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Tin oxide is a well-known wide band gap semiconductor that is used in particular in optoelectronic devices as SnO₂ nanocrystals dispersed in silica matrix [1]. The optical properties are directly related to the mean size of the nanocrystals [2]. We have elaborated such nanostructured materials using sol-gel process starting from alkoxide precursors [3]. After the synthesis at room temperature the amorphous bi-cationic material is homogeneous at the molecular level [4].

The aim of this communication is to present a detailed analysis of the phase separation process involving in such material synthesized far from the equilibrium state. This study has been realized through Small Angle X-ray Scattering (SAXS) in-situ measurements performed at the BM02 beamline at ESRF. Bulk samples were studied in transmission mode at 16 keV using a 2D detector. Isothermal and isochrones records of the SAXS curves were realized in a dedicated furnace between room temperature and 600°C.

A temperature increase of the thermal treatment induces decrease of the scattered intensity at low q values and simultaneously a clear increase of the signal in the high q range. A “cross over” is observed and its position shifts to low q value when the amount of tin oxide increases (see figure 1). This invariant point is due to the formation of a composition fluctuation related to the formation of tin-rich zones and the increases of the intensity in the high q range indicate an increase of the number of short Sn-Sn distances which means a tin enrichment of these zones.

Thermal treatment at temperature higher than 350°C induces a rapid modification of this self-organized microstructure (see figure 2). Indeed, the tin-rich zones grow rapidly and tin oxide particles appearing probably through a coalescence process.

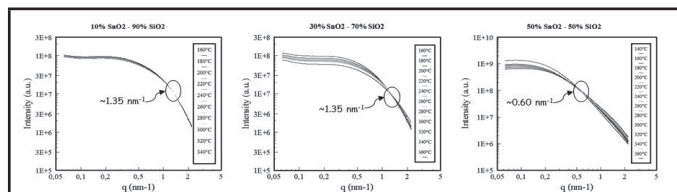


Figure 1. Direct in-situ SAXS observation of the phase séparation process.

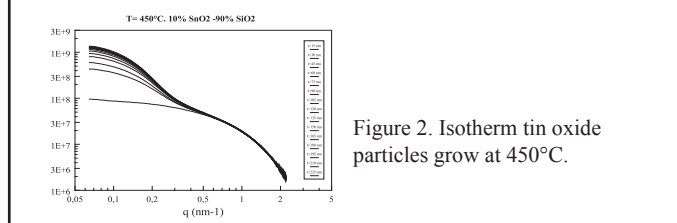


Figure 2. Isotherm tin oxide particles grow at 450°C.

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Block copolymer-mediated gold nanoparticles: small-angle scattering studies

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Combined application of small-angle neutron and x-ray scattering studies to characterize block copolymer mediated gold nanoparticles has been reported. These two techniques provide different contrasts for the different components and hence provide complementary information on the system. Neutron scattering sees the hydrogenous block copolymers and their micelles whereas X-ray scattering provides the structure of high-Z gold nanoparticles. We have shown that both gold nanoparticles and block copolymer micelles coexists and synthesis of gold nanoparticles can be controlled by tuning these populations.

The synthesis of the gold nanoparticles was carried out by varying the equi-concentration of gold salt (HAuCl₄.3H₂O) and trisodium citrate (Na₃C₆H₅O₇.2H₂O) in the range from 0 to 1 wt% for a fixed concentration of block copolymer [1 wt% P85 (EO₂₆PO₃₉EO₂₆)]. In the case when both gold nanoparticles and free block copolymer (unimers and/or micelles) coexist, the total scattering is determined by the sum of the individual components as

$$I_t(Q) = I_{np}(Q) + I_{bcp}(Q) \quad (1)$$

where the subscripts *np* and *bcp* correspond to nanoparticles and block copolymer, respectively.

In SANS data of 1 wt% P85 with varying gold salt and trisodium citrate concentration, the contrast with solvent (D₂O) for block copolymers is much higher than for gold nanoparticles. Also gold nanoparticles have much smaller number density (for given wt%, number density inversely depends on the density of the particle). This suggests that the scattering is dominated by block copolymers and no significant scattering occurs from gold nanoparticles [$I_t(Q) \sim I_{bcp}(Q)$ using equation (1)]. The changes in SANS data with varying gold salt concentration are because of the enhanced micellization at higher salt concentrations. Both the block copolymer unimers and micelles coexist in these systems and the fraction of block copolymer micelles increases (30 to 41%) as a result of enhanced micellization (salting out effect) with the salt concentration increase from 0.05 to 1 wt%. The micellar size is found to be almost similar having core radius of 40 Å surrounded by a PEO chain of radius of gyration of 12 Å and aggregation number around 70. Since the number density of gold nanoparticles is very small, the scattering from block copolymers stabilizing nanoparticles is therefore expected to be negligible.

In SAXS data on the same system, the high scattering length density difference between gold nanoparticle and solvent makes the scattering from nanoparticles dominant [$I_t(Q) \sim I_{np}(Q)$] even though the number density of the gold nanoparticles is small. Moreover, there exists almost no contrast for block copolymers in SAXS. The scattering increases as the number density of the gold nanoparticles increases with increasing gold salt concentration. The gold nanoparticles are fitted with polydispersed spherical particles. The particle size is found to increase (11.5 to 21.6 nm) with decrease in polydispersity (0.52 to 0.35) with increasing nanoparticle yield from 0.05 to 1 wt%.

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An examination of the structure of Fe₃O₄ using reverse Monte Carlo refinements

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