ORIENTED MESOPOROUS MATERIALS FROM LIQUID CRYSTAL TEMPLATES

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Swollen liquid crystals showing lamellar, cubic or hexagonal arrangement of micelles have been used as templates to direct the final morphology and texture of the ceramic material synthesized inside. In this route the inorganic sol precursor generates mesophases, which could assume the same structure of the micellar arrangement. The drawback of this route is the resulting weak interactions between particles forming these mesophases that hinders the structure keeping after organic phase extraction or thermal treatment.

This work reports the directional growth of macroscopic ceramic needles by combining a thermo-responsive zirconia sulfated hydrosol [1] with a swollen hexagonal liquid crystal (SHLC) [2] compared to that combined with a swollen hexagonal liquid crystal modified by urea (USHLC). The effect of the thermo-induction step and of the molar ratio $R_s = [Zr^{4+}]/[SO_4^{-2}]$ on the thermo-stability of both the SHLC and USHLC, and also on the nucleation and 1D-growth of ceramic particles was investigated. The SHLC templates were prepared as follows: the surfactant cetylpyridinium chloride was added in the concentrated zirconia sol (Zr^{4+}/SO^{4-} ratio = 15:1) under stirring; following the oil (cyclohexane) used as swelling agent was also added to form the emulsion, and the co-surfactant (pentanol-1) was added to form the microemulsion, that gels after changing the zirconia/sulfate ratio to 3/1. For the USHLC templates preparation, urea was added to the concentrated zirconia sol before surfactant addition, and the process followed as described.

The effect of the crystallization induction step on the thermo-stability of the structural array of the SHLC and USHLC containing the sulfated zirconia hydrosol prepared with different R_s was checked by *ex situ* and *in situ* small-angle X-ray diffraction (SAXD) measurements conducted at the SAXS beamline of LNLS, Campinas, Brazil. A bi-dimensional position-sensitive X-ray detector was used to record the scattering intensity, I(q), as a function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin\theta$, θ being half the scattering angle and λ = 1.6856 Å. For the *ex situ* measurement, before and after the induction step, the sample was placed inside a hermetic cell between two thin (10 µm) and parallel mica windows (cell thickness about 1 mm). The macroscopic particle growth inside the template was observed using a polarizing Olympus BX41-Pol microscope coupled to a digital camera (figure 1). The particle's nucleation is induced by heating the template to a moderate temperature (50℃), while the kinetics of the needle's growth is enhanced by increasing the $[Zr^{4+}]/[SO_4^{-2}]$ molar ratio. The effect of molar rate on the SAXD patterns shows the increase in R_s enhance the thermo-stability of the liquid crystalline structure of lyotropic hexagonal mesophases, the most stable being that modified by urea (figure 2).

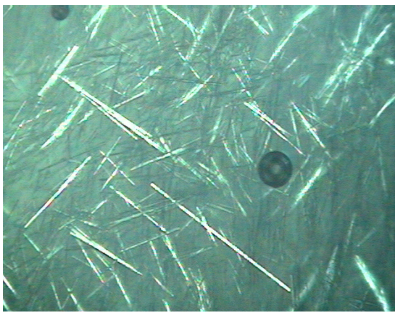

Figure 1: Optical microscopy of the formed fibers.

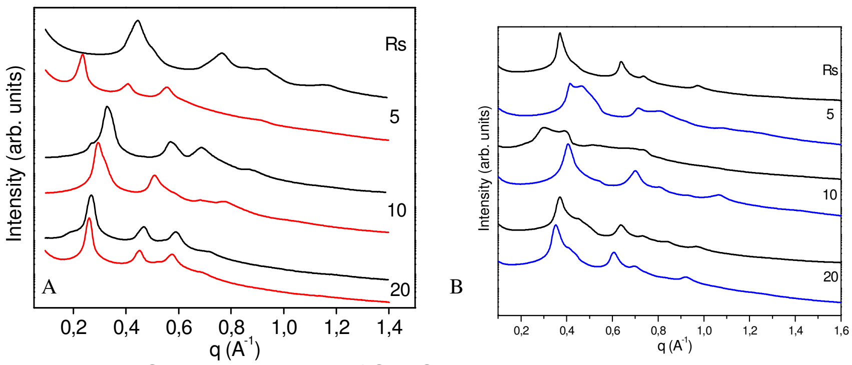

Figure 2: SAXD - (a) curves of SHLC prepared without (black) and with (red) induction temperature; (b) curves of USHLC prepared without (black) and with (blue) induction temperature.

References :

[1] CHIAVACCI, L. A. et al. The role of surface state and of structural feature on the thermoreversible sol-gel transition of a zirconyl aqueous precursor modified by sulfuric acid. **Chemistry of Materials**, v. 16, n. 21, p. 3995-4004, Oct. 2004.

[2] SANTOS, E. P. et al. Zirconia Needles Synthesized Inside Hexagonal Swollen Liquid Crystals. **Chemistry of Materials**, v. 16, n. 21, p. 4187-4192, Oct. 2004.