

The Two Faces of 2D: Functionalization Strategies for Janus 2D Materials



Alicia Forment-Aliaga

Instituto de Ciencia Molecular, Universitat de València, Paterna, Spain.



alicia.forment@uv.es



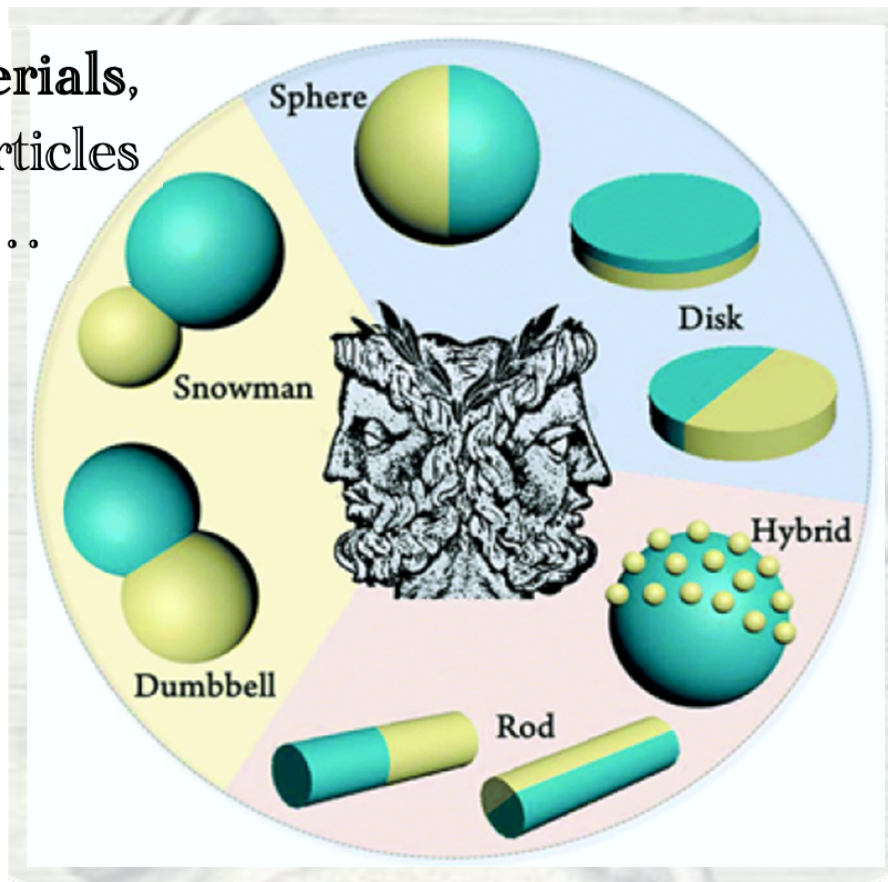
[@AFormentAliaga](https://twitter.com/AFormentAliaga)

In ancient
Roman religion,



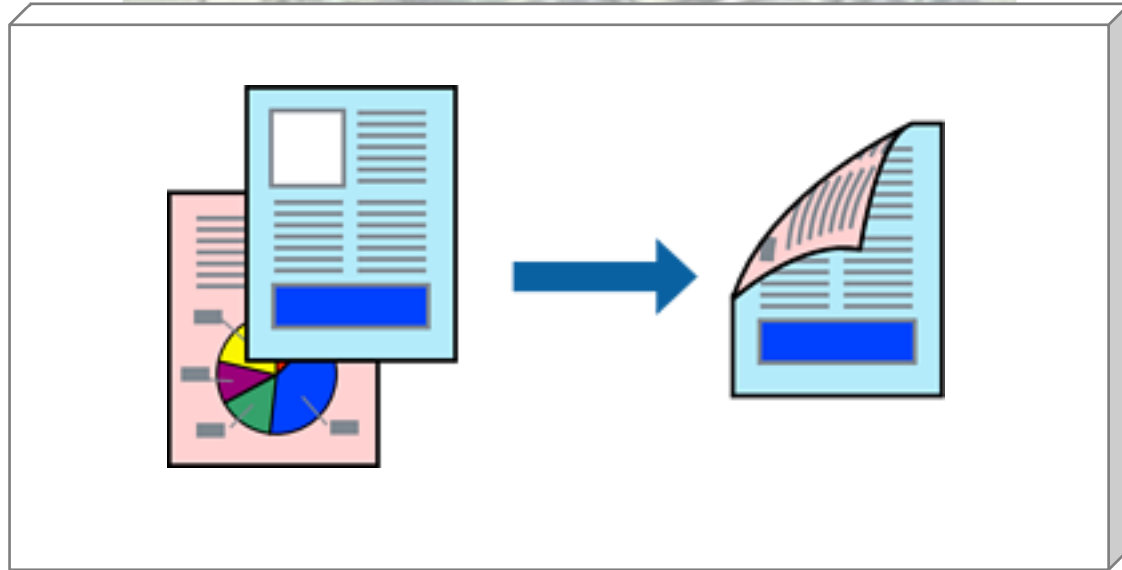
Janus is the god
of beginnings,
transitions, and
endings

In nanomaterials,
Janus nanoparticles
are those that...

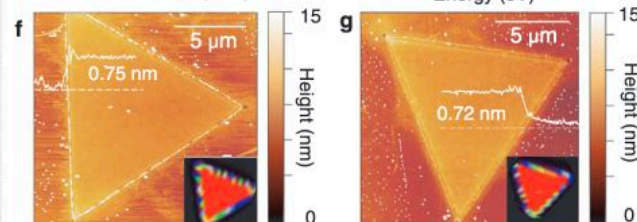
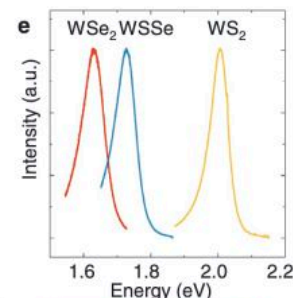
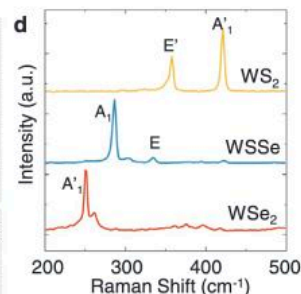
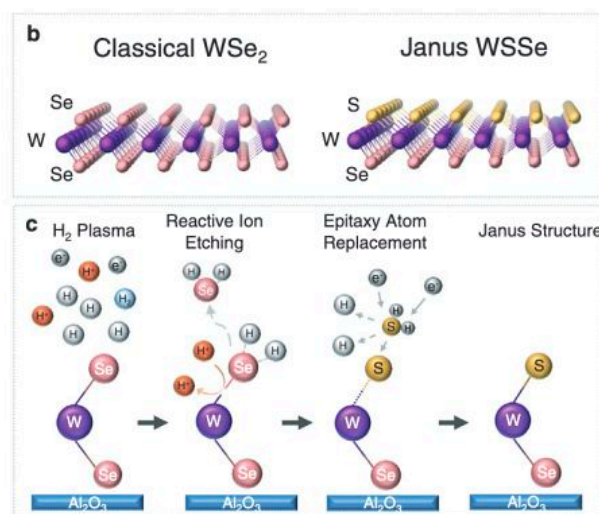
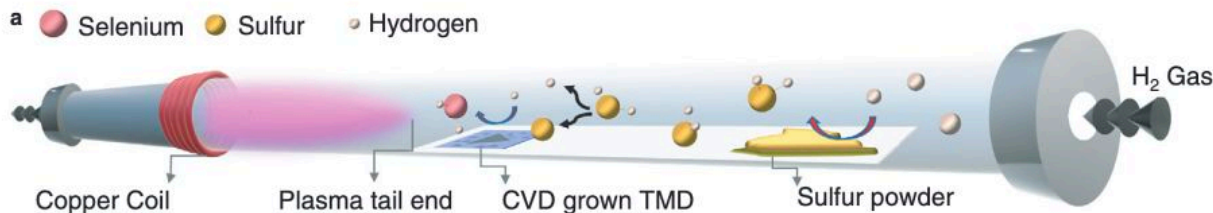


...exhibit two
(or more)
surfaces with
different, often
contrasting,
properties.

What about Janus 2D materials?

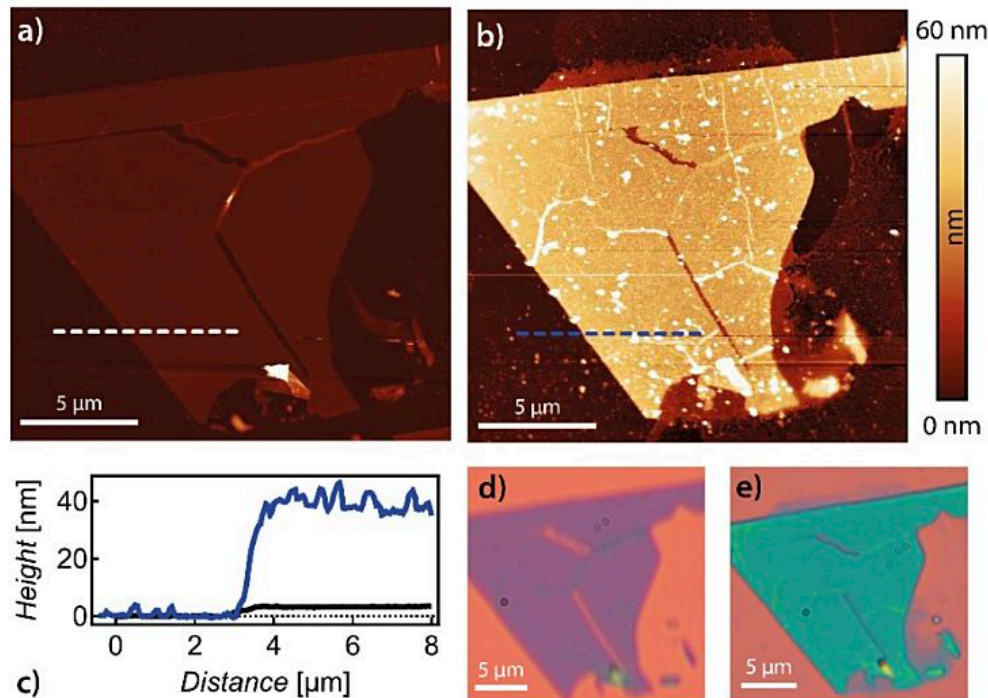
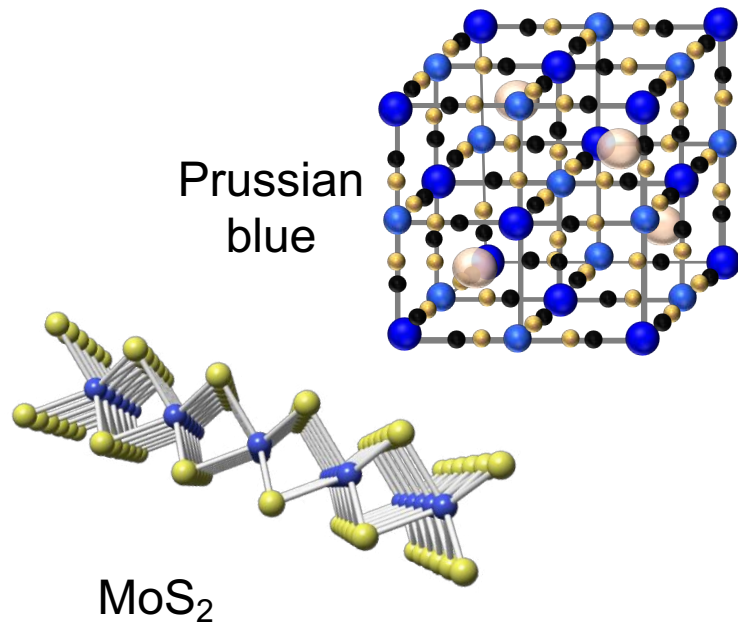


Asymmetric structure



D. B. Trivedy *Adv. Mater.* **2020**, *32*, 2006320

Asymmetric functionalization

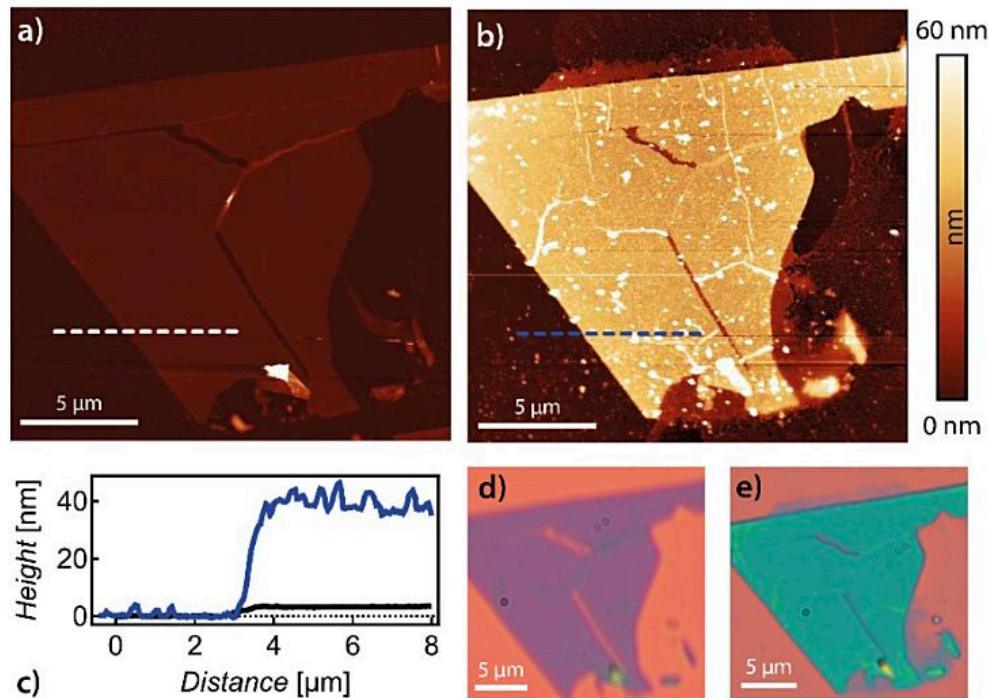
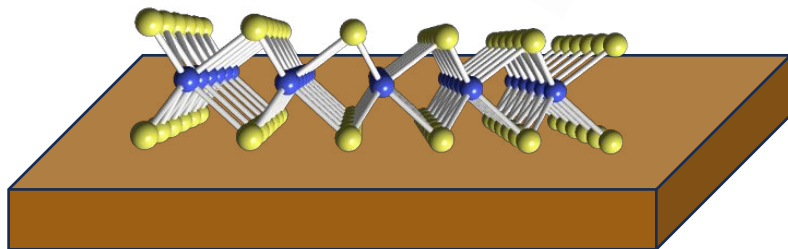
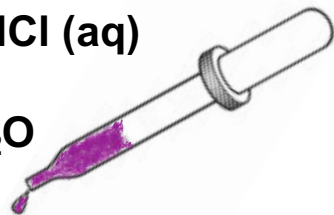


Asymmetric functionalization

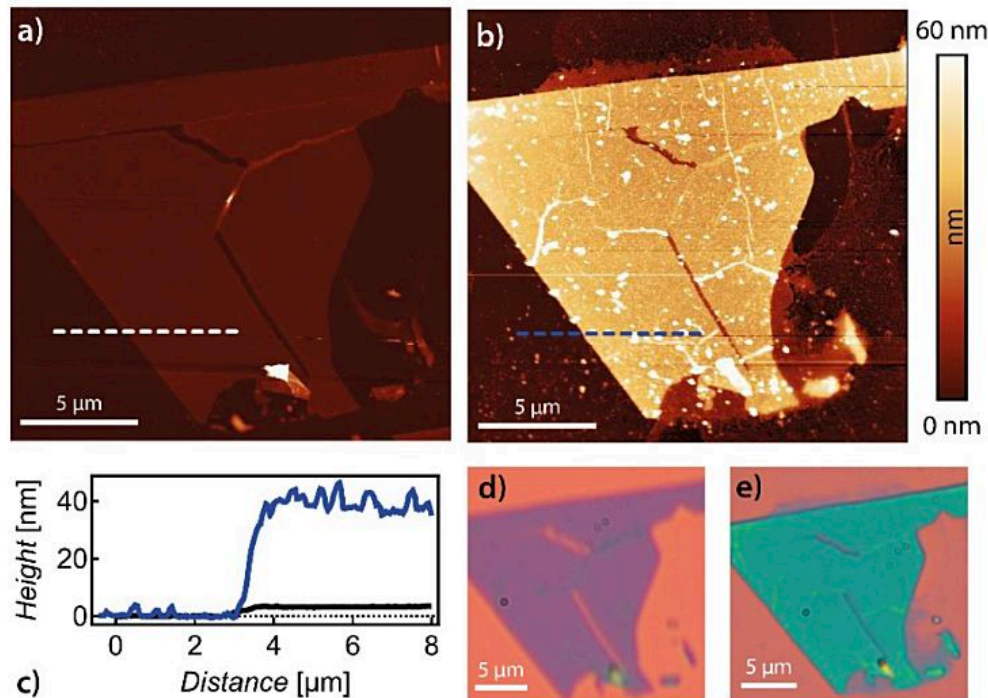
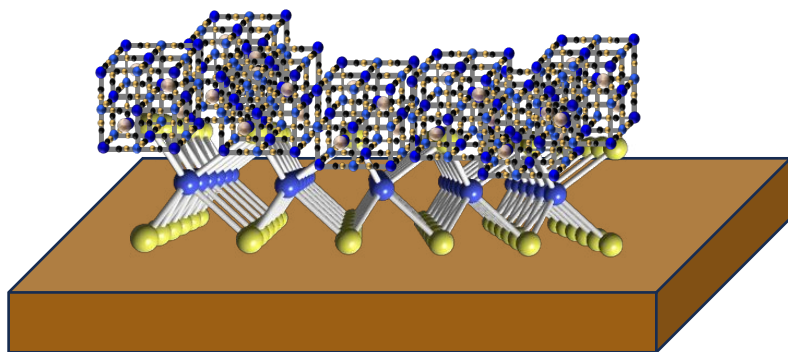
$[K_3Fe(CN)_6]$ in HCl (aq)

+

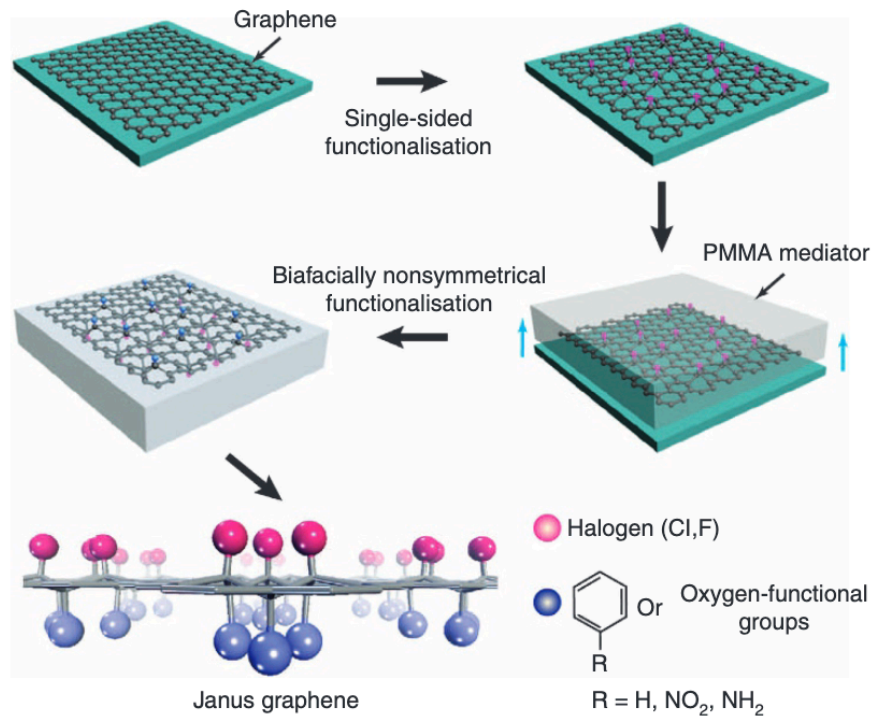
$FeCl_3$ in H_2O



Asymmetric functionalization



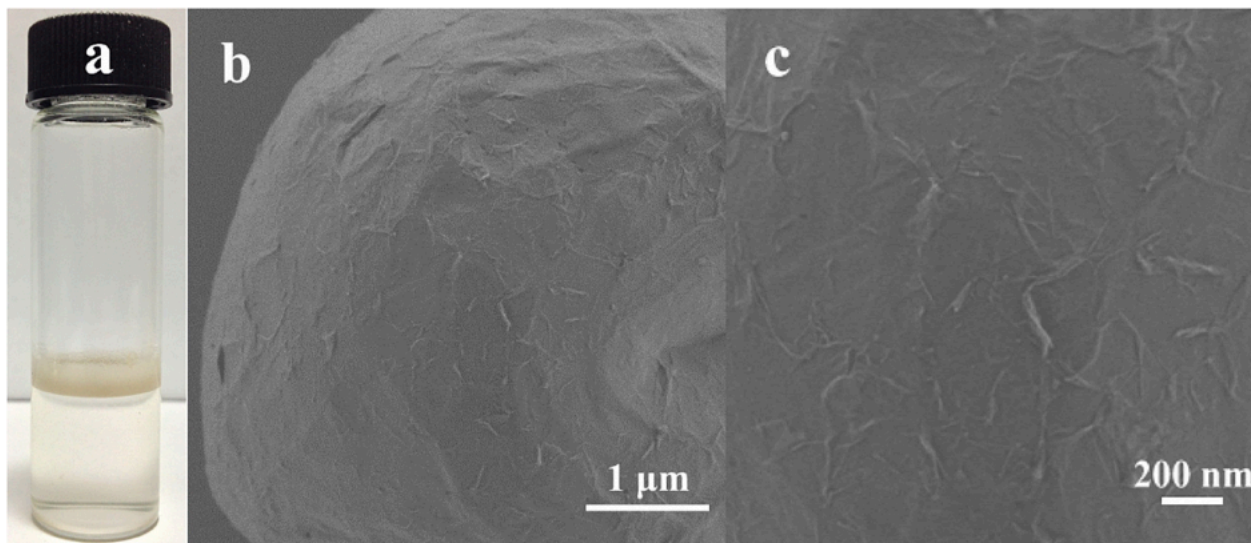
Asymmetric functionalization



Zhang, L. et al. Nat Commun, 2013, 4, 1443

Asymmetric functionalization **in solution**

Pickering emulsions strategy

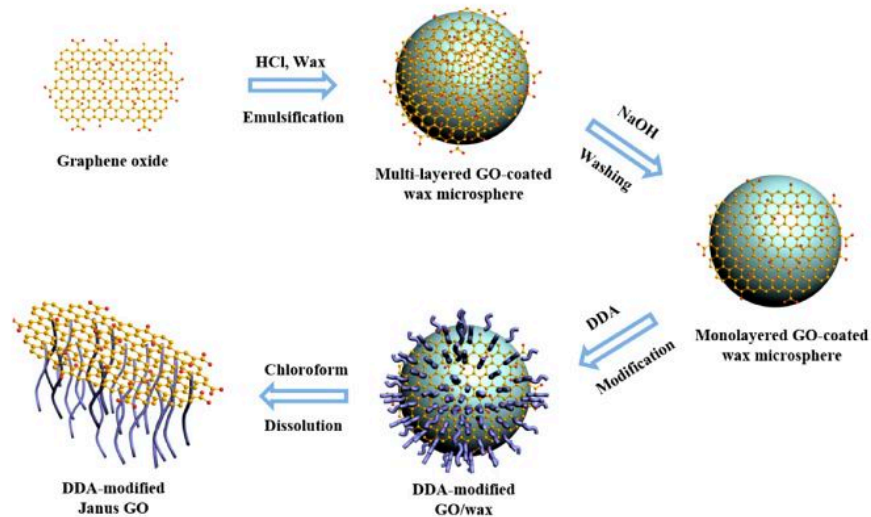


Wax-in-water emulsion stabilized by GO

Wu, H. et al. *Carbon*, **2015**, 93, 473

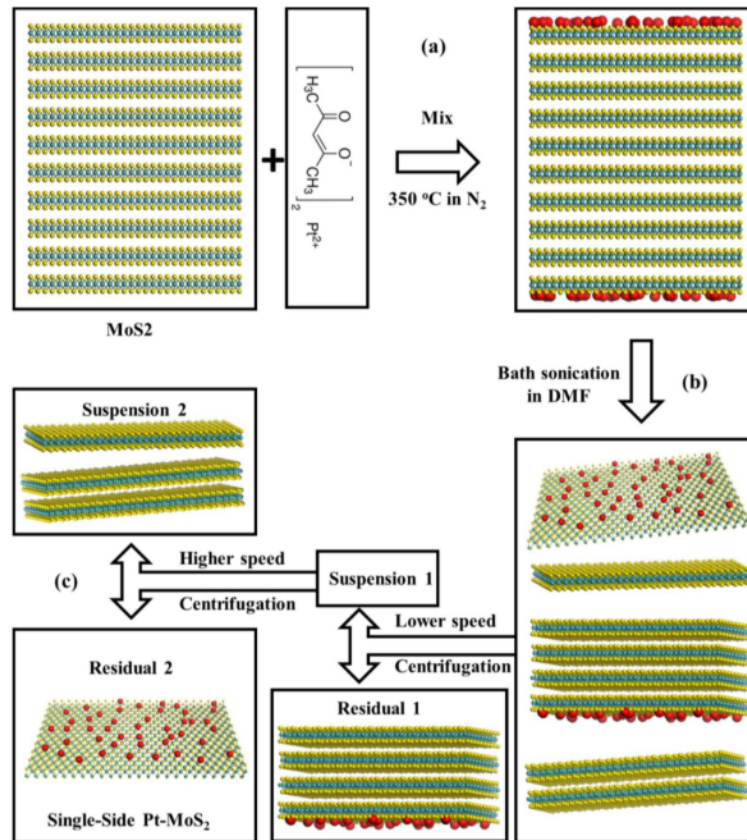
Asymmetric functionalization **in solution**

Pickering emulsions strategy



Wax-in-water emulsion stabilized by GO

Asymmetric functionalization in solution

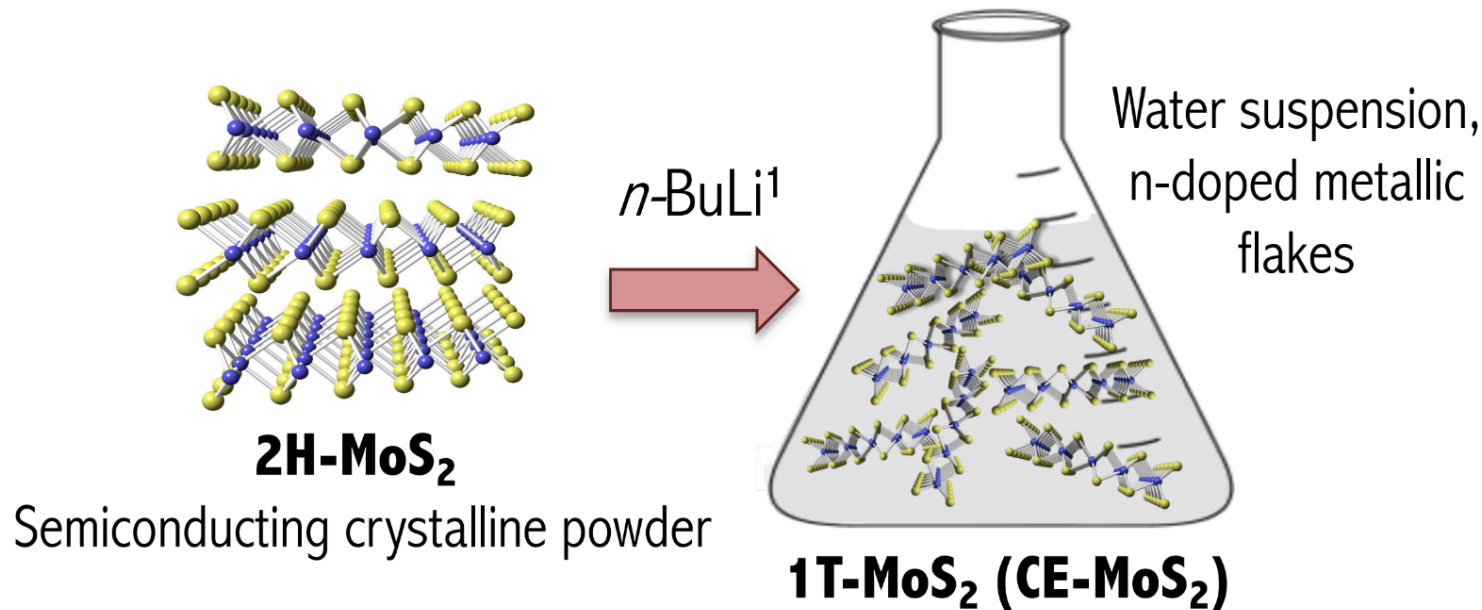


What about 2D materials?



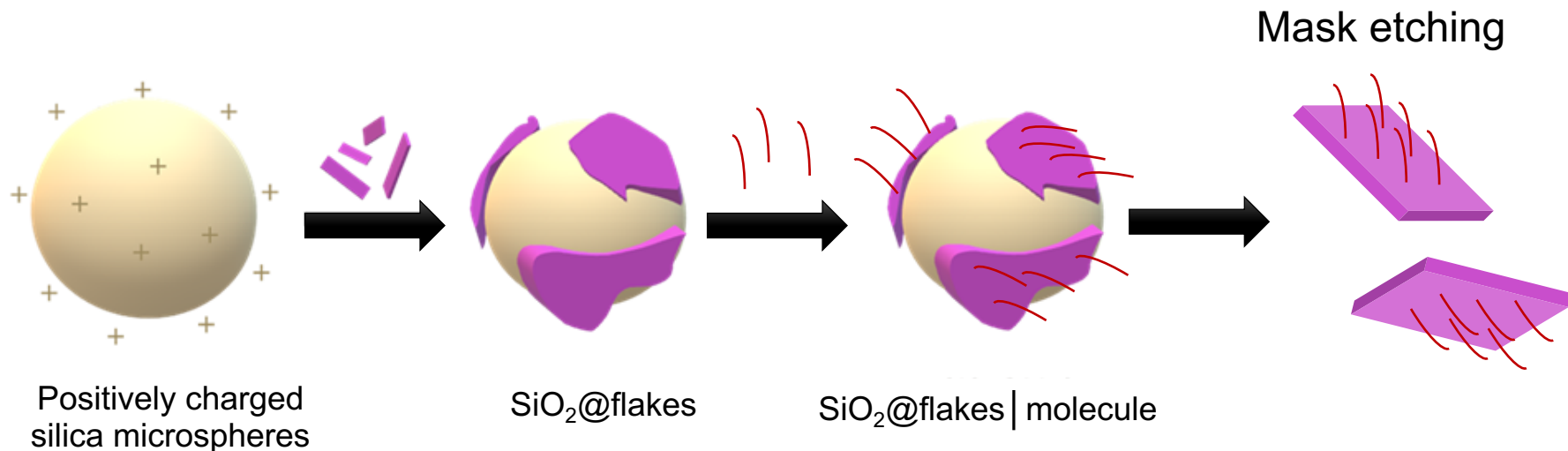
**Dr. Natalia
Vassilyeva**

OUR TARGET



Chemically exfoliated MoS₂

Our Strategy for JANUS 2D MoS₂

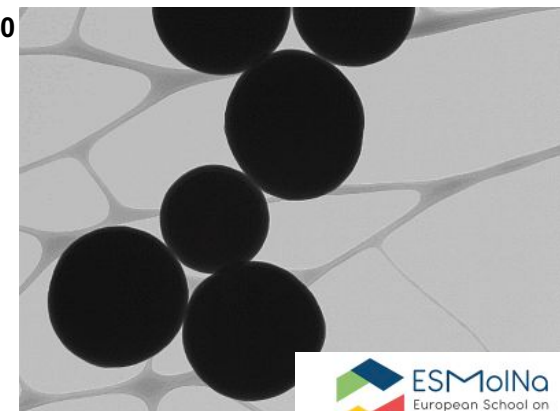
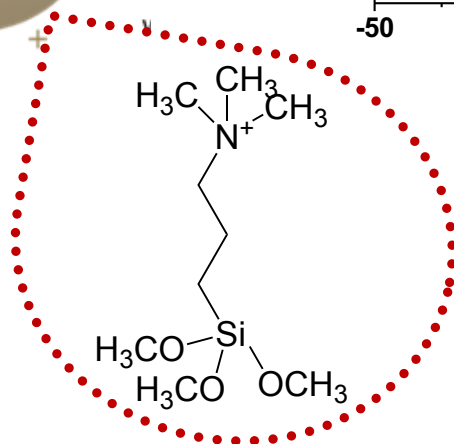
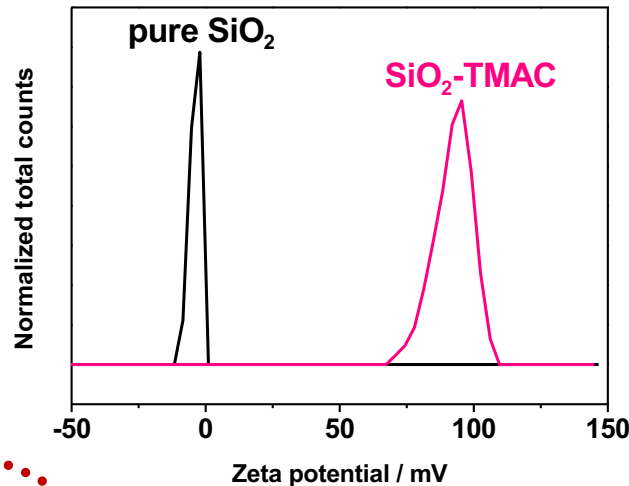
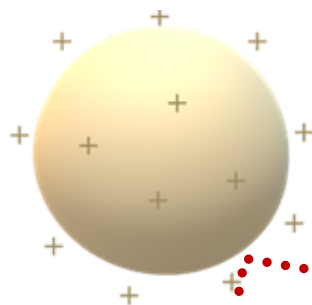


A solution approach

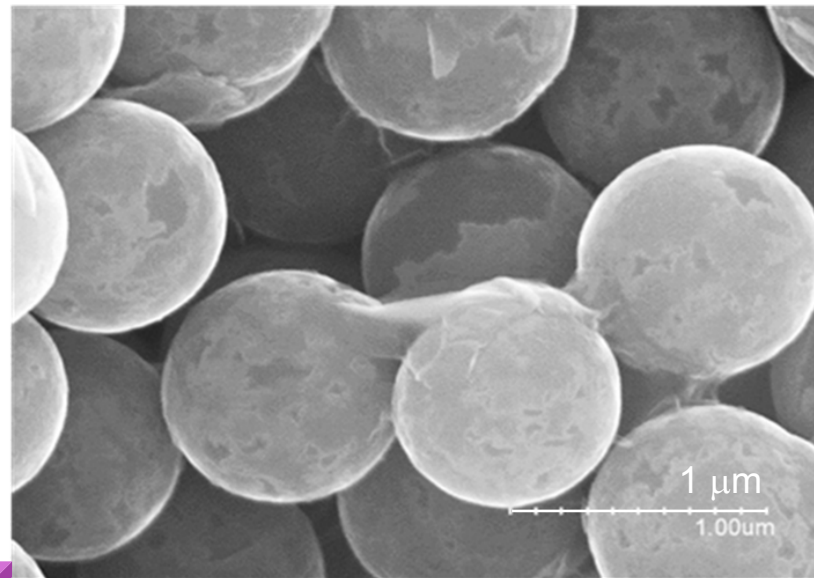
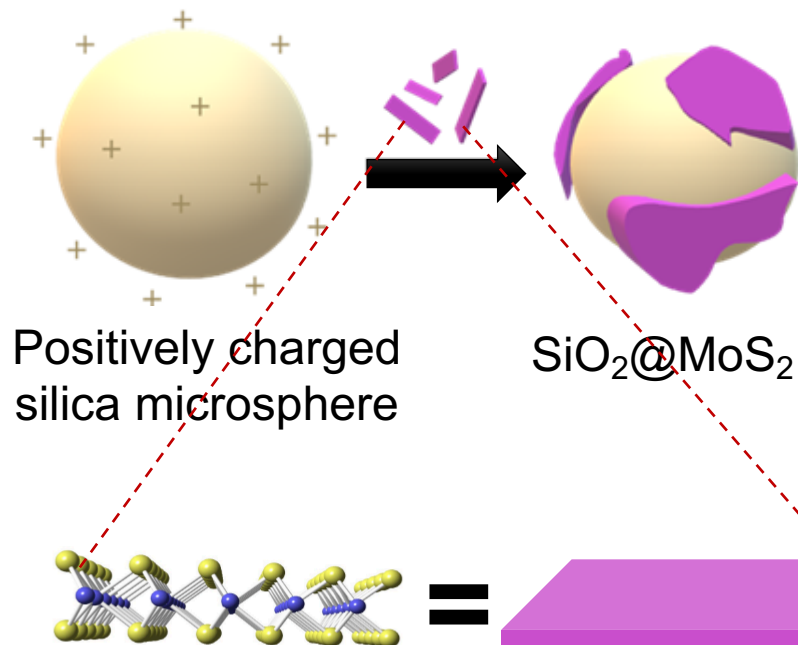
Our Strategy for JANUS 2D MoS₂

Our mask

Positively charged
silica microsphere

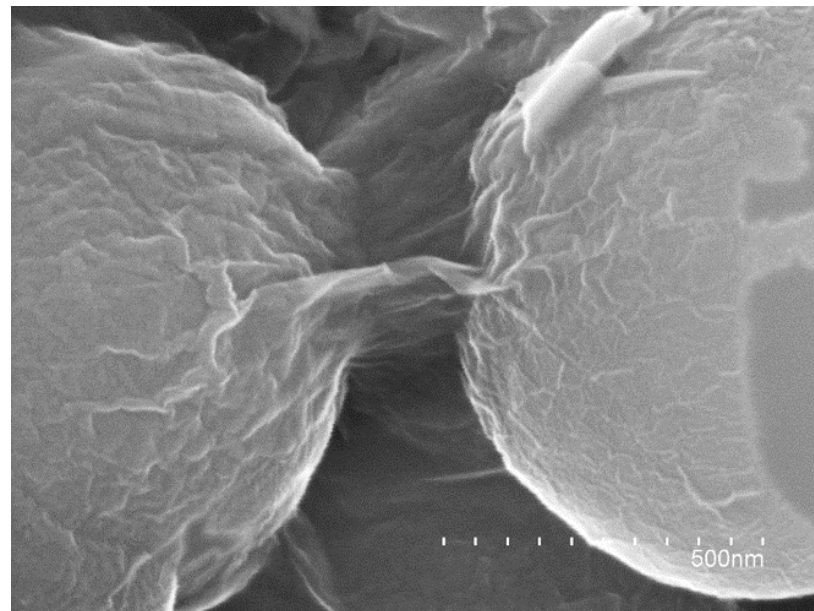
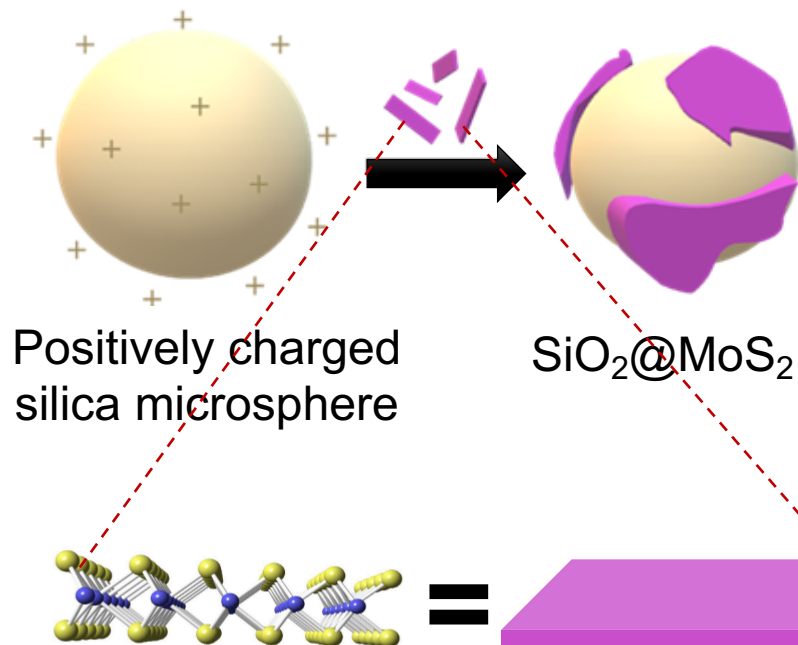


Our Strategy for JANUS 2D MoS₂



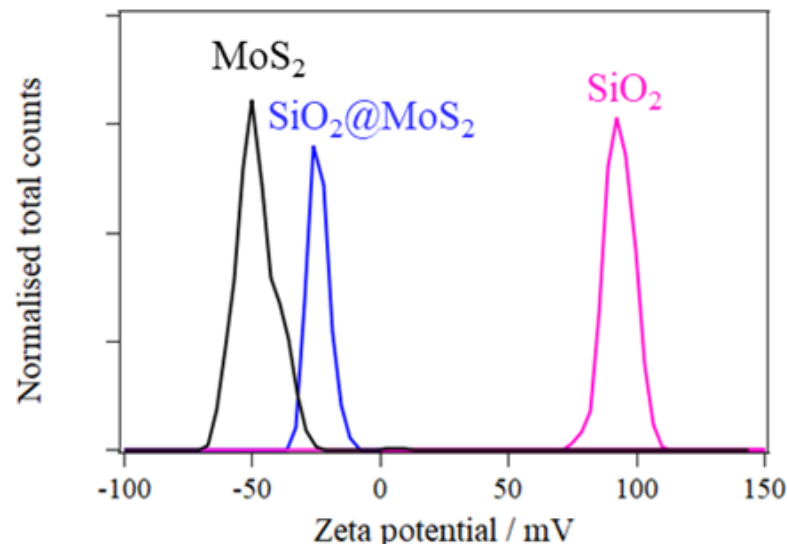
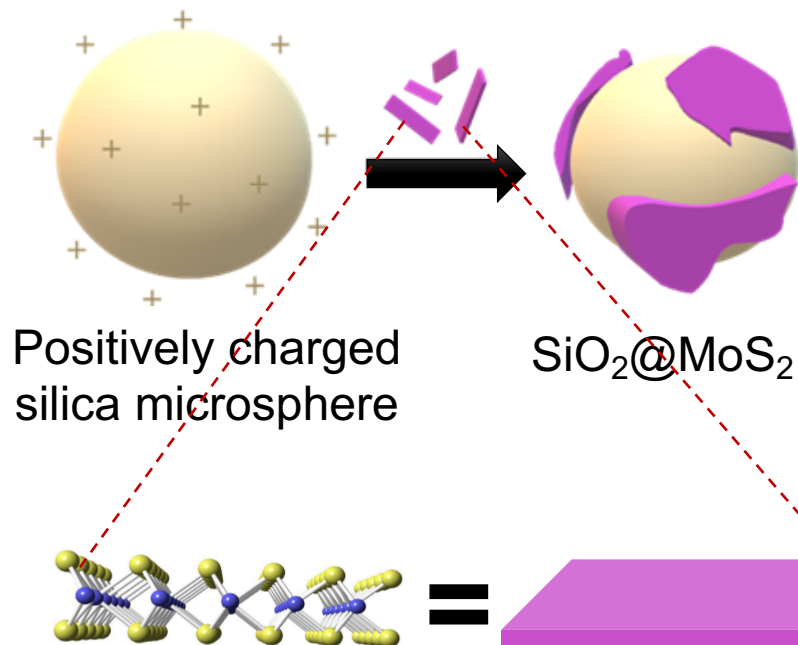
Wrapping silica spheres with MoS₂ layers

Our Strategy for JANUS 2D MoS₂



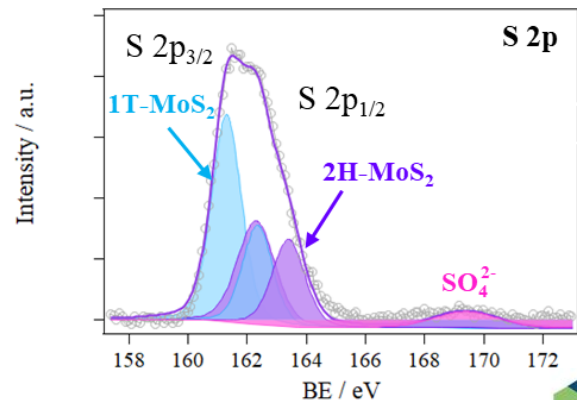
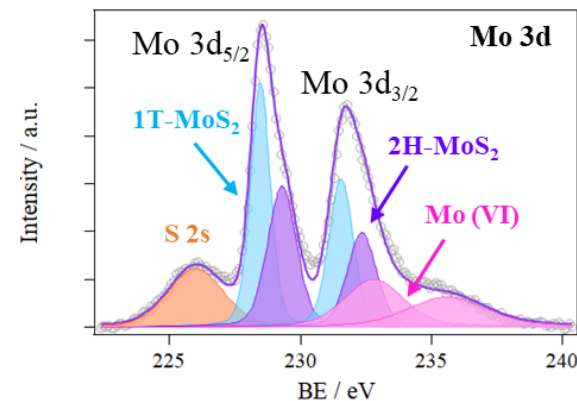
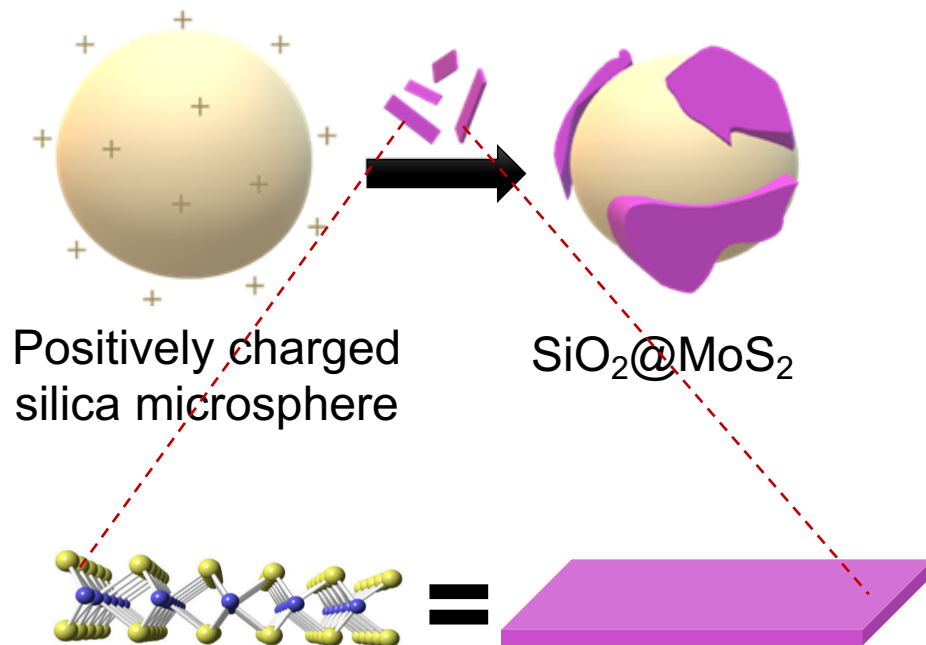
Wrapping silica spheres with MoS₂ layers

Our Strategy for JANUS 2D MoS₂

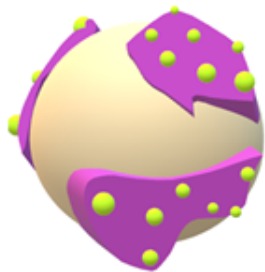
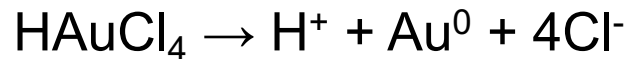


Wrapping silica spheres with MoS₂ layers

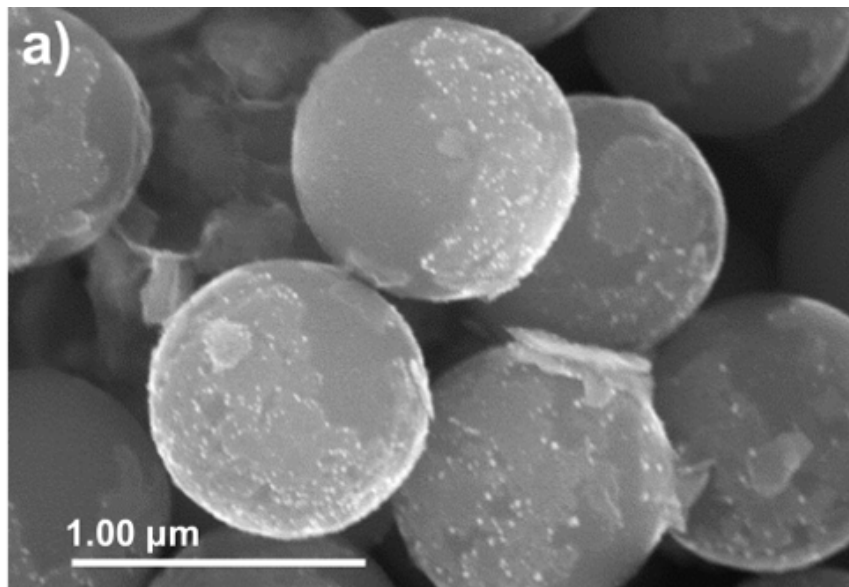
Our Strategy for JANUS 2D MoS₂



Our Strategy for JANUS 2D MoS₂

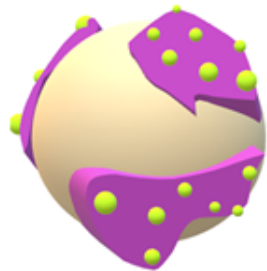


SiO₂@MoS₂|Au

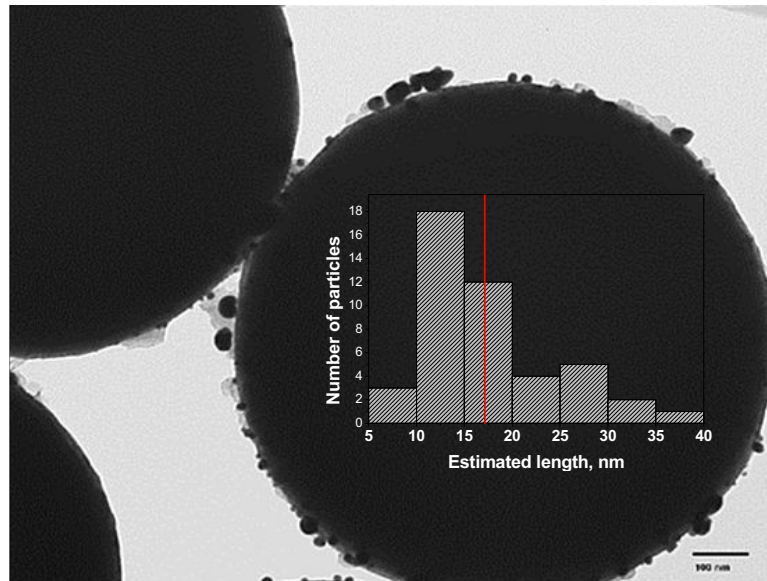
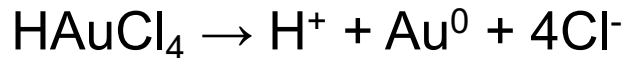


Growing Au NPs on MoS₂ layers

Our Strategy for JANUS 2D MoS₂



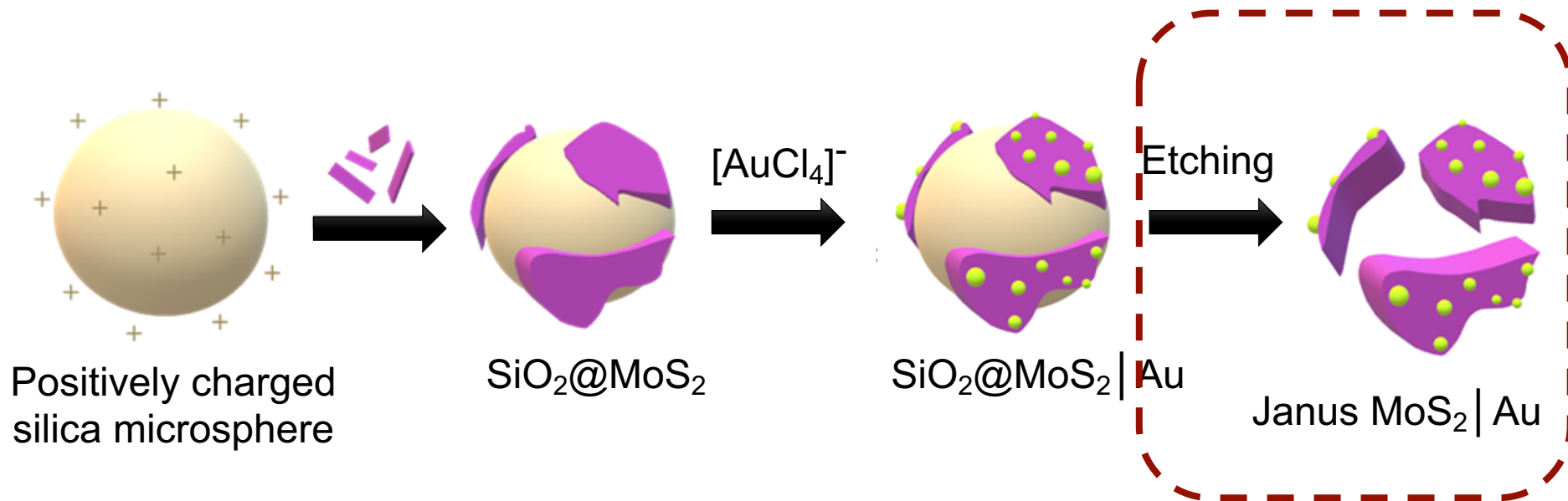
SiO₂@MoS₂ | Au



Average diameter = 17 nm

Growing Au NPs on MoS₂ layers

Our Strategy for JANUS 2D MoS₂



Flakes release

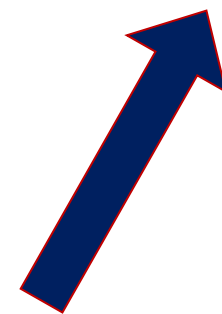
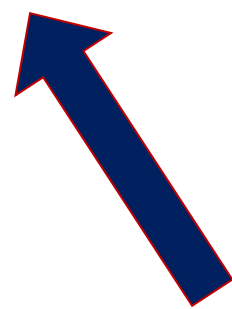
Our Strategy for JANUS 2D MoS₂

Basic media

Acid media

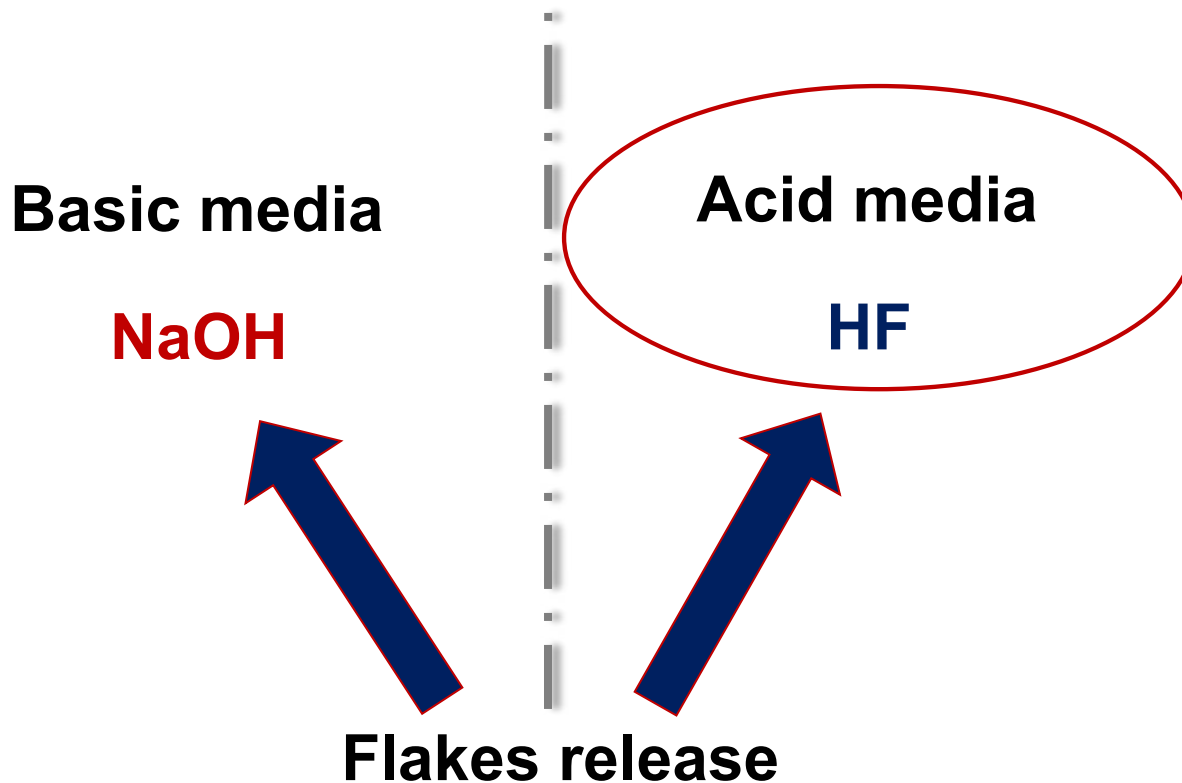
NaOH

HF

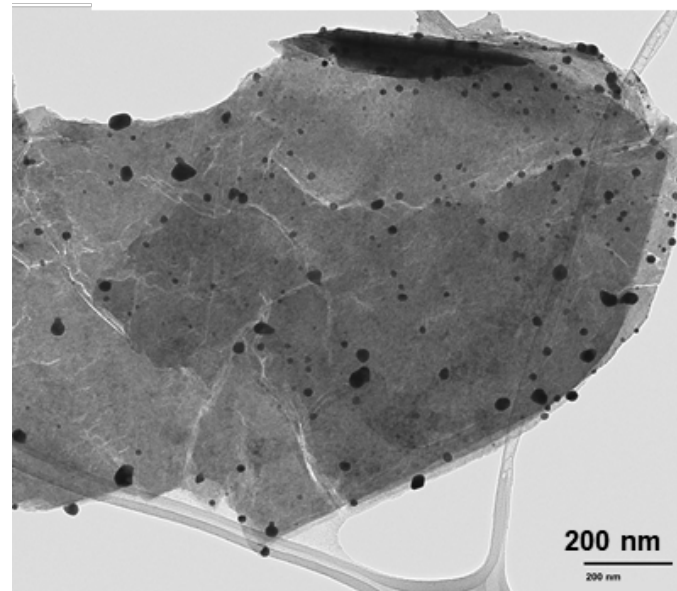
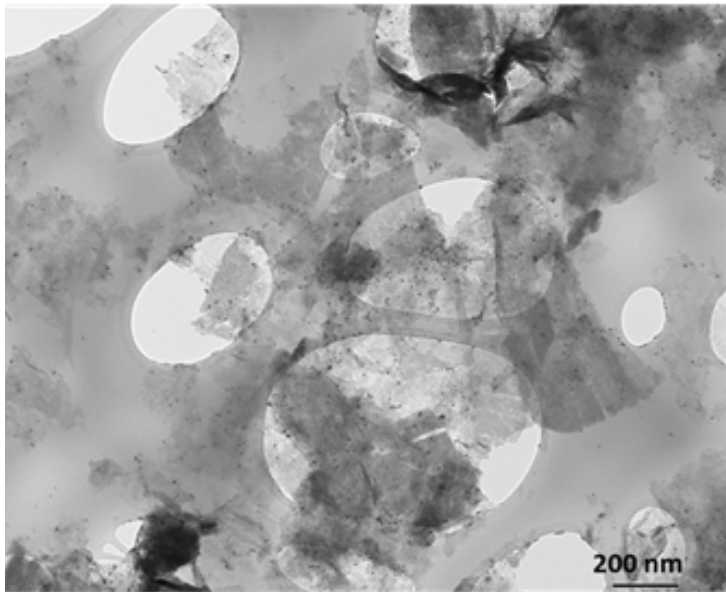


Flakes release

Our Strategy for JANUS 2D MoS₂

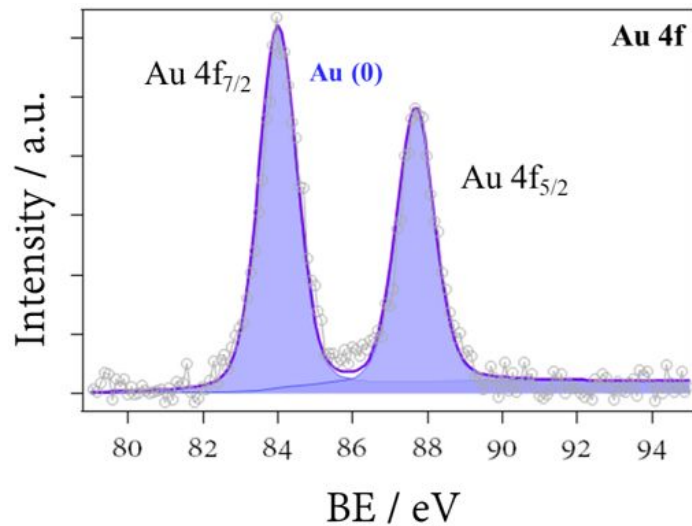
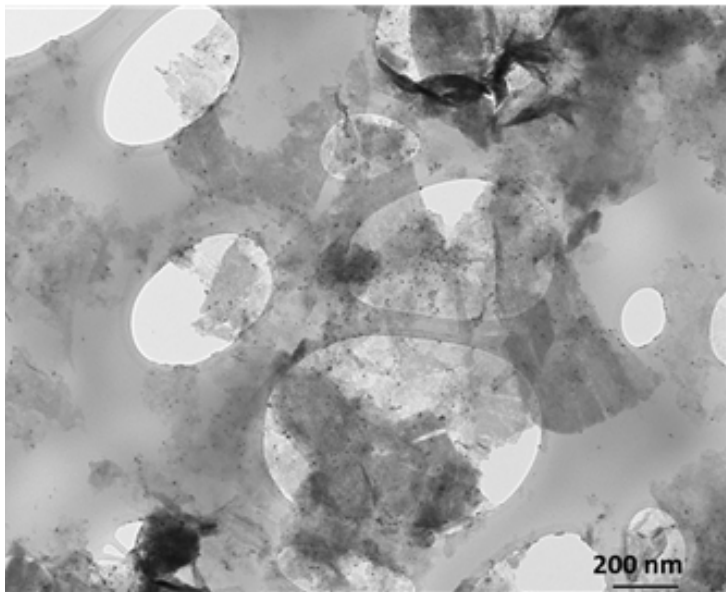


Our Strategy for JANUS 2D MoS₂



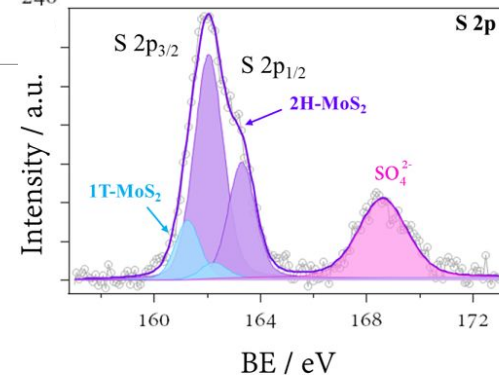
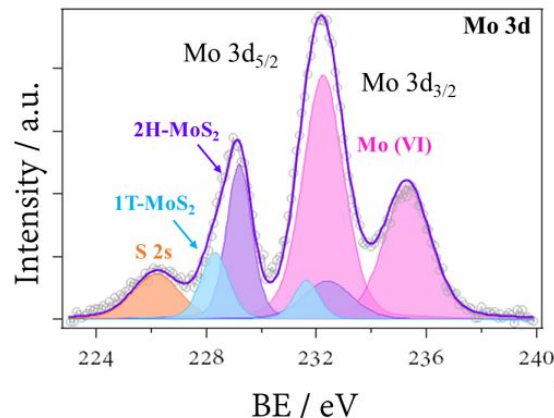
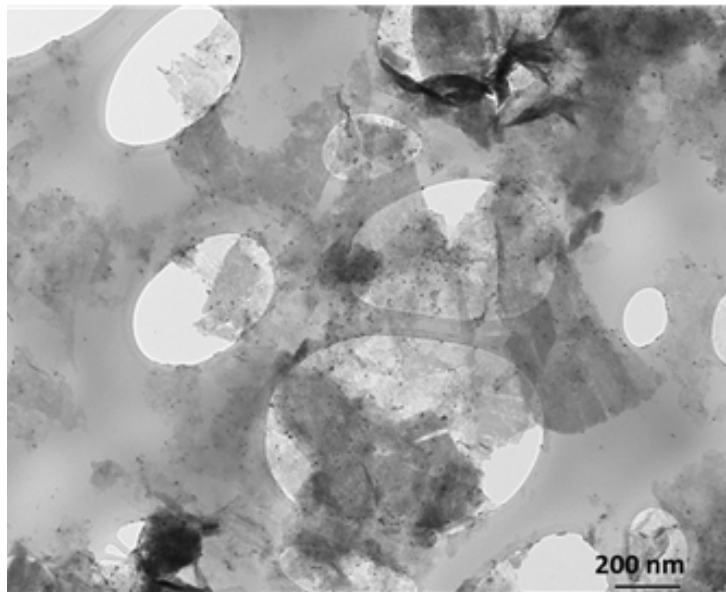
Flakes release

Our Strategy for JANUS 2D MoS₂



Flakes release

Our Strategy for JANUS 2D MoS₂



Flakes release

Our Strategy for JANUS 2D MoS₂

**How can we check the
asymmetric
functionalization?**



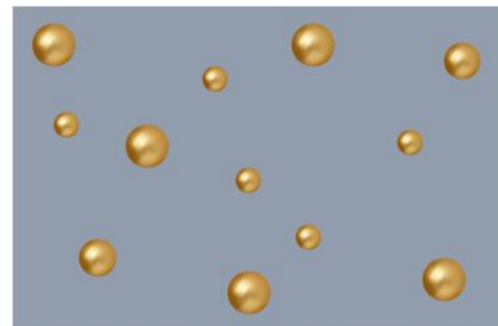
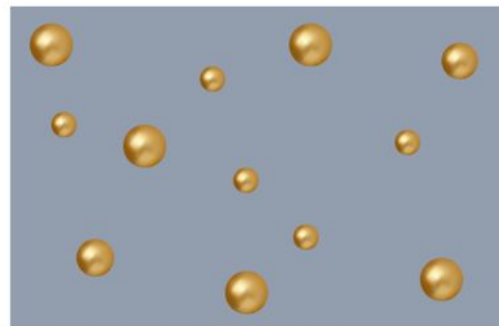
Our Strategy for JANUS 2D MoS₂

TEM

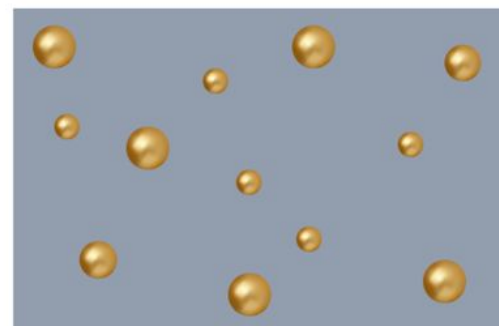
SEM



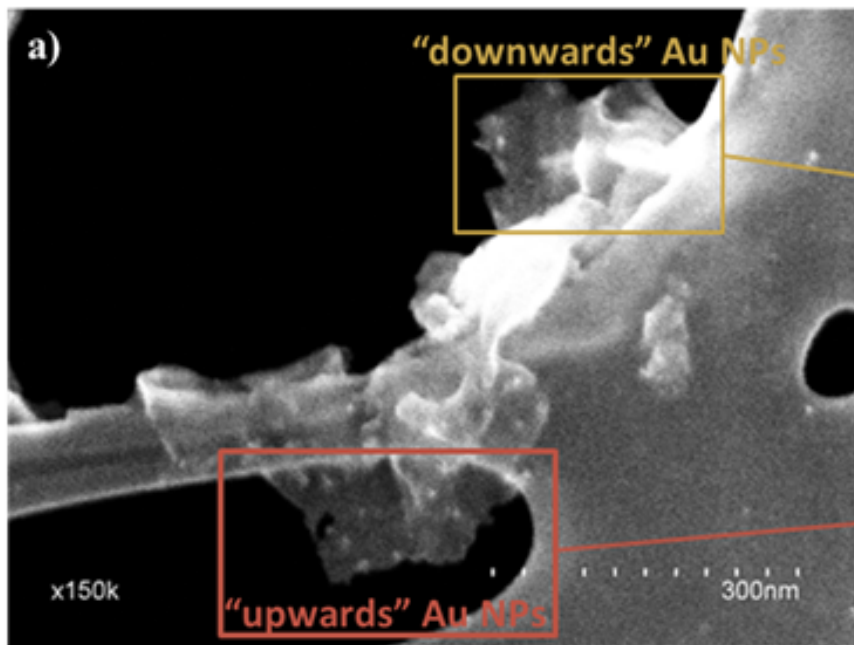
Top-oriented Au NPs



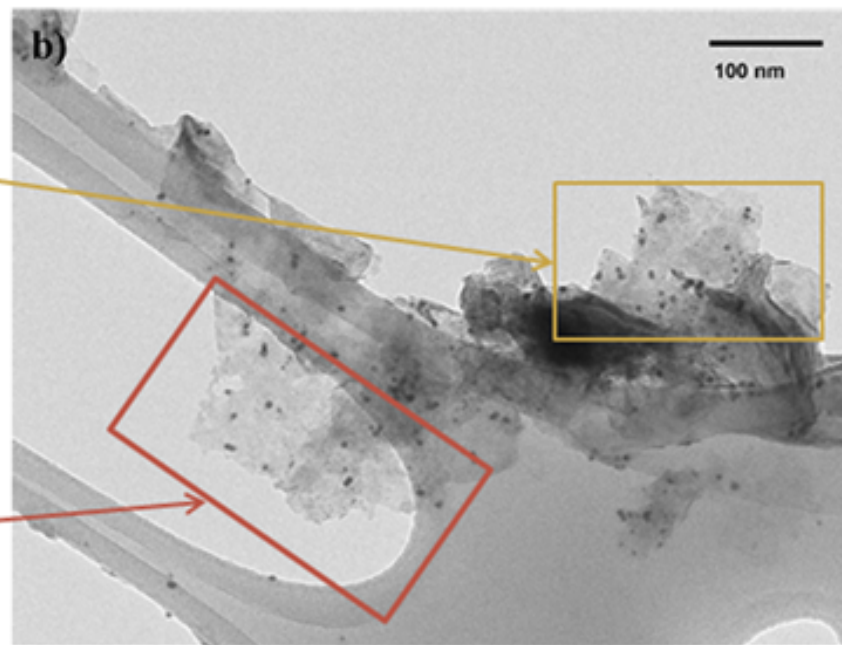
Bottom-oriented Au NPs



Our Strategy for JANUS 2D MoS₂

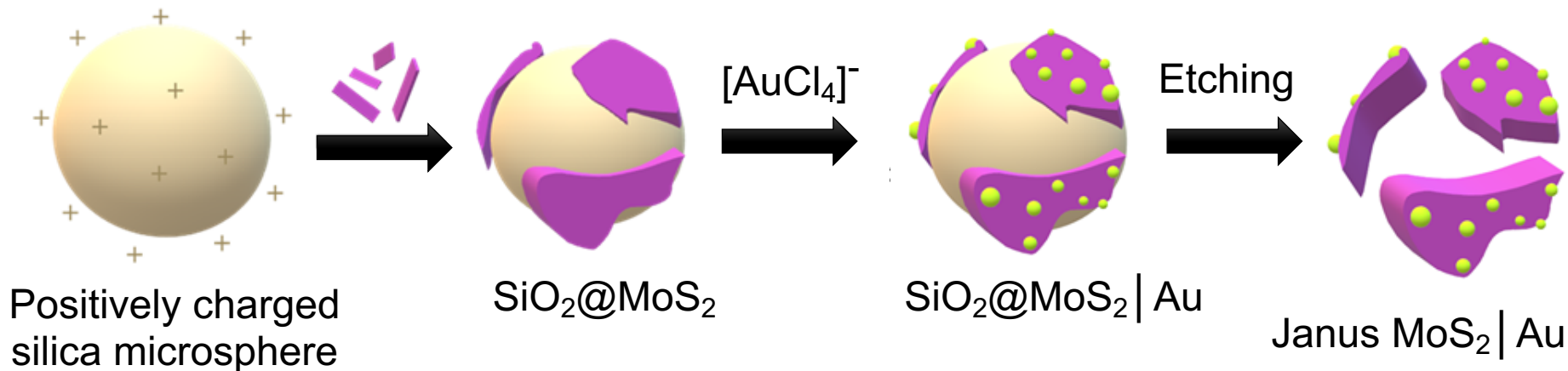


SEM



TEM

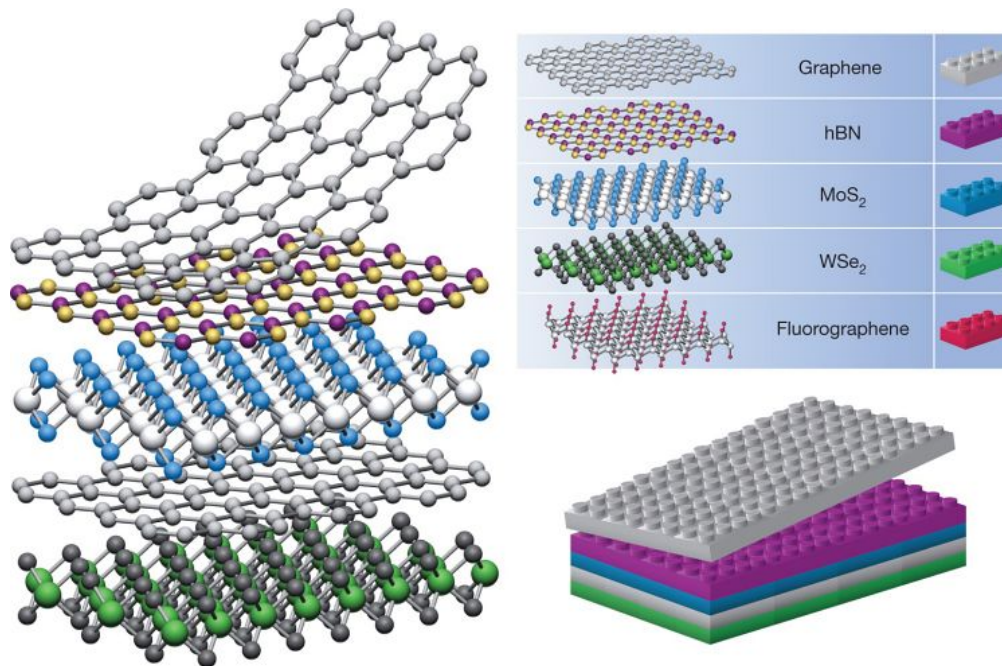
Summary



A facile and versatile strategy to asymmetrically decorate flakes in solution

Practical case

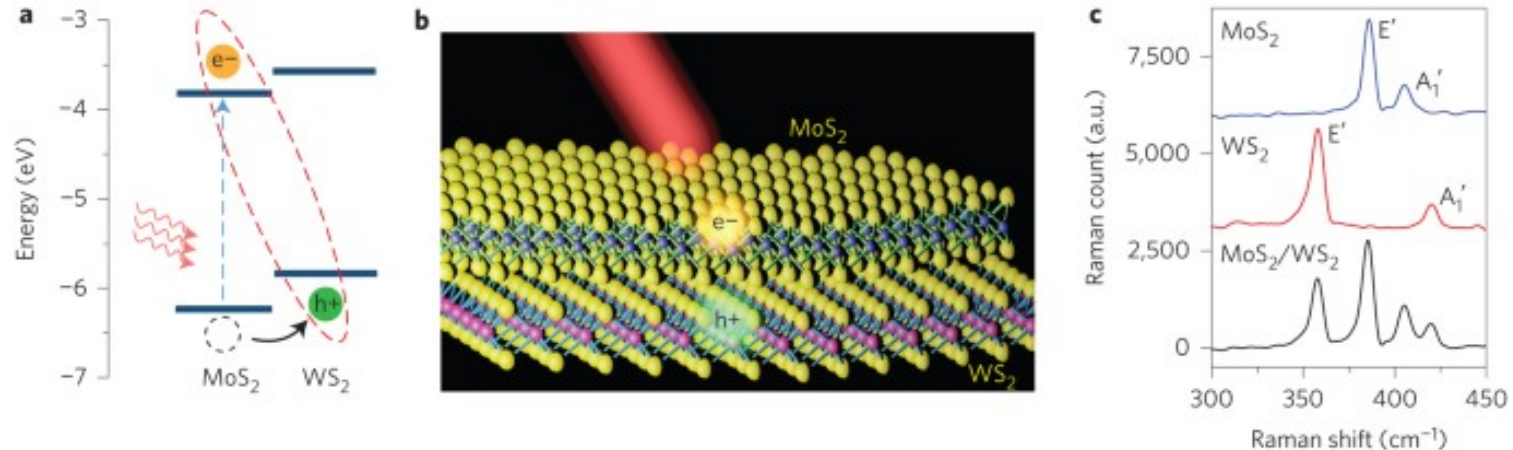
Van der Waals heterostructures



From Nature **499**, 419–425 (2013).

Van der Waals heterostructures

MoS₂/WS₂



Ultrafast charge transfer → two-dimensional devices for optoelectronics and light harvesting

Van der Waals heterostructures



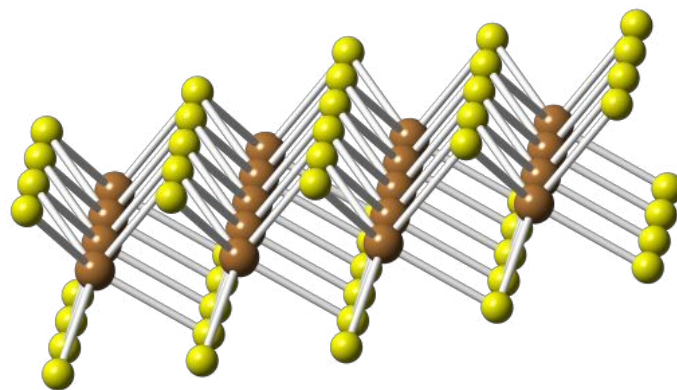
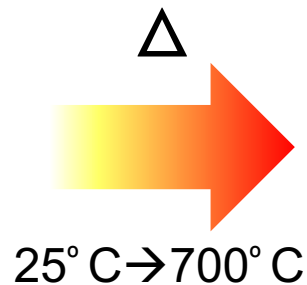
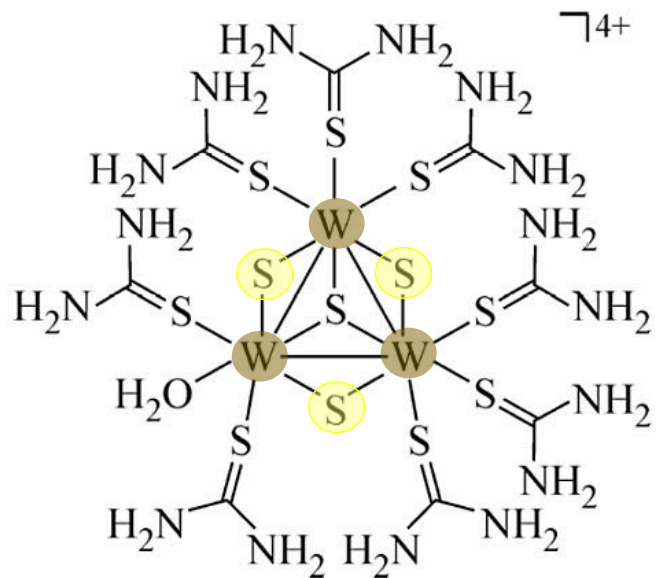
Can we do it in solution?

Ultrafast charge transfer → novel two-dimensional devices for optoelectronics and light harvesting

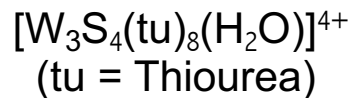
Nikita Y. Shmelev and Artem L. Gushchin
Nikolaev Institute of Inorganic Chemistry
Siberian Branch of Russian Academy of Sciences

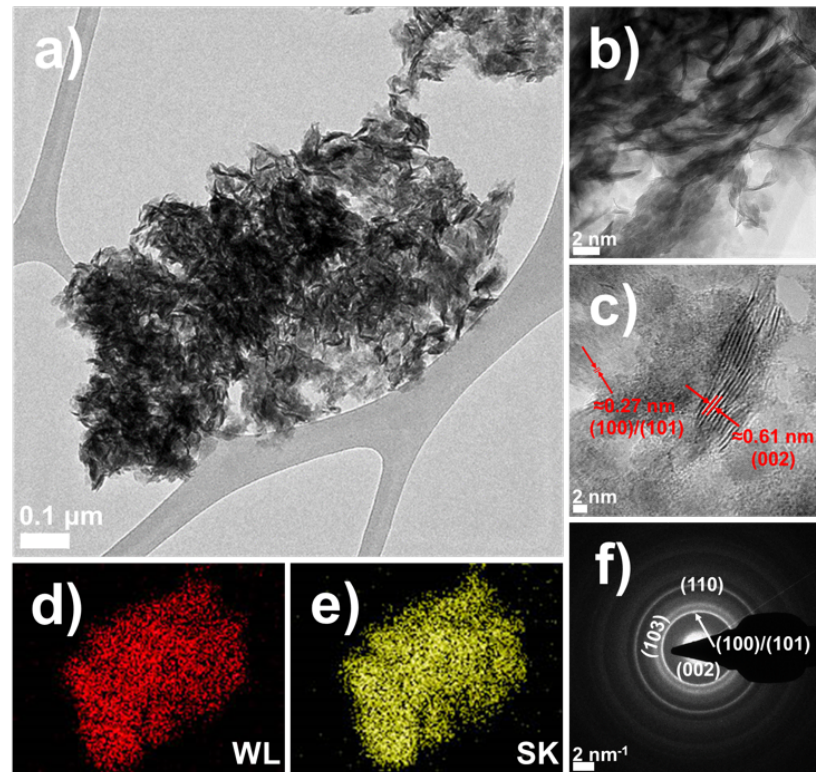
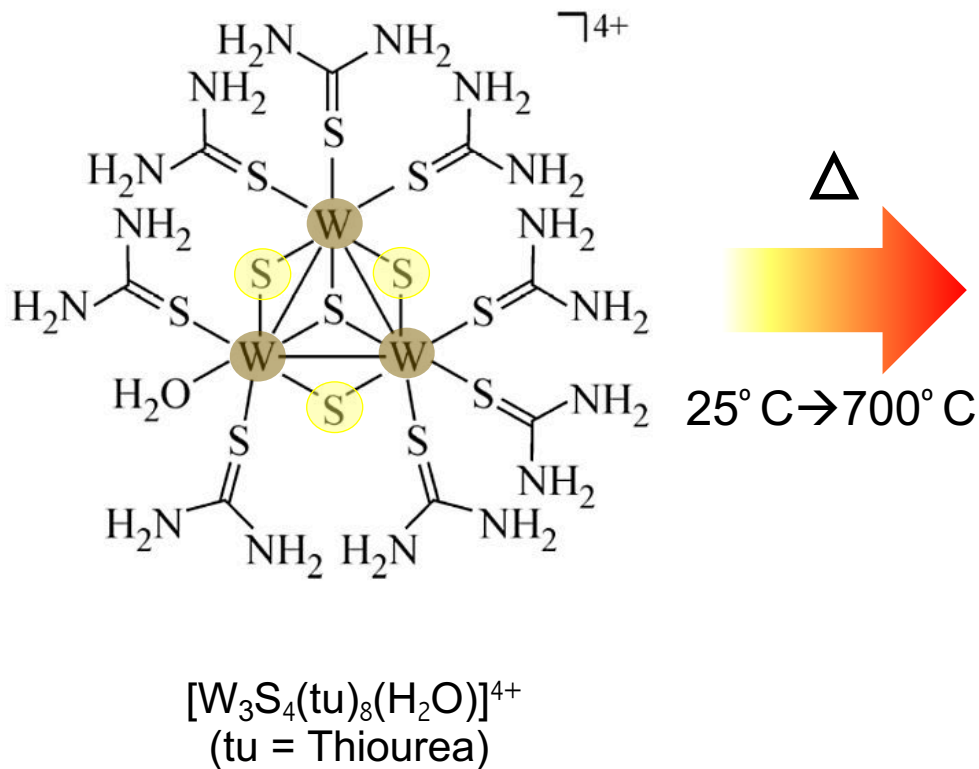


Dr. Marc
Morant-Gine

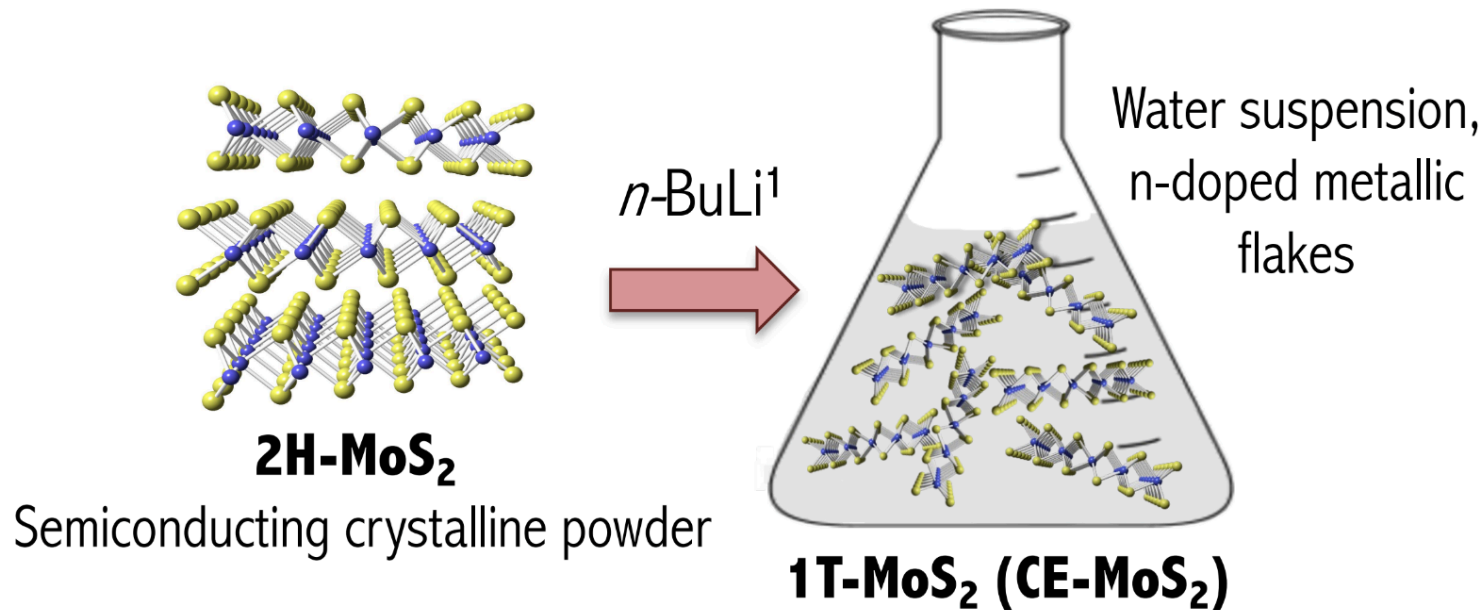


WS₂ flakes



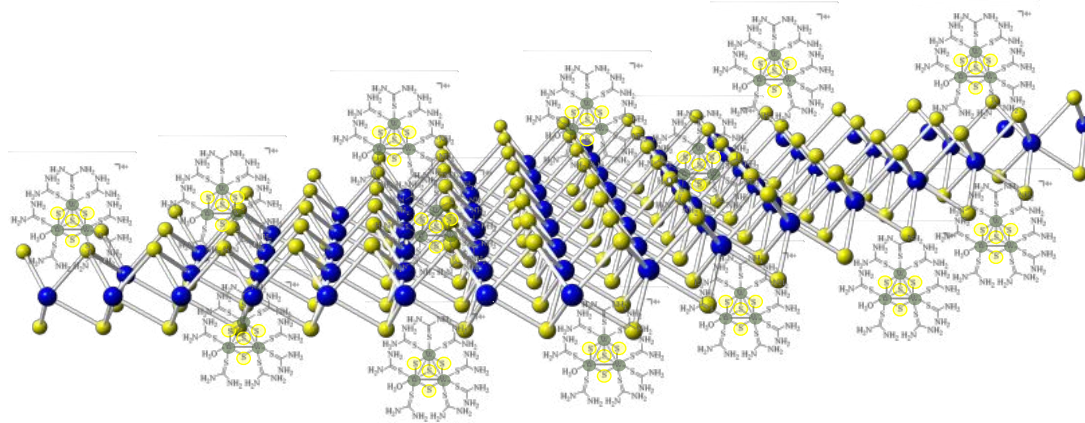


Looking for a driving force

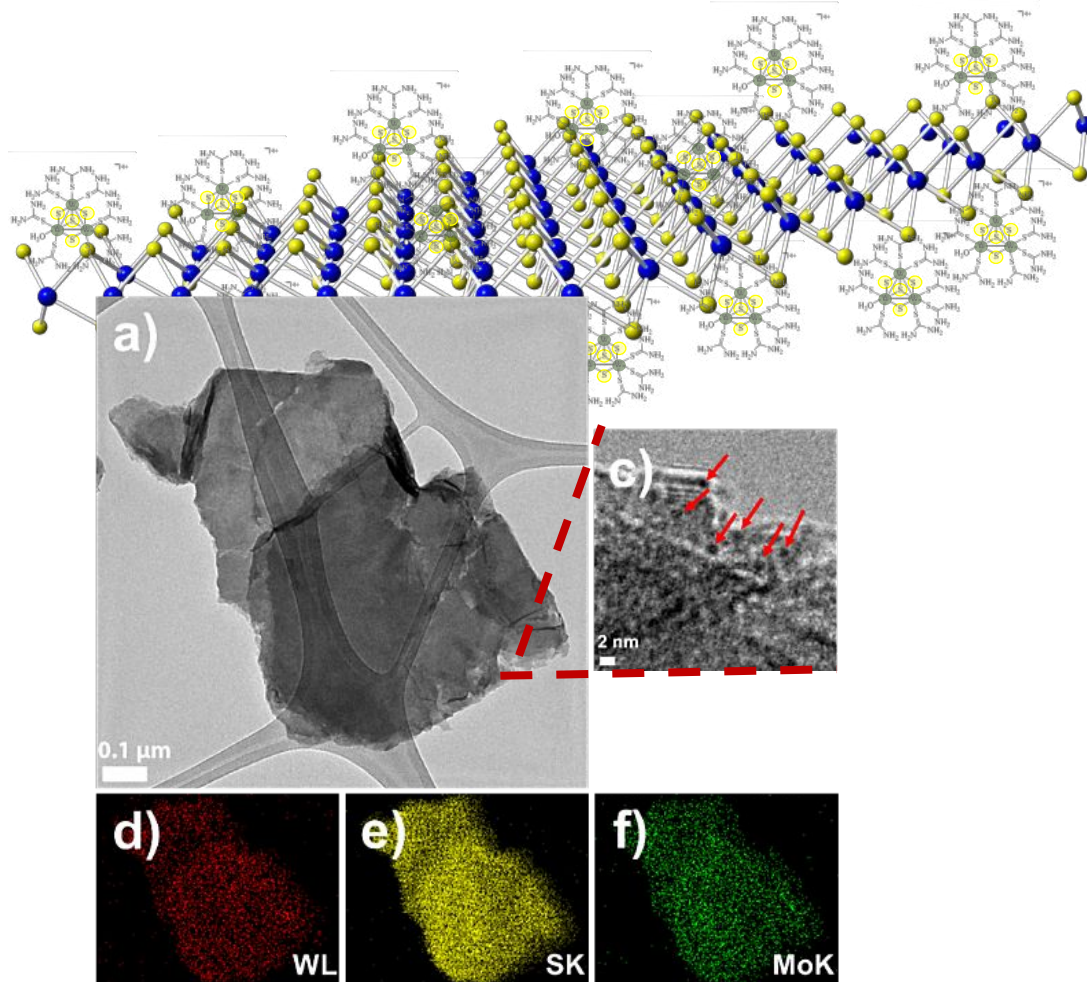


Chemically exfoliated MoS₂

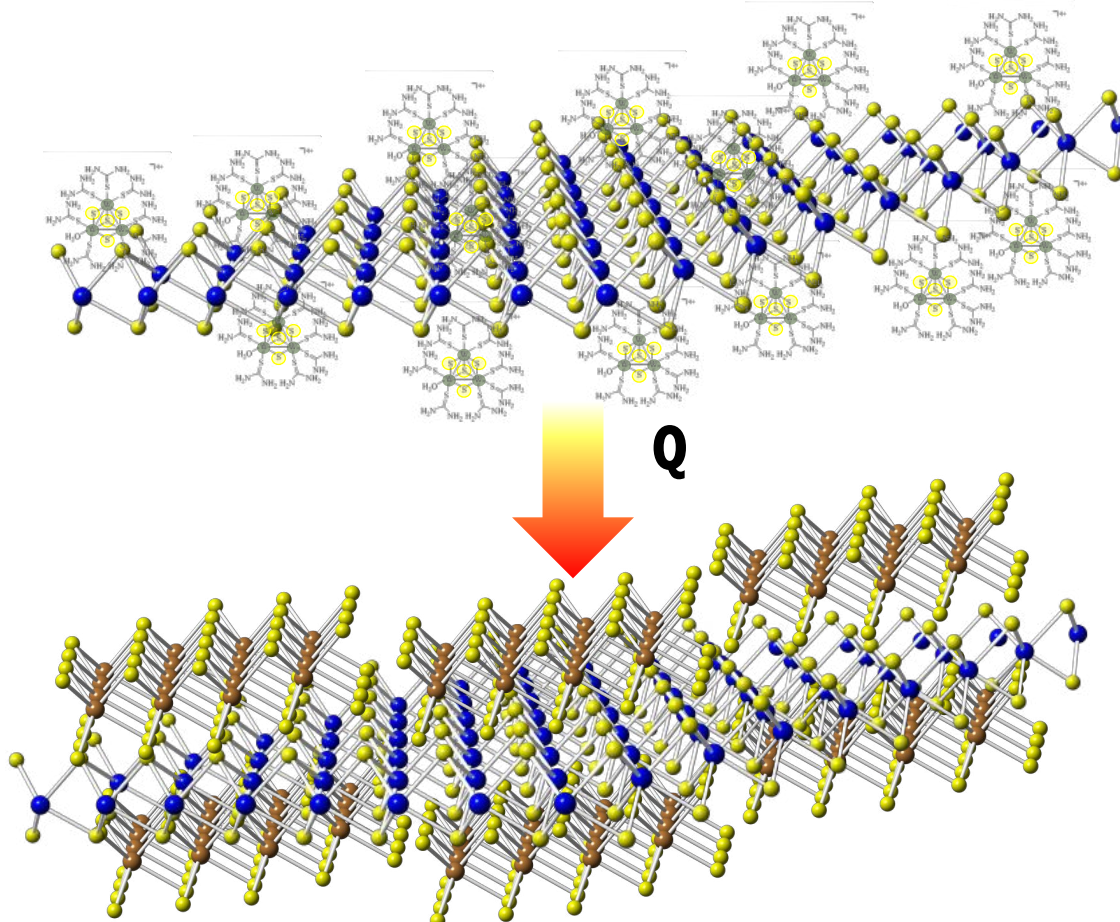
Driving force: Electrostatic Interactions



Driving force: Electrostatic Interactions

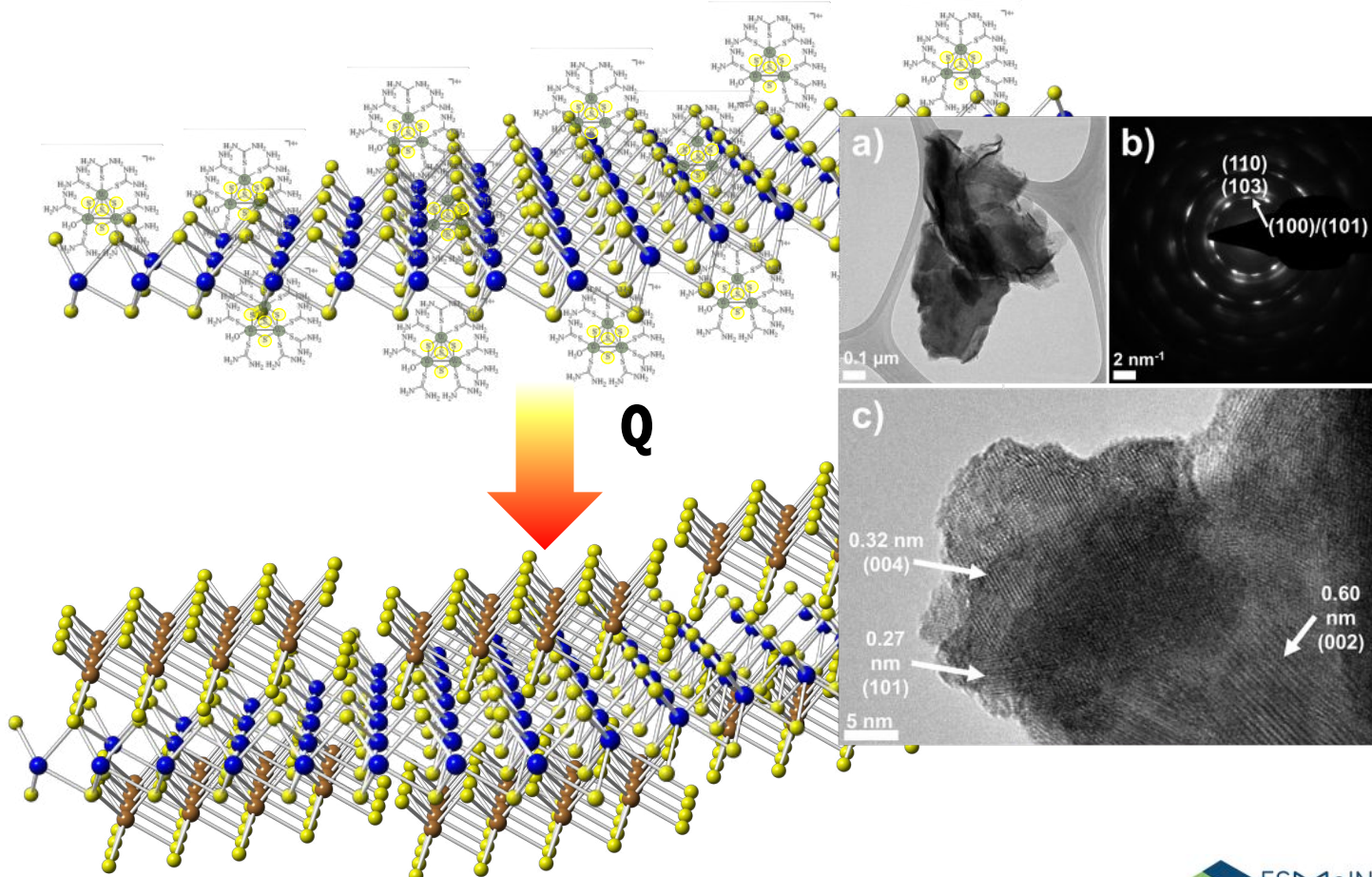


Driving force:
Electrostatic
Interactions

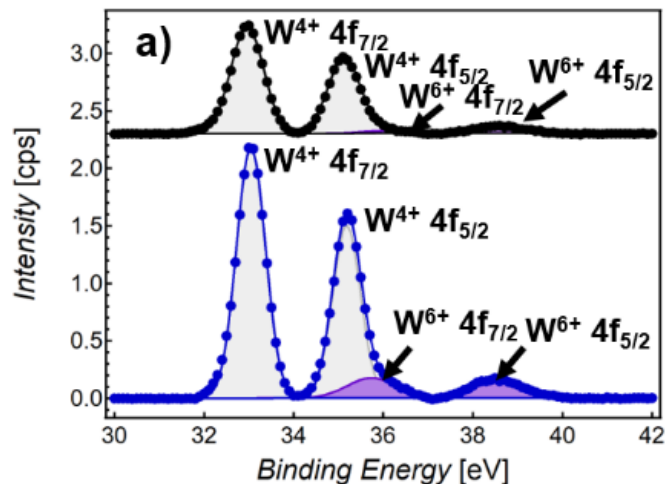
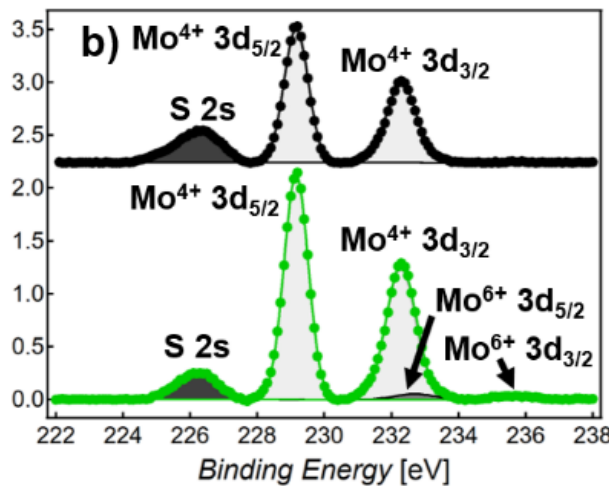
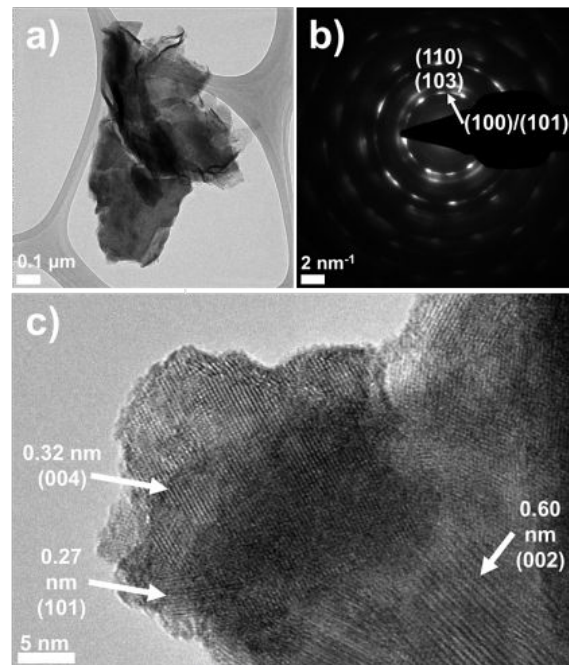


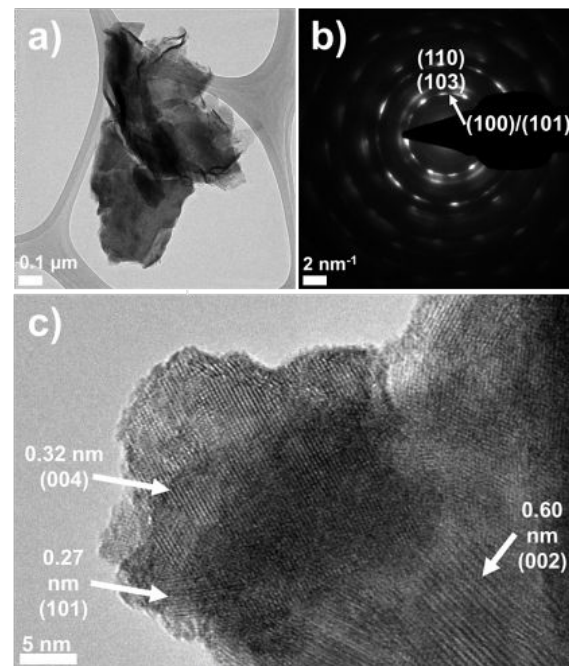
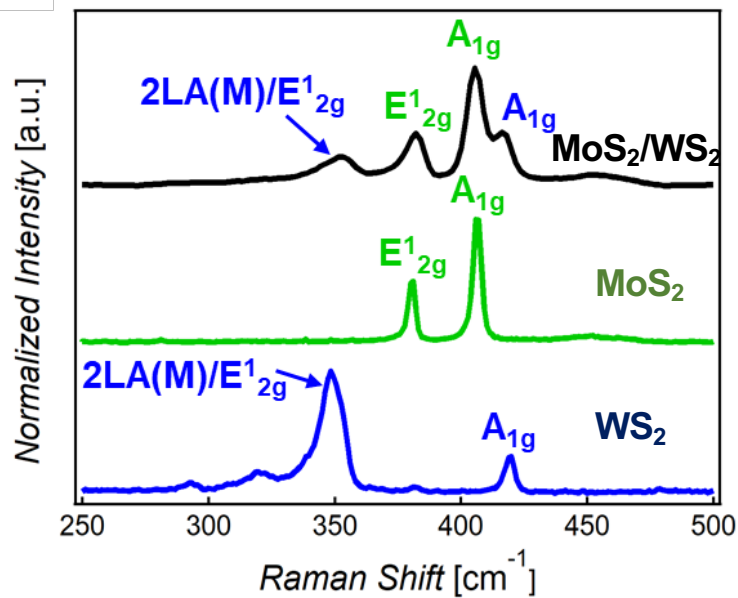
MoS₂/WS₂ stacked layers

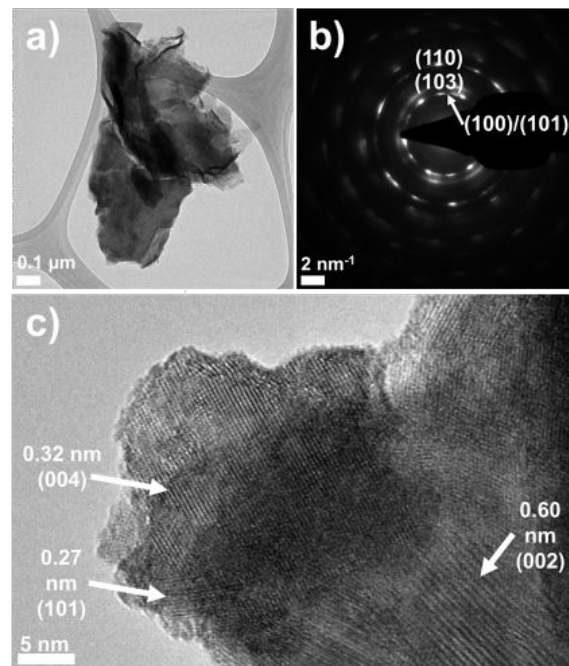
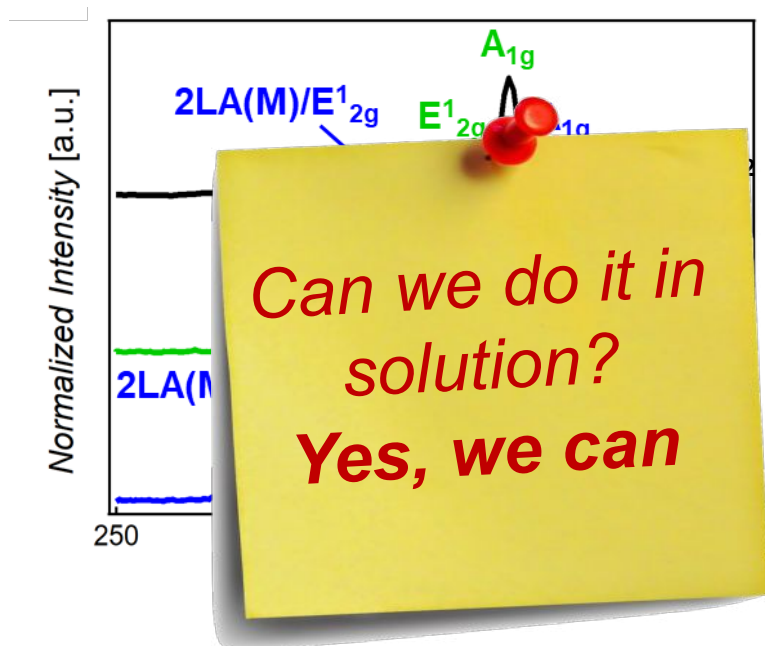
Driving force: Electrostatic Interactions

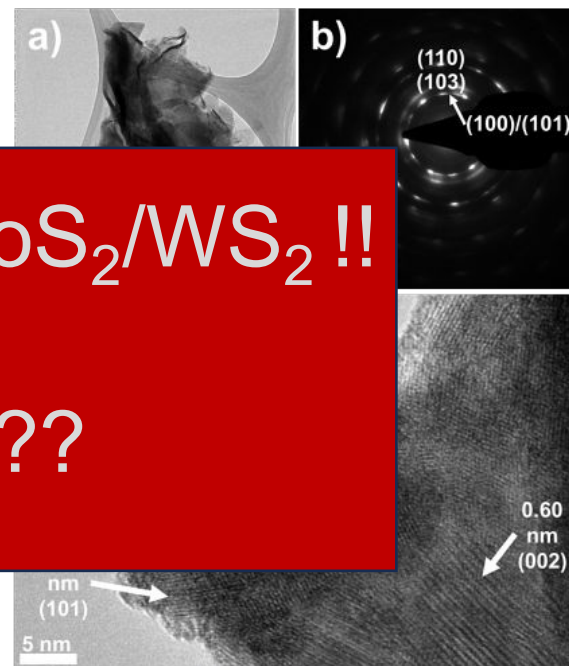
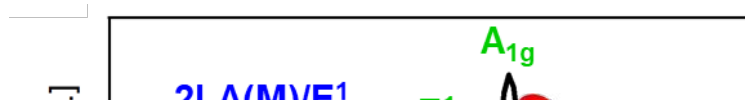


MoS₂/WS₂ stacked layers

MoS₂/WS₂WS₂MoS₂/WS₂MoS₂



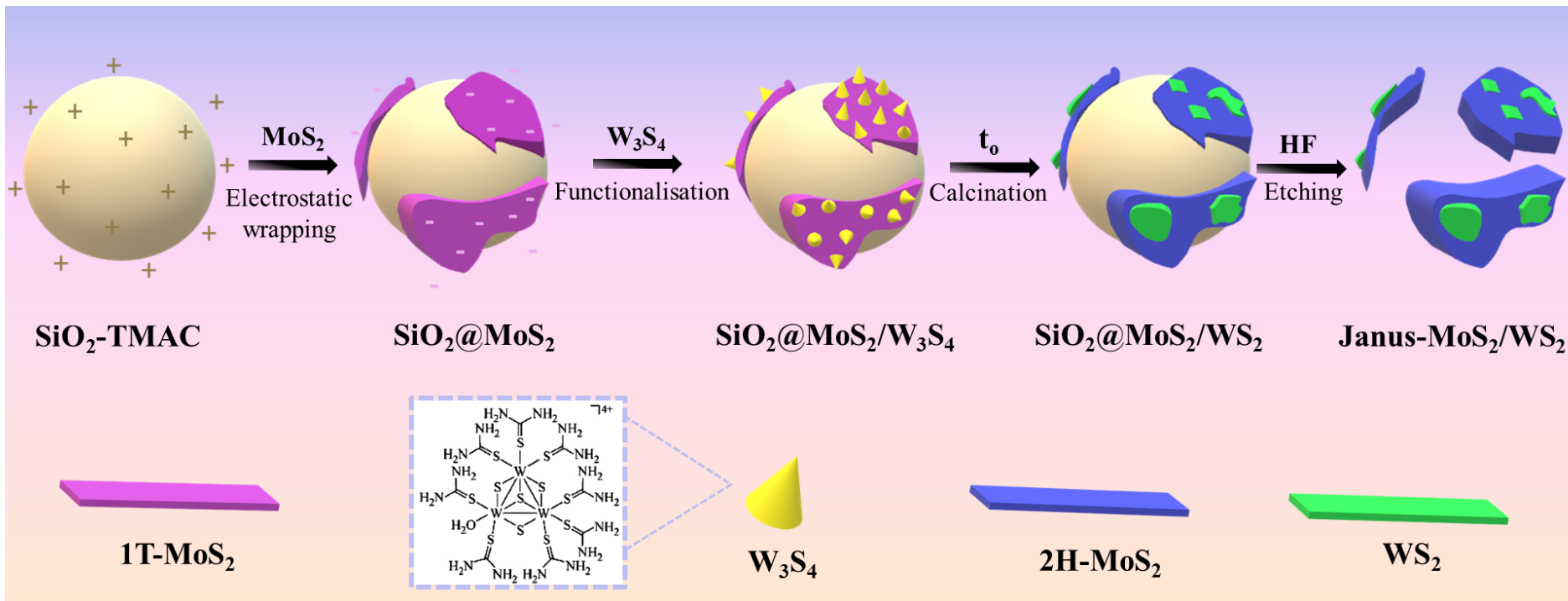


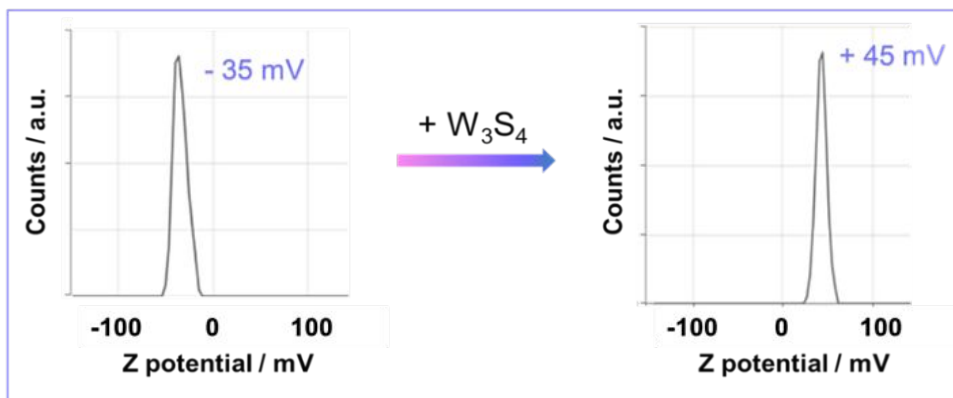


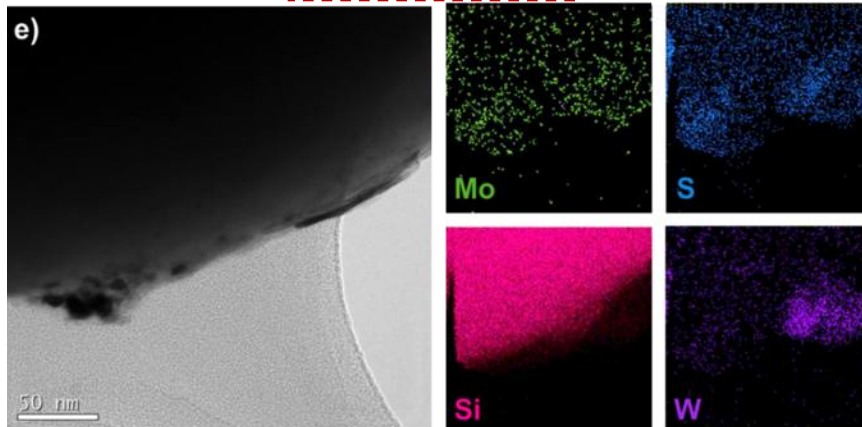
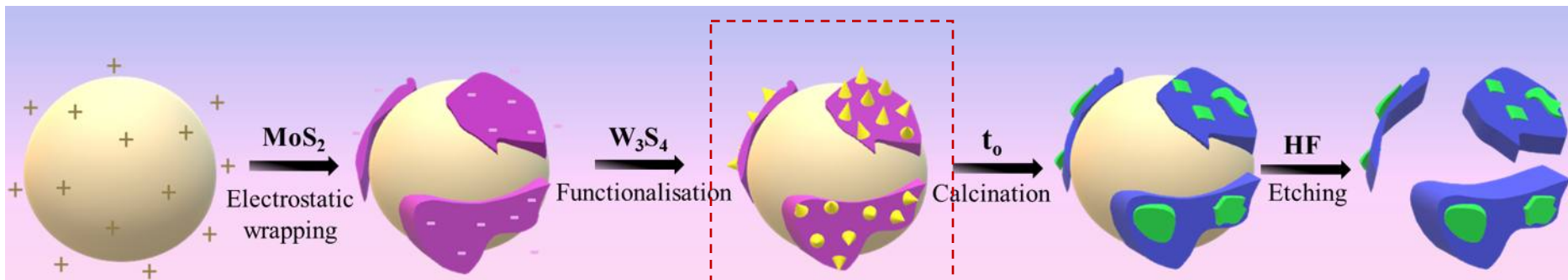
But this is actually $WS_2/MoS_2/WS_2$!!

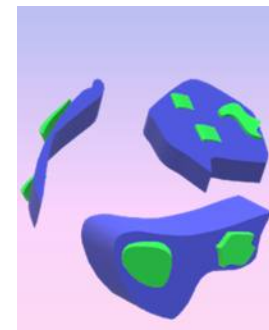
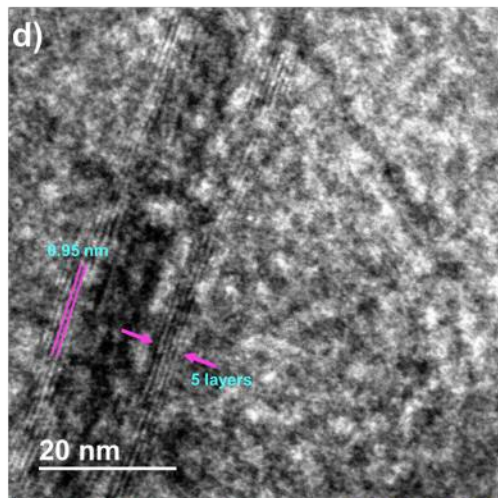
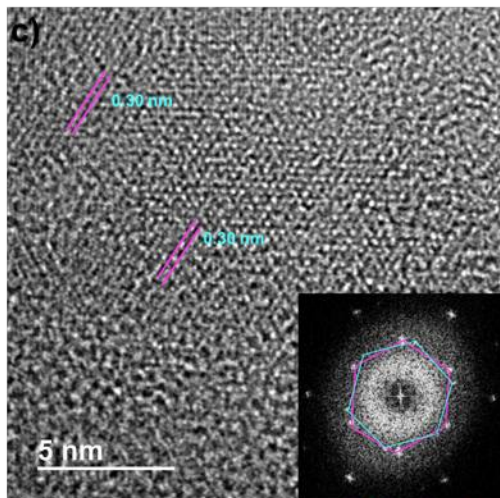
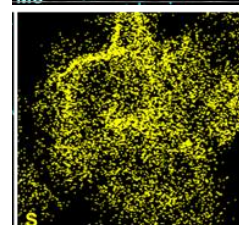
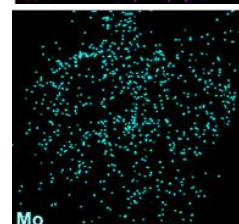
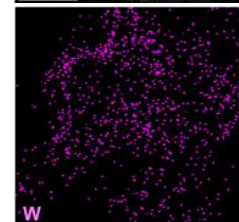
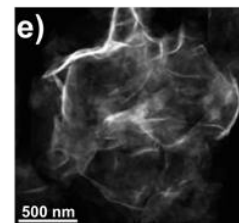
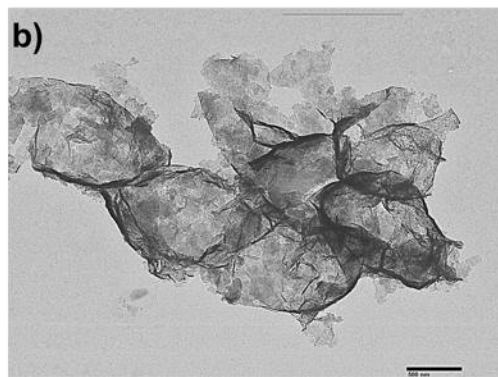
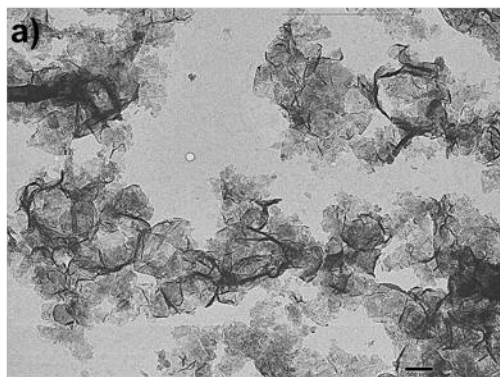
Can we solve this???

Plan

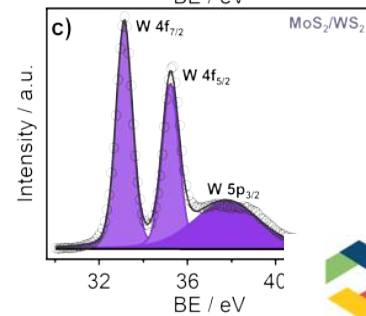
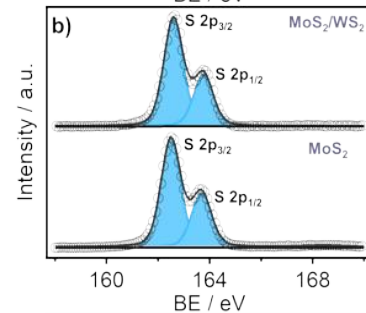
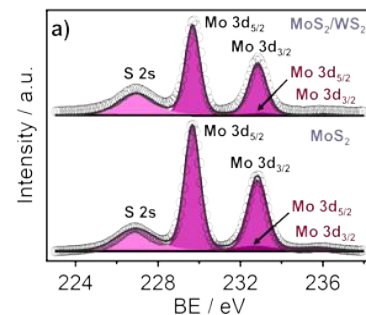
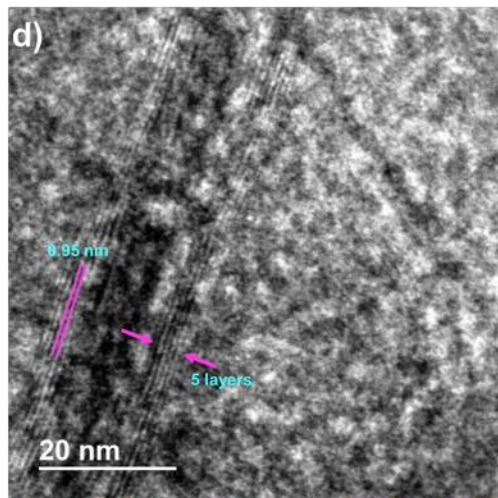
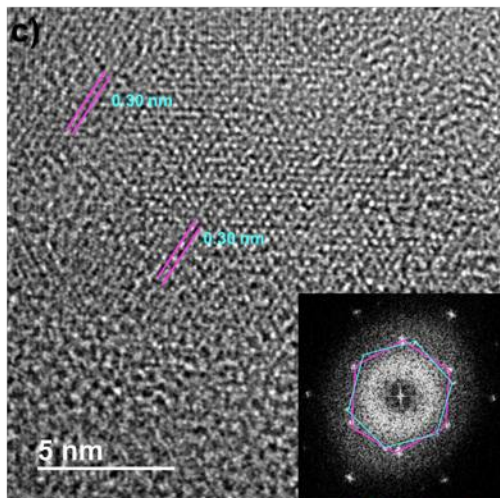
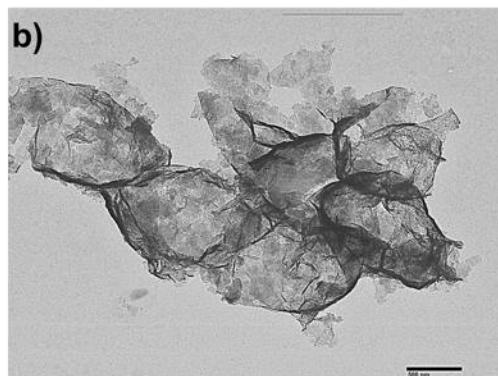
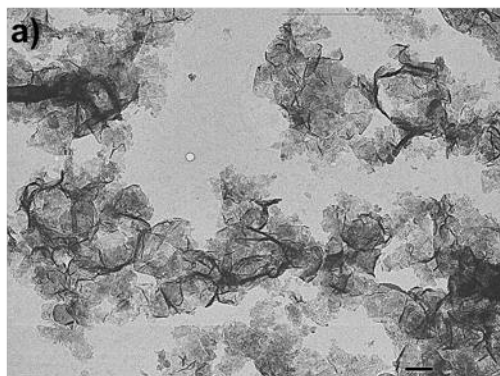


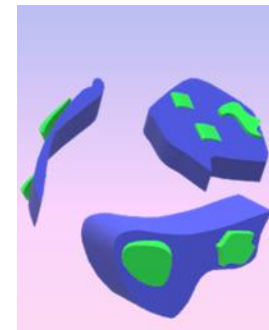
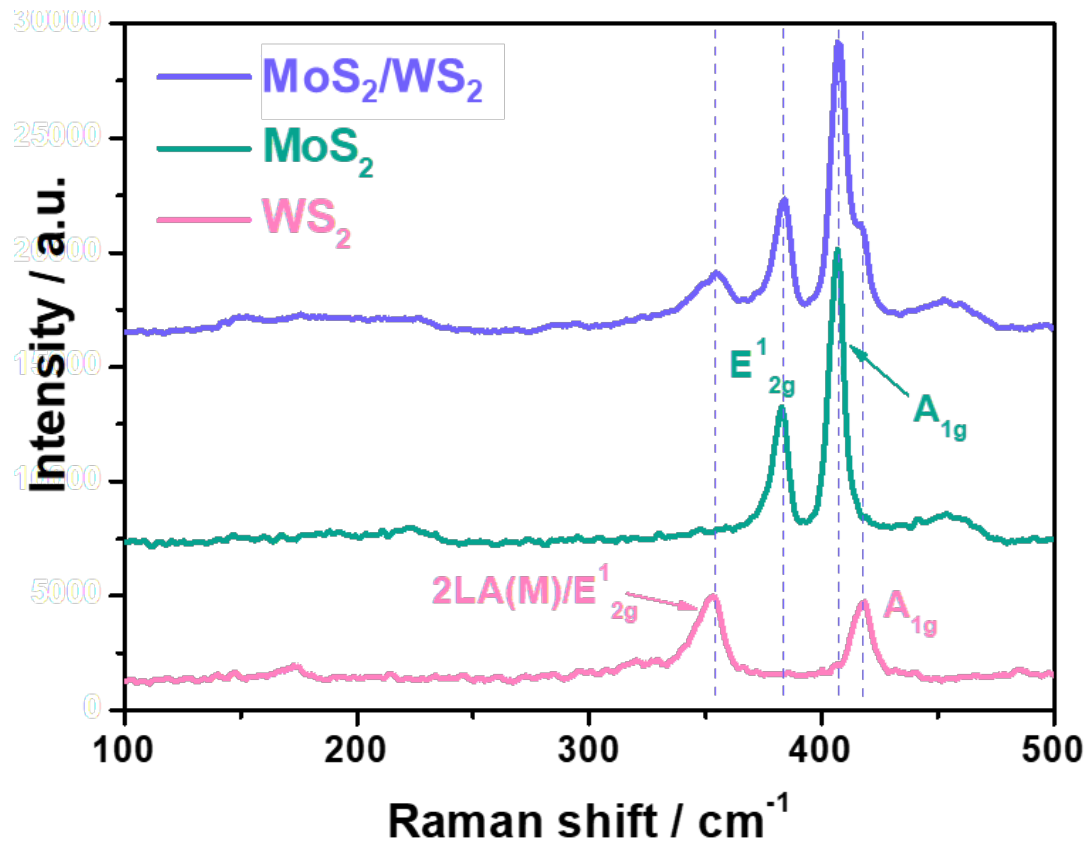


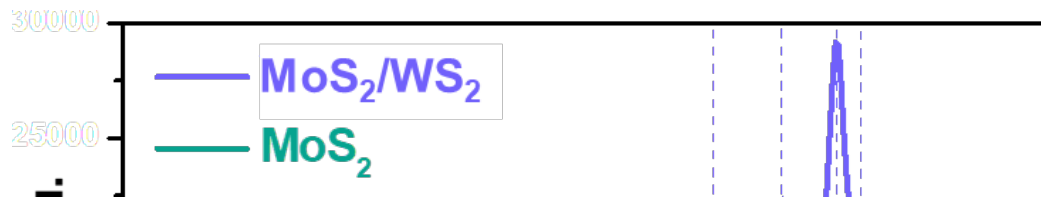




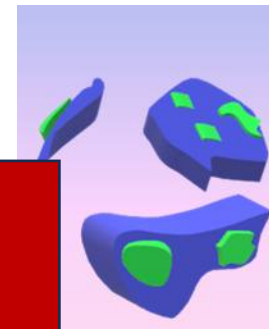
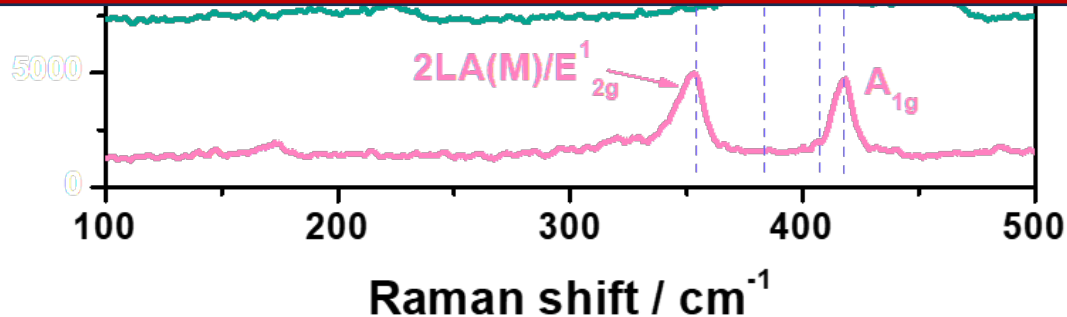
Janus MoS₂/WS₂



Janus MoS_2/WS_2



MoS₂/WS₂ heterostructure
can be prepared in solution

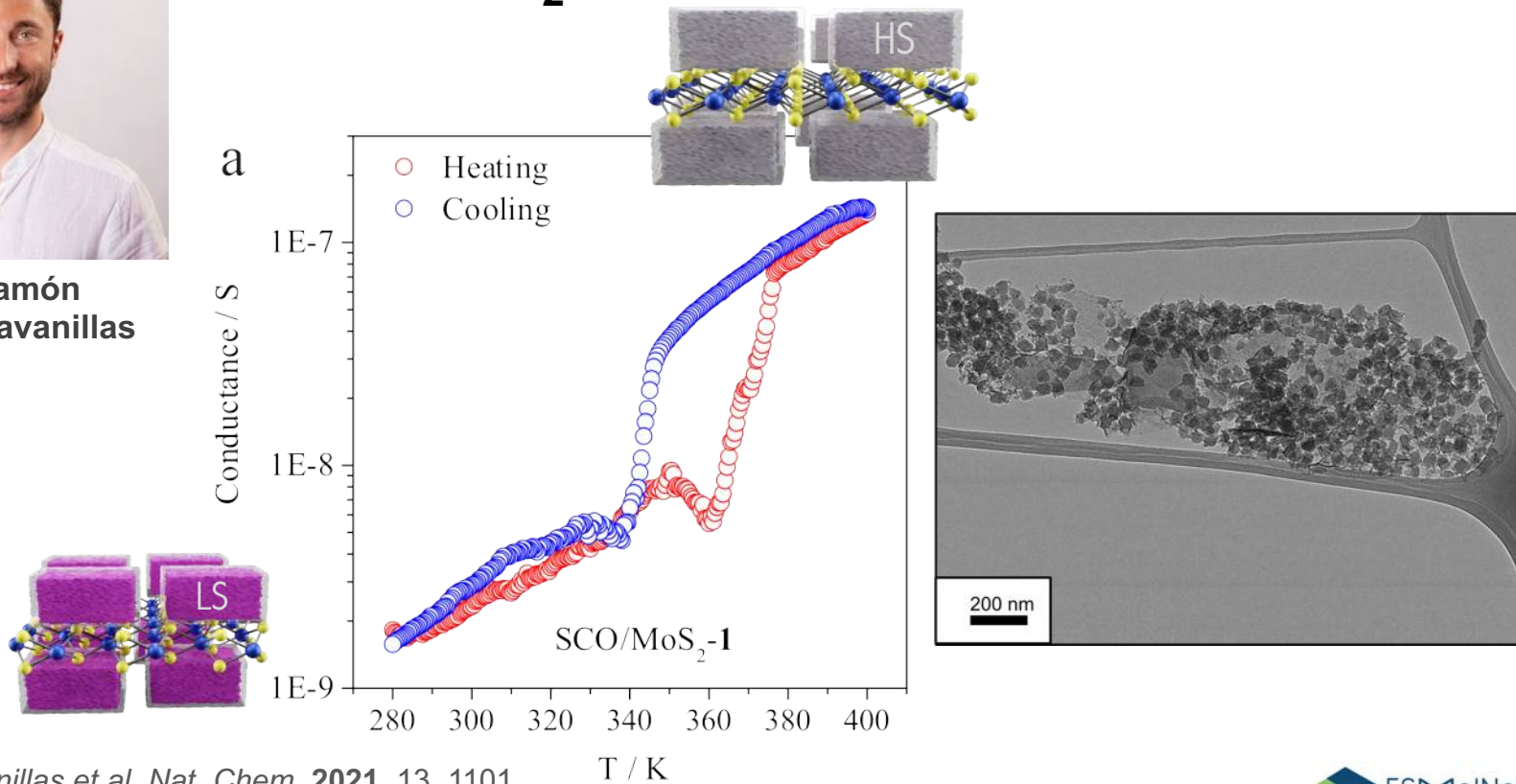


MoS₂/WS₂



Dr. Ramón
Torres-Cavanillas

MoS₂/SCO NPs





R. Torres



A. Regueiro



N. Vassilyeva

MoS₂/SCO NPs



Polystyrene (PS) spheres



R. Torres

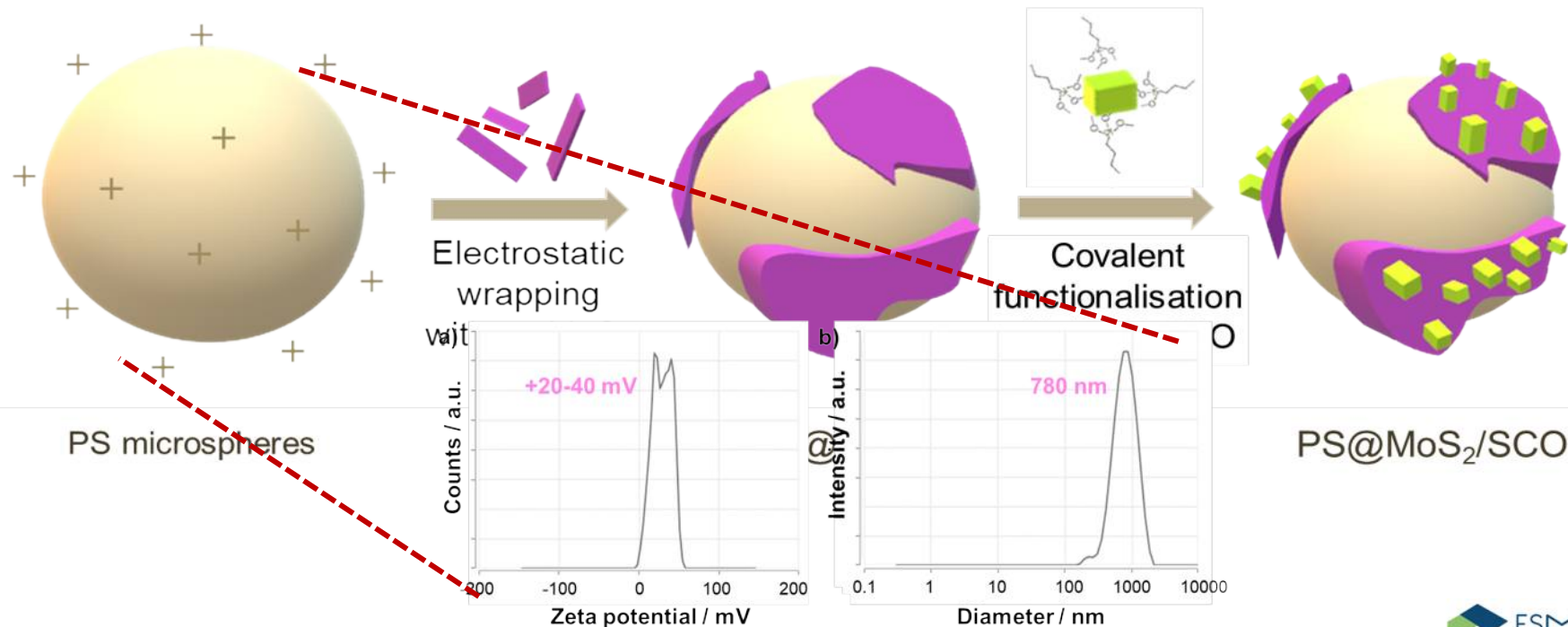


A. Regueiro



N. Vassilyeva

MoS₂/SCO NPs





R. Torres

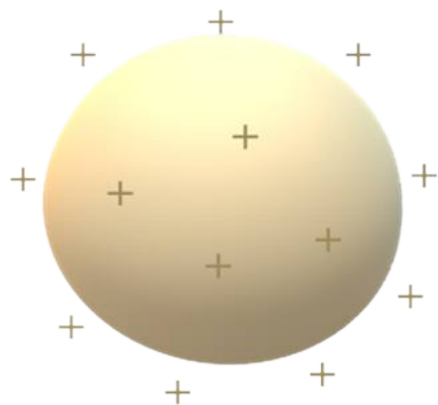


A. Regueiro

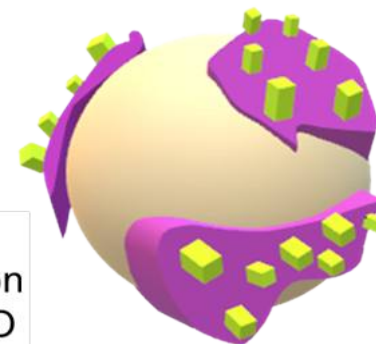
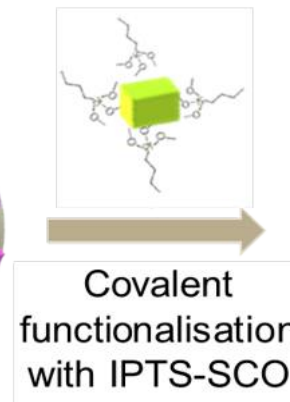


N. Vassilyeva

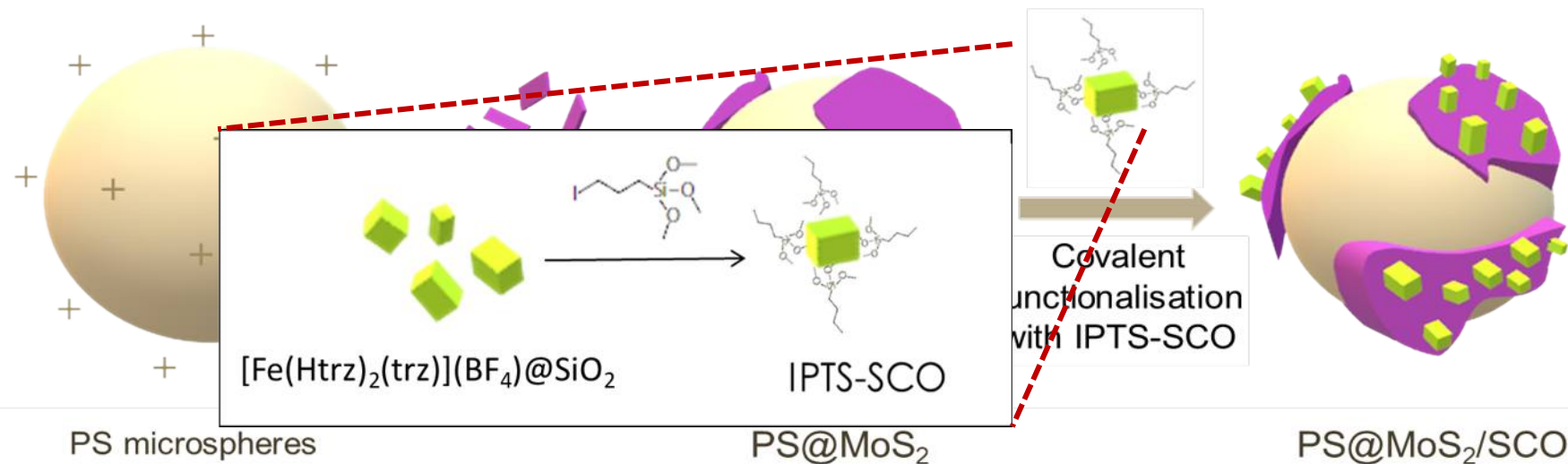
MoS₂/SCO NPs



PS microspheres

PS@MoS₂PS@MoS₂/SCO

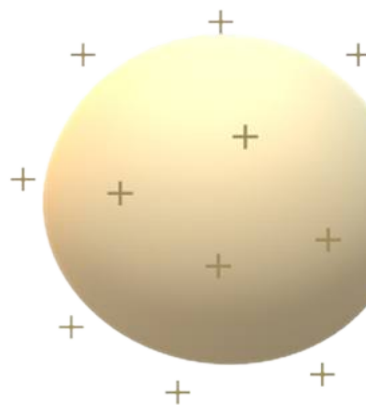
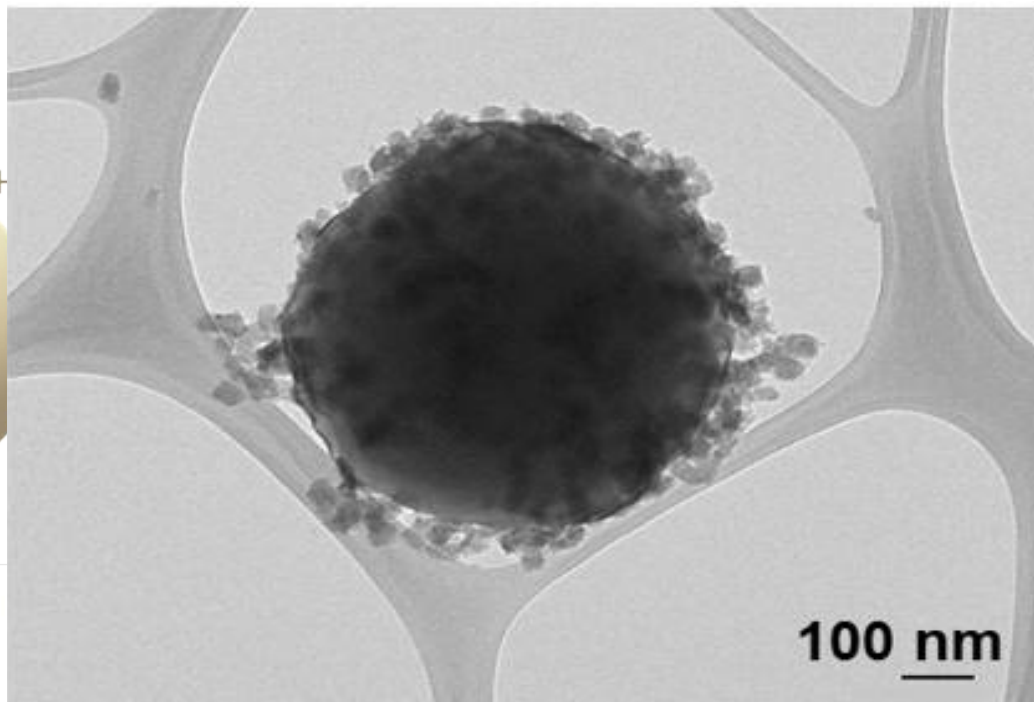
MoS₂/SCO NPs



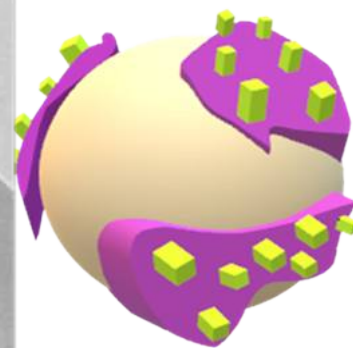
MoS₂/SCO NPs



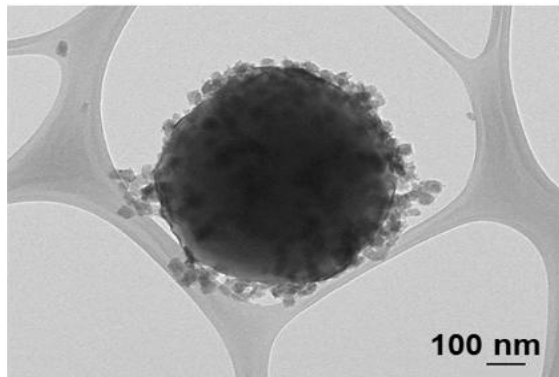
MoS₂/SCO NPs



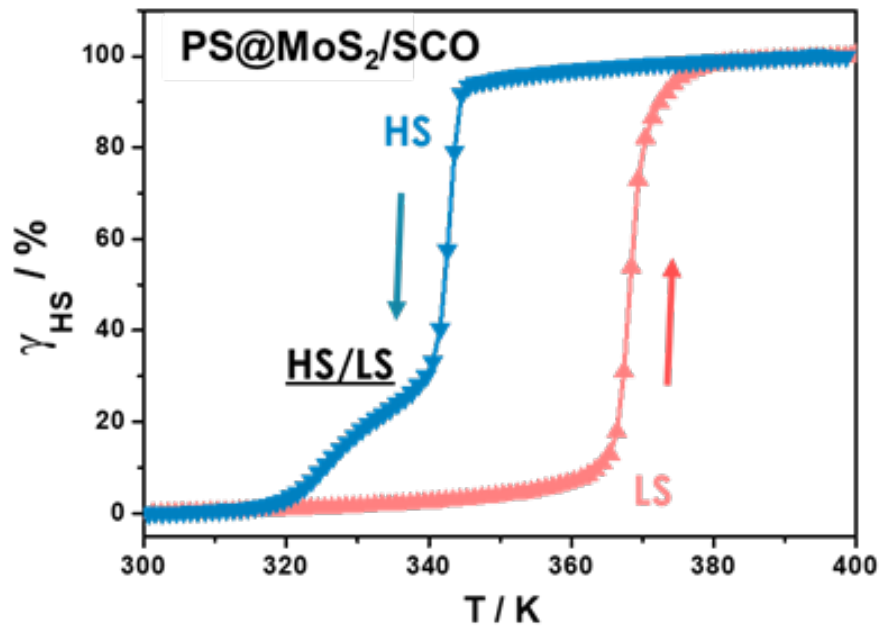
PS microspheres



PS@MoS₂/SCO

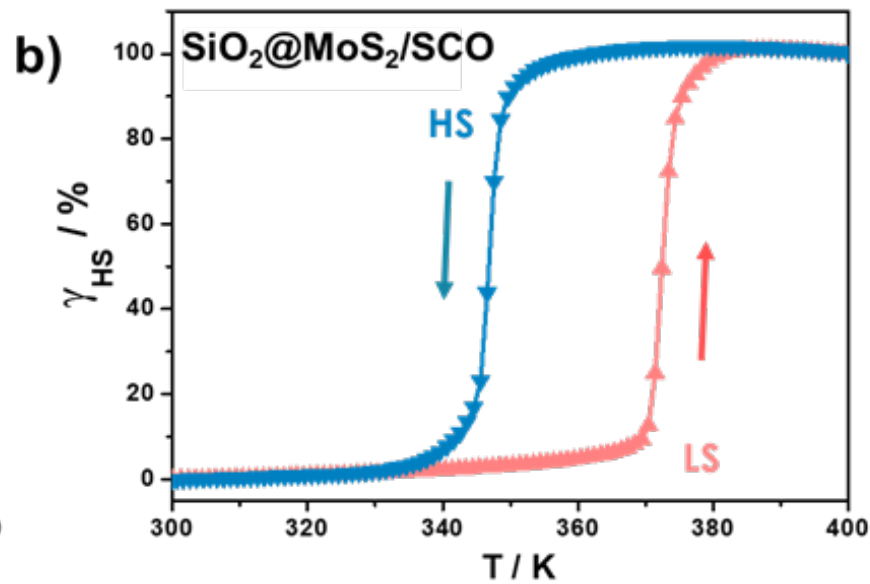
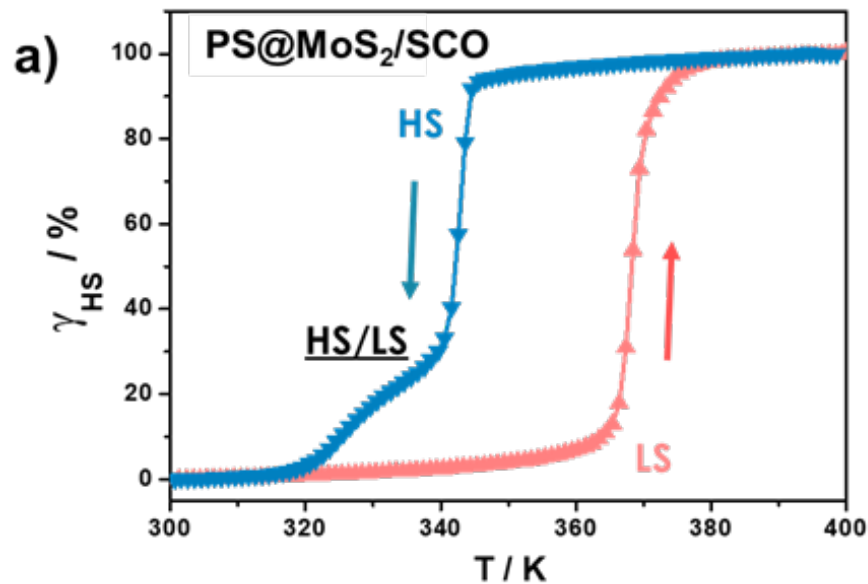


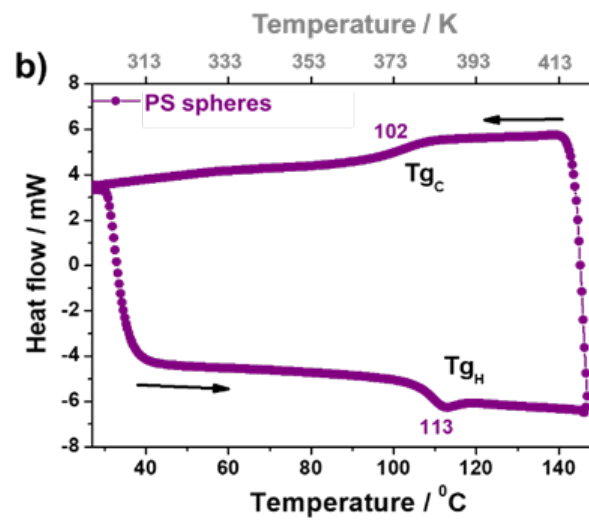
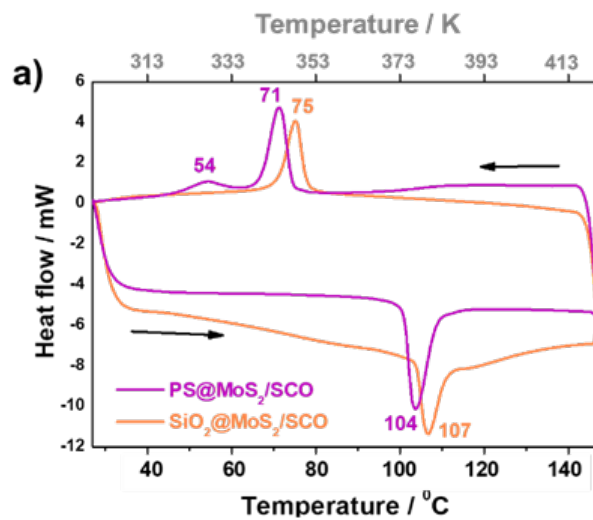
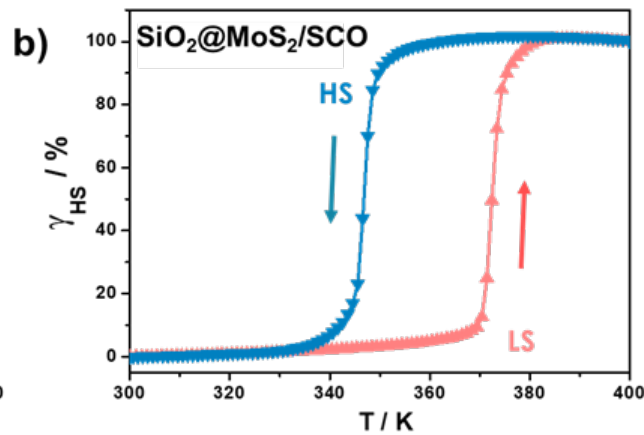
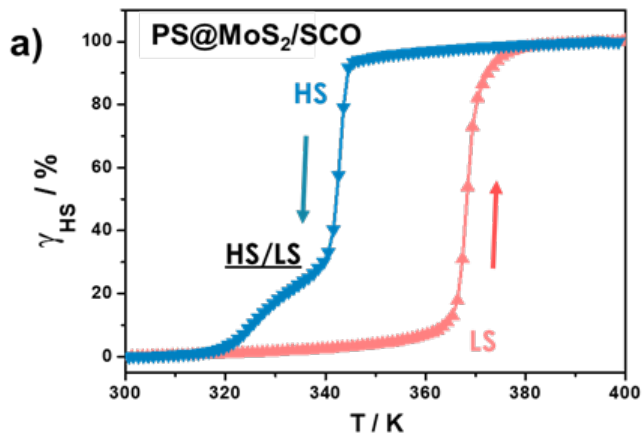
PS@MoS₂/SCO



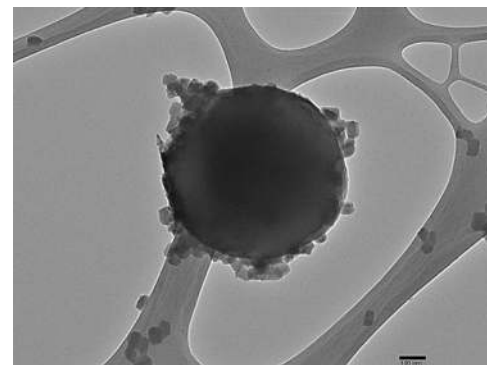
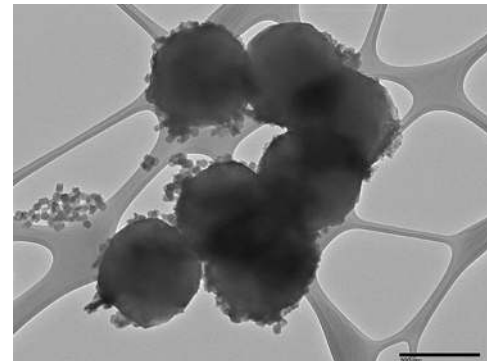
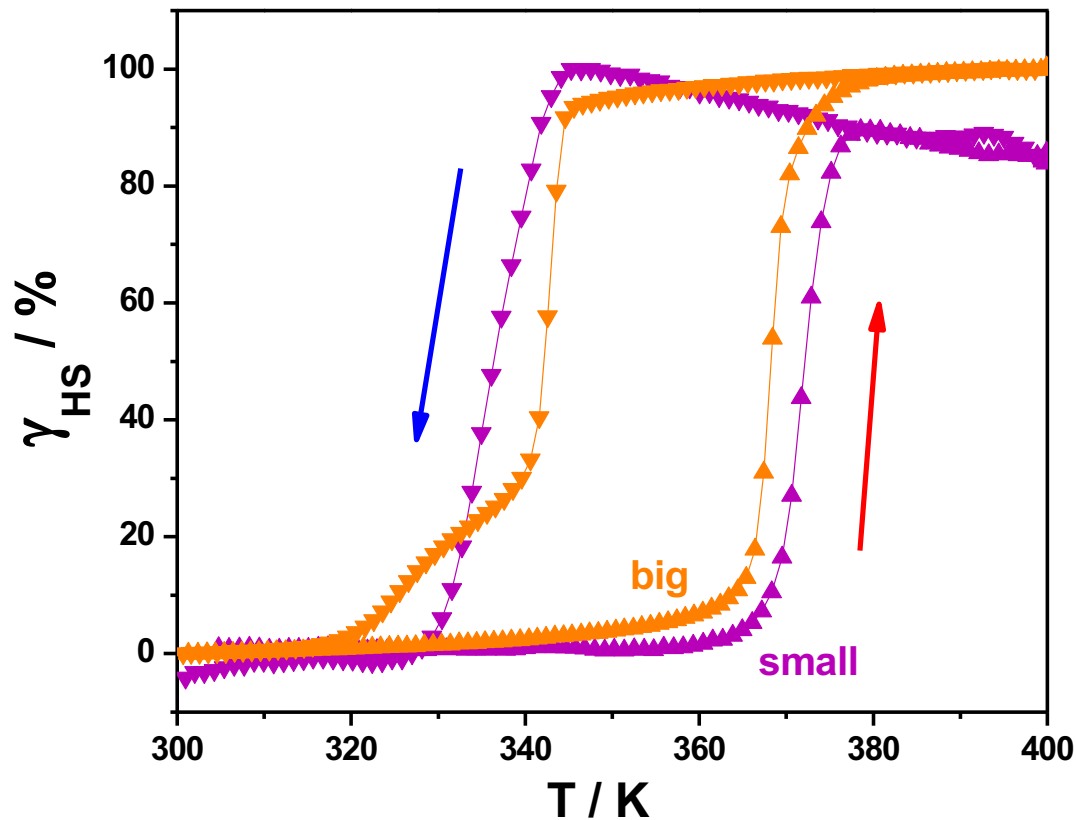
PS template

vs

SiO₂ template



PS@MoS₂/SCO with smaller SCO NPs



Summary of Ideas

Controlled growth of
2D/2D
heterostructures in
solution

*Pay attention to
the mask....
maybe not so
innocent*

Important people: Acknowledgements



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Brotons-Alcázar**



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**Beatriz Alba
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RTMM group (Coronado's Group at the ICMol)



**THANKS
FOR YOUR
ATTENTION**

The End