# A Crash Course on Transmission Electron Microscopy and Electron Energy Loss Spectroscopy

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https://sites.google.com/site/xinhuolin/Home

http://mods-n-hacks.wonderhowto.com/how-to/start-fire-with-your-water-bottle-0137955/

## Start a fire with a water bottle

MSAE E8235x: selected topics in materials science, Columbia University, Nov 18, 2015

# A Crash Course on Transmission Electron Microscopy and Electron Energy Loss Spectroscopy

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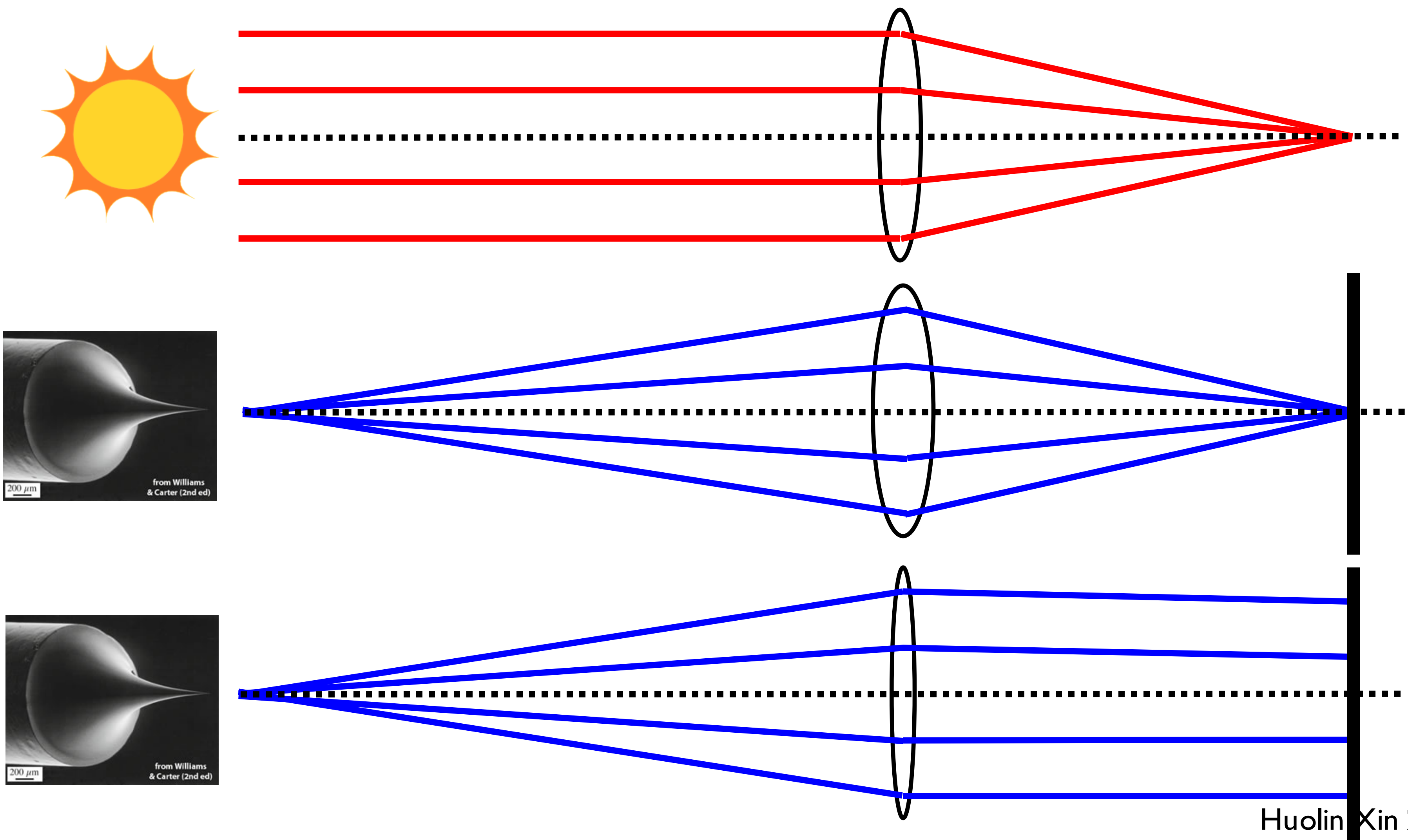
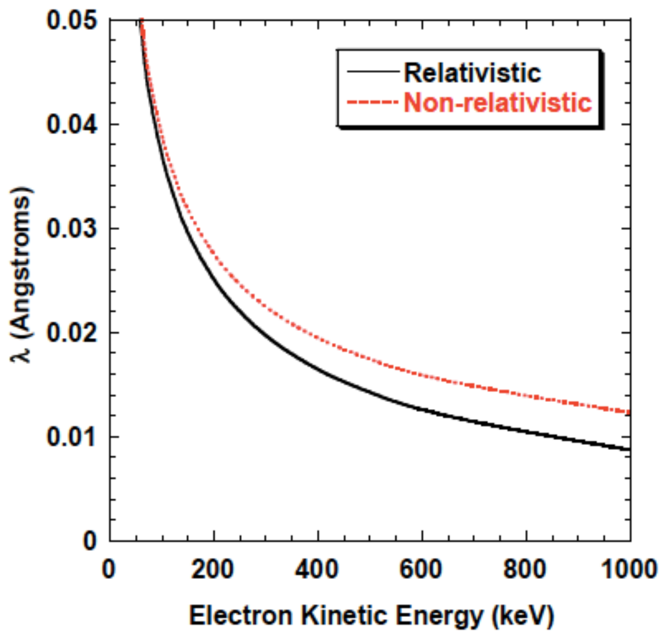


# Motivation for building an electron microscope

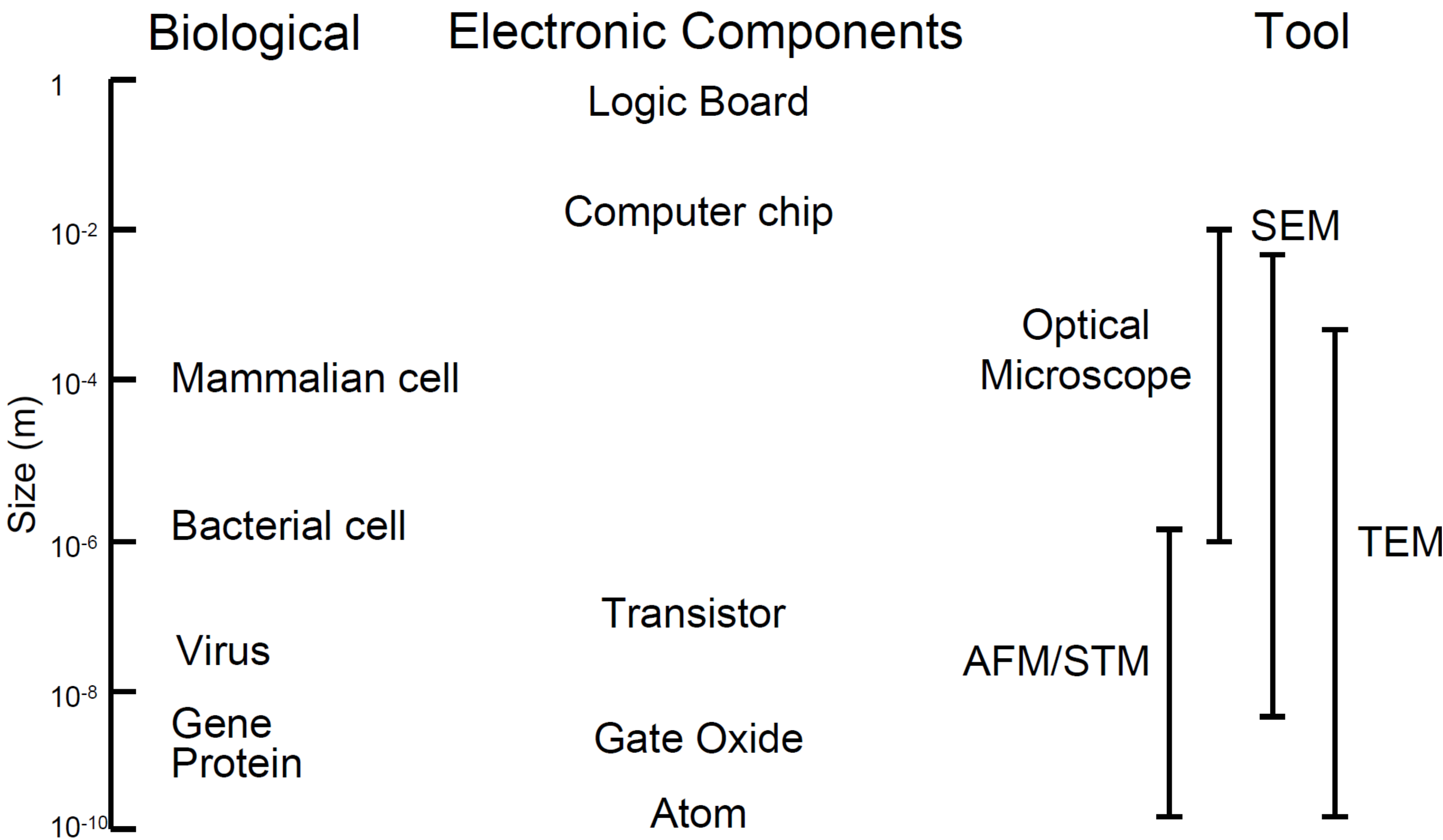





| Accelerating Voltage | v/c | λ (Å) |
|---|---|---|
| 1 V | 0.0019784 | 12.264 |
| 100 V | 0.0062560 | 1.2263 |
| 1 keV | 0.062469 | 0.38763 |
| 10 keV | 0.019194 | 0.12204 |
| 100 keV | 0.54822 | 0.037013 |
| 200 keV | 0.69531 | 0.025078 |
| 300 keV | 0.77653 | 0.019687 |
| 1 MeV | 0.81352 | 0.0087189 |

1. It is easy to accelerate electrons (charged particles)
2. It is easy to focus electrons (use magnetic or electric field)
3. Higher resolution than optical/X-ray microscopes—atomic resolution is routine now
4. Chemical and bonding imaging and spectroscopy
5. Radiation damage limits imaging resolution but it is not as bad as X-ray [ref: Henderson, Quarterly Reviews of Biophysics 28, 171 (1995)]

# Biological and Electronic Component Dimensions




Slide credit: DA Muller

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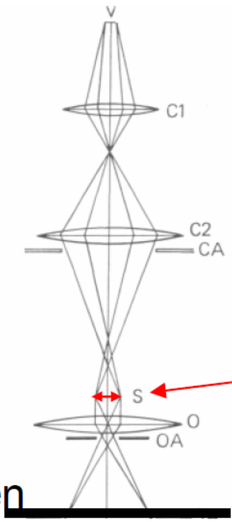
# Comparison of Optical and Electron Microscopes

## Light Microscope




## TEM

source

1st condenser

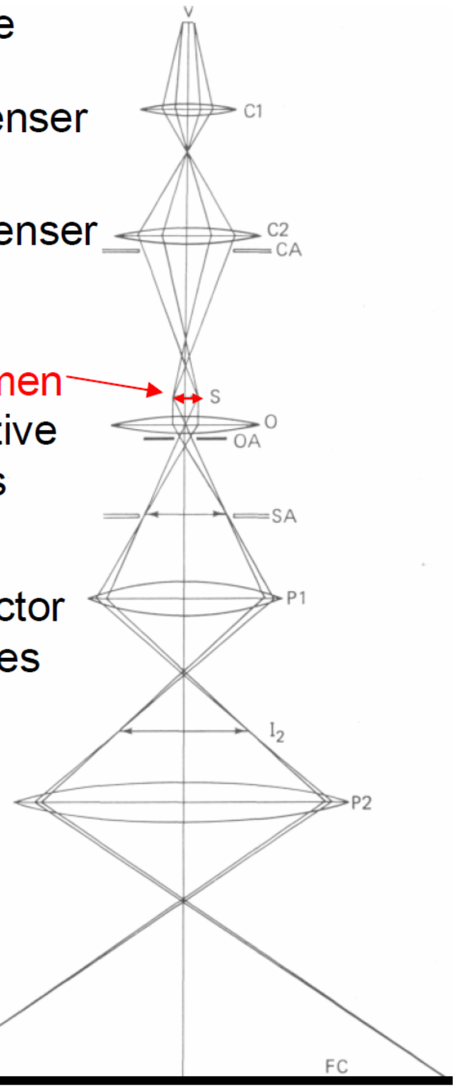
2nd condenser

specimen

Objective lens

Viewing screen Or CCD

Projector lenses




Viewing screen Or CCD

CA condenser aperture

OA objective aperture

SA selected area aperture

## SEM or STEM

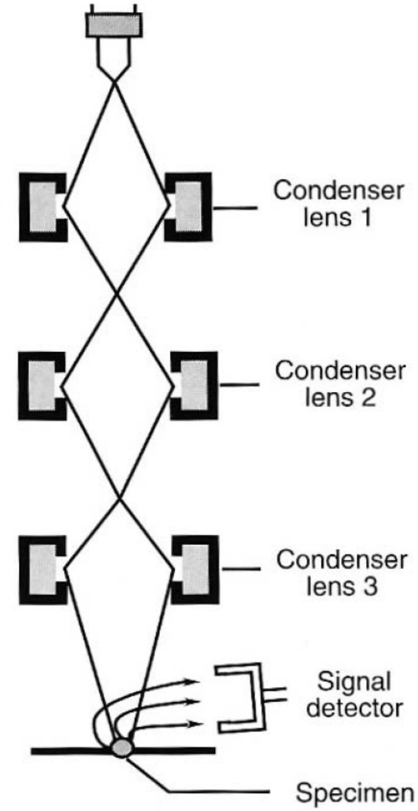
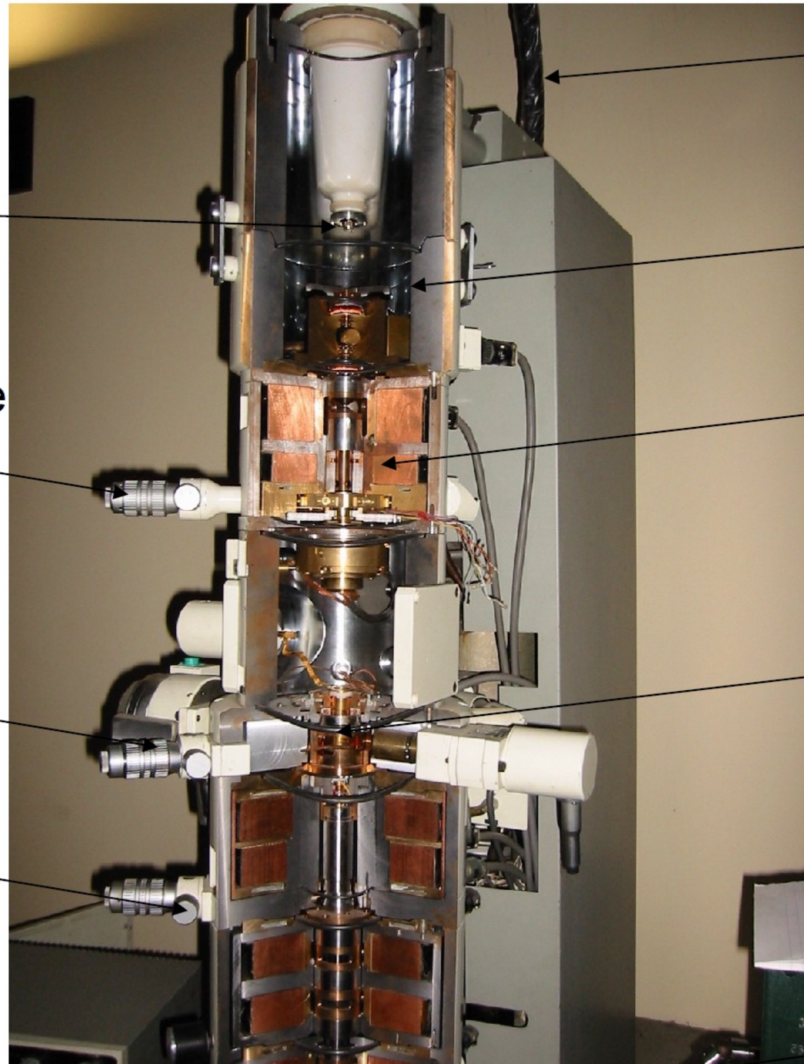



Image formed by scanning a small spot

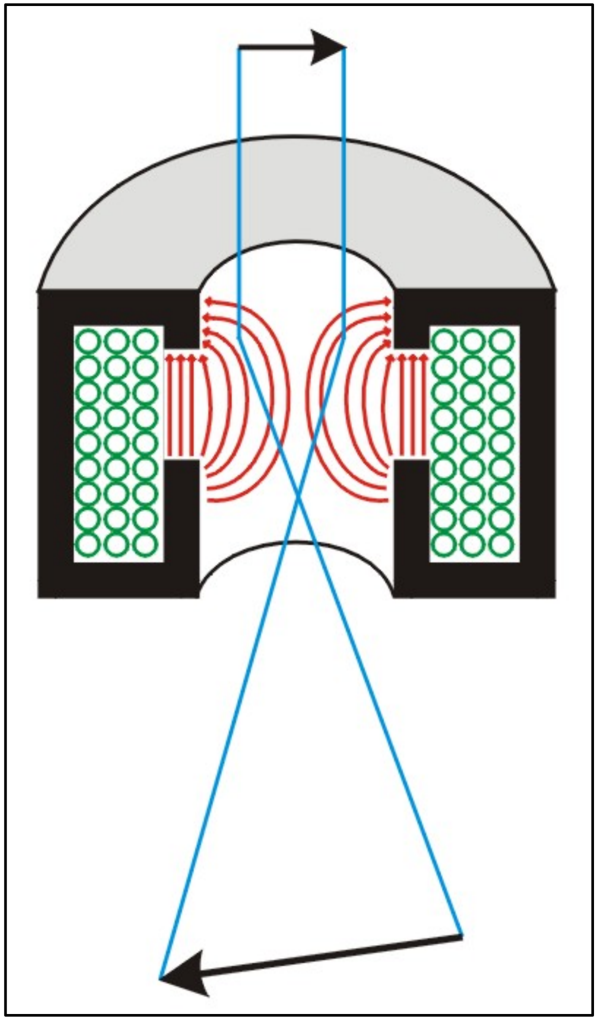
Slide credit: DA Muller

# The cross section of a real TEM



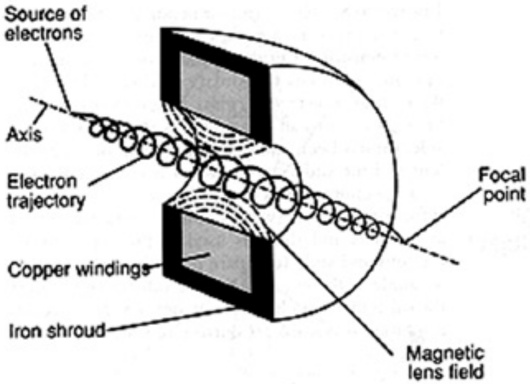

Slide credit: DA Muller

# Electromagnetic Lens



## Electromagnetic Lenses

Electromagnetic lenses are comprised of windings of wire through which electric current is applied. This creates a strong magnetic field through which negatively-charged electrons must pass.




Due to the magnetic field, the electrons follow a helical trajectory which converges at a fine focal point after it emerges from the lens. (DC-powered magnets behave similar to converging glass lenses)

Field Strength -determines the focal length which varies with:

(focal length) $f = K\,(V/i^2)$

K = constant based on the number of turns of lens coil wire and the geometry of the lens.

V = accelerating voltage

i = milliamps of current put through the coil

Potentiometer controls which vary the current to the various lenses are the means by which focus and magnification of the electron beam are achieved.

http://www.microscopy.ethz.ch/lens.htm http://www.udel.edu/biology/Wags/b617/tem/tem.htm

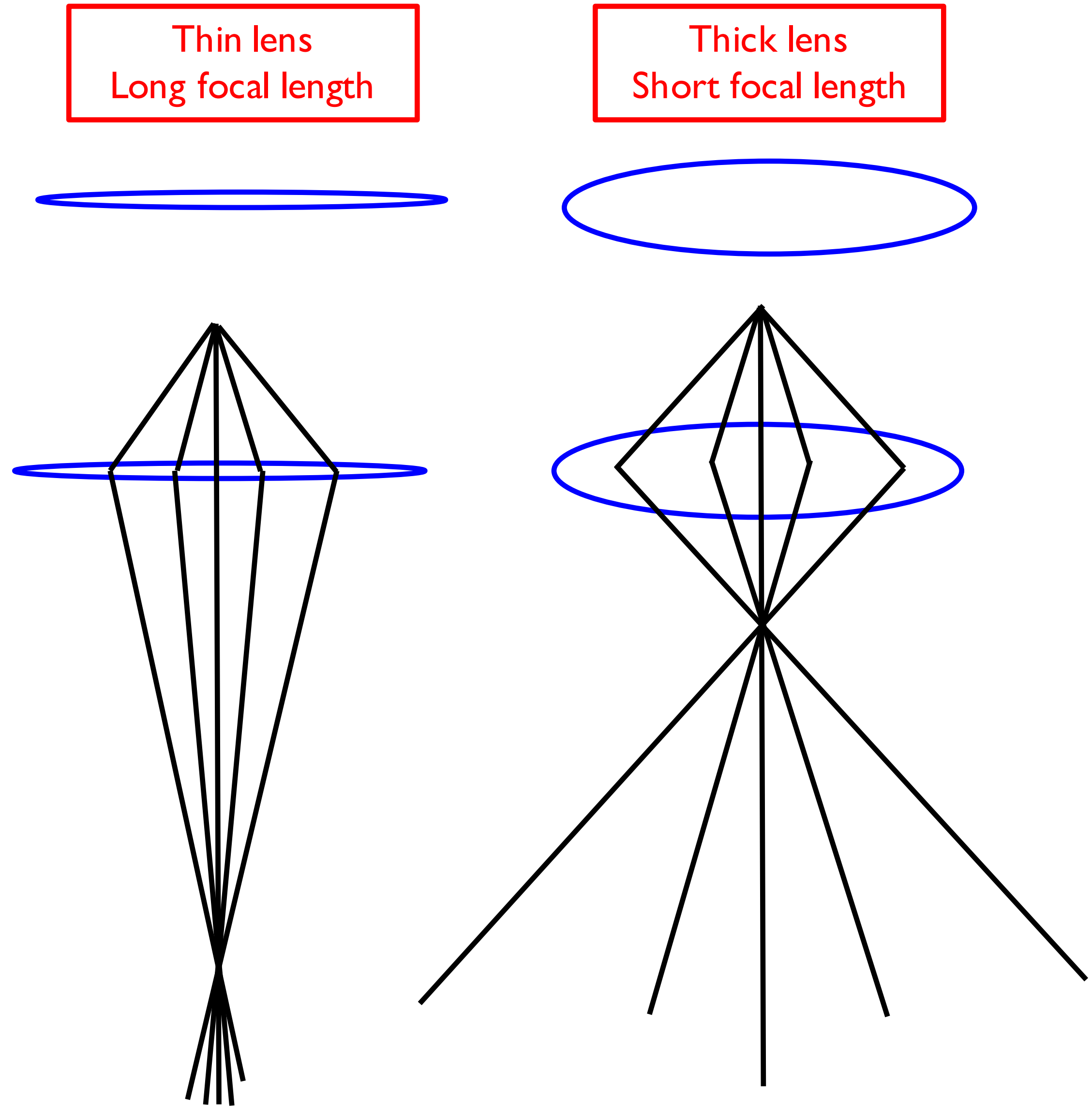
# Focal Length can be Changed in TEM

(focal length) $f = K\,(V/i^2)$

Constant:
Number of turns
and lens geometry

Accelerating voltage

Current

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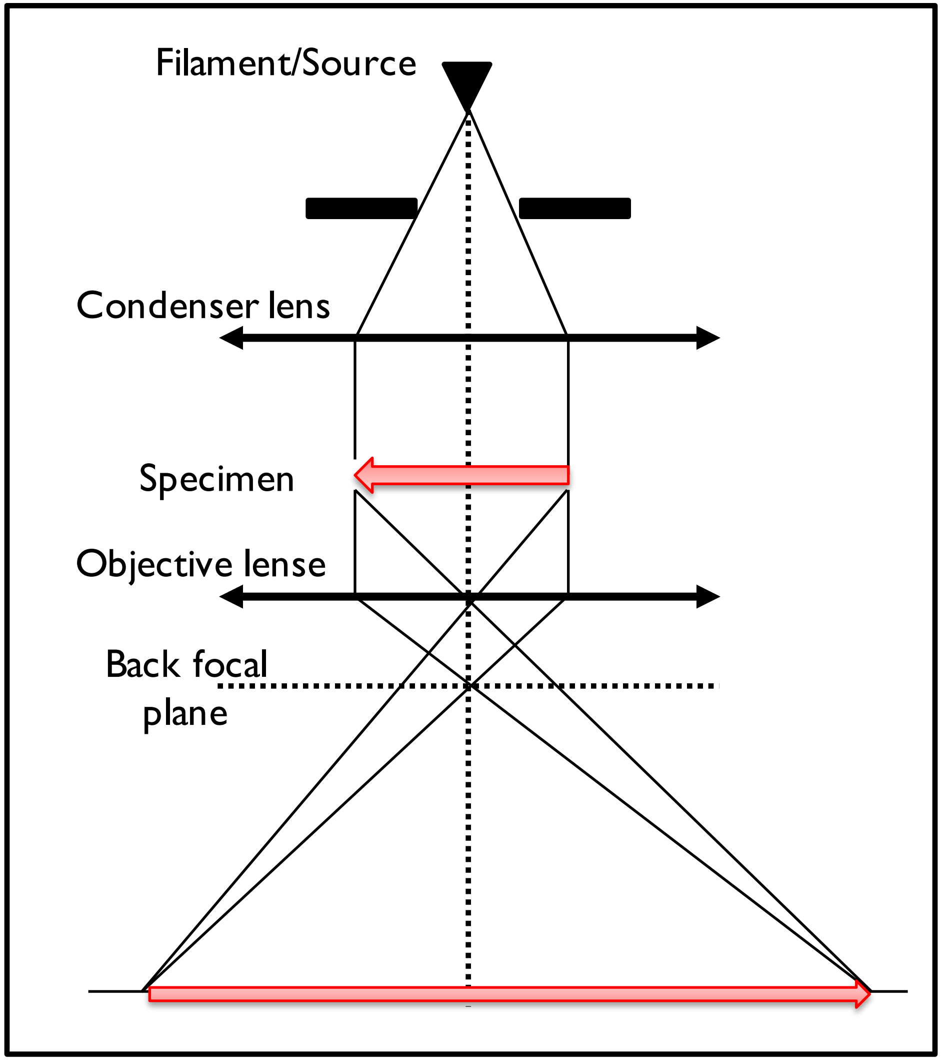
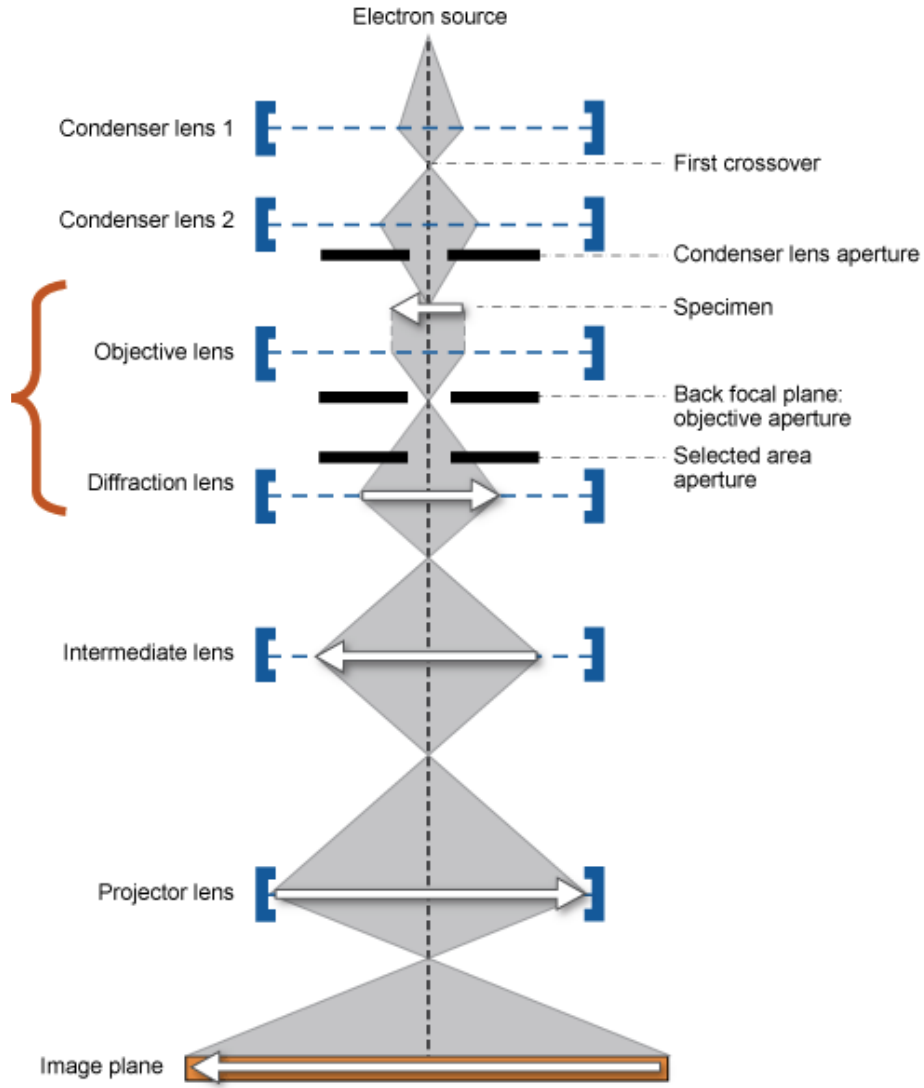
# A Transmission Electron Microscope




http://www.ammrf.org.au/myscope/images/tem/tem_beampath_stage_a.png

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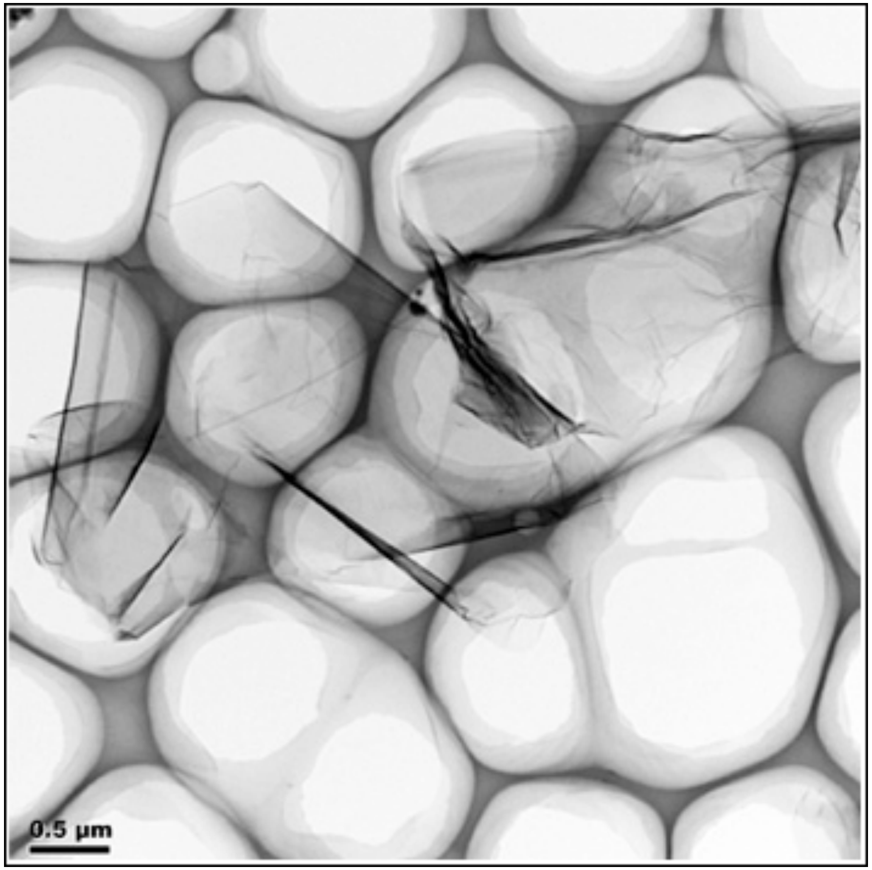
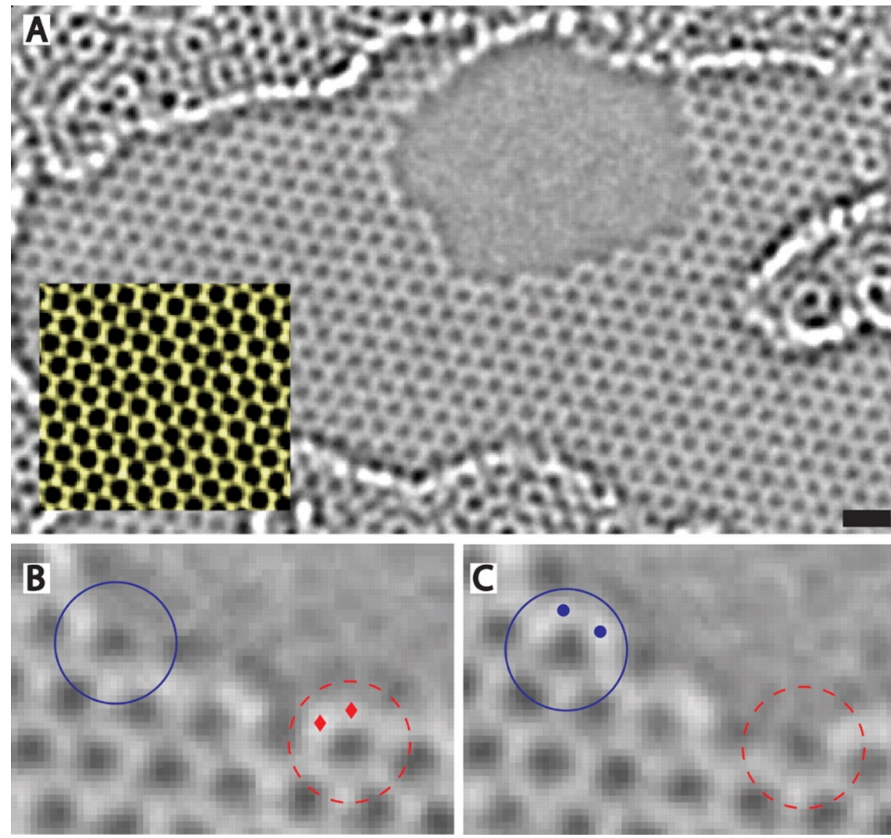
# From micrometers to atomic scales



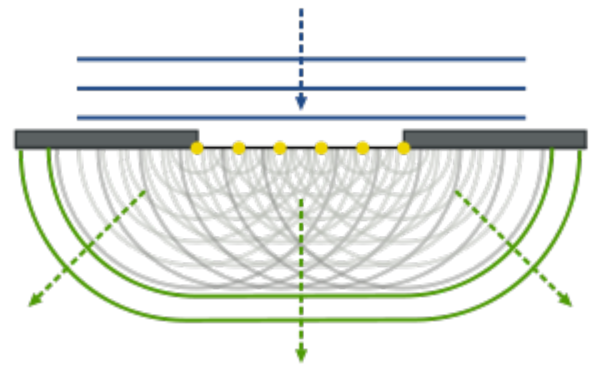

Science 27 March 2009:
Vol. 323 no. 5922 pp. 1705-1708

# Propagation of Wave Front

**Fresnel diffraction integral**

$$E(x,y,z)=\frac{z}{i\lambda}\iint_{-\infty}^{+\infty}E(x',y',0)\frac{e^{ikr}}{r^2}dx'dy'$$

**Huygens–Fresnel principle**



**Fresnel diffraction: near field**

$$E(x,y,z)=\frac{e^{ikz}}{i\lambda z}\iint_{-\infty}^{+\infty}E(x',y',0)e^{\frac{ik}{2z}[(x-x')^2+(y-y')^2]}dx'dy'$$

$$E(x,y,z)=\frac{e^{ikz}}{i\lambda z}e^{i\frac{\pi}{\lambda z}(x^2+y^2)}\mathcal{F}\left\{E(x',y',0)e^{i\frac{\pi}{\lambda z}(x'^2+y'^2)}\right\}\Big|_{p=\frac{x}{\lambda z};q=\frac{y}{\lambda z}}$$

**Fraunhofer diffraction: far field**

$$z\gg\frac{x'^2+y'^2}{\lambda}$$

$$E(x,y,z)=\frac{e^{ikz}}{i\lambda z}e^{i\frac{\pi}{\lambda z}(x^2+y^2)}\mathcal{F}\left\{E(x',y',0)e^{i\frac{\pi}{\lambda z}(x'^2+y'^2)}\right\}\Big|_{p=\frac{x}{\lambda z};q=\frac{y}{\lambda z}}$$

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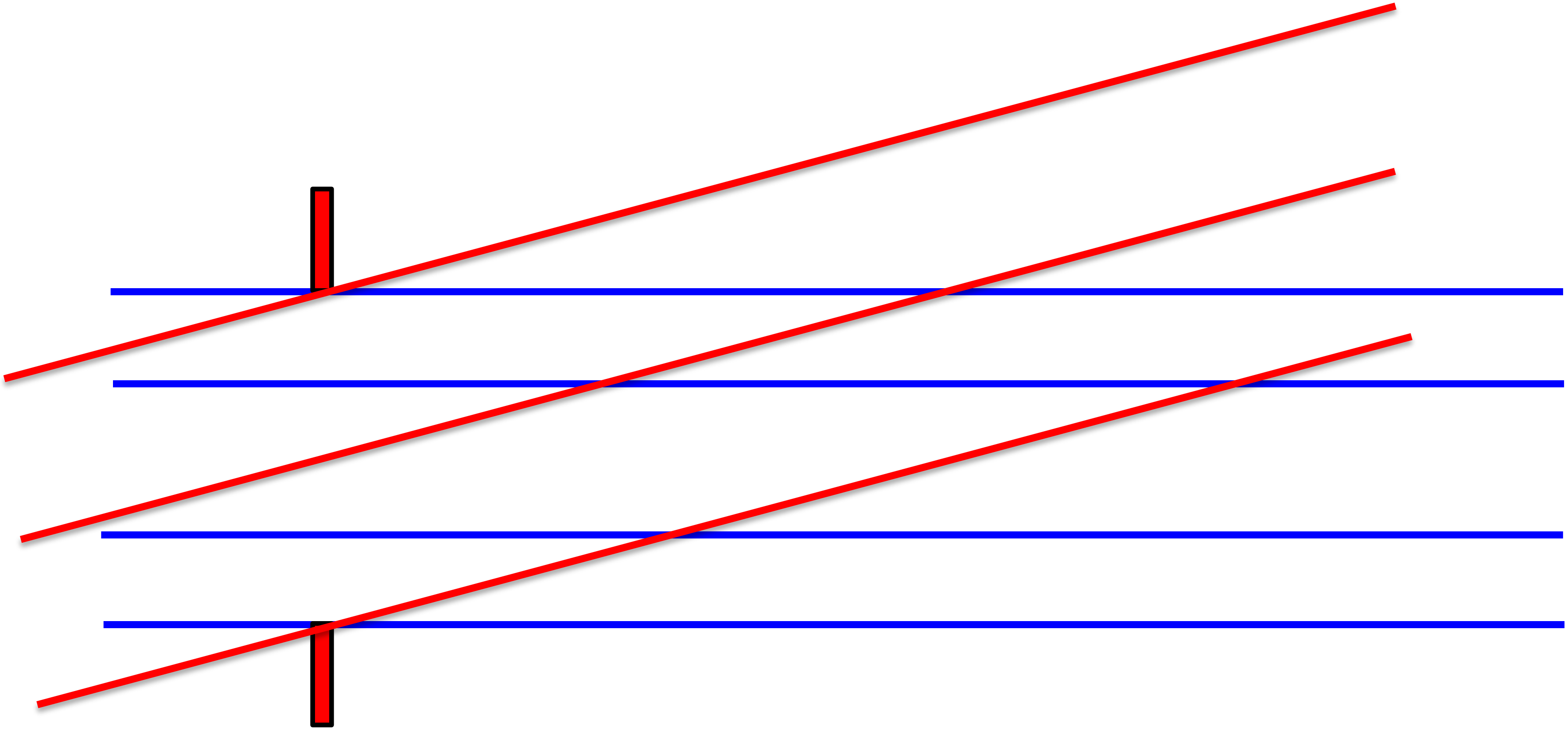
# What does a lens do?



**Fraunhofer diffraction: far field**

$$E(x,y,z) = \frac{e^{ikz}}{i\lambda z} e^{i\frac{\pi}{\lambda z}(x^2+y^2)} \mathcal{F}\left\{ E(x',y',0) e^{i\frac{\pi}{\lambda z}(x'^2+y'^2)} \right\}\Big|_{p=\frac{x}{\lambda z};q=\frac{y}{\lambda z}}$$

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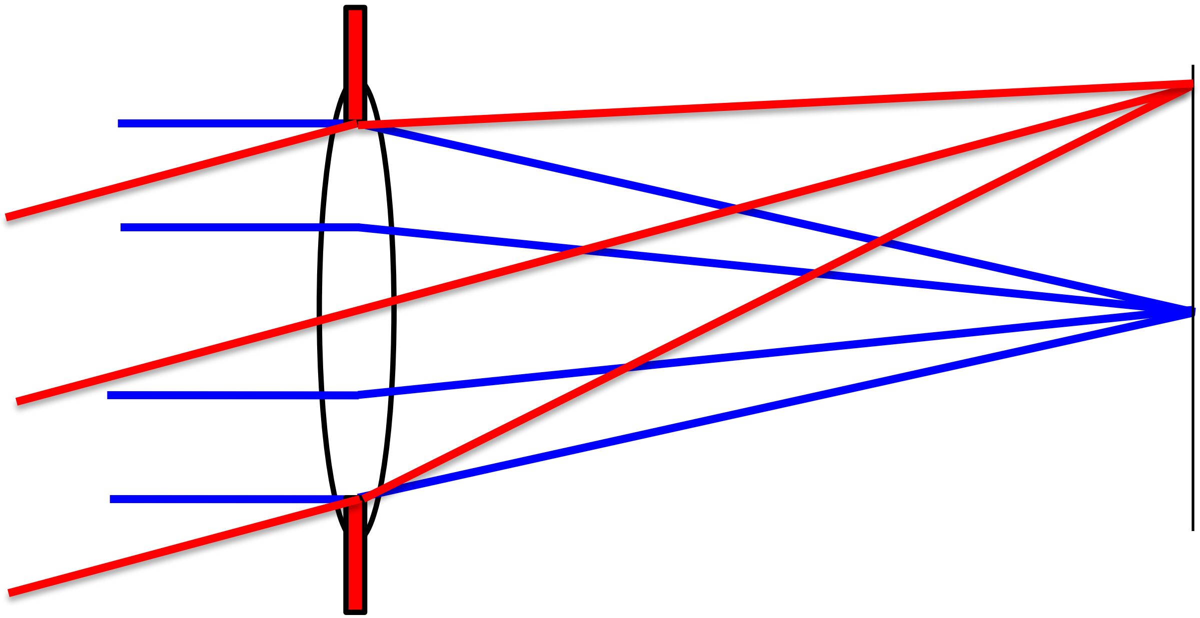
# What does a lens do?



- It focuses the Fraunhofer diffraction pattern to the back focal plane;

**Fraunhofer diffraction: far field**

$$E(x,y,z) = \frac{e^{ikz}}{i\lambda z} e^{i\frac{\pi}{\lambda z}(x^2+y^2)} \mathcal{F}\left\{ E(x',y',0) e^{i\frac{\pi}{\lambda z}(x'^2+y'^2)} \right\} \Big|_{p=\frac{x}{\lambda z};q=\frac{y}{\lambda z}}$$

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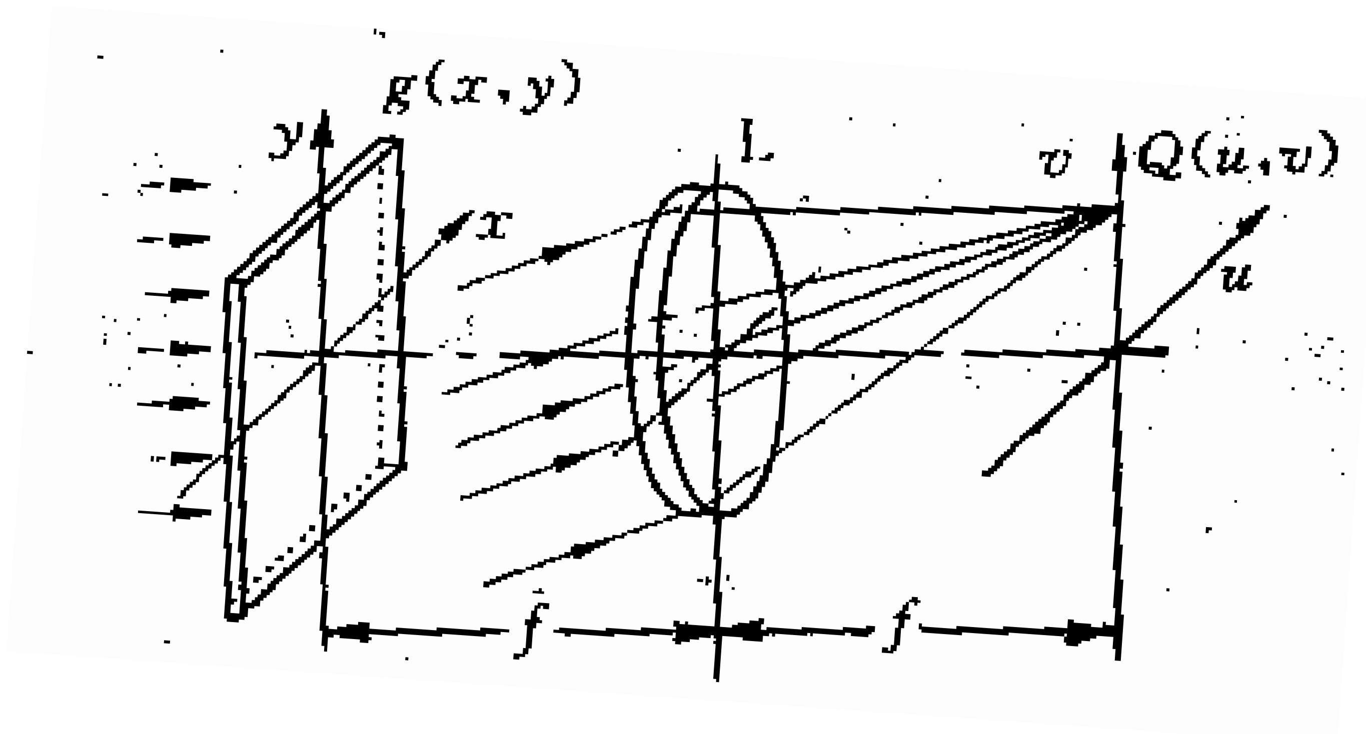
# A Converging Lens is Fourier Transform




$$\psi(u,v)=\frac{e^{ikf}}{i\lambda f^2}\iint_{-\infty}^{\infty}\psi_0(x,y)\exp\left[-i\frac{2\pi}{\lambda f}(xu+yv)\right]dxdy$$

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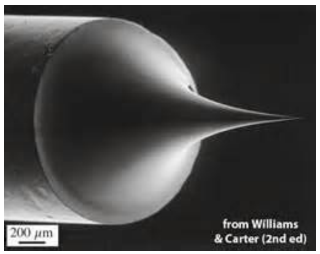
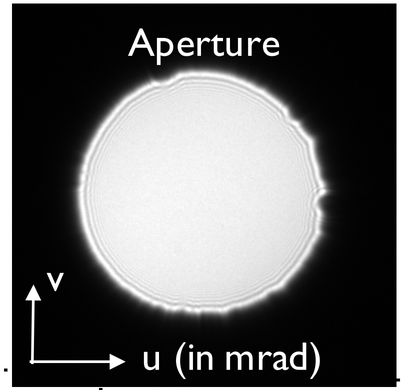
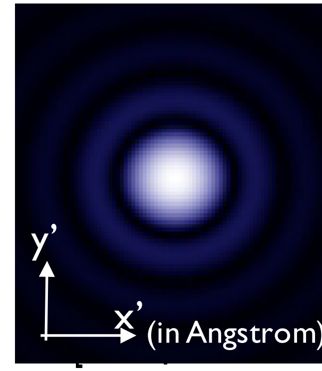
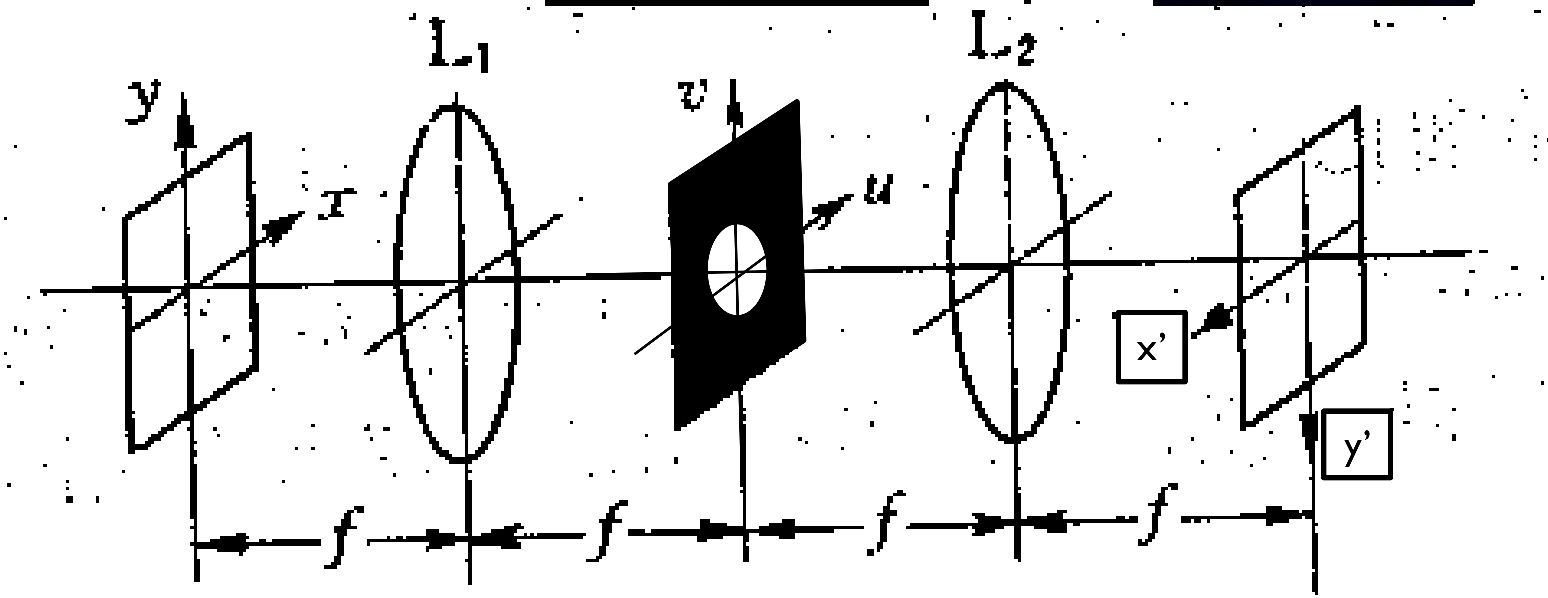
# How does a STEM create an electron probe



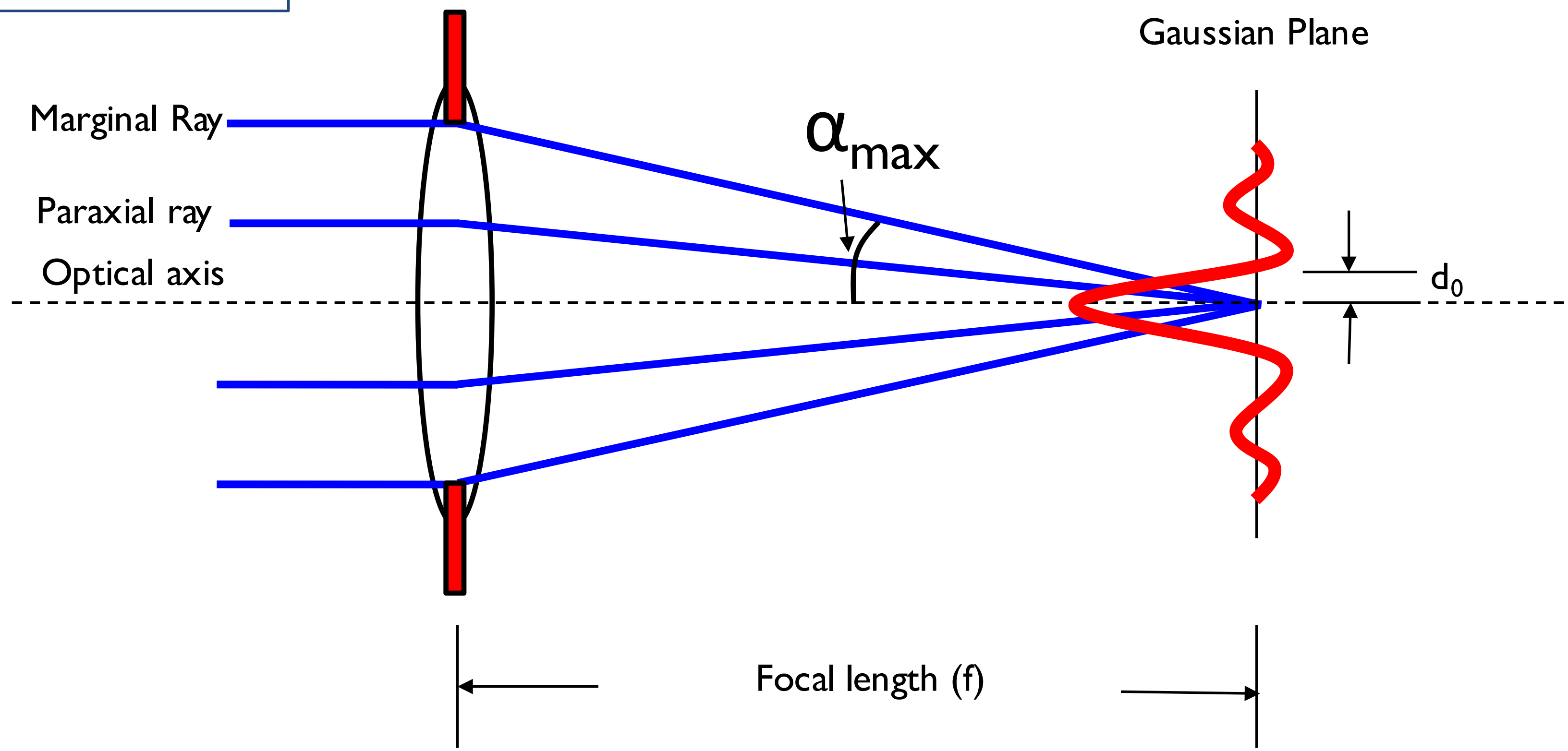




- The electron probe is a simple Fourier transform a round aperture

# Imaging with a perfect Lens

Source is far away




- The image of a point transferred through a lens with a circular aperture of semiangle $\alpha_{max}$ is an Airy disk of diameter

$$d_0 = \frac{0.61\lambda}{\alpha_{max}}$$

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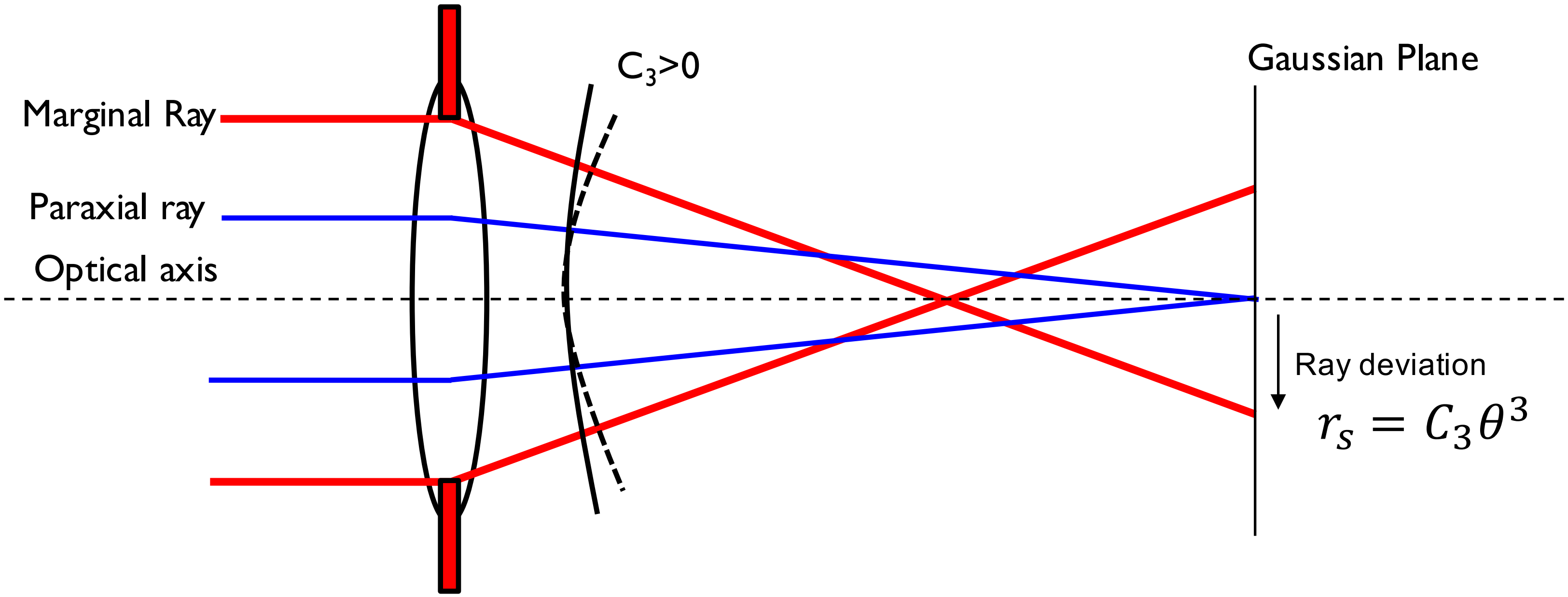
# Spherical Aberration

"For lenses made with spherical surfaces, rays which are parallel to the optic axis but at different distances from the optic axis fail to converge to the same point."

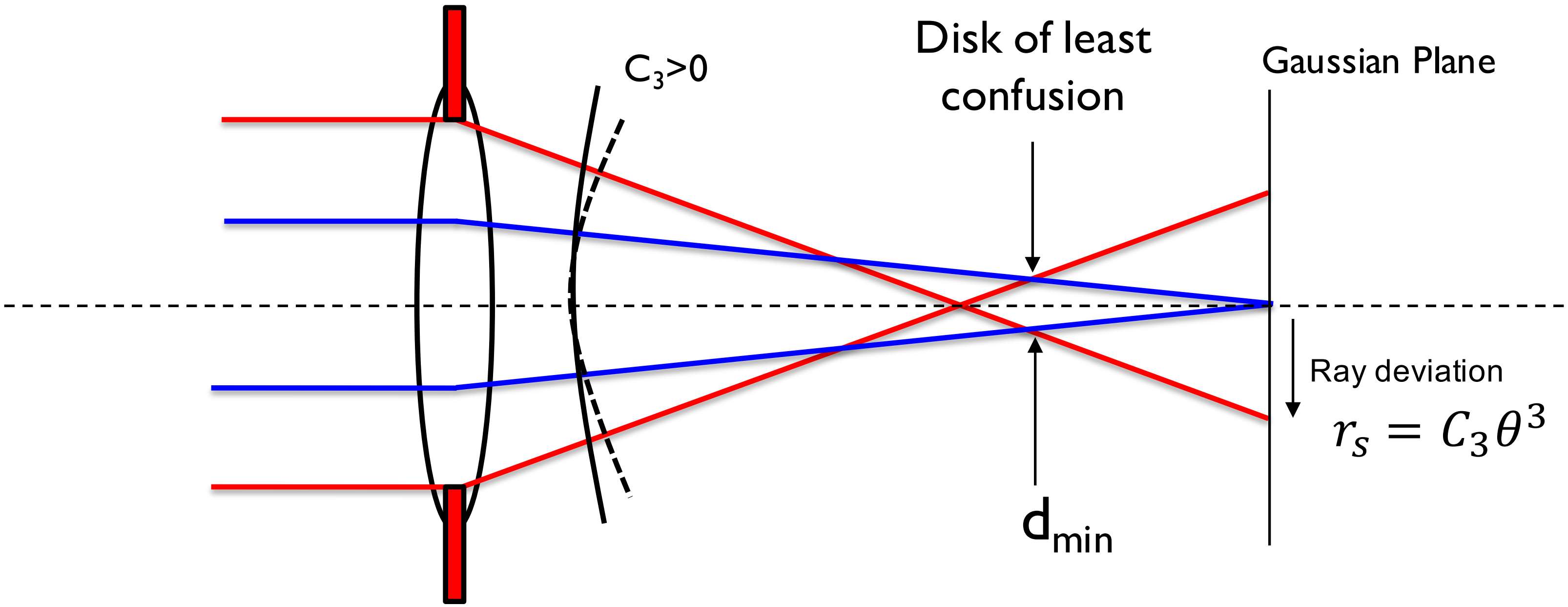



http://hyperphysics.phy-astr.gsu.edu/hbase/geoopt/aber.html

# Scherzer Theorem (1936)

- For electron optics: Scherzer showed that the expression for $C_s$ is a sum of squares (always positive) if:
  - The optical system is rotationally symmetric,
  - The system produces a real image of the object,
  - The fields of the system do not vary with time,
  - There is no charge on the axis.

# Resolution limits imposed by 3rd Order Spherical Aberrations




It is easy to proof

$$d_{min} = \frac{1}{2}C_3\alpha^3$$

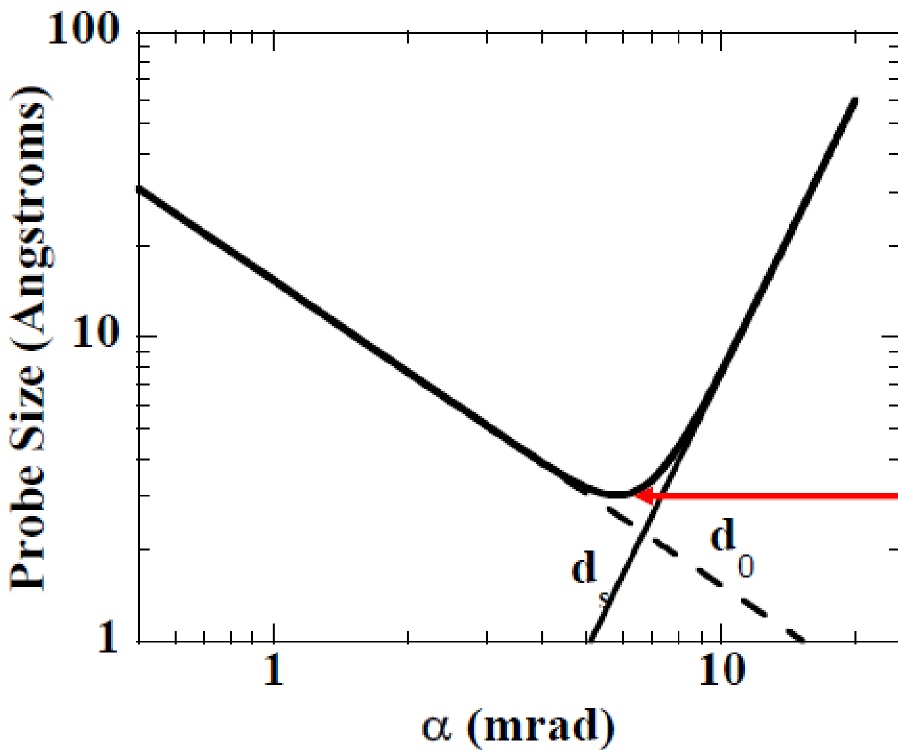
- So, FEI analytical pole piece: $C_3 = 1.2\ mm, \alpha = 9.2\ mrad$

$$d_{min} = 0.48\ nm$$

# Balancing Spherical Aberration against the Diffraction Limit

First Order Approximation

$$d^2 \approx d_{diff}^2 + d_{sph}^2 = \left(\frac{0.61\lambda}{\propto_{max}}\right)^2 + \left(\frac{1}{2} C_3 \alpha_{max}^3\right)^2$$




Optimal aperture
And minimum
Spot size

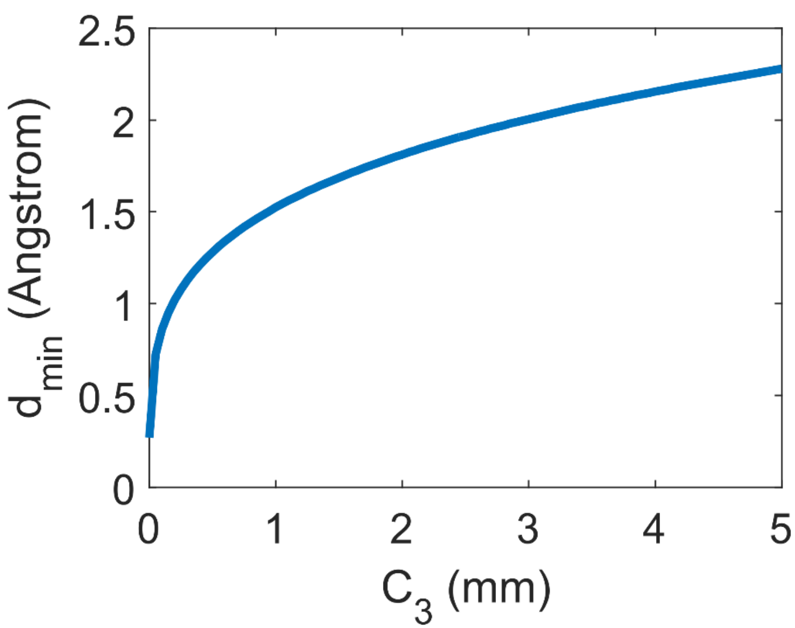
$$d_{\min} = 0.66\, C_3^{1/4} \lambda^{3/4}$$

# Balancing Spherical Aberration against the Diffraction Limit

A more accurate wave-optical treatment, allowing less than λ/4 of phase shift across the lens gives

Optimal aperture size: $$\alpha_{opt} = \left(\frac{4\lambda}{C_3}\right)^{1/4}$$

Minimum Spot size: $$d_{min} = 0.43 \times C_3^{1/4} \lambda^{3/4}$$



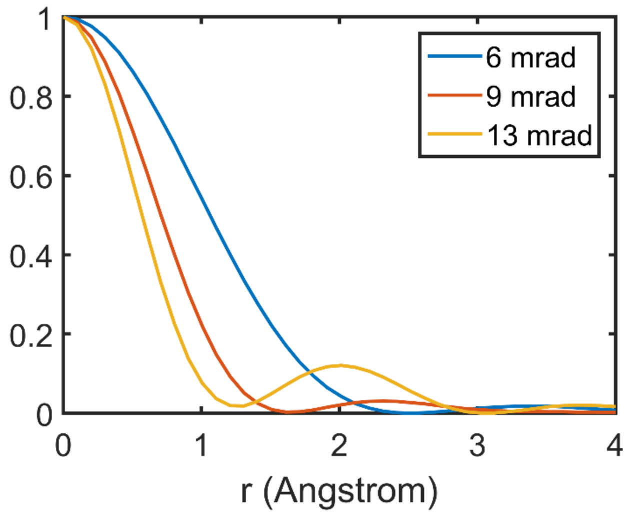

At 200 keV

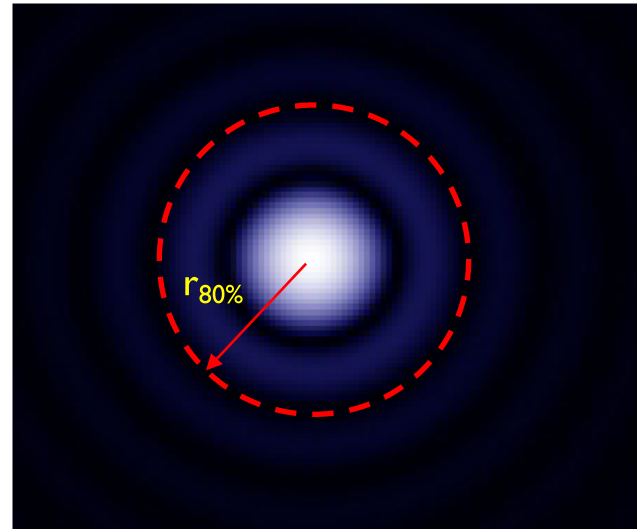
- C3 1.2 mm, 1.6 Angstrom
- C3 1.0 mm, 1.52 Angstrom
- C3 0.5 mm, 1.28 Angstrom
- C3 0.1 mm, 0.86 Angstrom

# Why you don't want to use too big an aperture

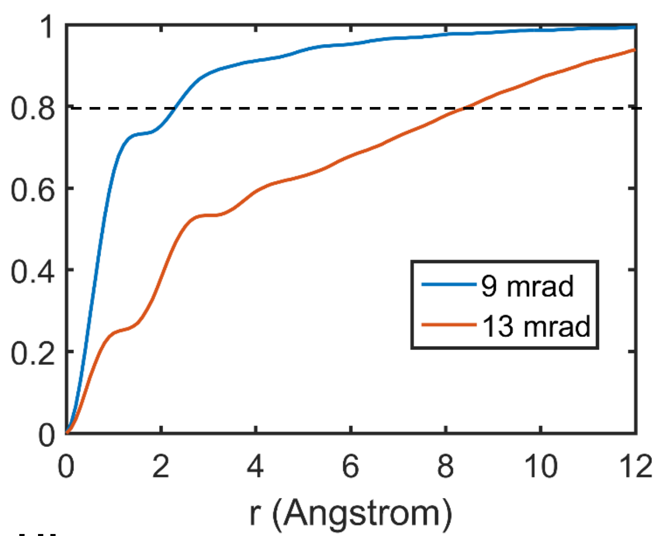
200 keV
C3 = 1.2 mm

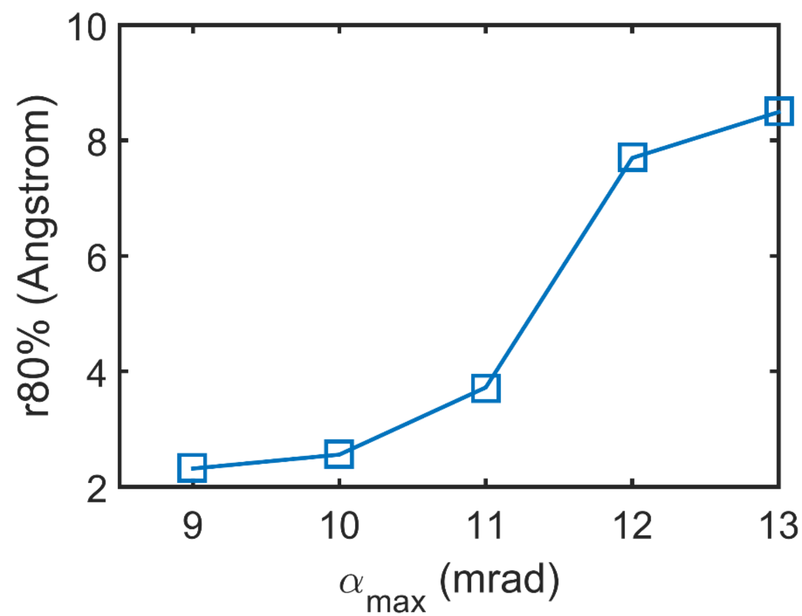
Point Spread Function




Cumulative Intensity

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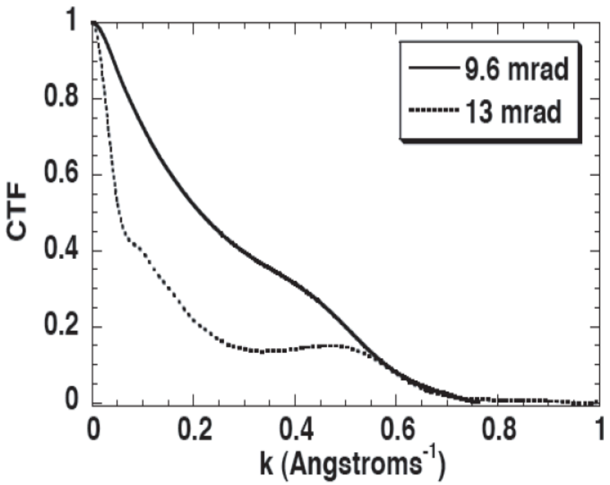
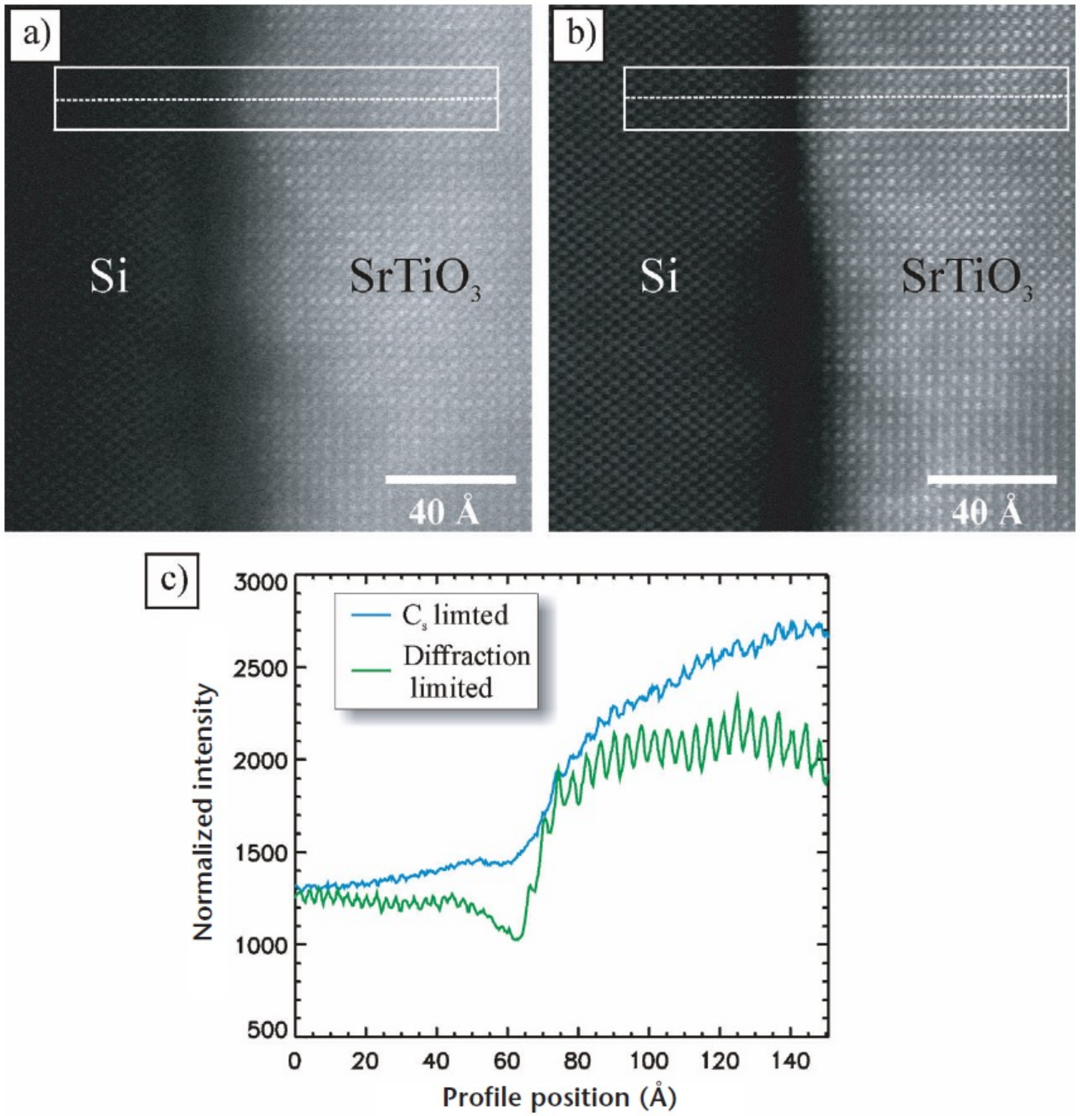
# Contrast Reduces if Aperture is Too Large



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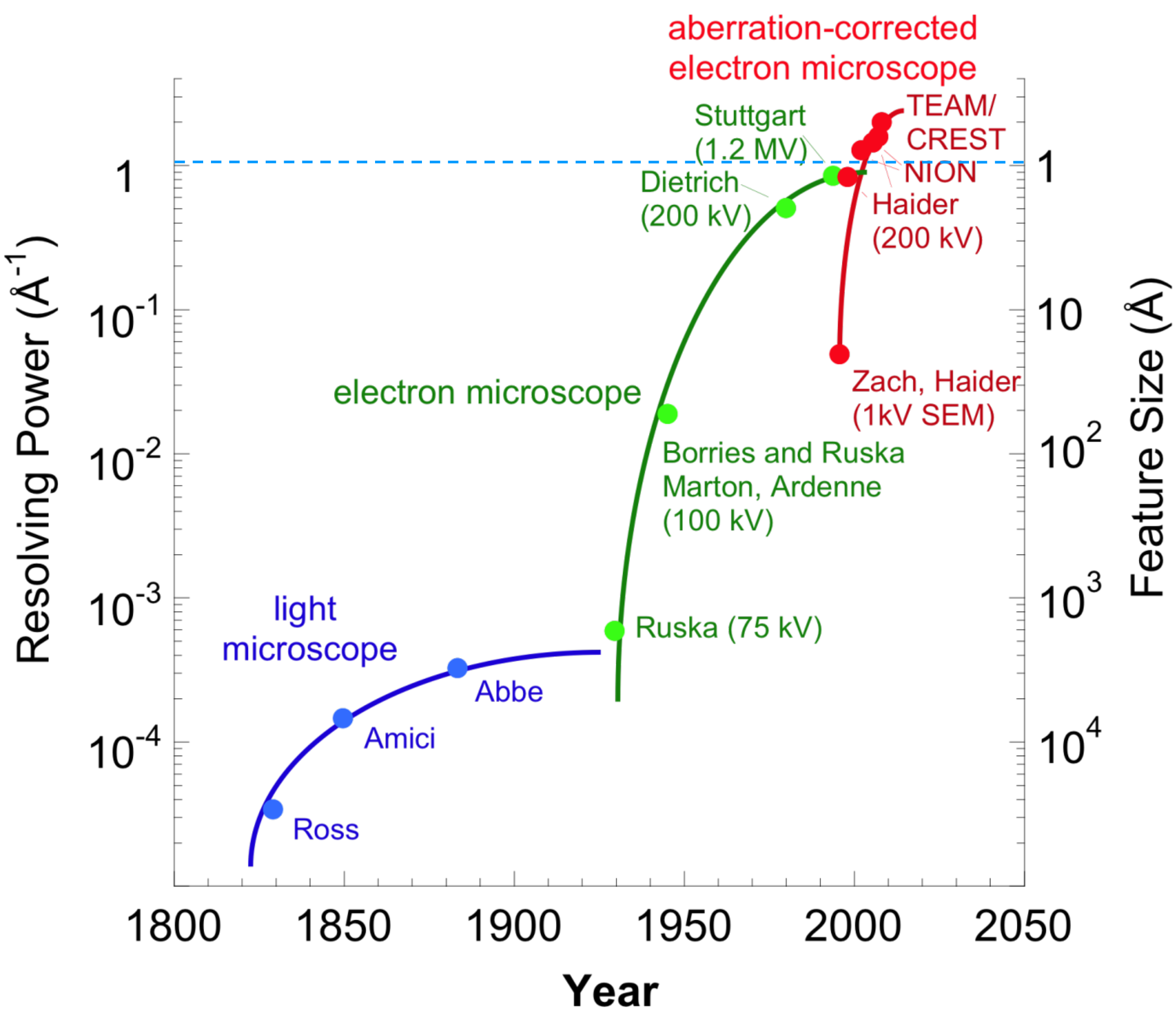
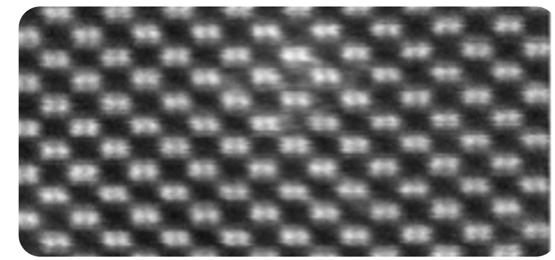
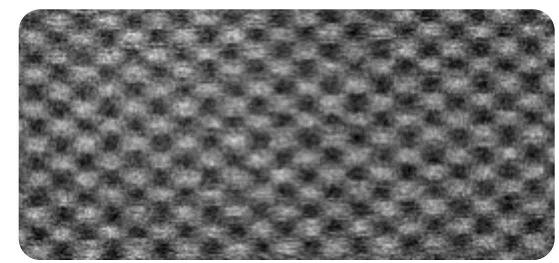
# Hardware Advances in Microscopy



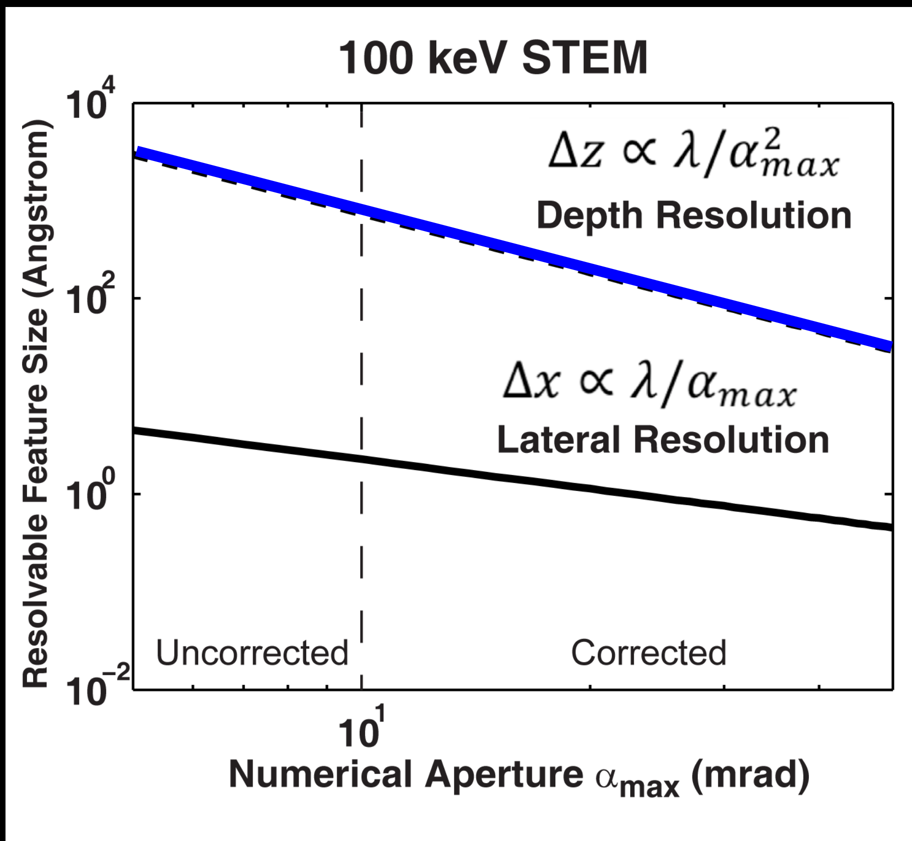





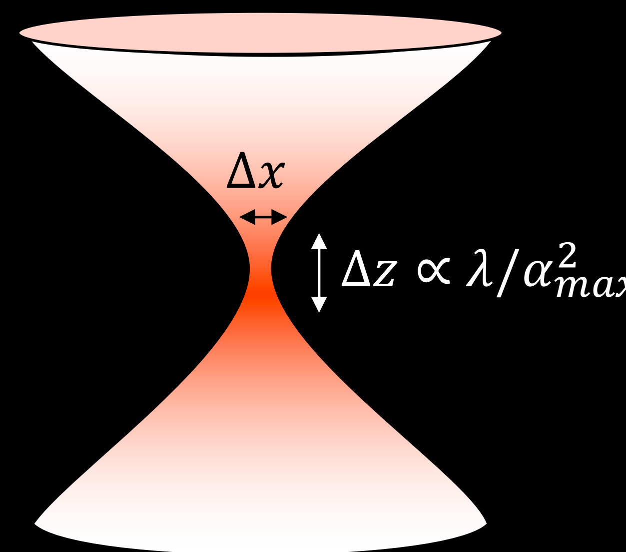
Corrected optics have enabled practical
Sub-Angstrom resolution

Muller, Nature Materials, (2009), Adapted from Rose (2009)

# Depth Sectioning and Confocal Imaging in an Aberration-Corrected S/TEM

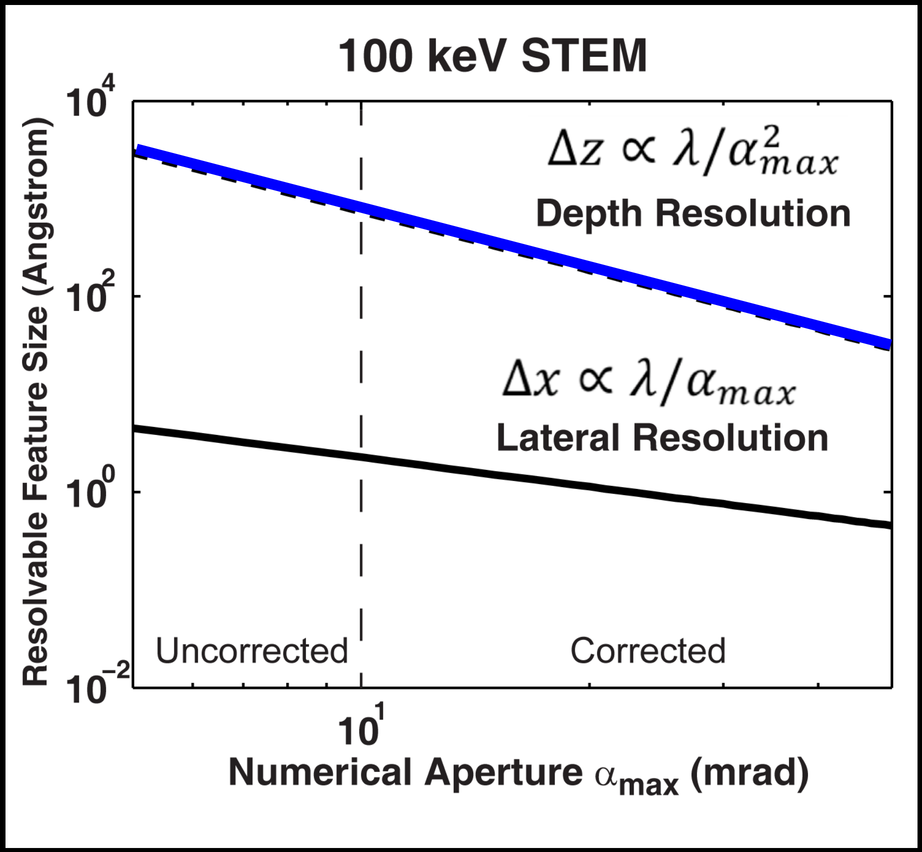



3D Point Spread Function of ADF-STEM

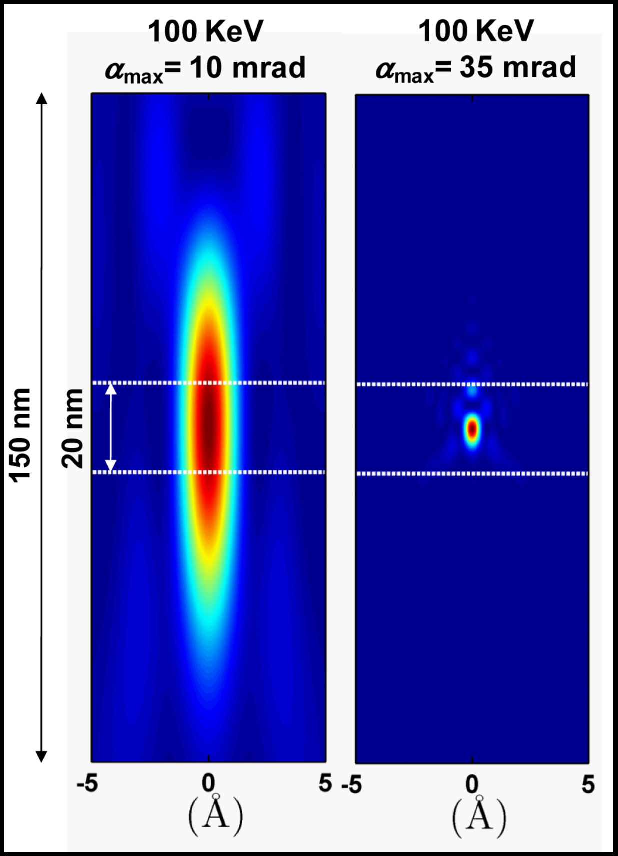



- The short depth of focus could potentially enable 3D reconstruction of nanomaterials through acquisition of a through-focal series in a similar manner to confocal microscopy.

# Depth Sectioning and Confocal Imaging in an Aberration-Corrected S/TEM




3D Point Spread Function of ADF-STEM




- The short depth of focus could potentially enable 3D reconstruction of nanomaterials through acquisition of a through-focal series in a similar manner to confocal microscopy.

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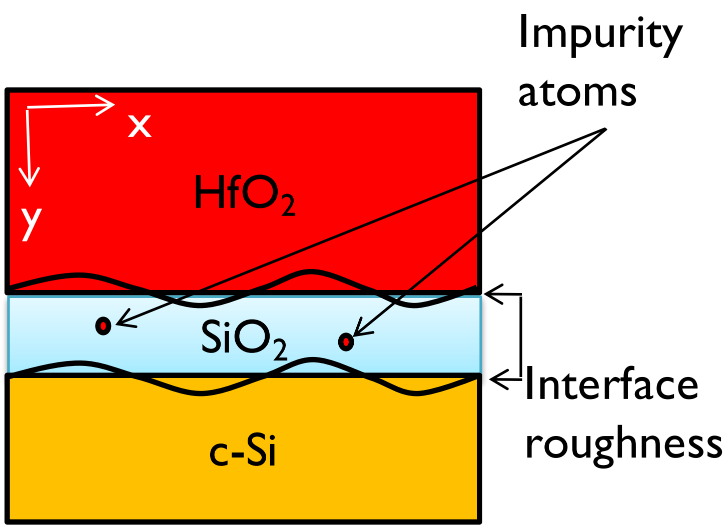
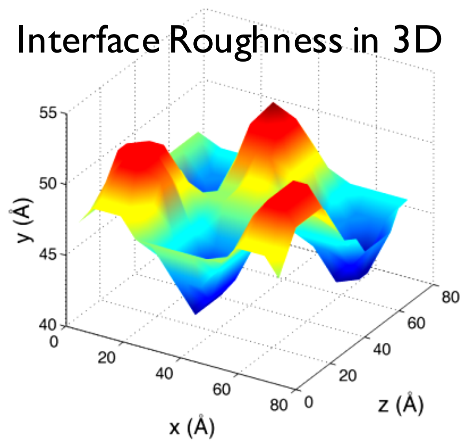
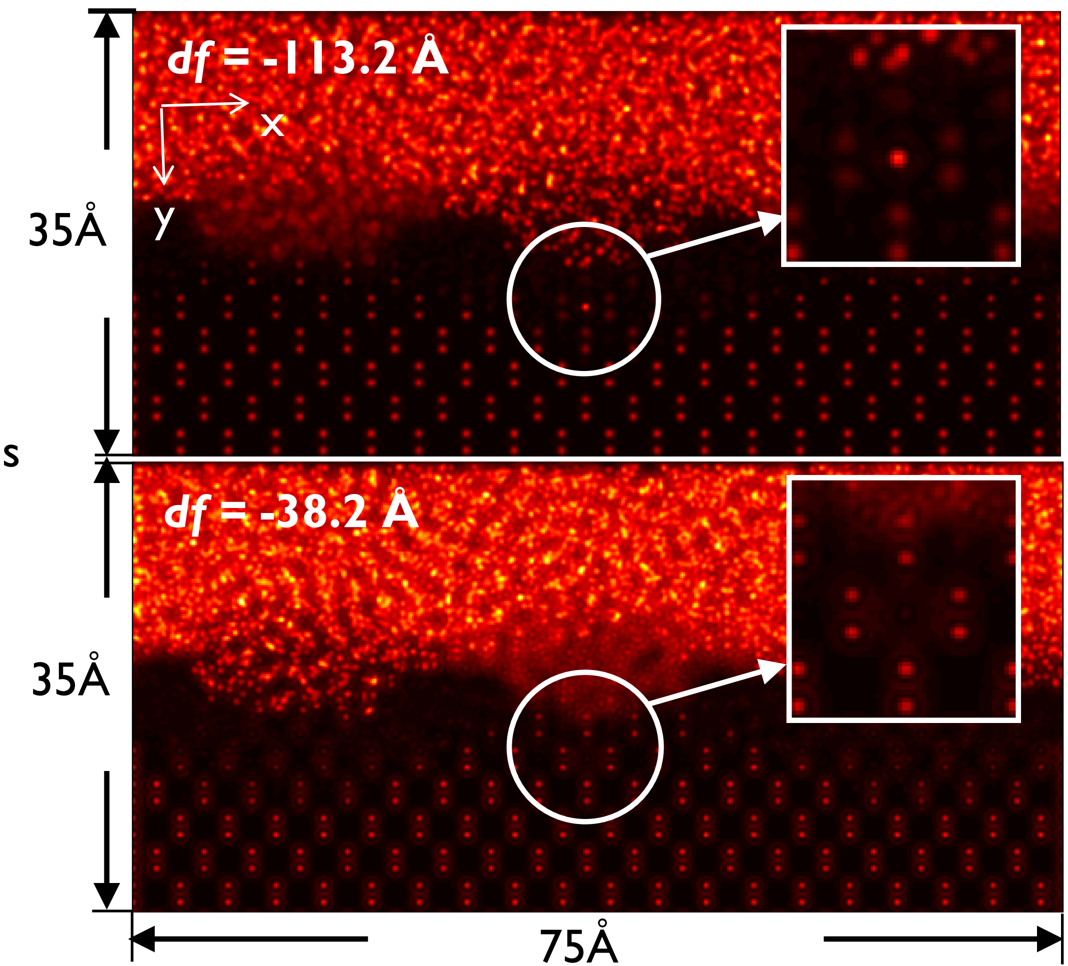
# Depth Sectioning of Impurity Atoms




*Xin, HL and et al, APL. 92, 013125 (2008)*

A 300KeV 23mrad aberration-corrected STEM can reveal the depth profile of a impurity atoms in amorphous layers (no electron channeling). Huolin Xin 2015

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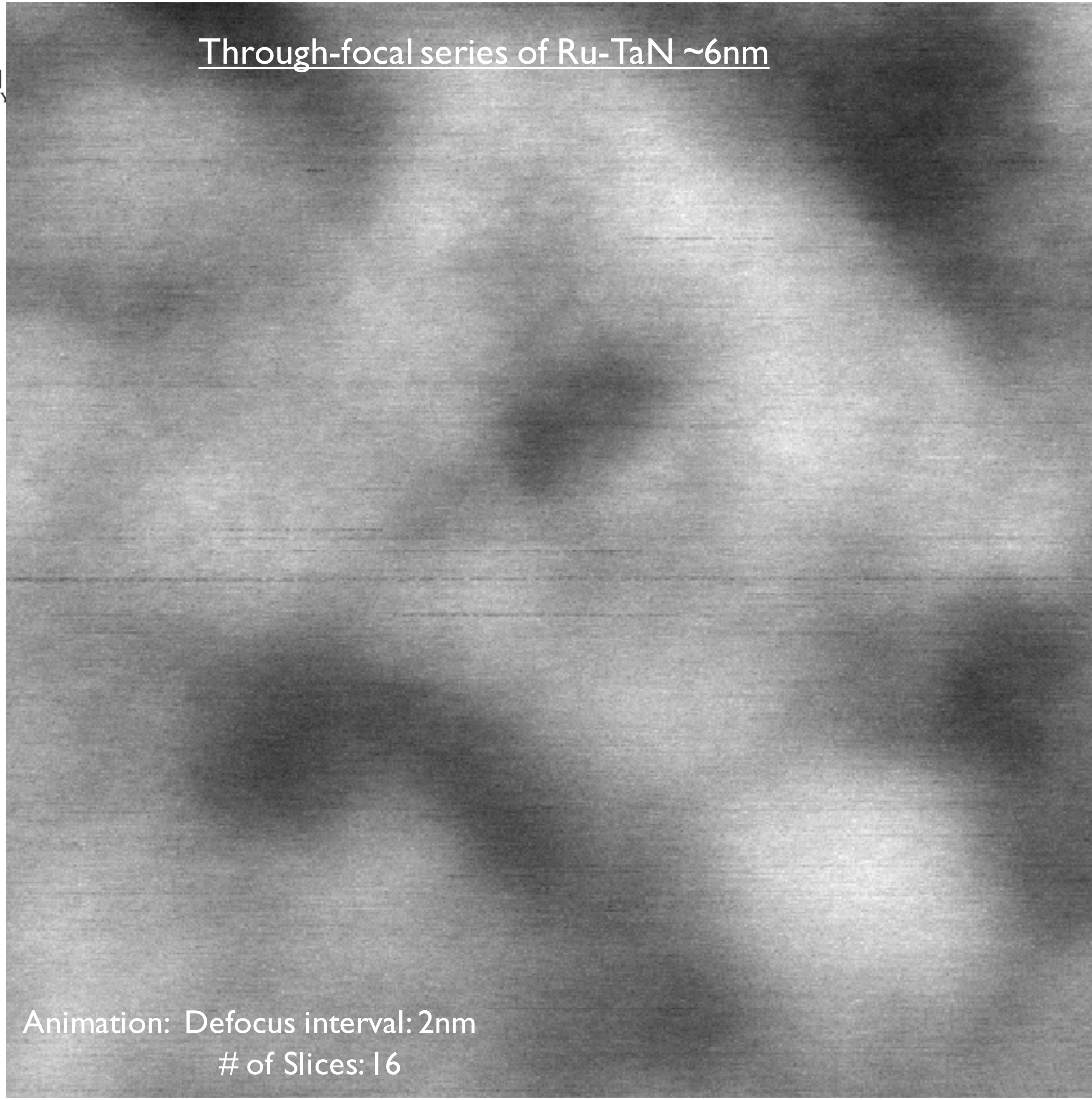
# Through-focal series of Ru-TaN ~6nm

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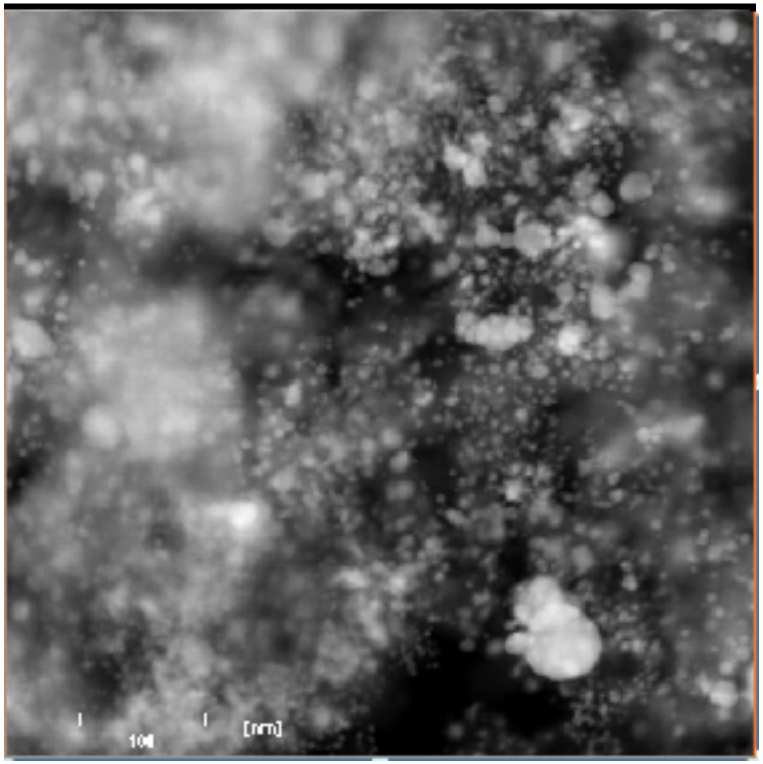
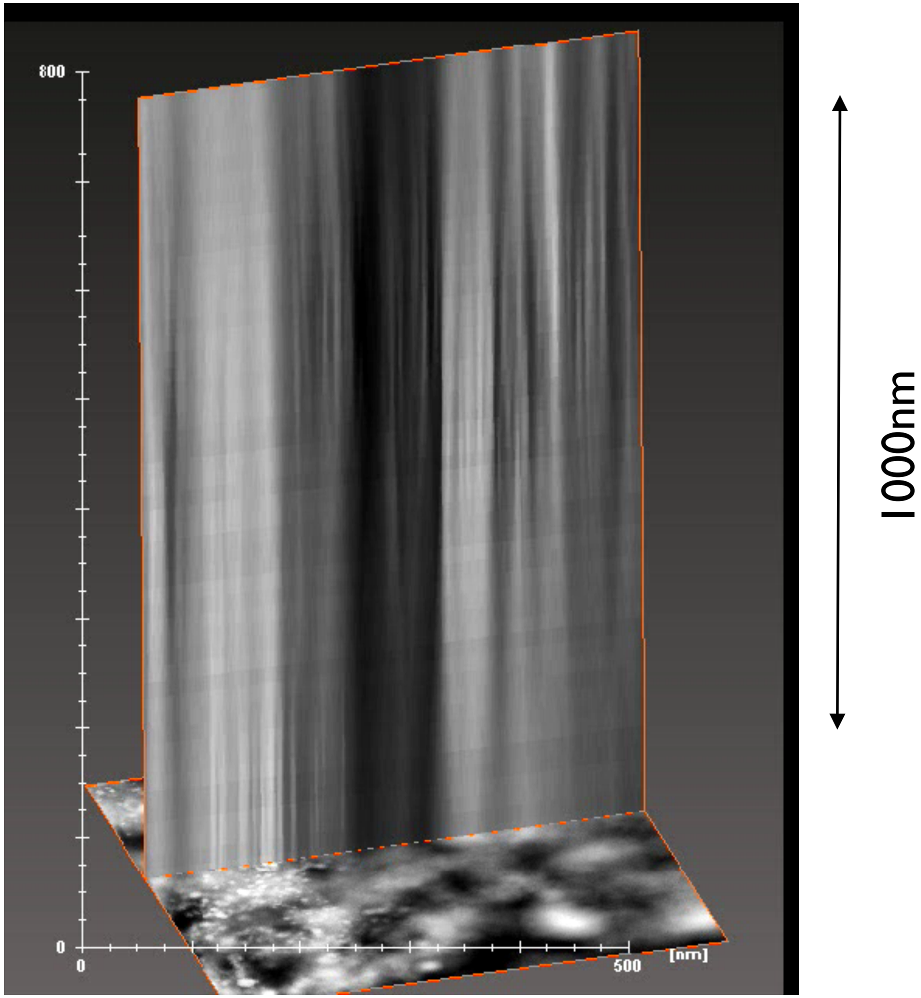
# Reconstruction of Extended Features by ADF-STEM Depth Sectioning

ADF-STEM Through-focal Series
Pt-Co Clusters on Carbon Support




100 KeV, 33 mrad, df = -500-500nm, 51 frames




- 5 nm particles are elongated to a few hundred nanomaters long.

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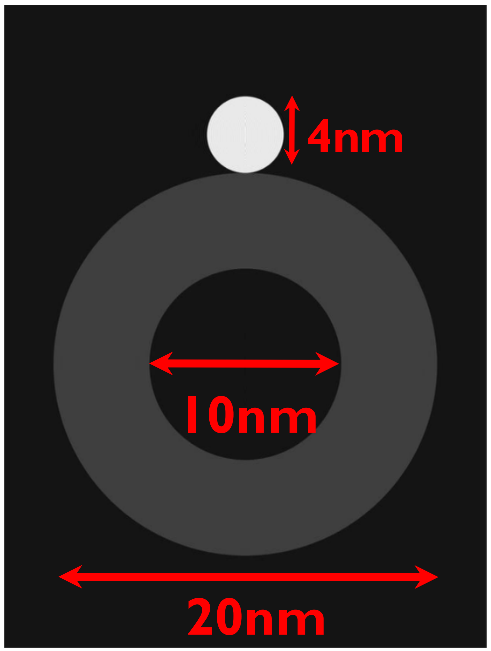
# Depth Sectioning Artifacts: Inside or Outside?

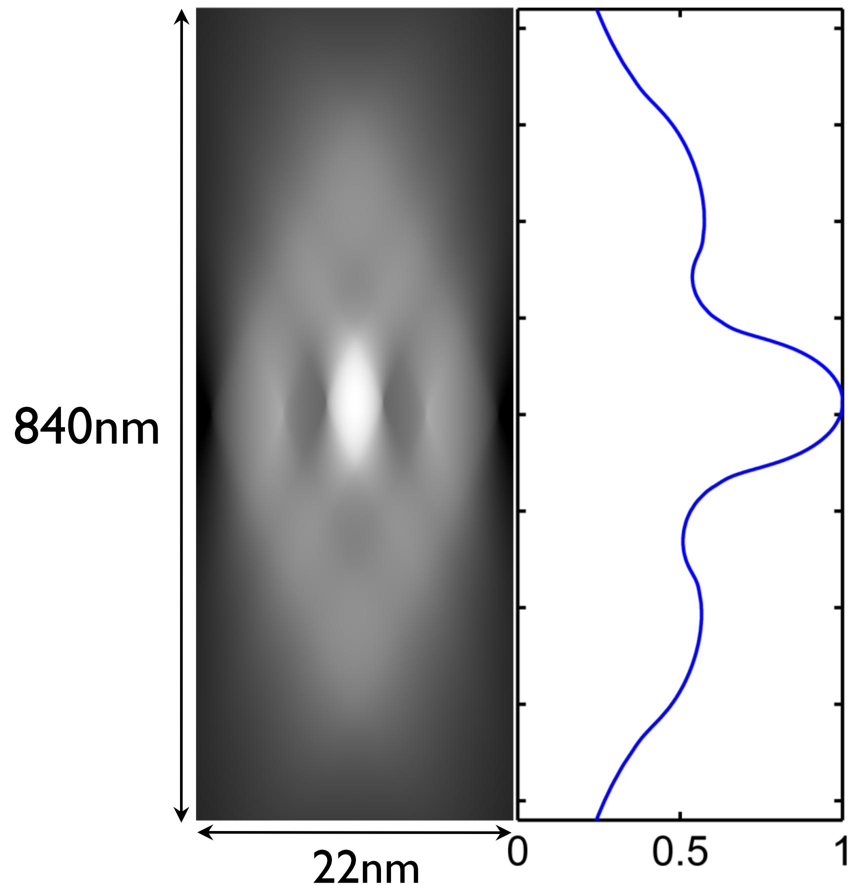
*Original Objects*

Catalyst Particle on a Low-Z Support




*STEM Depth Sectioning*

Z axis compressed by 15 fold

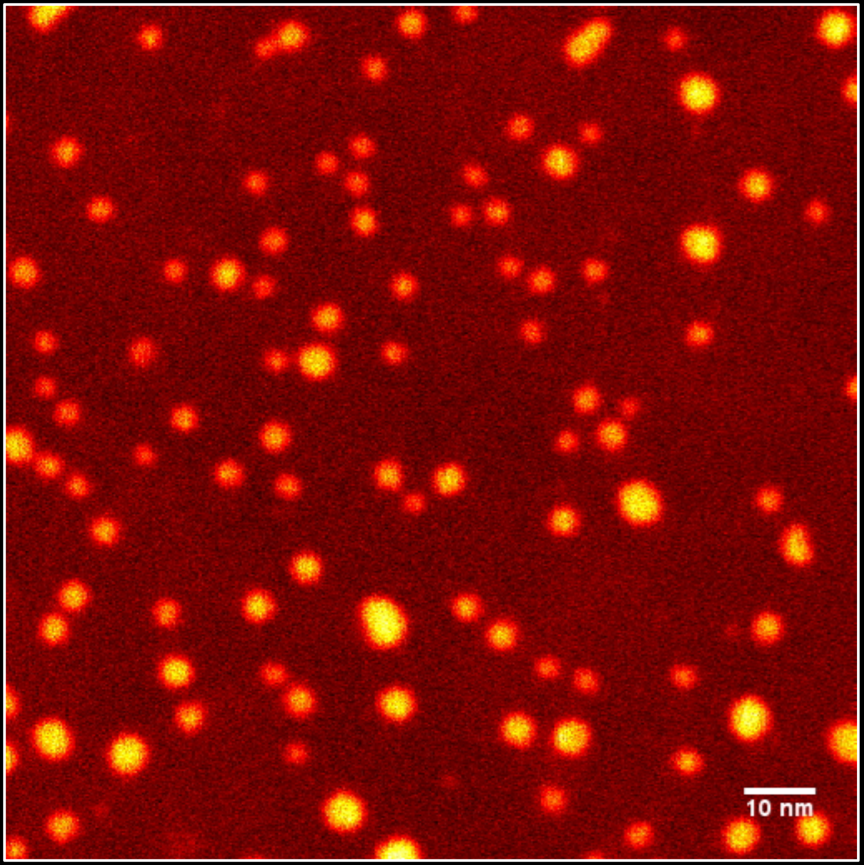



**STEM depth sectioning reconstruction can be confusing and not direct interpretable.**

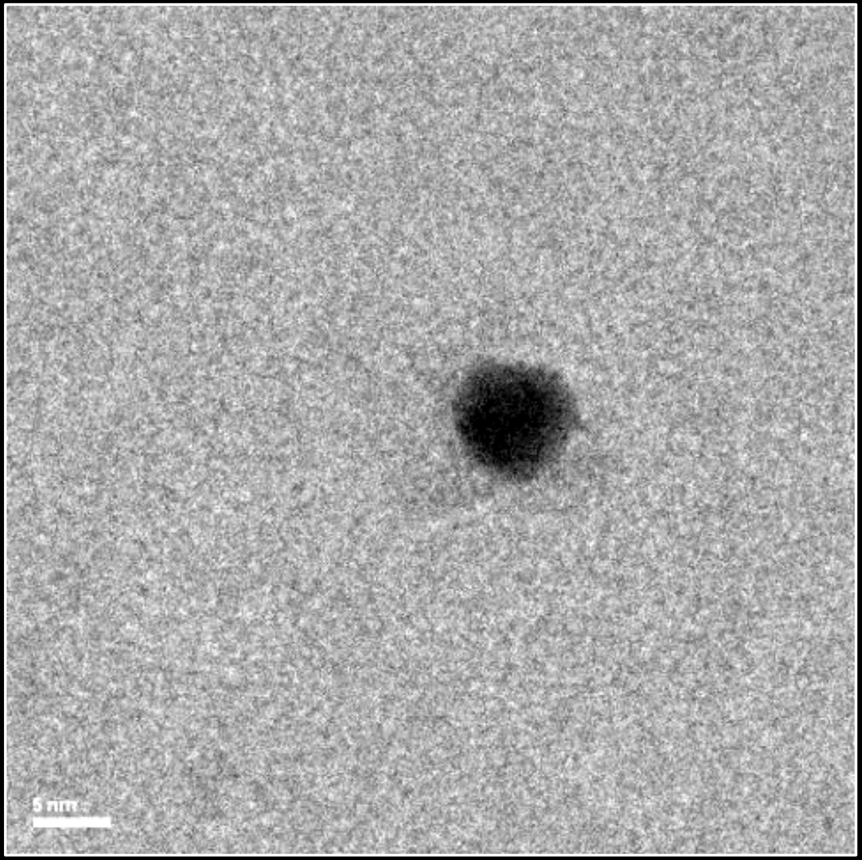
**HL Xin** and DA Muller, Journal of Electron Microscopy, **58**, 157 (2009)

# The T = 0 problem

Focused beam induced coarsening
at (>300 pA)




High-dose imaging in gas
4500/Ang.$^2$/sec




## Is it a pitfall of electrons?

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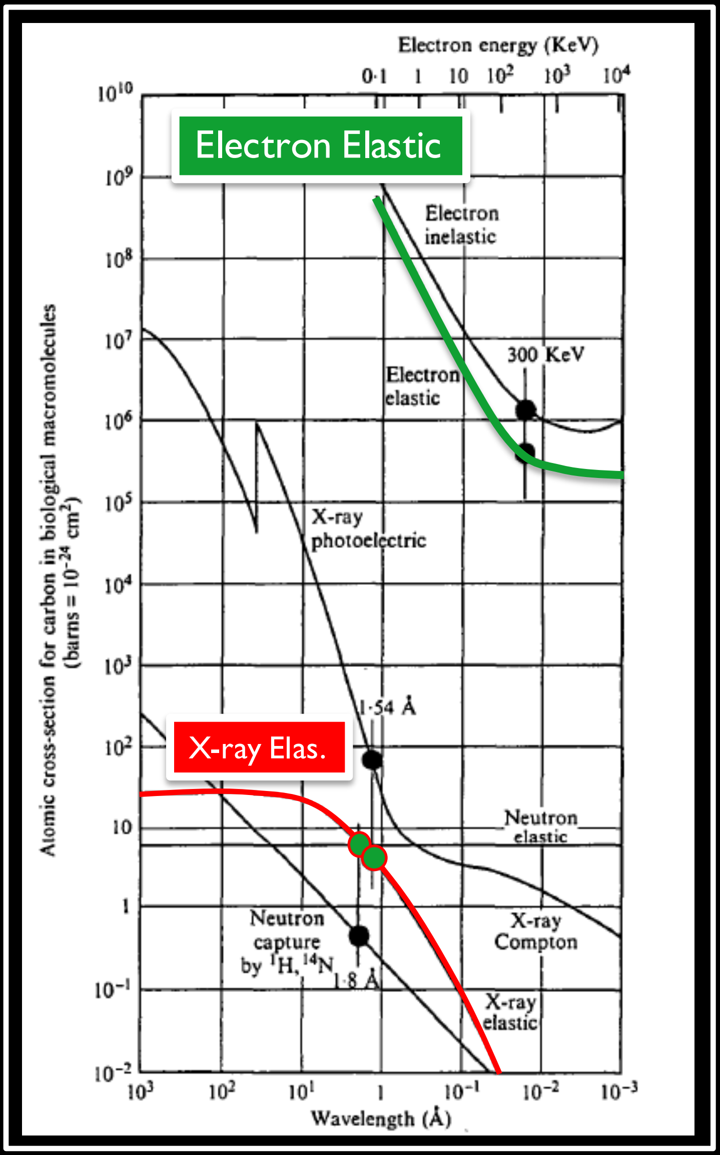
# Fast Electron vs. X-ray




It's not the **cross-section**, but

**How many damaging events per useful imaging event.**

Least Damage

Elastic Imaging – Electrons win

Inelastic imaging – Soft X-rays win

Henderson, *Quarterly Reviews of Biophysics* **28**, 171 (1995)

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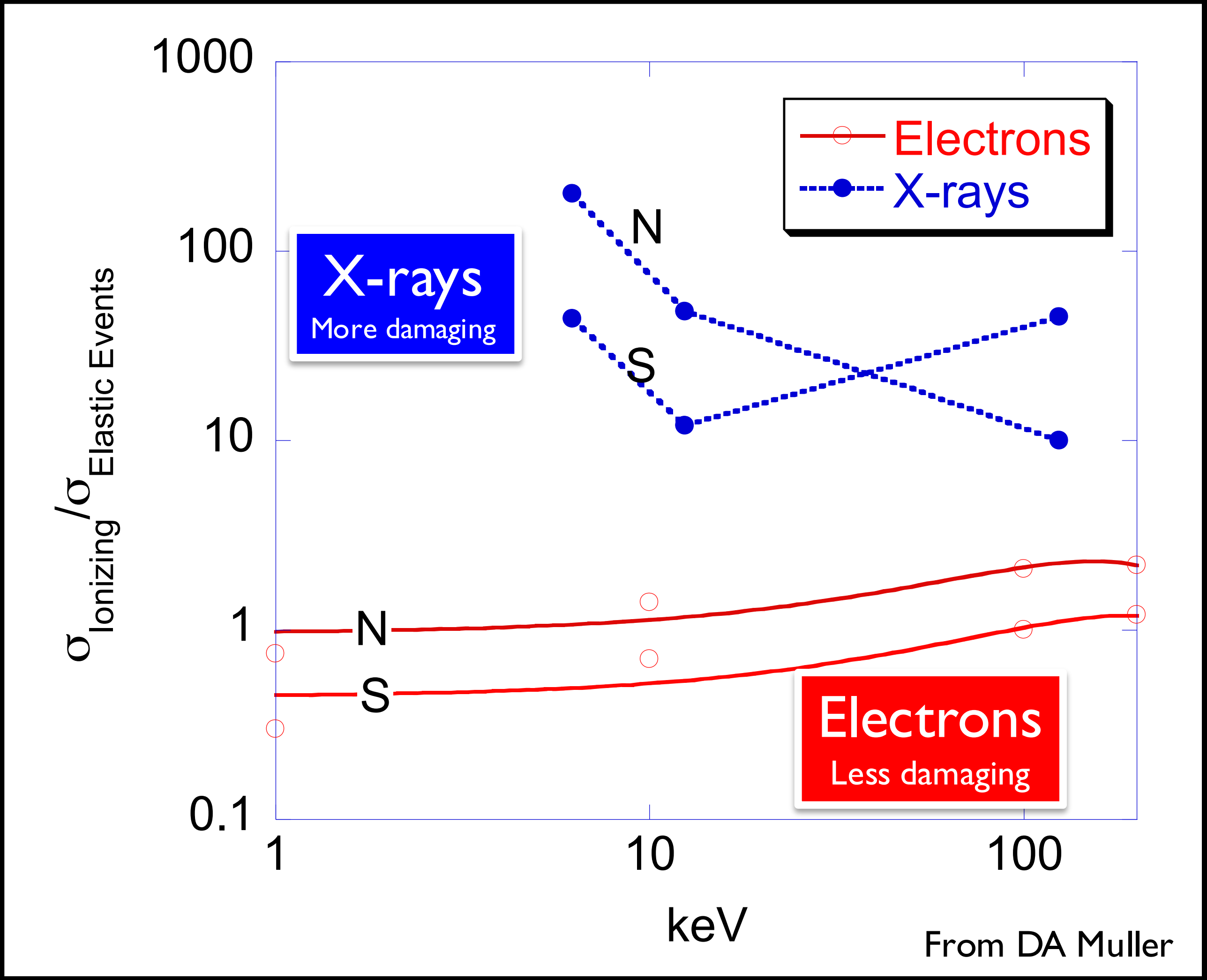
# Elastic information per damaging event (i.e. ionizing event)

Damaging / Useful




More elastic info per damaging event

- Can we do SLAC-type of protein crystallography with electrons?

Data from Breedlove and Trammell, Science 170 (1970) 1310

For electrons $\sigma_i/\sigma_e \sim \ln(E)$

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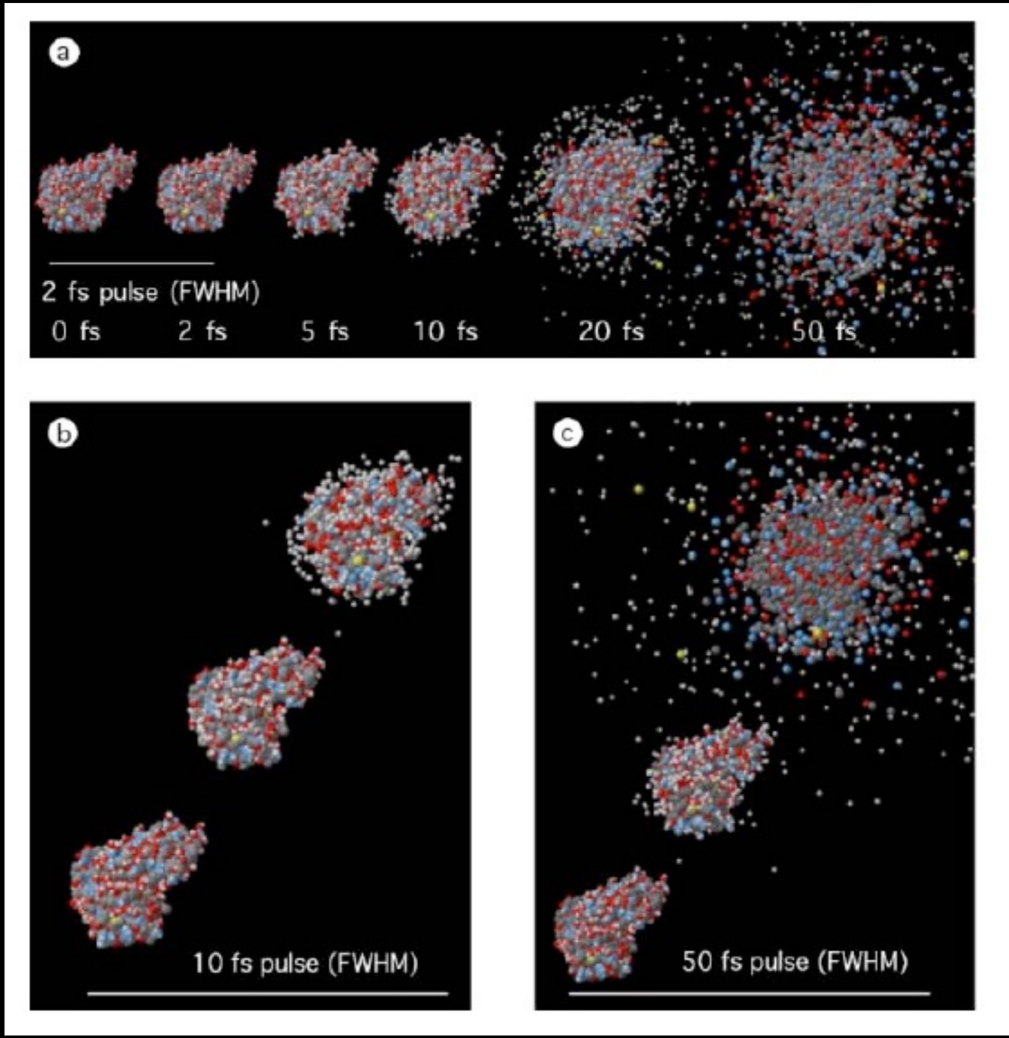
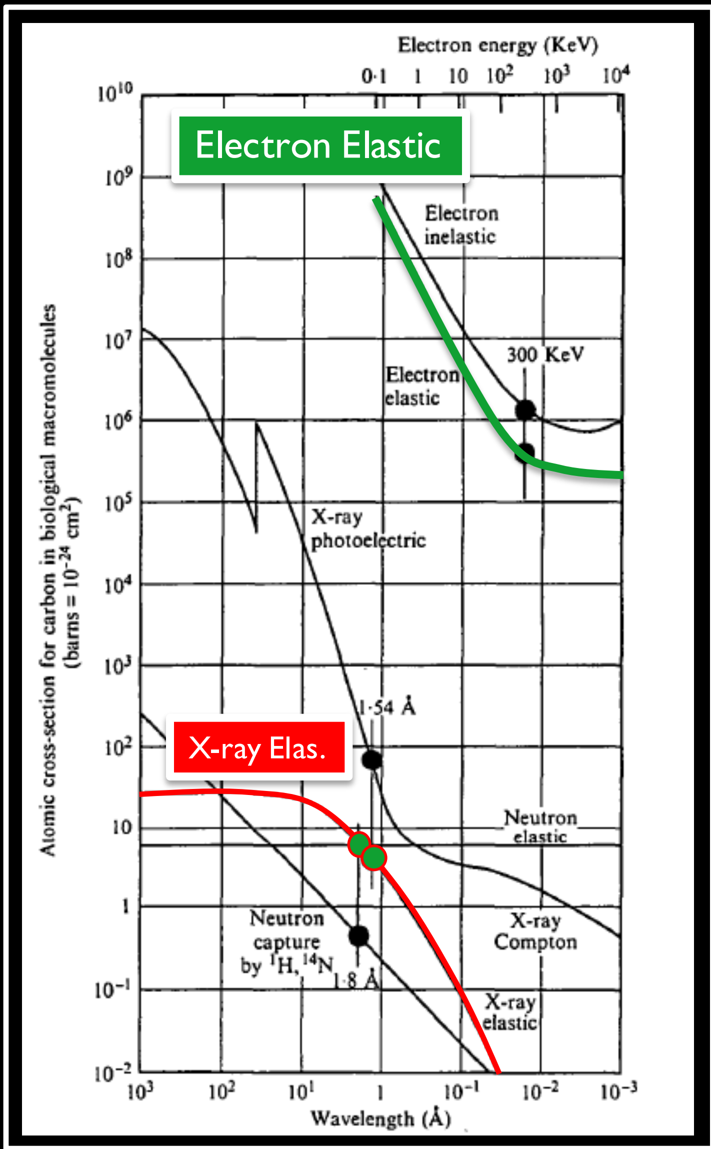
# Can we do Free Electron Laser-type of protein crystallography with short electron pulses?



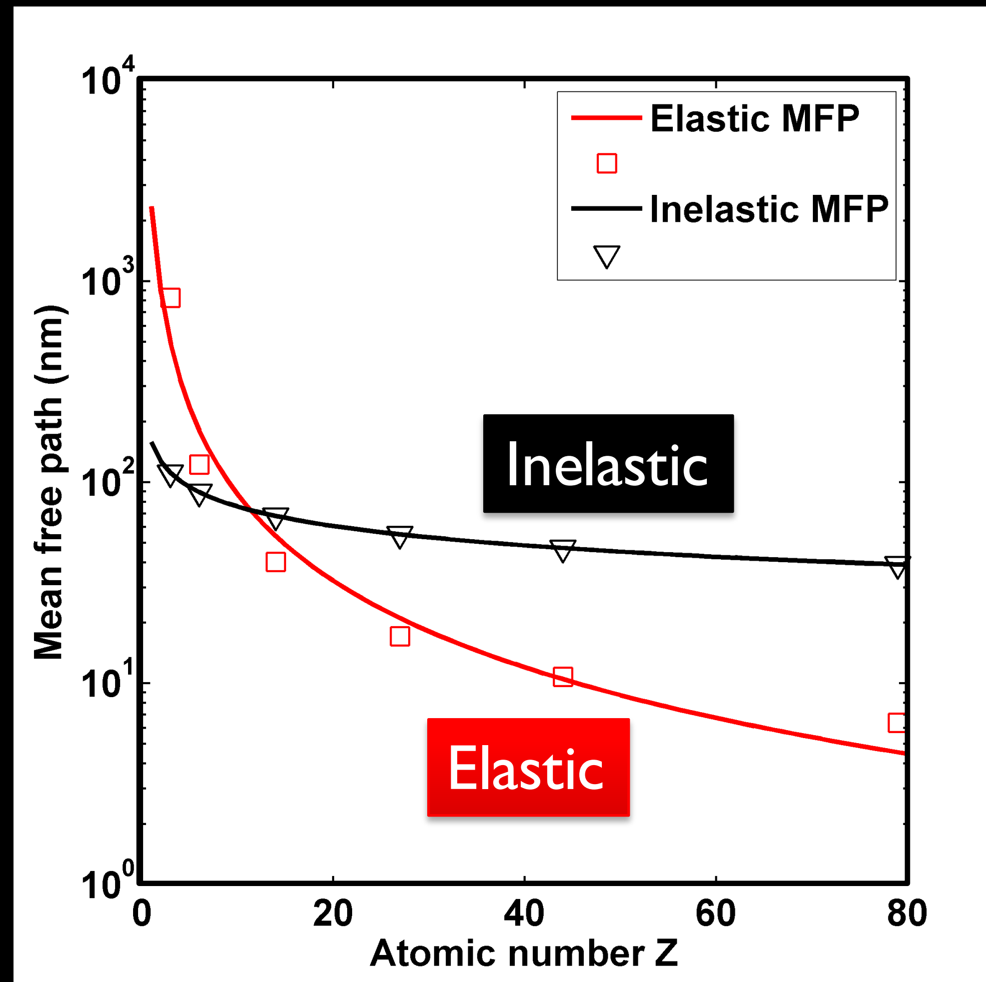

Proceedings of FEL 2006, BESSY, Berlin, Germany

- We have really good lateral and longitudinal **coherence** with electrons
- What are the limitations?

# Electron Mean Free Path




Mean free path for 100 keV electrons




Henderson, *Quarterly Reviews of Biophysics* **28**, 171 (1995)

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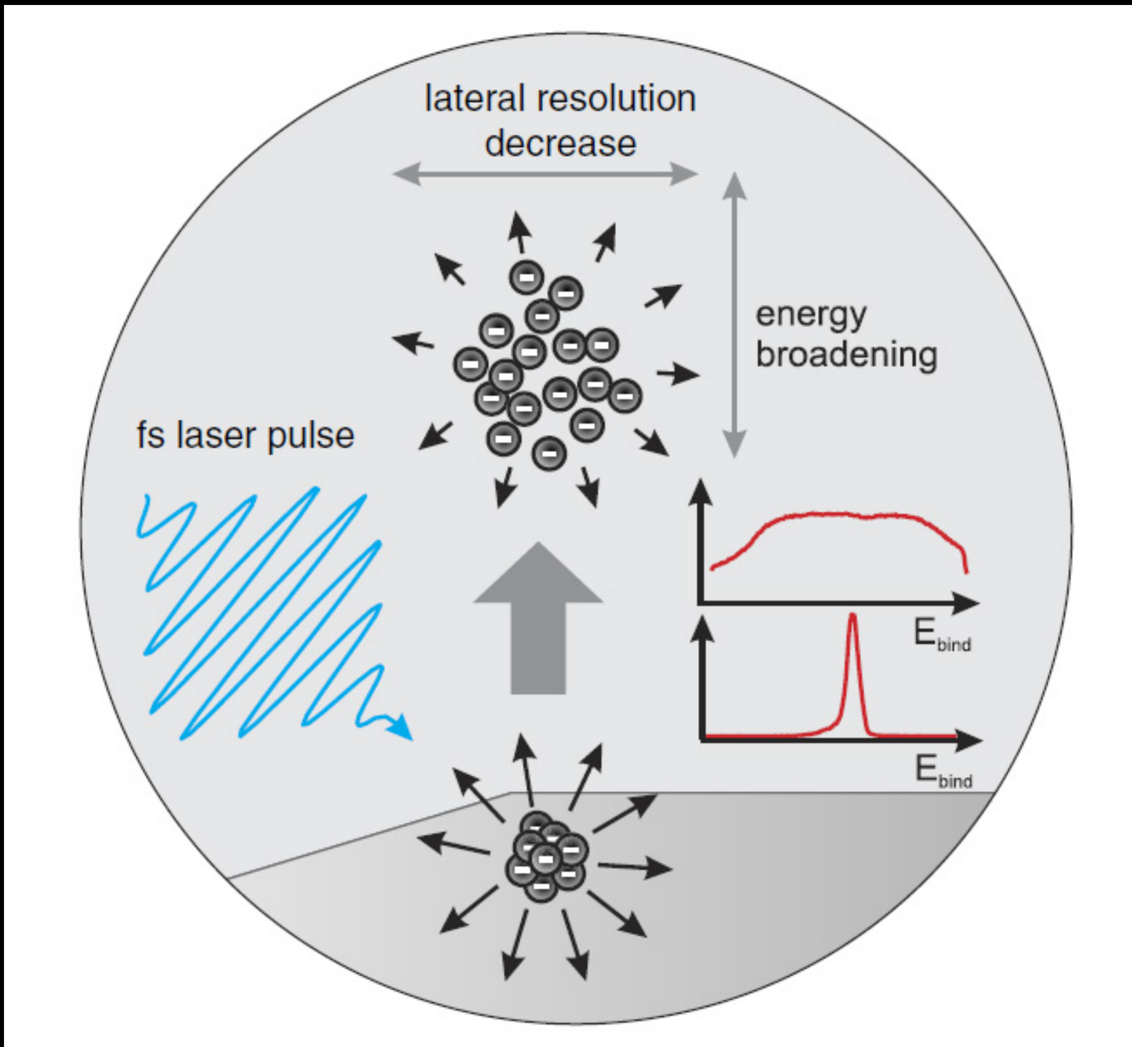
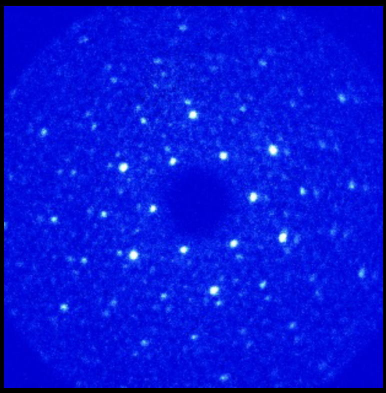
# Difficult Using Electron Pluses due to the Space Charge Effect



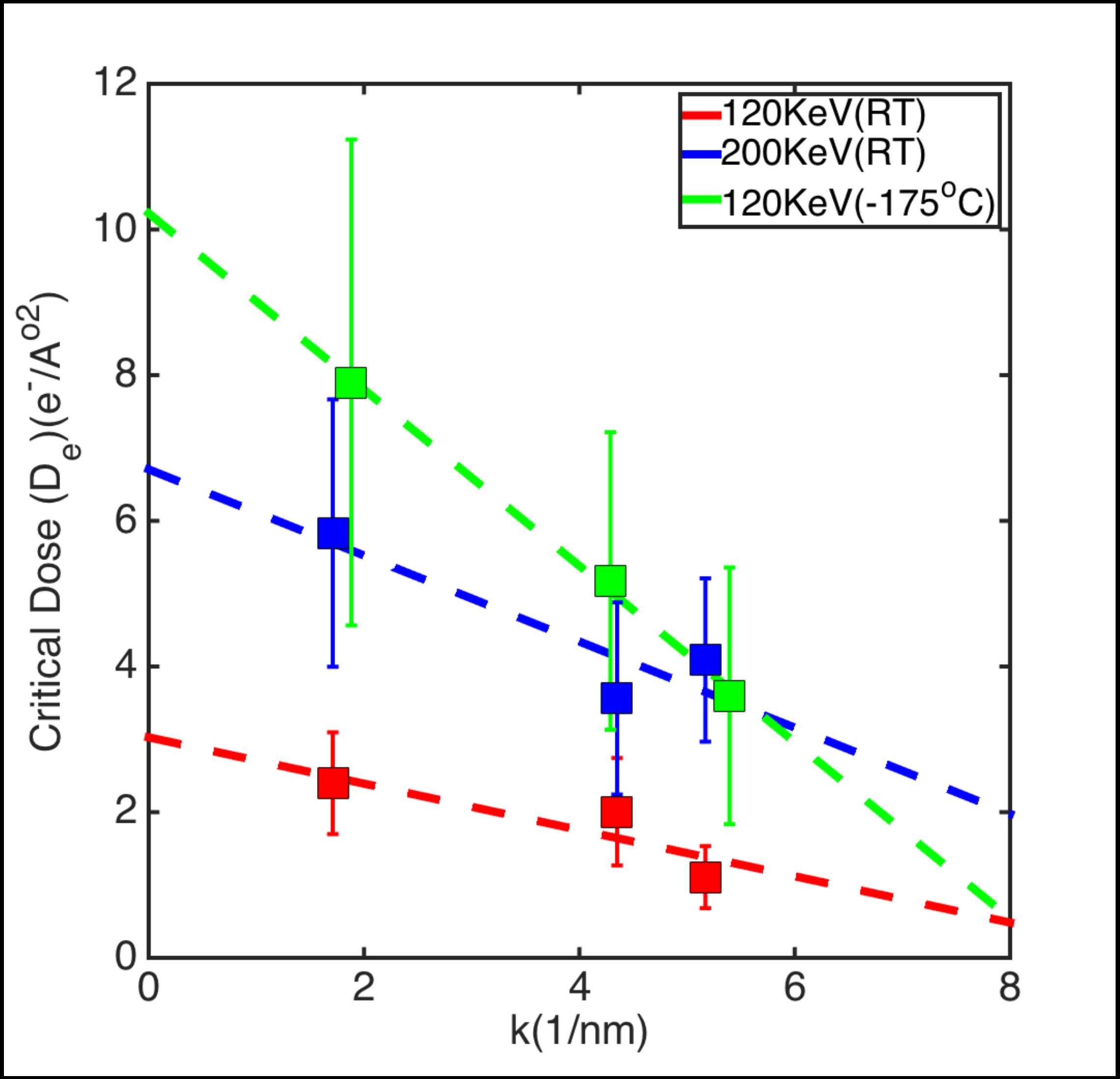

J. Phys.: Condens. Matter **21** (2009) 314003

- The temporal width of the electron pulses decreases quickly with the number of electrons



XJ Wang, J. Hill, and Y. Zhu et al, arXiv:1304.5176
Diffraction Patter of 1T-TaS2
40-120 fs single pulse of 3x10^4 2.8 MeV electrons

# Diffract but not Destroy




Critical dose is low,

but elastic scattering cross section is large.

Ratio between useful event vs. damaging event is high.

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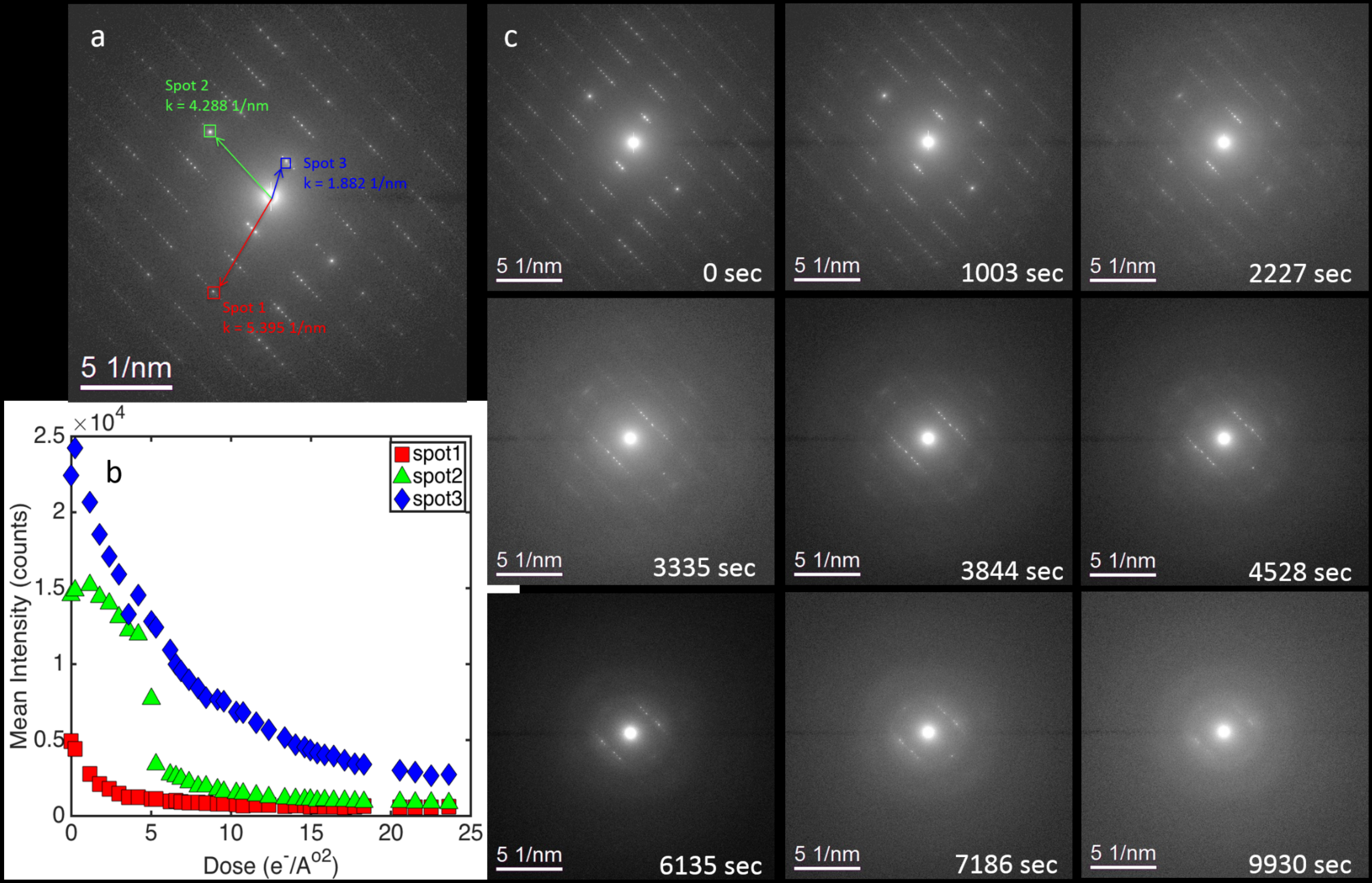
# Diffract but not Destroy

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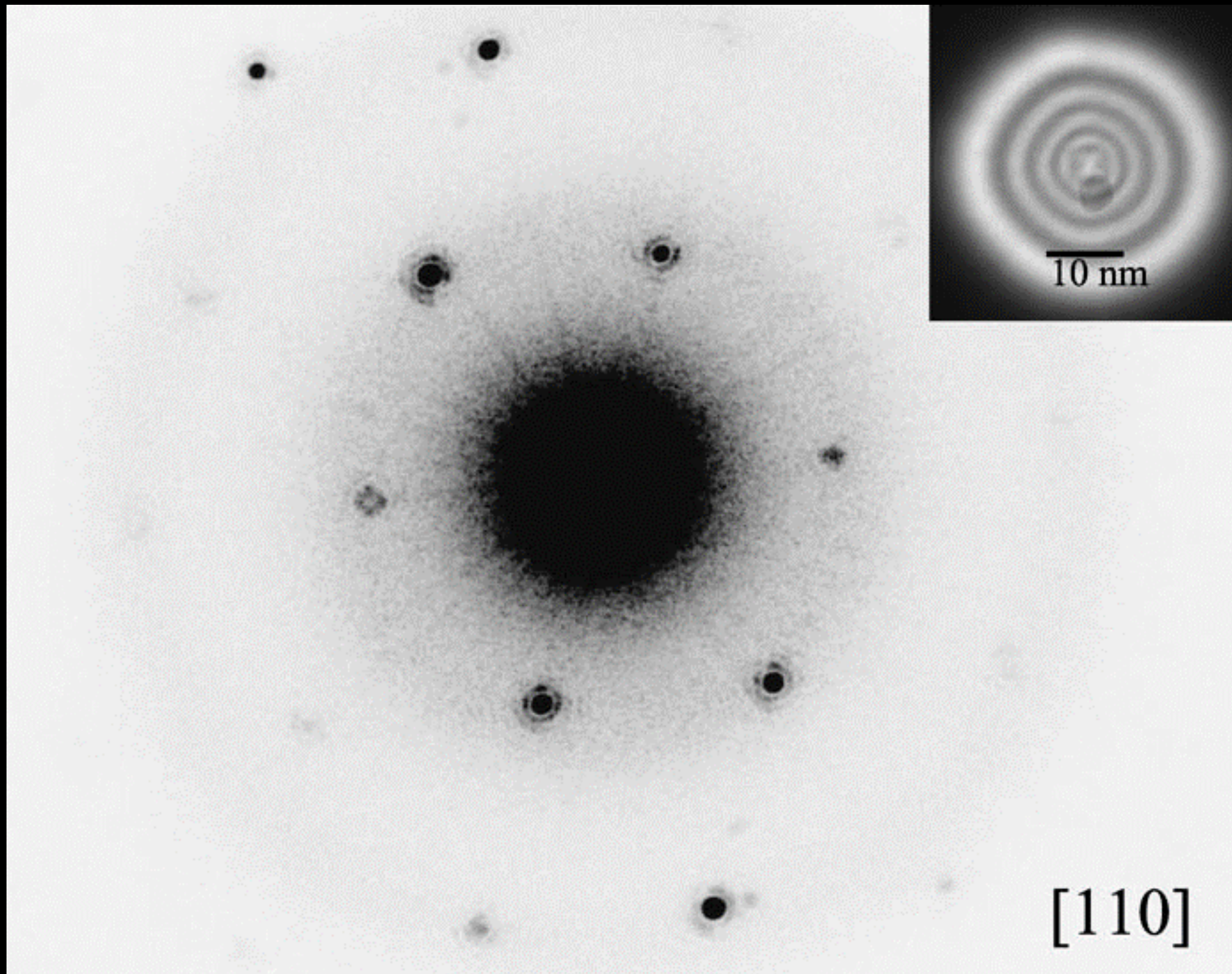
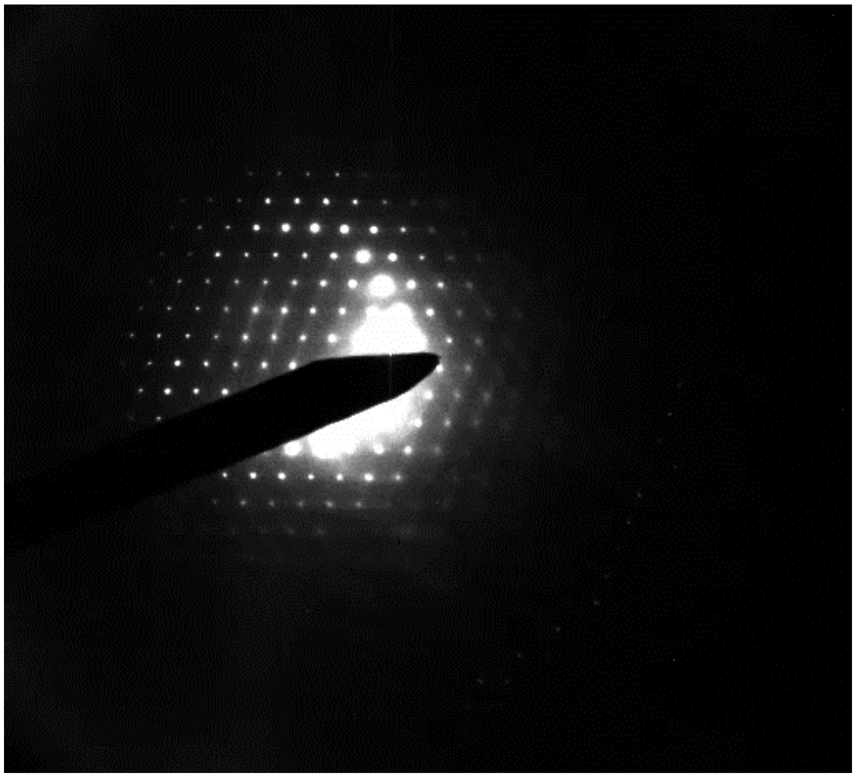
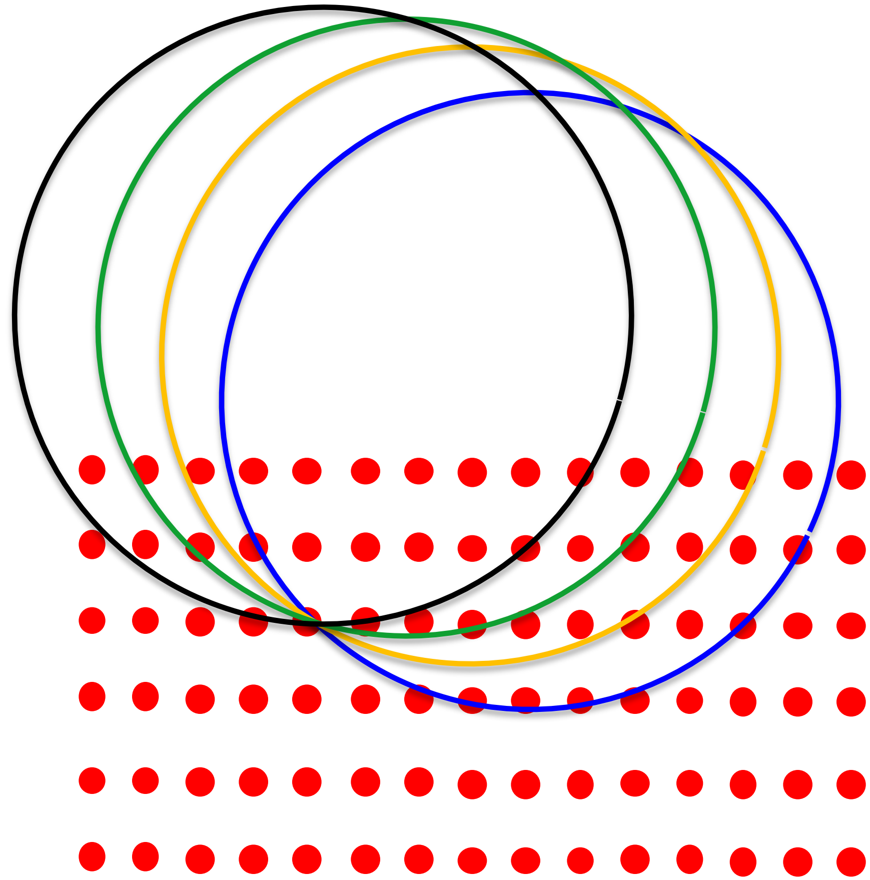
# Coherent diffraction from a single nanoparticle



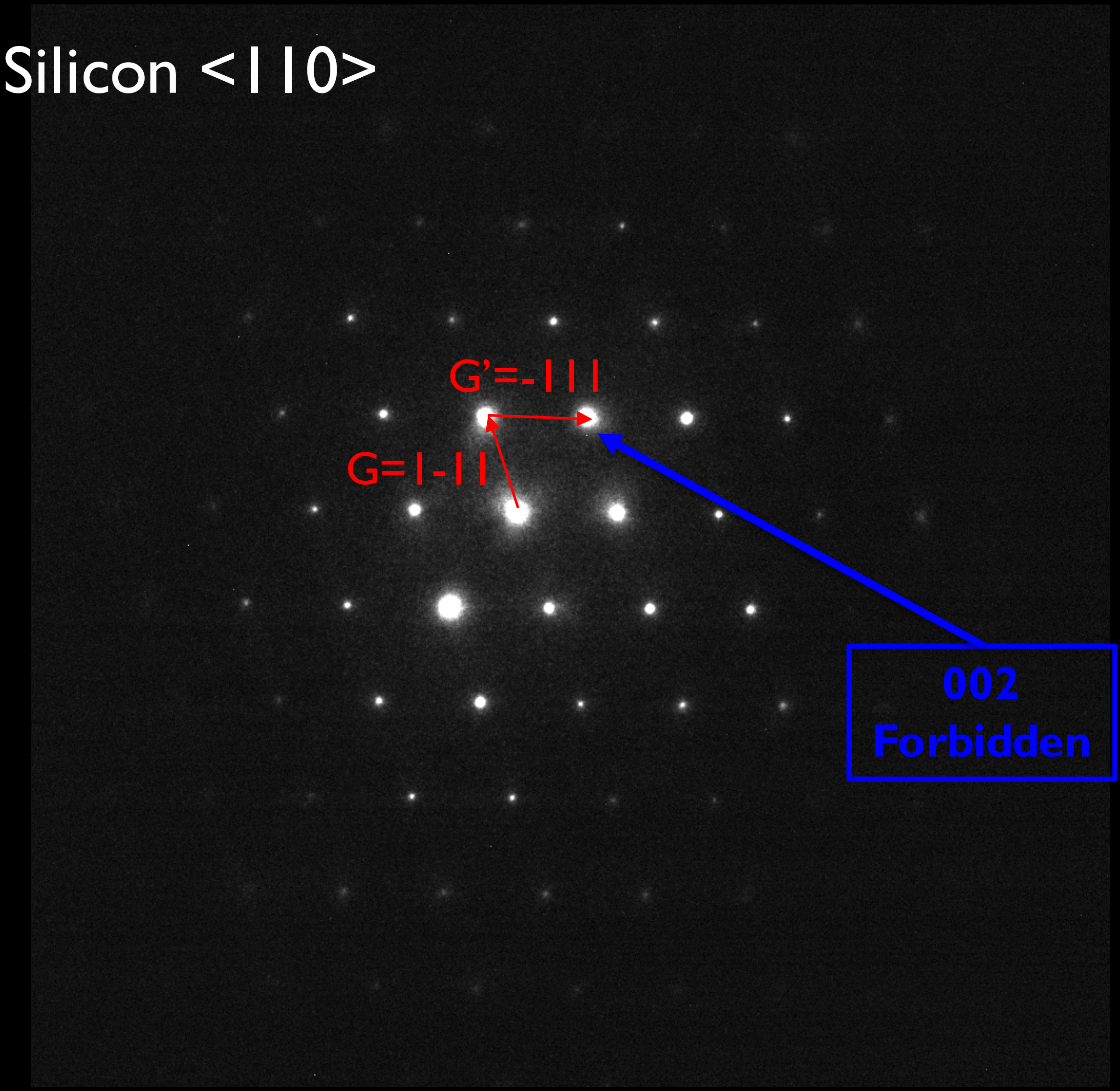

JM Zuo, Chapter on ELECTRON NANOCRYSTALLOGRAPHY

# Passing though a zone axis





# Electron Diffraction is Highly Dynamical

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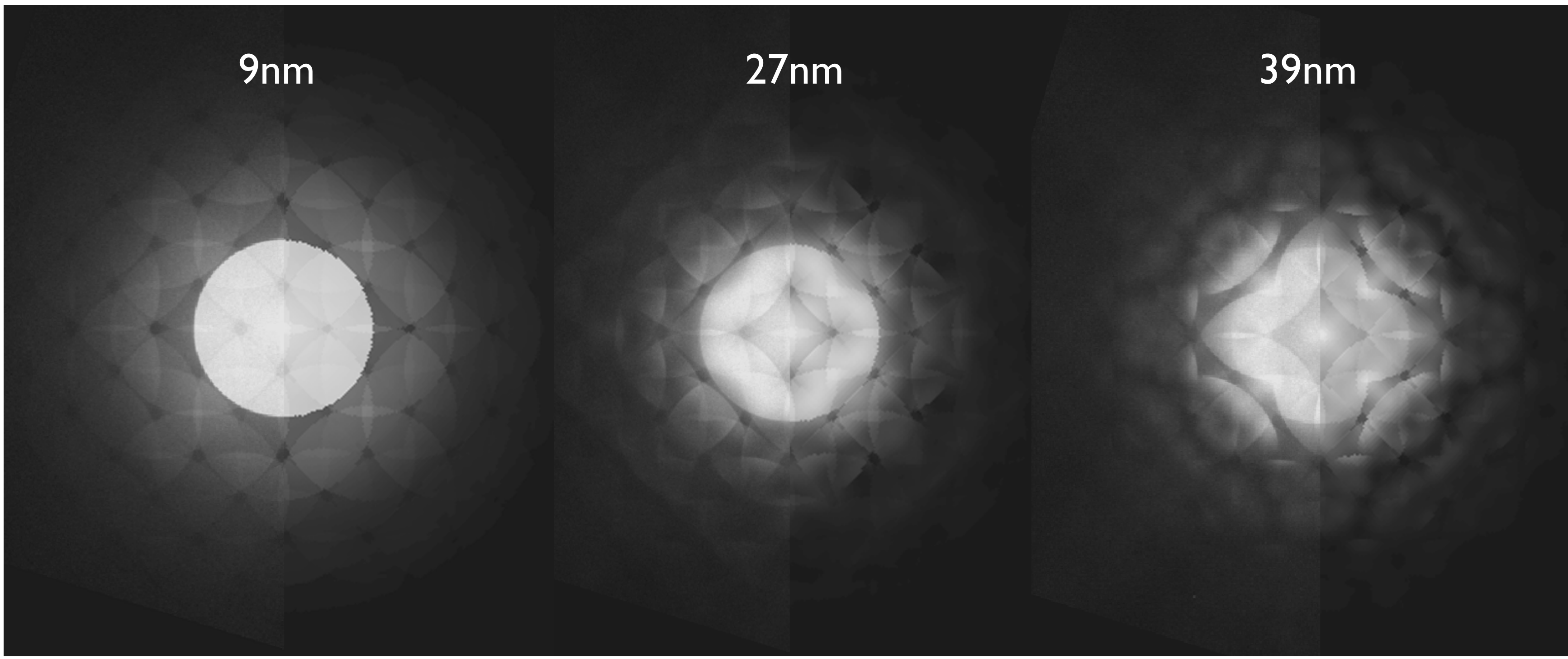
# Thickness fringes




Thicknesses determined by comparing position independent CBED (scanning probe CBED) with Block-wave CBED simulations.

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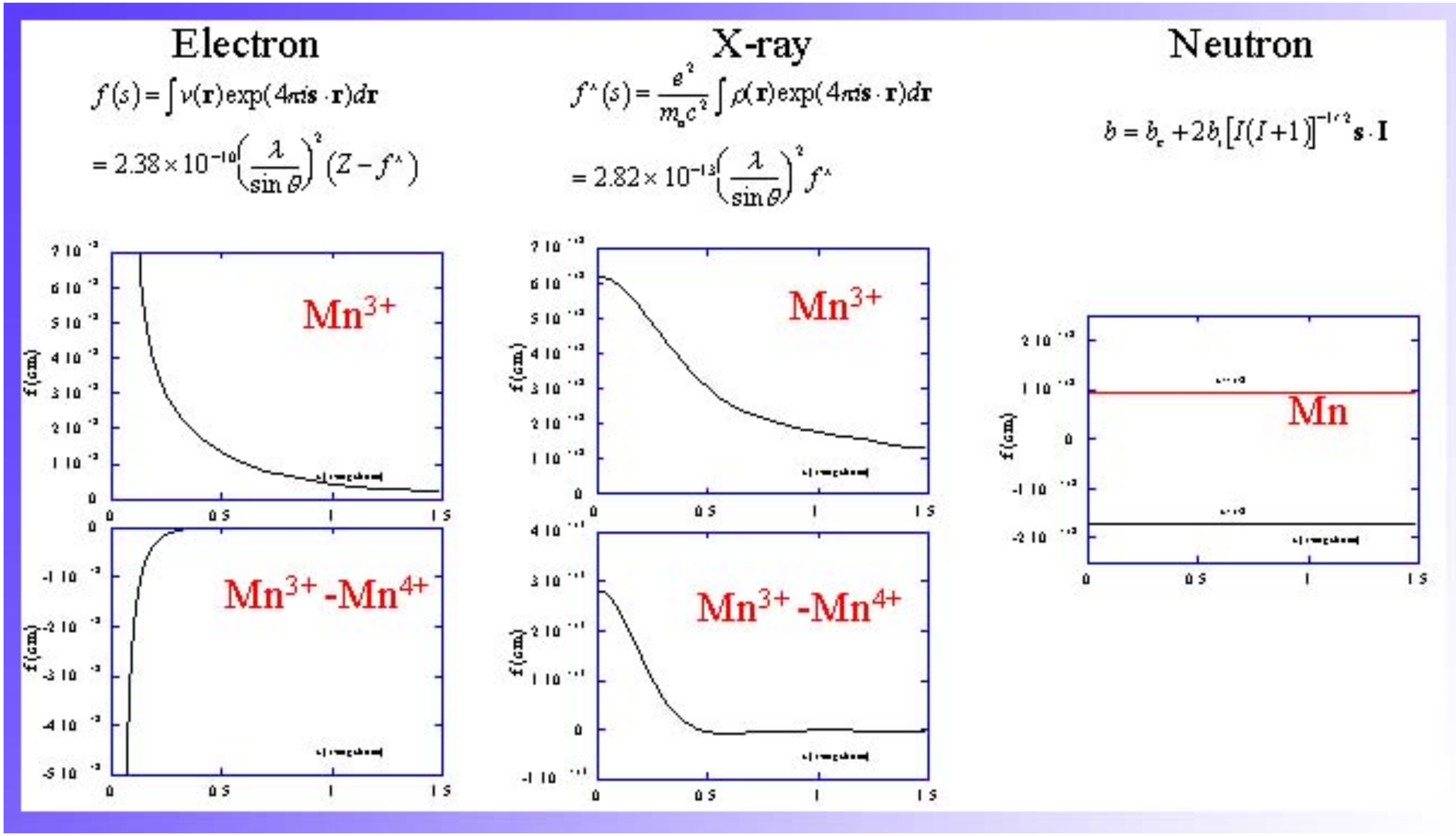
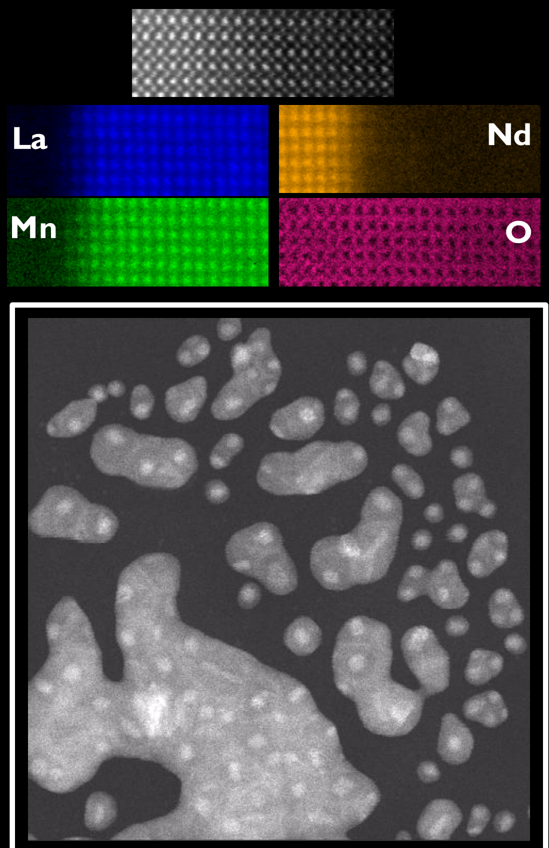
# Electron diffraction is sensitive to the change in lower-order structure factors.

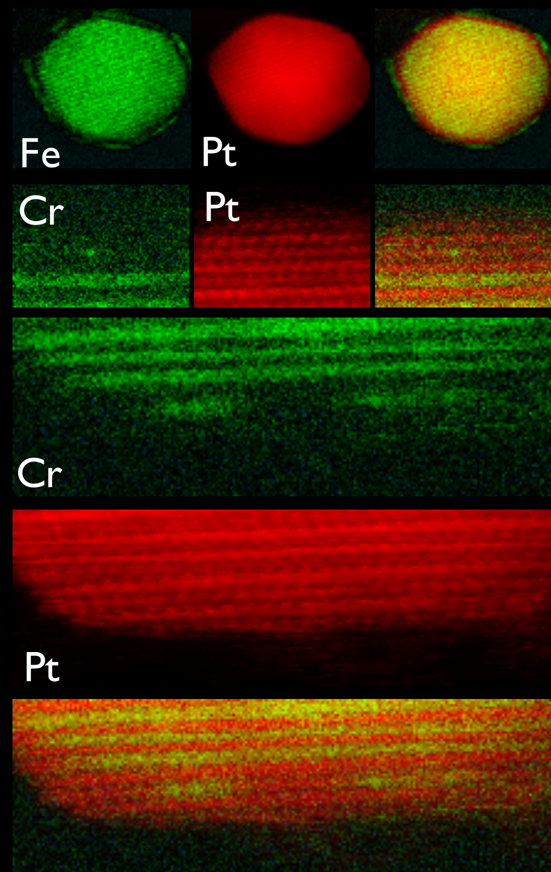


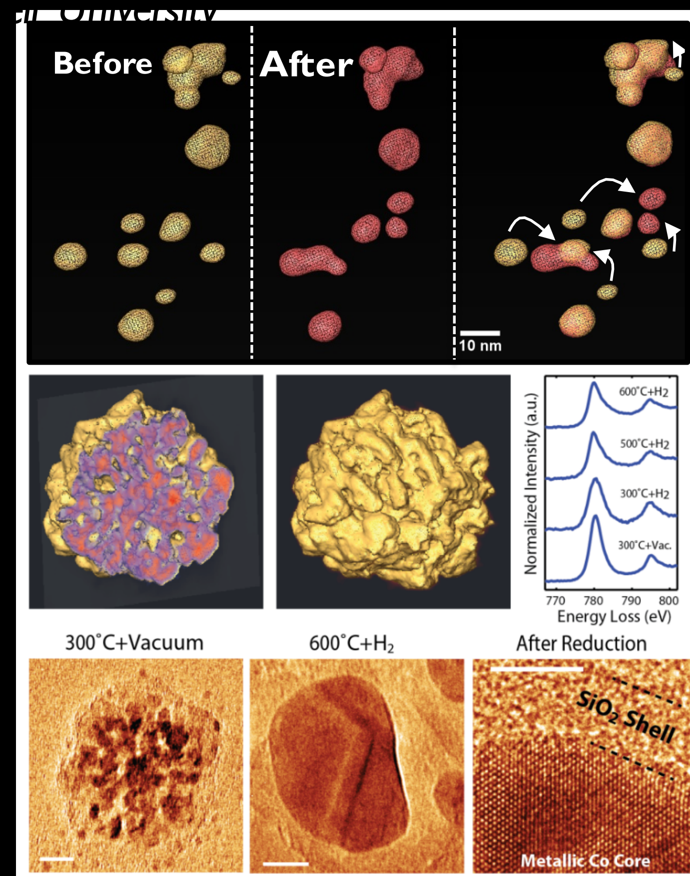

http://cbed.matse.illinois.edu/

- Quantitative electron diffraction is good for charge density reconstruction in a wide range of crystalline/poly-crystalline materials (sensitivity + spatial resolution)

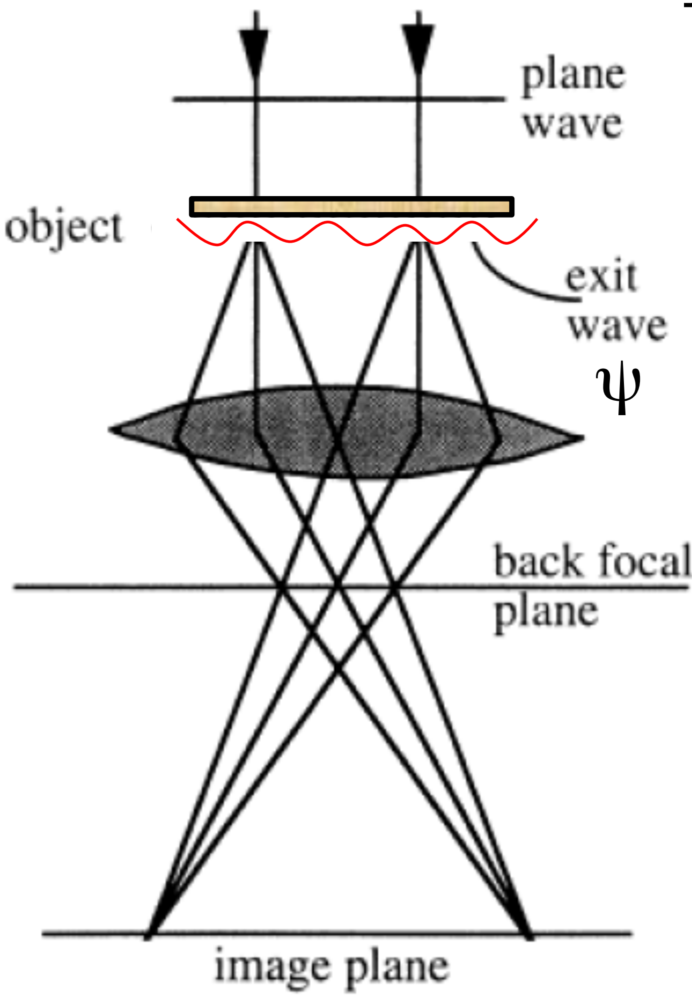
# Atomic-Resolution Spectroscopic Imaging and In Situ Environmental Study of Bimetallic Nanocatalysts



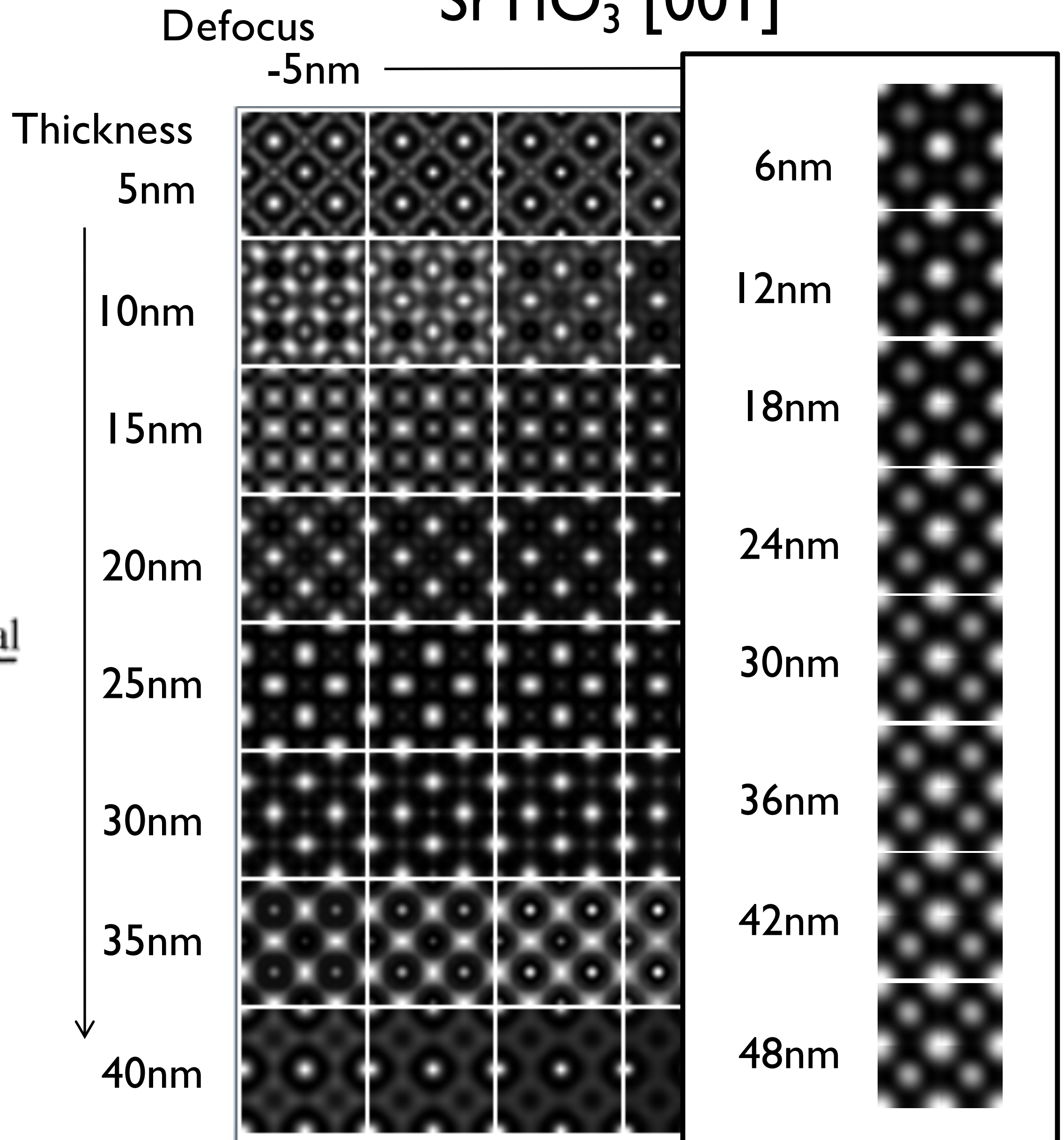



# Coherent Imaging (HRTEM) is Confusing




$|\psi \otimes P|^2$

## $SrTiO_3$ [001]

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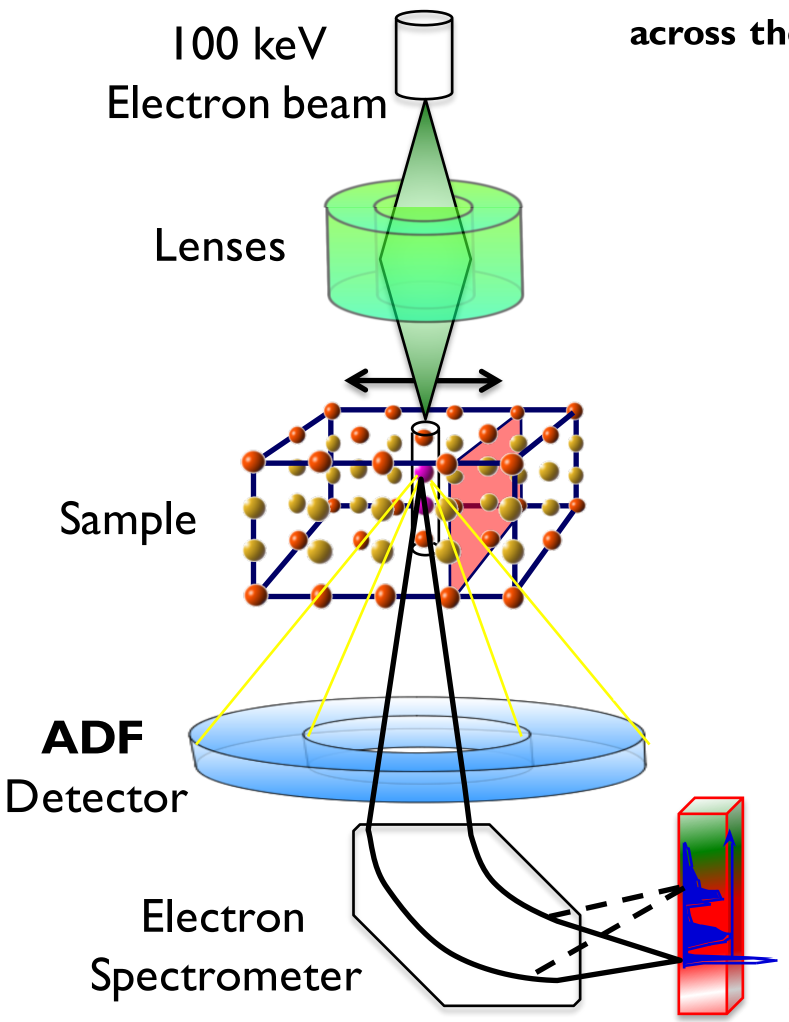
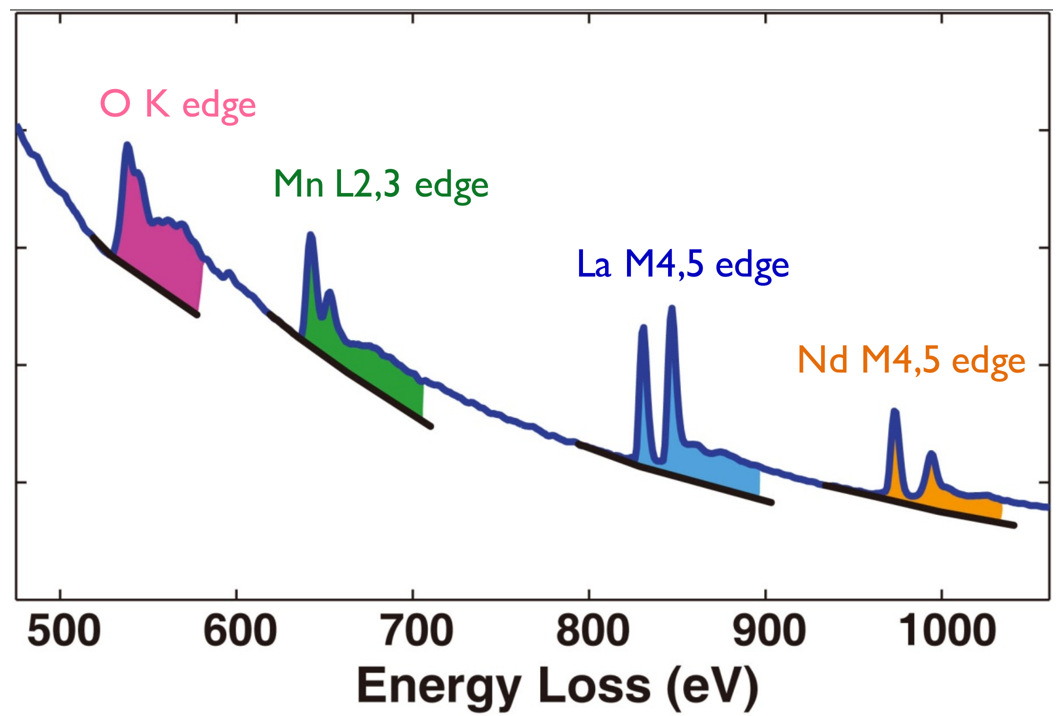
# Scanning Transmission Electron Microscopy

**1 atom wide (1 Å) beam is scanned across the sample to form a 2-D image**




Inelastic Scattering

**EELS**: Chemical Imaging

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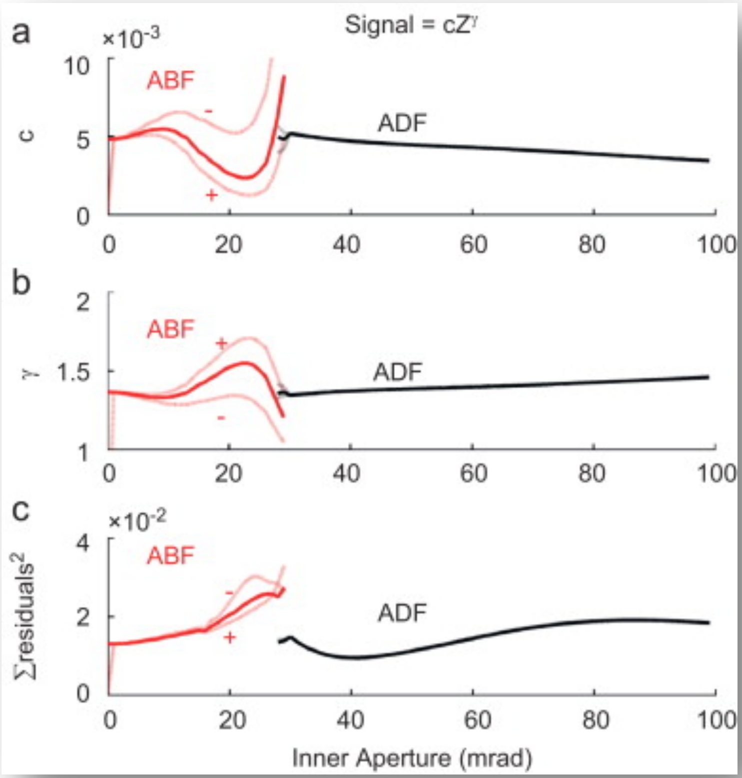
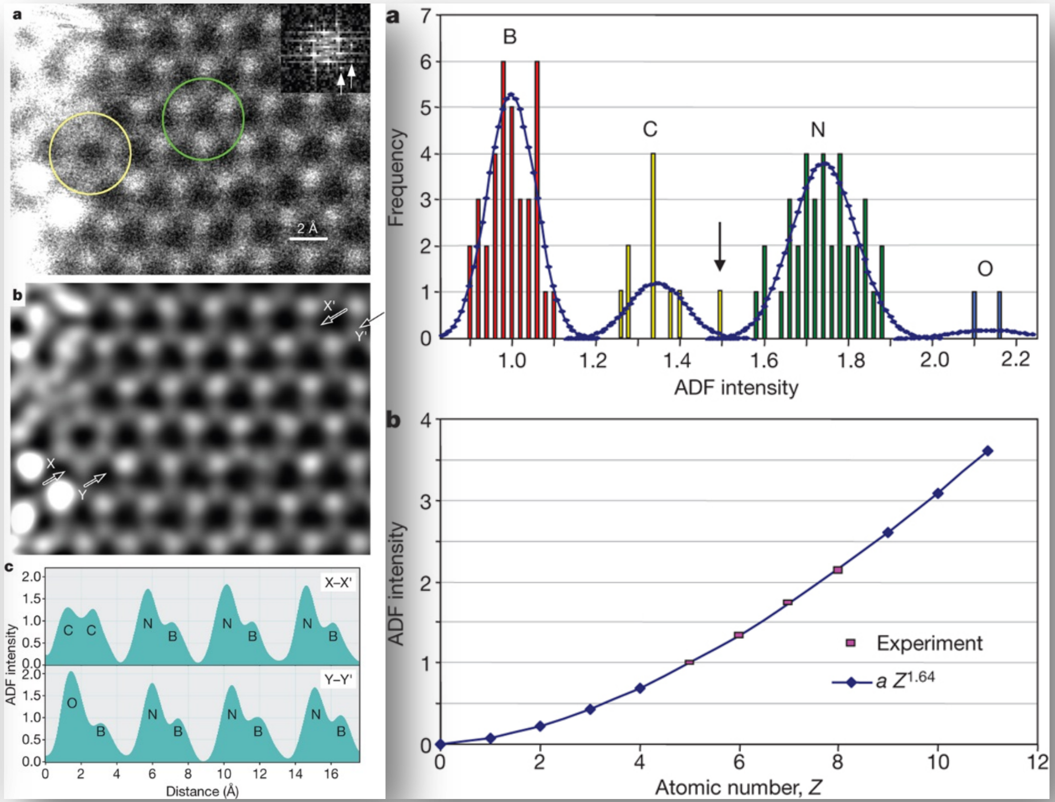
# Application of "Z-Contrast" – $Z^{\gamma}$

Thoery




Hovden et al, Ultramicroscopy 123, December 2012, Pages 59–65

Krivanek et al, Nature **464**, 571-574 (25 March 2010)

ADF detector (outer angle=240 mrad) varies with inner angle for a 60 keV STEM (convergence angle 30 mrad, $C_{S3}$=−0.018 mm, $C_{S5}$=20.0 mm, $df$=−30.4 nm).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# Not always "Z-Contrast"
# Caveat: Low-angle ADF and Strain Fields

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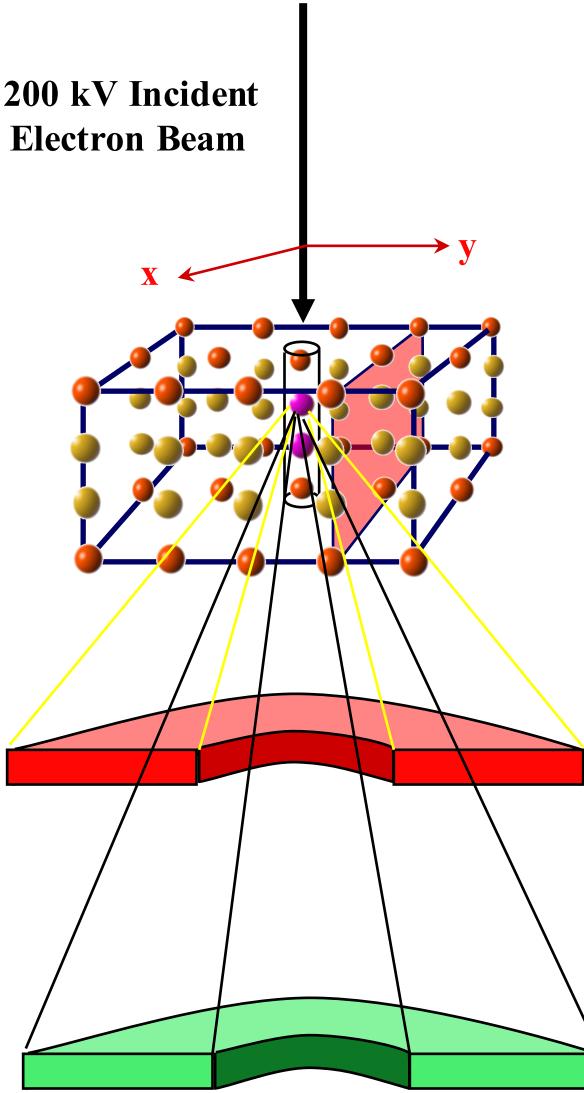
( grow 25 layers of $SrTiO_{3-\delta}$ on $SrTiO_3$, $\delta$=0.13 )

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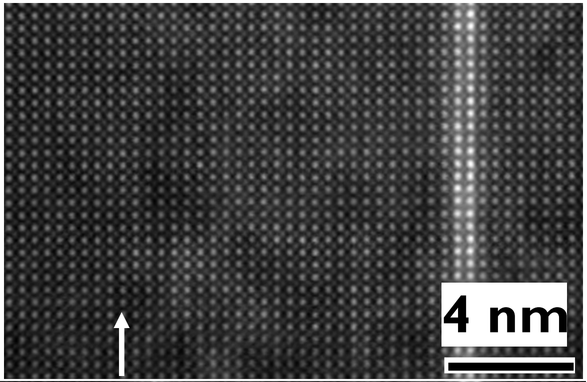
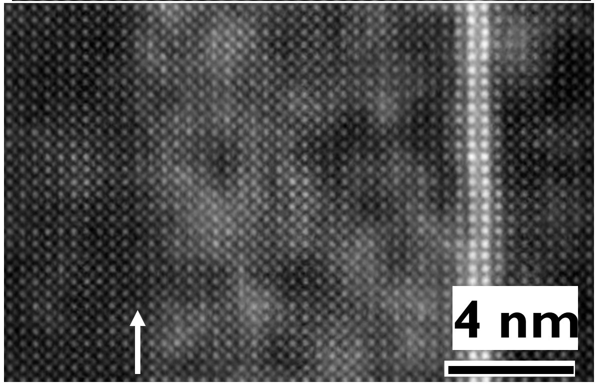
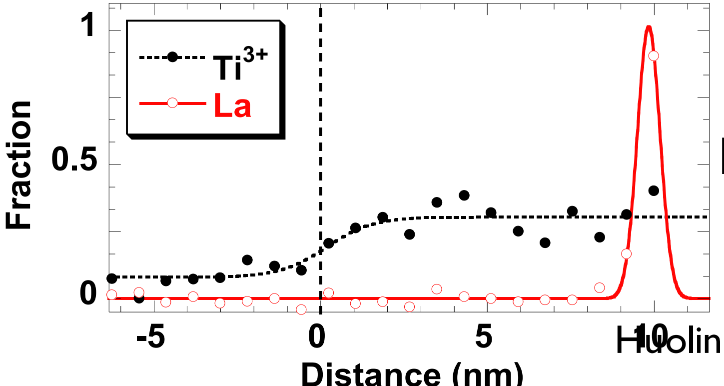
Collecting low anlge signals

HAADF
"Z" map




LAADF
"Strain" map
10±2 nm x/s




EELS

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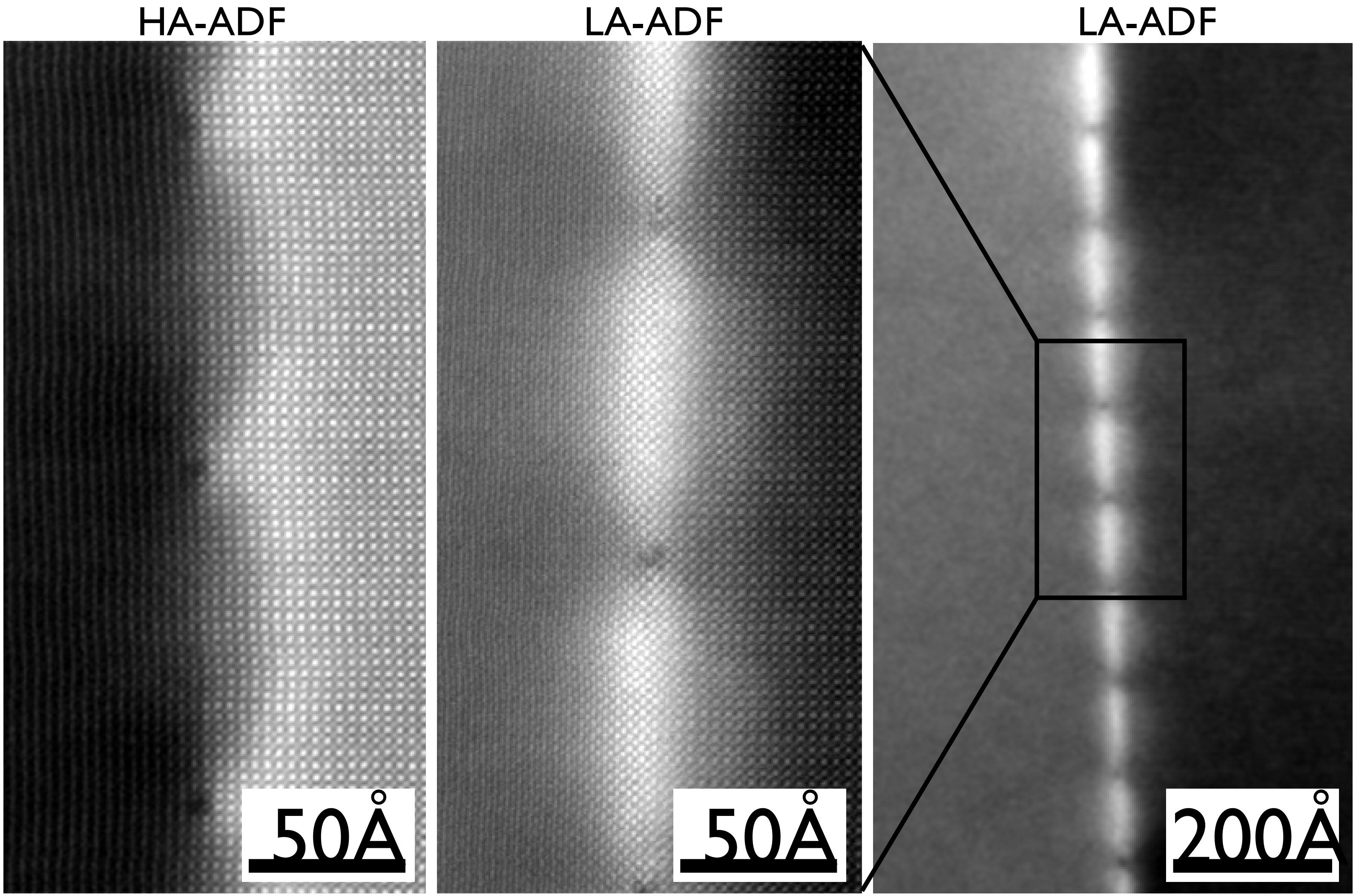
# Not always “Z-Contrast”
# Caveat: Strain Fields

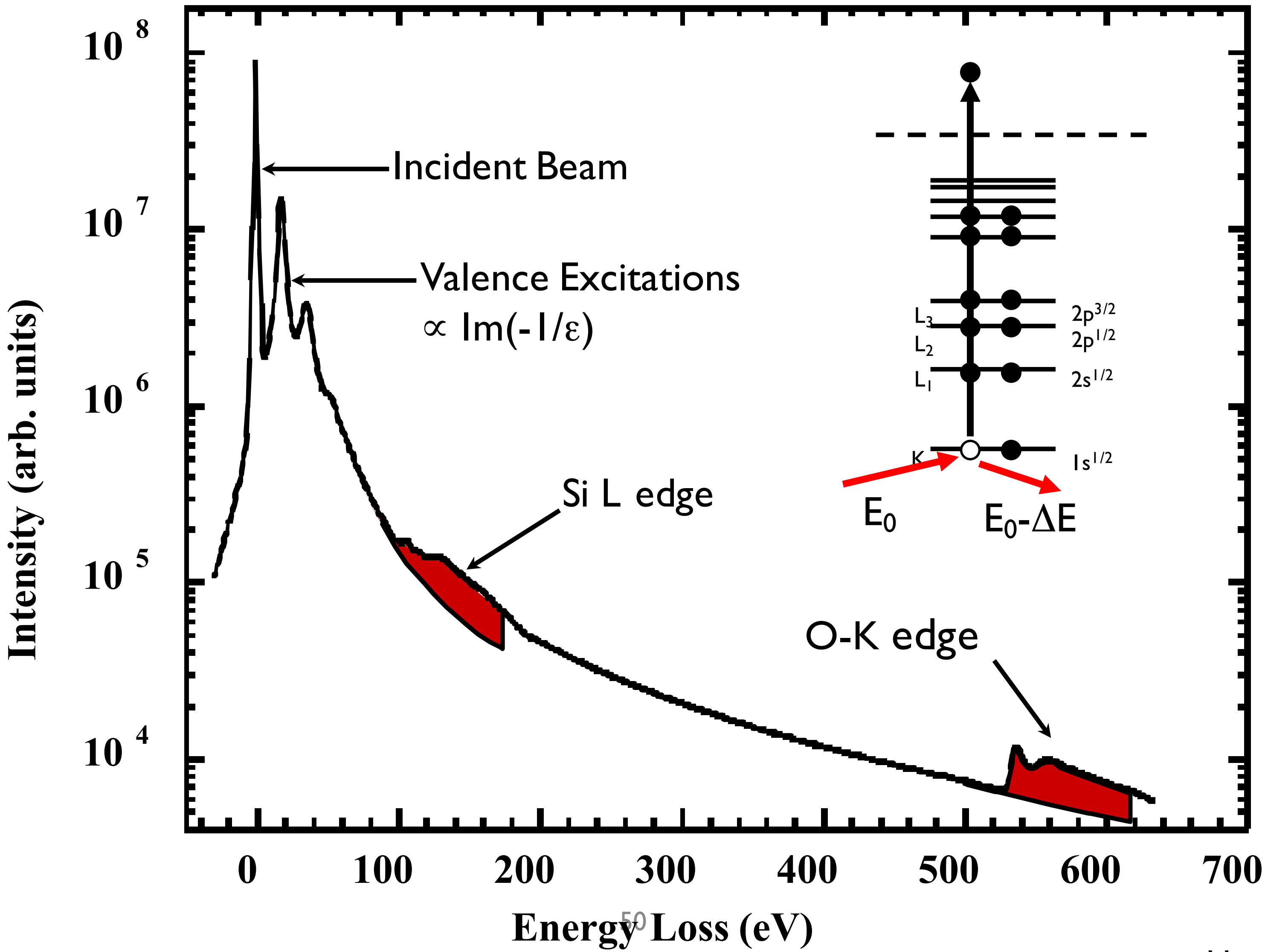
Strain Fields at the Tilt-Boundary






L. Fitting et al, Ultramicroscopy, 106, 1053 (2006)

# Electron Energy Loss Spectrum of $SiO_2$



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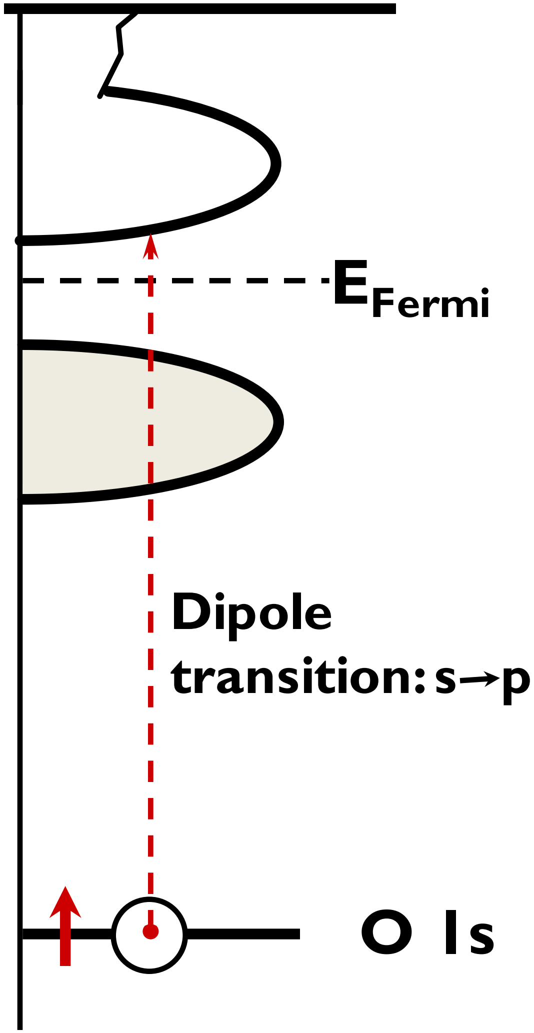
# Core-Level Near-Edge Electron Energy Loss Spectroscopy (EELS)




EELS measures the empty local density of states (the conduction band) partitioned by

- site - as the probe is localized,
- element - the core level binding energy is unique
- angular momentum - (s,p,d states separately)

HOWEVER

- DOS modified by presence of core hole

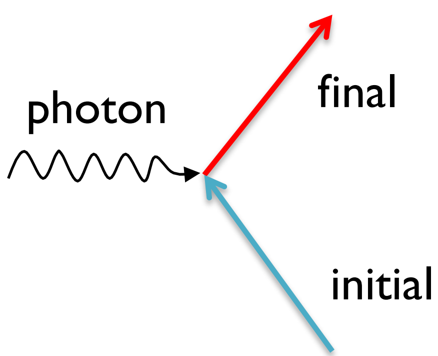
# X-ray absorption spectroscopy (XAS) vs EELS

## XAS

$$\sigma = \sum_{i,f} 4\pi^2 \hbar \alpha \omega |\langle f|\boldsymbol{\varepsilon} \cdot \mathbf{R}|i\rangle|^2 \delta(E + E_i - E_f),$$

Absorb a photon

Polarization vector $\boldsymbol{\varepsilon}$ is determined by your incident setup



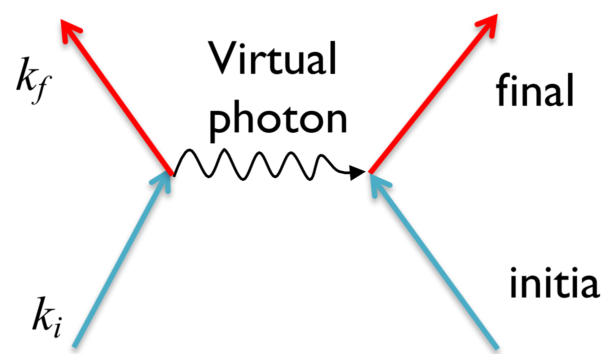

## EELS

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = \sum_{i,f} \frac{4\gamma^2}{a_0^2 q^4} \frac{k_f}{k_i} \left| \left\langle f \left| \sum_{j=1}^{n} e^{i\mathbf{q}\cdot\mathbf{R}_j} \right| i \right\rangle \right|^2 \delta(E_i - E_f + E)$$

$$\doteq \sum_{i,f} \frac{4\gamma^2}{a_0^2 q^4} \frac{k_f}{k_i} |\langle f|\mathbf{q} \cdot \mathbf{R}|i\rangle|^2 \delta(E_i - E_f + E), \qquad (1)$$

Absorb a virtual photon

The equivalent polarization vector $\mathbf{e}_q$ = $\boldsymbol{q}/q$ is determined by your collection setup

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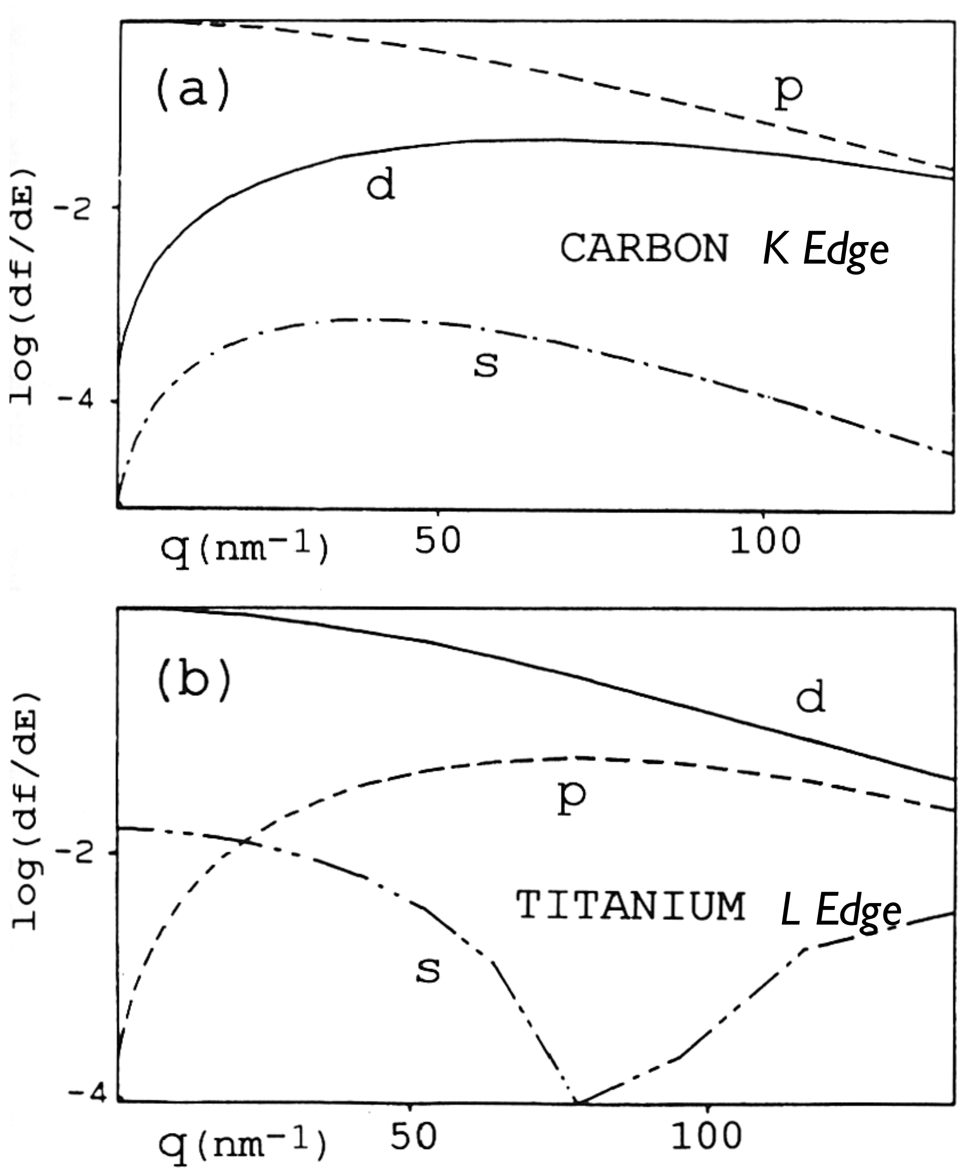
# *Dipole Approximation is good for Core Level EELS*

*(except when the probe < core orbital size)*




*1s->p dipole*
*1s->s monopole*
*1s->d quadrupole*

*2p->d dipole*
*2p->p monopole*
*2p->s dipole*

P. Rez, *Ultramicroscopy* **28** 1989 16-23

# Dipole vs. Multipole in Aberration-Corrected STEM-EELS

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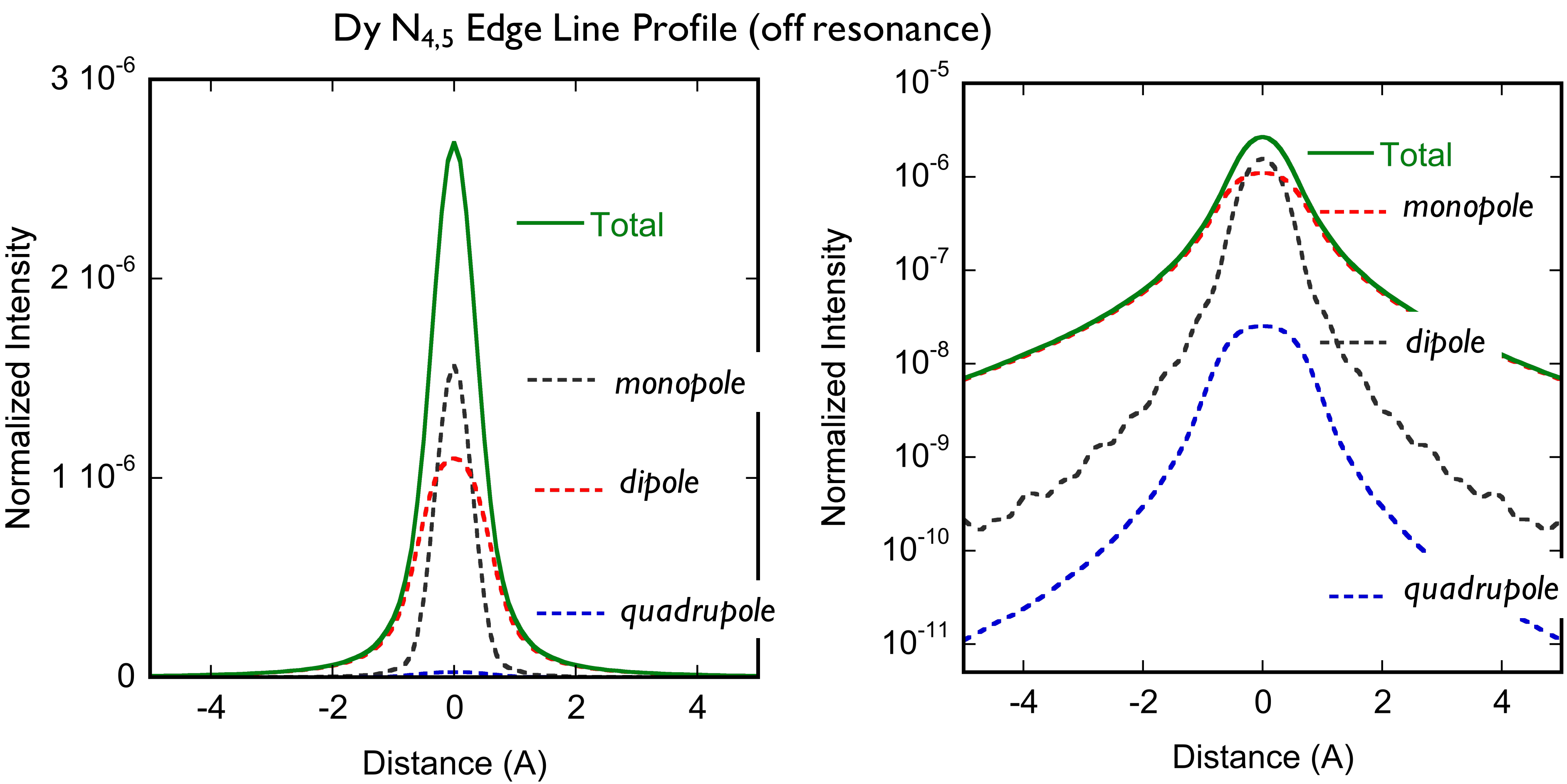


Dipole dominates the broad tails of the STEM-EELS profile: 80% of total intensity

Dipole gives upper bound to spatial resolution (monopole is a bit narrower)

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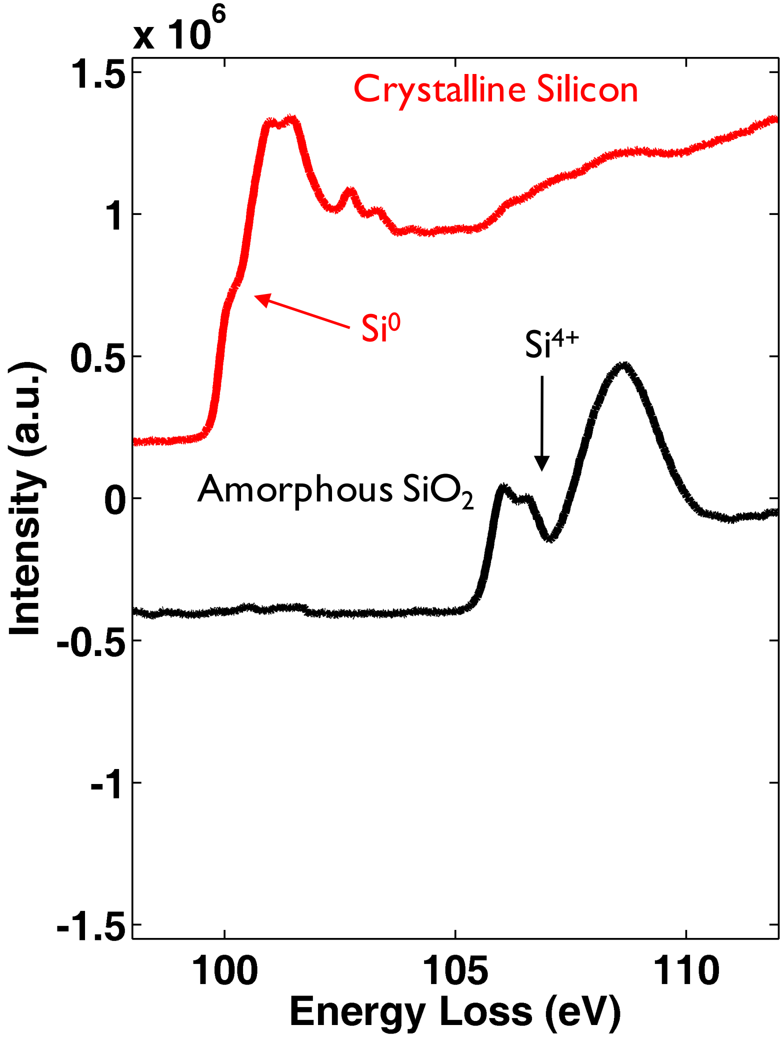
# Crystalline Si vs. $SiO_2$

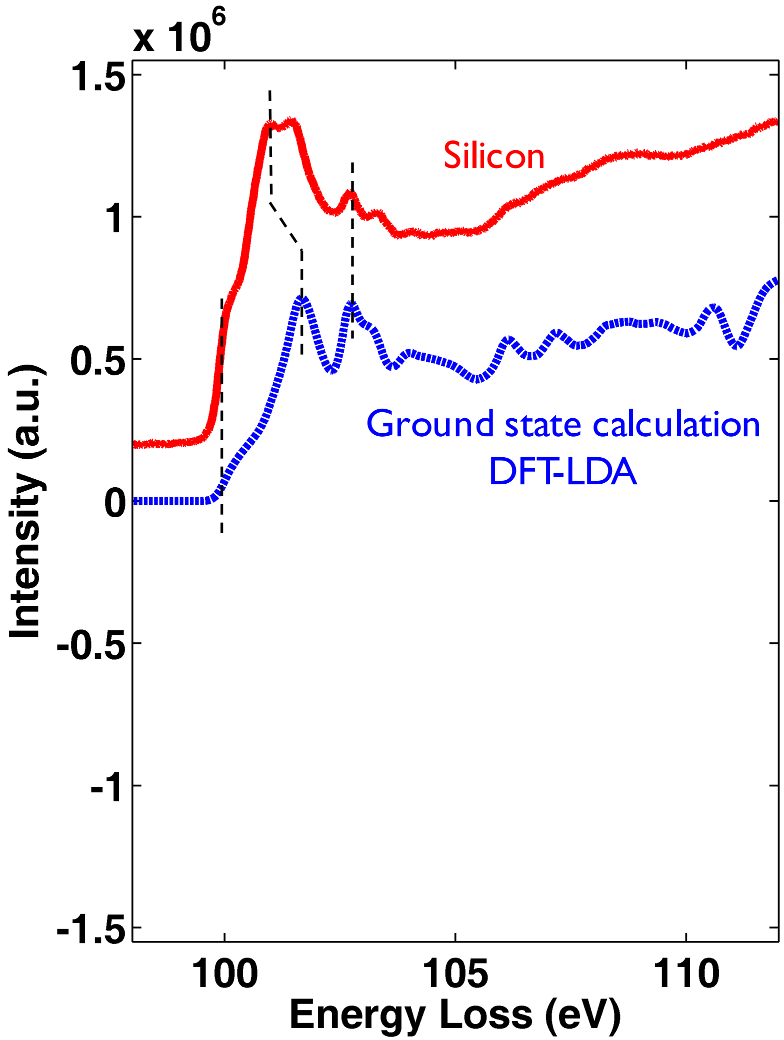
## Monochromated EELS

Energy resolution = 100 mV




- General rule: valence ↑
- edge onset ↑
- Edge onset shift however does not always track the magnitude of the core level shift (e.g. latter 3-d TM).
- Slightly more complicated for insulators due to the presence of excitonic features

# Crystalline Si vs. $SiO_2$




- Core-hole life time in c-Si is relatively short. The spectrum resembles the ground state calculation.

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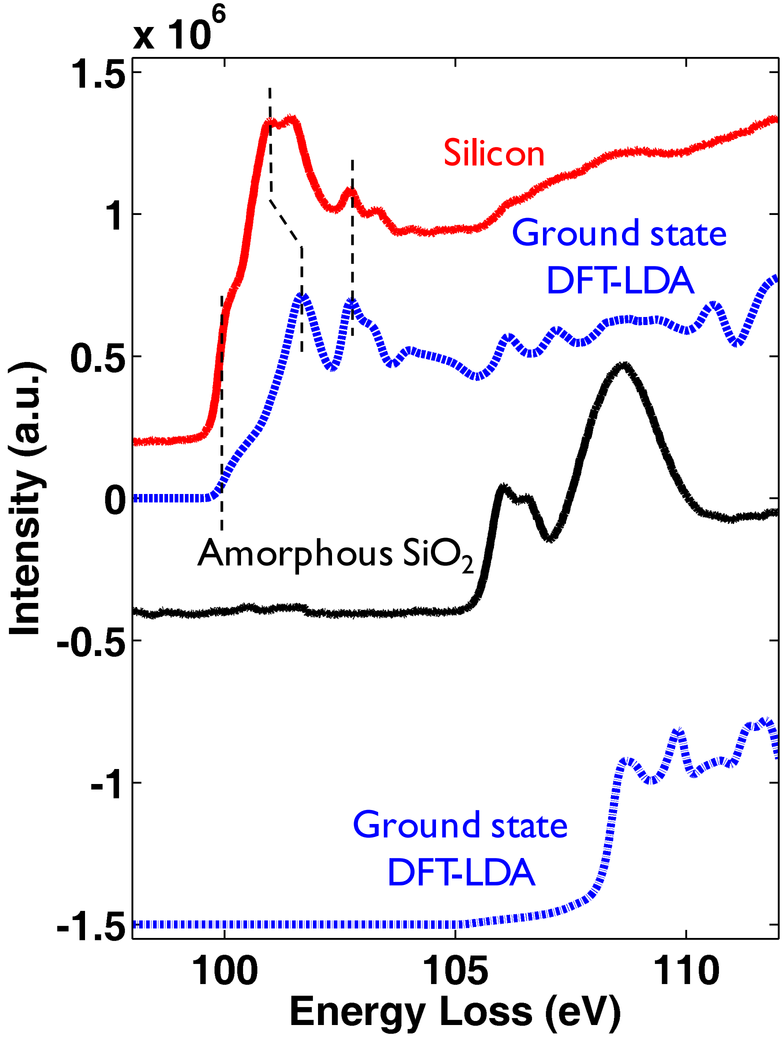
# Crystalline Si vs. $SiO_2$




- Strong core-hole effects on the silicon-L Edge in $SiO_2$

(it does not reflect the ground state)

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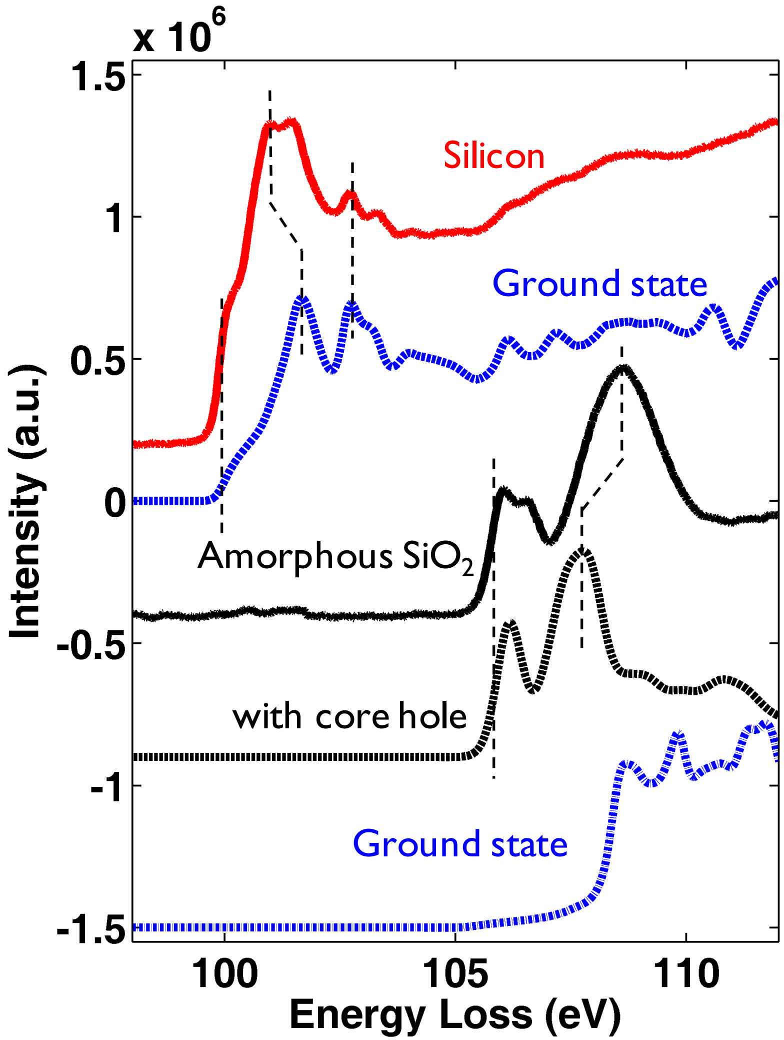
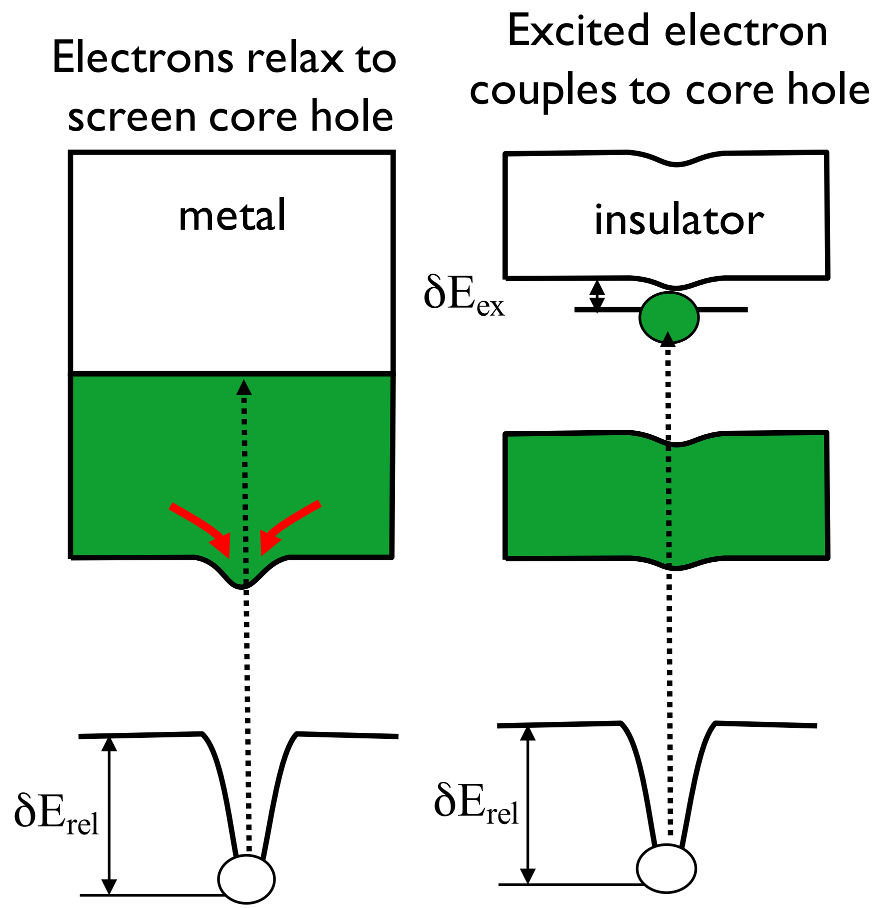
# Crystalline Si vs. $SiO_2$

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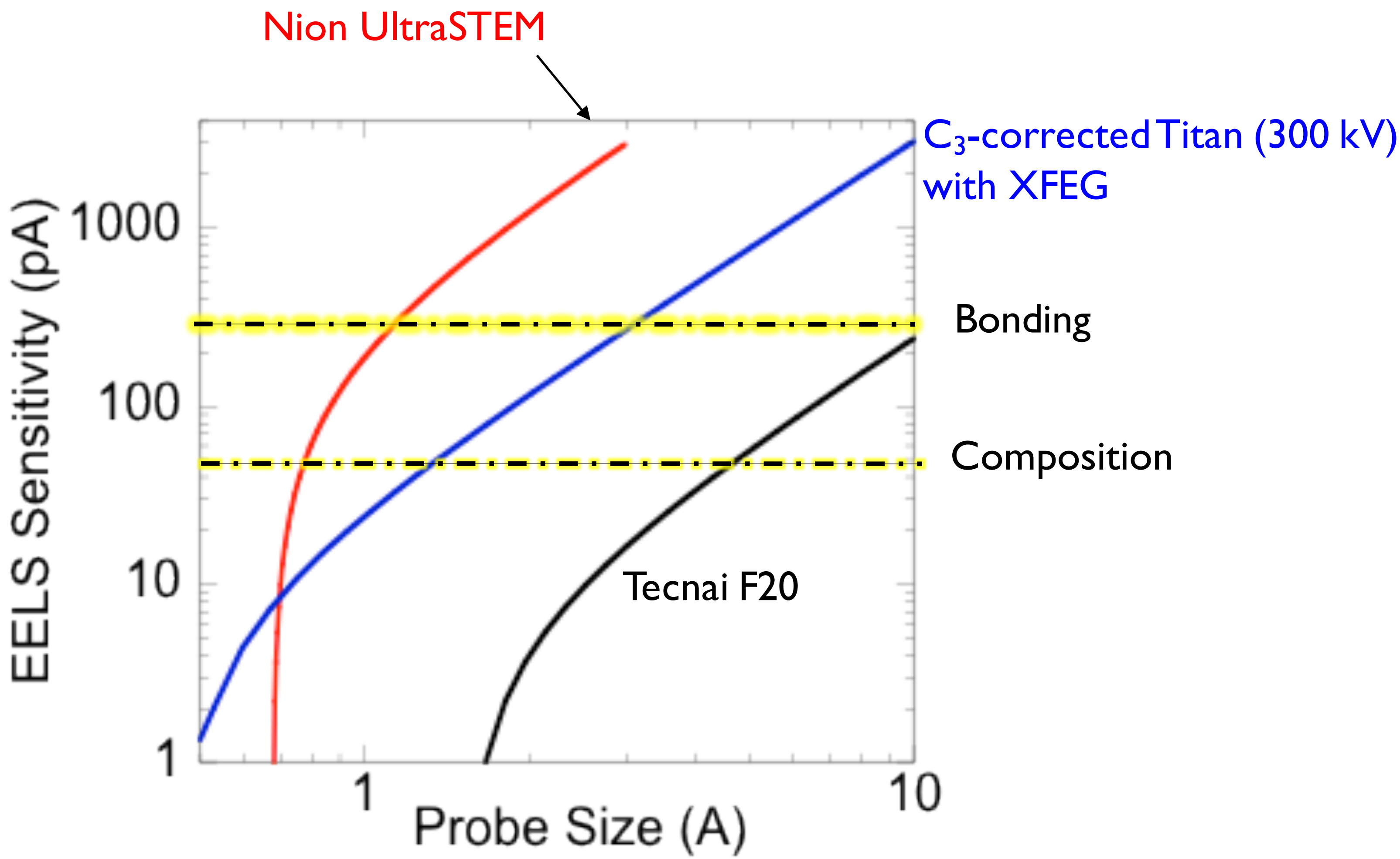
# Tradeoff: Probe Size for Beam Current

$I_{coll}$ = β x (Probe Area) x (Probe Solid Angle) x (Collection Efficiency)

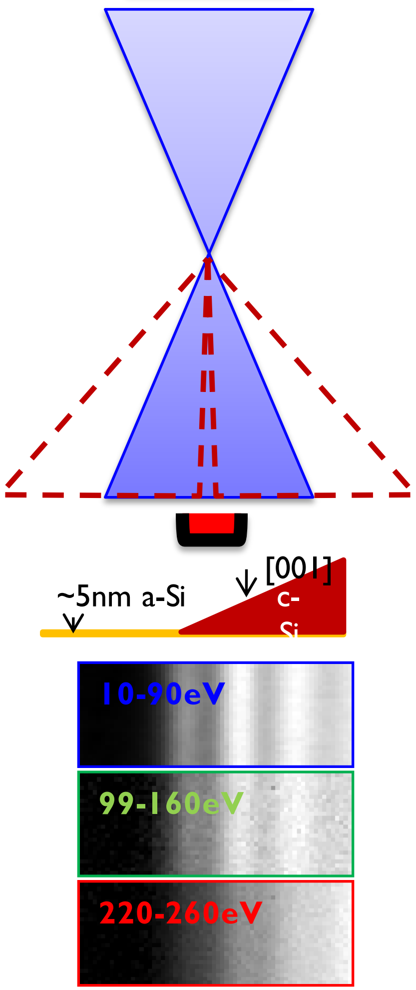



D. A. Muller, *Nature Materials*, **8**, 263 (2009)

# EELS Collection Efficiency

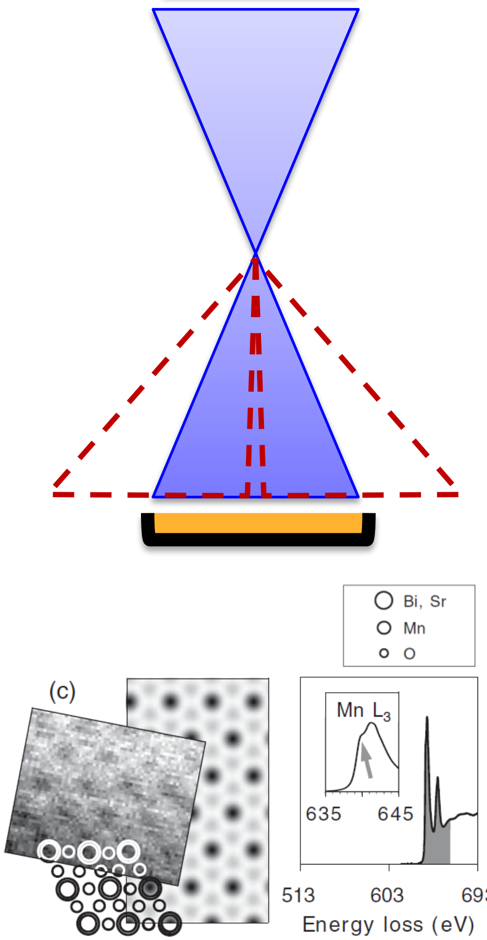
Improved Dose efficiency, improved interpretability

1st Gen 5-10%



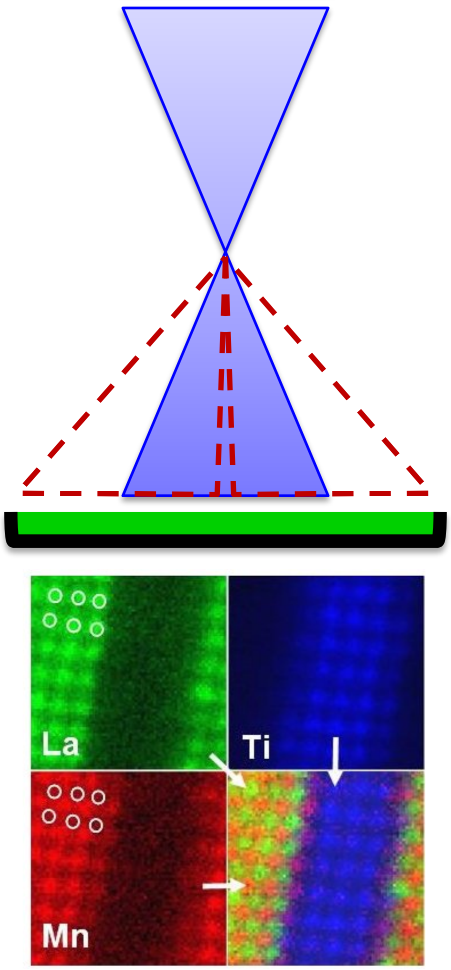

HL Xin, in prep.

2nd Gen 20-80%




M. Bosman *et al*, PRL, **99**, 086102 (2007)

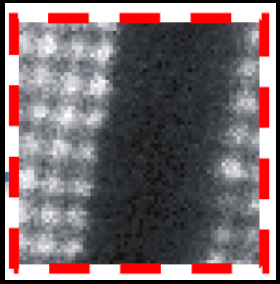
3rd Gen 50-100%



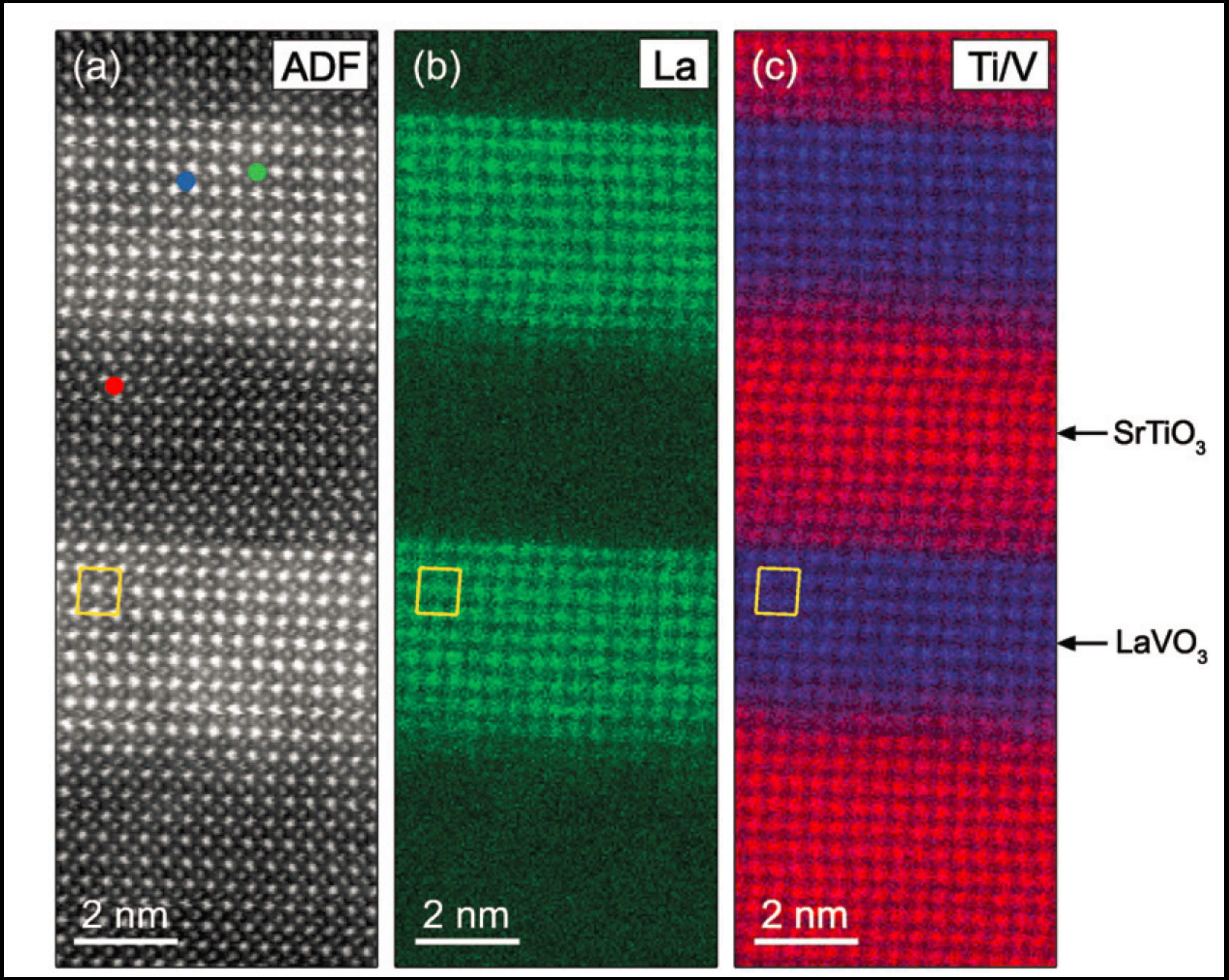

DA Muller *et al*, *Science* **319**, 1073–1076

Huolin Xin 2015

# Atomic Resolution Spectroscopic Imaging of STO/LVO Multilayer



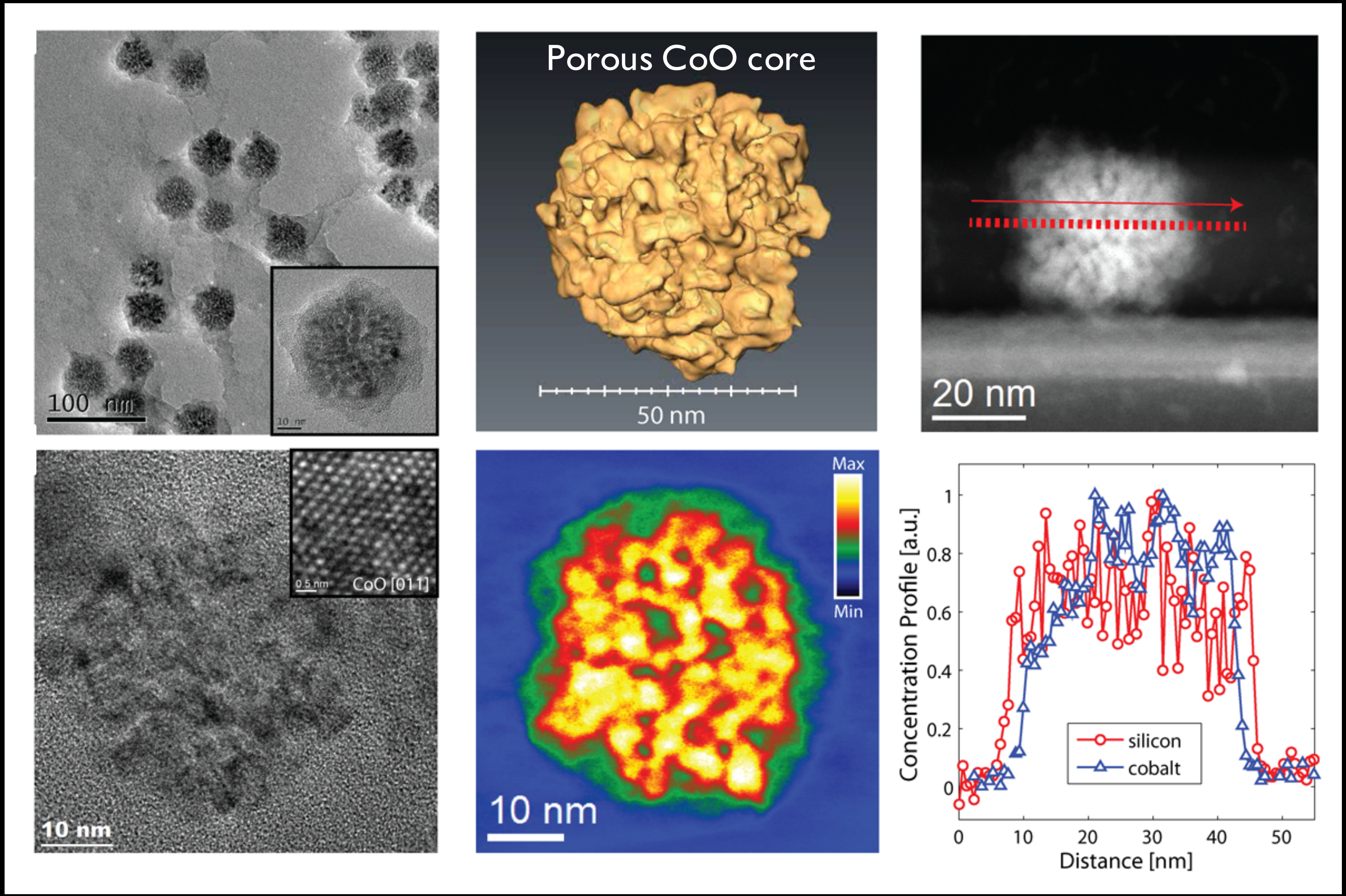

Science, 2008




- La in green, Ti in red, and V in blue.

*Kourkoutis, **Xin**, et all Phil. Mag.,* ***90****, 4731 (2010)*

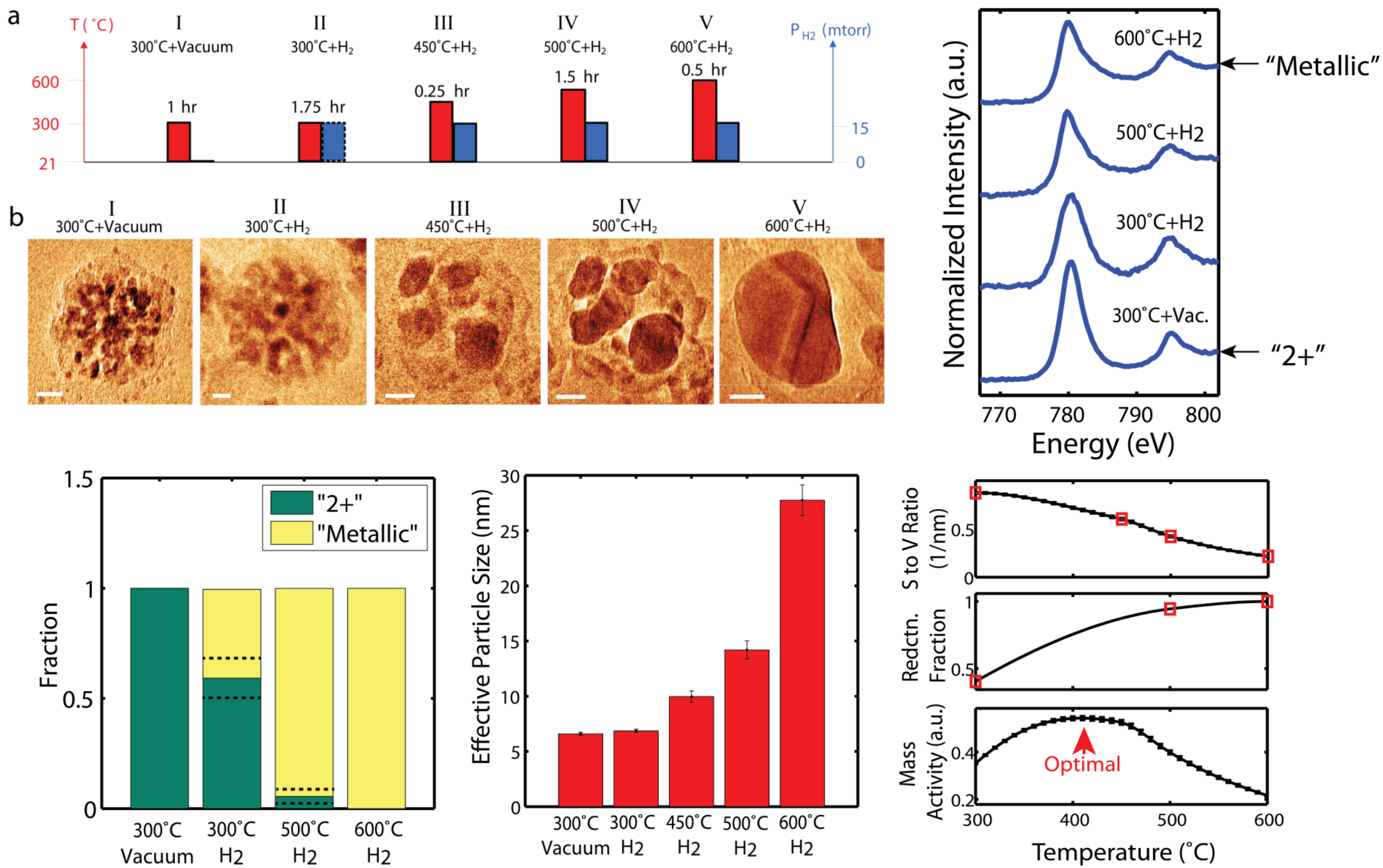
# Co/Silica Porous Catalyst for Carbon Monoxide (CO) Hydrogenation




HL Xin et al, ACS Nano, 6, 4241, (2012)

- Need to reduce Co oxide to metallic cobalt. What's the optimal reduction temperature?

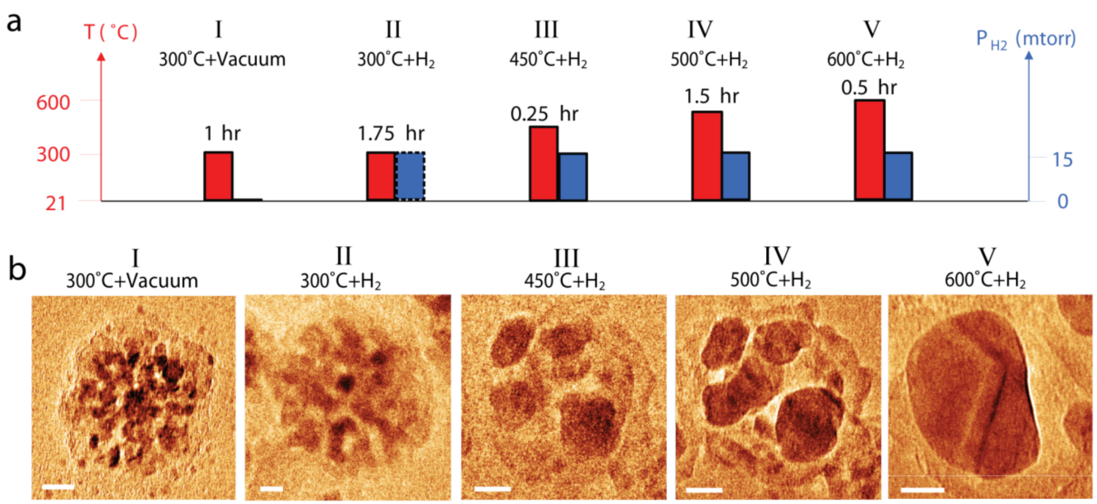
# Connecting In situ Imaging with Electronic Structures of the Materials

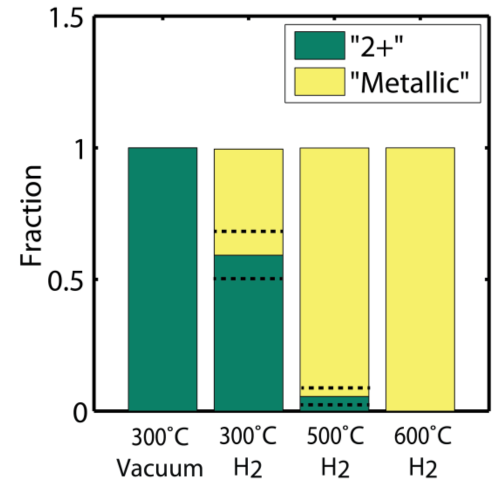


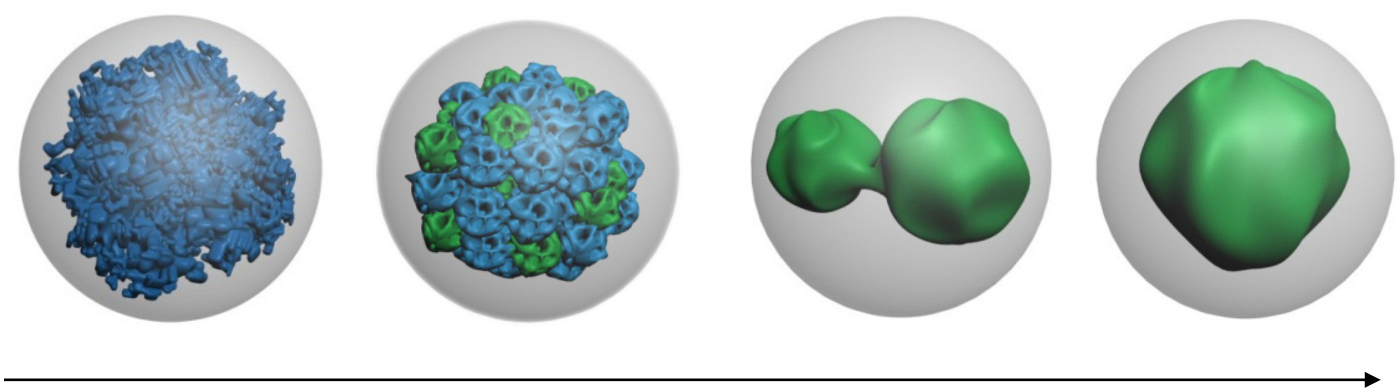

- Building a correlation between structural coarsening and valence state changes allow us to understand the underlying mechanisms in the catalyst optimization used in the industry

HL Xin et al, ACS Nano, 6, 4241, (2012)

# Reaction Pathway



$CoO + H_2 = Co + H_2O$

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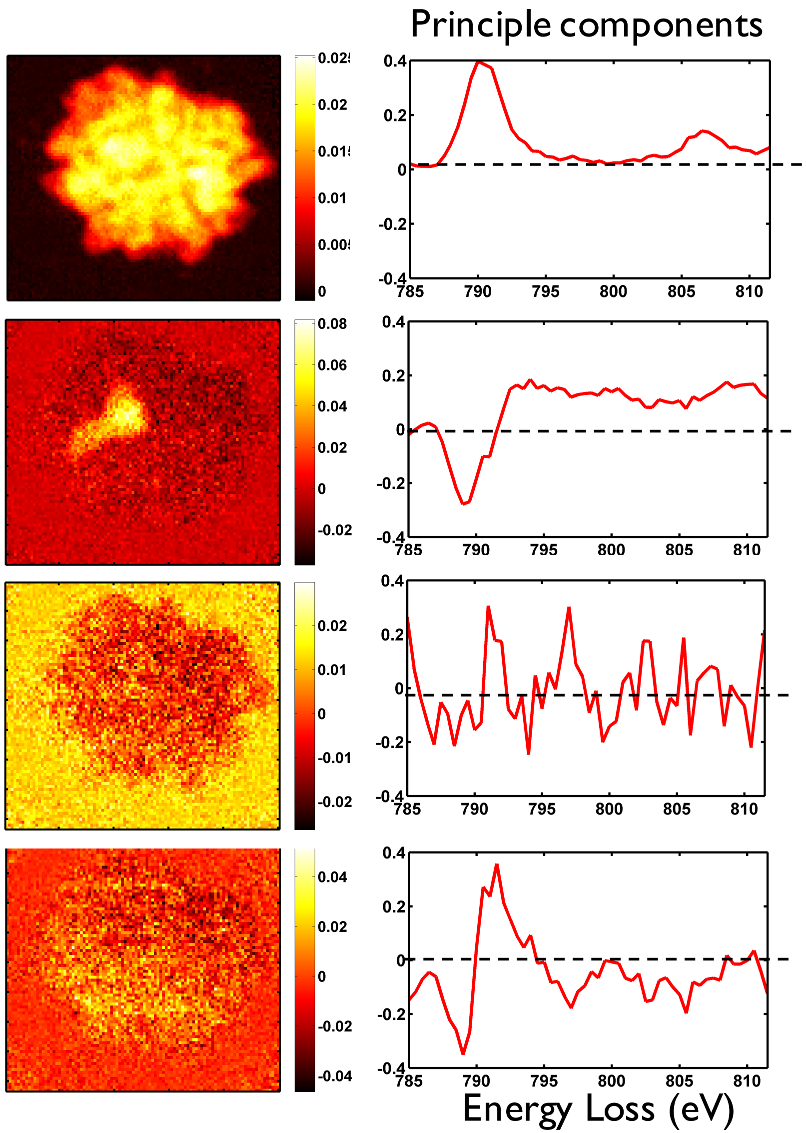
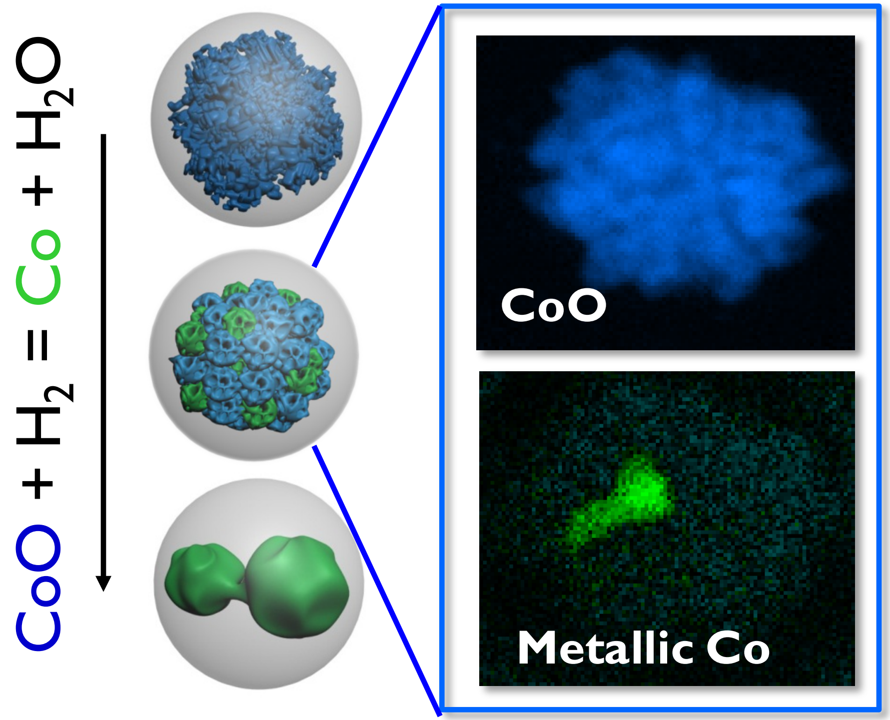
# Principle Component Analysis of Partially Reduced CoO Porous Networks




HL Xin et al, ACS Nano, 6, 4241, (2012)

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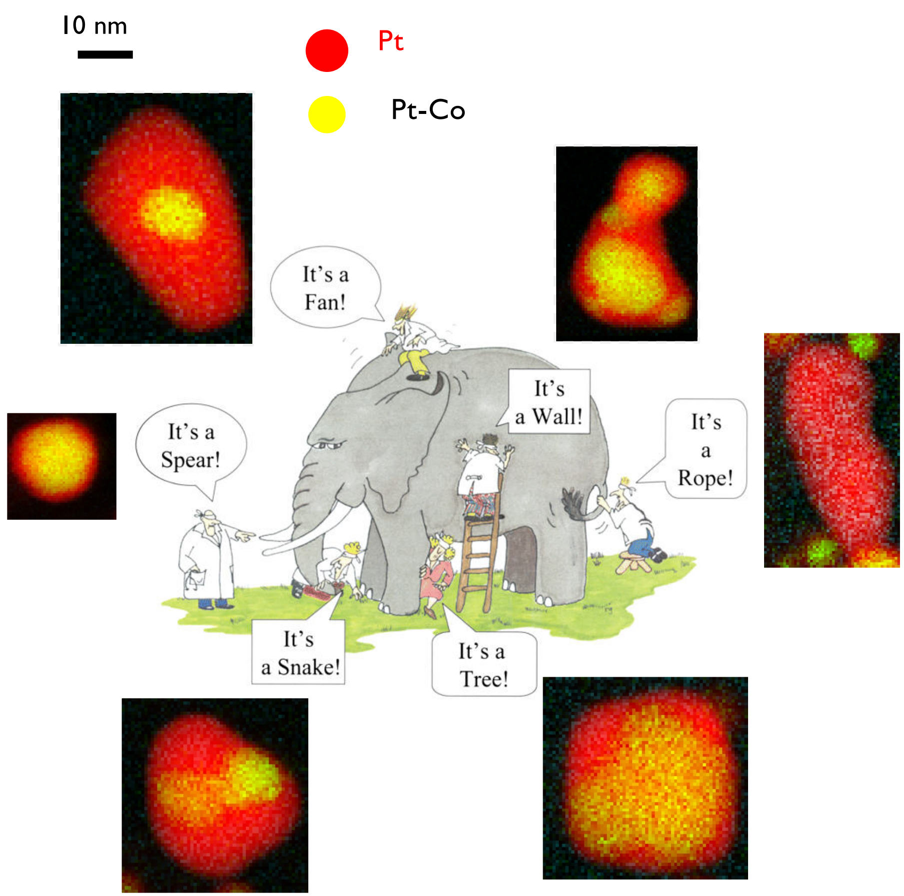
# Critical Thinking




and many more……

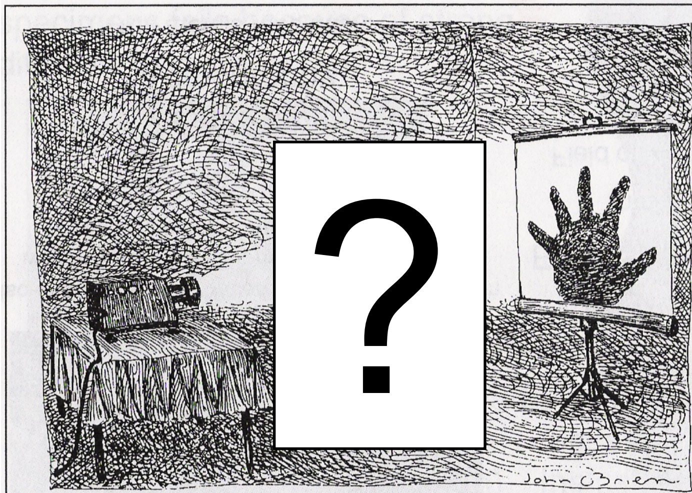



**Fig. 5.1.** A single projection image is plainly insufficient to infer the structure of an object. Drawing by John O'Brien; © 1991 The New Yorker Magazine.

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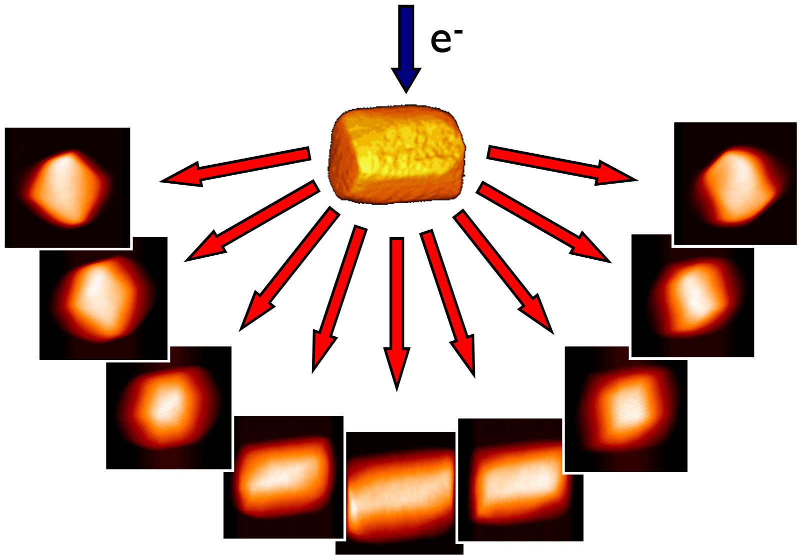
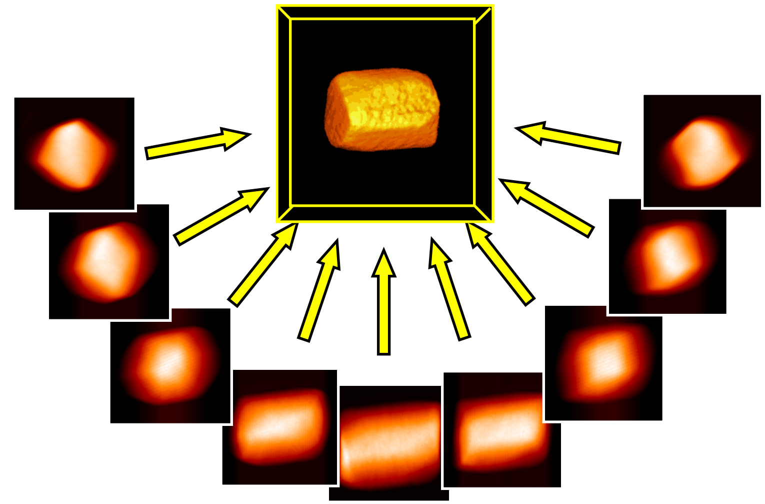
# Tomography Experiment




**Acquisition**



**Reconstruction**

## Slab Geometry:

- One image every 1-2° from ±70°
- 70 - 140 images

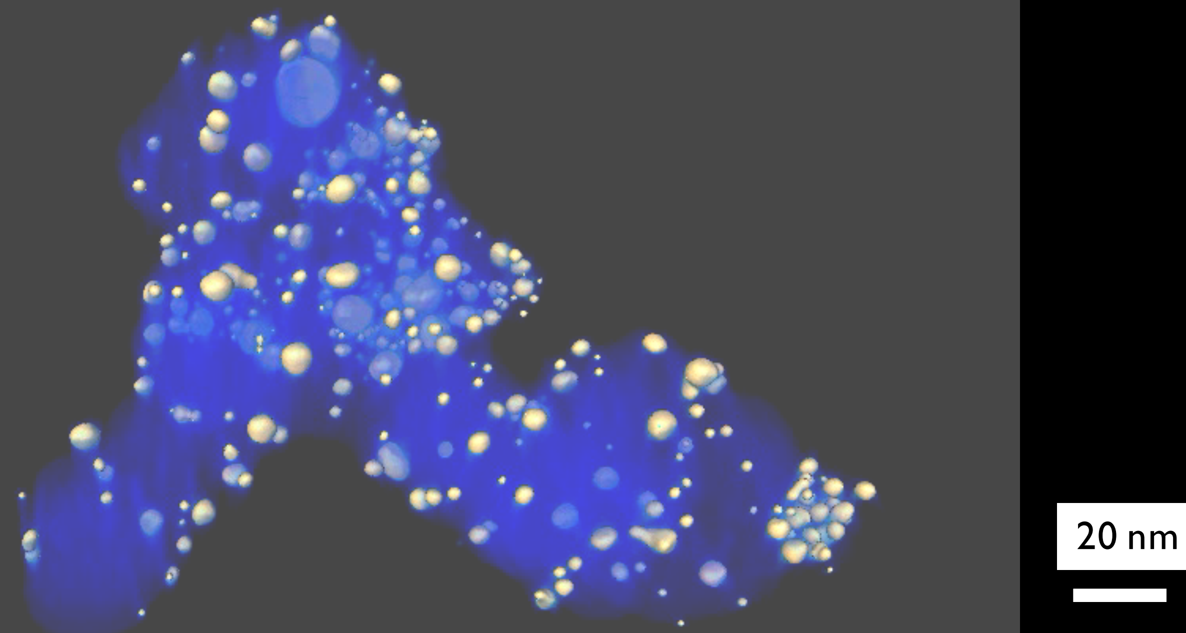
## Requirement:

- Image intensities vary monotonically with thickness

(STEM is superior to TEM for tomography because TEM suffers from phase contrast and diffraction contrast which breaks the monotony of the signal )

Huolin Xin 2015

# 3-D Reconstruction of Pt-Co particles on Support




Huolin Xin 2015

Huolin L. Xin et al, Nano Lett., 12, 490 (2011)

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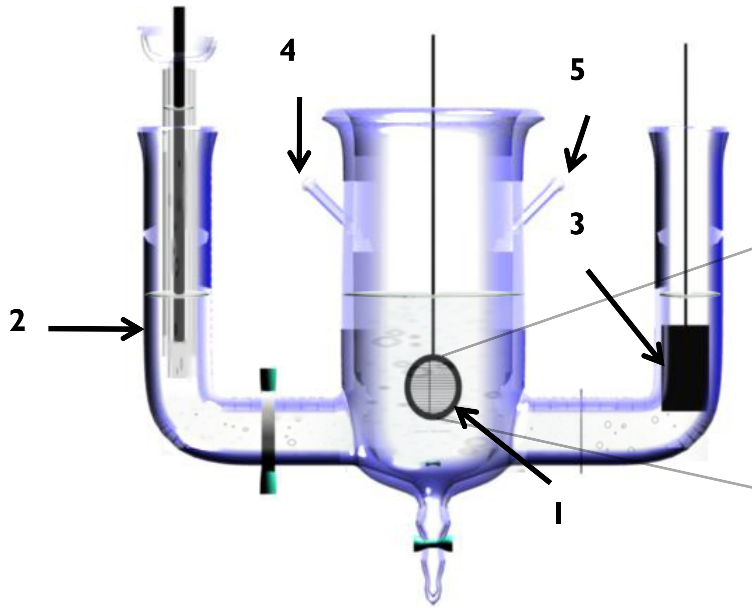
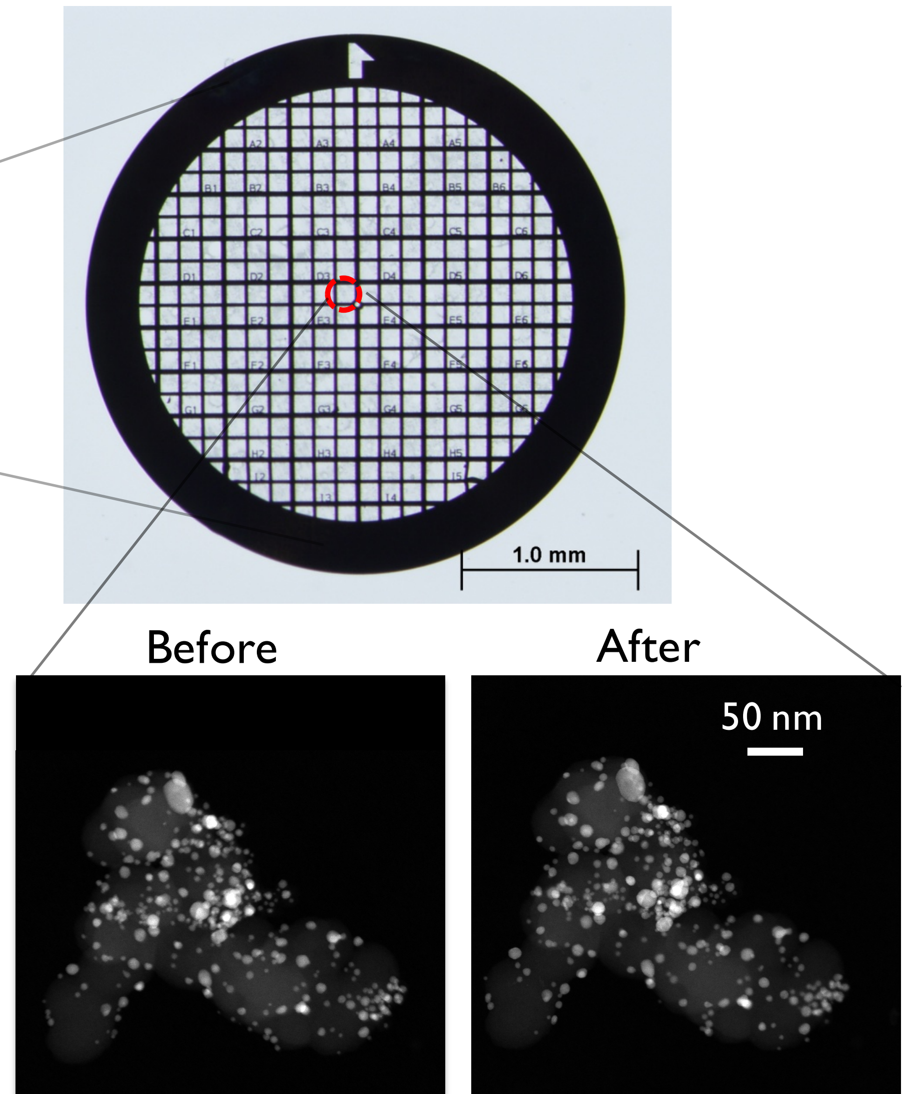
# Ex-Situ: Coarsening During Voltage Cycling




1. Gold index grid (working electrode)
2. Reversible Hydrogen Electrode (reference electrode)
3. Platinum foil (counter electrode)
4. Argon gas inlet
5. Argon gas outlet

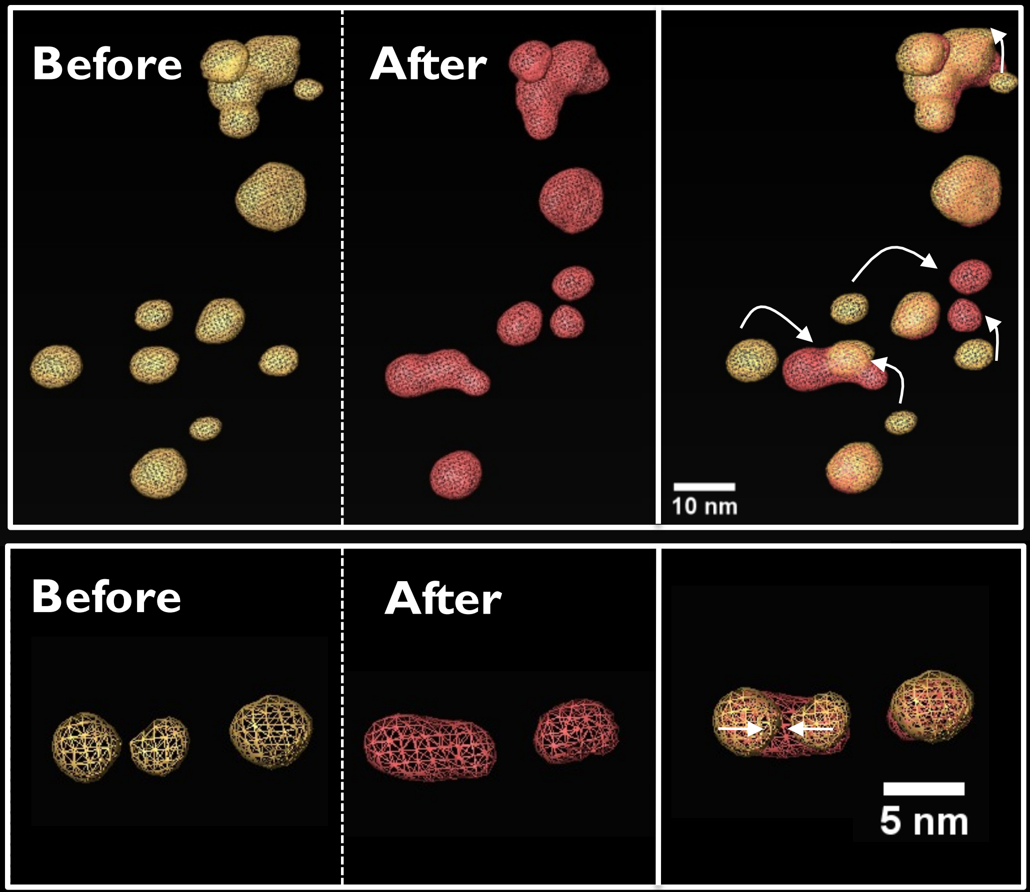


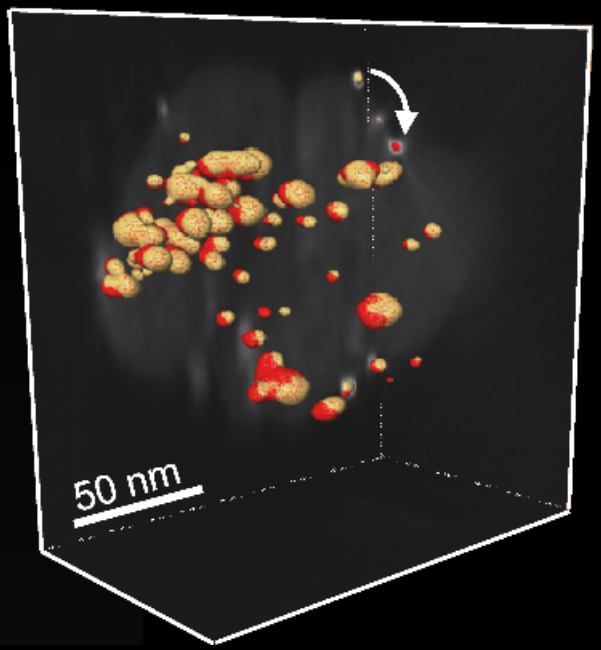

**3-D imaging for the first time the same region before and after electrochemical cycling**

Y. Yu*, **H. L. Xin*** (*cofirst author), Nano Lett., 12 (9), 4417-4423 (2012)

Huolin Xin 2015

# Observing Coalescence in 3-D




- ***Tracking individual particles and how they move on the support to coalesce***

Y. Yu*, **H. L. Xin*** (*equal), Nano Lett., 12 (9), 4417-4423 (2012)

Huolin Xin 2015

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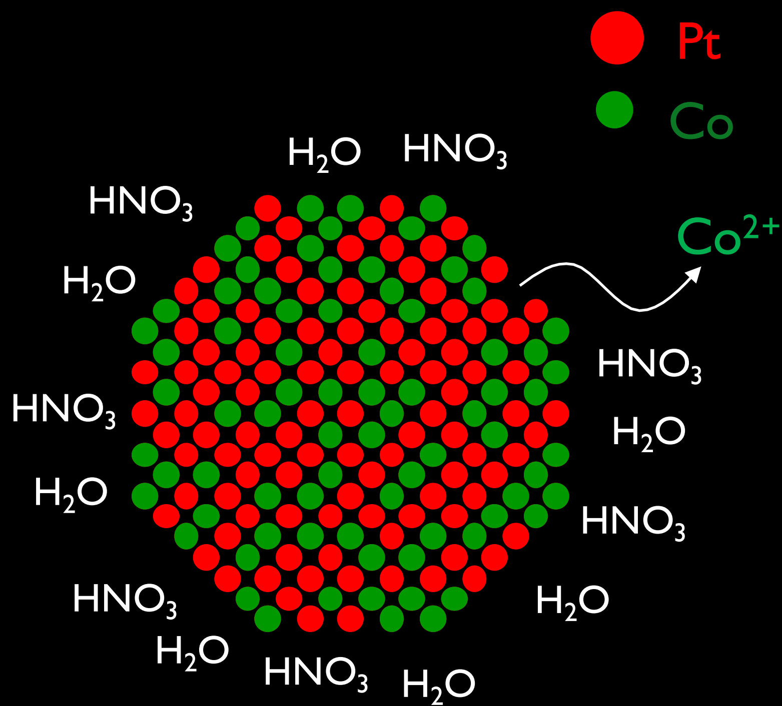
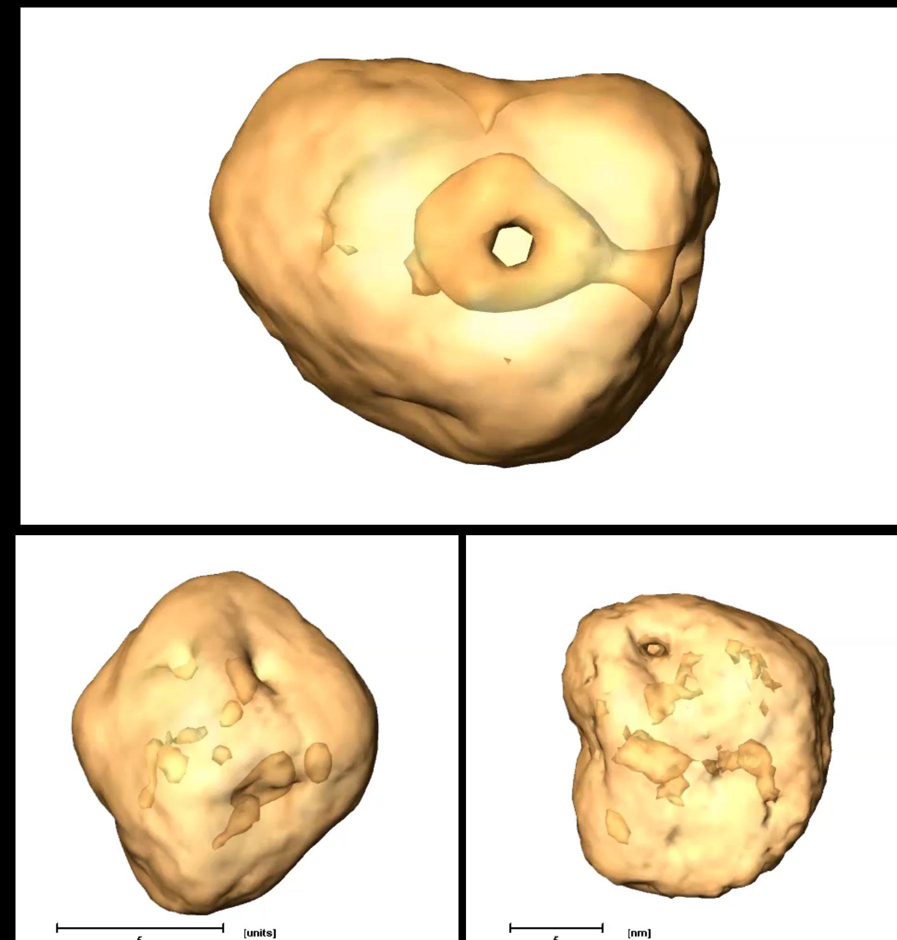
# Chemical Dealloying of Pt-Co Nanoparticles




- Leaching of Co left holes and divots in the remaining Pt

Vic Liu & HL Xin et al, Journal of The Electrochemical Society, 159, F554 (2012)

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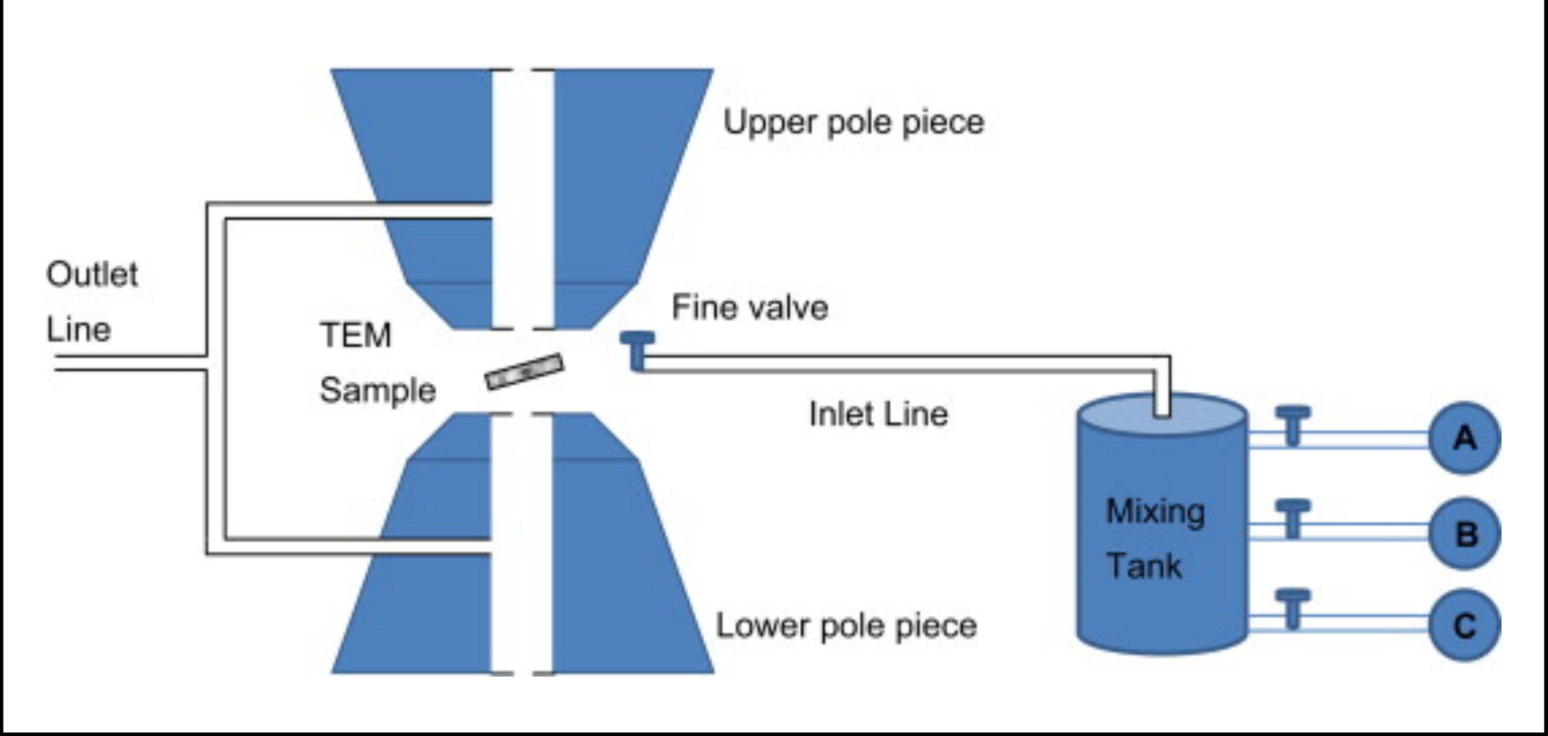
# A Schematics for ETEM




Crozier et al, Ultramicroscopy, **111**, 177 (2011)

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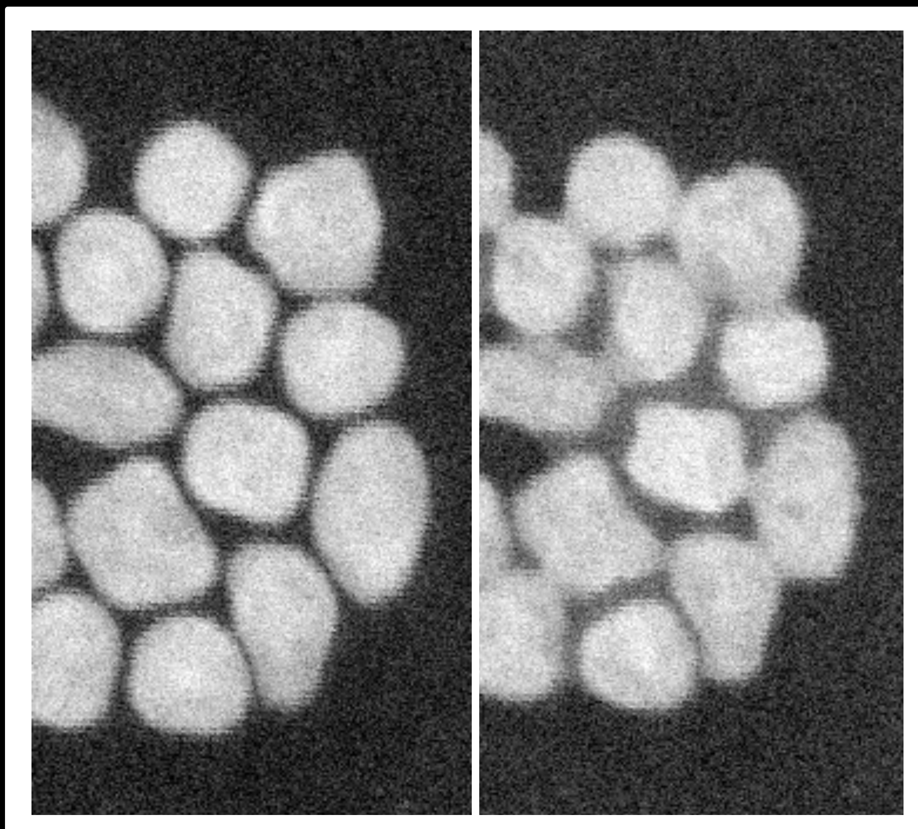
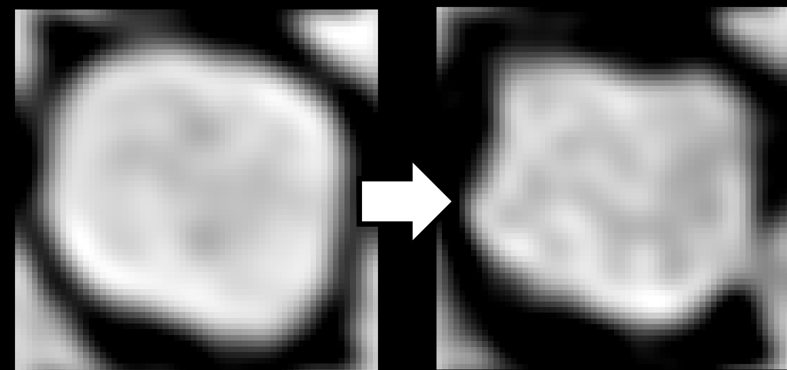
# Oxidation of 12nm PtCo Particles

400°C + 0.14 Torr $O_2$



Before After

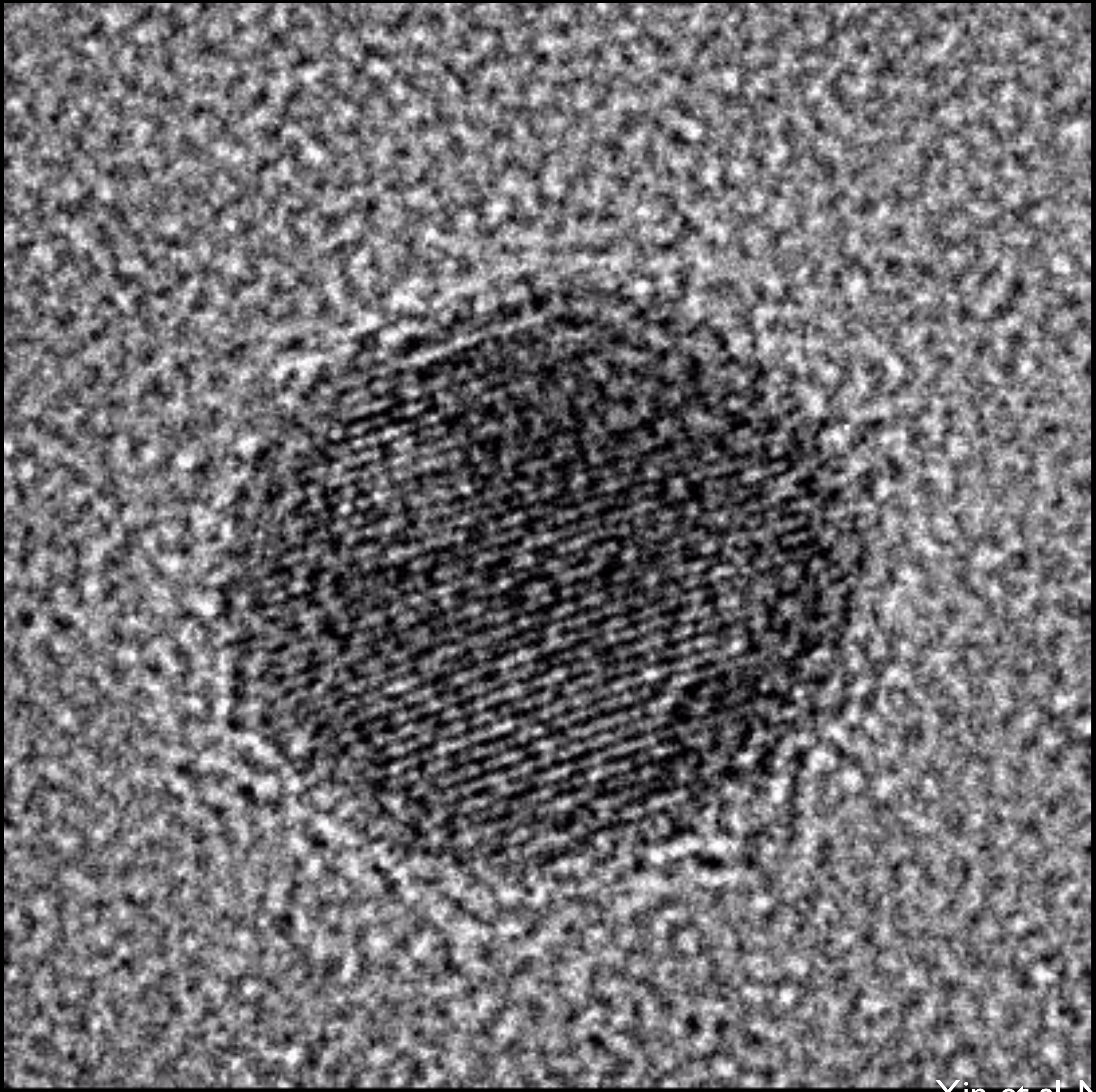


Ex situ Imaging


- Co diffuse out causing the Pt core to either shrink or forming holes

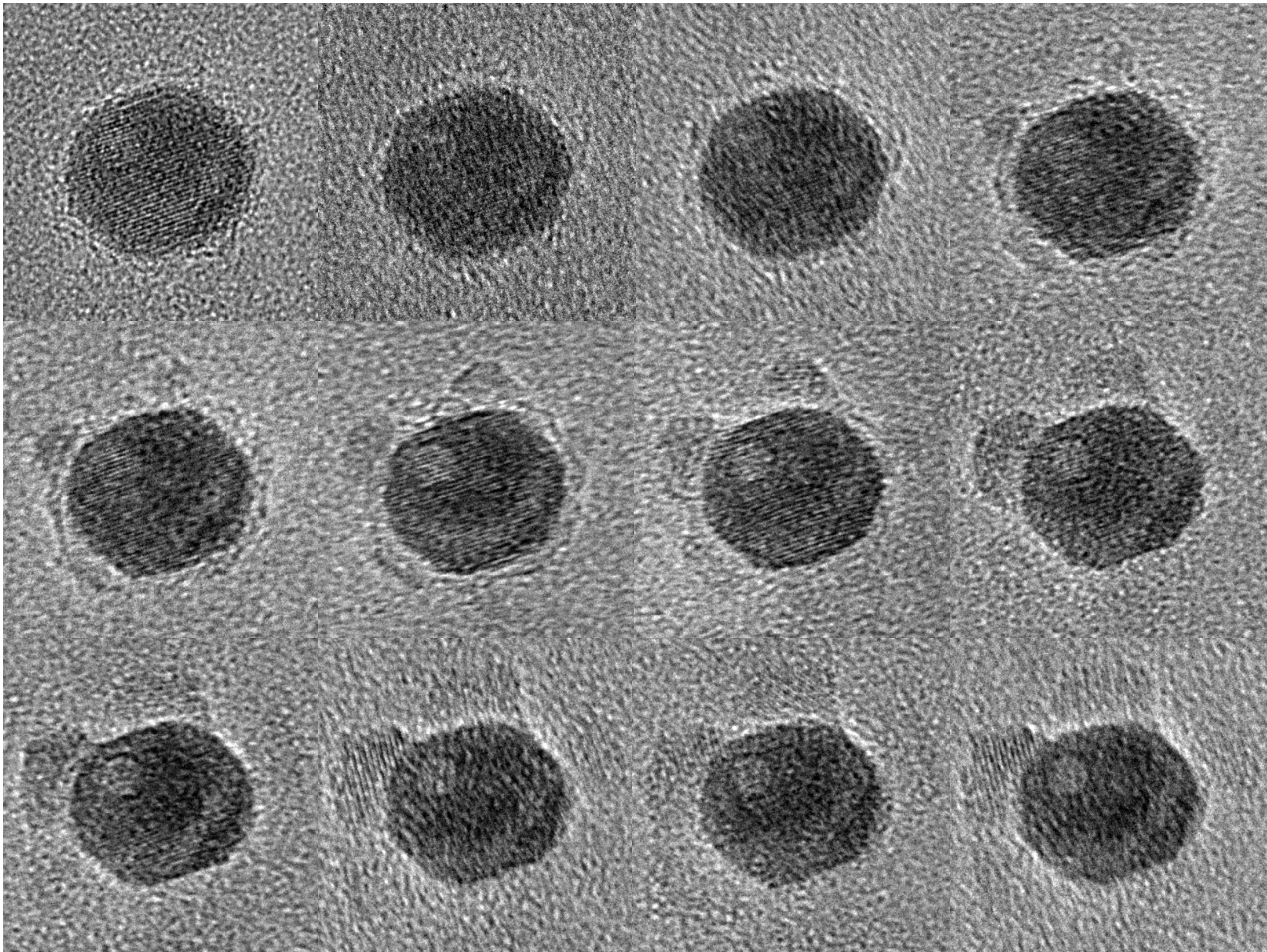
Xin et al, Nano Letters, 2014

# Atomic Scale Real Time Imaging of Oxidation of Individual Co-Pt Nanocatalysts



Huolin Xin 2015

Xin et al, Nano Letters, 2014



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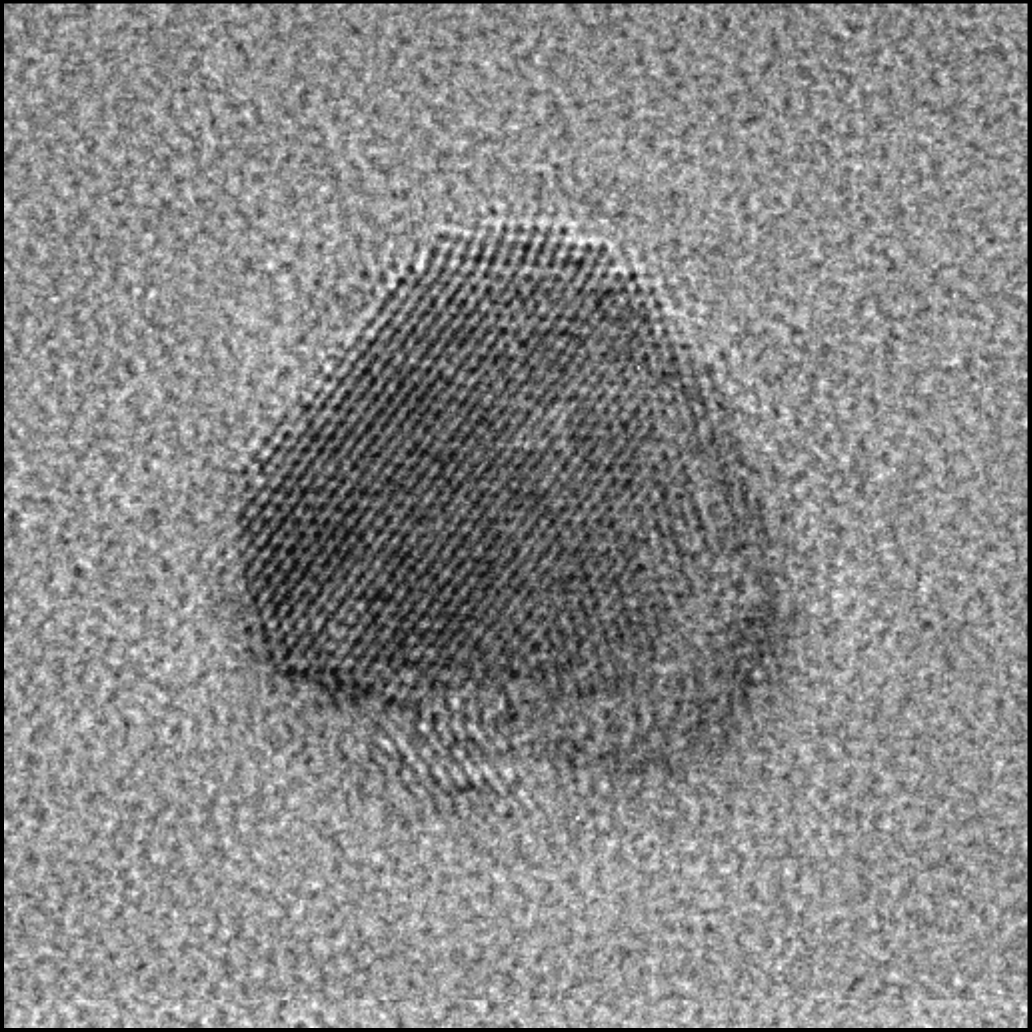
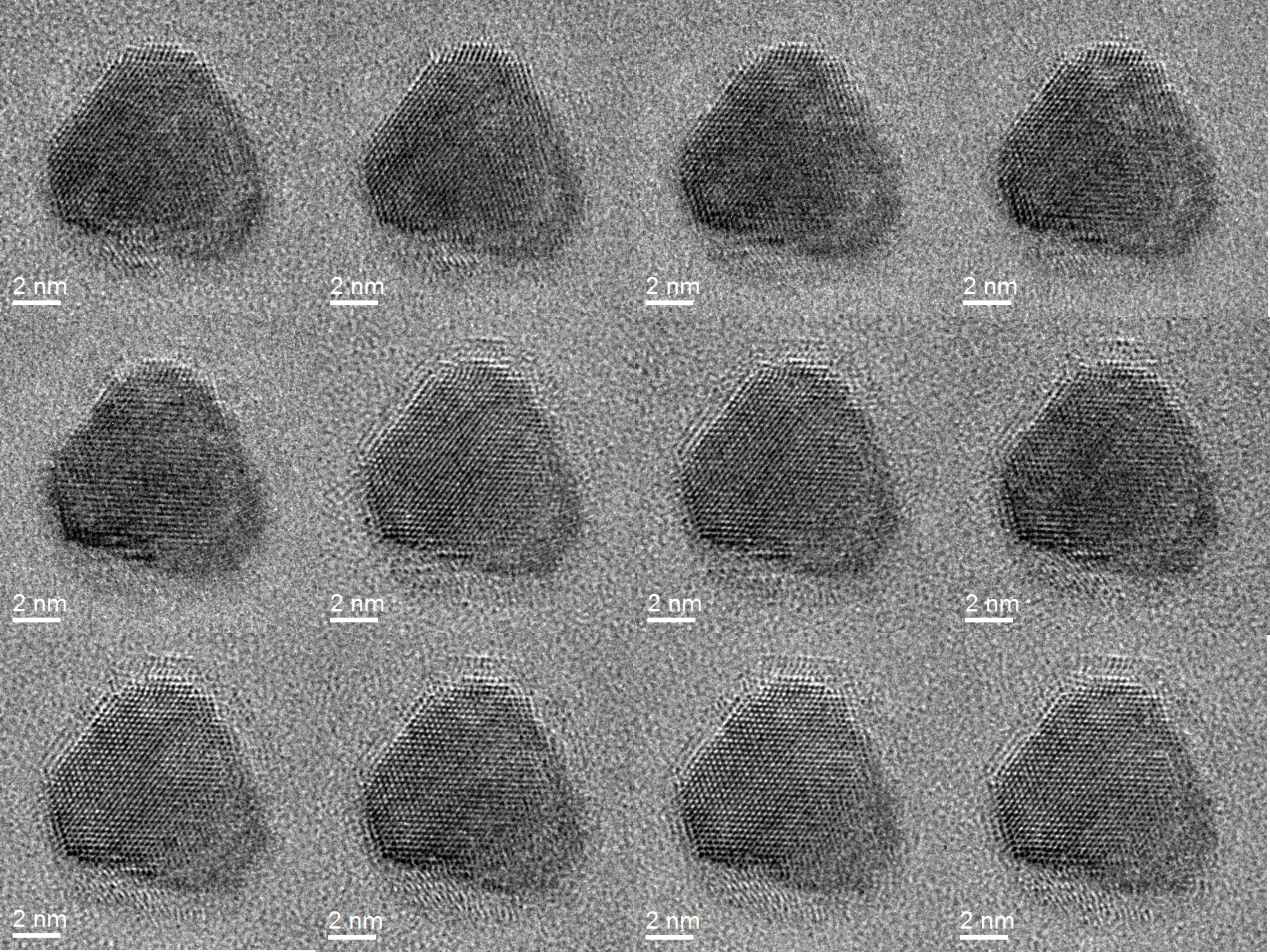


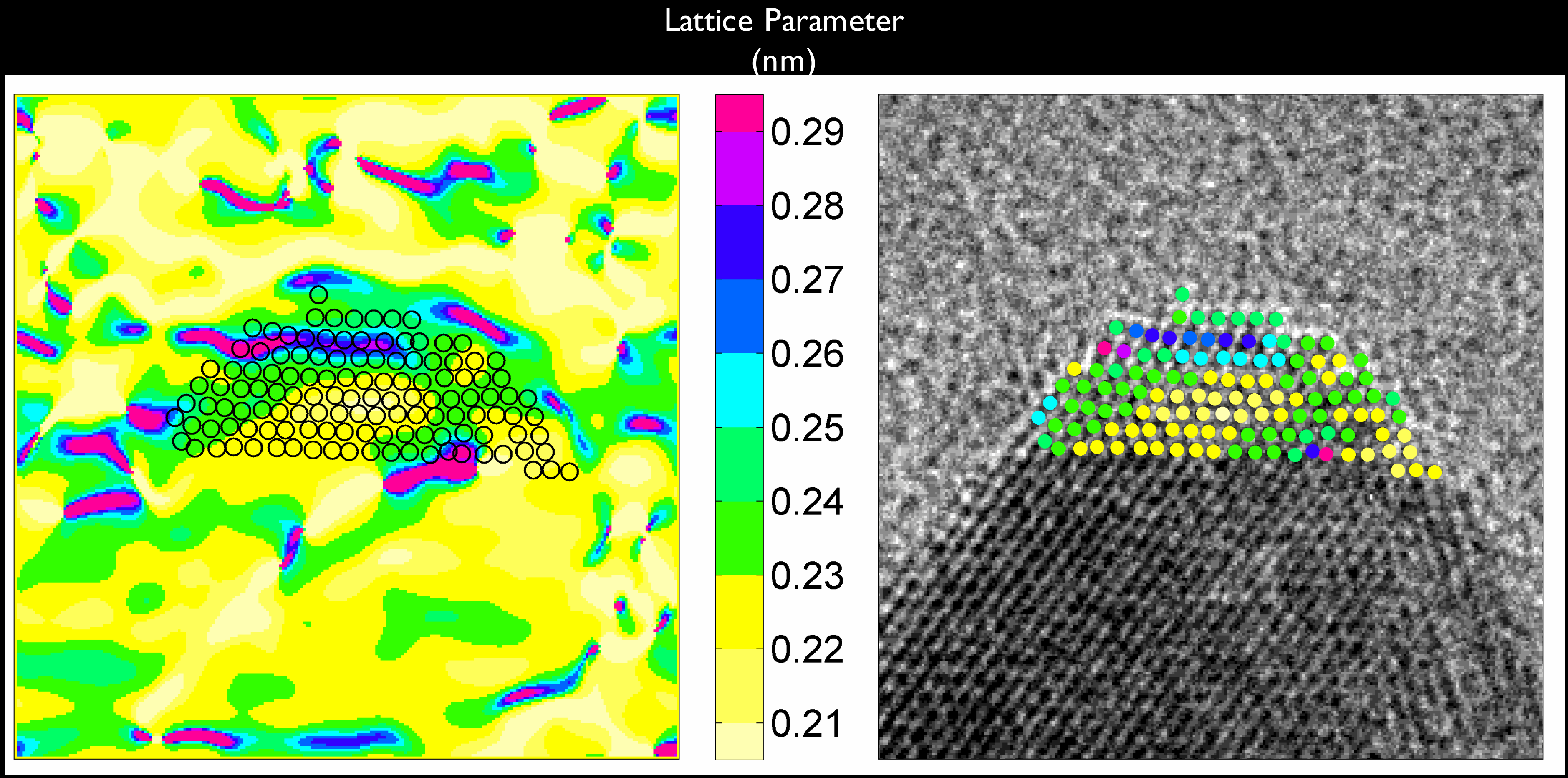
2 nm

~30X

- 250°C in 0.1 mbar $O_2$

Huolin Xin 2015

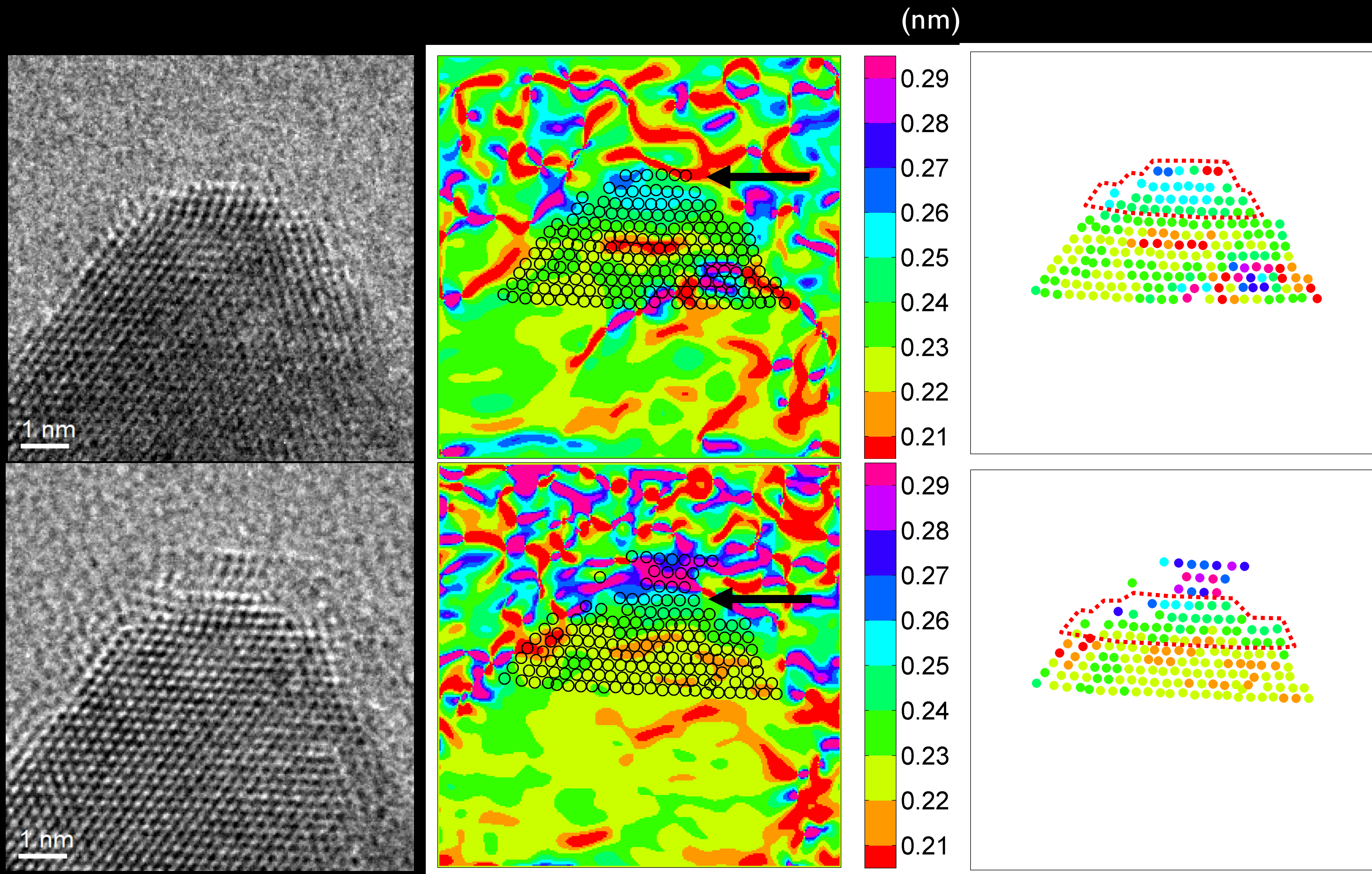

2 nm
2 nm
2 nm
2 nm
2 nm
2 nm
2 nm
2 nm
2 nm
2 nm
2 nm
2 nm




(Animated GIF. Play in presenting mode.)

Xin et al, Nano Letters, 2014

# GPA Strain Mapping

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Xin et al, Nano Letters, 2014

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# Low Concentration of Pt in Co

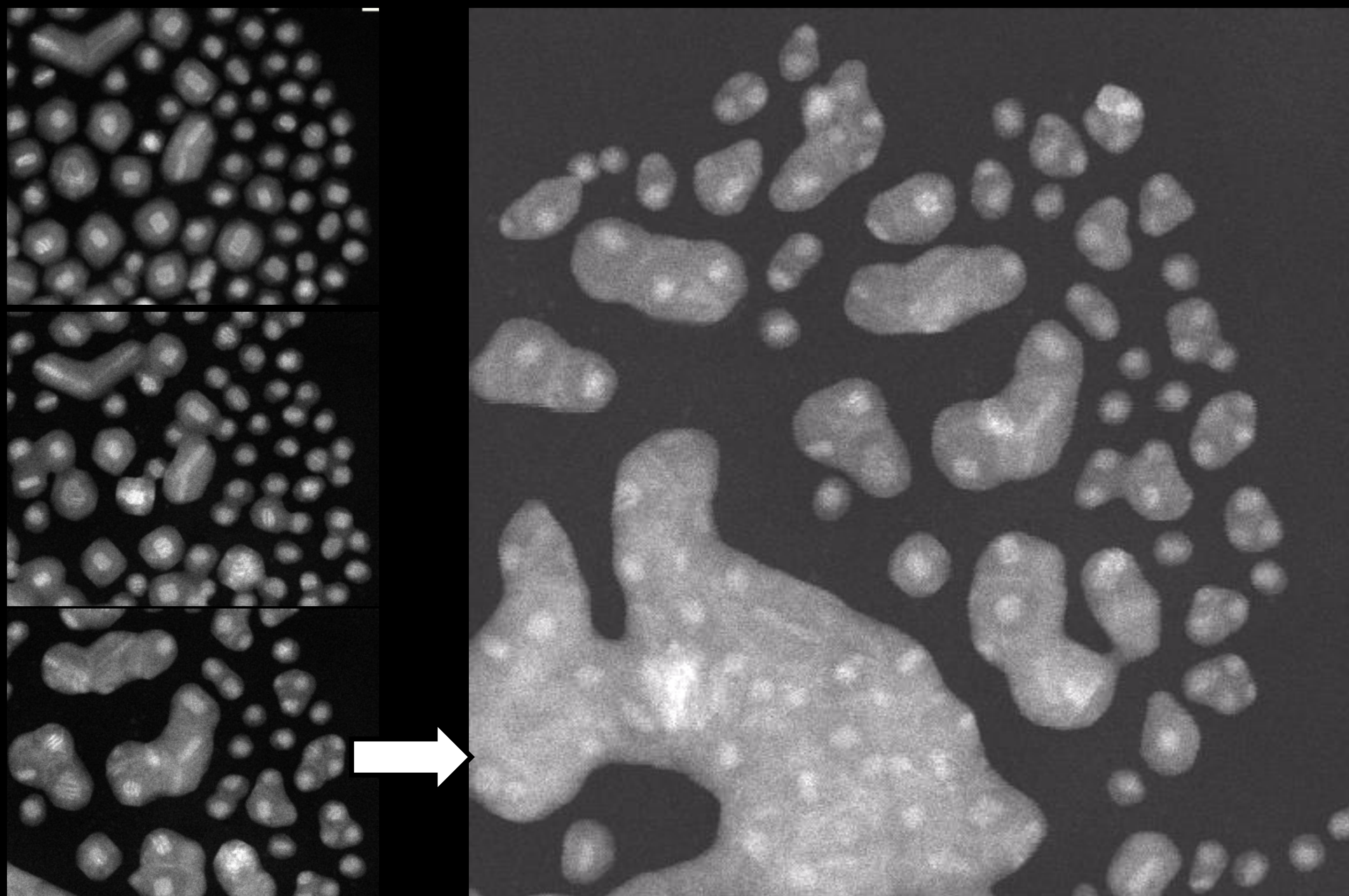
Initial Annealing (0.3 Torr $H_2$)

Oxidation (~30 mTorr $O_2$ + 300°C)

300 °C

400 °C

500 °C



- Much larger porousness in the dilute Pt system

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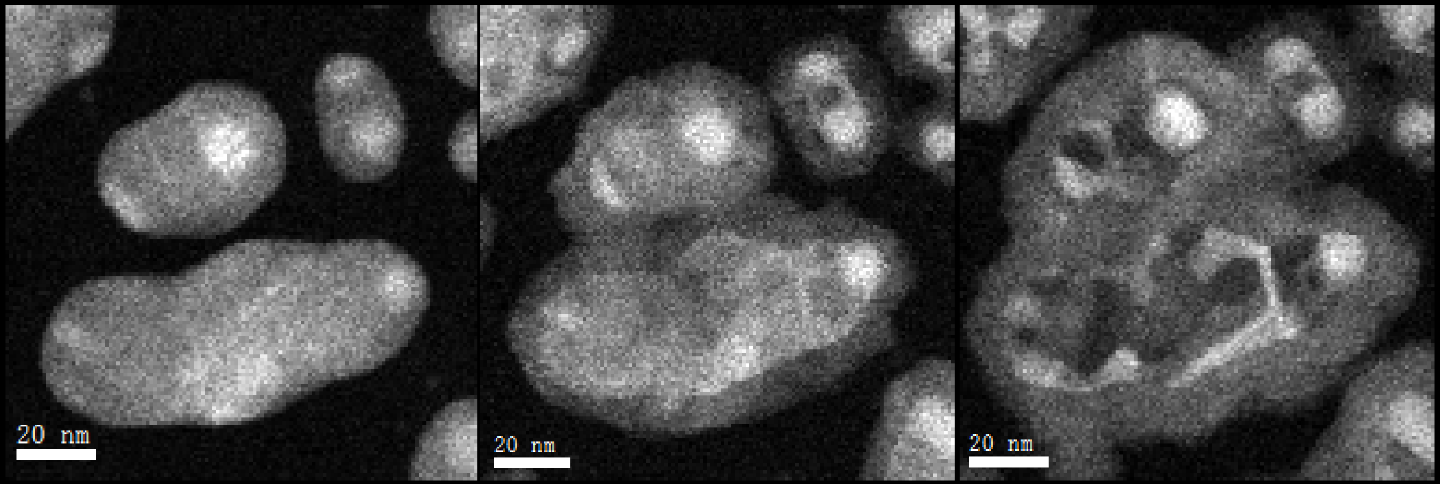
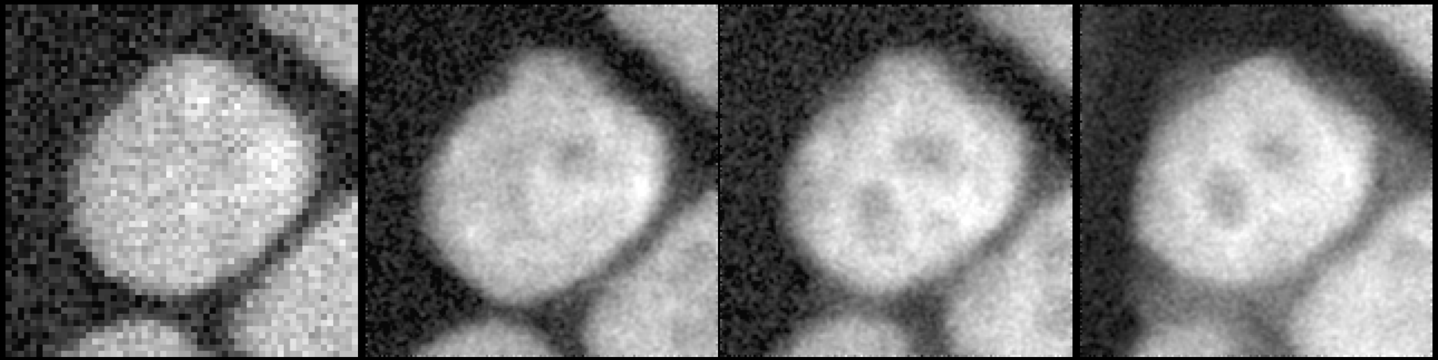
Samples provided by Chen Chen, PD Yang group

# Low Concentration of Pt in Co

Oxidation (~30 mTorr $O_2$ + 300°C)




Pt:Co = 1:1



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# Kirkendal Voids Forming Dynamics

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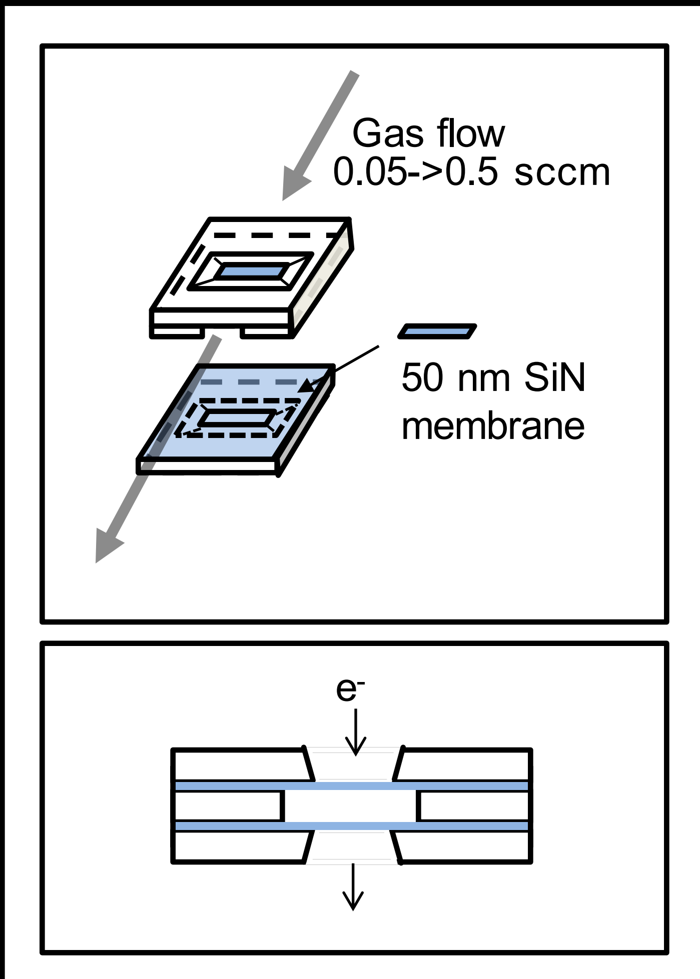
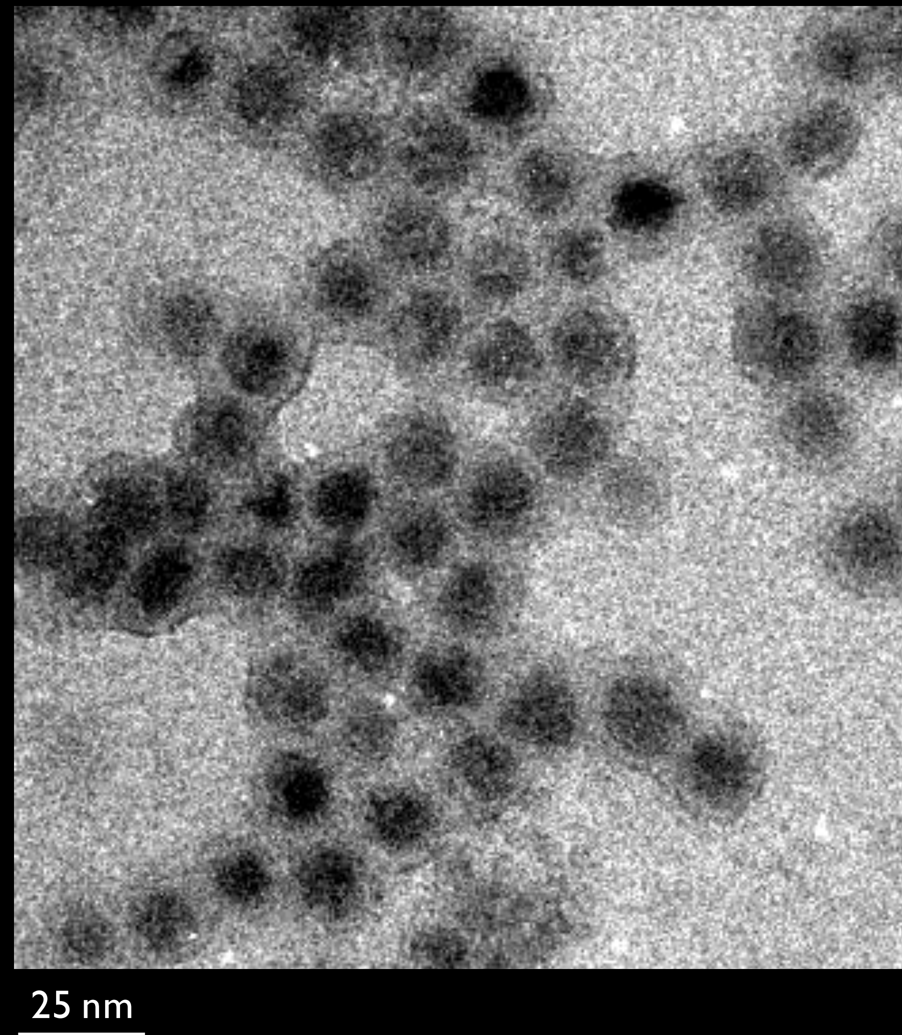
Ramping from 150 to 250°C in oxidation environment (1 atm)




- Oxidation dynamics of cobalt nanoparticles

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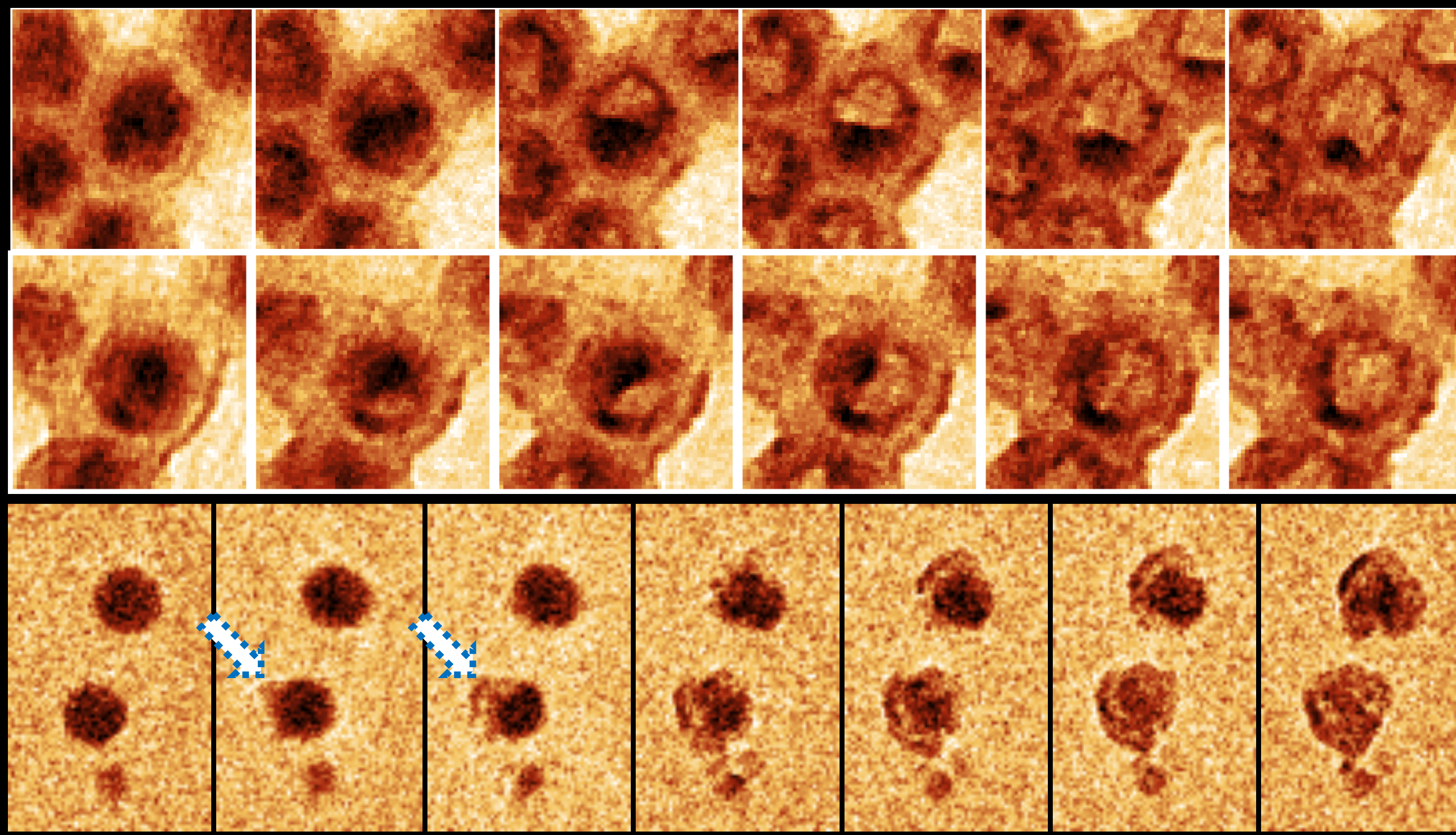
Xin et al, Microscopy and Microanalysis, 2013

# Gas Pressure Can Modify Spatial Dependent Reaction Kinetics

1 bar $O_2$

<0.1 mbar $O_2$



- Disclaimer: I have no intention to discredit differentially pumped ETEM.

Huolin Xin 2015