Project Thesis: Colloidal Synthesis and Real-Time Microscopy of Layered SnS and SnSe Nanosheets: Towards Large-Scale and Controlled Growth for Emerging Applications

Group IV chalcogenides (SnS, SnSe) have been investigated recently as they are van der Waals semiconductors showing promise as 2D thermoelectrics and ferroelectrics materials[1,2]. So far, they have been prepared predominantly by vapor transport processes. These processes yield large quantities of nanosheets but formation of large arrays of nanosheets with similar thicknesses and sizes is relatively hard to achieve. Colloidal synthesis of group IV selenide 2-dimensional nanosheets has been demonstrated for both SnSe and SnS and promises to overcome these limitations.

We propose to establish the colloidal growth of layered SnSe and SnS nanosheets with large sizes and narrow size and thickness distributions required by possible applications. Large-scale sustainable synthesis of few-layer (e.g., 1–10 layers) SnSe and SnS is a challenge, which also slows progress in understanding their properties as a function of the number of layers.

Synthesis (performed at Sorbonne University): The few existing protocols for colloidal synthesis of SnS and SnSe are based on complicated multi-step approaches[1,3,4]. We have recently achieved a 1-pot synthesis of SnS nanosheets using $SnCl_2$, an inexpensive tin salt, as the metal precursor and alkyl-thiols as sulfur precursor. All the products are dispersed in a mixture of oleylamine (OLA), oleic acid (OA) and octadecene and heated at high temperature 280°C. SnS square nanosheets were synthesized (Fig. 1A) with a thickness around 30 nm and a phase purity confirmed by the characteristic Raman modes at 160, 186, and 216 cm^{-1} (Fig. 1A, inset) and high-resolution transmission electron microscopy (TEM) (Fig. 1B).

We will further develop the approach by changing different synthesis parameters such as the reaction temperature, the amount of OLA and the nature of the chalcogenide precursor (S powder, octanethiol, dodecanthiol or thiocetamide) to achieve synthesis of nanosheets of controlled thicknesses and sizes. In particular, we will target uniform thicknesses in the range of 1- 20 monolayers (with a thickness lower than 10 nm) as such nanosheets show ferroelectricity. OLA is expected to control the growth of the nanosheet by a selective absorption on specific facets[5,6]. Decreasing OLA or increasing the reaction temperature will reduce the passivation effect, which will lead to the thickening of SnS

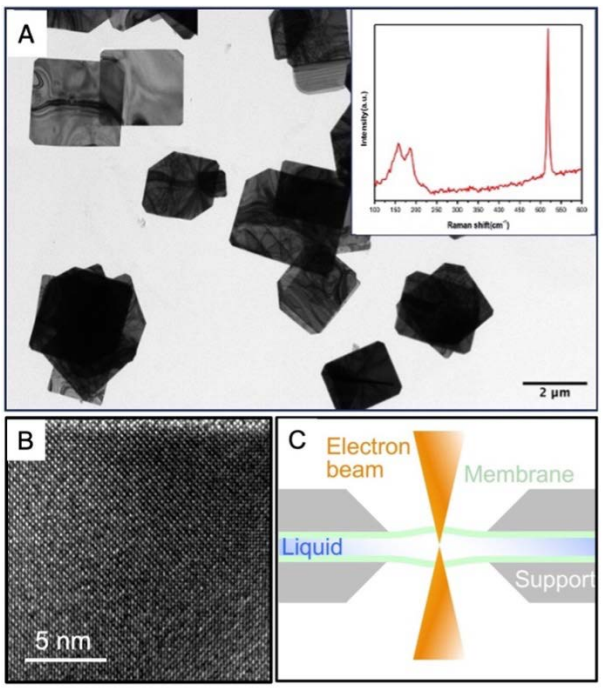

Figure 1: A. TEM image of SnS nanosheets synthesized by a one-pot synthesis at 280 °C. Inset: Raman spectrum of the SnS nanosheets. B. High-resolution TEM image of the single crystalline SnS flakes. C. Schematic representation of the in-situ LCEM set-up: microfabricated cells hermetically encapsulate bulk solutions between ultrathin electron transparent membranes that provide long-term protection from evaporation in the high-vacuum environment of the transmission electron microscope and allow observation of processes in liquids.

nanosheets. We have also found that the combination of OAm and OA ligands can influence the size distribution of SnS NCs. We will then extend the approach to the synthesis of SnSe by initially changing the chalcogenide precursor to Se powder dispersed in OLA or OA. Ributylphosphine-selenium (TBP−Se) and trioctylphosphineselenium (TOP−Se) could be also used as the precursors for the synthesis. The nature of the chalcogenide precursor can indeed influence the final morphologies of the SnSe nanoparticles. The crystal structure and morphology of the nanosheets will be investigated using TEM imaging and electron diffraction (both at Sorbonne University and University of Nebraska-Lincoln). The thickness will be monitored with AFM and thickness-dependent Raman measurements. The ferroelectric domain imaging both in SnS and SnSe will be performed by piezoresponse force microscopy (PFM) and in-situ low-energy electron microscopy (LEEM) at the University of Nebraska-Lincoln[2].

Real-time studies of nucleation and growth (performed at the University of Nebraska-Lincoln). Following the ex-situ characterization usually performed after the reaction is complete or by quenching the reaction at various time durations followed by TEM imaging, we will perform in-situ imaging during growth. We will use liquid cell electron microscopy (LCEM) to investigate the nucleation and follow the growth of nanosheets of SnSe and SnS in real time. LCEM is a powerful approach that allows observations of processes in liquids with sub-nanometer resolution [7].The LCEM studies will use as precursors the colloidal solutions prepared and validated by ex-situ experiments at Sorbonne University. These will be introduced in the liquid cell for the observations (Fig. 1C). Here, we expect that the real-time observations will allow us i) to follow the nucleation and evolution of the growing material; ii) to identify the shape, size and mobility of critical and stable nuclei; iii) to directly identify different growth processes, i.e. growth in the solution, on the seed surface, or combinations of the two for formation of 2-dimensional sheets as well as for other shapes and dimensionalities; iv) to determine attachment and growth rates at different surface sites on the seeds. The in-situ observations and their analysis will further inform the synthetic effort at Sorbonne University and allow to adjust the reaction parameters to optimize the growth of SnS or SnSe to the desired range of morphologies, thicknesses and sizes for harnessing of their properties in applications.

The high feasibility rate and the low proportion of risk of this project is above all due to the extensive experience on one hand in colloidal synthesis and characterizations by Prof Alexa Courty from MONARIS laboratory and in the other hand in van der Waals materials and nanostructures studied by in-situ electron microscopy, by Prof Eli Sutter from University of Nebraska-Lincoln. The two supervisors have been collaborating since around ten years[8,9].

Highly motivated candidates (expecting a master degree or equivalent with excellent academic records) with a background in Physical Chemistry and Material Science are strongly encouraged to apply. Knowledge of the candidate in colloidal synthesis, surface and electron microscopy characterization will also be appreciated.

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