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# 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.

## 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 macroporous 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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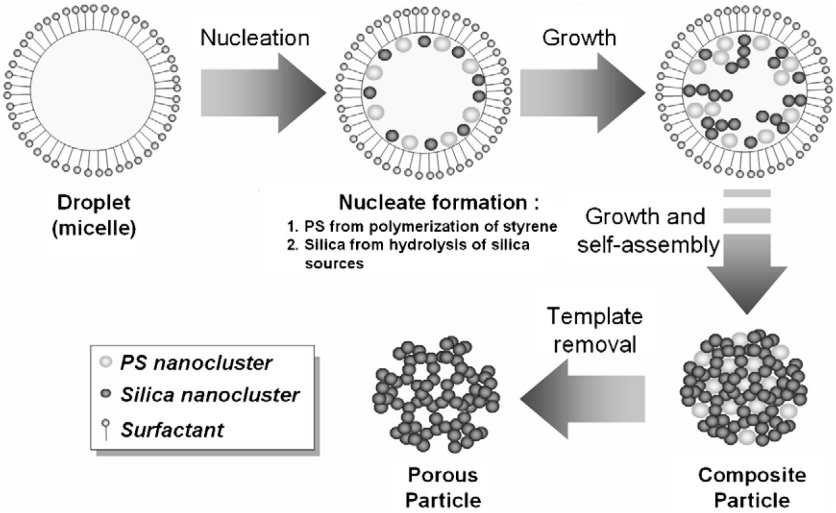

**Fig. 1.** Preparation of mesoporous silica nanoparticles.

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 homogenously 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-methylpropionamide) 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.