Synthesis of Artificial Opals with Uniform Mesoporous Silica Spheres

Chau-Nan Chen, Hong-Ping Lin,* Chih-Pin Tsai,[†] and Chin-Yuan Tang[††]
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 701
[†]*Department of Chemistry, National Taiwan University, Taipei, Taiwan 106*
[††]*Department of Zoology, National Taiwan University, Taipei, Taiwan 106*

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The mesoporous silica submicron-spheres (80–200 nm) with a small dispersion in diameter ($<10\%$) as the building blocks of the artificial mesoporous silica opals have been synthesized using quaternary ammonium surfactant as template in an aqueous solution of suitable polarity at near neutral condition of pH = 7.0–9.0.

Structures containing a three-dimension (3D) ordering of submicron-spheres have several applications in material sciences and optical devices.[1,2] When periodicity occurs in the submicron-size range, these structures demonstrate Bragg diffraction effects of visible light as well as the natural opals.[3] The brilliant colors of the opaline structures occur due to refractive index contrast between the spheres and the interparticle voids. Basically, the fabrication of the opaline structures involves two critical steps: (1) synthesis of monosized spheres, (2) 3D periodic packing. To obtain the highly uniform silica spheres, the well-know Stöber method have been widely utilized.[4–6] Although that method had been applied to synthesize the mesoporous silica spheres in highly alkaline ammonia solution,[7–10] the diameter dispersity of the mesoporous silica spheres is still relatively large. Herein, we propose a new chemical components to prepare the alkyltrimethylammonium surfactant (C_nTMAB, $n = 12$–16)-templated mesoporous silica spheres in a small diameter dispersity ($<10\%$) under a near neutral condition. Because of high uniformity, the mesoporous silica spheres were well-packed into a 3D periodic structure by centrifugation, which shows light-blue color or transparency in wet state regarded as an artificial mesoporous silica opals.

Mesoporous silica spheres in small dispersity were prepared in a dilute aqueous surfactant–silicate solution at 30–40 °C under near neutral-pH condition (pH = 7.0–9.0). Typically, a highly-alkaline sodium silicate solution, prepared from 0.88 g sodium silicate, 0.25 g NaOH, and 200.0 g H_2O, was quickly poured into a clear acidic alkyltrimethylammonium surfactant solution with the components of 1.15 g C_nTMAB surfactant ($n = 12$–16), 0.75 g acetic acid and, 75.0 g H_2O. After that, the pH value of that final solution was adjusted to the desired value in the range of 7.0–9.0 by adding a proper amount of dilute NaOH or acetic acid aqueous solution. The resulting clear solution was stirred for (3–6) h, and then that solution gradually turned to opaque but without precipitations. When using C_nTMAB surfactant with $n > 12$, (50–100) g ethanol was necessarily added to the C_nTMAB surfactant solution for the formation of high-uniformity mesoporous silica spheres. The solid products were recovered under a centrifugation rate of (6000–8000) rpm for (5–10) min. The organic templated was removed via a 560 °C-calcination in air.

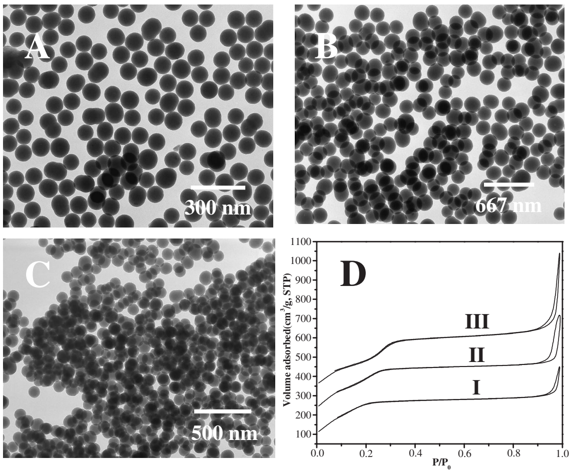

Figure 1. The TEM images and N_2 adsorption–desorption isotherms of the mesoporous silica spheres synthesized from C_nTMAB–sodium silicate–H_2O–ethanol components at different pH value. A. C_{12}TMAB, ethanol/H_2O = 0 g/ 275 g, pH = 8.0, the sphere size = 155 ± 15 nm. B. C_{14}TMAB, ethanol/H_2O = 70 g/275 g, pH = 8.0, the sphere size = 173 ± 17 nm. C. C_{16}TMAB, ethanol/H_2O = 80 g/275 g, pH = 8.0 the sphere size = 117 ± 10 nm, D. N_2 adsorption–desorption isotherms of A–C samples. The pore size analyzed by BJH method of sample A = 1.85 nm (I); the pore size of sample B = 2.30 nm (II); the pore size of sample C = 2.52 nm (III).

Figure 1 shows the representative transmission electron microscopic (TEM) images of the mesoporous silica spheres synthesized with different C_nTMAB surfactant in water-ethanol solution at pH value of 7.0–9.0. It is obvious that the sphere size is uniform. After counting about 100–200 spheres, the calculated deviation of the diameter in each sample is less than 10%. Because the small spheres can induce a large capillary condensation upon drying,[11] the mesoporous silica spheres tend to aggregate together. However, one can clearly see that the distinct sphere and mutually overlapped spheres rather than the apparently interspheres binding (i.e. forming the peanut-shaped particles). To confirm the silica spheres are porous, Figure 1D demonstrates the N_2 adsorption–desorption isotherms of these calcined samples. As the typical mesoporous silicas, the pore size increases with the chain length of the C_nTMAB surfactant, and the BET surface is about 1000 m^2/g. All samples possess the additional adsorption at $P/P_0 > 0.90$, which is ascribed to the textural porosity generated from the inter-aggregations between submicron-sized spheres upon drying.[11] Combining with the results of high-magnification TEM images and XRD patterns, the mesostructure of the mesoporous silica spheres is disorder.

Based on the experimental results, we concluded that the critical criteria to synthesize the uniform-sized mesoporous silica spheres are the highly-alkaline condition (pH > 11.5) and the hydrophobic property of the surfactants in the solution. The high pH value can prevent a fast silicate–surfactant precipitation to nanoparticulates in broad particle-size distribution. For the alkyltrimethylammonium surfactants,[12] the hydrophobicity of the surfactant is dependent both on the surfactant chain length and on the polarity of the solvent. In pure water solution, only the C_{12}TMAB can be used as the template to prepare the mesoporous silica spheres, while using C_{14}, and C_{16}TMAB surfactants gave the nanoparticles in an irregular shape. To reduce the hydrophobicity of the C_{14} and C_{16}TMAB surfactants, a proper amount of ethanol was added into the water as cosolvent to form a lower polarity aqueous solvent, which can lower the hydrophobicity of the surfactant. With a fine-tuning on the solvent polarity and surfactant chain length, the diameter of the mesoporous silica spheres in narrow size distribution increases with the added ethanol amount, and can be controlled within the size range of 80–200 nm. This behavior could be explained by an aggregative growth model in which uniformity in final particle size distribution is determined by inter-particles interaction strength.[13] The detailed study on the size control of the mesoporous silica sphere will be further developed.

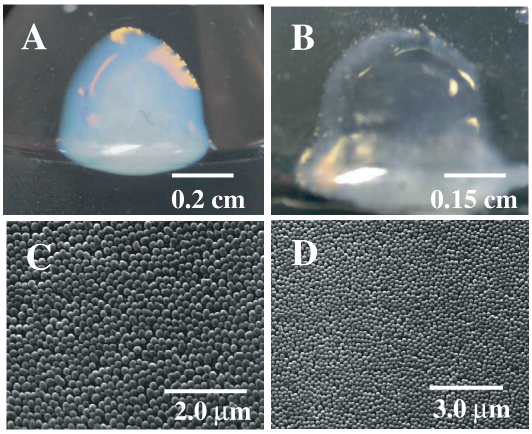

Figure 2. The optical (A, B) and electron-scanning microscopic (C, D) images of the artificial opals with mesoporous silica spheres in different diameter. A. A light-blue opals with mesoporous silica spheres of around 160–180 nm. B. A transparent opals with mesoporous silica spheres of around 100 nm. C. SEM image of the sample A surface. D. SEM image of the sample B surface.

Because the submicron spheres were not easily recovered by filtration, a high-speed centrifugation was usually performed to collect the solid products. Under a centrifugation field, these spheres would be compacted into a smooth and dense sheet attached on the centrifugation tube. It is surprising that a wet mesoporous silica sphere (MSS) sheet, obtained after proper centrifugation of the uniform mesoporous silica spheres with the diameter of about 160–180 nm, shows a brilliantly light-blue (Figure 2A). As the spheres diameter decreases to 100 nm, the wet MSS sheet created becomes transparent (Figure 2B). After drying, both MSS sheets turn to the opaque ones. The brilliant color and transparency can be returned by wetting these dried MSS sheets. With detailed SEM examinations on the surface of the MSS sheets, we found the densely packing of the mesoporous silica spheres (Figures 2C and 2D). Based on the brilliant color of the MMS sheet, the silica spheres were reasonably supposed to be well packed into a 3D periodic structure. As the smooth and shining appearance of the piece, the surface of the MSS sheet is almost crack-free but with some packing vacancy-defects. Based on these results, the opaline structure can be obtained with the uniform-sized mesoporous silica spheres under a proper centrifugation field.[1] Although the diameter-distribution of the mesoporous silica spheres is not as small as those ($<5\%$) in natural opals or artificial silica sphere opals, the uniformity need to be improved for obtaining high-quality artificial opals. To the best of our knowledge, it is first time to synthesize the mesoporous silica artificial opals at around neutral pH. This synthetic process could help ones to understand the growth mechanism of the biological opaline structure.

Here, we tried to theoretically explain the particular behaviors of the artificial mesoporous silica sphere opals. Different form the typical massive silica sphere with a refractive index of 1.46,[14] the mesoporous silica spheres consisted of surfactant and silica would have a refractive index less than 1.46. According to Bragg law, the wavelength of maximum reflected intensity is related to both the diameter of the spheres and the refractive index of the building spheres and voids.[15] Using the mesoporous silica spheres with larger diameter of about 180 nm generated a light-blue colored MSS sheets, which reflects the visible blue-light. In contrast, a transparent MSS sheet reflecting the shorter-wavelength UV light was obtained with spheres of smaller diameter of around 100 nm. After drying, the MSS sheets become opaque. That is because drying would lower the reflective index of the voids (from water ($n = 1.33$) to air ($n = 1.00$)) and increase the extent of light-scattering.

In conclusion, we have proposed a convenient method to obtain the monodispersed mesoporous silica spheres that can be compacted into an artificial opaline structure. Because the mesoporous silica spheres possess the advantages of high porosity and large surface area, the surface property could be tunable by simple surface modifications with different silanes or metal alkoxides to prepare the various refractive index mesoporous silica spheres as new optical materials or sensors. Besides, the nanochannel of the mesoporous silica spheres could be used as a solid host for incorporation with other optical materials to have multi-optical properties.[16]

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