

Super-insulating properties of porous ceramic particles fabricated by a self-assembly process using complex fluids

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Porous silica particles were synthesized by an emulsion-assisted self-assembly process. The templating materials, polymeric nanospheres or block copolymers, were self-organized with the precursor inside emulsions to prepare porous ceramic particles after calcination. The thermal insulating properties of mesoporous, macroporous, and meso-macroporous particles were compared by measuring their thermal diffusivity using a laser flash apparatus. The insulating properties of the porous particles could be controlled by changing the emulsification conditions using a rotating cylinder instead of a conventional homogenizer to induce a hollow interior structure of the porous particles. The lowest value of the thermal conductivity was recorded as roughly 10 mW/mK for the meso-macroporous particles, which is comparable to previous materials including aerogels. The porous ceramic particles additionally can be applied as coating materials for superhydrophobic surfaces via a lotus effect.

Key words: Self-assembly, Porous silica particles, Thermal insulators, Superhydrophobic surfaces.

Introduction

Porous materials have been extensively studied for various applications including separation media, catalytic supports, adsorbents, reflective pigments, and food industries [1-4]. In recent decades, various materials have been prepared in the form of porous structures, including polymers, ceramics, metals, and composites [5-7]. Recently, growing attention has been paid to porous structures, which are advantageous for applications such as thermal insulators, with the rise of energy costs and increasing concerns over greenhouse gases in relation to global warming.

In addition to use as construction materials, thermal insulators also can be applied as protective layers of spacecraft to maintain the temperature of the inner regions [8, 9]. Further research on thermal insulators is still imperative in that the effectiveness of the insulating properties should be improved, including at extremely high or low temperatures. Facile and economic fabrication of porous materials having a number of voids is thus a crucial task to produce effective thermal insulators with extremely low thermal conductivity.

The principle of thermal insulation is based on the low thermal conductivity of air voids or vacuum parts in the porous material, and has been applied to prepare thermal insulators such as polystyrene foams that can be used as low-cost insulators for versatile purposes.

However, these materials have a critical drawback that toxic gas can be emitted due to thermal decomposition of the organic material at high temperature, and low thermal stability is consequently inevitable due to the organic components. It is accordingly important to develop novel thermal insulators with excellent thermal resistance that can be used at high temperature.

For the realization of super-insulators, inorganic ceramic materials such as aerogels have been synthesized. However, harsh fabrication conditions are employed during the synthesis of aerogels including a supercritical drying step at high temperature and pressure [10]. It is thus necessary to develop new thermal insulators with sufficient resistance, including at high temperature that can be prepared under mild synthesis conditions.

In addition to aerogels and analogous materials such as xerogels, previous studies have been focused on fabricating mesoporous or hollow particles with high air content to prepare thermal insulators and limited to simple particle morphologies, thus making it difficult to optimize the thermal conductivities by controlling the porous shapes [11]. It is therefore essential to develop new nano-architecturing approaches based on the fabrication of macroporous or hierarchically porous particles to control the thermal conductivity.

In the present study, porous silica particles were synthesized using templating materials by evaporation-driven self-assembly from emulsion droplets for application to super-insulators. To generate emulsion droplets, a simple homogenizer as well as a rotating cylinder was adopted with batch-type or continuous operation mode. For macroporous particles, the polystyrene nanospheres having

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a narrow size distribution were synthesized by dispersion polymerization to be used as templates. A similar strategy was chosen to mesoporous or meso-macroporous particles using a triblock copolymer as a structure directing agent. The resultant porous particles fabricated using different templating materials were characterized by electron microscopy, and their thermal insulating properties were compared by laser flash analysis method. To avoid deterioration of the insulating properties due to humidity, fluorine treatment was performed to endow the porous particle films with superhydrophobicity.

Experimental Procedure

Sample preparation

Polystyrene particles were prepared by dispersion polymerization using the detailed synthesis conditions in Table 1. The temperature of the reactor was maintained at 70 °C and detailed methodologies can be found from elsewhere [12].

For the synthesis of porous particles, a continuous phase was prepared by dissolving 3 wt. % of emulsifier (Abil EM 90, Cosnet) in hexadecane. A suspension of PS beads was centrifuged and re-dispersed in ethanol by sonication. A precursor solution containing TEOS (tetraethylorthosilicate, Aldrich, 3.25 g) was prepared by adding an aqueous solution of hydrochloric acid (0.01 N, 1.687 g) with the PS suspension (7.5 g, 30 wt. %), followed by the addition of TEOS under stirring for 1 hour. Water (4.2688 g) was then mixed with this solution for another 30 minutes to prepare the dispersed phase, which was poured into the continuous phase with a volume ratio of 1 : 3 followed by homogenization for 60 seconds using a homogenizer (HG-15A-SET-A, Daihan Scientific, Korea). The dispersed phase was then evaporated by heating at 90 °C for 1 hour under mild stirring. The resultant composite particles were washed with hexane after sedimentation under gravity. Calcination was performed at 500 °C for 5 hours using a box furnace (Labhouse) to produce porous ceramic particles.

For mesoporous or meso-macroporous particles, a triblock copolymer, a Pluronic surfactant, was used as another templating material for the formation of mesopores. The block copolymer was dissolved in distilled water and mixed with ethanol/TEOS to prepare the dispersed phase.

Alternatively, a continuous oil phase was placed between two cylinders for emulsification. The dispersed phase containing precursors was then added while the

inner cylinder was rotating at 1,750 rpm. For continuous operation of the rotating cylinder, a syringe pump was used to continuously feed the input streams, that is, the dispersed and continuous phases. While the input streams were fed to the reactor, the inner cylinder was rotated at 1,750 rpm, producing an output stream of the complex fluid.

For the fabrication of porous film, the composite micro-particles after self-assembly were dried at room temperature for one day. The aqueous solution of Pluronic F108 was then added to the composite powder, and successive gentle sonication was performed to prepare a dispersion of the composite particles. After the particle suspension was deposited onto a glass substrate, drying and successive calcination at 500 °C for 5 hours resulted in the macroporous film. The film was then immersed into a solution of methanol containing 2 vol. % of fluorine-containing silane coupling agent (HDFTHDTS, (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) triethoxysilane, 97%, Aldrich) to prepare superhydrophobic film.

Characterizations

The morphologies of the porous silica particles were observed using FE-SEM (Hitachi-S4700) or TEM (Tecnai G20, F20). The specific surface area of the porous powder was analyzed using a Tristar II 3020 (Micrometrics, USA). The thermal conductivity of porous particles was measured using a LFA 457 (NETZCH). The contact angle of the water droplets on the porous silica film was measured using a contact angle meter (DCA-WZ, Kyowa Kaimenkagaku).

Results and Discussion

In this study, an emulsion-assisted process was adopted to synthesize porous silica particles by evaporation-driven self-organization of precursor materials. The emulsion droplets containing the precursors can be evaporated by supplying heat at a fixed temperature. The vaporization of the volatile solvent from the droplets induces inward capillary pressure, resulting in shrinkage of the emulsion and self-assembly. A dried powder can then be collected for successive heat treatment such as calcination. Fig. 1(a) presents the formation mechanism of the porous ceramic particles by droplet-assisted self-organization using water-in-oil emulsions. The porous silica micro-particles with high porosity and specific surface area can be applied to valuable industrial products such as thermal insulators.

Among various applications of the porous silica particles, thermal insulators are the most practical candidates, since the inorganic porous materials are heat-resistant at high temperature, unlike polymeric insulators such as foamed polystyrenes. When the porous particles are stacked on a substrate, a significant portion of heat flow can be blocked by the porous layer, since the air cavities act as insulating layers. Thus, we sought to apply

Table 1. Detailed synthesis conditions of polymeric particles by dispersion polymerization.

Sample	Styrene	MTC	Ethanol	Water	PVP	AIBN
Dispersion #1	50.3 ml	4.2 g	245 ml	122.5 ml	2.188 g	0.525 g
Dispersion #2	160 ml	16.8 g	980 ml	490 ml	8.752 g	2.1 g

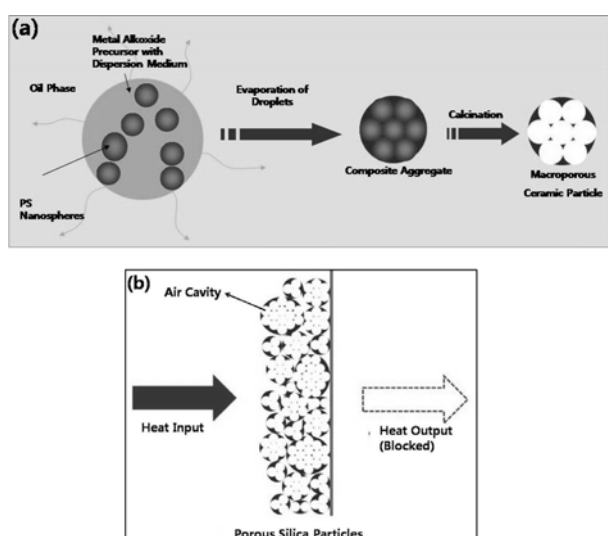


Fig. 1. Schematics of (a) the fabrication of macroporous ceramic particles by emulsion-assisted self-assembly. (b) the application of porous particles to thermal insulators.

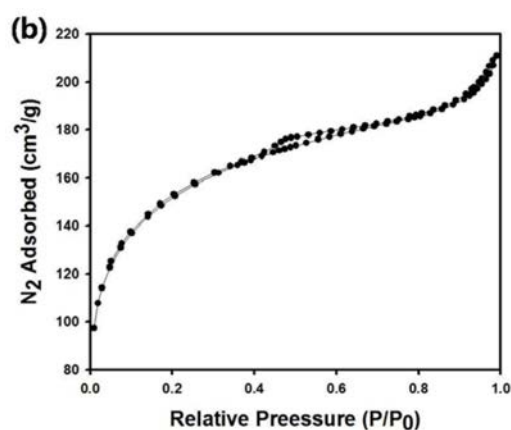
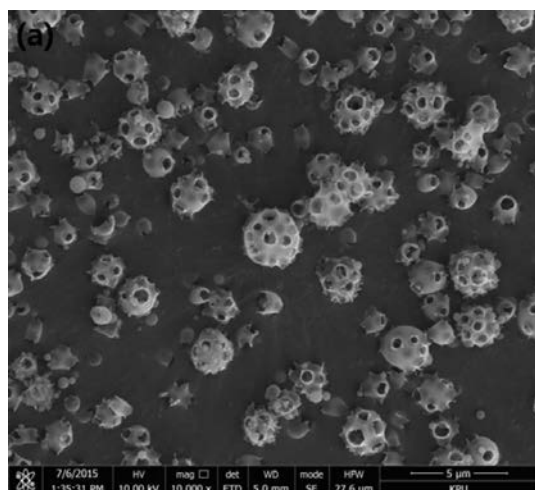


Fig. 2. (a) SEM image and (b) BET analysis result of macroporous silica particles. Scale bar indicates 5 μm. The porous particles were prepared by a mechanical homogenizer.

the porous particles as thermal insulators, as depicted schematically in Fig. 1(b).

In this study, polystyrene nanospheres were synthesized

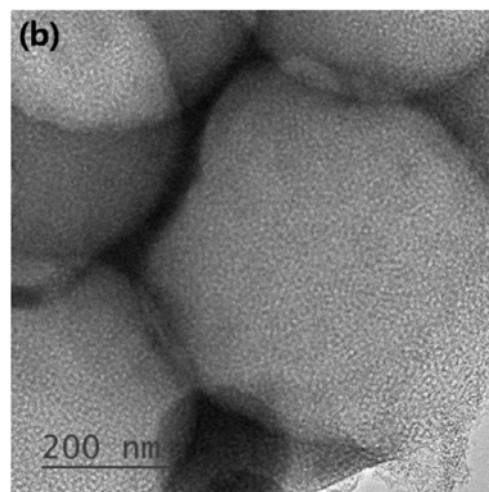
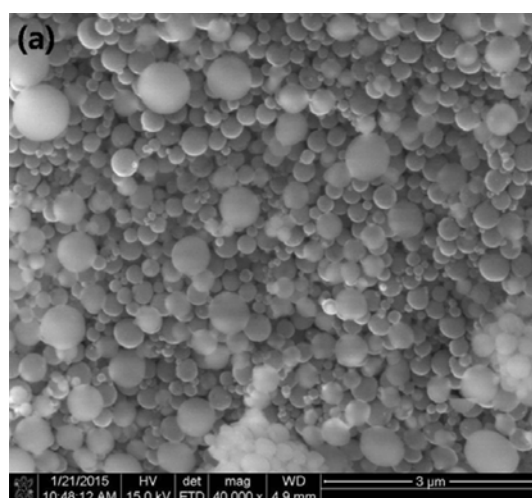


Fig. 3. (a) SEM and (b) TEM image of mesoporous and meso-macroporous silica particles, respectively. Scale bars indicate (a) 3 μm and (b) 200 nm, respectively.

by dispersion polymerization according to the conditions described in Table 1. By adjusting the reaction parameters, the particle size could be controlled as 640 and 800 nm. Latex particles with 800 nm diameter (dispersion #2) could be obtained by scale-up of the reactant compositions of the first sample (dispersion #1), indicating that the scale-up led to size enlargement of the polystyrene particles. These polymeric latex beads were adopted as templates for the formation of macropores of porous particles by producing emulsions using a conventional homogenizer for mechanical agitation. After the self-assembly process inside the droplets and the calcination step, macroporous silica particles could be obtained, as displayed in the SEM images of Fig. 2(a). In this study, the macropores could be formed using the polystyrene nanospheres of 800 nm diameter. The average size of the porous silica micro-particles was found to be polydisperse due to the non-uniformity of the original emulsions. The specific surface area of this sample was predicted by a BET analysis from the

adsorption and desorption of nitrogen, which is displayed in the graph of Fig. 2(b). Since the sample contained only macropores, the BET surface area was determined as $552.7 \text{ m}^2/\text{g}$.

Besides macroporous particles, mesoporous or meso-macroporous silica particles could be produced using a structure directing agent such as Pluronic P104 with or without the polystyrene nanospheres, respectively. Figs. 3(a) and 3(b) presents SEM and TEM images of the mesoporous and meso-macroporous silica particles, respectively, synthesized using a homogenizer for the formation of emulsions. For the case of mesoporous silica particles, a spherical powder material could be obtained, although meso-scale pores in the interior structure cannot be observed from the SEM image of Fig. 3(a). However, it is clear that the mesopores are successfully formed in the skeletal architectures of the meso-macroporous silica particles displayed in the TEM image of Fig. 3(b). These hierarchically porous particles were synthesized using the polystyrene nanospheres with 640 nm diameter.

In this study, the BET surface area of the meso-macroporous silica particles was also measured for the porous materials fabricated using Pluronic P104 and the polystyrene nanospheres with 800 nm diameter. Figs.

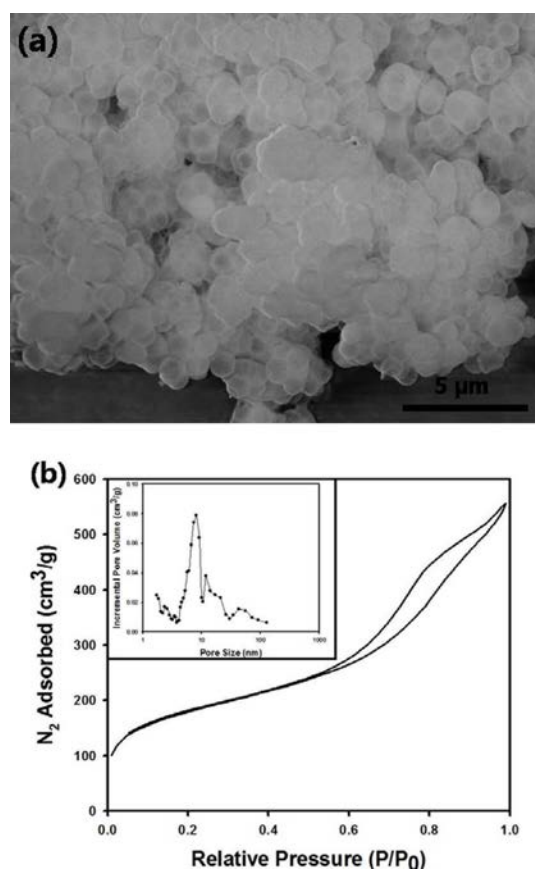


Fig. 4. (a) SEM image of meso-macroporous silica particles. Scale bar indicates 5 μm. (b) Nitrogen adsorption-desorption curve and pore size distribution of meso-macroporous silica particles.

4(a) and 4(b) present the morphology of the porous silica particles and nitrogen adsorption-desorption curve, respectively. The specific surface area was determined as $651.8 \text{ m}^2/\text{g}$ from the graph in Fig. 4(b), indicating that the surface area increased compared to simple macroporous particles after the formation of additional mesopores in the silica backbone. The inset graph of Fig. 4(b) presents the pore size distribution obtained by a BJH desorption analysis, showing that the mesopores could be detected with an average pore diameter of 5.57 nm.

Fig. 5(a) presents a SEM image of the macroporous silica micro-particles synthesized using rotating cylinder for the emulsification process. The dispersed phase contained the polystyrene nanospheres with 640 nm

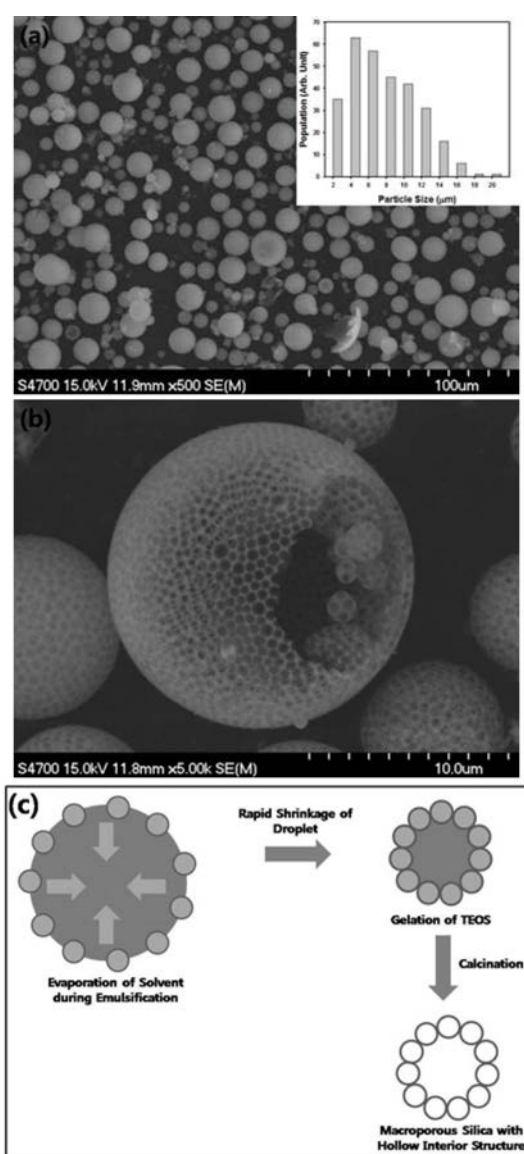


Fig. 5. (a) SEM images and size distribution of macroporous silica particles fabricated using a rotating cylinder system. Scale bar indicates 100 μm. (b) SEM image of the macroporous silica particles with a hollow interior structure. Scale bar is 10 μm. (c) Schematic figure of the formation of macroporous silica particles with a hollow inner structure.

diameter. This concentric cylinder system generated relatively crude emulsion droplets with large average diameter, resulting in the formation of the final macroporous particles with micron size. The size distribution of the porous particles is displayed in the inset graph of Fig. 5(a), showing that the average diameter was 7.3 μm .

It is also of note that the hollow inner structure could be observed from some porous particles with a fractured surface, as displayed in the SEM image of Fig. 5(b). During the rotation of the inner cylinder at 1,750 rpm, emulsification can be expected with mechanical agitation of the oil and dispersed phase. Simultaneously, the volatile solvent from the emulsions is evaporated between the concentric cylinders, causing insufficient migration time of the polystyrene beads into the central domain of the droplets, as shown schematically in Fig. 5(c). Thus, a hollow interior structure might be formed from the macroporous silica particles after calcination.

Mesoporous silica particles also can be synthesized using a structure directing agent such as the triblock copolymer Pluronic P104. In this study, a rotating cylinder was employed to control the size of the mesoporous particles via a self-assembly route. Particle size control could be achieved by changing the concentration of the precursor inside droplets generated by the rotation of the inner cylinder of the reactor at 1,750 rpm. Mesoporous silica particles fabricated using the emulsions with a precursor concentration of 24.7, 12.3, and 6.2 wt. %, respectively. As the concentration of the precursors inside the droplets decreased, the average size of the final mesoporous particles reduced, and the trend is plotted as a graph in Fig. 6, showing that the size increment is more sensitive in the low concentration regime of the precursor materials.

The mesoporous silica particles can be synthesized by not only batch operation but also in a continuous manner using the Taylor vortex reactor. In this study, two syringe pumps was used to feed the continuous oil phase dissolving the emulsifier and the dispersed phase to the Taylor vortex reactor, while the inner cylinder was rotated at a constant angular velocity of 1,750 rpm. The resultant emulsion droplets were collected by discarding from the top of the reactor, followed by heating for evaporation and self-assembly, as depicted schematically in Fig. 7(a). After calcination, the mesoporous silica particles could be obtained, as shown in the SEM images of Fig. 7(b). The inlet flow rate to the reactor was fixed at 8 ml/min, yielding a production rate of 0.48 l/hr. If a larger apparatus with robust scale-up conditions were employed, practical production of the emulsions would be possible for industrial purposes.

Thermal conductivity of materials can be defined as the heat flow rate per unit temperature difference and layer thickness. Table 2 lists the thermal conductivity data of the porous silica particles with three types of

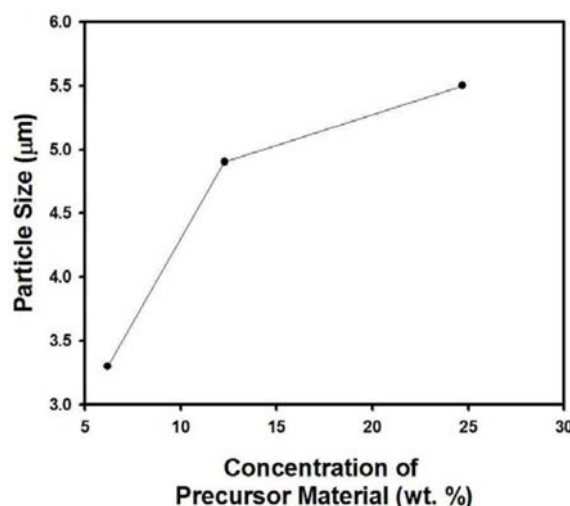


Fig. 6. The change of the average size of the mesoporous silica particles fabricated using a rotating cylinder as a function of the precursor concentration inside the emulsions.

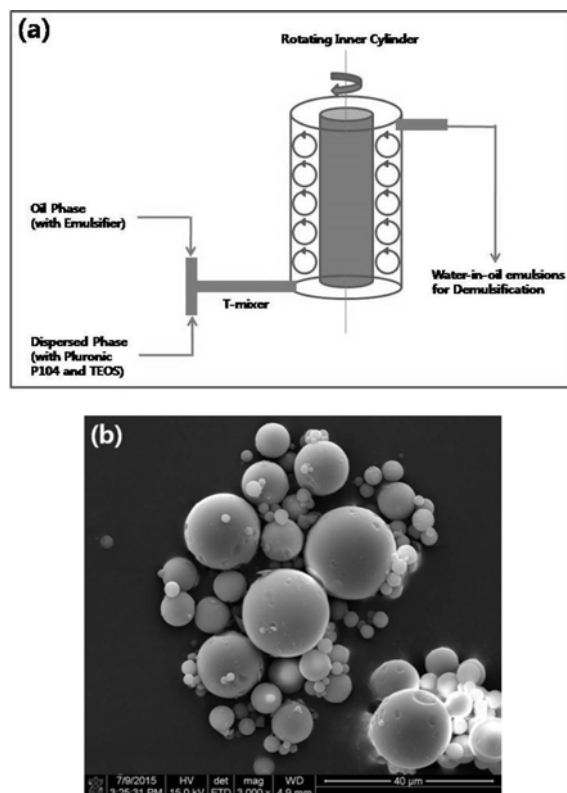


Fig. 7. (a) Schematic figure of the continuous production of mesoporous silica particles by an emulsion-assisted self-assembly. (b) SEM image of mesoporous silica particles fabricated using a Taylor vortex reactor with continuous operation mode.

samples fabricated by a simple homogenizer. For the formation of mesopores and macropores, Pluronic P104 and the polystyrene nanospheres with 800 nm diameter were applied as templating materials.

Before estimating the thermal conductivity of the porous particles, heat capacities of the particles were determined by DSC measurement. The thermal

Table 2. Thermal insulating properties of various porous silica particles fabricated by simple homogenizer.

Sample	Density ρ	Thermal Diffusivity α	Thermal Conductivity k
Macroporous Silica	0.189 g/cm ³	0.084 mm ² /s	24 mW/m·K
Mesoporous Silica	0.545 g/cm ³	0.063 mm ² /s	31 mW/m·K
Meso-macroporous Silica	0.102 g/cm ³	0.070 mm ² /s	10 mW/m·K

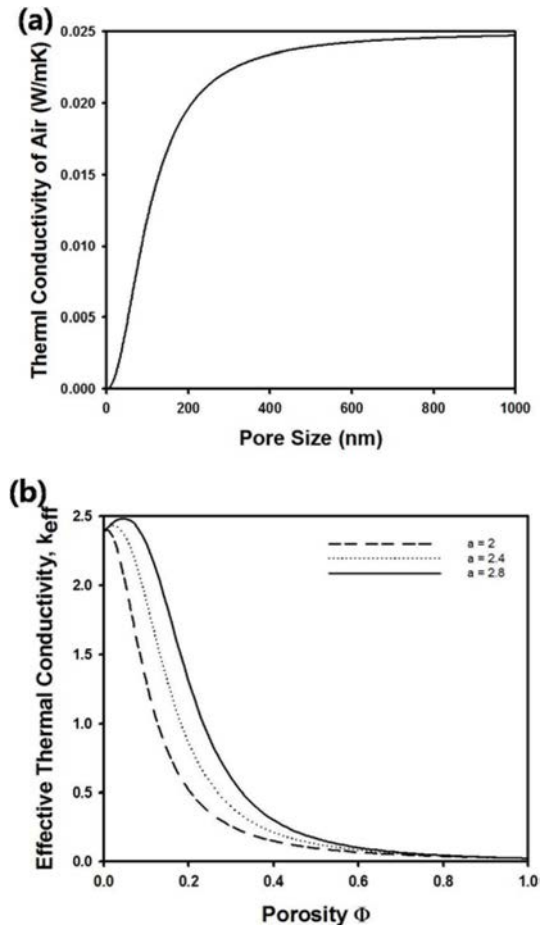
conductivity (k) of the porous silica particles could then be predicted from the definition of the thermal diffusivity, $\alpha = k/(\rho C_p)$. Here, ρ denotes the apparent density of the porous silica powder, which was measured by using a microbalance and a mass cylinder. The LFA (laser flash analysis) technique was applied to measure the thermal diffusivity of the porous materials, and finally the thermal conductivity of the porous particles was predicted from the definition. As presented in Table 2, the thermal diffusivity of the mesoporous silica particles was the smallest among the three kinds of porous materials. However, the mesoporous particles showed the largest value of thermal conductivity due to having the highest value of apparent density. The effect of density was also clear, with the meso-macroporous silica particles showing the smallest value of thermal conductivity, as displayed in Table 2. It can be concluded that the hierarchically porous architecture of the meso-macroporous silica particles resulted in the lowest value of thermal conductivity, suggesting that they can be applied as an efficient insulator. Since the following equation indicates that the thermal conductivity of air contained in pores with extremely small sizes decreases drastically, the introduction of mesopores to macroporous particles would enhance the insulating properties of the particles.

$$k_{\text{gas}} = \frac{k_{\text{gas},0}}{1 + 2\beta Kn} \quad (1)$$

Here, k_{gas} and $k_{\text{gas},0}$ denote the thermal conductivity of gas inside pores and the thermal conductivity of gas at standard temperature and pressure (STP), respectively. β is a coefficient to characterize the collision energy transfer efficiency between molecules and pore walls [13]. Since the Knudsen number Kn increases as the size of pores decreases, as shown in the following equation, the thermal conductivity of air contained in the mesopores would be smaller compared to that of air trapped in macropores [13].

$$Kn = \frac{k_B T}{\sqrt{2} \pi d p \delta} \quad (2)$$

Here, δ represents the characteristic size of pores, T and P denote temperature and pressure inside pores, while d and k_B denote the collision diameter of gas

**Fig. 8.** (a) The change of thermal conductivity of air trapped inside pores as a function of the pore size. (b) The effective thermal conductivity of porous material as a function of porosity Φ . The pore size was assumed as 800 nm.

molecules and the Boltzmann constant. Fig. 8(a) presents the change of the thermal conductivity of air trapped in pores as a function of the pore size, calculated using equations (1) and (2). The graph indicates that a dramatic decrease of thermal conductivity of air can be obtained when the size of the pores becomes smaller than about 300 nm. In this study, mesopores of about 5.57 nm were introduced into the frameworks of macroporous structures to enhance the thermal conductivity of porous silica particles using hierarchically porous architectures.

Besides pore diameter, the porosity of the particles is another important factor to determine the thermal conductivity of porous materials. As suggested by Matiasovsky et al, the porosity Φ should be considered to calculate the effective thermal conductivity of a porous medium k_{eff} , as shown in the following equation [14].

$$k_{\text{eff}} = \frac{1}{\frac{(1-1.1\Phi)^s}{k_s} + \frac{(1.1\Phi)^a}{k_a}} \quad (3)$$

Here, k_s and k_a denote the thermal conductivity of the

Table 3. Thermal insulating properties of various porous silica particles fabricated by rotating cylinder system.

Sample	Density ρ	Thermal Diffusivity α	Thermal Conductivity k
Macroporous Silica	0.174 g/cm ³	0.07 mm ² /s	23 mW/m·K
Mesoporous Silica	0.304 g/cm ³	0.076 mm ² /s	25 mW/m·K

silica backbone and air, respectively. The exponent s and a represent the fractal dimension of high and low conductivity zones of a porous material, respectively. Fig. 8(b) shows the change of effective thermal conductivity of porous silica as a function of Φ obtained by equation (3) by fixing the fractal dimension s as 1 and considering three different values of a . The graph reveals a dramatic decrease of the effective thermal conductivity with increasing porosity when the size of the macropores is assumed as 800 nm. It is thought that the low thermal conductivity of the meso-macroporous silica particles, as listed in Table 2, originates from the combined effect of high porosity due to macropores and the decrease of the conductivity of air contained in mesopores.

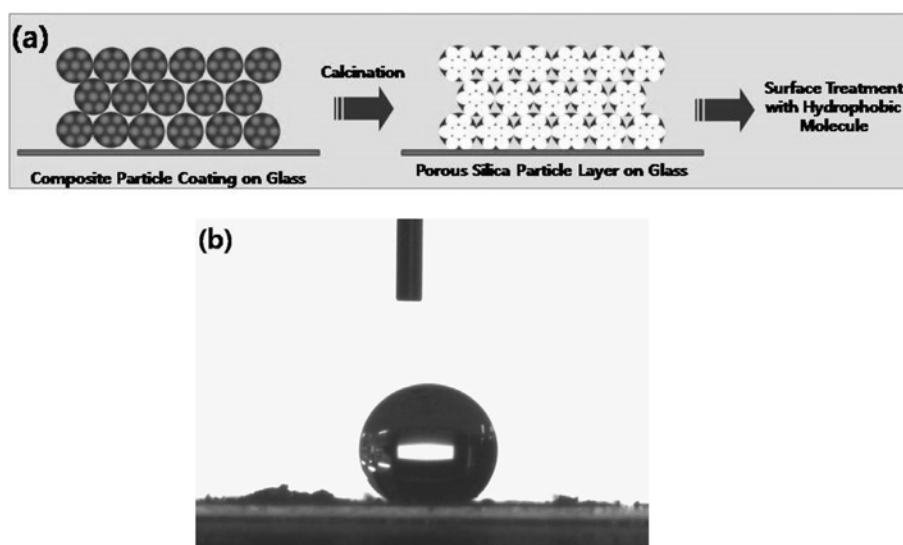
In this study, porous silica particles synthesized using a rotating cylinder were analyzed by a LFA apparatus to predict their thermal conductivities. The hollow nature of the porous silica particles synthesized by the rotating cylinder may be more advantageous than simple porous particles fabricated by a homogenizer. Table 3 lists the thermal conductivity data of the porous particles with hollow interior architectures by the Taylor vortex reactor, showing a decrease of the conductivity values compared to the data in Table 2. Since the hollow interior structure may increase the air volume of the porous particles, it is expected that the thermal insulating property can be improved. For macroporous

silica particles, only a slight decrease of the thermal conductivity was observed, whereas mesoporous particles revealed much smaller conductivity, as found in Table 3. Unlike macroporous particles, the thermal conductivity of the mesoporous particles decreased by more than 19% due to the formation of hollow structures by the fast evaporation of the emulsion. However, the decrease of thermal conductivity of macroporous particles was only about 4.2% after changing the emulsification apparatus, suggesting that the macropores generated by polymeric beads act as effective air voids in the same manner as hollow interior structures.

For application of the macroporous silica particles, superhydrophobic surfaces were created from a coating film composed of the porous powder material. A macroporous film with a superhydrophobic property could be obtained and characterized by measuring the water contact angle, as displayed schematically in Fig. 9(a). A water droplet could be stably posed on the film, as shown in the photograph of Fig. 9(b), and the measurement was possible with a contact angle of about 155°. Since the thermal conductivity may increase when the porous materials are exposed to humid environments, it would be advantageous to impose superhydrophobicity to the porous films to maintain insulating properties. Thus, the technologies of porous inorganic particles and a superhydrophobic film can be combined to develop novel advanced materials that will be useful for energy-saving buildings and specialty components such as

Table 4. XPS analysis results of the film composed of porous silica particles after surface treatment.

Element	C1s	O1s	F1s	Si2p
Atomic Concentration (%)	24.92	17.75	48.03	9.29

**Fig. 9.** (a) Schematic figure of the fabrication route of a superhydrophobic film composed of macroporous silica particles. (b) The contact angle of the water droplet on the superhydrophobic surface of macroporous particles.

spacecraft with good insulating layers.

The existence of fluorine atoms after the treatment with HDFTHDTS was confirmed by a XPS analysis of a film composed of porous particles, as displayed in Table 4. The atomic concentration of fluorine was most abundant with 48.03%, among all possible components, indicating that the surface treatment using the fluorine-containing silane coupling agent was successful.

Conclusions

In this study, porous silica particles were synthesized by self-assembly inside emulsions to fabricate super-insulators with low thermal conductivity. To produce the droplets, a simple mechanical homogenizer or a rotating cylinder was used for the emulsification process. Three types of porous particles could be fabricated with a nano-architecturing approach, and meso-macroporous particles had the lowest thermal conductivity, about 10 mW/mK.

Using the rotating cylinder system, porous particles with hollow interior structures could be obtained, possibly due to the rapid evaporation of the emulsions as heat generated during the rotation of the inner cylinder. The thermal-insulating properties of the resultant porous particles were slightly lower than those of the porous materials fabricated by a homogenizer without hollow architectures. Continuous production of porous particles was also possible using the same apparatus by feeding the dispersed and continuous phases separately.

The porous particles were deposited as a thick film for the creation of a superhydrophobic surface with water-repelling property. After fluorination treatment of the porous film with multiple length scales, a superhydrophobic surface was created with a water contact angle of 155°, and the superhydrophobicity was conceptually analyzed in light of the lotus effect.

Acknowledgments

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