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Synthesis and characterization of multi-wall silica nanospheres

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Abstract

Multi-wall silica nanospheres have been synthesized from non-ionic surfactant, and TEOS as precursor under acidic and reflux conditions. The wall-to-wall distance inside the “onion-like” texture is close to 10 nm while the nanoscale objects depict polydisperse particle sizes ranging from 80 to 300 nm. Nitrogen physisorption measurement demonstrates a Brunauer-Emmet-Teller (BET) surface area of 691 m² g⁻¹ associated to a total pore volume of 0.8 cm³ g⁻¹.

Keywords: Silica; Mesoporous; Nanoparticles; Morphosynthesis; Sol-gel

1. Introduction

Mesostructuration of inorganic materials is today a rather well established method [1]. To achieve both a higher degree of control and a hierarchically organized texture, mineralization can be confined at macroscopic interfaces as demonstrated by the on-growing field of bio-inspired materials [2]. In such context two main routes can be extracted. The first one makes the use of macroscopic pattern via metastable thermodynamic systems (emulsions [3], reverse emulsions [4] and air-liquid foams [5]) whereas the other one is still based on mesoscopic supramolecular templating approaches where the inorganic texturation extends to higher length scales. Those strategies are both leading to the newly chemistry of shapes concept or synthesis over all length scales [6]. In this last issue multi-wall silica nanospheres have been synthesized in aqueous acidic conditions by using a Pluronic P123 (EO20-PO70-EO20) solution in the presence of 1,3,5-trimethylbenzene

(TMB), general procedure already mentioned to produce mesocellular siliceous foams [7].

2. Experimental

2.1. Synthesis

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without purification. 1,3,5-Trimethylbenzene (TMB) has been kindly provided by BASF. Tetraethoxy-orthosilane (TEOS) was purchased from Aldrich.

In a typical synthesis, 4 g of P123 is first mixed with distilled water (105 ml) then 19.5 ml of HCl (37%) is added to the aqueous phase. In a second step, this mixture is brought to 35 °C and let under agitation to complete polymer dissolution. In a third step, 0.8 g (930 ml) of TMB and then 8.6 g of tetraethoxy-orthosilane (TEOS) are added to the polymeric aqueous solution. For this specific condition, the ratio TMB/P123 is equal to 0.2. It is important to note that an increase or decrease of the TMB amount does not induce any more this “onions” texturation discussed in this work, but rather promote two dimensional lyotropic organization (TMB/P123=0.05) at lower ratio

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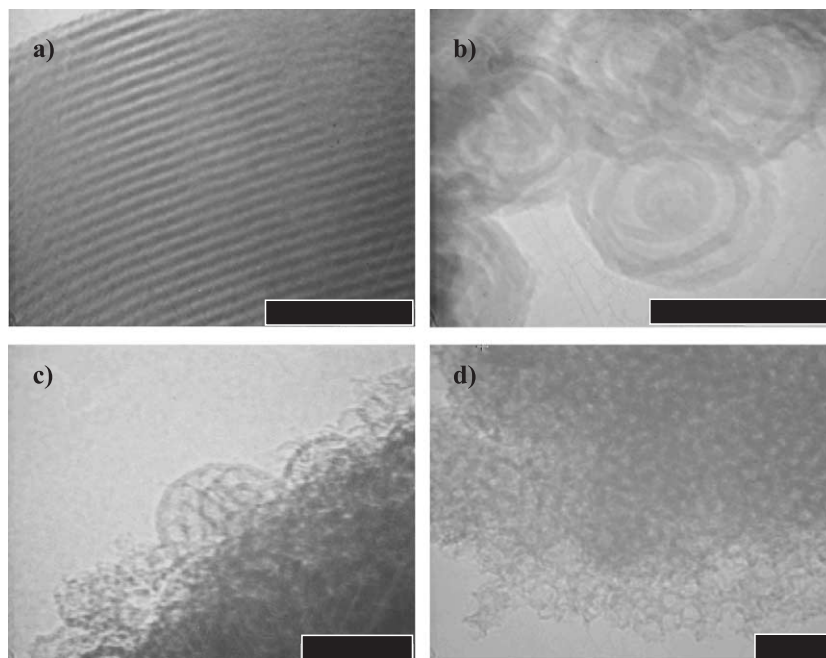


Fig. 1. TEM pictures of the compounds mesoscale organization. (a) TMB/P123 ratio of 0.05, (b) TMB/P123 ratio of 0.2, (c) TMB/P123 ratio of 0.5 and (d) TMB/P123 ratio of 1. The scale bars represent 100 nm.

whereas for higher ratio (TMB/P123=1) the texturation is closed to previous study on mesocellular siliceous foams [7]. Those mixtures are then let under reflux during a 24 hours period. Final powders are recovered by filtration and washed three times with tetrahydrofuran (THF). Finally those objects are calcinated at 600 °C in order to remove the organic part.

2.2. Characterization

TEM experiments were performed with a Jeol 2000 FX microscope (accelerating voltage of 200 kV). The samples were prepared as follows: silica scaffolds in a powder state were deposited on a copper grid coated with a formvar/carbon membrane. SEM observations were performed with a Jeol JSM-840A scanning electron microscope operating at 10 kV. The specimens were

gold-coated or carbon-coated prior to examination. Surface areas and pore characteristics at the mesoscale were obtained with a Micromeritics ASAP 2010 employing the Brunauer-Emmett-Teller (BET) method. X-ray diffraction experiments were carried on a 18 kW rotating anode X-ray source (Rigaku-200) with use of Ge (111) crystal as monochromator. The scattered radiation was collected on a two dimensional detector (Imaging Plate system from Mar Research, Hamburg). The sample-detector distance was 500 mm.

3. Results and discussion

As discussed in the synthetic part, the mesoscale textures are strongly related to the amount of TMB employed during the procedures (Fig. 1).

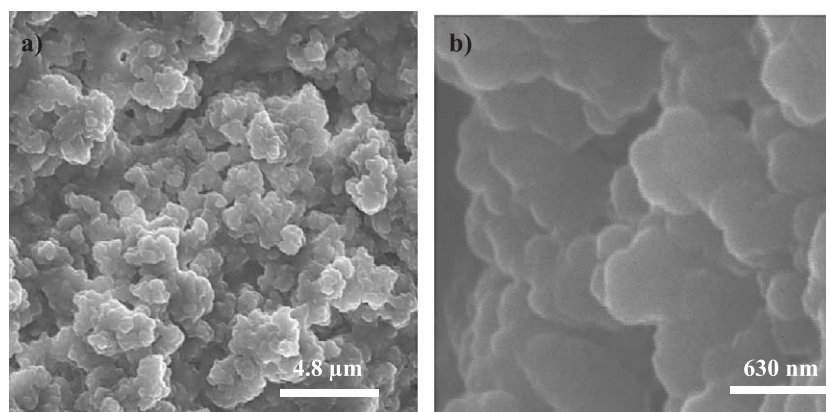


Fig. 2. SEM pictures of the as-prepared materials with a TMB/P123 ration of 0.2.

These differences in topology suggest a synergistic effect between the TMB and the P123 lyotropic mesophases, interaction certainly disturbed by the sol reflux constraint. We do not recover the highly organized mesocellular foam previously observed [7] where the reflux is not employed during the synthesis procedures. Textures observed for the TMB/P123 ratio different from 0.2 do not offer new insight in siliceous mesoscopic organization and are not associated to a specific shape at the nanoscale. This is the reason why this study is especially dealing with the materials obtained with a TMB/P123 ratio of 0.2. The hybrid materials obtained with this specific TMB/P123 ratio of 0.2 depict spherical shapes and a polydisperse nanoscale size (Fig. 2).

To remove the organic supramolecular-type templates, the hybrid organic–inorganic materials were treated at 650 °C during a period of 6 h. The heat rate was monitored to 2 °C/min with a first plateau at 200 °C during 2 h. The cooling process was uncontrolled and directed by the oven inertia. The texture of those inorganic objects has been observed by TEM (Fig. 3). With those TEM micrographs, performed on calcined samples, we can observe the multi-wall texture that resembles the “onion-like” lyotropic mesophases obtained within high surfactant concentration conditions upon a shear flow [8]. With the TEM micrograph we can consider that the wall-to-wall distance is closed to 10 nm.

In order to better quantify this evaluation we did perform small angle X-ray diffraction profile experiments (Fig. 4). The scattering curves exhibit a large peak at about 0.048 Å⁻¹ (12.5 nm) for the hybrid organic–inorganic materials (Fig. 4a) that shifts to 0.055 Å⁻¹ (11 nm) after the calcination treatment (Fig. 4b). This peak is in good agreement with wall-to-wall distance extracted from the TEM observation and the shift of the d-spacing (from 12.5 to 11 nm) induced

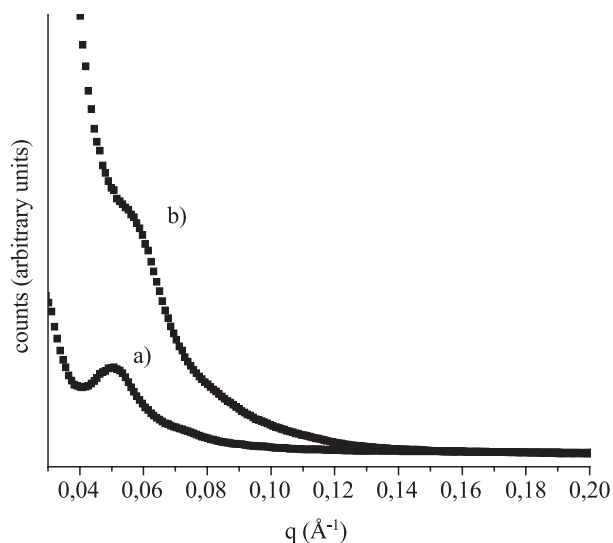


Fig. 4. Small angle X-ray diffraction patterns (a) before calcination, (b) after calcination.

by the calcination treatment is associated to the inorganic core sintering effect [9]. It is worthwhile to notice that the starting acidic pluronic-TMB solution does not depict the X-ray diffraction profile signature of this nanoscale organization, meaning that the multi-wall texture observed within the solid state materials is induced by a non-direct morphosynthesis between the organic template and the mineralization process. If we consider Fig. 3d (see black arrow) we can hypothesize that the first silica spinning clusters locally increase the non-ionic surfactant concentration, which process is commonly admitted for mesoscale micellar templating texturation or structuration [9]. Beyond this synergy effect between the organic and inorganic

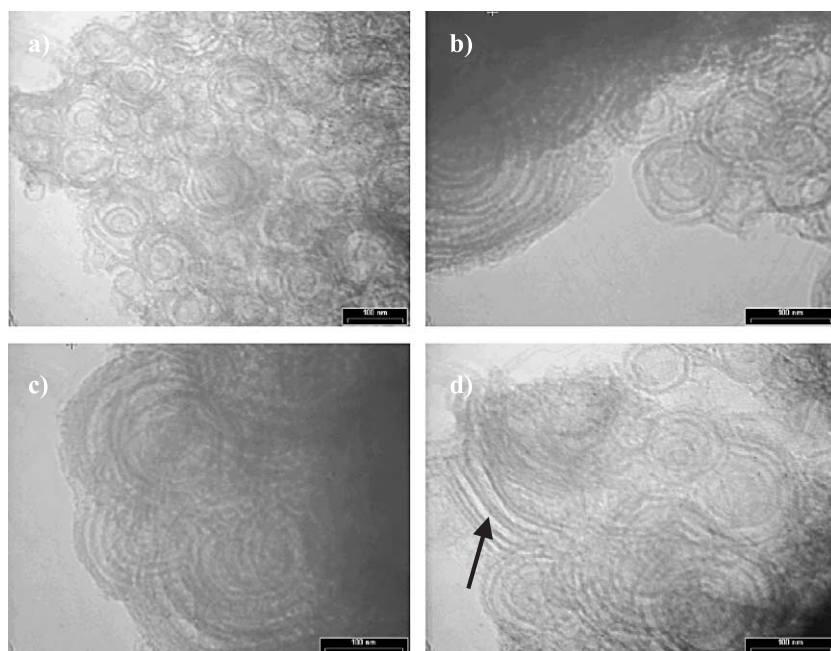


Fig. 3. TEM micrographs of the silica multi-wall nanospheres. The scale bars represent 100 nm.

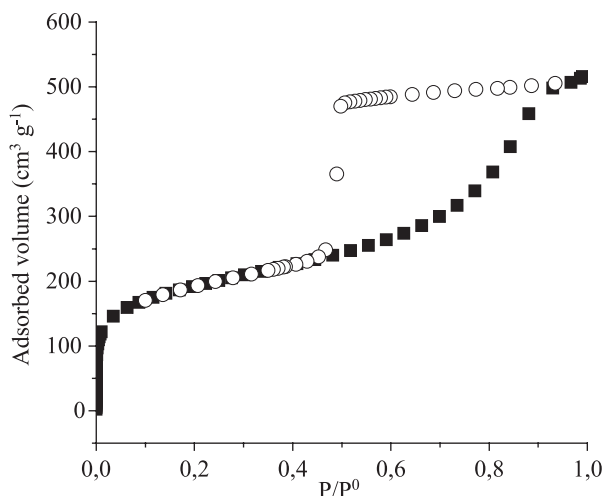


Fig. 5. Nitrogen adsorption and desorption isotherms of the multi-wall silica nanospheres, ■ adsorption curve, ○ desorption curve.

growing phases, the aqueous shear flow induced either by the stirring bar or the reflux convection flow during the synthesis, might promote the “onion-like” texture in the same way that it does for the typical organic lyotrope “onion-like” mesophases texturation [8], in this context the TMB is certainly present within the hydrophobic part of the multilamellar vesicles.

Also, taking into account both TEM and SAXS experiments we do not observe any void spaces within the walls of those nanoscopic objects associated with any kind of porous meso-structuration signature. The main emerging porosity should be induced by silica amorphous character, namely intra-walls microporosity. To quantify this porosity we did perform N₂ adsorption-desorption experiments (Fig. 5).

For the silica multi-wall nanospheres N₂ adsorption at 77 K rises slowly in the relative pressure range (0.1–0.8) followed by a strong additional nitrogen adsorption at higher relative pressure values above 0.7 (Fig. 5). An hysteresis loop can be observed between the adsorption and desorption curves, above relative pressure of 0.5 and up to 1.0. Overall, the N₂-adsorption measurements performed at 77 K reveal a composite type I+type IV isotherm shape [10], including both micro- and mesoporosity. The Brunauer-Emmet-Teller (BET) surface area and total pore volume were estimated to be 691 m² g⁻¹ and 0.8 cm³ g⁻¹, respectively. The microporous character of the sample was assessed by nitrogen t-plot analysis, which leads to a microporous surface and volume of about 310 m² g⁻¹ and 0.13 cm³ g⁻¹, respectively. The BJH adsorption and original density functional theory pore size distributions are rather broad and furnish a mean pore diameter of about 10 nm. Furthermore, the BJH adsorption cumulative surface area of pores taking into account only pore diameters larger than 25 Å and up to 500 Å reports a surface area of 260 m² g⁻¹.

Consequently, the origin of the mesoporosity observed can be rationalized as the inter-walls space. This result is consistent both with the TEM photographs which shows inter-walls distance of about 10 nm (Fig. 3) and SAXS measurement that confirms this value (Fig. 4).

In conclusion, we have synthesized for the first time, using a sol-gel process and lyotropic templates associated to 1,3,5-trimethylbenzene, multi-wall silica nanospheres associated to intra-walls microporosity and inter-walls mesoporosity. Extension of this work towards other metal oxide materials, more precisely to TiO₂ and ZrO₂, is underway and will be published in due time.

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References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710; J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, et al., *J. Am. Chem. Soc.* 114 (1992) 10834.
- [2] S. Mann, *Nature* 332 (1988) 119; D.D. Archibald, S. Mann, *Nature* 364 (1993) 430; P. Feng, X. Bu, G.D. Stucky, D.J. Pine, *J. Am. Chem. Soc.* 122 (2000) 994; H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, G.A. Ozin, *Nature* 379 (1996) 703.
- [3] a) A. Imhof, D.J. Pine, *Nature* 389 (1997) 948; S. Schacht, Q. Huo, I.G. Voigt-Martin, G.D. Stucky, F. Schüth, *Science* 273 (1996) 768; b) F. Carn, A. Colin, M.-F. Achard, M. Birot, H. Deleuze, R. Backov, *J. Mater. Chem.* 14 (2004) 1370.
- [4] G. Fornasieri, S. Badaire, R. Backov, O. Mondain-Monval, C. Zakri, P. Poulin, *Adv. Mater.* 16 (2004) 1094.
- [5] F. Carn, A. Colin, M.-F. Achard, H. Deleuze, R. Backov, *Adv. Mater.* 16 (2004) 140.
- [6] S. Min Yang, I. Sokolov, N. Coombs, C.T. Kresge, G.A. Ozin, *Adv. Mater.* 11 (1999) 1427; G.A. Ozin, *Chem. Commun.* (2000) 419; S. Mann, G.A. Ozin, *Nature* 382 (1996) 313.
- [7] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, D.G. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [8] O. Diat, D. Roux, F. Nallet, *J. Phys. II* 3 (1993) 1427; D. Roux, T. Gulik, J. Dedieu, C. Degert, R. Laversanne, *Langmuir* 12 (1996) 4668.
- [9] C.J. Brinker, G.W. Scherer, *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*, Academic Press, San Diego, 1990.
- [10] a) P.A. Webb, C. Orr, *Surface area and pores structure gas adsorption*, Analytical Methods in Fine Particles Technology, Micromeritics, 1997; b) F. Rouquerol, J. Rouquerol, K. Sing, *Adsorption by Powders and Porous Solids*, 1999 Academic Press, London, p. 204.