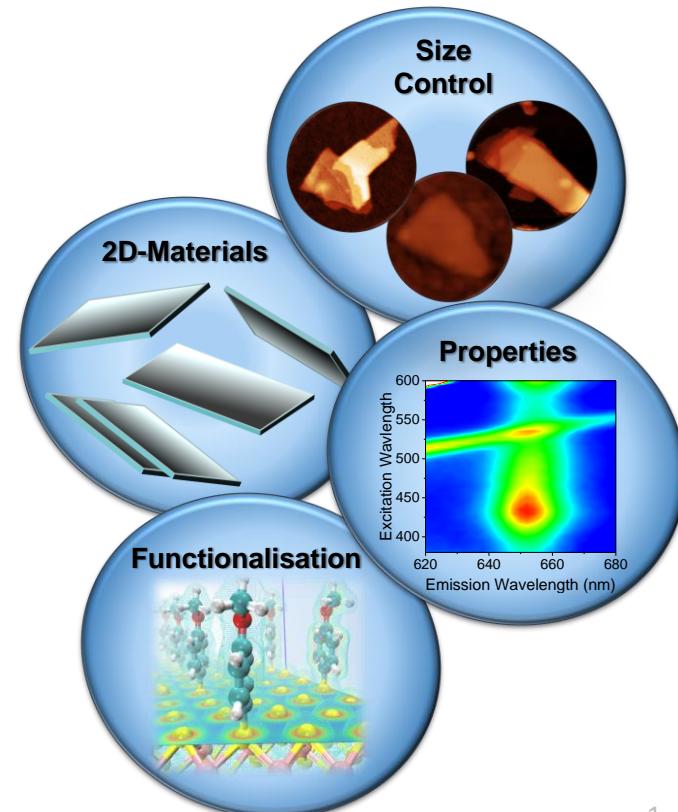


Nachwuchsgruppe Dr. Claudia Backes

In Lösung exfolierte anorganische Schichtmaterialien (z.B. MoS₂, GaS, schw. P) als Bausteine für funktionale Architekturen

Themengebiete:

- **Prozessoptimierung der Exfoliierung**
- **Größenselektion (Zentrifugation...)**
- **Spektroskopische Eigenschaften
→ Quantitative Größenbestimmung!**
- **Funktionalisierung, chemische Dotierung**
- **Hierarchische Strukturen:
“mix and match”**



Acknowledgement

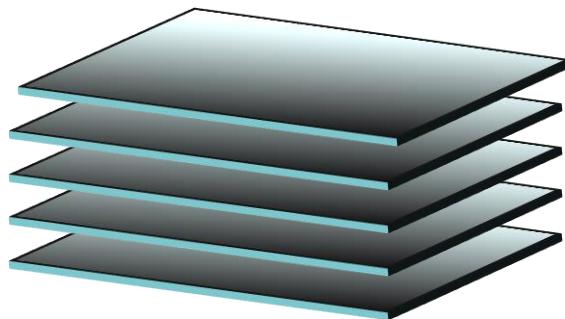


**Lehrstuhl Angewandte
Phys. Chemie (Zaumseil)**



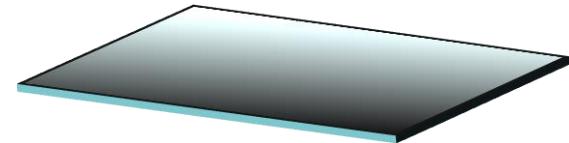


2D-materials

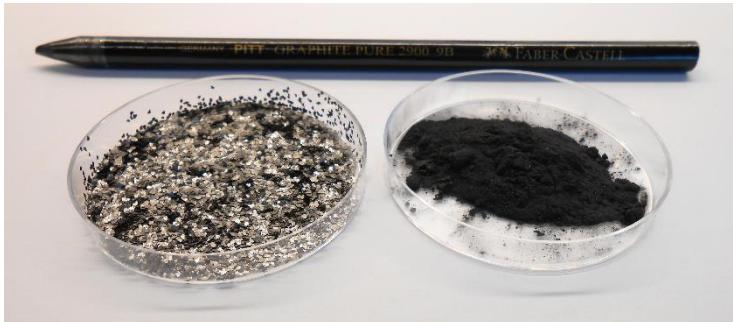


Graphite

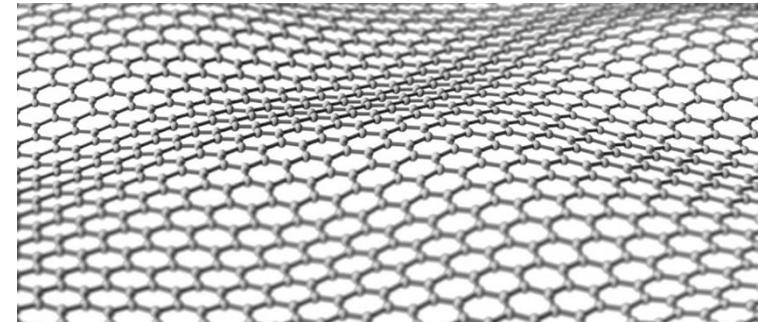
Exfoliation



Graphene



→

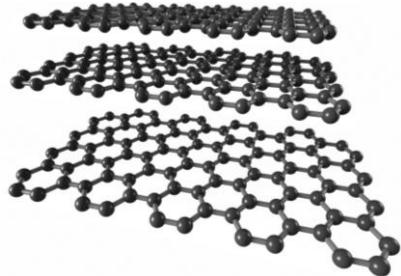


- Exciting physics and spectroscopy due to quantum confinement in 2D
- Huge surface area: Old materials with new chemistry!
- Application potential in diverse areas (electronics, catalysis, energy)

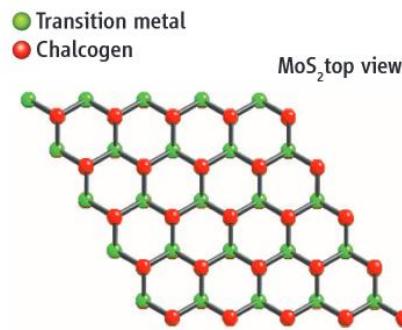
Spectroscopic metrics library



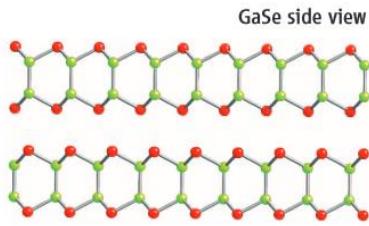
Graphite/Graphene



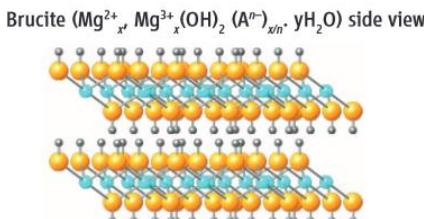
Transition metal dichalcogenides



III-VI semiconductors



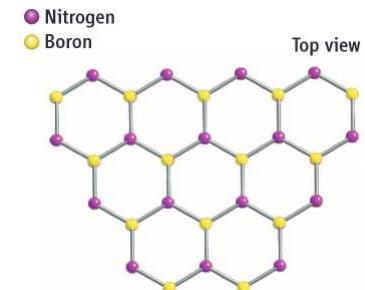
Layered hydroxides



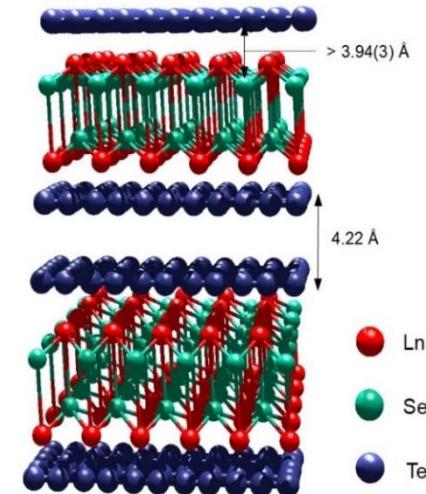
Single element; e.g. P, Sb



Hexagonal boron nitride

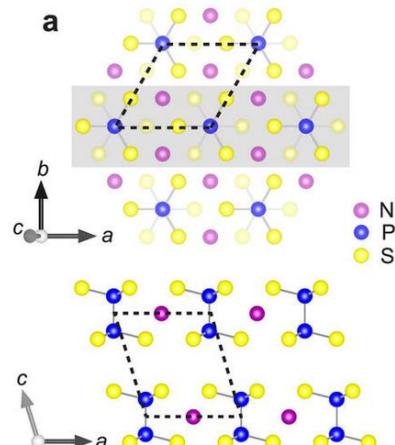


Rare earth polychalcogenides



Thomas Doert, TU Dresden

Transition metal phosphorus trisulfides

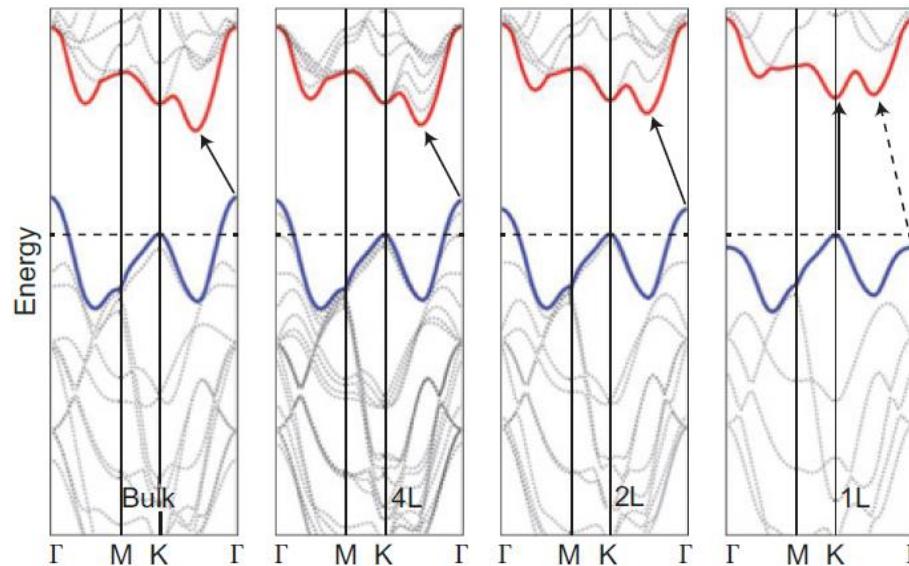
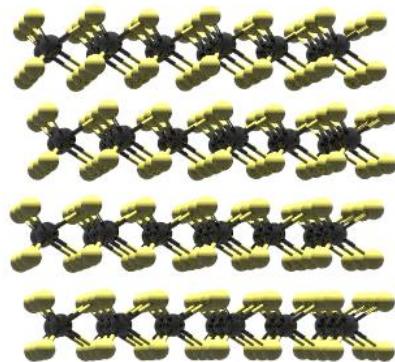


Wolfgang Bensch, Uni Kiel

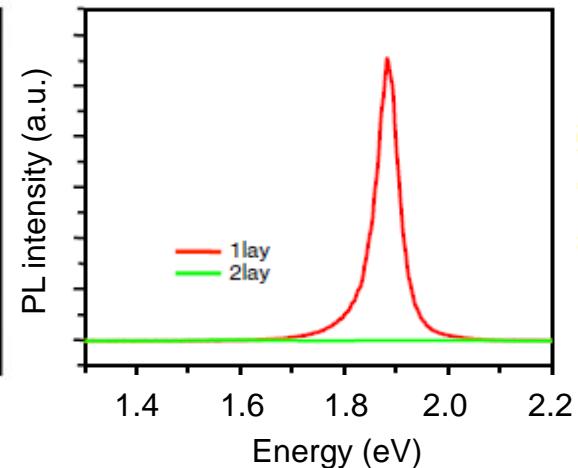
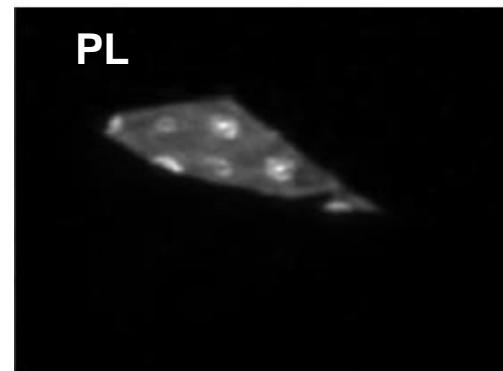
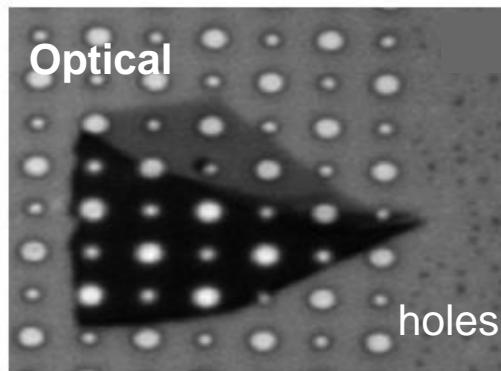
2D-Transition metal dichalcogenides



Quantum confinement in 2D materials



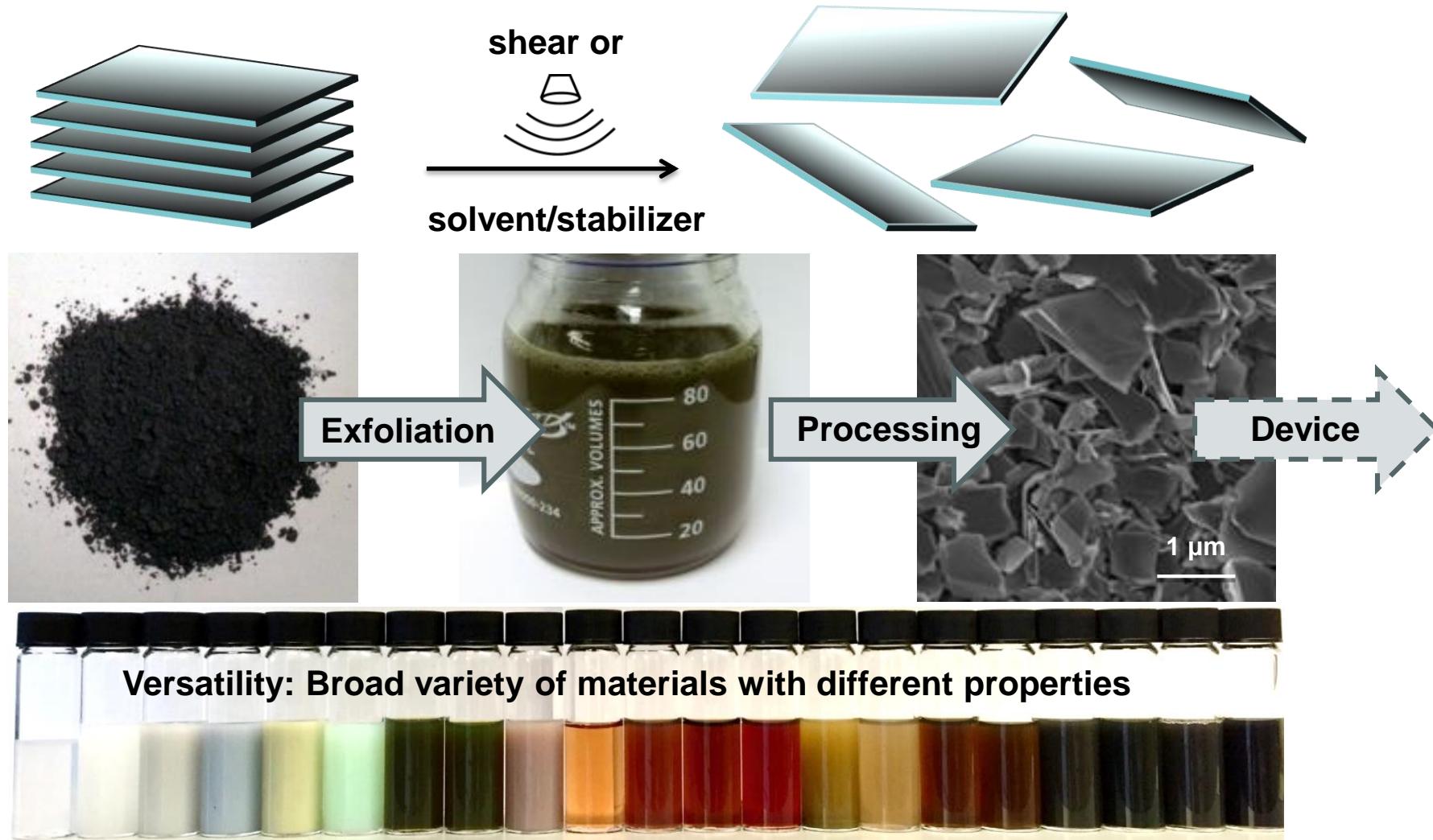
- Direct gap
Semiconductor
→ High absorption
→ Higher PL yield
→ Large exciton binding energy





Liquid exfoliation

Liquid exfoliation: bulk quantities



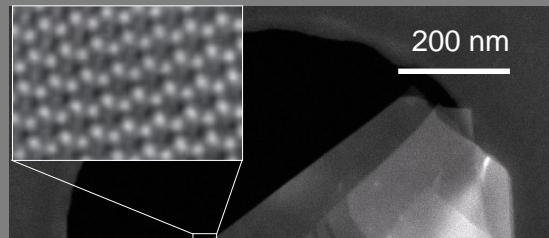
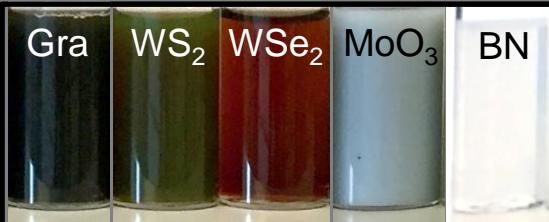
Coleman et al., *Science* 2011, 331, 568.
Bonaccorso et al., *Adv. Mater.* 2016, 28, 6136.

Backes et al. *JOVE* 2016
Backes et al. *Chem. Mater.* 2016



Process chain 2D-materials

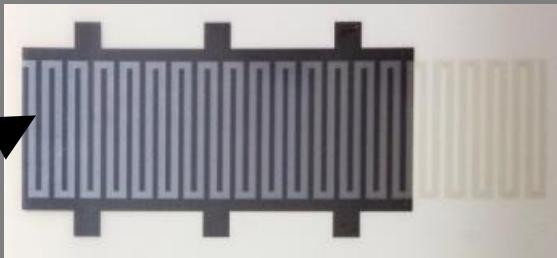
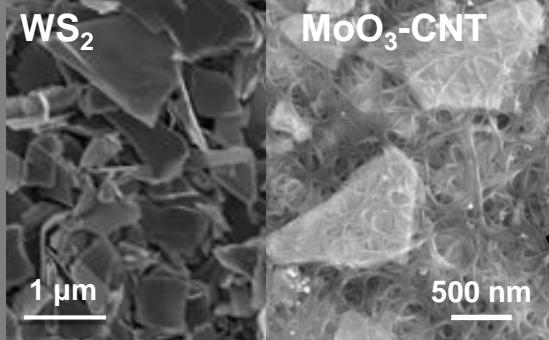
NANOSCALE



Synthesis
Exfoliation and
ink formulation

Size control
Functionalisation

MESOSCALE



Deposition
Thin film formation
Hybrid & composite
preparation

MACROSCALE



(Opto)electronics

Energy storage &
conversion

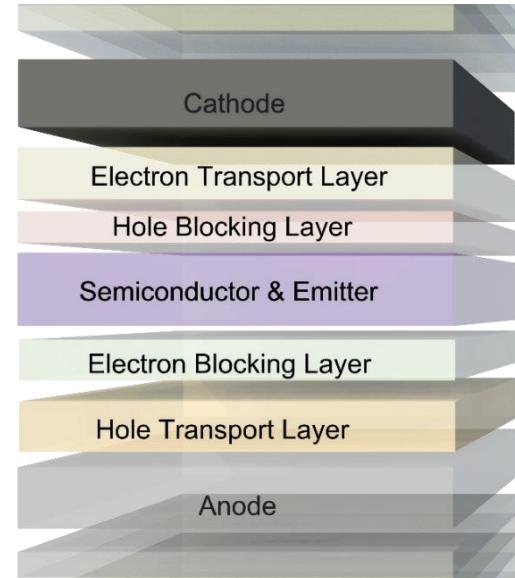
Catalysis



Challenges example

Solutions to challenges by using chemistry

Challenges (before device fabrication)



1. High quality samples (monolayers!)
2. Prevent restacking in films
3. Improve charge transport in layer
4. Tune emission properties (doping, quantum yield)
5. Understand and avoid degradation



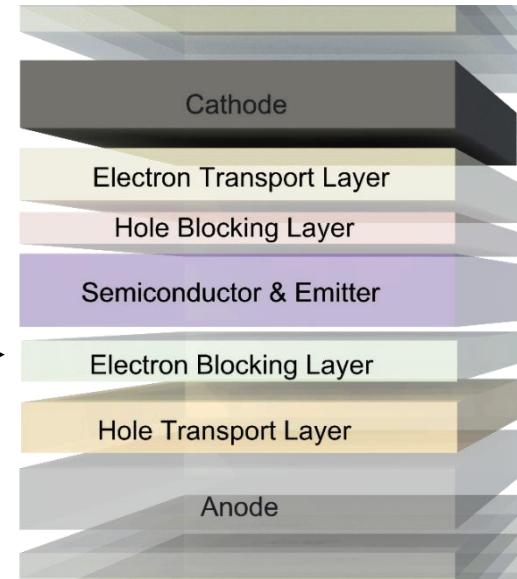
Challenges example



- Size control
- Size measurement

??

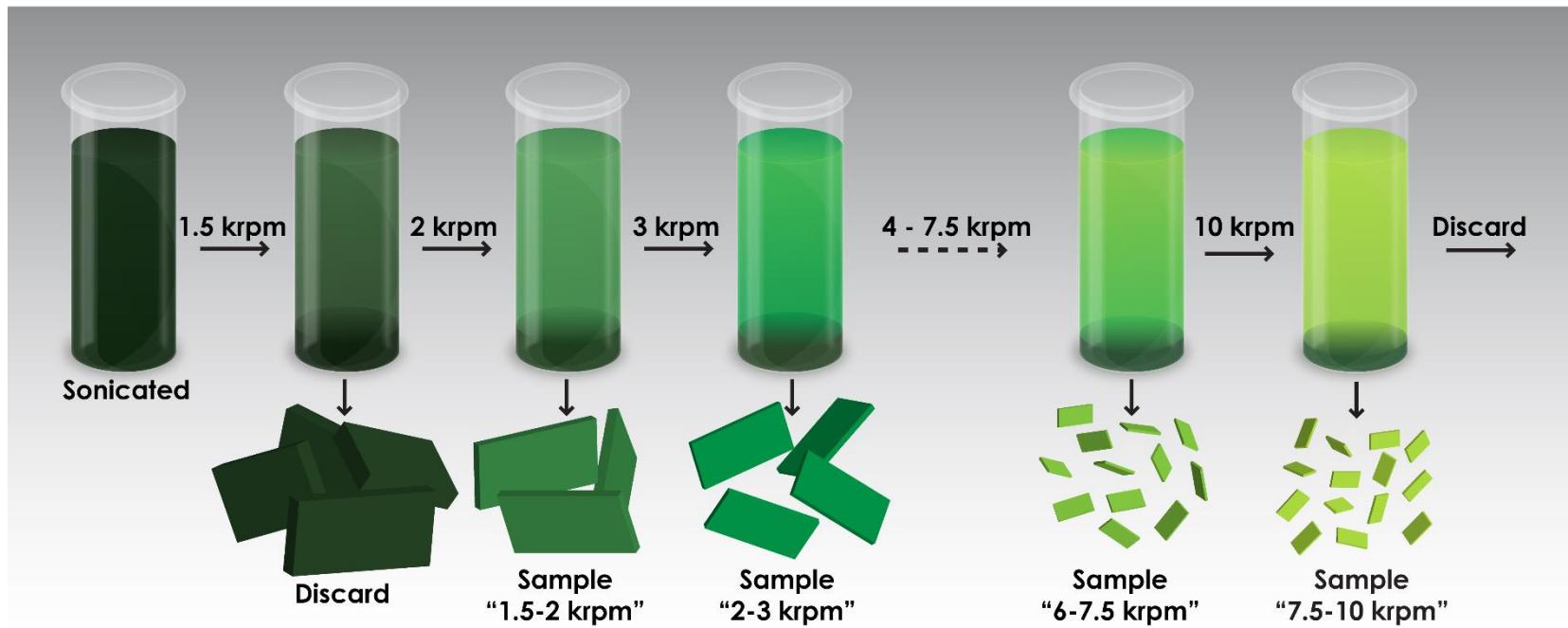
Pre-defined size,
Monolayers





Size selection and measurement

Liquid cascade centrifugation



Advantages

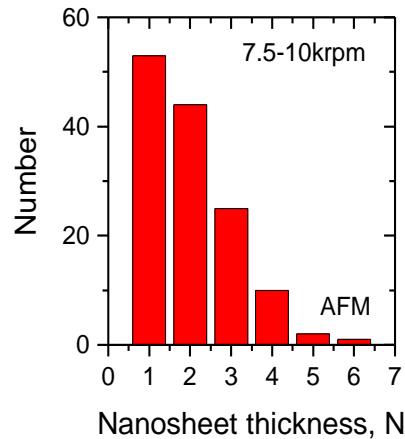
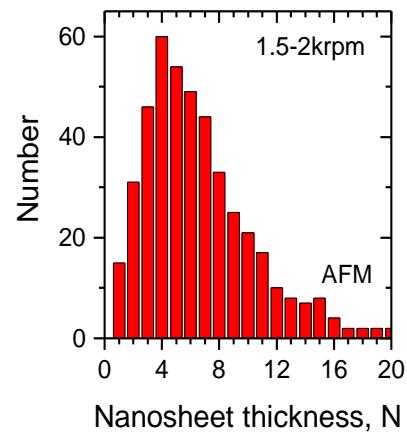
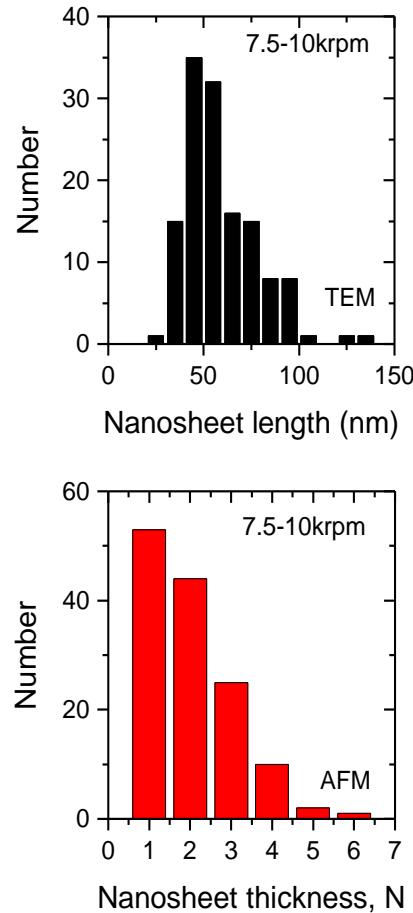
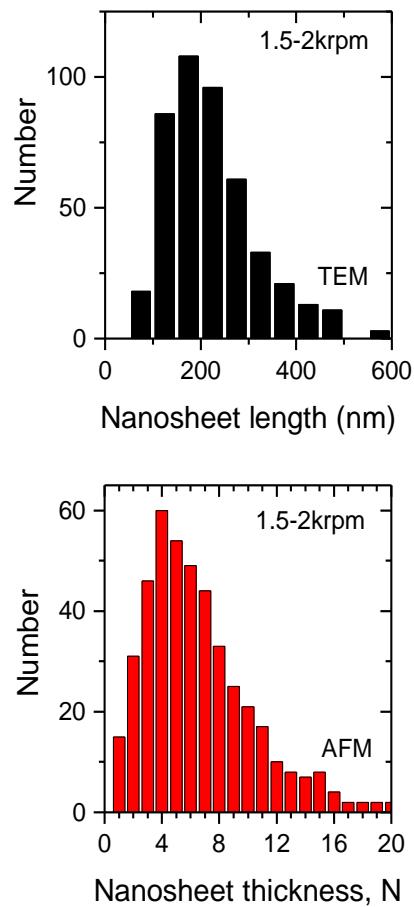
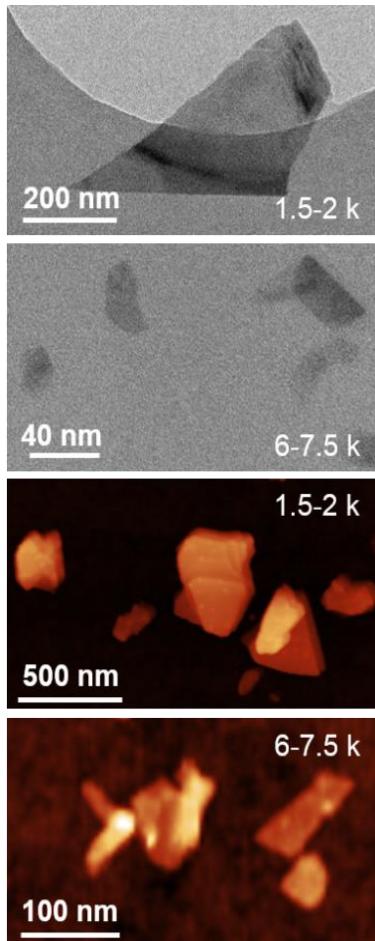
- Universally applicable (solvent, surfactant, any material)
- Scalable and simple
- No wastage of material
- Depending on design, either size selection or monolayer enrichment



Size selection and measurement

Liquid cascade centrifugation: WS₂

- Size and thickness measured by statistical microscopy





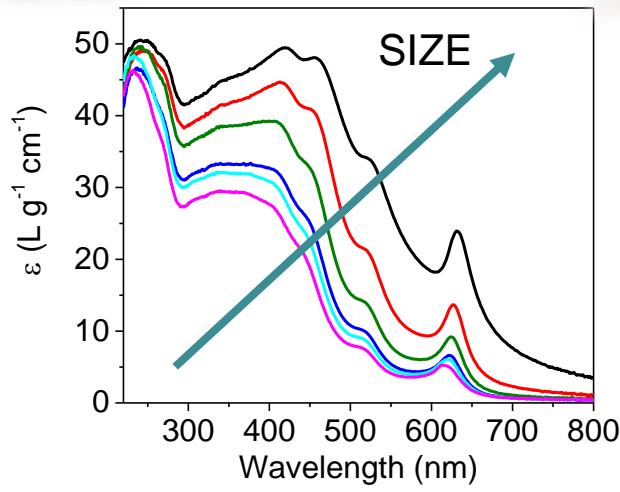
Spectroscopic metrics



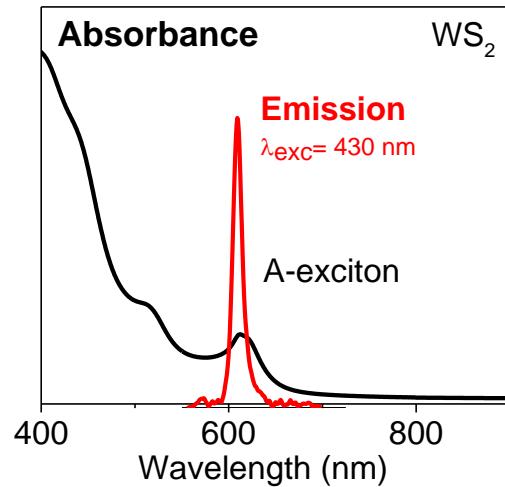
- Size control
- Size measurement

??
Metrics

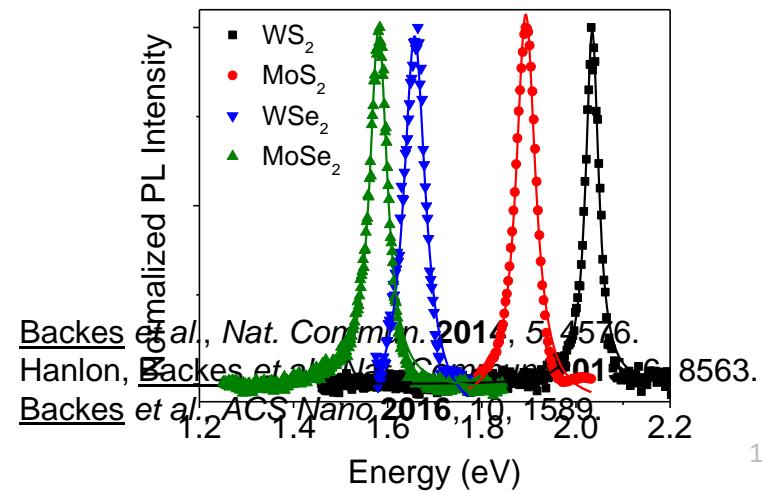
**Pre-defined size,
Monolayers**



High monolayer content



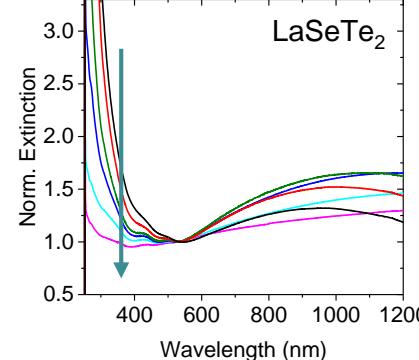
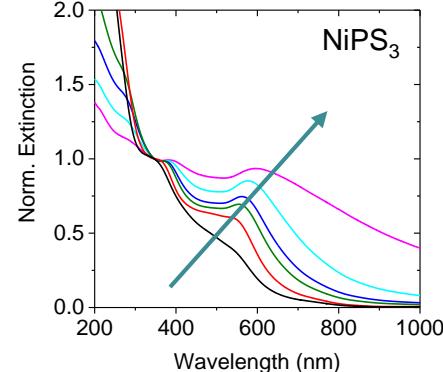
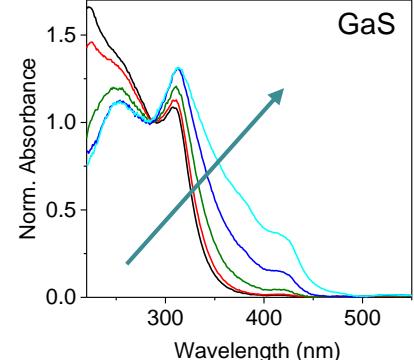
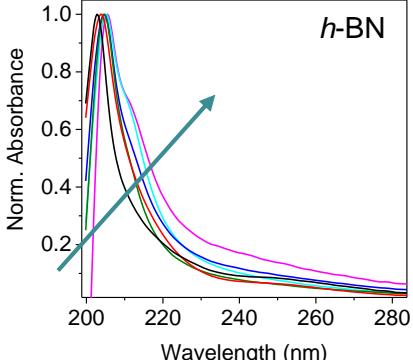
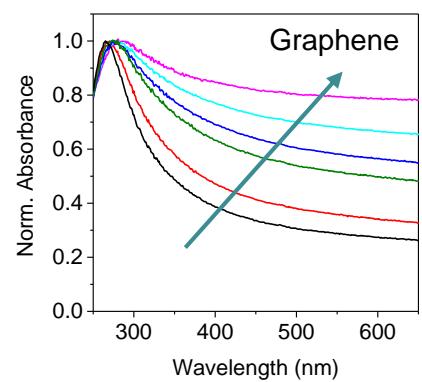
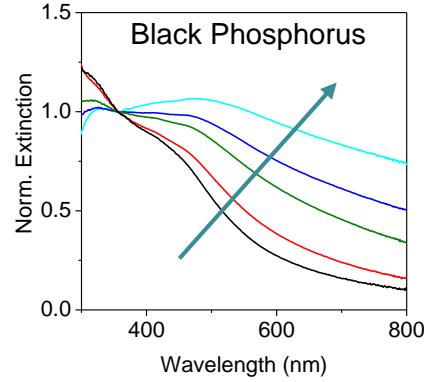
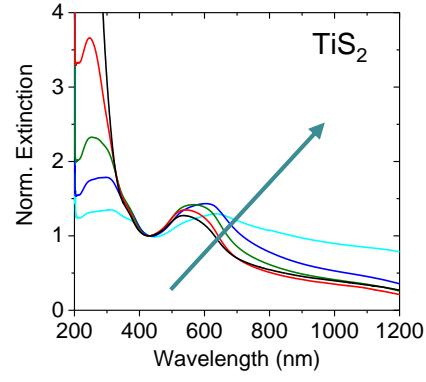
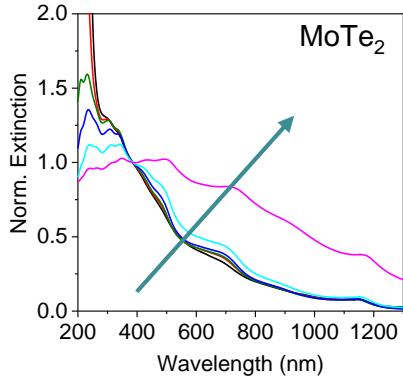
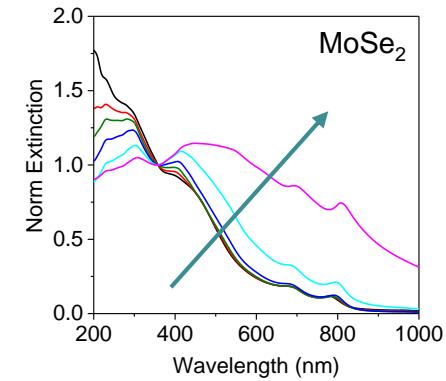
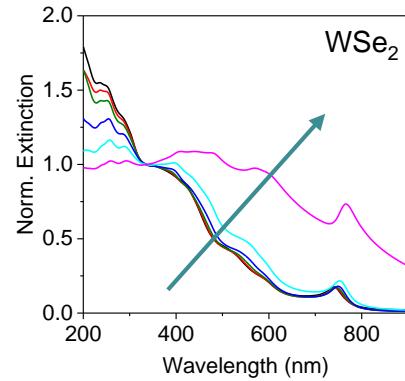
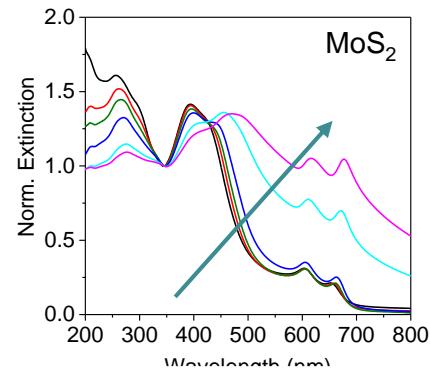
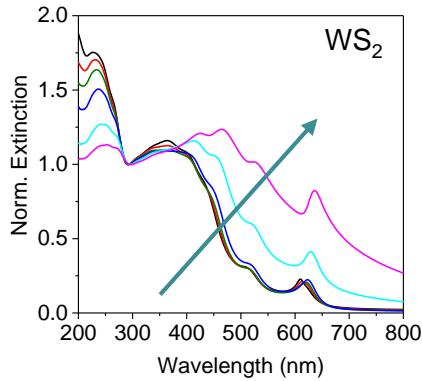
Applicable to various TMDs





Spectroscopic metrics

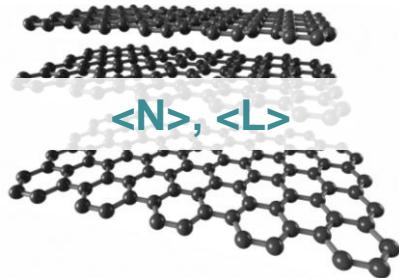
Extinction/absorbance spectra various 2D-materials



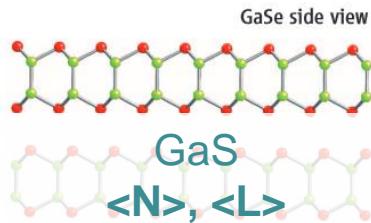
Spectroscopic metrics library



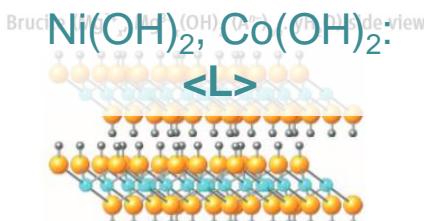
Graphite/Graphene



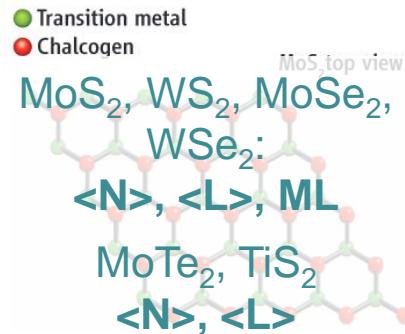
III-VI semiconductors



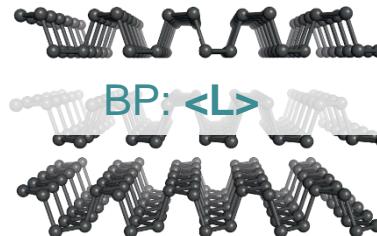
Layered hydroxides



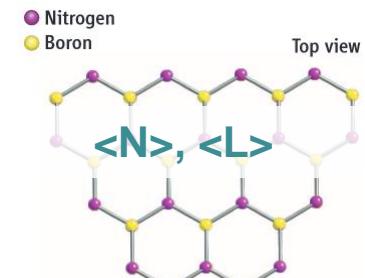
Transition metal dichalcogenides



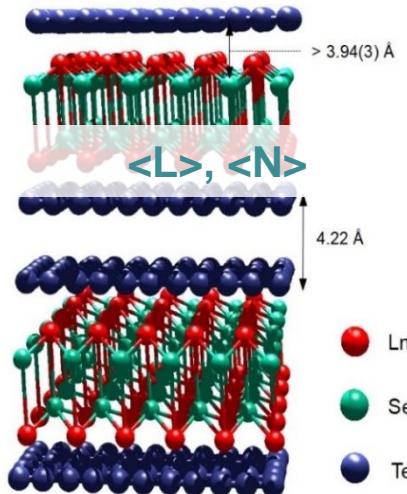
Single element; e.g. P, Sb



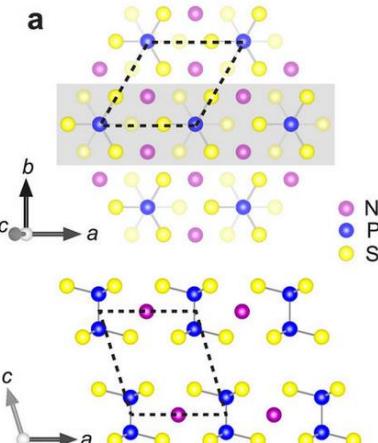
Hexagonal boron nitride



Rare earth polychalcogenides



Transition metal phosphorus trisulfides

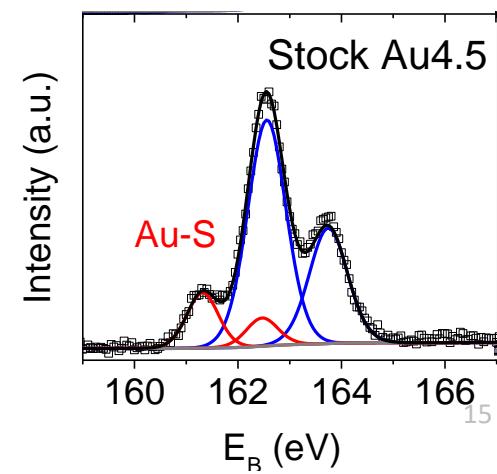
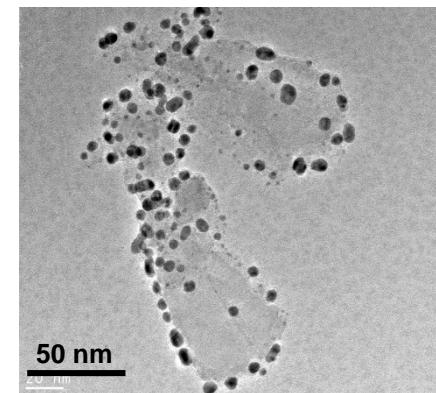
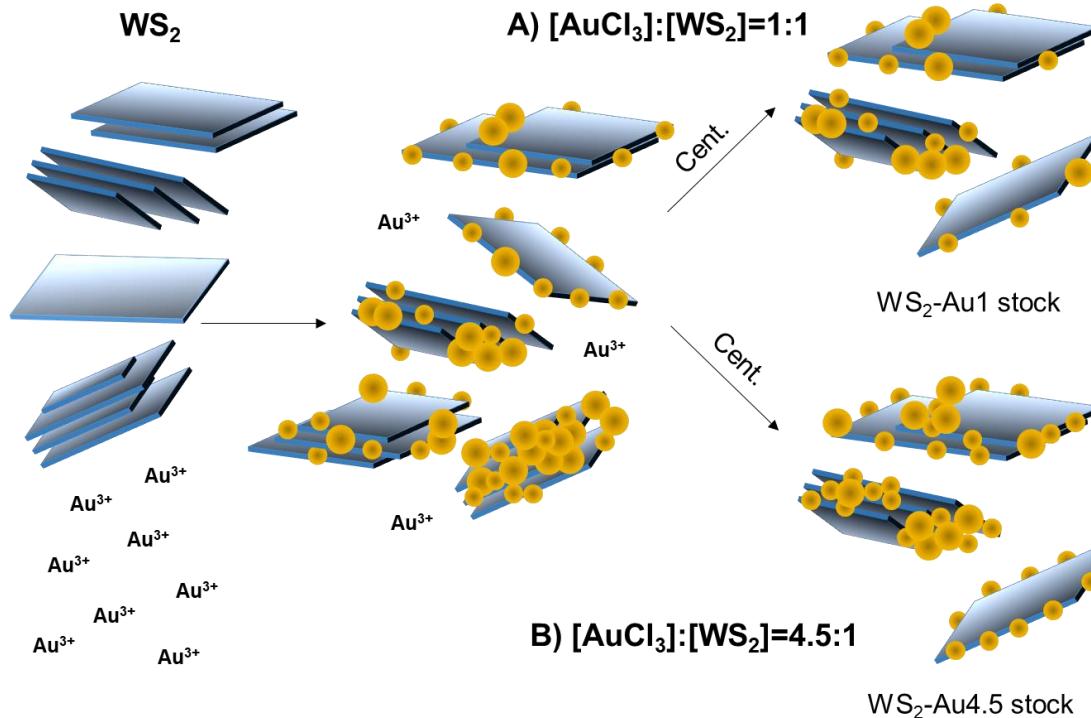


Functionalisation of TMDs



Edge decoration with Au nanoparticles

- Spontaneous reaction of WS_2 with AuCl_3
- Formation of covalently bound Au nanoparticles predom. at edges
- Tuning of reaction conditions possible to change Au decoration density

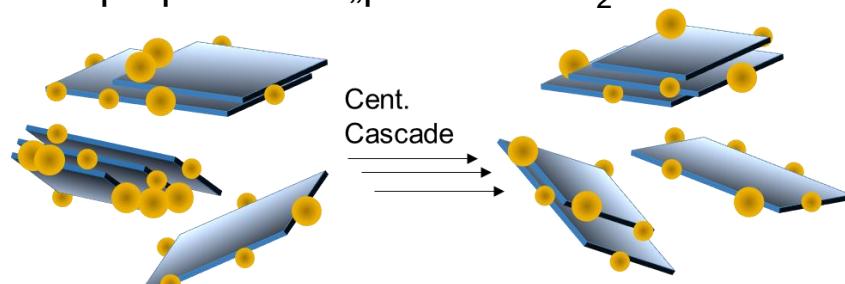




Functionalisation of TMDs

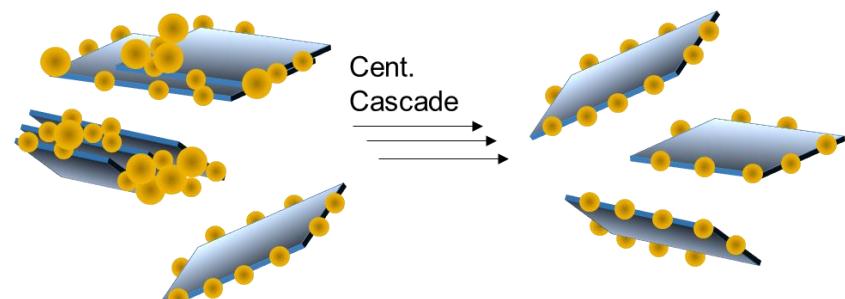
Edge decoration with Au nanoparticles

- Heavily Au decorated WS_2 removed by centrifugation
- Likeliness of NPs to merge higher on few-layer nanosheets
→ **monolayer enrichment** (tunable lateral size)
- Optical properties of „pristine“ WS_2



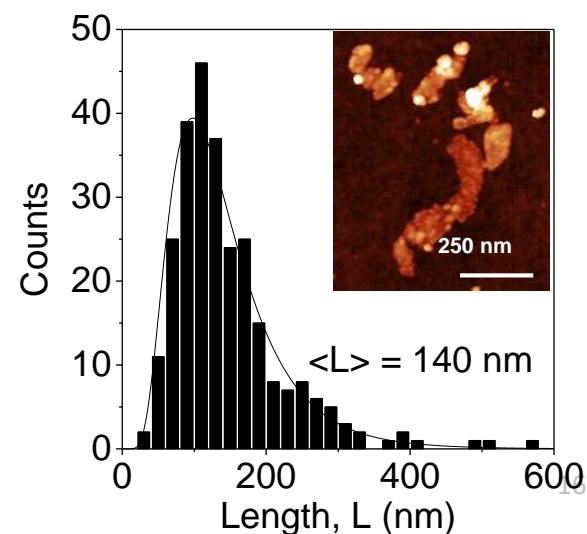
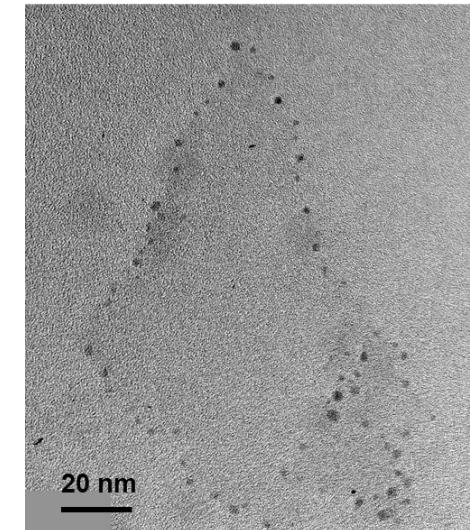
$\text{WS}_2\text{-Au}1$ stock

Purified $\text{WS}_2\text{-Au}1$



$\text{WS}_2\text{-Au}4.5$ stock

Purified $\text{WS}_2\text{-Au}4.5$



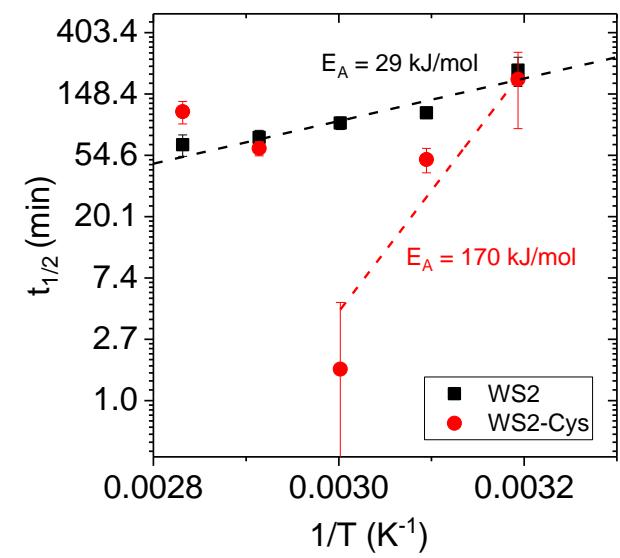
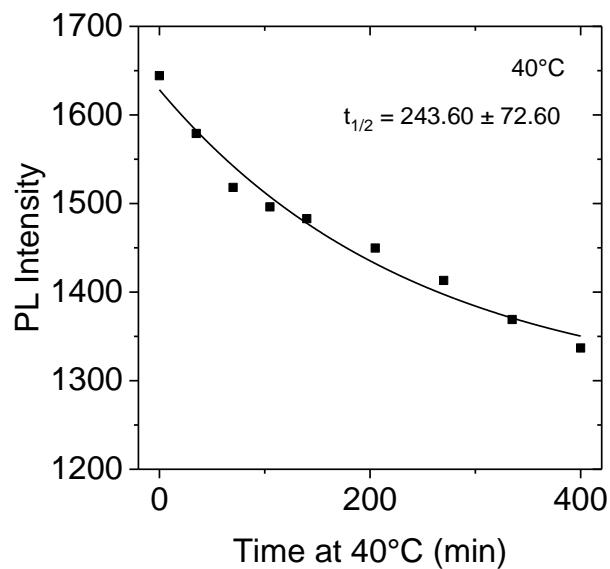
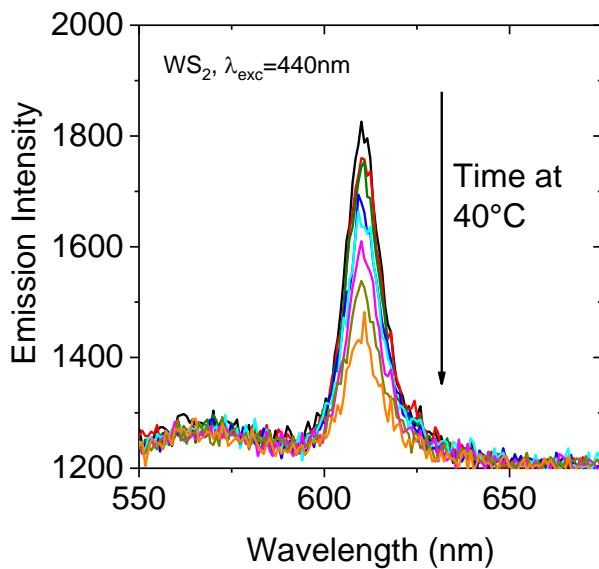
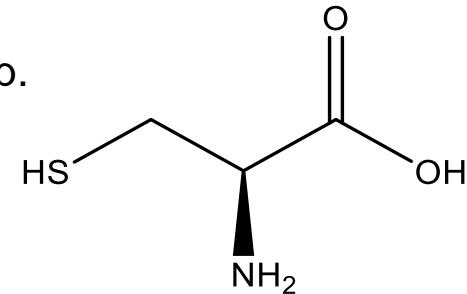
Functionalisation of TMDs

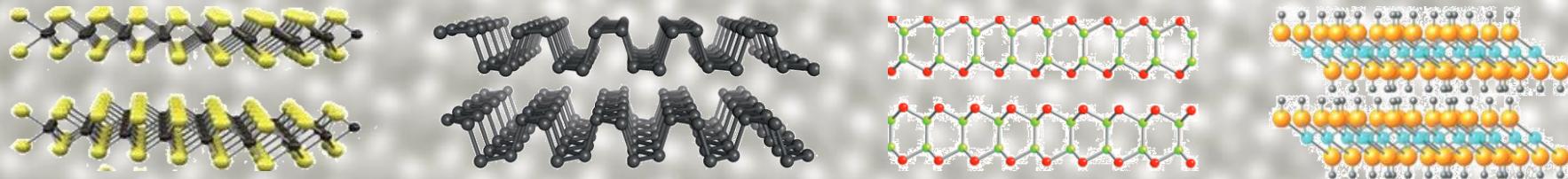


Defect passivation

- TMD monolayer degrade in ambient conditions at elevated temp.
- Can be followed by decay of photoluminescence
- Measurements at different temperatures yield activation energies in the range of 30 kJ/mol for WS_2

→ Defect passivation for example by cysteine can improve stability!



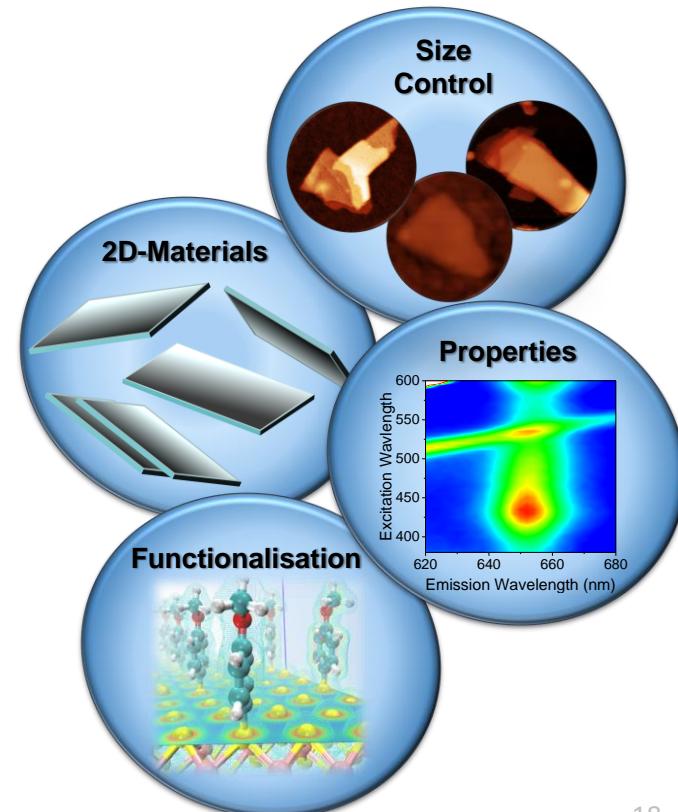


Nachwuchsgruppe Dr. Claudia Backes

In Lösung exfolierte anorganische Schichtmaterialien (z.B. MoS₂, GaS, schw. P) als Bausteine für funktionale Architekturen

Themengebiete:

- **Prozessoptimierung der Exfoliierung**
- **Größenselektion (Zentrifugation...)**
- **Spektroskopische Eigenschaften
→ Quantitative Größenbestimmung!**
- **Funktionalisierung, chemische Dotierung**
- **Hierarchische Strukturen:
“mix and match”**



Helping hands are always welcome!

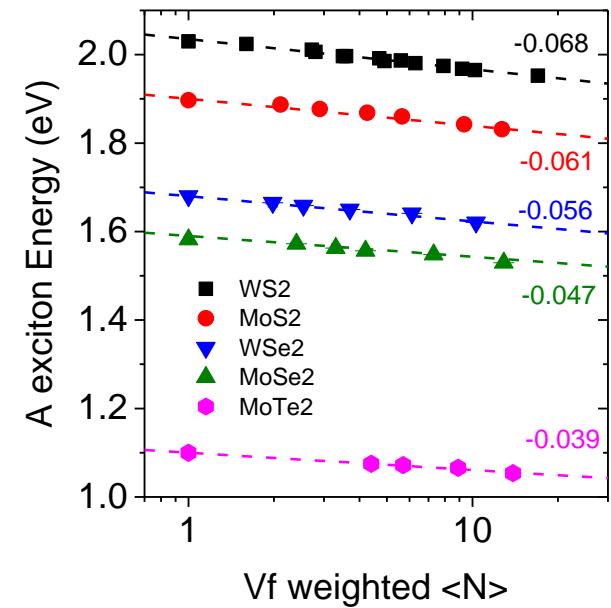
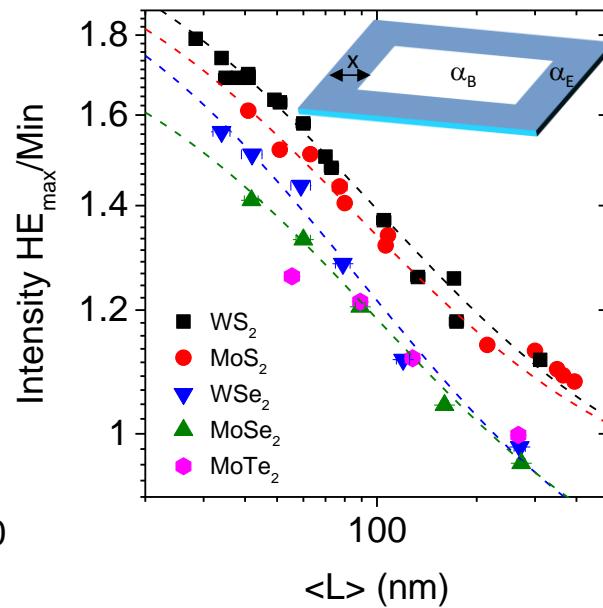
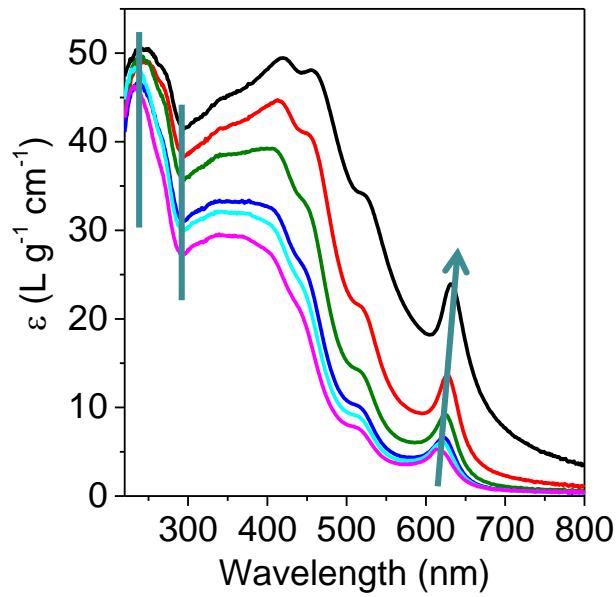
Thank you for your attention!



Spectroscopic metrics

Metrics from extinction spectra

- Changes in extinction peak intensity ratios due to edge effects → metrics for lateral size
- A-exciton shift due to confinement → thickness metric



$$\frac{Ext_1}{Ext_2} = \frac{\alpha_{B,1} + 4x\alpha_{E,1}/L}{\alpha_{B,2} + 4x\alpha_{E,2}/L}$$