Probing in situ the formation mechanism of semiconducting nanoplatelets by time resolved SAXS/WAXS (SC3356) : experimental report

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Experiment date and duration : July 13th to July 15th 2012. 8 shifts.
People present during the experiment : From LPS, Orsay : Benjamin Abécassis, Doru Constantin, Patrick Davidson. From LPEM, ESPCI, Paris : Cécile Bouet and Nicolas Lequeux.
Local contact : Diego Pontoni.

1 Overall assessment of the experiment

During the 3 days, all the experimental aspects relevant to the ID2 beamline and to the synchrotron in general worked smoothly. The beam has been stable for the whole course of the experiment and all the end-station elements operated correctly during the run. Hence, we used all the beamtime to acquire data without being troubled by side issues.
The measurement set-up (which is described in more details in the following) that we decided to use also worked faultlessly.
Overall, we investigated around 20 different synthesis conditions (dilution, temperature mostly) for CdSe spherical nanoparticles and nanoplatelets. The data are being processed at present but as far as the data acquisition is concerned we are very satisfied.
In the following, i first describe the experimental set-up that we used. In a second part, i describe preliminary observations that were made during a first look at some datas.

2 Experimental set-up

The aim of the experiment was to probe *in situ* the formation mechanism of CdSe nanoplatelets. To do so, we needed to use a sample environment which makes possible the the heating of the precursor solution at temperature comprised between 150 and 250°C. After initial searches to build a custom sample environment which would pump the hot solution from an agitated reactor and inject it through a glass capillary, we finally decided to use a Linkam hotstage (figure 1).

This solution has several advantages. First, it is a commercial solution and it is easy to set-up. Furthermore, the ID2 staff had already some experience on interfac-

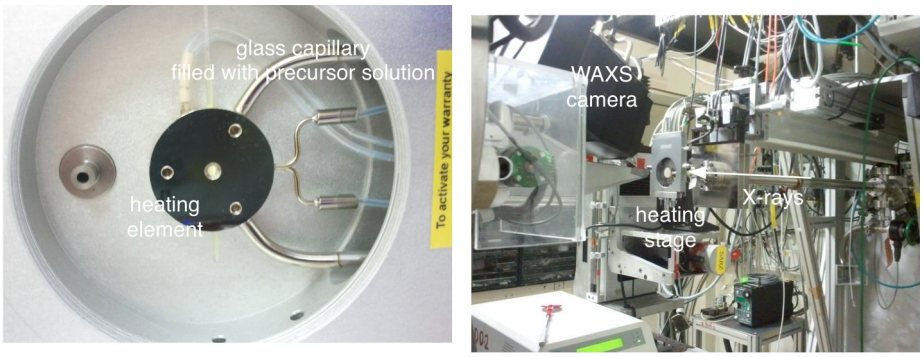

Figure 1: Left : Linkam hostage with a capillary filled with a precursor solution. The metal round part can be heated at the deisred temperature and the X-rays go through the capillary through the hole at the center of the heated piece. Right : the hot stage set-up

ing the hot stage with the beamline. Second, the temperature control is very precise (0.1 °C) and the temperature evolution inside the hot-stage is very reproducible. The maximum temperature heating rate is 60 °C/min. This high value makes the transient regime between the ambient temperature and the goal temperature as short as possible. Finally, it is perfectly suited for the use of glass capillary traditionally used for SAXS experiments.

A typical experiment happens as follow. First, the precursor solutions are mixed together and inserted in the glass capillary which is afterwards filled with dry argon and sealed with rubber. The capillary is then inserted in the hot-stage. Starting from ambient temperature, the capillary is then heated at the maximum heating rate while acquisition of SAXS patterns is triggered. Hence, we acquire SAXS patterns during the heating up of the solution and when the temperature reaches its maximum value. Typically, 500 SAXS/WAXS patterns are acquired during one experiment for a reaction time of 30 minutes.

3 Preliminary results

We now discuss preliminary data treatment on a typical platelet synthesis occurring at 200 °C/min. This section will be augmented as the data analysis is made in the near future.

We first start to plot the average intensity and the invariant ($\int I(q)q^2dq$) as a function of time (or the SAXS acquisition number). These graphs are plotted to identify the different phases during the formation of the nanoparticles. We identiy three phases. First, the scattered intensity decrease while the temperature increases. From the SAXS patterns (data not shown) we see that the small angle region exhibit a bq^{-4} behavior with b decreasing with time. We think this is due to metal precursors which are not

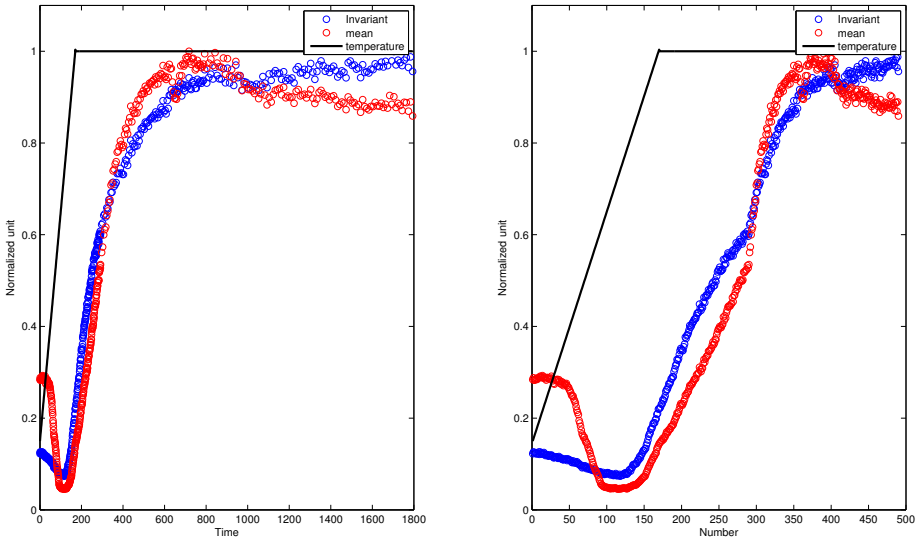

Figure 2: Normalized average intensity, invariant and temperature as a function of time (left) and SAXS pattern number (right). The difference in the abscissa is due to the fact that the frequency of acquisition is higher at the beginning of the sequence and is switched to a smaller value to look at "long" times.

fully solubilised in the solvent at ambient temperature but which solubility is increased as temperature raises. After that, the intensity remains constant for around 30 seconds while the temperature is reaching its maximum value. This induction period precedes the formation of the nanoplateletes. During this third phase the average intensity and the invariant are increasing steadily before reaching a plateau.

For the SAXS intensity to be properly analyzed we need to subtract the background intensity to keep only the intensity scattered by the platelets. We chose to subtract the intensity during the induction to all the subsequent SAXS patterns. The subtracted SAXS patterns are showed on figure 3.a). We see that the intensity at low q increases while a q^{-2} regimes appears at high q. This is the signature of the formation of platelet nanoparticles. On the WAXS side (figure 3.b) Bragg peaks are appearing during the reaction while the broad peak visible at 13 nm^{-1} is due to the solvant (octadecene).

These patterns will be analyzed in a more quantitive fashion in the coming weeks but from these first steps we are confident that the data we acquired during this experiment are of high quality and that the treatment will lead to the important new results.

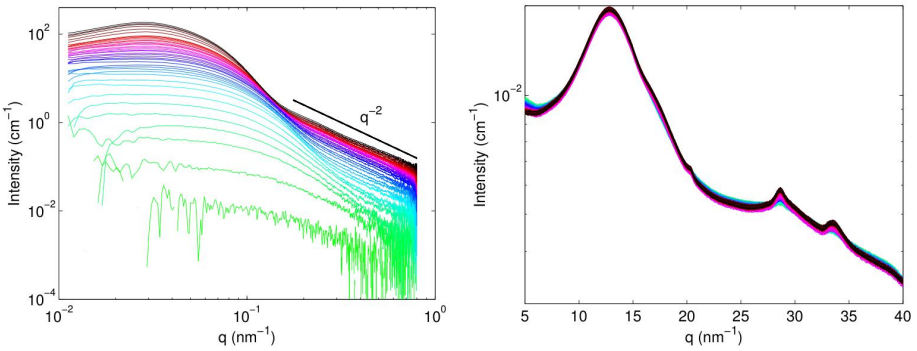

Figure 3: Left : a series of substracted SAXS patterns during the formation of CdSe nanoplatelets.Right : WAXS patterns.

4 Conclusion and perspectives

In conclusion, at this point of the data treatment, we consider that we will be able to obtain significant new experimental results on the formation mechanism for CdSe nanoparticles and CdSe nanoplatelets. More specifically, effect of temperature and concentration have been explored in both case. These will be compared to several theories which have been published in the literature recently. More parameter variation would be of great interest to get a wider picture of the formation mechanism of nanoplatelets For example, exploring the chemical reactivity of the precursors and looking to other materials of the same family (such as CdS or CdTe) should be appealing. A new proposal has been submitted along these lines.