

Synthesis of spherical mesoporous silica nanoparticles with nanometer-size controllable pores and outer diameters

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ABSTRACT

Spherical mesoporous silica particles with tunable pore size and tunable outer particle diameter in the nanometer range were successfully prepared in a water/oil phase using organic templates method. This method involves the simultaneous hydrolytic condensation of tetraorthosilicate to form silica and polymerization of styrene into polystyrene. An amino acid catalyst, octane hydrophobic-supporting reaction component, and cetyltrimethylammonium bromide surfactant were used in the preparation process. The final step in the method involved removal of the organic components by calcinations, yielding the mesoporous silica particles. Interestingly, unlike common mesoporous materials, the particle with controllable pore size (4–15 nm) and particle diameter (20–80 nm) were produced using the method described herein. The ability to control pore size was drastically altered by the styrene concentration. The outer diameter was mostly controlled by varying the concentration of the hydrophobic molecules. Relatively large organic molecules (i.e. Rhodamine B) were well-absorbed in the prepared sample. Furthermore, the prepared mesoporous silica particles may be used efficiently in various applications, including electronic devices, sensors, pharmaceuticals, and environmentally sensitive pursuits, due to its excellent adsorption properties.

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1. Introduction

The synthesis of mesoporous materials has been of great interest due to an ever-expanding list of uses, ranging from chemical sensors to drug delivery [1]. In the past decade, many mesoporous have been developed. One of the well-developed mesoporous materials is silica. Silica is attractive because it is chemically inert, thermally stable, harmless, and inexpensive [2].

Many preparation methods of mesoporous silica materials with various morphologies from thin film, sphere, fiber, as well as bulk-form, such as the MCM series [3] and the SBA series [4], have been reported. In these synthetic reactions, the organic template-driven synthesis process is commonly used [5]. Although the previously reported methods are feasible for industry, they have several disadvantages: (i) use of harmful chemicals (e.g. ammonia [6,7] or N_2H_4 [8] as a catalyst) that can be a problem for bio-applications; and (ii) the difficult preparation of spherical particles with controllable size less than 100 nm in diameter.

Methods for circumventing the above problems have been suggested by several research groups [9], such as utilizing functional amines as “bio”-catalysts, which reduce the diameter to approximately 50 nm. However, even with the current method, synthesis

of spherical particles smaller than 50 nm remains difficult. Furthermore, the pore size of the prepared particle has been limited to less than 5 nm. In this range of pore size, difficulties associated with mass transfer, diffusivity, and penetration of molecules into or out of the pore system are well-known, limiting several applications [10]. In addition, while current methods have been used to create porous particles, to the best of our knowledge, reports of materials comprised of spherical particles with controllable particle size in the nanometer range and controllable pore size greater than 5 nm are virtually non-existent. Meanwhile, with a pore size of the greater than 5 nm, many applications (such as adsorbing large molecules) could be possible. Given a size in the nanometer range, a higher surface area could be gained. Further, we also can control the pore size with the prospect of controlling the optical properties, such as the refractive index.

In our previous studies, we prepared several meso- and macro-porous inorganic particles with diameters in the submicron range using a spray method and polymer particles as the template. The morphology of the resulting prepared particles is controllable and the pore size is greater than 30 nm [11–14]. The purpose of the present study was to develop a method for the preparation of spherical nano-sized silica particles (Hiroshima Mesoporous Material, HMM) with a tunable pore size ranging from 4 to 15 nm and a tunable particle size in nanometer range (20–80 nm) using an organic template method in a water/oil phase. Nano-sized particles

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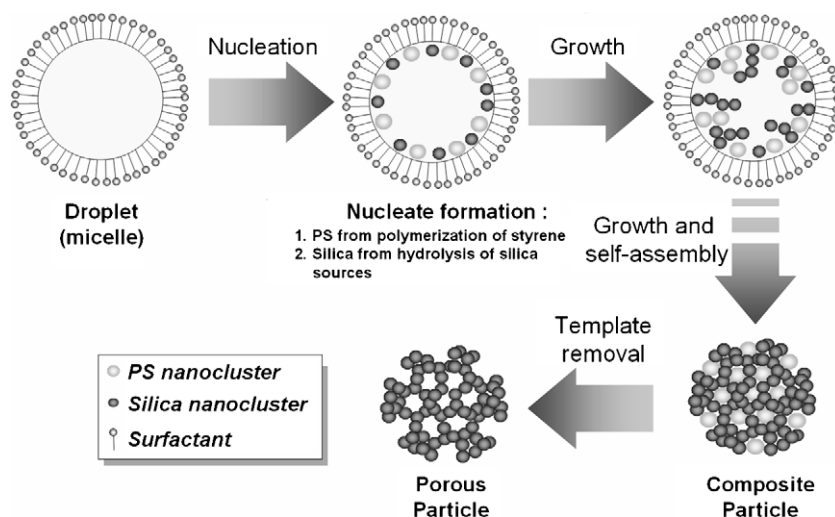


Fig. 1. Preparation of mesoporous silica nanoparticles.

are desirable because they exhibit new and unique properties such as a high-surface area. The unique properties, such optical transparency, could also be obtained if nano-size particles are homogeneously dispersed into the solution [9]. Moreover, tunable pore size is important because it extends the range of possible applications, such as selective adsorption or catalytic activity [15]. Further, when the particle pore size and outer diameter can be controlled, the refractive index can also be controlled. Then, when the particle is composed of polymer material, the new optical properties (with controllable refractive index) are possible, such as a plastic lens.

The preparation method described in this paper involves the hydrolytic condensation of tetraorthosilicate (TEOS) to form silica and the polymerization of styrene into polystyrene (PS). The process uses an amino acid as the catalyst, octane as the hydrophobic-supporting reaction component, and cetyltrimethylammonium bromide (CTAB) as the surfactant. The reactions took place simultaneously in the micelle, resulting in a composite silica/PS particle with CTAB as the as-prepared product. In the final step, the organic components (CTAB and PS) were removed by calcination to yield the mesoporous silica particles (Fig. 1). An amino acid was utilized to control silica formation due to its ability to cover the prepared silica after the reaction [16]. With the amino acid covering, silica growth could be controlled, the silica nanocluster could be obtained, and agglomeration was inhibited. These advantages were different with another catalyst (e.g. ammonia or N_2H_4), which only catalyzed the silica sources so that smaller particles are difficult to produce. Furthermore, the use of the amino acid compound minimized the disadvantages associated with the use of harmful catalysts required by the current Stober method. The ability to control both the pore size and outer diameter was drastically altered by the styrene concentration and by varying the hydrophobic molecule concentration, respectively. In addition, the adsorption of large organic molecule (i.e. Rhodamine B) by the prepared mesoporous particles was also investigated.

2. Experimental

The mesoporous particles were synthesized from the following raw materials: TEOS (98%, Aldrich, USA) as the silica source; L-lysine (lysine, Aldrich, USA) as the catalyst; styrene monomer (Kanto Chemical Co., Inc., Japan) as the template; CTAB (Merck, Germany) as both a template and surfactant; and, 2,2'-Azobis (2-methylpropanamide) dihydrochloride (AIBA, Aldrich, USA) as the initiator of

styrene polymerization. Lysine was used as a catalyst because it can control silica in the nanometer range [16]. We also tried other catalysts such as Ammonia and N_2H_4 . However, bigger silica particles were produced, with an outer size larger than 100 nm.

In the experimental procedure, first, a mixed solution was prepared by dissolving and heating 0.1 g CTAB in 30 ml of aqueous solution at 60 °C in three-necked flask reactor. After a clear solution was obtained (about 30 min of mixing), octane (Aldrich, 98%, USA), styrene monomer, lysine, TEOS, and AIBA were subsequently added to the system. The styrene monomer was pre-washed with 2.5 M NaOH to remove the stabilizer prior to use. Octane was added and varied to the mixed solution with the initial octane/water mass ratios ranging from 0.04 to 0.84. For example, 14.4 ml of octane was added to 30 ml of aqueous solution to obtain a mesoporous silica particle with an outer diameter of 44 nm. The reaction was allowed to proceed for 3 h under an N_2 atmosphere at 60 °C. Then, the heating was stopped and the suspension was cooled naturally to room temperature. The cooled suspension was decanted for one night (about 12 h) and purified by centrifugation (at a rate of 15,000 rpm). The suspension was centrifuged twice to insure that the particle was well purified. Ethanol was used to wash the centrifuged particle. Finally, the template was completely removed by heat treatment at 500 °C under atmospheric conditions. The mass ratio of $H_2O/TEOS/L$ -lysine/CTAB was maintained at 310:10:0.22:1. 0.39–55 mg/ml of styrene monomer and 0.84 mg/ml of AIBA were added to the solution to control the pore size at 5–15 nm.

The morphology and particle size of the prepared mesoporous silica nanoparticles were characterized using a scanning electron microscope (SEM, S-5000 and S-5200, Hitachi, Tokyo, Japan, operated at 20 kV) and a transmission electron microscope (TEM, JEM-3000 F, JEOL, Tokyo, Japan, operated at 300 kV). From SEM and TEM photographs, the pore sizes and outer diameters were measured using the Feret measurement, and detailed definitions are represented in Fig. 2. The chemical composition of the prepared particles was investigated using Fourier transform infra red (FTIR, Shimadzu FTIR 8700). In addition, nitrogen adsorption isotherms at 77 K were measured using a conventional volumetric apparatus (Bel Japan, BELSORP 28SA).

To determine the large-molecule-adsorption performance of the prepared porous particles, the following experimental procedure was conducted. First, the calcined particle was grinded softly to break the soft agglomeration after calcination. Then, the particle was re-dispersed into the water with concentration of 600 ppm.

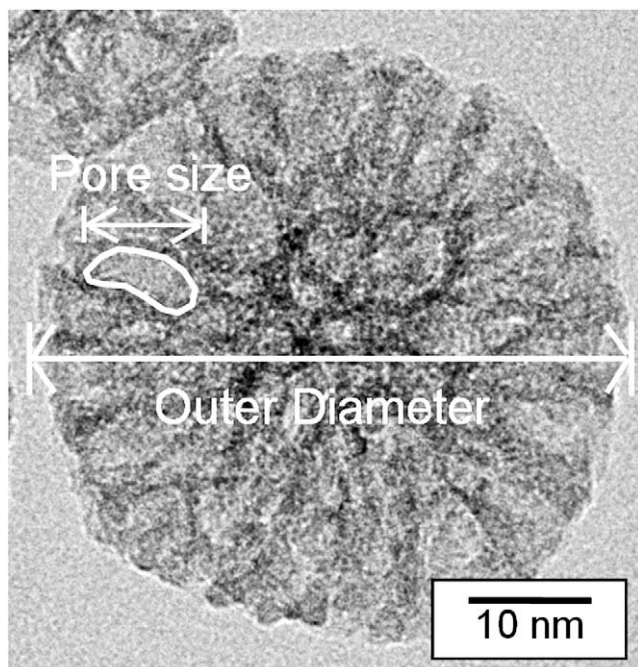


Fig. 2. Definition of pore size and outer diameter using Feret diameter.

On the other hand, RhB (Wako Pure Chemicals Industries Ltd., Osaka, Japan) was dissolved in water with a concentration of 1200 ppm, separately. After both suspensions were dispersed well, they were mixed with a volume ratio of 1:1 using a vigorous stirrer for 1 min. Then, the sample was immediately measured using spectroscopy (Shimadzu UV-Vis Spectrophotometer, UV-3150). In addition, for the standard comparison, the RhB sample was also dissolved in water with a concentration of 600 ppm. In addition, the duration time for the measurement was no more than 3 min. The measurements were repeated continuously until 100 min and then several hours and days. Thus, the results could be analyzed as function of time. To corroborate the first time adsorption, we also checked the mixture of the initial concentration for several samples, which compared with the RhB solution in the same calculated concentration. To investigate the effect of pores and morphology, different types of particles (different pore size) were used as an adsorbent.

3. Results and discussion

The morphology and particle size of the prepared particles were analyzed with scanning and transmission electron microscopy as shown in Fig. 3. Nearly monodispersed spherical particles with a mean diameter of 41 nm and a standard deviation of 6.72 nm were obtained (Fig. 3a). From the results shown in this figure, it also confirm that present method can be used to prepare particles with porous surface structures.

To verify the porous structure of the particle, the prepared particles were also characterized using TEM. As shown in Fig. 3b, the TEM images indicate that the prepared particles contained pores that were approximately 5 nm in size, which were larger than that the pores observed in previously reported results [17]. The porous morphology of particles (as assessed by SEM) was similar to the TEM results. The high-resolution TEM confirmed the existence of pores both on the particle surface and inside the particle. Self-assembly structures were obtained in all prepared particles. In addition, after thermally removal of the organic templates, no particle swelling or shrinking was observed. This result confirmed that heat treatment is a reasonable method for removal of the organic templates, as it had no effect on particle morphology and size.

Fig. 4 shows the sorption properties of the prepared particles. The calcined particle exhibited a characteristic type-IV curve,

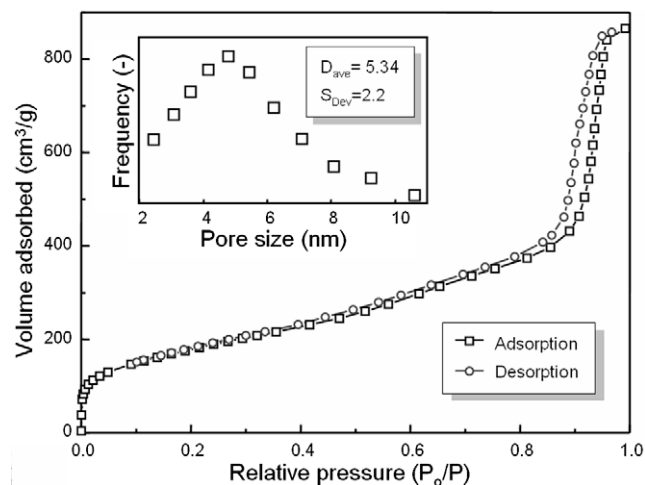


Fig. 4. Nitrogen adsorption of mesoporous silica particles.

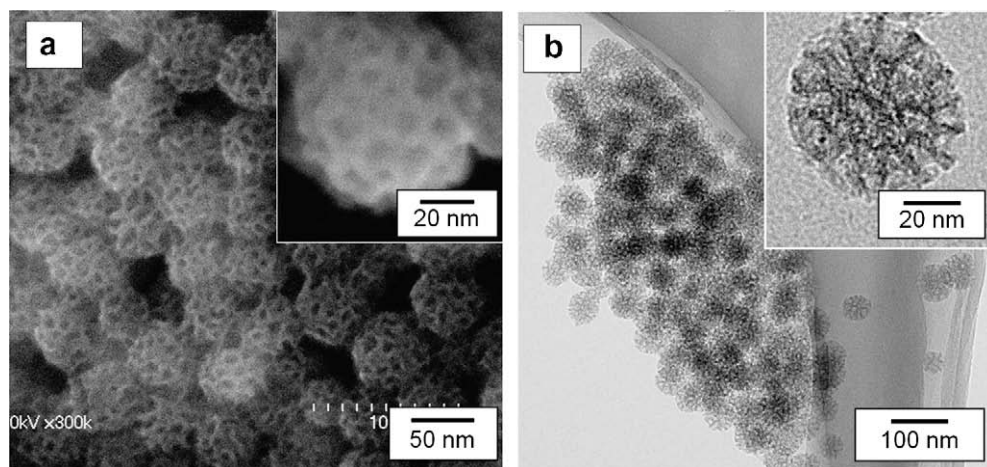


Fig. 3. SEM (a) and TEM (b) images of prepared mesoporous silica nanoparticles. The insert image is a high-resolution electron microscope image of a single silica particle.

which was indicative of the mesoporous material. The specific surface area (BET) was about $600 \text{ m}^2 \text{ g}^{-1}$ and the average pore size was 5 nm. After measuring the pore size distribution using BET, it was concluded that the measured average pore size from BET analysis was consistent with the Ferret diameter measured in the TEM photographs (Fig. 3b). The BET result also revealed that the prepared particles had a greater specific surface area and larger pore size than previously reported [16]. In addition, comparison of the specific surface area and mesopore size with MCM-41 [18], implies that the particle has a closed mesopore channel.

Because the reaction was occurred in an oil/water phase in the presence of surfactant, micelle formation occurred during the process. The micelle morphology (i.e. size and shape) could be easily controlled by changing the chemical structure of the surfactant molecules, and by varying the conditions of the dispersed phase, e.g., pH, ionic strength, and temperature [19–21]. We expected the prepared particles to be easily controlled by changing the ratio of octane/water during preparation. Thus, the effect of mass ratio of octane/water on the outer particle diameter was investigated (Fig. 5). Based on the TEM images in Fig. 5a and b, relatively monodispersed spherical mesoporous silica nanoparticles were successfully prepared using different octane ratios. As expected, the desired result was obtained, revealing a strong relationship between the mass ratio of octane/water and the porous particle diameter (Fig. 5c). Moreover, the presence of octane molecules might be responsible for the increase in particle size by controlling sphere growth as follows: (i) homogenization of the hydrophobic

molecules (styrene and TEOS); (ii) slight retardation of the electrostatic interaction between silicate species; and, (iii) protonation of the amino groups [16]. The measured particle sizes were 20, 28, 45, and 75 nm for the initial octane/water mass ratios of 0.05, 0.17, 0.32, and 0.84, respectively. These results demonstrate that a significant advantage of this method is that particles of any size can be readily obtained.

Fig. 6 shows the effect of styrene concentration on both the pore size and outer diameter of the prepared particles. Fig. 6a–c correspond to the TEM micrographs of silica porous particles that were prepared using different styrene concentrations; while Fig. 6d shows the relationship between styrene concentration, pore size and diameter. The TEM analysis shows that spherical particles with nearly monodispersed (outer diameter/standard deviation were 43 nm/6.43 nm; 43 nm/4.98 nm; 58 nm/9.53 nm; and, 63 nm/9.60 nm using styrene concentration of 3.88; 9.64; 22.80; and, 54.93 mg/ml, respectively) were obtained. From the result, it also obtained that the size of the pores of the particles prepared using the present method could be controlled with relatively larger than the pore sizes commonly reported in the literature [22].

The Ferret diameter measured in the TEM images revealed that the mean pore sizes were 5.6, 9.4, and 14.6 nm for initial styrene concentrations of 0.39, 9.64, and 55 mg/ml, respectively. Although the experiments were performed under the same conditions, the resulting pore size of the particles was markedly influenced by variation in styrene concentration. Thus, it was confirmed that pore size increases when additional styrene template is provided.

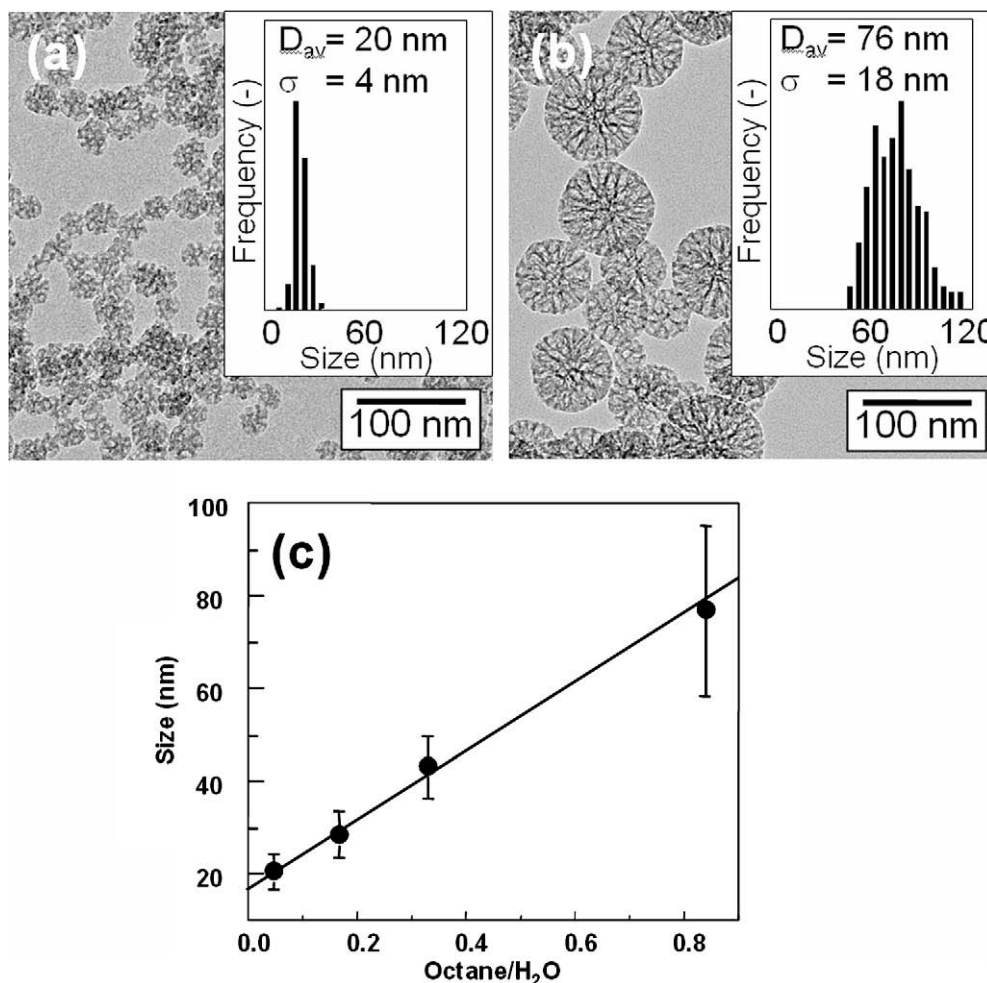


Fig. 5. TEM images of porous silica nanoparticles as function of the mass ratio of octane/water: (a) 0.04; and (b) 0.84. (c) Average particle and pore size as a function of the octane/water ratio. All samples were using the mass ratio of H₂O/TEOS/l-lysine/CTAB of 310:10:0.22:1; 0.39 mg/ml of styrene monomer; and 0.84 mg/ml of AIBA.

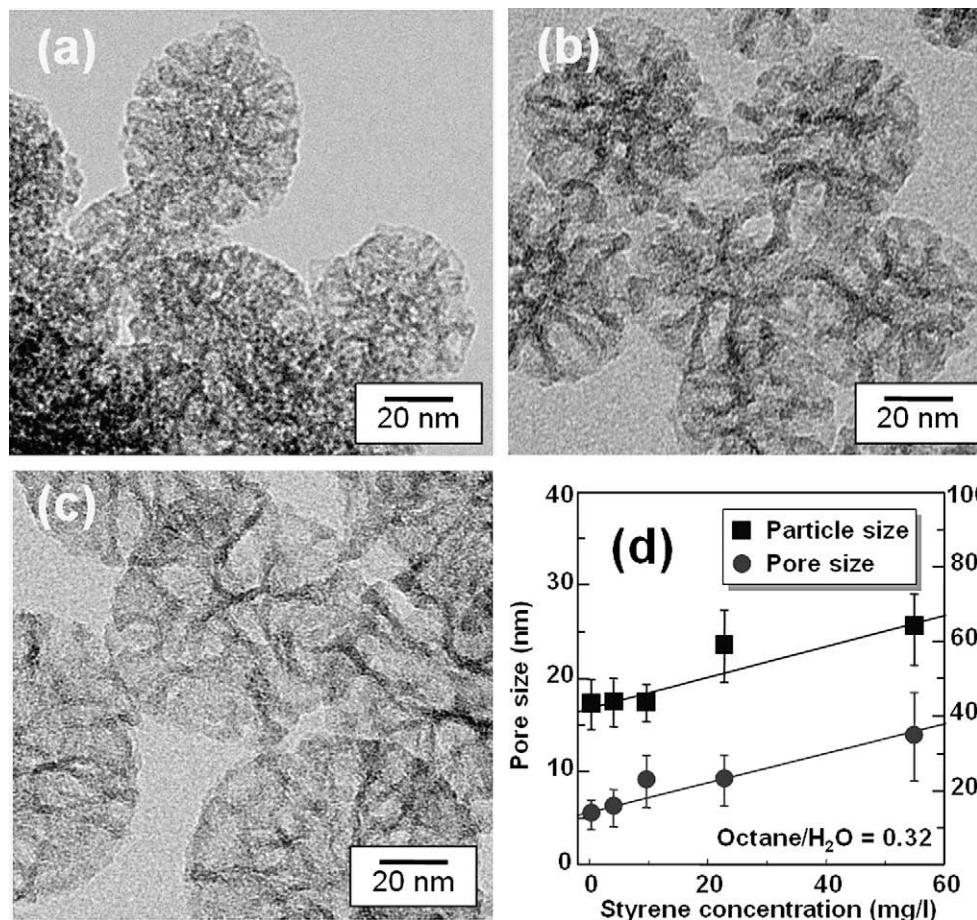


Fig. 6. TEM images of various mesoporous silica particles using (a) 0.39, (b) 9.64, and (c) 55 mg/ml of styrene. (d) Average particle and pore size as a function of styrene concentration. All samples were using the mass ratio of H₂O/TEOS/L-lysine/CTAB of 310:10:0.22:1; 0.84 mg/ml of AIBA; and the ratio of octane/water of 0.46.

According to our hypothesis, during the formation of monomeric silica nucleate, the styrene monomer is also polymerized into PS. These reactions are thought to occur inside the micelles. The silica nucleate enrichment grows, coalesces with the PS, and forms the silica/PS composite particle. Besides, several factors, such as electrical charging on the nanocluster surface and the existence of amino acids, were also considered to be self-assembly triggering factors inside the micelle. Then, after removal of the organic compounds by calcination, the mesoporous structure was produced. Based on this scenario, it is feasible that increasing the styrene concentration would result in an increase in the size of the polymer that formed within the composite silica/PS particles, due to greater polymerization of the styrene monomer [23], which led to larger pores after removal of the PS.

To confirm the chemical structure in the particle as the effect of styrene concentration, FTIR spectroscopy analysis of particles prepared using different styrene concentrations was conducted. As shown in Fig. 7, different peaks were observed by changing the styrene concentration. The intensities of alkyl ($-C_nH_{2n+1}$) groups (in the range of 2800–2900 and 2900–3000 cm) peaked and the Si-NH₂ bond (about 1540 cm) increased as the styrene concentration increased. Those peaks completely disappeared following the thermal removal process. Besides, there are also another peaks (e.g. Si-O-Si (in the range of 1200–1400 cm), Si-OH (in the range of 3200–3400 cm)) were also observed and maintained after additional heat treatment. This FTIR result also indicates that PS (confirmed by alkyl molecules peak) was controlled during assembly, occupied the particle, and was removed after heat treatment.

The excellent adsorption properties of porous silica materials have been ascribed to their high-surface area [24]. However, the appropriate pore size is also important because it is critical to cap-

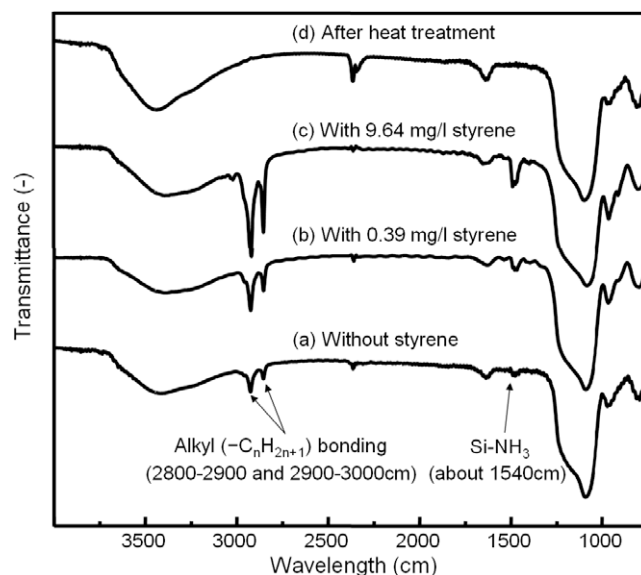


Fig. 7. IR spectra of as-prepared particles [with styrene of 0 mg/l (a); 0.39 mg/l (b); and 9.64 mg/l] and (b) heat-treated particles.

Table 1
Analyzed concentrations of RhB in the aqueous solution before and after adsorption treatment.

Sample	Pore size (nm)	Ratio of C/C _{initial} (%)				
		Before additional adsorbent	As-additional adsorbent*	After treatment		
				1 h	15 h	100 h
No adsorbent	–	100	100	100	100	100
XL**	–	100	100	100	100	100
HMM-4	4	100	78	59	29	22
HMM-5	5	100	83	58	31	20
HMM-10	10	100	89	54	30	27
HMM-15	15	100	94	65	51	51

* The sample which analyzed at the first time ($t < 1$ min) after the silica porous particle as adsorbent was added.

** Commercial silica nanoparticle (XL, $D_{\text{average}} = 50$ nm, Nissan Chemical Industry Co. Ltd.).

illary and chemical diffusivity effects. Hence, the adsorption ability of the prepared mesoporous silica particle was also investigated. RhB was selected as a sample dye because it has a molecular weight that is intermediate to that of simple molecules (i.e. N_2 , H_2O , etc.) and usual polymers. The absorption spectra of the RhB solution during its adsorption by prepared silica particles were observed using a UV–Vis spectrometer. To determine the concentration of RhB in the solution, Beer's law was used and the data were normalized to the absorbance at 555 nm, which implies a red color [13]. Table 1 shows the RhB concentration during adsorption (with elapsed time) using different pore size of prepared particle as the adsorbent. For comparison, RhB adsorption using a commercial non-porous silica nanoparticle (50 nm in diameter) was also investigated. As shown in the table, RhB was well-adsorbed by the prepared porous particles, but not by the commercial particles. When prepared porous particles were used as the adsorbent, the RhB concentration decreased gradually with the adsorption time.

The adsorption performance of the prepared particles with different pore sizes was compared (i.e. about 4 nm, 5 nm, 10 nm pore size). Silica with 10-nm pores exhibited the fastest RhB adsorption. However, after several hours, the amount of RhB remaining in the suspension was almost similar among the porous material samples. The differences in the rate of organic loading on the inside surface is caused by differences in the diffusivity rates of molecules reaching the inside of the pores. In the case of prepared particles with 15-nm pores, the expected result was obtained, mostly due to the low surface area of the adsorbent. The adsorption rate using this porous particle was lower than the 10-nm pore size. In another case, when we used commercial particle, almost no decreasing of RhB concentration from the suspension was observed. From these results, it is obvious that when the pore size is too large, then "RhB-loading" can more easily result in desorption. Therefore, there are only a few regions of the surface that can load and hold RhB in the particle.

It was hypothesized that since no adsorption was measured for the non-porous commercial silica particles, it could be expected that the RhB was adsorbed due to the existence of a porous structure. In addition, the size of the RhB was $1.44 \text{ nm} \times 1.09 \text{ nm} \times 0.64 \text{ nm}$ [25]. This size actually can penetrate a pore size larger than 3 nm. However, the RhB needed more space in order to adsorb inside the pore without blockage. Thus, the appropriate pore size is required in order to adsorb to the inside pore and to hold against the desorption process. In general, when the pore size is too small for adsorption, the adsorption only occurred on the outer surface. By contrast, if the pore size is too large, desorption occurred and caused the release of RhB. This hypothesis is in good agreement with the results from when a particle with a 15 nm pore size was used. By contrast, when the prepared silica with a pore size of about 15 nm was used, lower adsorption properties resulted than with a pore size of less than 10 nm. Further, when commercial silica particles were used, almost no adsorption was observed, which was caused by the easy desorption of RhB.

The spectra for all samples were decreased gradually by the adsorption time (Table 1). It concluded that an increase in adsorption time would allow for enhanced loading of organic contaminants onto the inside surface of the particles. The RhB reaches the deepest pores of the adsorbent after several times. Therefore, with commercial non-porous particles, there is no decreasing RhB concentration because RhB adsorbs only on the particle surface and is easily released as there is no holding place for RhB. Then, further additional adsorption time (15 h) proved that the prepared porous particle could adsorb up to 70% of the RhB.

A previously described adsorption process that uses mesoporous silica [26], showed a lower adsorption capacity (approximately 3.5 mg/g). This result was observed because no surface treatment was used to ensure that only physical adsorption occurred. Thus, it is reasonable to conclude that the adsorption capacity should be increased with additional surface modification.

Although the effect of the pore size can be confirmed by the adsorption of RhB, the mixed sample/RhB was directly characterized using spectrophotometry. Therefore, there was a concern that an error may have been created by the measurement of unprecipitated silica (dispersed silica). The additional purification can produce misleading results because separation takes longer than adsorption. Besides, it is possible that another error was created by the coagulated or agglomerated porous particles as adsorbent. For this reason, additional studies are required to verify the adsorption/desorption rates, its ability in re-dispersing chemical ability after adsorption process, and the solubility of particles after calcination (e.g. using bead mill process [27] to re-disperse porous particle for adsorbing RhB). In addition, although the diameter and pore size of the mesoporous particles can be controlled, additional investigations aimed at controlling size in a monodispersed range, porous structure performance (e.g. effect of porous structure and sizes on adsorption ability, refractive index, etc.), and other properties (i.e. solubility, mechanical strength, additional functional chemical for increasing the adsorption ability, etc.) also are important and will be investigated in our future work.

4. Conclusion

In summary, mesoporous particles (Hiroshima Mesoporous Material (HMM)) with controllable pore size (4–15 nm) and outer diameter (20–80 nm) were successfully prepared in a water/oil phase using an organic template method. The spherical, nearly monodisperse and agglomeration-free particles were obtained from the simultaneous hydrolytic condensation of TEOS to form silica and polymerization of styrene into PS, using an amino acid catalyst, octane as the hydrophobic-supporting reaction component and CTAB as the surfactant. The adsorption properties of the prepared porous silica particle were excellent compared with those of non-porous silica particles. The mesoporous particles prepared

in this study are expected to be useful in many industrial applications, especially those related to bio-applications, due to their adsorptive activity.

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