EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Formation of semiconductor nanocrystals through hot-injection	**Experiment number**: HC-3725
Beamline: ID02	**Date of experiment**: from: 09-03-2018 to: 12-03-2017 from: 27-07-2018 to: 29-07-2018	**Date of report**: 13-09-2018
Shifts: 9+9	**Local contact(s)**: Thomas Zinn	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We have performed SAXS measurements to study the formation mechanism of CdSe semiconductor nanocrystals (NCs) through the hot injection synthesis. There are few reports on the formation mechanism of NCs but either only *via in/ex situ* optical absorption spectroscopy data or with reaction setups not accurately reproducing the hot-injection conditions. In this experiments we have performed the synthesis of CdSe NCs in a custom made setup to reproduce exactly the same synthesis conditions used in the laboratory and, at the same time, probe the growing NCs *in situ* with a ms time resolution.

The synthesis of semiconductor NCs, or quantum dots, is typically performed with a hot-injection method. In this method, a solution of one of the two precursors is quickly injected in a thermally activated solution of the second precursor. Due to the harsh synthesis conditions (high temperatures, oxygen and water free atmosphere) and due to the very fast formation timescale (ms), it is very challenging to study the formation of these particles with synchrotron-based X-ray scattering techniques. For this reason there are only few reports on this kind of measurements, and in all of them the NCs are either already formed (static measurements) or they are produced *in situ* through the prior mixing of the precursors and their heat up in capillaries (*i.e.* in a different synthesis environment and not with a hot injection procedure). To perform this experiment in exactly the same conditions used in the lab, we developed a custom built setup to perform a hot injection synthesis while probing the sample with X-rays. For this purpose we designed a three neck flask with an indentation for the transmission of the X-rays, heated with a heating ribbon and connected to a remotely

controlled liquid/powder injector (Figure 1). With this setup we studied the formation of CdSe NCs (spherical and platelet-like) through Small Angle X-ray Scattering (SAXS) experiments at a detector distance of 0.8m.

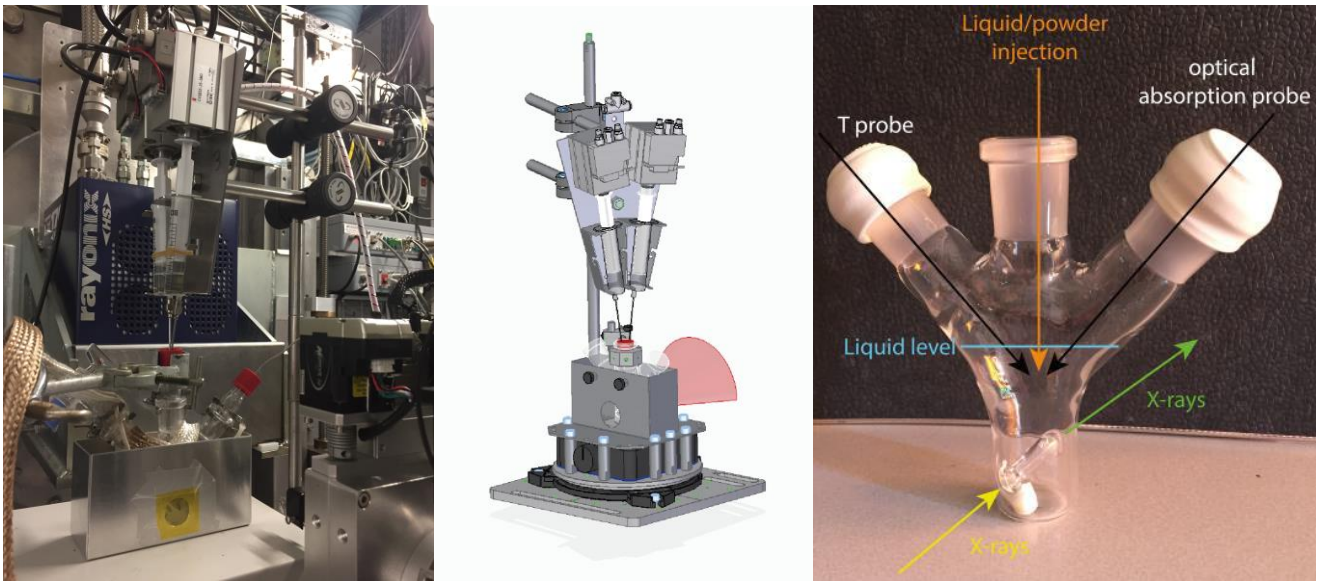

Figure 1: Experimental setup used in the experiments.

For the nanoplatelet geometry, we performed three syntheses with different formation temperature and injecting our precursors at different recation times, while probing the reaction mixture with a time resolution of 1 s (Figure 2). From the evolution of the scattering pattern we can extract information about the formation mechanism of the nanoplatelets. In particular the preliminary analyses highlight the formation of semiconductor NCs in the early stages of the reaction, followed by the injection of the precursor (peak at 6 nm^{-1}), which dissolved over time thus triggering the two dimensional growth (highlighted by the increased scattering at small q values). At very long reaction times (>1350 s) we observe the appearance of structure factor peaks associated to the stacking of the nanoplatelets. Further analysis will be required in order to separate the scattering contributions of the NCs to the one of the nanoplatelets, thus allowing us to unravel the exact formation mechanism of the two dimensional CdSe nanoplatelets.

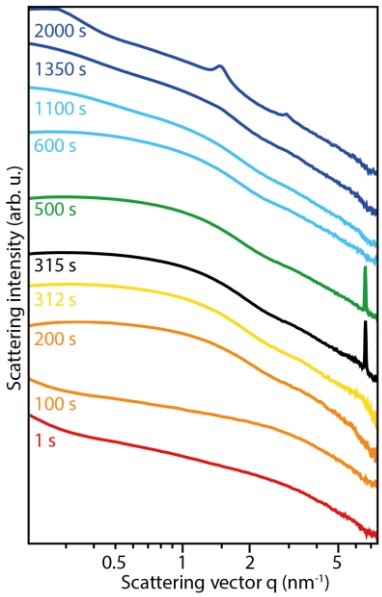

Figure 2: Time resolved X-ray scattering patterns of forming NPLs. Evolution of the temperature of the reaction flask during the synthesis. Each stage of the reaction is identified with a color coding. The black dot identifies the moment where the cadmium acetate has been injected in the reaction flask. The oscillations of the temperature over time are due to the temperature controller trying to keep the temperature constant.

Concerning the formation of the NCs, we performed several hot injection syntheses with different synthesis parameters (quantity of precursors, injection temperature, growth temperature) while probing the reaction

mixture through SAXS with a time resolution as small as 0.122 s (Figure 3). From the evolution of the scattering pattern with reaction time, we observe the appearance of spherical form factor minima associated to the nucleation of the NCs, and their shift toward smaller q values over time, indicating growth. A preliminary fitting of the scattering patterns over time allowed us to extract the evolution of the concentration of the NCs in the reaction mixture, as well as of their radius and of their size distribution. Further analyses will be required to extract all the useful information necessary to develop a formation mechanism model.

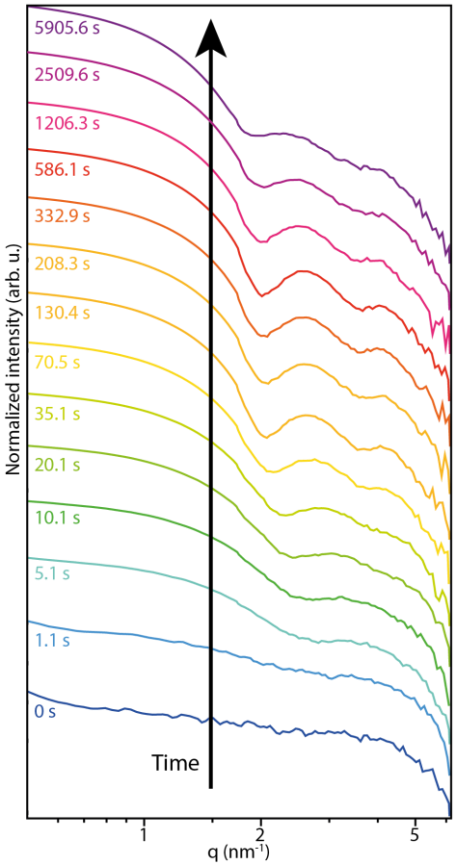

Figure 3: Time resolved X-ray scattering patterns of QDs synthesized through hot injection. (a) Small angle X-ray scattering patterns of the reaction mixture at different times.

To summarize, we performed, for the first time, a study on the formation kinetics of NC systems with a hot injection method *in situ*, in real time and in experimental conditions similar to the ones used in the laboratory with time resolutions as high as 122 ms. Although the results deserve a more detailed and more quantitative analysis, preliminary considerations show that our experiments were successful in following the growth of the CdSe NCs and nanoplatelets. Further analysis are required to extract all the information from the scattering patterns and thus allow a complete reconstruction of the formation mechanism.