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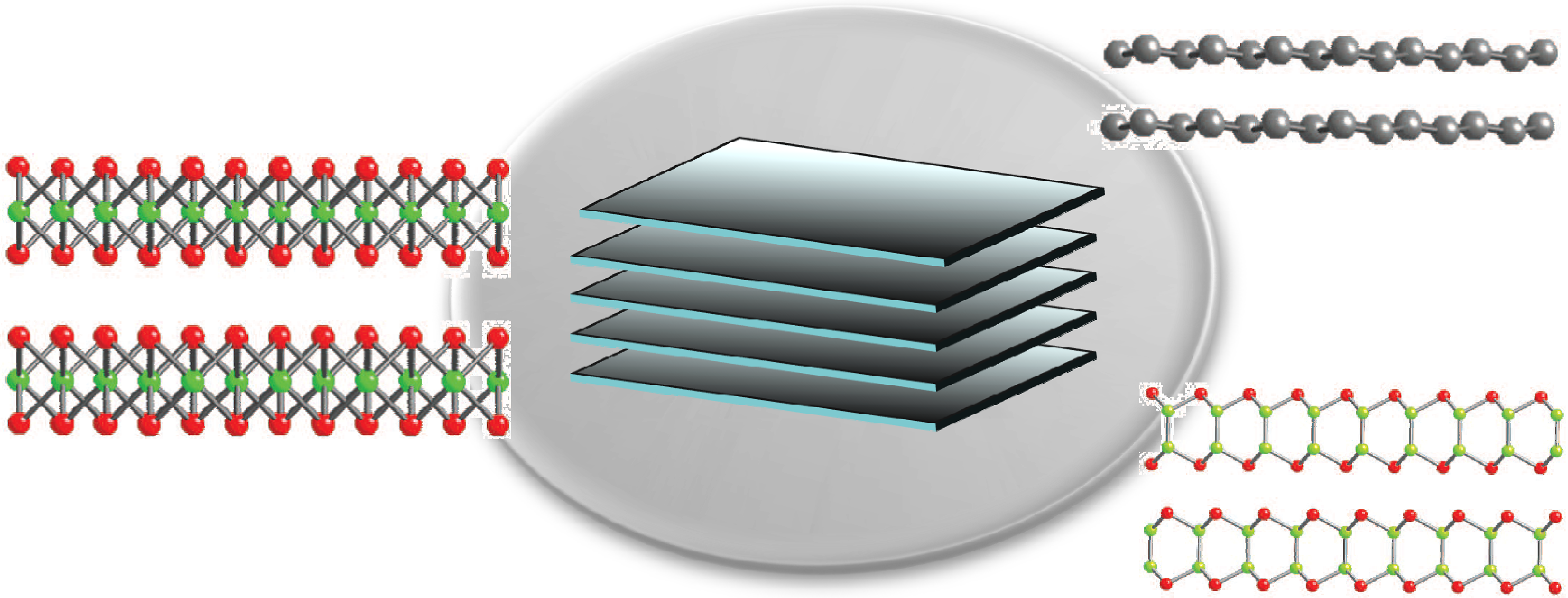
Spectroscopic metrics to detemine size and thickness of liquid-exfoliated nanosheets in dispersion



Claudia Backes, J. N. Coleman

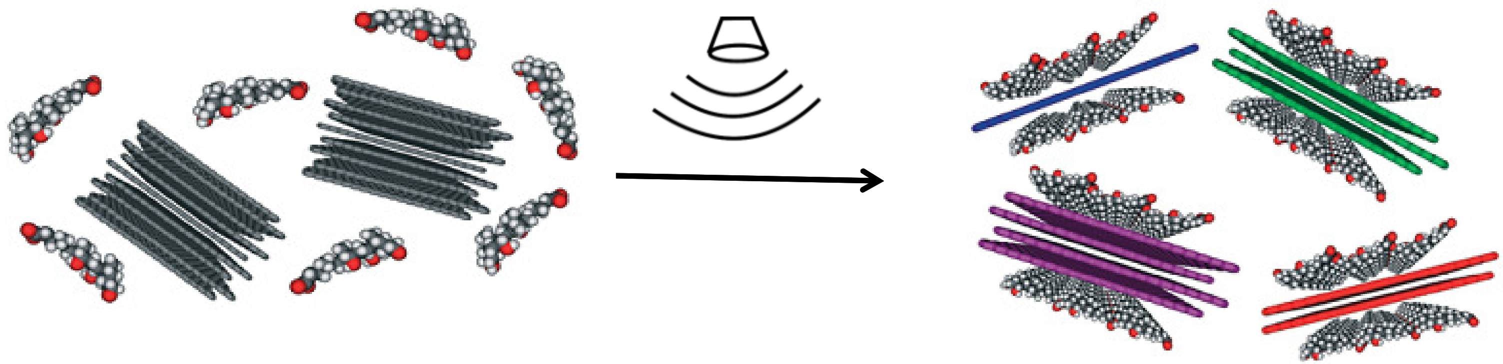
Trinity College Dublin, Ireland

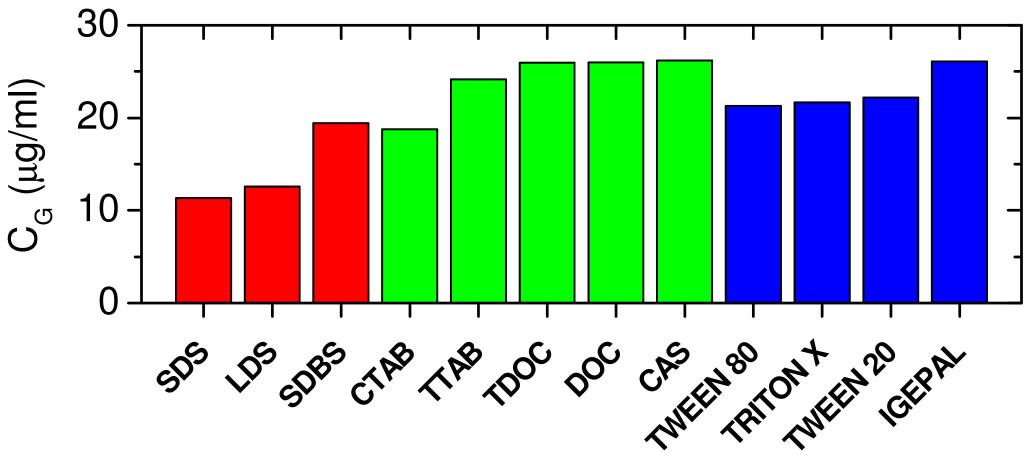
07/10/2014

Liquid-phase exfoliation

Dispersion of graphite/graphene in surfactants

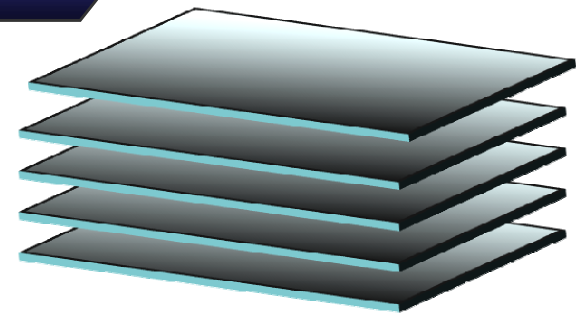
- **Reaggregation can be prevented by the use of surfactants**



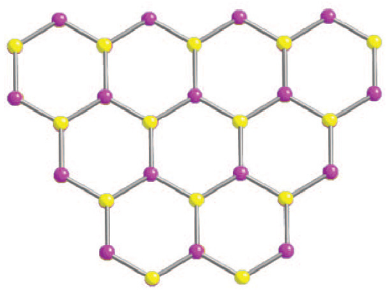


R. J. Smith, M. Lotya, J. N. Coleman, *New Journal of Physics* **2010**, *12*, 125008.
M. Lotya, P. J. King, U. Khan, S. De, J. N. Coleman, *ACS Nano* **2010**, *4*, 3155-3162.

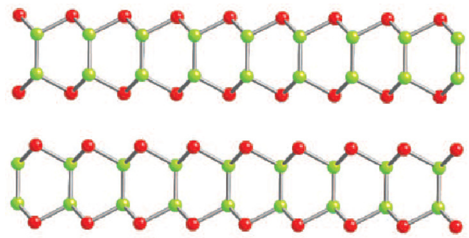
Layered inorganic materials



- **Boron Nitride**



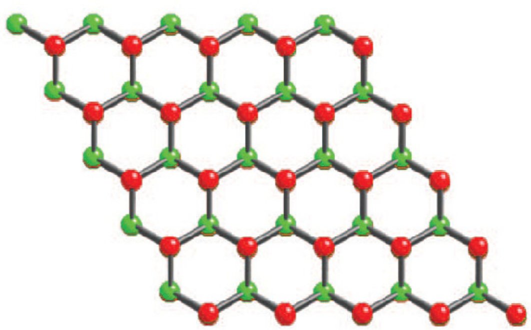
- **III-VI semiconductors (e.g. GaS)**

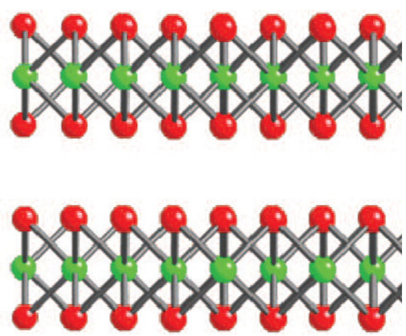


● = Ga, In

● = S, Se, Te

- **Transition metal dichalcogenides**





● = S, Se, Te

● = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Tc, Re, Ni, Pd, Pt

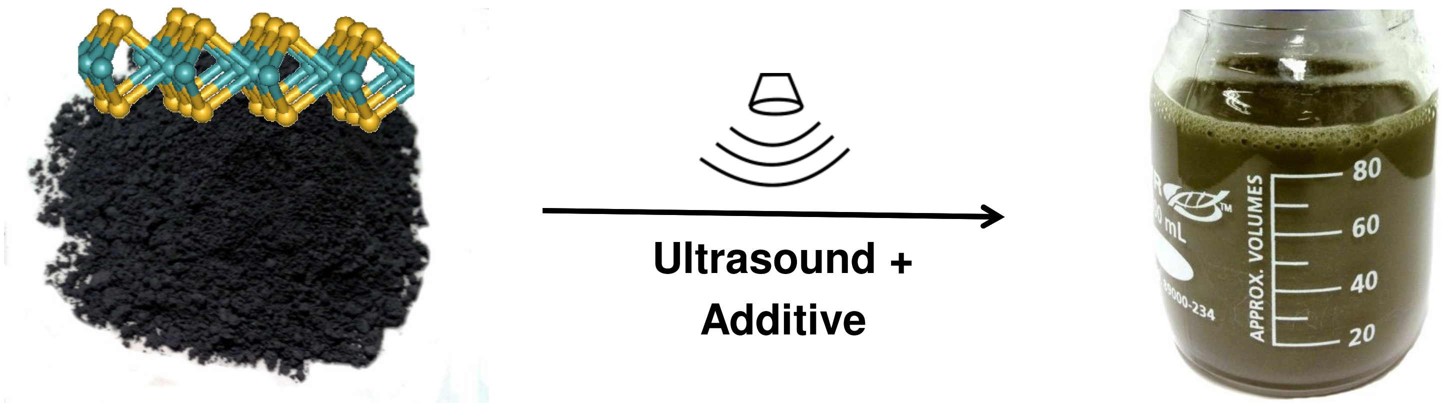
Blue = semiconducting
Red = Metallic
Green = Both depending on S, Se, Te

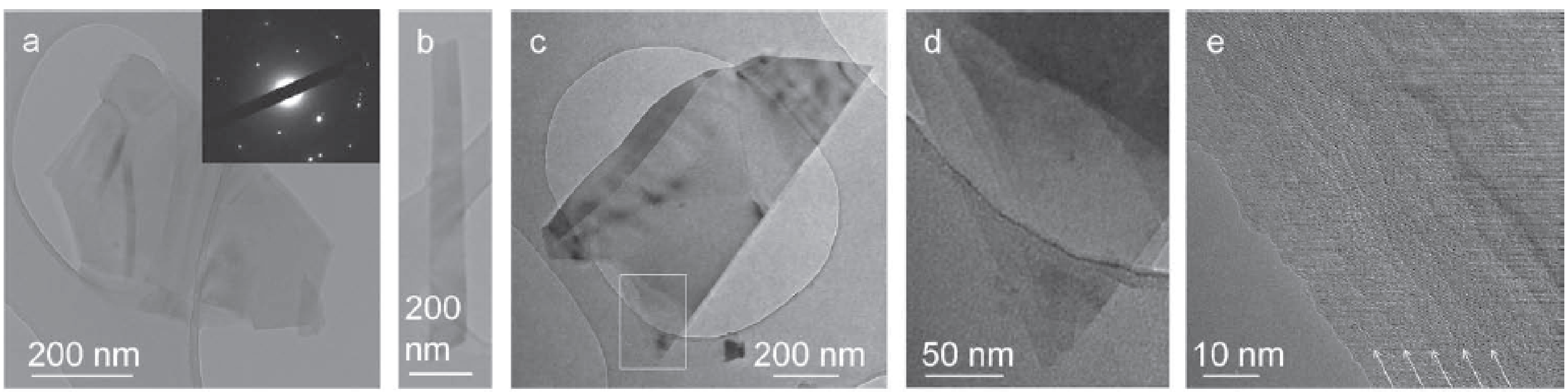
- **Also TMOs (MoO_3, MnO_2, $TiNbO_5$ etc), halides (e.g. $MoCl_2$)…**

Liquid-phase exfoliation

Surfactant-exfoliated MoS_2

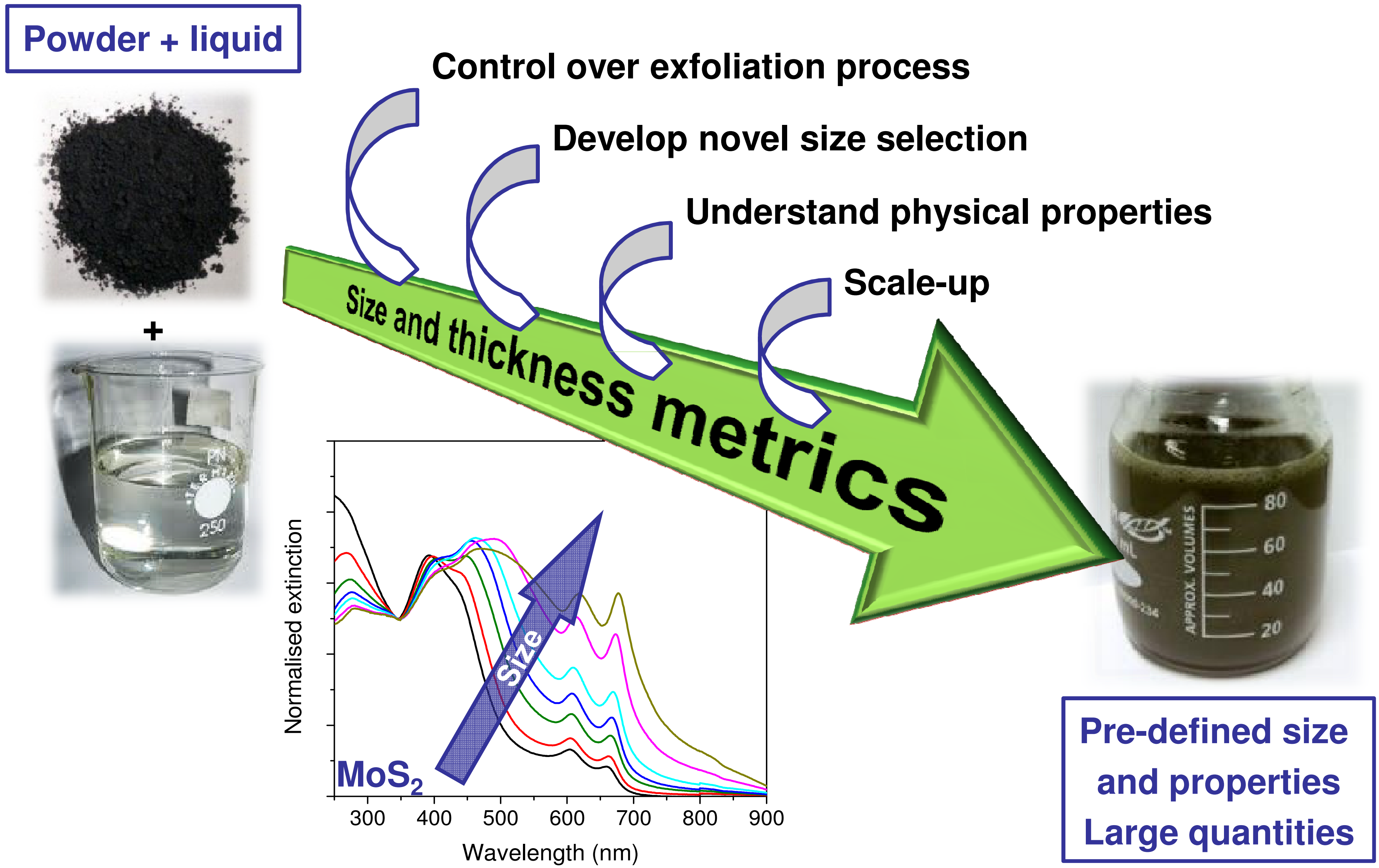
- **Layered materials can be exfoliated in aqueous surfactant solution**





R. J. Smith, …. J. N. Coleman, *Adv. Mater* **2011**, *23*, 3944-3948.

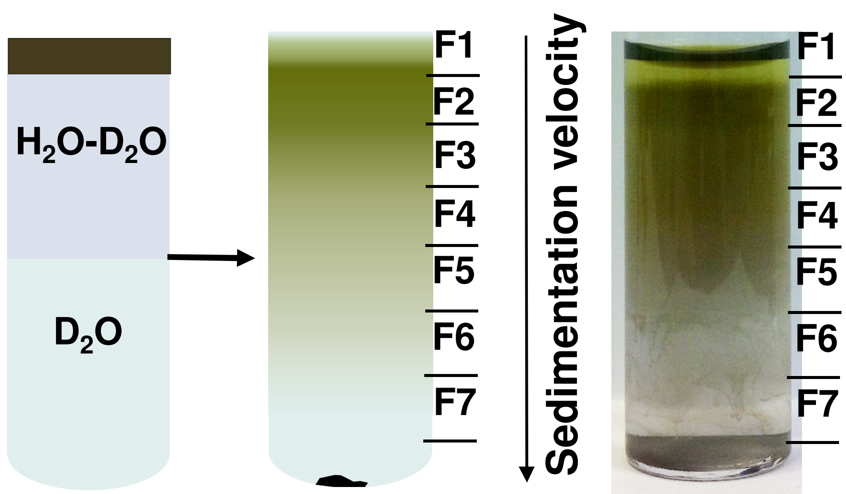
Targets and challenges in liquid exfoliation

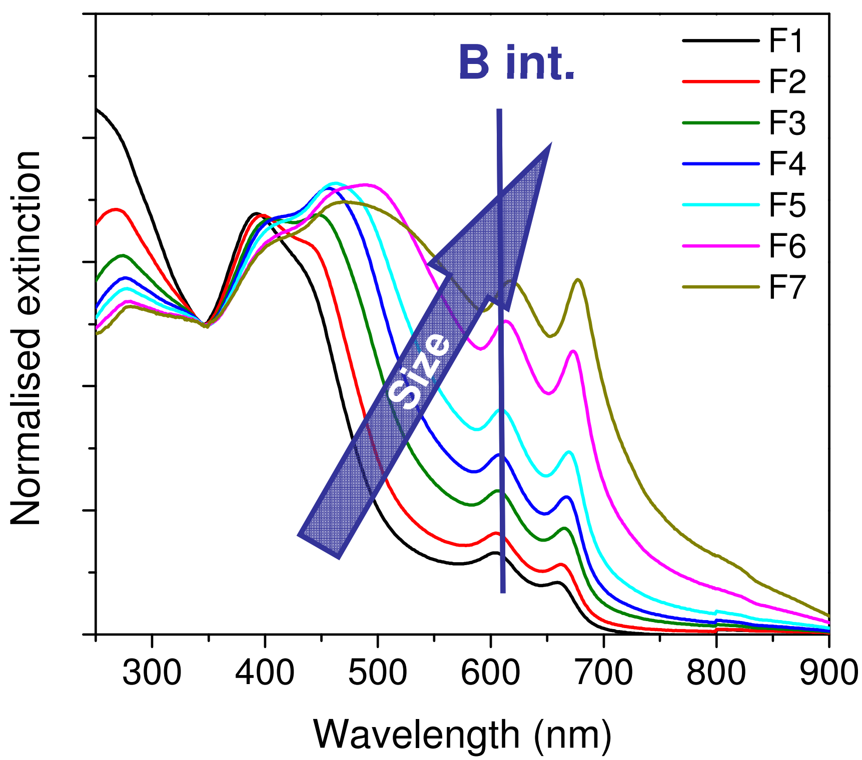


MoS_2 metric

Band sedimentation (rate zonal centrifugation)

- **Access to different size and thickness distribution within minutes**
- **Extinction spectra change as a function of size**
  → can we use this as a metric??



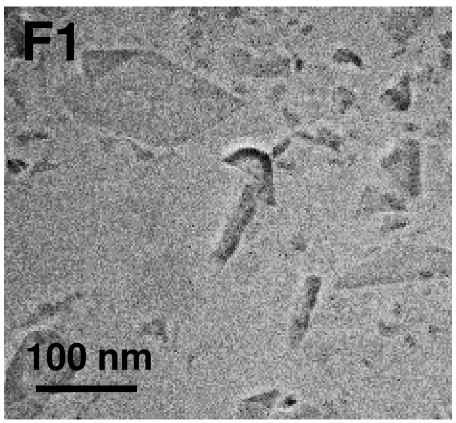


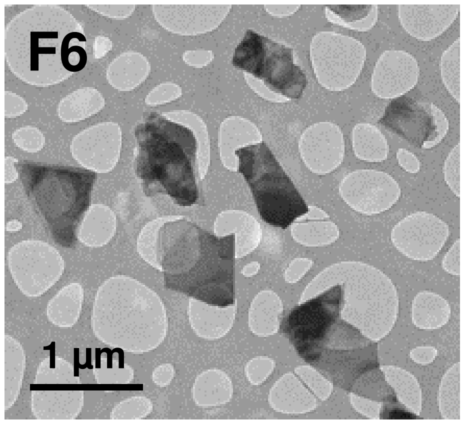
C. Backes... J.N. Coleman, *Nat. Comm.* **2014**, 5, 4576.

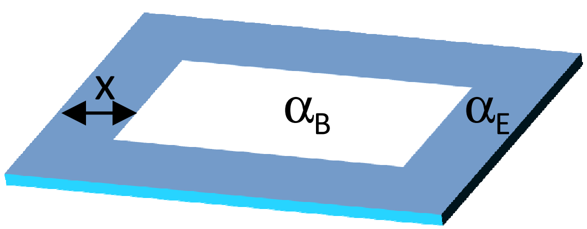
MoS_2 metric

Peak intensity metric

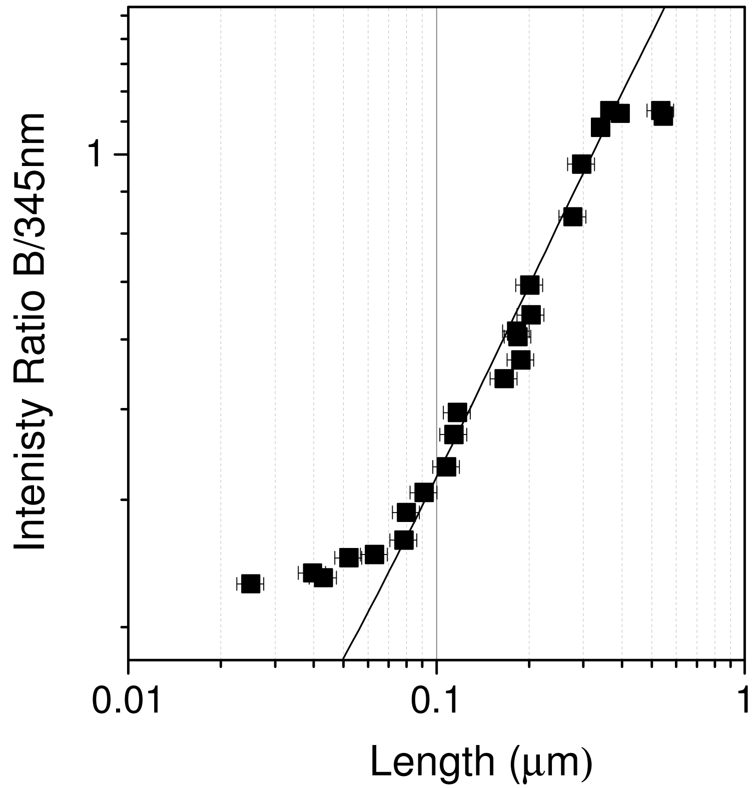
- Intensity ratio of B-exciton / 345 nm as a function of length → fits model very well







$$\frac{A_B}{A_{345nm}} = \frac{\alpha_{B,B} + 4x\alpha_{E,B}/L}{\alpha_{B,345nm} + 4x\alpha_{E,345nm}/L}$$

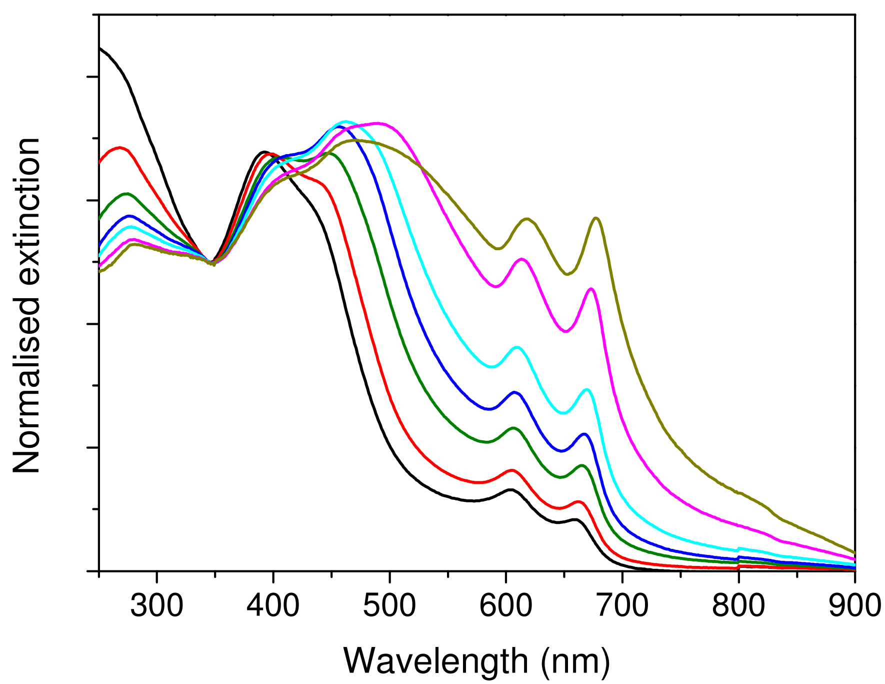


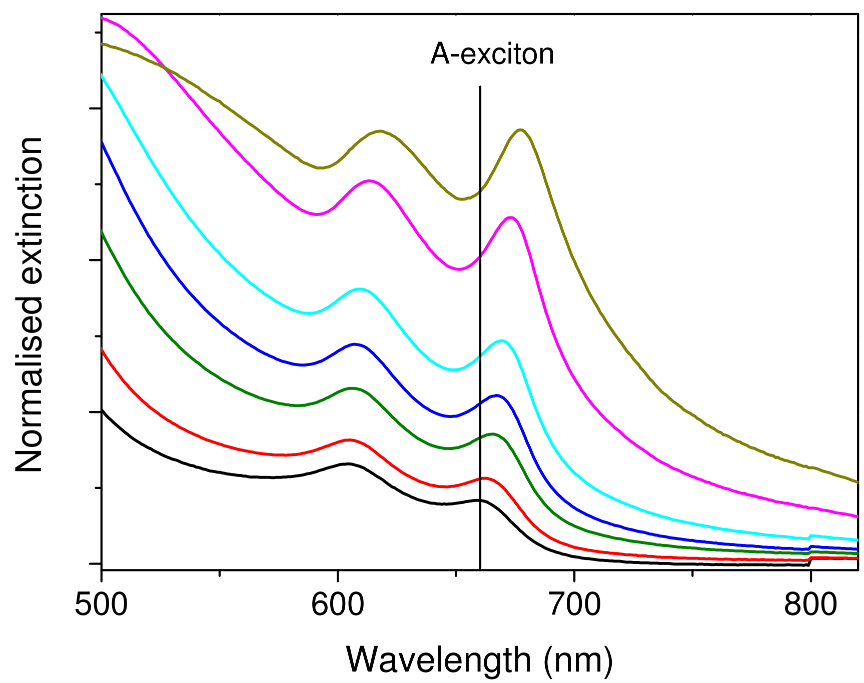
C. Backes... J.N. Coleman, *Nat. Comm.* **2014,** 5, 4576.

MoS_2 metric

Peak position metric

- **Zoom in in region of A-exciton position**
- **Experimentally observed in Lit.: A-exciton position depends on thickness**





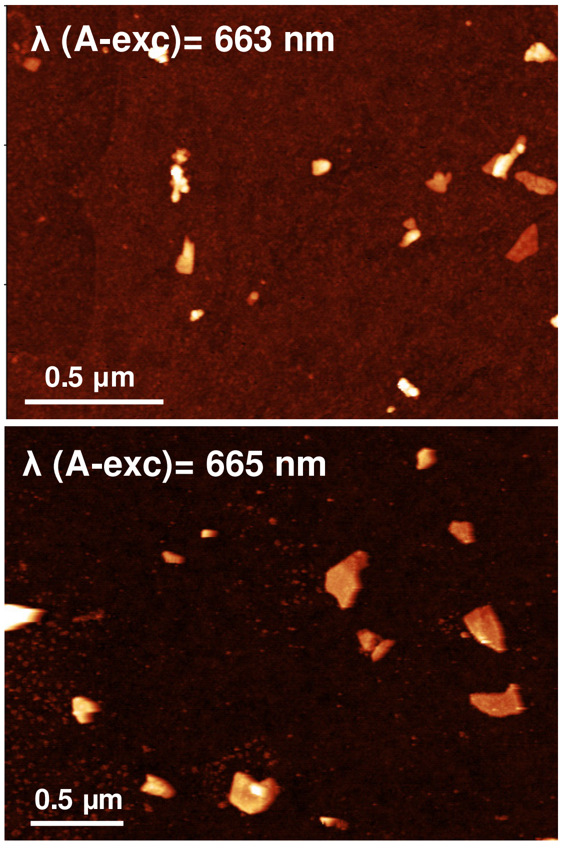
G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, *Nano Letters* **2011**, *11*, 5111-5116.

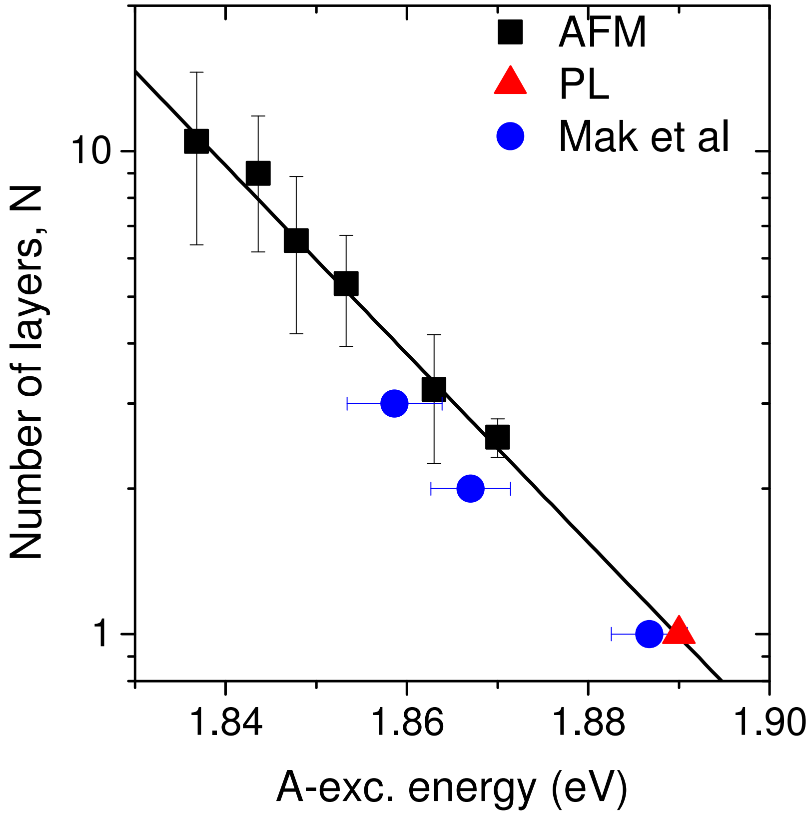
K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Physical Review Letters* **2010**, *105*, 136805.

MoS_2 metric

Peak position metric – correlation to thickness?

- **AFM height statistics → correlation of A-exciton position to thickness/ number of layers**



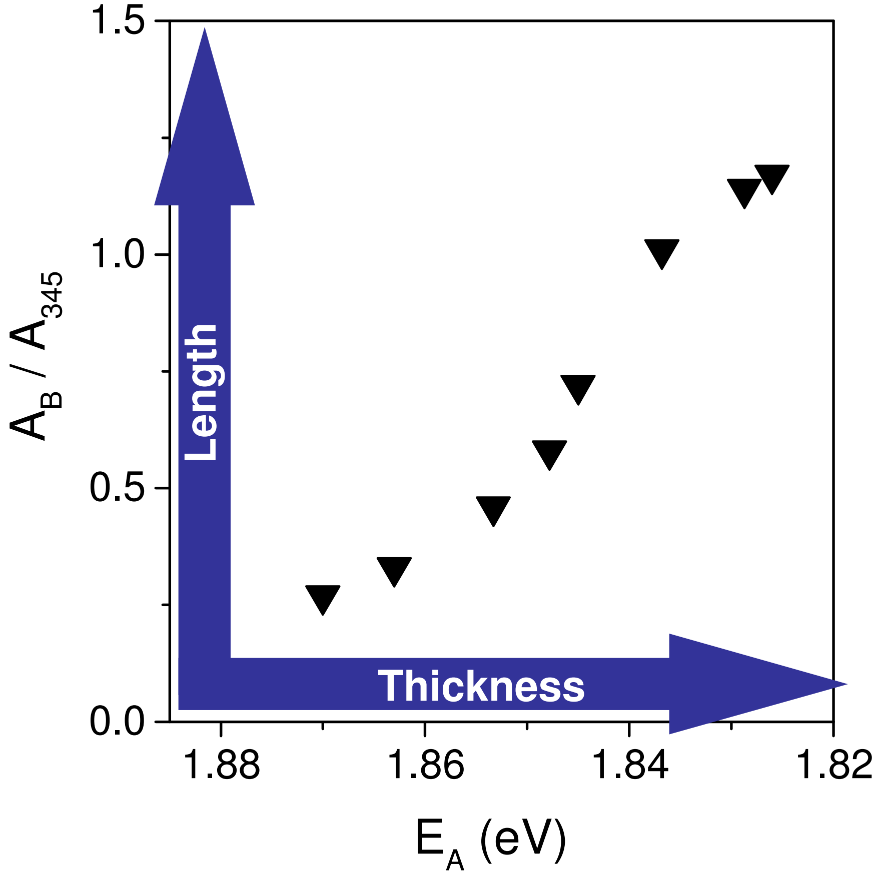


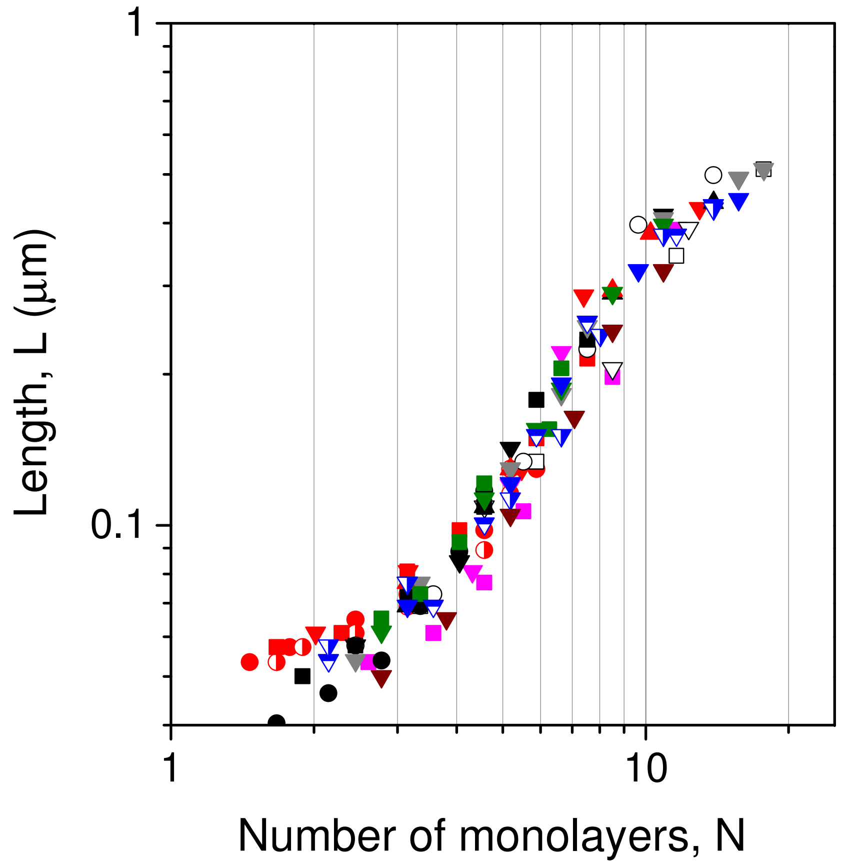
Nat. Comm. **2014**, 5, 4576.

MoS_2 metric

The final metric plot

- **With calibration curves, SIZE AND THICKNESS can be quickly determined**

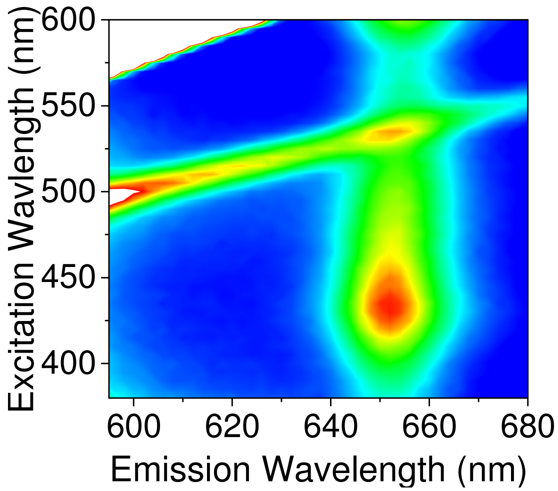




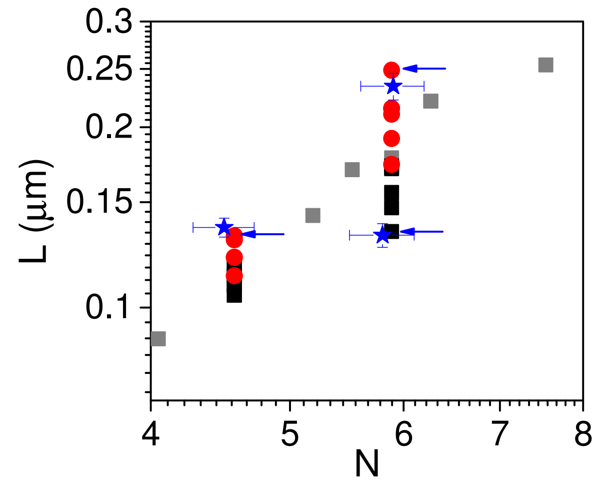
Nat. Comm. **2014**, 5, 4576.

What for?

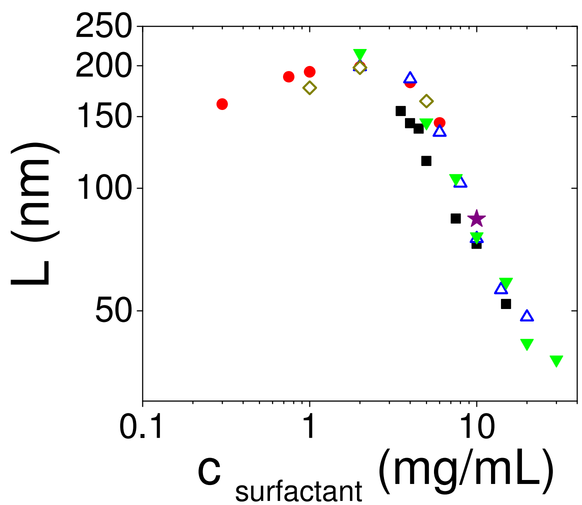
Luminescence in dispersion



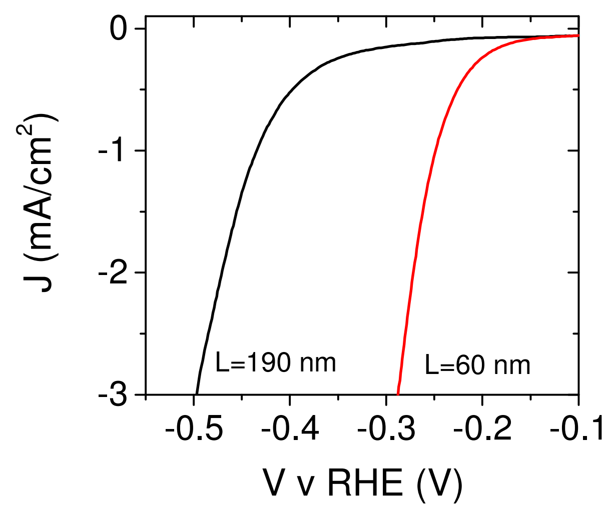
New size selection techniques



Understand exfoliation

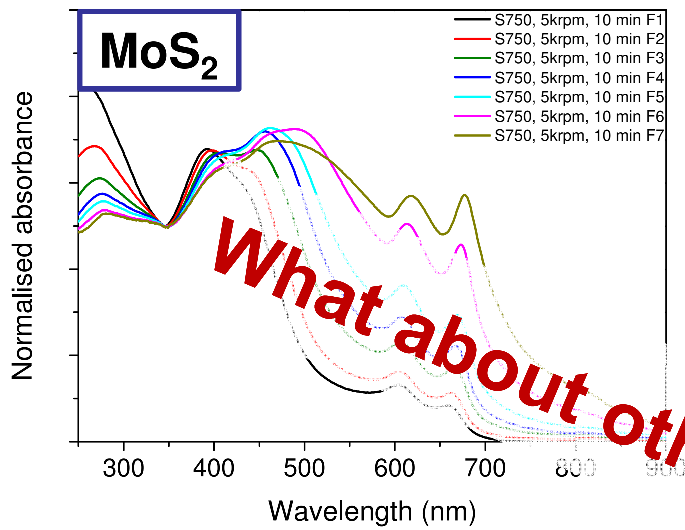


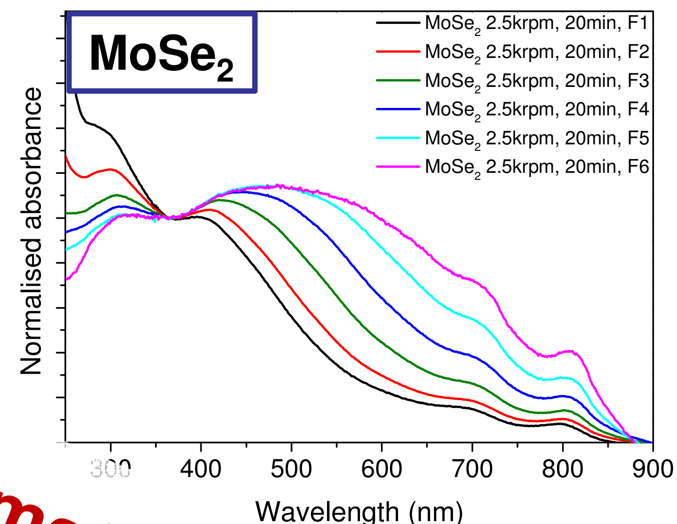
Defined sizes → Applications (HER)



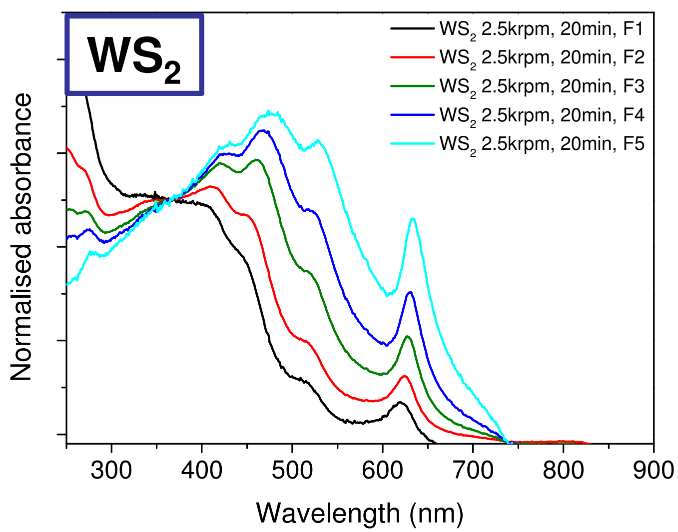
Other TMDs

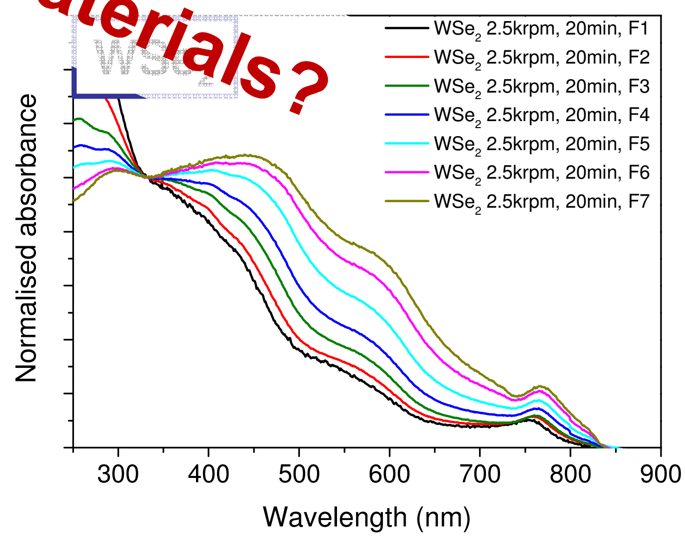
Band sedimentation and extinction with other materials



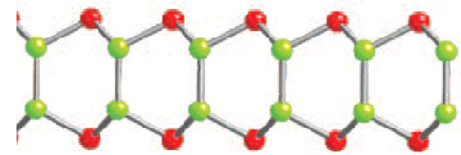


What about other materials?

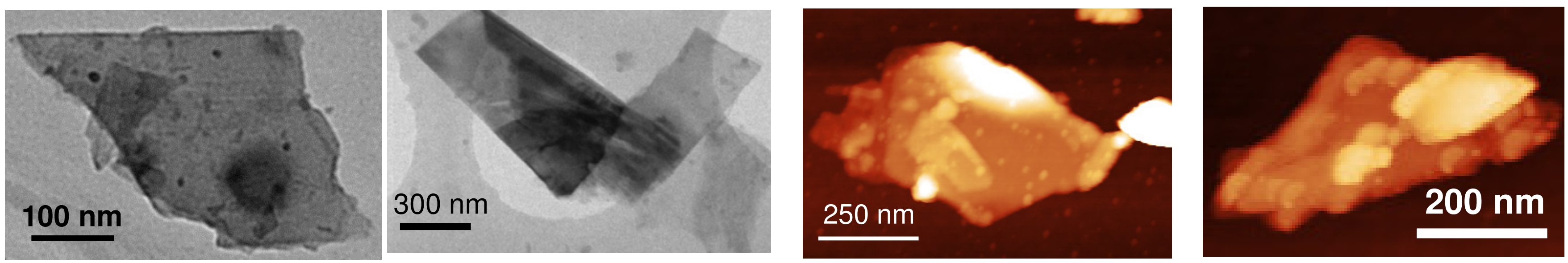


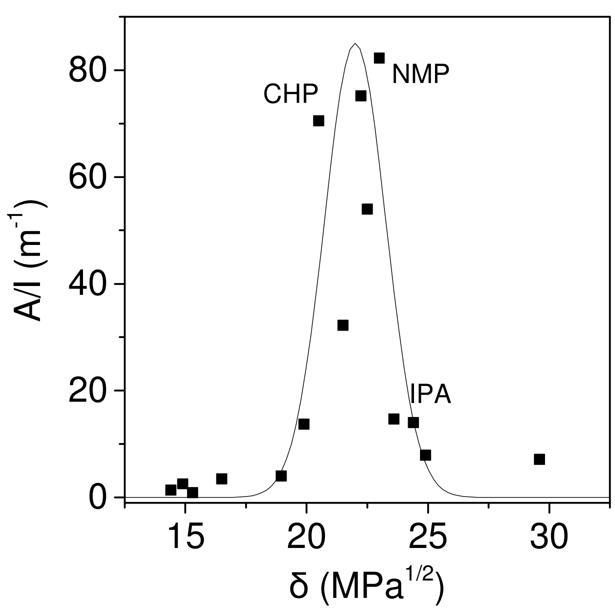


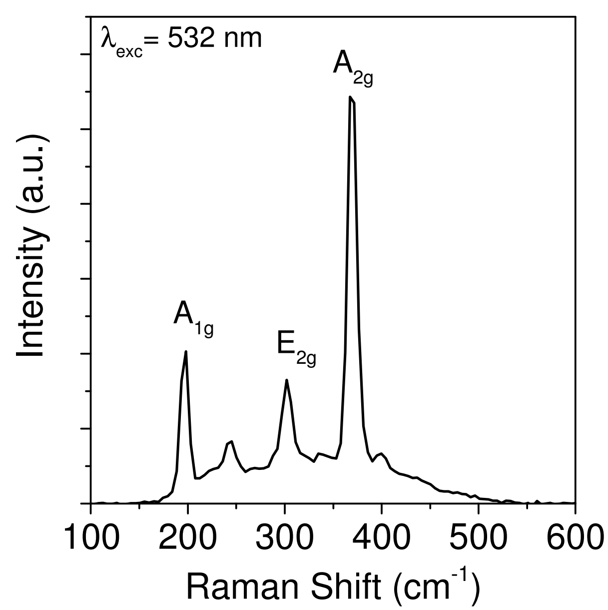
GaS

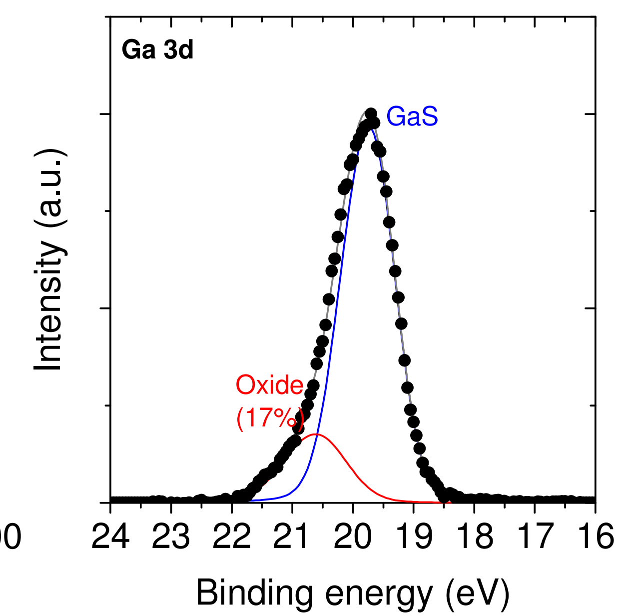


Liquid-exfoliation of GaS









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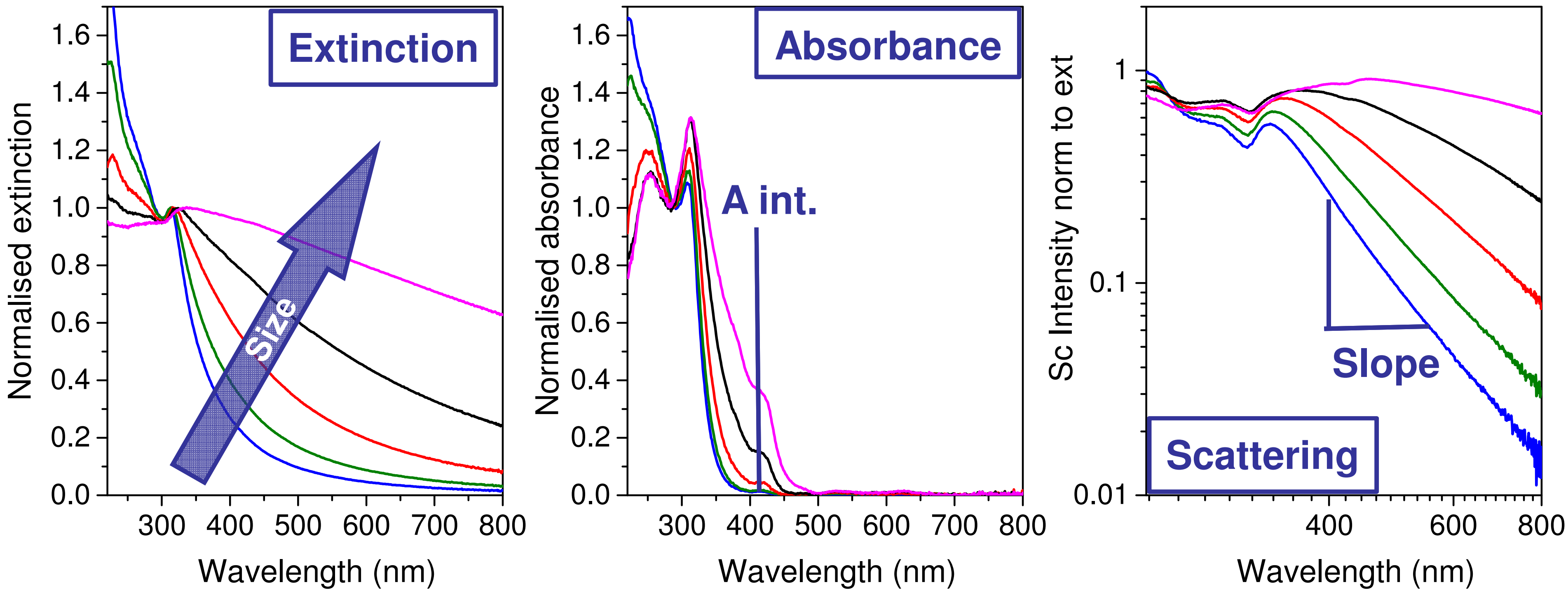
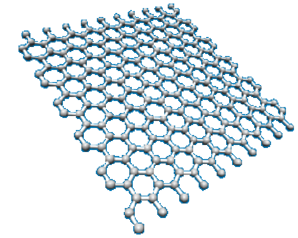
GaS

Absorbance/extinction/scattering L metric for GaS

- **Size selection → extinction spectra change as a function of size**
- **Also very clear: scattering and absorbance spectra change with size**



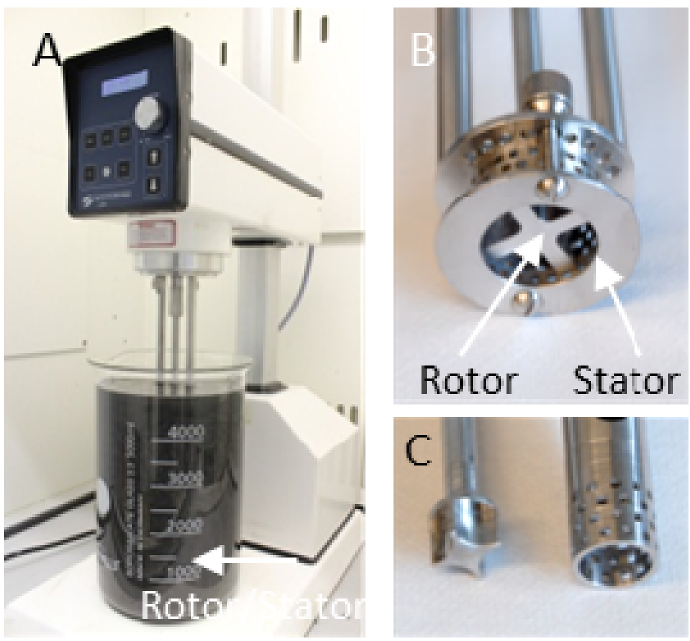
Graphene



Scalable production

THOMAS SWAN
PERFORMANCE & SPECIALITY CHEMICALS

- **Graphite exfoliated to few-layer graphene by shear mixing → scalable!**

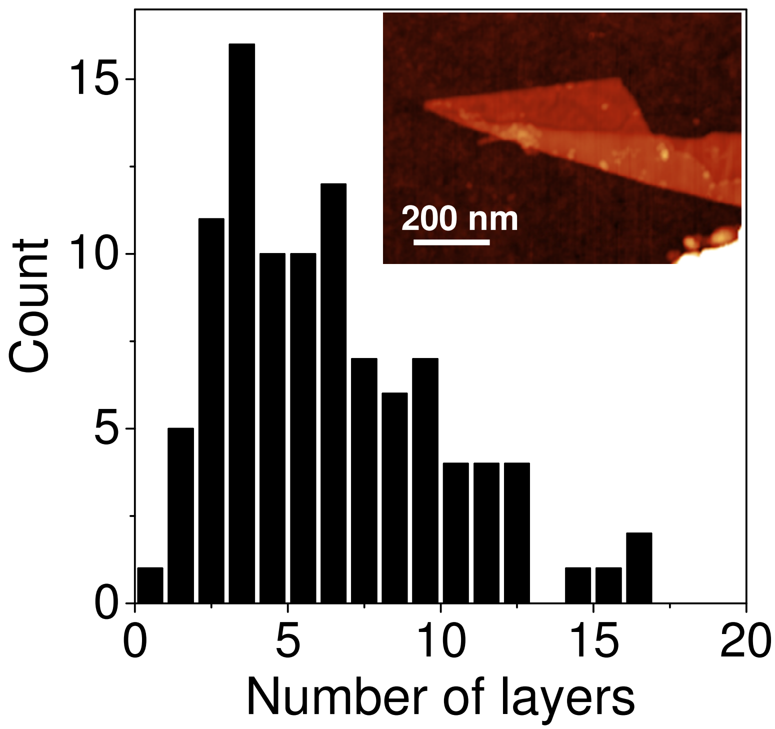


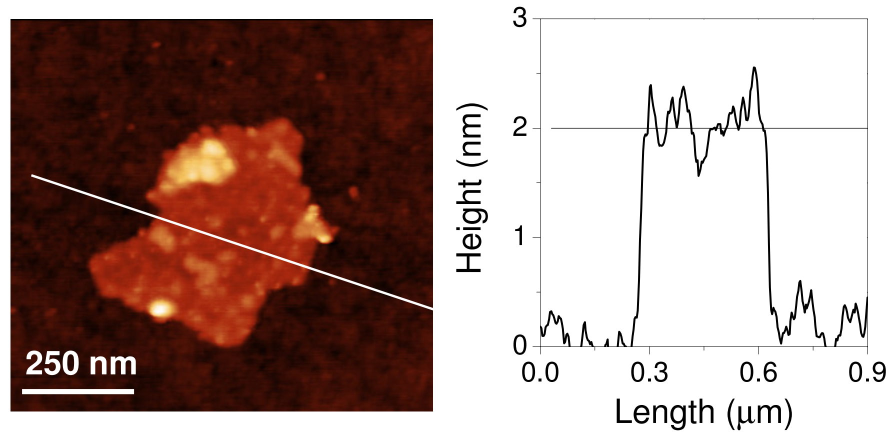
K. Paton, E. Varrla, C. Backes... J.N. Coleman, *Nat. Mater* 2014, *13*, 624-630.

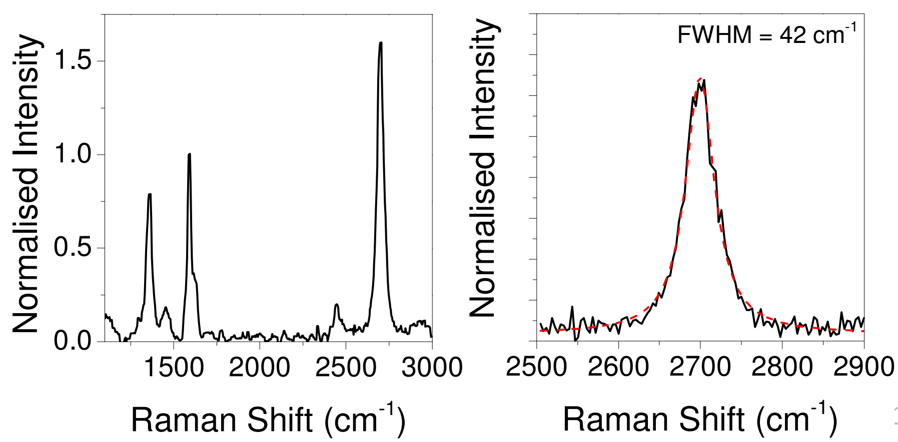
Liquid-phase exfoliation

Scalable production: shear exfoliation

- **What is dispersed? Few layer graphene (7-8 layers, 300-500 nm)**





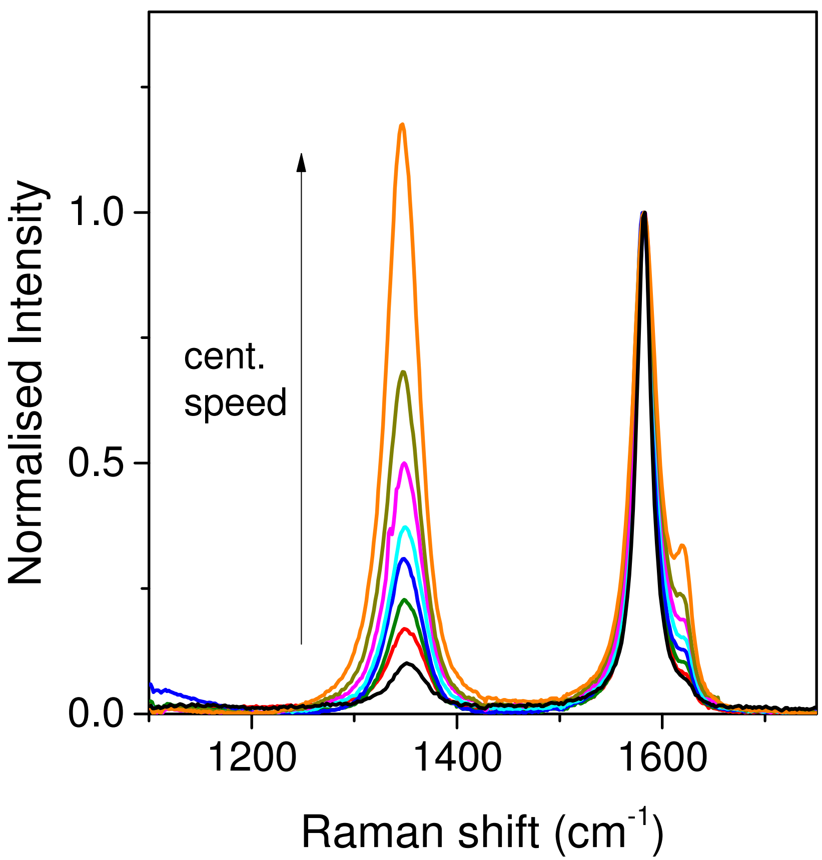


K. Paton, E. Varrla, C. Backes... J.N. Coleman, *Nat. Mater* **2014**, *13*, 624-630.

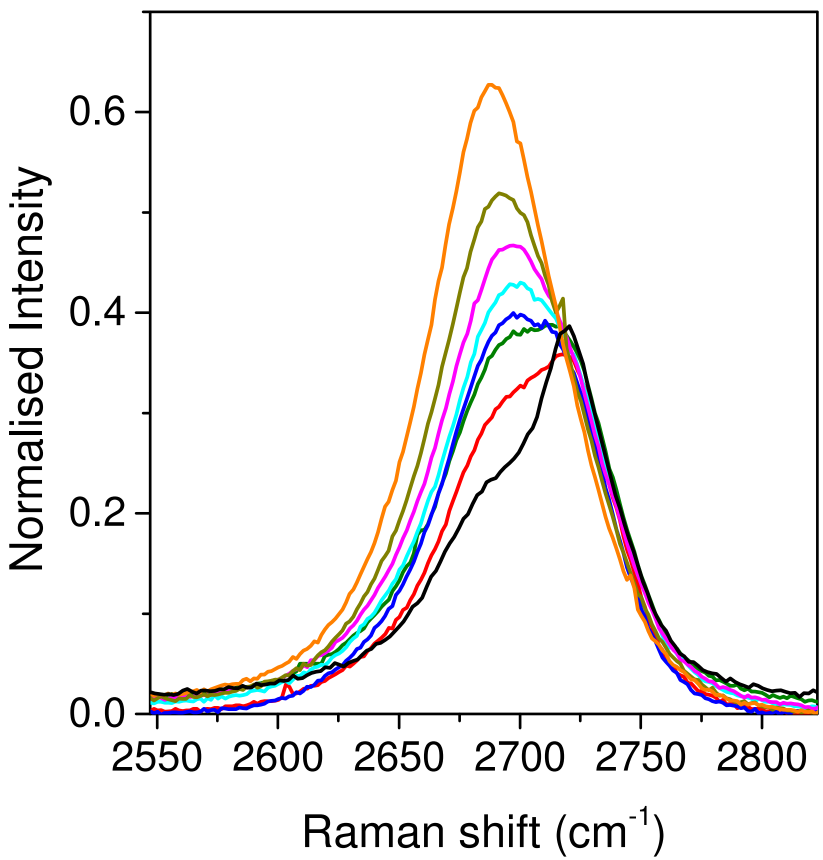
Graphene

Size selection by controlled centrifugation

Raman D/G: changes in L



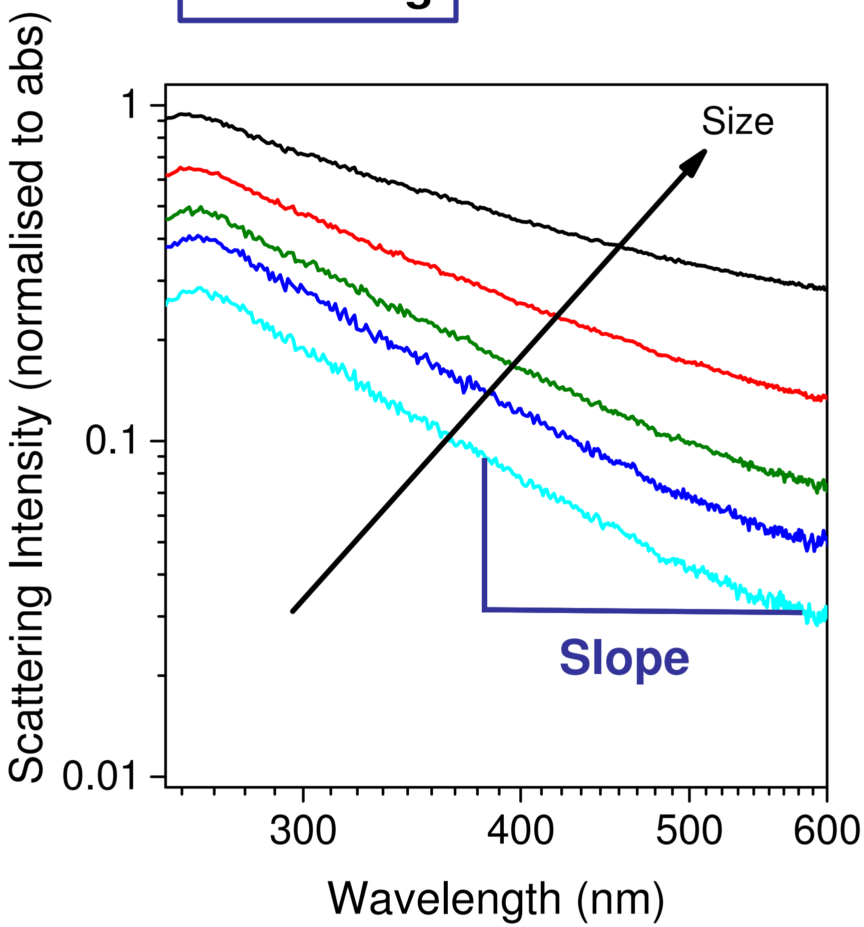
Raman 2D: changes in N



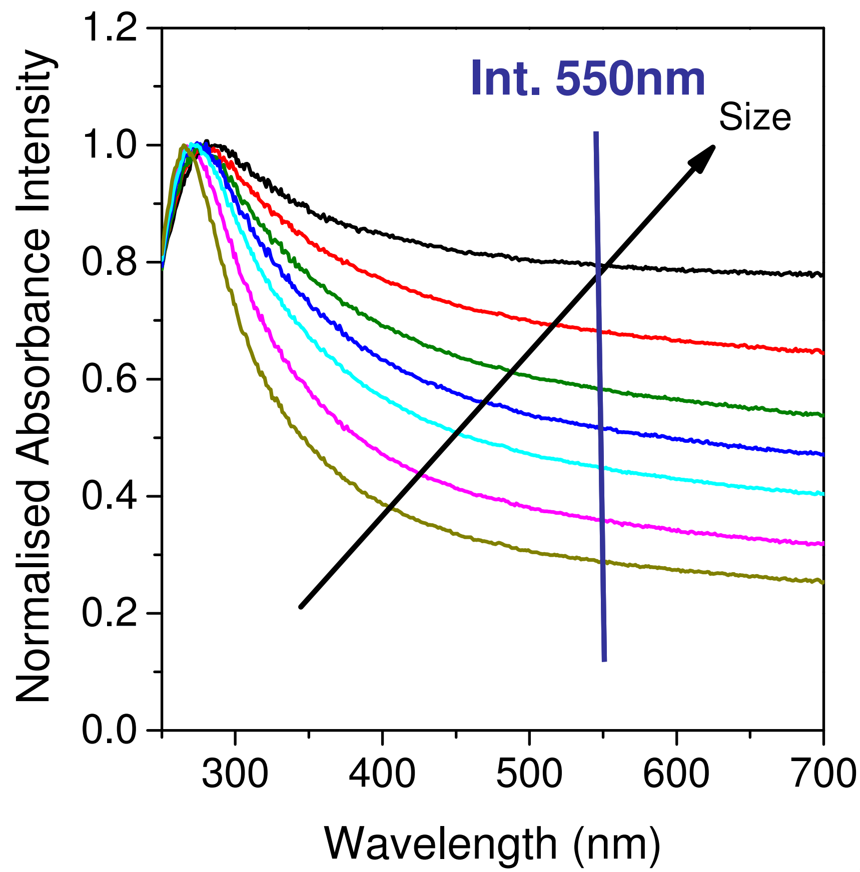
Graphene

Extinction/absorbance metric FLG

Scattering



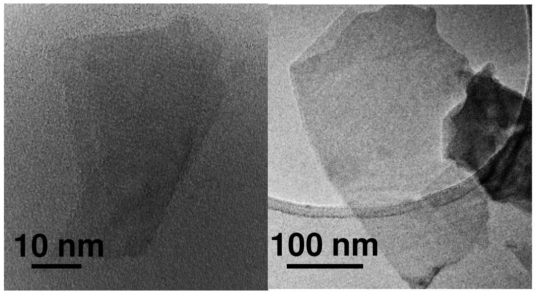
Absorbance

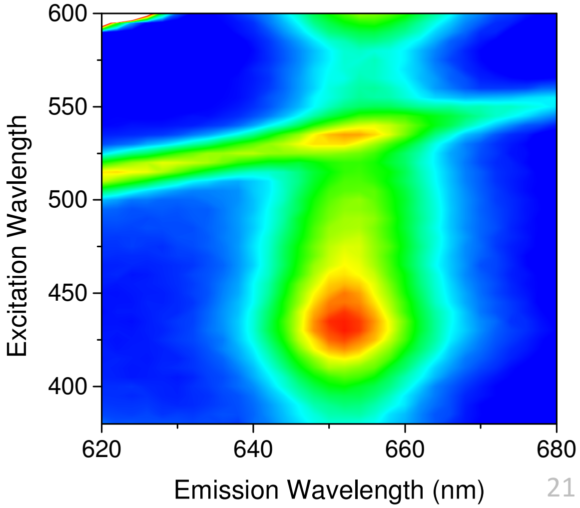


Metrics help!

Summary

- **Liquid exfoliation: it works for sooo many materials!**
- **Size selection allows production of samples with varying mean size and thickness**
- **Metrics are everywhere to determine size and/or thickness *in situ***
- **Huge step forward in understanding dispersion conditions, improving sample preparation etc**
  → e.g. Observation of PL of TMDs in liquid
  → Varying N and L independently
  → Samples with predefined properties
- **Similar metric for other materials!!!!!**





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Acknowledgements

DFG

- Funding (postdoc fellowship)

- Jonathan Coleman + group
  esp. Ronan, Damien, Keith, Andrew, Eswar, Valerie, Tom, Zahra....
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  esp. Nina Berner, Niall McEvoy
- John Donegan + group,
  esp. David McCloskey
- Valeria Nicolosi + group,
  esp. Hannah Nerl, Evie Doherty
- Werner Blau + group,
  esp. Beata Szydłowska

CRANN

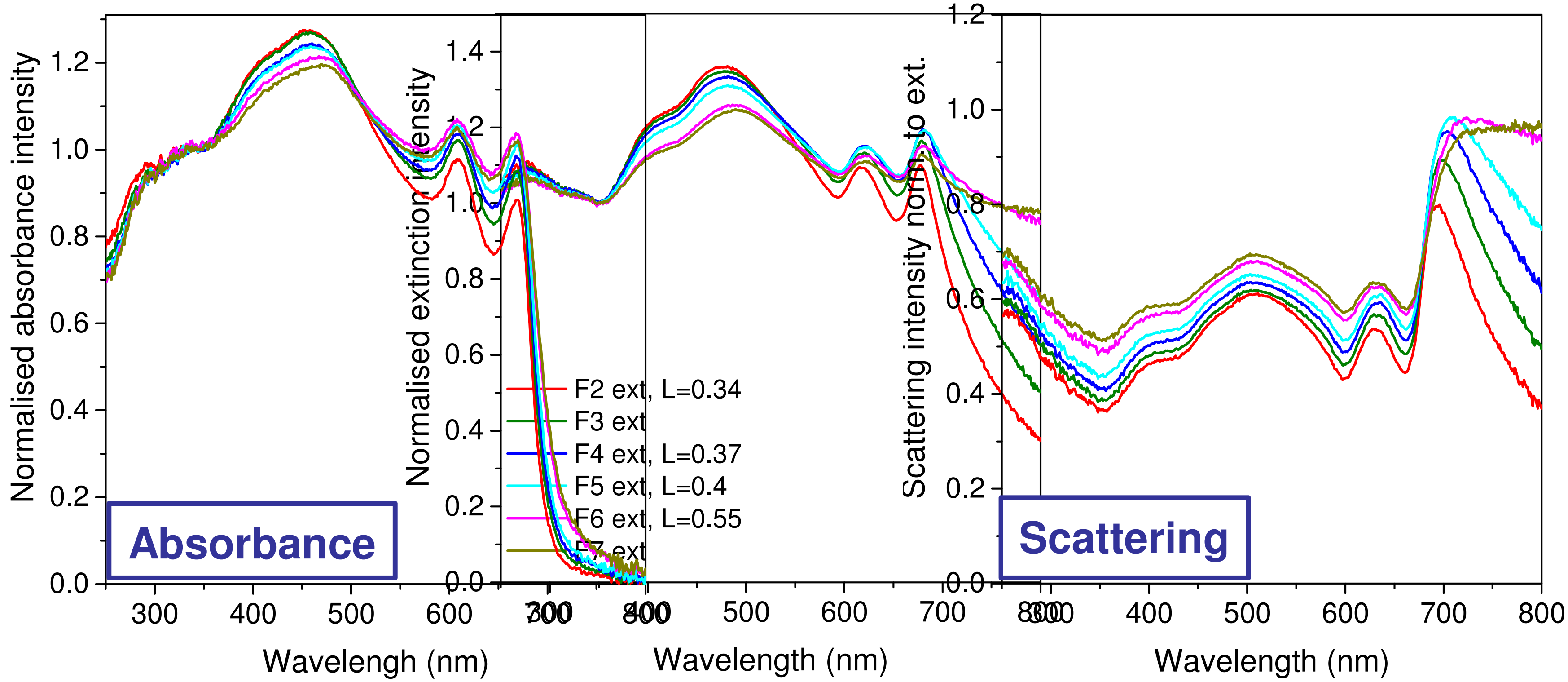
- Nils Scheuschner and Janina Maultzsch

Thank you for your attention!

MoS_2 metric

Overcoming limitations to length metric: large flakes

- **Large flakes: only minor changes in extinction spectra → metric limited**
- **Measurement of absorbance in integrating sphere helps!**

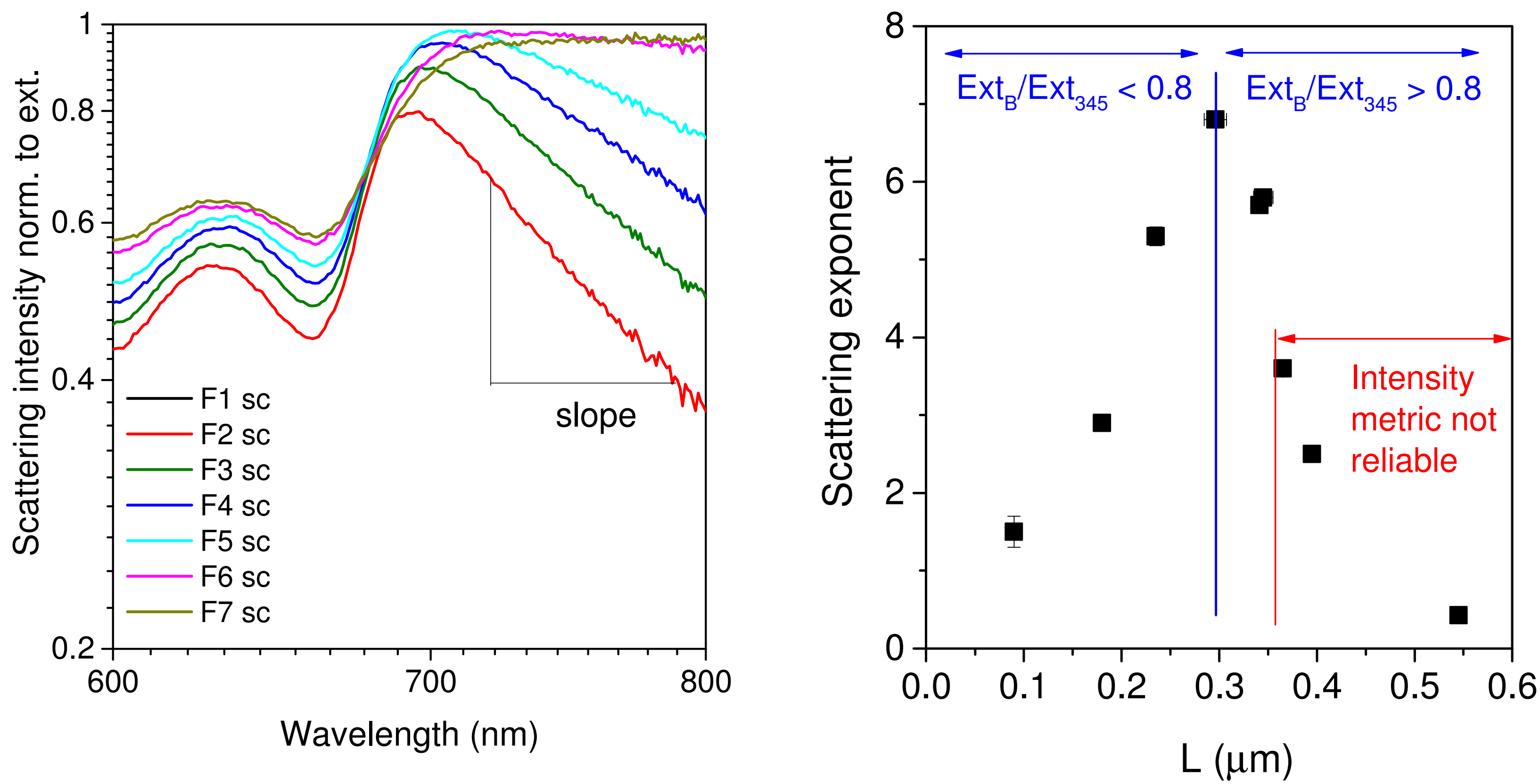


David McCloskey, John Donegan

MoS_2 metric

Overcoming limitations to length metric: large flakes

- **Scattering exponent is an excellent alternative metric for L!**

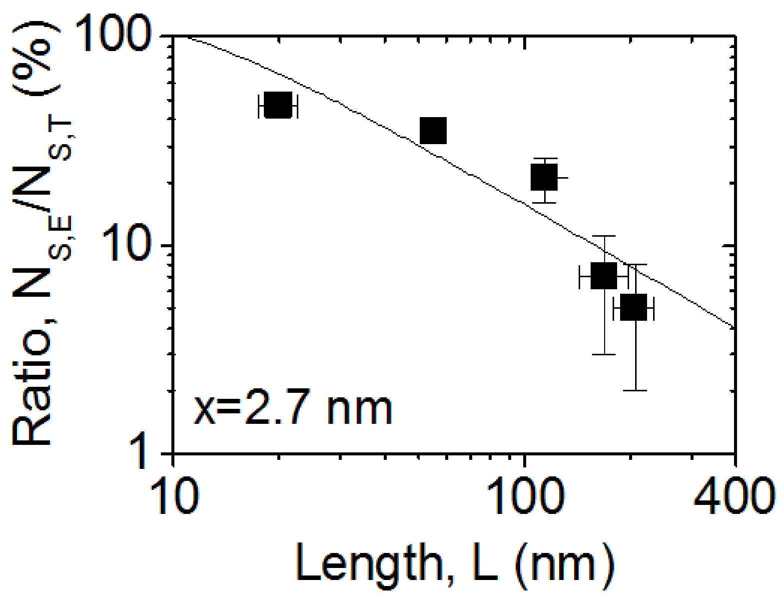


David McCloskey, John Donegan

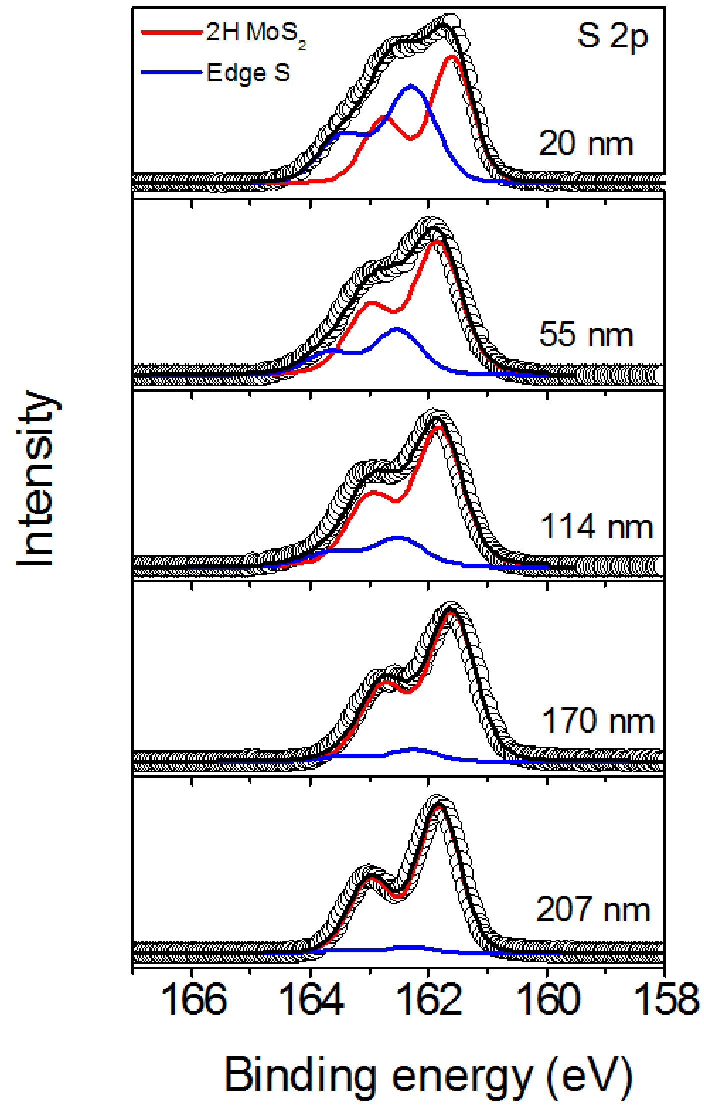
MoS_2 metric

Further evidence for edge effects: XPS

- **XPS says 3 nm**



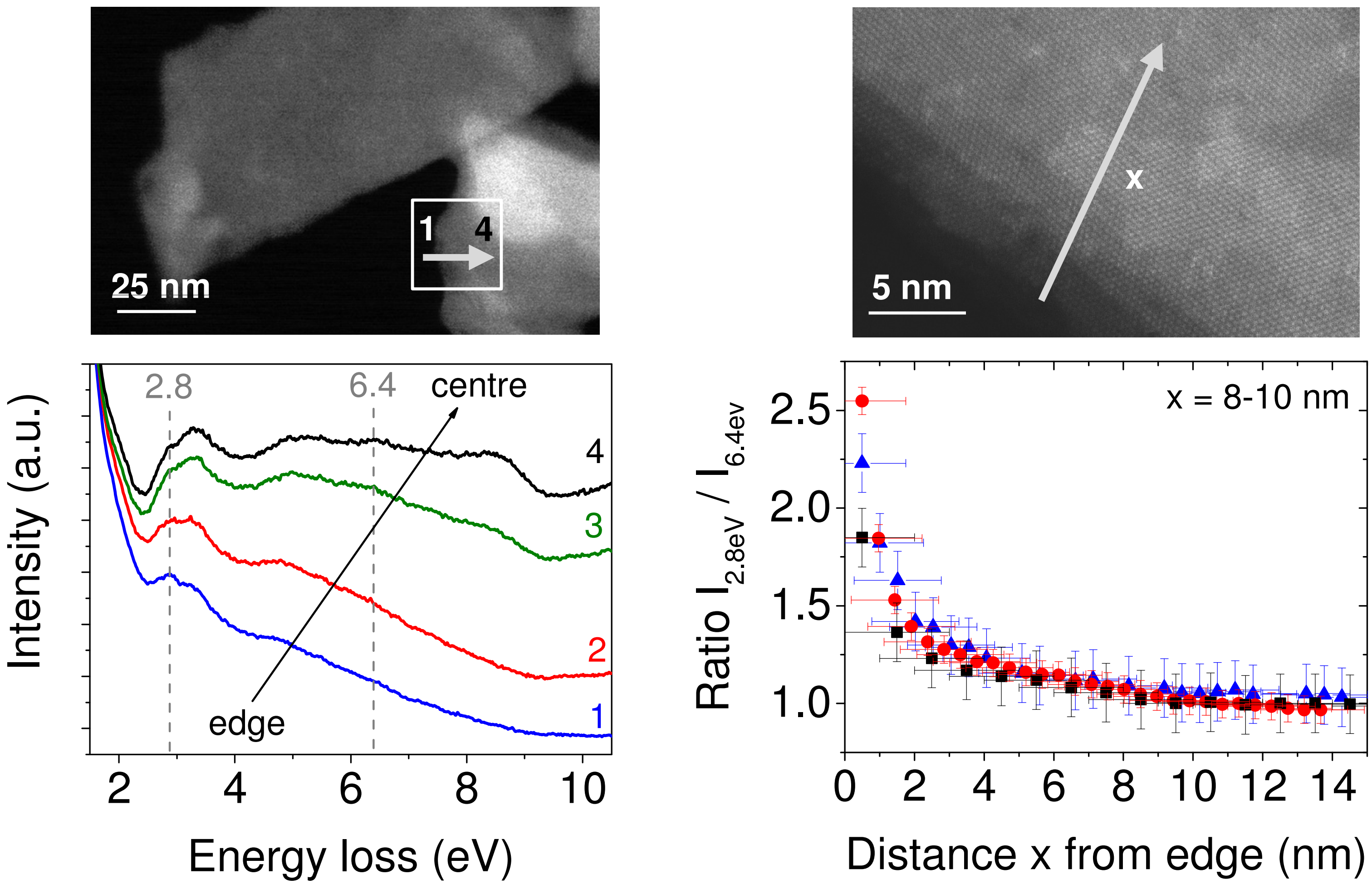
$$\frac{N_{S,E}}{N_{S,T}} = \frac{2x}{L}\left[1 + k\left(1 - \frac{2x}{L}\right)\right]$$



Nina Berner, Georg Duesberg

MoS_2 metric

Further evidence for edge effects: EELS

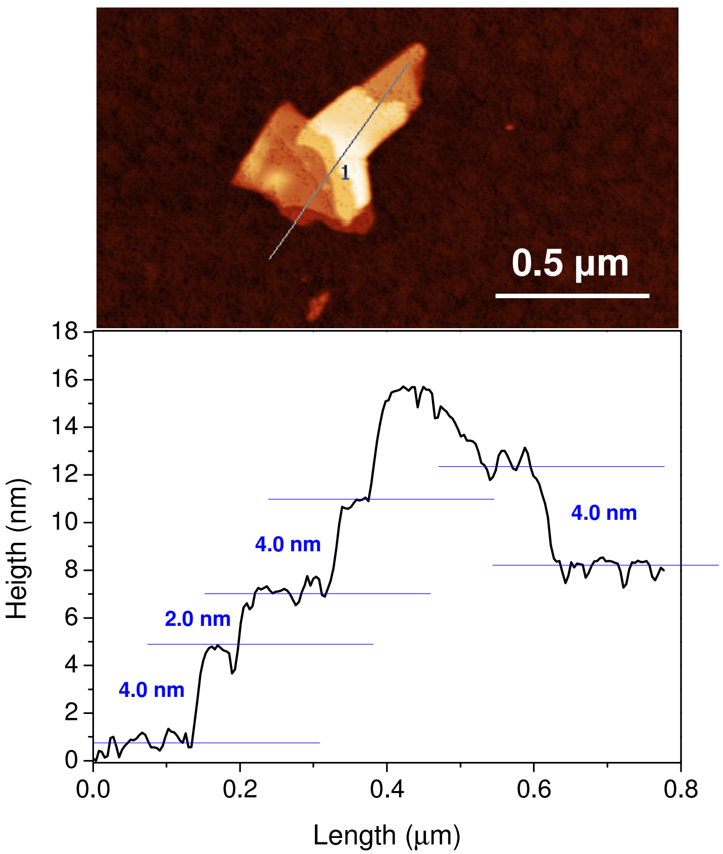


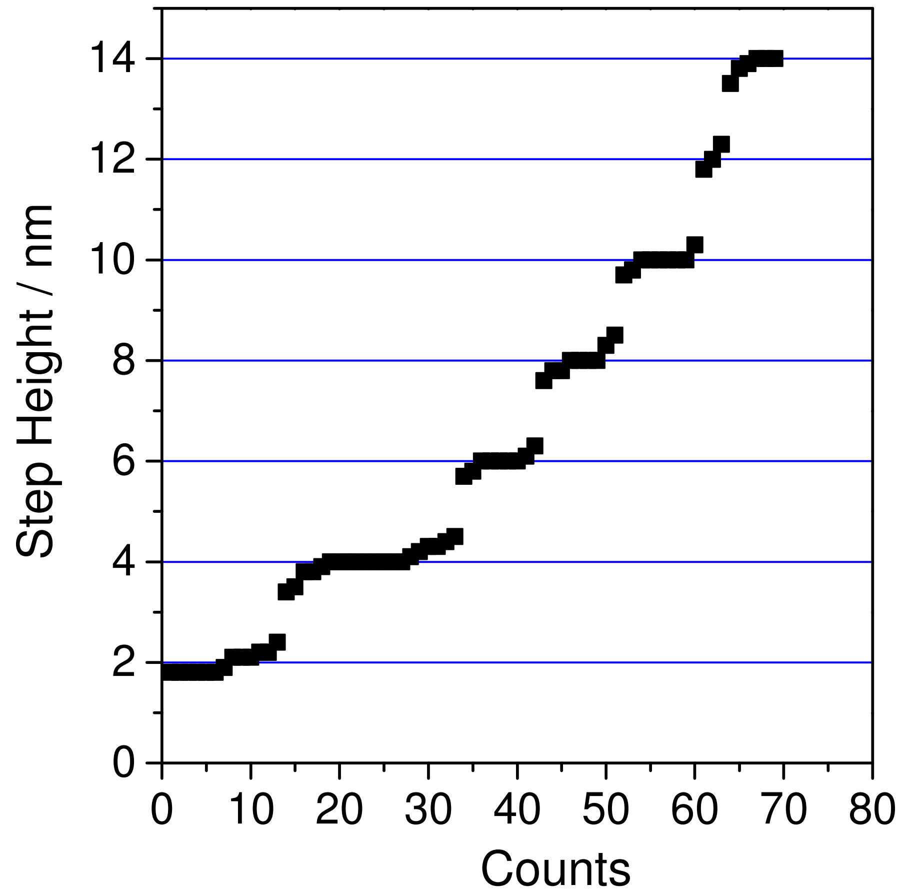
Hannah Nerl, Valeria Nicolosi

MoS_2 metric

AFM height: correlation to layer number

- **Analysis of step heights: step height is a function of ~2 nm**





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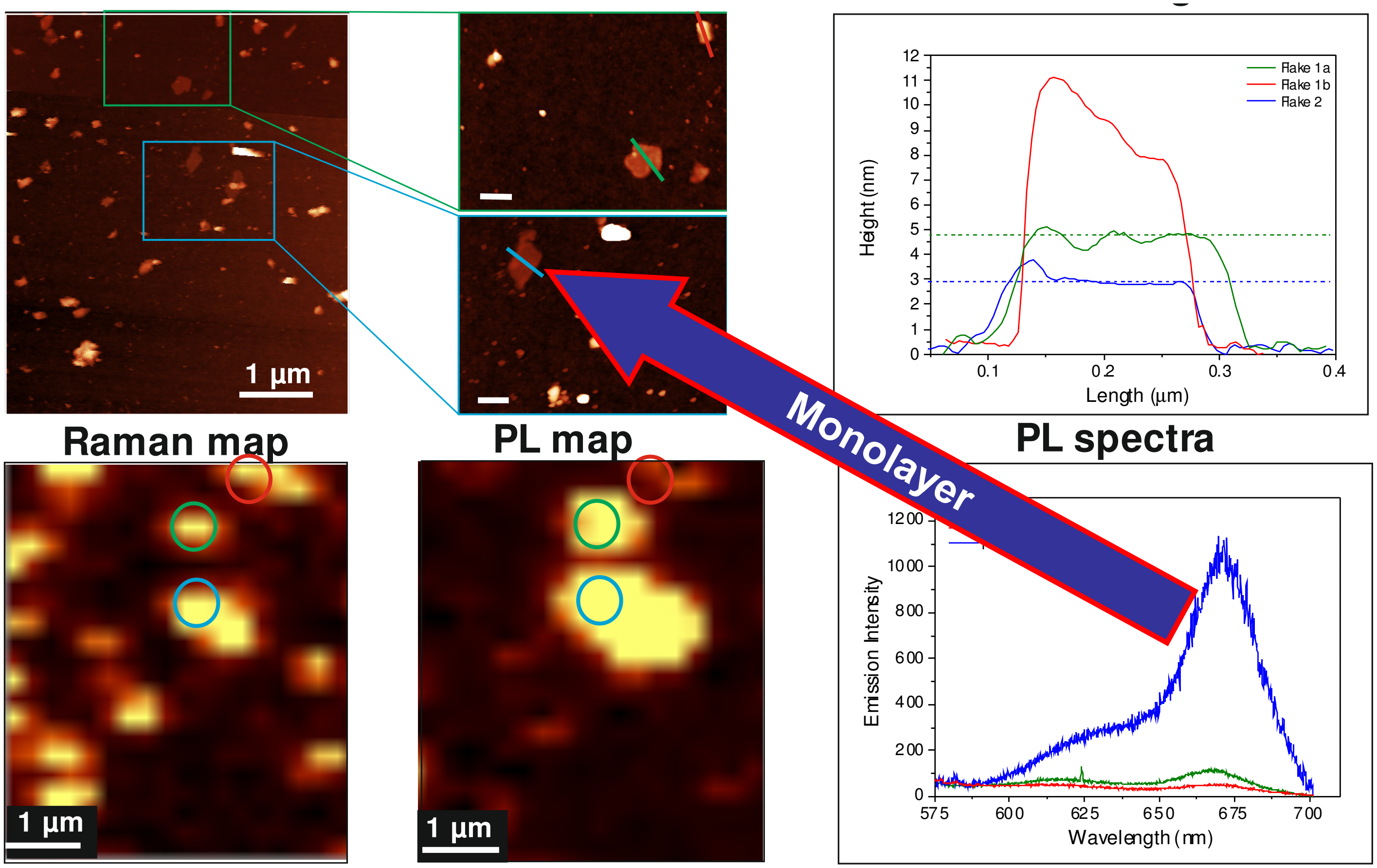
MoS_2 metric

AFM height: correlation to layer number

- Height of thinnest flakes 3-4 nm → monolayer?!

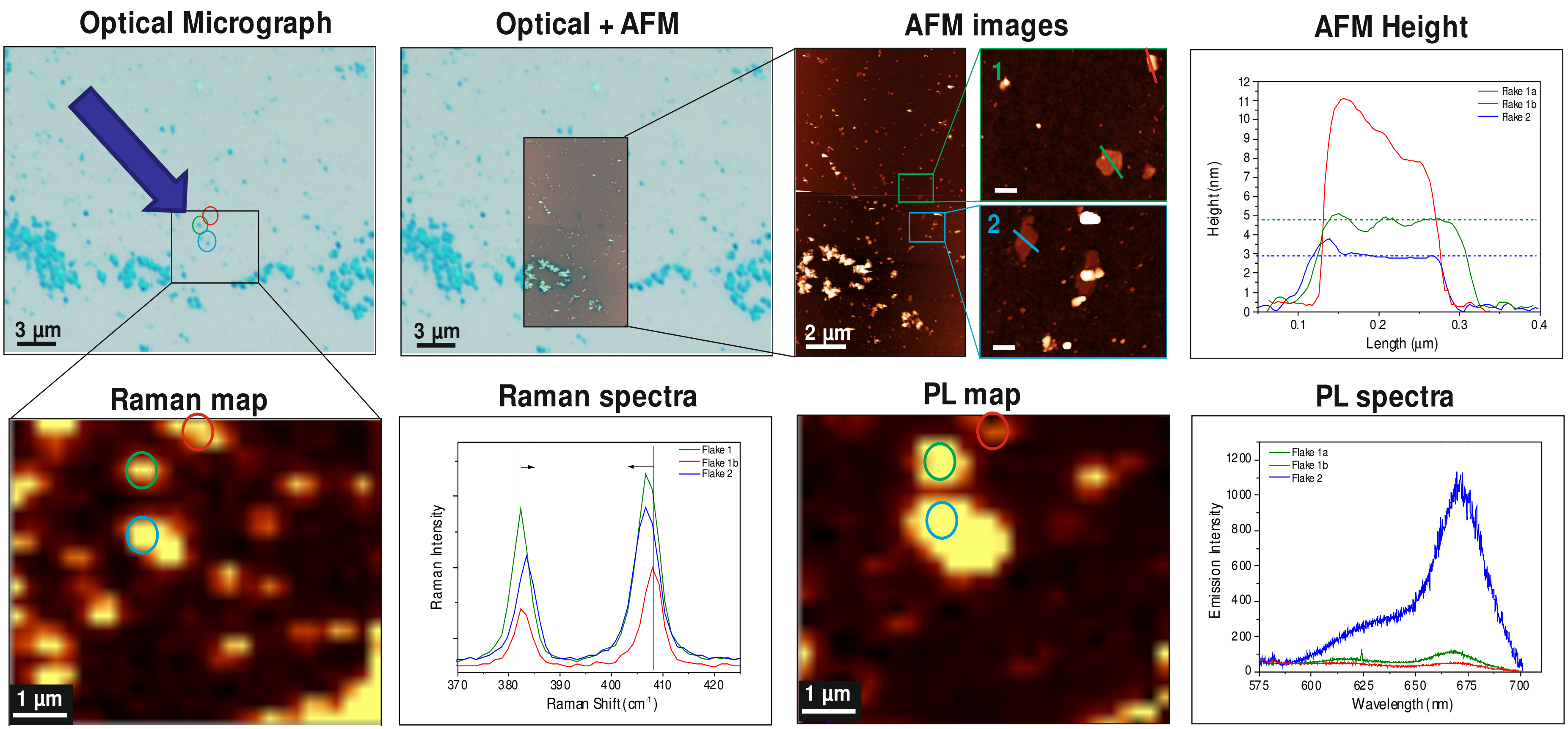


Niall McEvoy, Georg Duesberg

Absorbance Metric

AFM height: correlation to layer number

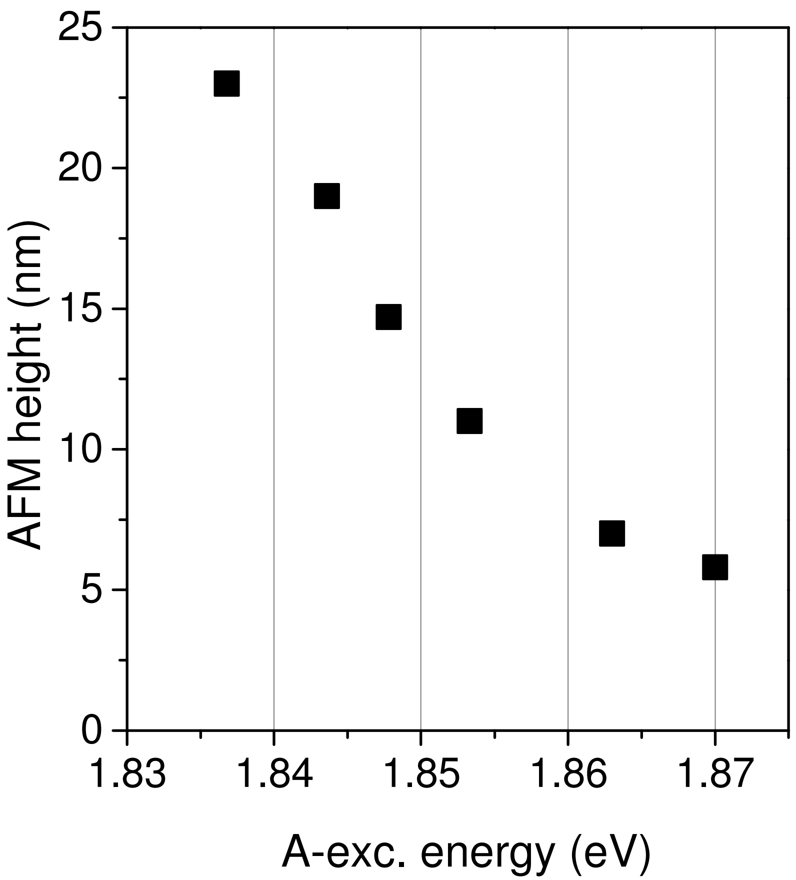
- **Height of thinnest flakes 3-4 nm → monolayer?!**

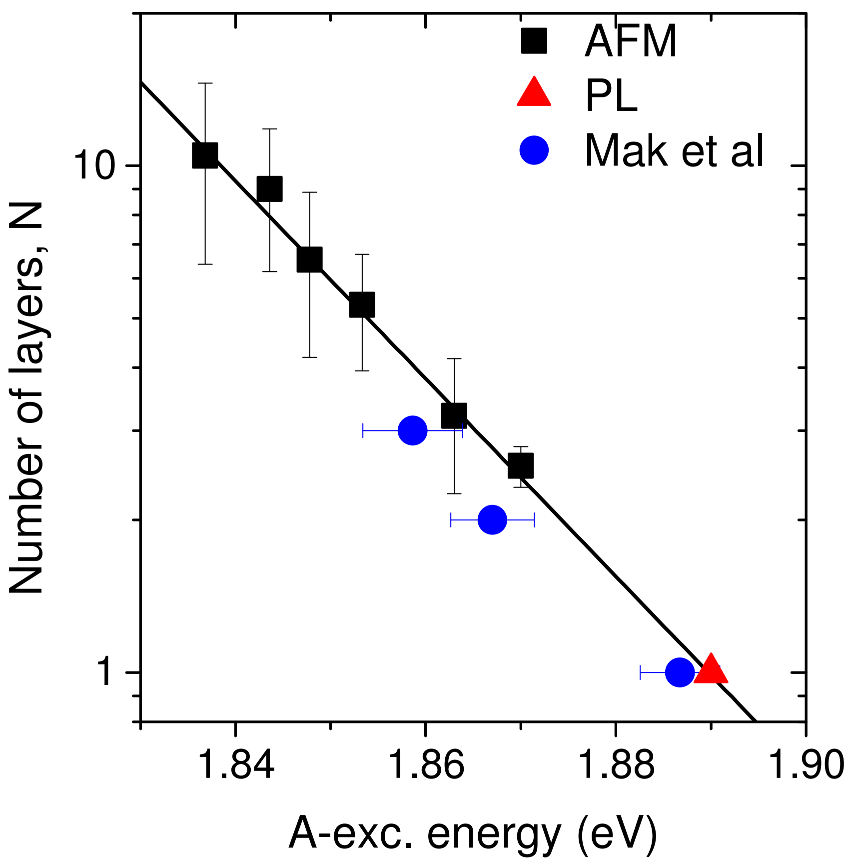


MoS_2 metric

Peak position metric – Correlation to thickness!

- **Apparent height can be converted to number of layers**

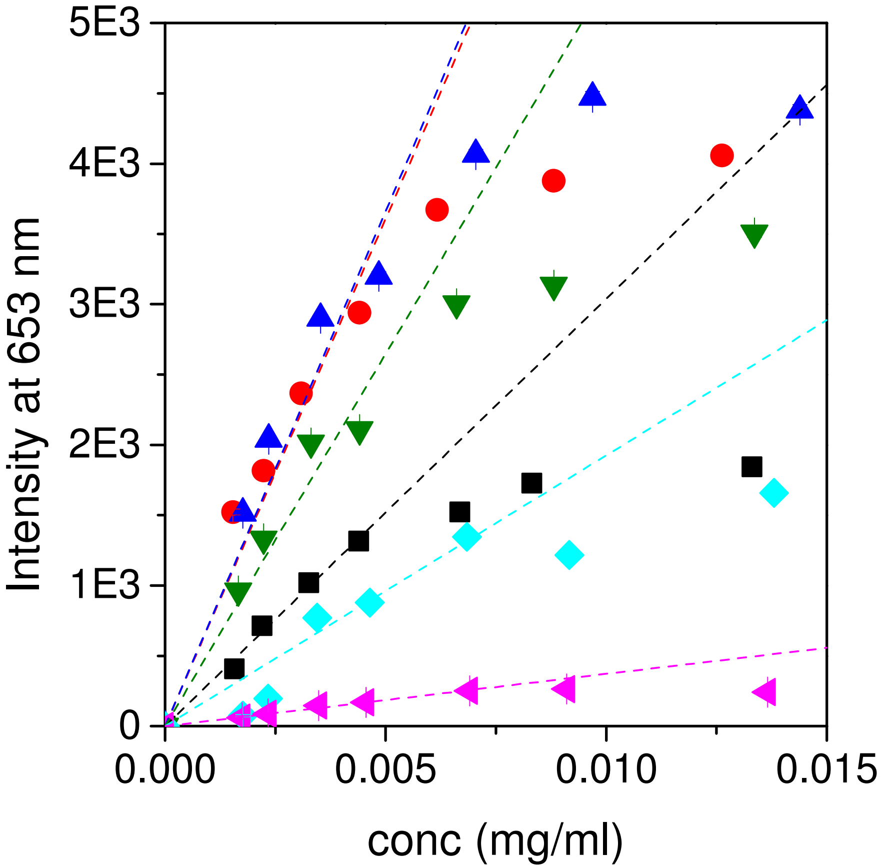


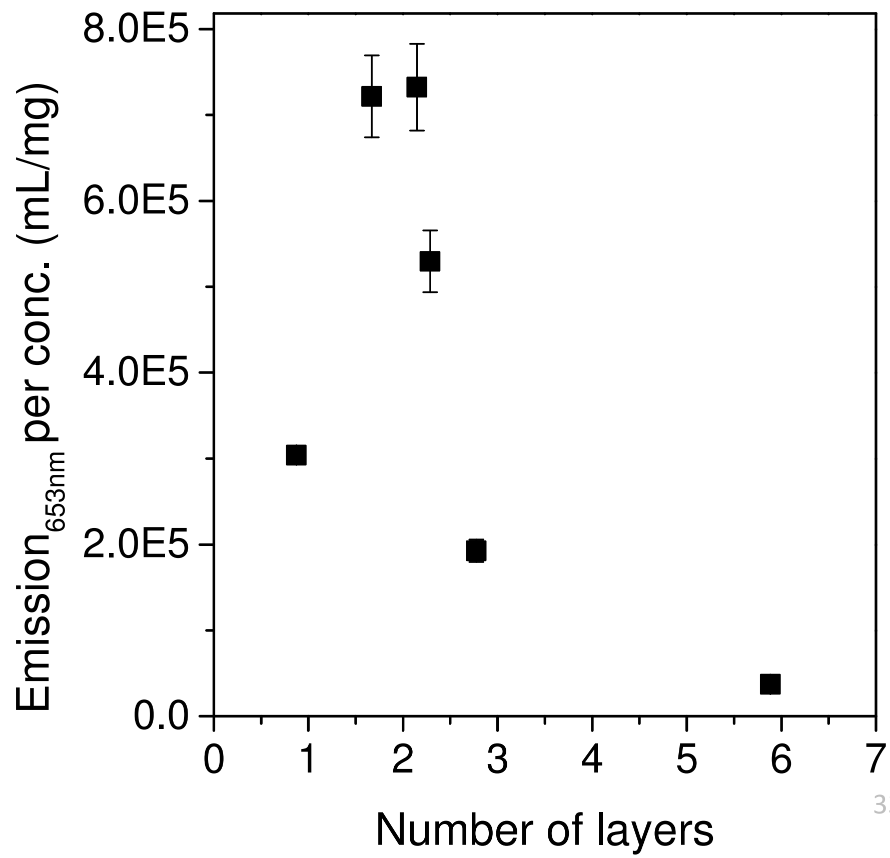


MoS_2 metric

Fluorescence in dispersion

- **PL intensity as a function layer number → reduced for very small flakes → PL quenching at edges**

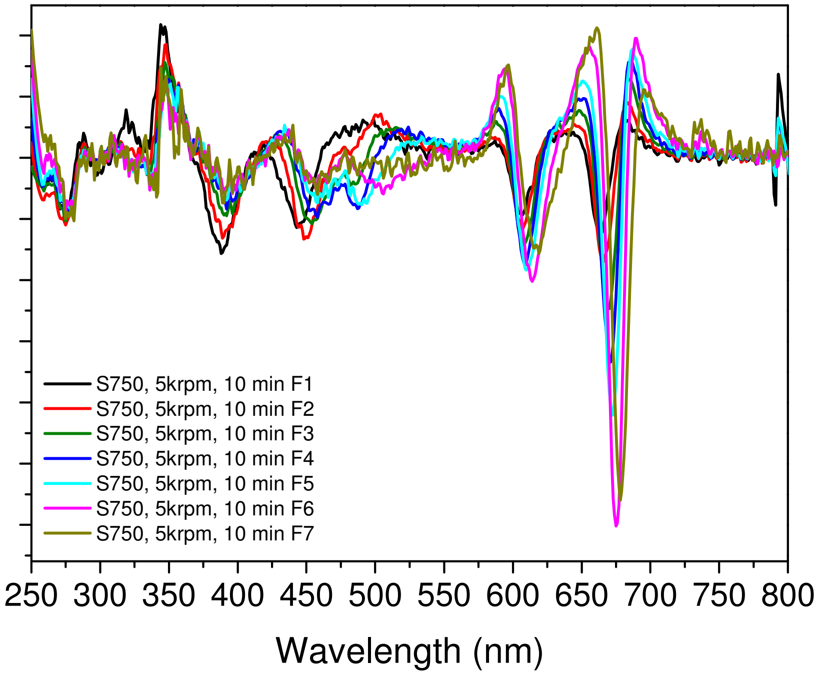


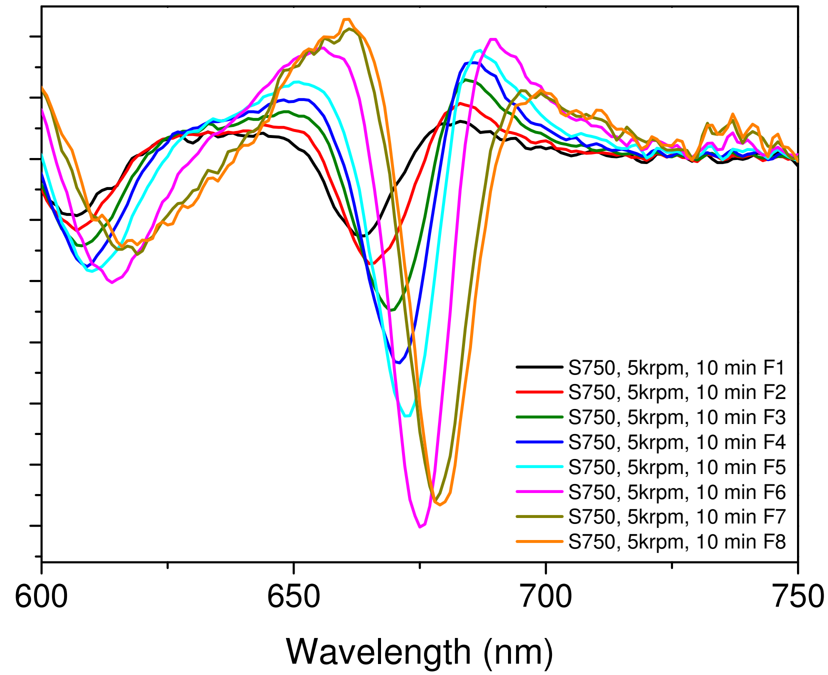


Absorbance Metric

Determination of peak position A-exciton

- **Contribution from scattering background (then, peak position not independent from lateral sizes) → peak position of second derivative**

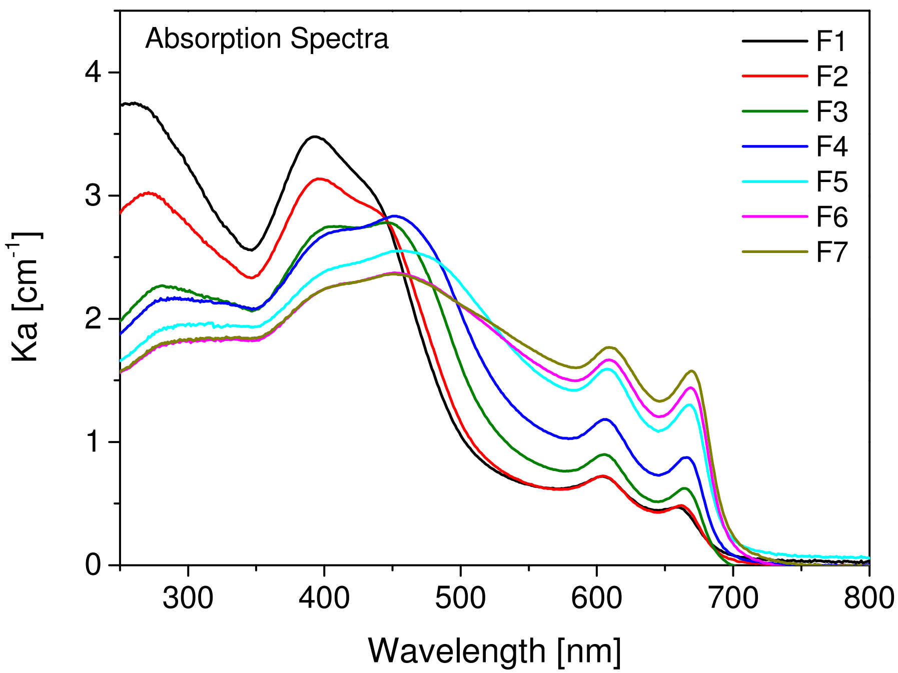


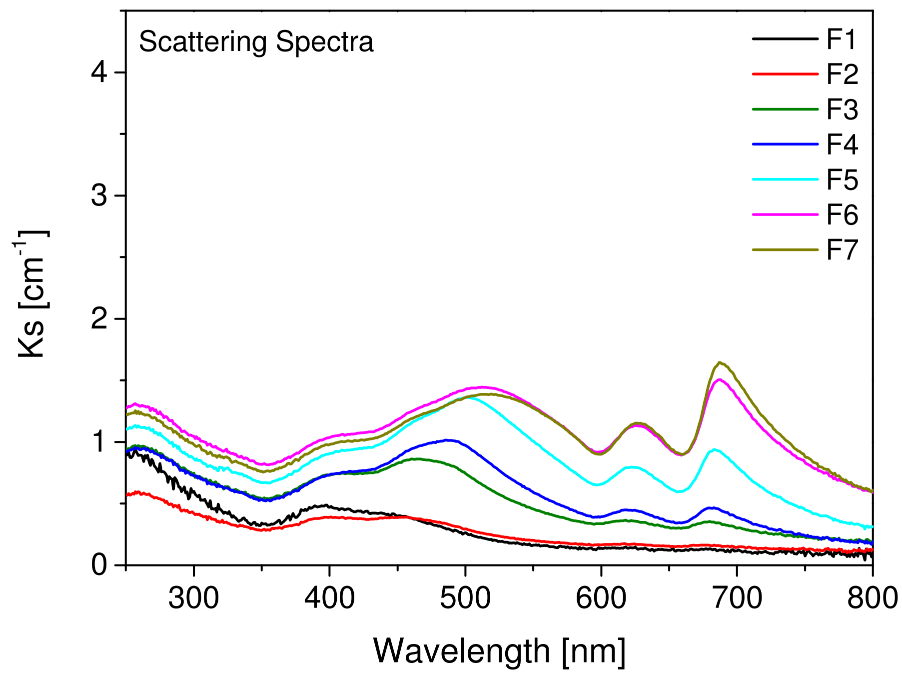


Scattering contribution

Absorbance and scattering spectra

- **Similar to extinction spectra, absorption and scattering spectra also change as a function of size in a similar way**

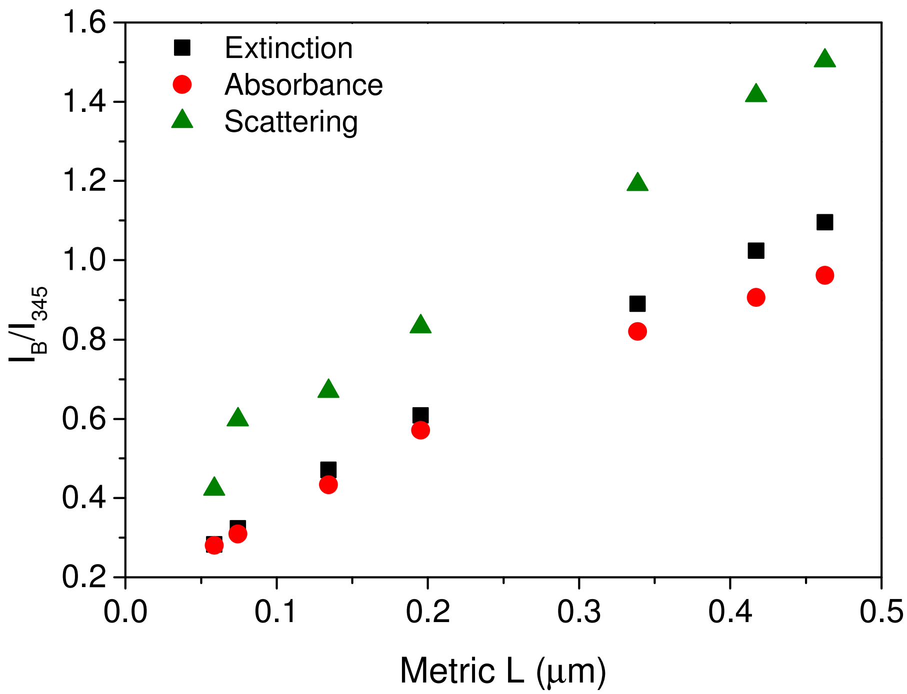


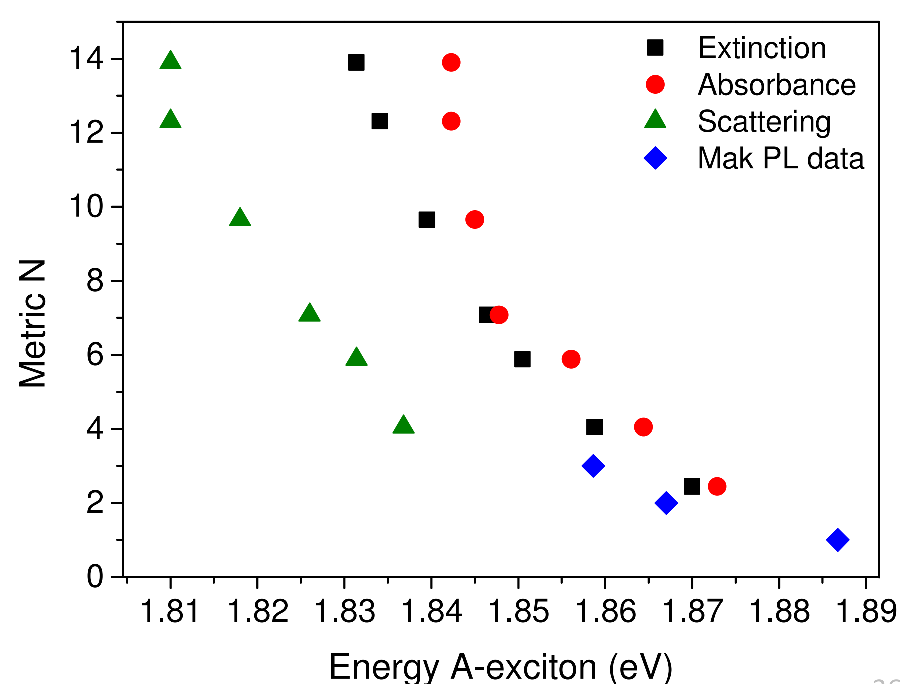


Scattering contribution

Metric plots from absorbance and scattering

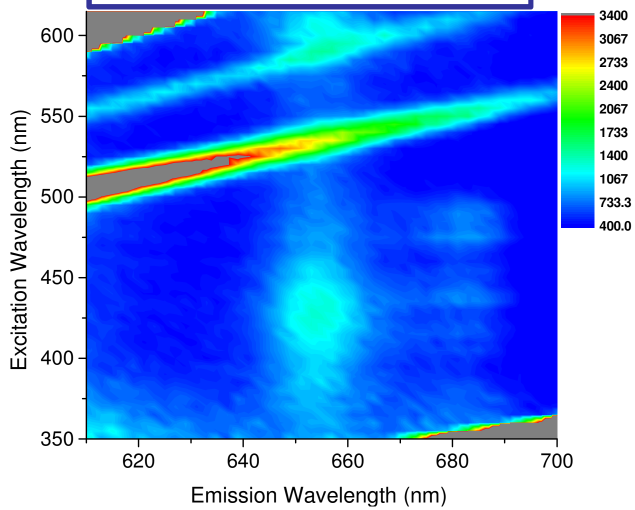
- For L metric, absorbance, scattering and extinction spectra follow same curve shape
- For N metric, for N>8, shift is caused by scattering



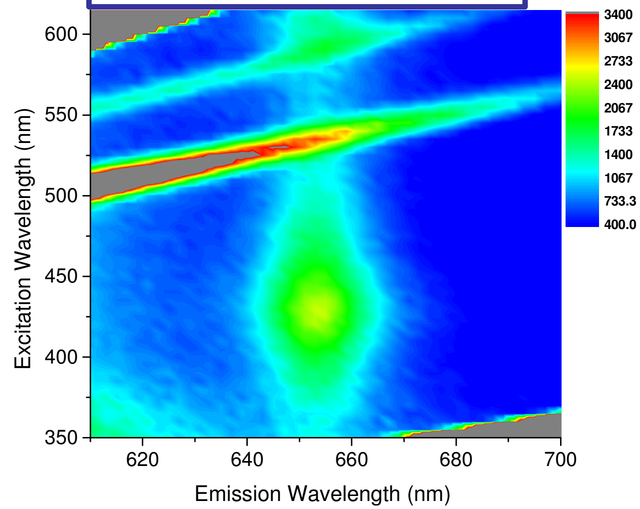


PL maps

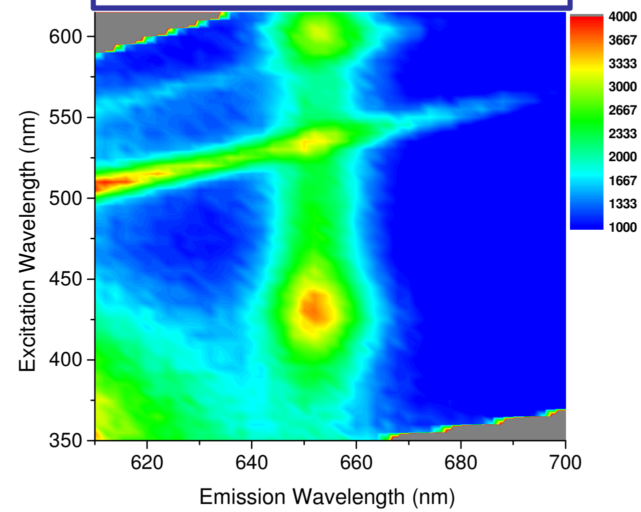
UC P, 0.008 mg/ml



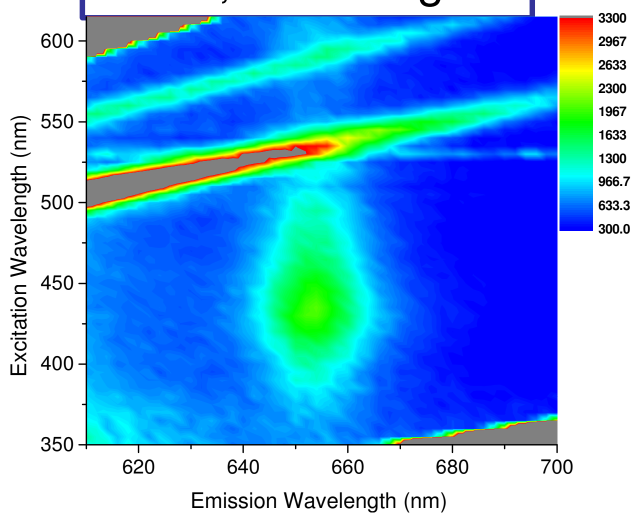
15kP, 0.009 mg/ml



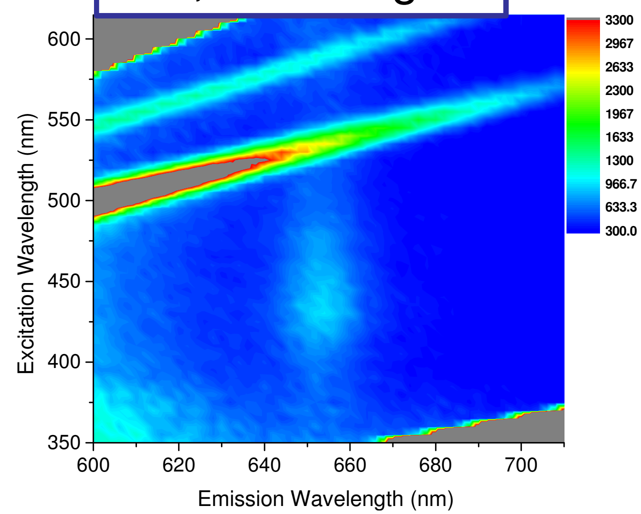
12.5kP, 0.009 mg/ml



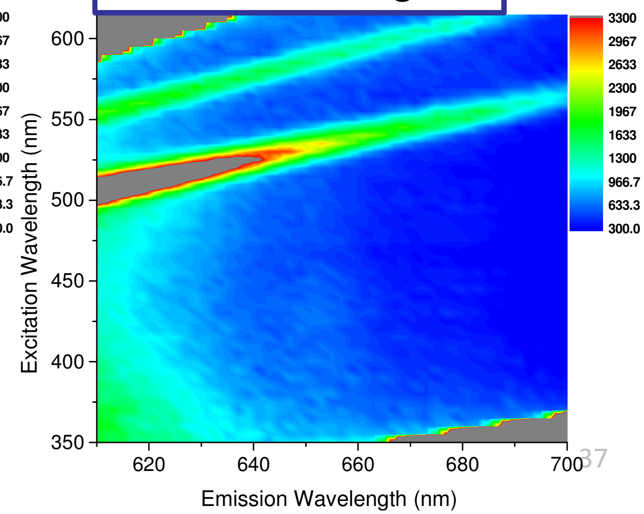
9.5kP, 0.008 mg/ml



5kP, 0.009 mg/ml



3kP, 0.009 mg/ml



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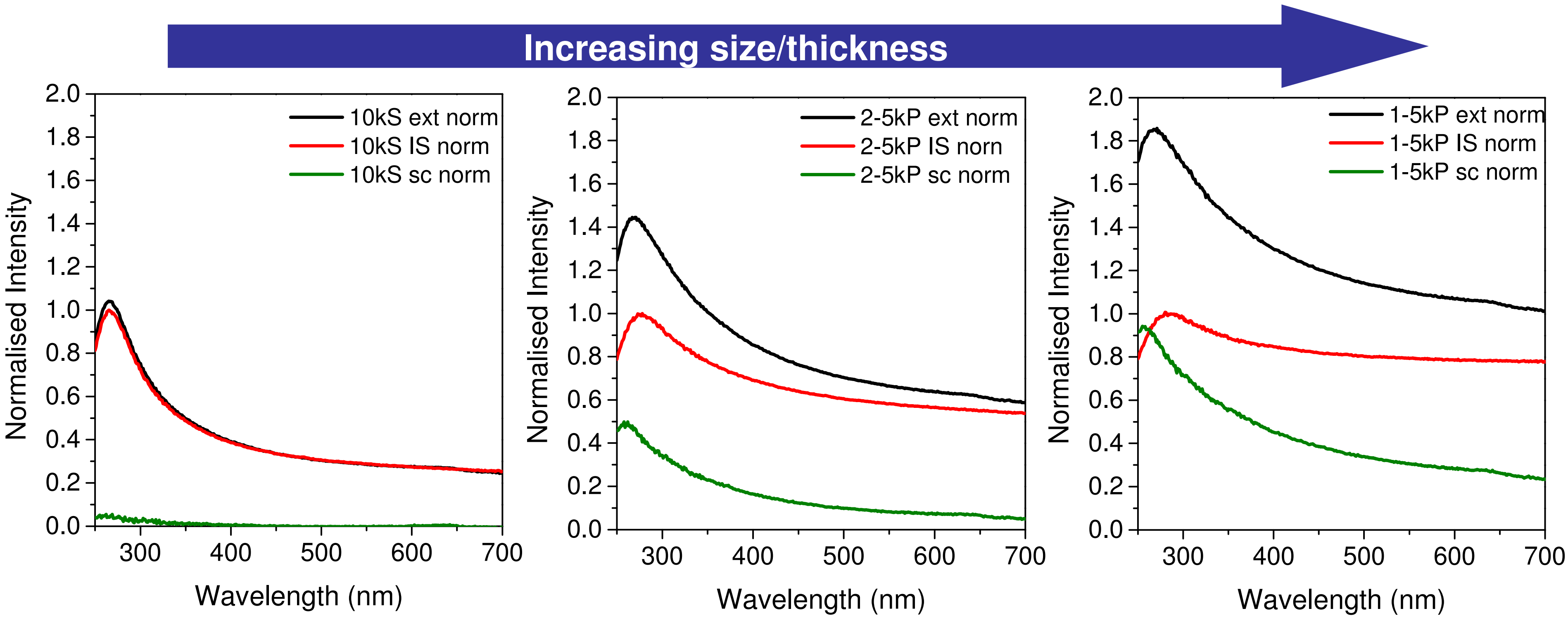
Graphene

Extinction/absorbance metric FLG

- **Descrimination between scattering and absorbance to extinction spectra by measurement in integrating sphere**



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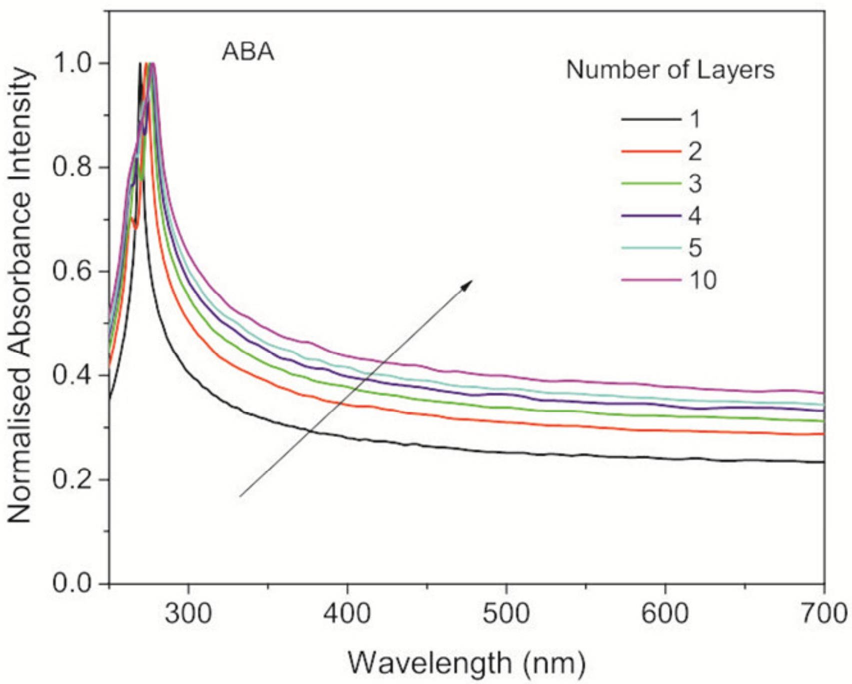
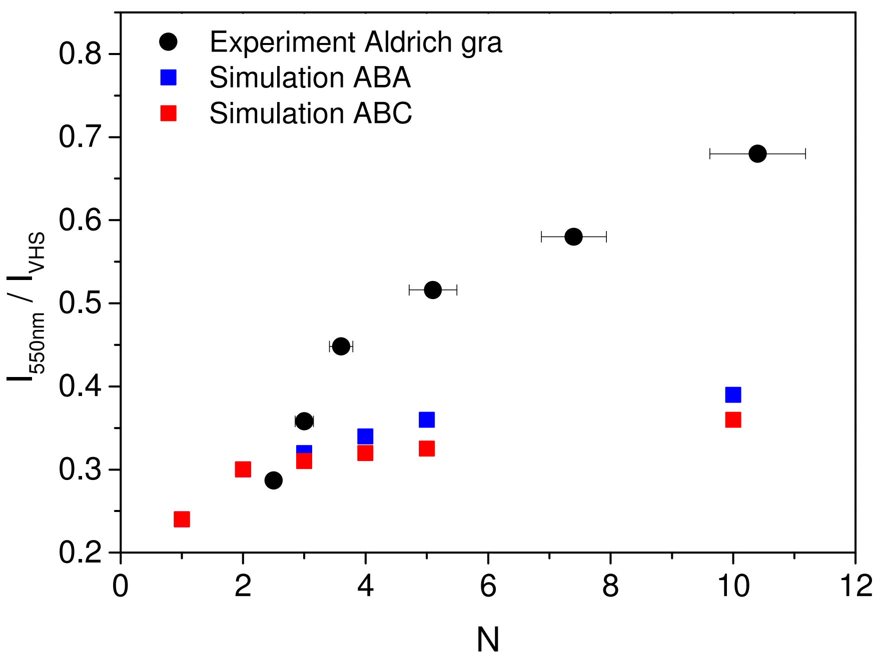
Graphite N metric

Comparison to simulation

- **Simulation qualitatively confirms trend of abs spectra changing as function of N**





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