TWO DIFFERENT APPROACHES FOR THE SYNTHESIS OF ORDERED MESOPOROUS SILICA NANOPARTICLES WITH TUNABLE DIAMETER AND PORE SIZE

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Abstract

Two combined approaches of Stöber method and supramolecular assembly of surfactant molecules, under assistance of different organic solvents, have been exploited for the synthesis of ordered MSNs with spherical morphology between 60- 200nm and pore size from 2.7 to 8nm.

Keywords: Mesoporous silica nanoparticles; Stöber method; micelle; CTAB

Mesoporous silicas prepared by the synthesis of supramolecular assembly of molecules by means of surfactants, as templates, have been extensively studied due to their large surface area and uniformity of pore size, as adsorbents, catalysts and nano-reactors. The morphology of these mesoporous materials is a very important issue for their practical application. In fact, this type of material has a network of well-defined channels of nanoscale dimensions (2-50nm). The use of surfactant molecular aggregates, as micelles organized in an orderly fashion, it is known since the early '90s and has been developed by researchers at Mobil Oil Corporation [1] for the preparation of silica and mesoporous ordered silica-alumina. These materials have the characteristic of possessing, in addition to a large surface area created by channels of variable size, reactive surface silanol groups. This particular architecture with the presence of Si-OH groups makes them suitable candidates to host, a variety of organic or inorganic molecules.

An example is the use of porous silicas as matrices for the gradual release of drugs or cosmetics. The silica, SiO_2, is not only atoxic and biocompatible but also the elimination of the matrix is not dangerous for the organism. The drug, after being adsorbed inside the silica matrix, may be issued only in a specific area, depending on conditions such as pH, temperature, and avoiding the potentially harmful contact, among the drug and not involved tissues. The size and morphology of these MSNs is of paramount importance for these applications. It was demonstrated that monodisperse silica particles in spherical geometry that vary in size between 60-500 nm are the most suitable for being able to penetrate cell membranes.

In this work two different combined approaches of Stöber method and supramolecular assembly of surfactant molecules (CTAB) that act as templates, respectively under assistance of n-hexane, n-octane or toluene, have been used to lead to the formation of ordered MSNs with spherical morphology between 60-200nm and pore size ranging from 2.7 to 8nm.

The methods (named here A and B) both rely on the hydrolisis and condensation reactions of the silica precursor (TEOS) in alcaline solution, but differ in the actual approach: in the method A, modified from that of Shengpu et al. [2], n-hexane or n-octane act as both the swelling agent for the micelles and the phase in which alkoxyde is solubilized, thus allowing the slowdown of the hydrolysis rate by reducing TEOS-water contact time.

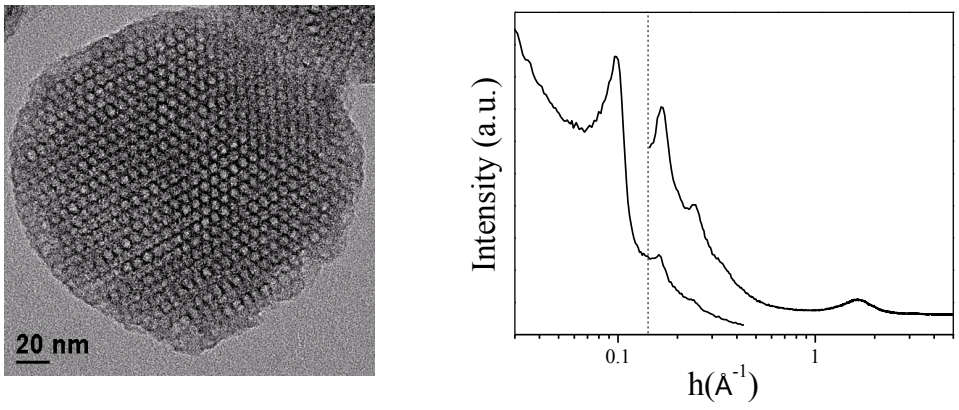
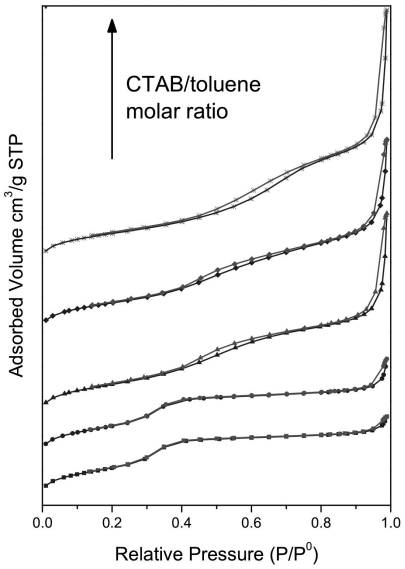


Fig. 1: TEM micrograph and SAXS-WAXS diffractograms of MSNs prepared using method A

In the method B, modified from that of Qiao et al. [3], TEOS is dissolved in a mixture of water and ethanol, while the swelling effect is accomplished by toluene.



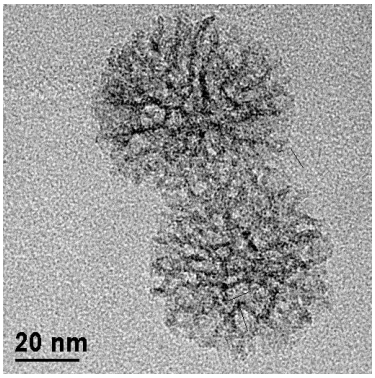


Fig. 2: Adsorption-desorption N_2 isotherms of samples synthesized according to method B with different amount of toluene and TEM micrograph of a selected sample.

In order to remove the organic fraction the final product is obtained both by calcination or via acidic extraction.

Characterization was carried out by several techniques as Thermogravimetric Analysis, TGA-DTG and DRIFT-IR spectroscopy, the morphology and porosity of the spherical nanoparticles have been investigated by means of Electron Microscopy techniques (SEM, TEM), N_2-adsorption/desorption and X-ray diffraction (SAXS, WAXS).

The mesoporous silica spherical nanoparticles (MSNs) characterization confirms that it is possible a fine tuning of both the size of the spherical particles and of the pore of the MSNs silicas.

References

[1] 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 and E. W. Sheppard, *Journal of the American Chemical Society,* 114 (1992) 10834.

[2] M. Shengpu, Y. Wang and Y. Zhu, *Journal of Porous Materials*, 18 (2011) 233.

[3] Z. A. Qiao, L. Zhang, M. Guo, Y. Liu and Q. Huo, *Chemistry of Materials*, 21 (2009) 3823.