# Synthesis of Highly Uniform Mesoporous Sub-Micrometric Capsules of Silicon Oxycarbide and Silica

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The synthesis of uniform hollow spherical materials in the sub-micrometric size range has attracted widespread attention because they offer the possibility of encapsulating a variety of substances (i.e., drugs, catalysts, enzymes, dyes, etc.) within their macroporous core. Such core/shell composites have enormous potential as drug storage and delivery carriers[1] or as high-performance catalysts.[2]

Various synthetic methods have been reported for the fabrication of carbon,[3] metal,[4] inorganic,[5] and polymeric[6] hollow materials. As a result of their high thermal, chemical, and mechanical stability spherical hollow materials with a silica framework have generated special interest.[7] The applicability of such materials is enhanced when they are of uniform size within the sub-micrometric size range (<500 nm) and the shell contains penetrating pores that guarantee the facile transport of species between the core and the outside of the capsules. However, the preparation of uniform spherical porous silica capsules in the sub-micrometric size range is not easy. Indeed, although a large number of procedures for synthesizing silica hollow particles have been reported, only a few of them lead to porous silica capsules of a uniform size below 500 nm. The procedures usually employed to synthesize hollow silica particles with the above-mentioned characteristics are based on the polymerization of silica precursors (i.e., tetraethoxysilane), in the presence of surfactants, on the surface of polyestyrene spherical nanoparticles, followed by calcination.[8] This synthetic strategy involves complex steps that include the synthesis of uniform polyestyrene spherical latexes and their surface functionalization. Thus, the development of simpler synthetic routes toward uniform porous silica capsules is still an important challenge. Accordingly, in the present work we report a simple and novel method to synthesize uniform sub-micrometric spherical silica capsules with a hollow macroporous core and a porous shell structure. This synthetic scheme allows uniform hollow porous capsules of silicon oxycarbide (SOC) to be obtained. To the best of our knowledge, this is the first time that the fabrication of porous capsules of SOC has been reported.

Sub-micrometer-size solid core/mesoporous shell (SCMS) silica particles were prepared as reported by Unger et al.[9] (see Figure S1 in Supporting Information for the structural characteristics of SCMS particles). In a typical synthesis, 0.5 g of polycarbomethylsilane (PCMS, FW 800, Aldrich) was dissolved in xylene (10 mL). A total of 2.5 g of SCMS particles were then added to the solution, and the mixture was magnetically stirred in a closed vessel, under $N_2$ atmosphere, for 2 h. Next, the solvent (xylene) was evaporated under a nitrogen flow at room temperature. The PCMS/SCMS composite obtained was heated under $N_2$ according to the following program: (i) at a heating rate of 3 K·min$^{-1}$ up to 100 °C (4 h), (ii) 2 K·min$^{-1}$ up to 200 °C (5 h), and (iii) 2 K·min$^{-1}$ up to 1000 °C for 2 h. To dissolve the silica template, the samples were treated with hydrofluoric acid (40%). The resulting material consisted of porous SOC capsules, which were converted into silica capsules by means of a simple heat treatment in air at 700 °C. The synthetic scheme employed to obtain these porous SOC and silica capsules is illustrated in Figure 1.

Elemental analysis of the product obtained after the removal of the silica framework in the pyrolyzed PCMS/SCMS composite was performed by using a microanalyzer for C and H (Leco CHNS-932) and by means of a thermogravimetric analyzer for Si (see Figure S2 in Supporting Information for details). The sample contained Si, C, H, and O in the following amounts (wt %): Si, 28.1; C, 34.3; H, 3.2; and O (by diff.), 34.4. The empirical formula deduced for this material is $SiC_{2.9}H_{3.2}O_{2.2}$. Taking into account that this product was obtained after the HF etching, it is obvious that it does not contain silica. It should therefore

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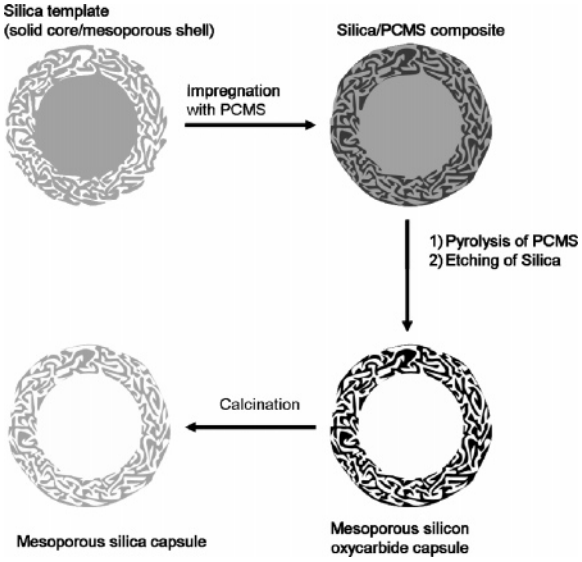


**Figure 1.** Illustration of the synthesis procedure used for mesoporous SOC and silica capsules.

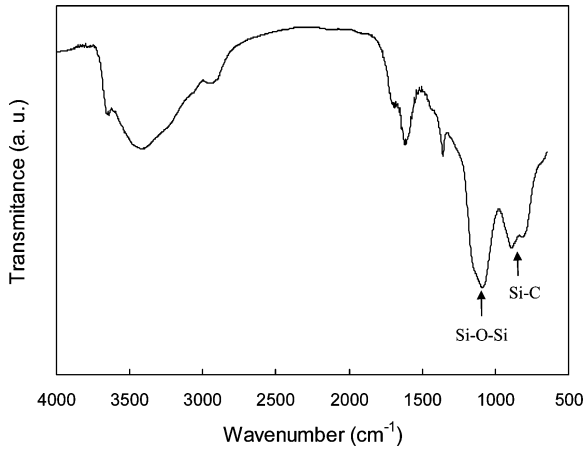


**Figure 2.** FTIR spectrum of the SOC sample.

be considered a SOC compound rather than a silica−carbon nanocomposite. This is confirmed by the Fourier transform infrared (FTIR) spectrum obtained for this sample (Figure 2), which shows two main peaks due to the inorganic structure, one at ∼1100 $cm^{-1}$ attributed to Si−O−Si bonds and the other at ∼850 $cm^{-1}$ assigned to Si−C bonds.[10] The scanning electron microscopy (SEM) images obtained for the SOC sample reveal that it is made up of very uniform microspheres with a diameter of ∼350−400 nm (Figure 3a). During the removal of the silica, a certain degree of shrinkage takes place as deduced by comparing the diameter of SOC particles with that of the pyrolyzed PCMS/SCMS material (diameter: ∼500 nm, see Figure S1c in Supporting Information). These microspheres exhibit hollow cores as is clearly shown by the TEM images in Figure 3b,c. The diameter of the macroporous core is around 270−320 nm. The shell of these capsules, which has a thickness of ∼40 nm, contains confined pores, as evidenced by the high-magnification transmission electron microscopy (TEM) image showed in Figure S2a (Supporting Information). The textural characteristics of these SOC porous capsules were examined by means of nitrogen sorption isotherms and pore size distribution (Figure 4). It can be seen that there is a large nitrogen uptake for $p/p_0 > 0.8$, revealing a large textural porosity related to the interparticle voids between the hollow particles. This material has a large BET surface area of 660 $m^2 \cdot g^{-1}$ and a high pore volume of 0.72 $cm^3 \cdot g^{-1}$ (0.34 $cm^3 \cdot g^{-1}$ corresponding to the shell-confined pores as can be deduced from the $\alpha_s$-plot analysis of the adsorption branch). Moreover, the porosity is made up mesopores with a size in the ∼2−10 nm range being the maximum centered at 3.4 nm (see Figure 4, inset).

When the SOC sample was heat treated in air at temperatures up to 700 °C, the SOC decomposed and the color of the sample changed from brown to white. A significant weight loss occurred during this process as illustrated in

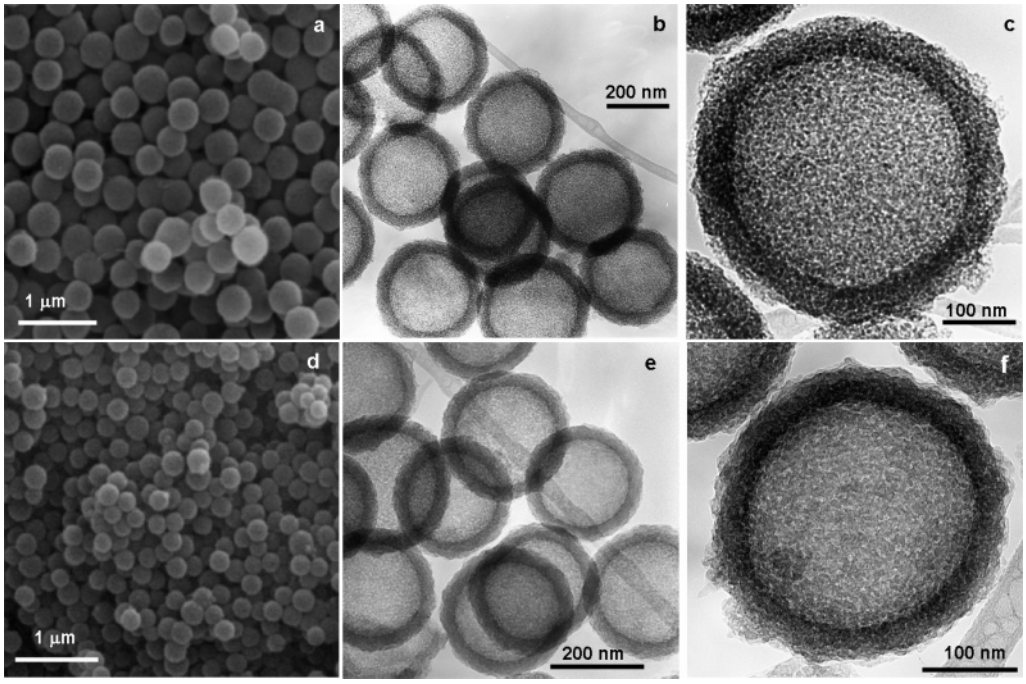


**Figure 3.** SEM and TEM images obtained for SOC (a, b, and c) and silica (d, e, and f) capsules.

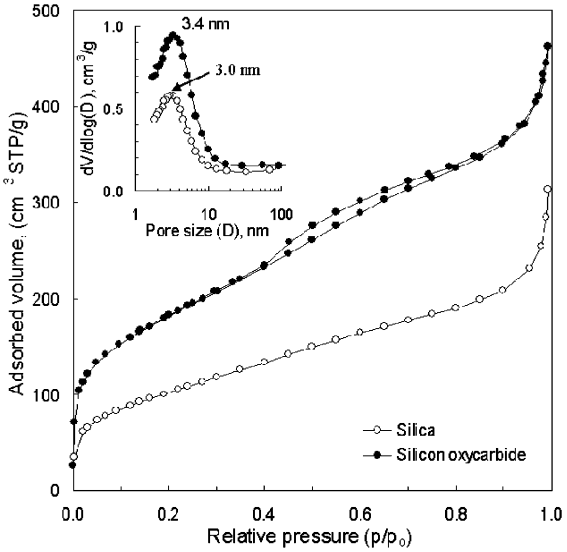


**Figure 4.** Nitrogen sorption isotherms and pore size distributions (inset) of the SOC and silica capsules.

Figure S3 (Supporting Information) which shows the variation in the weight of the sample and the rate of weight loss with temperature. The weight loss (∼40%) mainly takes place in the temperature range of 300−700 °C as can be deduced from the variation in the rate of weight loss with temperature. Energy-dispersive X-ray spectroscopy (Figure S4 in Supporting Information) reveals that the white product obtained after the calcination of the SOC sample is silica. The complete removal of the carbon present in the SOC sample was verified by the elemental analysis of calcined product. This silica sample consists of spherical hollow particles of a very uniform size as evidenced by the SEM (Figure 3d) and TEM images in Figure 3e,f. Comparison of the images for the SOC sample (Figure 3a−c) with those obtained for the silica capsules (Figure 3d−f) shows that during the calcination step a shrinkage of the hollow particles took place. Thus, the silica capsules have a diameter of ∼250−300 nm, which is smaller than that of the hollow SOC particles (∼350−400 nm). The shell thickness for both types of capsules is similar (∼40 nm). Like the SOC capsules, the shell of the silica capsules also contains penetrating pores, which connect the macroporous core with the outside of the capsule. These pores are illustrated in the high-magnification TEM image shown in Figure S2b (Supporting Information). Figure 4 shows the nitrogen sorption isotherm and the pore size distribution (Figure 4, inset) obtained for the silica capsules. This material has a BET surface area of 370 $m^2 \cdot g^{-1}$ and a total pore volume of 0.49 $cm^3 \cdot g^{-1}$, the volume of the shell-confined pores being ∼0.2 $cm^3 \cdot g^{-1}$. The porosity of the shell structure is made up of mesopores (∼2−10 nm) with a size centered at around 3 nm (see Figure 4, inset).

In summary, we have illustrated a nanocasting route for successfully fabricating very uniform SOC and silica capsules with a structure consisting of a hollow macroporous core and a mesoporous shell. The procedure employed is based on the impregnation of sub-micrometer-size SCMS silica particles with a preceramic polymer (PCMS). The pyrolysis and subsequent etching of the silica template allows mesoporous silicon oxycabide capsules to be synthesized. Capsules with a silica framework were also obtained after the calcination of the SOC hollow particles. Both types of capsules exhibit very uniform diameters, which are ∼350−400 nm for SOC and ∼250−300 nm for silica. The shell of these hollow particles has a thickness of ∼40 nm, and it contains penetrating mesopores (∼2−10 nm), which are important for the transport of species between the inner macroporous core of the capsule and the outside.

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**Supporting Information Available:** Physical properties of the sub-micrometer-size SCMS silica particles, high-magnification TEM images of hollow particles, thermogravimetric experiments of calcination of SOC, and energy-dispersive X-ray (EDX) spectrum for the silica sample (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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