BROOKHAVEN NATIONAL LABORATORY

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Monitoring Galvanic Replacement of Ag Nanoparticles by Pd using Low Dose In Situ Liquid S/TEM

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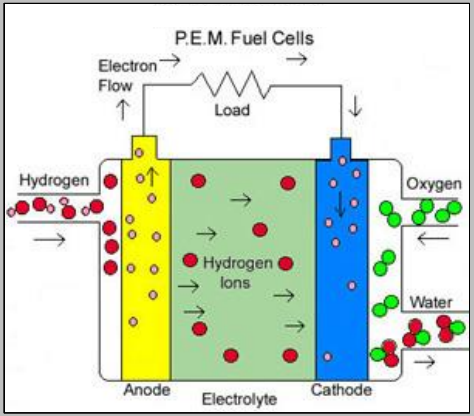
Center for Functional Nanomaterials

Overview

- Nanoparticles for increased catalytic activity in the Oxygen Reduction Reaction
  - High surface area
  - Reduce amount of Pt loading on the surface
  - AuPd core shell to deposit a Pt ML on the surface
  - Pd hollow nanoparticles for larger surface area Pt ML
- In Situ liquid S/TEM to image the deposition and galvanic displacement processes
  - STEM/EELS to measure the thickness of the aqueous solution in the liquid cell
  - Electron beam damage causing the formation of aqueous electrons in solution
  - Understanding the interaction of the aqueous electrons with colloidal nanoparticles in the liquid cell
  - Minimize the formation of radiation species in STEM using reduced beam current and magnification
- Understanding the morphological and compositional changes during pit formation
  - TEM vs. STEM imaging of pit process at low electron doses
  - Comparison of in situ particles to ex situ reaction under similar reaction times



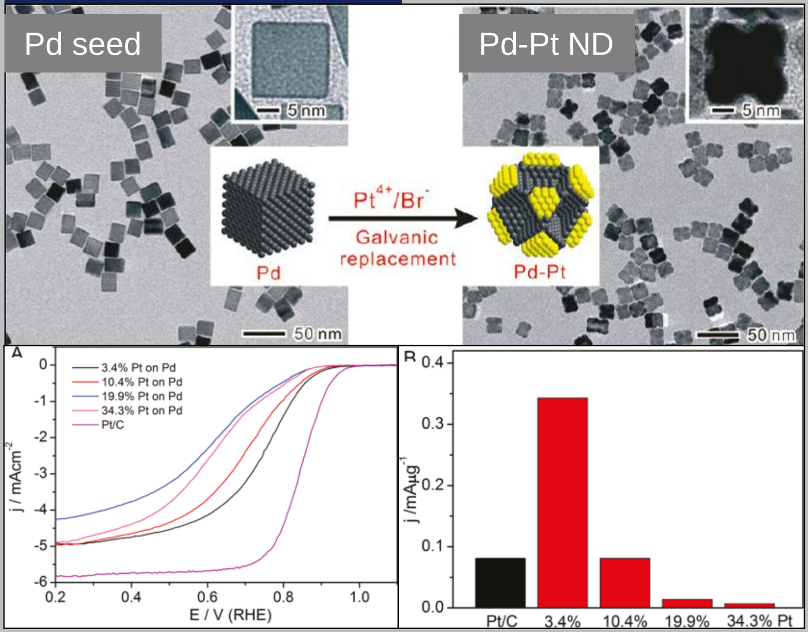
www.americanhistory.si.edu/fuelcells/basics.htm

Catalyst Materials	Ag	Pd	Pt	Au
Cubic Structure	FCC	FCC	FCC	FCC
Lattice constant (Å)	4.090	3.890	3.920	4.080
Reduction Potential (V)	0.80	0.99	1.20	1.69

High Activity Catalysts for Oxygen Reduction Reaction

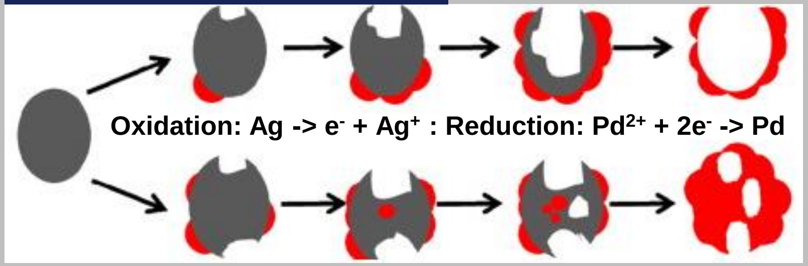
$$O_2 + 4H^+ + 4e^- \xrightarrow{catalyst} H_2O$$

Pd-Pt Nanodendrites



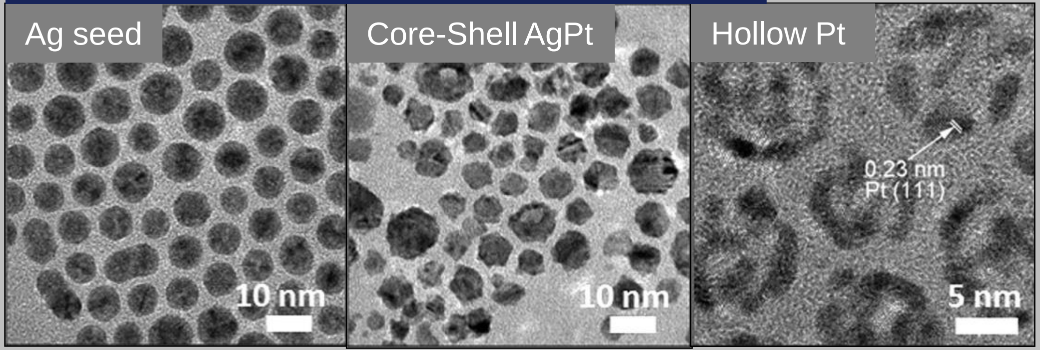
Zhang et al., J. Am. Chem. Soc. **2011**, 133, 6078-6089.

Galvanic Displacement



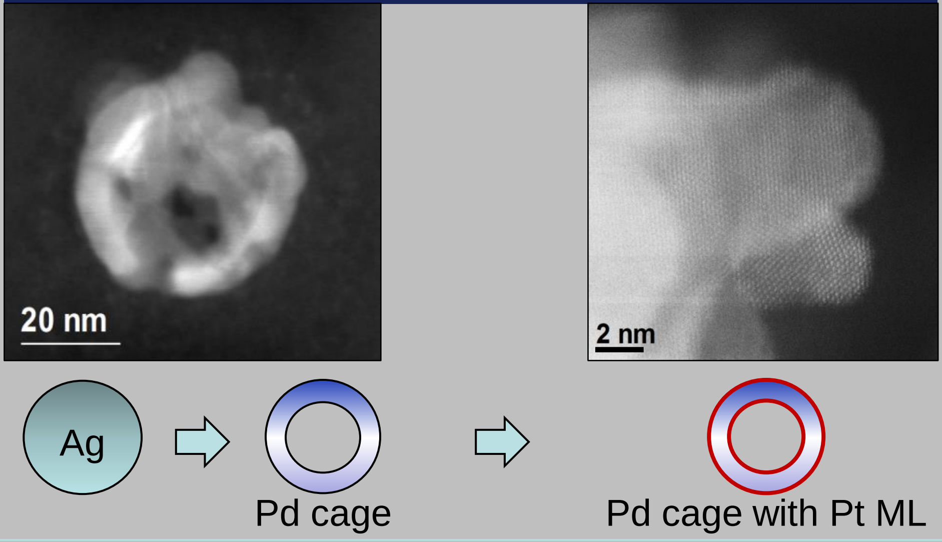
Clay et al., Materials Letters **2012**, 88, 143-147.

High Surface Area: Hollow Pt Nanocages



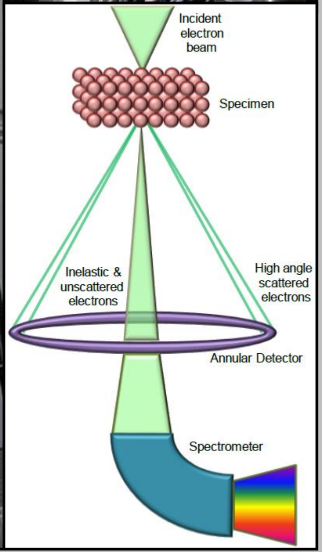
Qu et al., Int. J. Hyd. Ener. **2012**, 37, 13191-13199.

Hollow Pd Nanocages for Pt Monolayer Deposition



Develop hollow Pd nanostructres with Pt ML surfaces for high activity catalysts

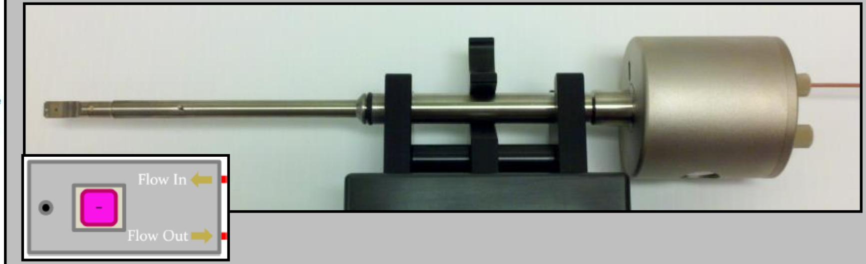
Titan Environmental TEM



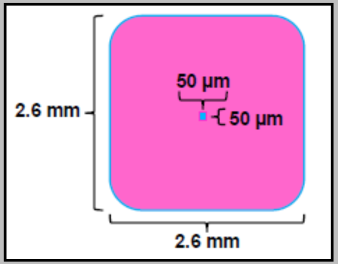
FEI Titan 80-300 kV C_s-corrected ETEM
- Operated at 300 kV
- STEM resolution: 1.4 Å
- Probe current: 0.37 nA

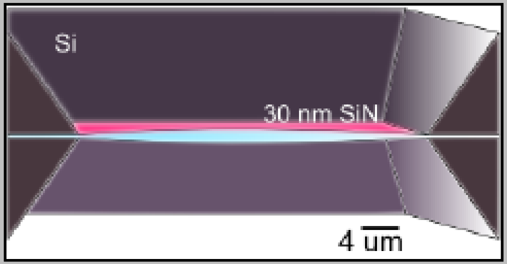
Gatan Tridiem EEL Spectrometer
- Energy resolution: 1.6 eV

Hummingbird Scientific Liquid Holder
- Microfluidic pumping



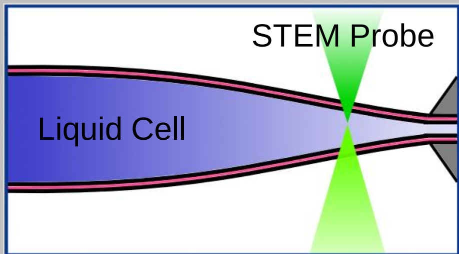
SiN Membrane Windows from Norcada
- Window Area: 50 x 50 µm
- SiN thickness: 30 nm
- Spacers: 90 nm polystyrene beads dried at the corners

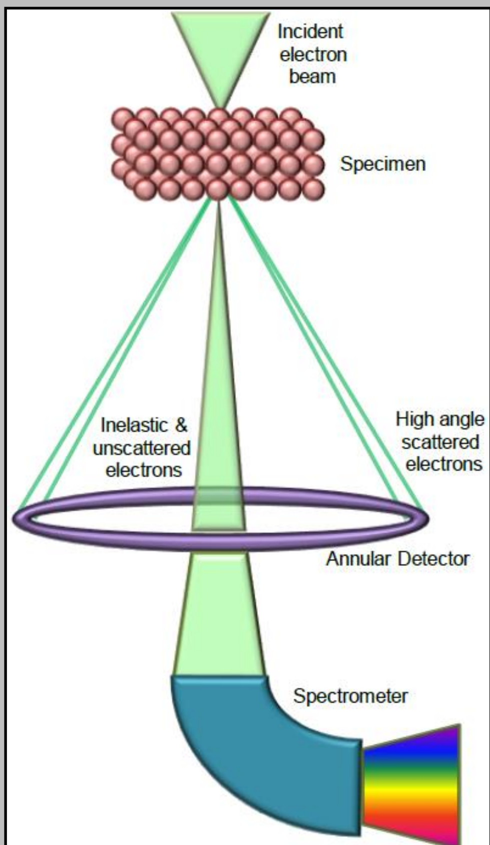




STEM/EELS allows for liquid thickness measurements during imaging

Water Thickness Measurement in the Liquid Cell





t/λ_i values : measured using EELS
t : thickness of material (nm)
λ_i : inelastic mean free path of e^- through the material

Atomic Number Formula

$$Z_{eff} = \frac{\sum f_n Z_n^{1.3}}{\sum f_n Z_n^{0.3}}$$

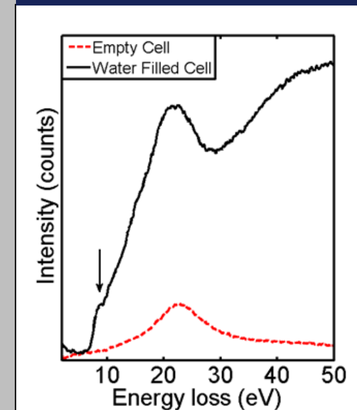
$$E_M = 7.6Z^{0.36}$$

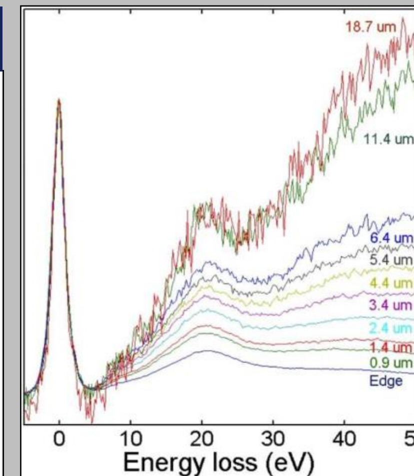
$$\lambda_i = \frac{106FE_0}{E_M \ln((2\beta E_0)/E_M)}$$

Z_{eff}: Effective atomic number
f_n: Atomic fraction of element n
Z_n: Atomic number of element n
E_M: Average energy loss (eV)
Z: Average atomic number
λ_i : Inelastic mean free path length
E_o: Accelerating voltage
β: Collection angle (mrad)
F: Relativistic correction factor

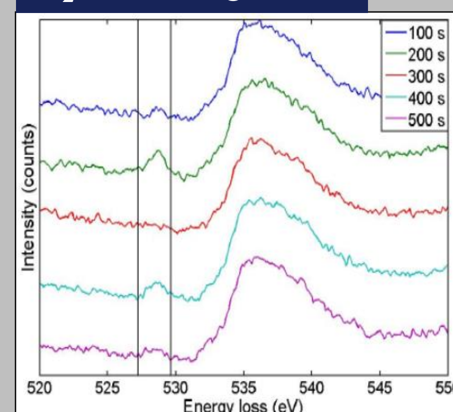
Malis et al. *J. of Elec. Micro. Tech.* **8**, 193-200 (1988).

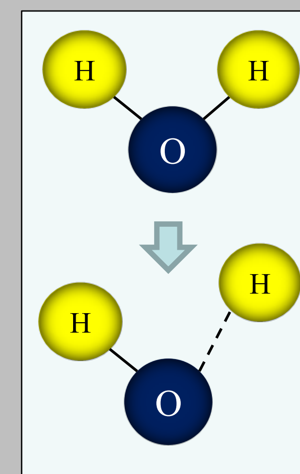
Low Energy Loss





H_2O: O k-edge

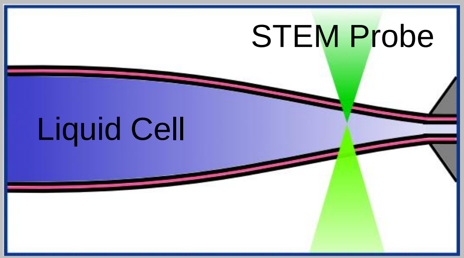




Jungjohann et al., Micro. Microanal. **2012**, 18, 621.

STEM/EELS provides estimated fluid thickness and evidence of damage to water

Electron Beam Ionization of Water

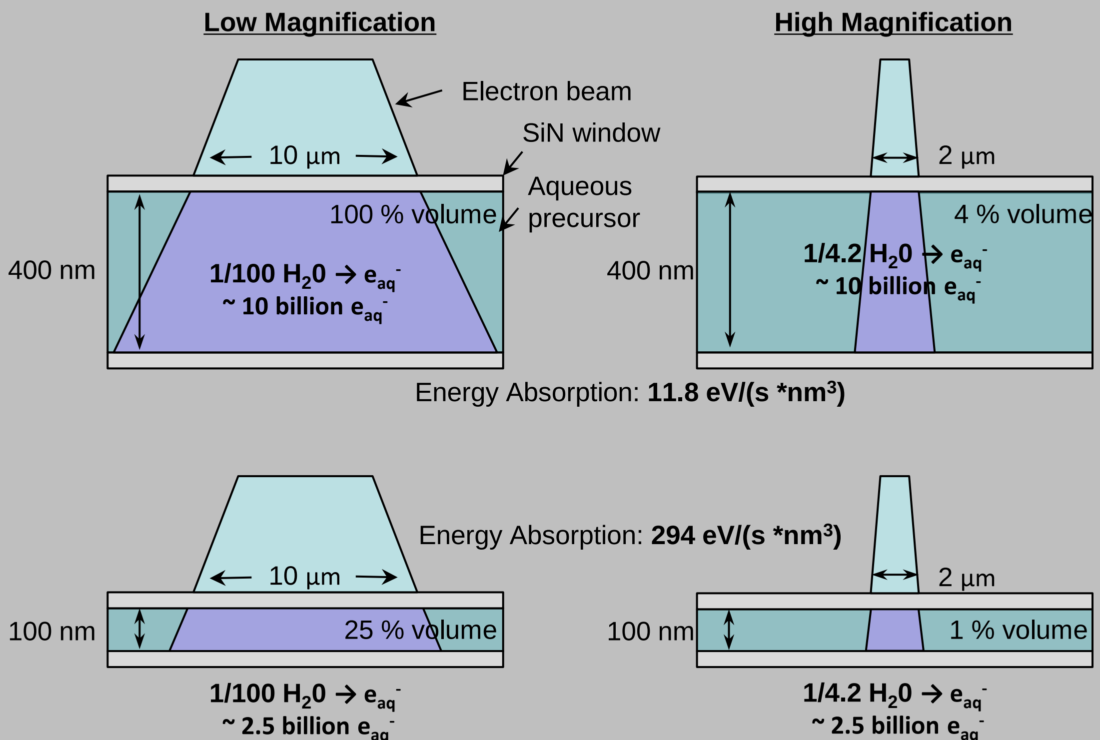


$$H_2O \rightarrow 2.7\ e_{aq}^- + 2.7\ H^+ + 0.61\ H + 0.43H_2 + 2.87OH + 0.61\ H_2O_2 + 0.026HO_2$$

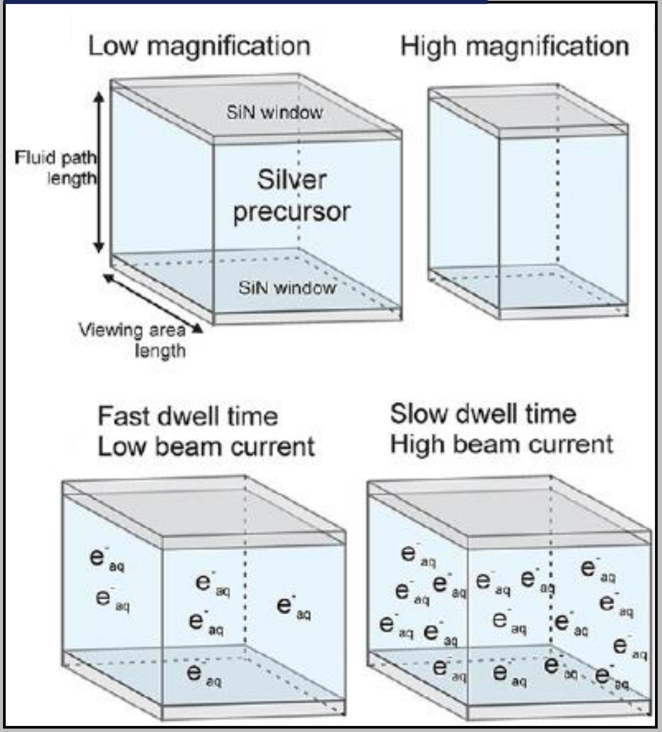
* values represent # species formed for 100 eV absorbed energy

- Main reducing specie: e_{aq}^- formed at 4×10^{-13} s
- Majority of primary species quickly react before diffusion occurs

TEM Electron Exposure



STEM Electron Exposure

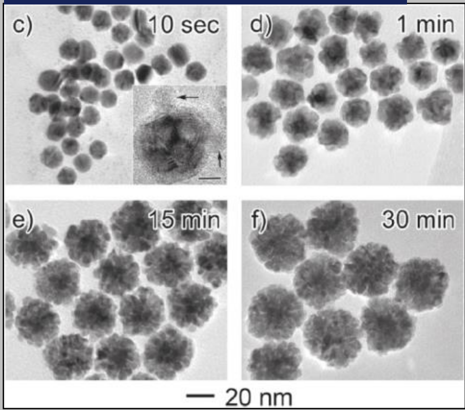


Woehl et al. ACS Nano **6**, 8599 (2012).

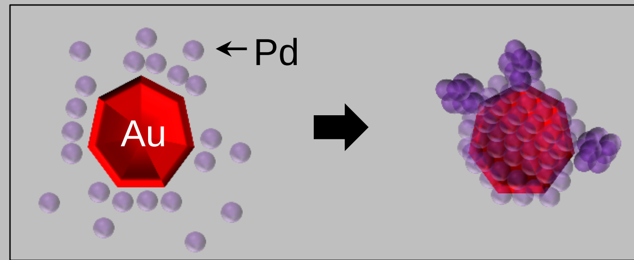
Electron probe generates reducing species in water during imaging

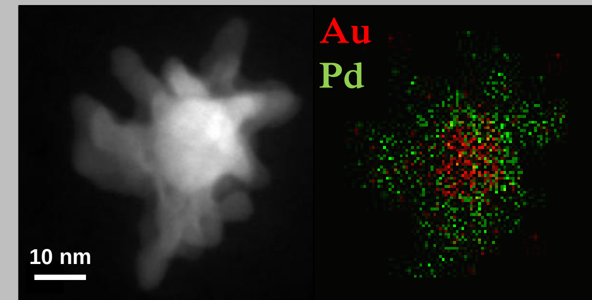
Pd Shell Structure Comparison by Au Template Size

Ex Situ Au-Pd Growth

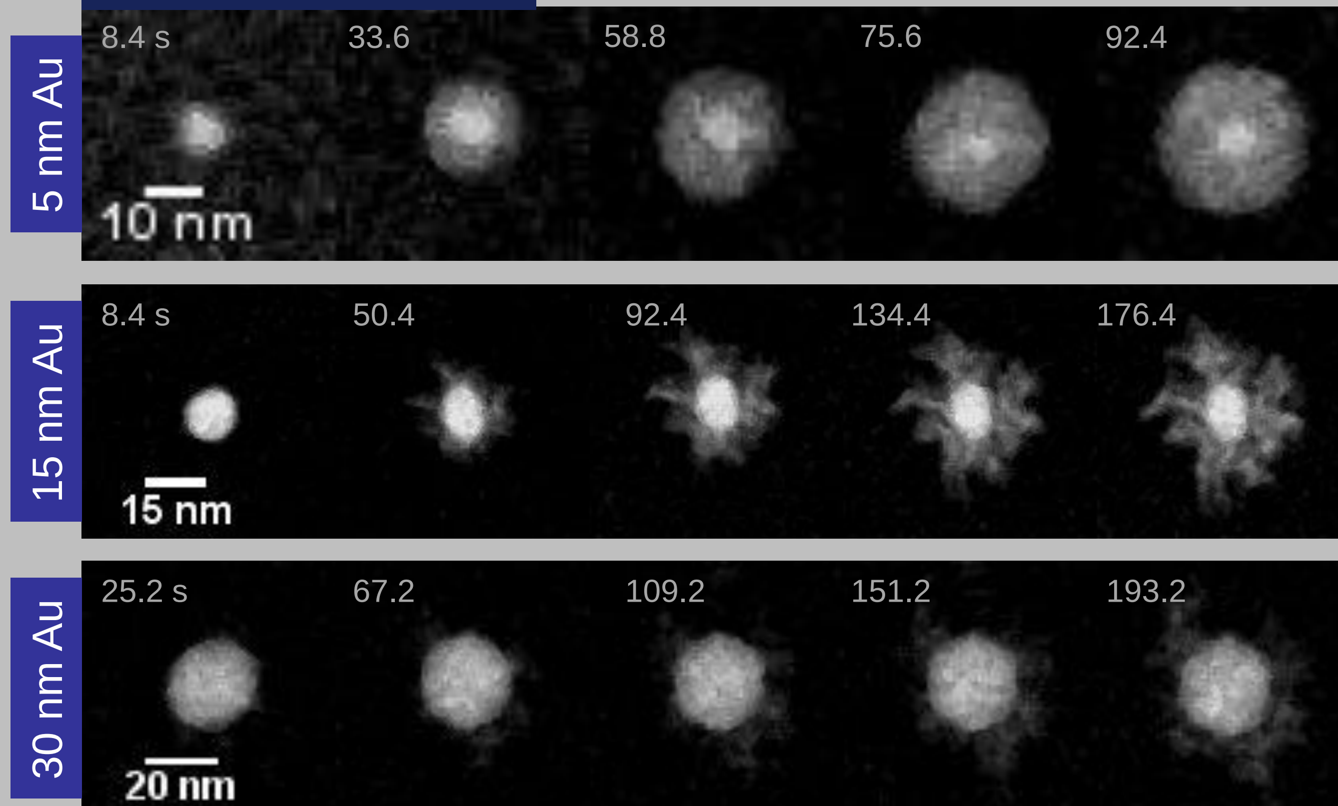


Xu et al., ACS Nano **2011**, 5, 6119.



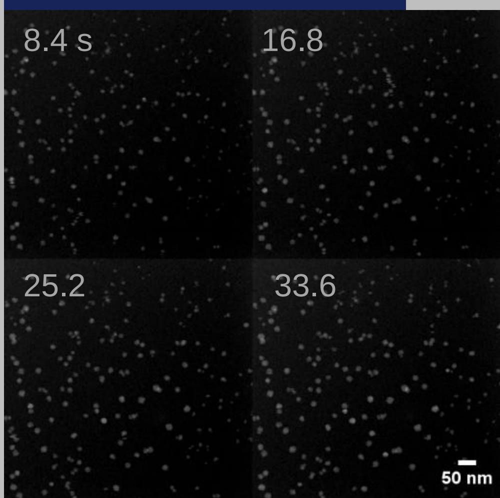


In Situ Dark-Field STEM



K. Jungjohann et al. Nano Lett. **2013**, 13, 2964.

10 µM $PdCl_2$ Aqueous

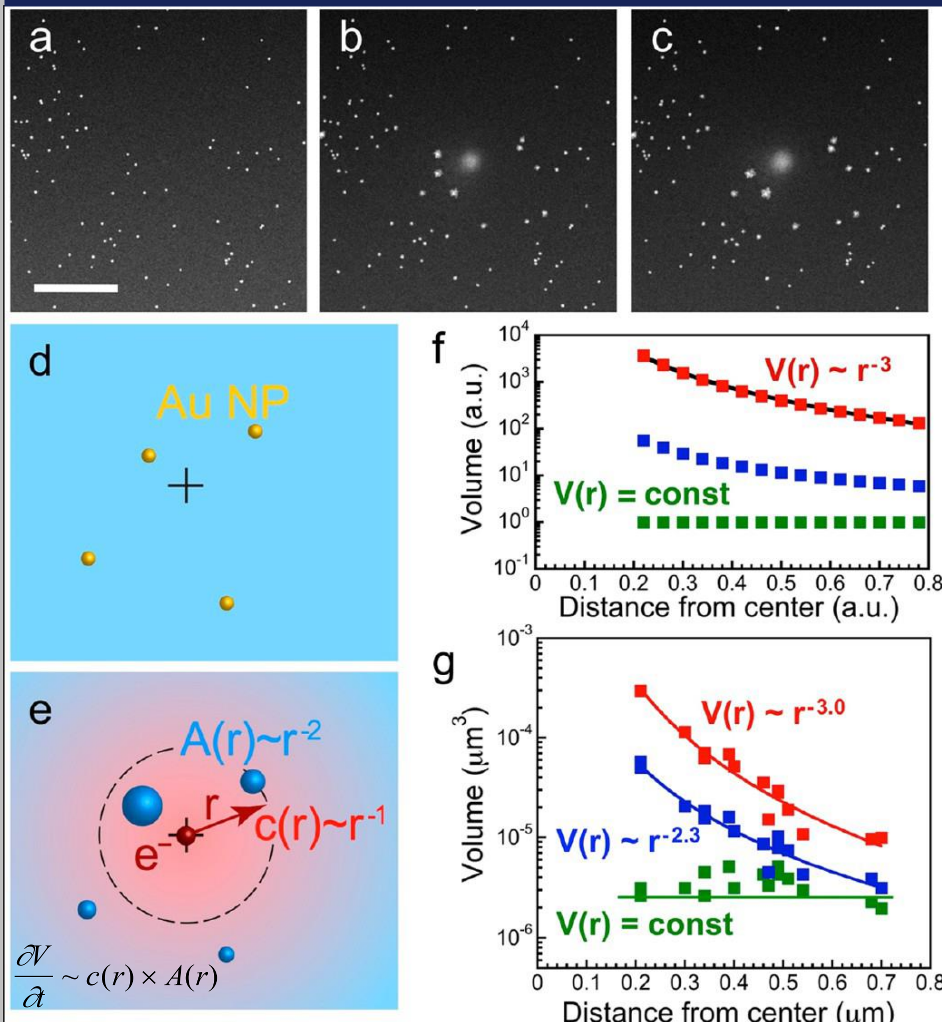


10 µM $PdCl_2$ solution
Fluid thickness: 40 nm

Pd shell morphology varies strongly by gold template size (surface structure)

Mobility of Aqueous Electrons in Liquid Cell

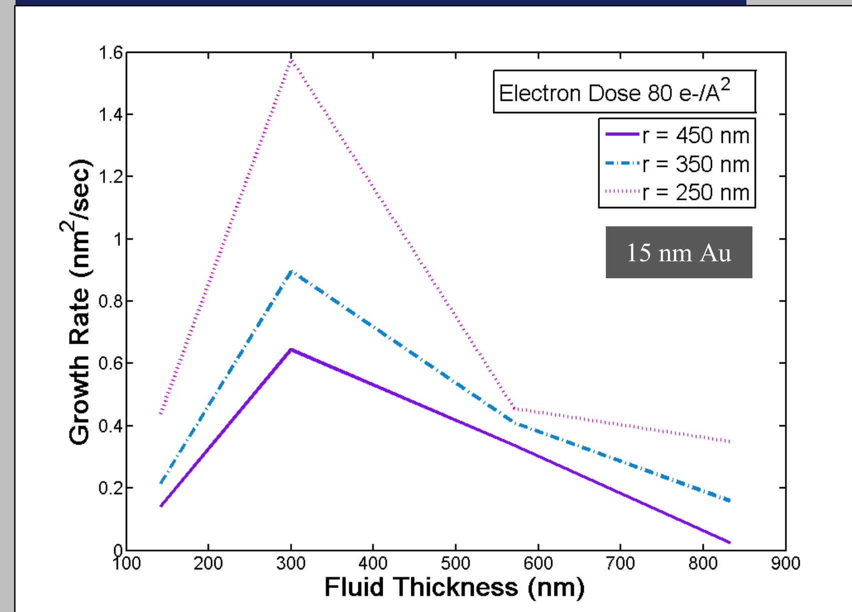
Aqueous Electron Dynamics Control the Growth Rate



$c(r) = \frac{c_a}{r} + c_b$

K. Jungjohann et al. Nano Lett. **2013**, 13, 2964.

Pd Shell Growth Rate vs. Fluid Thickness



Initial state: $V(r) \sim r^{-2.3}$

Steady state: $V(r) \sim r^{-3}$

Pd deposition rate on 15 nm Au dependence

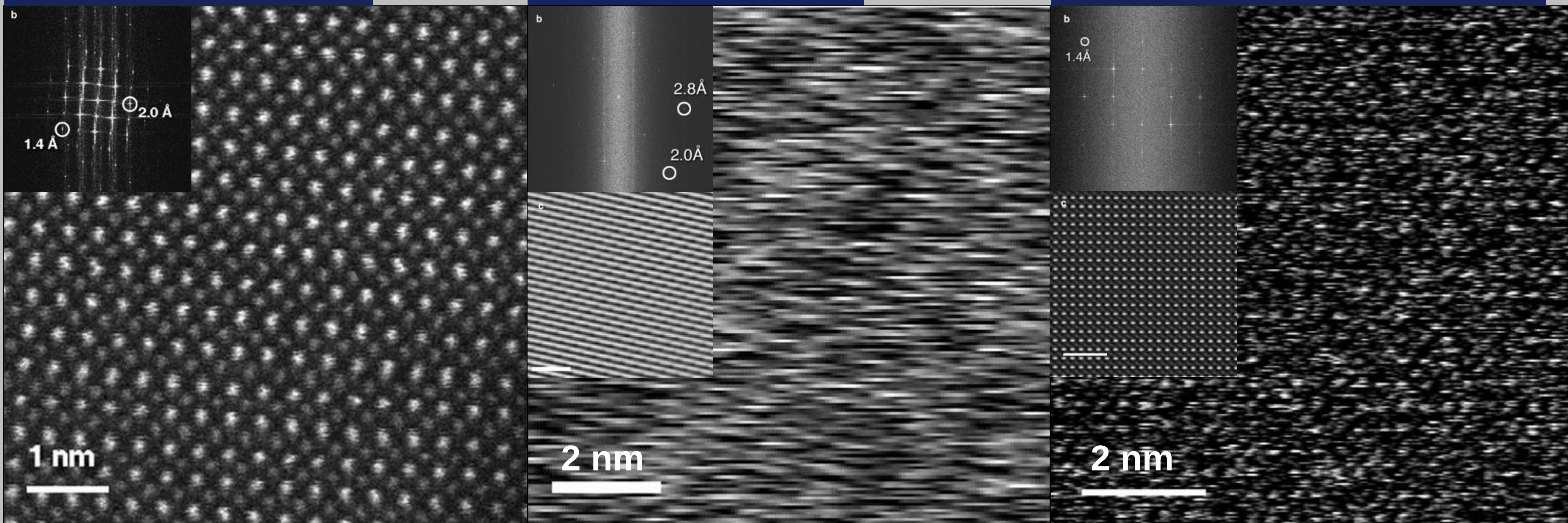
- Distance from beam exposure
- Shadowing of closer nanoparticles
- Thickness of liquid in cell

e_{aq}^- dynamics determine the growth rate of particles in solution

Low Dose Imaging to Reduce Beam Effects

Demonstrated with $SrTiO_3$

C_s Image: 1×10^8 $e^-/Å^2$ | Fast Scan: 450 $e^-/Å^2$ | Lower Beam Current: 220 $e^-/Å^2$

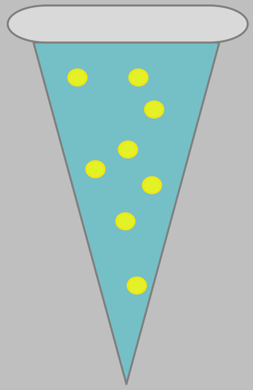


Buban et al., J. Ele. Microsc. **2010**, 59, 103-112.

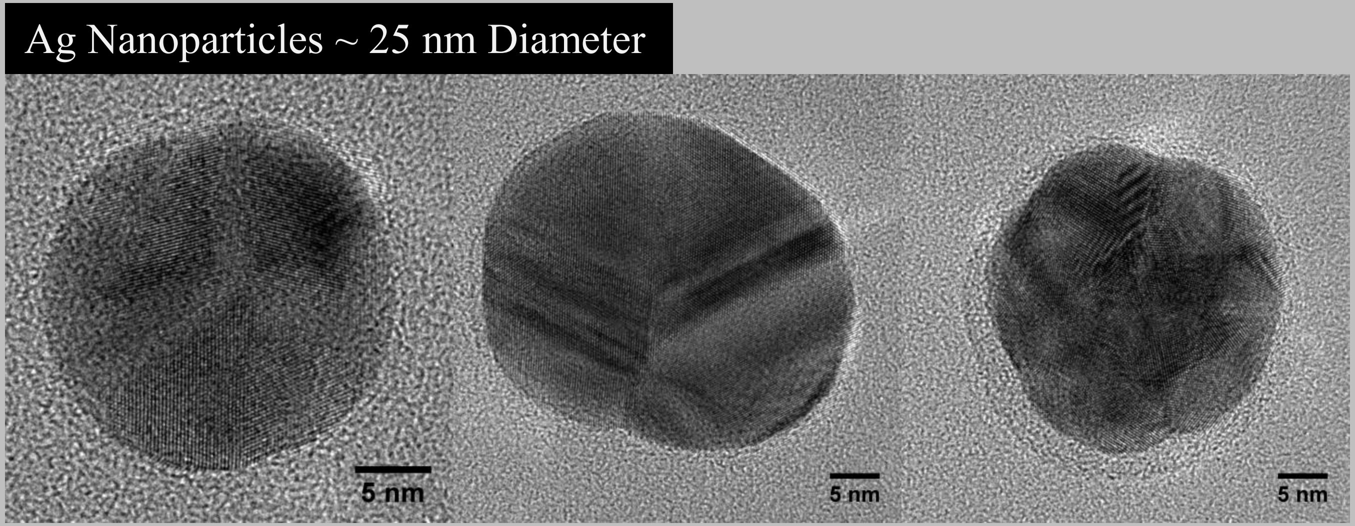
	1×10^8 $e^-/Å^2$	450 $e^-/Å^2$	220 $e^-/Å^2$
Beam Current (pA)	50	50	2
Pixel Dwell Time (μs)	20	0.5	2
Pixel Size ($Å^2$)	0.05	0.3	0.11

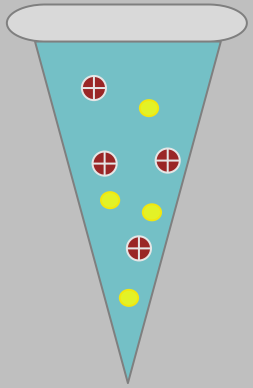
Limit the electron dose to image non-beam induced processes

Ex Situ Hollow AgPd Formation at Room Temp

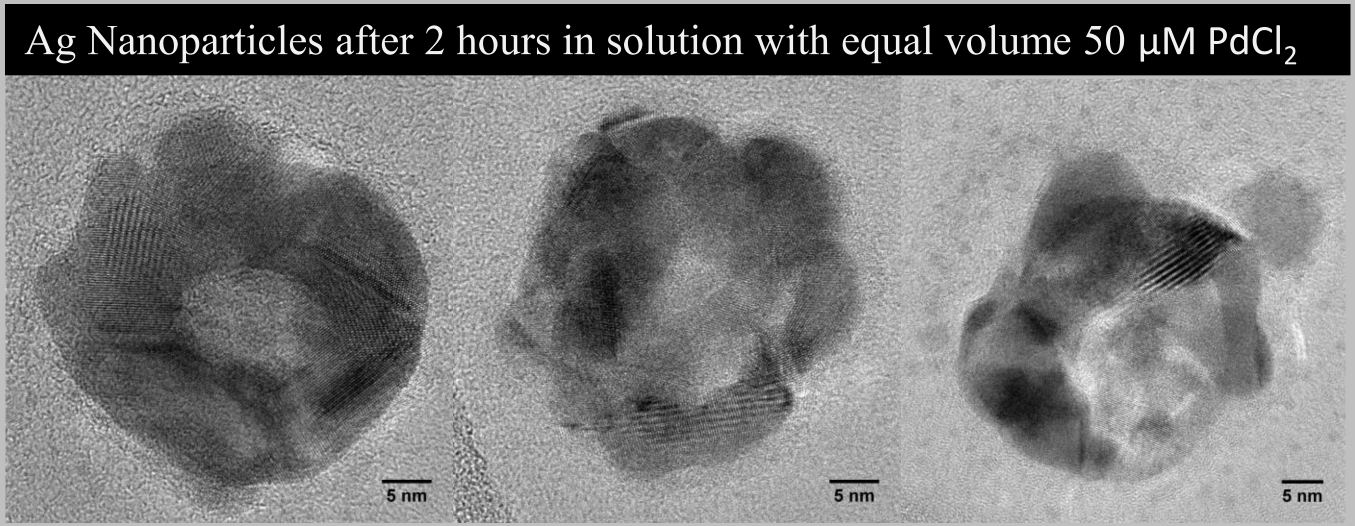


5 x 10^9 Ag particles/μL





2.5 x 10^9 Ag particles/μL
25 μM $PdCl_2$

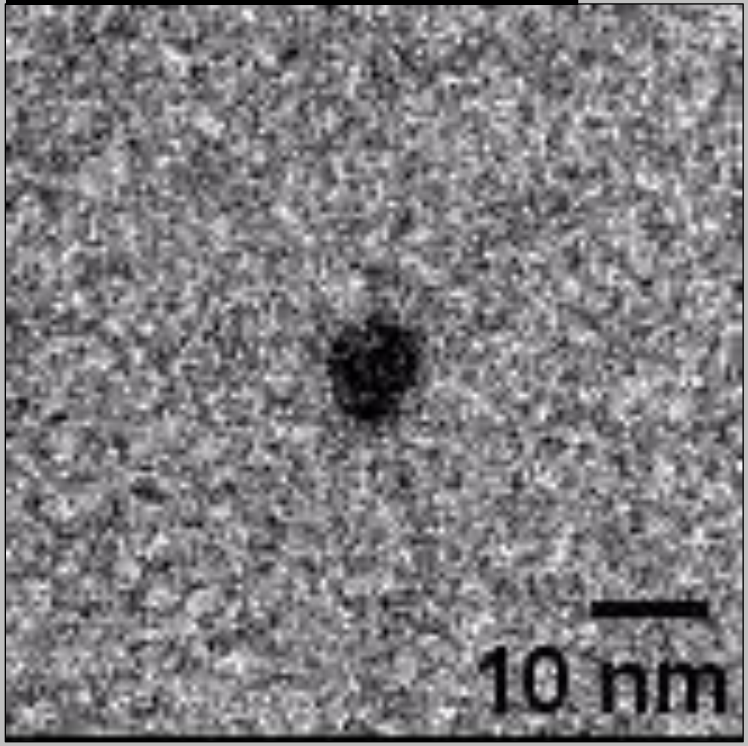


~ 81% Ag &19 % Pd ~ 35 nm Diameter

Hollow structures formed after 2 hours of exposure to $PdCl_2$

Hollow AgPd Alloy Nanoparticles

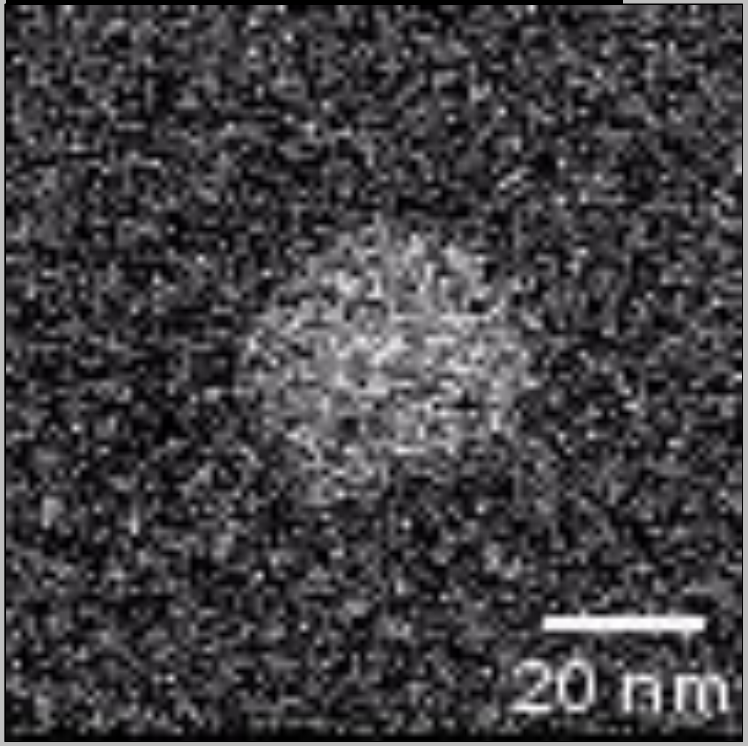
TEM: 50 μM $PdCl_2$ (5.2 $e^-/Å^2$)



Video played at 3x real-time

Acquired at 3 frames/second

STEM: 10 μM $PdCl_2$ (40.9 $e^-/Å^2$)



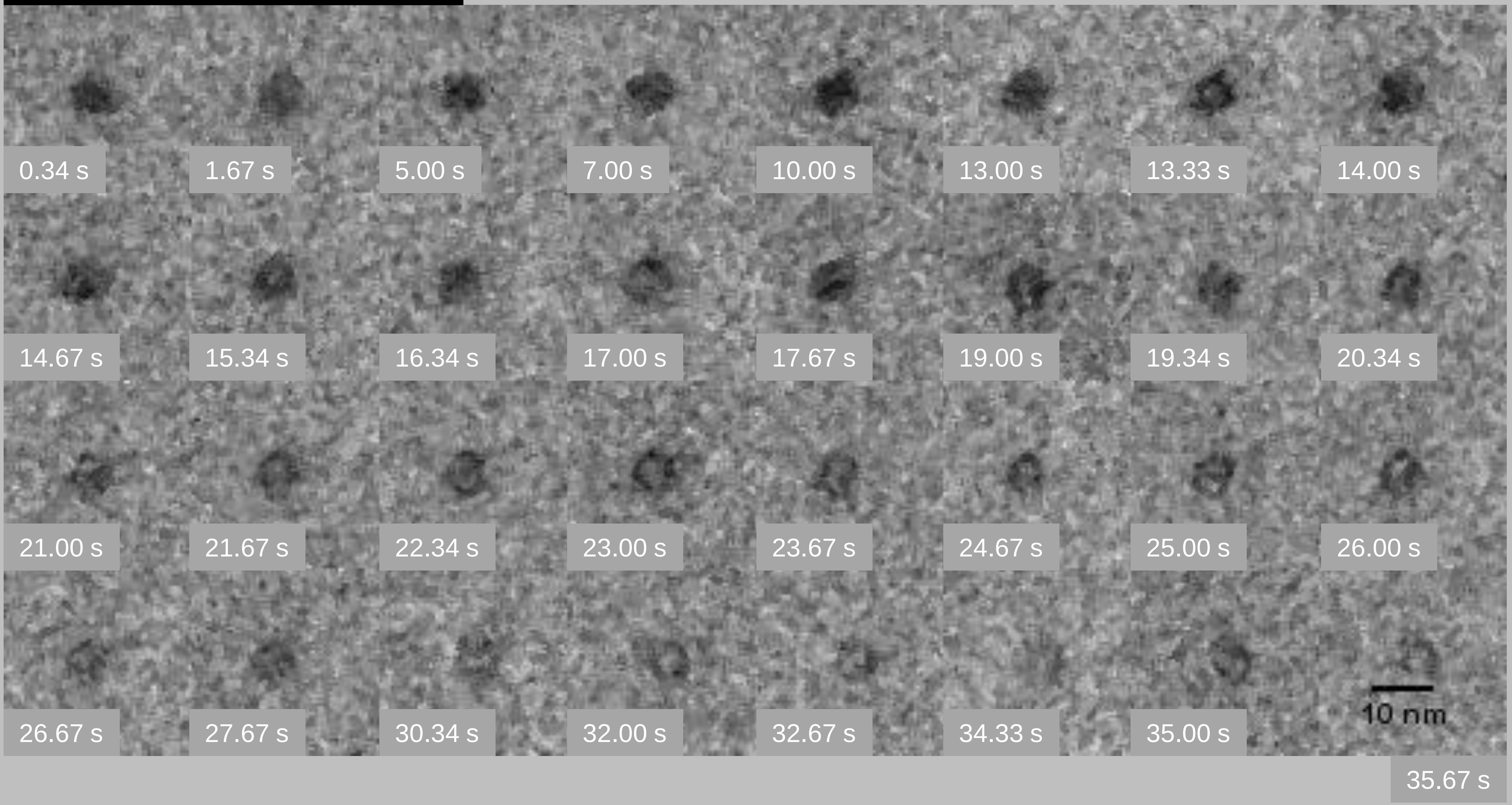
Video played at 3x real-time

Acquired at 1 frame/second

Slow process of pit formation, followed by rapid dissolution of Ag core

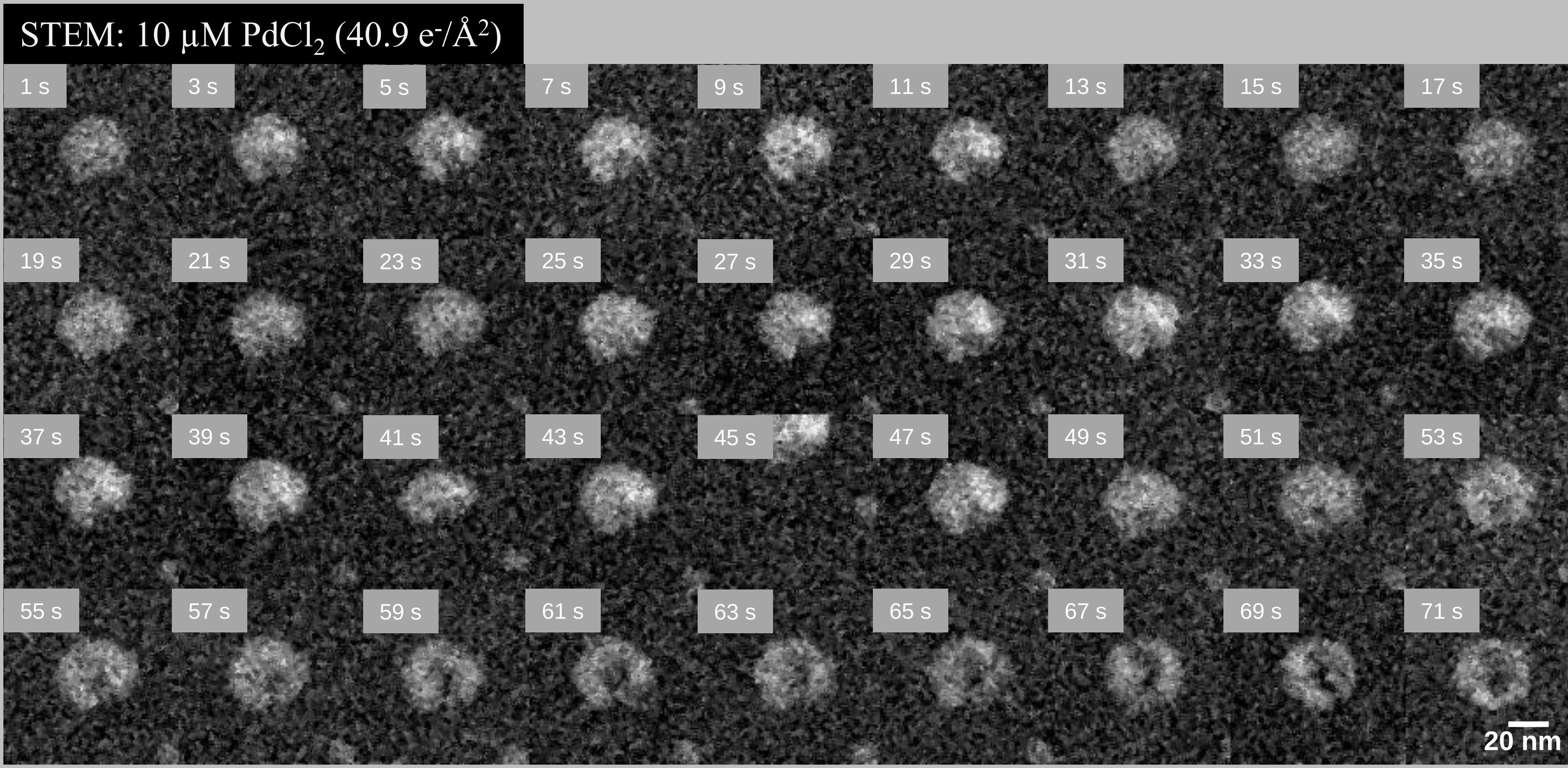
Hollow AgPd Alloy Nanoparticles

TEM: 50 μM $PdCl_2$ (5.2 $e^-/Å^2$)



Low dose TEM observes process with higher frame rate than STEM

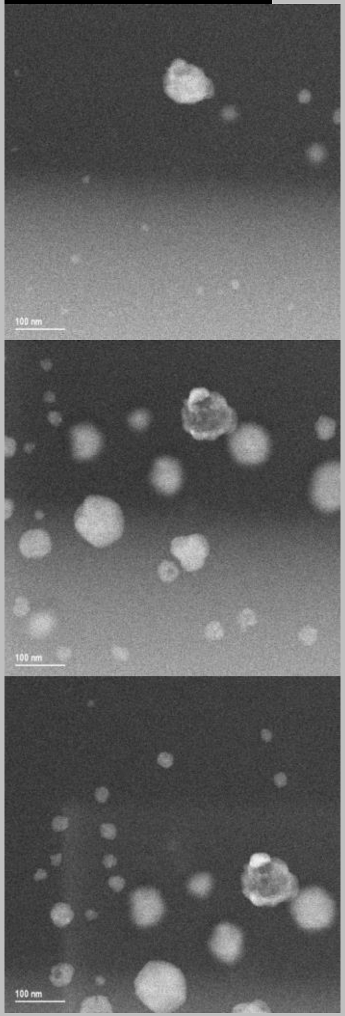
Hollow AgPd Alloy Nanoparticles



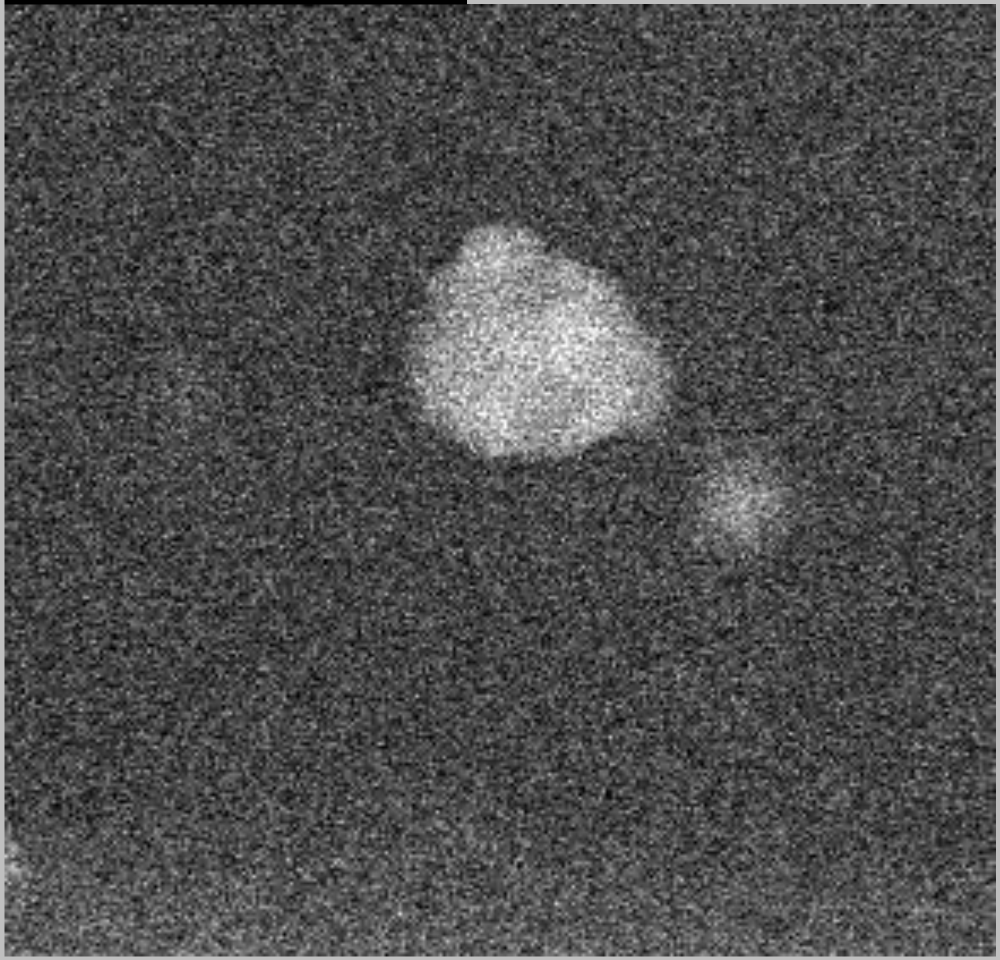
Low dose STEM provides high contrast and controlled exposure area

Hollow AgPd Alloy Nanoparticles

50 µM $PdCl_2$

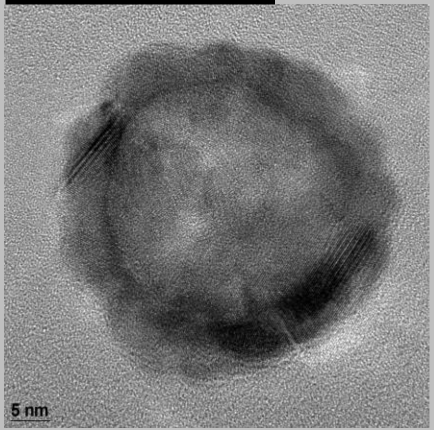


In Situ DF STEM Video



Video played at 3x real-time   Acquired at 1 frame/ seconds

Ex Situ TEM

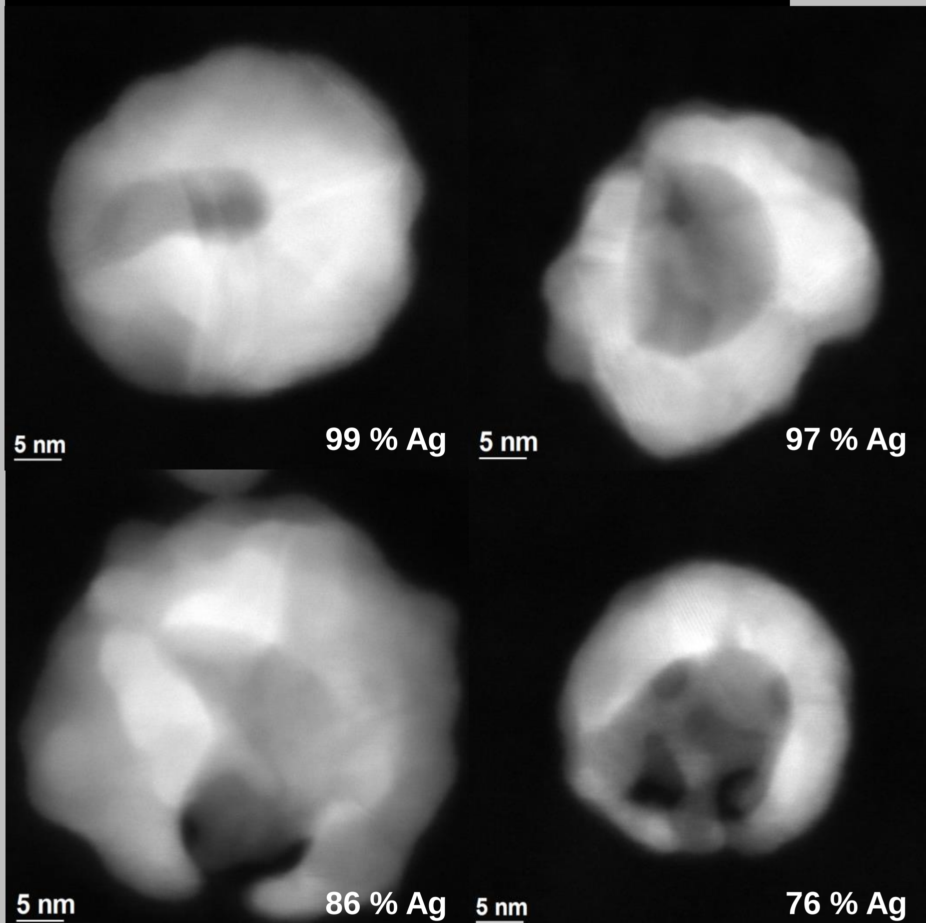


- Particle ~ 70 nm
- Cage composed of many small nanoparticles
- Ag metal dissolves in solution, is reduced by the electron beam along with free Pd ions in solution during imaging
- Out of focus particles deposited on the bottom SiN membrane
- Some nanoparticles were already hollow when began imaging in region

Hollowing of Ag from the nanoparticle core occurred within seconds

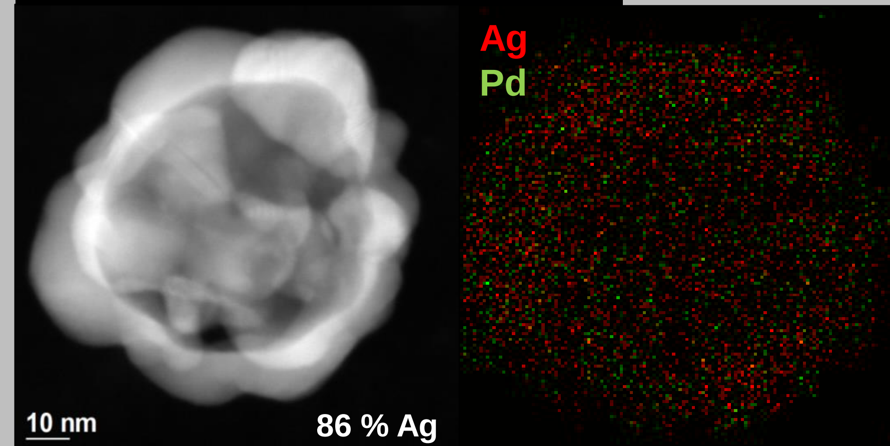
Hollow AgPd Alloy Nanoparticles

Analysis after *In Situ* STEM: 25 μM $PdCl_2$

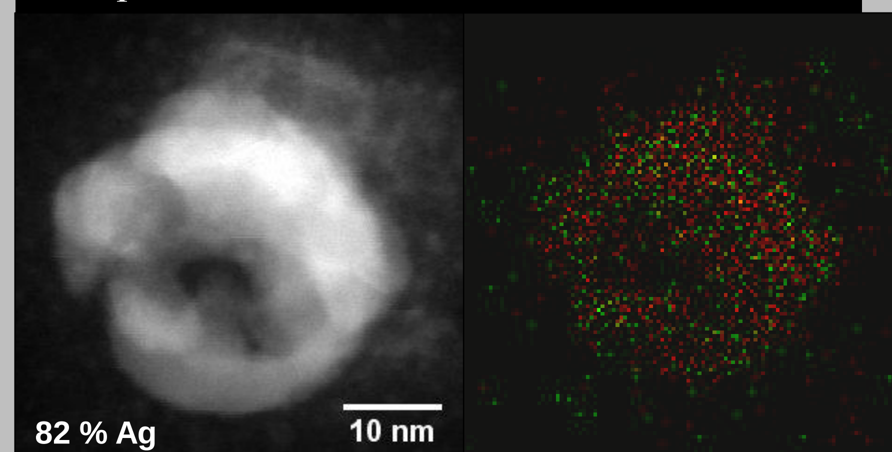


Extent of Ag replacement depends on the shape of the Ag core

Composition of *In Situ* Particles



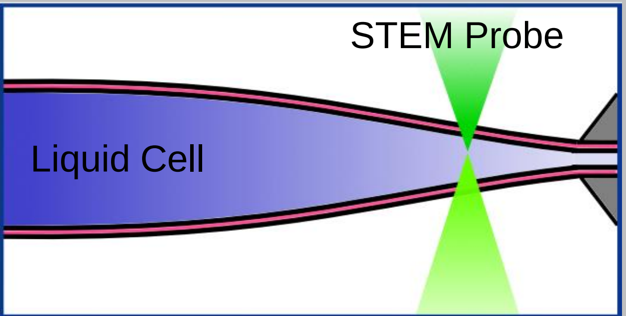
Composition of *Ex Situ* Particles after 2 Hours

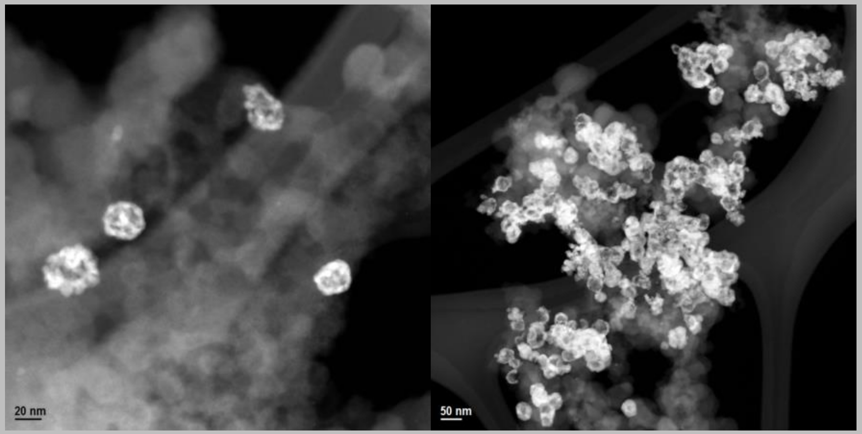


Ex situ structure and composition matches *in situ* hollow structures

Conclusions

- In situ liquid STEM/EELS allows for real-time imaging and simultaneous collection of thickness measurements from nanomaterial reactions
- Minimize electron beam induced processes by lowering the beam current for imaging, less beam effects observed in STEM vs. TEM
- The structure, size and composition of the hollow AgPd nanoparticles was comparable for the in situ TEM and ex situ reactions
- Future analysis of the kinetics related to hollowing of the interior Ag, control structure using Br ions to mask some Ag surfaces
- The Center for Functional Nanomaterials (CFN at BNL) and the Center for Integrated Nanotechnologies (CINT at SNL & LANL) provide access to scientific staff and facilities at no fee to approved users via a peer-review process for research





Acknowledgements

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