Environmental TEM at the U

1. Liquid/electrochemical TEM sample holder

   U of U Research Instrumentation Fund proposal

2. Heatable gas cell TEM sample holder

   Defense University Research Instrumentation Program (DURIP) proposal

Goals: E-TEM

Nanoscale imaging under realistic reaction conditions

- Effects of temperature on nanoparticle stability, shape, etc.
- Effects of adsorbates on NP structure
- Growth or dissolution of nanostructures
- NP diffusion and agglomeration
- Effects of electrochemical potentials on NP structure, stability, and activity

Approaches:

- Dedicated e-TEM instrument
  - Cost $nM, plus annual maintenance
- Environmental sample holders – convert existing STEM
  - Cost ~$200k, Protochips, Hummingbird Scientific, DENS Solutions

Complete gas-cell TEM system

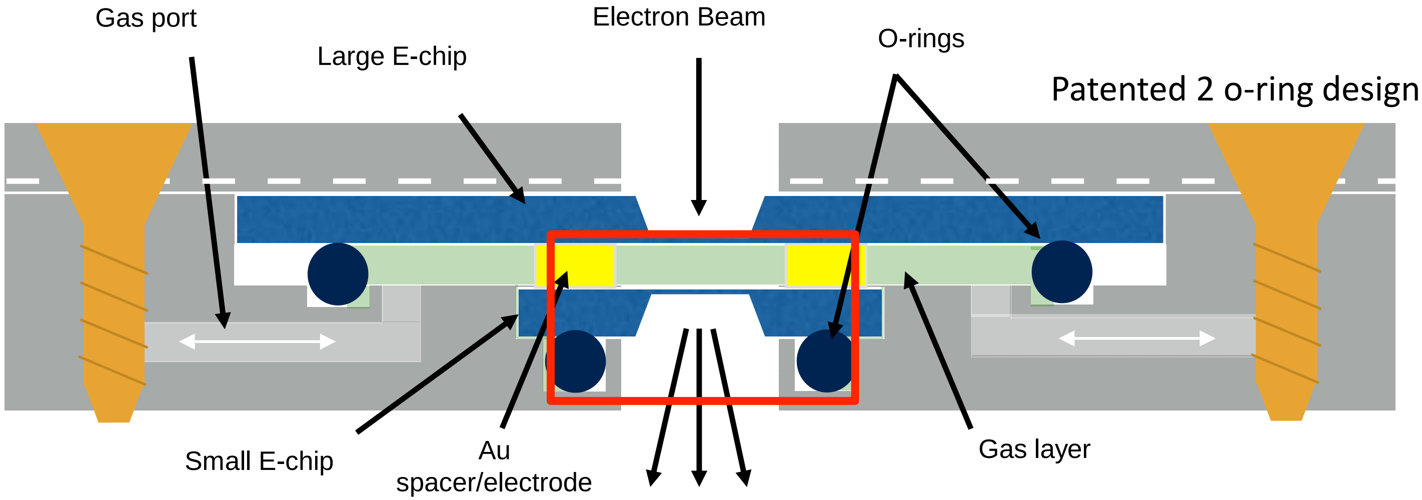
TEM Holder

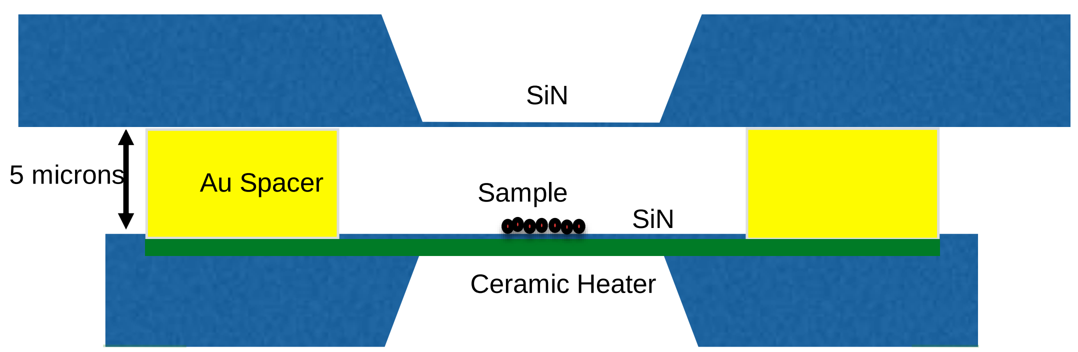
E-chips

Atmosphere Software

Gas Manifold

Holder Tip - Assembly and Design





Pressures to 1 atm, temperature to 800 or 1000 °C, depending on vendor

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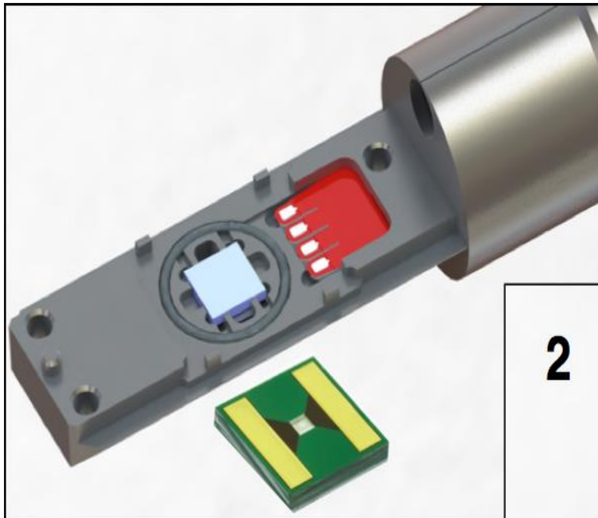
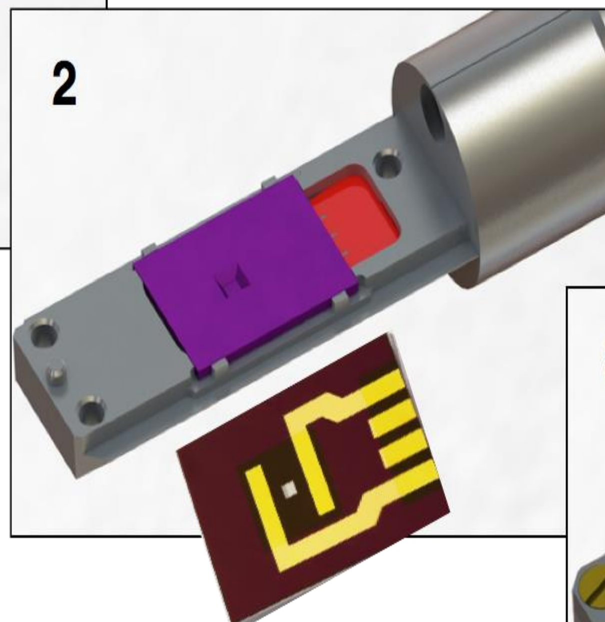
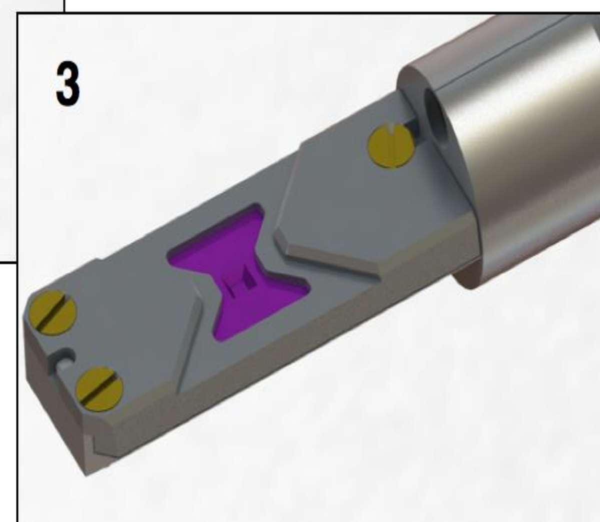
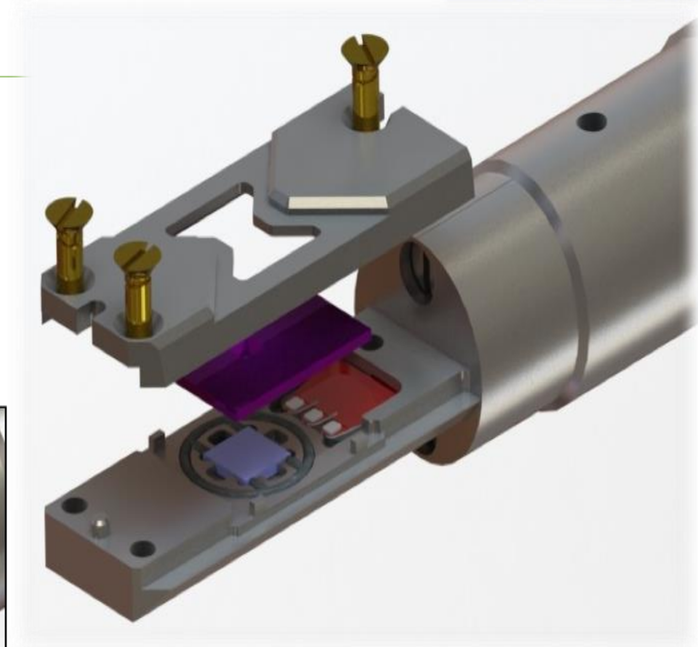






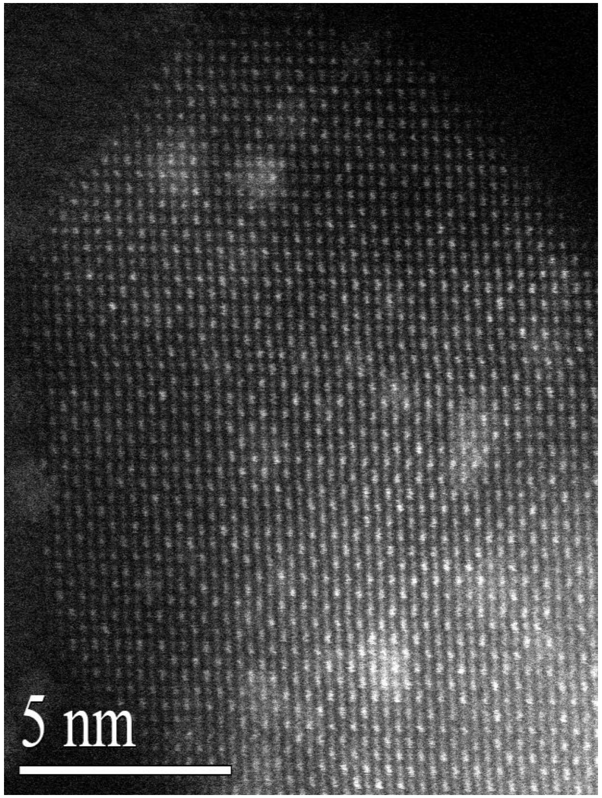


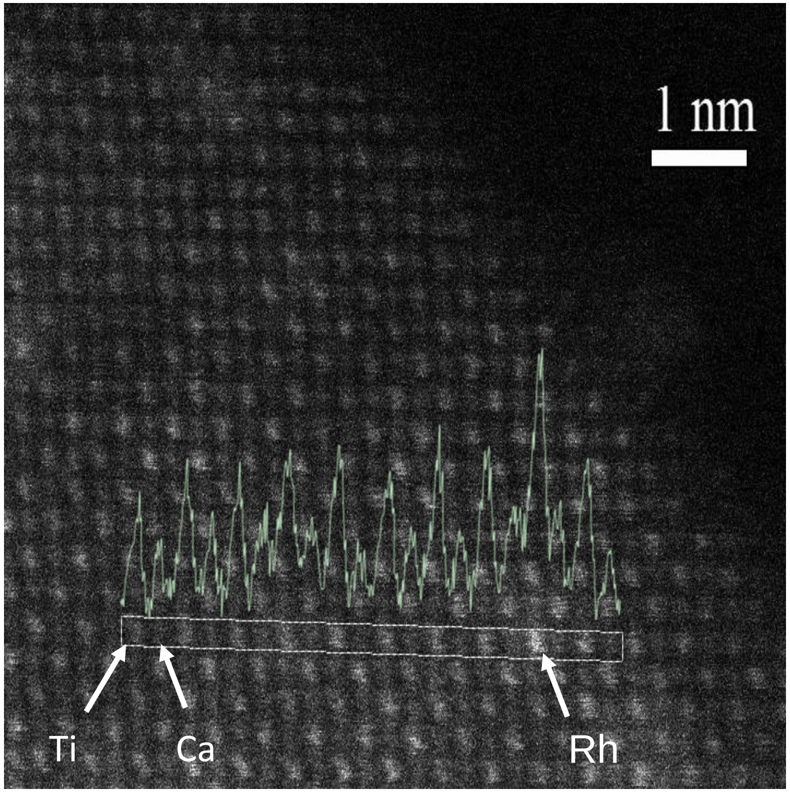
CASE: Perovskite/Metal Catalysts

Solution: Atmosphere system with 95/5 N_2/H_2 and O_2 gas supplies

Results: See the **regeneration of metal NP catalysts** directly under meaningful conditions in a single microscopy session with atomic scale resolution, including **Z-contrast.**

Calcium Titanate (CTO)
Doped with Rhodium
$CaTi_{0.95}Rh_{0.05}O_3$
1 atm 95/5 N_2/H_2 & 550 ºC





200 kV JEOL 2100F
Images courtesy of Shuyi Zhang,
X. Pan group, University of Michigan

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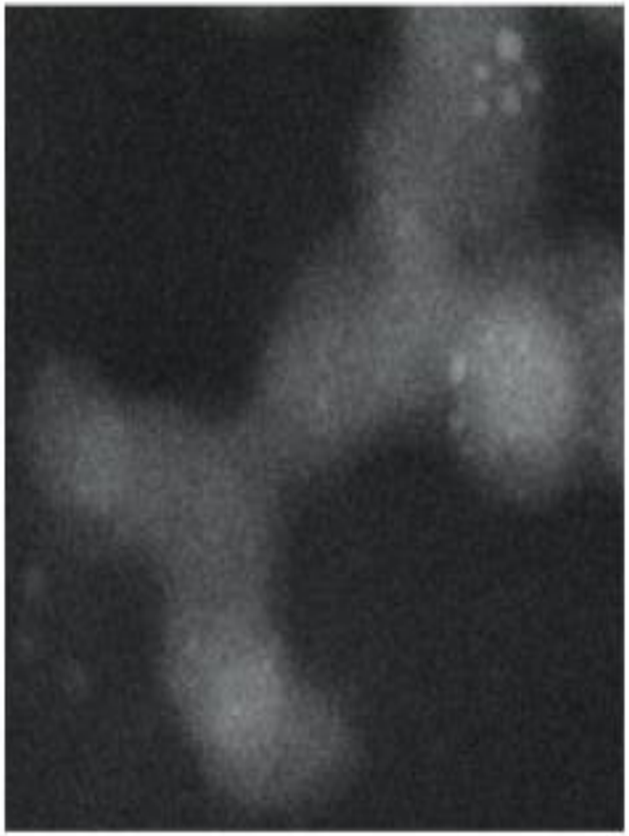

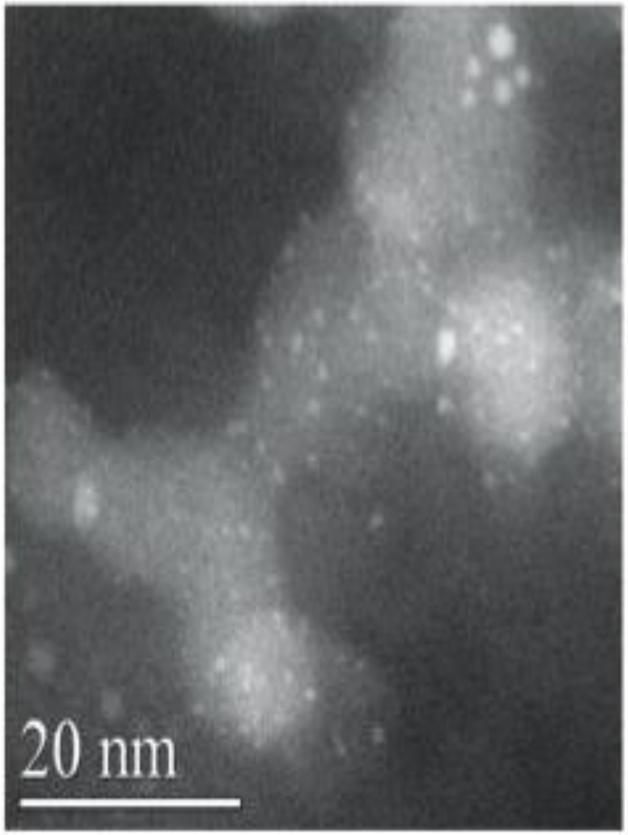

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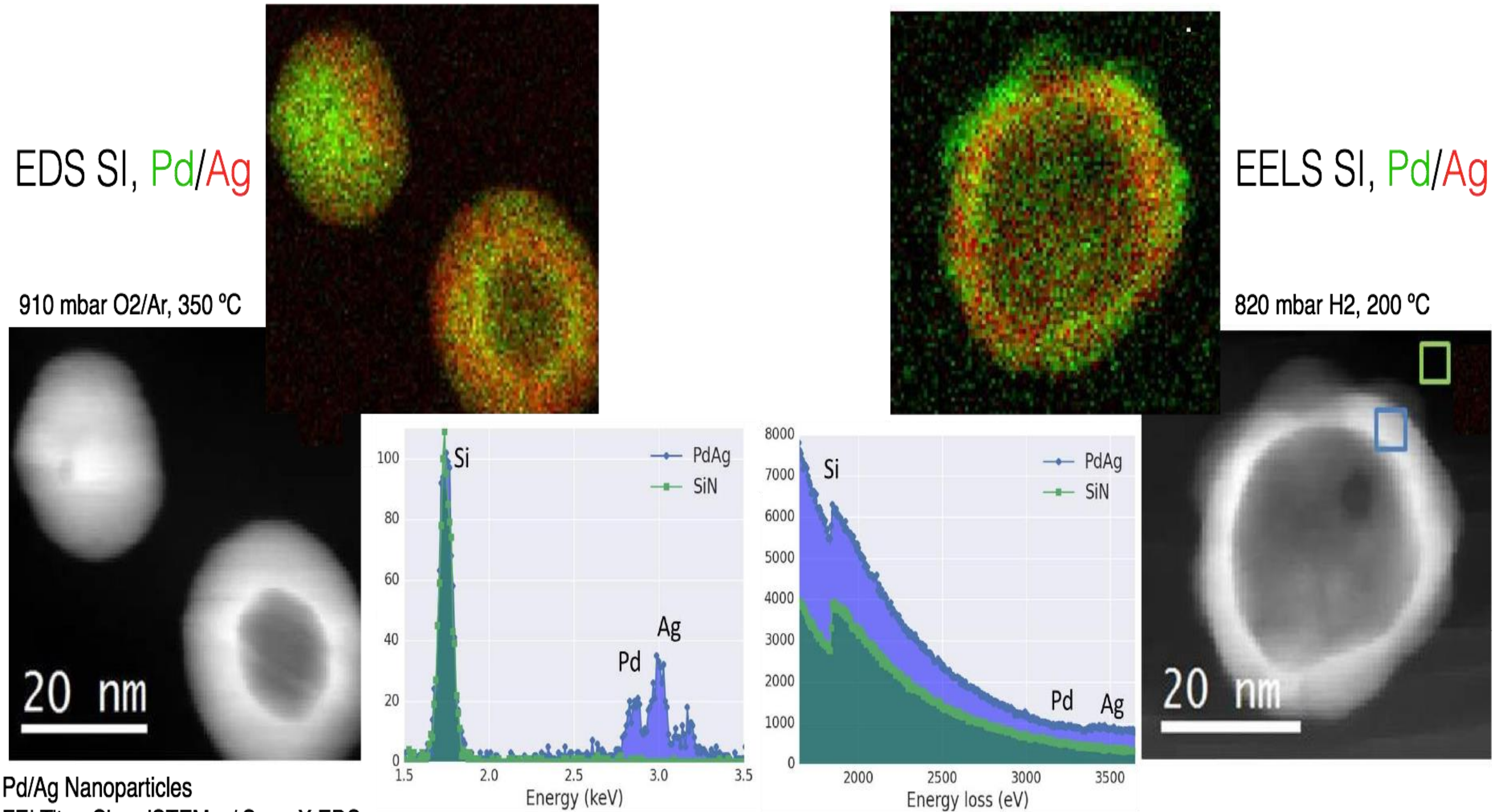
EDS & EELS Compatible



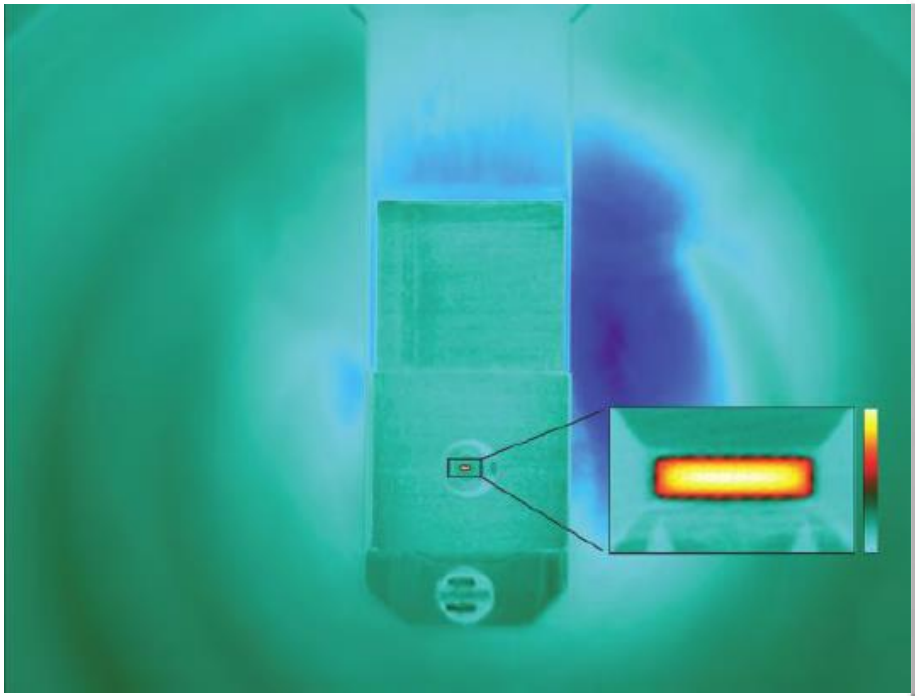
Pd/Ag Nanoparticles
FEI Titan ChemiSTEM w/ SuperX EDS
Image courtesy U Manchester

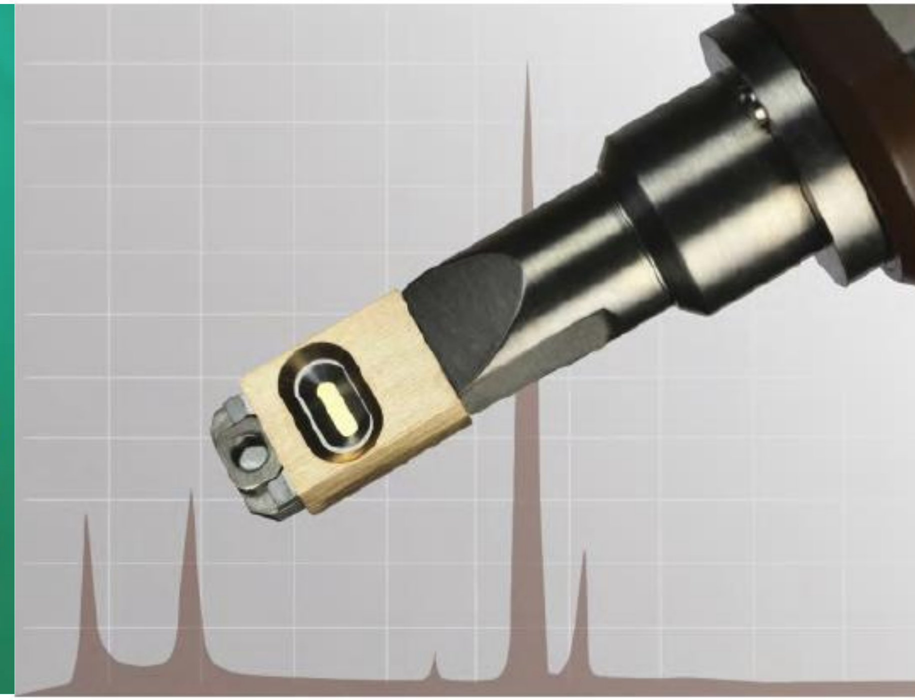
HUMMINGBIRD SCIENTIFIC

Liquid Cell

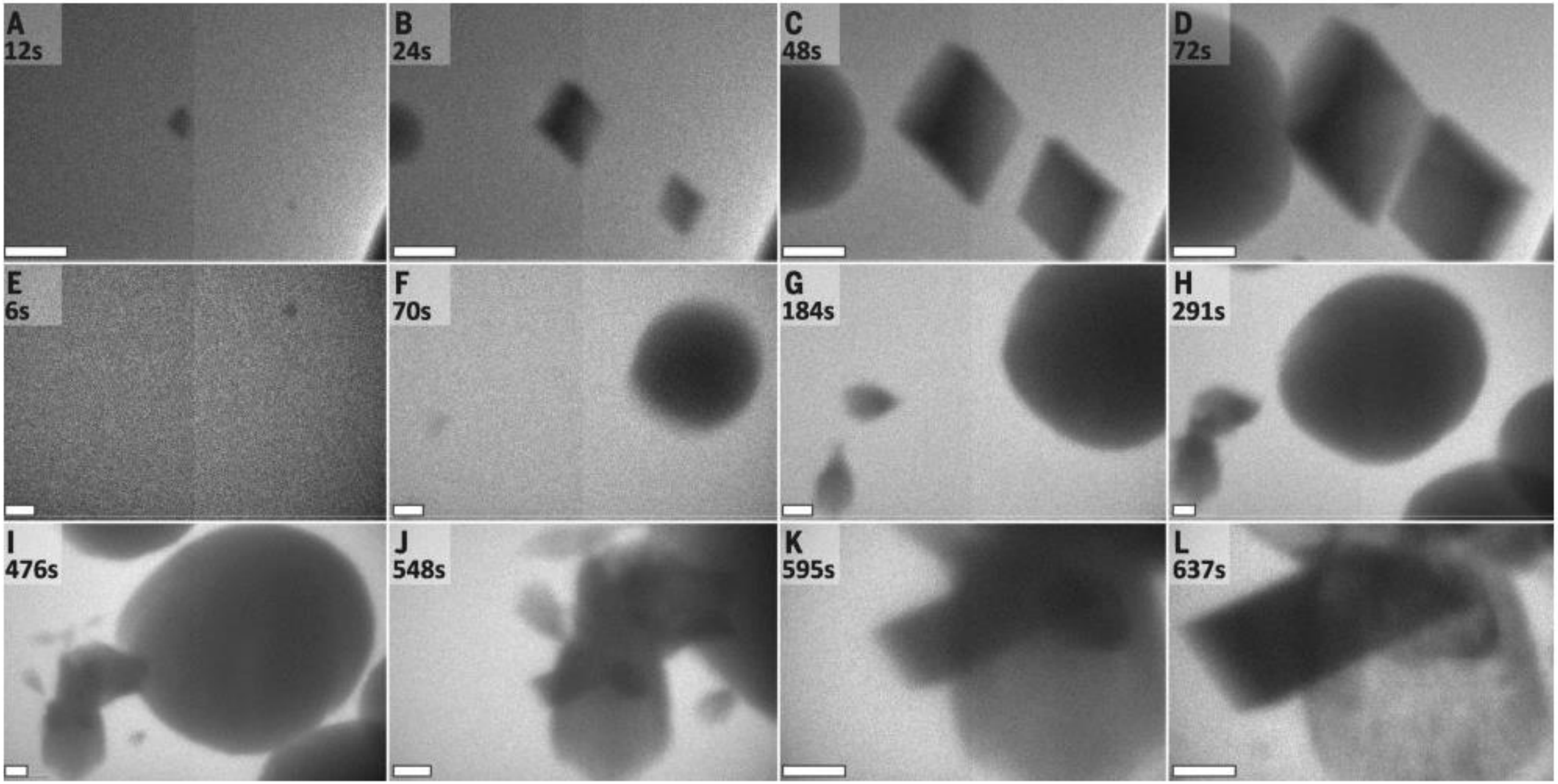
Number of Inlets	1 or 2 depending on model, single outlet
Biasing Contacts	3 or 4 depending on model
Tubing Type	Replaceable microfluidic tubing
Delivery System	Variable speed liquid delivery system
Tip Type	Removable tip
Flow Type	Continuous flow or static liquid
EDS Compatible	Yes

Heating *In situ* spectroscopy





Example $CaCO_3$ nucleation and growth

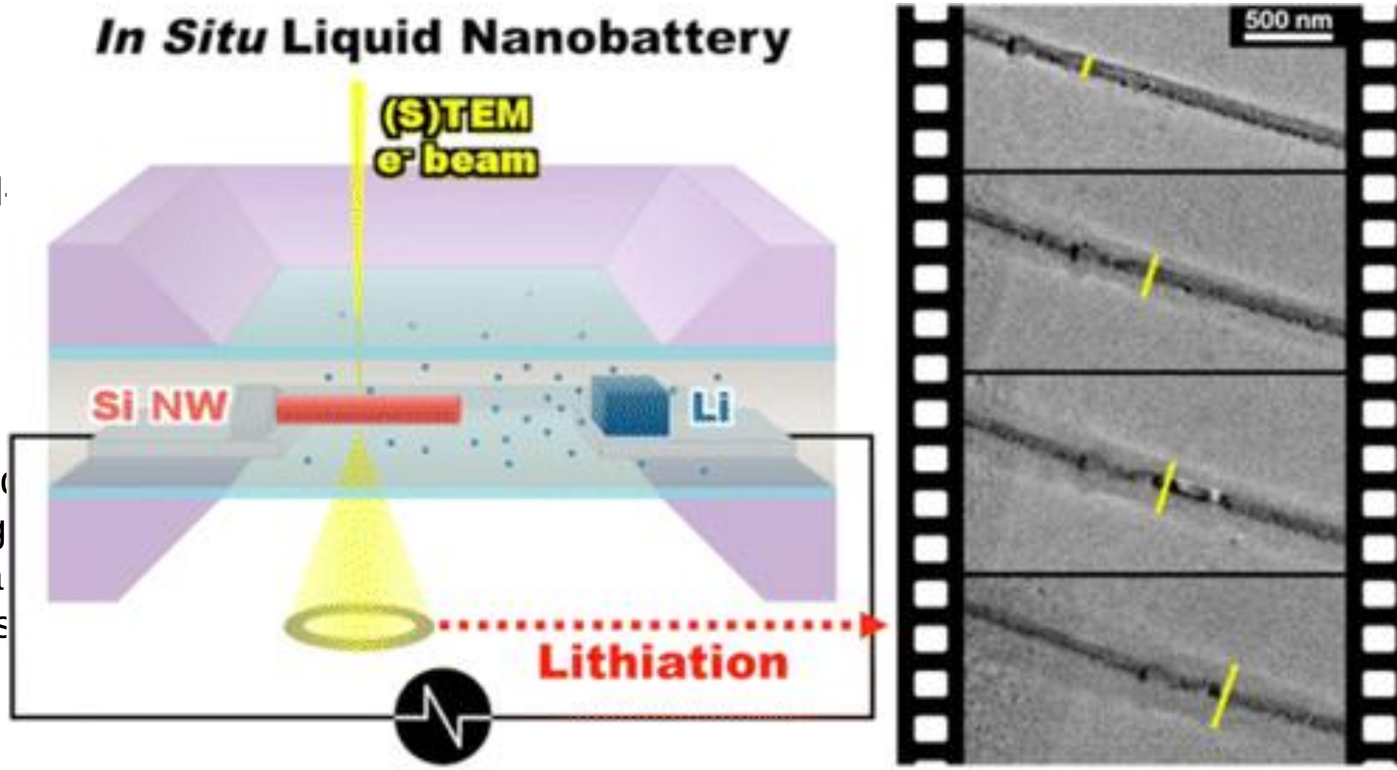


Concurrent formation of multiple phases. All scale bars are 500nm

M.H. Nielsen, S. Aloni, J.J. De Yoreo. "In situ TEM imaging of CaCO3 nucleation reveals coexistence of direct and indirect pathways," Science vol. 345 iss. 6201 (2014) pp. 1158-1162

In-Situ Liquid Nanobattery

Left: Schematic of a liquid nanobattery cell used to study the lithiation and delithiation of Si nanowire electrodes.
Right: Time-series images of the lithiation of Cu coate Si nanowires during testing This experiment employs a configuration that simulate a real battery.



Reference: M. Gu, L.R. Parent, B.L. Mehdi, R.R. Unocic, M.T. McDowell, R.L. Sacci, W. Xu, J.G. Connell, P. Xu, P. Abellan, X. Chen,Y. Zhang, D.E. Perea, J.E. Evans, L.J. Lauhon, J.G. Zhang, J. Liu, N.D. Browning, Y. Cui, I. Arslan, and C.M. Wang. “Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy Observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes.” *Nano Lett.* 13:12 (2013) pp. 6106–6112.

Timing

- Will learn about the liquid cell proposal in early November
- Will learn about the heatable gas cell proposal in July