Project Thesis: Optimizing Colloidal Synthesis and Growth of SnS and SnSe Nanosheets for Ferroelectric Applications.

Group IV chalcogenides (SnS, SnSe) have recently attracted attention as van der Waals semiconductors with potential applications in 2D thermoelectrics and ferroelectrics [1,2]. While vapor transport processes have been primarily used for their preparation, they often result in nanosheet arrays with limited uniformity in size and thickness. In contrast, colloidal synthesis of 2D SnSe and SnS nanosheets has been demonstrated, offering a promising solution to overcome these limitations. This project aims to establish a reliable colloidal synthesis of SnSe and SnS nanosheets with controlled size and thickness distributions, necessary for their application in various devices. Large-scale, sustainable synthesis of few-layer SnS and SnSe (e.g., 1–10 layers) remains a challenge, slowing progress in understanding their properties as a function of layer number.

Synthesis (performed at Sorbonne University): Existing protocols for colloidal synthesis of SnS and SnSe are complex and involve multi-step procedures[1,3,4]. We have recently developed a simple one-pot synthesis method for SnS nanosheets using $SnCl_2$ (an inexpensive tin salt) as the metal precursor and alkyl thiols as sulfur sources. The products are dispersed in a mixture of oleylamine (OLA), oleic acid (OA), and octadecene and heated to 240°C. Well-crystallized SnS square nanosheets, approximately 30 nm thick, were successfully synthesized (Fig. 1A), with their phase purity confirmed by Raman peaks at 160, 186, and 216 cm^{-1} (Fig. 1A, inset) and their crystallinity verified by HR-TEM (Fig. 1B).

We will refine this approach by varying key synthesis parameters, such as reaction temperature, OLA concentration, and the nature of the chalcogenide precursor (e.g., sulfur powder, octanethiol, dodecanethiol, or thioacetamide). The goal is to achieve nanosheets with controlled thicknesses and sizes, targeting thicknesses ranging from 1 to 20 monolayers, with a desired thickness of around 10 nm, which is known to exhibit ferroelectric properties. OLA is expected to influence the growth of the nanosheets by selectively adsorbing onto specific facets[5,6] and modifying its concentration or increasing the temperature will reduce the passivation effect, leading to thicker nanosheets. Recent findings suggest that the combination of OLA and OA ligands also affects the size distribution of SnS nanosheets. We will extend this method to synthesize SnSe nanosheets by adjusting the chalcogenide precursor, such as Se powder dispersed in OLA or OA. Alternative precursors like ributylphosphine-selenium (TBP-Se) and trioctylphosphine-selenium (TOP-Se) will also be explored, as they can influence the final morphology of the SnSe nanoparticles.

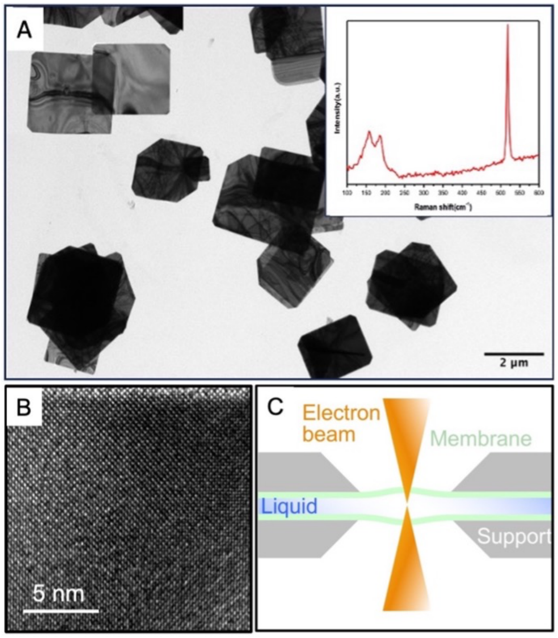

Figure 1: A. TEM image of SnS nanosheets synthesized by a one-pot synthesis at 280 °C. Inset: Raman spectrum of the SnS nanosheets. B. High-resolution TEM image of the single crystalline SnS flakes. C. Schematic representation of the in-situ LCEM set-up: microfabricated cells hermetically encapsulate 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.

The crystal structure and morphology of the nanosheets will be analyzed using TEM, X-ray diffraction, and phase purity will be assessed with EDS and Raman spectroscopy. AFM and thickness-dependent Raman measurements will be used to monitor nanosheet thickness.

Real-time studies of nucleation and growth (performed at the University of Nebraska-Lincoln). 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. The LCEM study will use as precursor the colloidal solutions prepared at Sorbonne University. These will be introduced in the liquid cell for the observations. In-situ observations will shed light on the nucleation, the shape, size and mobility of critical and stable nuclei, the possible growth pathways for formation of 2-dimensional sheets as well as for other shapes and dimensionalities. These will further inform the synthetic effort at Sorbonne University and allow to adjust the reaction parameters to optimize the growth of very thin nanosheets of SnS or SnSe.

Ferroelectric properties: Piezoresponse force microscopy (PFM) and in-situ low-energy electron microscopy (LEEM) at the University of Nebraska-Lincoln will be used to investigate the ferroelectric domain structures, switching behavior, and the impact of nanosheet thickness on ferroelectricity.[2] Ferroelectricity in few-layer SnS and SnSe arises from interlayer interactions and symmetry breaking, with ultrathin layers (below 20 monolayers) exhibiting polarization. Additionally, the distortion of the SnX (X = S, Se) lattice in these layers modulates spontaneous polarization, potentially enabling tunable ferroelectric devices. Cathodoluminescence (CL) will complement PFM and LEEM analyses to probe the optoelectronic properties expected to be different in the ferroelectric flakes.

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 have collaborated for more than a decade[7,8].

Research program

The primary goals of this project are to:

- Synthesize SnS and SnSe nanosheets with controlled thickness and phase purity.
- Investigate the nucleation and growth mechanisms of nanosheets and other shapes.
- Achieve exceptional properties, including ferroelectricity, in ultrathin materials.

To achieve these objectives, the PhD candidate will:

- Synthesize SnS nanosheets with controlled size and thickness, performing chemical and structural characterization.
- Extend the synthesis to SnSe nanosheets with controlled size and thickness.
- Conduct in-situ LCEM studies of nucleation and growth processes.
- Study the ferroelectric domain structure of SnS and SnSe nanosheets using PFM, LEEM, and CL.

References

[1] Z. Li, Q. Wang, X. Yang, S. Song, J. Wang, S.-F. Wang, *Chemical Engineering Journal* 2022, *430*, 133049.

[2] P. Sutter, H. P. Komsa, H. Lu, A. Gruverman, E. Sutter, *Nano Today* 2021, *37*, 101082.

[3] X. Hu, G. Song, W. Li, Y. Peng, L. Jiang, Y. Xue, Q. Liu, Z. Chen, J. Hu, *Materials Research Bulletin* 2013, *48*, 2325.

[4] X. Liu, Y. Li, B. Zhou, X. Wang, A. N. Cartwright, M. T. Swihart, *Chem. Mater.* 2014, *26*, 3515.

[5] L. Shi, Q. Li, *CrystEngComm* 2011, *13*, 6507.

[6] M. Cao, K. Yao, C. Wu, J. Huang, W. Yang, L. Zhang, F. Lei, Y. Sun, L. Wang, Y. Shen, *ACS Appl. Energy Mater.* 2018, *1*, 6497.

[7] K. Ouhenia-Ouadahi, A. Andrieux-Ledier, J. Richardi, P.-A. Albouy, P. Beaunier, P. Sutter, E. Sutter, A. Courty, *Chemistry of Materials* 2016, *28*, 4380.

[8] E. Sutter, K. Jungjohann, S. Bliznakov, A. Courty, E. Maisonhaute, S. Tenney, P. Sutter, *Nat Commun* 2014, *5*, 4946.