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Liquid Scanning / Transmission Electron Microscopy

Katherine Jungjohann

Center for Integrated Nanotechnologies, Sandia National Laboratories, kljungj@sandia.gov

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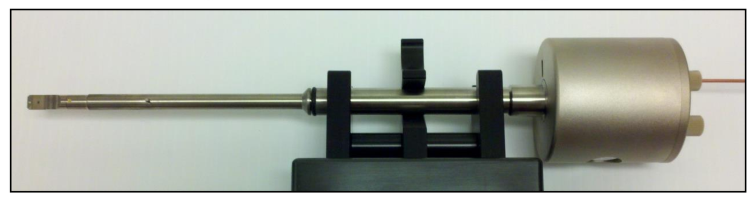
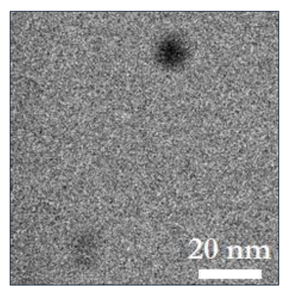
Imaging Specimens in Liquid using S/TEM

Nanomaterial structural analysis and dynamics in liquids with high resolution imaging is possible using a liquid cell holder. The types of samples that may be studied using this technique include:

- Colloid Dynamics
- Nanoparticle Growth
- Nanostructured Assemblies
- Solid-Liquid Interfaces
- Electrochemistry
- Microfluidics
- Whole Biological Cells
- Biological Macromolecules

Hummingbird Scientific Liquid Stage

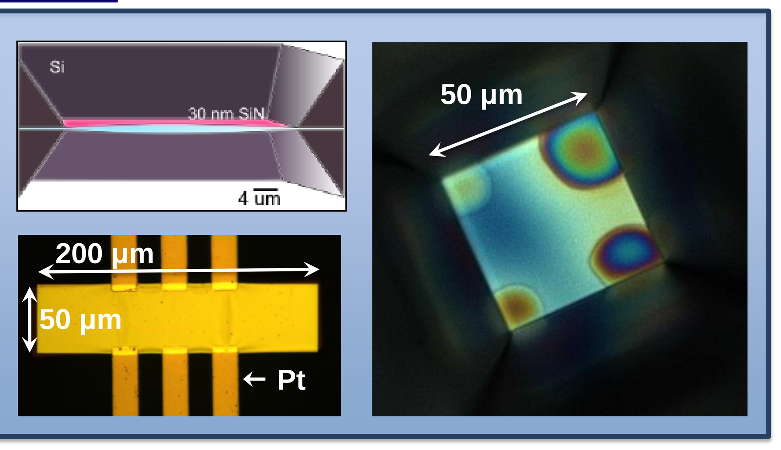




BF STEM of unstained ferritin and apoferritin in a thin water layer

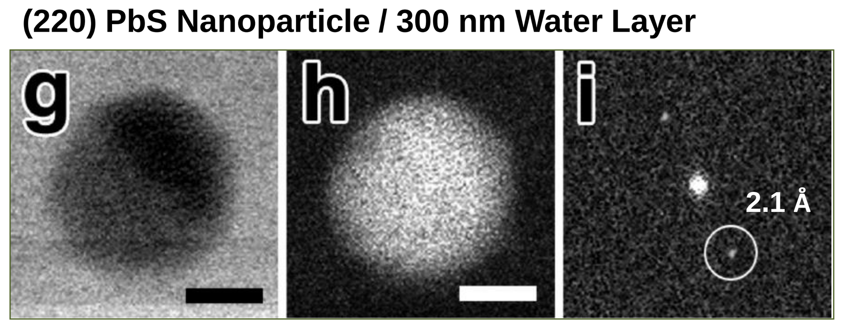
Thin Film SiN Membrane Windows

- Window Area: 20 – 200 µm
- Window Thickness: 10 – 50 nm
- Spacers: > 50 nm tall
- Spacer Composition: variable
- SiN Surface Treatment
- Electrodes: variable composition and patterns
- Microfluidic channels

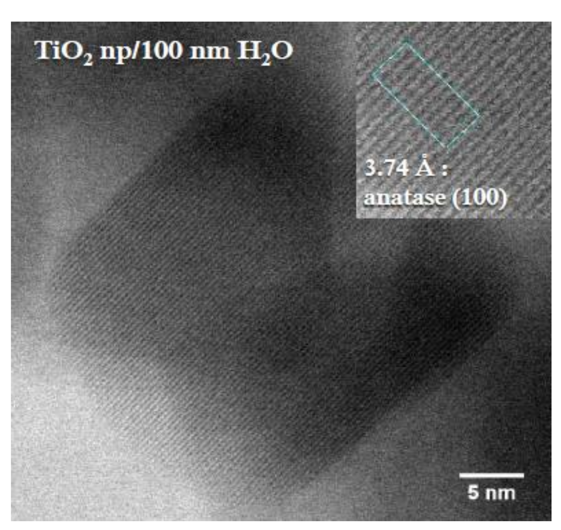


Atomic-scale imaging is possible on stable structures within thin fluid path lengths.

(220) PbS Nanoparticle / 300 nm Water Layer



Evans, J. E.; Jungjohann, K. L.; Browning, N. D.; Arslan, I. Nano Lett. **2011**, 11, 2809.



Electron Beam Radiolysis to Aqueous/Electrolyte Solutions within Liquid Cell

$$4.14H_2O \rightarrow 2.7\ e_{aq}^- + 2.7\ H^+ + 0.61\ H + 0.43H_2 + 2.87OH + 0.61\ H_2O_2 + 0.026HO_2$$

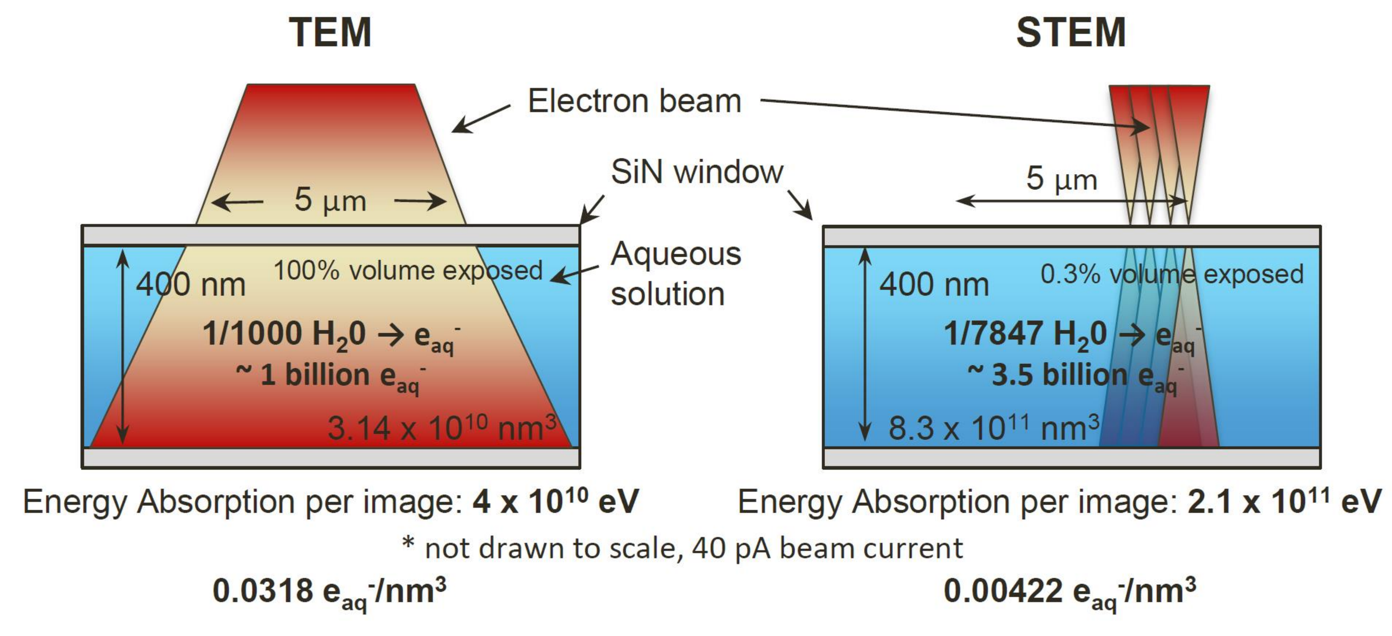
* values represent # species formed / 100 eV absorbed energy that escape recombination

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

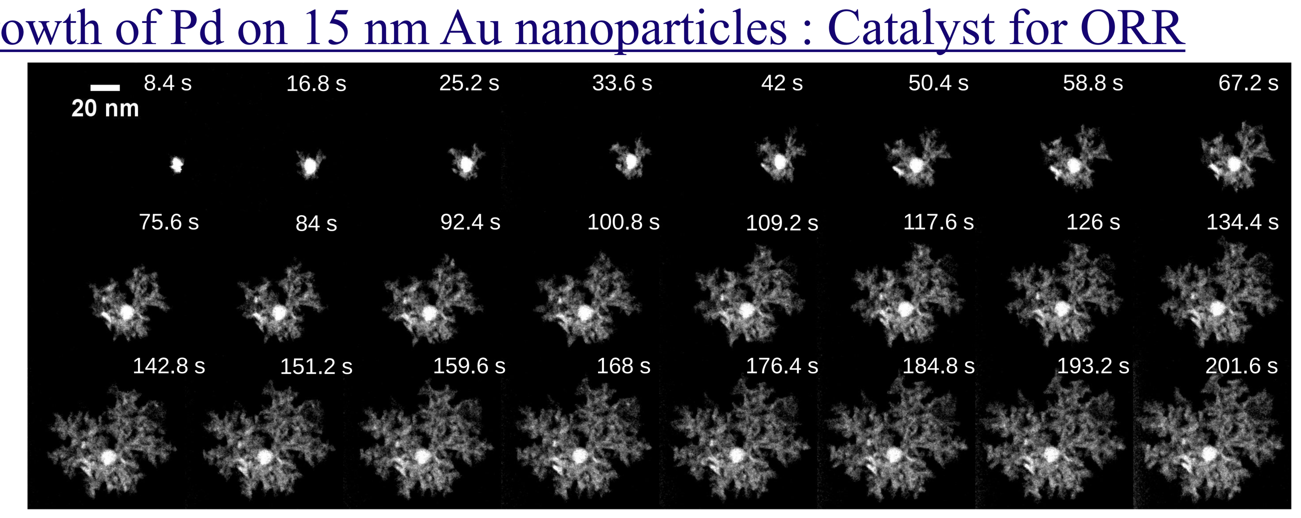
• Most abundant species in a spur are H_3O^+, OH and e_{aq}^-

* Water containing O_2 will form the superoxide radical, an extremely reactive specie

Electron Dose Comparison between TEM and STEM Modes of Imaging



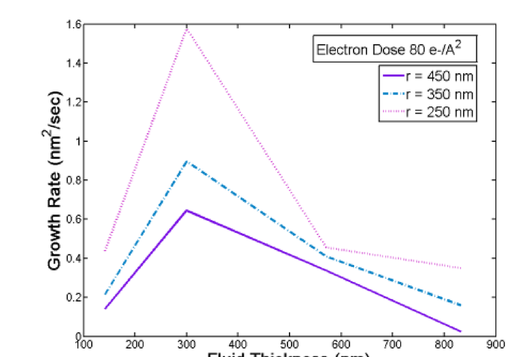
Growth of Pd on 15 nm Au nanoparticles : Catalyst for ORR

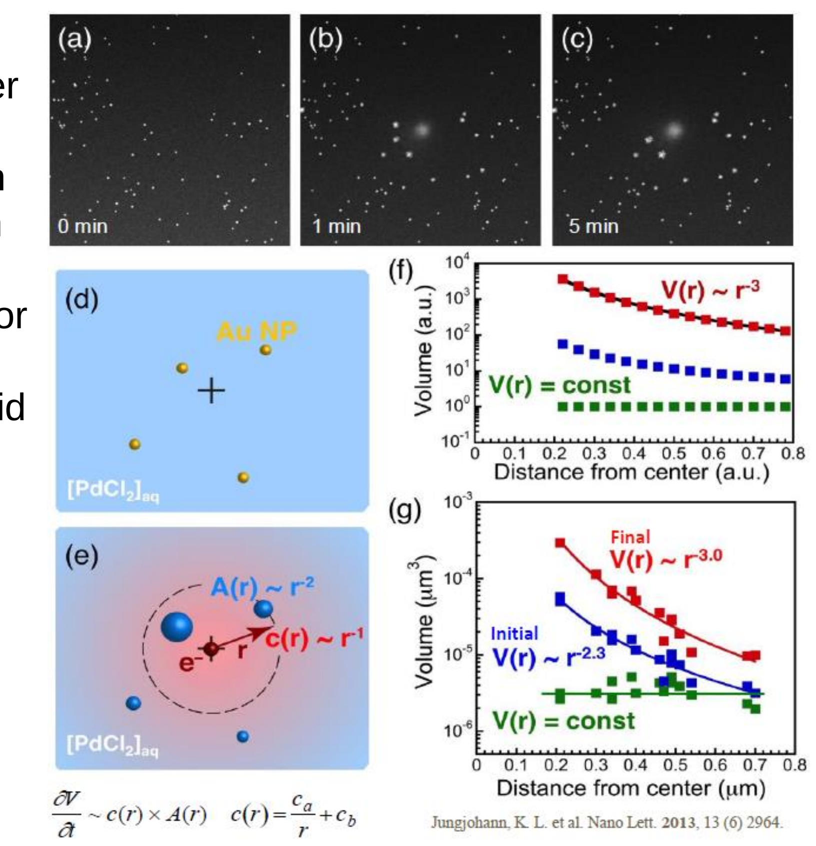


Mobility of the Aqueous Electrons Created in Solution

- e_{aq}^- produced through radiolysis will reduce species in solution
- Interaction of e_{aq}^- with nanoparticles in the liquid cell depends on the distance from the formation of the e_{aq}^- and the fluid layer thickness

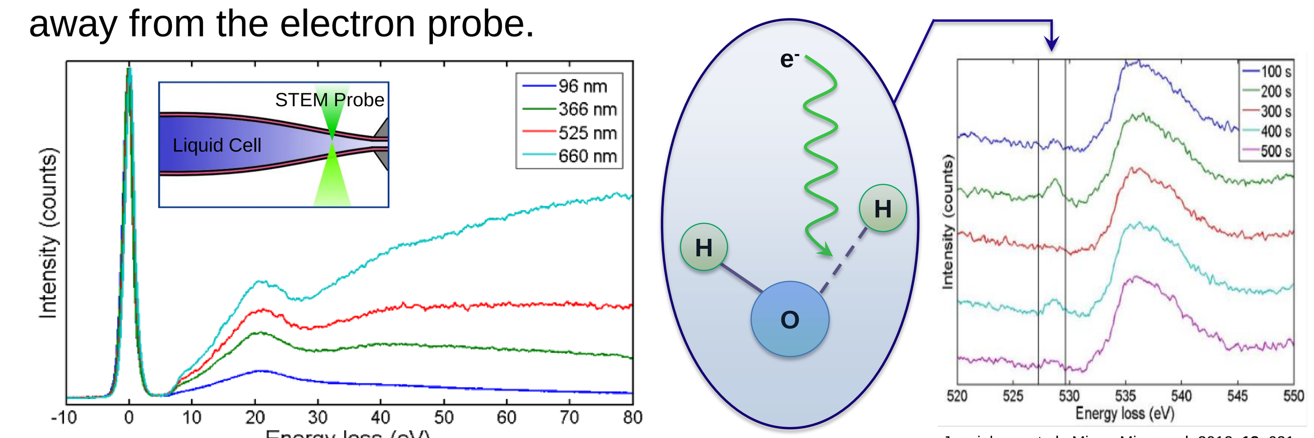
In STEM, the electron beam was left stationary in the center of colloidal 15 nm Au nanoparticles with Pd^{2+} ions in solution. Through the diffusion of e_{aq}^-, Pd reduced on the Au. The growth rate was highest for nucleation sites close to the formation of e_{aq}^- and within fluid thicknesses around 300 nm.





Electron Energy Loss Spectroscopy of Aqueous Solutions

Low-loss EELS provides a thickness measurement of the liquid layer at any location during STEM imaging. Core-loss EELS at the oxygen K-edge in water displayed a pre-edge feature that arose by radiolysis of the oxygen-hydrogen bond. Over time, either radiolysis species recombined or diffused away from the electron probe.



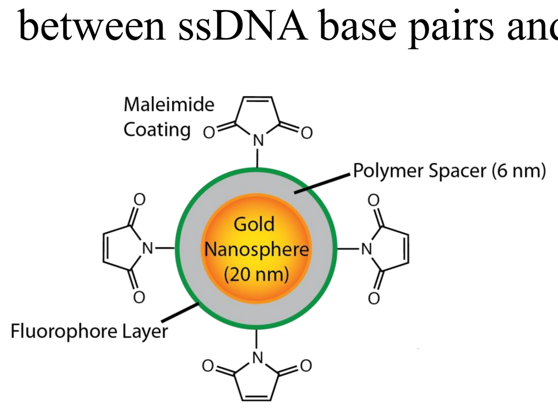
Au Nanoparticle DNA Assemblies

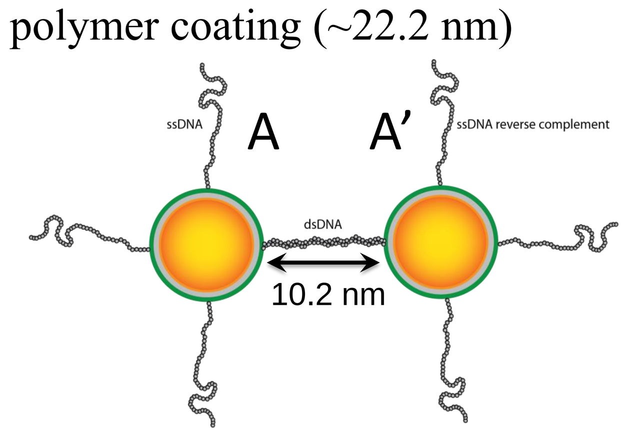
RA2013A0028

Angela Rudolph, Washington State University

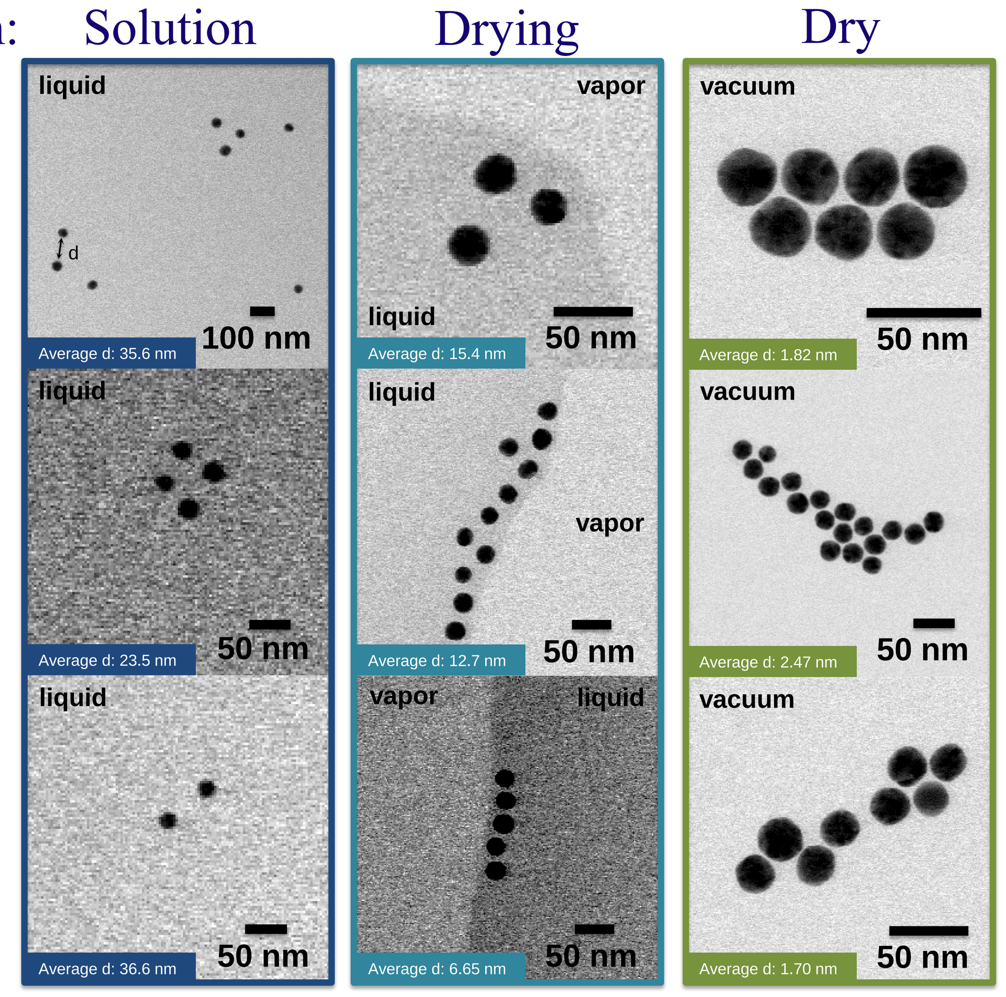
Susan Brozik and David Wheeler, Sandia National Laboratories

- DNA was used to create Au nanoparticle assemblies using a combination of base pair hydrogen bonding and the length of ssDNA strands
- Distances between the Au nanoparticles in assemblies was found to be very different for wet vs. dry STEM imaging
- Images acquired while the solution was drying demonstrates the grouping of the nanoparticles at the liquid-vapor interface
- Distances between the particles provides evidence that the dry assemblies (~2 nm) are not representative of lengths defined by the connection between ssDNA base pairs and polymer coating (~22.2 nm)



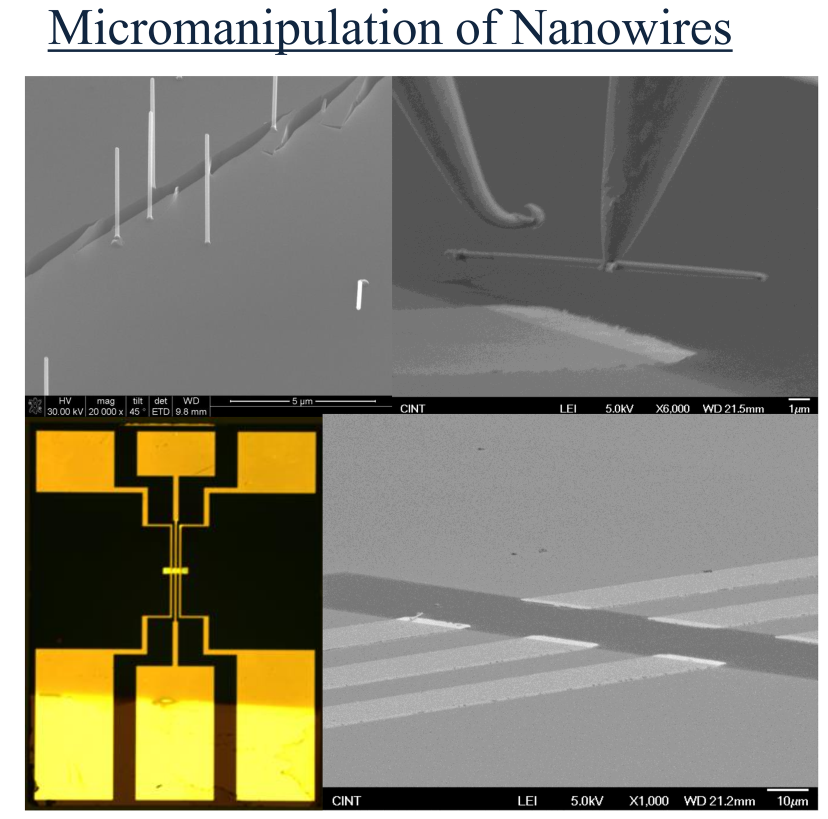


Assemblies in: Solution / Drying / Dry



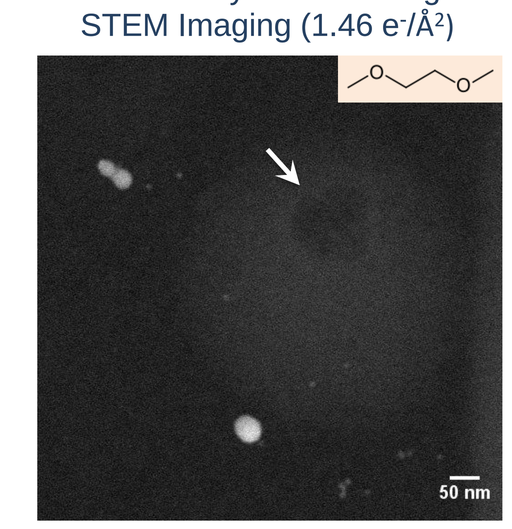
Towards Electrochemistry in Organic Solvents

Micromanipulation of Nanowires

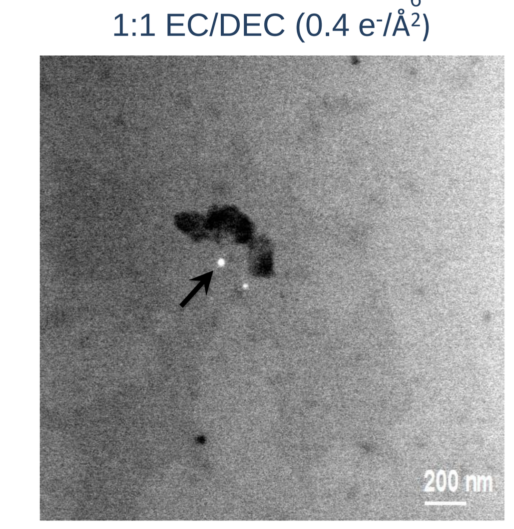


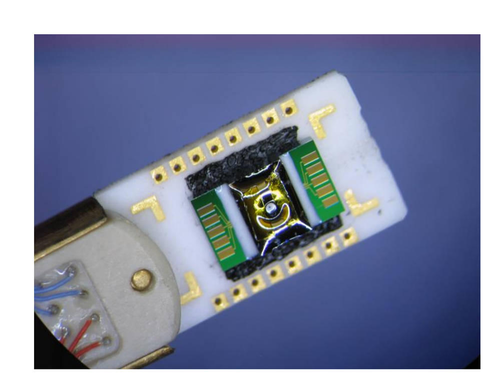
Integration with the expertise of Brian Swartzentruber to place individual nanowire structures on a precise location of the Pt electrode on the SiN membrane window. Electrodes were masked using CINT's clean room facilities.

Bubble Formation in Dimethoxyethane during STEM Imaging (1.46 e⁻/Å²)



Hole Formation in SiN Membrane in 1 M $LiPF_6$ in 1:1 EC/DEC (0.4 e⁻/Å²)





Development of imaging conditions for quantitative electrochemistry within the Electrochemical TEM Discovery Platform. Organic electrolytes are more beam sensitive than aqueous solutions, producing a larger amount of radiation species which react during imaging. Therefore, low-dose high-contrast HAADF STEM imaging is used.

Los Alamos National Laboratory EST. 1943

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