

Electronic Supplementary Information (ESI)

Colloidal Janus Nanoparticles by Asymmetric Capping of Mesoporous Silica with Phenylsilsesquioxane

Hiroto Ujiie,^a Atsushi Shimojima*^a and Kazuyuki Kuroda*^{a, b}

^aDepartment of Applied Chemistry, Faculty of Science and Engineering, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169-8555, Japan, ^bKagami Memorial Research Institute for Materials Science and Technology, Waseda University, Nishiwaseda-2, Shinjuku-ku, Tokyo, 169-0051, Japan

Fax: +81-3-5286-3199; Tel: +81-3-5286-3199; E-mail: kuroda@waseda.jp

Materials

Cetyltrimethylammonium bromide (C₁₆TMABr) and triethanolamine (TEA) were purchased from Wako Pure Chemical Industry. Tetraethoxysilane (TEOS: Si(OC₂H₅)₄, Guaranteed Grade) was purchased from Kishida Chemical. Phenyltriethoxysilane (PTES, Purity > 99 %) was purchased from Tokyo Kasei. Acetic acid (AcOH) and ethanol (EtOH) were purchased from Kanto Chemical. All materials were used without any further purification.

Characterizations

Dynamic light scattering (DLS) measurements were conducted with a HORIBA Nano Partica SZ-100-S at room temperature. Zeta-potential measurements were conducted with an Otsuka Electronics ELSZ-1 at room temperature. TEM images were taken on a JEOL JEM-2010 microscope operating at 200 kV. SEM images were taken on a HITACHI S-5500 electron microscope operated at an acceleration voltage of 3–30 kV. Samples for TEM and SEM measurements were dropped and dried on a carbon-coated micro-grid (Okenshoji Co.). X-ray diffraction (XRD) patterns of dried powder samples were obtained on a RIGAKU UltimaIV with Fe K α radiation (40 kV, 30 mA). Nitrogen adsorption-desorption measurements were performed with an Autosorb-1 instrument (Quantachrome Instruments) at 77 K. Samples were preheated at 120 °C for 24 h under 1×10^{-2} Torr. The Brunauer-Emmett-Teller (BET) surface area was calculated from adsorption data in relative pressure range from 0.05 to 0.20. The pore volume was calculated at $P/P_0 = 0.95$ in order to exclude the volume due to interparticle pores. The pore

size distribution was evaluated using the adsorption branch with non-local density functional theory (NLDFT). CHN elemental analysis was performed with a Perkin-Elmer 2400 Series II. FT-IR spectra were obtained by using a JASCO FT/IR 6100 spectrometer by a KBr method.

Preparation of colloidal mesostructured silica nanoparticles as cores for the preparation of Janus nanoparticles

Detailed procedure for the preparation of CMSS is described here. First, 0.420 g of TEA and 2.00 g of C₁₆TMABr were added to 240 mL of water and the solution (pH 9.5) was stirred at 80 °C. After 2 h, 11 mmol of TEOS was added to the solution and the mixture was stirred vigorously at 80 °C for 12 h. Finally, the colloidal suspension (pH 8.2) was filtered with a filtering paper (No. 5) to remove very tiny amounts of aggregates. Virtually, no noticeable aggregates can be observed on the filtering paper after filtration, and all the colloidal particles were recovered in the filtrate. The molar composition of the precursor solution was 1 TEOS: 0.50 C₁₆TMABr: 0.25 TEA: 1200 H₂O. From the TEM image of CMSS (Fig. S1 left), the contrast in brightness due to mesostructures was observed in a particle whose average diameter is *ca.* 30 nm. The XRD pattern (Fig. S1 right) proved the mesostructure ($d = 5.6$ nm). The sharp peak observed at $2\theta = 4.2^\circ$ ($d = 2.6$ nm) is originated from a small amount of C₁₆TMABr crystals deposited upon drying.

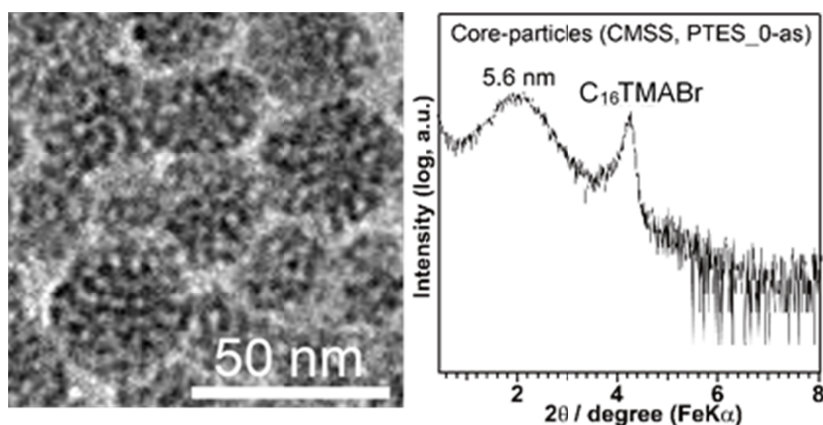


Fig. S1. TEM image (left) and XRD pattern (right) of CMSS (PTES_0-as).

Selective dissolution of silica in PTES_0.5-dia

First, 50 mL of PTES_0.5-dia was transferred into a dialysis membrane. The dialysis membrane containing the colloidal solution was then immersed in 250 mL of 0.6 M aqueous Na₂CO₃ solution (pH 11.5) at 80 °C for 30 min (Y. Chen, H. Chen, L. Guo, Q. He, F. Chen, J. Zhou, J. Feng and J. Shi, *ACS Nano*, **1**, 529 (2010)). The process was repeated twice. Aggregates were formed during these processes. Next, the dialysis membrane containing the aggregates was

immersed in 250 mL of pure water at room temperature, and the outer solution was replaced with 250 mL of fresh pure water every 30 min until the pH value of outer solution approached to *ca.* 7. Finally, the aggregates were dried.

Hydrolysis of PTES under an acidic condition

PTES was added to an acidic aqueous solution containing of EtOH and AcOH (PTES : water : EtOH : AcOH = 1 : 50 : 10 : 0.1, PTES = 5.5 mmol, pH = 2.8), and the mixture was stirred for 6 h. The mixture was an emulsion at the early stage of the reaction, but became transparent (after 4–5 h) as PTES was hydrolyzed.

Liquid-state ^1H NMR of the solution after stirring for 6 h showed that peaks assigned to ethoxy groups (3.88–3.82 ppm: $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiPh}$, 1.22–1.19 ppm: $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiPh}$,) were not observed (data not shown). Liquid-state ^{29}Si NMR of the solution (Fig. S6) showed the peak assigned to $\text{PhSi}(\text{OH})_3$ at -51.9 ppm (see Y. Sugahara, T. Inoue and K. Kuroda, *J. Mater. Chem.*, 7, 53 (1997)). These data suggest that PTES was fully hydrolyzed.

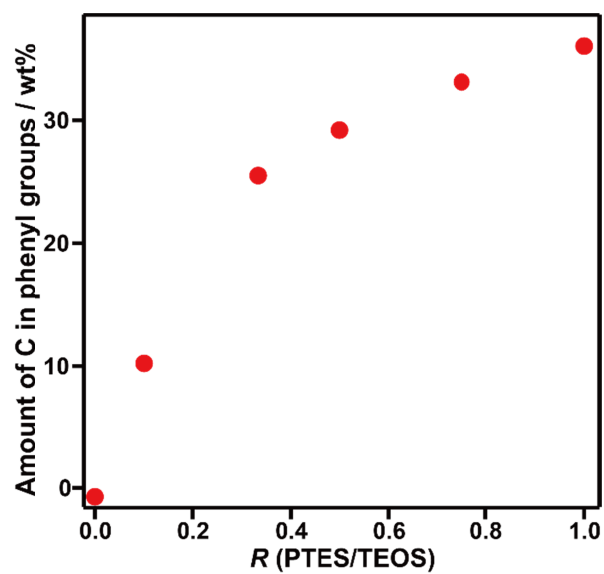


Fig. S2. C contents in PTES_ R -dia calculated by CHN elemental analysis.

Table S1 C contents of the samples shown in Fig. 3

Lapse time	C contents corresponding to phenyl groups / mass%
0 min	5.0
2 min	13.7
5 min	16.2
10 min	24.9
30 min	29.7
1 h	30.9
3 h	31.0
6 h	30.6
12 h	29.2
(PTES_0.5-dia)	

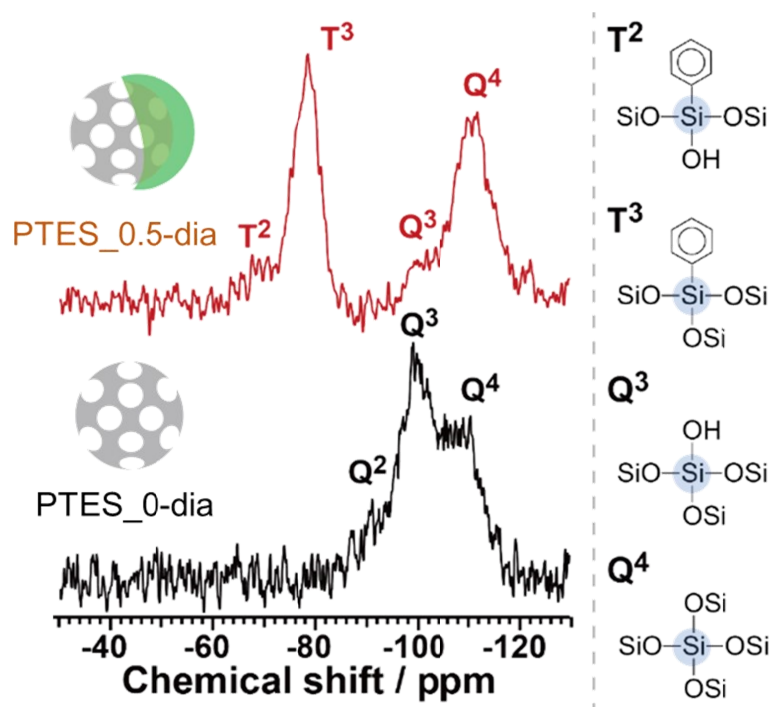


Fig. S3. ^{29}Si CP/MAS NMR spectra of PTES_0-dia and PTES_0.5-dia

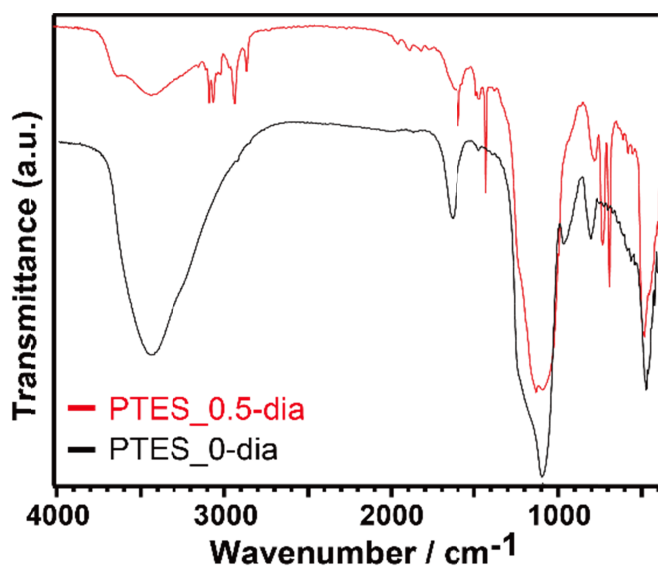


Fig. S4. FT-IR spectra of PTES_0-dia and PTES_0.5-dia. In the IR spectrum of PTES_0.5-dia, the peaks assigned to C-H stretching vibrations of phenyl groups ($C=C-H$) are observed at 3000–3100 cm^{-1} . The stretching vibrations of $-C=C-$ in aromatic rings are observed at 1596 cm^{-1} and 1431 cm^{-1} . The bands at 739 cm^{-1} and 697 cm^{-1} are also characteristic of mono-substituted benzene. On the other hand, the bands at 2850–2950 cm^{-1} are possibly due to the residual surfactant (CTA cations) in the sample.

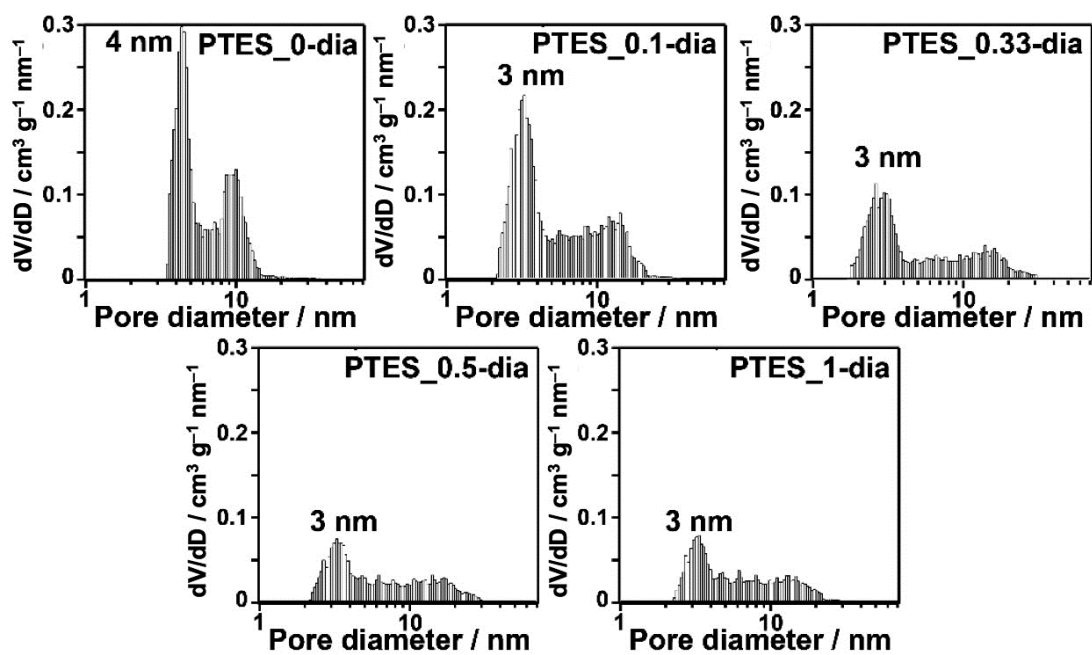


Fig. S5. Pore size distributions of PTES_*R*-dia calculated by NLDFT method.

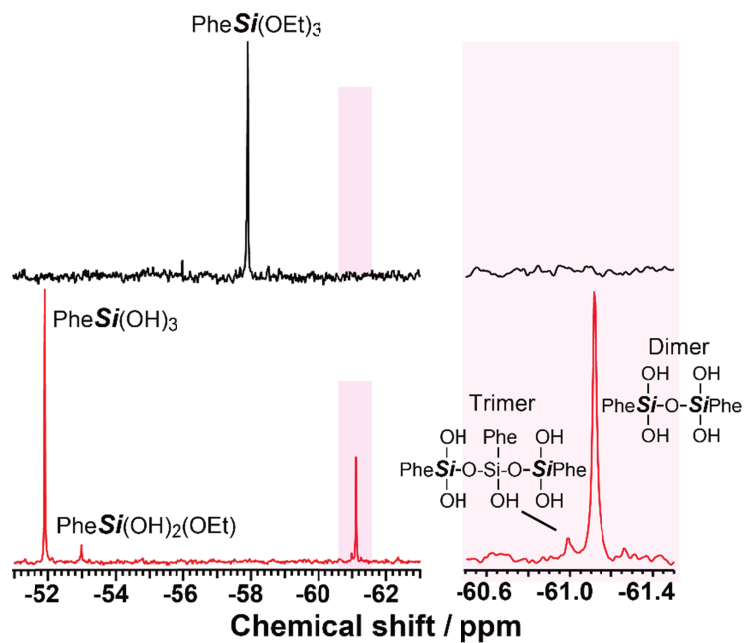


Fig. S6. Liquid-state ^{29}Si NMR spectra of PTES (top) before and (bottom) after hydrolysis.

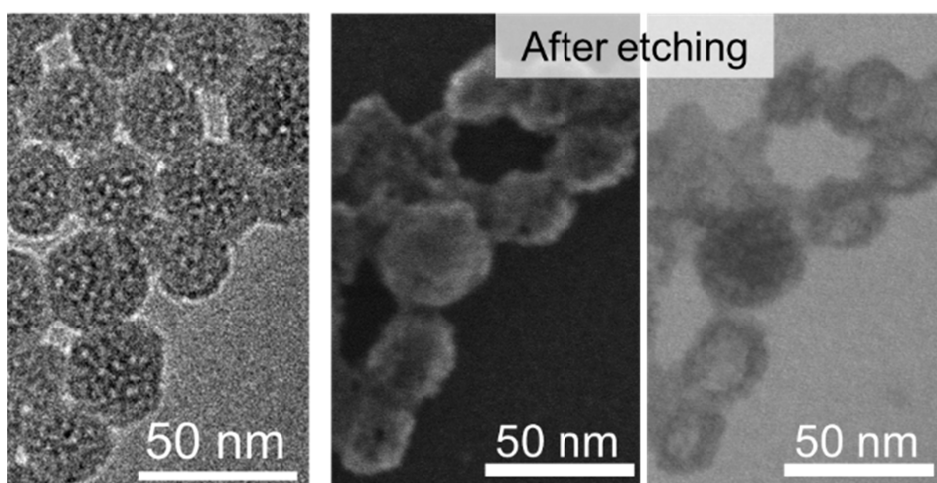


Fig. S7. (left) TEM image of mesoporous nanoparticles prepared by modification of CMSS with pre-hydrolyzed PTES. (middle and right) SEM and STEM images of the nanoparticles after dissolution of silica region, respectively. The formation of hollow spheres suggests that the shell formation occurred symmetrically.