Synthesis of siliceous hollow spheres with large mesopore wall structure by supercritical CO_2-in-water interface templating

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Hollow silica spheres with large mesopore wall structures have been synthesized *via* CO_2-in-water emulsion templating in the presence of PEO–PPO–PEO block copolymers under supercritical fluid conditions.

Hollow spherical materials with ordered pore channels are currently attracting attention due to their potential application in drug-delivery, adsorption, and catalysis.[1] Emulsion templating is a widely used method for the preparation of hollow spherical materials.[2] However, a significant drawback of normal emulsion templating approaches is that large quantities of water-immiscible oil or organic solvent, such as 1,3,5-trimethylbenzene, are required as the internal phase. A further disadvantage of the oil phase is that it is often environment-unfriendly and difficult to remove from the templated material after reaction.[3]

Near critical and supercritical carbon dioxide ($scCO_2$) has been promoted as a suitable replacement of some industrial organic solvents, because it is nontoxic, nonflammable, and naturally abundant.[4] Carbon dioxide has been recently exploited in the preparation of porous materials.[3,5] For example, $scCO_2$ has been used as swelling agent, during the silica hydrolysis process, to tailor the pore size of hexagonal mesoporous silica.[6] Mesoporous silica has also been prepared by pre-organized block copolymer templates dilated with $scCO_2$.[7] Here we describe a novel and efficient synthesis approach to hollow silica spheres which possess large pore mesoporous wall structures *via* templating with CO_2-in-water emulsion under high pressure. Under the high pressure conditions, the CO_2 exists as a supercritical fluid (SCF). It is worth noting that under ambient pressure conditions, hierarchical ordered strings of mesoporous silica spheroids are obtained from CO_2-in-water emulsion systems.[8]

The mesoporous silica hollow spheres were prepared in CO_2-in-water emulsion systems in the presence of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO–PPO–PEO) block copolymers. Firstly, triblock copolymer $EO_{20}PO_{70}EO_{20}$ was dissolved in HCl and deionized water. When the copolymer was fully dissolved, tetraethyl orthosilicate (TEOS) was added under vigorous stirring for 1 min, after which the stirring rate was lowered. The mixture was stirred for a further 10 minutes at room temperature, after which it was transferred to a high-pressure autoclave. The autoclave was heated to 40 °C and pressurized (with CO_2) to a pressure of 200 bar. The autoclave was then hydrothermally treated (at 40 °C) for 45 h under stirring to maintain the CO_2-in-water emulsion. After 45 h, the pressure in the autoclave was reduced slowly. The resulting white powder was recovered by filtration, washed with water and dried in air at room temperature. In order to remove occluded organic species, the dry powder was calcined in air at 500 °C for 6 h to obtain the final silica material.

The scanning electron microscopy (SEM) images in Fig. 1 reveal that the calcined silica samples prepared in the CO_2-in-water system consist of spherical particles that are intact or fractured/broken. The spherical particles have an outer diameter (particle size) of 5–10 μm (Fig. 1). The broken or fractured spherical particles reveal hollow cores indicating that hollow silica spheres are formed from the CO_2-in-water system. The hollow spheres have very thin walls whose thickness appears to be uniform around the shell and smooth outer surfaces. The formation of broken/fractured hollow spheres is probably due to the effects of pressure changes during the pressure release step.

The existence of hollow spheres in the silica prepared from the CO_2-in-water system was also evidenced by transmission electron microscopy (TEM) images as shown in Fig. 2. Spheres with thick edges (outer shells) are clearly observed. The edge thickness contrasts with the core of the spherical particles due to the higher density of the silica outer shell thus confirming that the interior of the spheres is indeed hollow.

The nitrogen sorption isotherm of the calcined silica hollow spheres, shown in Fig. 3, is of type IV and displays a clear hysteresis loop. The sorption isotherm has a broad adsorption–desorption hyteresis loop which is characteristic of mesoporous materials with cage-like pores.[9] The adsorption step at relative pressure (P/P_o) between 0.6 and 0.9 indicates the presence of

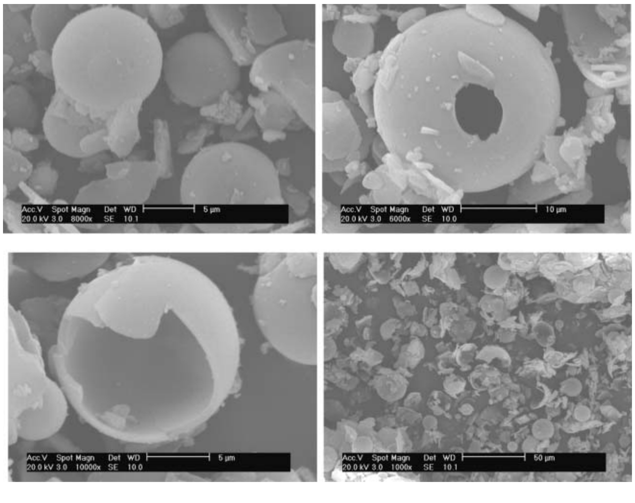

Fig. 1 Representative SEM images of calcined silica hollow spheres.

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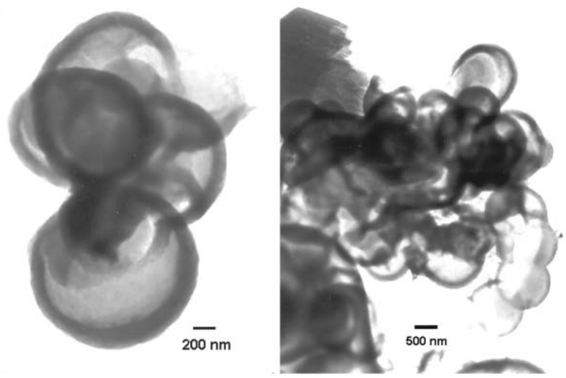


Fig. 2 Representative TEM images of calcined silica hollow spheres.

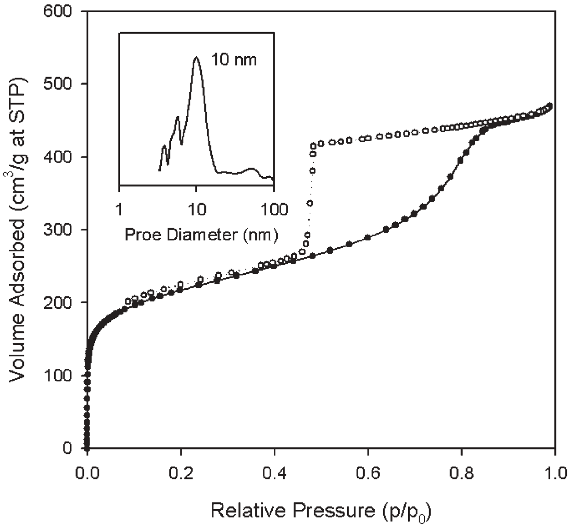
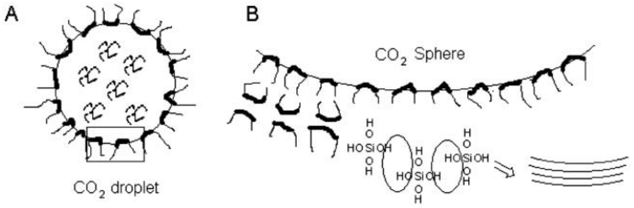


Fig. 3 Nitrogen adsorption (●) and desorption (○) isotherm curves and pore size distribution curve (inset) of calcined silica hollow spheres.



Scheme 1 (A) The CO_2 drops in the CO_2-in-water emulsion containing dissolved TEOS; the emulsion is stabilized by the surfactant at the interface; thick lines represent the CO_2-philic PPO moiety while thin lines represent the hydrophilic PEO moiety. (B) At the interface [boxed area in (A) expanded], TEOS is hydrolyzed and solidified to form mesopores. The morphology of the final product is more or less molded on the original CO_2 droplet.

mesopores with a relatively narrow pore size distribution. The silica spheres had a surface area of 700–800 m^2 g^{-1} and a pore volume of 0.7–0.8 cm^3 g^{-1}; these textural properties are typical for well-ordered mesoporous silicas.[9,10] A large mesopore average pore diameter of *ca.* 10 nm was calculated from BJH analysis of the adsorption isotherm. It is worth noting that a pore size of between 4 and 6 nm is usually observed for mesoporous silicas (*e.g.*, SBA-15) templated with block copolymers under synthesis conditions similar to those used here but in the absence of $scCO_2$. This suggests that the $scCO_2$ played a significant role as a swelling agent that caused pore expansion in the mesostructured hollow silica. We note that similar $scCO_2$-induced pore size expansion in mesoporous silicas has previously been reported.[6]

In our method, the surfactant is the most important factor for the successful synthesis of hollow silica spheres with *mesoporous* wall structure; PEO–PPO–PEO triblock copolymer is a good structure-directing agent for the synthesis of highly ordered mesoporous silicas.[10] The copolymer family of surfactants is also known to form CO_2-in-water and water-in-CO_2 emulsions under high pressure.[11] In such cases, the poly(propylene oxide) block is CO_2-philic and the poly(ethylene oxide) block is CO_2-phobic. CO_2/water emulsion systems have been used as templates for the preparation of well-defined porous polymers *via* polymerization.[12] Silica precursors, such as TEOS, have high solubility in $scCO_2$ because the silicone group is CO_2-philic.[13] Based on the known chemical interactions between copolymer surfactants, CO_2 and TEOS, we propose the mechanism illustrated in Scheme 1, which is based on an emulsion templating pathway, for the formation of the large pore hollow silica.

In Scheme 1, we propose that under our synthesis conditions, TEOS was dissolved in CO_2 and the CO_2-in-water emulsion generated by stirring. The concentration of the block copolymer surfactant was enriched at the CO_2–water interface thus stabilizing the CO_2-in-water emulsion droplet. The PEO–PPO–PEO triblock copolymers formed lamellar vesicles with the CO_2-philic PPO blocks shielded from the aqueous phase by hydrophilic PEO blocks protruding out from the vesicle wall on both sides.[2c] However, in the CO_2-in-water system, CO_2 was adsorbed into the polymer core of the surfactant micelle thus causing expansion and hence an increase in pore size.[7] The TEOS was hydrolyzed in the prevailing acidic conditions at the interface and formed the mesostructure under the influence of the surfactant (Scheme 1B). During the pressure release step, any CO_2 trapped in the siliceous hollow spheres escaped through the porous wall or by fracturing the spherical shells.

In conclusion, hollow silica spheres with large mesopore wall structures have been synthesized *via* CO_2-in-water emulsion templating in the presence of PEO–PPO–PEO block copolymers. The technique presented here adds a new dimension in the application of supercritical fluids in material processing. The ability to tune the solvent (SCF) properties by varying the pressure enables control of the pore size and morphology. Hollow spheres of mesoporous silica are likely to find application in catalysis, adsorption and drug delivery.

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