Revealing the potential of transition metal dichalcogenides for thermoelectric applications through nanostructuring and confinement

MELODICA

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Partner	Country	Institution/ Department	Name of the Principal Investigator (PI)	Name of the co-Investigators	Other participants
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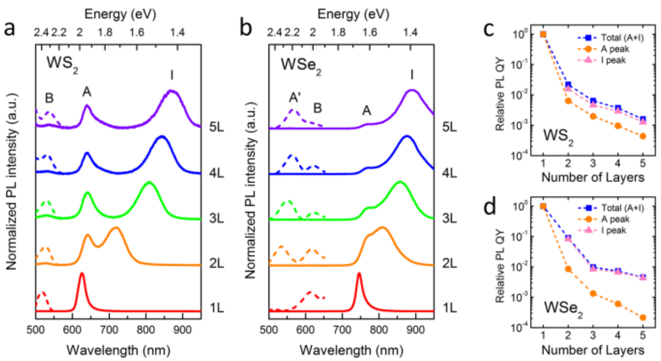
Starting points:

1.

The electronic structure of TMDs is <u>observed</u> to change dramatically from bulk to few ML samples: e.g. indirect-to-direct band gap crossover in ML semiconducting TMDs (MoS_2, WS_2, WSe_2, $MoSe_2$), changes in magnitude of the band gap, exciton binding energy, spin-orbit splitting



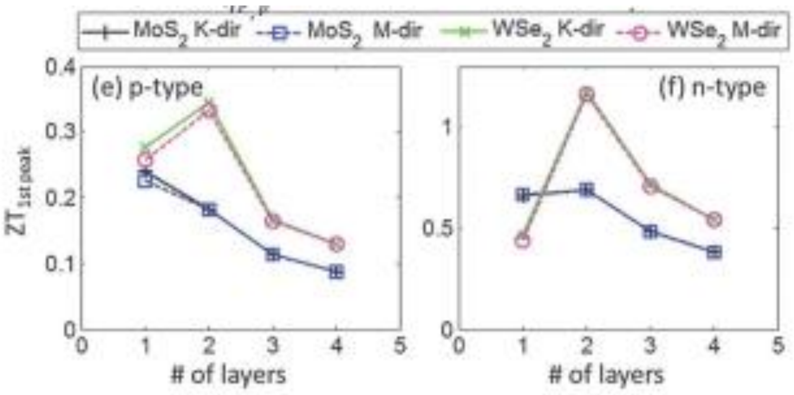
W. Zhao et al., ACS Nano Lett. 7, 791 (2012)

2.

Thermoelectric properties are <u>predicted</u> to improve from bulk to few MLs (e.g. in MoS_2, WSe_2). In particular, 2D confinement is predicted to decrease κ and increase ZT

A. Arab et al. Sci. Rep. 5, 13706 (2015)

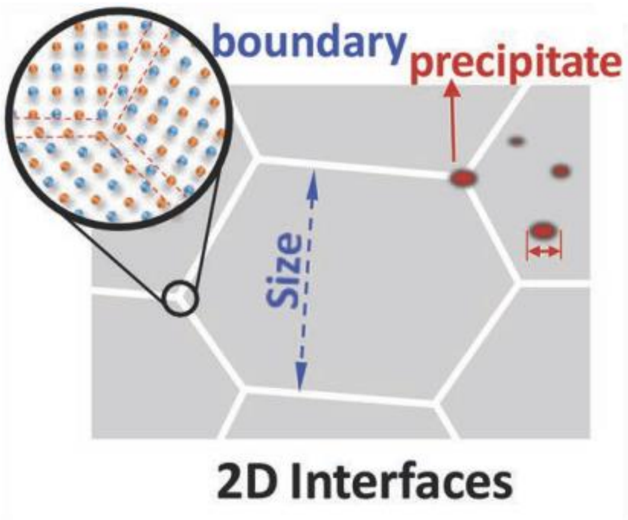
W. Huang et al., Phys. Chem. Chem. Phys. 16, 10866-10874 (2014)



W. Huang et al., Phys. Chem. Chem. Phys. 16, 10866-10874 (2014)

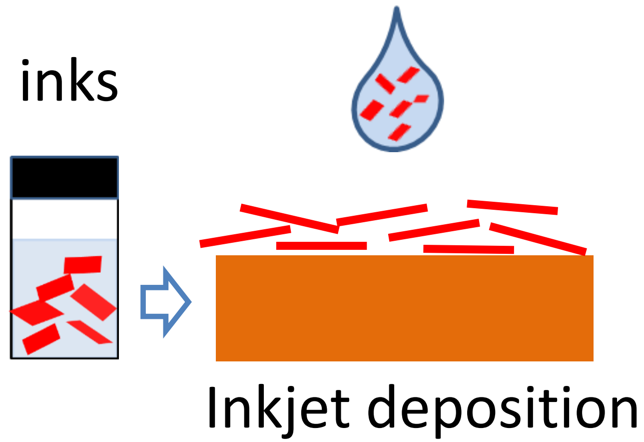
3.

Nanostructuring is an effective and widely pursued route to induce scattering of low-frequency phonons, thus decreasing κ_L in a number of thermoelectric compounds



4.

TMD flakes can be produced by liquid phase exfoliation (LPE) and restacked nano-flake assemblies can be obtained by inkjet printing or drop-casting



Aim of the proposal:

confinement

studied in MBE deposited films

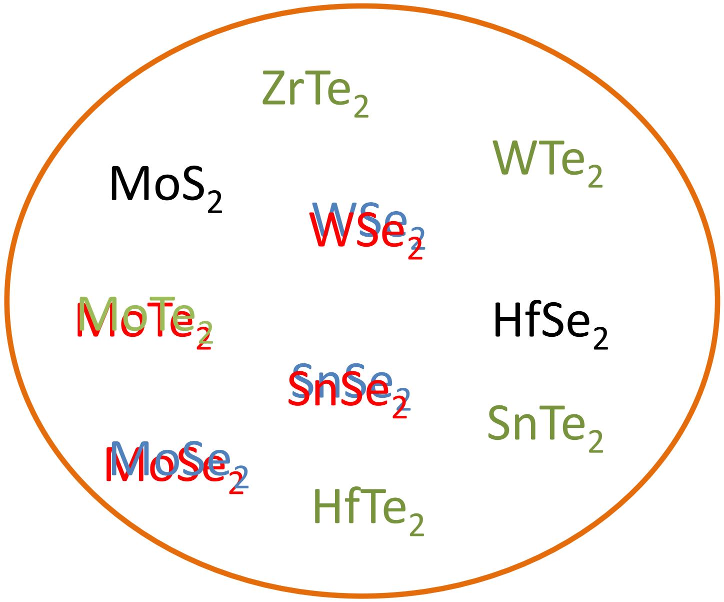
nanostructuring

studied in restacked nanoflakes assemblies

→ **Possibly improved thermoelectric figure of merit $ZT=S^2\sigma T/\kappa$ for applications of TMDs in energy conversion and cooling**

This project explores the potential of tuning electronic confinement and nanostructured morphology in view of enhancing the thermoelectric performance of transition metal dichalcogenides (TMDs). By combining experimental measurements on samples in different forms (single flakes, films, heterostructures and restacked nano-flake assemblies) and theoretical calculations (first principles calculations for electron and phonon states, statistical approach to model transport across interfaces in nano-flake assemblies), we aim at obtaining a comprehensive understanding of the physical mechanisms into play and a realistic assessment of TMDs as thermoelectric materials for device applications in energy conversion or cooling, such as thermoelectric micro-coolers.

TMD compositions



Restacked nanoflakes by LPE
Epitaxial films by MBE (starting material)
Epitaxial films by MBE (in a second stage)

We will consider also preparing less common TMDs, such as **$ZrTe_2$, $TiTe_2$, $ZrSe_2$, $TiSe_2$**, whose more complex trigonal u.c. should be associated to smaller κ_L

Sample forms

- Single crystals
- Epitaxial thin films and heterostructures
- Restacked nano-flake assemblies

Characterization methods

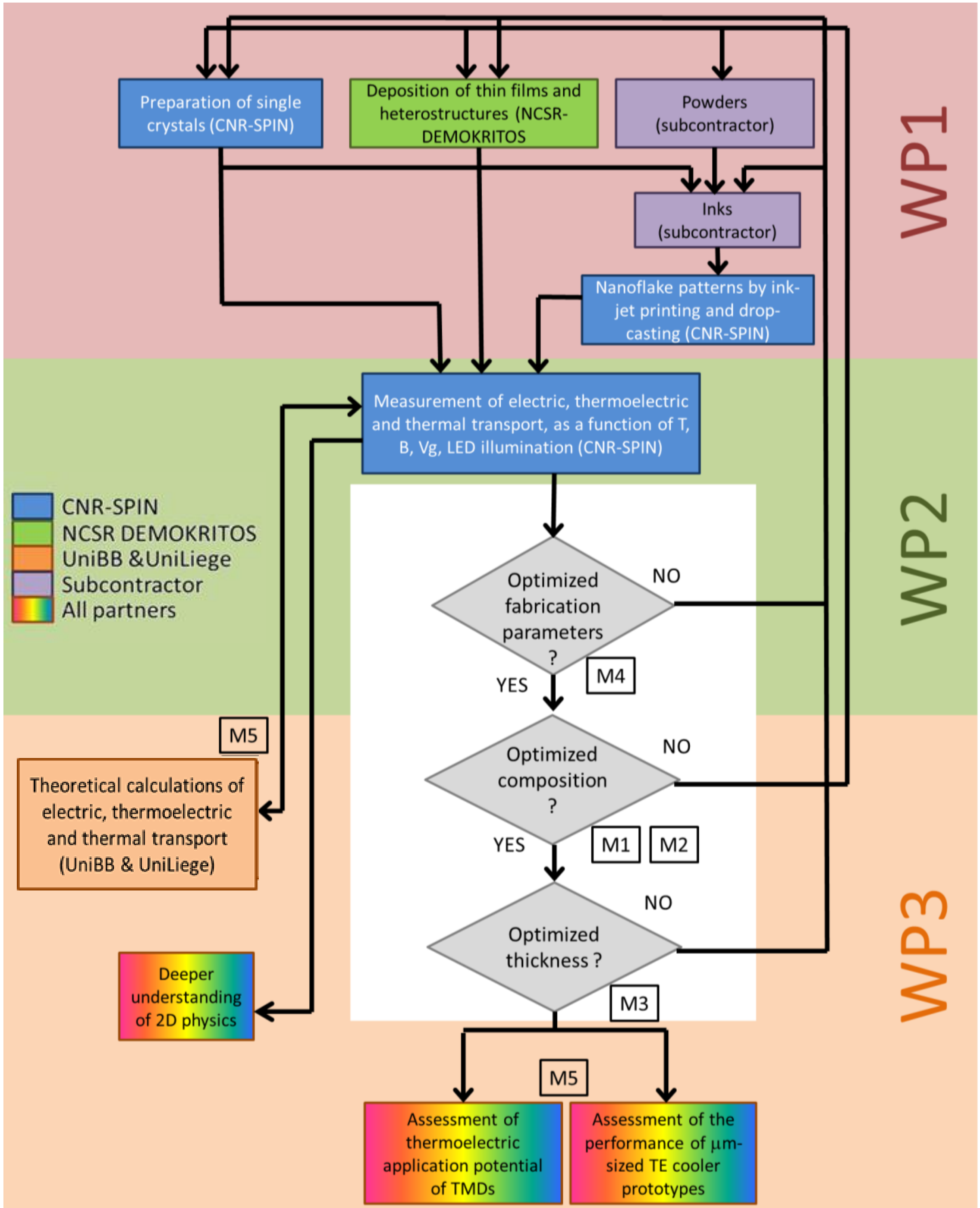
- Electric , thermoelectric and thermal transport (T, H, V_{gate}, LED illumination)
- SEM, AFM, XPS, ARPES, UHV-STM, microRaman

Theoretical calculations

- first principles calculations for electron and phonon states, velocities, and scattering rates (microscopic description)
- statistical approach to model transport across interfaces in nano-flake assemblies (mesoscopic description)

Design of a TE module

- Finite element simulation of a μm-size TE cooler based on p-n legs, working as solid-state heat pump



WP1: sample preparation

WP2: characterization of electric, thermoelectric and thermal transport

WP3: theoretical calculation of electric, thermoelectric and thermal transport and assessment

Main goals

- **Optimization of sample fabrication (TRL3)**
  - for nanoflake assemblies: inkjet and dropcast processing, effect of metal additions to improve σ, effect of flake shape anisotropy and orientation-dependent κ of grain boundaries to lower κ, …
  - for films: growth rate, protocol for transfer to another substrate, …
- **Understanding (TRL1-2)** thermoelectric and thermal transport in TMDs samples of different forms (focus on the role of interfaces and grain boundaries and of confinement)
- **Assessment** of TMDs as thermoelectric materials
- **Design (TRL3)** and simulate the performance of a solid state heat micro-pump based on p-type and n-type TMDs, operating at 300K-500K

Success criteria

- κ at room temperature ~ few $Wm^{-1}K^{-1}$ in nanoflake assembiles and < 30 $Wm^{-1}K^{-1}$ in films (literature values in single flakes are mostly ~ tens $Wm^{-1}K^{-1}$, record value 0.73 $Wm^{-1}K^{-1}$ in MoS_2 granular films)

- S ~ hundreds mV/K in films at room temperature and in the depletion regime (in literature ~30 mV/K in ML MoS_2)

- $S^2\sigma$ ~ 10-100 $\mu W\ cm^{-1}\ K^{-1}$ in films at room temperature (in literature ~ hundreds $\mu W\ cm^{-1}\ K^{-1}$ in ML MoS_2 and WSe_2)

- ZT in the range of unity at room temperature (in literature ~ 0.13 in SnS_2 nanosheets)

Interaction with the Flagship

Alignment of the activities and objectives of the project with the work-programme of the Flagship:

- Liquid phase exfoliation technologies for the production of Graphene Related Materials (GRMs) inks in quantities sufficient to be used for large scale production in printed electronics and deposition and integration of GRMs onto various technological substrates. This project deeply investigates the GRMs flake aggregation process upon ink drying, which is a fundamental prerequisite to obtain reliable fabrication methods.

- Obtained results will be important for the established activity of the flagship, in term of material development, heterostructures, devices, general understanding of physical mechanisms.

- The project follows a direction, not yet covered by the flagship, of natural expansion to kindred materials and their application in the field of energy conversion (TMDs, possibly having κ much smaller than that of graphene). On the other hand, the project may take advantage of the scientific and technological achievements, as well as close connection with the industry, gained with graphene in the field of energy generation and storage.