Metal hydride nanoparticle synthesis

In liquid cell TEM

NU*ANCE* November Tech Talk
November 18, 2026

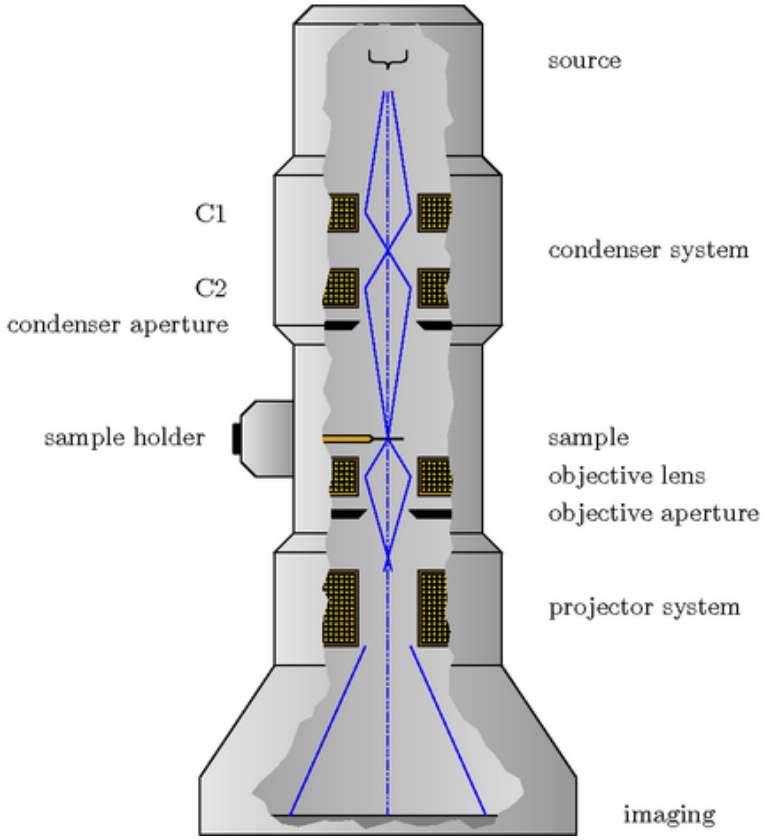
Jaeyoung Hong
Postdoctoral Research Associate
NU*ANCE* Keck-II

Outline

- Liquid cell compatible with a standard TEM holder
  - K-kit
  - Graphene liquid cell / carbon film liquid cell

- Utilize electron beam-induced effect in liquid cell TEM
  - Palladium hydride nanoparticle formation in liquid
  - Maximize hydrogen production in liquid by boosting radiolysis of

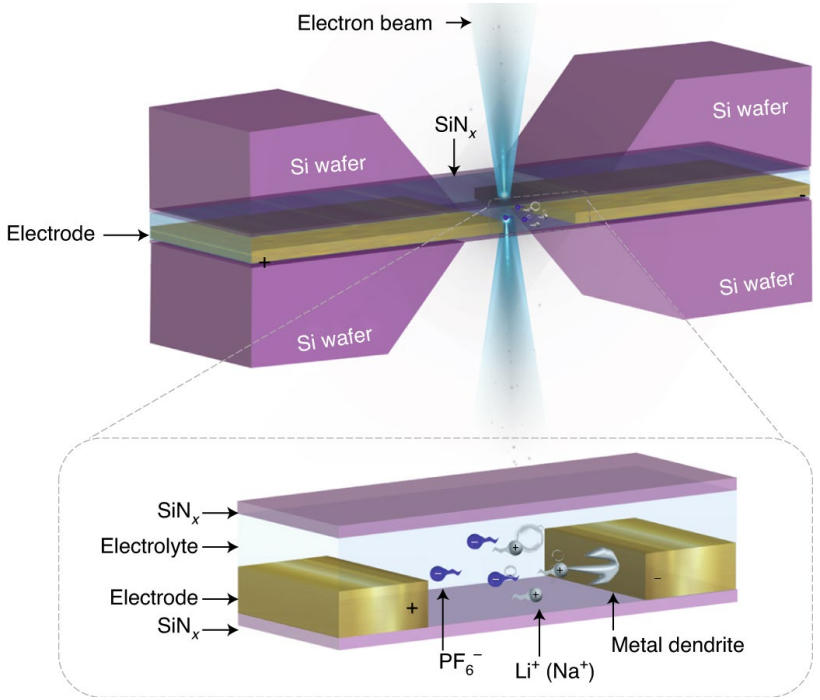
Transmission electron microscope (TEM)



https://texample.net/tikz/examples/transmission-electron-microscope/

- High vacuum inside column: ~$10^{-6–8}$ torr

- Special container is needed to keep liquid or gas inside TEM column for in situ and operando analysis

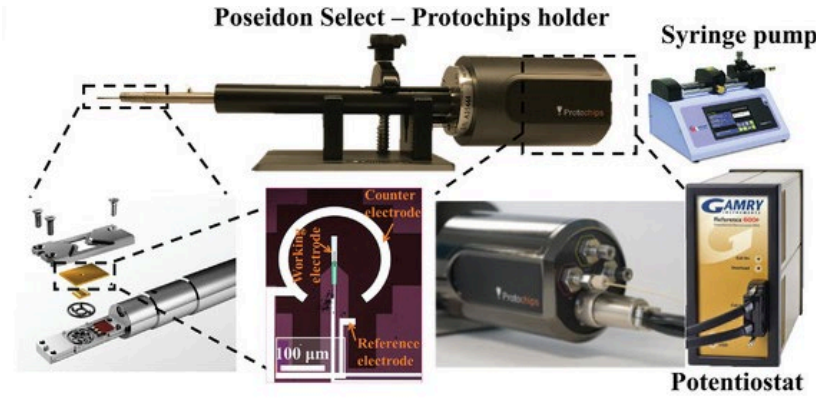


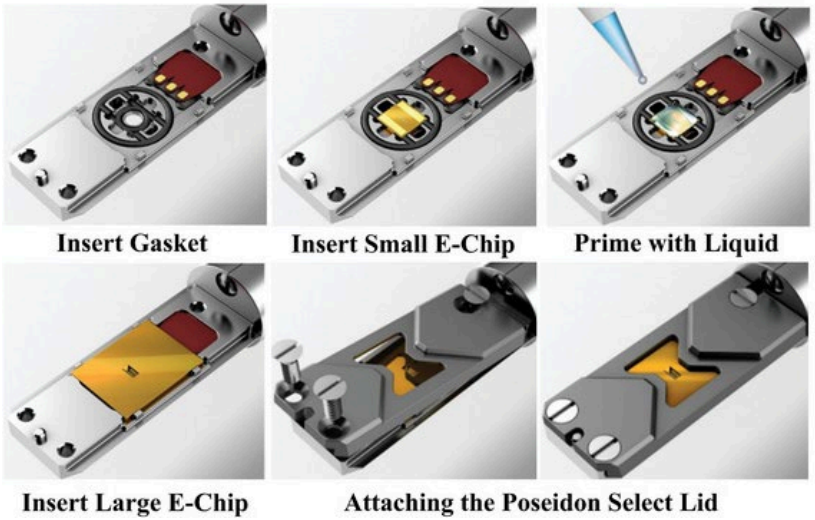
R. Yang et al., *Nat. Protoc.* 18 (2023)

- In situ gas/liquid TEM cell

- Imaging window:
  thin & robust

Commercial in situ liquid TEM holder

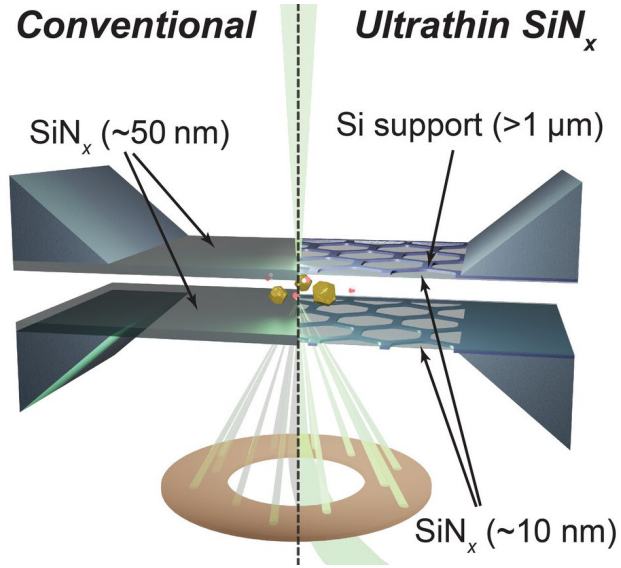




A.M. Abdellah et al., *Small Methods* (2025) Protochips

➢ Pros

- Liquid flow
- Liquid thickness control
- Electrochemical experiment
- Heating

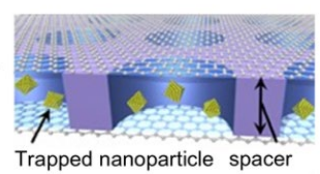


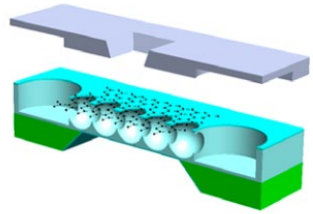
K. Koo et al., *Sci. Adv.* 10 (2024)

➢ Cons

- Limited imaging window thickness
  SiN_x ~ 50nm
  → Can be reduced to ~ 10 nm or substituted with graphene through chip customization (Fab needed)

- Holder is not cheap
  NU*ANCE* center liquid holder: Hitachi TEM

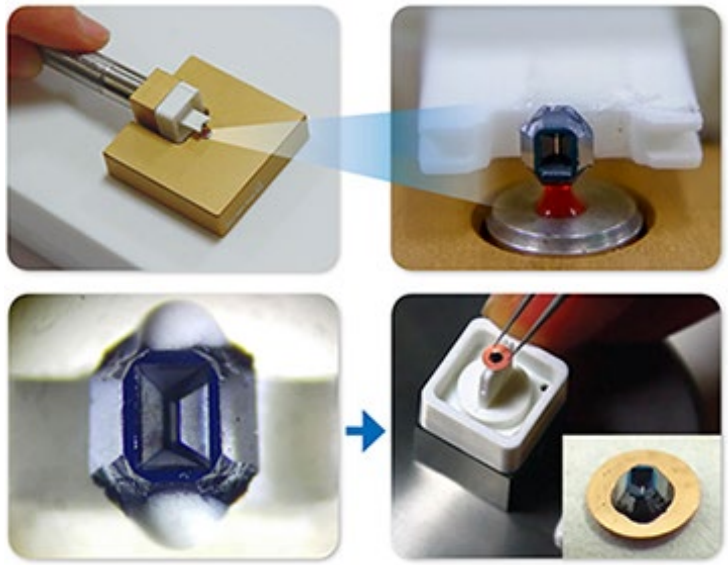




H. Ma et al., *Small Sci.* 5 (2025)

Liquid TEM cell compatible with standard TEM holder

- **Silicon nitride liquid cell (e.g. K-kit)**

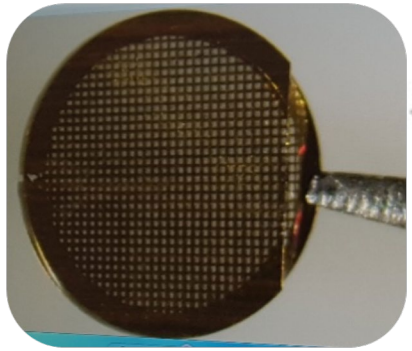


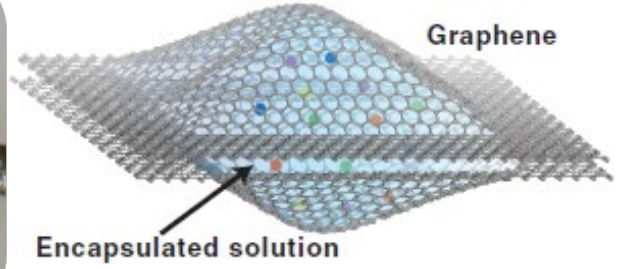
https://www.tedpella.com/k-kit_html/k_kit.aspx

- SiN_x window ~30 nm

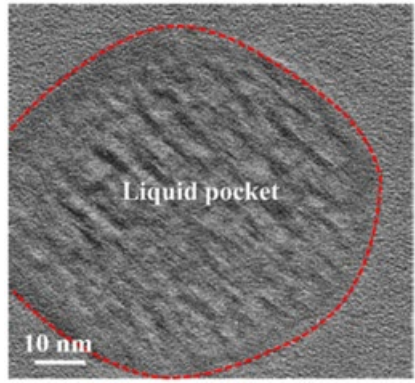
- Liquid thickness: 0.1, 0.2, 0.5, 1, 2, 5 µm

- **Graphene liquid cell (GLC) / filmliquid cell**





J.M. Yuk et al., *Science* 336 (2012)



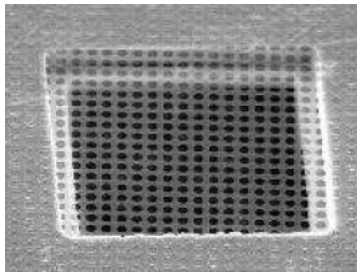
C. Zhu et al., *Nat. Commun.* 9 (2018)

- Carbon-based window: Graphene monolayer/multilayer Carbon film
- Random liquid thickness

- No liquid flow
- No electrochemical experiment
- No heating (unless heating holder is accessible)

GLC fabrication

1.



Quantifoil®

Holey carbon
Au grid

graphene
Cu foil
graphene

2.



Plasma cleaner

graphene
Cu foil
graphene

Plasma etching

3.

Isopropanol

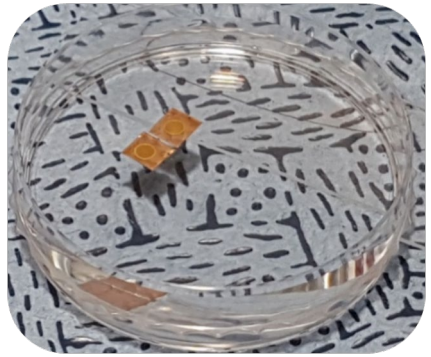
Au grid
Holey carbon
graphene
Cu foil



4.

Au grid
Holey carbon
graphene
Cu foil

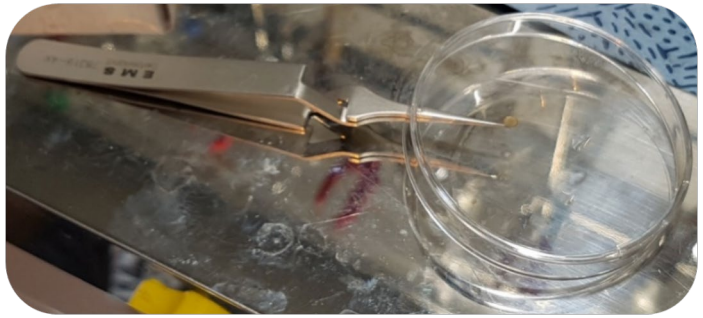
Etchant



Cu foil etching
e.g. Ammonium persulfate, $FeCl_3$

5.

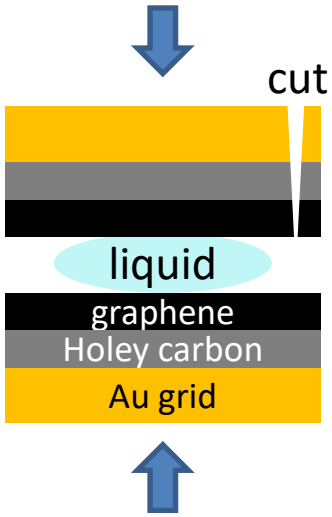
graphene
Holey carbon
Au grid



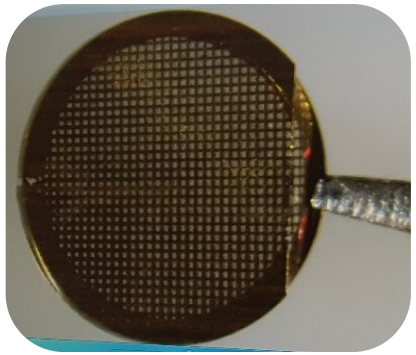
Dry graphene TEM grid after rinsing with DI water

GLC fabrication

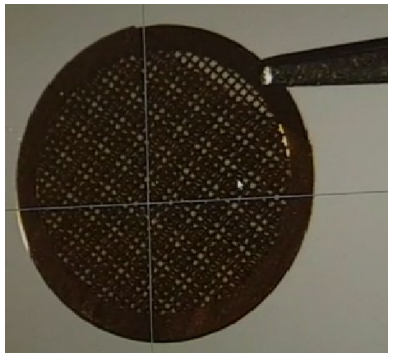
6.



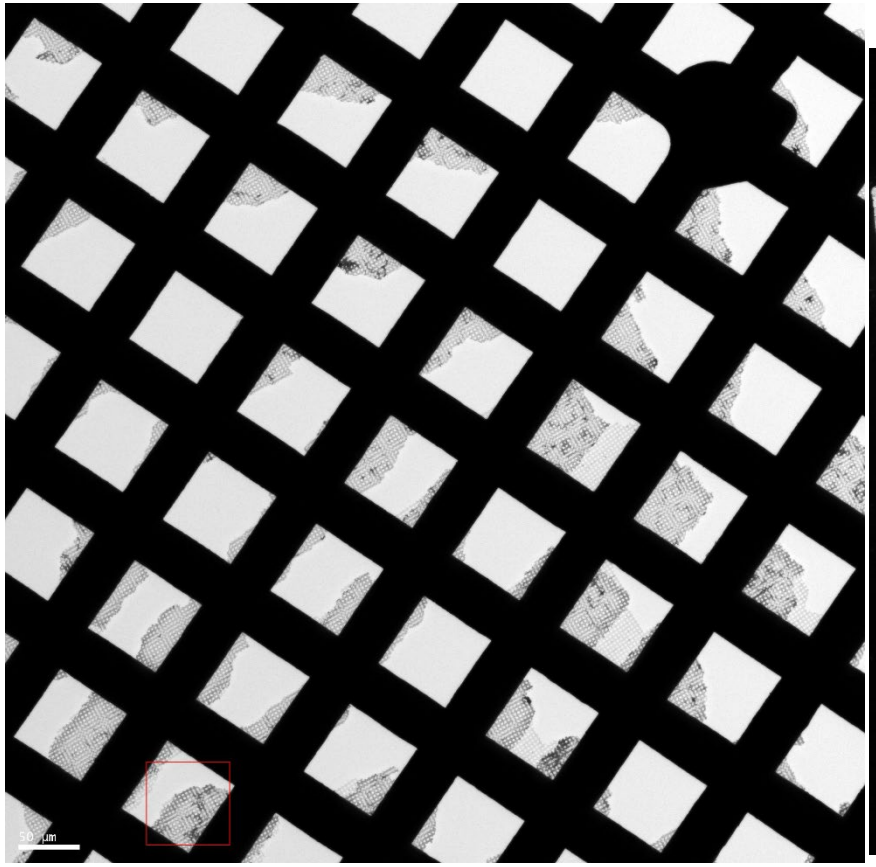
Sandwich



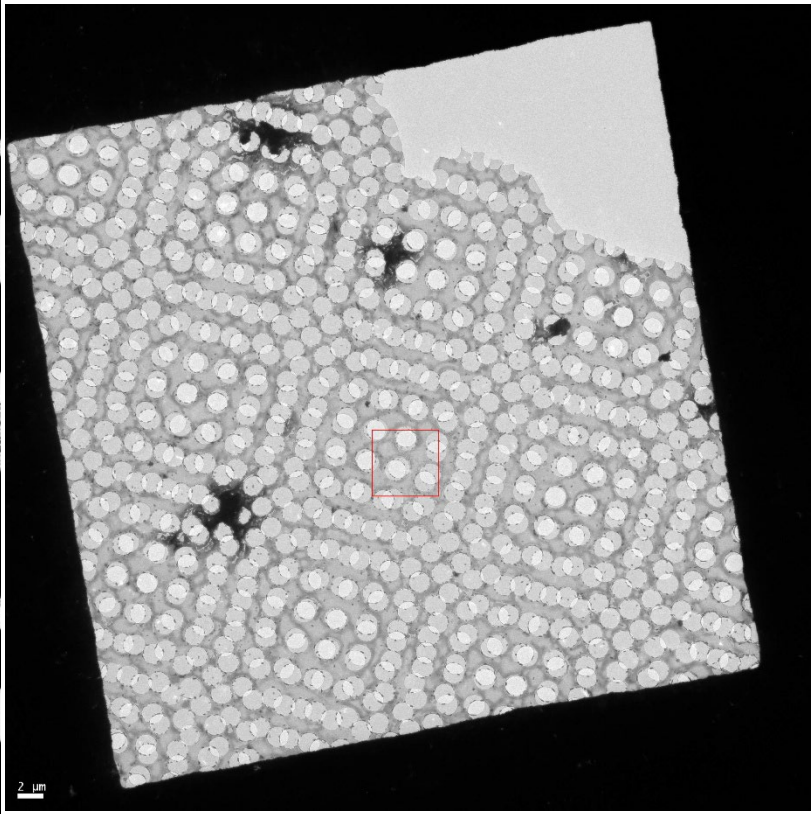
Aligned



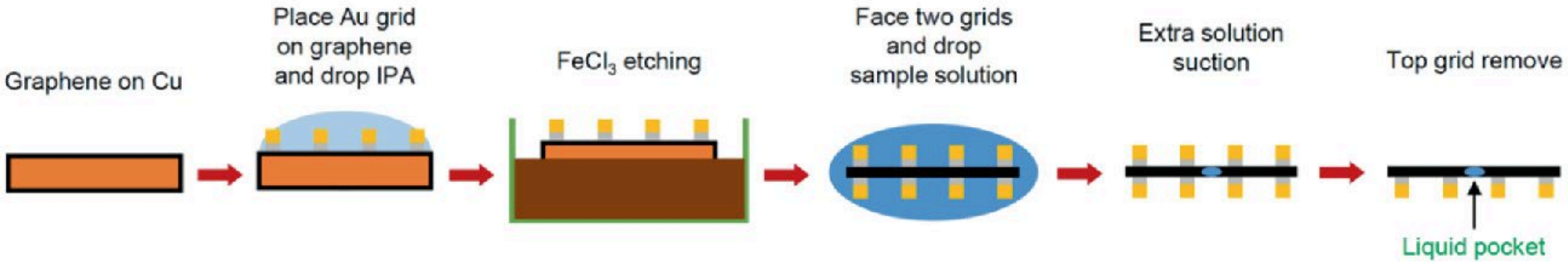
Misaligned



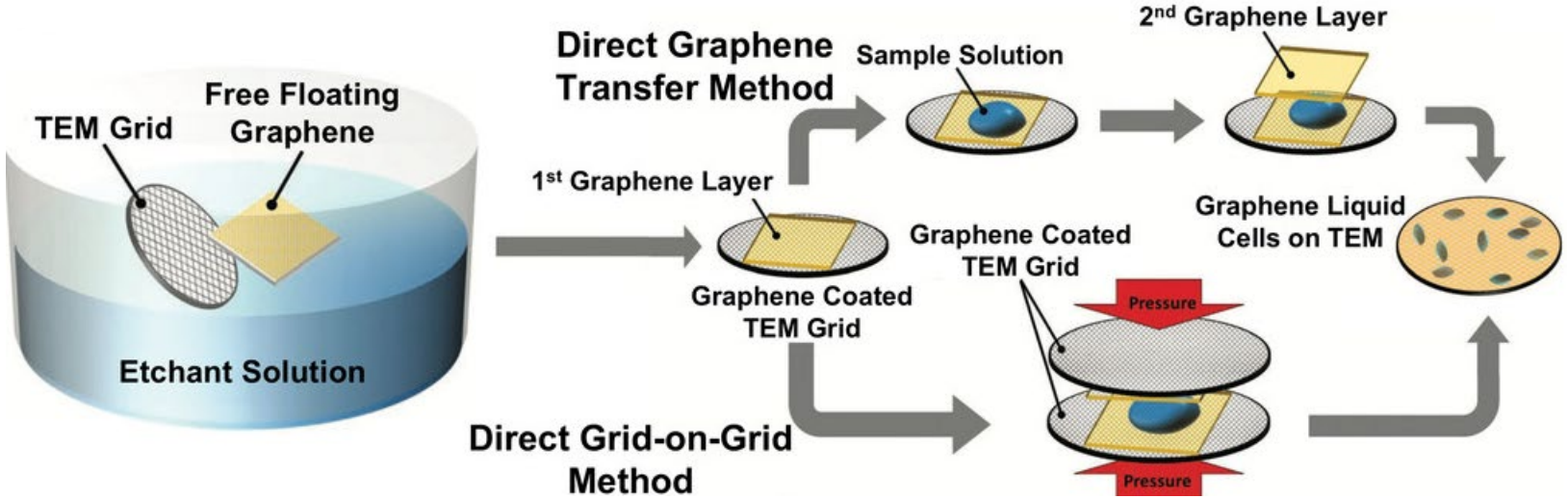
If one grid is removed



GLC fabrication – other methods



C. Zhu et al., In-situ transmission electron microscopy (2023)

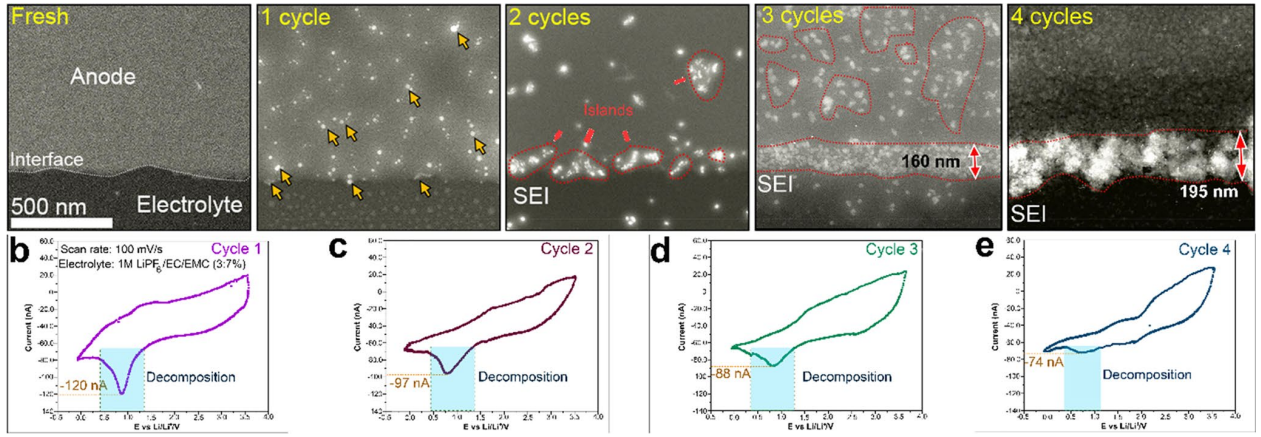


H. Ma et al., *Small Sci.* 5 (2025)

Electron beam-sample interaction

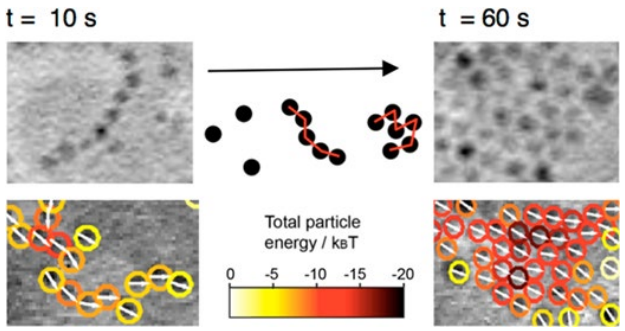
➢ Case 1. Need to minimize beam-induced artifacts

- Electrochemical reaction

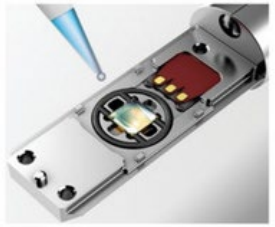


W. Dachraoui et al., *ACS Nano* 17 (2023)

- Self assembly



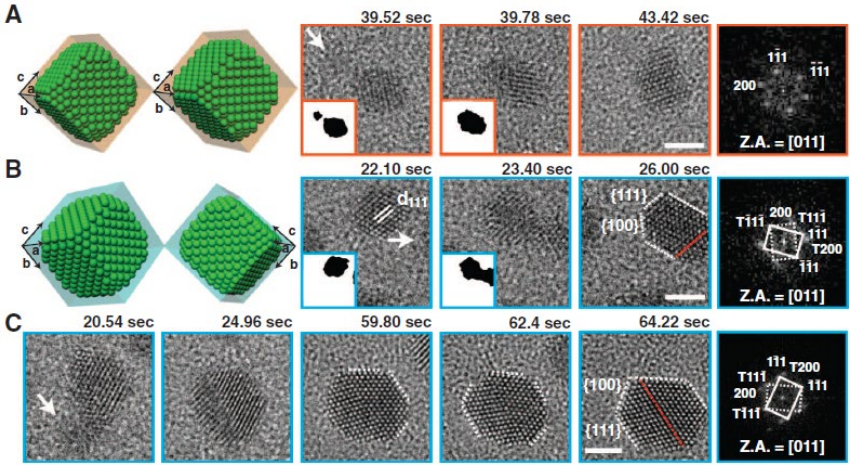
A.S. Powers et al., *Nano Lett.* 17 (2017)



Sample shouldn't be affected by electron beam to capture true nature of the phenomena

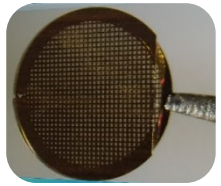
➢ Case 2. Utilize beam-induced effect

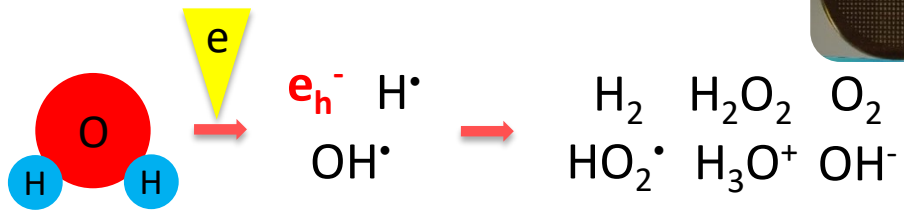
- Particle growth



J.M. Yuk et al., *Science* 336 (2012)

- radiolysis of water

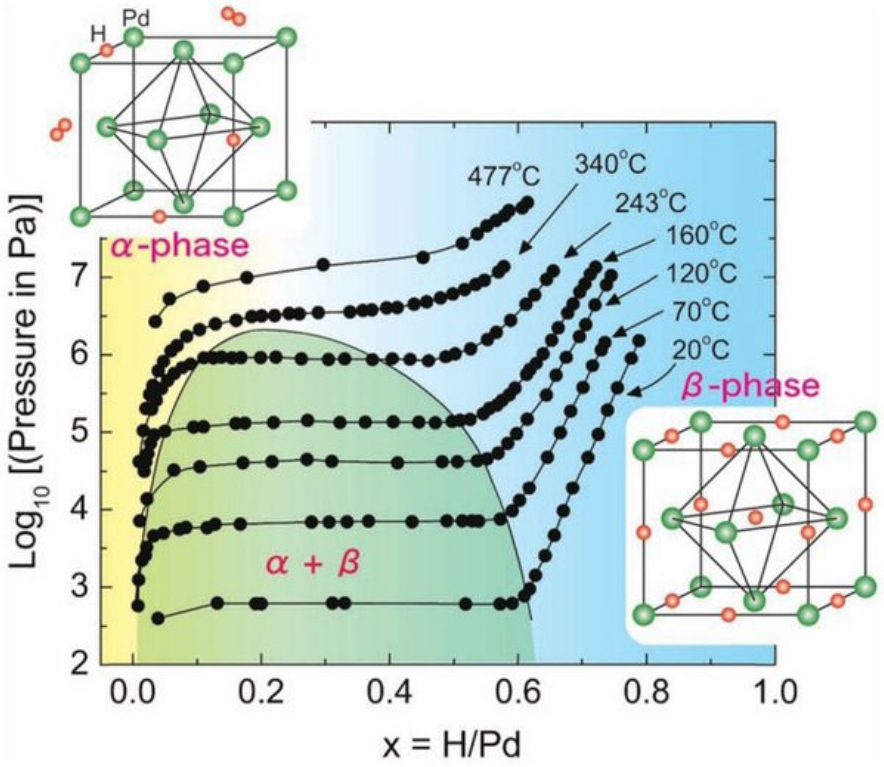




e_h^-: reducing agent

Interaction between hydrogen and metal

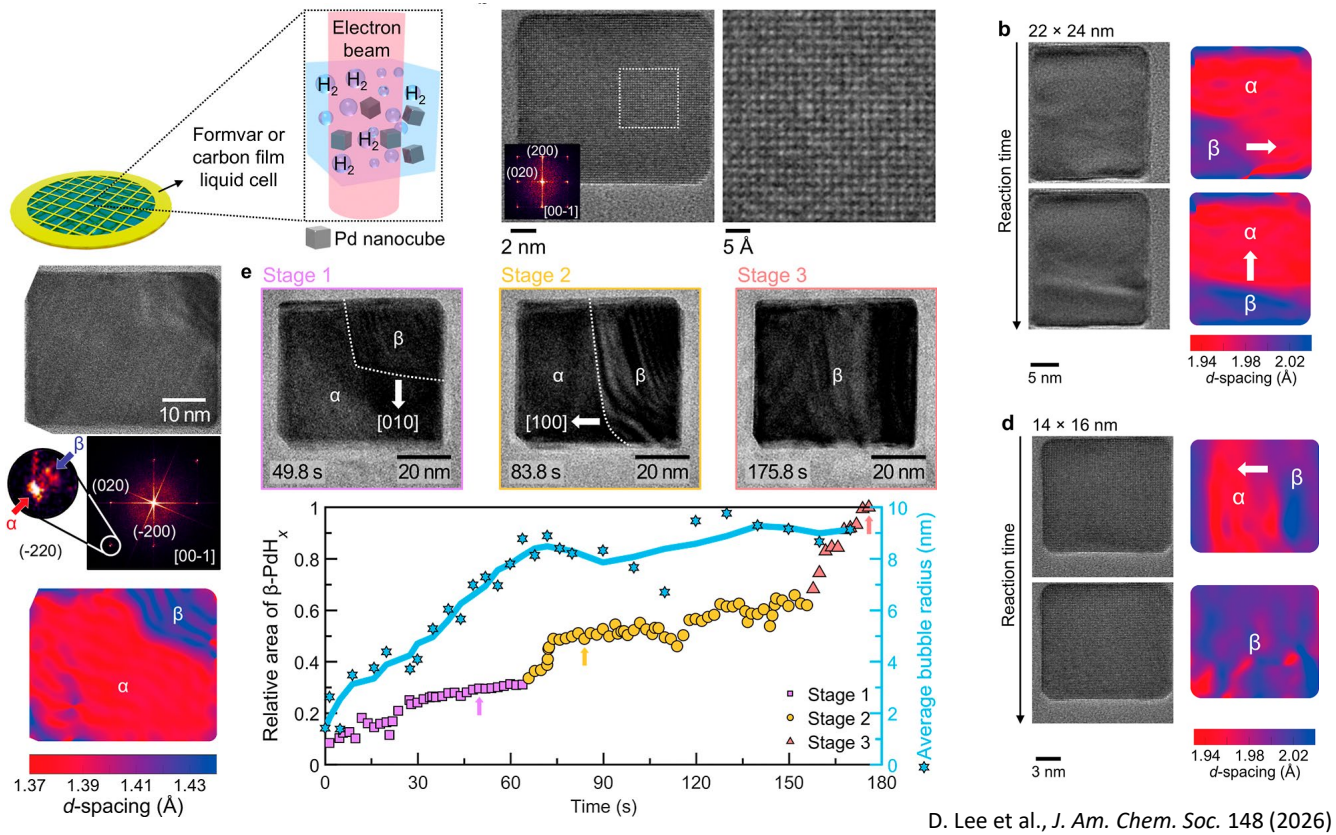
➢ Palladium



H. Akiba et al., *Phys. Rev.* 92 (2015)

Exceptional hydrogen affinity

➢ Hydrogen absorption in water

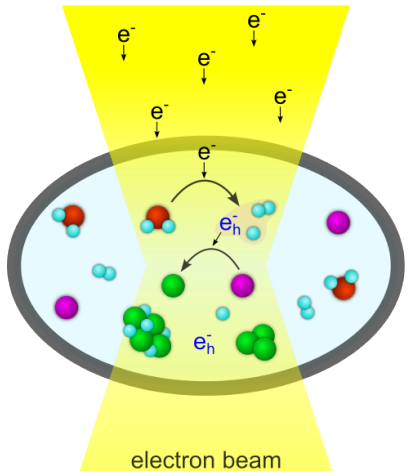


D. Lee et al., *J. Am. Chem. Soc.* 148 (2026)

Hydrogen produced due to electron beam

Boost radiolysis reaction

➢ Pd NP growth in H-rich environment

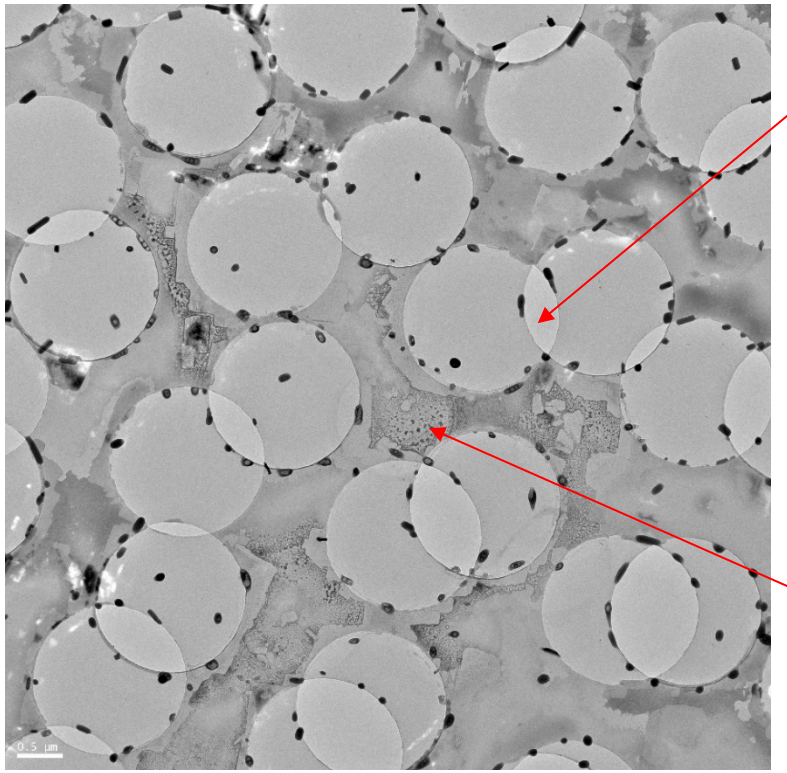


J. Hong, X. Su, *J. Am. Chem. Soc.* 146 (2024)

Electron beam irradiation on Na_2PdCl_4 aq. solution

Typically, GLC users set accceleration voltage to 60 or 80 kV to minimize the damage to graphene

➢ Used GLC as carbon film liquid cell



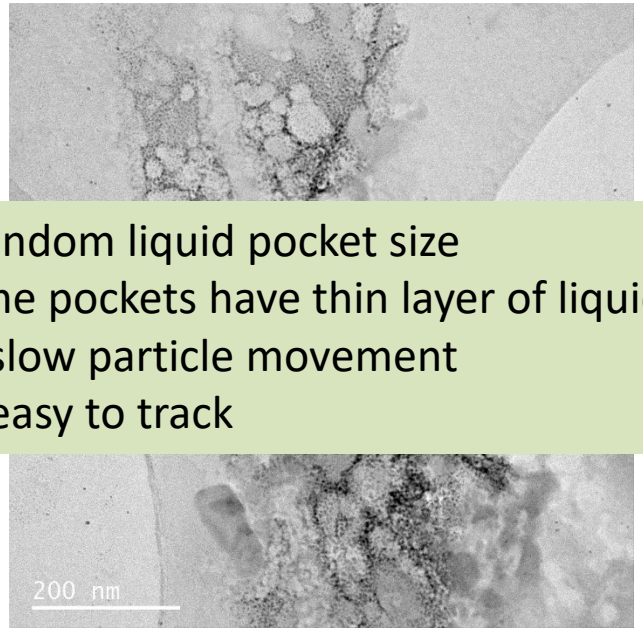
Graphene only area

Area I used

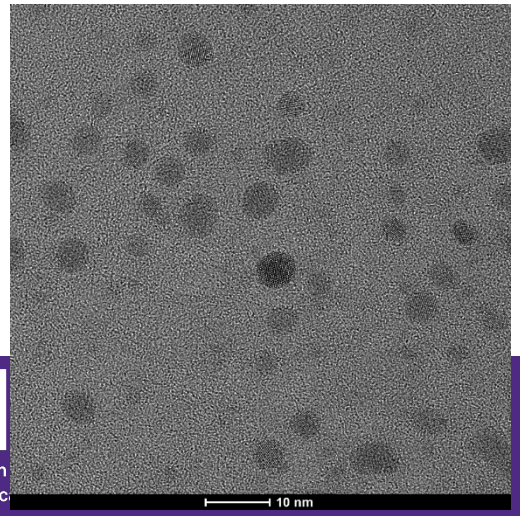
Adopted acceleration voltage : 300 kV
Electron dose rate > 600 e^- $Å^{-2}$ s^{-1}
Irradiation 20 – 30 m

In situ observation

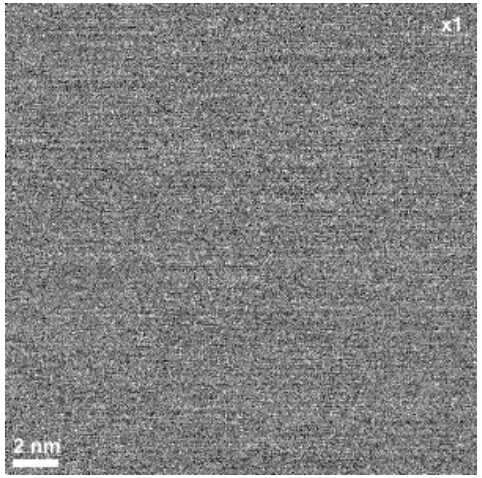
➢ After irradiation

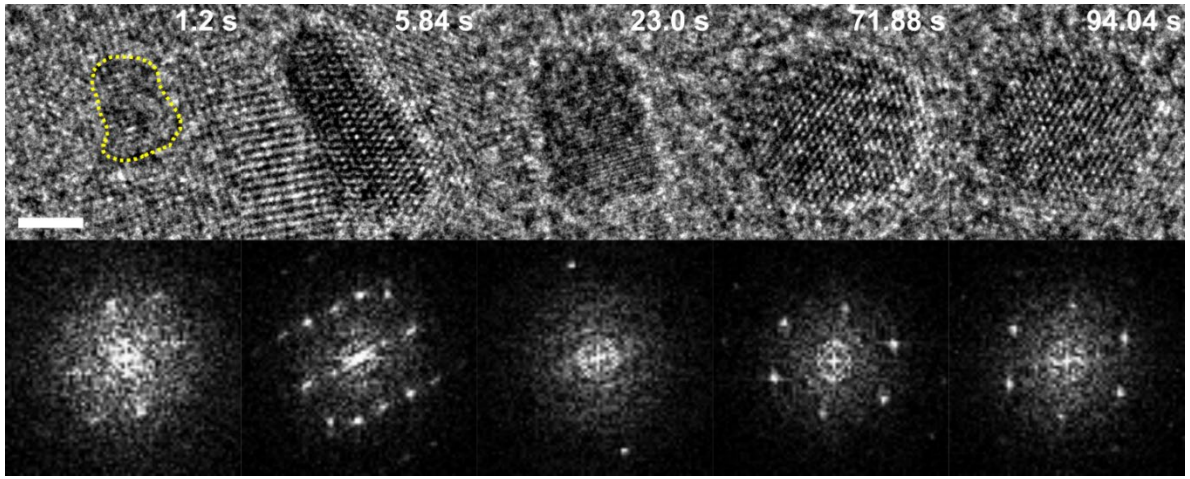


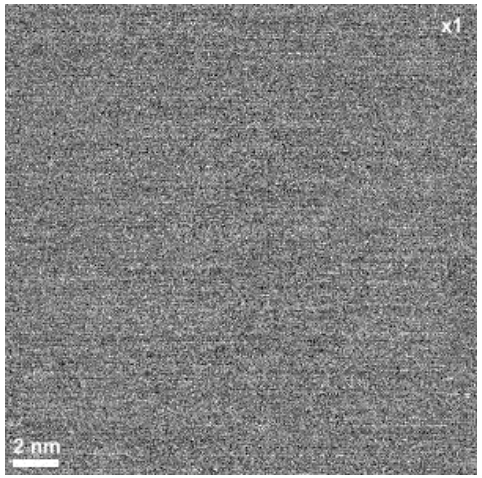
- Random liquid pocket size
Some pockets have thin layer of liquid
→ slow particle movement
→ easy to track

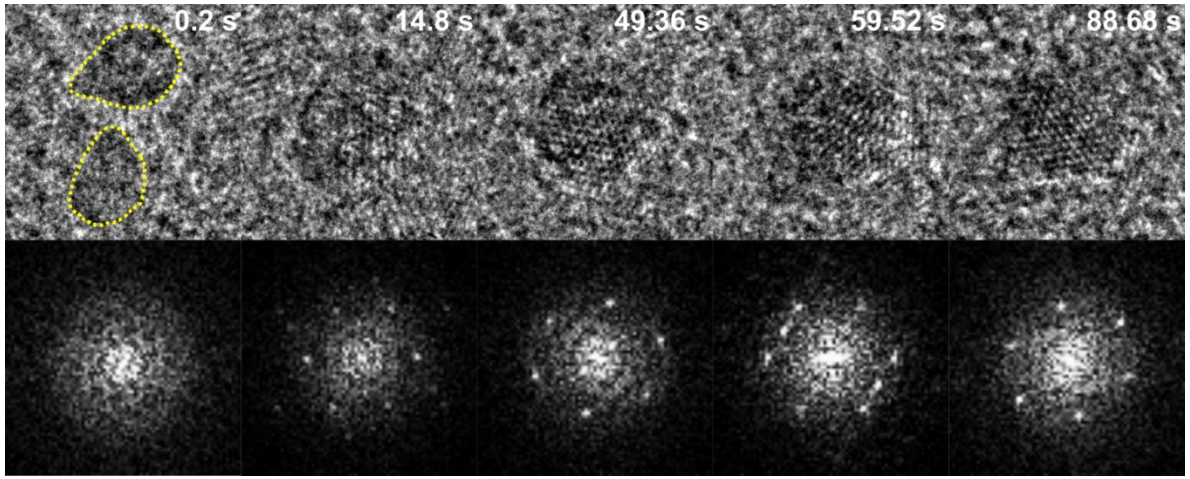


➢ During irradiation





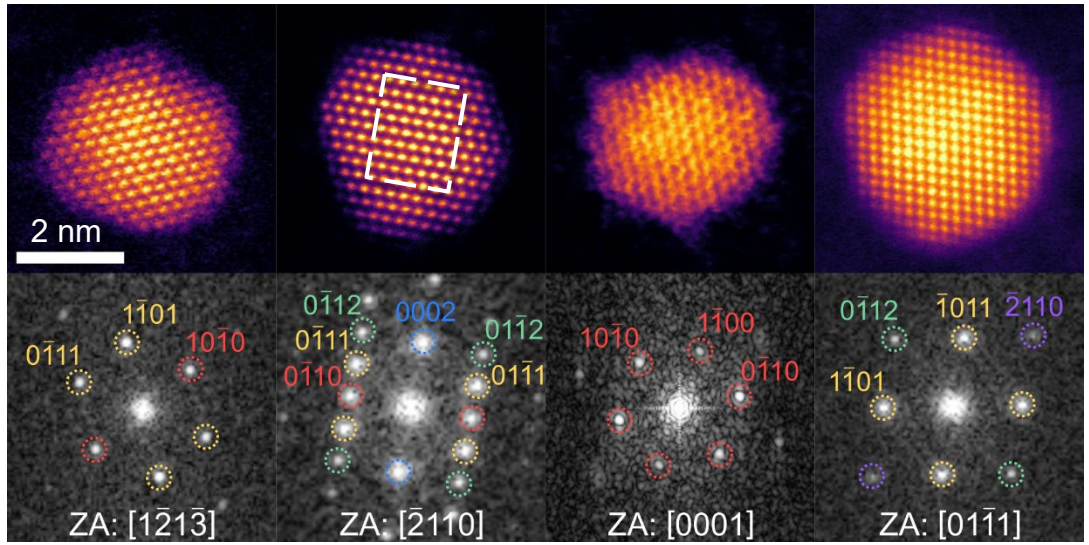




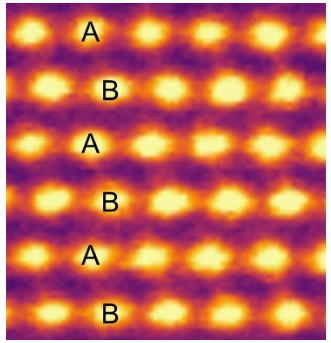
J. Hong et al., *Nature* 603 (2022)

Hexagonal close-packed (hcp) particles

➢ hcp zone axis patterns

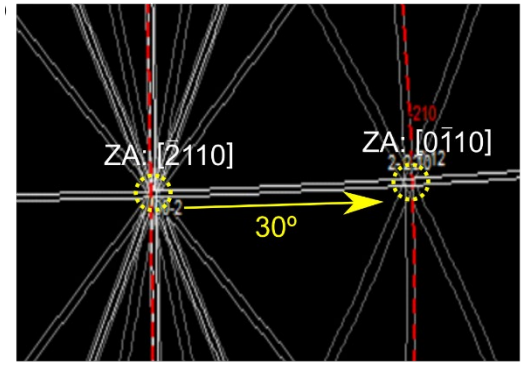


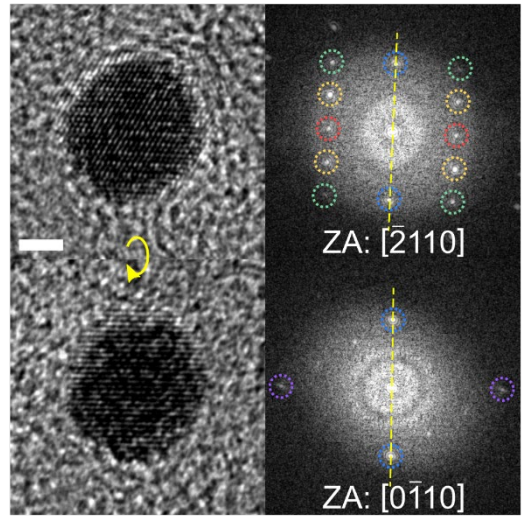
Particles are hcp,
not fcc



ABAB stacking

➢ Rotation test



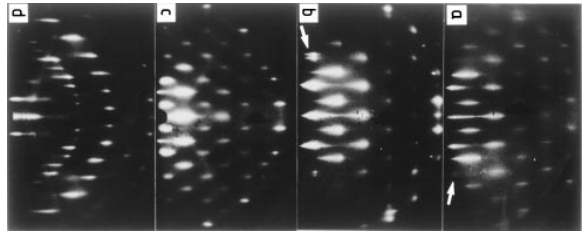


Match with
hcp Kikuchi pattern

J. Hong et al., *Nature* 603 (2022)

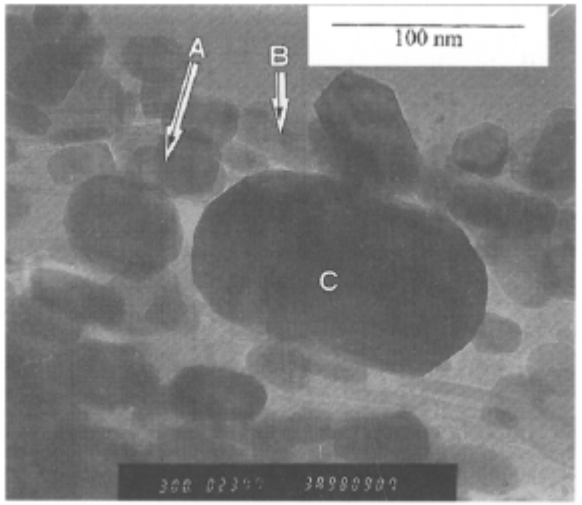
Hcp palladium compound

- **Hexagonal Pd thin film on W(100)**



H. Wormeester et al., *Phys. Rev. Lett.* 77 (1996)

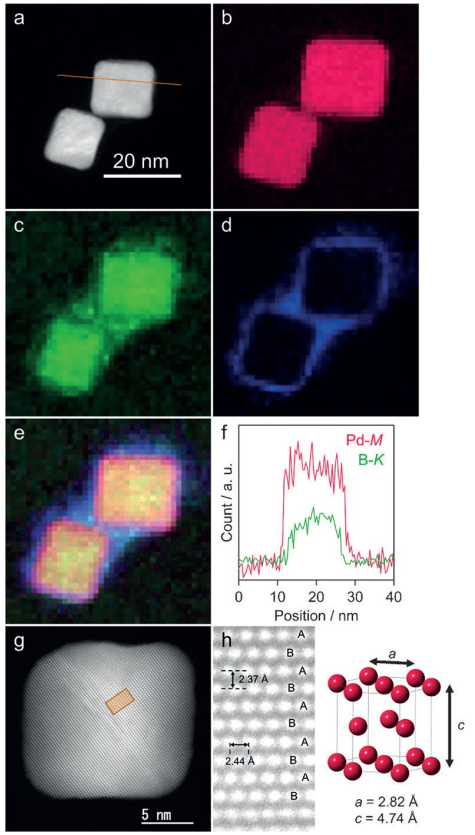
- **Quasi-2D hcp Pd nanoparticles encapsulated in graphite**



J. Walter et al., *Phys. Lett.* 254 (1999)

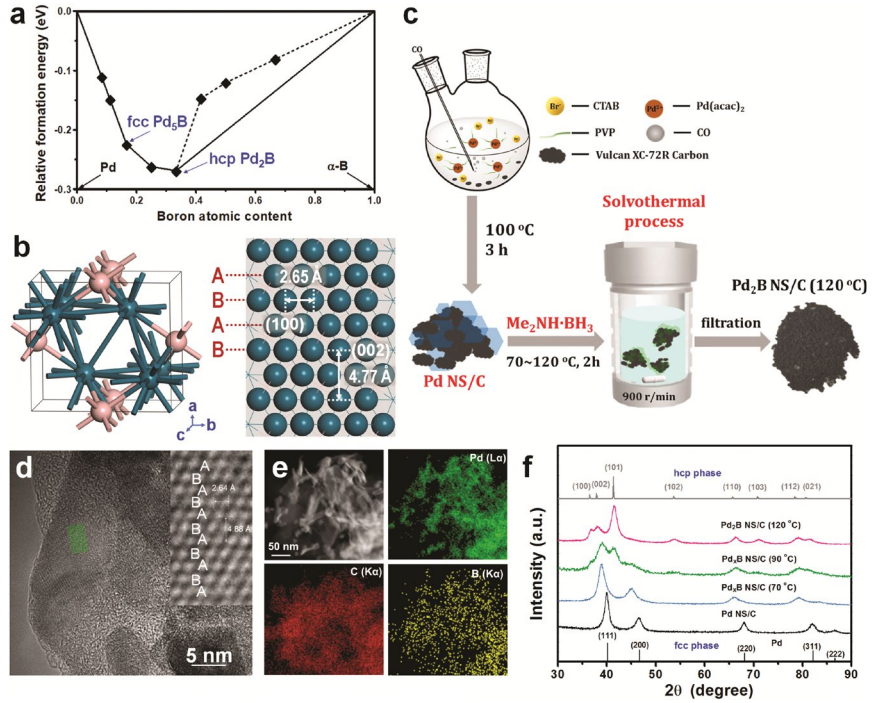
Not clearly characterized

- **hcp Pd-B nanoparticles**



K. Kobayashi et al., *Angew. Chem. Int. Ed.* 56 (2017)

- **hcp Pd_2B nanoparticles**

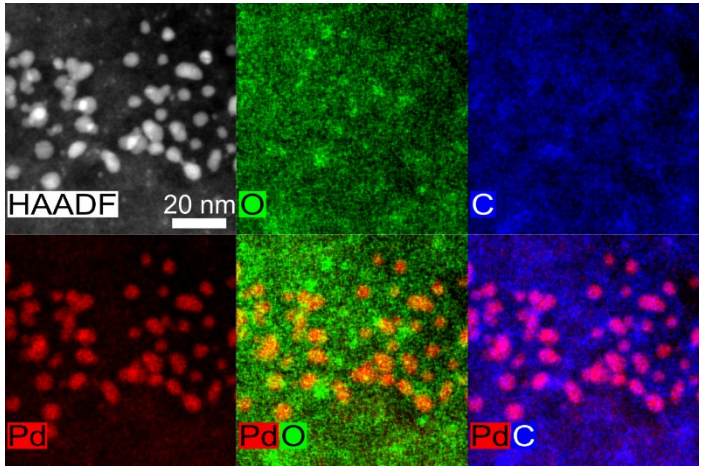


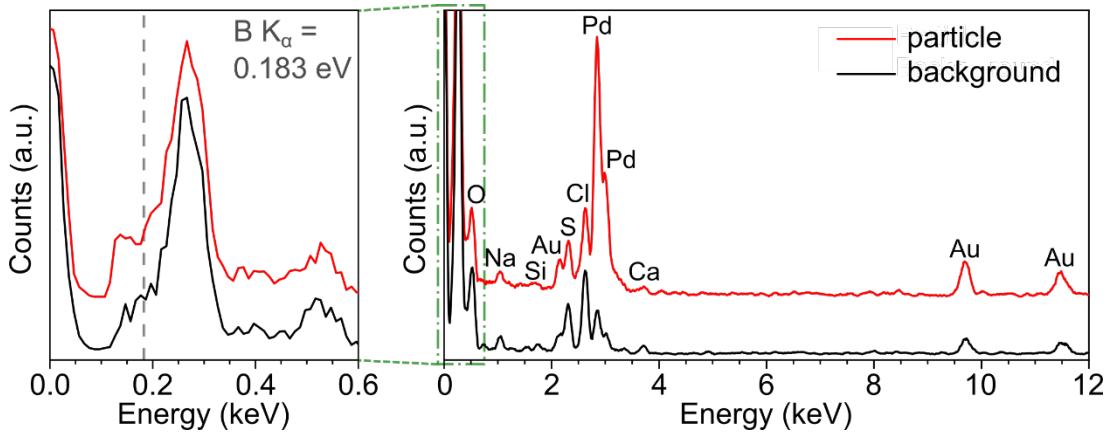
L. Chen et al., *Energy Environ. Sci.* 12 (2019)

Pd-B compound

Hcp palladium hydride

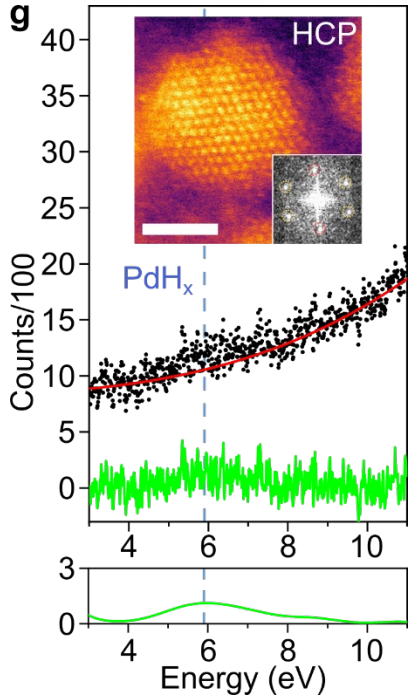
➢ EDS – Boron-free



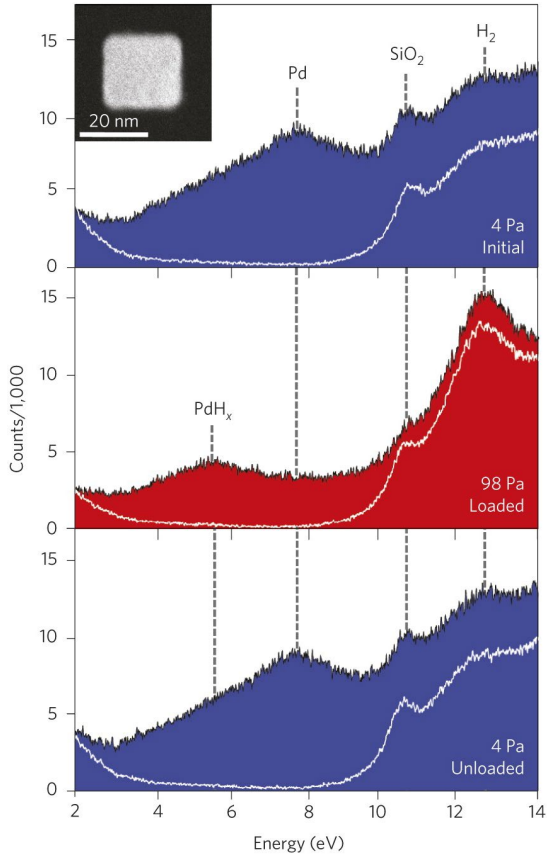


EDS: H, He, Li, Be undetectable

➢ EELS – Palladium hydride



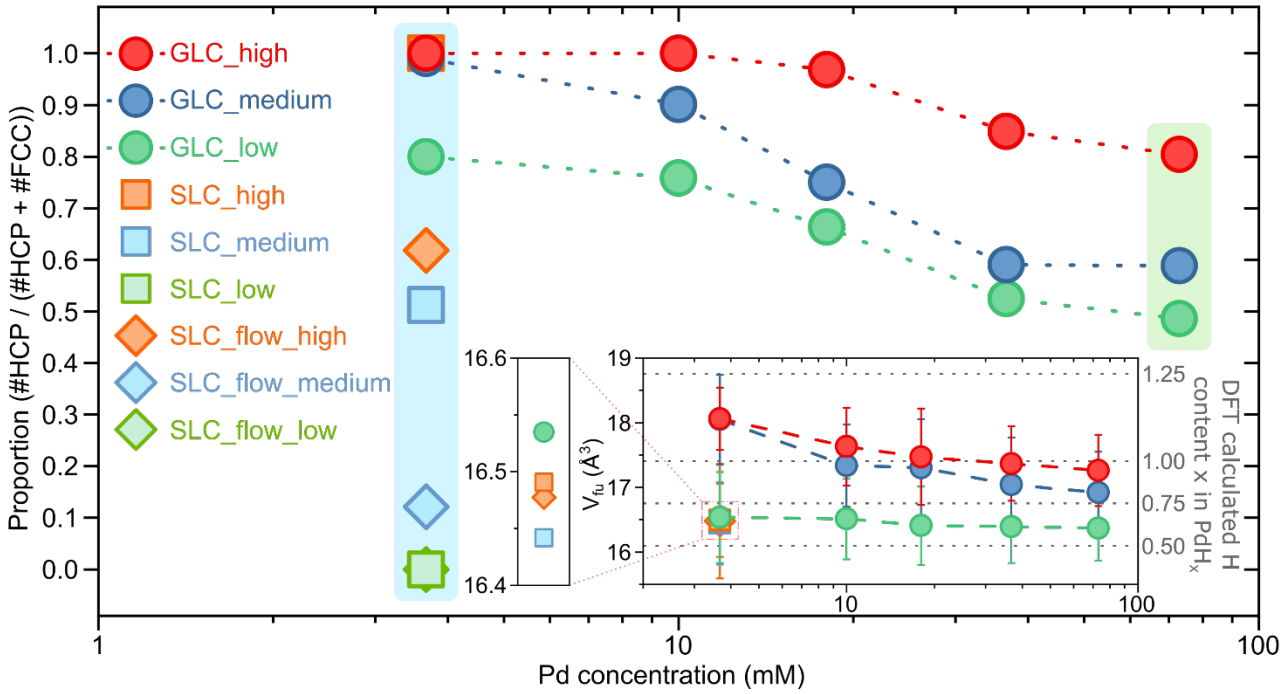
hcp PdH_x



A. Baldi et al., *Nat. Mater.* 13 (2014)

J. Hong et al., *Nature* 603 (2022)

What cause the formation of hcp PdH_x



1. Substrate effect

GLC: graphene SLC: SiN_x

hcp formed in both cells

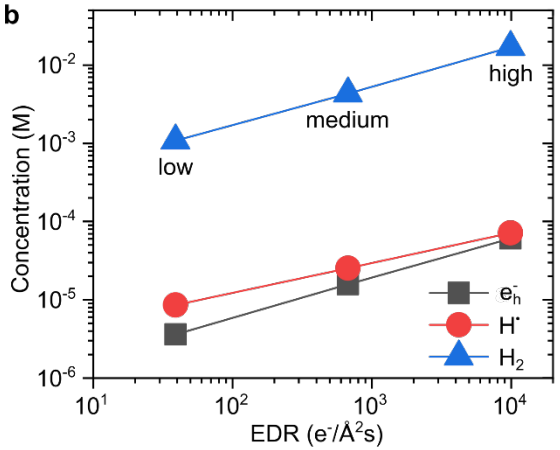
→ **Substrate doesn't matter**

2. Electron dose rate (EDR)

Higher EDR

→ Higher [H]

→ **Higher hcp fraction**



3. Pd concentration in liquid

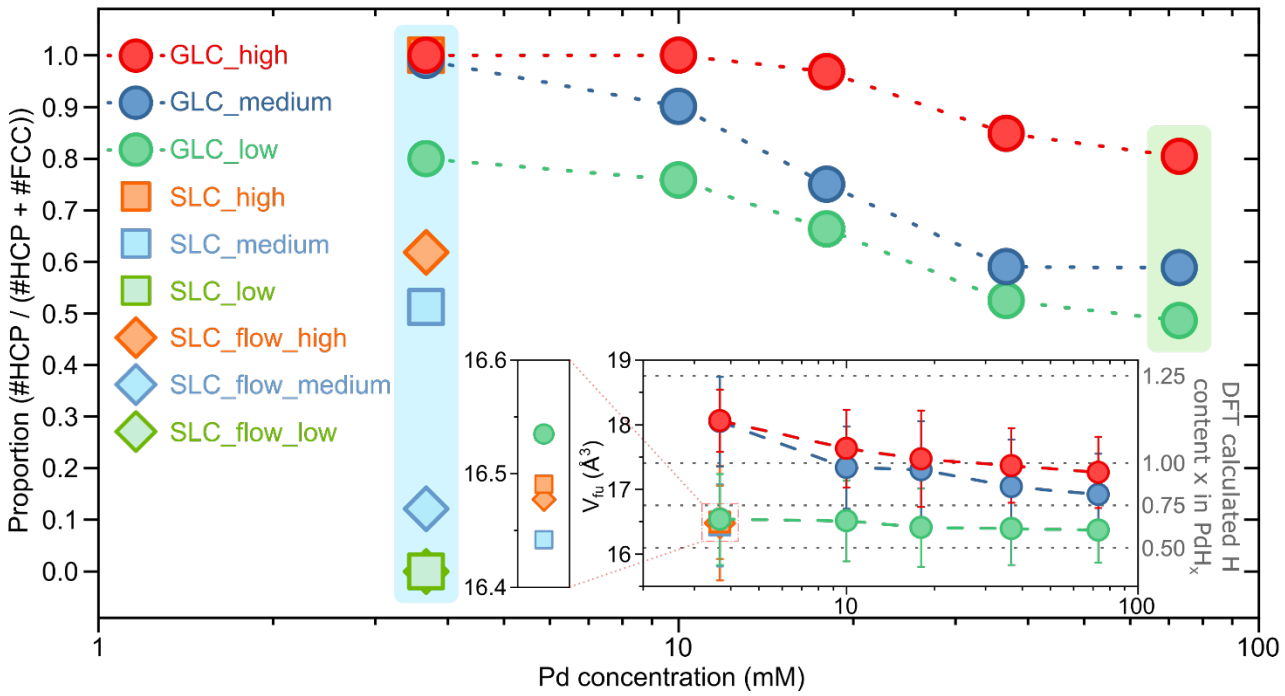
Higher [Pd]

→ **Lower hcp fraction**

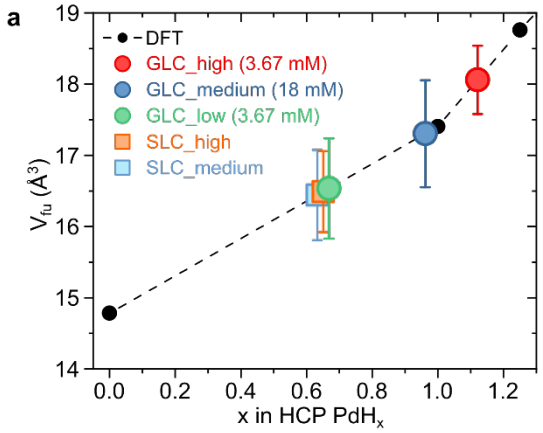
Higher [H]/[Pd] ratio → Higher hcp fraction

J. Hong et al., *Nature* 603 (2022)

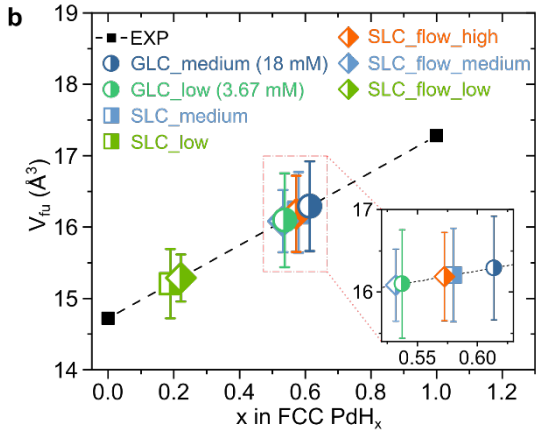
What cause the formation of hcp PdH_x



hcp

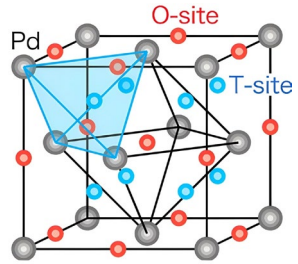


fcc



H fraction estimation

x: 0 – 1.0
Octahedral site
x: > 1.0
Tetrahedral site



H. Akiba et al., *J. Am. Chem. Soc.* 138 (2016)

though H also goes to T site in fcc PdH_x nanoparticles

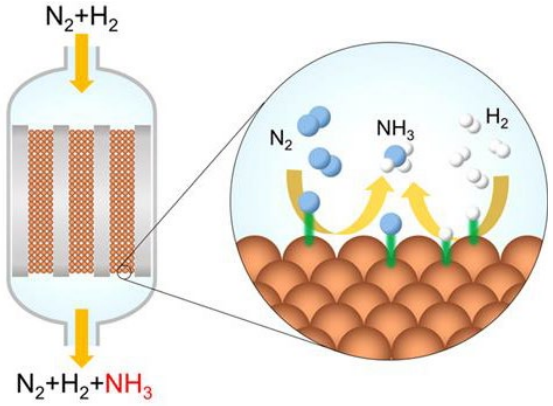
Higher [H]/[Pd] ratio → Higher H fraction in hcp PdH_x

J. Hong et al., *Nature* 603 (2022)

Liquid cell TEM as synthetic scheme design tool

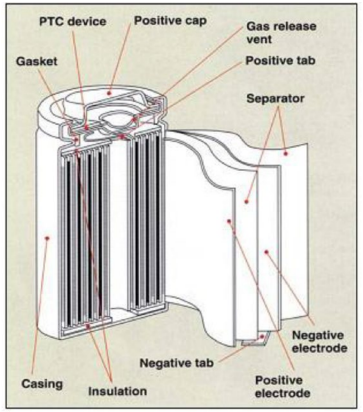
- **To get deeper understanding**

- Catalytic reaction



L. Mascaretti, A. Naldoni, *J. Appl. Phys.* 128 (2020)

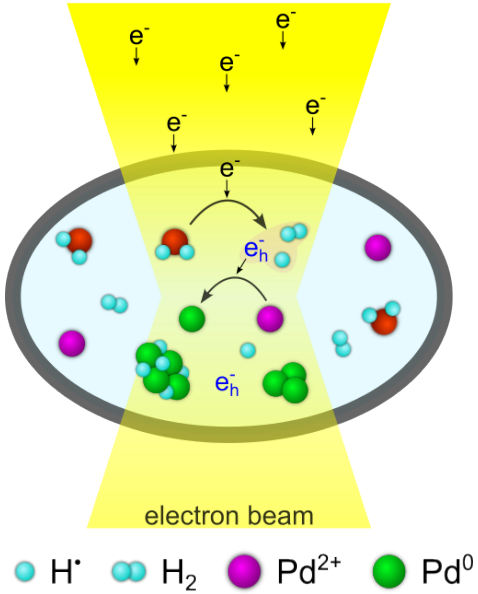
- Battery

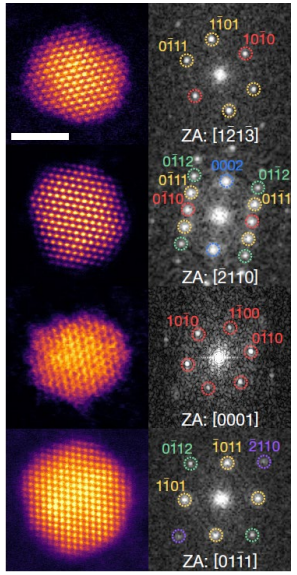


L. N. Trinh, D. Lee, *Materials* 13 (2020)

To understand process occurring outside TEM

- **Suggesting new synthetic scheme**



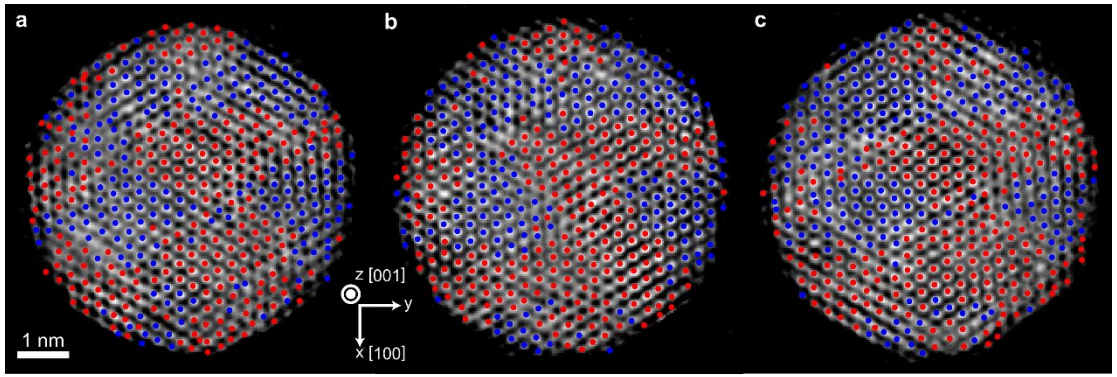


From TEM to outside TEM

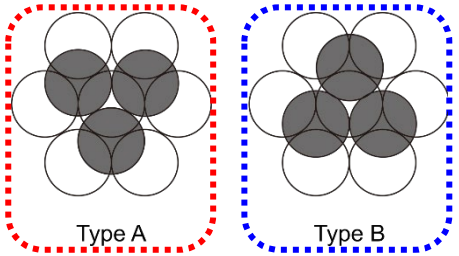
J. Hong et al., *Nature* 603 (2022)

Tomography

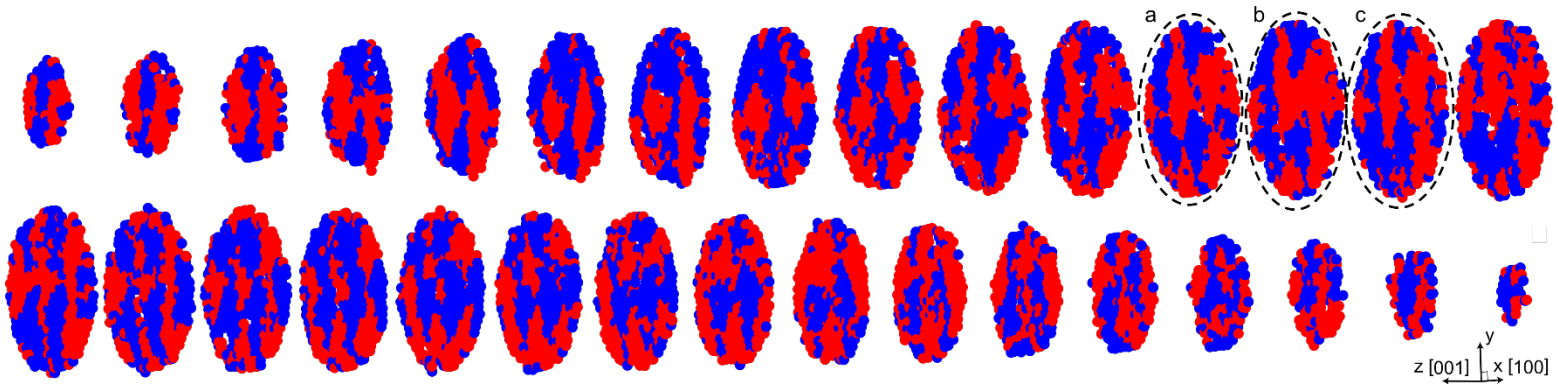
- **Multidomain structure of a single particle**



..ABABAB.. ..CACACA..

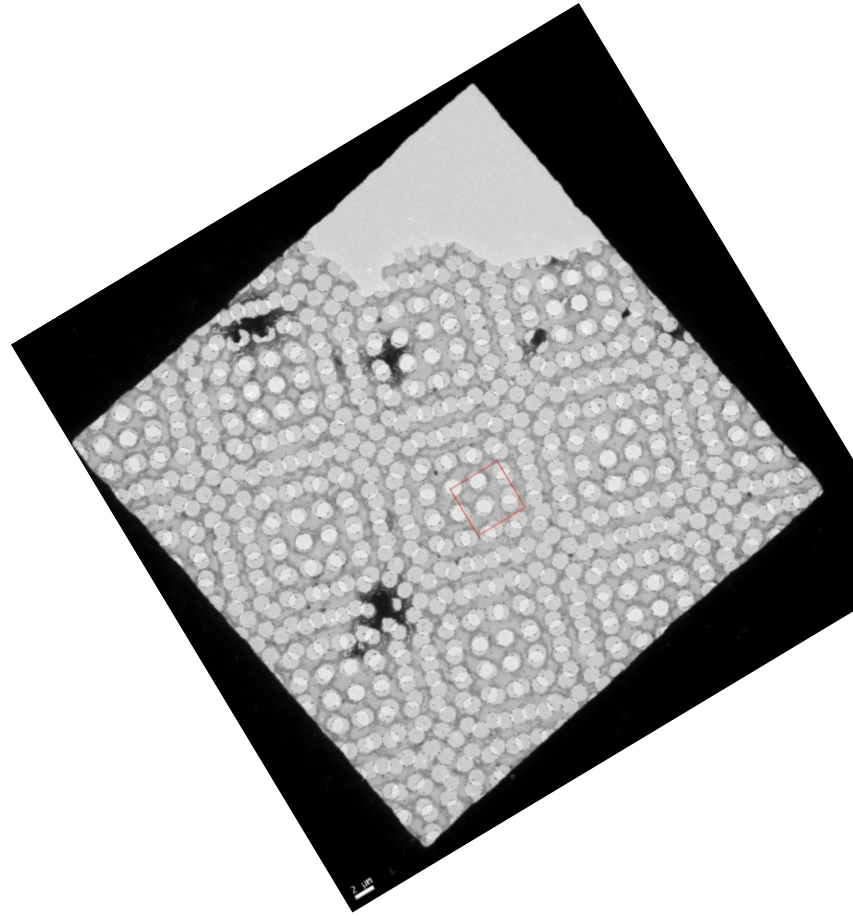


Colored depending on stacking type



each domain size < 2 nm

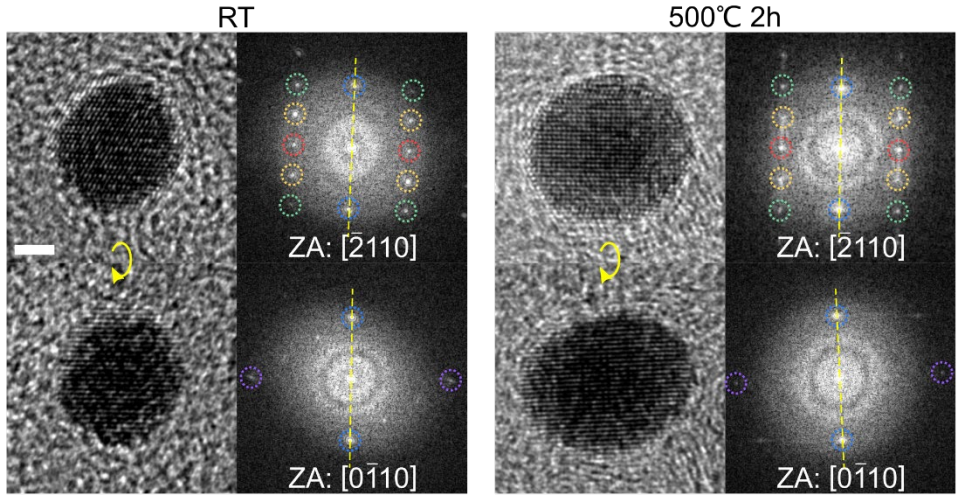
Multidomain stabilized hcp nanoparticle with D > 2 nm



-70° to 70 ° with 300 mesh grid
Need to choose a particle in the center of a mesh

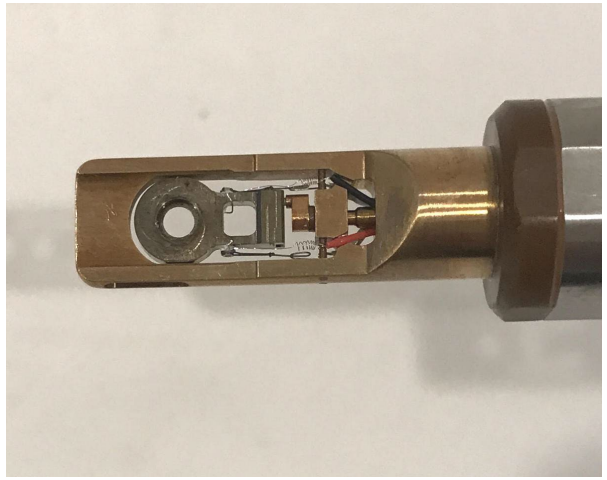
J. Hong et al., *Nature* 603 (2022)

Heating



No phase transition after 500°C annealing
→ Metastable but sturdy





https://tem-service.com/product/gatan-652-double-tilt-heating-holder/

Heating holder for standard TEM grid

J. Hong et al., *Nature* 603 (2022)

Thank you for your attention!