

Light on dynamics

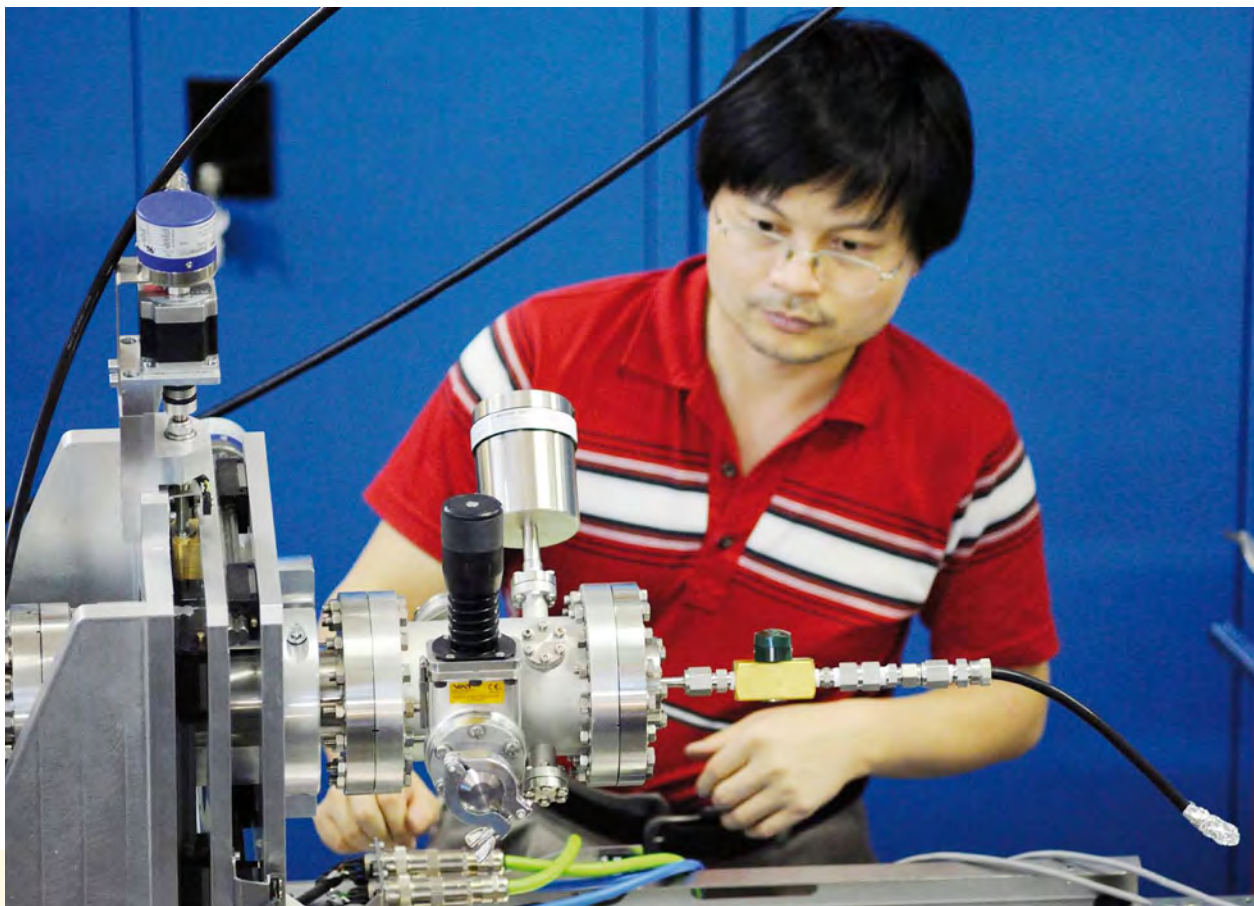


Dynamics at SOLEIL involves a very wide timescale, ranging from milliseconds to a few hundred femtoseconds! Similarly, it covers a wide range of applications, since it starts with the study of atomic motion and the local properties of atoms and moves on to phase transition at the macroscopic scale by using cooperative or reactional effects that develop at different times.



Light on dynamics

Xiaojing Liu, scientist on PLEIADES beamline, setting up the isolated nano-objects source based on an aerosol generation technique, which is developed for the Nano-PLEIADES ANR project.



Synchrotron radiation is an ideal tool for developing time-resolved studies both because it has a naturally pulsed structure (the pulses are a few tens of ps, or even a few ps in low-alpha mode or about 100 femtoseconds in slicing mode), but also because its brightness allows acquisitions with very short integration times (a few seconds or a few milliseconds or tens of microseconds with ad hoc detectors), allowing, for example, reaction monitoring. Another complementary approach, from the point of view of quantum mechanics, is to develop spectroscopic studies at very high spectral resolution. It is then possible, following the uncertainty principle, to access temporal information at even shorter time scales, as far as the total achieved resolution is good enough. The examples brought together here are certainly not exhaustive (almost all beamlines are presently or will be in-

involved in dynamic studies) but help to illustrate some of these general considerations, over a wide scientific field.

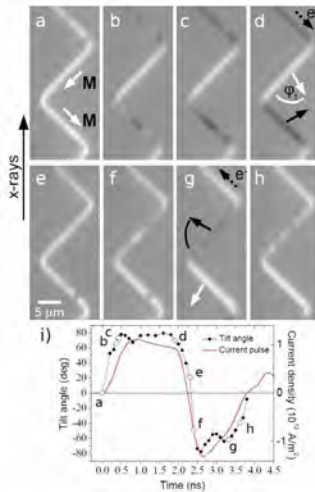
Studies of nano-objects

The strong interest in nano-objects, which have unique properties related to confinement effects linked to their size, has prompted numerous dynamic studies aimed at understanding both nucleation and growth phases. Experiments carried out on SAMBA and SWING, combining time-resolved absorption and scattering, or on ODE (XANES dispersive mode), further our understanding of these complex phenomena which often involve transient states. The aim of such studies, through greater control of the nucleation conditions, is to control the synthesis of nanoparticles and to optimize their final properties. Studies on aerosols and free nanoparticles (DESIRS, PLEIADES) will complement these approaches.

TEMPO

Magnetization dynamics in nanowires revealed by time-resolved XMCD-PEEM

Figure 1: Time-resolved XMCD-PEEM images of the magnetic domains in the NiFe layer of a 400 nm wide nanostructure. The upper part of the figure presents 8 of the tens of images recorded, every 100 ps, during the bipolar current pulse (4.5 ns). Part (i) of the figure shows with what time delays these images were recorded, together with the magnetization tilt angle ϕ_t .



Domain walls in magnetic nanowires have been proposed to constitute a new type of fast and cheap magnetic storage medium, the so-called race-track memory [1]. The displacement of the domain walls in these nanowires is induced by short current pulses, through the so-called spin-transfer-torque (STT) effect. Many experimental studies have used magnetic

microscopy to investigate current-induced domain wall motion, but all of them used quasi-static measurements, imaging the position and shape of the magnetic domain wall before and after a current pulse. For a better theoretical and experimental understanding of the interaction between spin polarized currents and domain walls it is crucial to directly observe the magnetic configuration of the nanowires during the current pulses.

The time structure of the SOLEIL synchrotron radiation

source and the equipment of the Louis Néel Laboratory in Grenoble have been used to perform time-resolved x-ray photoemission electron microscopy (PEEM) experiment in real time, with 100 ps time resolution. In pump/probe experiments, the effect of nanosecond current pulses applied to spin-valve-like FeNi/Cu/Co magnetic nanostructures was directly observed. The microscope images have been taken during the current pulses and clearly reveal a tilt of FeNi magnetization in the direction perpendicular to the stripe. It is associated to the Oersted field accompanying the current pulse. For 400 nm wide stripes, average current densities of 10^{12} A/m² lead to tilt angles as large as 80 degrees. These measurements give the first direct evidence for the importance of Oersted fields for current-induced domain wall motion in these trilayered structures. This effect should also play a role for samples where the magnetic layer is surrounded by metallic buffer or protection layers.

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Dynamics modelisation

The example described on the DISCO beamline involves a completely different field because it is the in situ measurement of the diffusion dynamics of trace elements within complex systems such as food, for example. A major challenge for public health is the problem of food contamination by certain additives found in their packaging. The objective behind modeling their dynamics at the molecular level, based on these measurements, is to understand the role that the size of these solutes plays in their diffusion rate.

Pump-probe

Much shorter time-scale studies involve more fundamental aspects. While in the previous examples, the element triggering the temporal process to be followed did not require extensive synchronization, this is no longer the case for very short time scales, where this

“THE OVERARCHING QUESTION IN STRUCTURAL DYNAMICS IS TO UNDERSTAND HOW ATOMIC AND ELECTRONIC INTERACTIONS DRIVE MOLECULAR MACHINES.”

FRANCESCO SETTE, DIRECTOR GENERAL OF ESRF, GRENOBLE.

synchronization is usually obtained by pump-probe type experiments. In short, very fast excitation is created by interaction of the system with a pulsed laser, and further evolution of the system is probed means of synchrotron radiation, by adjusting the delay between two pulses. This type of experiment, based on sufficient

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PLEIADES

Circularly polarized light - a probe of nuclear dynamics in achiral species

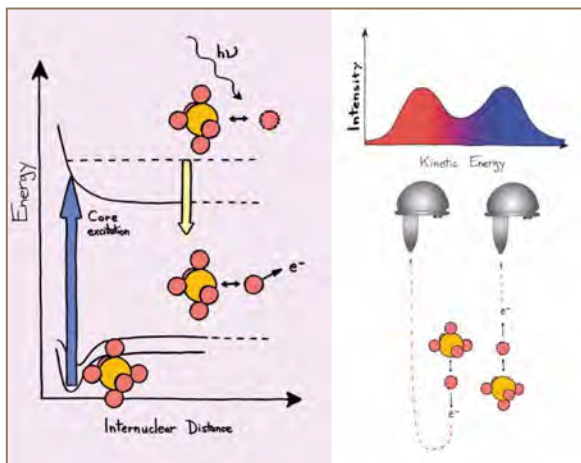


Figure: Left panel: Schematic diagram of the ultrafast dissociation and formation of atomic-like Auger lines observed in Resonant Auger Spectroscopy (RAS).

Right panel: Schematic diagram of the Auger-Doppler effect observed in RAS due to the emission of electrons from the forward/backward travelling core-excited atomic fragments.

Circularly polarized light (CPL) finds numerous applications ranging from modern displays and RealD 3D cinema technology, to circular dichroism of magnetic materials or chiral macromolecules in structural biology, and allows addressing the fascinating origin of the homochirality of life.

For the first time, on the PLEIADES beamline, circularly polarized light has been used to probe nuclear dynamics of highly excited neutral molecules, which dissociate within a few femtoseconds (10^{-15} s) only after absorption of the X-ray photon.

The highly excited SF_6 species $F1s^{-1}a''_{1g}$ experience electronic relaxation by emitting a valence electron, a so-called "Auger electron". However, since the fragmentation process is very fast, the ejection of the Auger electron may occur from already dissociated fragments.

As it has been observed before

using linearly polarized light, one is able to distinguish Auger electrons ejected from the fragment atoms moving either towards or away from the electron detector owing to the small differences in their kinetic energies. This effect, called Auger-Doppler by analogy with acoustical Doppler effect, is observed for the first time using CPL despite the uniform distribution of the dissociating chemical bonds induced by the CPL.

Based on the present results, it will be possible to use the circular dichroism in Auger-Doppler profiles as an efficient probe of the photoionization dynamics as well as of the molecular structure and chemical environment, even in achiral species.

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statistical analysis, requires the recording of a large number of measurements and thus applies only to reversible phenomena in the analysis time window. In materials science, we can thus probe phase transition dynamics using a photo-triggered system recording time-resolved diffraction patterns. The CRISTAL beamline will soon be equipped with such a system for dynamic studies of a few ps and a eventually a few fs (see prospects offered by the slicing project). The PLEIADES and TEMPO beamlines are, or soon will be, equipped with lasers synchronized with the synchrotron pulses for experiments in dilute phase (fragmentation dynamics) and surface dynamics (reactivity, magnetism) again on a scale of a few tens of ps (then fs with slicing). The insert, showing results from studies on the TEMPO

beamline, concerns the magnetization dynamics induced by injecting current into magnetic nanowires. These studies form part of the optimization of materials for information storage of ever increasing density and with switching times as short as possible. It should be noted that, for these studies, the temporal resolution (here about 100 ps) is combined with the spatial resolution (sub-micron) using the XPEEM technique, the magnetic properties being revealed by circular dichroism analysis.

An electronic hole used as an internal clock

The example described on the PLEIADES beamline belongs to another category as it concerns dynamic effects

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DISCO

In-situ measurements of trace diffusion coefficients in polymers

Determining the relationship between the chemical structure of solutes with intermediate molecular weights (e.g. monomers, plastic additives, residues) and trace diffusion coefficients (D) in polymers is of significant concern in various domains including the contamination of food products by packaging constituents, polymer ageing, reactivity in solids... For a reason that is still not completely understood, the molecular mass dependence is found much greater in semi-crystalline than in melts. The general goal of this study is to contribute to the development of single-molecule spectroscopy technique that can be applied to monitor trace diffusion in polymer or nanocomposite materials on DISCO beamline.

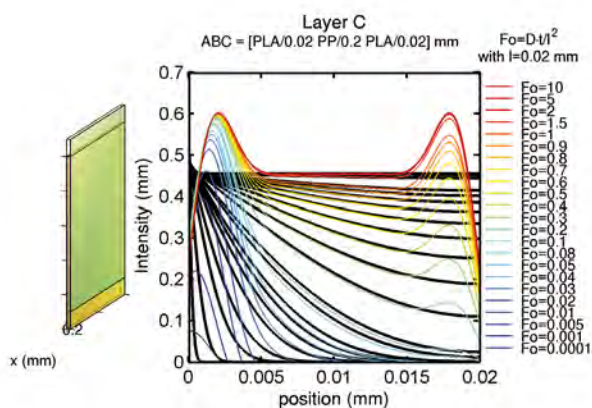
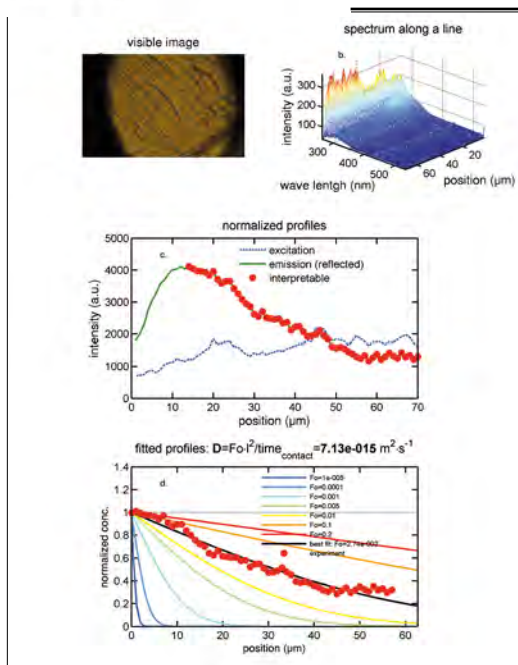


Figure 1: Conditions of diffusion (B=source, A=C=destination) and simulated profiles (black lines= concentration profile without diffraction, colored lines=intensity profiles as measured including light diffraction).

Figure 2: Typical profiles: a) overview of the cross-section of B (PP) in the visible range, b) spectra along a line, c) integrated intensities, d) numerical fitting.



As an intermediate step, a reference was devised and a microscopic technique tailored to assess D values for arbitrary homologous series of tracers and diffusion coefficients as low as $10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$. The developed methodology relies on 2D spectra profile (wavelength \times position) measurements in epi-configuration along cross-sections of materials. The only requirements are that the studied substances present some absorption bands (e.g. aromatic rings or conjugated double-bonds) in the energy range accessible on DISCO beamline, and a corresponding fluorescence that can be separated from the natural fluorescence of the polymer or of its constituents. Three layers of materials, denoted ABC, are put in contact in controlled thermodynamic conditions (Fig. 1 shows one of the tested configurations) and subsequently microtomed for observations. Layer B is formulated with the desired substance by a prior sorption experiment, and acts as a source. A and C are reception layers that do not contain the substance to test. Determined fluorescence intensities along each sample thickness are compared to numerical solutions of a transport model by diffusion (including partitioning effects if required). In practice, light diffraction due to defocus (imperfect cutting, non-planar samples) and optical aberration must be included.

A typical fit is described in Fig. 2 for an excitation wavelength of 275 nm. A semi-supervised method has been developed to extract baselines, to integrate specific emission peaks (Figs. 2b and 2c) and finally to fit D values or equivalently layer dimensionless Fourier numbers, Fo .

Plotting activation energies and D scaling relationships identified on DISCO beamline for a series of biphenyl molecules in polypropylene (PP) and in poly(lactic acid) (PLA), it appeared that adding one carbon between two phenyls lower D values by a factor 3. This scaling was unexpected. Such results that do not depend on polymer details (similar slopes) are currently analyzed by molecular dynamics simulation to reach a theory.

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ODE

Gold nanoparticles: subsecond kinetics and mechanisms of formation

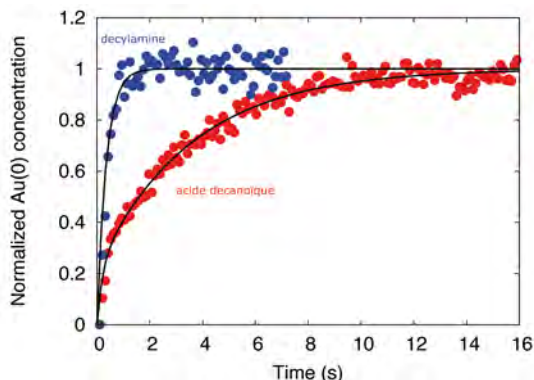
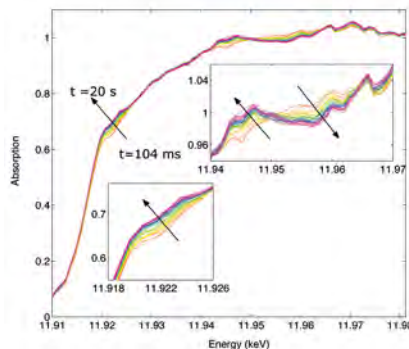


Figure 1 : (left): Formation rate of Au(0) in solution for the 2 ligands (decanoic acid or decylamine) resulting from in situ XANES experiments (right): absorption spectra (XANES) at the L(III)-gold edge for different time periods of gold nanoparticle synthesis in the presence of decanoic acid.

The potential applications of gold nanoparticles aim to exploit their unique intrinsic properties (color, reactivity, etc.) due to their large surface to volume ratio, their shape and polydispersity. Many synthetic routes can be used to obtain these nanoparticles, though it is difficult to control their size distribution and the underlying mechanisms are still poorly understood. The first stages of synthesis are difficult to observe experimentally and, as a result, there is very little control over the nucleation phase. Studies on ODE fall within this context and aim to develop in situ follow-up experiments on the formation of gold nanoparticles in terms of the structure of



the material being formed and the chemical speciation of the medium. The goal is to understand the mechanisms of metallic nanoparticle formation in order to control their synthesis. One of the approaches was to couple X-ray absorption near-edge structure (XANES) with a rapid mixing stopped-flow Bio-Logic © system by developing a cell adapted to gold concentration ranges (3 mM). Nanoparticles were formed by borohydride reduction of a solubilized gold salt. These reactions can be very fast (one to a few seconds for spherical particles). The measurement of the absorption spectrum in dispersive mode achieved at the near-edge of gold (XANES) was used to

quantitatively access the different oxidation states of gold (Au (III), Au (I), Au (0)) during the synthesis of nanoparticles in the presence of ligands (decanoic acid or decylamine) (Fig 1).

The very high temporal resolution (~ 100 ms) of these experiments helped establish the rules of Au (0) formation rate in the solution, and demonstrate its fundamental role in controlling the final size of nanoparticles. In particular a very strong transient supersaturation of Au (0) monomers was shown to occur at the peak of nanoparticle nucleation (1s), and a lack of secondary aggregation for this synthesis process. These key experiments to understand the reaction mechanisms involved in the formation of nanoparticles are also used to understand the development of anisotropy.

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using so-called sub life-time spectroscopy applied to an isolated molecule. In short, the very short life time of a hole created in the inner shell of an atom is used as the internal clock of the changes in the core excited system. The condition required to extract the relevant information, is to combine an overall resolution, both in terms of excitation and analysis that is less than the widening induced by the finite lifetime of the inner hole (in this example 100 meV corresponds to dynamics of tens of femtoseconds).

To conclude this brief overview of opportunities offered at SOLEIL in the field of time-resolved studies, we would like to point out two future actions over the longer term:

- Plans for a beamline optimized for short time kinet-

ics for nanomaterials in heterogeneous catalysis and energy (batteries). This project, accepted by the EQUIPEX call for proposals, will give communities the opportunity to use rapid X absorption (QuickEXAFS) techniques under *in situ* conditions.

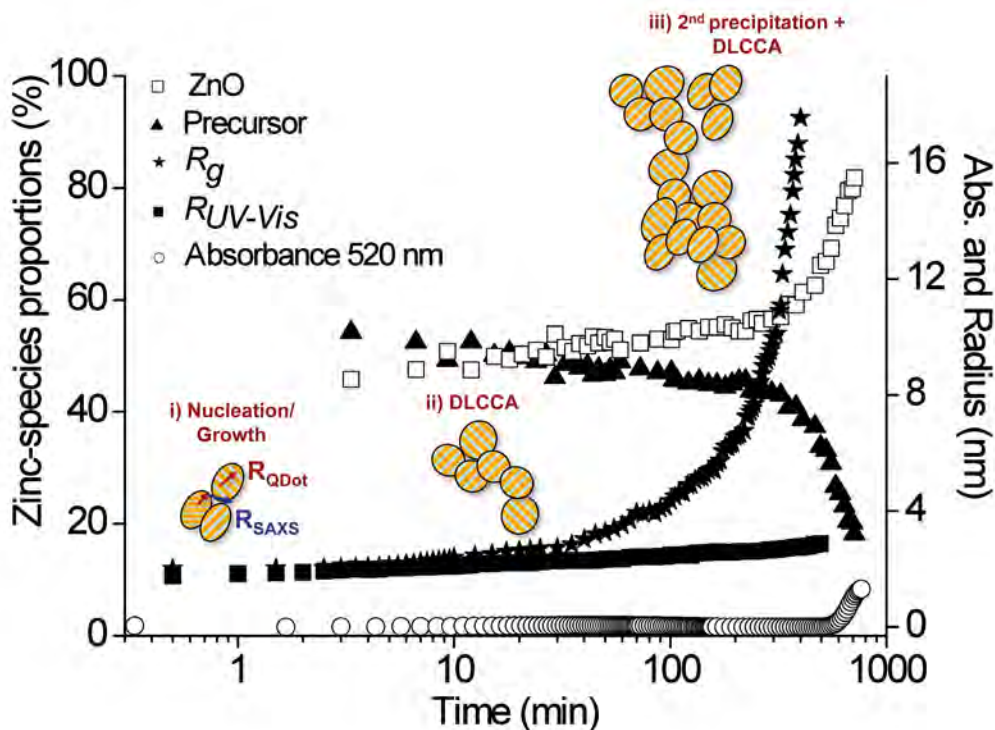
- Generation of femtosecond pulses by interaction of a high-intensity fs laser with the electron bunch stored in the ring. The X-ray pulses thus generated in the TEMPO and CRISTAL insertions will then be extracted on these beamlines for dedicated pump-probe experiments (see article p.11).

These actions will directly benefit from specific developments undertaken at the detection level (Xpad detector, local beam deviation, etc.)

SAMBA- SWING

In situ UV-Vis/SAXS and UV-Vis/XAFS Time-Resolved Studies of ZnO Quantum Dots Formation and Growth

Figure 1 :
Time evolution
of the proportion
of different
zinc species
determined by
EXAFS (ZnO Q-dots
and precursors),
of the absorbance
value at 520 nm
and of the
radius of Q-dots
determined by UV-
Vis, RUV-Vis, and
of the gyration
radius of scatters
determined by
SAXS, R_g .



In recent years, the synthesis of nanoparticles has strongly attracted the attention of researchers due to their electronic, luminescent, optoelectronic and catalytic properties varying significantly with particle size. The study of increasing band gap with decreasing particle size is one of the most studied in the field of semiconductor nanoparticles. The understanding of the nucleation and growth processes of such nanoparticles is of prime importance for tailoring their size and then their properties. In this context, the results gathered at SOLEIL using both the SWING and SAMBA beamlines during the in situ monitoring of the formation of ZnO quantum dots (Qdot), induced by the addition of KOH solution ($[\text{OH}]/[\text{Zn}] = 0.5$) to zinc oxy-acetate ethanolic solution at 40°C,

were successfully combined in order to unravel the complexity of the involved mechanisms. In situ time-resolved UV-Vis absorption was combined with Small Angle X-ray Scattering (SAXS) and X-ray Absorption Fine Structure (XAFS) techniques and enabled to link both synchrotron radiation techniques by rescaling both time-resolved experiments. The monitoring by XAFS allowed to determine the proportion of Zn-based phases present as a function of time (herein ZnO Qdots and unreacted zinc oxy-acetate precursors) and to reveal stepped transformations i) with fast increase of ZnO Qdots (~47%) at the expense of precursors, ii) then a steady state with no increase of the amount of ZnO Qdots but with increasing radii as revealed by UV-Vis and iii) a new increase of the quantity

of ZnO Qdots up to ~82% in a time period where UV-Vis revealed aggregation or huge particle growth. Regarding the analysis of SAXS in the context of the conclusions drawn from XAFS and UV-Vis, it has been evidenced that the stepped processes occurring during the formation of colloidal ZnO nanocrystals are: i) ZnO Qdot nucleation and growth; ii) growth of compact ZnO Qdot aggregates followed by the growth of fractal aggregates described by a cluster-cluster diffusion limited growth; iii) and finally secondary nucleation and fractal aggregation.

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