

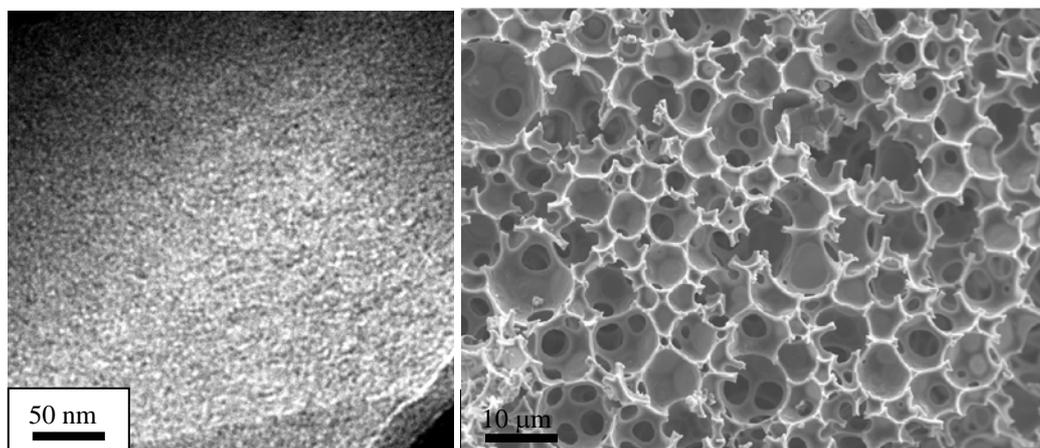
PREPARATION OF MESO/MACROPOROUS SILICA IN HIGHLY CONCENTRATED EMULSIONS BY SINGLE-STEP METHODS

J. Esquena^{}, J. Nestor, C. Solans*

*¹Institut d'Investigacions Químiques i Ambientals de Barcelona (IIQAB)
Consejo Superior de Investigaciones Científicas (CSIC)
Jordi Girona, 18-26, 08034 Barcelona*

() E-mail: jemqci@iiqab.csic.es*

The main objective of the present research has been to study the preparation of silica materials with high pore volume and high specific surface area. This can be achieved by reactions in the continuous phase of highly concentrated emulsions to obtain dual meso/macroporous materials. Such emulsions possess volume fractions of the dispersed phase higher than 0.74, which is the critical value of closed-packed monodispersed undeformed droplets [1-2]. Consequently, highly concentrated emulsions have a foam-like structure that consists of deformed and/or polydispersed droplets, separated each other by a thin film of continuous phase [1-3], and the content of the dispersed phase can be very large, as much as 99.5 %. Therefore, highly concentrated emulsions are very interesting media to be used as templates for the preparation of solid materials because dual meso/macroporous materials, with very high pore volume, can be obtained by carrying out reactions in its continuous phase. The meso/macroporous dual materials combine the advantages of high specific surface, due to the presence of mesopores, with the accessible diffusion pathways associated with macroporous structures [3-5]. Therefore, these meso/macroporous materials are very appropriate in applications with macromolecules (enzymes, polymers, etc.), because they have higher pore volumes than zeolite-type materials. In our first studies, materials with dual meso/macroporous structures were successfully obtained, in a two-step process, by polymerizing in highly concentrated emulsions to obtain polystyrene solid foams [6], which were later impregnated with inorganic precursor solutions containing block copolymer surfactants to form the mesopores [7]. However, in industrial applications it is also very important to obtain such materials by simple and cost-effective methods. Recently, silica materials with dual meso/macroporous structures were obtained, directly in a simple single-step process, by polymerizing tetraethyl orthosilicate (TEOS) in O/W highly concentrated emulsions where the continuous phase was a cubic liquid crystal, which allowed obtaining high specific surface areas. However, TEOS generates ethanol as a by-product, which affects considerably the emulsion stability and the structure of the continuous phase. More recently, meso/macroporous silica has been obtained in a single-step process in highly concentrated emulsions, by using new silica precursors that does not generate any type of alcohol, and the original structure of the emulsions is preserved during the reactions. Surfactant composition has been optimized in order to prepare highly concentrated emulsions with enough stability to carry out the reactions of silica formation. The results show that porous silica with dual meso/macroporous structure is obtained, with relatively small concentrations of surfactant and high specific surface areas can be achieved.



(a)

(b)

Fig. 1. Examples of TEM (a) and SEM (b) images of a dual meso/macroporous material, in which mesopores (a) and macropores (b) are visible at different magnifications.

References:

- [1] K. L. Lissant, *J. Colloid Interface Sci.*, 1966, 22, 462-468.
- [2] C. Solans, R. Pons, H. Kunieda, In: *Modern Aspects of Emulsion Science*; B. P. Binks, Ed.; The Royal Society of Chemistry: Cambridge, UK, 1998; pp 367-394.
- [3] C. Solans, J. Esquena, N. Azemar, *Current Opinion in Colloids and Interface Sci.* 8 (2003), 156.
- [4] G. J. Soler-Ilia, E.L. Crepaldi, D. Grosso, C. Sanchez, *Current Opinion in Colloid and Interface Science*, 8, 2003, 109.
- [5] J. Esquena, C. Solans, In: *Emulsions and Emulsion Stability*; J. Sjöblom, Ed.; Taylor and Francis, New York, 2006.
- [6] J. Esquena, G.S.R.R. Sankar, C. Solans, *Langmuir* 19 (2003), 2983.
- [7] H. Maekawa, J. Esquena, S. Bishop, C. Solans and B.F. Chmelka, *Adv. Mater.* 2003, 15, 591.