Preparation of Propanethiol-Modified Nanoporous Silica Spherical Particles

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Spherical particles of nanoporous silica (with a diameter of 600 nm) containing mercaptopropylsilyl groups on the pore surface were synthesized by a modified Stöber method and subsequently silylated using (3-mercaptopropyl)-trimethoxysilane. The spherical particles of organosilica formed an artificial opal structure by simply casting the suspension (water dimethylformamide mixture) on a mercaptopropylsilylated Si wafer.

After the discovery of nanoporous silicas prepared by supramolecular templating, the control of nanostructure, chemical composition, and morphology has been investigated and possible applications of nanoporous silica have been proposed.[1–6] Since morphology is a key issue for certain applications, the preparation of nanostructured and nanoporous silicas in such controlled morphologies as films, fibers, and monoliths have been actively investigated.[7–10] Nanoporous silica spherical particles have been prepared by utilizing various synthetic approaches including those based on emulsion chemistry,[11] morphology templates,[12] and spraying,[13–18] and the control of particle size has been investigated. The Stöber method,[19] which was developed for the preparation of mono-dispersed silica spherical particles with controlled particle size from tens to hundreds of nm, has successfully been applied to prepare nanoporous silica spherical particles.[20–34] Due to the controlled size and size distribution of nanoporous silica spherical particles, their applications as chromatography stationary phase, building block of colloid crystals (or photonic crystals), drug support toward controlled release, and catalyst supports seems to be promising.[35–39] These future possible applications motivate researchers to prepare nanoporous silica spherical particles with further variation including varied chemical composition, particle size and size distribution, and surface functionalization.

The modification of mesoporous silicas by complexation with functional units both within the silica wall and in the nanopore is a possible way to tune the properties.[1–6] Accordingly, nanoporous organosilica spherical particles have been prepared by both post synthetic grafting and direct co-condensation.[40–43] Such organic groups as alkyl, amino, and mercapto groups have been introduced so far. Since mercapto groups are known to complex with heavy metal ions and noble metal particles, their introduction into nanoporous silica spherical particles may lead to materials for separation, catalyst supports, and other applications.[42–52] Although there are several reports of the successful introduction of mercapto groups into the spherical particles of silica-based materials, there remains room for further research on this kind of material. The preparation of materials with nanoscale to macroscale hierarchically designed architectures and the structure–properties relationship of the resulting materials are worth investigating. The present paper reports the preparation of mercaptopropylsilylated derivatives of nanoporous silica spherical particle by post-synthetic grafting. The grafting led to improved dispersion stability of the particles leading to densely packed particle aggregate on a flat substrate by drying.

Experimental

Materials. Tetraethoxysilane (abbreviated as TEOS) and hexadecyltrimethylammonium chloride [$(C_{16}H_{33})(CH_3)_3NCl$; abbreviated as CTAC] was obtained from Tokyo Kasei Kogyo Co., Ltd. (3-Mercaptopropyl)trimethoxysilane was purchased from Sigma-Aldrich. Sodium hydroxide, methanol, toluene, dimethylformamide, and 28% aqueous ammonia solution were obtained from Kanto Chemical Co., Ltd. All the chemicals were used as received.

Sample Preparation. The synthesis of the nanoporous silica was conducted by the combination of reported procedures for the preparation of spherical silica particles[34,53,54] and the attachment of mercaptopropylsilyl groups on mesoporous silicas.[45,46] CTAC (0.845 g), deionized water (5.2 g), methanol (400 mL), and 28% aqueous ammonia solution (119.6 g) were mixed in a sealed vessel and the solution was shaken for 15 s at room temperature. To the solution was added TEOS (1.472 mL) and then the mixture was shaken for 3 s. The mixture was subsequently aged at room temperature for 20 h. The molar ratio of TEOS:CTAC:deionized water:methanol:ammonia was 1:0.4:774:1501:288. After aging, products were separated by vacuum filtration using a membrane filter (pore diameter: 200 nm; Toyo Roshi Kaisha, Ltd.) and washed with methanol. Organic modification was conducted by the reaction of the as synthesized spherical particles (500 mg) with (3-mercaptopropyl)trimethoxysilane (MPTS). 500 mg of the spherical particles were mixed with a toluene solution of MPTS (1 g of MPTS in 25 mL of toluene) and the mixture was allowed to react at 110 °C for 48 h with magnetic stirring. The operation was done under nitrogen flow. Prior to the silylation, the particles were dried at 80 °C for 3 h under reduced pressure. The product was separated

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by vacuum filtration and washed with toluene and ethanol in order to remove remaining silane coupling reagent and CTAC. After washing, the product was dried at 60 °C. As a reference, nanoporous silica spherical particles were also prepared by calcination of the surfactant–silica spherical particles at 550 °C in air. These particles are refered to as calcined particles in the present paper.

The organothiol-modified nanoporous silica spherical particles were dispersed in a mixture of dimethylformamide and water (3:1 in volume) and the suspension was spread on a Si wafer modified with MPTS and subsequently dried.

Characterization. Scanning electron micrographs (SEM) were obtained on a Hitachi S-2380N scanning electron microscope. Prior to the measurements, the samples were coated with gold. Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a Rigaku TG-8120 instrument at a heating rate of 10 °C min^{-1} and using α-alumina as standard materials. The nitrogen adsorption/desorption isotherms of the thiol-modified particles were measured at −196 °C on a Belsorp 28SA instrument (Bel Japan Inc.). Prior to the measurements, the samples were dried at 60 °C under vacuum for 3 h. Surface area and pore size distribution were determined by the Brunauer–Emmett–Teller method[56] and the Barrett–Joyner–Halenda method[55] from nitrogen adsorption isotherms, respectively. CHN analysis was conducted with a Perkin-Elmer PE2400II instrument. Solid-state ^{29}Si MAS NMR spectra were recorded on a JEOL JNM-EX270 spectrometer at a resonance frequency of 79.42 MHz with a 45° pulse and a recycle delay of 300 s. The spinning speed was 6 kHz. Solid-state ^{13}C CP/MAS NMR spectra were recorded on a JEOL JNM-EX270 spectrometer at a resonance frequency of 104 MHz and a recycle delay of 5 s with a sample rotation of 5 kHz and a 90° pulse. The ^{29}Si and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm. FT-IR spectra of KBr discs were recorded on a FT-IR8000PC spectrometer (Shimadzu).

Results and Discussion

SEM images of the products (before and after the silylation) are shown in Figure 1, which shows the products are spherical particles of 600-nm diameter with narrow particle size distribution. The particle morphology did not change during reaction with MPTS.

The infrared spectrum of the silylated product is shown in Figure 2, where an absorption band ascribable to C–S stretching vibration was observed at 686 cm^{-1} in addition to those ascribable to SiO_2 and methylene groups. The ^{29}Si MAS NMR spectrum (Figure 3a) showed signals due to Q^3 (–O**Si**(OSi)$_3$) and Q^4 (**Si**(OSi)$_4$) environments of Si at around −102.6 and −109 ppm, respectively. New signals at −50.5, −57.7, and −65.1 ppm, assigned to T^2 (R**Si**(OSi)$_2$O−) environments of Si, were observed for the silylated product. The ^{13}C CP MAS NMR spectrum of the product is shown in Figure 3b, where signals ascribable to propyl groups were observed at 30.2 and 46.6 ppm. These observations indicated the successful immobilization of mercaptopropylsilyl groups on the nanopore surface. It should be noted here that the possible oxidation of thiol to disulfide has been suggested for mercaptosilylated mesoporous silicas.[57,58] In the present materials, signals which suggest possible disulfide group formation were not clearly distinguished, while the ^{13}C signals were broad possibly suggesting the presence of disulfide. The surface functional groups may play an important role in the dispersion and aggregation of the particles, which will be described below. In addition, the loading amount of the mercaptopropylsilyl group may also affect the surface properties. Further study on the variation of the surface modification and the quantitative characterization of the surface functional groups is worth conducting.

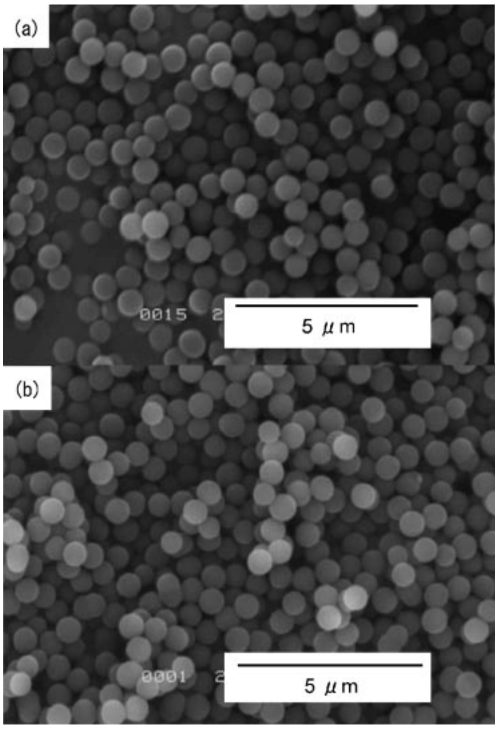

Figure 1. The SEM image of the particles (a) before and (b) after the silylation.

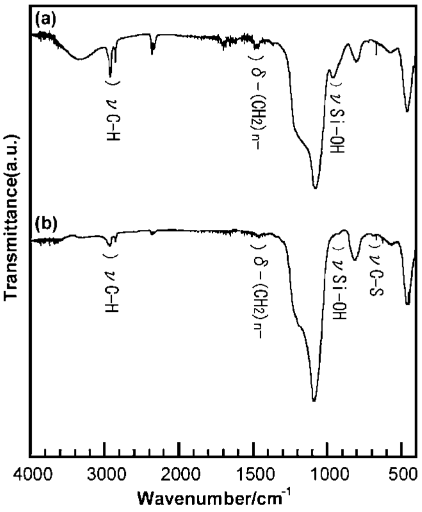

Figure 2. FT-IR spectra of the particles (a) before and (b) after the silylation.

The TG-DTA curves of the product are shown in Figure 4a. As a reference, TG-DTA curves of nanoporous silica spherical particles are shown in Figure 4b. The weight loss starting from room temperature was due to the dehydration. The weight loss at this temperature range was very small for the

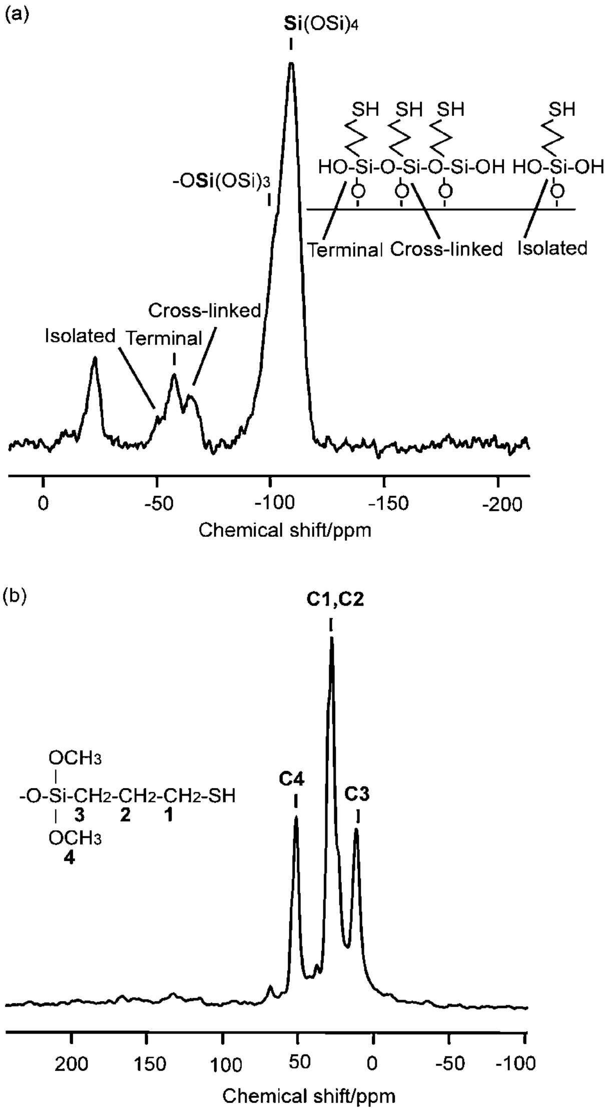

Figure 3. (a) ^{29}Si MAS NMR spectrum and (b) ^{13}C CP MAS NMR spectrum of the silylated product.

silylated product compared to that observed for nanoporous silica (Figure 4b) without organic modification, indicating the occupation of the organosilyl group on the nanopore surface made the nanopore hydrophobic. The weight loss observed in the 150–300 °C region was ascribed to the oxidative decomposition of the organothiol group, since exothermic reaction was observed in the corresponding DTA curve. The chemical composition of the product was determined by CHN analysis (C, 14.0; N, 0.2 mass %). The absence of nitrogen indicates that the hexadecyltrimethylammonium cation was completely leached out during the silylation procedure and the detected C was due to the immobilized mercaptopropylsilyl groups.

The nitrogen adsorption/desorption isotherms of the product are shown in Figure 5a. The nitrogen adsorption isotherm of the calcined particle showed BET surface area of 530 $m^2 g^{-1}$. Taking the composition determined from the CHN analysis into account, the density of organic groups on the surface was calculated to be 2.6 groups nm^{-2}. The BJH pore size of the modified nanoporous silica (Figure 5b) was determined to be 1.5 nm, while the BJH pore size of the nanoporous silica prepared in the same procedure without organic modification was 2 nm. The smaller pore size of the thiol-modified product reflects the immobilization of mercaptopropylsilyl groups on the nanopore surface.

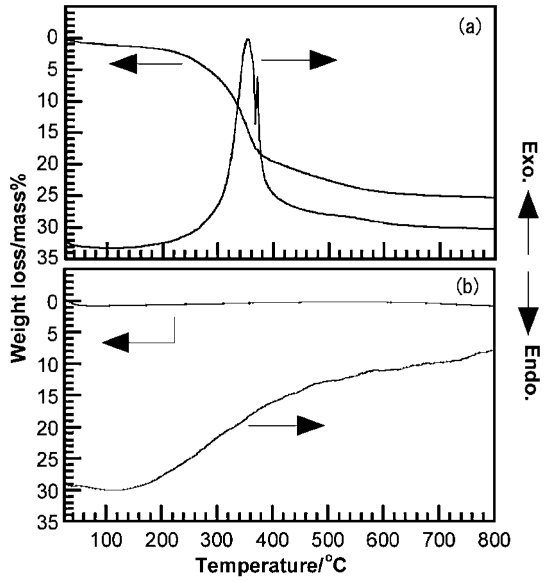

Figure 4. TG-DTA curves of (a) the silylated and (b) calcined particles.

The sample was dispersed in DMF/water mixture to give a suspension, which is stable without precipitation for several hours. The unmodified nanoporous silica spherical particles tend to precipitate easily. An aliquot of the suspension was dropped onto a Si wafer modified with MPTS and dried in air to make a film. A photograph and the SEM image of the film are shown in Figures 6a and 6b, respectively.

The structural color was developed for the film as shown in Figure 6a. For nanoporous silica spherical particles without organic modification, it is not easy to fabricate such an artificial opal structure. In very recent reports on the artificial opal structure of nanoporous silica spherical particles, a special technique was utilized to fabricate the nanostructures.[25,26] Simple sedimentation was reported to be effective, while the sample shape and regularity of the particle arrangement were not well defined.[24] Thus, it is worth noting as a merit of the present method to prepare an artificial opal structure by simple casting. It was shown that the mercaptopropylsilyl group on the particle surface played an important role for the dispersion in the water/DMF mixture and the periodic packing on Si wafer.

Conclusion

Spherical particles of nanoporous silica organically modified with mercaptopropylsilyl groups were synthesized by precipitation of silica–surfactant spherical particles and post-synthetic silylation using (3-mercaptopropyl)trimethoxysilane. By simply casting the suspension of the present particle on a thiol-modified Si wafer, homogeneous film composed of closely packed and regularly arranged nanoporous silica spherical particles formed.

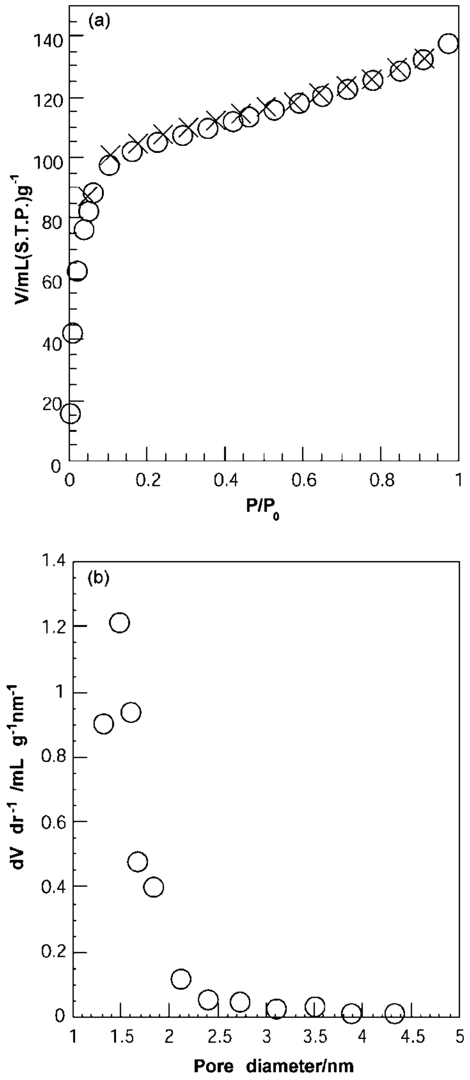

Figure 5. (a) Nitrogen adsorption (○)/desorption (×) isotherms and (b) BJH pore size distribution of the silylated product.

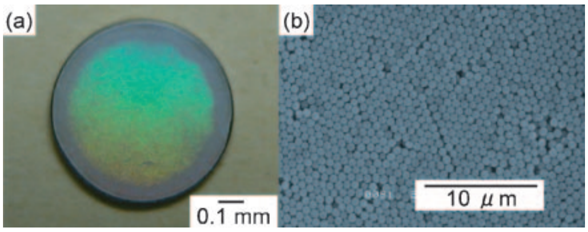

Figure 6. (a) Photograph and (b) SEM image of the thin film of the silylated product on organically modified Si wafer.

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