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EPSRC Engineering and Physical Sciences Research Council

erc European Research Council

Through Graphene and beyond
(finding unexpected atoms in a pencil trace)

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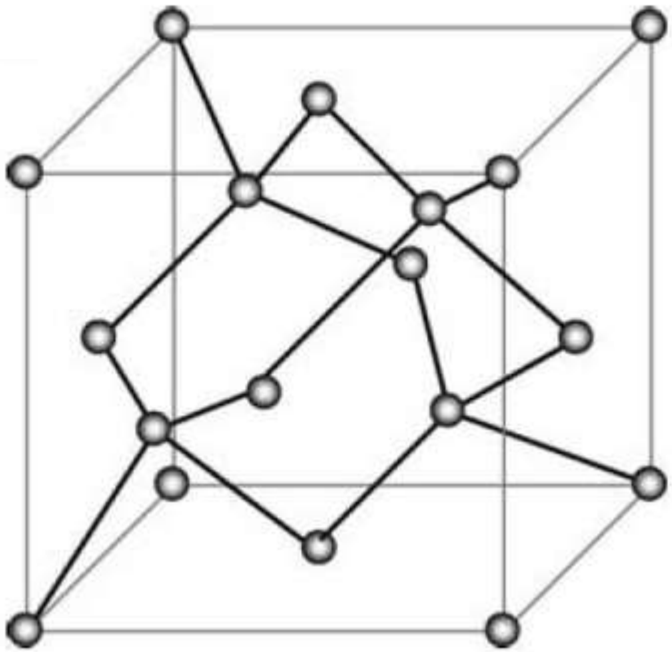
M I Katsnelson, A N Rudenko (Radbound University, Netherlands)

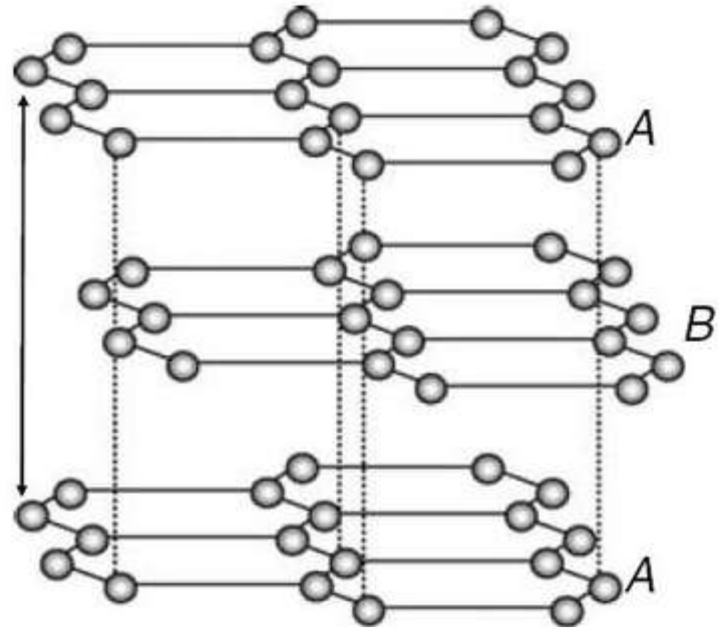
F Ding, W Zhao (Hong Kong Polytechnic University)

Outline

- **Reminder/Introduction to Graphene**
- **An new 2D approach to engineer Functional Electronics**
- **Fast flow properties of 2D channels**
- **What can we do with a Graphene Sandwich?**

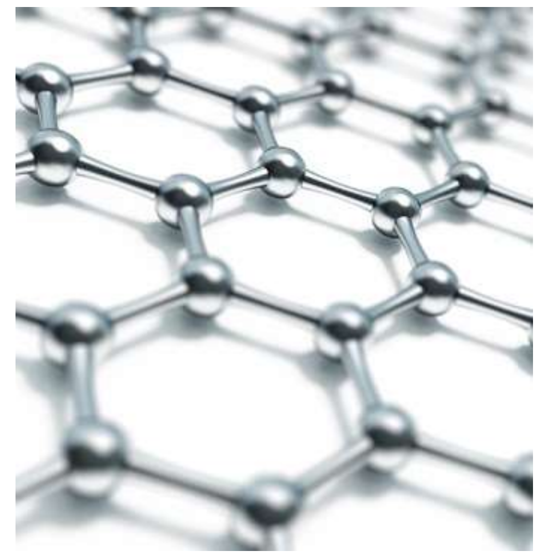
Carbon allotropes





If you peel a **one atom thick layer** from graphite
it has some **amazing new properties** and is known as

Graphene



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Graphene's Properties

- ***thinnest imaginable material***
- ***strongest material ever measured*** **(theoretical limit)**
- ***stiffest known material*** **(stiffer than diamond)**
- ***most stretchable crystal*** **(up to 20% elastically)**
- ***highest thermal conductivity*** **(outperforming diamond)**
- ***highest current density at room T*** **(million times copper)**
- ***highest electrical conductivity*** **(100 times more than in Si, *conducts electricity in the limit of no electrons*)**
- ***most impermeable*** **(even He atoms cannot squeeze through) …**
- ***Almost entirely transparent*** **(97.3 %)**

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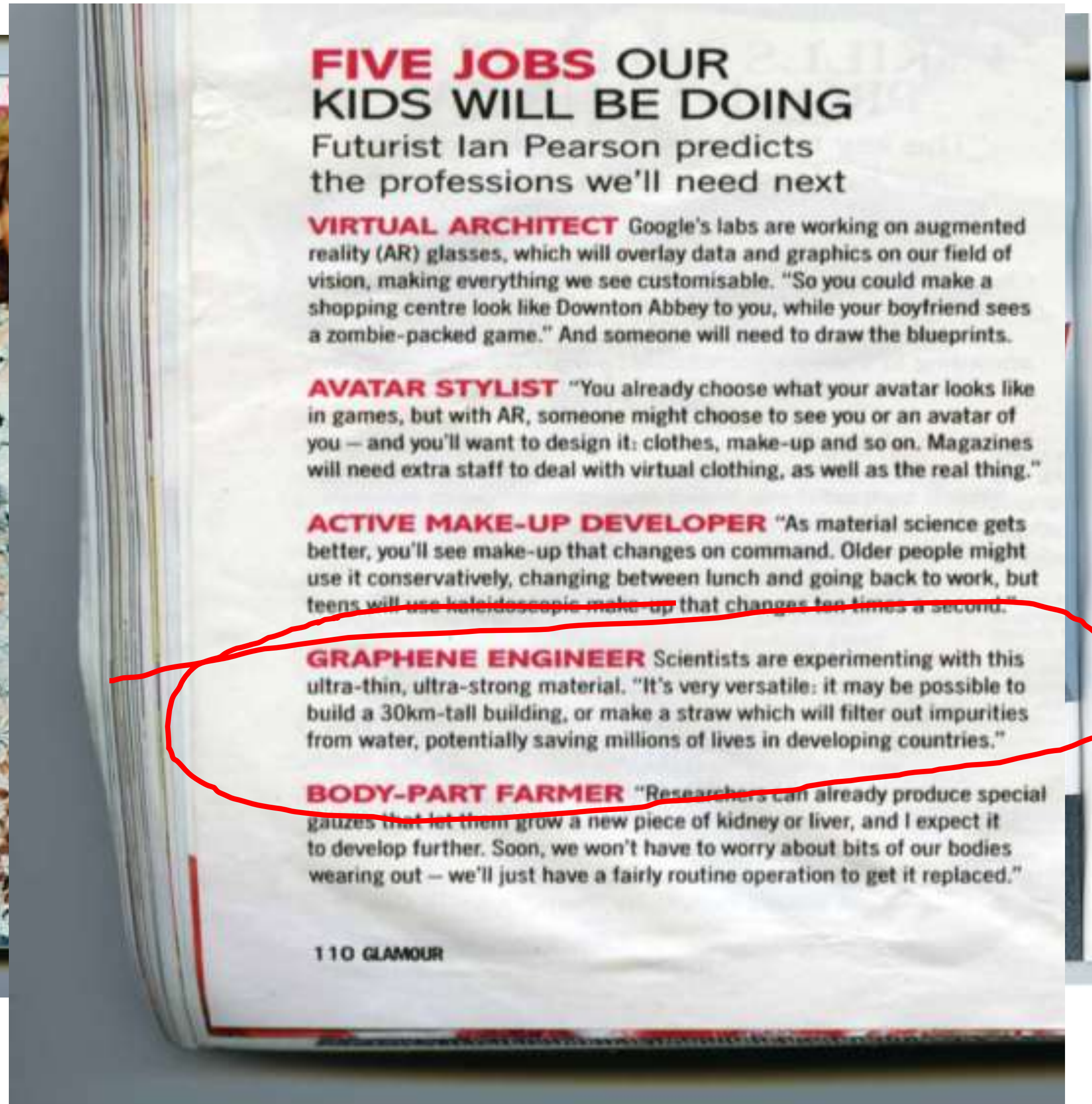
Graphene career?



FIVE JOBS OUR KIDS WILL BE DOING

Futurist Ian Pearson predicts the professions we'll need next

VIRTUAL ARCHITECT Google's labs are working on augmented reality (AR) glasses, which will overlay data and graphics on our field of vision, making everything we see customisable. "So you could make a shopping centre look like Downton Abbey to you, while your boyfriend sees a zombie-packed game." And someone will need to draw the blueprints.

AVATAR STYLIST "You already choose what your avatar looks like in games, but with AR, someone might choose to see you or an avatar of you – and you'll want to design it: clothes, make-up and so on. Magazines will need extra staff to deal with virtual clothing, as well as the real thing."

ACTIVE MAKE-UP DEVELOPER "As material science gets better, you'll see make-up that changes on command. Older people might use it conservatively, changing between lunch and going back to work, but teens will use kaleidoscopic make-up that changes ten times a second."

GRAPHENE ENGINEER Scientists are experimenting with this ultra-thin, ultra-strong material. "It's very versatile: it may be possible to build a 30km-tall building, or make a straw which will filter out impurities from water, potentially saving millions of lives in developing countries."

BODY-PART FARMER "Researchers can already produce special gauzes that let them grow a new piece of kidney or liver, and I expect it to develop further. Soon, we won't have to worry about bits of our bodies wearing out – we'll just have a fairly routine operation to get it replaced."

110 GLAMOUR

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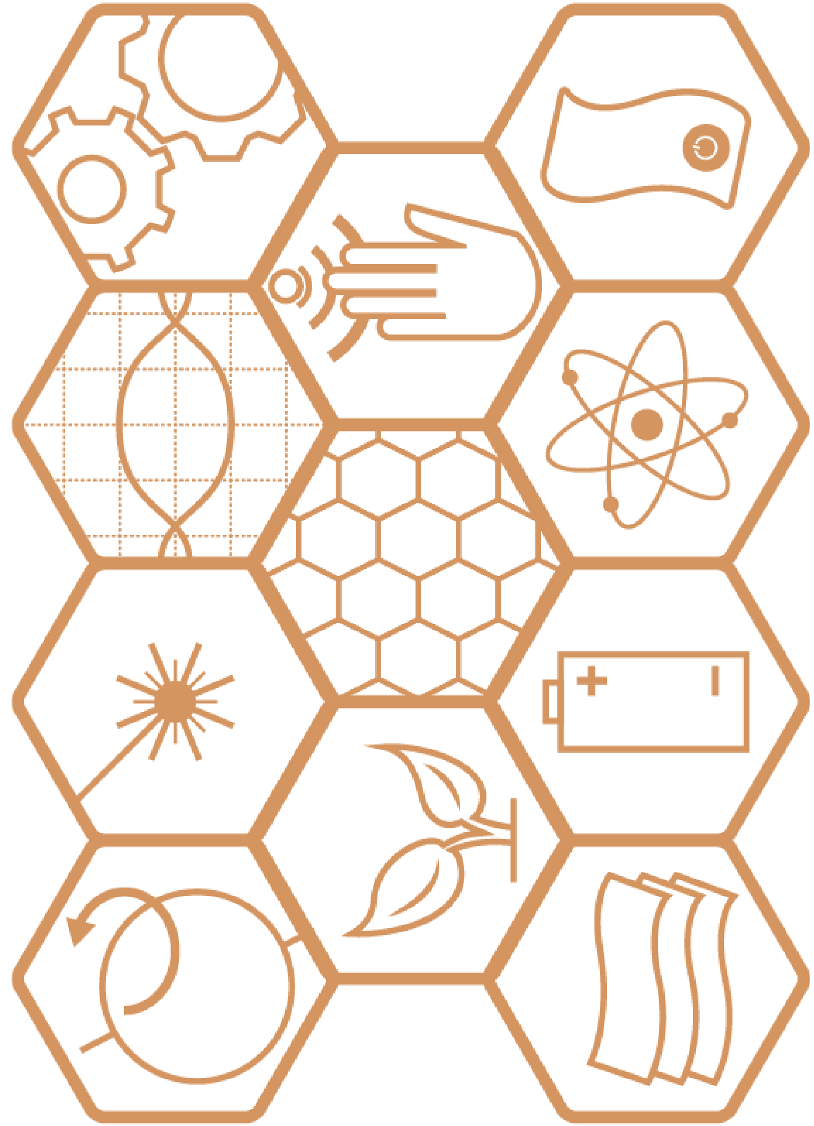
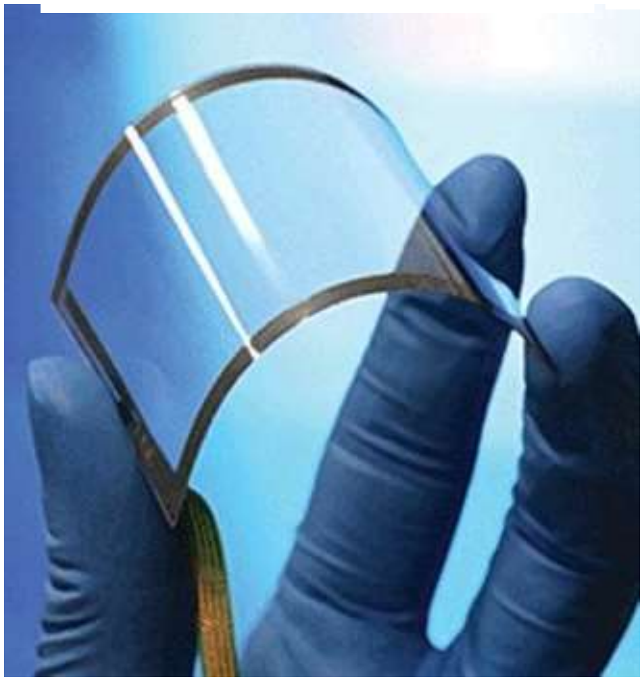
Applications of GRAPHENE

1. **Electronics – faster transistors, semiconductors, flexible electronics.**
2. **Bioapplications – Targeted drug delivery, ’smart implants’, DIY health-testing kits.**
3. **Sensors – Multifunctional sensors, enhanced gas/chemical/ biological detection.**
4. **Composite – Lightweight, strong composites, conductive paints, inks and rust-proof coatings.**
5. **Energy – Batteries, Supercapacitors, wearable power supplies.**
6. **Membranes– Improving water filtration, gas separation, desalination.**



Applications of GRAPHENE

Graphene touch-screen

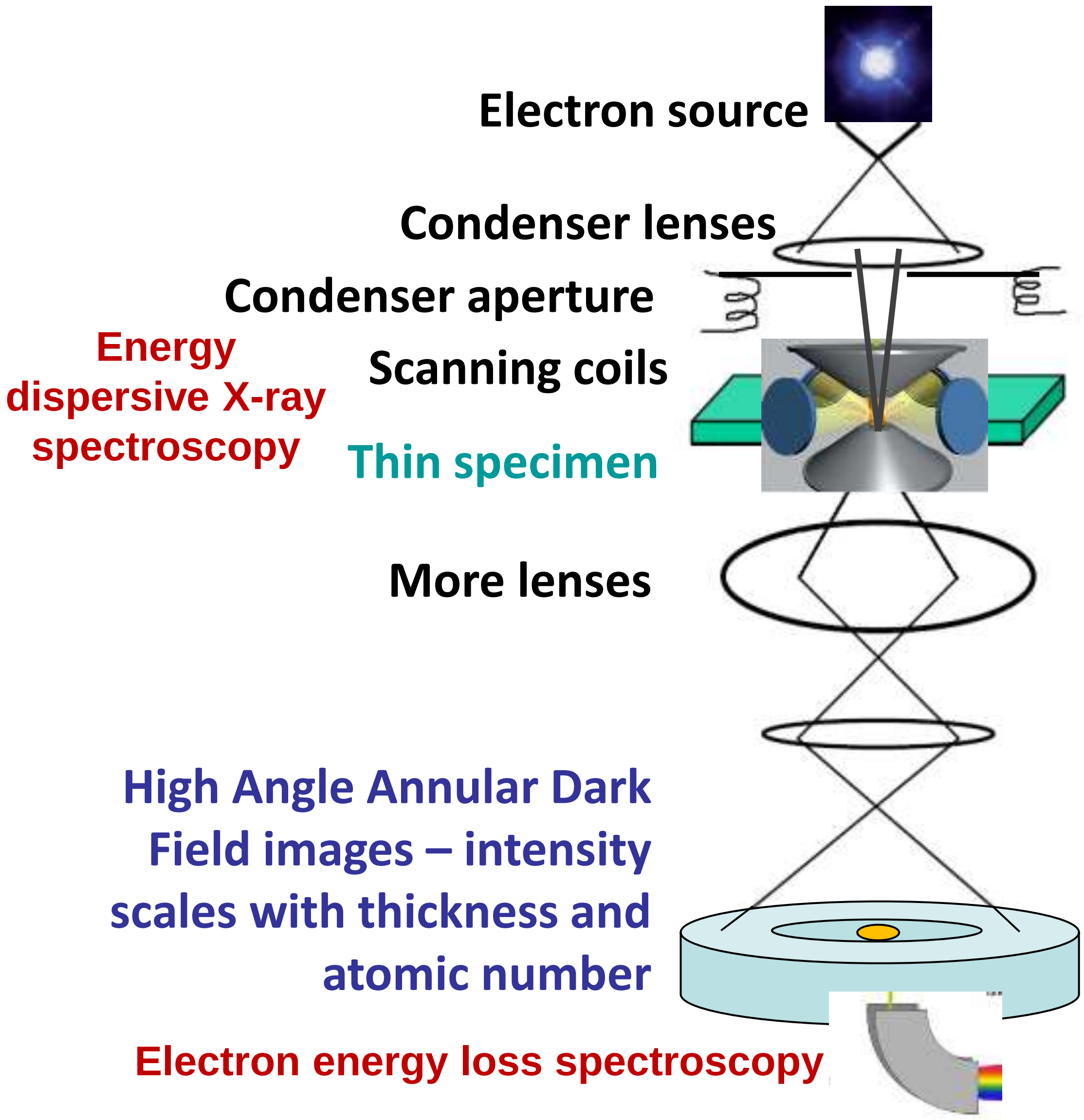


Graphene light bulb

Graphene trainers

However engineering optimal properties for graphene requires detailed characterisation at the atomic scale

(Scanning) Transmission Electron Microscopy



$$\text{Figure of merit for a lens} = \frac{\text{diameter of primary optical element}}{\text{precision of wavefront}}$$

Titan = 1×10^8

Cost = ~$3M

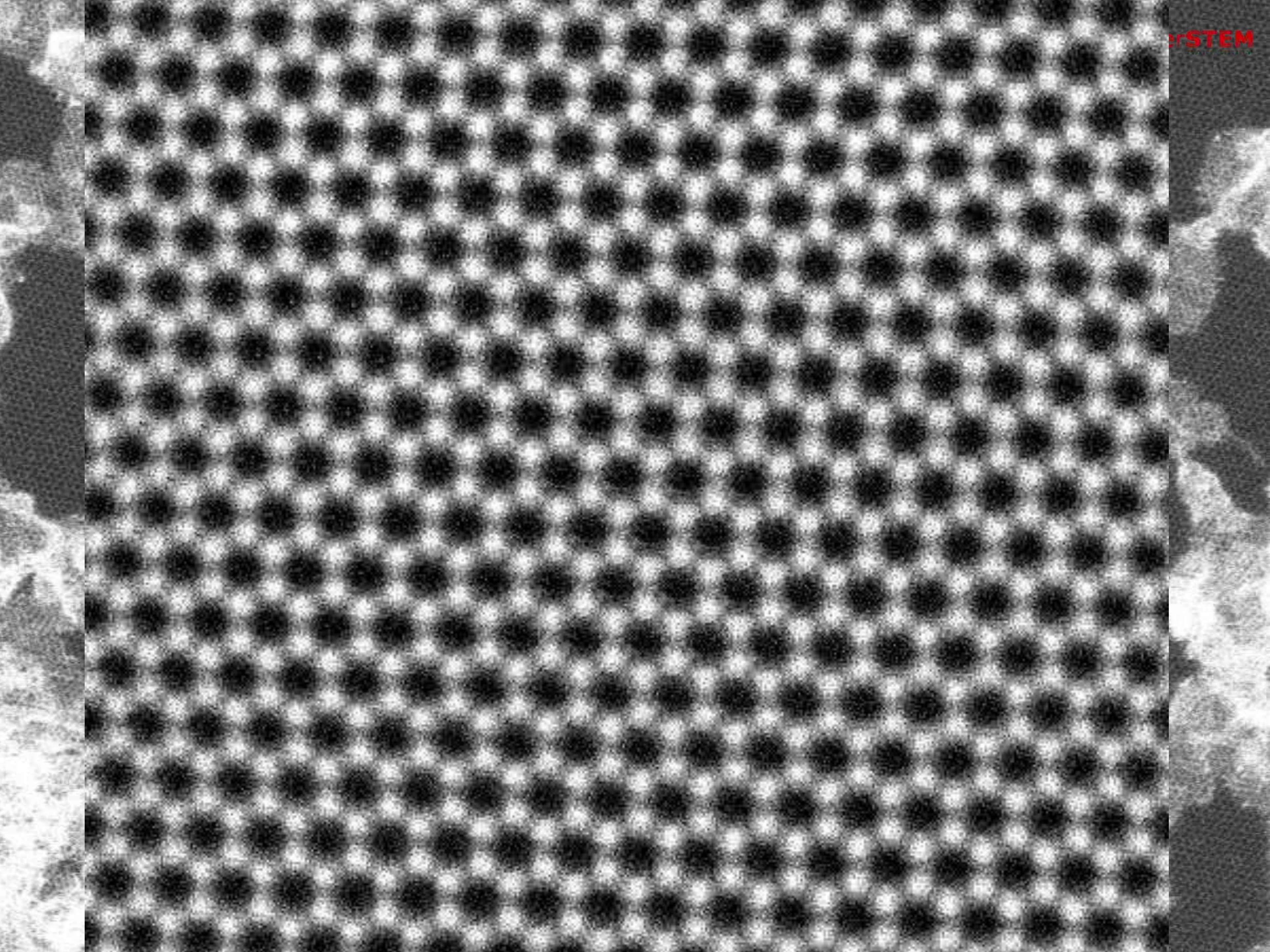
Value for money = 33

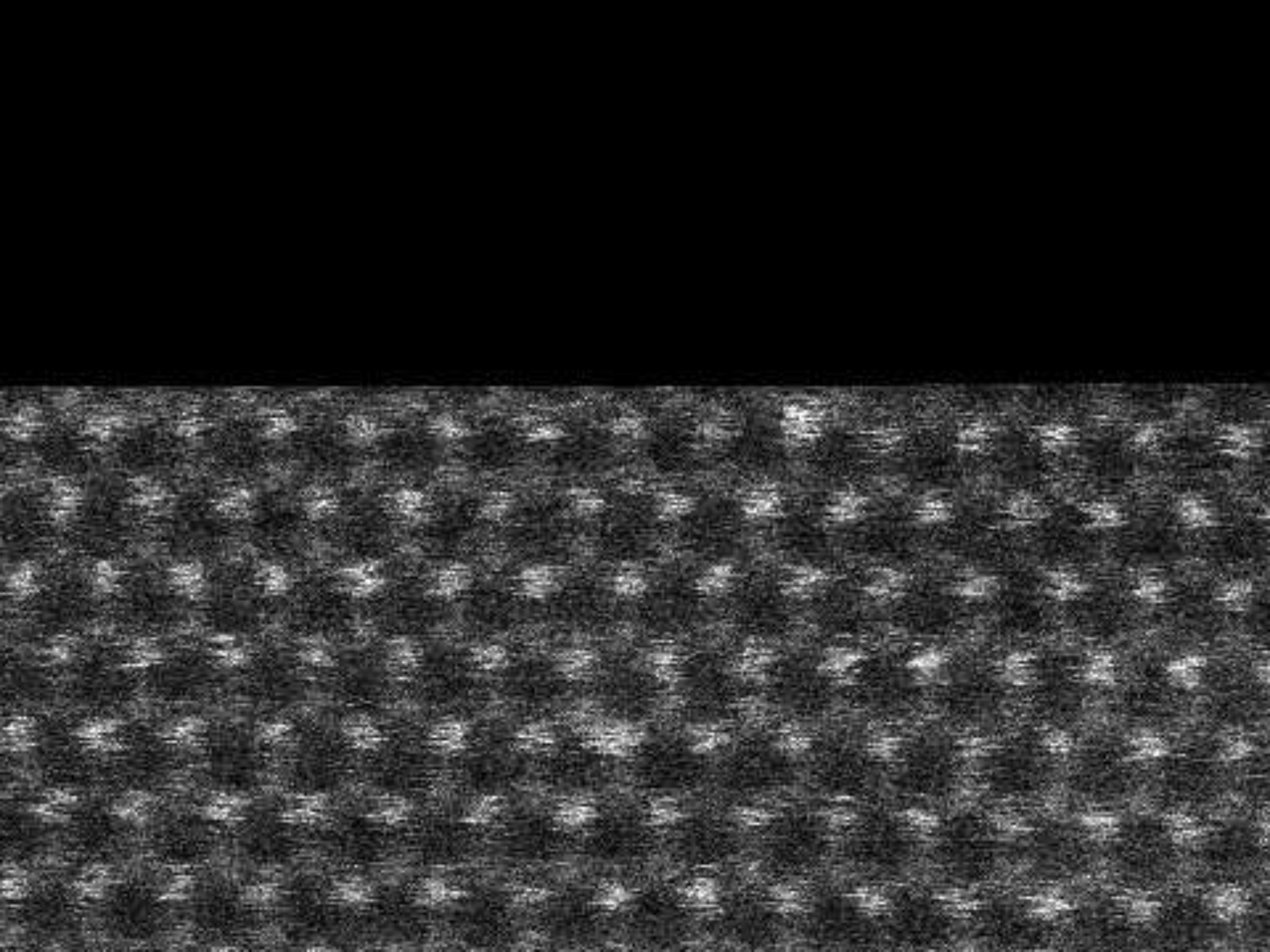
Hubble = 3×10^7

Cost = ~$2000M

Value for money = 0.0125

Data courtesy of Dr. P Nellist





Outline

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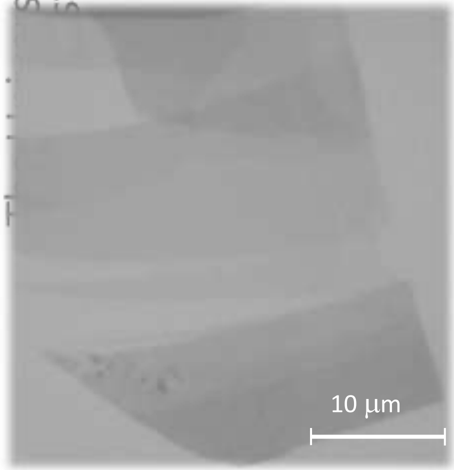
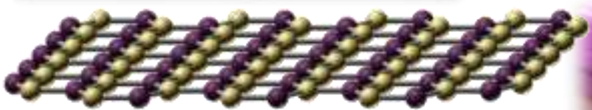
Beyond Graphene

2D boron nitride

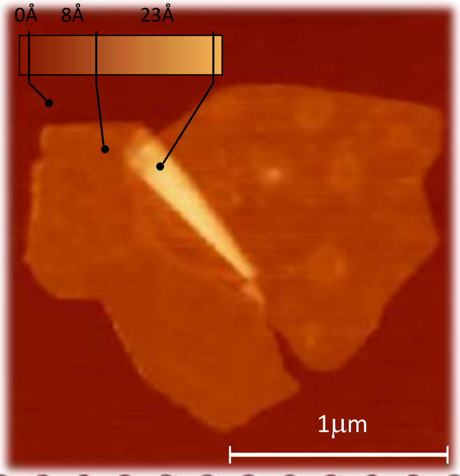


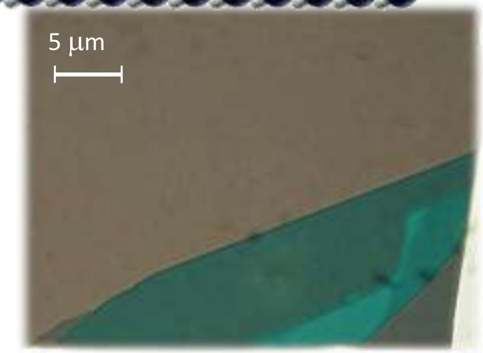


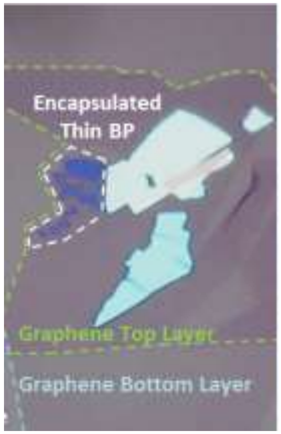
2D From 3D systems

Novoselov et al PNAS (2005)

2D $NbSe_2$





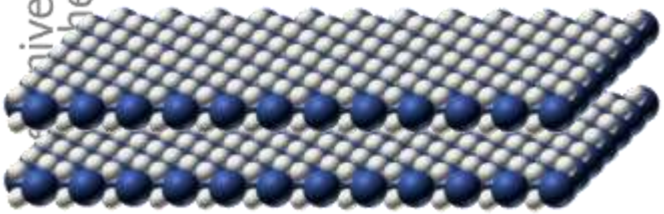


Black Phosphorus (BP)

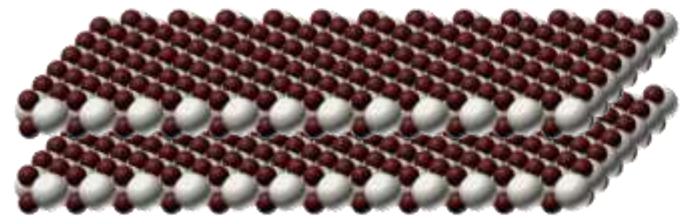
2D MoS_2

Slide courtesy of K Novoselov

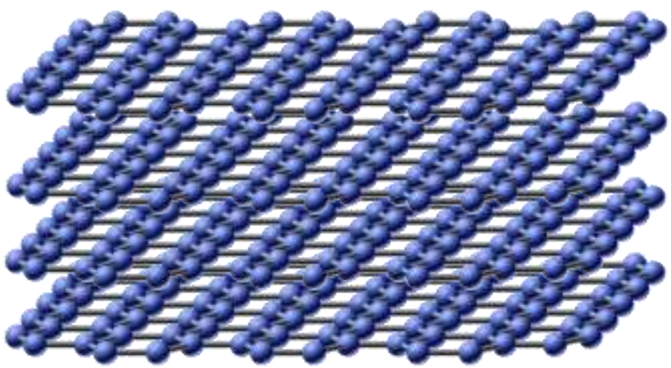
2D-Crystal Heterostructures



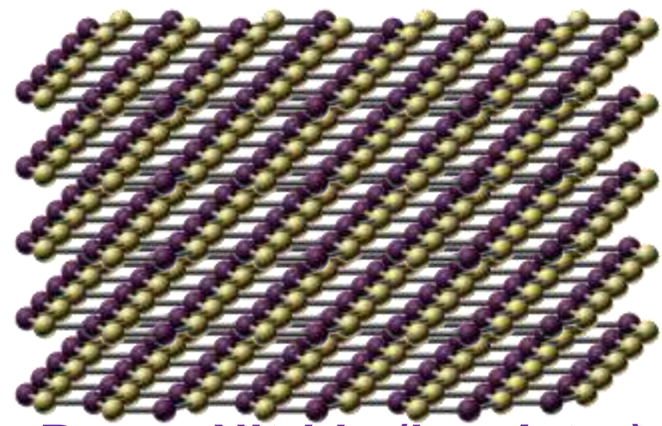
MoS_2 (semiconductor)



$NbSe_2$ (superconductor)

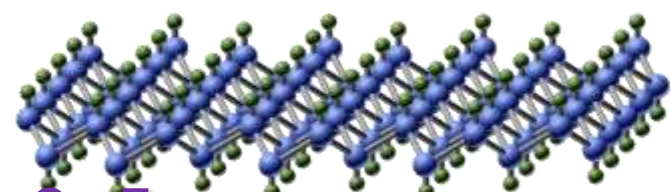


Graphene (conductor)



Boron-Nitride (insulator)

Etched Graphene



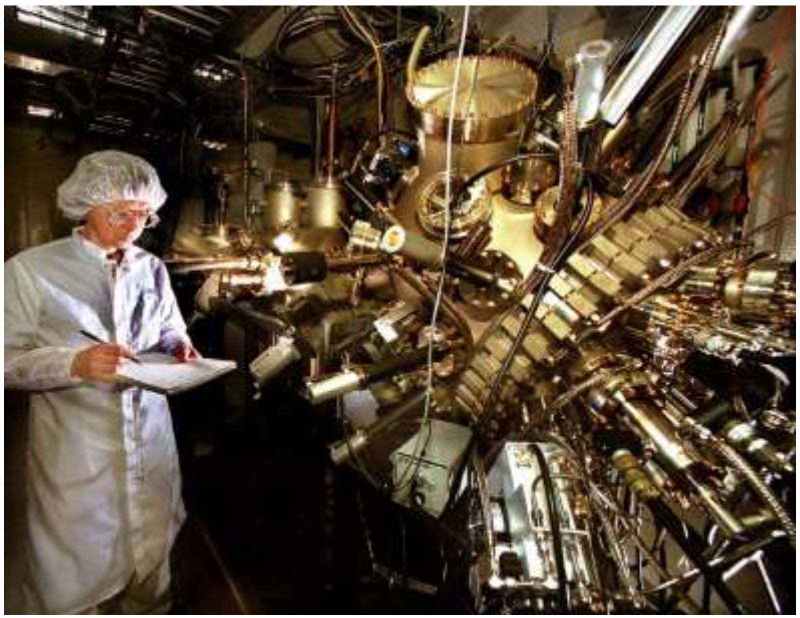
GraFane

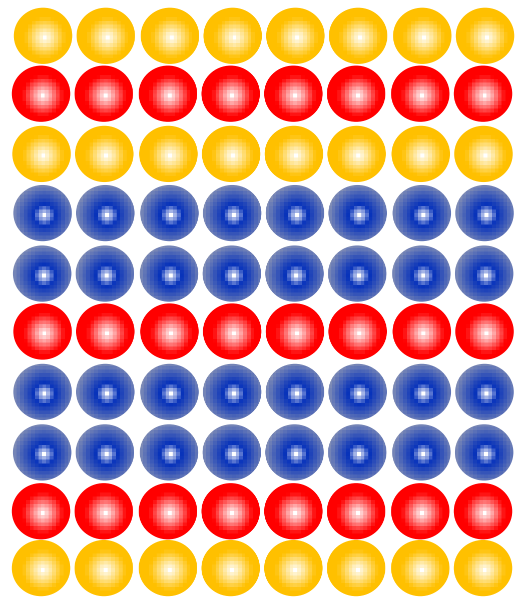
A.K. Geim & I Grigorieva Nature 2014

Current layer by layer engineering

Traditionally manufacturing of many electronic devices relies on atomic layer growth

E.g molecular beam epitaxy

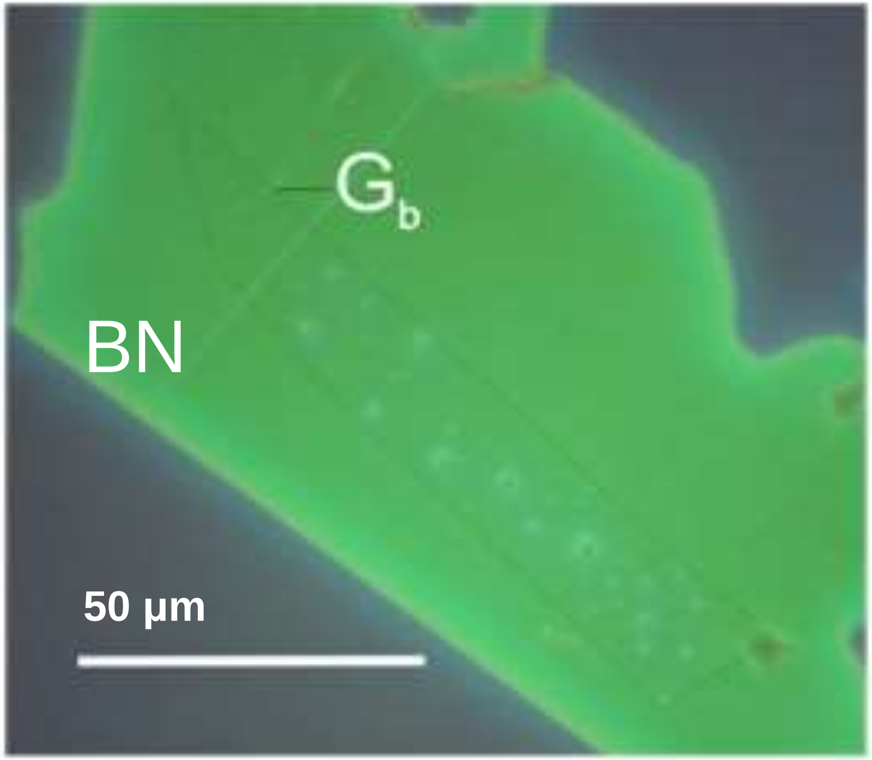


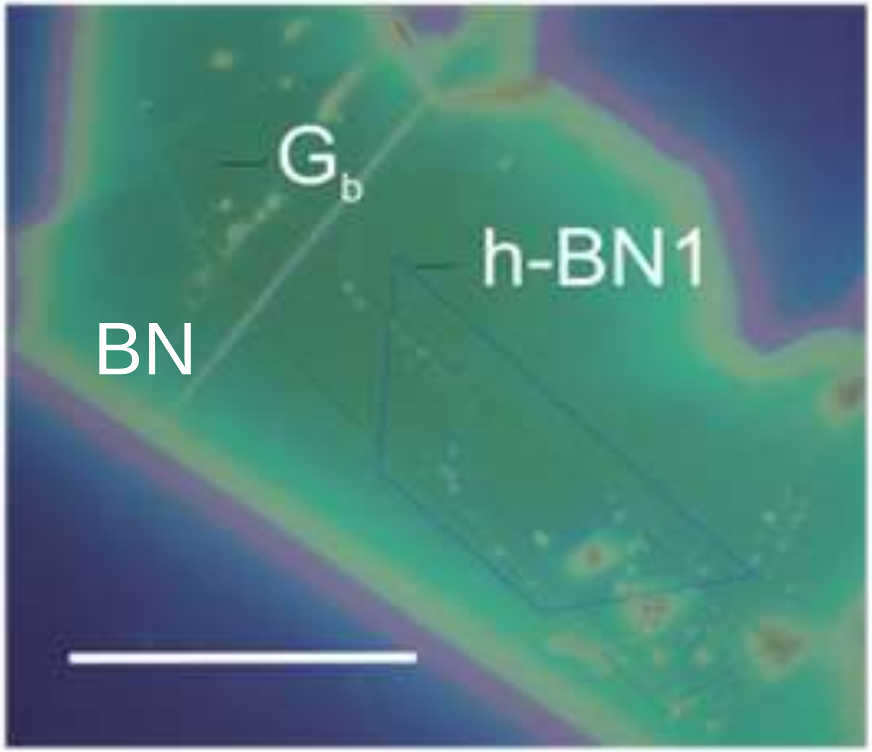


sensor
solar cell
transistor
interconnect
laser

But this requires sequential layers to have similar atomic structures which limits efficiency and structures that can be produced

Mechanical Exfoliation:
Layer by layer device manufacture

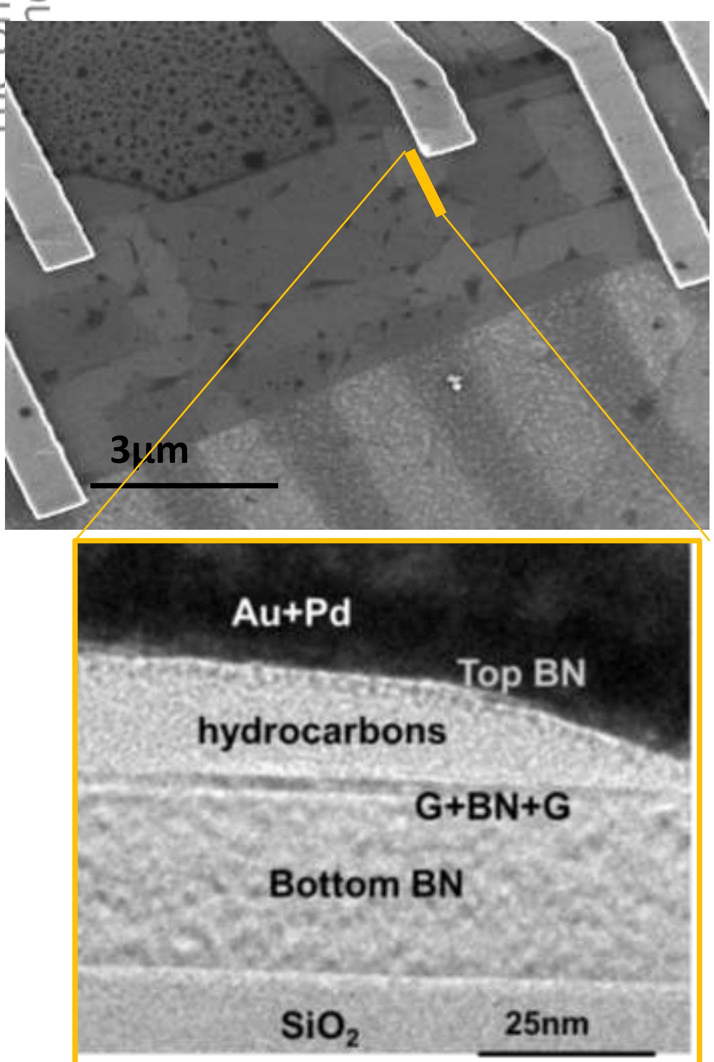


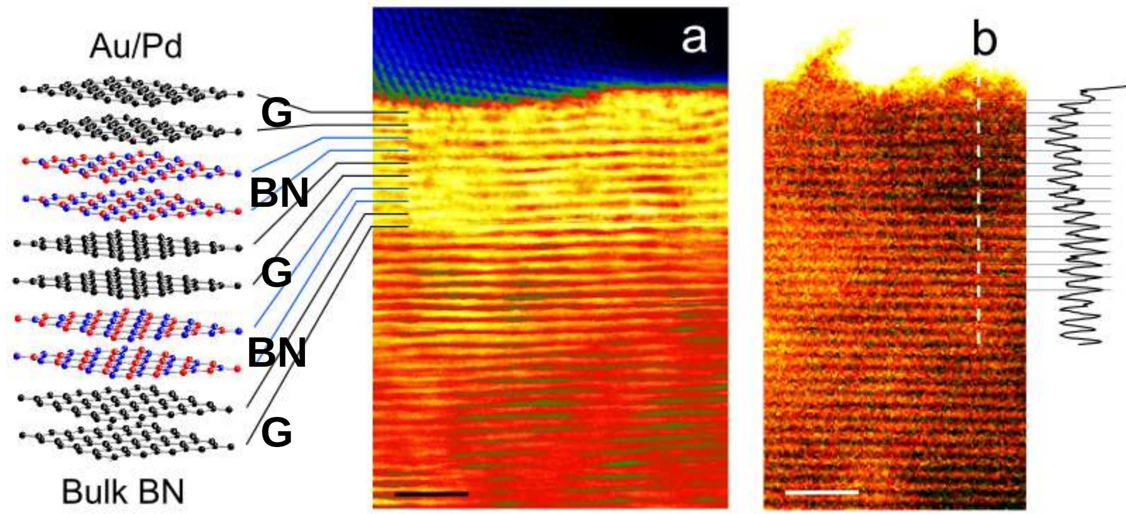


F. Withers *et al.*, *Nat Mater*, 2015, 14, 301-306.

Atomic Crystal

2D Heterostructures produced by mechanical exfoliation



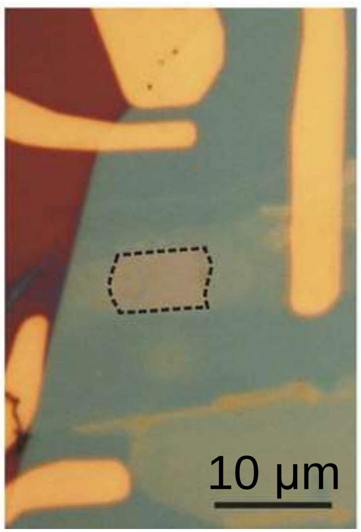


In Graphene – Boron Nitride heterostructures the contamination layer segregates into pockets leaving "perfect" atomic interfaces

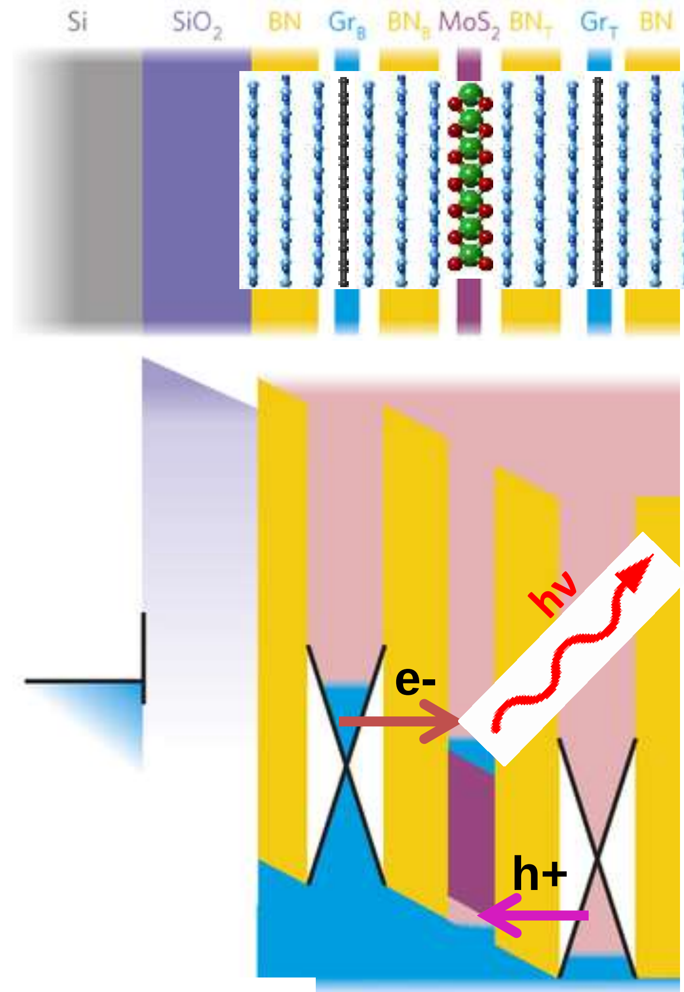
Haigh *et al.*, *Nat Mater*, 2012, 11,764–767 .

Building LEDs from 2D crystal heterostructures

Optical image



Electroluminescense image

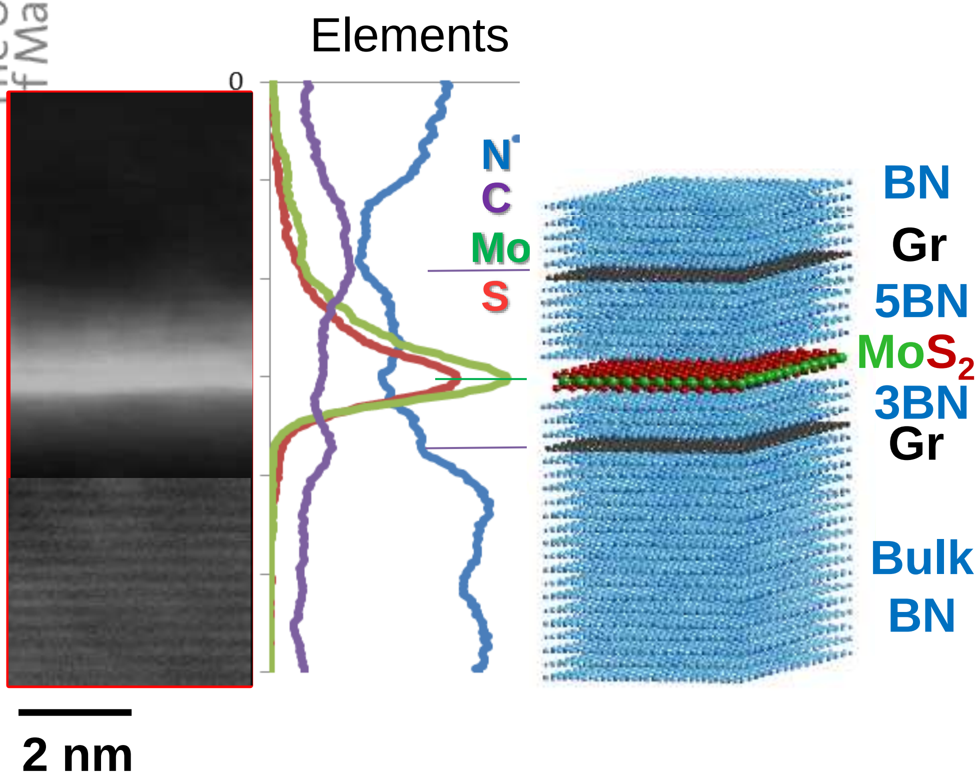


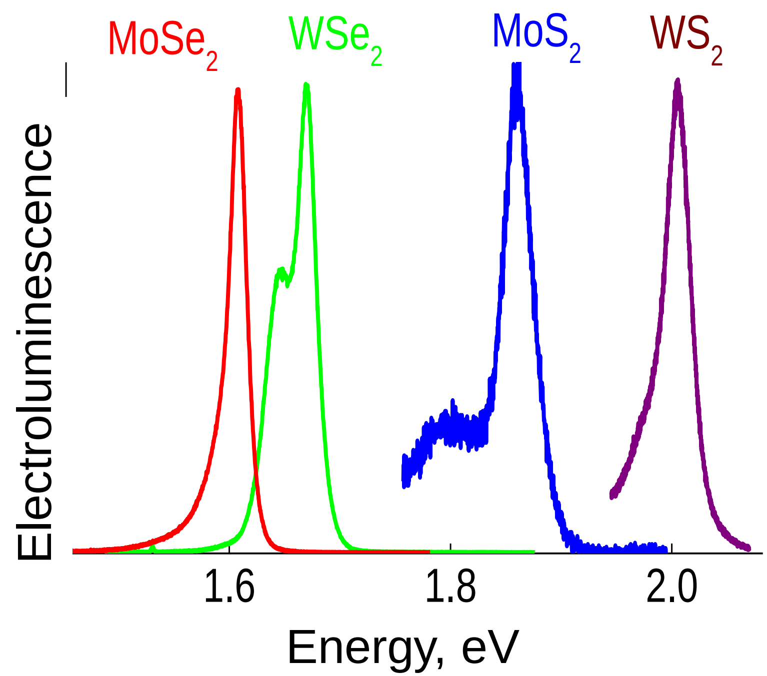
$+2.4V_b$

Operational LED device with **single MoS_2 quantum well structure**: $Si/SiO_2/hBN/Gr_B/3hBN/MoS_2/3hBN/Gr_T/hBN$ (dashed lines outline the complete heterostructure area).

F. Withers *et al.*, *Nature Materials*, 2015, 14, 301-306.

Building LEDs from 2D crystal heterostructures





- **Different 2D crystals give different wavelengths**
- **Total LED thickness ~10 nm (~30 atoms)**
- **Quantum efficiency ~1%.**

F. Withers *et al.*, *Nature Materials*, 2015, 14, 301-306.

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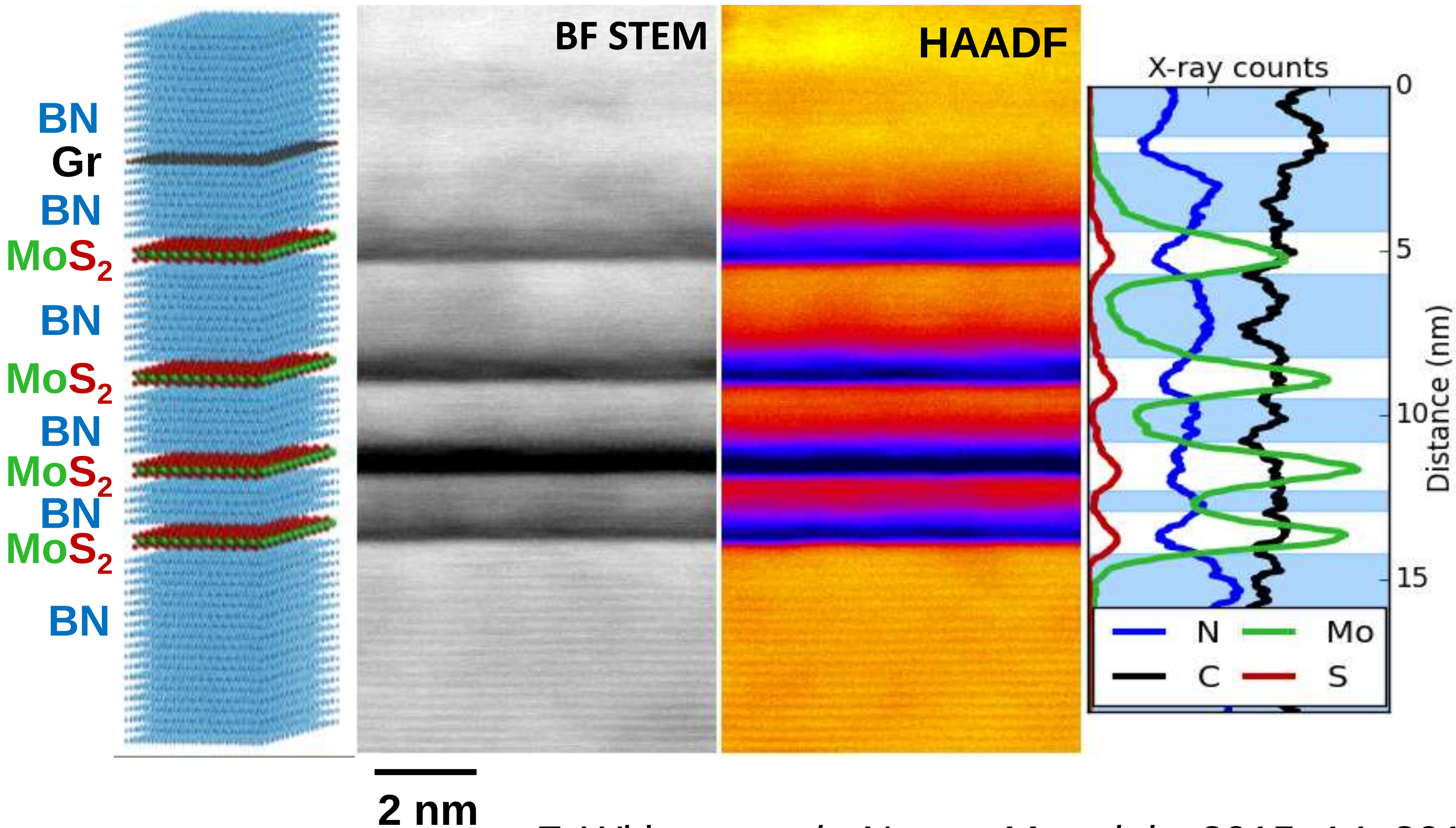
Building LEDs from 2D crystal heterostructures

Stacking 13 2D crystal layers (including 4 MoS_2 Quantum Wells) gives LED with quantum efficiency up to 8.5%.



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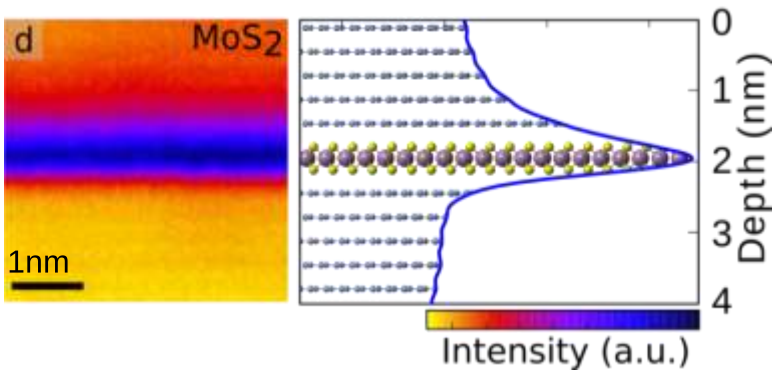
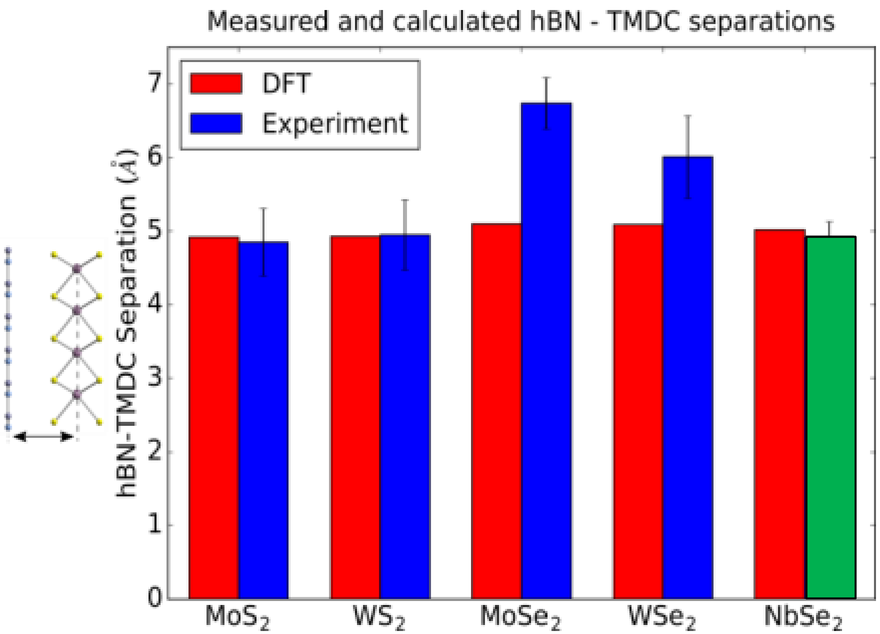
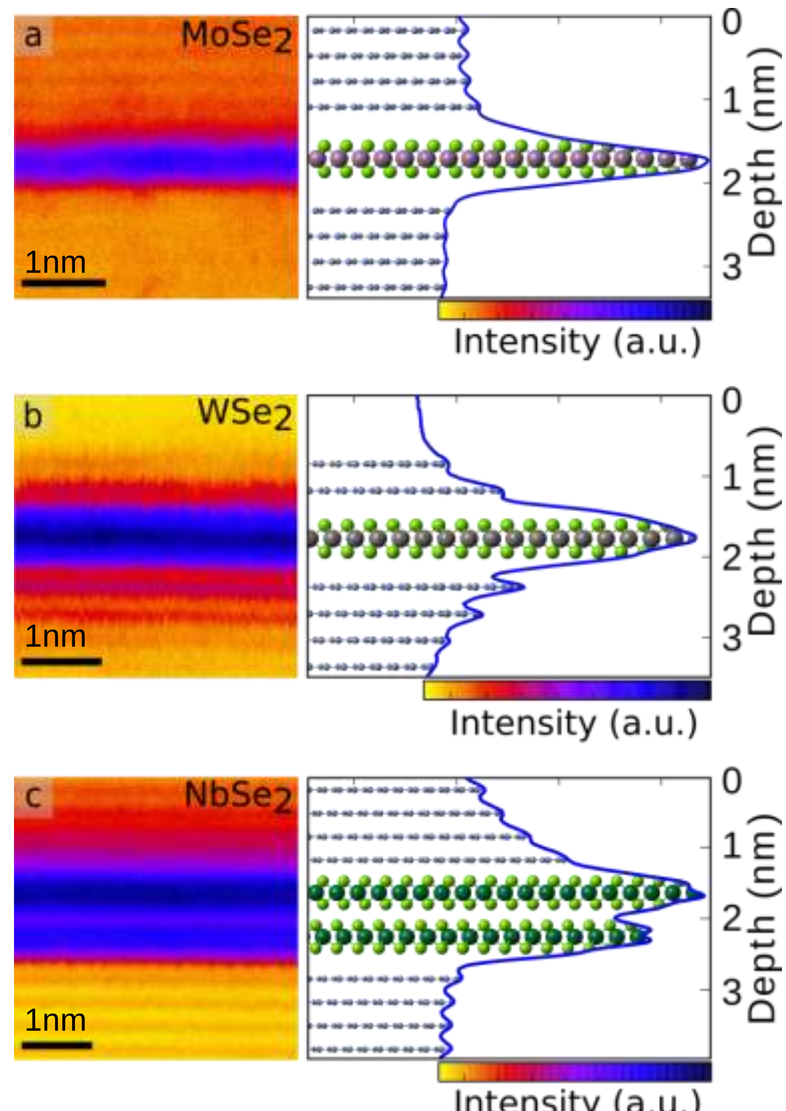
Measuring interlayer separations in Van der Waals heterostructures



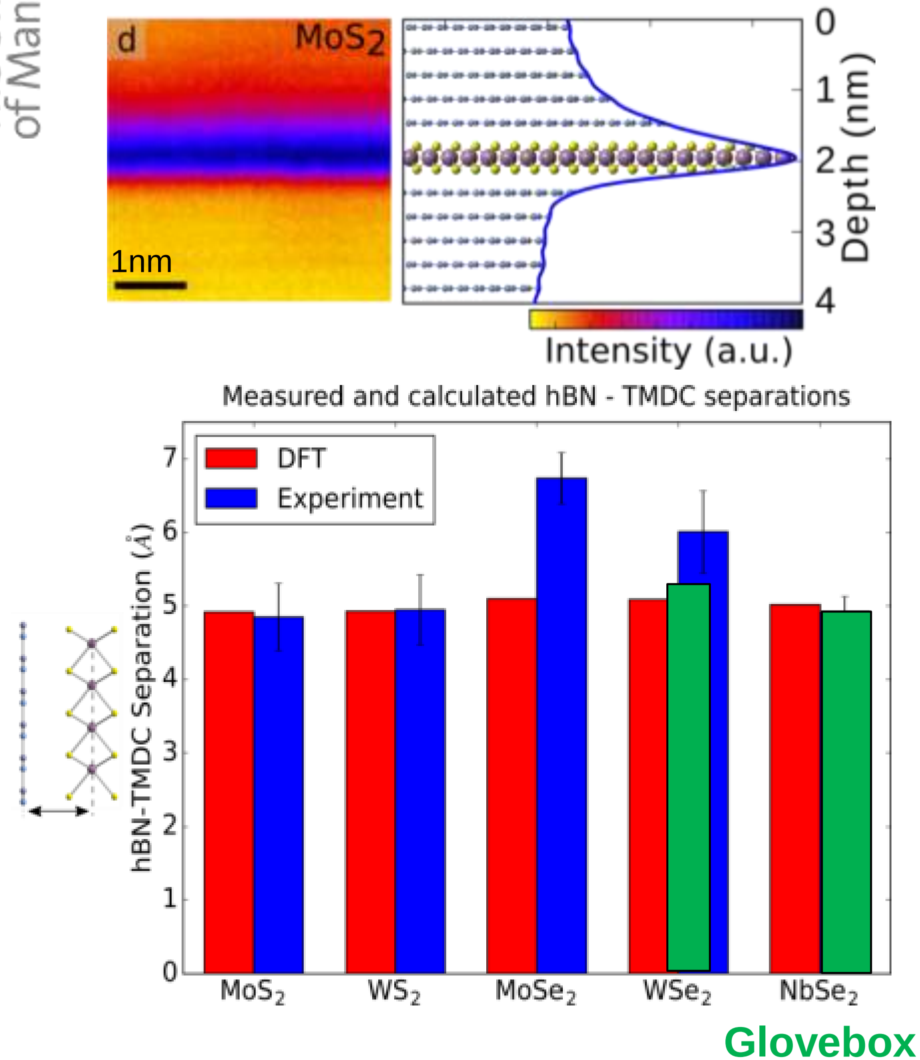


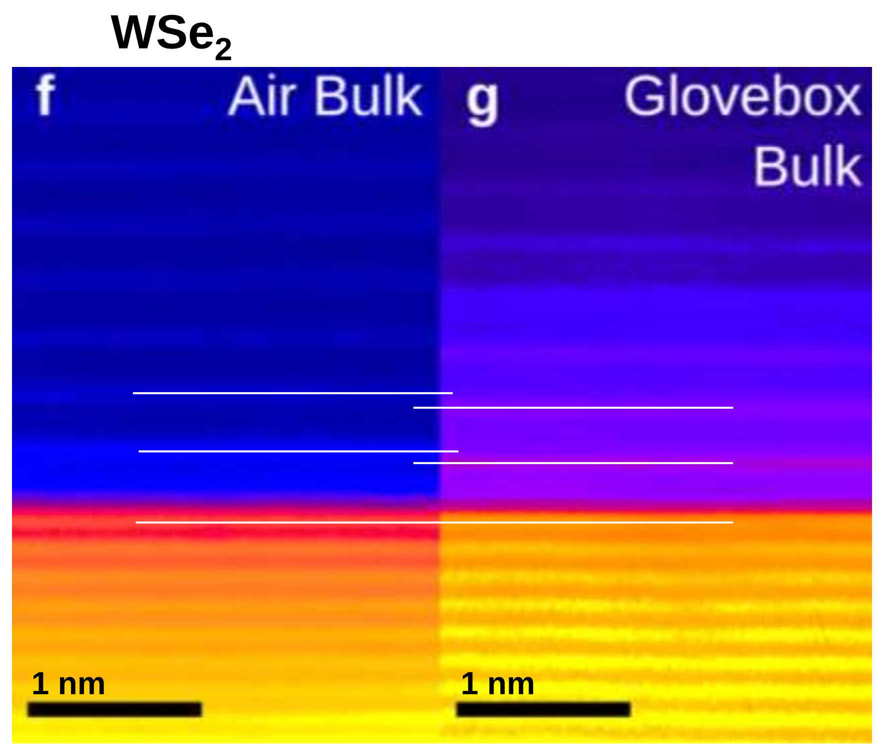
Glovebox



Rooney *et al.*, Nano Letters, 2017.

Measuring interlayer separations in Van der Waals heterostructures





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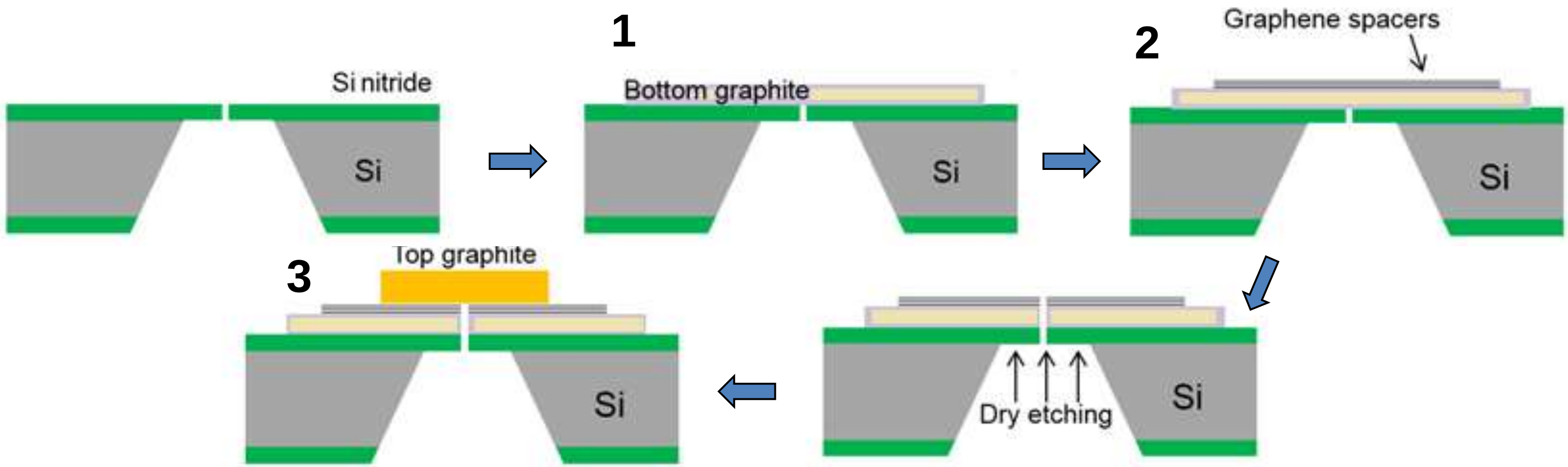
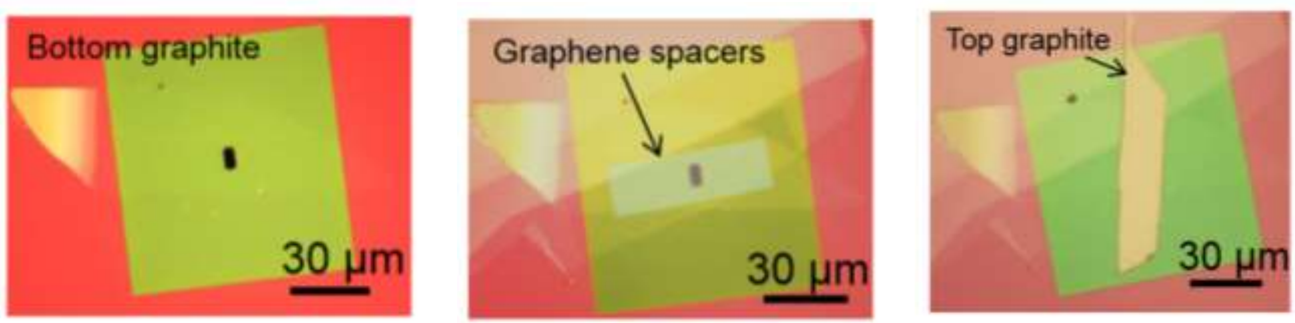
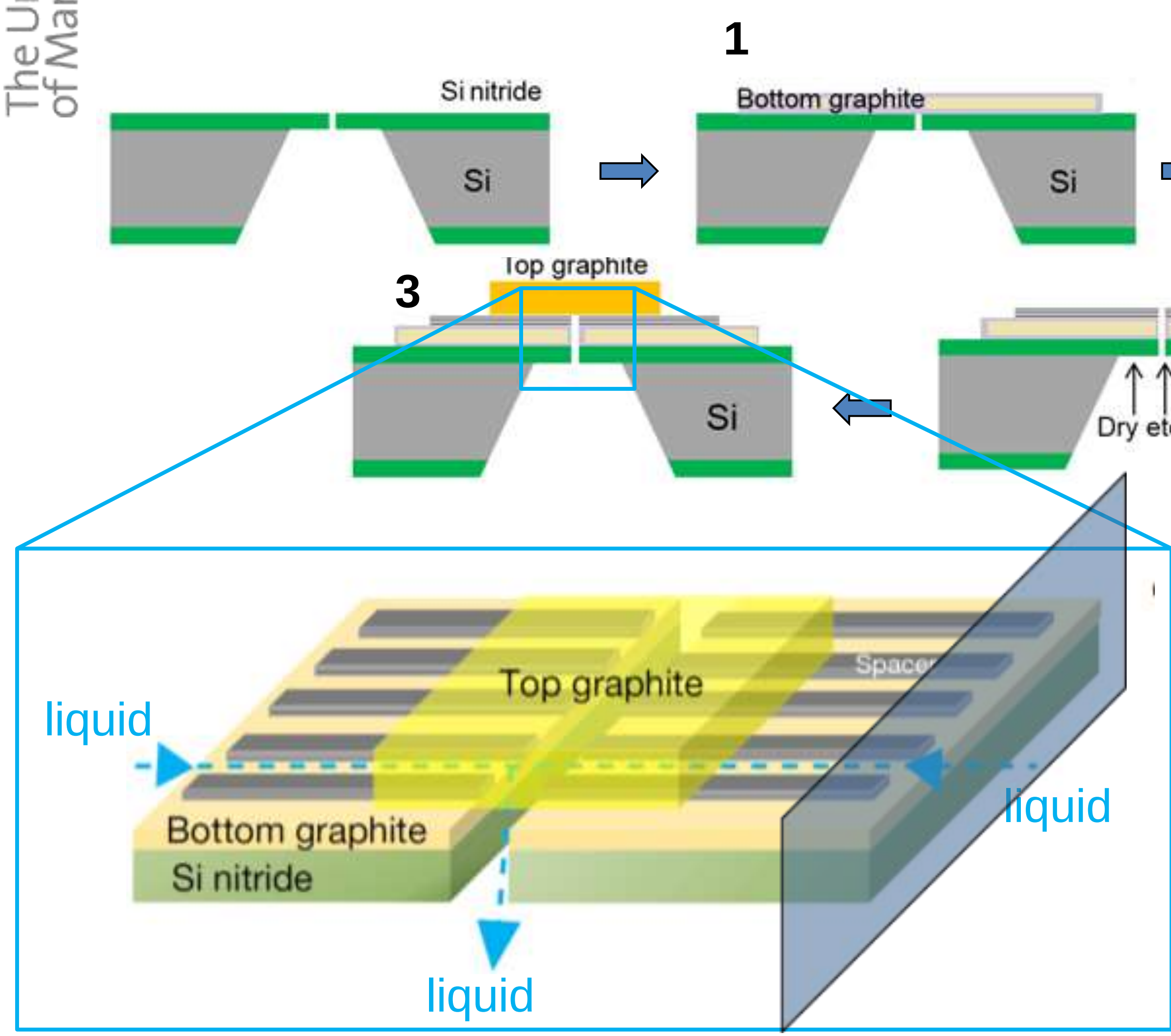
Graphene nanocapillaries





Boya et al Nature 2016

Graphene nanocapillaries

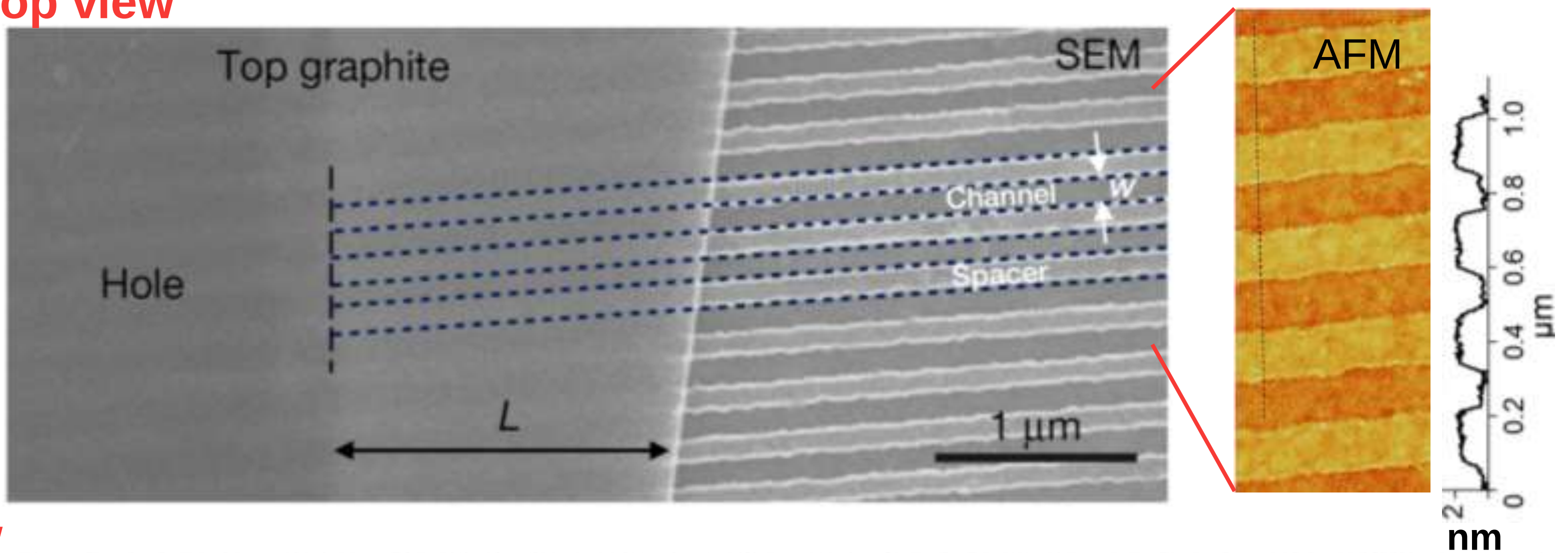


- Atomically flat surfaces (usual limit is surface roughness)
- Atomically defined height dimensions (better than lithographic)

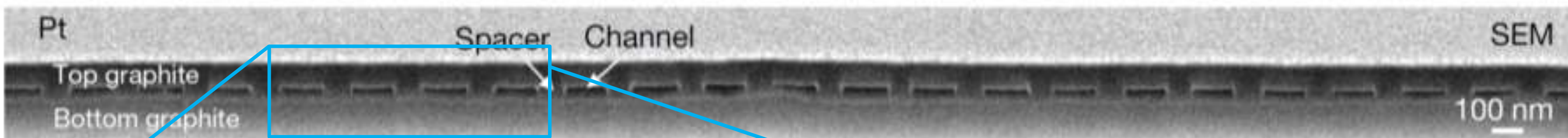
Boya et al Nature 2016

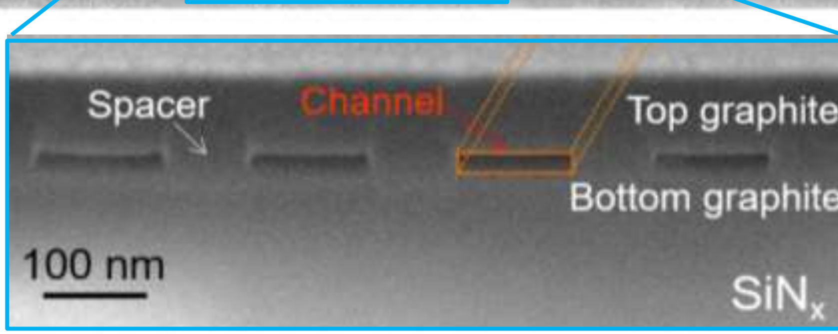
Graphene nanocapillaries

Top view



Sideview



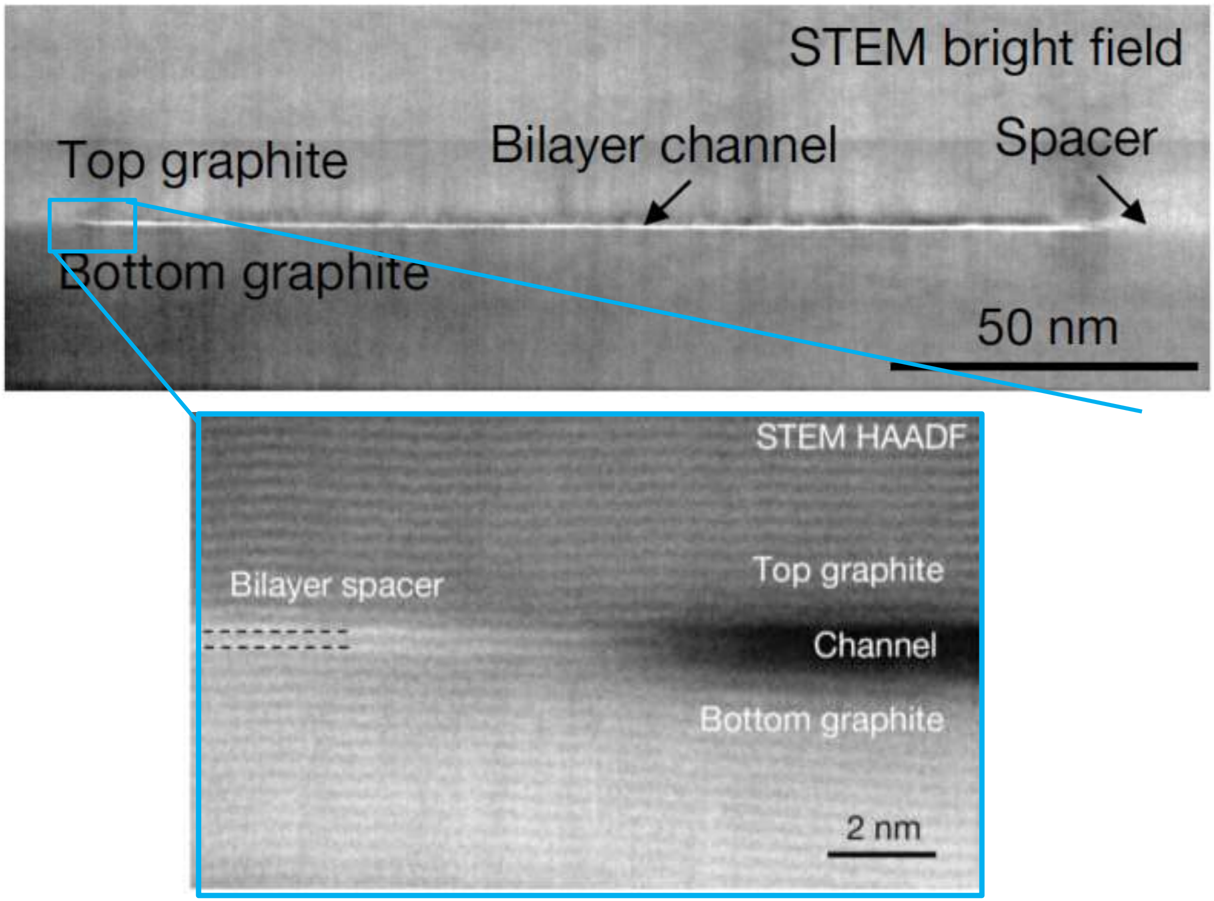


- Graphene spacer stack thickness **(N layers)** is important as it governs the calibration of liquid transport
- **Graphene top layer** is important as bowing occurs if the top layer is too thin.

Boya et al Nature 2016

Graphene nanocapillaries

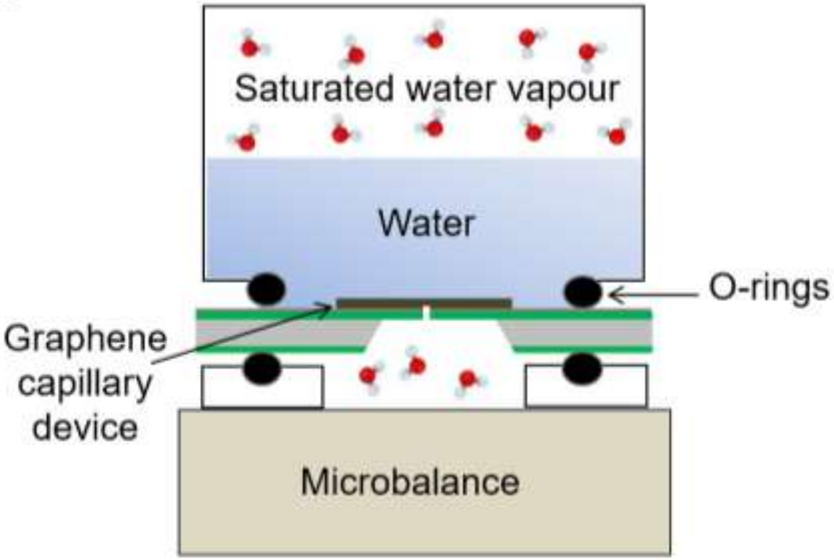
- **Smallest channel height (N<5) are most interesting and most challenging and beyond the resolution of SEM.**
- **After >2 yrs and >40 samples…….**

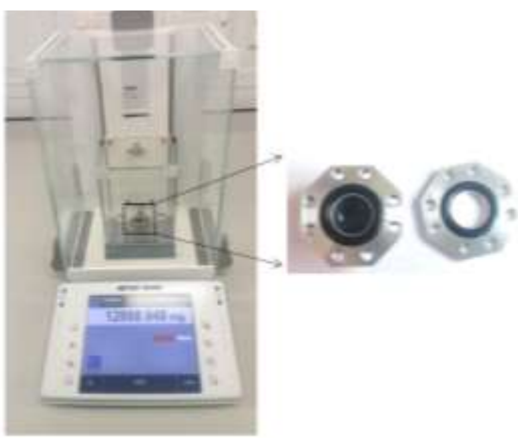


Boya et al Nature 2016

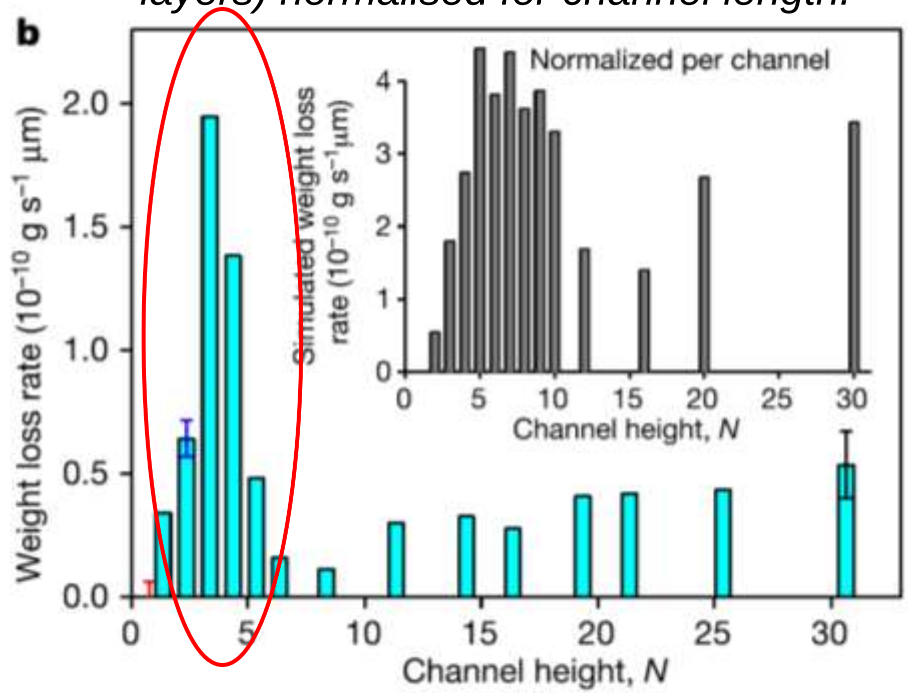
Graphene nanocapillaries

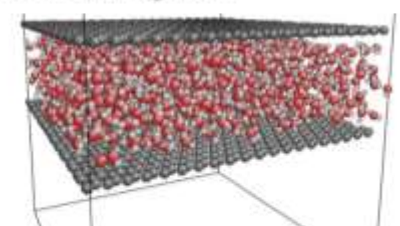
Liquid flow Gravimetric measurements





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





Boya et al Nature 2016

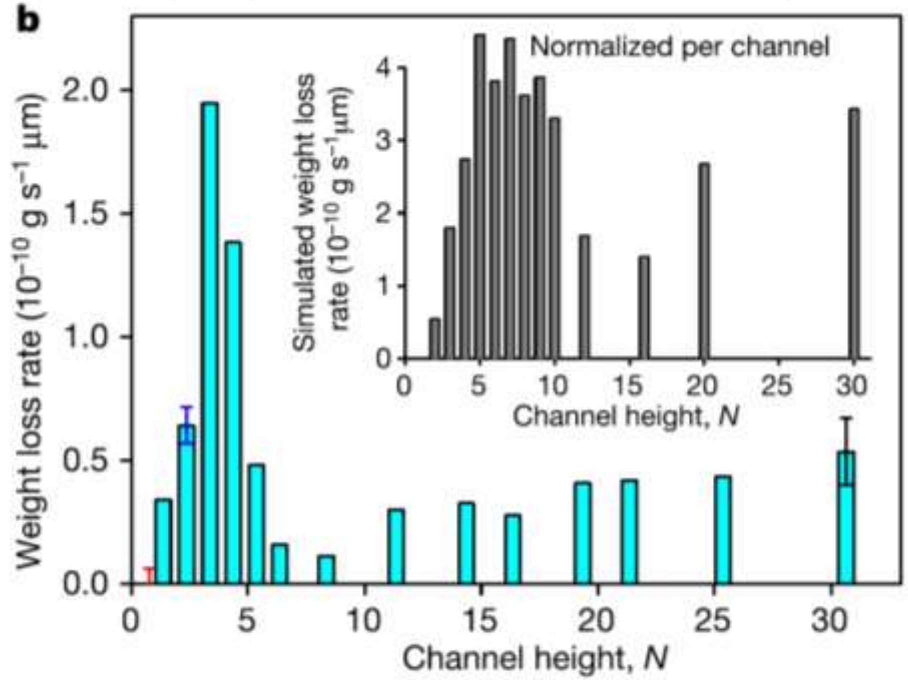
Graphene nanocapillaries

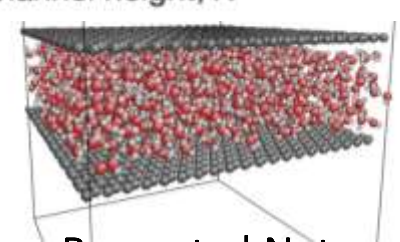
Liquid flow Gravimetric measurements

- 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.

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

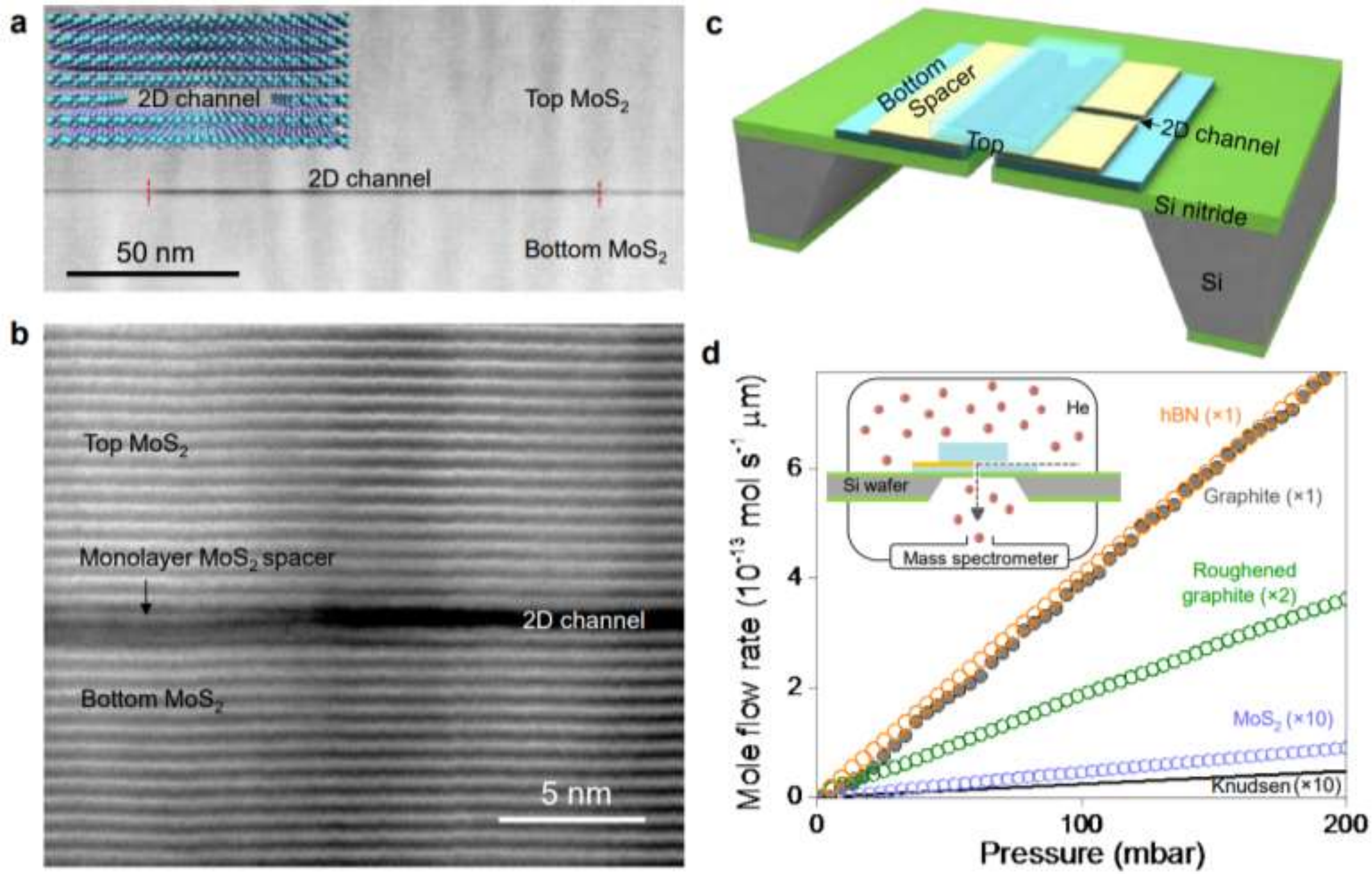




Boya et al Nature 2016

Graphene nanocapillaries

Gas flow measurements – specular scattering or Knudsen flow



Keerthi et al Nature 2018

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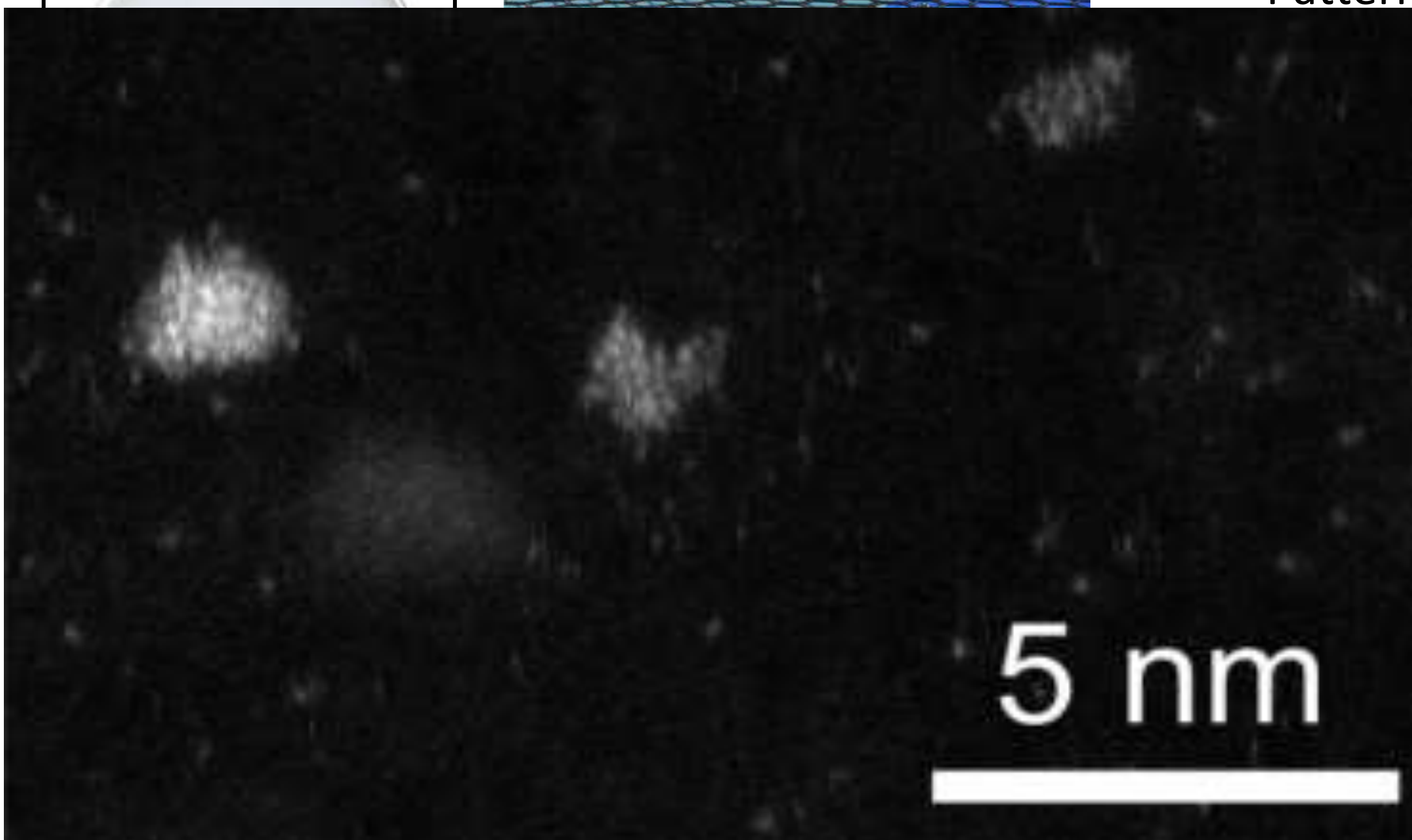
Engineered Graphene Liquid Cells

(A TEM compatible graphene petri dish)



- Patterned boron
spacer allows
over liquid
ions
- ne forms
ic seal on
lly flat thin
stals
- ible with flow
ing …

Please come and discuss at my poster

Kelly et al Nano Letters 2018 ……

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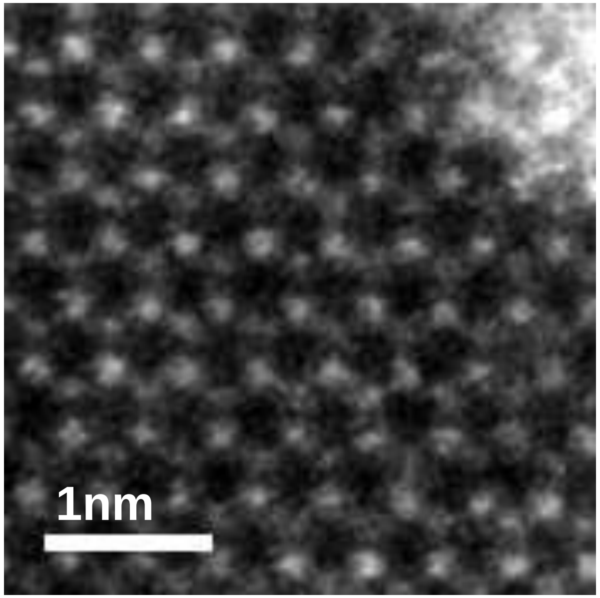
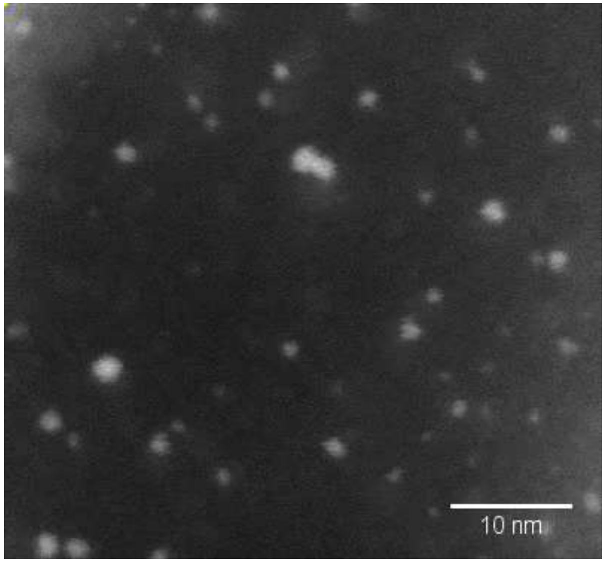
Take home messages

- The library of 2D crystals is rapidly expanding (beyond graphene) and **2D material heterostructures provide an exciting playground** to probe the properties of matter and to engineer new functionality
- **(Scanning) Transmission Electron Microscopy** is a powerful tool to help develop these and other materials to tackle scientific problems from smart screens and shoes to cleaner water and fuel.





Thank you

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