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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.

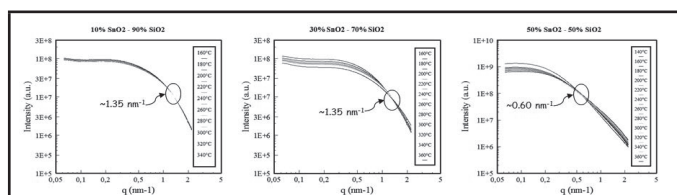


Figure 1. Direct in-situ SAXS observation of the phase séparation process.

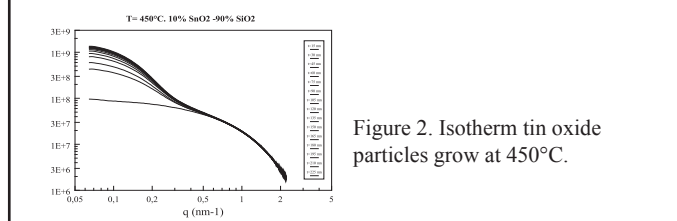


Figure 2. Isotherm tin oxide particles grow at 450°C.

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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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Fe₃O₄ (magnetite) is a ferrimagnetic material that has been known to man for thousands of years, and was used to make the first magnetic compasses as early as the 8th century AD. In more recent times it has been greatly studied by the scientific community, with much effort going into investigation of the Verwey transition [1] and the associated structural changes [2]. Despite this, a definitive model for the low temperature structure has remained elusive.

In this study neutron total scattering data from a highly stoichiometric powder sample collected at 10K have been used to perform reverse Monte Carlo (RMC) refinements using the program RMCProfile [3]. These refinements produce large box atomic configurations consistent with experimental data on both local and average length scales. Atoms may be translated and magnetic moments swapped and rotated during the refinement, allowing both the atomic and magnetic structures to be refined.

The results and their implications are discussed within the context of charge ordering models and space group assignments produced by previous studies.

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Keywords: diffraction, magnetite, RMC

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Studying the 3-dimensional structure of proteins in solution by small-angle X-ray scattering

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Small-angle X-ray Scattering (SAXS) is an important method for the characterization of biological macromolecules. Usually, the structure of proteins is characterized by protein crystallography and NMR. However, the results obtained with these methods do often not reflect the protein structure and its behavior in the native state. With SAXS, the 3-dimensional structure of proteins in solution, i.e. under biological conditions can be determined. The method determines the size and shape of proteins and protein complexes. Furthermore, SAXS is very sensitive to any structural or size changes caused e.g. by external effects (changed temperature or pH, ligand binding, etc.).

The main challenge for measuring proteins in solution with laboratory SAXS systems is the low contrast of these samples (contrast in SAXS is the difference in electron density between the nanoparticle and the matrix). Therefore, the design, collimation concept [1] and quality of the SAXS system is crucial for achieving excellent data quality at reasonable measurement times.

In this contribution we will show some examples of structural characterization of proteins in solution with the SAXSess mc² laboratory system. These examples include the determination of the overall protein size, of the folding state and of the 3-dimensional envelope describing the structure of the protein in solution. The determined solution structures can be well compared with structural data from protein crystallography.

SAXSess mc² is ideally suited for the analysis of e.g. low-concentrated protein solutions or drug delivery systems within minutes. Therefore, it can be used for time-resolved monitoring of

structural changes. Furthermore, many samples can be screened by use of a fully integrated autosampler.

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Keywords: SAXS, Proteins, 3D-envelope

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New GI-SAXS capabilities for the home-lab

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Grazing-incidence small angle X-ray scattering (GI-SAXS) is an established technique for the characterization and analysis of nano-structured surfaces and thin films. Typical applications include thin organic films, quantum dot arrays or nanomaterials deposited and arranged on surfaces. However, GI-SAXS is mainly performed on dedicated synchrotron (GI-)SAXS beamlines due to the requirement of high primary beam intensity and parallel-beam requirements.

In this contribution we will present the new GI-SAXS stage for the SAXSess mc² laboratory small- and wide-angle X-ray scattering system. The precise GI-SAXS stage in conjunction with the SAXSess mc² system enables to perform GI-SAXS experiments even in the home laboratory. Samples with a nano-structured surface can be precisely tilted in order to perfectly obtain grazing incidence conditions. In addition, samples can be rotated in-plane in order to study the arrangement of the nanostructured surface. We will discuss technical aspects of the GI-SAXS stage and will present selected results of nanostructured thin film samples.

Keywords: GI-SAXS, grazing incidence, surface

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Non-crosslinking aggregation of DNA-functionalized nanoparticles

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Recently, it was discovered that DNA-functionalized nanoparticles assemble by hybridization in a non-crosslinking configuration. When single-stranded (ssDNA) molecules grafted on the nanoparticles hybridize to the complementary ones, the resulting nanoparticles, which are covered with double-stranded DNA (dsDNA), assemble immediately at high salt concentrations without molecular crosslinking, while the nanoparticles with ssDNA molecules remain stable. The colloidal stability is very sensitive to the terminal base-pair of DNA duplex. When the tethered ssDNA hybridizes with a single-base mismatched DNA, the nanoparticles still disperse stably at the high salt concentrations. However, the mechanism of the non-crosslinking aggregation has not been understood yet. In this study, the non-crosslinking aggregation was explored from the structural point of view, using mainly small-angle X-ray scattering (SAXS). The structural characterization of the gold nanoparticles with ss- or dsDNA was performed, and the effects of DNA length, core size, and temperature on the non-crosslinking aggregation were also investigated.

Gold nanoparticles (ca. 5, 15 and 40 nm) were functionalized with ssDNA. Here, the DNAs with various bases were used. The functionalized gold nanoparticles were suspended in 10 mM phosphate