



Controlled synthesis of monodispersed mesoporous silica nanoparticles: Particle size tuning and formation mechanism investigation



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ABSTRACT

In this work, systematic studies were performed to investigate the effects of experimental parameters (e.g. reaction temperature, stirring rate and concentration of triethanolamine (TEA)) on the particle sizes of mesoporous silica nanoparticles (MSNs). Results revealed that the stirring rate played a key role in the size-controlling of MSNs. Additionally, both the reaction temperature and the concentration of TEA showed relatively obvious influence on the sizes of MSNs. We supposed that the MSNs particles were formed by the aggregation and condensing of silica-surfactant micelles and the diameters of MSNs were dependent on the concentration of silica-surfactant micelles. In order to obtain MSNs with small sizes, low reaction temperature and rapid stirring rate were adopted to reduce the concentration of silica-surfactant micelles and suppress the growth of MSNs. As a surface capping ligand, TEA could suppress the particle growth and prevent the particle aggregation of MSNs. By simply controlling the synthetic parameters, MSNs with adjustable size from 20 to 110 nm were obtained. Moreover, the obtained MSNs displayed narrow size distribution and well dispersity in water, which made them highly promising in biomedical applications.

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1. Introduction

Since the discovery of ordered mesoporous silica in the 1990s, mesoporous silica nanoparticles (MSNs) have attracted much attention because of their unique mesostructural features, such as high specific surface area, large pore volume, tunable particle size and facile functionalization [1–6]. In particular, the applications of MSNs in biology-relevant fields, including cell imaging, diagnosis, bio-analysis and drug/gene/protein delivery, are highly desirable due to their chemical inertness and excellent biocompatibility [7–10]. In order to realize the applications of MSNs in biology, especially for *in vivo* diagnosis and therapeutics, discrete particle size and excellent dispersity in physiological conditions are critical requirements [11,12]. It's important and urgently needed to synthesize MSNs with controllable particle size and excellent

monodispersity to meet the critical requirements of biomedical applications.

As well documented in previous studies, mesoporous silica could be easily obtained in the presence of assembled cationic surfactant micelle templates, which served as structure-directing agents for polymerizing silica component by electrostatic interaction. Generally, the obtained mesoporous silica displayed micrometer dimension or wide size distribution. In order to get MSNs with smaller diameters and discrete size distribution, efforts should be focused on the restriction of particle growth and the controlling of size distribution. Up to now, several approaches have been developed successfully to synthesize mesoporous silica with controlled particle sizes in the range of tens of nanometers to tens of micrometers by altering some experimental parameters, e.g. reaction temperature, the concentration of surfactants and base, stirring rate, to control the nucleation and growth of MSNs [12–21]. For example, Yu and co-workers have synthesized well-ordered mesoporous silica with diameters ranging from 30 to 500 nm through a surfactant-templating approach [12]. However, this method needed diluted TEOS and low surfactant concentration in ammonia solution, which brought difficulties in products collection

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and extremely low productivity. In addition, MSNs tended to aggregate when their sizes less than 50 nm, which resulted in polydispersity and wide size distribution [18]. Although Ma and co-workers have successfully synthesized monodispersed ultra-small sub-10 nm MSNs, PEG-silane was required and the ultra-low concentration of precursor led to low yields and complex post-treatment process [19,20]. To resolve the issue of agglomeration, diluted concentration of reagent and special silane were frequently adopted in the synthesis of MSNs with small size (below 50 nm), which inevitably resulted in low yields, complicated post-treatment and high cost.

Previously, Bein et al reported that triethanolamine (TEA) can act as a complexing agent for silica-base species, which could affect the nucleation of MSNs and avoid the particle agglomeration [21]. Thus, TEA was applied as a substitute of base catalyst for the hydrolysis of TEOS in this study. In consideration of facile and precisely controlling the particle sizes of MSNs, we conducted systematic studies to investigate the effects of synthetic parameters on the particle sizes of MSNs. Taking the widely applied micelle-templating approaches as example, synthetic parameters (e.g. temperature, stirring rate and concentration of TEA) were varied to control the sizes of MSNs. The diameters of obtained MSNs were varied from 20 nm to 110 nm with narrow size distribution by simply controlling the synthetic parameters without any additional reagents. The obtained MSNs displayed favorable dispersity in aqueous solution without aggregation due to the surface capping of the TEA. Moreover, the formation mechanism of MSNs based on the micelle-templating approach was proposed, and the sizes of MSNs were supposed to be dependent on the concentrations of silica-surfactant micelles.

2. Experimental section

2.1. Chemicals and materials

Tetraethoxysilane (TEOS), ethanol, hydrochloric acid (HCl, 38%), Hexadecyl trimethyl ammonium chloride (CTAC) were purchased from Sinopharm Chemical Reagent Co. Ltd. Triethanolamine (TEA) was purchased from Aladdin Industrial Inc. Deionized water was used in the experiments.

2.2. Synthesis of mesoporous silica nanoparticles

MSNs with controlled particle sizes were synthesized by using cationic surfactants as the structure-directing agent under base conditions. In a typical synthesis process, firstly, 0.5 g CTAC and appropriate amounts of TEA were dissolved completely in 20 mL distilled water at 95 °C under different stirring rate for 1 h. Then, 1.5 mL TEOS was added at a speed of 1 mL/min. After continuous stirring for 1 h, the as-synthesized MSNs were collected by centrifugation at 12,000 rpm for 30 min and then washed with ethanol to remove the residual reactants. To remove surfactants completely, the as-synthesized MSNs were dispersed under ultrasound for 20 min and refluxed in a mixed solution of ethanol (12 mL) and hydrochloric acid (36–38%, 1.5 mL) at 60 °C for 4 h, and then centrifuged and washed several times with ethanol. The same operation was repeated two times. The final product was dried by freeze-drying. MSNs with different particle sizes were synthesized by controlling the reaction temperature, stirring rate and dosage of TEA. Detail synthesis parameters were listed in the Table 1.

2.3. Characterization

TEM images were taken on a Tecnai F20 electron microscope with an acceleration voltage of 200 kV. Hydrodynamic particle sizes

Table 1

Brief summary of the experimental parameters and the corresponding average particle size of the obtained MSNs. (Other synthetic parameters were kept identical: 0.5 g CTAC was dissolved in 20 ml water to prepare the micelle templating solution, and 1.5 ml TEOS was added as silica precursor.)

| No. | Temperature (°C) | Stirring rate (rpm) | TEA (g) | TEM average diameter (nm) |
|---------------|------------------|---------------------|---------|---------------------------|
| MSNs-40 °C | 40 | 700 | 0.06 | 21 ± 3 |
| MSNs-60 °C | 60 | 700 | 0.06 | 27 ± 4 |
| MSNs-80 °C | 80 | 700 | 0.06 | 30 ± 3 |
| MSNs-95 °C | 95 | 700 | 0.06 | 38 ± 4 |
| MSNs-100 rpm | 95 | 100 | 0.06 | 111 ± 13 |
| MSNs-200 rpm | 95 | 200 | 0.06 | 95 ± 10 |
| MSNs-300 rpm | 95 | 300 | 0.06 | 65 ± 6 |
| MSNs-400 rpm | 95 | 400 | 0.06 | 48 ± 5 |
| MSNs-700 rpm | 95 | 700 | 0.06 | 38 ± 4 |
| MSNs-1000 rpm | 95 | 1000 | 0.06 | 38 ± 5 |
| MSNs-0.02 g | 95 | 400 | 0.02 | 57 ± 4 |
| MSNs-0.06 g | 95 | 400 | 0.06 | 48 ± 5 |
| MSNs-0.12 g | 95 | 400 | 0.12 | 46 ± 6 |
| MSNs-0.20 g | 95 | 400 | 0.20 | 41 ± 5 |

and size distributions were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS operated at 25 °C. Each sample was measured three times in DI water. Small angle X-Ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-2000 X-ray powder diffractometer (Japan) using Cu K α (1.5405 Å) radiation. The nitrogen adsorption/desorption isotherms were measured at 77 K using an ASAP 2020 M analyzer. Prior to the measurement, the samples were degassed at 473 K for 400 min. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and the pore size was calculated by the Barrett–Joyner–Halenda (BJH) model.

3. Results and discussion

During the past decades, numerous researches have been conducted on the size controlling of nanoparticle to fully exploit the size-dependent properties of nanomaterials. The appropriate understanding of the growth mechanism has provided useful knowledge to design and tailor particles with smaller size and unique morphologies for a broad range of applications. Chemical synthesis of nanoparticles involved complicate processes, including precursor conversion, nucleation, particle growth, monomer diffusion, etc. Synthesis parameters (such as reaction temperature, concentration of precursors, mixing rate, etc.) could affect more than one processes, and finally display contradictory effects on the particle sizes. Herein, we studied the effects of reaction temperature, stirring rate and the concentration of TEA on the particle size of MSNs systematically. The diameter of the obtained MSNs was observed by TEM and the results were summarized in Table 1. By varying the synthetic parameters, the particle diameters of MSNs can be varied from 20 nm to 110 nm. MSNs with different sizes was further characterization with small-angle XRD, a broad XRD peaks could be observed (Fig. S1). The XRD results demonstrate that the as-prepared MSNs lack a long-range order. The pore structures of the as prepared MSNs were characterized by the N₂ adsorption–desorption isotherms. All the obtained MSNs had similar pore sizes, and the specific surface area and pore volume decreased with the particle sizes of MSNs due to inter-particle space relatively decreased.

As an important parameter in chemical synthesis of nanoparticles, reaction temperature shows obvious impacts on the rates of precursor conversion, nucleation and growth of nanoparticles. Therefore, the temperature effects on the particle size of MSNs were investigated firstly. Fig. 1 shows TEM images of samples

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