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Nucleation and Growth of Metal Oxides Nano- and Microparticles studied by metal K-edge XANES/EXAFS spectroscopy

L. Vayssieres, J. Guo, J.-E. Rubensson, and J. Nordgren (Uppsala University)
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Introduction: A novel concept[1] has been developed in order to create a new generation of smart materials (i.e. purpose-*built nanomaterials*), modeled, designed and engineered to match the physical and structural requirements of their applications. This concept, well-sustained by a thermodynamic model, monitoring the nucleation, growth and ageing process through the control of the interfacial free energy of the system allows to control the particle size and its surface morphology as well as the ability to thermodynamically stabilized metastable crystal phases in solution. The experimental outcome of such concept for the thin film processing of metal oxide materials is of great interest both for fundamental and applied research purposes since the influence of parameters such as particle size, shape and orientation as well as the overall film texture and porosity may be probed and demonstrated for instance, on the electronic structure and/or catalytic activity of various transition metal oxides. Moreover, designing well-controlled materials allows tuning and optimizing the physical properties of current devices as well as the ability to create novel and improved devices.

The use of EXAFS spectroscopy at metal K-edge to study the structural properties at various stages of the chemical growth of transition metal oxides in suspension will represent a great advantage for the understanding of the mechanisms of nucleation and growth processes from molecular level to the solid state. Indeed, probing the local environment (distance between metal-metal and metal-oxygen and number of surrounding atoms) is of essential importance to achieve a significant structural description of amorphous compounds and clusters as well as the early stages of the hydrolysis-condensation of metal salts likewise organometallic complexes (alkoxide). Moreover, the study of these precursors may lead to great fundamental information concerning the structural conformation (monomer, dimer…), which in turns gives information on the kinetics of the hydrolysis-condensation processes. Information on the symmetry of the metal atoms can be reached (e.g. the absence or presence of an inversion center, respectively tetrahedral or octahedral symmetry, will result in the presence or the absence of intense pre-peak in the XANES spectra. Indeed, the position, the intensity and the multiplicity of the pre-peak is directly correlated to the nature of the ligand surround the metal as well as their numbers (ligancy) and the symmetry of the metal. Therefore, fundamental knowledge will arise and will contribute to a comprehensive fundamental understanding of the species and mechanisms involved in the chemical growth of nanoparticles of various crystallographic symmetry, particle size and shape.

Methods and Materials: The basic ideas, well-illustrated on the controlled growth of spinel iron oxide (magnetite) nanoparticles in aqueous solution[2], have been successfully applied to the development of a template-free, aqueous chemical growth techniques using metal salts and complexes as precursors, which allows to generate at large scale and low-cost, novel designed and ordered thin film materials with a complex architecture such as, three-dimensional crystalline arrays of oriented nanorods of ferric oxide (hematite and akaganeite)[3], three-dimensional crystalline arrays of highly oriented microrods[4] and microtubes[5] of ZnO (zincite) grown on various substrates such as glass, conducting glass (TCO), single crystalline silicon and silicon dioxide wafers or sapphire for photovoltaic and photoelectrochemical devices. Typically, the aqueous synthesis is conducted in a laboratory oven in a teflon or polypropylene bottle containing various composition of metal salts, pH and ionic strength and/or metal/complex ratio heated at a temperature varying from room temperature to approximately 100C. The samples are then transferred in a sealed mylar bag and K-edge spectra are recorded in transmission mode.

Results: At this stage, the complete aqueous chemical growth of a II-VI semiconductor (ZnO nanorods and microrods) as well as nanoparticles of a metallic oxide (RuO_2) from the molecular precursors state to the solid phases has been investigated by EXAFS at metal K-edge and crucial results have been recorded that shall lead to the identification of the symmetry and oxidation state of the intermediate species of the nucleation and growth process of such important metal oxides.

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