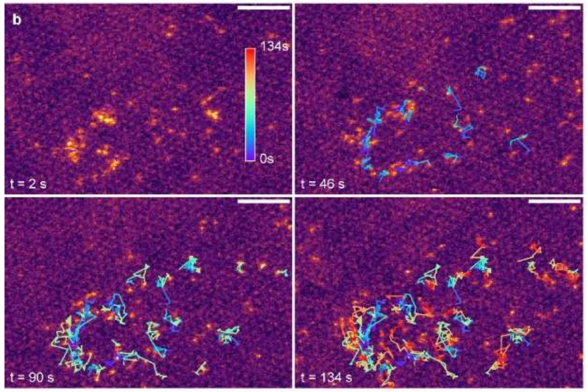
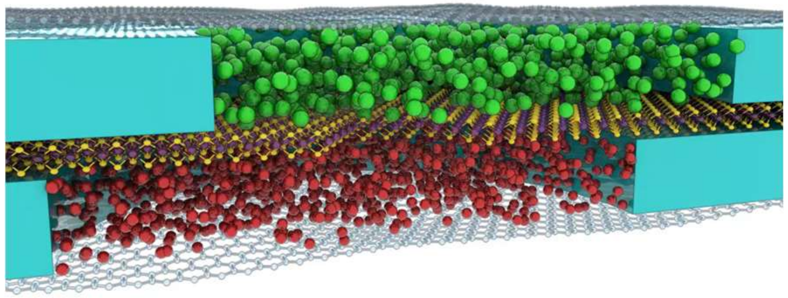
Probing atomic behaviour in liquids with STEM : opportunities for machine learning

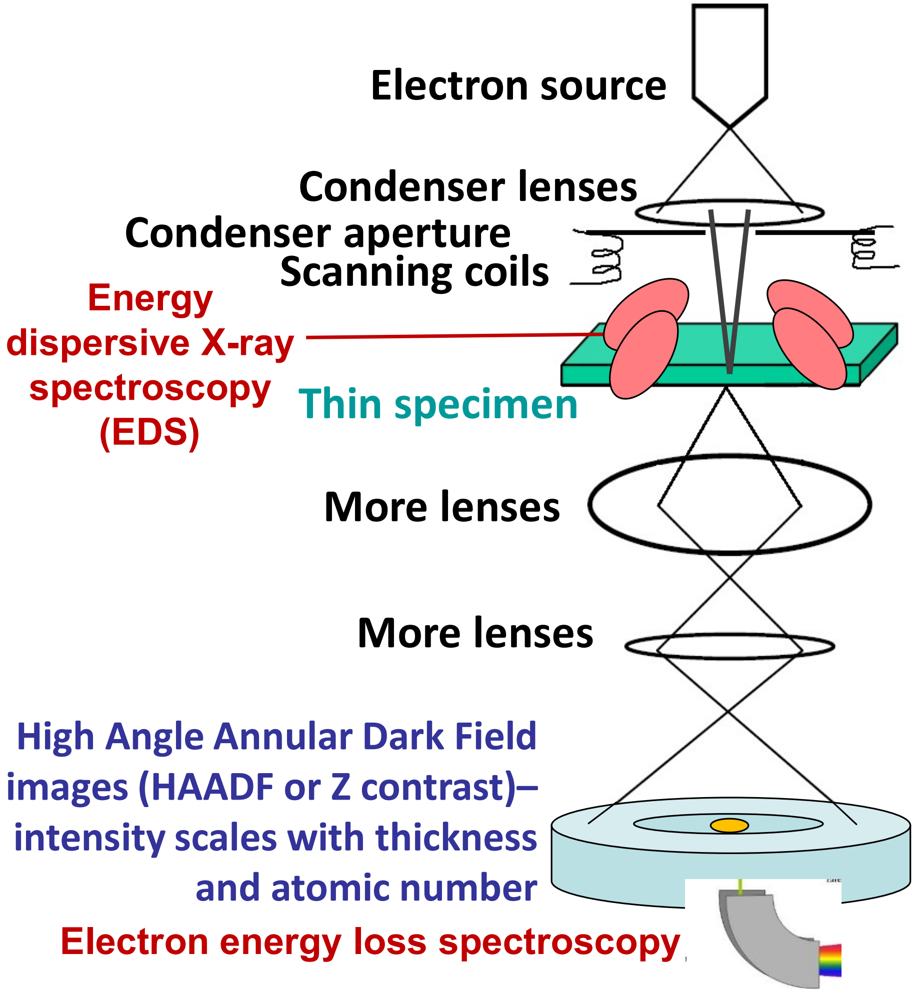


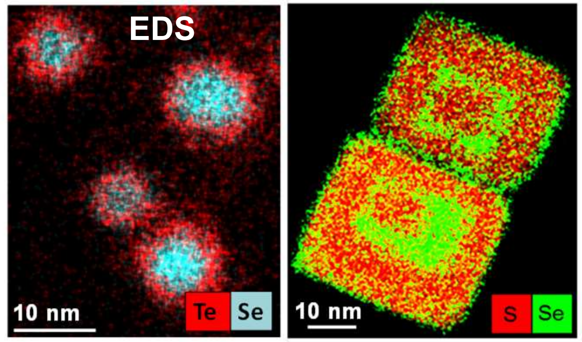
Sarah Haigh
University of Manchester

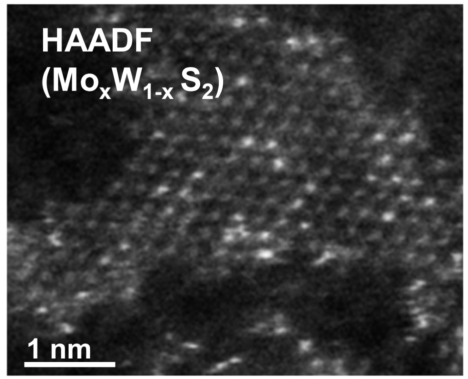


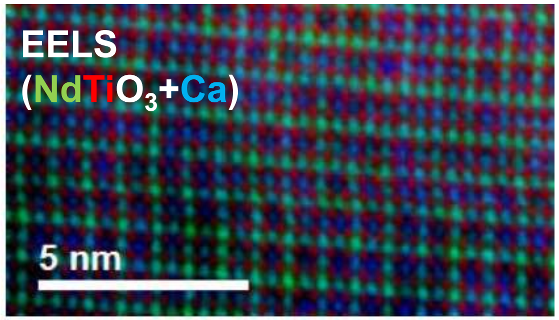
Y. Zou, L. Nguyen, D. Kelly, N. Clark, D. Hopkinson, A.P. Rooney, S. Fairclough, A. Rakowski, A. Weston, Z. Li, M. Zhou, M. Hamer, L. Mogg, A. Kozikov, A. Summerfield, D. Terry, R. Gorbachev, A. Mishchenko, K.S. Vasu, V Sreepal, M. Zhu, D. A. Bandurin B. Radha, I. Grigorieva, K.S. Novoselov, A.K.Geim, R. Nair, R. Young, M Lozada-Hidalgo.
V Zólyomi, V. Enaldiev, S. Magorrian, V Fal'ko (Manchester)
T. Slater, C. Allen, M. Danaie (ePSIC)
M I Katsnelson, A N Rudenko (Radbound University, Netherlands)
Prof Denis Gebauer (Institute of Inorganic Chemistry, Leibniz University of Hanover)

Scanning Transmission Electron Microscopy (STEM)







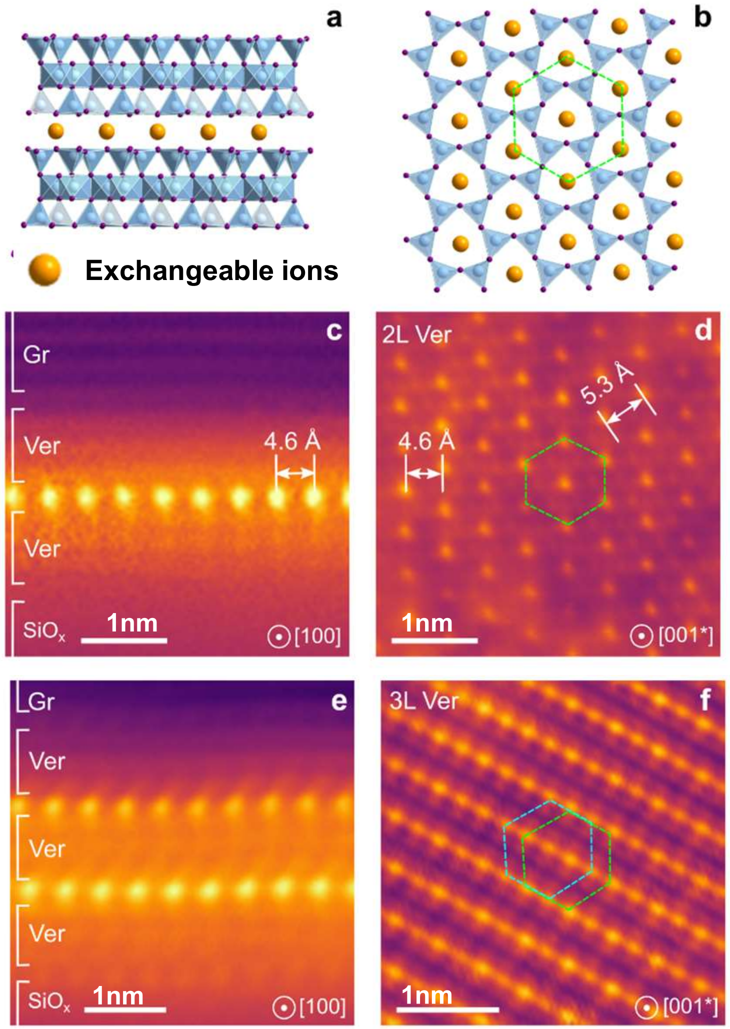


Outline

- **Dynamics of ion exchange in few layer clays**
- **TEM Imaging in liquids**
- **2D Heterostructure Liquid Cells**
  - **Imaging of liquid-liquid mixing reactions**
  - **Tracking single surface adatoms in liquids**
- **3D reconstruction in liquid cells**

Interlayer ion exchange in atomically thin clays and micas

- Many minerals consist of aluminosilicate layers weakly held together by interlayer cations
- Cations can be exchanged by immersion in solution. Takes seconds to decades depending on ion, mineral and solution concentration.
- Essential materials for:
  - Filtration membranes
  - Fuel cells
  - Radioactive waste storage
- Cation exchange mechanism is controversial



2 silicate layers, 1 interlayer

3 silicate layers, 2 interlayers

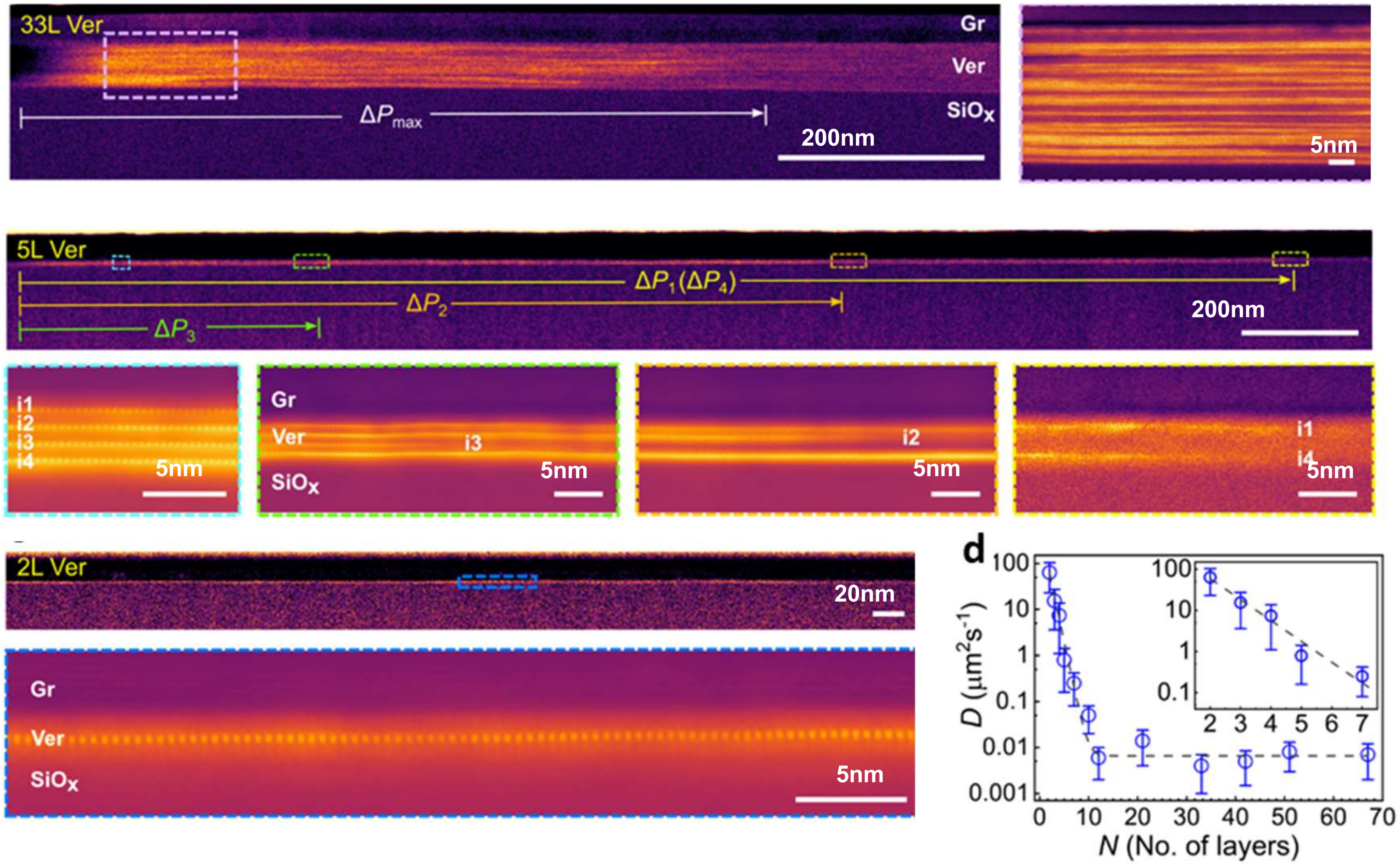
Yi-Chao Zhou et al Nature Materials, 20, 1677–1682 (2021)

Can few-layer thick clays improve membrane performance?

33 layers thick (bulk)

5 layers thick

2 layers thick

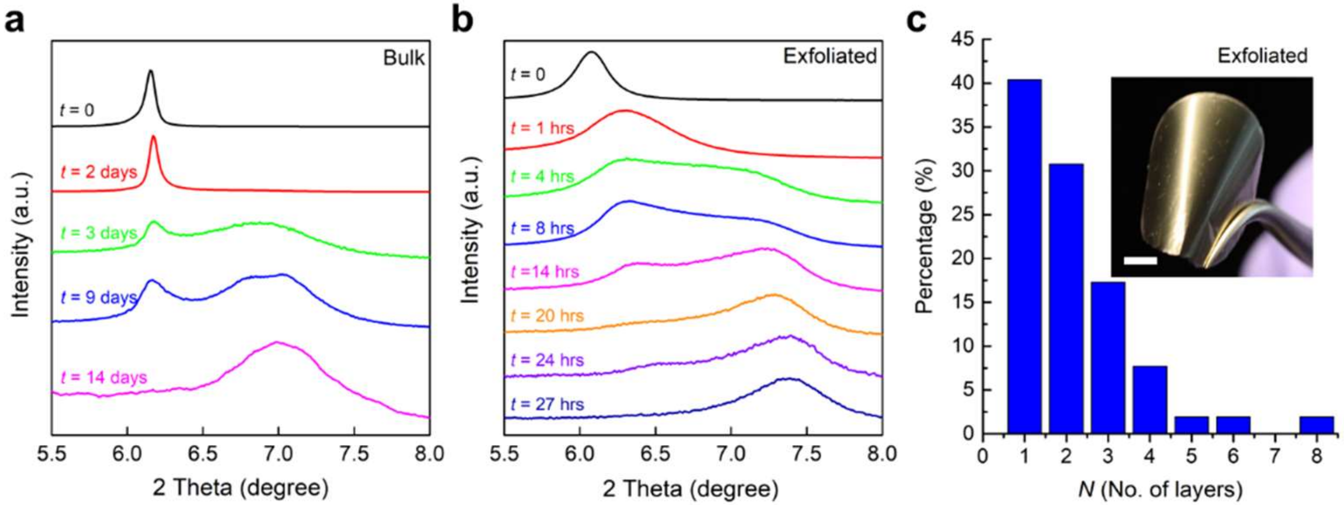


Exchanged Cs is visible as bright contrast in cross sectional ADF imaging

Analysis as a function of crystal thickness (@10s ion exchange) reveals 4 orders of magnitude faster in bilayer than in bulk

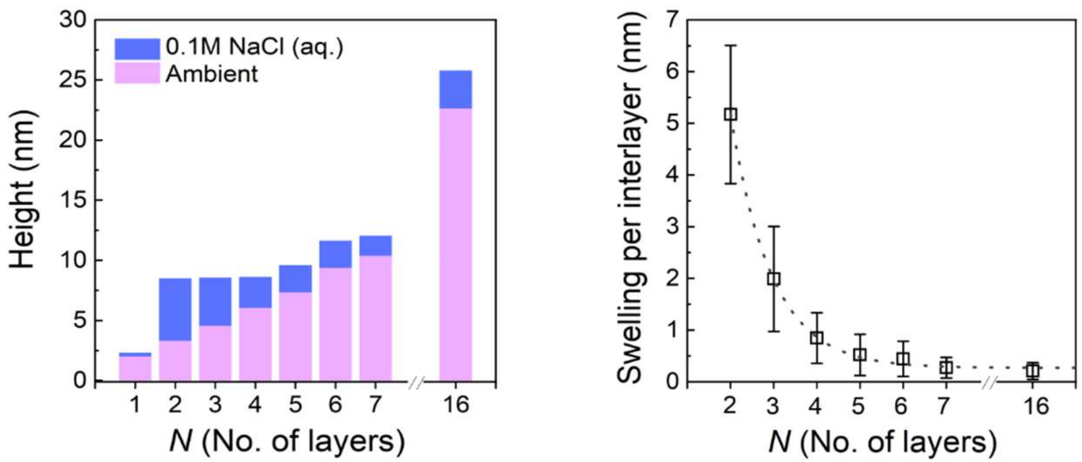
Yi-Chao Zhou et al Nature Materials, 20, 1677–1682 (2021)

Can few-layer thick clays improve membrane performance?



Measurements from membranes made from few layer crystals are fully exchanged in ~24 hours compared to ~14 days for bulk counterparts

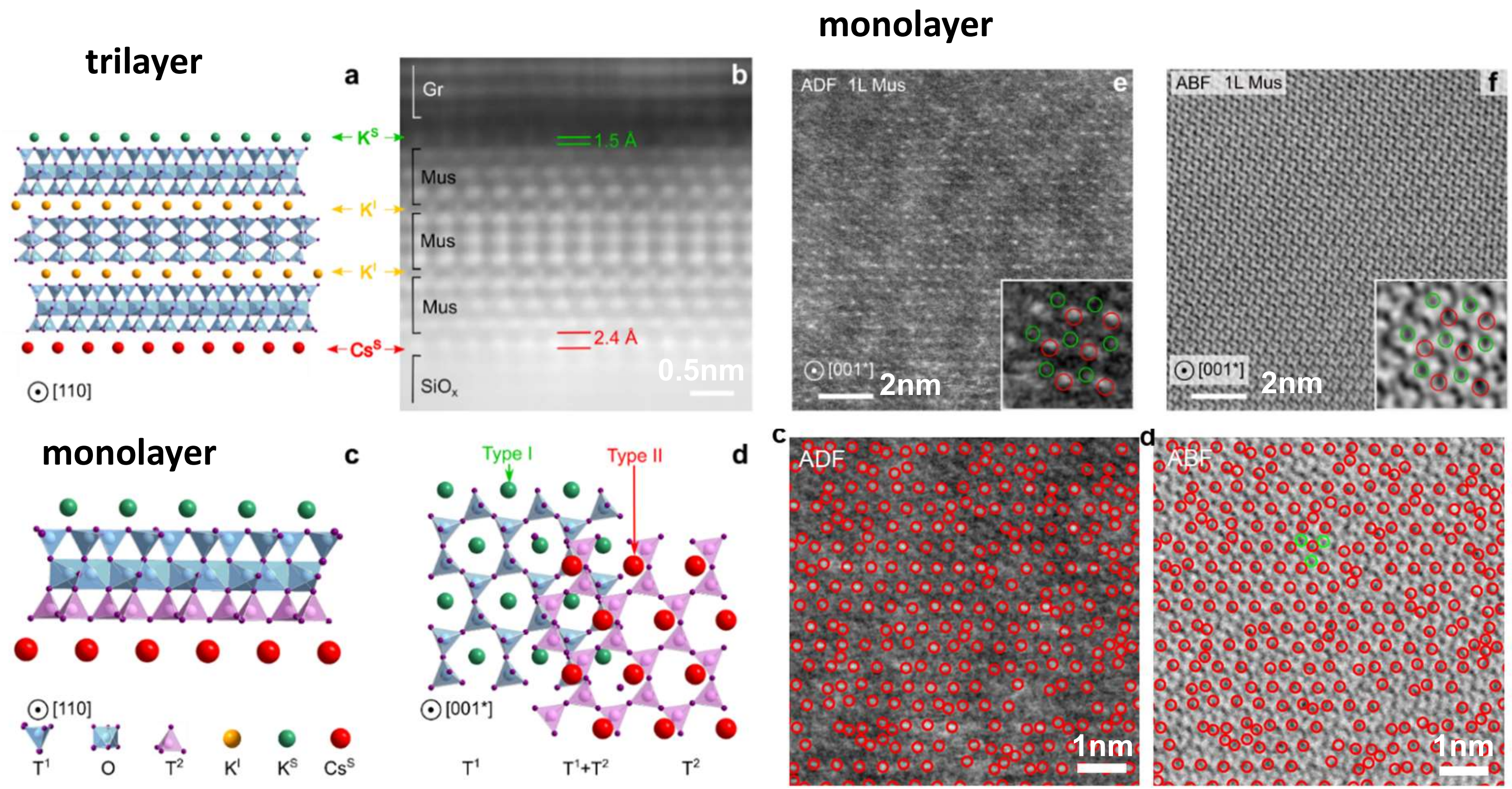
Why?



AFM measurements in liquid show that interlayer swelling is greatest in bilayer – facilitating fast ion diffusion

Yi-Chao Zhou et al Nature Materials, 20, 1677–1682 (2021)

Imaging individual surface cations on monolayer muscovite



- Cs^+ ions visible in ADF STEM image (highlighted by red circles)
- K^+ ions and TOT lattice visible in ABF STEM image

Yi-Chao Zhou et al Nature Materials, 20, 1677–1682 (2021)

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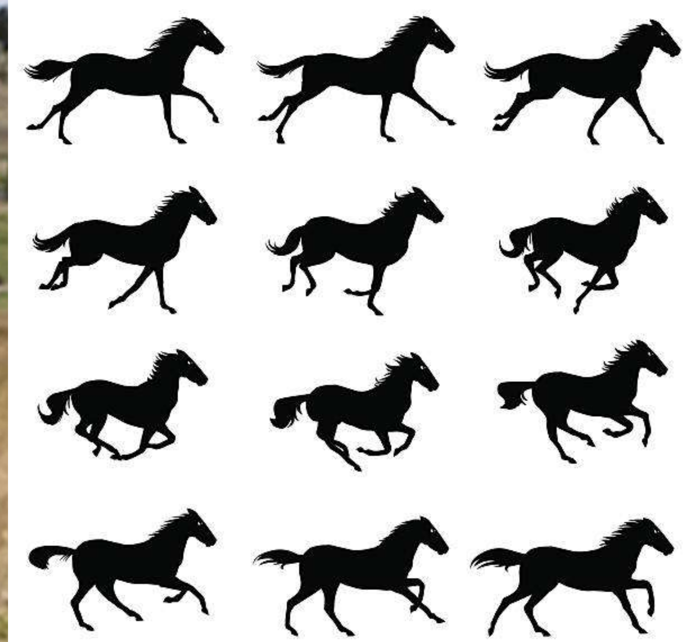
Why do we need in situ?

Theodore Gericault's "The Derby at Epsom" (Photo by WikiArt) (France, 1791-1824)

https://bestspb.ru/en/russian_troika.en.php, (St Petersburg, 1879)

Why do we need in situ?



Why do we want to image solids in liquids environments?

Chemistry: ion exchange, electrochemistry, wet synthesis of nanostructures, redox reactions, self-assembly, liquid phase catalysis,

Physics: motion of nanostructures in solutions, particle interactions, electrostatic forces, electronic and chemical properties of water

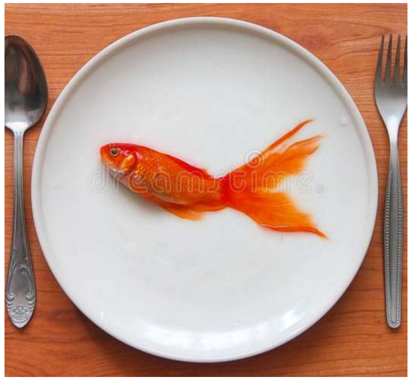
Materials: corrosion, etching

Biology: dynamics of hydrated viruses, peptides etc

Why do we need in-situ environmental cell TEM?

Vacuum TEM

Experiment:



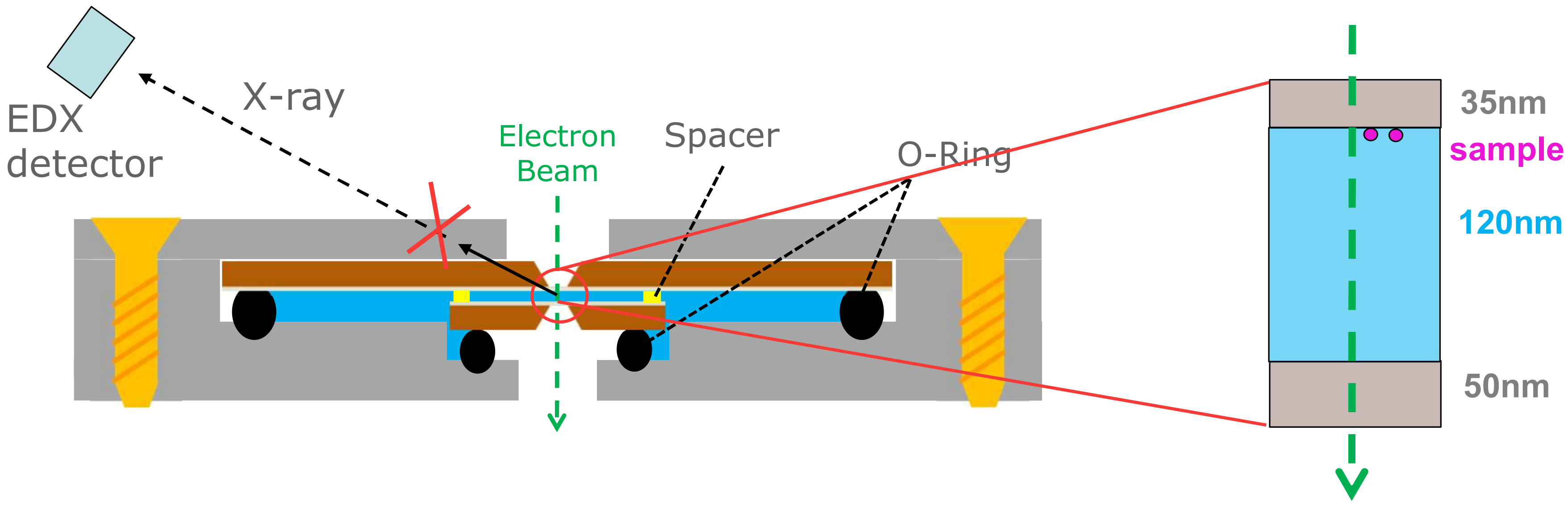
Cryo TEM

2D Liquid cells

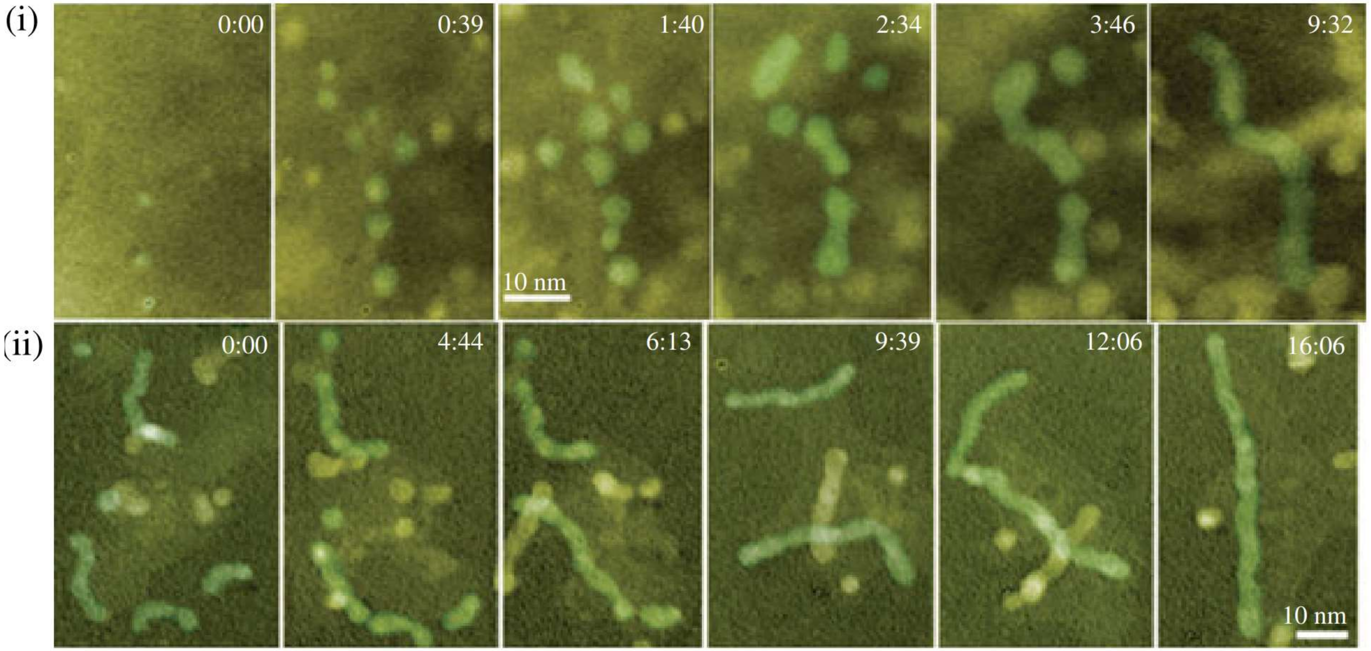
Liquid cell TEM holders

Poseidon E-chips

Syringe Pump



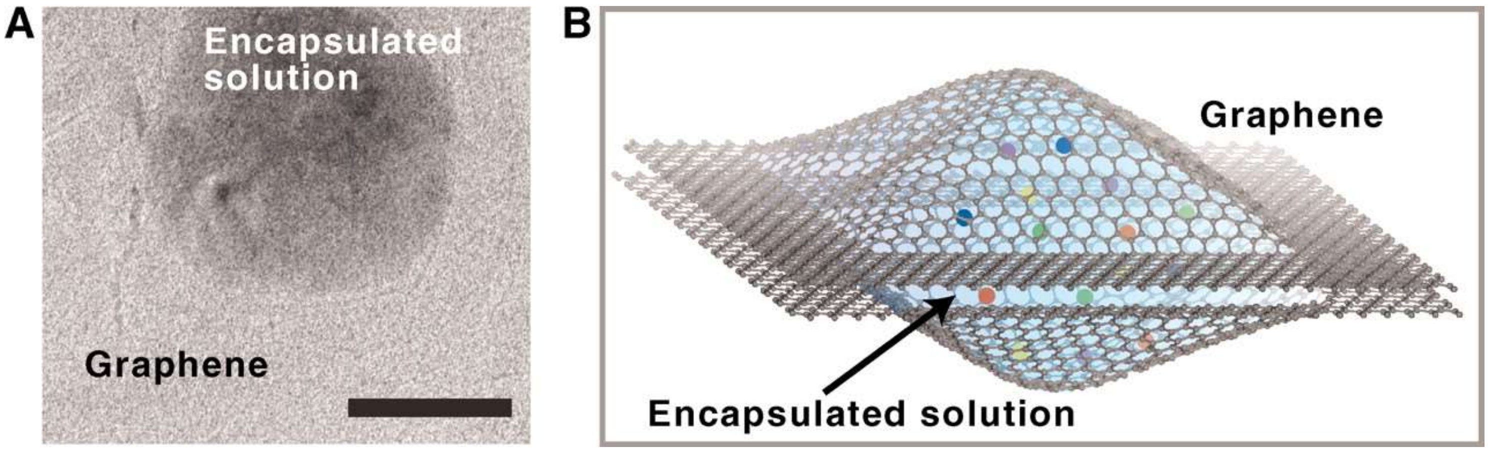
Liquid cell TEM imaging of nanoparticle coalescence

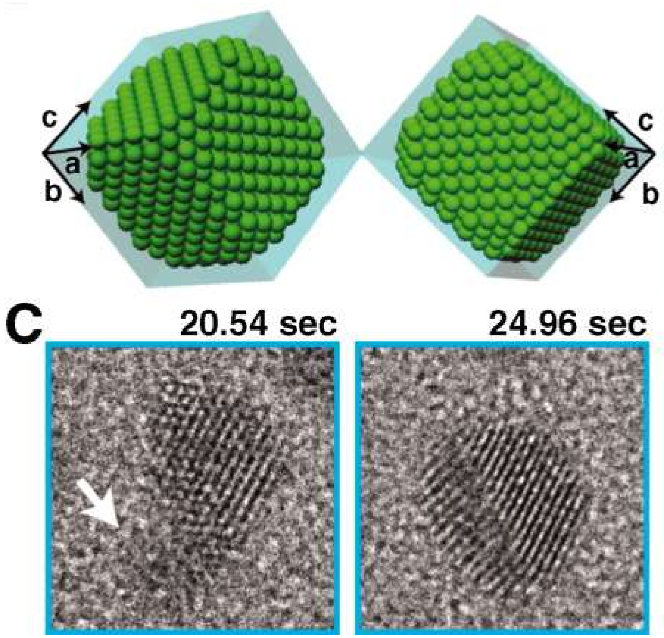


Real-time imaging of Pt_3Fe nanorod formation. (i) Nucleation and growth of Pt_3Fe particles followed by their assembly into a nanorod. Particles contributed to the nanorod are highlighted in green. (ii) The growth of a long Pt_3Fe nanorod from the assembly of several short nanorods

[Liao H-G, et al. 2014 Science 345, 916–919. (doi:10.1126/science.1253149)].

Graphene Liquid Cells





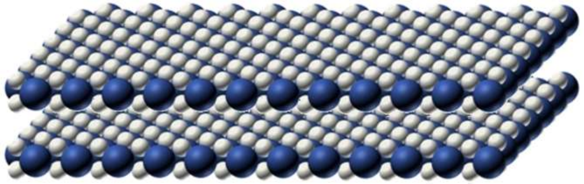
TEM image of a Graphene Liquid Cell; laminated graphene layers immobilize a blister of encapsulated stock solution (dark region).

Still snapshots from movie of Pt nanocrystal growth via coalescence and crystal-structure evolution observed with atomic resolution in a graphene liquid cell

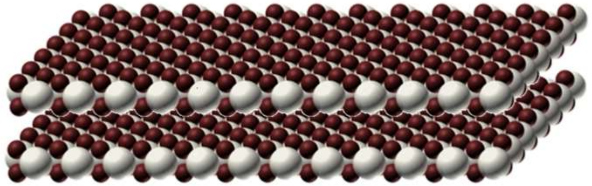
[Jong Min Yuk et al. Science 2012;336:61-64]

Can we improve on this?

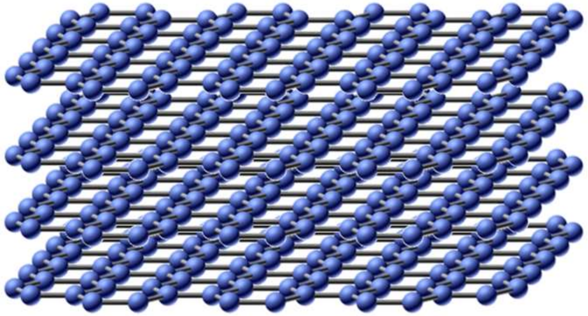
2D-Crystal Heterostructures



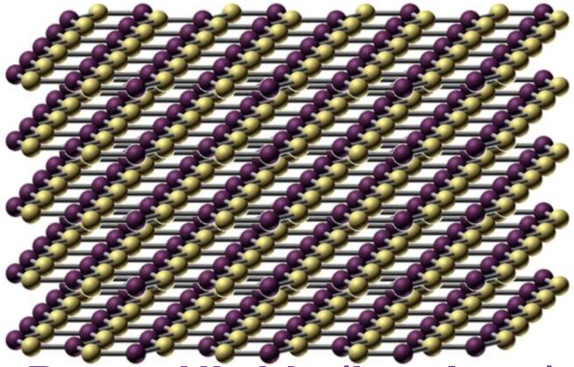
MoS_2 (semiconductor)



$NbSe_2$ (superconductor)

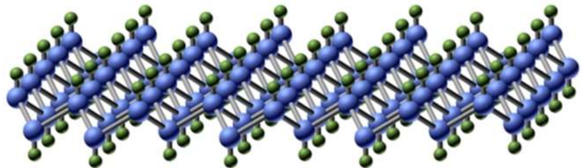


Graphene (conductor)



Boron-Nitride (insulator)

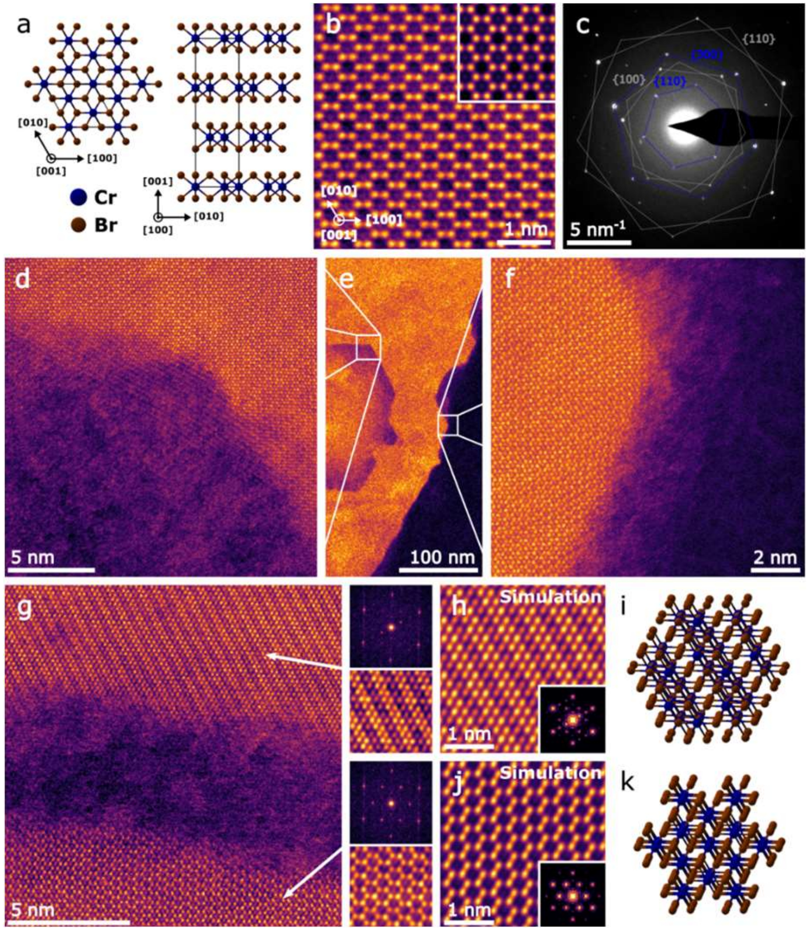
Etched Graphene



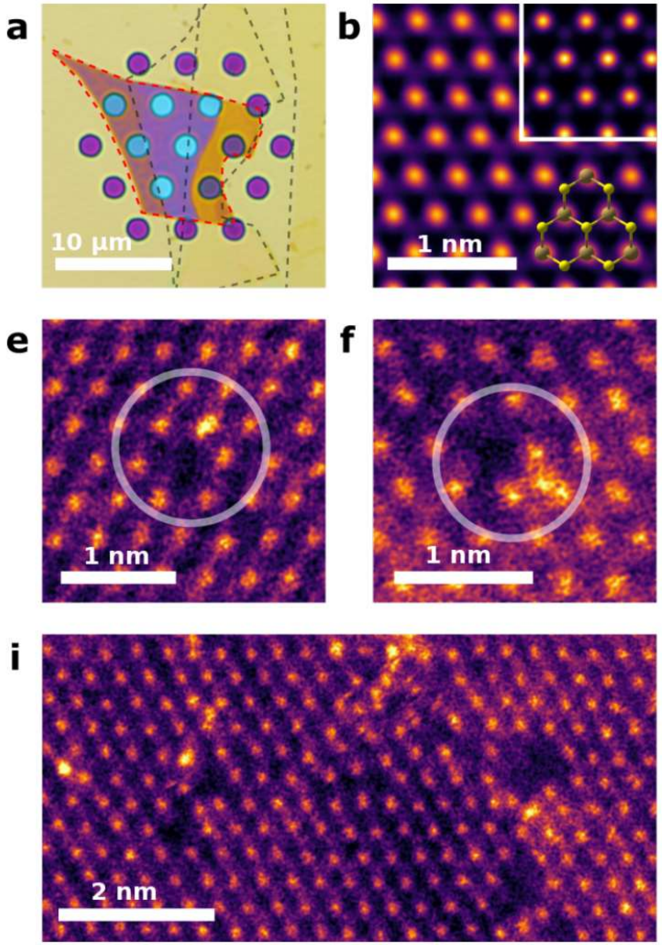
GraFane

A.K. Geim & I Grigorieva Nature 2014

Air sensitive 2D crystals imaged using graphene encapsulation



Atomic Resolution Imaging of $CrBr_3$ Using Adhesion-Enhanced Grids, *M Hamer, et al,* Nano Letters, *20, 9, 6582–6589 (2020)*



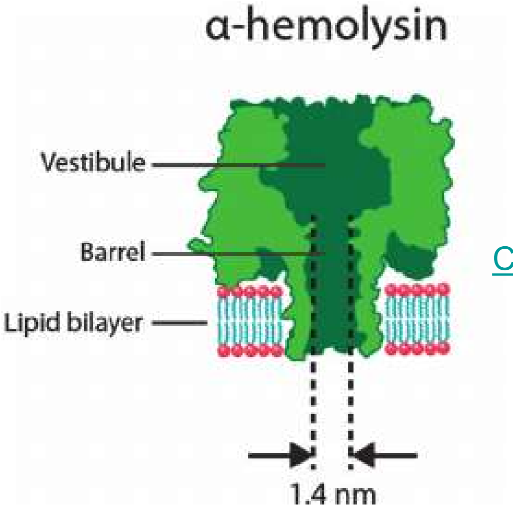
Enhanced Superconductivity in Few-Layer TaS_2 due to Healing by Oxygenation. Bekaert et al. Nano Letters, 20, 5, 3808–3818, (2020)

Motivation for 2D Nanofluidics

- **Nanofluidics is the study of fluid behaviour when in confined spaces (1-100 nm = few-100s atoms wide)**
- **Small dimensions cause properties not observed in bulk**

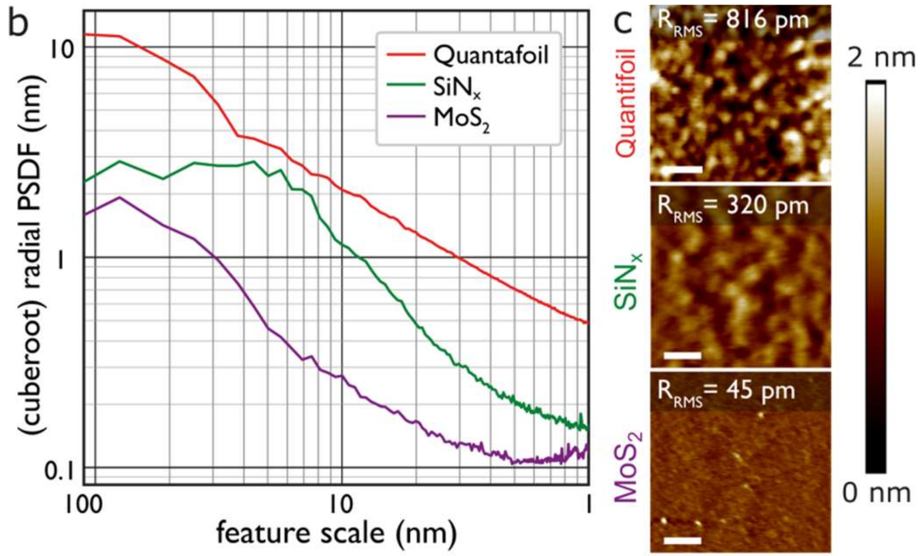
Flow in nanometre size pores is crucial for:

- **battery and fuel cell operation**
- **separation membranes**
- **small fluid volumes**
- **lab on a chip diagnostics**



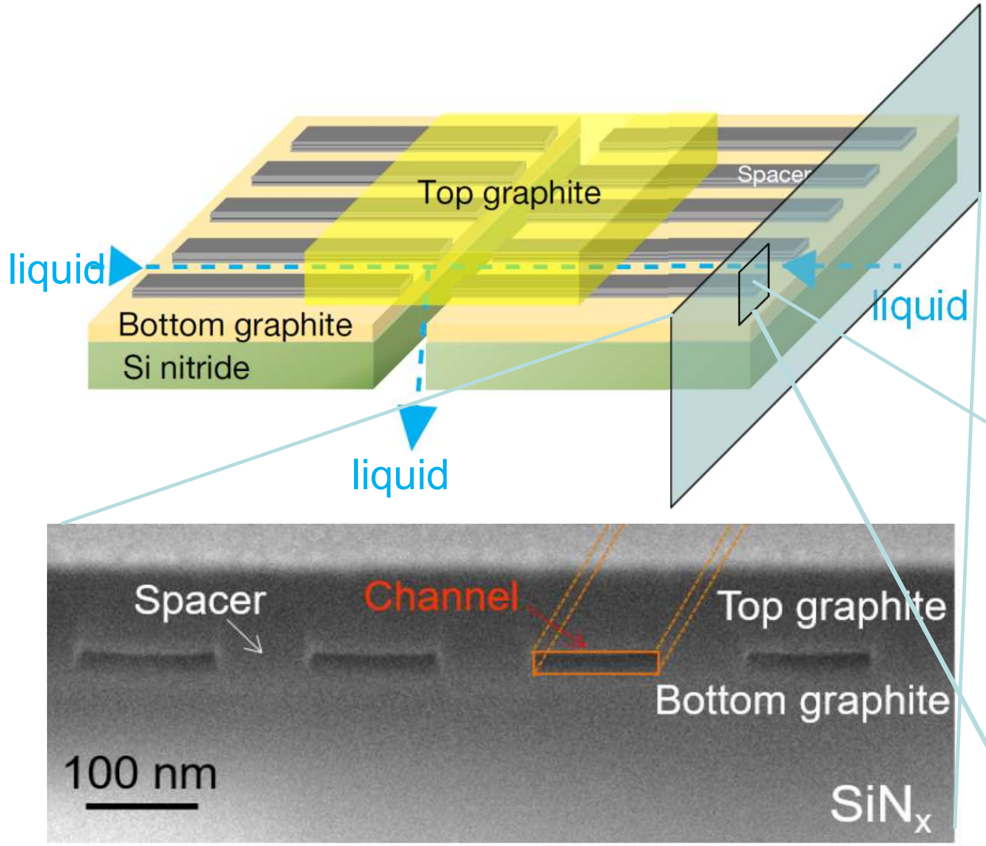
Chemical Society Reviews 2012
DOI: 10.1039/C2CS35286A

Problem is that
Silicon oxide or nitride patterned structures have surface roughness of 1-10 nm

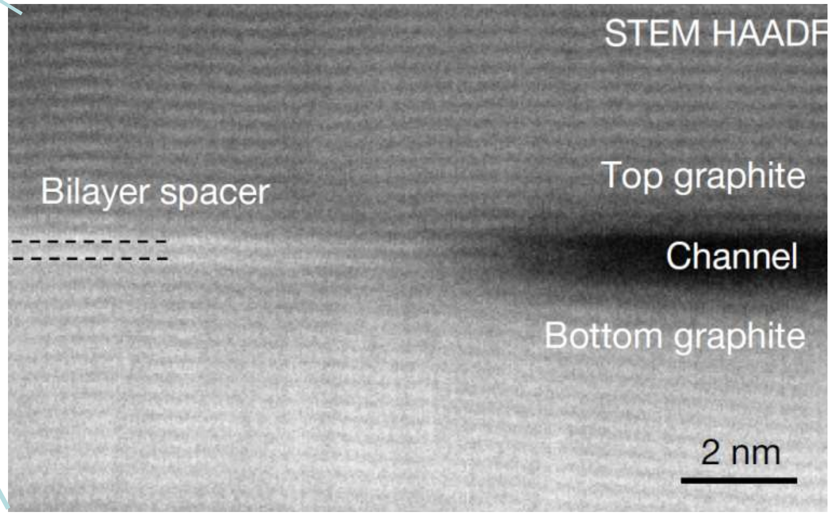


M Hamer, et al **Nano Letters 2020,** 20, 9, p6582**,** doi:10.1021/acs.nanolett.0c02346

A 2D approach to nanofluidics

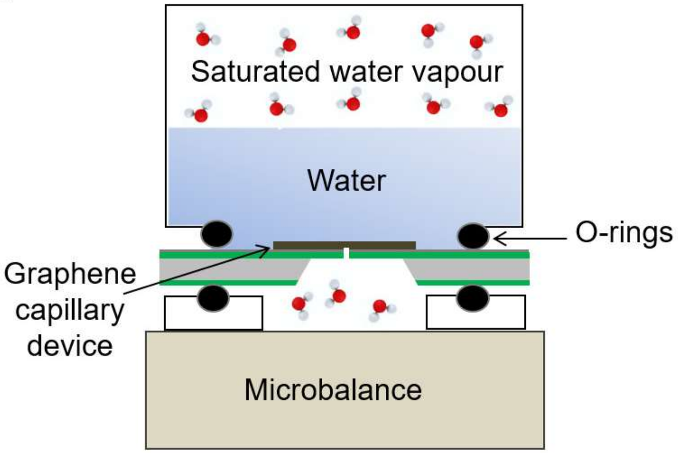


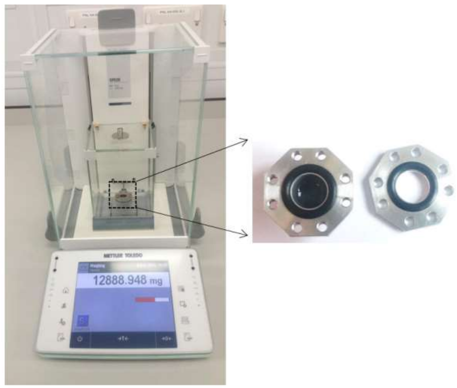
- **Etched channels in a 2D heterostructure allow precise measurements of flow through controlled pore sizes for atomic dimensions**
- **Channels have atomically flat surfaces and atomically defined height (better than lithography)**
- **Most interest (few-layer high) require TEM imaging to develop fabrication methodology**



Boya et al Nature 2016

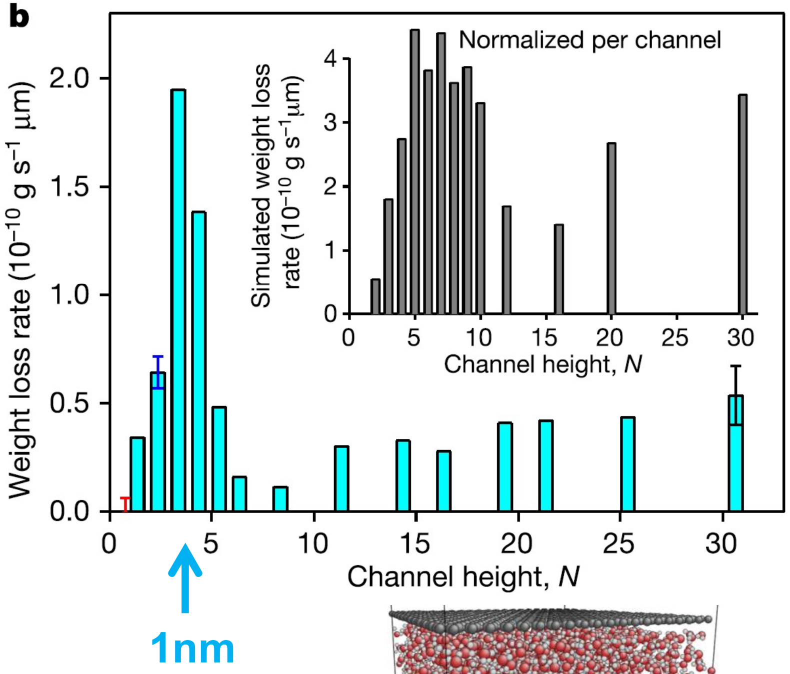
A 2D approach to nanofluidics

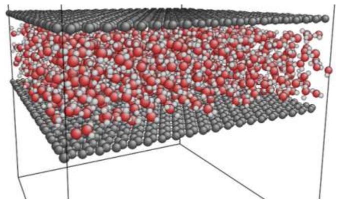




Liquid flow Gravimetric measurements

Weight loss rate for different spacer heights (N layers) normalised for channel length.



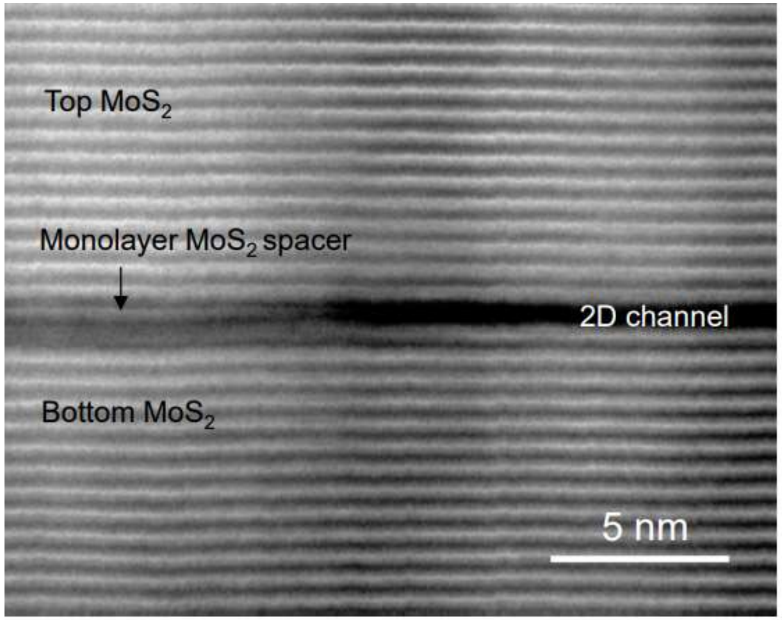


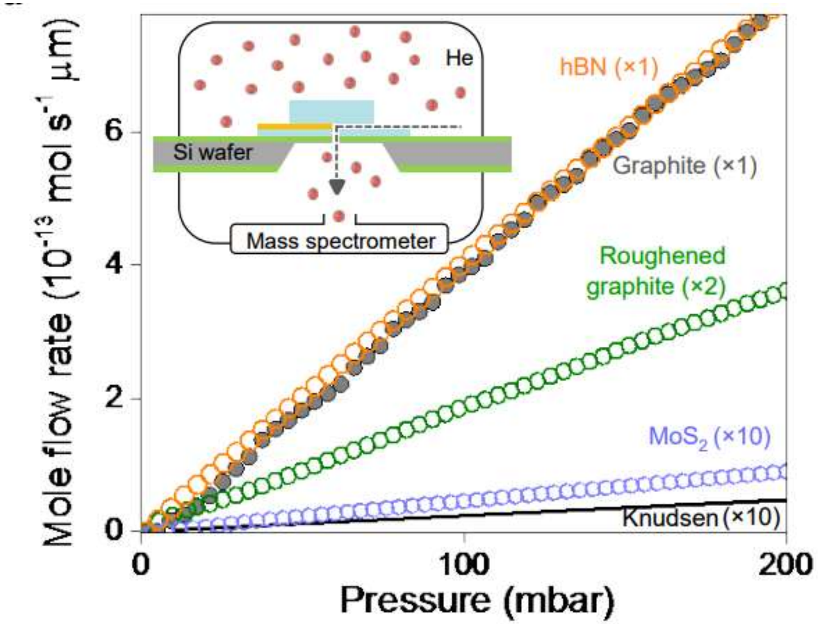
Water transport through the channels, has **unexpectedly fast flow** (up to 1 ms^{-1}) that we attribute to **high capillary pressures** (about 1,000 bar) and large slip lengths.

For channels that accommodate only a few layers of water (N<5), the flow exhibits **a marked enhancement** that we associate with an increased structural order in nanoconfined water.

Boya et al Nature 2016

Gas flow nanofluidics



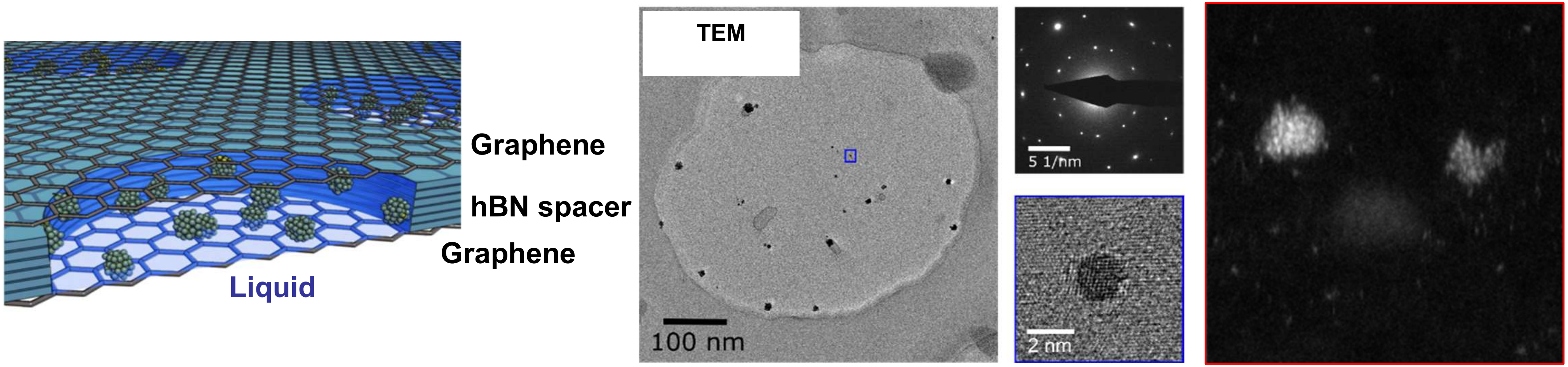


Measurements of gas flow though "2d" channels with atomic dimensions show exceptionally fast gas flow for graphene and hBN but not MoS_2.

Atomic flatness of graphene/hBN causes specular rather than diffuse scattering

Keerthi et al **Ballistic molecular transport through two-dimensional channels**. **Nature** 558, 420–424 (**2018**).

Engineered Graphene Liquid Cells

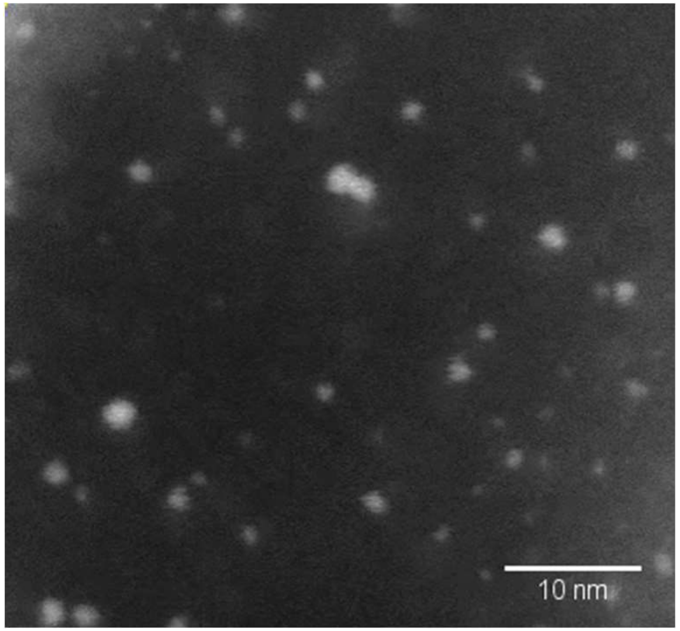


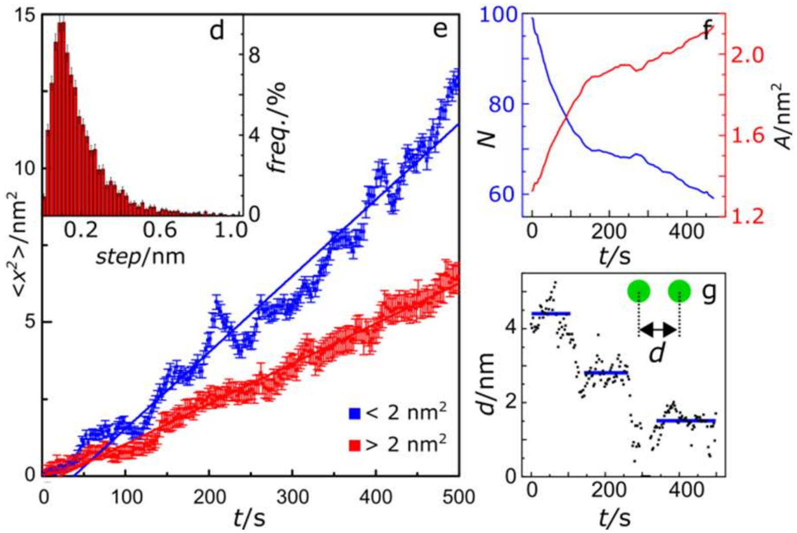
- Robust - seal is exceptionally strong due to atomic flatness of hBN crystals
- Precise dimensions controlled by thickness of hBN and lithography pattern
- Reliable fabrication procedure established for 2D heterostructure stacks
- Compatible with mixing …. and flow ….

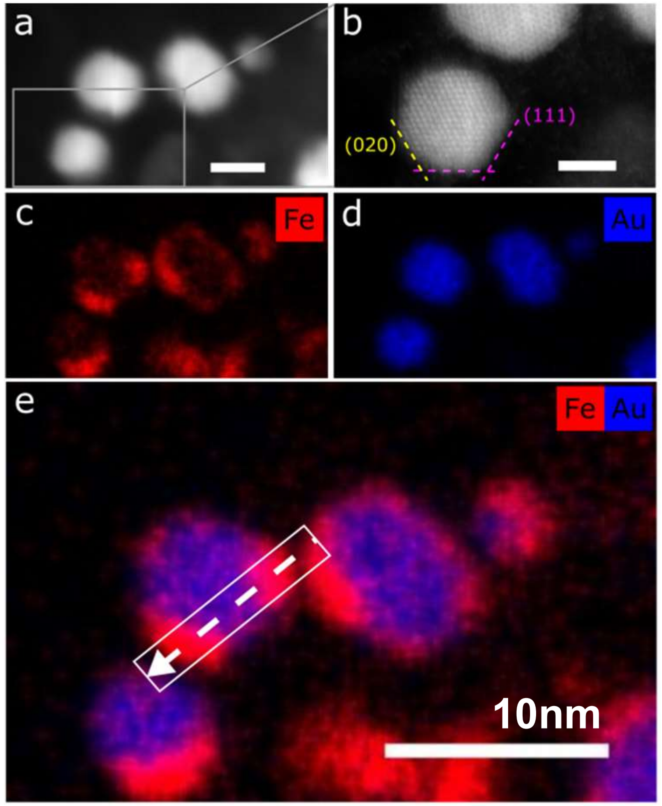
Kelly et al Nano Letters 2018, 18, 2, 1168

Engineered Graphene Liquid Cells

Imaging nanoparticle motion on graphene in water





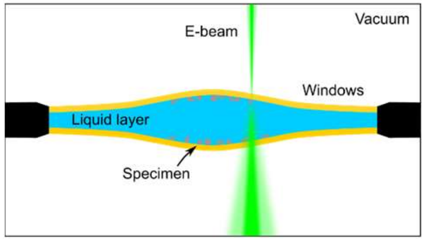


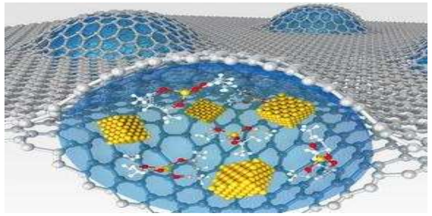
- Allows tracking of dynamic surface motion in liquid of nanoparticles with diameters of <1nm
- STEM-EDX mapping quality better than in vacuum

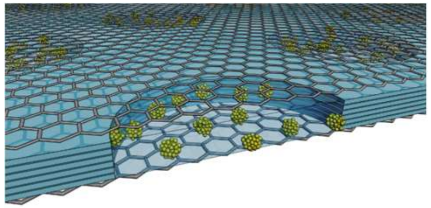
Kelly et al Nano Letters 2018, 18, 2, 1168

Comparing TEM liquid cell technologies

Ideal experiment	Conventional Liquid Cells	Conventional Graphene Liquid Cells	Engineered Graphene Liquid Cells







	Conventional Liquid Cells	Conventional Graphene Liquid Cells	Engineered Graphene Liquid Cells
External Stimuli?	✓	✗	Work in progress
Atomic Resolution?	Difficult	✓	✓
Spectroscopy?	Partial	✓	✓

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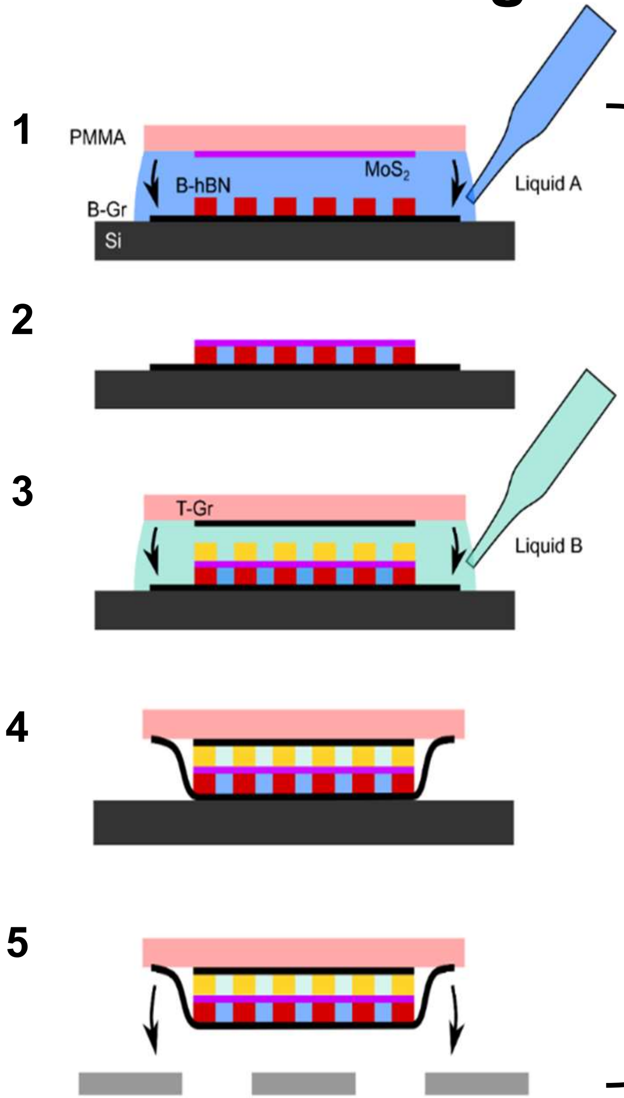
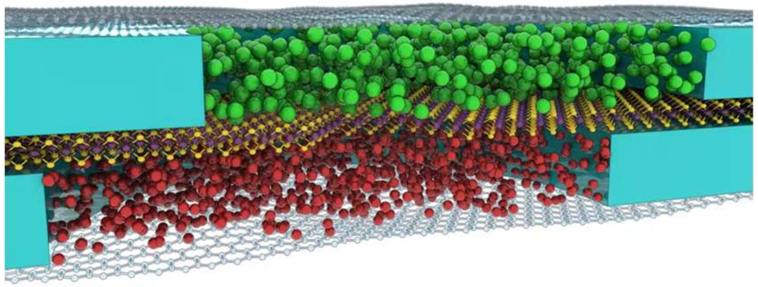
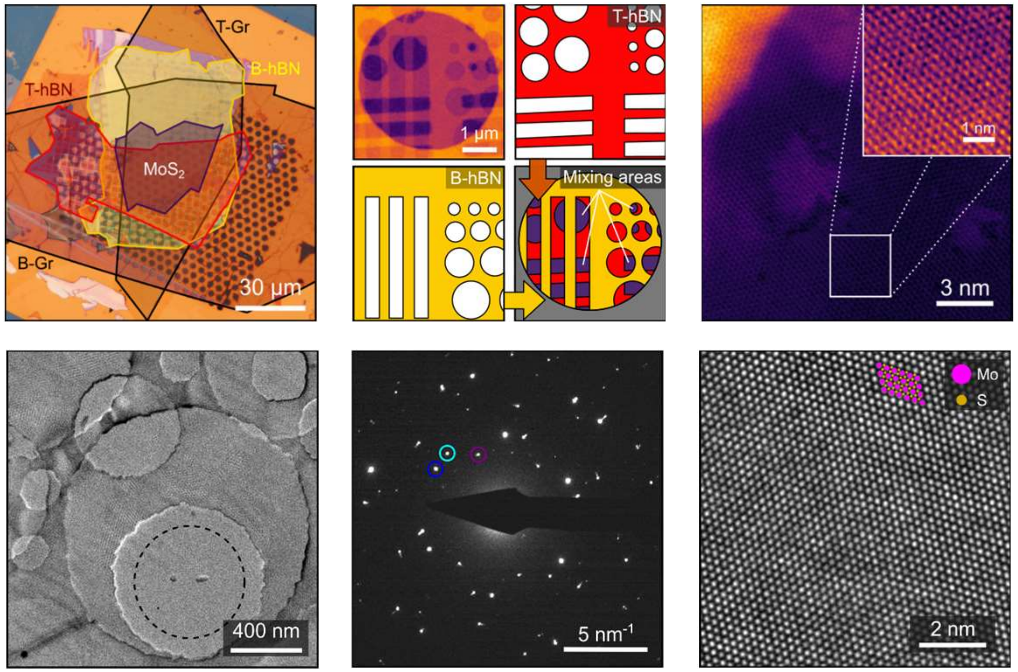
Engineered Graphene Liquid Mixing Cells



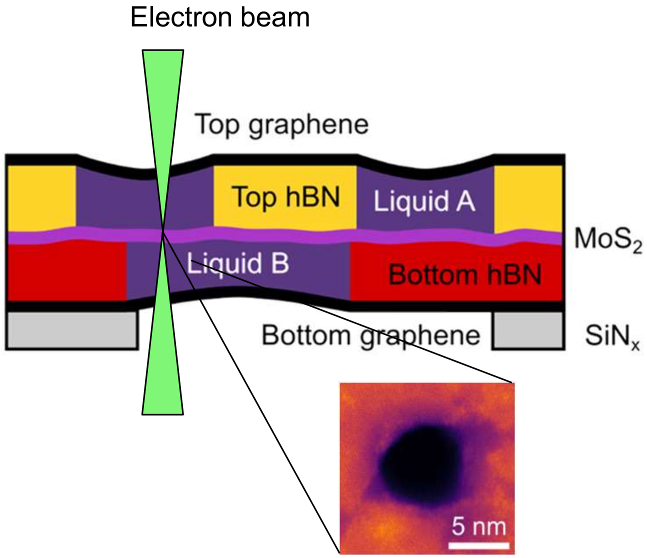
Few layer graphene (~1.5nm)
hBN(~20nm)
monolayer or bilayer MoS_2
hBN(~20nm)
Few layer graphene (~1.5nm)

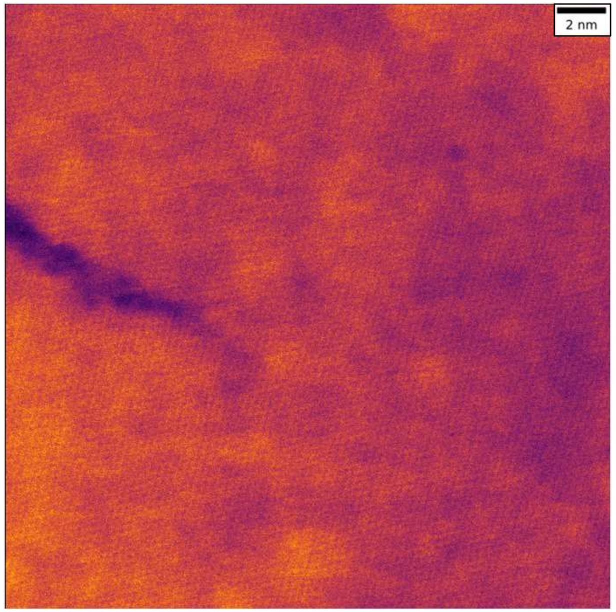


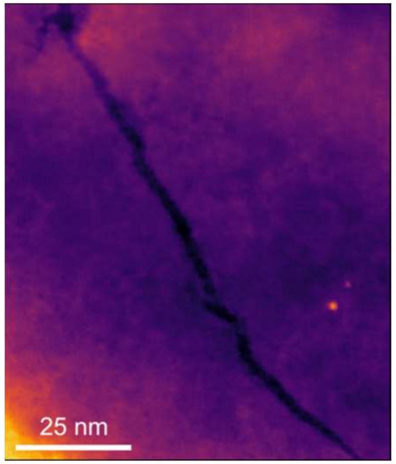


Daniel Kelly et al Advanced Materials 2021 (doi:10.1002/adma.202100668)

Engineered Graphene Liquid Mixing Cells



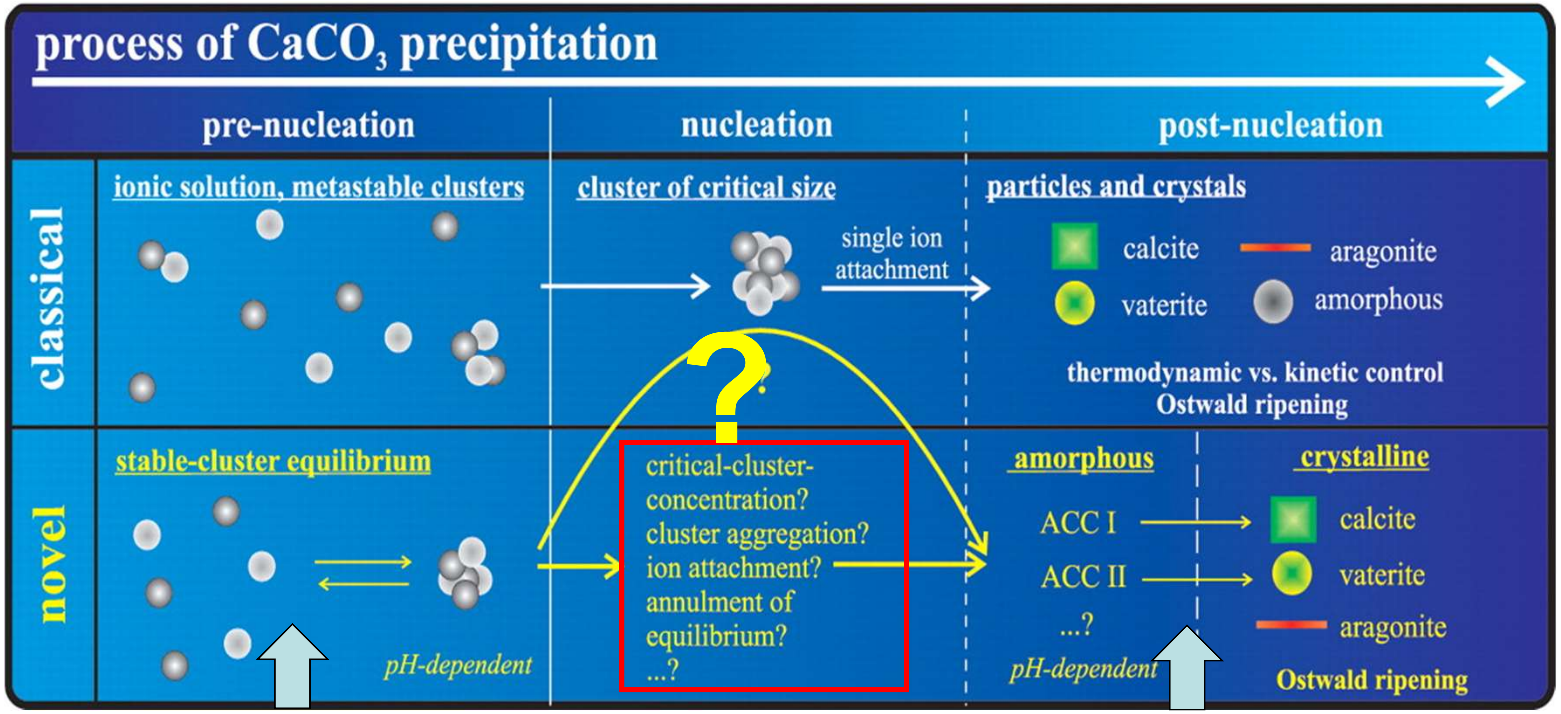




- **Use electron beam to pierce MoS_2 separation membrane – triggering nanofracture and liquid mixing under or near to the electron beam (rather than in a reservoir as conventional liquid cells)**
- **allows first imaging of the earliest stages of nucleation**
- **Graphene windows and small liquid thickness (total ~70 nm) maintains high resolution and analytical capabilities.**

Engineered Graphene Liquid Mixing Cells

Calcium carbonate precipitation – complex reaction that occurs through a non-classical nucleation mechanism



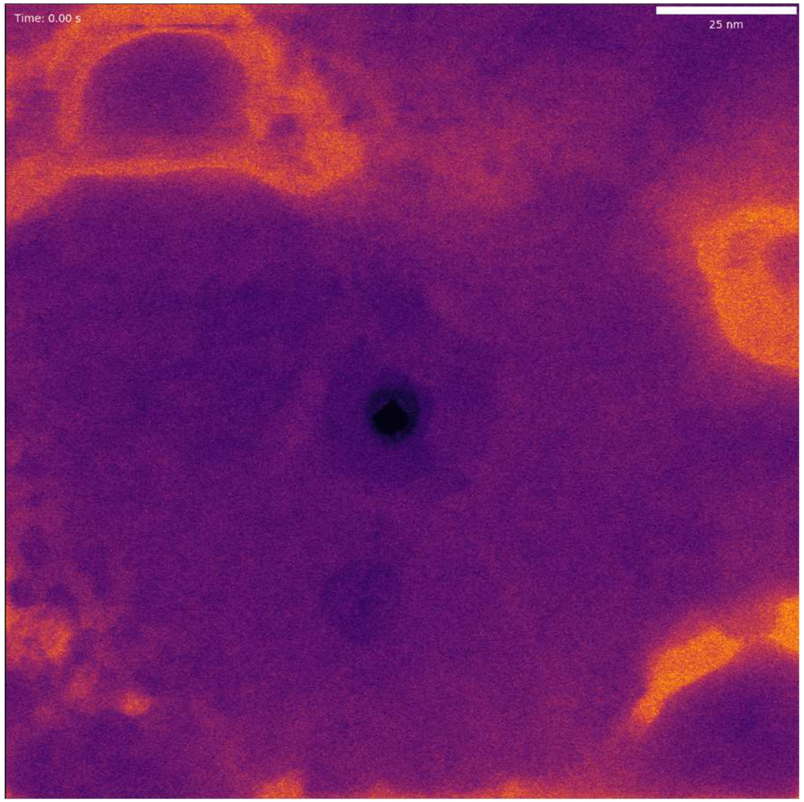
Static images accessible via cryo-TEM

Dynamics are accessible to conventional liquid cells

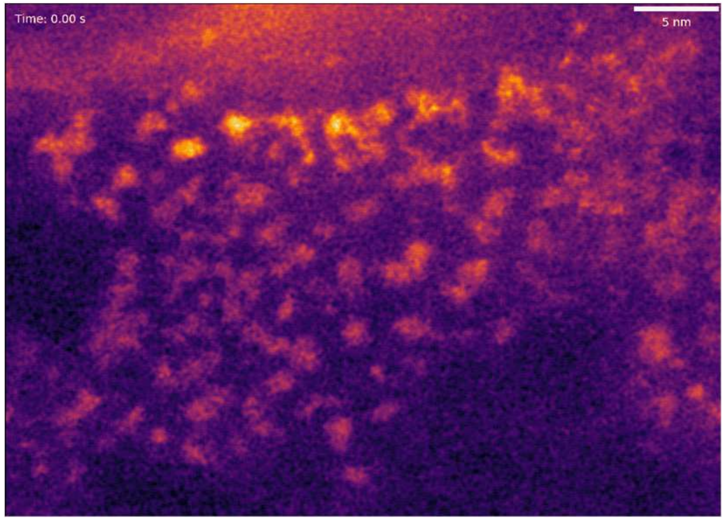
D. Gebauer, A. Völkel, H. Cölfen, *Science* 2008, *322*, 1819.

In situ imaging of early stage $CaCO_3$ precipitation

$CaCl_2$ (aq) + Na_2CO_3 (aq) = ?



Beam current: 120 pA, Dwell time: 1.0 µs, Flux: 1500 $e^- Å^{-2} s^{-1}$



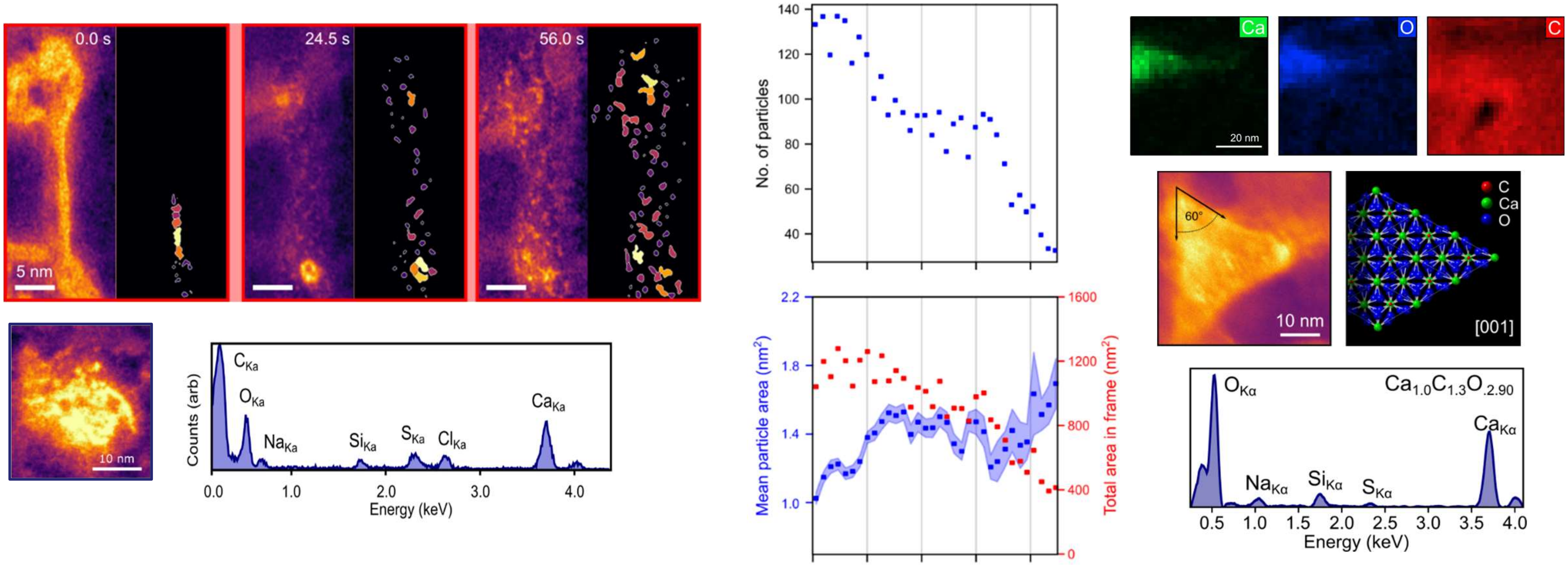
Beam current: 60 pA, Dwell time: 1.0 µs, Flux: 732 $e^- Å^{-2} s^{-1}$

<u>Observations during mixing</u>

- Early stage = formation of dense liquid globules
- Dehydration near pore
- Deposition of subnanometre particles
- Formation of ionic clusters
- Full crystallisation only when electron beam is blanked after mixing.

Daniel Kelly et al Advanced Materials 2021 (doi:10.1002/adma.202100668)

In situ imaging of early stage $CaCO_3$ precipitation



- **Early-stage species are not pre-nucleation clusters but rather phase-separated nanodroplets that form as spinodal decomposition products equilibrate toward a binodal composition**
- **Our observations provide first direct confirmation of liquid-liquid phase separation theory**

Daniel Kelly et al Advanced Materials 2021 (doi:10.1002/adma.202100668)

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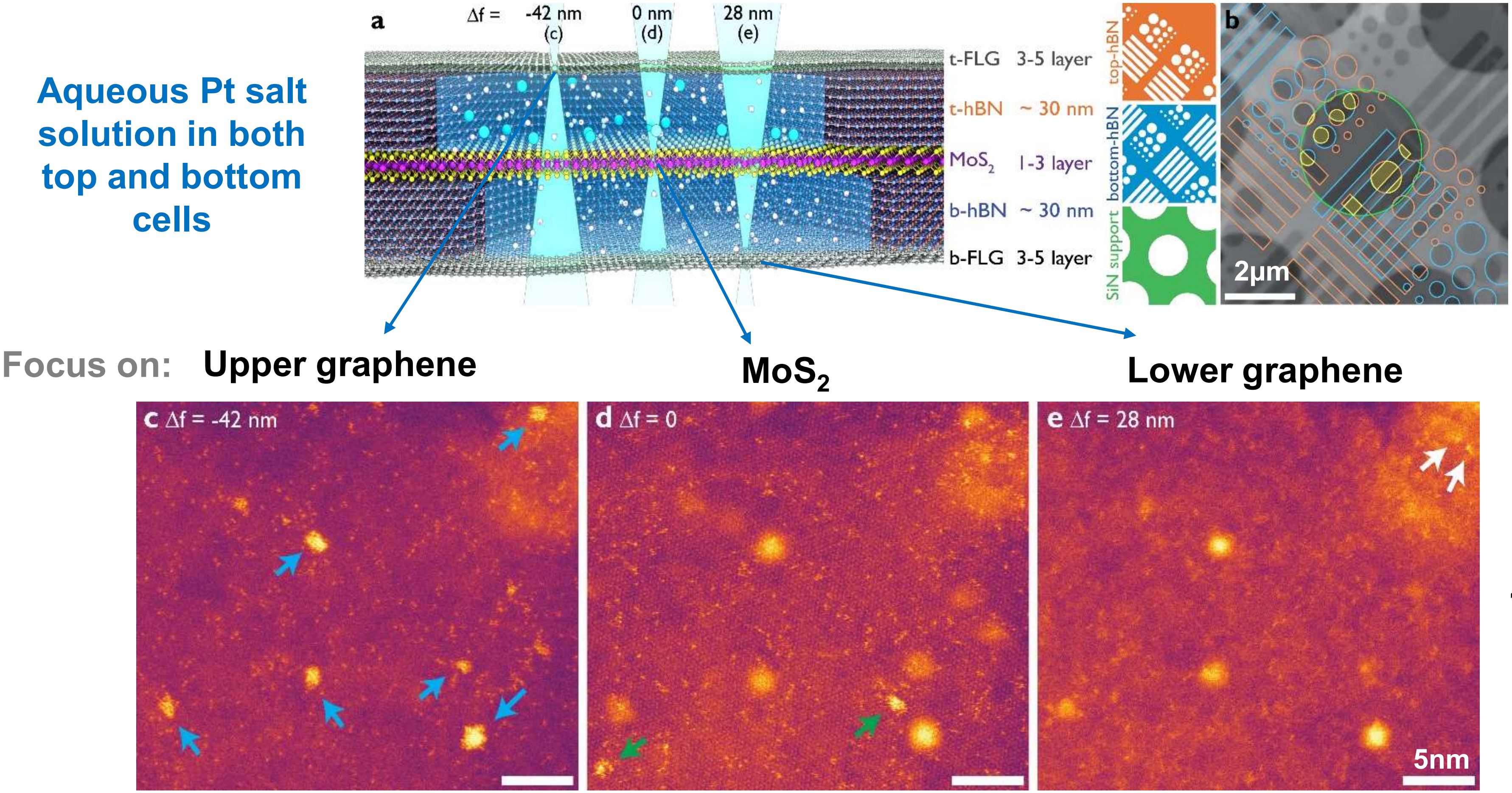
  - **Imaging of liquid-liquid mixing reactions**
  - **Tracking single surface adatoms in liquids**
- **3D reconstruction in liquid cells**

Tracking single surface atoms inside double Graphene Liquid Cells

Aqueous Pt salt solution in both top and bottom cells

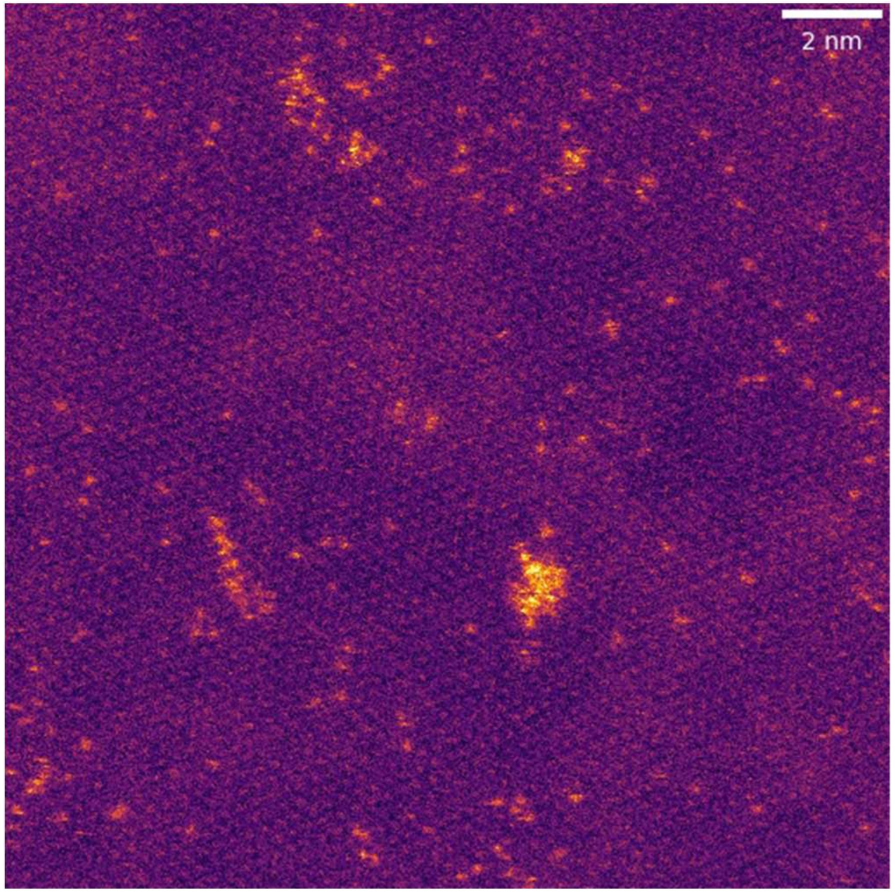


Double graphene cell design (total liquid thickness ~70nm) creates fully submerged internal MoS_2 membrane

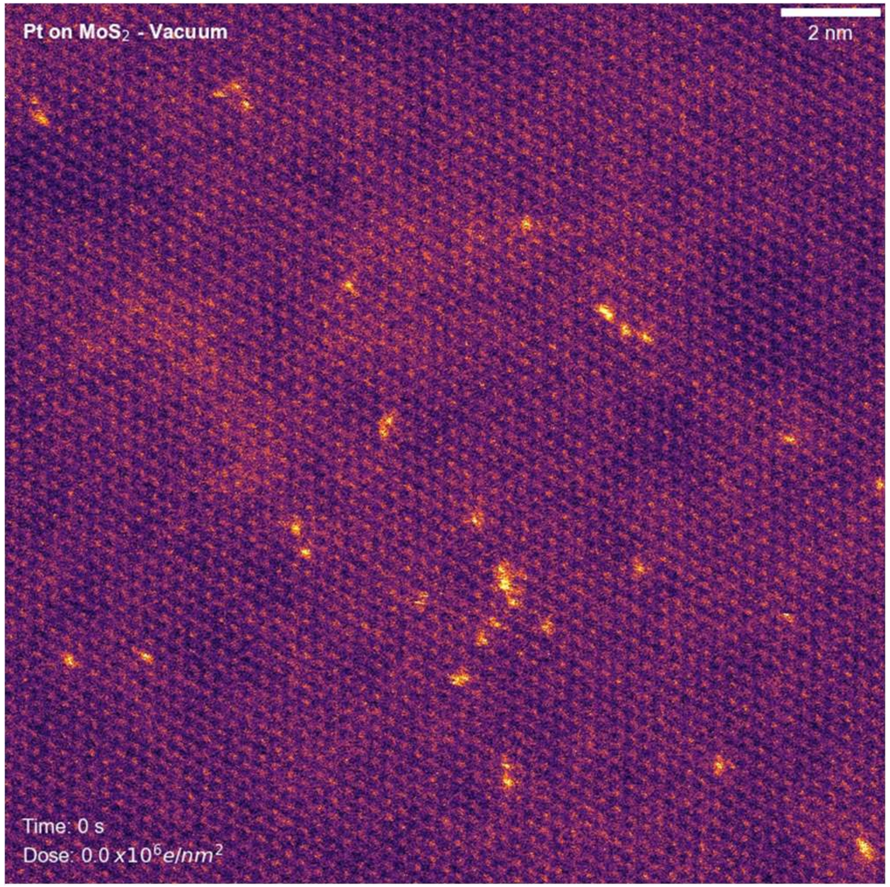
Nick Clark et al. Nature (2022), “Tracking single adatoms in liquid in a TEM”

Comparison between Pt on MoS_2 behaviour in vacuum and in liquid

In aqueous PtCl salt

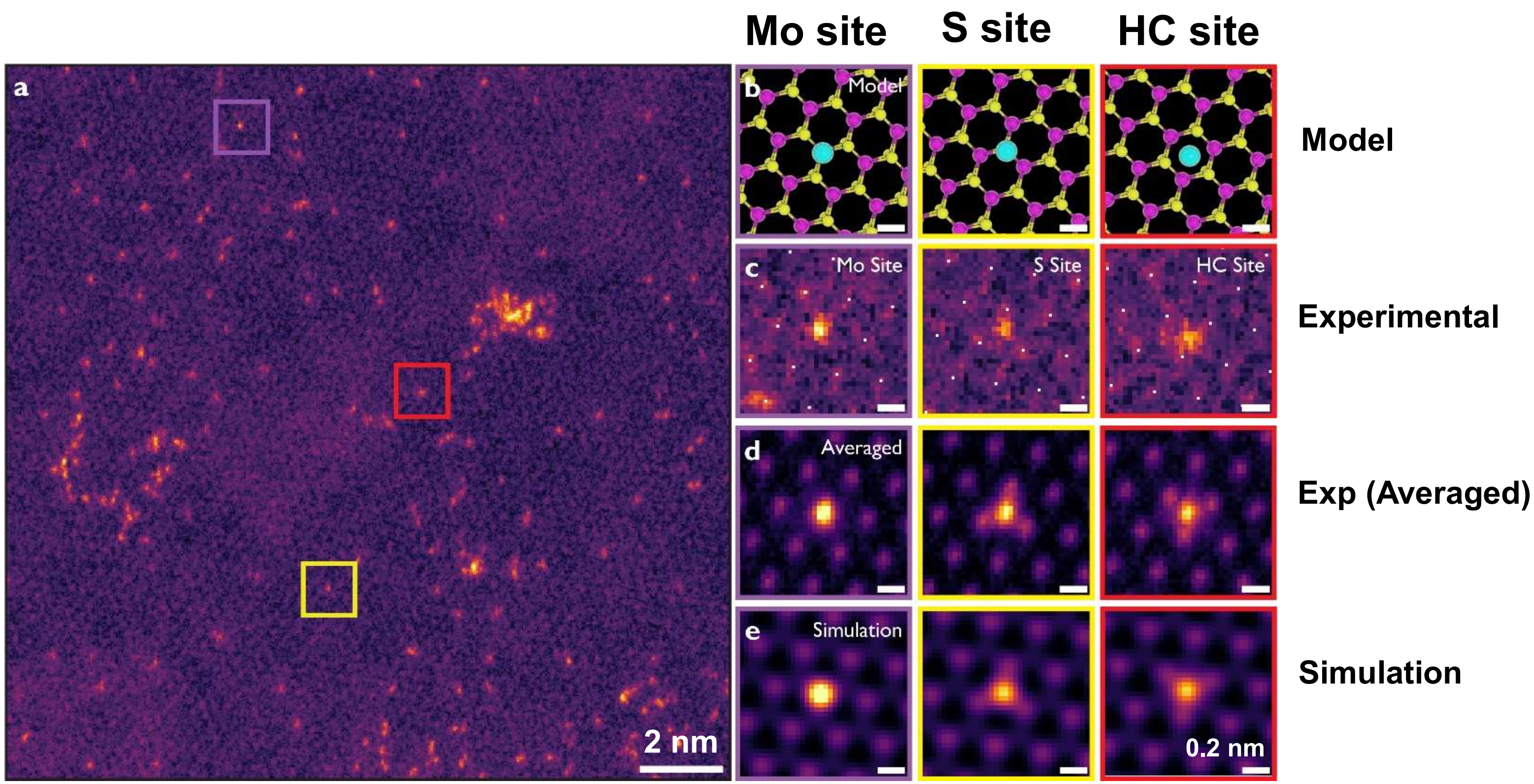


Vacuum



Nick Clark et al. Nature (2022), "Tracking single adatoms in liquid in a TEM"

Preferred sites for Pt adatoms on MoS_2 in Liquid Water

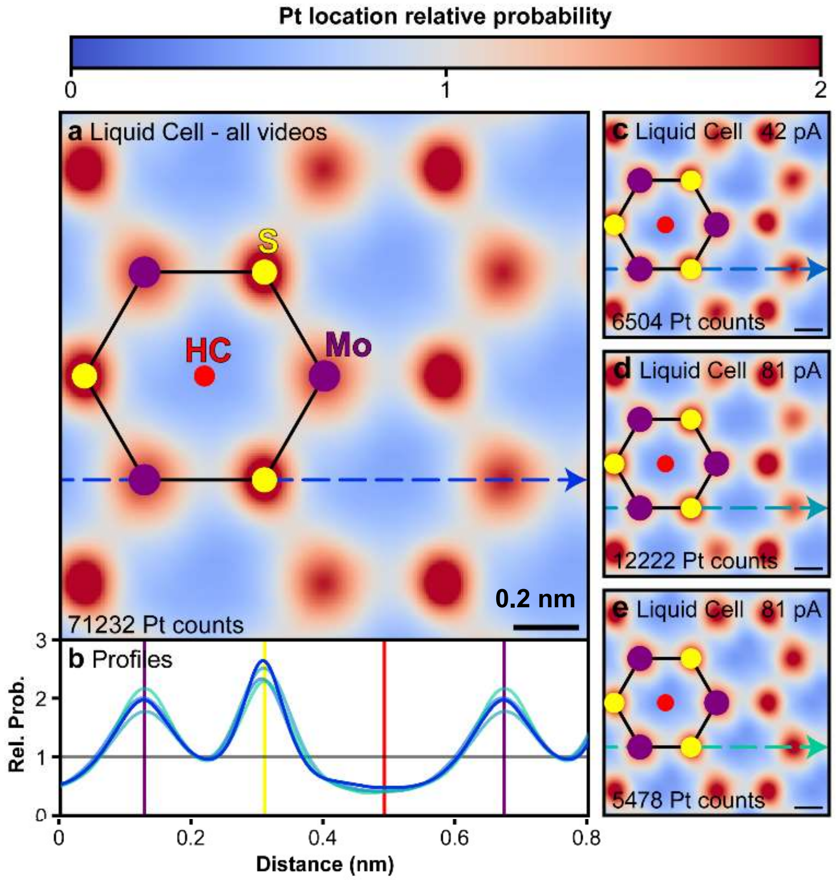


- Robust enough for extended atomic resolution imaging of Pt atoms on submerged MoS_2 monolayer
- Majority of Pt adatoms can be assigned to one of the high symmetry atomic sites (Mo, S or hexagonal centre)

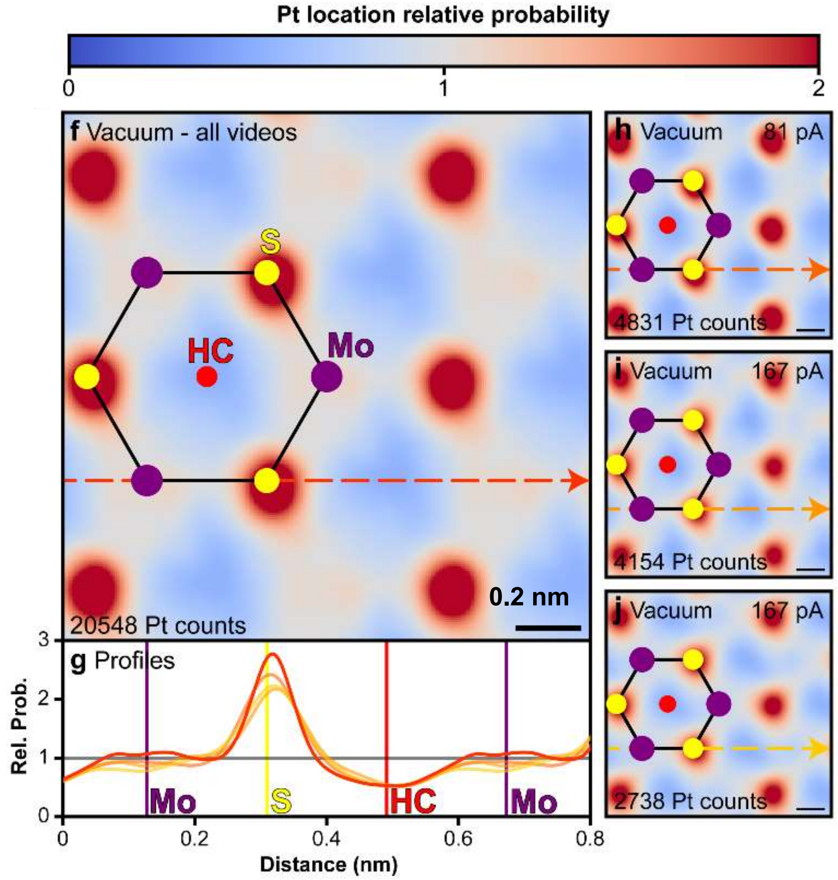
Nick Clark et al. Nature (2022), “Tracking single adatoms in liquid in a TEM”

Preferred sites for Pt adatoms on MoS_2 in Liquid compared to measurement in vacuum

In aqueous PtCl salt



Vacuum

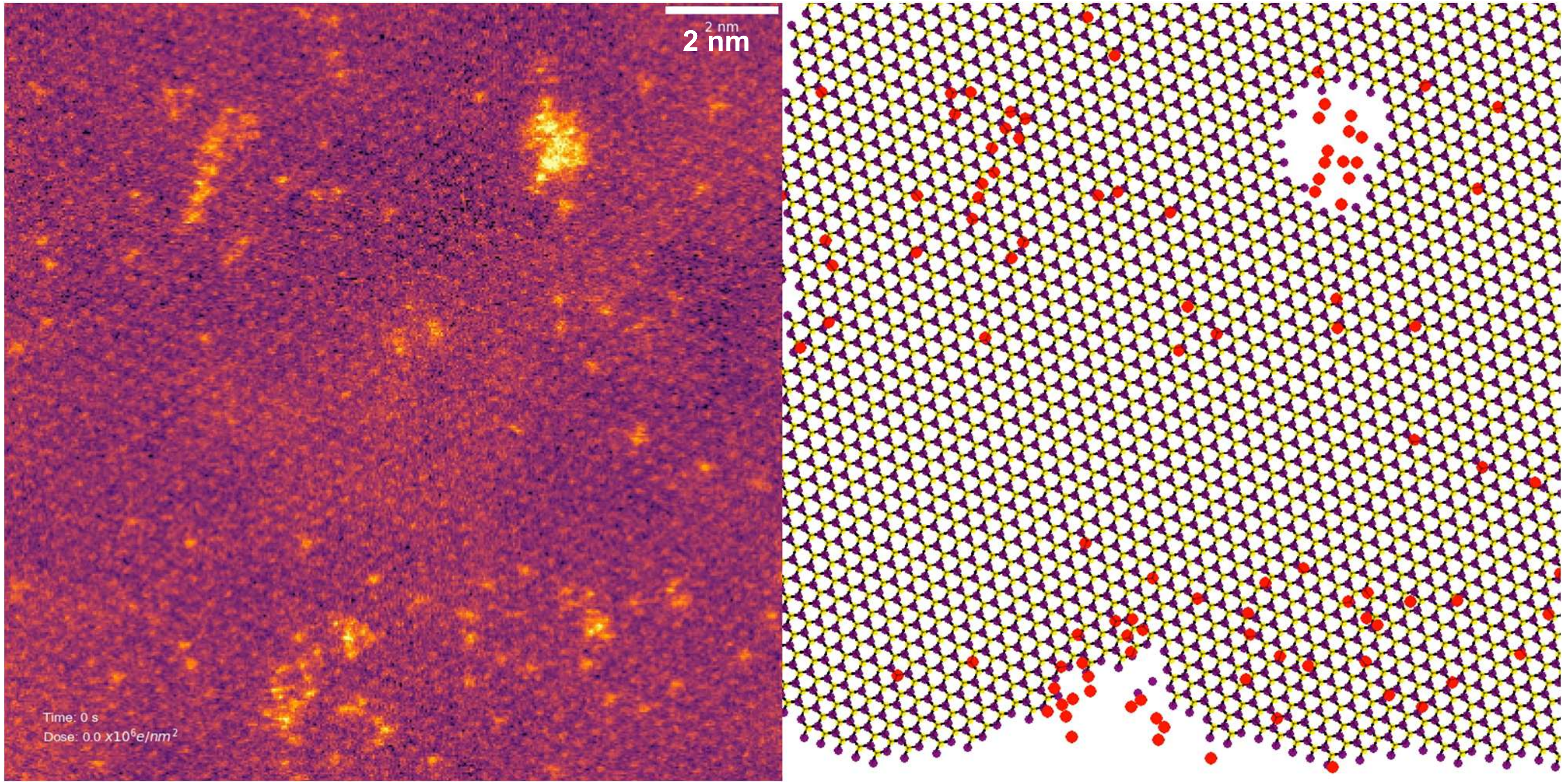


Averaged Pt adatom positions (>90,000 measurements)

(dehydration of graphene liquid cell by drilling hole, then leaving in vacuum overnight recovers vacuum behaviour)

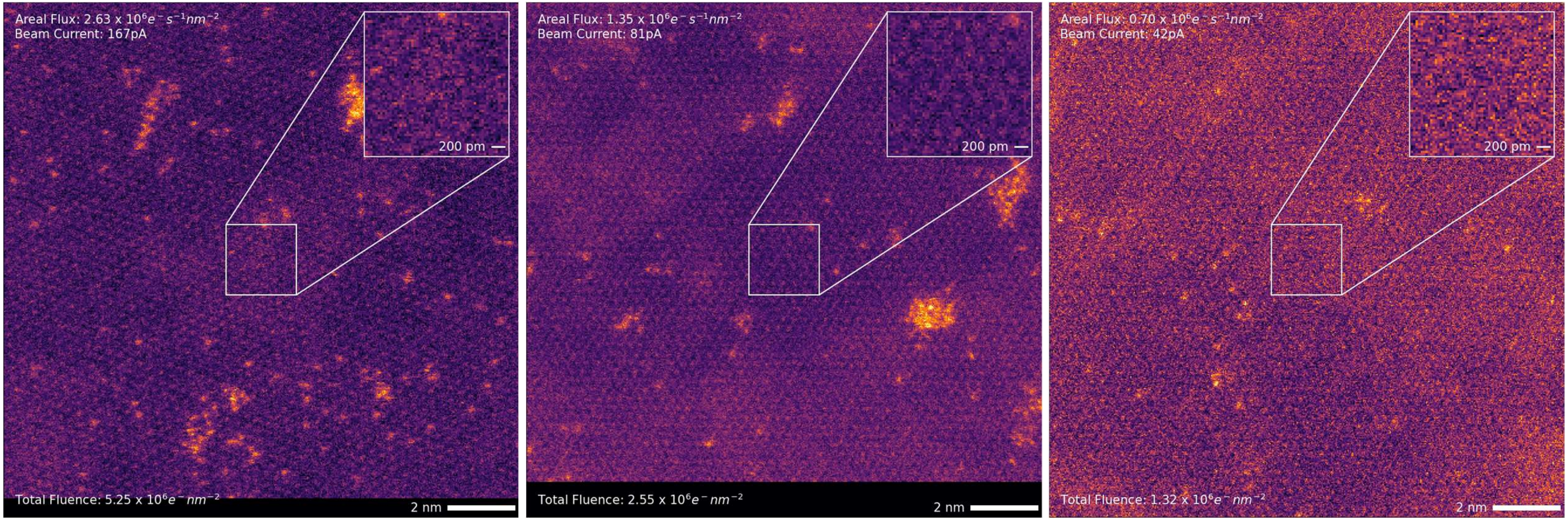
Nick Clark et al. Nature (2022), "Tracking single adatoms in liquid in a TEM"

Tracking dynamic motion of Pt adatoms on MoS_2 in liquid



Nick Clark et al. Nature (2022), “Tracking single adatoms in liquid in a TEM”

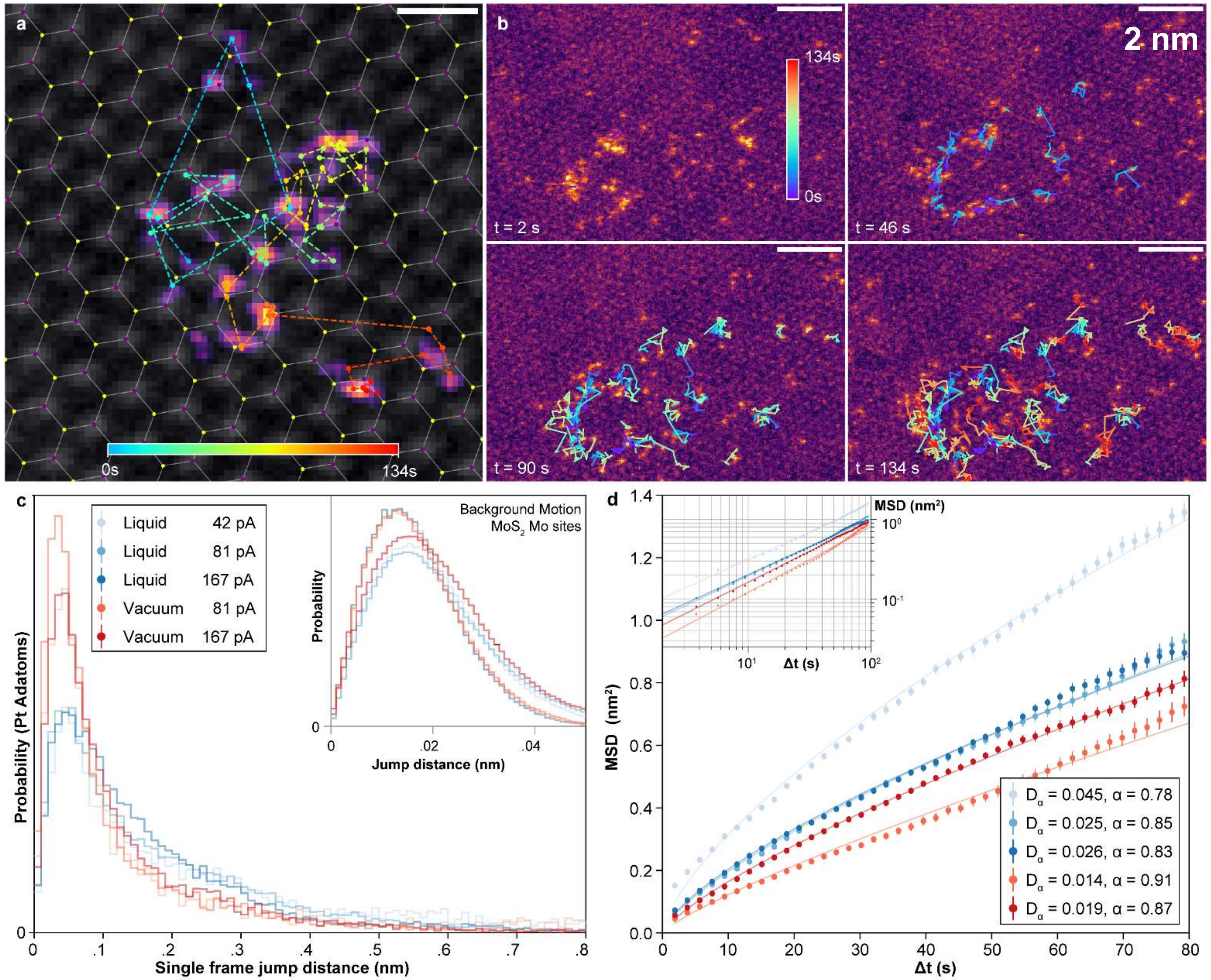
Tracking dynamic motion of Pt adatoms on MoS_2 in liquid



High Dose
High SNR

Low Dose
Low SNR

Tracking dynamic motion of Pt adatoms on MoS_2 in liquid



Detailed atomic tracking reveals big difference in atomic motion for liquid cell data compared to vacuum

(dehydration of graphene liquid cell by drilling hole, then leaving in vacuum overnight recovers vacuum behaviour)

Lowest probe current gives fastest adatom motion in liquid

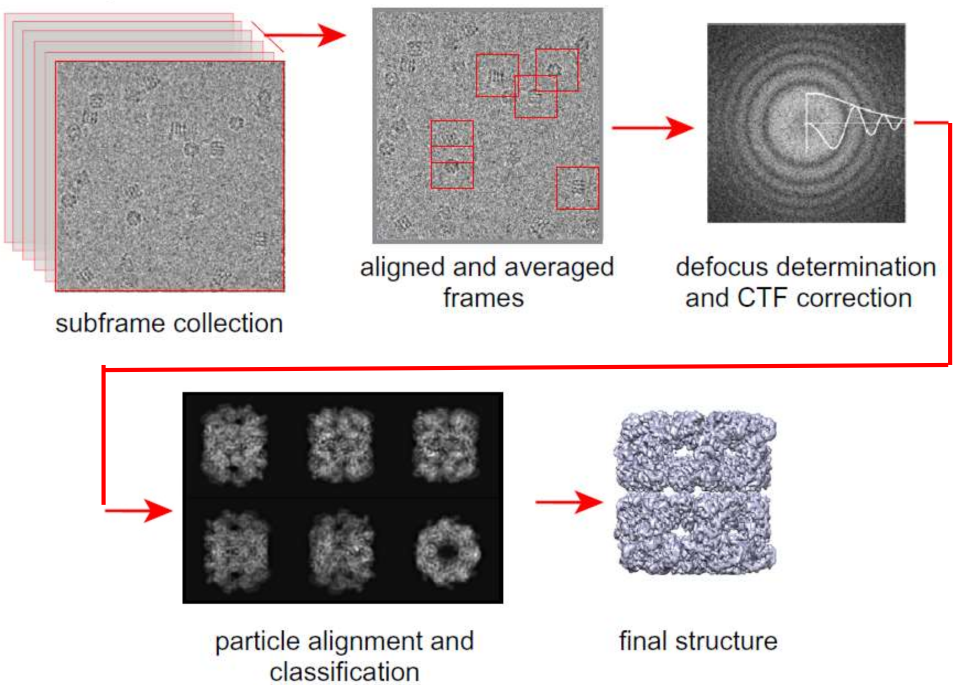
Nick Clark et al. Nature (2022) "Tracking single adatoms in liquid in a TEM"

Outline

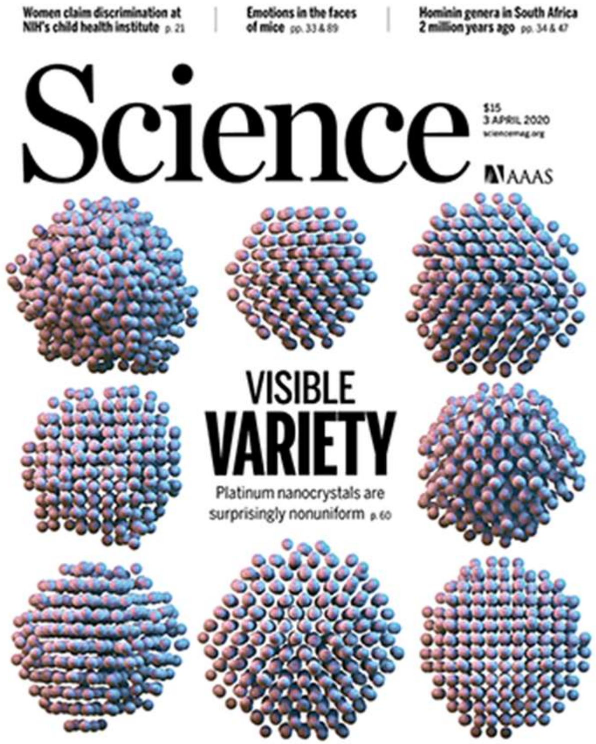
- **Dynamics of ion exchange in few layer clays**
- **TEM Imaging in liquids**
- **2D Heterostructure Liquid Cells**
  - **Imaging of liquid-liquid mixing reactions**
  - **Tracking single surface adatoms in liquids**
- **3D reconstruction in liquid cells**

3D reconstruction in liquids?

Cryo EM Single Particle Reconstruction (SPR) is technique commonly used for proteins which are much more beam sensitive than inorganic particles



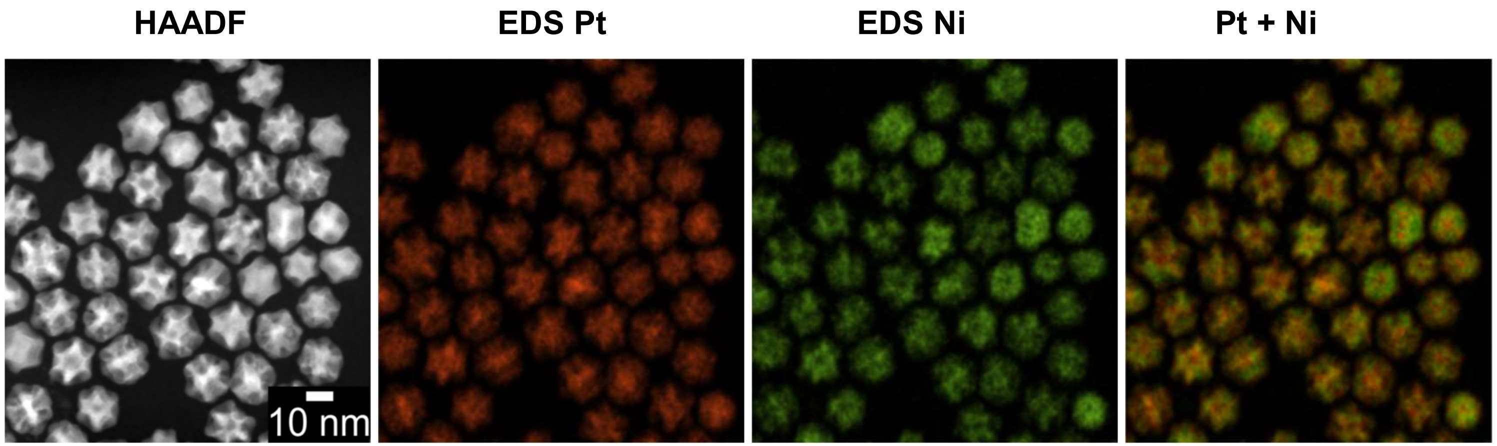
From Marta Carroni, Helen R. Saibil, Methods, 95, p78 (2016)



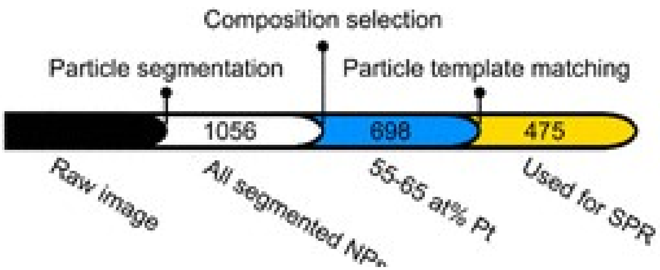
Byung Hyo Kim et al Science 2020

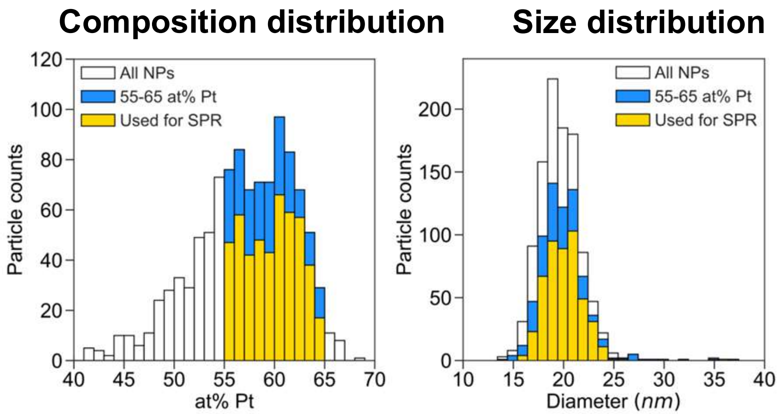
https://www.science.org/doi/10.1126/science.aax3233

Segmenting inorganic nanoparticle populations for SPR



Nanoparticle population segmented based on mean composition and template matching

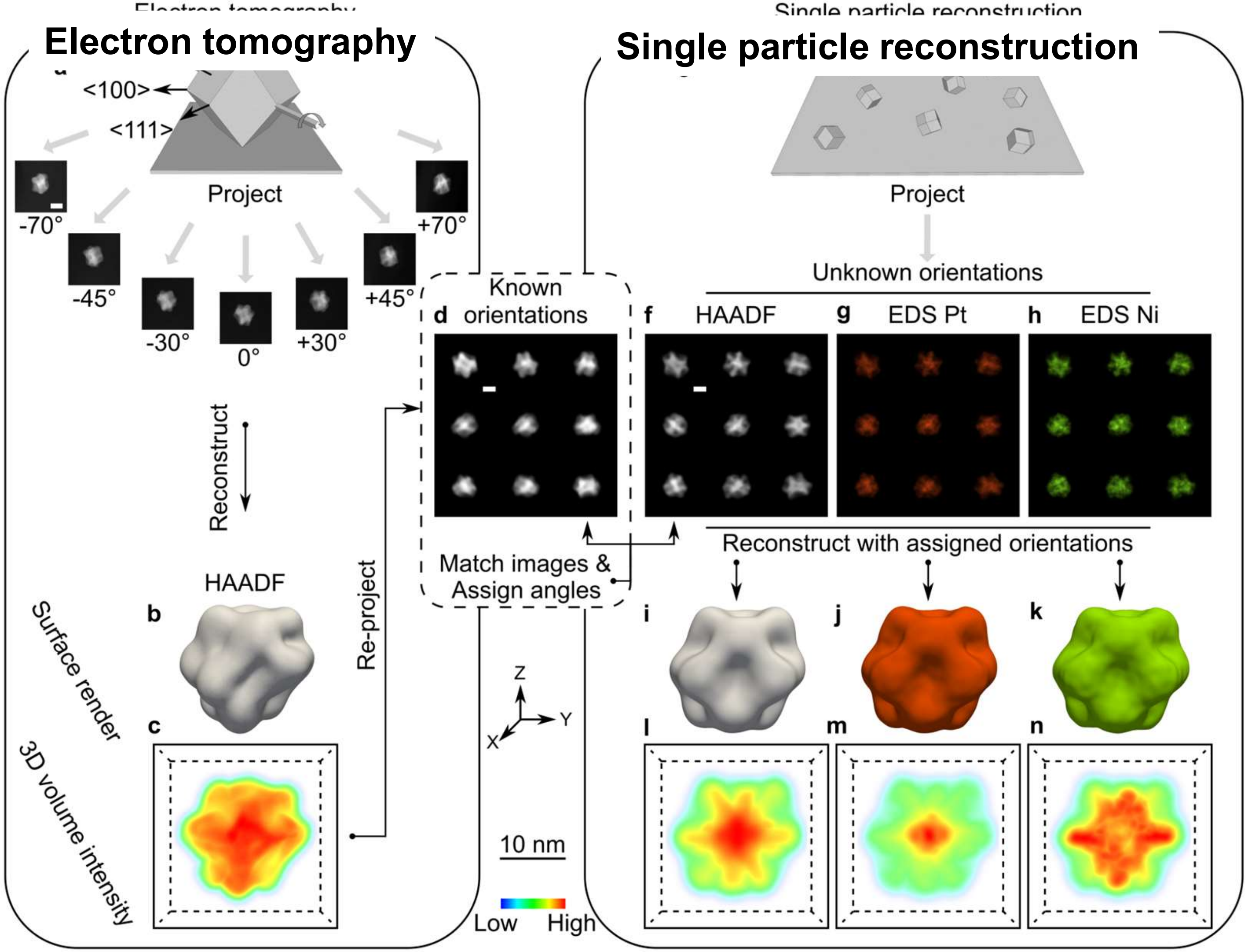




SPR requires approximation of homogeneity therefore only ~50% of segmented particles are used

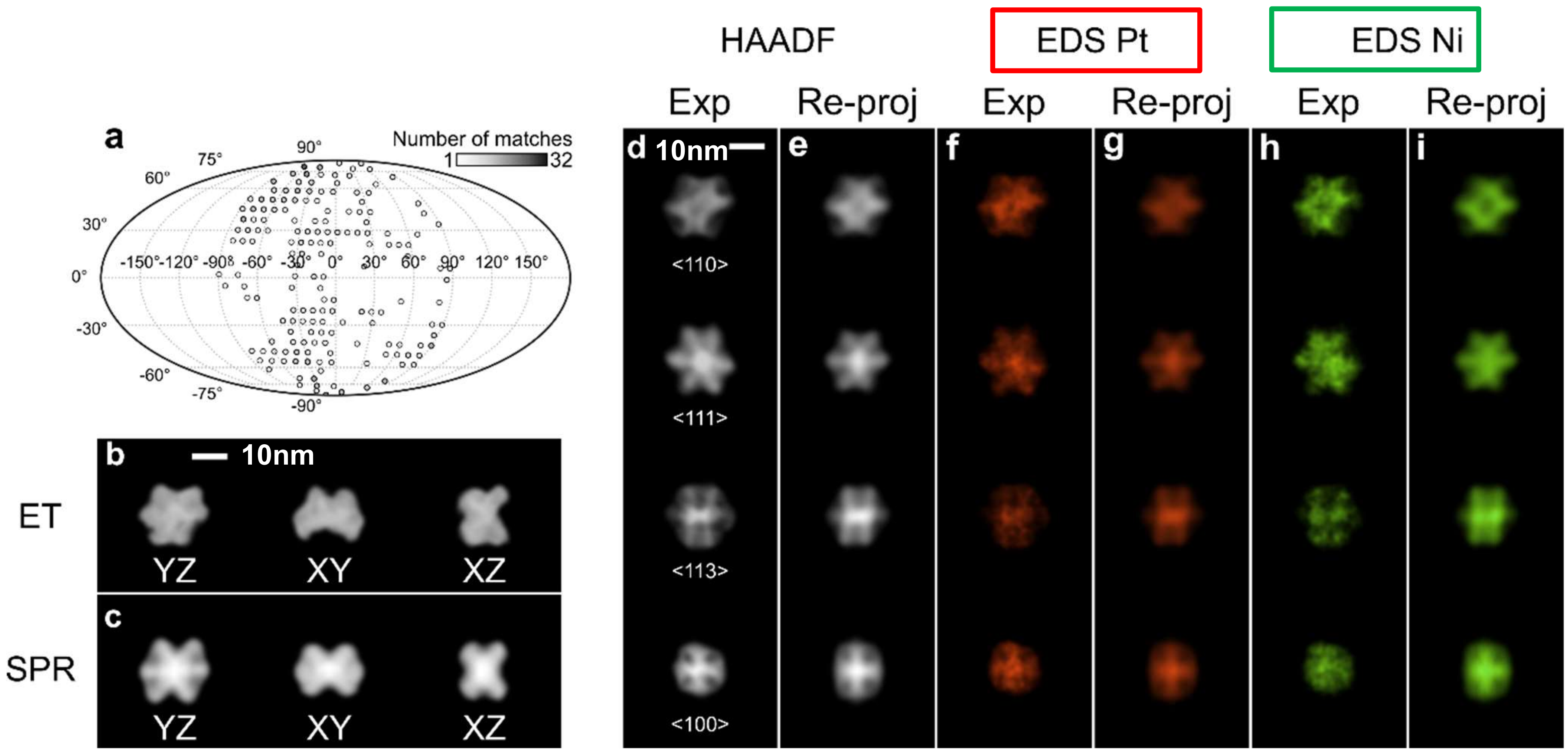
Wang et al Nano Letters (2019), 10.1021/acs.nanolett.8b03768

Workflow for spectroscopic single particle reconstruction



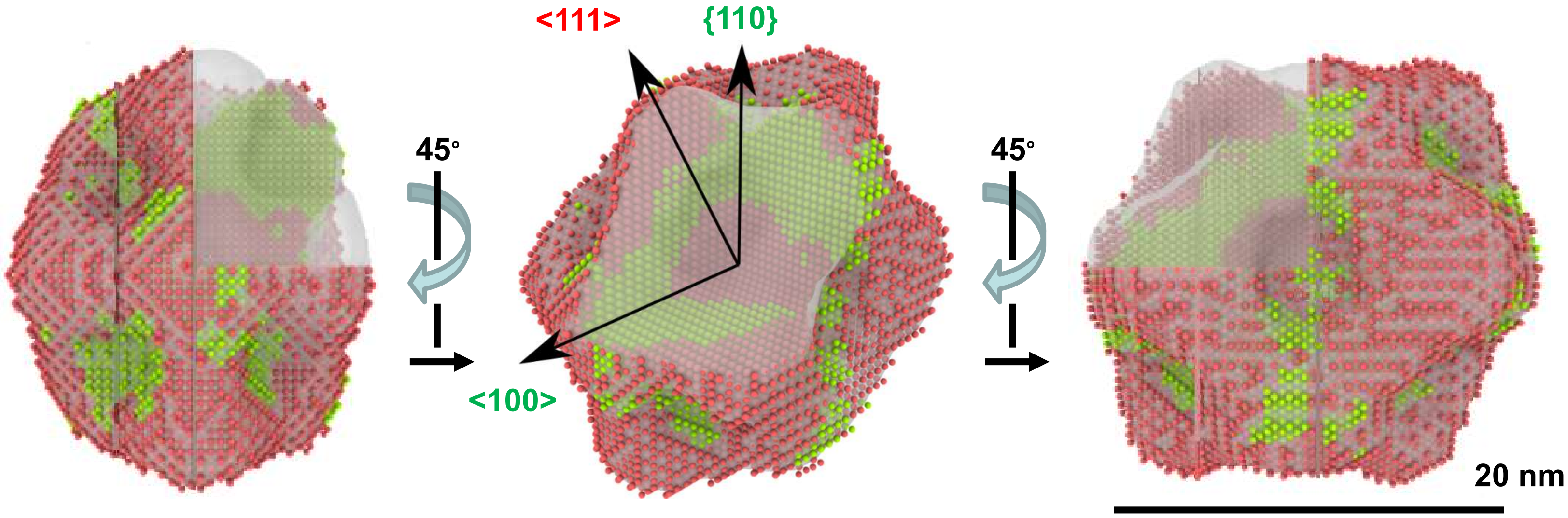
Wang et al Nano Letters (2019), 10.1021/acs.nanolett.8b03768

Verifying fidelity of spectroscopic single particle reconstruction (SPR) vs experiment and Electron Tomography (ET)



Wang et al Nano Letters (2019), 10.1021/acs.nanolett.8b03768

Visualisation of 3D chemical segregation



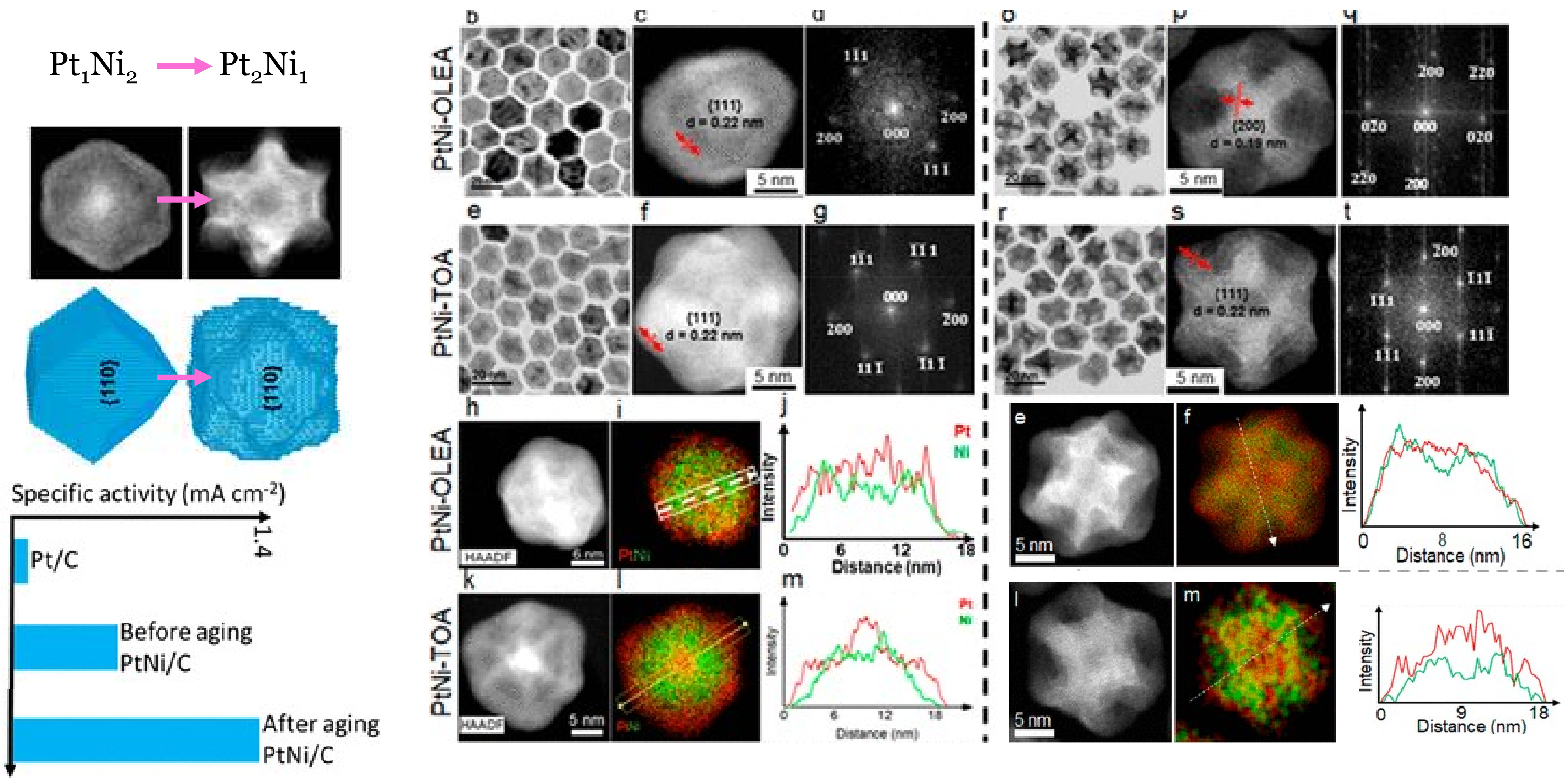
From inside to outside:
- Pt-rich core
- Ni-rich hollow octahedral intermediate shell
- Pt-rich rhombic dodecahedral skeleton framework

In terms of surface segregation:
- Pt rich at <111> vertices
- Ni rich at <100> vertices and {110} facets

Kinetically produced growth seed	Surface ligand interactions	Faster leaching of Ni from surfaces	Pt has the larger lattice parameter so strain reduction at vertices

Wang et al Nano Letters (2019), 10.1021/acs.nanolett.8b03768

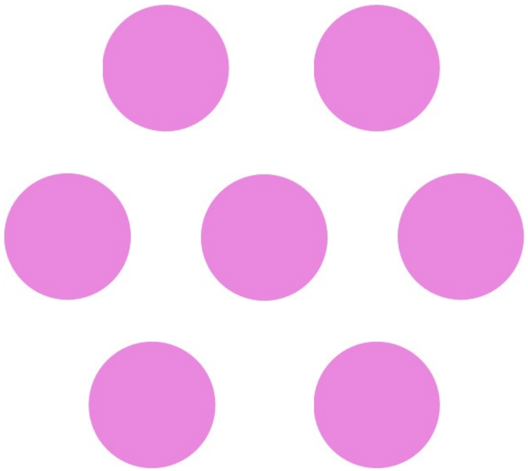
3D chemical segregation evolution during aging in Oleylamine solution

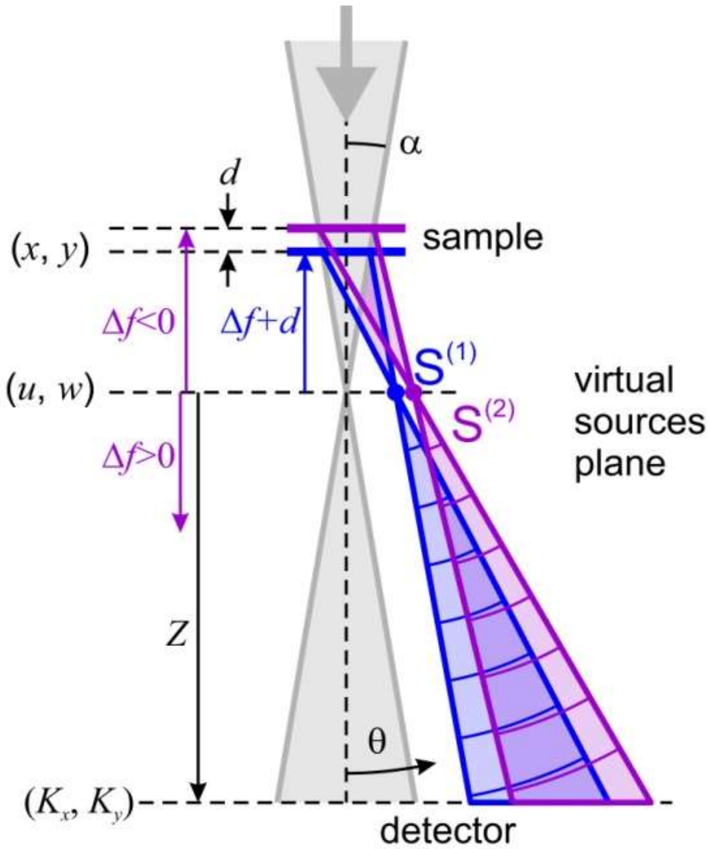


Leteba et al Nano Letters (2021), 10.1021/acs.nanolett.1c00706

Recovering 3D information from Convergent Beam Electron Diffraction (CBED)

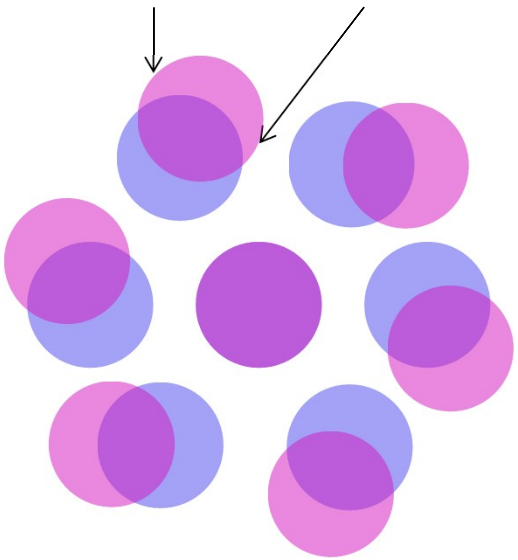
CBED
Graphene





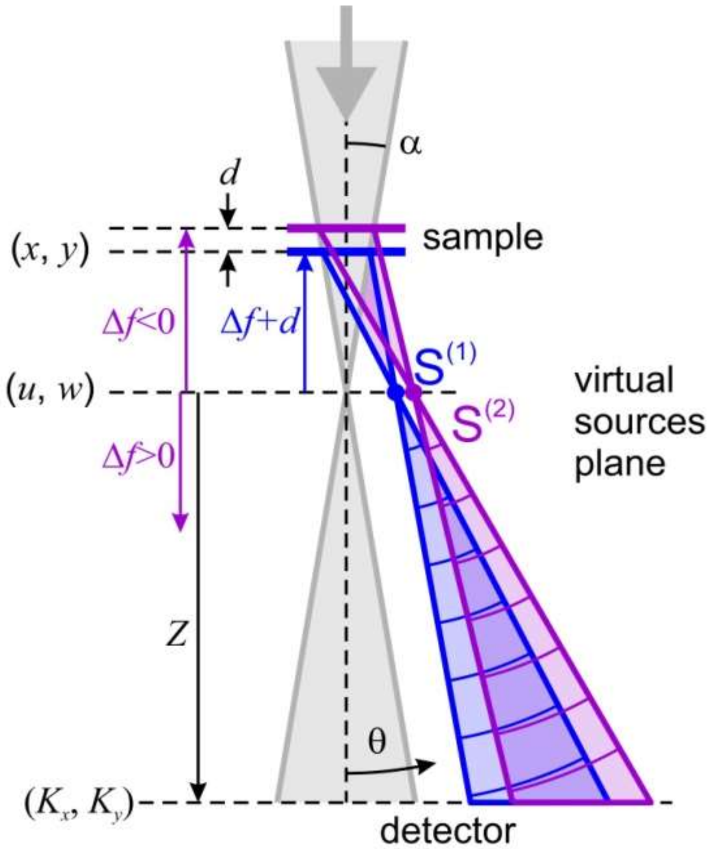
T. Latychevskaia et al PNAS 2018
Latychevskaia T, *Carbon*. 2023; 201: 244-250.

Recovering 3D information from Convergent Beam Electron Diffraction (CBED)



Twist Rotation

Interference between diffraction discs gives holographic contrast = phase information

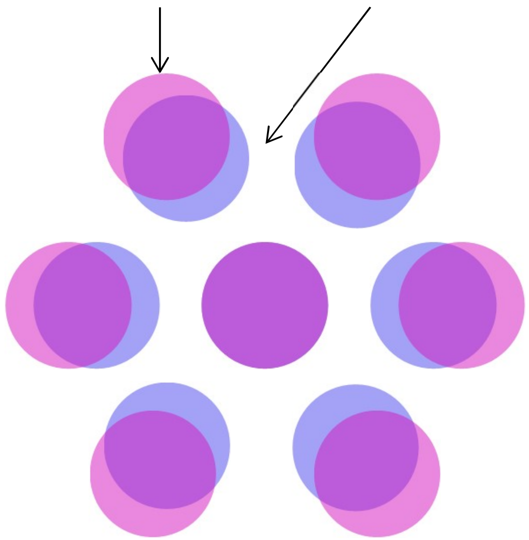


T. Latychevskaia et al PNAS 2018

Latychevskaia T, *Carbon*. 2023; 201: 244-250.

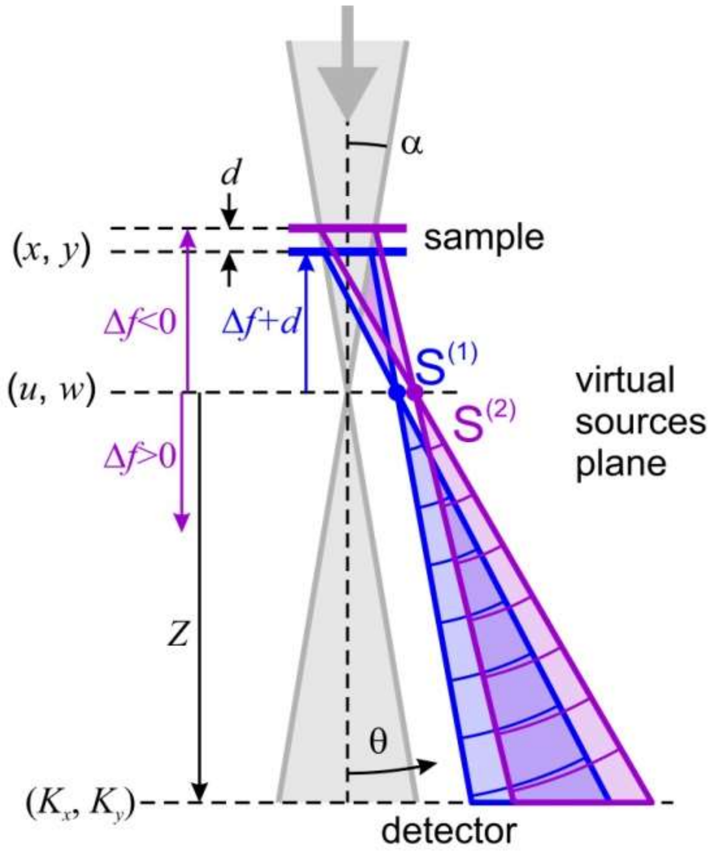
Recovering 3D information from Convergent Beam Electron Diffraction (CBED)

CBED
Graphene + hBN



No rotation

Interference between diffraction discs gives holographic contrast = phase information

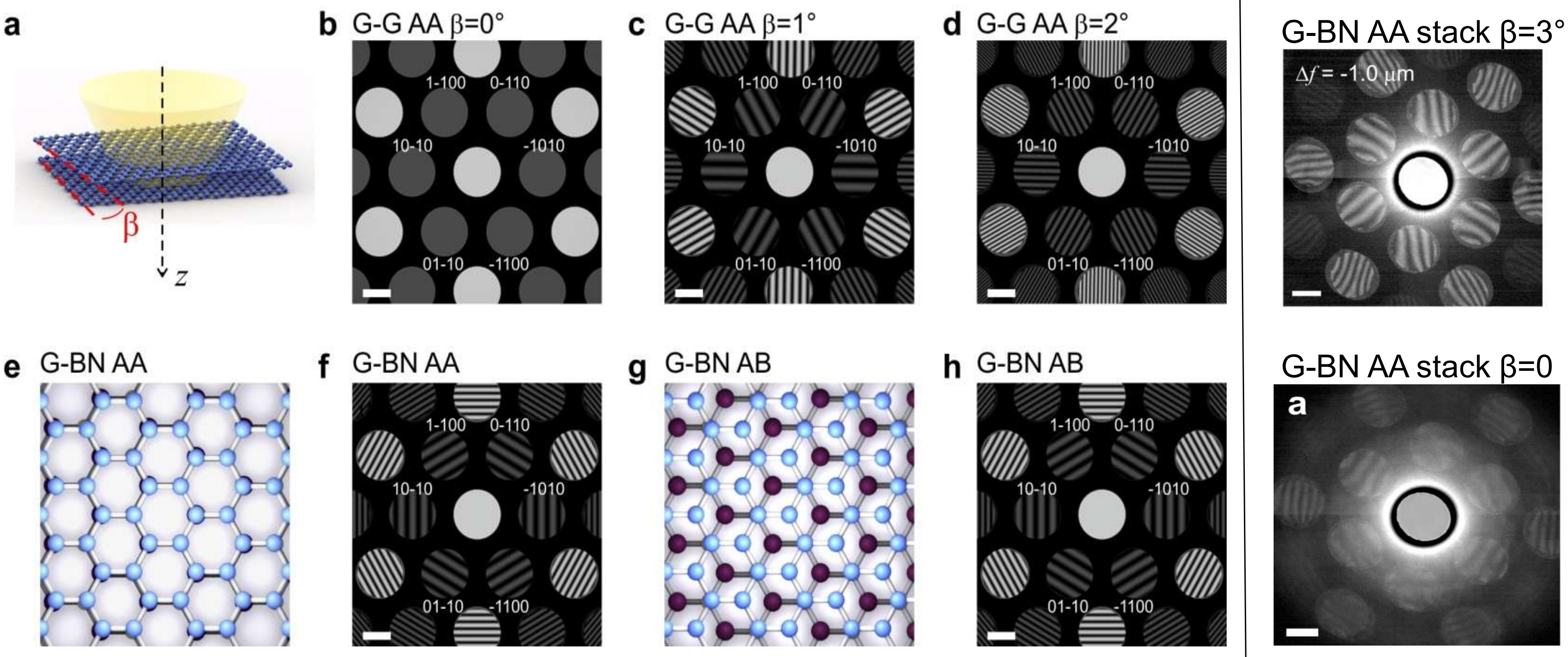


T. Latychevskaia et al PNAS 2018

Latychevskaia T, *Carbon*. 2023; 201: 244-250.

CBED is highly sensitive to bilayer rotation and local stacking

Simulations | **Experiment**

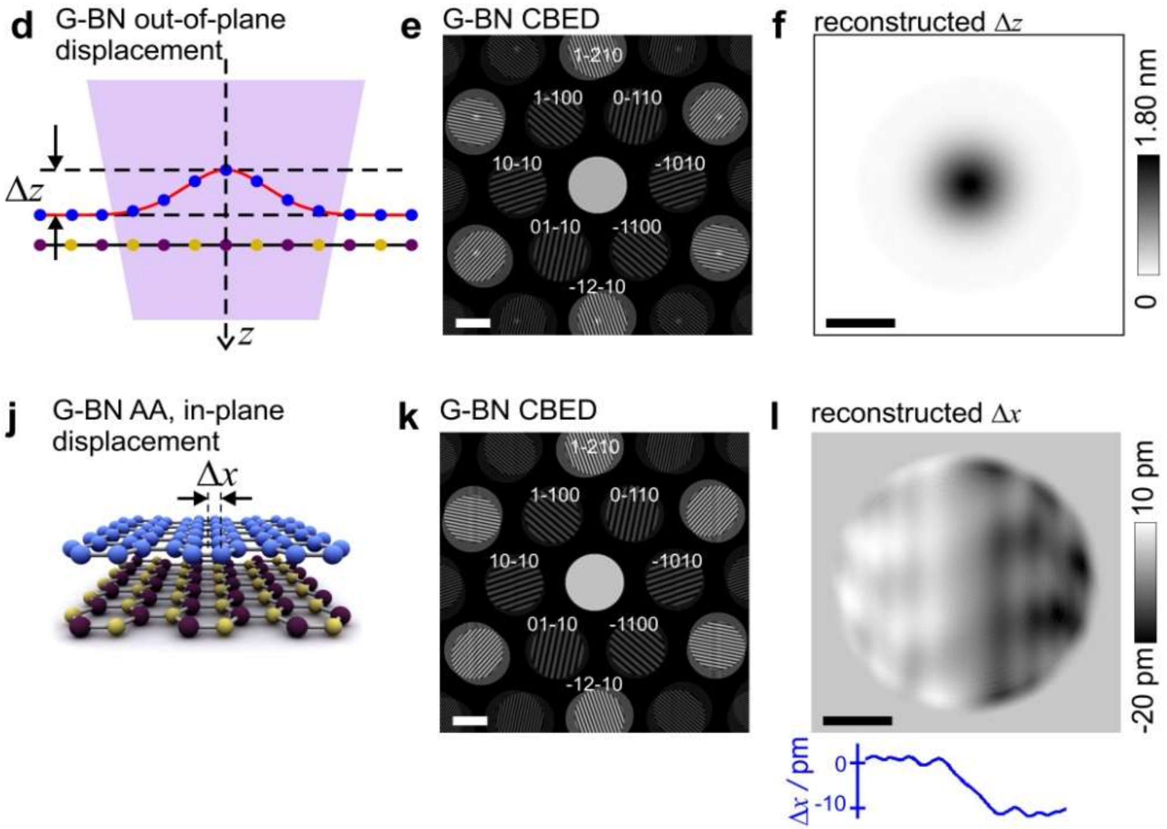


T. Latychevskaia et al PNAS 2018

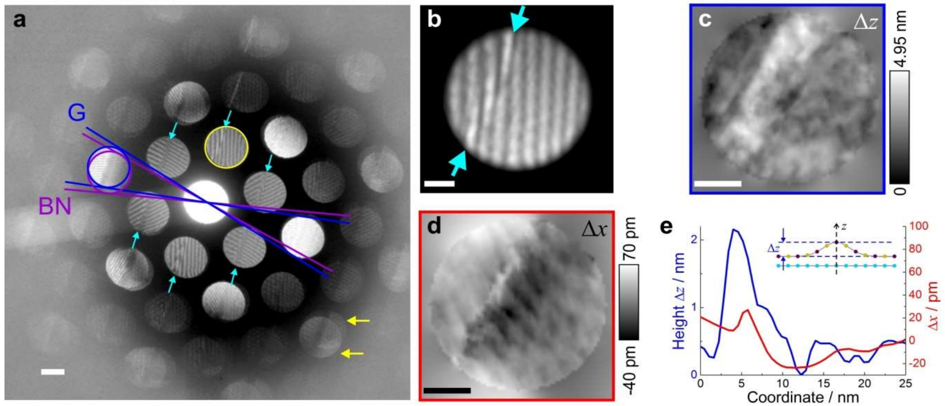
Latychevskaia T, *Carbon*. 2023; 201: 244-250. https://doi.org/10.1016/j.carbon.2022.09.003

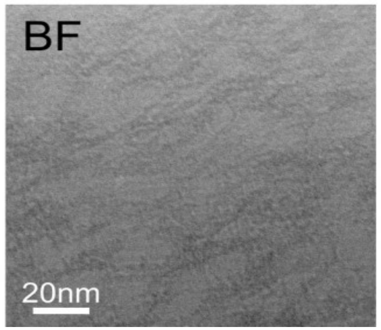
CBED is highly sensitive to ripples and local strain in 2D heterostructures

Simulations



Experiment





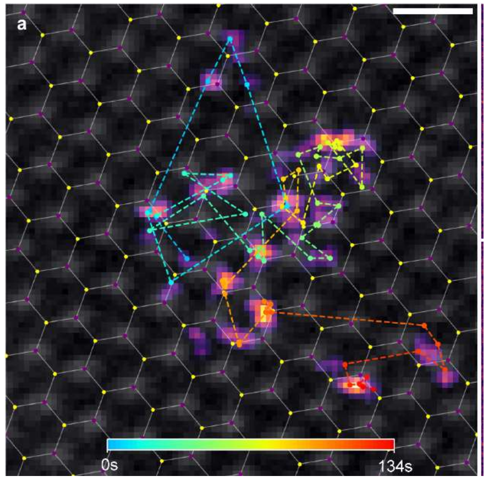
Experimental CBED patterns reveal quantitative height information on local ripple disorder- in G-hBN

T. Latychevskaia et al PNAS 2018

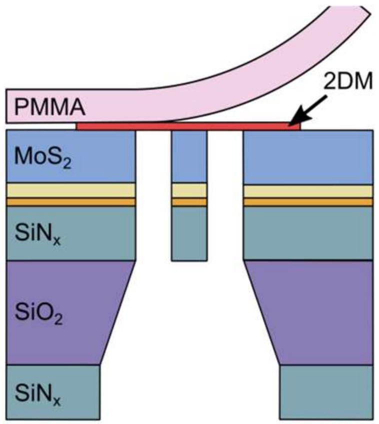
Latychevskaia T, *Carbon*. 2023; 201: 244-250. https://doi.org/10.1016/j.carbon.2022.09.003

Take home messages

- **The 2D heterostructure in situ TEM platform provides ability for atomic resolution imaging of the earliest stages of chemical reactions, chemical synthesis and adatom motion at solid liquid interfaces**
- **New opportunities to understand role of disorder on adsorption behaviour for these systems**
- **Combination with ML would enable reduction of electron beam flux and improved understanding**



Nick Clark et al https://arxiv.org/abs/2203.04906
(now accepted in Nature)



Improved transfer success for 2D heterostructures

M Hamer, et al **Nano Letters 2020,** 20, 9, 6582**,**

Thank you

D. Hopkinson, A.P. Rooney, Y. Zou, L. Nguyen, D. Kelly, N. Clark, S. Fairclough, A. Rakowski, A. Weston, Y. Li, M. Zhou, M. Hamer, Kozikov, A. Summerfield, D. Terry, R. Gorbachev,Mishchenko, K.S. Vasu, E. Khestanova, J. Birkbeck, L Mogg, M. Zhu, D. A. Bandurin B. Radha, I. Grigorieva, K.S. Novoselov, A.K.Geim, R. Nair, R Young, M Lozada-Hidalgo, V Sreepal, R Nair, V Zólyomi, V. Enaldiev, S. Magorrian, V Fal'ko (Manchester) **A Michaelades S** (Cambridge) **C. Bacaksiz, S. Milanovic, F. Peeters, J Bekaert, M.V. Milošević,** (Antwerp, Belgium) **Prof D. Gebauer** (Leibniz University of Hanover) **T. Slater, C. Allen, M. Danaie** (ePSIC)

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