particles

Monodisperse PTMS particles were prepared by the procedure described in earlier report [7]. The particles (0.5 g), ca. 300 nm in size, were added to an 80 mL of ethanolic solution. After sonication for 30 min in ultrasonic bath, an aqueous solution of ammonium hydroxide (28%) in the range of 0.2–2.0 mL was added to the dispersion with stirring. To the mixture solution was

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added 10 mL of ethanolic solution containing 1 mL of TEOS (molar ratio of PTMS/TEOS = 0.73). And then the solution was continuously stirred at ambient temperature for 2 h. The resultant particles were collected with a membrane filter and washed with ethanol several times. The obtained particles were dried in a vacuum oven at 80°C for 4 h.

2.2. VTMS (or MTMS)-Modified PTMS Particles

An aqueous solution containing nitric acid (61–62%, 0.1 mL) was placed in isothermal bath at 60°C. Phenyltrimethoxysilane (1.0 mL) was added to the solution with stirring and then the mixture solution was continuously stirred for 1 min. An aqueous ammonium hydroxide solution (28%, 40 mL) was added to the resulting transparent solution, leading to a milky solution immediately. After stirring for 1 h, VTMS (or MTMS) (1.0 mL) was added to the mixture solution (molar ratio of PTMS/VTMS and PTMS/MTMS = 0.82 and 0.77, respectively). The reaction was continued for 1 h more, and then the resultant particles were collected with a membrane filter and washed with deionized water several times. The particles as prepared were dried in a vacuum oven at 80°C for 4 h.

2.3. Characterization

The morphology and size of the particles were observed using field emission scanning electron microscopy (FE-SEM, JEOL JEM-6340F) and transmission electron microscopy (TEM, JEOL EM-2000EXII). The chemical analyses of the obtained particles were performed by solid-state nuclear magnetic resonance (NMR, VARIAN UnityInova 300 MHz) spectroscopy using MAS technique (spinning rate: 3.5 kHz). ^{29}Si MAS NMR spectra were obtained at 59.617 MHz with a 50 kHz spectral width, a pulse width of 4.7 μs and a relaxation delay of 10 s. The ^{13}C CP MAS NMR experiments (75.463 MHz) were recorded with a relaxation delay of 30 s and a spectral width of 60 kHz. Tetramethylsilane was used as the external reference for all MAS NMR spectra.

3. Results and Discussion

Figure 1 shows the schematic procedure of the preparation of surface-modified PTMS particles with TEOS,

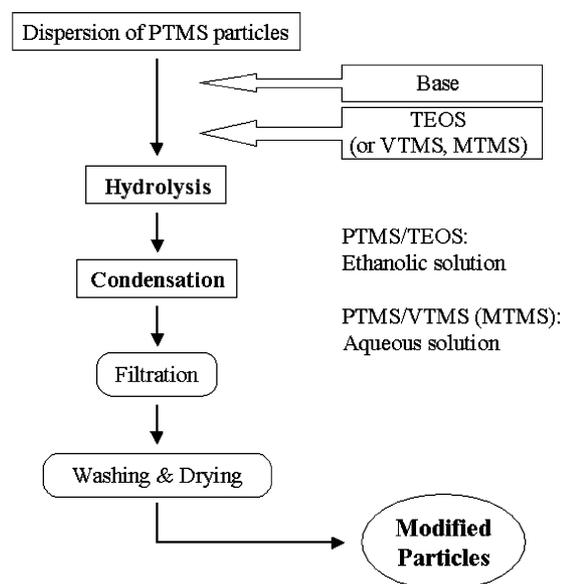


Figure 1. Schematic procedure of the surface modification of PTMS particles with TEOS, VTMS, or MTMS monomer.

VTMS, or MTMS monomer. Surface modification of PTMS particles with TEOS monomer was performed in an ethanolic solution, while that with VTMS or MTMS monomer was done in an aqueous solution. This is because formation of silica particles cannot arise from TEOS monomer in an aqueous solution without alcohol [8, 9]. Figure 2 shows the effect of added aqueous NH_4OH solution on morphology of TEOS-modified PTMS particles. Monodisperse and smooth particles were obtained with decreasing the amount of added aqueous NH_4OH solution. Higher R ($[\text{H}_2\text{O}]/[\text{monomer}]$) value caused by increase of the amount of aqueous NH_4OH solution leads to increase the condensation rate of TEOS monomer resulting in the occurrence of secondary nucleation. This secondary nucleation produces pure silica particles through particle growth procedure, and the obtained particles, in consequence, have a bimodal particle size distribution. And, the size of TEOS-modified PTMS particles as prepared also increased with decreasing the amount of aqueous NH_4OH solution. Using a feature of PTMS particles described in earlier report [7], hollow TEOS silica could be prepared from TEOS-modified PTMS particles as shown in Fig. 3. The particles have hollows in the range of 120–180 nm after washing with ethanol. With sonication in acetone for 3 h, the hollows of the particles increased to the size of 290–300 nm, and continuous sonication overnight resulted

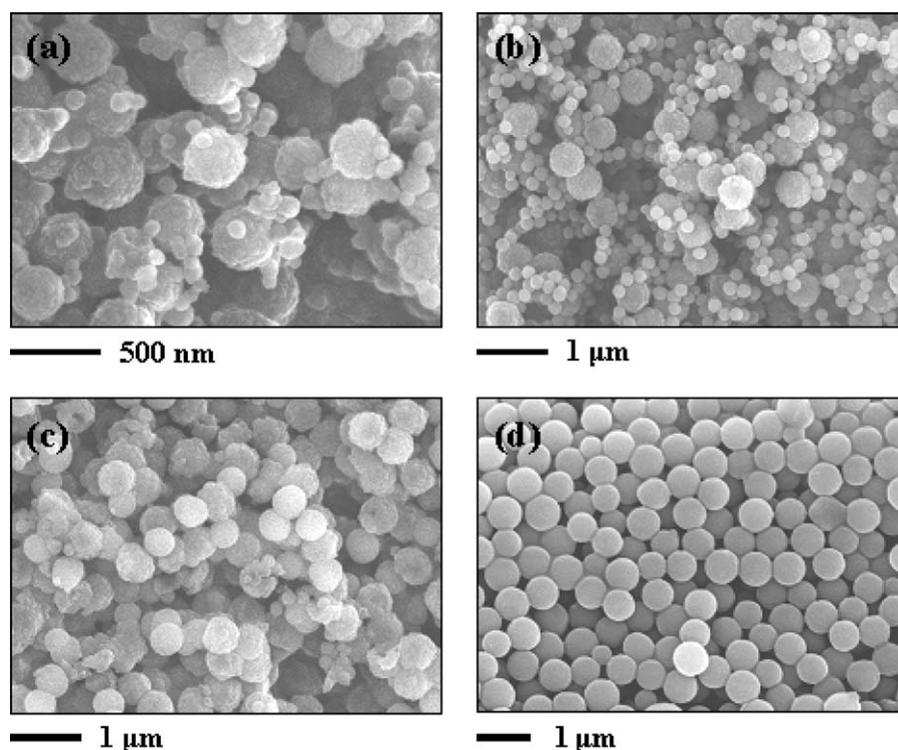


Figure 2. SEM images of TEOS-modified PTMS particles obtained with the variation of aqueous NH_4OH added: (a) 2 mL, (b) 1 mL, (c) 0.5 mL, and (d) 0.2 mL.

in the formation of channeled hollow silica particles. Figure 4 shows solid-state ^{29}Si NMR spectrum of TEOS-modified PTMS particles as prepared. Two signals at -76.5 ppm and at -103.5 ppm in the spectrum can be assigned to T^3 silicon site resulted from PTMS and Q^4 silicon site from TEOS, respectively. It demonstrated with the increase of particle size that sur-

face modification of PTMS particles with TEOS was achieved.

The preparation of VTMS-modified PTMS particles was performed in an aqueous solution. As mentioned in experimental, PTMS particles were synthesized in an aqueous solution, and the surface modification of the particles was progressed through subsequent

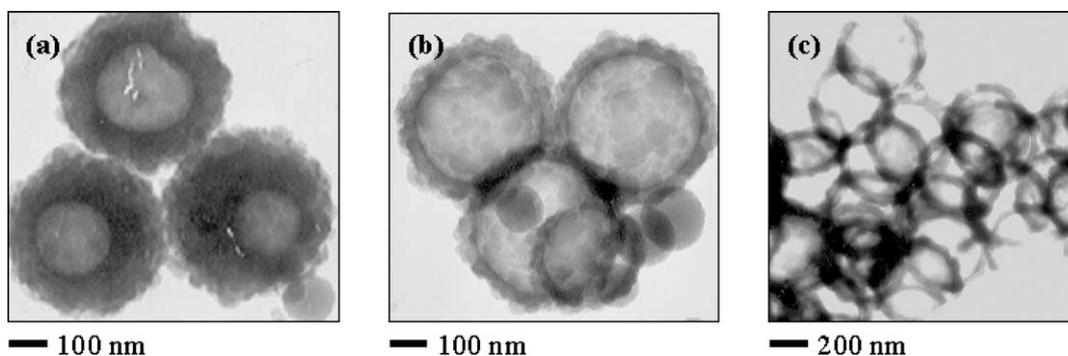


Figure 3. TEM images of hollow particles resulted from TEOS-modified PTMS particles after sonication in ethanol for 2 h (a), and after sonication in acetone for 3 h (b) and overnight (c).

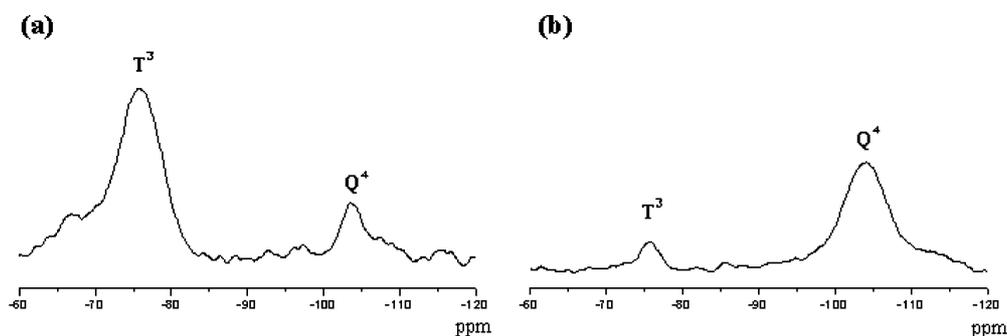


Figure 4. Solid-state ^{29}Si NMR spectra of TEOS-modified PTMS particles (a) before and (b) after acetone treatment.

addition of VTMS monomer. The VTMS-modified PTMS particles, produced from PTMS particles in size of ca. 400 nm, have a smooth surface and a monodisperse size distribution (600–700 nm). The resultant particles could also be made the channeled hollow particles by sonication in acetone for 3 h. The channeled hollow VTMS particles obtained are shown in Fig. 5(a)–(c).

The surface modification of PTMS particles with MTMS monomer exhibited similar results to that with

VTMS mentioned above. As shown in Fig. 5(d) and (e), MTMS-modified PTMS particles were obtained in size of ca. 600 nm, and the channeled MTMS particles with the hollows of ca. 400 nm were resulted from sonication in acetone for 3 h. Figure 6 shows solid-state ^{13}C NMR spectra of pure PTMS particles and MTMS-modified PTMS particles. The signals at near 130 ppm are due to the carbons in phenyl groups of PTMS particles. Moreover, the spinning side bands (ssb) of phenyl signals are

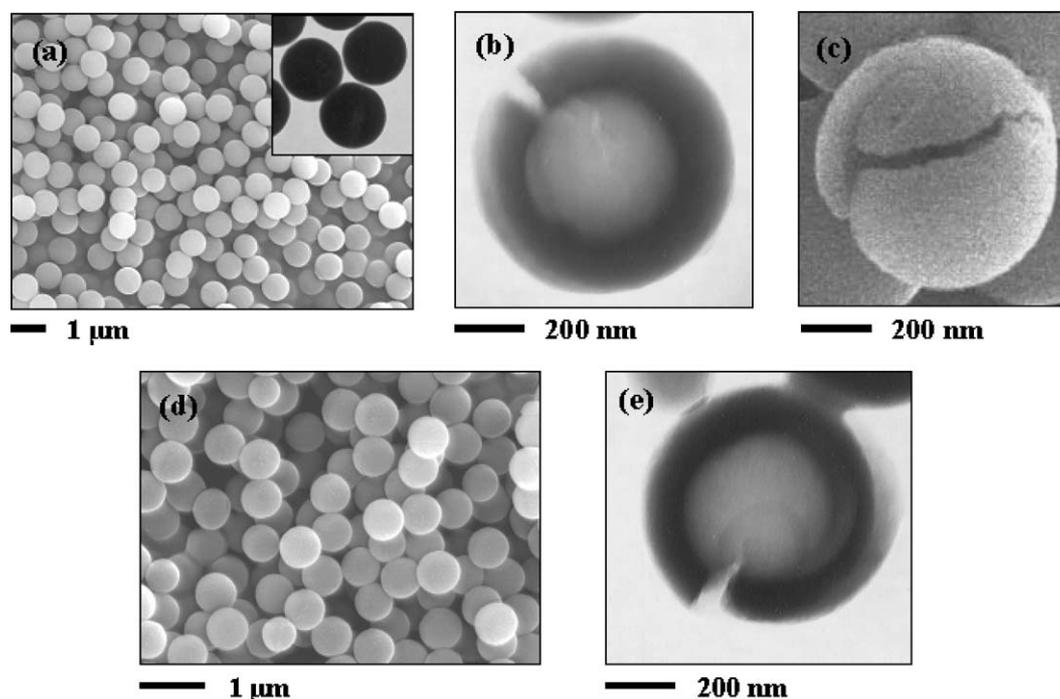


Figure 5. SEM and TEM images of (a)–(c) VTMS- and (d) and (e) MTMS-modified PTMS particles. (a) and (d): the images before acetone treatment; (b), (c) and (e): the images after acetone treatment.

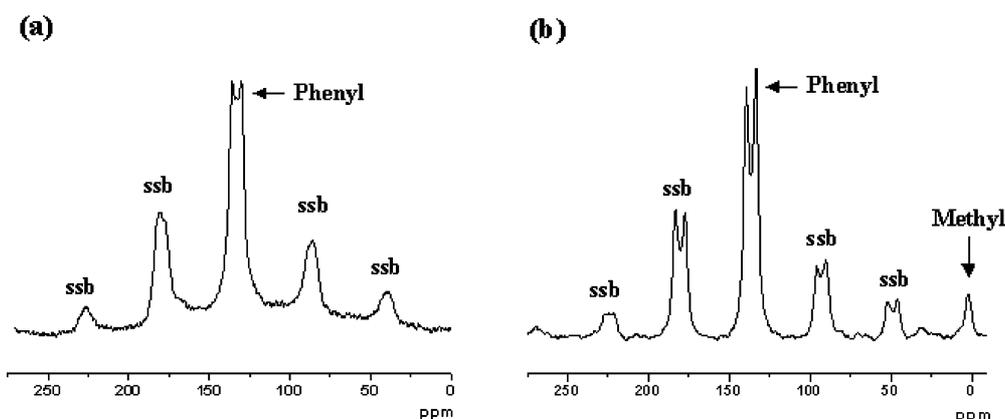


Figure 6. Solid-state ^{13}C NMR spectra of (a) pure PTMS particles and (b) MTMS-modified PTMS particles prepared. The ssb represents a spinning side band.

also shown symmetrically in Fig. 6. The as-synthesized MTMS-modified PTMS particles, however, have one more signal at near 1.7 ppm that can be assigned to the carbons in methyl groups of the particles. This demonstrated the surface modification of PTMS particles with MTMS monomer.

4. Conclusions

The surface modification of PTMS particles was performed in an ethanolic solution or in an aqueous solution with silane monomers such as TEOS, VTMS, and MTMS. The resultant surface-modified PTMS particles have smooth surfaces and monodisperse size distributions. Using a feature of PTMS particles, selective solubility in organic solvents, TEOS-, VTMS-, and MTMS-modified PTMS particles could be made the channeled hollow particles.

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