

# Synthesis of Double Mesoporous Silica Nanoparticles and Control of Their Pore Size

## 이중 다공성 실리카 나노입자 합성 및 공극 크기 조절

Dae Keun Park, Jung Hwan Ahn

### Abstract

In this study, monodispersive silica nanoparticles with double mesoporous shells were synthesized, and the pore size of synthetic mesoporous silica nanoparticles was controlled. Cetyltrimethylammonium chloride (CTAC), N, N-dimethylbenzene, and decane were used as soft template and induced to form outer mesoporous shell. The resultant double mesoporous silica nanoparticles were consisted of two layers of shells having different pore sizes, and it has been confirmed that outer shells with larger pores (Mean pore size > 2.5 nm) are formed directly on the surface of the smaller pore sized shell (Mean pore size < 2.5 nm). It was confirmed that the regulation of the molar ratio of pore expansion agents plays a key role in determining the pore size of double mesoporous shells.

*Keywords: Silica Nanoparticle, Double Mesoporous, Core-Shell, Pore Size Control*

### I. Introduction

Until recently, many studies have been underway to reduce the effluent of hazardous materials such as waste including fine dust. Many types of nanomaterials have been reported to be able to absorb harmful substances efficiently as a means of them [1]-[3]. Typically for silica nanoparticles, a very uniform mesoporousity (2~50 nm) can be generated, making it a key ingredient in commonly used adsorption filter [4]-[6]. Recent studies have reported a variety of silica materials with dual pores, such as micro-meso [7], macro-meso [8], and meso-meso [9], because the material properties from the interconnection structure of the small-to-large pores in terms of mass transport efficiency can be superior to those of single porous materials. Usually the bimodal porous silica material is synthesized using colloidal crystals and soft templates [10] such as polymer foam, emulsion, or hard template [11] for the formation of pores with different sizes.

Over the past 20 years, studies of mesoporous silica particles have been carried out in several study groups [12]-[15]. However, as a result, the material is not uniform in size (reasonably polydispersive), and the diameter is limited to a range of more than 500 nm. Silica nanoparticles of these core-shells are spherical particles of uniform pore size, but they consist only of single-sized mesoporous, and the synthesis of silica nanoparticles composed of double mesoporous structures is quite limited.

Here, we report the synthesis method of core-shell silica nanoparticles with double mesoporous. Synthesized double mesoporous silica nanoparticles were spherical, monodispersive and consist of two different-sized mesoporousity that coexist in each

nanoparticle. The double mesoporous silica nanoparticles were synthesized through the process of using CTAC, N, N-dimethylbenzene (DMB), and decane as an organic template solution in addition to the inner mesoporous shells formed using only CTAC in silica nanoparticles. The pore sizes of double mesoporous silica nanoparticle can be easily adjusted by controlling the molar ratio of organic templates.

### II. Experiments

#### A. Synthesis of Silica Nanoparticles

Uniform-sized and monodispersive silica nanoparticles were synthesized by referring to the generally well-known synthesis method [16] utilizing initial silica nanoparticles as a seed, and then added tetraethylorthosilicate (TEOS) to silica nanoparticle mixture and composing them by overnight stirring at room temperature. The molar ratio of TEOS, 28 wt.% NH<sub>4</sub>OH, distilled water, and EtOH used in this process was 1.0:1.7:6.0:190.0 respectively. 5 ml of silica seed solution was prepared for the synthesis of monodispersive silica nanoparticles and the seed solution was added to NH<sub>4</sub>OH/H<sub>2</sub>O/EtOH mixture with stirring for 30 minutes, and added 5 ml of TEOS to the mixture with further for 6 hours under the same conditions. Finally, 10 ml of TEOS was additionally added and stirred for another 12 hours.

### Article Information

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The Authors are with KEPCO Research Institute, Korea Electric Power Corporation, 105 Munji-ro Yuseong-gu, Daejeon 34056, Republic of Korea

Correspondence Author: Dae Keun Park (dkpark01@kepco.co.kr)



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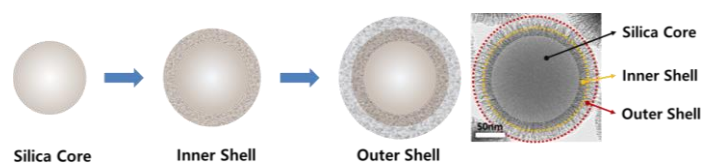


Fig. 1. Schematic illustration of mesoporous silica nanoparticles with double shells, and TEM image (right side)

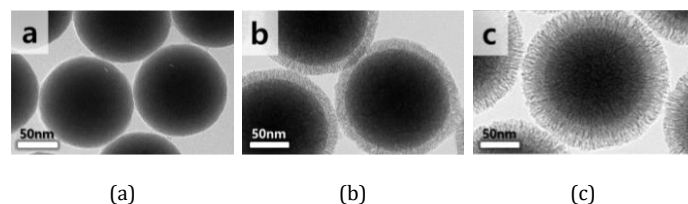


Fig. 2. TEM images of silica nanoparticles with no shell (a), single mesoporous shells (b), and double mesoporous shells (c).

### B. Formation of Inner Mesoporous Shell

The inner mesoporous shells (single shell silica nanoparticle) were synthesized on the surface of initial silica nanoparticles through their own assembly with sol-gel reactions from pore expansion agents such as *N,N* dimethylbenzene and decane. To form the mesoporous of silica nanoparticles, 10 ml of previously synthesized silica nanoparticles was added to 30 ml of mixture containing 28 wt.%  $\text{NH}_4\text{OH}$  (0.2ml) and distilled water. Dissolved CTAC, DMB, and Decane solution in the DI  $\text{H}_2\text{O}$  and  $\text{EtOH}$  mixture (2:1) was added to prepared silica nanoparticle solution and stir for 30 minutes. TEOS was then added to the mixture with vigorously stirring. The reacted mixture was stirred for 30 minutes and then overnight at room temperature. The molar ratio of TEOS:CTAC:DMB:decane was adjusted to 1.00:0.43:0.45:0.45 respectively, and the synthesized inner mesoporous shells were retrieved using centrifuges and dried at room temperature overnight. The inner mesoporous shells, which were calcined at  $550^\circ\text{C}$  for 5 hours, were immediately used to form the outer shell.

### C. Formation of Outer Mesoporous Shell

To further synthesize the double mesoporous shell, a surfactant mixture (CTAC:DMB:Decane) solution was further added to inner mesoporous shell following the above manner with a molar ratio of 1:0.2:0.2, 1:0.4:0.4, 1:0.8:0.8 and 1:1.2, respectively. Then add 1 mol of TEOS was added to the mixture and stirred for 30 minutes. The reaction procedure was then carried out in the same way as the synthesis of inner mesoporous shells.

## III. Result and Discussion

Fig. 1 shows the order in which the double mesoporous shell is formed through core-shell silica nanoparticles with single mesoporous shell from silica nanoparticles. The double mesoporous shell silica nanoparticles were obtained by directly forming larger-sized pores on the surface of a single mesoporous shell by introducing a mixture solution of CTAC as pore generating template and pore expansion agent. The resultant was found to be implemented as a double mesoporous consisting of inner shell

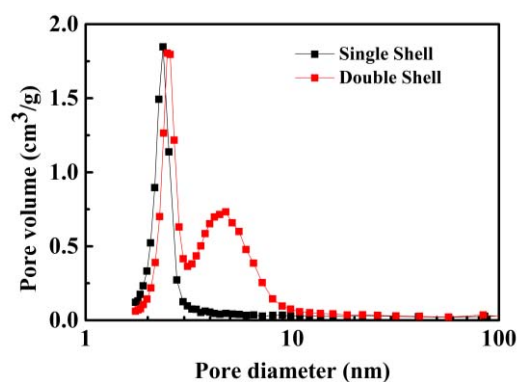


Fig. 3. Pore diameter distribution curves of silica nanoparticles with single and double shells.

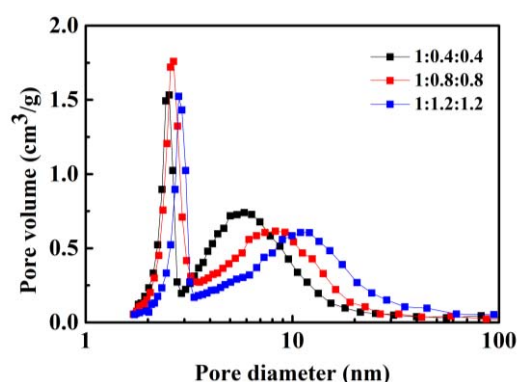


Fig. 4. Pore diameter distribution curves of silica nanoparticles with different molar ratio of pore expansion agents.

(smaller pore size) and outer shell (larger pore size). The double pore structure was obtained by forming an outer shell with a larger mesopore (pore size  $> \sim 2.5$  nm) on the inner shell surface with a smaller mesopore (pore size  $< \sim 2.5$  nm).

Transmission electron microscopy (TEM) images of synthesized silica nanoparticles as core structure, inner mesoporous shell, and outer mesoporous shell were observed in Fig. 2. The mean pore size (2.5 nm) of single mesoporous shell was obtained using the pore size distribution (PSD) in the case of inner mesoporous shells.

To form the double mesoporous shell structure such as the illustration of Fig 1, silica nanoparticles which were about 210 nm in size, were previously synthesized (Fig. 2a). The inner mesoporous shells were produced by sol-gel reactions of CTAC and TEOS for the next process. The thickness of the inner shell was found to be  $\sim 15$  nm (Fig. 2b), followed by the combination of CTAC/DMB/Decane (Fig. 2c). Double mesoporous shells in Fig. 2c have hierarchically doubled, whose thickness was  $\sim 15$  nm/ $\sim 23$  nm, respectively.

The PSD curve (Fig. 3) clearly shows that the outer pore size after synthesized the double mesoporous shell has been formed with a larger size than the pore size of the inner mesoporous shell (mean pore size: 5.2 nm). On the other hand, the pore size of the inner mesoporous shell has become very slightly larger due to the addition of the pore expansion agent which infiltrated at the surface of inner mesoporous shells in the stage of forming the double shell.

In addition, it was confirmed that pore size of the outer mesoporous shell can be controlled by adjusting the molar ratio of the pore expansion agents during the formation stage of the outer shell.

The PSD results in Fig. 4 show that the higher the concentration ratio of pore expansion agents, the larger the pore size could be made. Each of these outer pore sizes was measured at 5.9 nm, 8.8 nm, and 11.6 nm, and at the same time, the pore size of the existing inner shell was slightly increased. This suggests that the higher the concentration of agents, the more involved the expansion of the outer shell pores as well as the expansion of the inner porosity.

#### IV. Summary

In summary, we implemented double shells consisting of smaller and larger mesoporous on the surface of each silica nanoparticle and controlled the pore size by adjusting the molar ratio of pore expansion agents. An analysis of the pore size of the synthetic double mesoporous silica nanoparticles found that the outer pore size formed on the surface of the silica nanoparticle was larger than the pore size of the inner shell. It has been confirmed that the higher the concentration ratio of pore expansion agents, the larger the pore size of outer and inner shell. Further research is underway to utilize these hierarchical nanostructures for research such as catalyst support and hydrogen storage, including the adsorption of harmful substances. Our findings, which can easily adjust the pore size, are expected to be useful not only for catalysts, hydrogen but also for bio applications such as drug delivery and cosmetics.

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