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Report:

In order to design functional nanoparticles, it is necessary to tailor their properties, hence it is crucial to understand their formation processes. During the last 15 years supercritical fluids have shown great potential for the production of tailor-made nanoparticles [1,2]. Synthesis in sub- and supercritical fluids (*i.e.* reactions at elevated pressure and temperature) is superior to conventional synthesis techniques in terms of product uniformity, reaction kinetics, and monodispersity. However, the fundamental understanding of particle nucleation, growth and agglomeration in sub- and supercritical fluids to a great extent still remains elusive. Time-resolved X-ray *in situ* studies are highly useful for understanding details of fundamental processes and offer insight into the formation of nanoparticles under challenging conditions. In previous studies we have performed combined *in situ* SAXS and WAXS studies in our home-built synthesis reactors [3,4]. Information on the mechanism behind particle growth, size, and crystallinity was obtained for various functional materials such as battery materials, catalysts, and thermoelectrics [5,6]. However, most of the conclusions were based on information on the crystallized nanoparticles alone.

EXAFS can provide structural information on the initial state of a reaction *i.e.* on formation of the amorphous nucleus from solutions of simple metal salts. Moreover, EXAFS can give unique information on the local structure around dopant atoms in materials. Simultaneous WAXS can provide information on the crystalline phase, particle size, and crystallinity and hence motivate combined *in situ* EXAFS/WAXS studies.
The first combined EXAFS/WAXS experiment exploring reactions in sub- and supercritical fluids were performed at BM01B (SNBL) at the ESRF in July 2011. The growth of nanocrystalline yttria stabilized zirconia (YSZ) and ceria zirconium oxide (CZO) [5] solid solutions was studied. EXAFS data were collected on the *K*-edges of zirconium, yttrium, and cerium in transmission mode, and WAXS data were collected with six crystal analyzers. The quick changeover between the EXAFS and WAXS monochromators and fast scanning times enabled carrying out quasi-simultaneous EXAFS/WAXS experiments. In a typical experiment a sequence of 5-6 quick EXAFS scans and one WAXS dataset was collected repeatedly for approximately 30 min.

Preliminary results on the *in situ* EXAFS/WAXS study of the formation of YSZ (8% yttrium) are shown in Figure 1. EXAFS data on the zirconium edge shows that the zirconium precursor solution is extremely ordered as three well-defined coordination shells were observed before the solution was heated. When heat is applied and the reaction initiated, only one coordination shell around Zr, most likely Zr-O, was observed. The intensity of the second shell coordination peak (corresponding to Zr-Zr/Y) increases with reaction time which shows that the nanoparticles grow and become more crystalline with time. Even at the end of the reaction, only two peaks are observed indicating that the product consists of small particles. EXAFS data on the yttrium edge (not shown here) reveal that the local environment around yttrium in the precursor solution is much less ordered than zirconium in the precursor as only one peak (Y-O) appears in the Y-spectra for the precursor. During the reaction, however, a second peak (Y-Zr/Y) increases with time as ytrrium is incorporated into the nanoparticles as they grow. The particle growth is illustrated by the evolution of one Bragg peak as a function of time. After the first WAXS scan the peak width decreases revealing particle growth, but after the second diffraction scan, the crystallite growth is very slow indicating that ripening does not occur. The peaks are broad revealing small particles in agreement with findings from the EXAFS data.

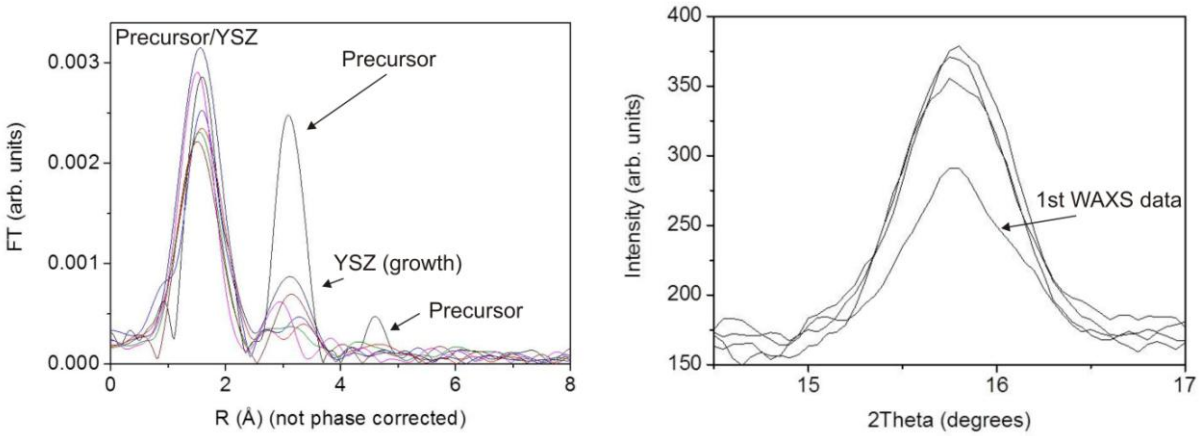

Figure 1. Selected data from the synthesis of YSZ (8% yttrium) with a total duration of ca. 30 min. are shown. *(left)* EXAFS data on the Zr-edge and *(right)* WAXS data (one Bragg peak) of nanocrystalline YSZ.

The only thing that did not turn out succesfully from the beamtime was trying to combine the EXAFS/WAXS experiments with Raman spectroscopy. A Raman laser is installed at BM01B, hence development of combined EXAFS/WAXS/Raman experiments were attempted even though we did not initially propose this experiment. Raman spectroscopy could have contributed to these experiments by distinguishing between the tetragonal and cubic polymorphs of zirconia, which may be difficult by powder diffraction from small nanoparticles due to peak broading. The reason that the Raman spectroscopy attempts were unfruitful is due to the materials of which our reactor cells are composed: amorphous silica or single crystalline sapphire. The amorphous silica tubes gave a large background in the Raman spectra, whereas sapphire tubes gave very noisy EXAFS data.

The experiment at SNBL was very succesful, and proof-of-concept was given that fast hydrothermal reactions can be followed *in situ* by combined EXAFS/WAXS. The experimental setup with the two monochromators, the high flux at high X-ray energies, the fast scanning time of especially the EXAFS data collection, and experimental support makes BM01B a unique beamline for performing these experiments. New information on the fundamental understanding of chemical processes was obtained. The data analysis is in progress, and the work will be published in a peer-reviewed paper.

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