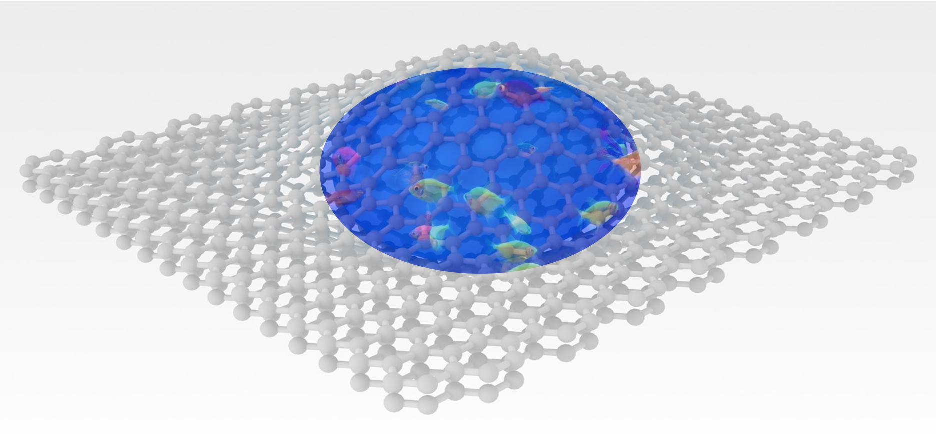
Graphene Liquid Cell (GLC) TEM:

Observing atoms in the graphene aquarium



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Aug 18, 2022   11:00 CST

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- Liquid-loading strategies for EM
  - Open cell and closed cell liquid TEM
- The Graphene Liquid Cell
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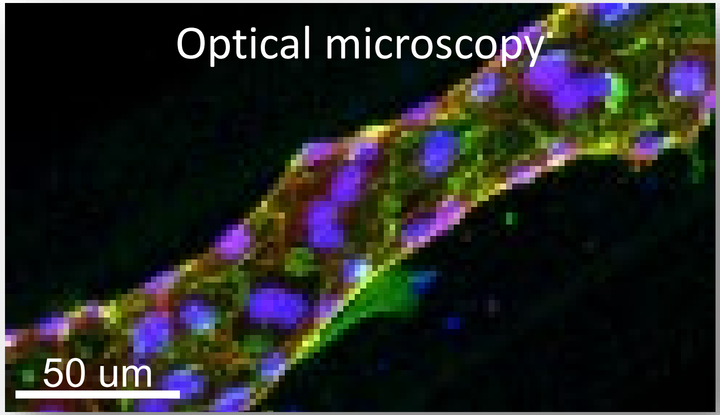
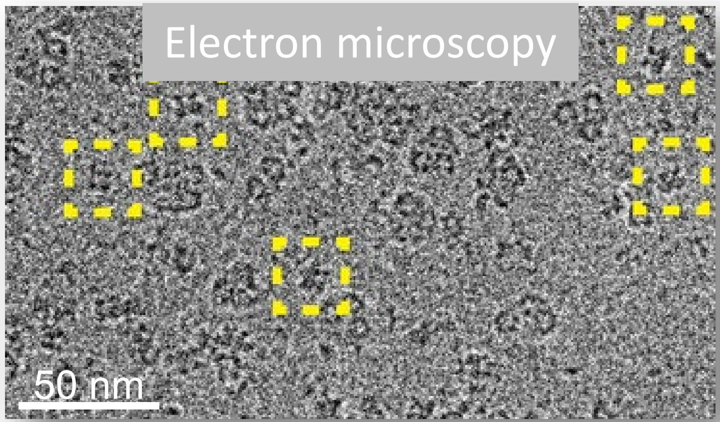
  - How to make?
  - Real-world examples

The LP-TEM

Conventional techniques



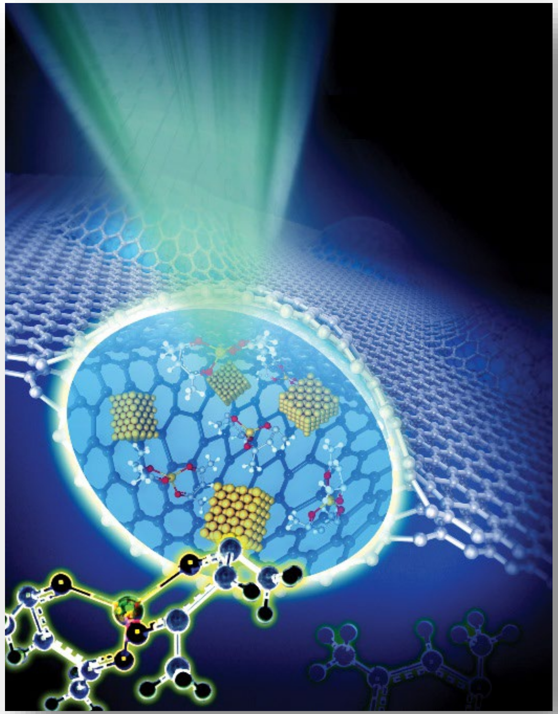
Live imaging, poor image resolution



HR imaging, fixed samples

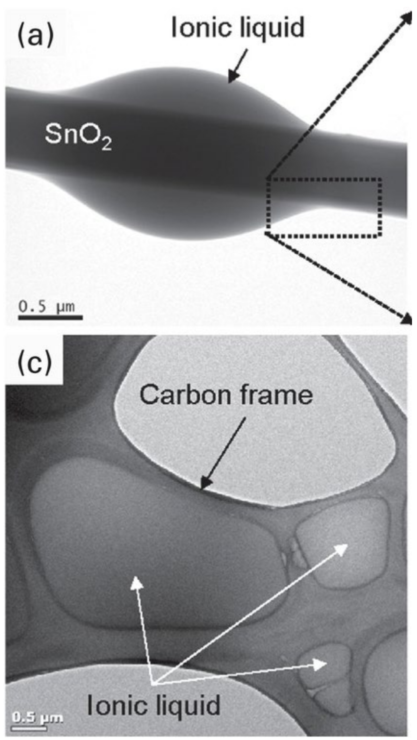
Solution

Liquid-phase TEM (LP-TEM)

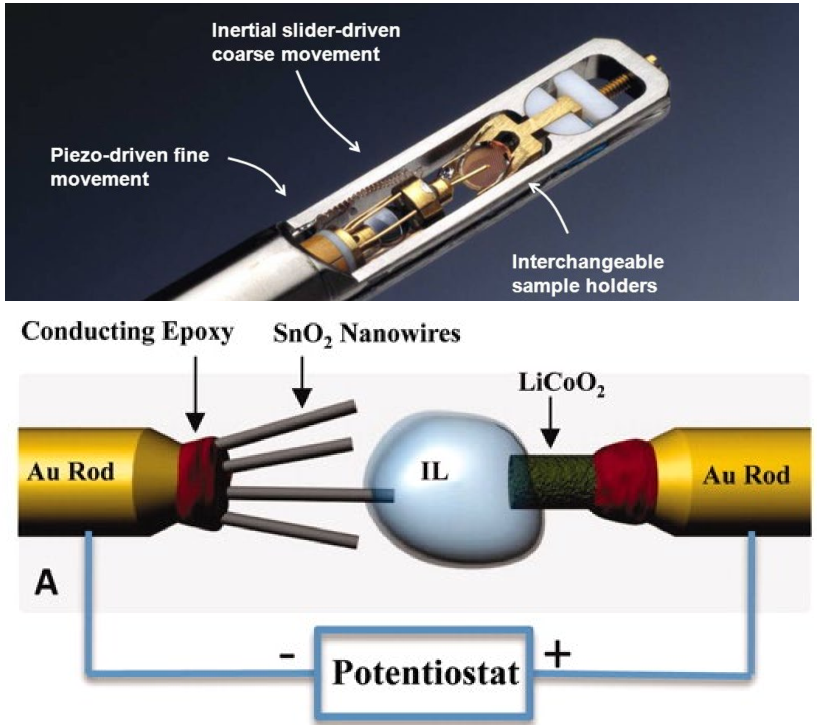


Visualization of the transformative kinetics of biomolecules with the unprecedented spatial (~ 10^{-9} m) and temporal (~ 10^{-3} s) resolution, in their native liquid environment !!

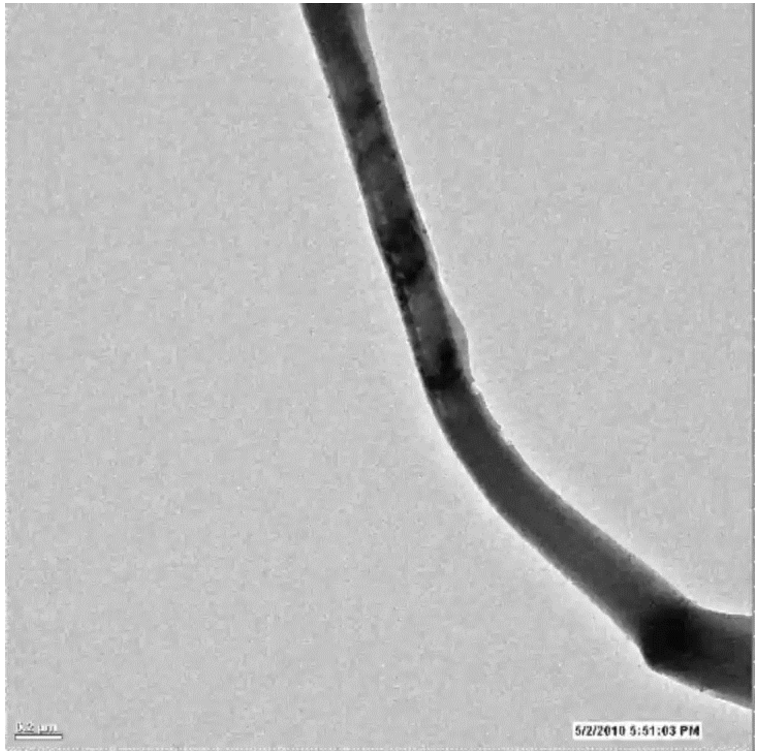
Open Cell Liquid TEM



C. Wang *et al.*, *J Mater Res* (2010)



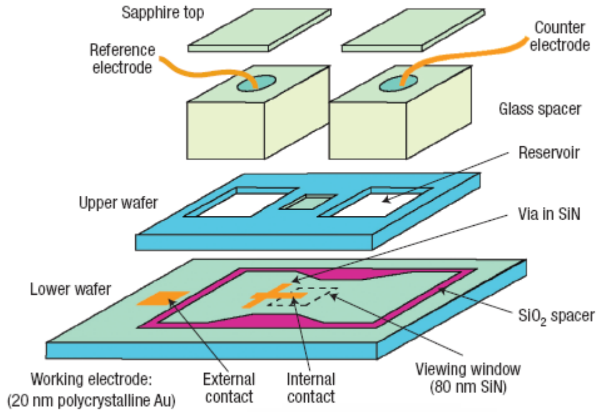
J. Y. Huang *et al. Science* (2010)

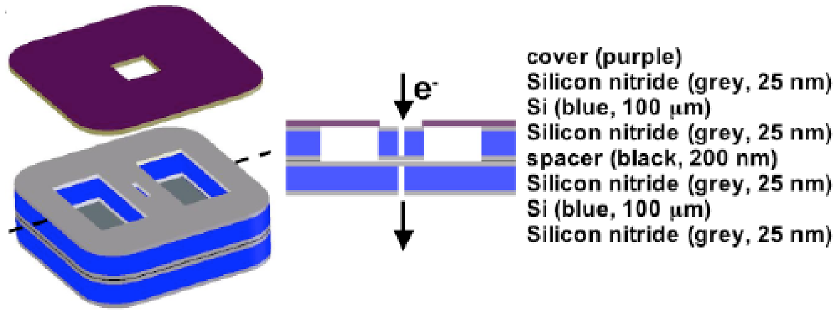


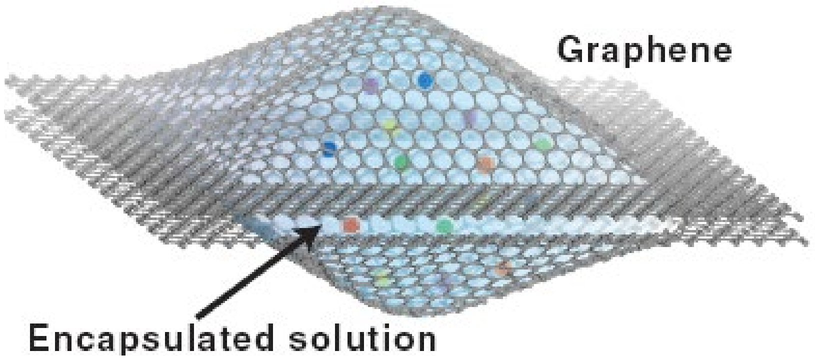
- Some ILs having low enough vapor pressure(~10^{-5} Pa) can be loaded without encapsulation
- Most of aqueous, *organic solvent cannot be used*

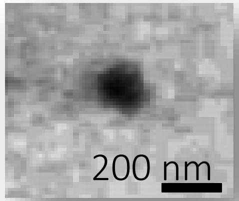
Closed cell LP-TEM Techniques

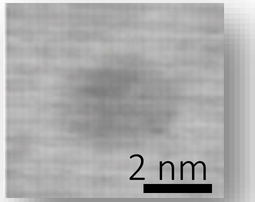
2003 | 2009 | 2012

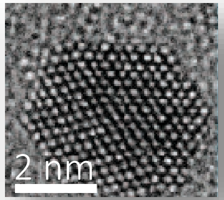












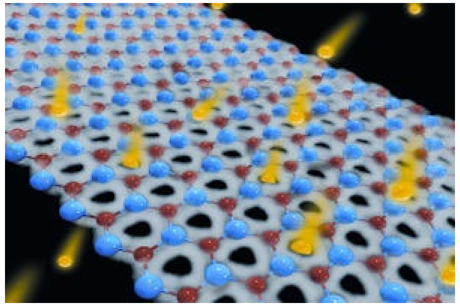
Window material	SiN	SiN	Graphene
Window thickness	160 nm	50 nm	~ 1 nm
Liquid thickness	0.5 – 1 um	> 1 um	< 100 nm
Resolution	~ 5 nm	~ 1 nm	~ 0.1 nm

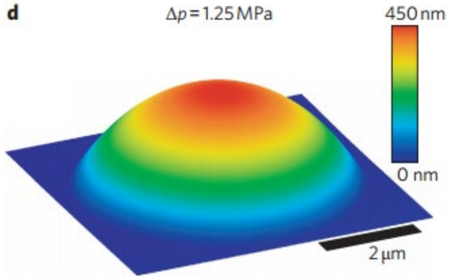
Williamson *et al. Nature Mater.* (2003) | Zheng *et al. Science* (2009) | Yuk *et al. Science* (2012)

The Benefits of Graphene for a Liquid Cell

1. Physically robust

- Impermeable
- High flexibility and strength (E ~ 1 TPa)

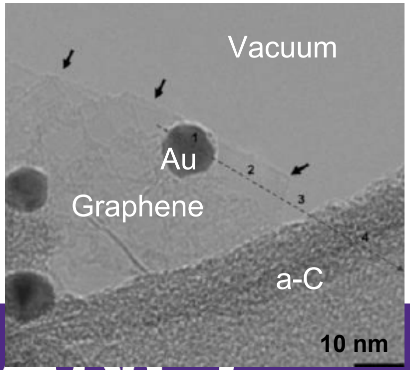


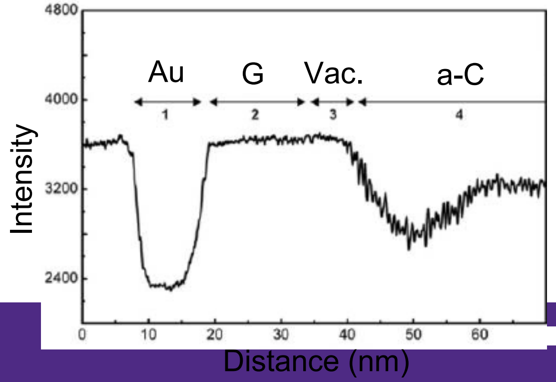


Hu *et al. Nature* (2014) Koenig *et al. Nat. Nanotech.* (2011)

2. Low background contrast

- Carbon (Z=6) material
- Two-dimensional thin (0.34 nm) material

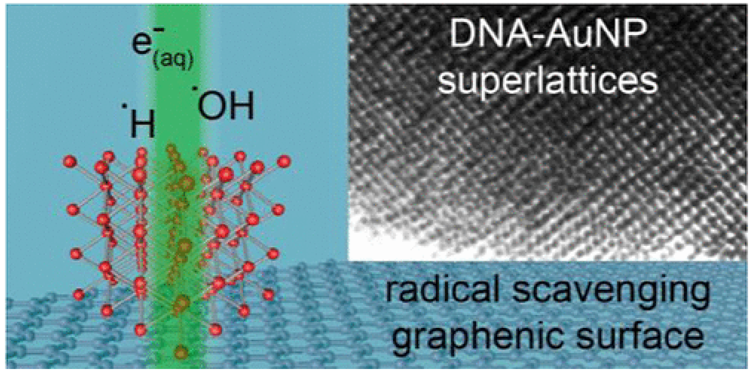




Lee *et al. Nano Lett.* (2009)

3. Radical scavenger

- Reduces secondary damage from reactive radicals



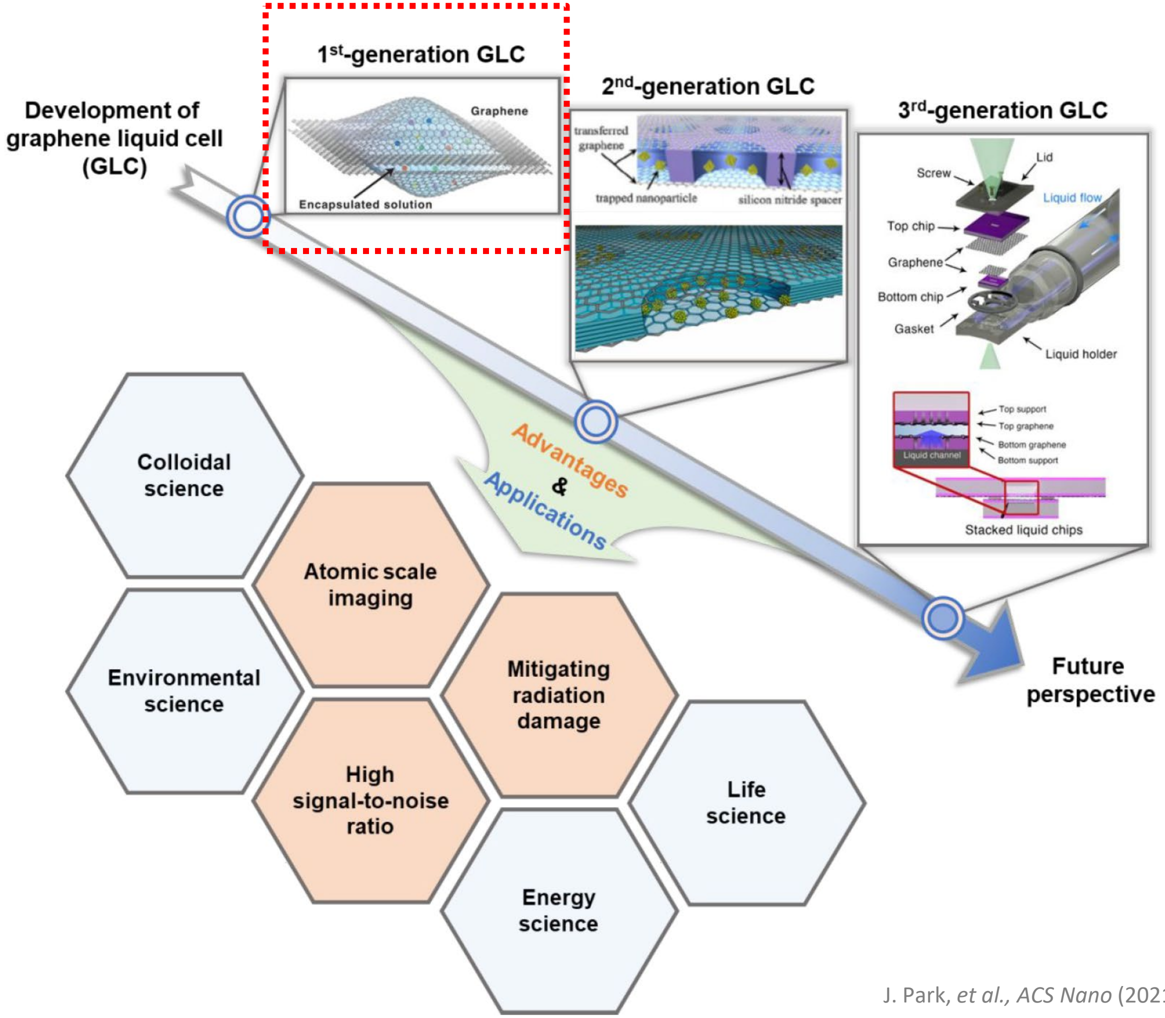
H. Cho, *et al., ACS Nano* (2017)

4. Decrease of heating and charging effect

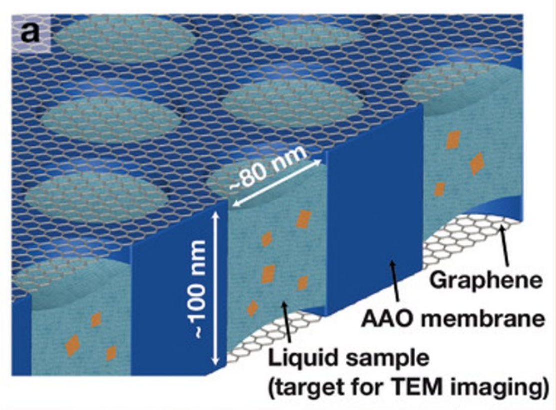
- Electrically and thermally conductive material

"Graphene is the **best material** for liquid encapsulation"

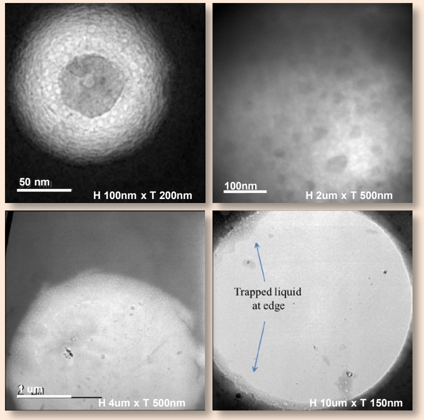
Various Graphene Liquid Cell Techniques



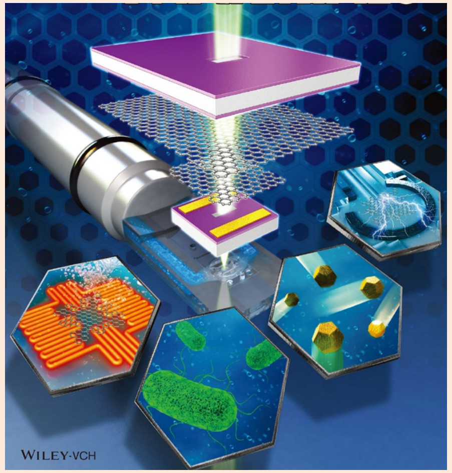
J. Park, *et al.*, *ACS Nano* (2021)

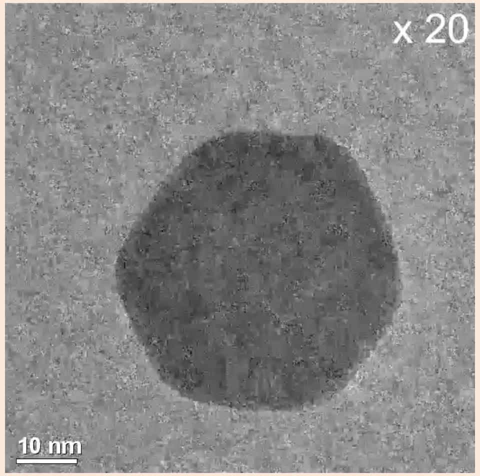


K. Lim, *et al.*, *Adv Mater* (2020)



N. Noh, *et al.*, *Lab on a chip* (2020)



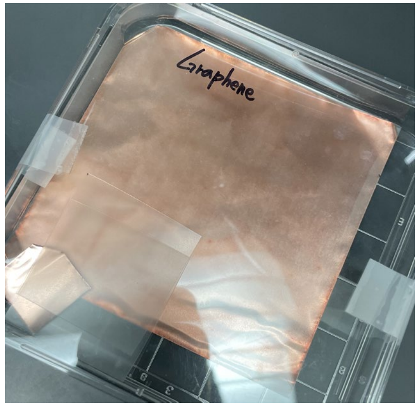


K. Koo, *et al.*, *Adv Mater* (2021)

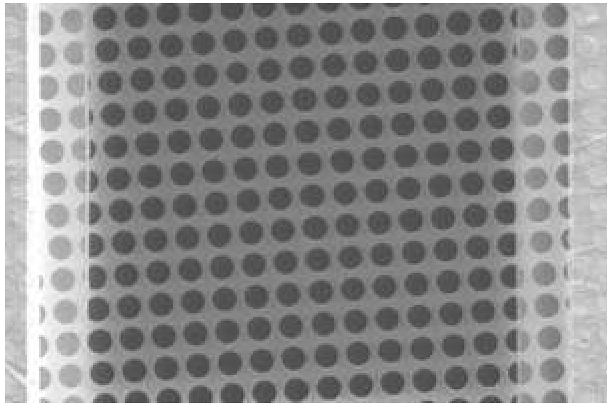
How to Make?

- J. Chang *et al.*, *JoVE* (**2019**) – Preparation of Graphene Liquid Cells for the Observation of Lithium-ion Battery Material

- Material *(or you can buy Graphene grid)*
  - High quality SL graphene on Cu
  - Au Quantifoil ® Grid
  - Ammonium Persulfate $(NH_4)_2S_2O_8$
  - Your solution
- Tools
  - Pt wire loop
  - Glassware, hotplate, PPEs, etc..



RTCVD graphene



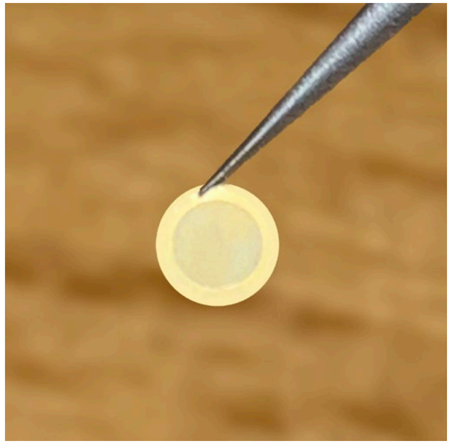
Quantifoil or C-Flat grid 2/2

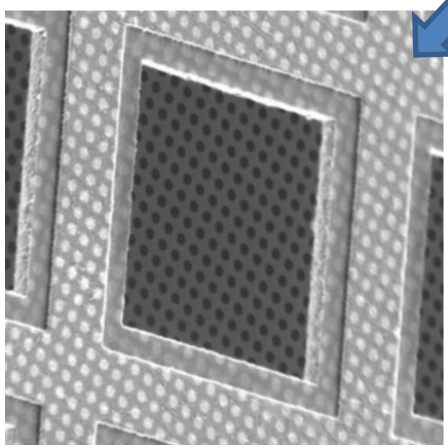
Pt wire

S/S wire loop - corrosion

Graphene Semi-wet Transfer

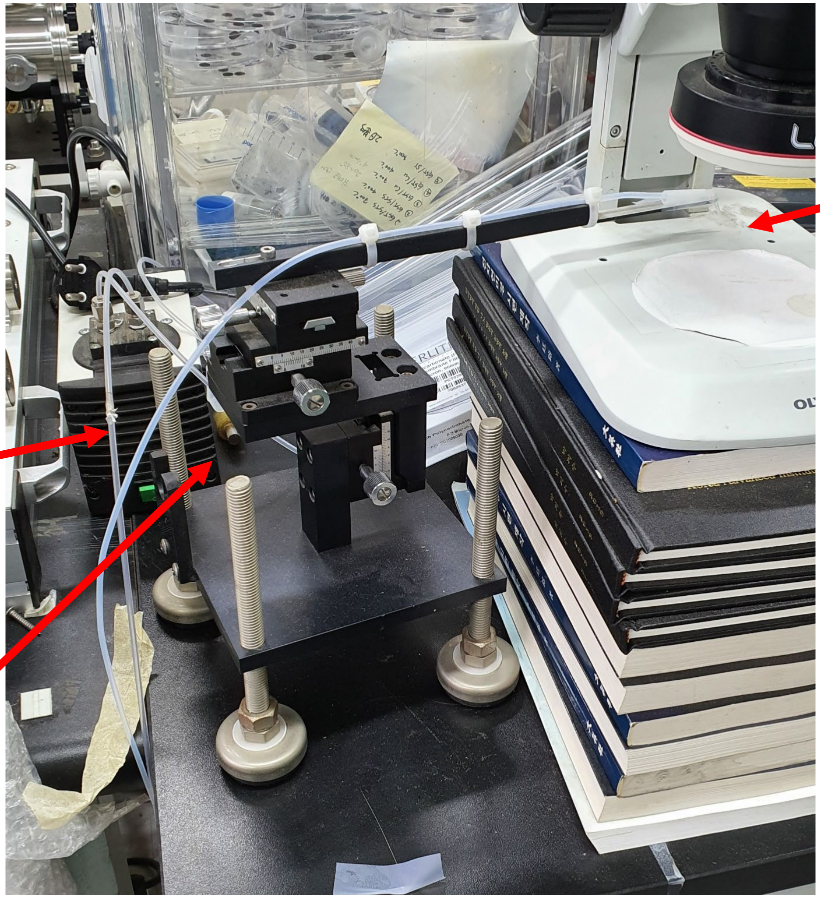
Film side (gray side)





Grid film side (gray side) down
Contacted with Gr/Cu

Optional suction for extra adhesion



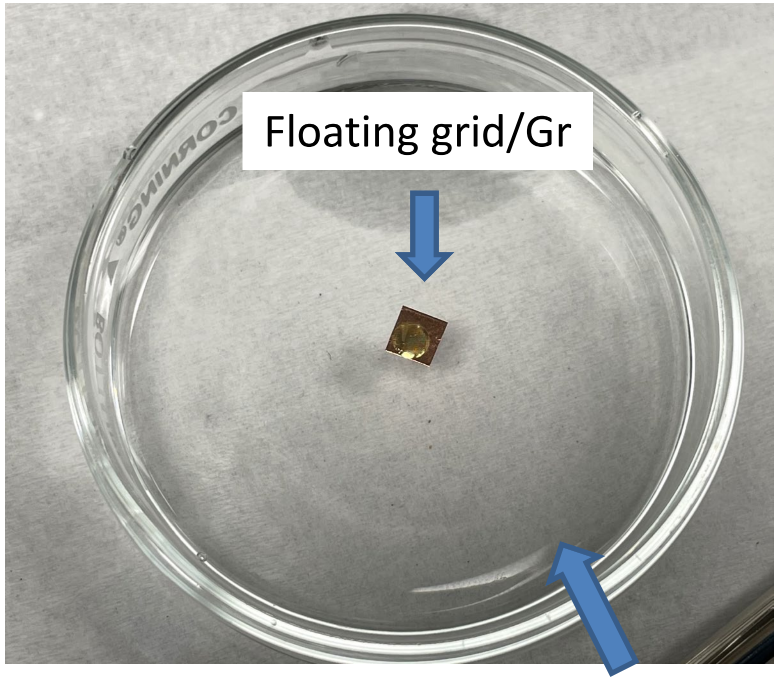
Pipette tip

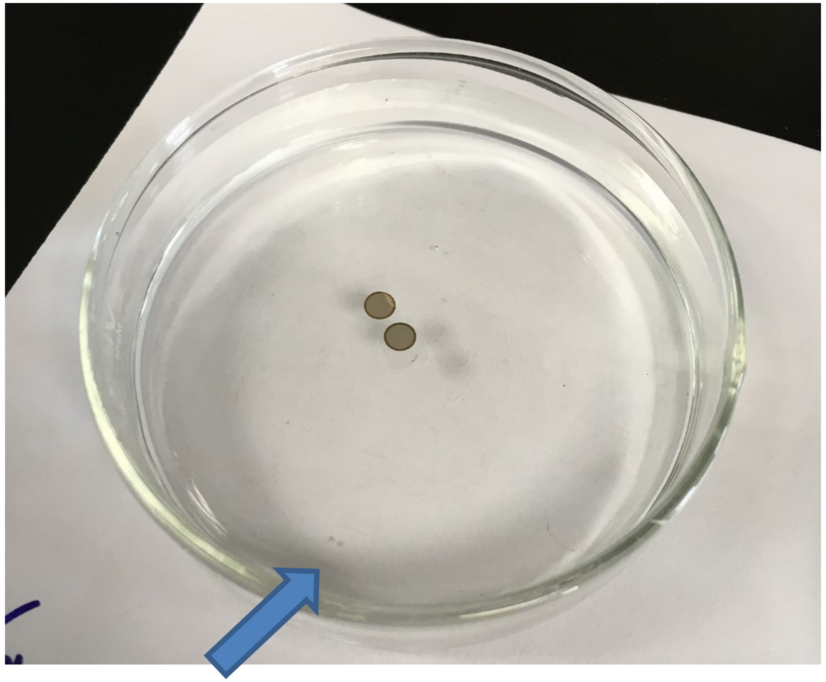
Liquid pump

Manipulator

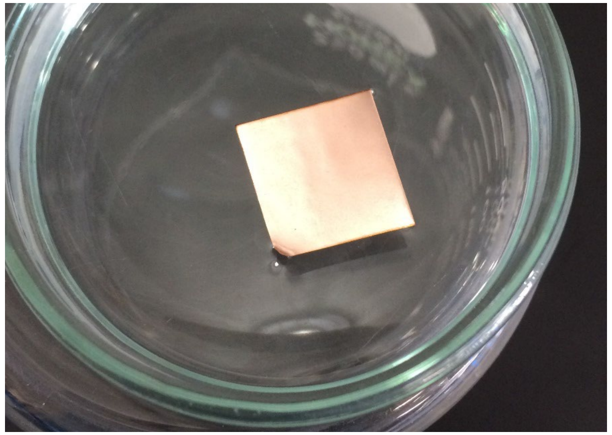
Graphene Etch

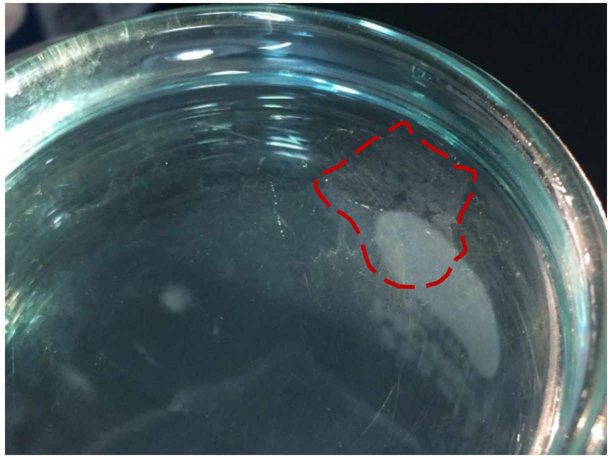
- Metal-containing Cu etchant ($FeCl_3$, $Na_2S_2O_8$) can induce metal ion residue within GLC





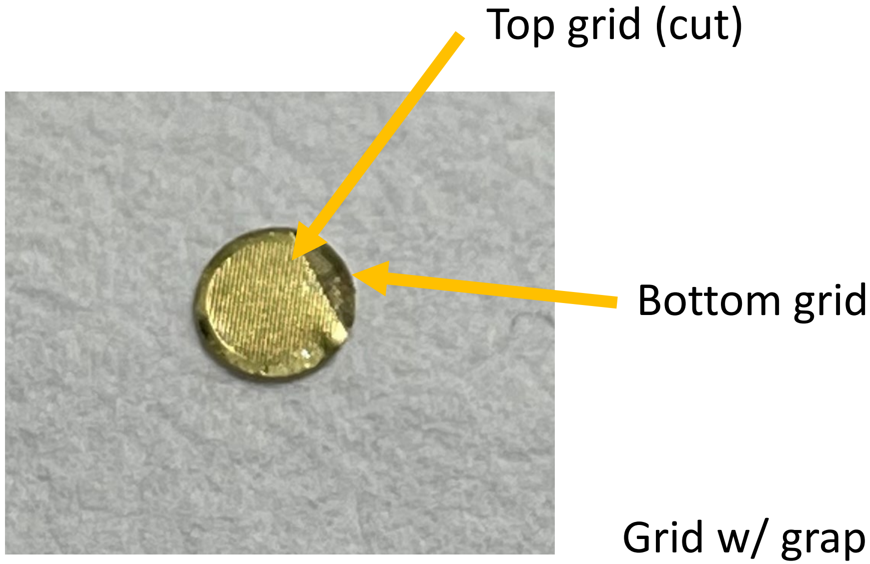
0.1-0.2 M APS solution



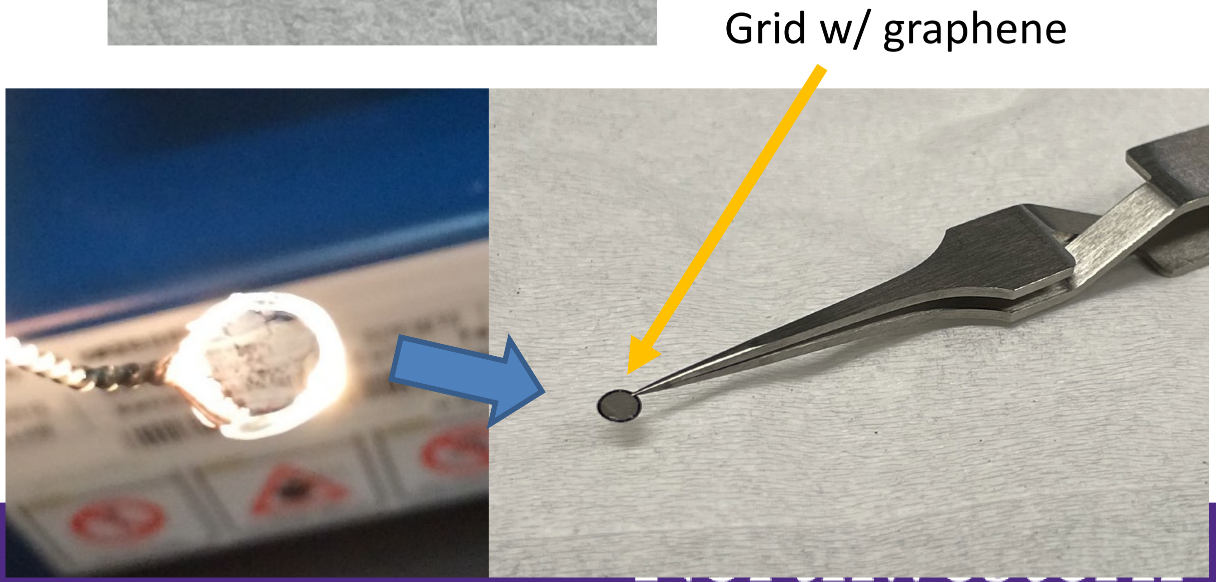


GLC Assembly – Two Ways

- Imposing two graphene grid
  - Aligning of hole and mesh
  - Small quantity of liquid
  - Delamination



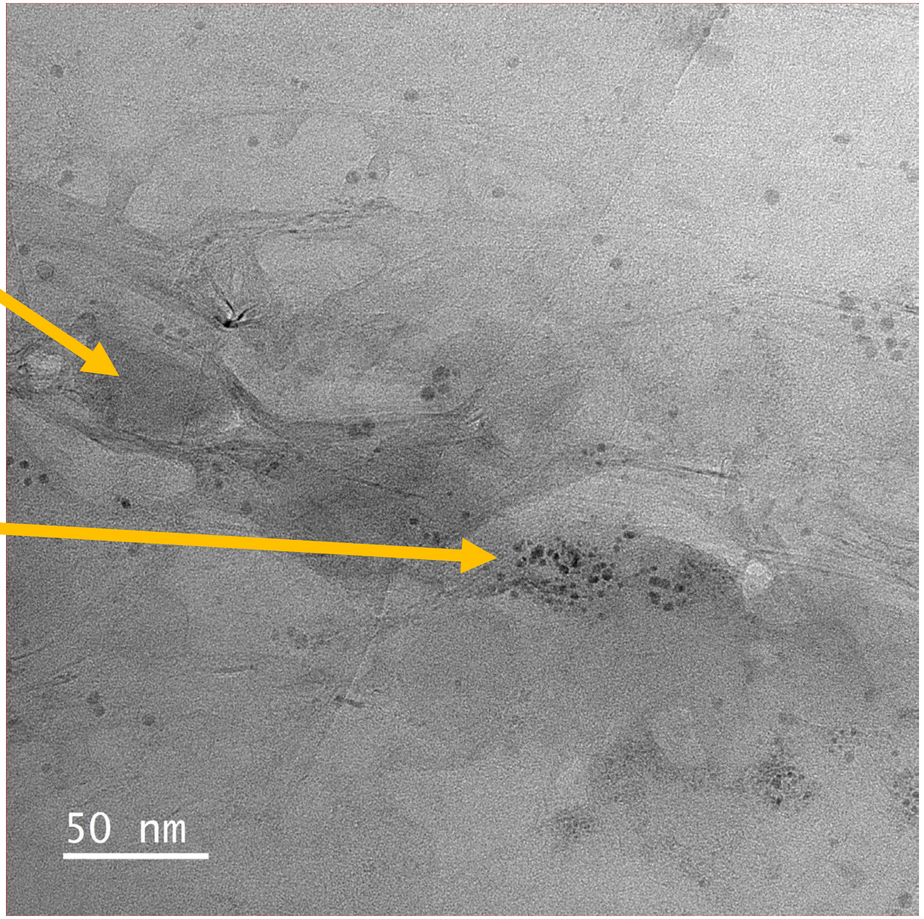
- Scooping graphene
  - Aqueous solution trap easy
  - Nasty shape

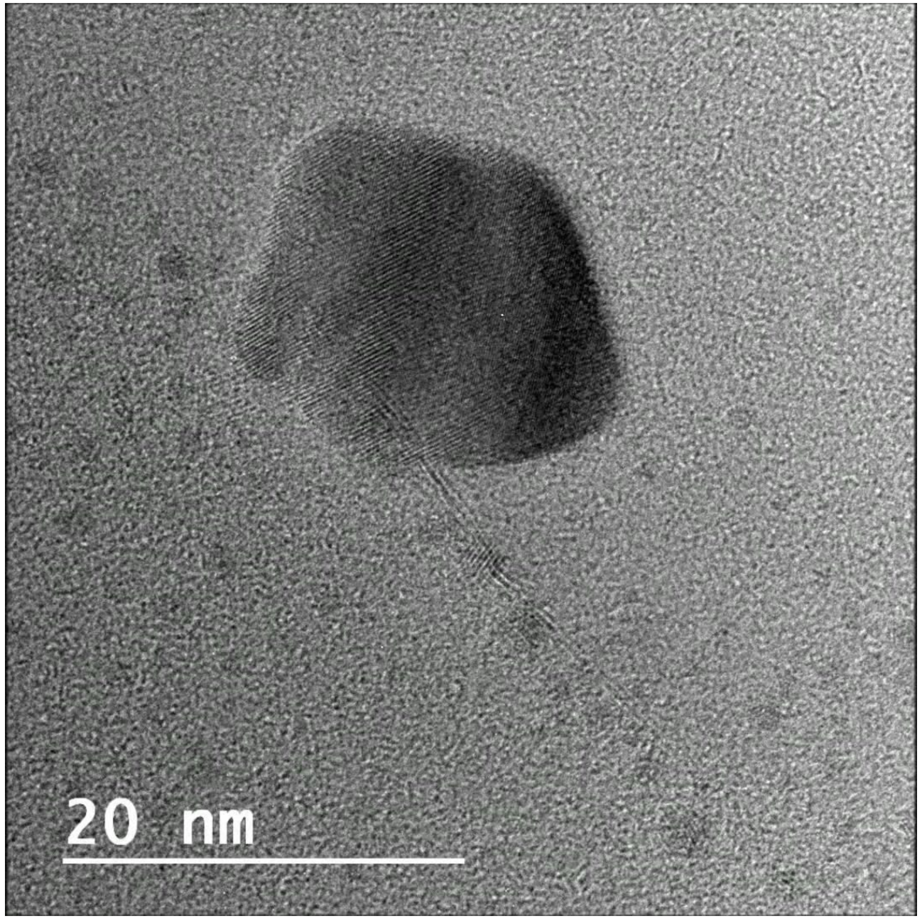


GLC Formation by Scoop

Your liquid

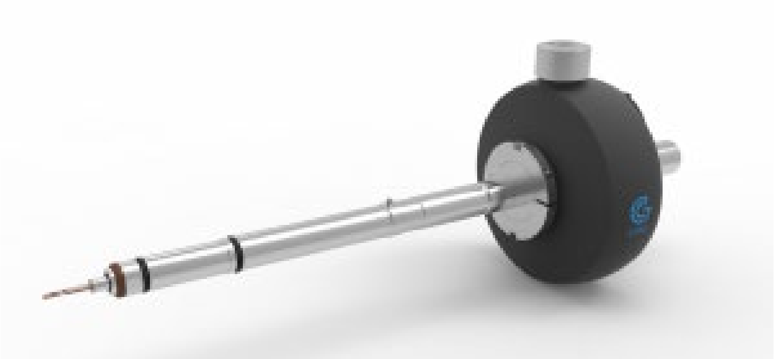
Particle





S. Y. Kim et al., PSS A (2018)

Specimen Rods for GLC in *EPIC*



Gatan Cryo-transfer holder

Controlled cooling down to LN_2 temp

Example : Formation of ice, phase transition, etc..

Gatan heating holder

Furnace heater up to 1300 deg C
Double tilt capability

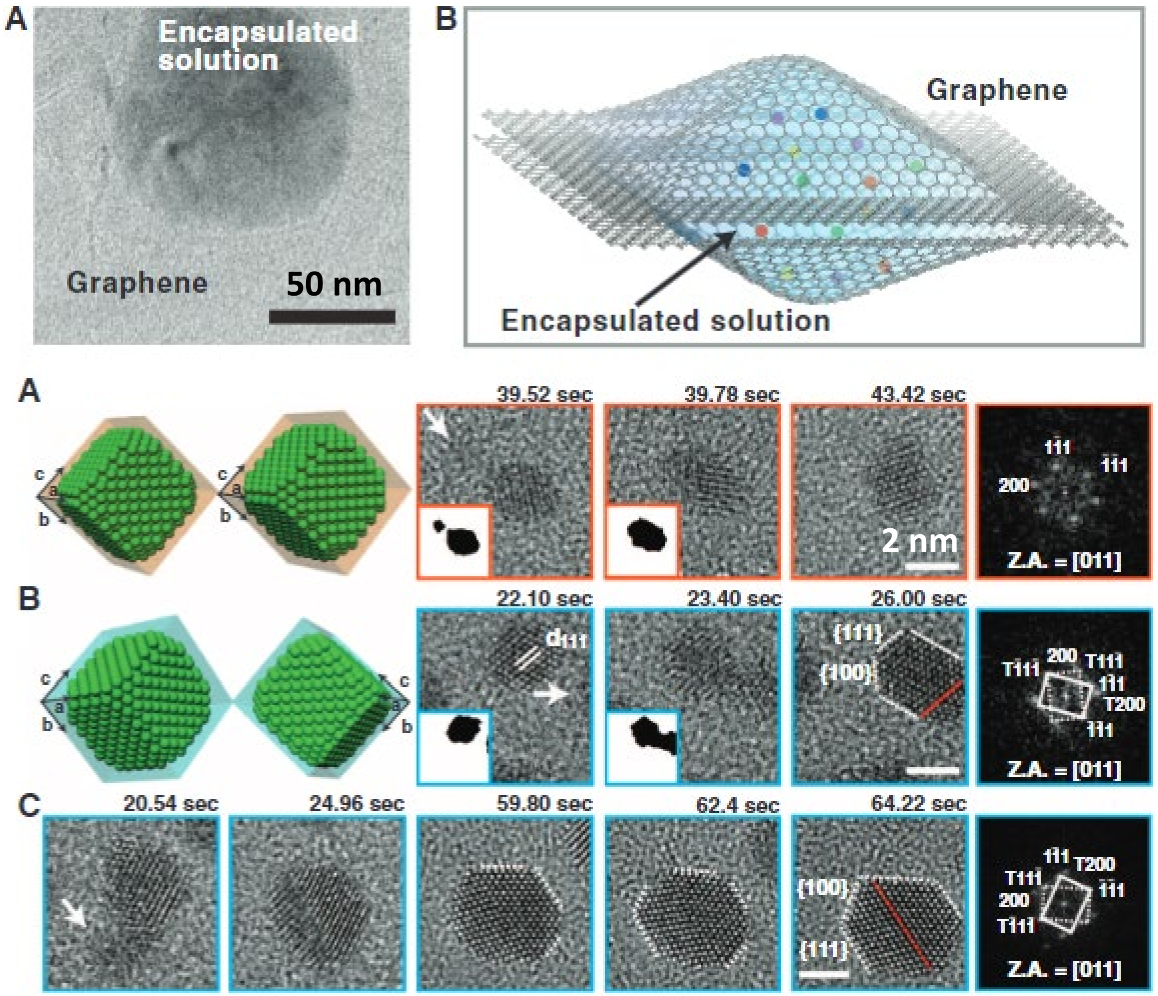
Example : Etch, formation of NPs, etc …

Also for the DT holder for crystallographic studies…

1: Crystal Growth

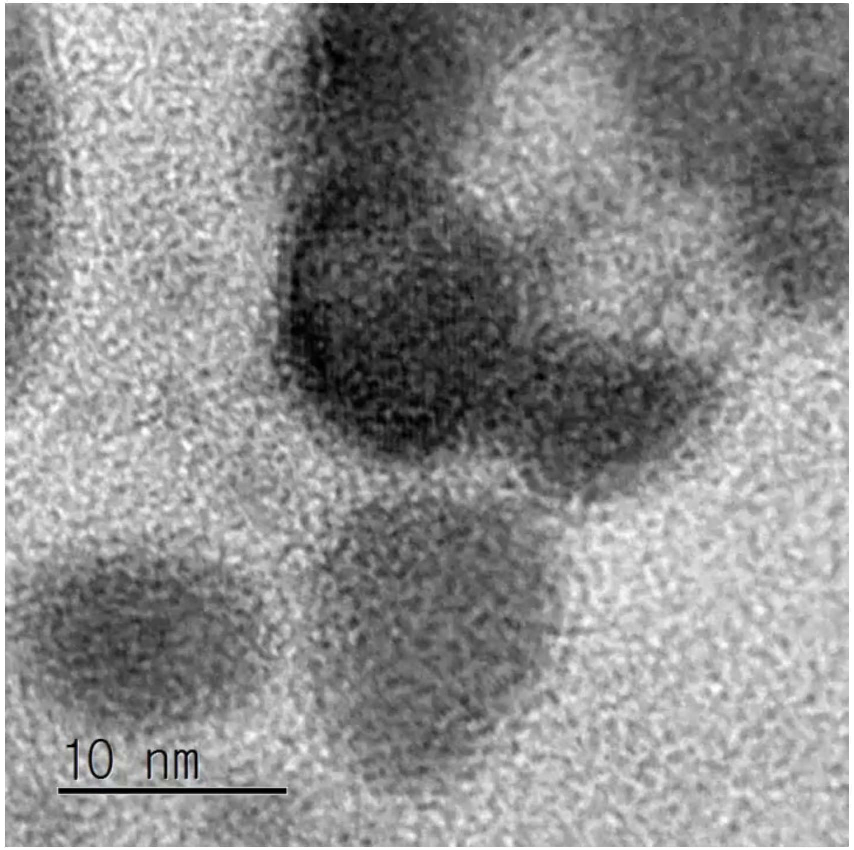
- Electron beam induced formation of Pt
- Non-classical growth along the {111} plane (growth by coalescence)

Yuk *et al.*, *Science* (2012)

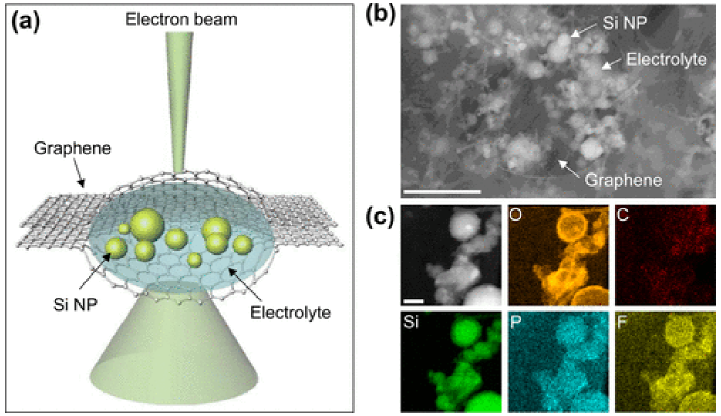


2: Energy Application

Lithiation of SnO_2 Nanoparticle



Chang *et al.*, *ACS Omega* (2017)



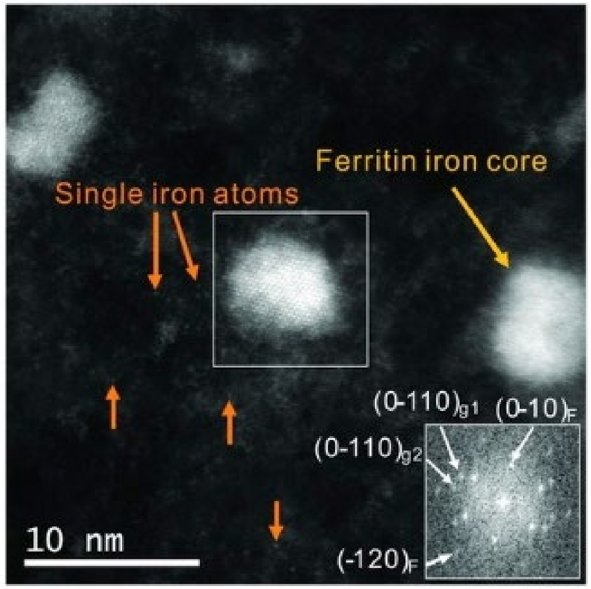
Yuk *et al.*, *ACS Nano* (2014)

- Direct-biasing of material inside of GLC pocket is very hard, thus e-beam induced chemical lithiation is frequently used

- Most common studies are related to ***orientation-preferred lithiation***, develop of ***SEI layer***, and ***crystallographic study during alloying-lithiation …***

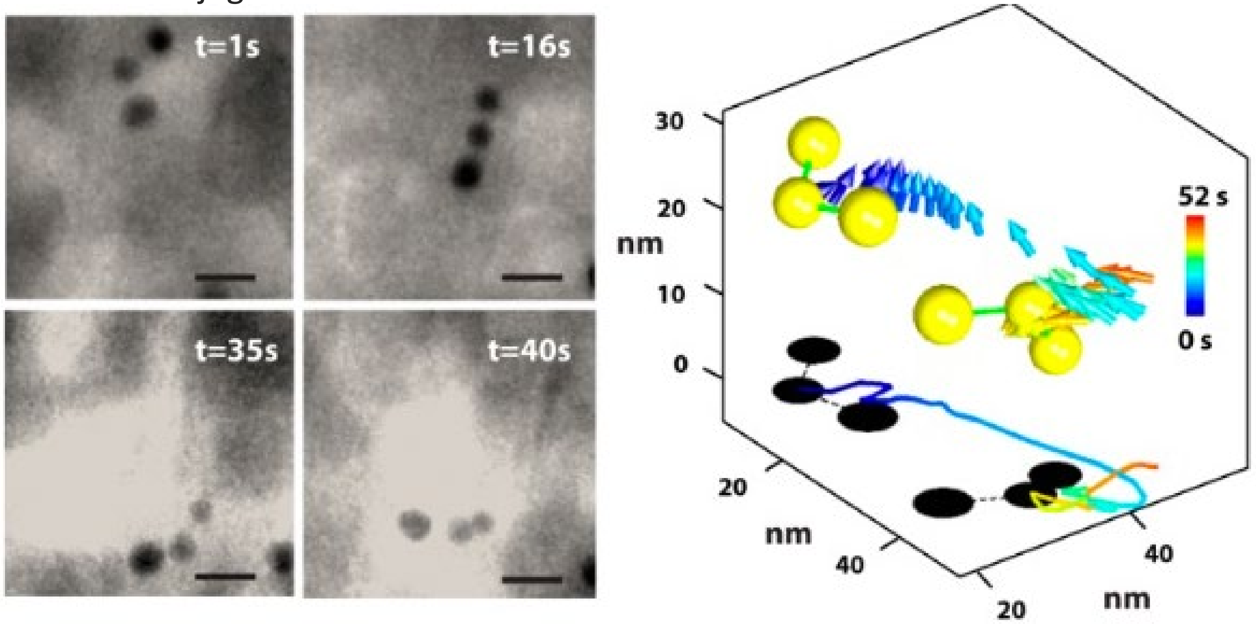
3: Bio Application

Protein



C. Wang, *et al.*, *Adv. Mater.* (2014)

DNA-Au Conjugates



Q. Chen, *et al.*, *Nano Lett.* (2013)

- Hydrated biomolecules can be visualized with GLC
- Radical scavenging property prolongs observation time

Reading Materials for Better GLC Skills

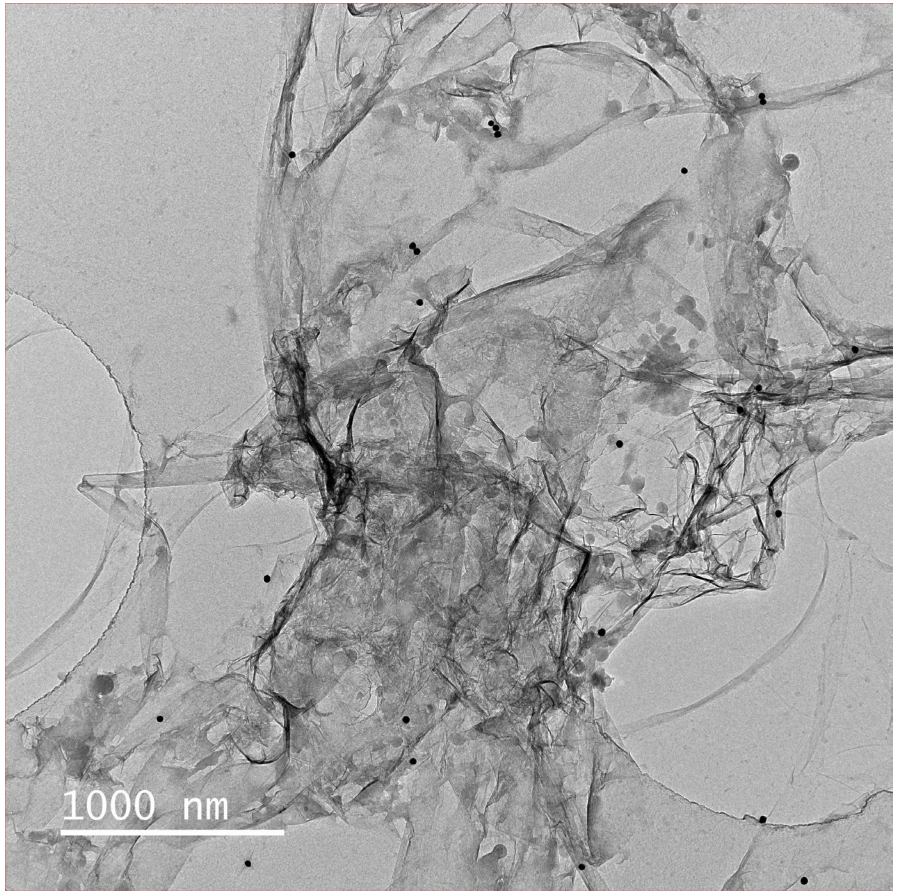
- J. Yuk *et al.*, *Science* (**2012**) - High-Resolution EM of Colloidal Nanocrystal Growth Using Graphene Liquid Cells
- J. Chang *et al.*, *JoVE* (**2019**) – Preparation of Graphene Liquid Cells for the Observation of Lithium-ion Battery Material
- M. Textor *et al.*, *Nano Letters* (**2018**) - Strategies for Preparing Graphene Liquid Cells for Transmission Electron Microscopy
- J. Park *et al.*, *ACS Nano* (**2021**) – Graphene Liquid Cell Electron Microscopy: Progress, Applications, and Perspectives
- K. Koo *et al.*, *Adv Mater* (**2021**) - Liquid-Flowing Graphene Chip-Based High-Resolution Electron Microscopy

Questions From the Mailbox -1

- Q1 : How large are the volume pockets examined?
  - Generally, **few attoliters (10^{-18} L) in volume**. Typical area and thickness of the liquid pocket is in 100 nm scale. ($(10^{-7})^3 \times 1000$ L/m^3)
- Q2 : How are you sure your liquid cell is examined and has not dried/undergone radiolysis?
  - Most easy way to confirm liquid is **bubble generation** sample dried away will not create bubbles upon illumination. **You must consider there is always radiolysis** while you are doing liquid experiment, but generation rate (controlled dose) and alleviating (scavenging) is more important.
- Q3 : How do you prepare your GLCs?
  - Explained in slide/ please refer nice JoVE video.

Questions From the Mailbox -2

- Q4 : How do you avoid the folding of graphene and maintain high purity?
  - Scooping (wet transfer) of graphene will always incorporate folding but some liquid cell can be also formed inside fold (not always bad).
  - Imposing two transferred-graphene have less folds but sometimes it is hard to capture depends on its wettability on graphene.
  - Use metal ion free etchant, and rinse it thoroughly to avoid contamination



Thank you for your attention!

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