

Synthesis of ultra-large-pore ordered mesoporous materials using Pluronic surfactants and judiciously selected swelling agents

Michal Kruk

Department of Chemistry, College of Staten Island, City University of New York, 2800 Victory Boulevard, Staten Island, NY 10314 and Graduate Center, City University of New York, 365 Fifth Avenue, New York, NY 10016

Micelle swelling agents (expanders) have been extensively applied in the surfactant-templated synthesis of ordered mesoporous materials. The micelle expander is solubilized in the hydrophobic cores of the micelles and thus it increases their diameter and volume, leading to the enlarged pore size and increased pore volume of the surfactant-templated material. However, the micelle expansion process is often accompanied by the loss of size uniformity or by the change in shape of the micelles, which affords heterogeneous or disordered porous materials. Recently, we proposed that the synthesis of well-defined materials with appreciably enlarged mesopores can be facilitated by selecting a swelling agent that is solubilized in the micelles to an appreciable extent, but not to an excessive extent. Further, we proposed to select swelling agent candidates from series of organic compounds that exhibit gradually increasing extent of solubilization in the solution of the surfactant of interest. In particular, the solubilization of alkyl-substituted benzenes in Pluronic surfactants, which serve as templates for many ordered mesoporous materials, increases as the number and size of alkyl substituents on the benzene ring decreases. Therefore, one can identify promising pairs of block copolymer surfactants and micelle expanders according to the criteria outlined above. In particular, the synthesis of 2-D hexagonal ultra-large-pore SBA-15 silicas (ULP-SBA-15) was developed using Pluronic P123 surfactant ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and 1,3,5-triisopropylbenzene (TIPB) swelling agent. ULP-SBA-15 silicas with (100) interplanar spacings tunable in the range from 13 to ~27 nm and with pore diameters adjustable from 11 up to ~26 nm with narrow pore size distributions were obtained. 2-D hexagonal periodic mesoporous methylene-, ethylene-, ethenylene- and phenylene-bridged silicas (PMOs) with similarly large (100) interplanar spacings and with a wide range of pore diameters (10-20 nm) were also synthesized. Ultra-large-pore FDU-12 (ULP-FDU-12) silicas with face-centered cubic structure of spherical mesopores were developed using Pluronic F127 surfactant and xylene or ethylbenzene as a swelling agent, and exhibited pore diameters up to 37 nm and unit cell parameters up to ~55 nm. The same block copolymer was used to synthesize large-unit-cell PMOs with face-centered cubic structures. The size of entrances to the spherical and cylindrical mesopores can be adjusted by using hydrothermal treatments. Closed-pore ordered mesoporous silicas can be derived from some of the above large-pore silicas and PMOs through the thermally induced pore closing. Moreover, there emerges an opportunity for the synthesis of single-micelle-templated nanospheres and nanotubes simply through the adjustment of the framework-precursor/surfactant ratio.