In situ probing of transition metal dichalcogenide monolayers nucleation and growth using time-resolved SAXS and WAXS

The experiments performed on the beamline ID02 in November 2021 have provided a large amount of positive results. *In situ*, time-resolved, SAXS/WAXS sequences were obtained by inserting the precursors in sealed capillaries, heated up using a linkham hotstage, up to a final temperature.

1) First, we obtained the last results required to study in depth the effect of water in the synthesis of 2-dimensional In_2S_3 nanocrystals. We previously demonstrated that the addition of small amounts of water in the synthesis progressively modifies the shape of the final product, from small hexagons (without water) to long nanoribbons less than 1 nm thick and more than 1 µm long.

In comparison to our previous experiments on this system, we performed similar syntheses with a detector further away from the sample (10 m), in order to acquire the signal over the appropriate q range for such long particles. During this beamtime, we performed several sequences modifying the amount of water and the final temperature. Our previous results seemed to indicate an unreported synthesis mechanism to explain the precisely controlled sub-nanometre thickness. These new results will particularly help us understand the lateral growth of the particles.

2) We performed preliminary experiments on 2-dimensional CeF_3 nanotriangles. In the same way as to our work on In_2S_3, we performed *in situ* SAXS/WAXS to get insights on their synthesis (Fig. 1). Although all the chemicals are different, the synthesis mechanism might be similar to In_2S_3, which would be the first demonstration of a universal mechanism for the synthesis of 2D nanocrystals.

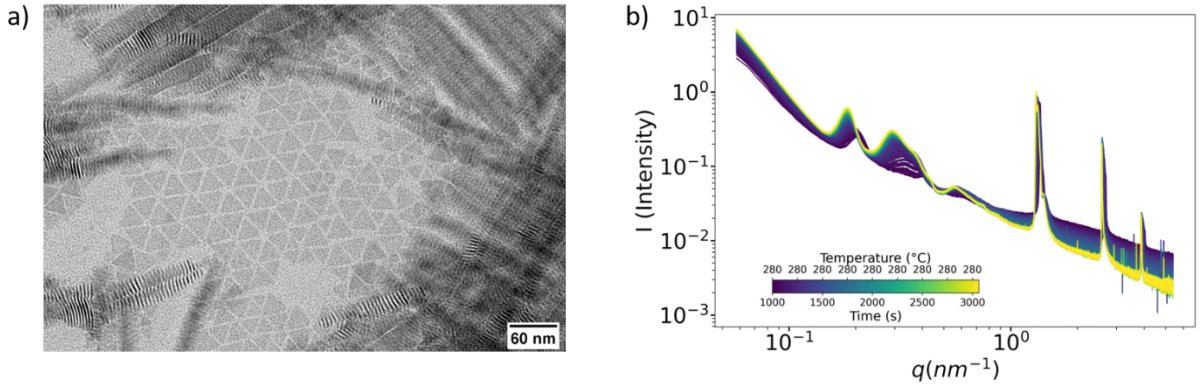

Figure 1. (a) TEM of 2D CeF_3 nanotriangles. (b) In situ SAXS measurements during the synthesis of the particles shown in panel a.

3) Additional preliminary experiments to follow particle synthesis were performed on CdSe wurtzite, PbS, WSe_2 and WS_2-WSe_2 heterostructures. In particular, CdSe wurtzite and PbS gave interesting results we would like to investigate in further details. CdSe wurtzite was studied ex-situ as the synthesis lasts for 24 hours. The synthesis was performed in the chemistry lab and aliquots were extracted every few hours and measured by SAXS. We still observe the appearance of Bragg peaks suggesting an early lamellar self-assembly which could explain the controlled sub-nanometre thickness, as seen with In_2S_3 and CeF_3 (Fig. 2a). The in-situ PbS synthesis does not show Bragg peaks but rather intriguing oscillations of the SAXS signal throughout the sequence (Fig. 2b), which we would like to investigate in more details.

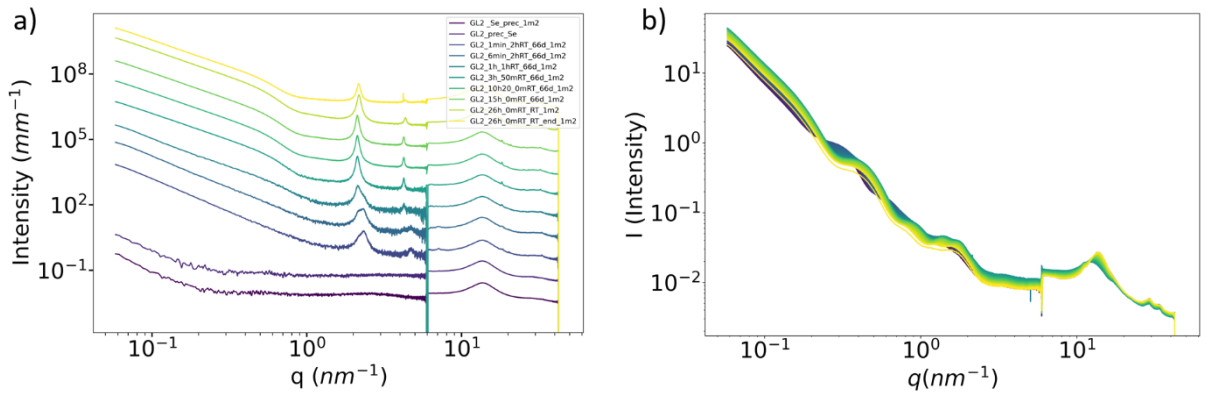

Figure 2. a) Ex situ SAXS measurements during the synthesis of 2D CdSe wurtzite nanoplatelets. b) In situ SAXS measurements during the synthesis of PbS nanocrystals (13 minutes at 168°C).

4) One of the goals of our project is to understand and control 2D nanoparticle deformation. To achieve this, we studied the effect of surface chemistry on pre-synthesised CdSe nanoplatelets. Fig. 3a shows how different surface chemistry drastically modifies the shape, and consequently the SAXS pattern, of CdSe nanoplatelets. For example, for a single particle surface chemistry (purple curve), we observe a dozen oscillations. We will use these data to determine the spatial geometry of the different nanoplatelets. Fig. 3b shows a modification of the CdSe nanoplatelets SAXS pattern when increasing the temperature from 25 to 280°C. We want to how the temperature modified the deformation of the structure and whether it is reversible.

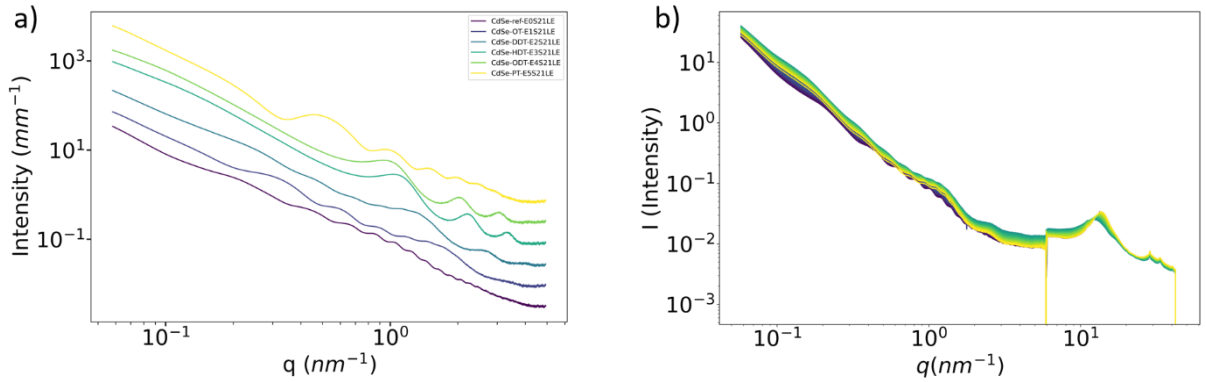

Figure 3. a) Effect of the surface chemistry of the shape of 2D CdSe nanoplatelets. b) Effect of the temperature (from blue to yellow, corresponding to 25 to 280°C)