SAND2016-0114C

Advanced electron microscopy techniques for *in situ* liquid imaging of metal nanoparticles towards water-phase catalysis

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and ***Ilke Arslan***

Water-Phase Energy Production

How can we view this chemical conversion process within a reactor (environmental control) to investigate catalyst performance with sub-nanometer resolution?

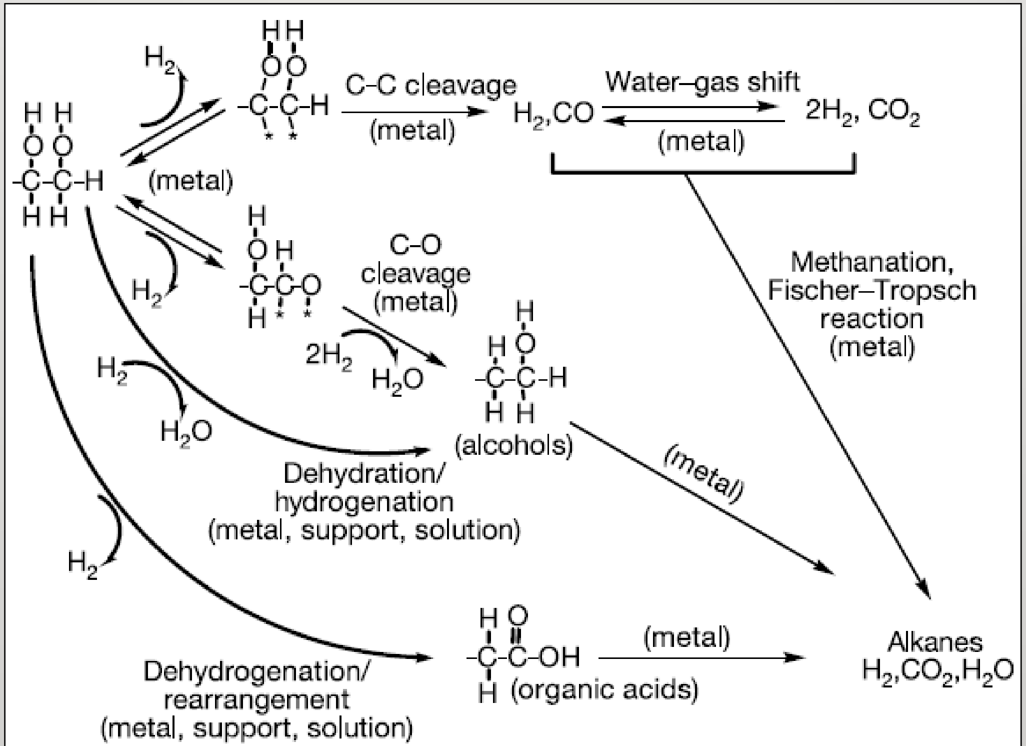


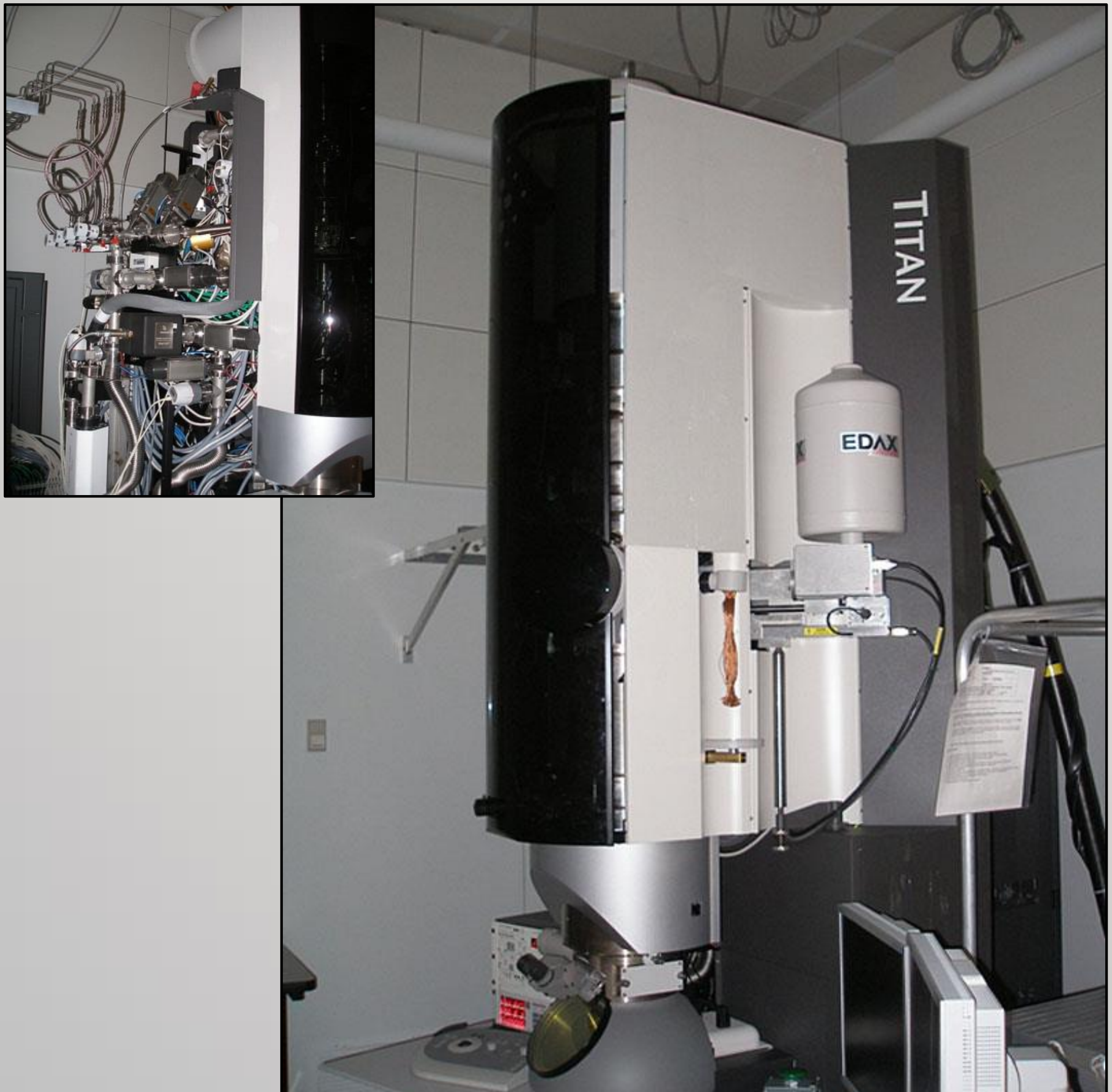
Figure 1 Reaction pathways for production of H_2 by reactions of oxygenated hydrocarbons with water. (Asterisk represents a surface metal site.)

- Liquid control
- Gas control
- 500 K
- Nanoscale imaging of Pt metal catalyst on support material

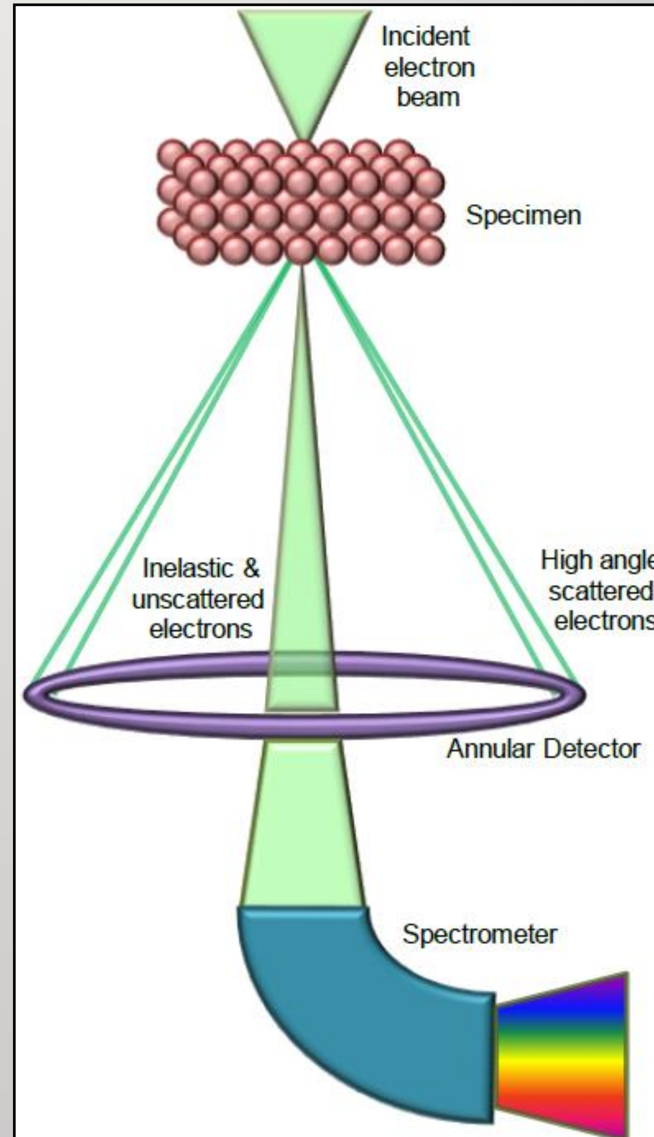
Cortright et al. *Nature* **2002.**

Environmental TEM

FEI Titan 80-300 kV C_s-corrected ETEM

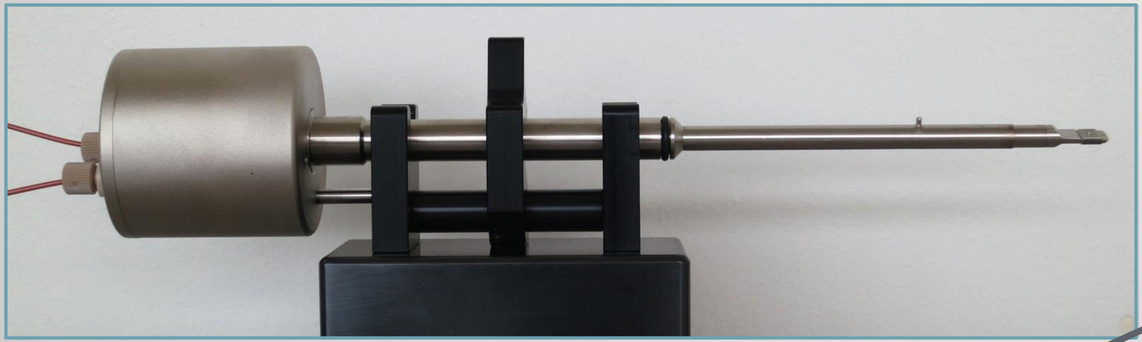


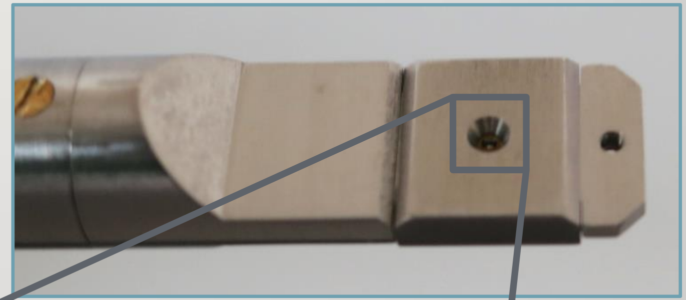
Scanning TEM



In-situ TEM Liquid Cell

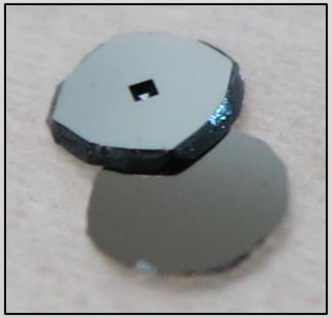
Hummingbird Scientific Microfluidic TEM Liquid-Cell Stage



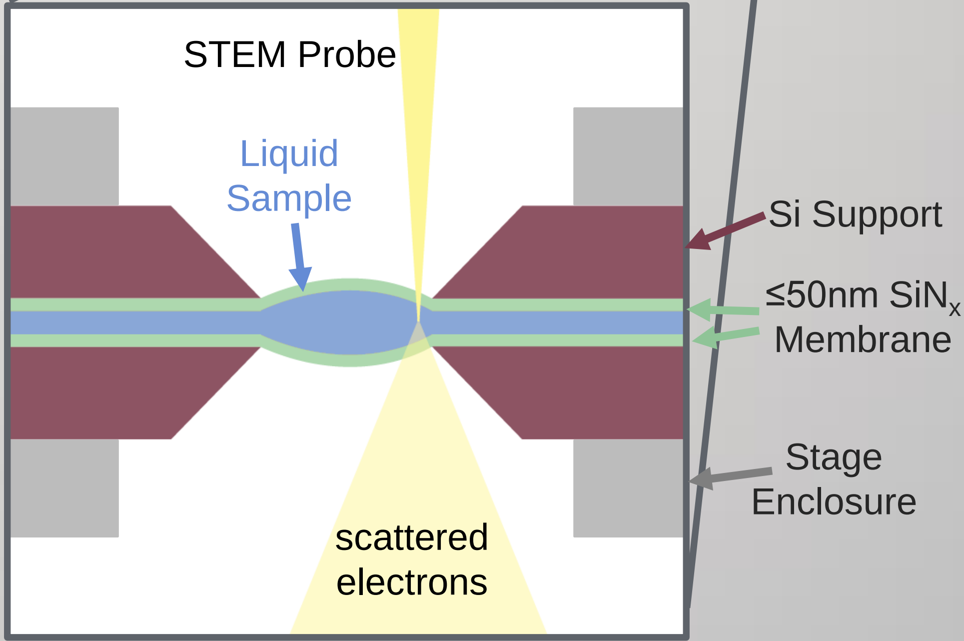


Sample Solution

SiN_x Windows

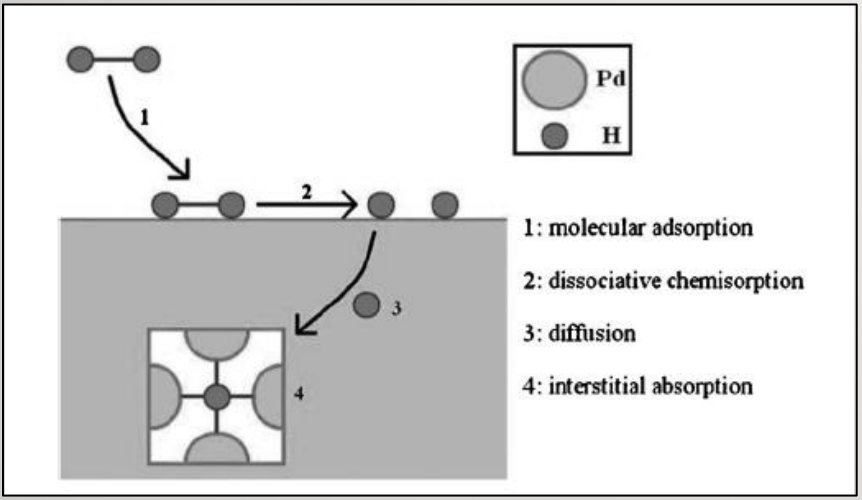


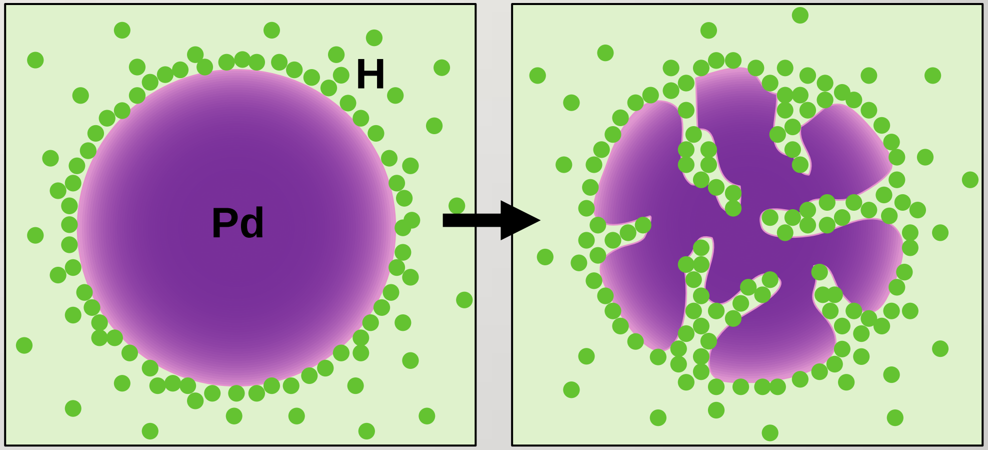
Cross-section



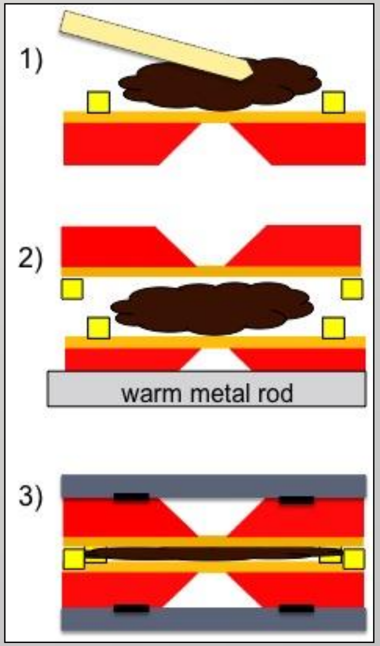
Pd Catalyst Growth for High Surface Area

Pd for Hydrogen Storage





R. Delmelle et al. *J. Phys. Chem. Chem. Phys.* **2010**.



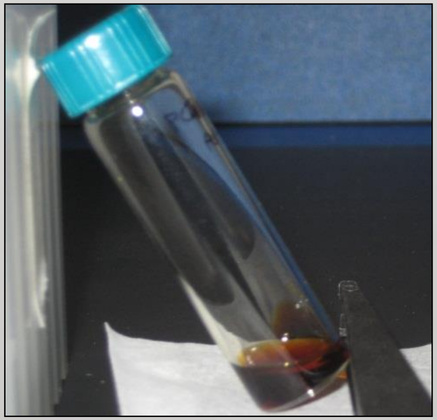
Desirable Aspects of Mesoporosity:

•More rapid hydrogen transport than with dense Pd particles

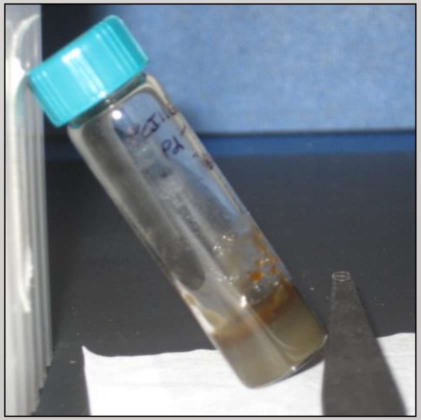
•High surface area for electrochemical applications

•Greater tolerance to volume change

Pd-salt solution (liquid)

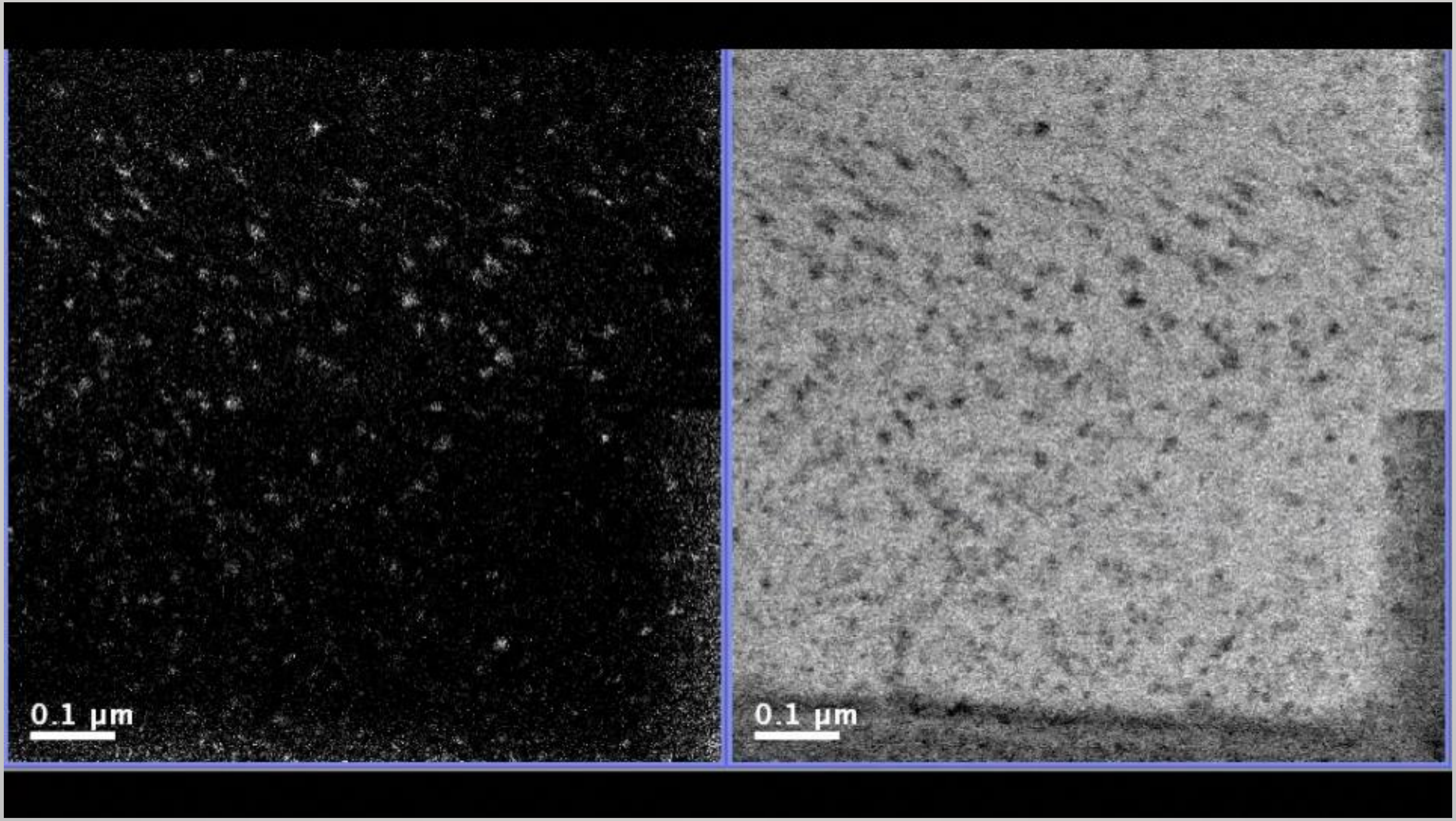


Pd-salt/micelle template (waxy)



L.R. Parent et al. *ACS Nano* ***2012***.

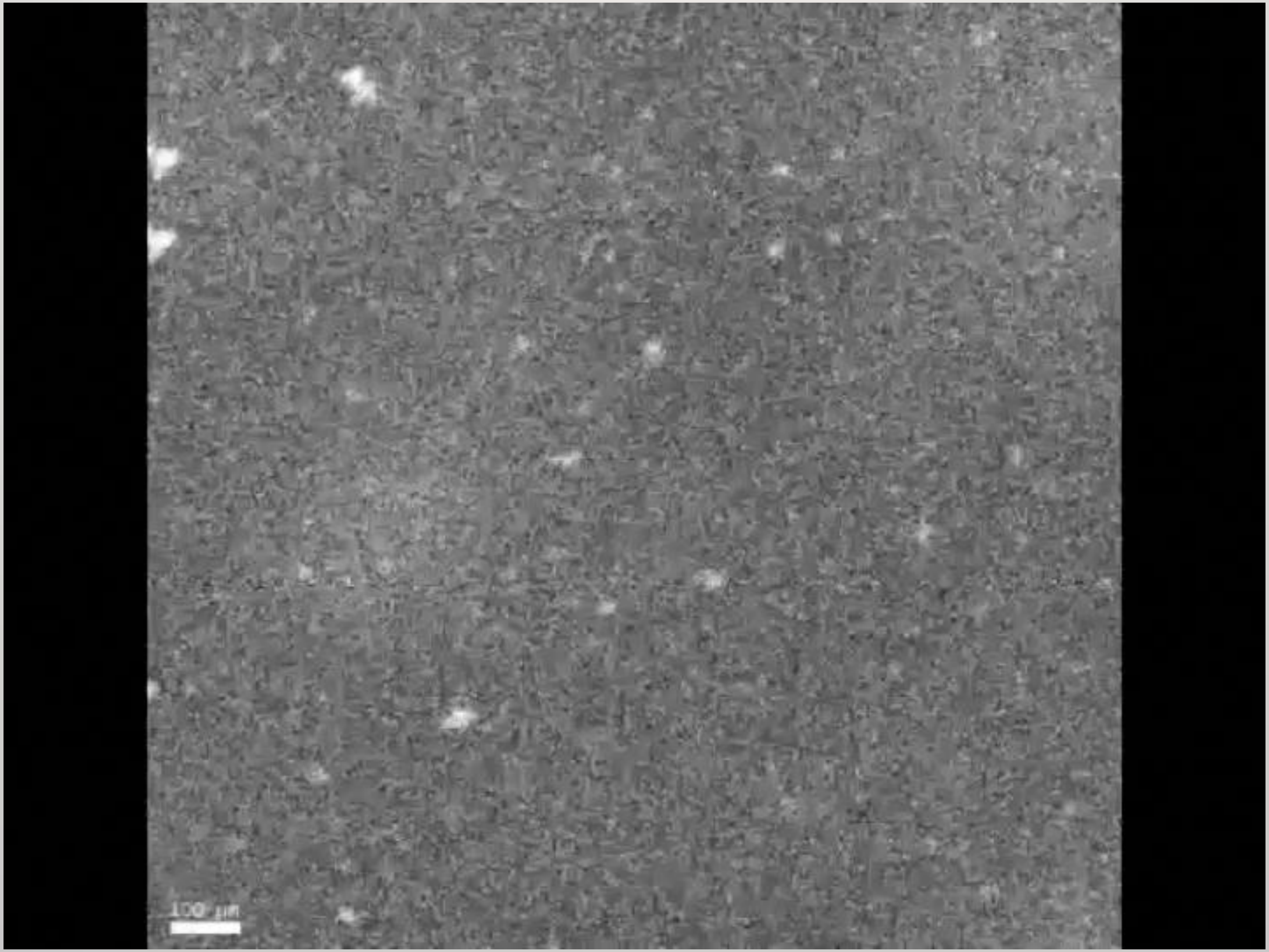
Pd-salt Electron-Beam Induced Growth



- x200k magnification
- First 8 sec at x4 speed, last 6 sec at x8 speed (~80 sec real time)

L.R. Parent et al. *ACS Nano* ***2012***.

Pd-salt/Template E-Beam Induced Growth

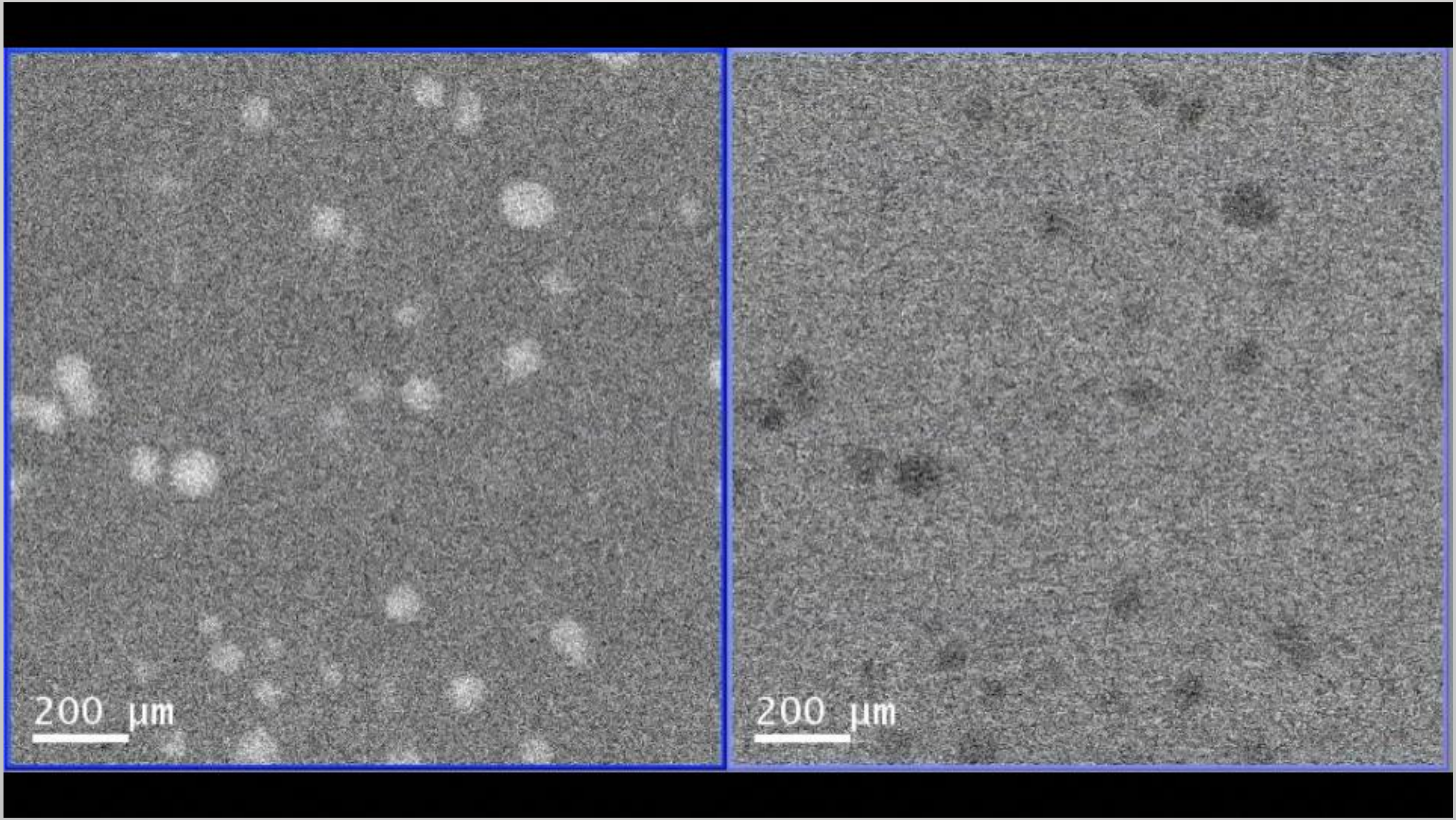


- x400k to x800k magnification
- First 7 sec at x24 speed, last 15 sec at x48 speed (~15 min real time)

L.R. Parent et al. *ACS Nano* ***2012***.

Partial Chemical Reduction

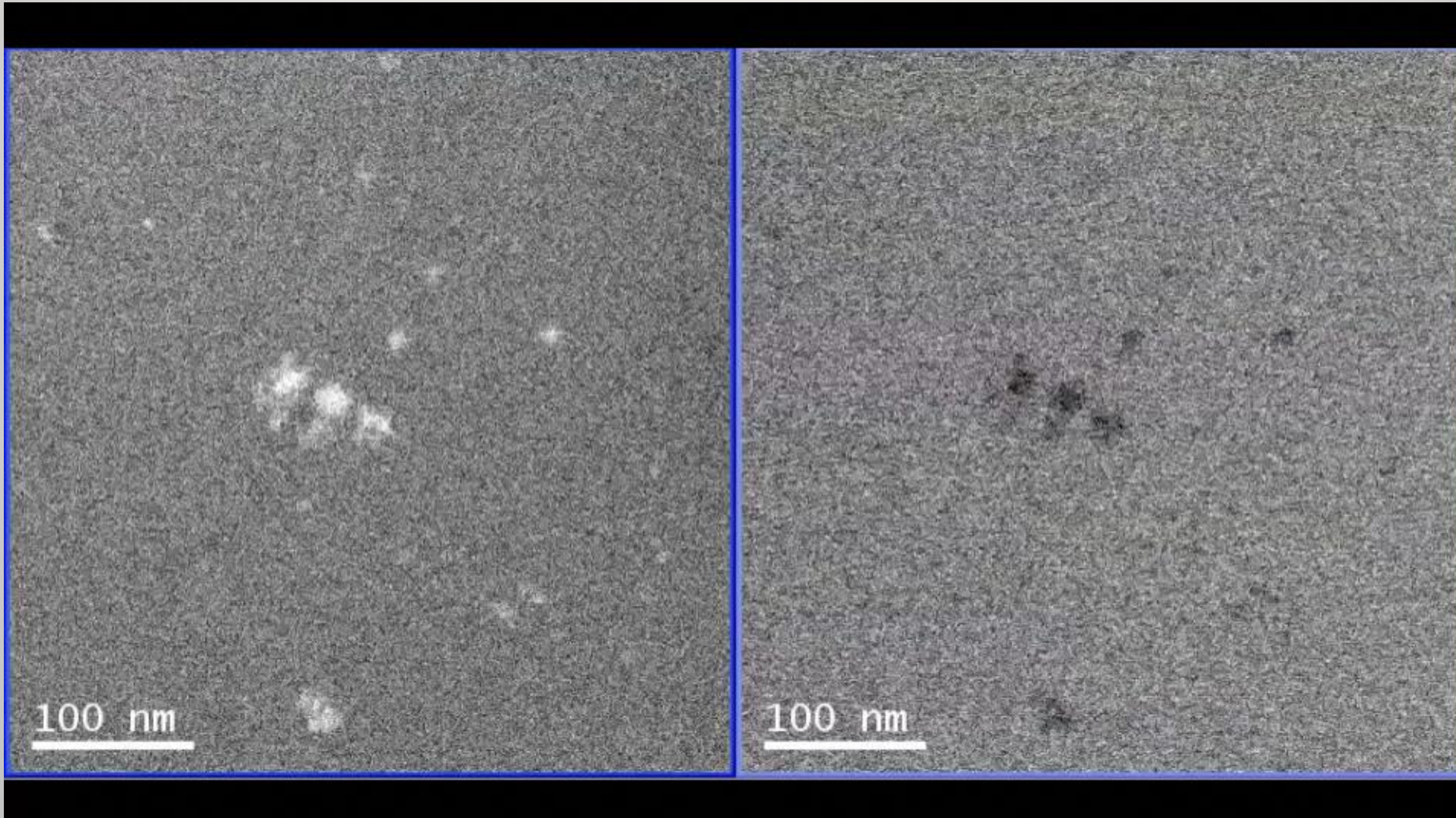
Pd/surfactant paste is mixed with ascorbate (2:1) 2 hrs prior to STEM imaging



- x1.5M to x5M magnification, x8 speed (~2 min real time)

L.R. Parent et al. *ACS Nano* ***2012***.

Partial Chemical Reduction: Later Stages of Growth

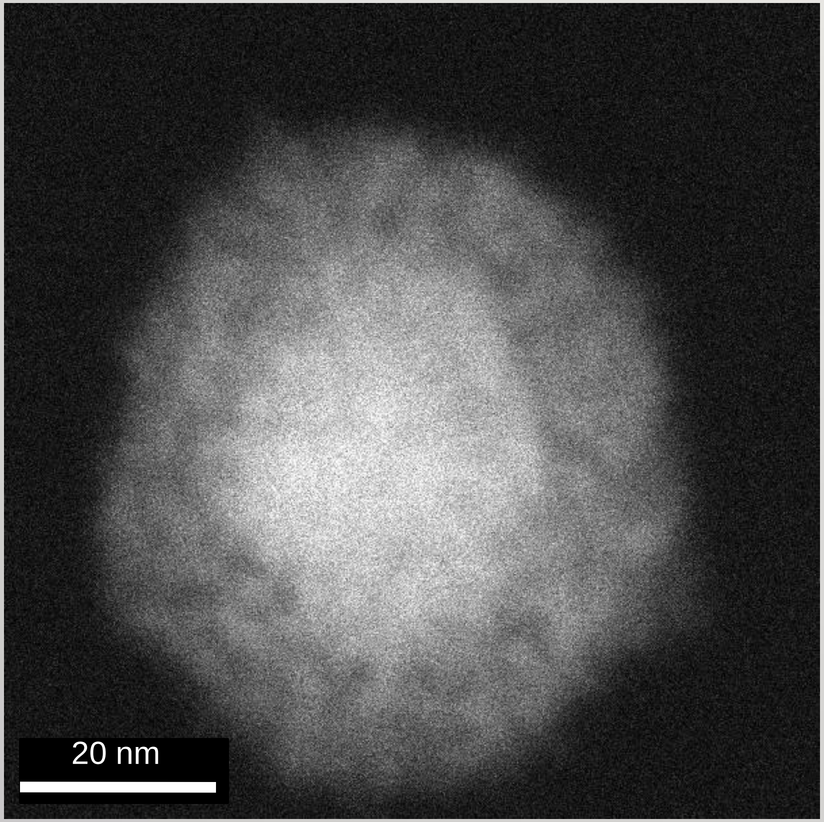


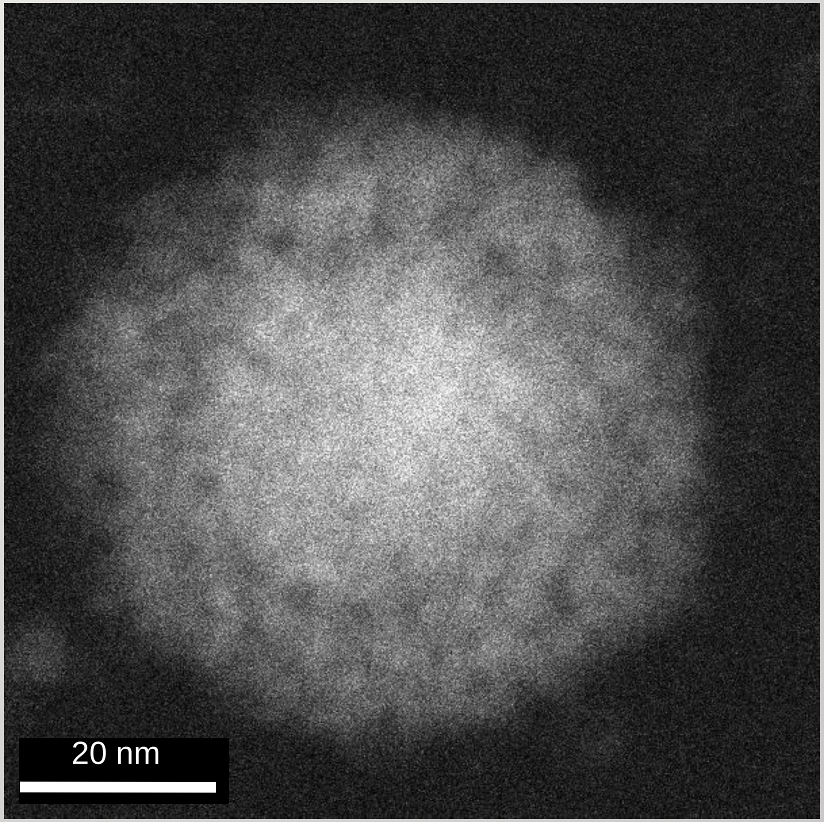
- x1M to x1.2M to x2M magnification
- x32 speed (~7.5 min in real time)

L.R. Parent et al. *ACS Nano* **2012**.

Complete Chemical Reduction in Liquid Stage

Formed with ascorbate *in situ* produces same morphology as *ex situ* growth



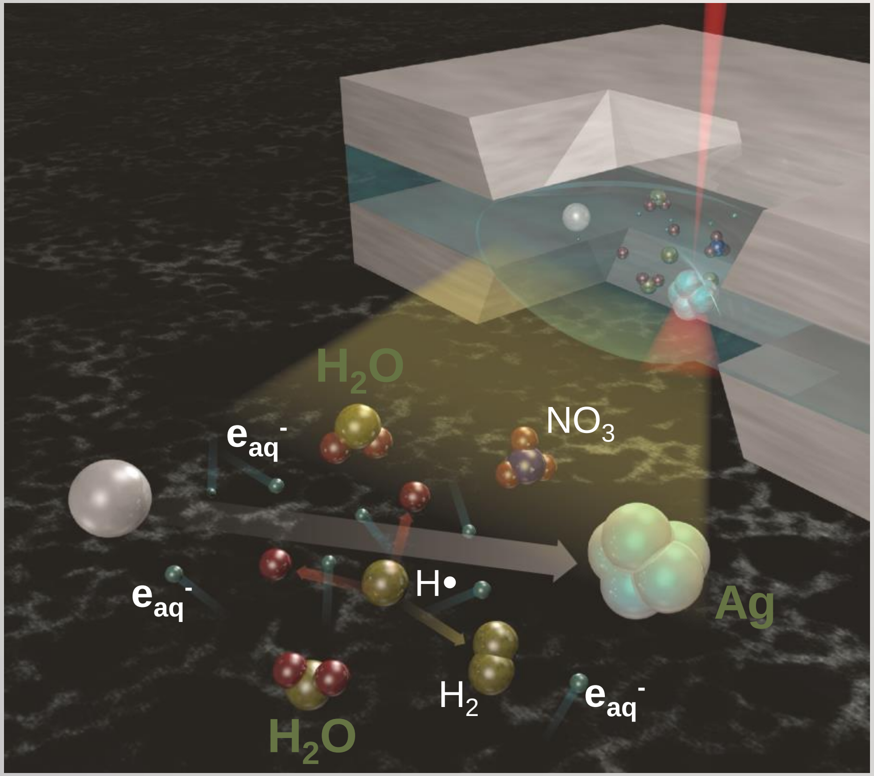


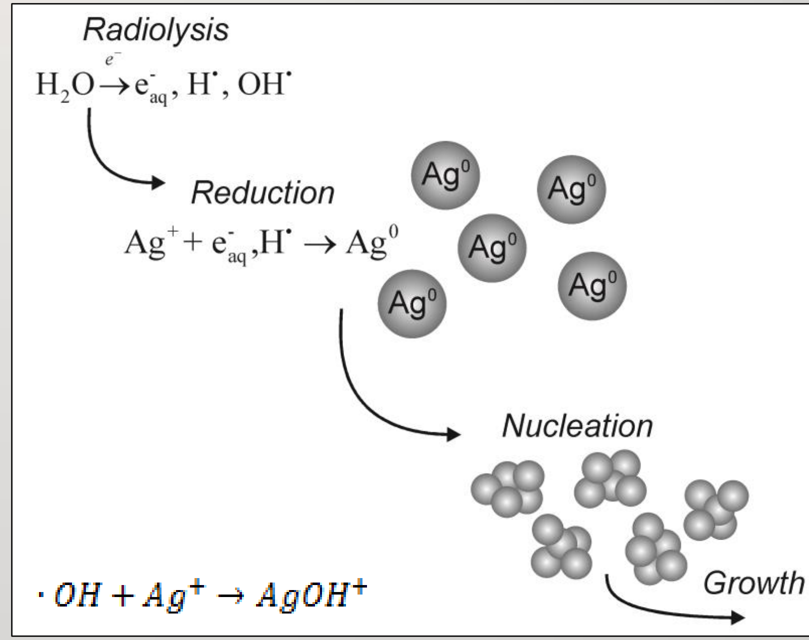
Porous, highly spherical nanoparticles are formed by complete ascorbate reduction

L.R. Parent et al. *ACS Nano* ***2012***.

Generation of Reactive Species by the e⁻ Beam

Radiolysis of water and Ag reduction from $AgNO_3$





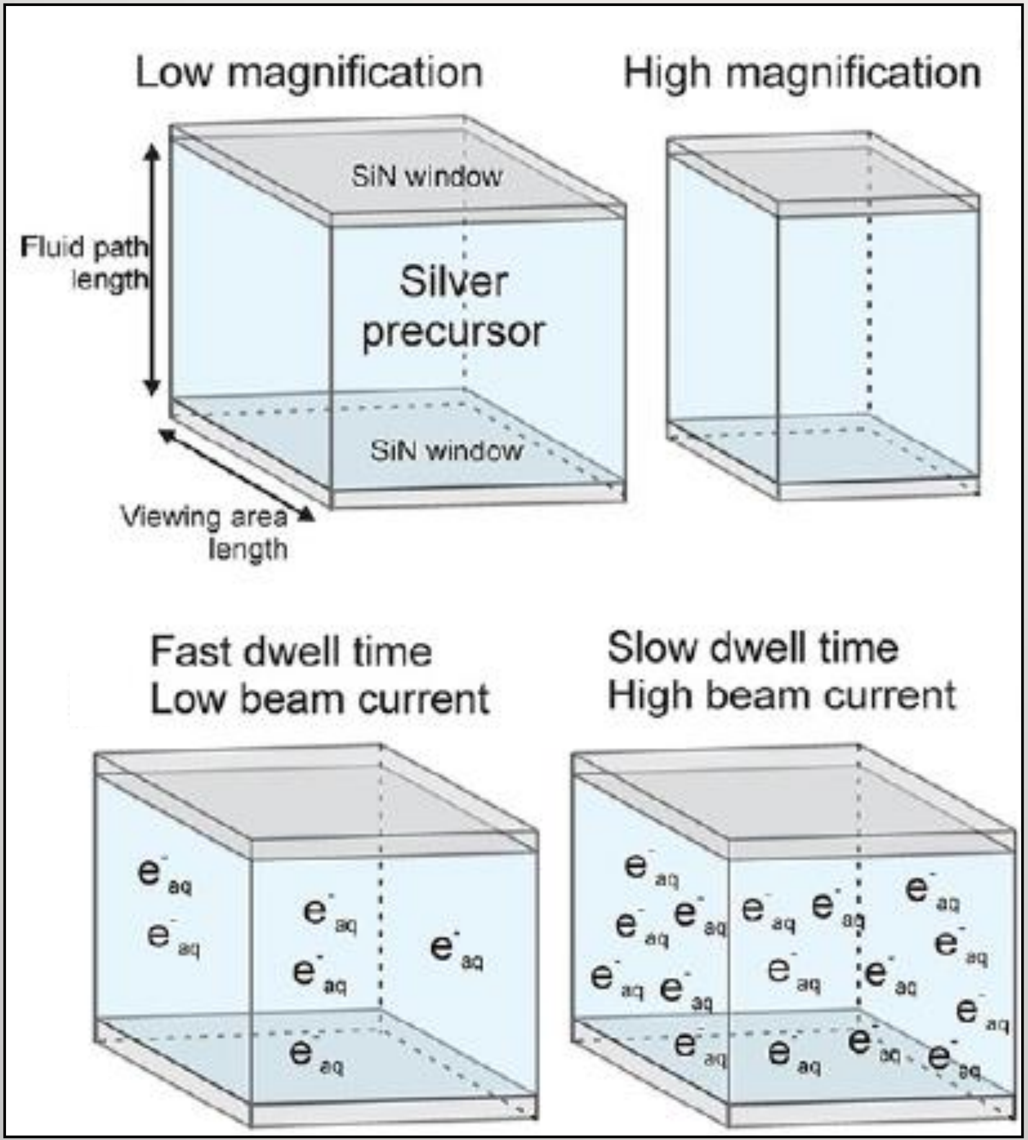
Woehl *et al. ACS Nano* **2012**.
Abellan et al. *ChemComm.* **2014**.

Amount of products formed depends on the electron dose

$$H_2O \rightsquigarrow 0.28\ e_{aq}^-, 0.062\ H^\bullet, 0.28\ {}^\bullet OH, 0.047\ H_2, 0.073\ H_2O_2, 0.28\ \mu mol\ J^{-1}$$

Buxton, *VCH Weinheim* **1987**.

Use Scanning TEM to Control Dose



Woehl et al. *ACS Nano* **2012.**

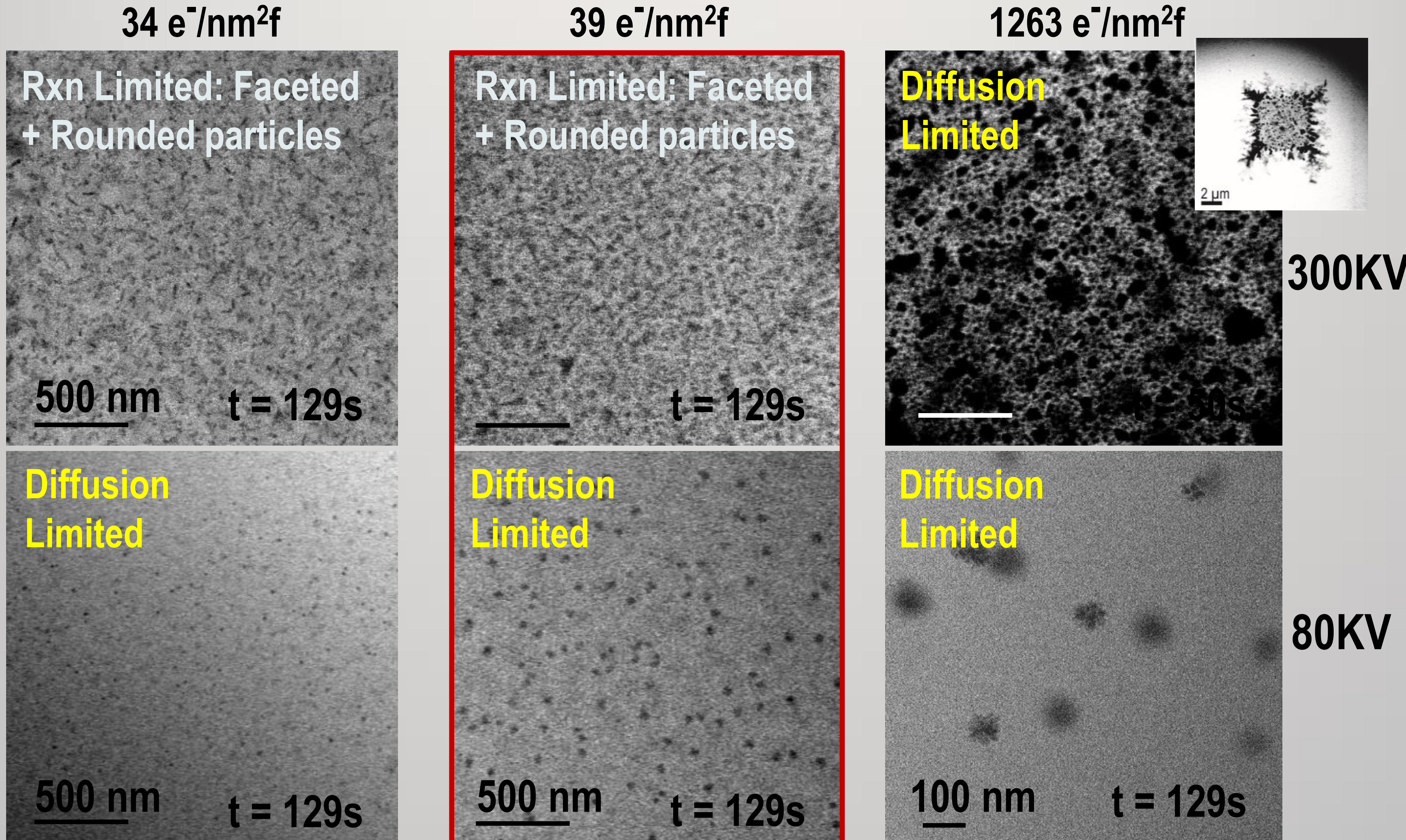
- Electron beam current
- Pixel dwell time
- Magnification

Limited electron exposure can produce not enough reducing agent for observable nucleation and growth

* At 200 kV ~ 10 $e^-/\text{Å}^2$

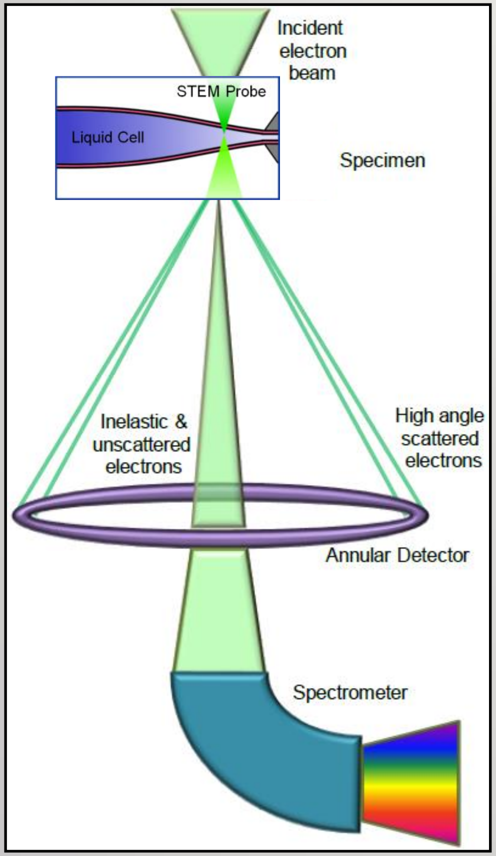
Requires quantification of imaging conditions, accelerating voltage, electron dose, and liquid thickness

Effect of Beam Energy



Abellan et al. *CISCEM* **2014**.

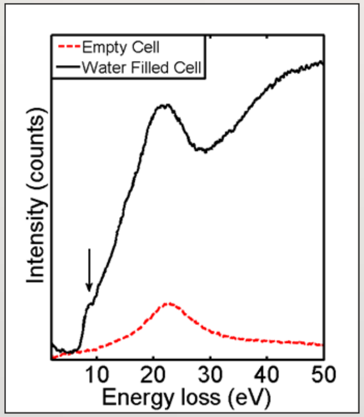
Cell Water Thickness Effect on Growth



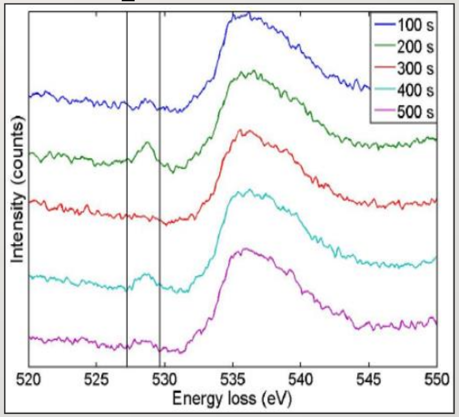
t/λ_i values : measured using EELS
t : thickness of material (nm)
λ_i : inelastic mean free path of e^- through the material

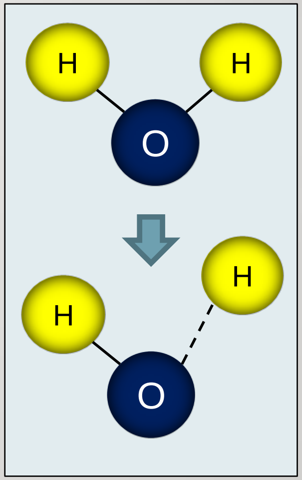
Malis et al. *J. of Elec. Micro. Tech.* **1988**.

Low Energy Loss

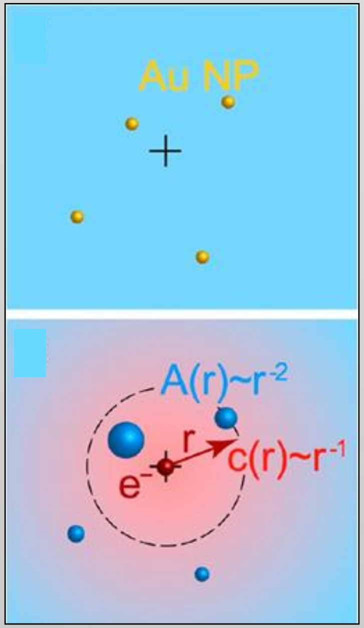


H_2O: O k-edge

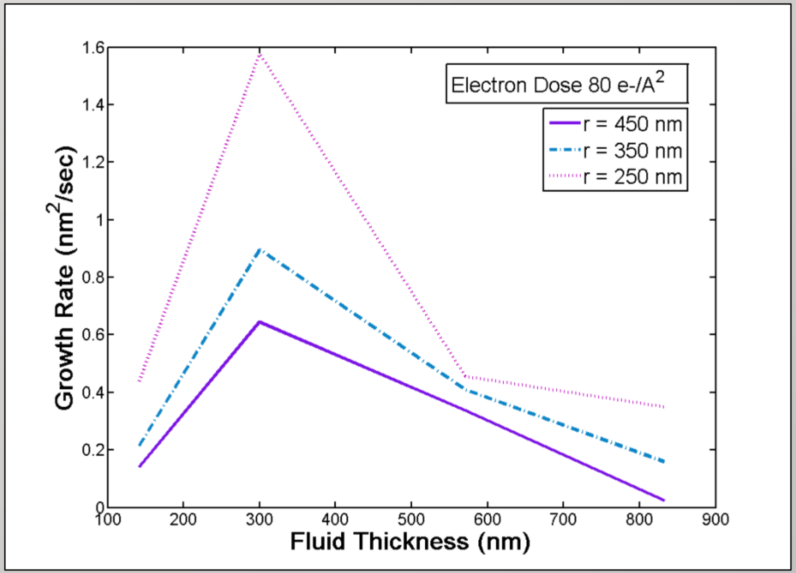




Jungjohann et al. *Micro. Microanal.* **2012**.

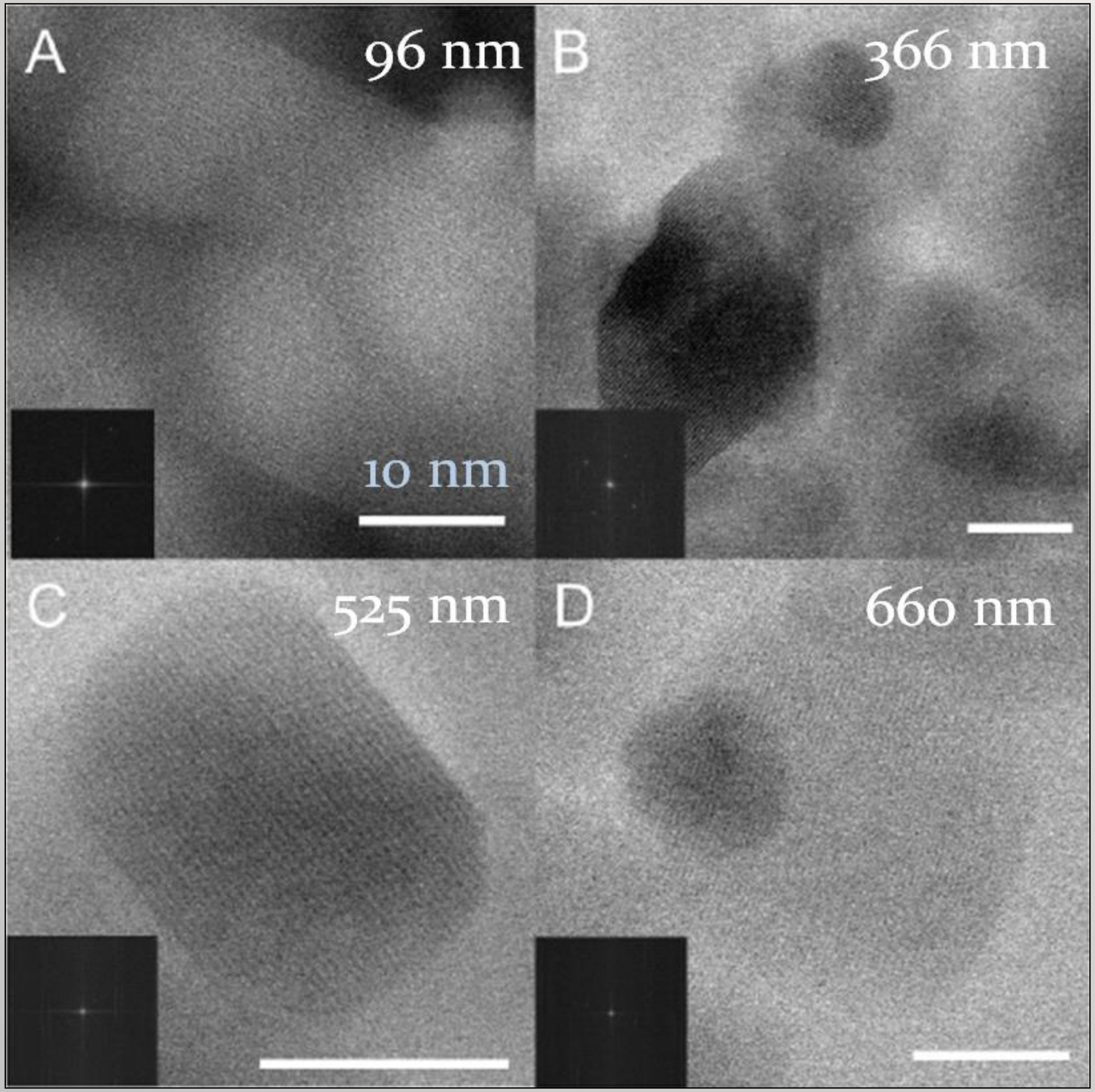


Effect of Cell Thickness on NP Growth



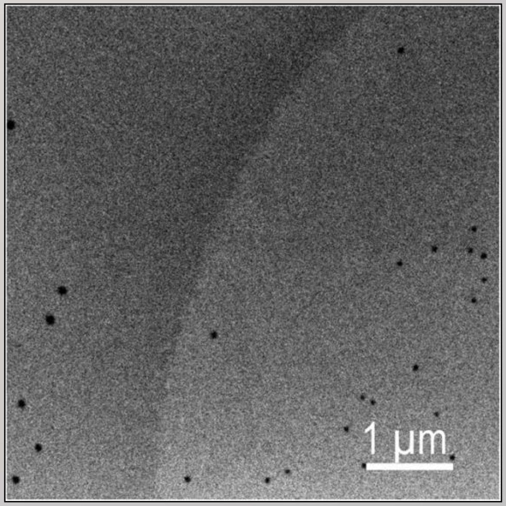
Jungjohann et al. *Nano Lett.* **2013**.

Resolution and Limitations



<u>TiO_2 nanoparticles in water</u>

- 30 nm SiN membrane windows
- Water thickness increased
    - 96 nm
    - 366 nm
    - 525 nm
    - 660 nm
- Contrast from fringes decreases with increased background scattering from water

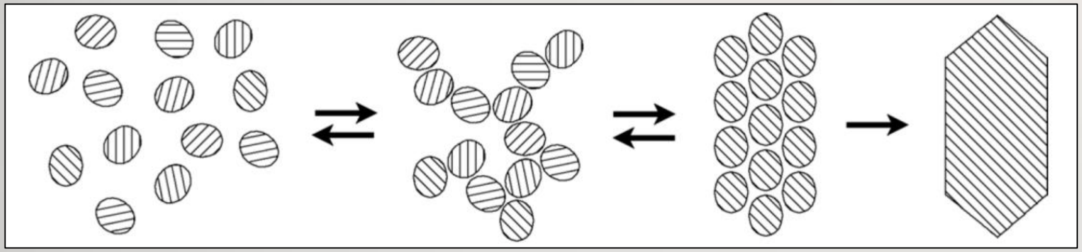


E-beam radiolysis damage produces hydrogen gas bubbles

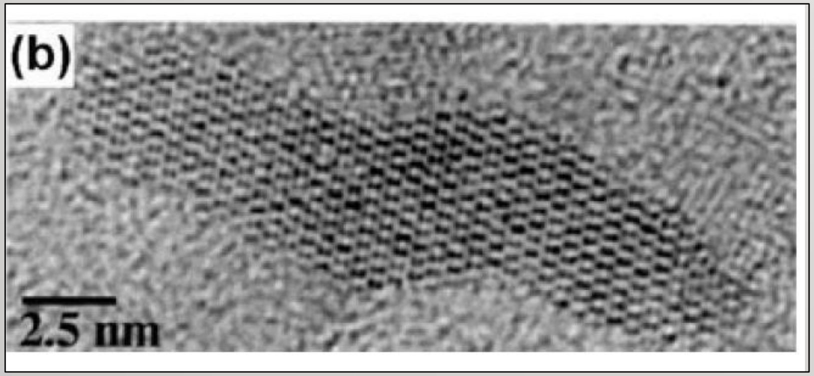
Abellan et al. *ChemComm* **2014**.

Non-classical 'Particle-mediated' Growth

Oriented attachment



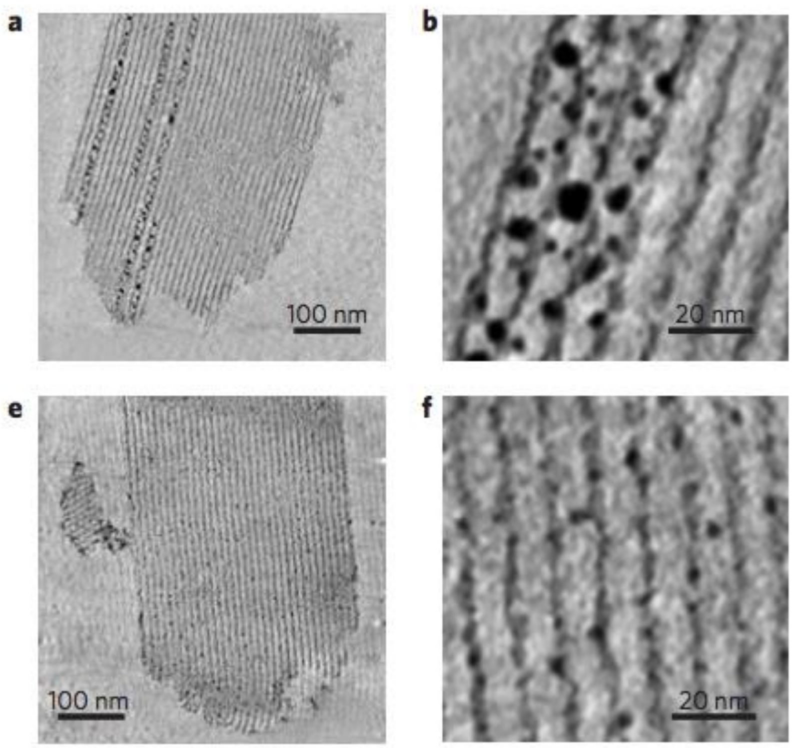
Penn and Soltis, *Crysengcomm* **2014**.



Banfield and Penn, *Geochim cosmochim*. *Acta* **1999**.

Coalescence and growth

Catalysis nanoparticle degradation

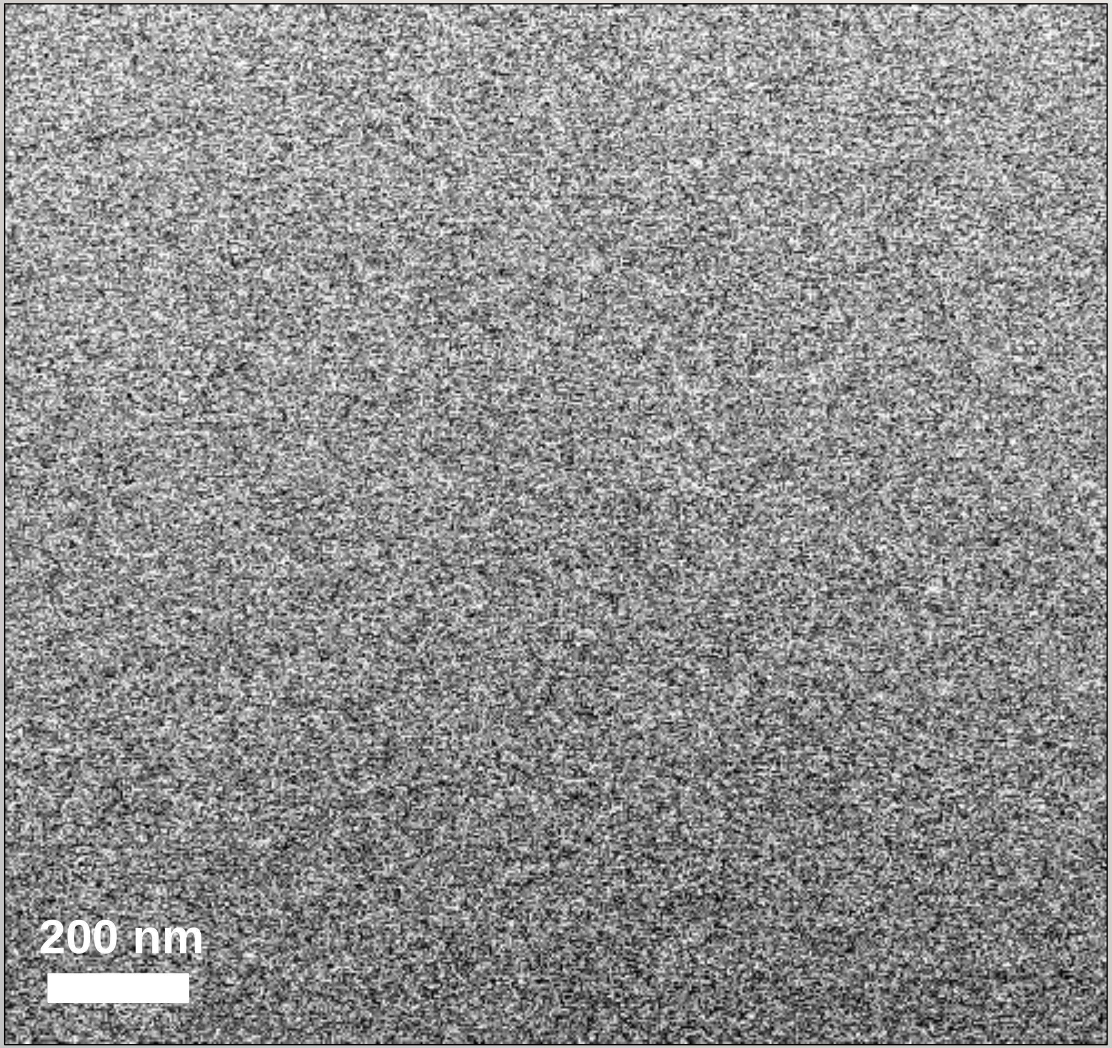


Prieto et al. *Nature Materials* **2013**.

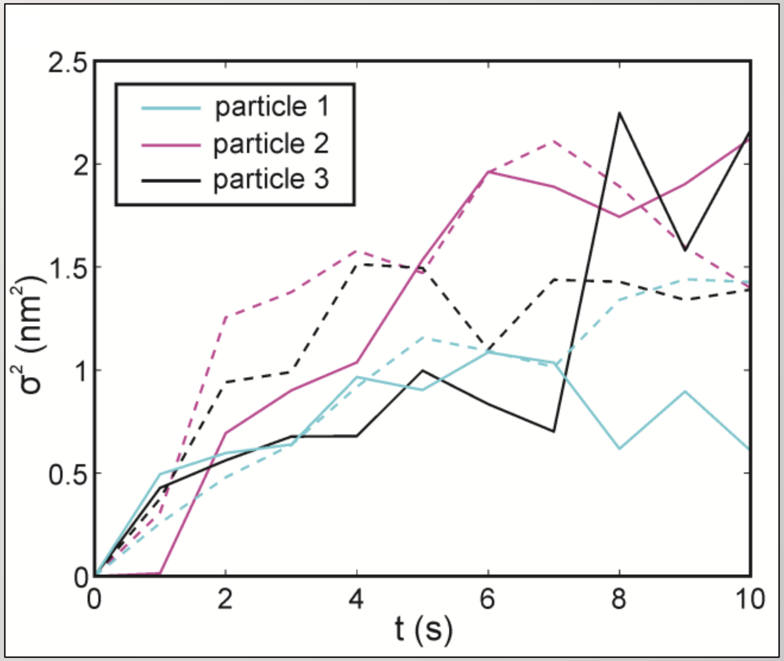
Non-classical nanoparticle growth mechanisms control growth of many natural and synthetic nanomaterials

Ensemble-Scale Growth of Ag Nanoparticles

$$Ag^{+} + e^{-}_{aq}, H^{\bullet} \rightarrow Ag^{0}$$



Tracking Individual NP Mobility



<u>Diffusion coefficient</u>

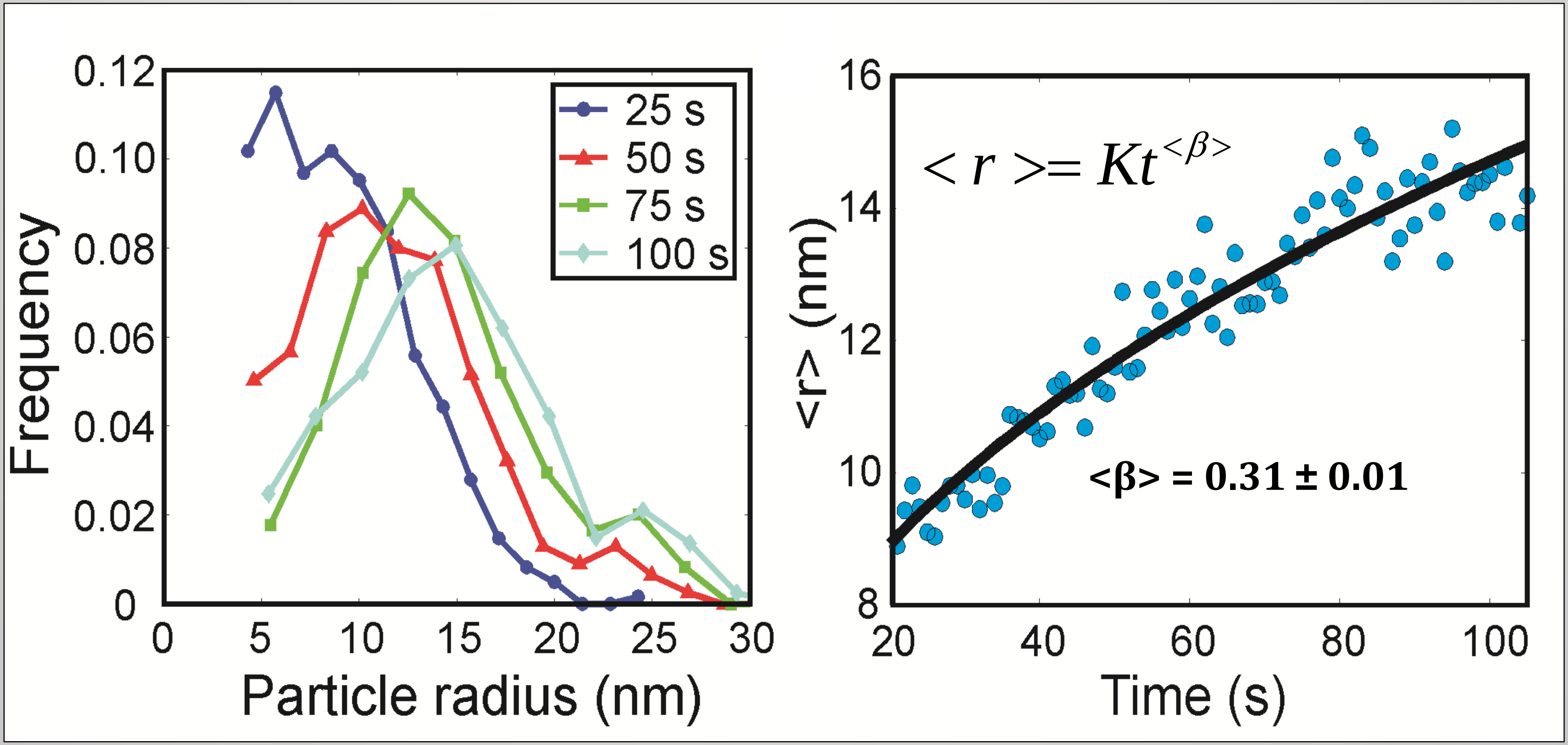
$$D_{exp} = \sigma^2/2t \approx 10^{-19}\ m^2/s$$

<u>Stokes-Einstein prediction</u>

$$D_{th} = k_b T/6\pi\mu a \approx 10^{-11}\ m^2/s$$

Woehl et al. *Nano Letters* **2014**.

Ensemble-Scale Growth Rate and PSD



Lifshitz-Slyozov-Wagner (LSW) Model for Ostwald Ripening

$\langle\beta_{LSW}\rangle = 1/3$

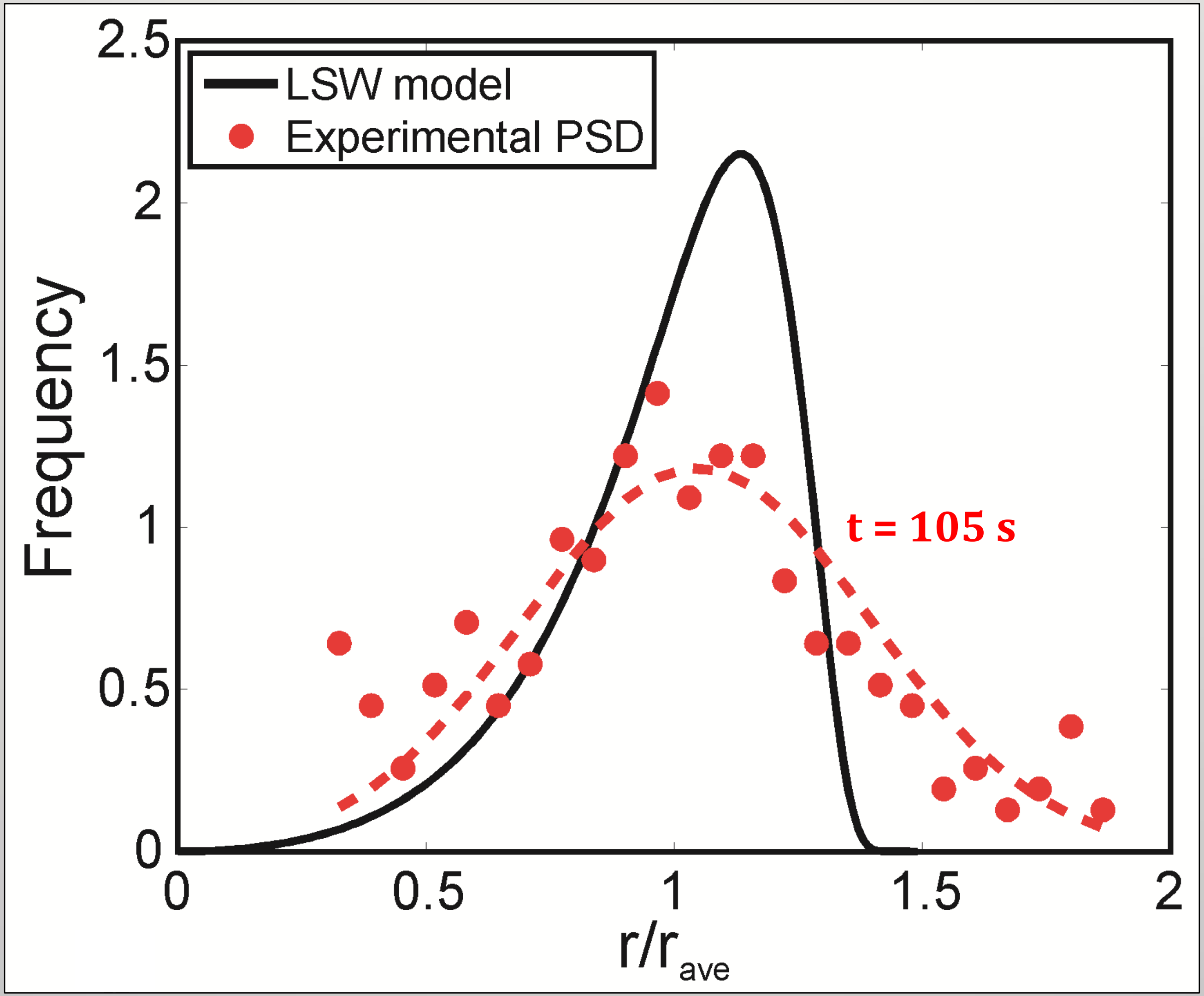
How does the PSD compare to the LSW model?

Lifshitz and Slyozov, *J Phys. Chem. Sol*. **1961**.

Woehl et al. *Nano Letters* **2014**.

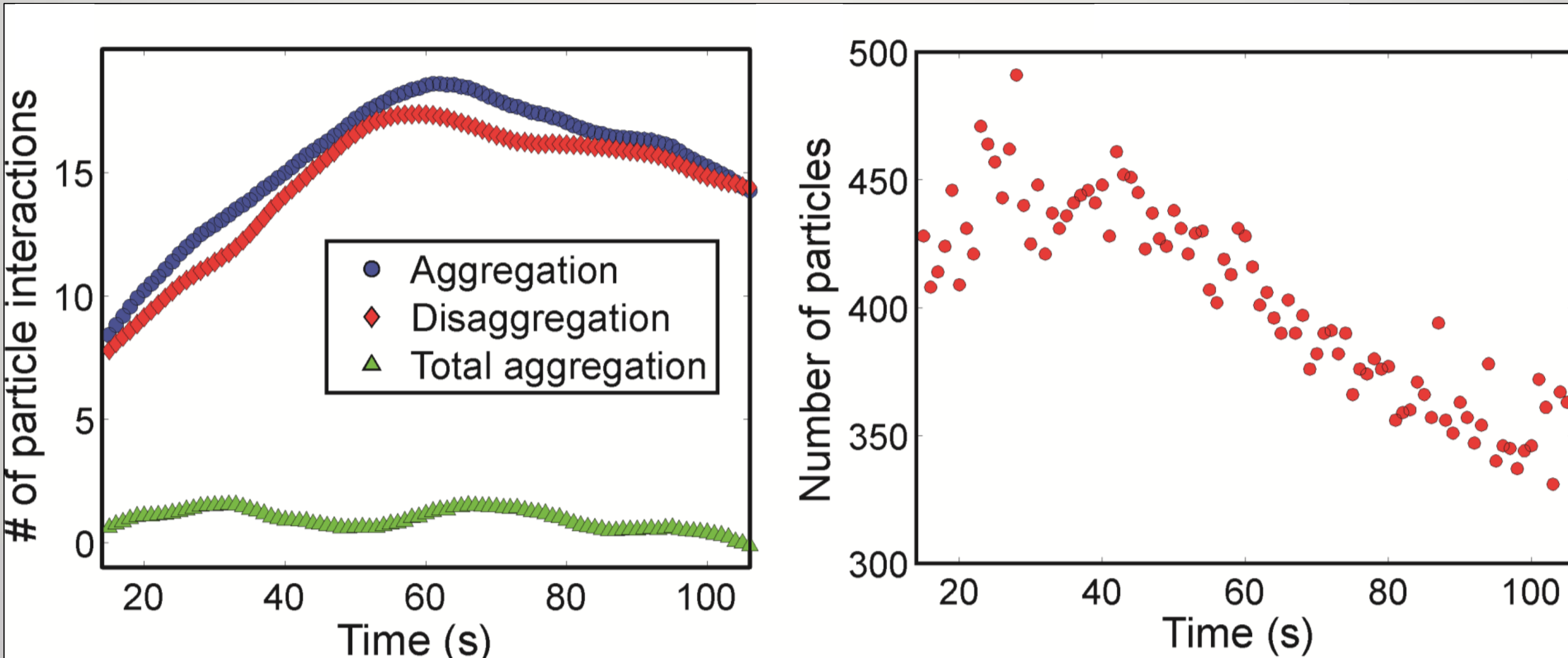
Experimental PSD Deviates from the LSW Model

Long time asymptotic LSW PSD



Woehl et al. *Nano Letters* **2014.**

Nanoparticle Aggregation Kinetics



30% decrease in number of particles due to aggregation

Woehl et al. *Nano Letters* **2014.**

Proposed growth mechanism

Hypothesis: Nanoparticle growth occurs by monomer attachment *and* ensemble-scale aggregation

Woehl et al. *Nano Letters* **2014**.

Smoluchowski Coagulation Kinetics

$$\frac{d}{dt}n_s(t) = \frac{1}{2}\sum_{s'} K\left(s', s - s'\right) n_{s'}(t) n_{s-s'}(t) - n_s(t)\sum_{s'} K(s,s') n_{s'}(t)$$

$n_{s,}$ concentration of clusters of size s

Increase in n_s due to collision of clusters of s' and s-s'

Decrease in n_s due to collision of clusters of s and s'

von Smoluchowski, M. *Physikalische Zeitschrift*, 1916

Smoluchowski kinetics yield a closed form PSD and power law growth

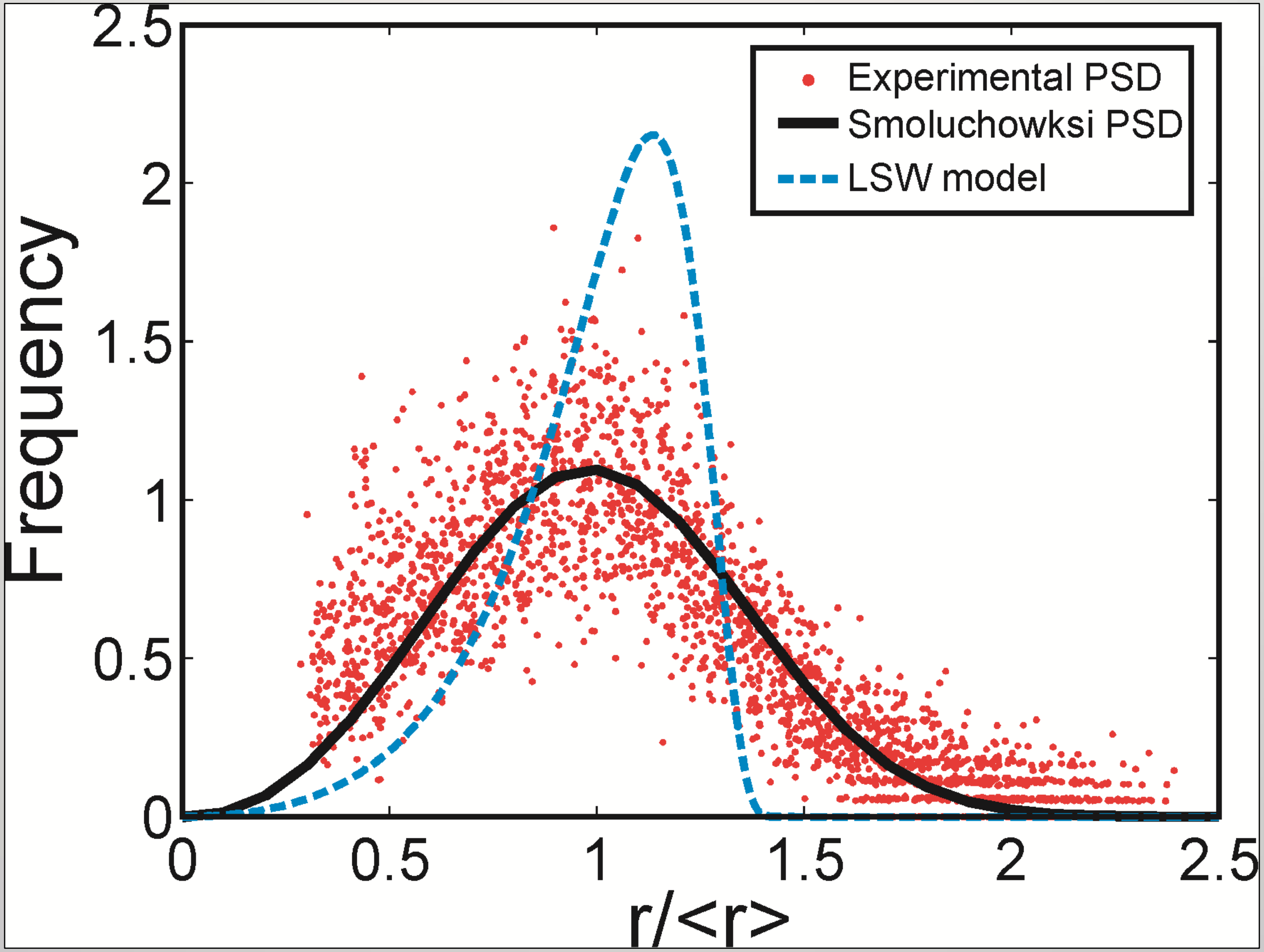
Power-law growth

$$\langle r \rangle \sim t^{\alpha}$$

Sholl and Skodje, *Physica A* **1996.**

Woehl et al. *Nano Letters* **2014.**

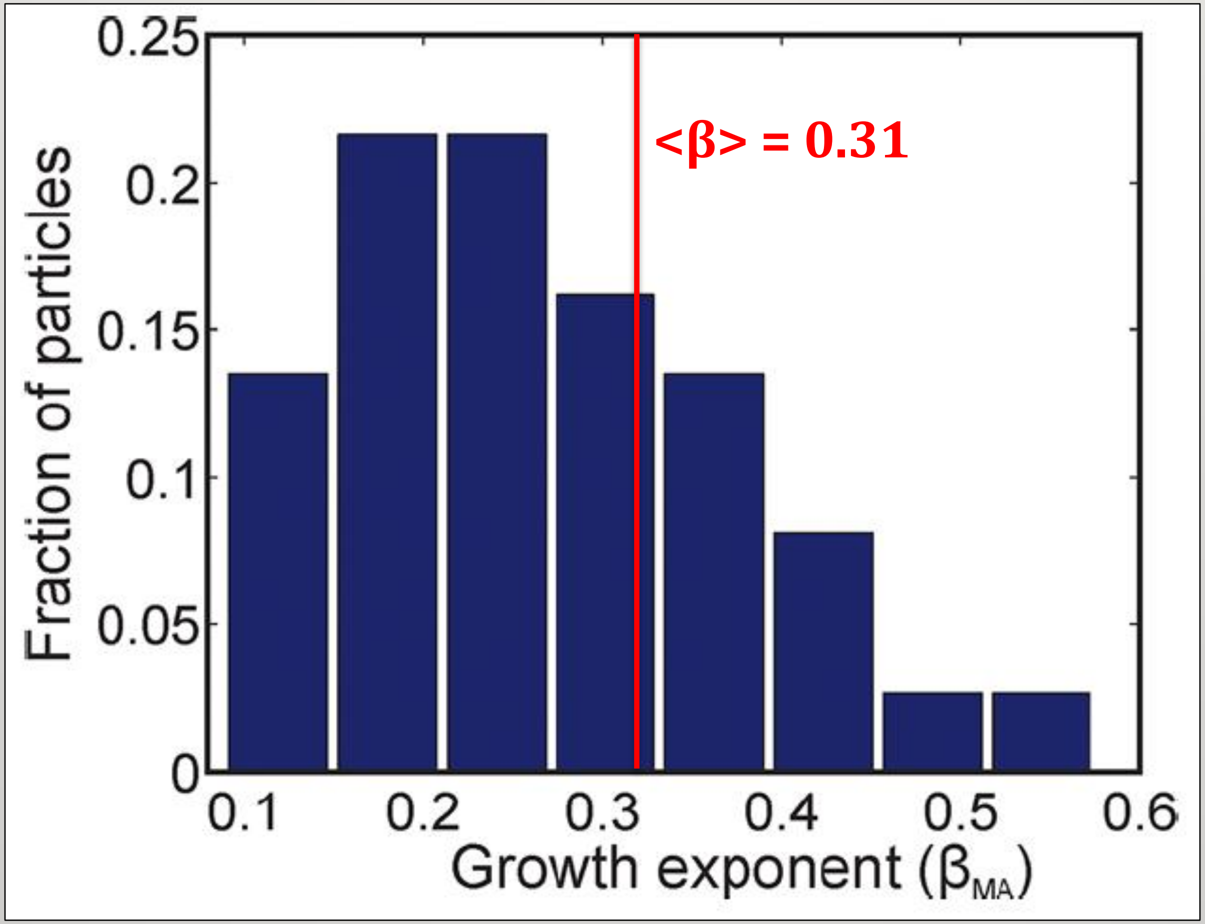
Smoluchowski PSD Quantitatively Fits Experimental PSD



***no fitting parameters, used the experimentally determined power law <β> = 0.31**

Woehl et al. *Nano Letters* **2014**.

Ensemble Growth Rate Exceeds Monomer Attachment Rates



Individual particle
Growth rates

$$r = Kt^{\beta_{MA}}$$

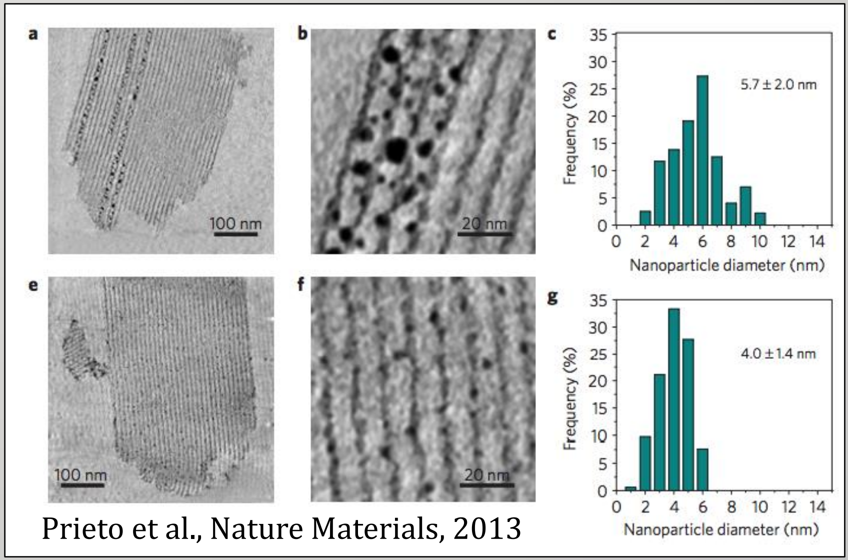
Aggregation expedites nanoparticle growth on the ensemble scale
(relative to growth by monomer attachment)

Woehl et al. *Nano Letters* **2014**.

Ag Growth Model Conclusions

- <β> was consistent with LSW model for Ostwald ripening, but not the PSD
- Numerous aggregation events caused the number of nanoparticles to decrease by 30 % over the growth time
- Smoluchowski coagulation kinetics quantitatively described the mean growth exponent and the experimental PSD

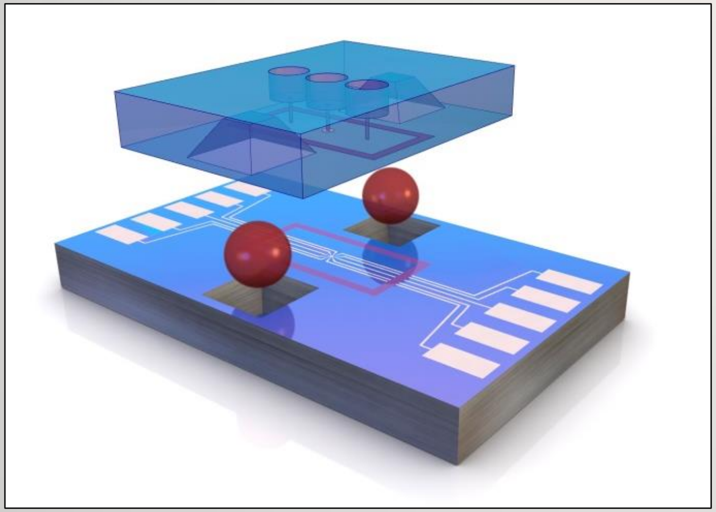
<u>Future application:</u>
Understanding nanoparticle catalysis degradation



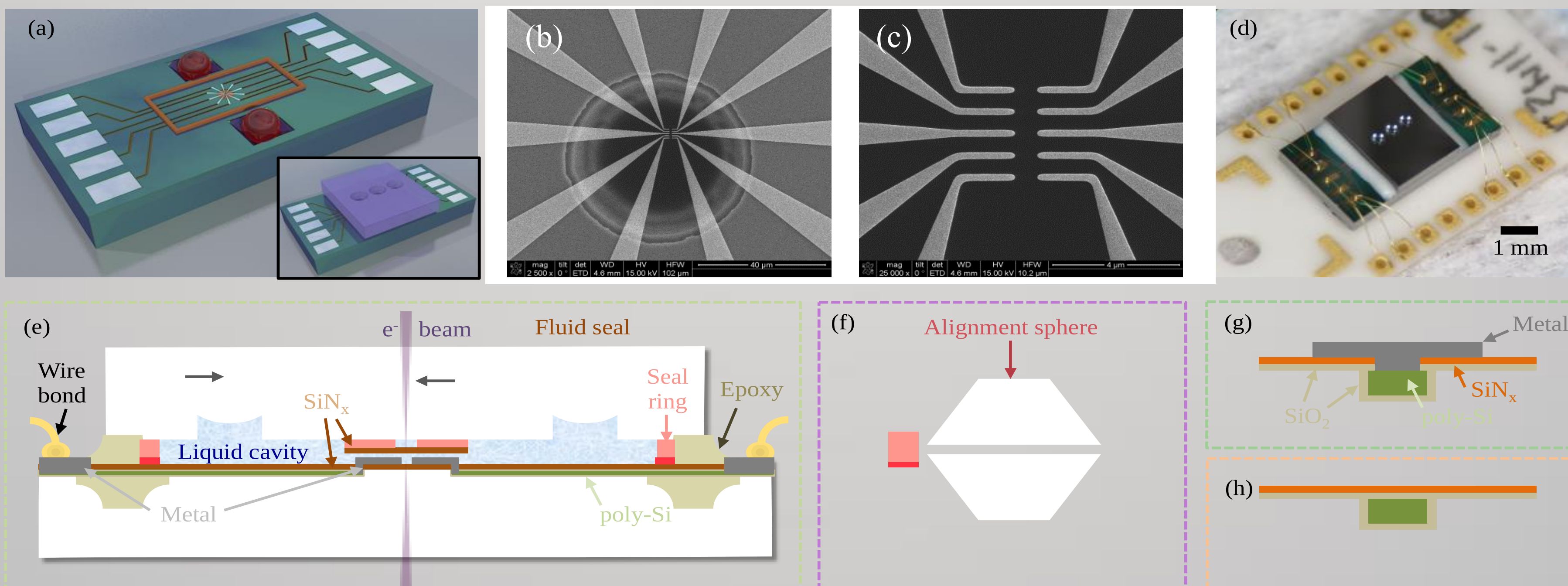
Prieto et al., Nature Materials, 2013

Woehl et al. *Nano Letters* **2014.**

CINT Electrochemical Discovery Platform

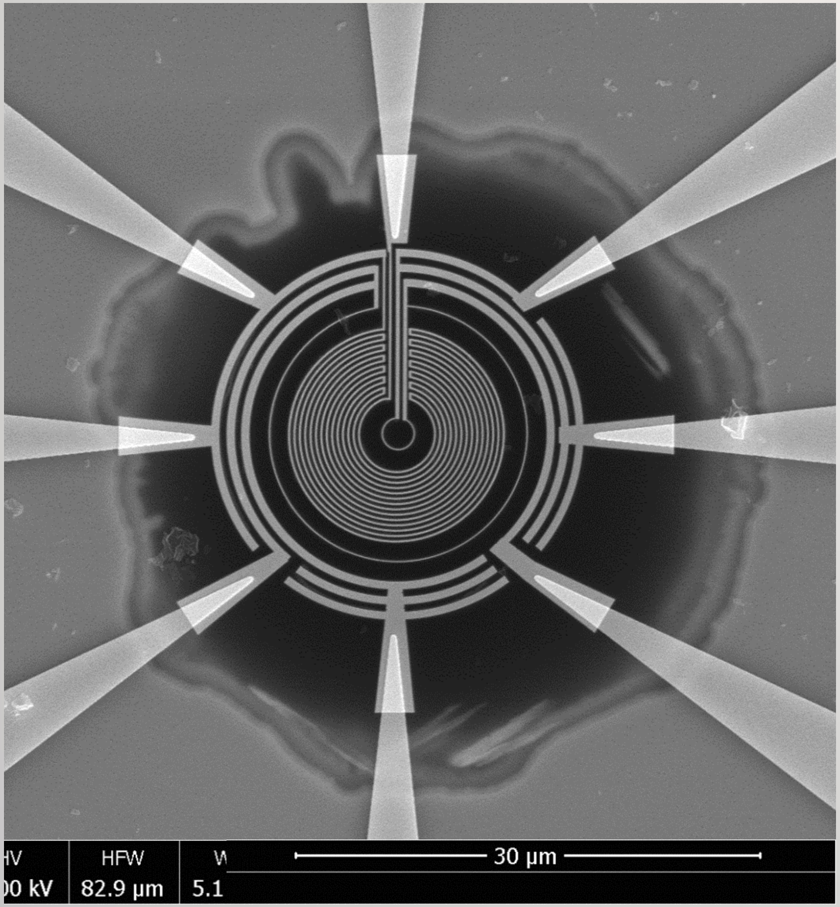


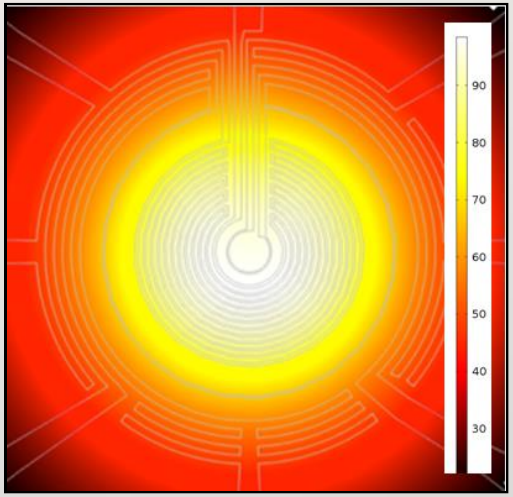
- 10 Custom Designed Electrodes
- Beads Simplify Window Alignment
- Liquid Thickness > 120 nm
- Passivated Leads to localize electrochemistry
- Picoampere Current Control
- Chemical compatibility with cell
- Conduct *in situ* & *ex situ* testing

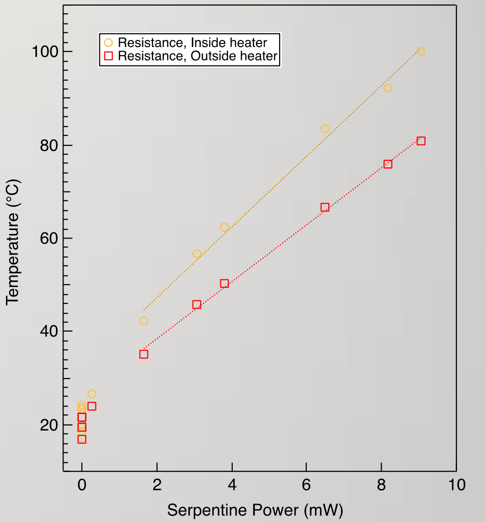


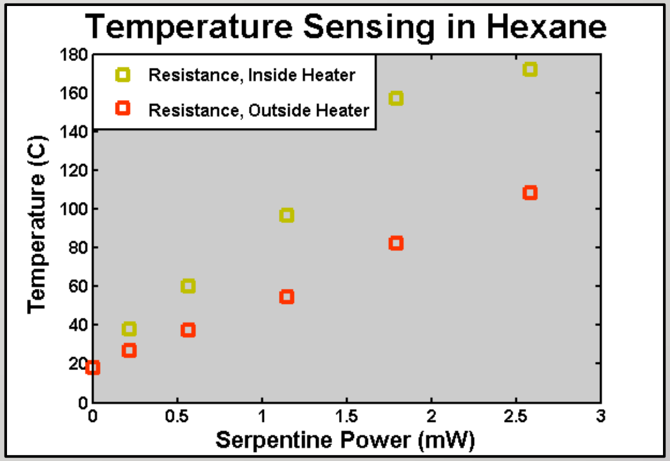
Leenheer et al. *JMEMS* **2015**.

Temperature Control up to 200˚C









445 K

Liquid thickness plays a larger role in heating calibration than the liquid thermal conductivity, therefore measurement of the temperature changes on column is preferable

Towards Visualizing Water-Phase Energy Production

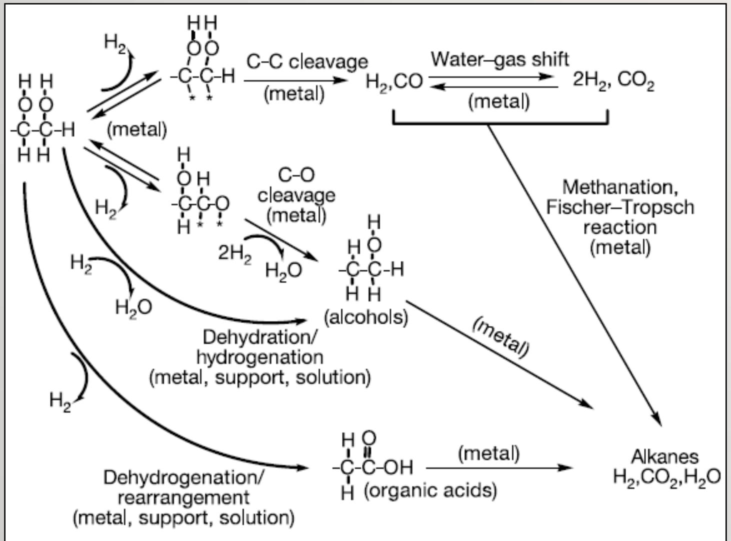


Figure 1 Reaction pathways for production of H_2 by reactions of oxygenated hydrocarbons with water. (Asterisk represents a surface metal site.)

Cortright et al. *Nature* **2002**.

How can we view this chemical conversion process within a reactor (environmental control) to investigate catalyst performance with sub-nanometer resolution?

H_2 Production Requirements	In-situ TEM Capability
Temperature: 500 K	Temperature: 290 – 445 K
Pressure: 10 atm	Pressure: <1 atm (0.001 atm)
Nanoscale catalyst	Nanoscale catalyst
Gas inlet	Redesign for gas and liquid inlet
RGA	RGA

Acknowledgements

PNNL: Nigel Browning, James Evans

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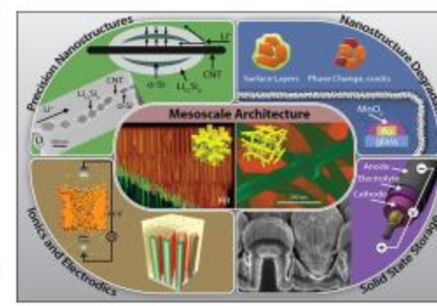
Florida State U: Chiwoo Park

Sandia: David Robinson, Andrew Leenheer, John Sullivan, Mike Shaw, and Tom Harris

Nanostructures for Electrical Energy Storage
A DOE Energy Frontier Research Center

NEES major research areas

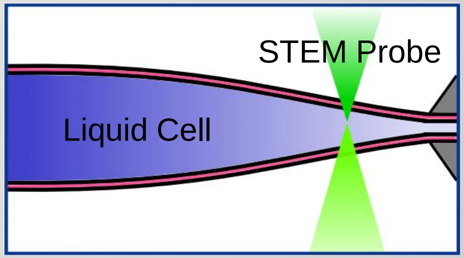
- Nanostructure Interface Science
- Mesoscale Architectures & Ionics
- Nanostructure Degradation Science
- Solid State Energy Storage



This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science.

Outline

- What is in-situ liquid EM imaging?
  - Instrumentation, resolution, limitations
  - Calibration of electron dose



- Why is this characterization technique useful for catalysis?
  - Nanoparticle catalyst synthesis in solution
  - Dynamic observations in solution

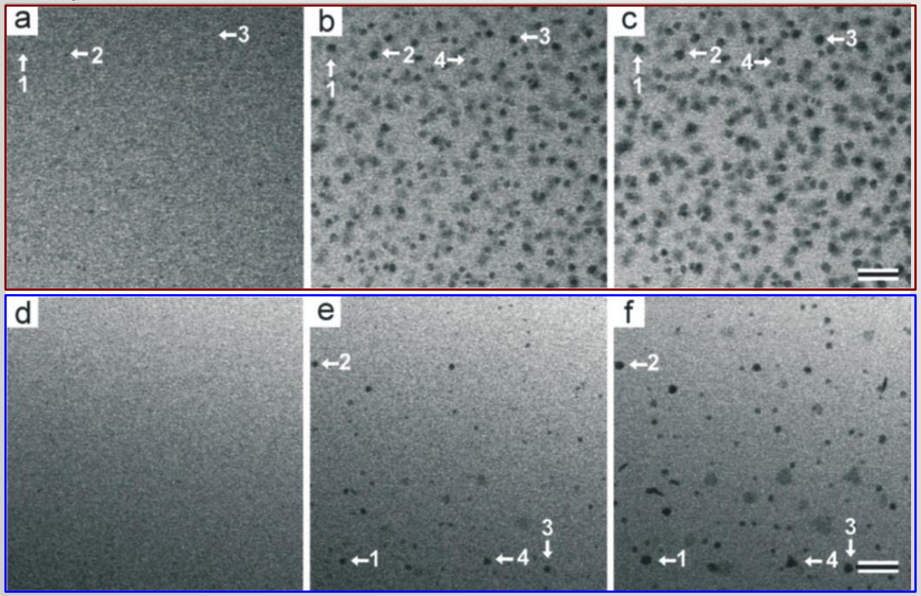
- What is the future for water-phase catalysis characterization?
  - Elevated temperature and pressure in cell
  - In-situ vs. operando

Water-phase Catalysts

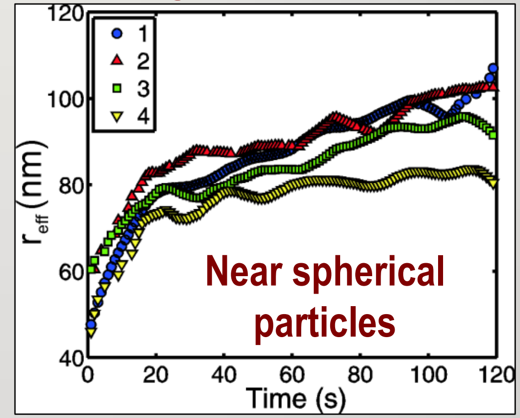
- Oxidation and hydrogenation (treat with H2 in presence of catalyst (Ni, Pd, or Pt) to remove double bonded carbon) processes
- TiO_2 assisted photocatalysts, and red mud as a catalyst
- Higher surface area to improve catalytic activity
- How to improve catalyst activity and durability? Active and stable? Lower temperature than gas phase
- Surface plays an important role in reaction rate, therefor support material is important
- Materials: metal (Ru, Pt, Rh, Ir, and Pd) and metal oxides (Cu, Mn, Co, Cr, V, Ti, Bi, and Zn, zeolite (Na,K, Ca, Sr, and Ba) and silicate materials) good electrical conductivity, high stable oxidation states. Metal oxides are usually less active but more resistant to poisoning
- Characteristics: high activity, resistance to poisiong, stability at prolonged use and temp, mechanical stability and resistance to attrition (reduce strength or effectiveness), non-selectivity, physical and chemical stability
- Support: for metal (activated carbon, TiO_2, alumina, cerium oxide, lead oxide and MgO), role for immobilizing active catalyst. Functions: increase surface area of catalytic material, decrease sintering and improve hydrophobicity and thermal, hydrolytic, and chemical stability of the material, govern the useful lifetime of the catalyst. May act as co-catalyst.
- Problems: rapid deactivation by poisoning, sintering or leaching. Noble metals are sensitive to poisoning by halogens, sulfur, or phosphorous containing compounds.
- Reaction temperatures up to 325C, but many reactions below 200C
- Radicals produced by the electron beam are similar to those produced by a photocatlyst
- Future: Bi-metallic catalysts and high-porosity supports

Using Dose to Control Growth

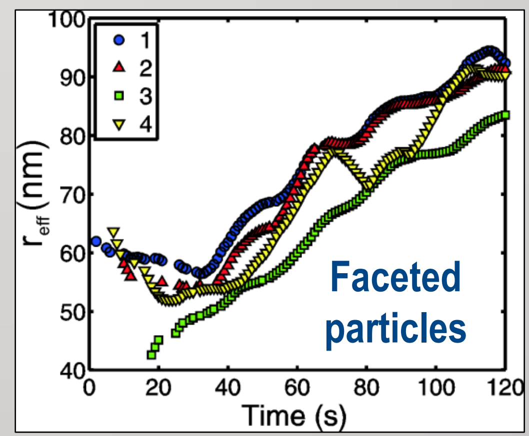
$d_{ind} > \sim 28\ e^-/Å^2$; $0.5\ e^-/(Å^2 s)$

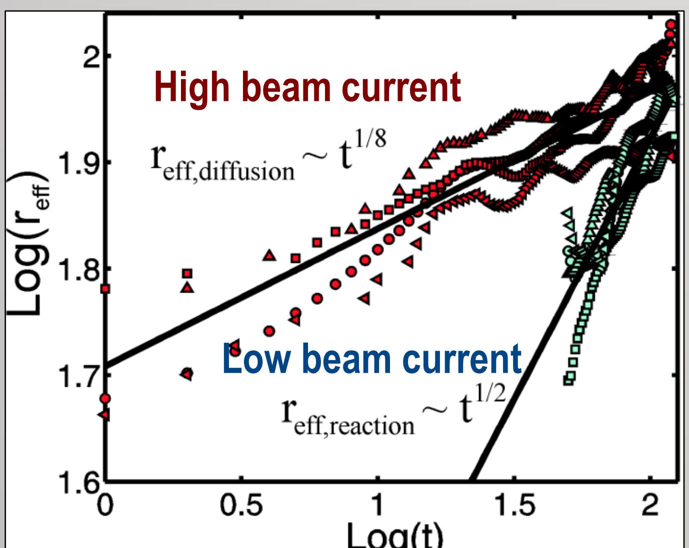


High beam current



Low beam current



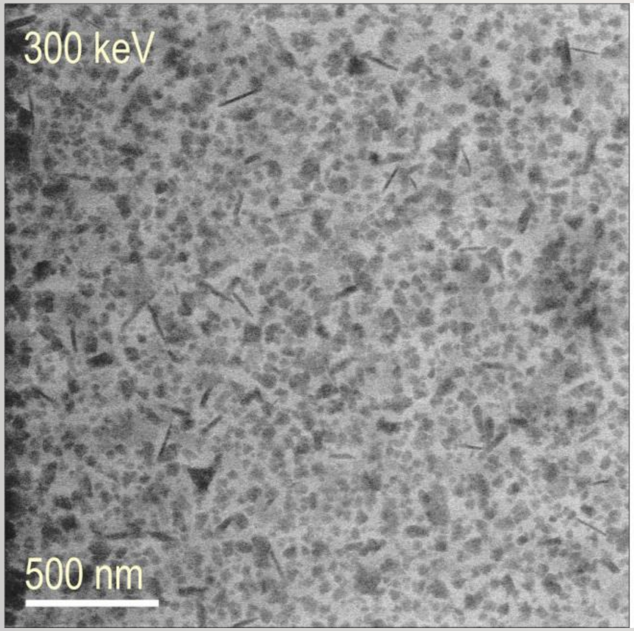


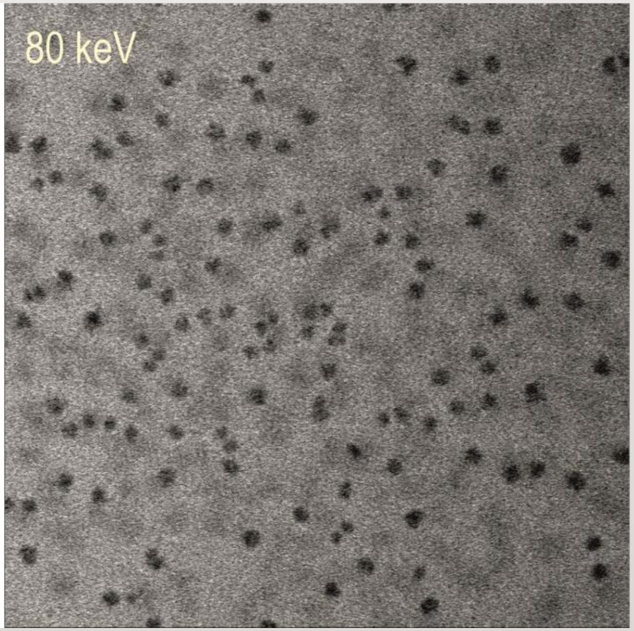
Reaction limited growth follows LSW growth mode

Diffusion limited growth slower than predicted by LSW model. Finite confinement of liquid by cell may play a role.

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

Effect of Beam Energy





Dose 39.1 e^-/nm^2 per frame

Based on final particles morphology, higher kV is equivalent to applying a lower reductive dose.

However, overall Ag area higher at 300kV. Higher effect of back reactions at lower kV.

Stopping power of water

NIST website (and references therein)

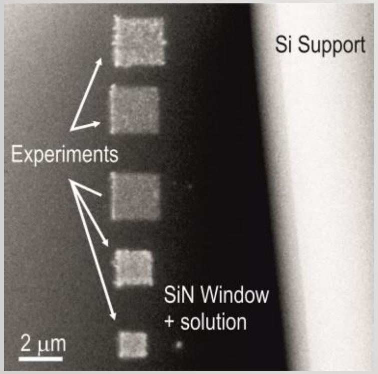
S_{80KeV} = **4.76** MeV cm^2/g

S_{200KeV} = 2.798 MeV cm^2/g

S_{300KeV} = **2.36** MeV cm^2/g

Abellan et al. ChemComm 2014

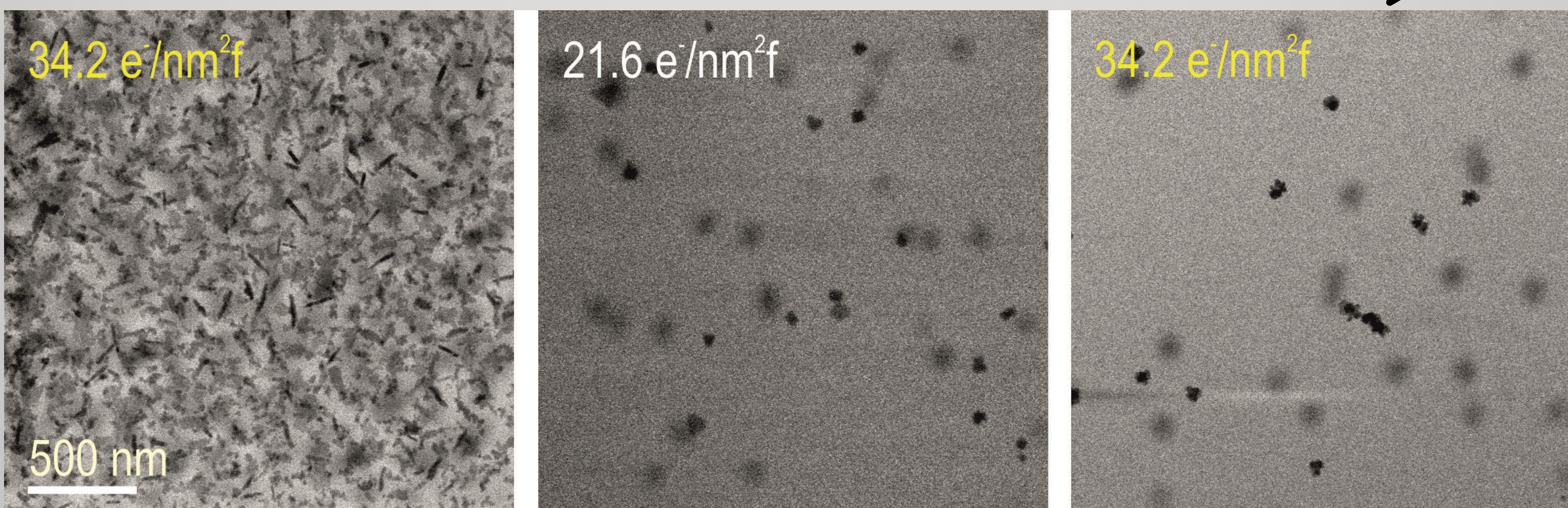
Liquid Samples Memory (of Irradiation)



Radiolytic species move, ultimately producing solution depletion and an increasing number of excess unreacted radicals.

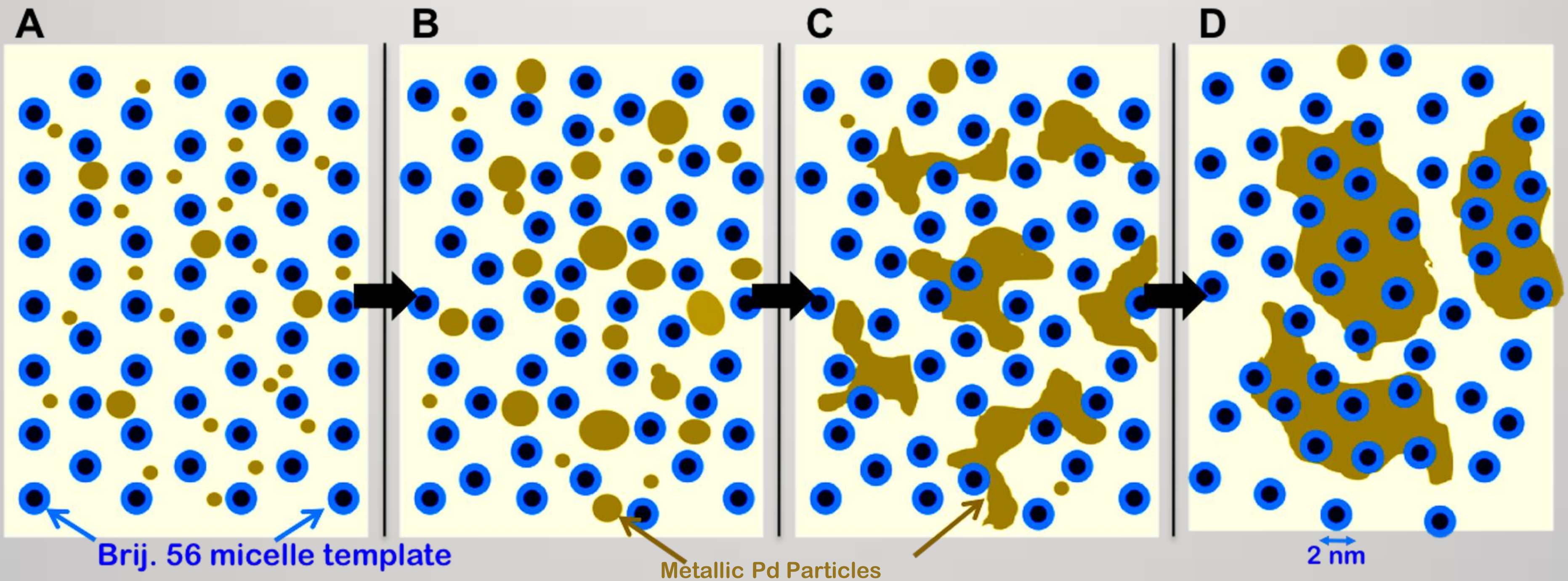
Total dose on the cell is important

1st **(…)** **Sequence of experiments** **Nth**



Abellan et al. ChemComm 2014

Templated Growth Model



L. R. Parent et. al., *ACS Nano*, 6, 3589 (2012).