

## COLLECTION OF INDUSTRIAL OIL USING NANOPARTICLES AND POROUS POWDERS OF SILICA

Industrial oil was collected using hydrophobic silica powders. Silica nanopowder was modified with octadecyltriethoxysilane (OTS) using spray pyrolysis reactor continuously. Besides nanoparticles, mesoporous silica powder synthesized using Pluronic P104 was adopted as another oil adsorbents. Spherical macroporous or meso-macroporous silica particles were prepared by self-assembly for the removal of oil. The effects of the amount of powder on the oil adsorption were studied and compared with the results of various silica powders. The meso-macroporous silica particles were found to be the most efficient, indicating that both specific surface area and porosity played crucial role.

*Keywords:* Silica nanopowder, Surface modification, Porous silica, Oil removal

### 1. Introduction

Silica nanopowder with large surface area can be applied to various purposes. For instance, hydrophobic silica particles can be used to electronics or the fabrication of hybrid colloids by self-assembly [1]. Since the surface modification of the nanopowder is usually performed by batch-type reactor, the continuous operation should be studied in detail to produce functional particles efficiently. For this purpose, spray pyrolysis apparatus can be considered as important candidate since the modification of the nanoparticles can be conducted within short processing time in continuous manner.

Recently, various environmental problems have been caused by oil contaminants. Some oil is so toxic that living organisms in the ocean are endangered and human beings are threatened due to food chains. Thus, it is essential to develop the techniques to remove oil practically. Porous silica materials such as aerogels have been applied for the adsorption of oils with high removal efficiency [2]. However, researches on novel materials are still necessary since harsh synthesis conditions such as supercritical drying are required for aerogels.

In this study, the adsorption capabilities of silica nanoparticles and porous silica materials with meso or macropores were compared for the removal of industrial oil. Porous silica powders or nanoparticles were fabricated and modified to prepare adsorbent to collect the oil. Additionally, hierarchically porous silica particles could be synthesized by self-assembly, and surface treatment was conducted using silane coupling agent. The amount

of oil removed by the hydrophobic powders was monitored as a function of the amount of the powder.

### 2. Experimental

#### 2.1. Surface modification of silica nanoparticles

Silica nano-colloid (Ludox HS-40) was mixed with nitric acid, ethanol, and octyltrimethoxysilane (OTS). The mixture was fed to spray pyrolysis reactor at 300°C using two fluid nozzle to produce aerosols. Argon was used as carrier gas to collect the OTS-treated silica particles. The collected hydrophobic particles were centrifuged and dried.

#### 2.2. The synthesis of hydrophobic mesoporous silica powder

Mesoporous powder was prepared using tetramethylorthosilicate (TMOS) and Pluronic P104 as precursor and structure directing agent, respectively. Nitric acid (1 M) was added for gelation of the precursor and the sample was heated at 60°C for 24 hours. Then, calcination was performed at 500°C for 5 hours to prepare the mesoporous powder, which was modified using OTS to obtain hydrophobic silica. After 72 hours, the powder was collected and washed with ethanol followed by drying at room temperature.

\* DEPARTMENT OF CHEMICAL ENGINEERING AND BIOTECHNOLOGY, KOREA POLYTECHNIC UNIVERSITY, 237 SANGIDAEHAK-RO, SIHEUNG-SI, GYEONGGI-DO 15073, REPUBLIC OF KOREA

\*\* DIVISION OF POWDER AND CERAMICS, KOREA INSTITUTE OF MATERIALS SCIENCE, SANGNAM-DONG, CHANGWON 641-831, REPUBLIC OF KOREA

# Corresponding Author: yscho78@kpu.ac.kr

### 2.3. The synthesis of hydrophobic macroporous or meso-macroporous silica particles

As templating material, polystyrene nanospheres were synthesized to form macropores using styrene as monomer and AIBA ( $\alpha$ ,  $\alpha'$ -azodiisobutyramidine dihydrochloride) as initiator. According to Table 3, emulsion polymerization was conducted to synthesize polystyrene nanospheres with 210 or 670 nm in diameter. To synthesize macroporous silica particles, emulsion-assisted self-assembly was adopted using hexadecane as continuous medium dissolving Abil EM90 as emulsifier. The dispersed phase was prepared by mixing TEOS, PS suspension in ethanol, and aqueous HCl solution. After homogenizing the continuous and dispersed phase, evaporation-driven self assembly was conducted, followed by calcination at 500°C for 5 hours to remove the templates. Similar approach was performed by the addition of Pluronic P104 into dispersed phase for meso-macroporous particles.

For the surface modification of the porous silica particles, 2.5-ml OTS was dissolved in 10-ml toluene. Then, the porous powder was added to the solution, followed by heating at 60°C under stirring. After modification, the powder was collected and dried at room temperature.

### 2.4. Oil adsorption

Industrial oil was stained using Sudan III dye with red color. Then, it was placed on top of water in vial. After hydrophobic powder was added to the oil-water mixture, adsorption of oil was induced to remove the oil from water. As the amount of powder increased, the liquid oil became gel-like mixture due to the addition of hydrophobic powder by the selective mixing with

ally, continuous operation can be conducted, which is adequate for practical industries. Table 1 summarizes the modification conditions of silica nanopowder using aerosol reactor. The amount of OTS was adjusted to control the hydrophobicity of the nanopowders while other conditions were fixed. To avoid the decomposition of silane coupling agent inside the reactor, relatively low temperature such as 300°C was maintained.

Fig. 1a contains the size distribution of the silica nanoparticles dispersed in the mixture of ethanol and water. Though the primary particle size is about 10 nm, the secondary particles formed by aggregation showed much larger diameter such as 330 nm. However, the atomization of the mixture was possible without clogging nozzle. Fig. 1b contains the SEM image of the silica nanoparticles modified with OTS according to Table 1. In this image (sample #1 in Table 1), the contrast difference can be recognized near the boundary of the nanoparticles, indicating the OTS molecules are adsorbed on the surface of the nanopowders. The contrast difference was reduced as the amount of OTS decreased during modification (sample #2 in Table 1) as displayed in Fig. 1c. Fig. 1d displays the graph of the adsorbed amount of oil on the surface of the silica nanopowder as a function of the amount of the nanoparticles. Hydrophobic silica nanopowder was added to the oil-water mixture for the adsorption of the oil to form the solid-like oil-nanopowder mixture. The results were plotted in Fig. 1d, and it can be concluded that the nanoparticles modified with larger amount of OTS (sample #1 in Table 1) can be used more effectively compared to the nanopowder treated with less amount of OTS (sample #2 in Table 1). Thus, sufficient amount of OTS will be effective for the modification of the silica nanopowder, since the nanoparticles modified with larger amount of OTS revealed superior adsorption capability.

TABLE 1

Experimental Conditions of Surface Modification of Commercial Silica Nanopowders

	Silica Nanoparticle Suspension	Aqueous HNO <sub>3</sub> Solution (60%)	Ethanol	OTS	Furnace Temperature	Feeding Rate of Precursor Mixture	Feeding Rate of Carrier Gas
#1	1 g	0.1 ml	70 ml	13.0 g	300 °C	1 ml/min	1 L/min
#2	1 g	0.1 ml	70 ml	6.5 g	300 °C	1 ml/min	1 L/min

oil. Since the powder is hydrophobic, water-repelling property caused the formation of oil-powder mixture. The mass of powder to form stable oil-powder mixture was recorded to determine adsorption capability.

## 3. Results and discussion

To obtain hydrophobic particles by alcoholysis, silica nanopowder was mixed with water, ethanol, and OTS, followed by the atomization of the mixture through the nozzle of spray-pyrolysis reactor [3]. This aerosol-assisted modification is advantageous in that simple process can be employed inside droplets due to the reaction between the surface silanol groups and OTS. Addition-

ally, continuous operation can be conducted, which is adequate for practical industries. Table 2 summarizes the synthesis and modification conditions of mesoporous silica powder. The amount of TMOS, Pluronic P104, and nitric acid were fixed, whereas the amount of OTS was changed, as written in Table 2. Fig. 2a,b contains the SEM and TEM image of the mesoporous silica powder, respectively, before the modification with OTS (sample #2 in

TABLE 2

The Synthesis and Surface Modification Conditions of Mesoporous Silica Powder

	TMOS	Pluronic P104	Nitric Acid (1 M)	OTS
#1	5.515 g	4 g	12 g	2.5 ml
#2	5.515 g	4 g	12 g	5 ml

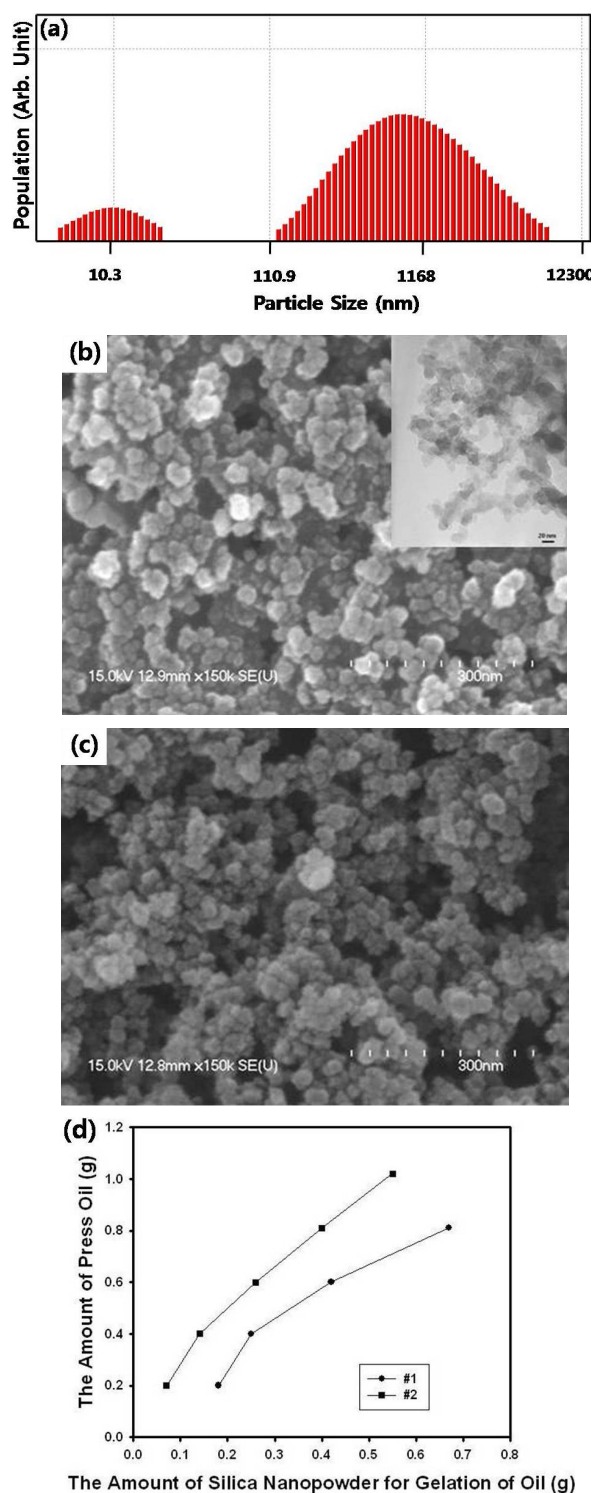


Fig. 1. a) The size distribution of silica nanoparticles dispersed in the mixture of ethanol and water. b) and c) SEM image of the silica nanopowders modified with OTS. (b) Sample #1 and c) Sample #2 in Table 1). d) The adsorbed amount of oil as a function of the amount of hydrophobic silica nanopowder

TABLE 3

The Synthesis Conditions of Monodisperse Polystyrene Nanospheres

	Styrene	Water	AIBA	Polymerization Temperature	Particle Size
#1	5.61 g	112.5 g	0.04625 g	80°C	210 nm
#2	39.375 g	393.75 g	0.3238 g	70°C	670 nm

Table 2). The skeletal structure of silica was formed by the phase separation of the precursor during the sol-gel reaction. Although the results were not reproduced here, the mesoporous structure was observed after the modification with OTS, showing that the micron-sized powders are aggregated and several voids were formed between the powders.

Fig. 2c contains the nitrogen adsorption-desorption of the hydrophobic mesoporous silica powder (sample #2 in Table 2). The specific surface area of the powder was estimated as 755.2 m<sup>2</sup>/g, and the average pore size was determined as 3.4 nm, as displayed in the inset graph. Since the average pore size is in the size range of mesopores, it can be confirmed that the hierarchical pores of the silica is formed with macro-voids between the skeletal backbones shown in Fig. 2a. Fig. 2d contains the adsorbed amount of oil as a function of the amount of the porous silica powder. The amount of the powder for the gelation of the oil was measured using sample #1 and #2 in Table 2 to compare the effect of the amount of OTS. As shown in Fig. 2d, the adsorption capacity of the powder was enhanced when larger amount of OTS was used during the modification. The saturation behavior of adsorption was observed, indicating the initial adsorption capacity was increased drastically.

In this study, porous particles having hierarchical structures with mesopores and macropores were also utilized as adsorbents for oil removal. For this purpose, meso-macroporous silica particles were synthesized from emulsions. The synthesized particles were modified using OTS to increase the hydrophobicity to use as oil adsorbent. It has been reported that several methods can be adopted for the modification of porous particles. For instance, simple mixing of porous silica and activated carbon followed by calcination resulted in the formation of carbon-modified porous silica particles [4]. PDMS-modified silica xerogels could be also prepared by the sol-gel process using PDMS and TEOS [5]. The modification with biocides on mesoporous silica particles was also studied by physisorption [6]. In this study, solution-phase modification was conducted to form the chemical bonding of OTS on the silica surface. This is advantageous in that various functional groups can be attached using silane coupling agents [3].

Fig. 3a contains the TEM image of the meso-macroporous silica particles synthesized by self-assembly, indicating that the macropores are surrounded with silica frameworks containing mesopores to form hierarchical structures. The ordered arrays of the mesopores can be considered as hexagonal structure, which were generated from the self-assembly of Pluronic P104. Fig. 3b contains the results of the oil adsorption using meso-macroporous silica particles in Fig. 3a. Before the adsorption, the hierarchically porous particles were modified with OTS to enhance the hydrophobicity. Fig. 3b contains the result on the amount of the porous particles required for the adsorption and gelation of the oil. In Fig. 3b, the adsorption capacity of the meso-macroporous particles was the highest among the samples due to the hierarchical structure of the particles.

For the comparison of the adsorption capacity of meso-macroporous silica particles, macroporous particles were

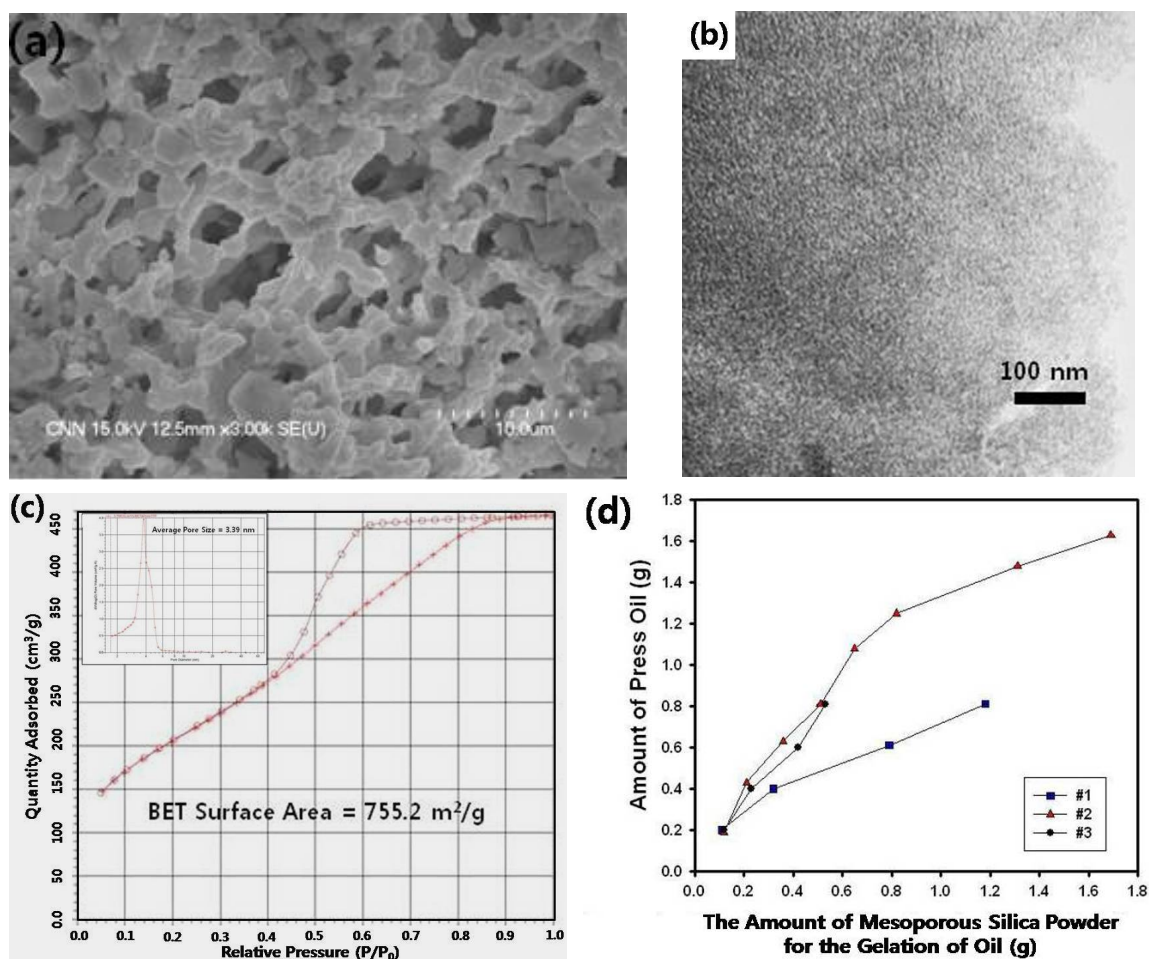


Fig. 2. a) SEM and b) TEM images of mesoporous silica powder with skeletal voids. Scale bars indicate 10 μm and 100 nm, respectively. c) The nitrogen adsorption and desorption curve of the hydrophobic mesoporous silica powder. The inset figure displays the pore size distribution. d) The adsorbed amount of oil as a function of the mass of the hydrophobic mesoporous silica

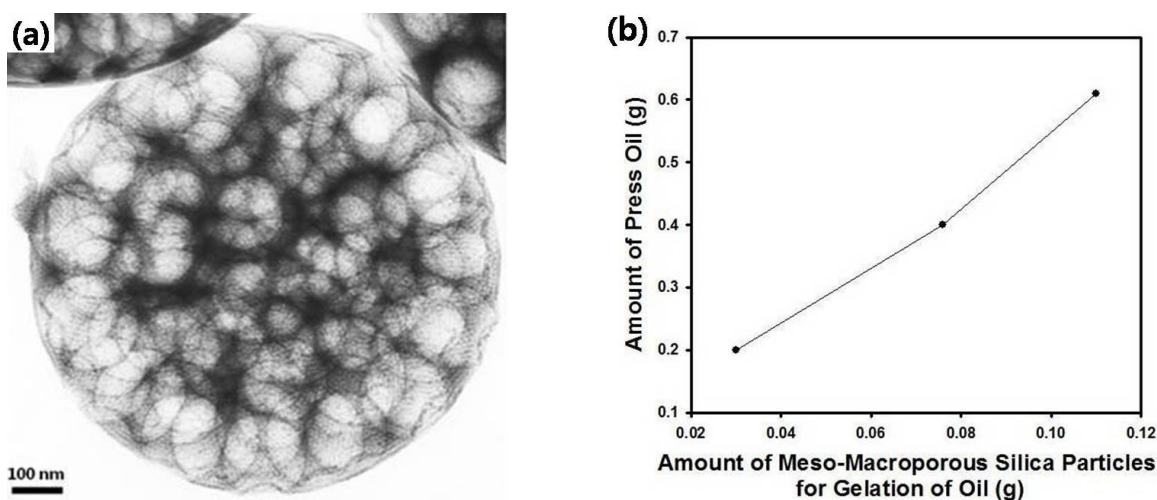


Fig. 3. a) TEM image of meso-macroporous silica particles synthesized using polystyrene nanospheres with 210 nm in diameter. Scale bar indicates 100 nm. b) The amount of adsorbed oil as a function of the mass of the hydrophobic meso-macroporous silica

adopted for the adsorption of oil. Before the test, the surface of the particles was also modified with OTS. Fig. 4a contains the SEM image of the macroporous particles synthesized using polystyrene nanospheres with 670 nm in diameter as templates. After the colloidal templating, the nano-structured particles with

open pores could be observed in Fig. 4a, and the oil was adsorbed onto the particles through the porous channels. Fig. 4b contains the amount of the adsorbed oil as a function of the amount of the macroporous powder. In Fig. 4b, the adsorption capacity of the macroporous particles was inferior to that of the meso-

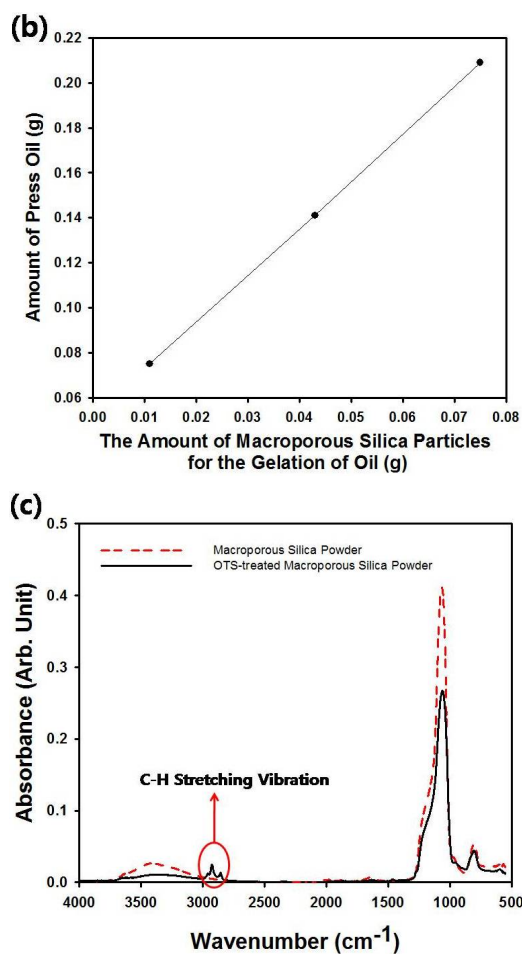
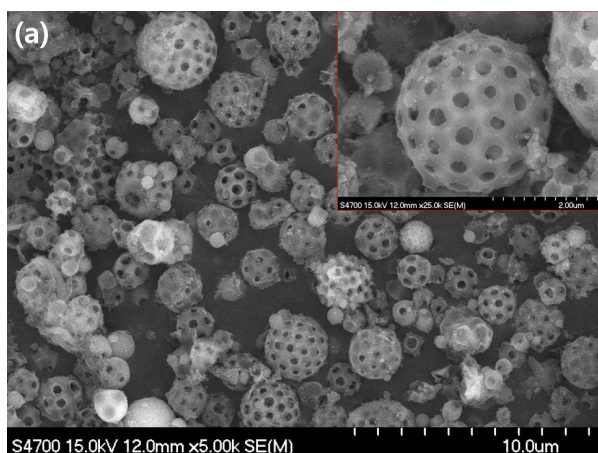


Fig. 4. a) SEM image of macroporous silica particles synthesized using polystyrene nanospheres with 670 nm in diameter as templating materials. b) The amount of adsorbed oil as a function of the amount of hydrophobic macroporous silica particles. c) FT-IR spectrum for the macroporous silica powder before (dashed line) and after (solid line) OTS treatment

macroporous particles in Fig. 3a. Since much more pores exist in the meso-macroporous silica compared to the simple macroporous particles, the adsorption of oil on the meso-macroporous powder could be enhanced compared to the particles having only

macropores. These porous particles can be potentially applied as porous supports for antifungal purposes [7].

To confirm the covalent binding of OTS on the surface of macroporous silica particles, the FT-IR analysis was performed before and after the treatment with OTS, as displayed in Fig. 4c. After the modification with OTS, new peaks at 2,607 and 2,801  $\text{cm}^{-1}$  were detected due to the stretching vibration of C-H, indicating that the modification was successful.

#### 4. Conclusions

The surface of silica nanoparticles was modified using OTS by spray pyrolysis reactor. Continuous production of the hydrophobic nanopowder was possible for the application as adsorbent of industrial oil. Mesoporous silica powder could be also synthesized using TMOS and Pluronic P104 for modification by alcoholysis of OTS to apply as adsorbent of oil. Spherical porous particles could be also utilized for the removal of the oil after the modification with OTS. Macroporous or meso-macroporous silica particles were synthesized by self-assembly using polystyrene nanospheres or triblock copolymer as sacrificial templates. The adsorption capability of the meso-macroporous particles was found to be much larger than that of macroporous particles due to their hierarchical structure.

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