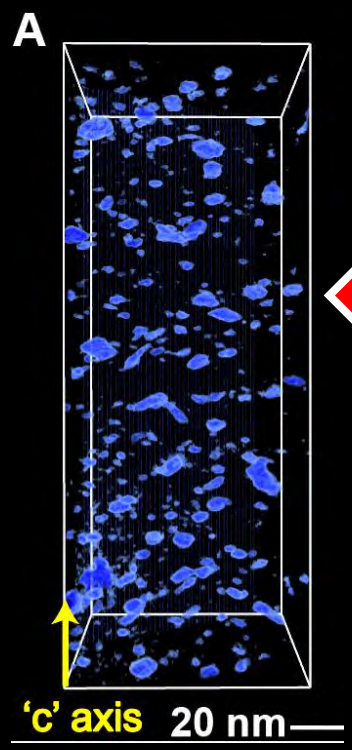
Strategies for atomic-resolution and three-dimensional electron microscopy imaging of soft-hard material interfaces

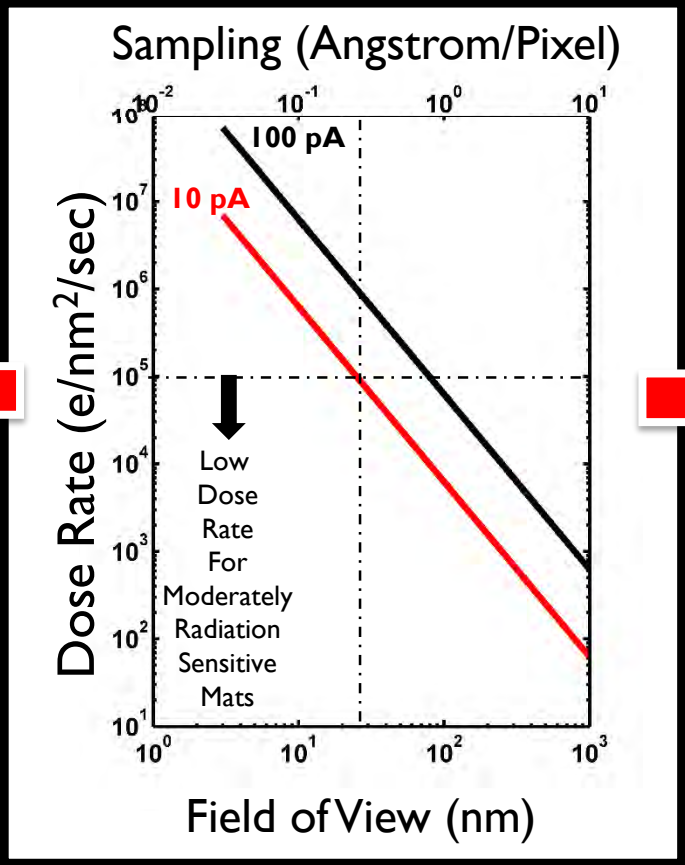
Huolin L. Xin

Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY

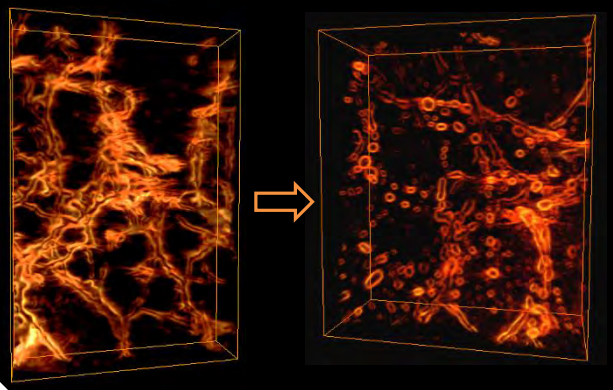
Biogenic Calcite

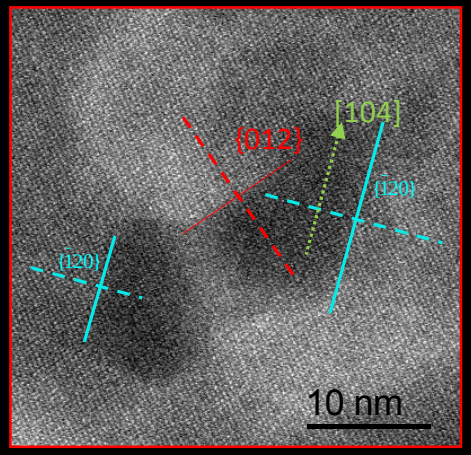


Adv. Funct. Mater., 21 (2011) 2028



Bio-inspired Calcite



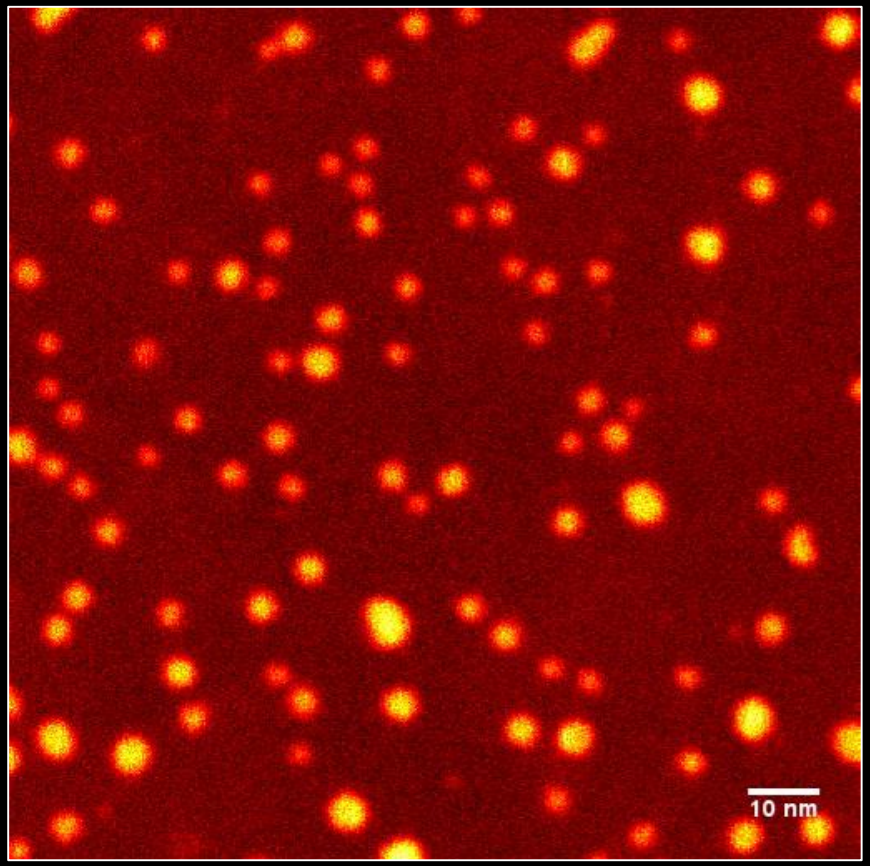


Science 326 (5957), 1244

Pitfalls of Fast Electrons

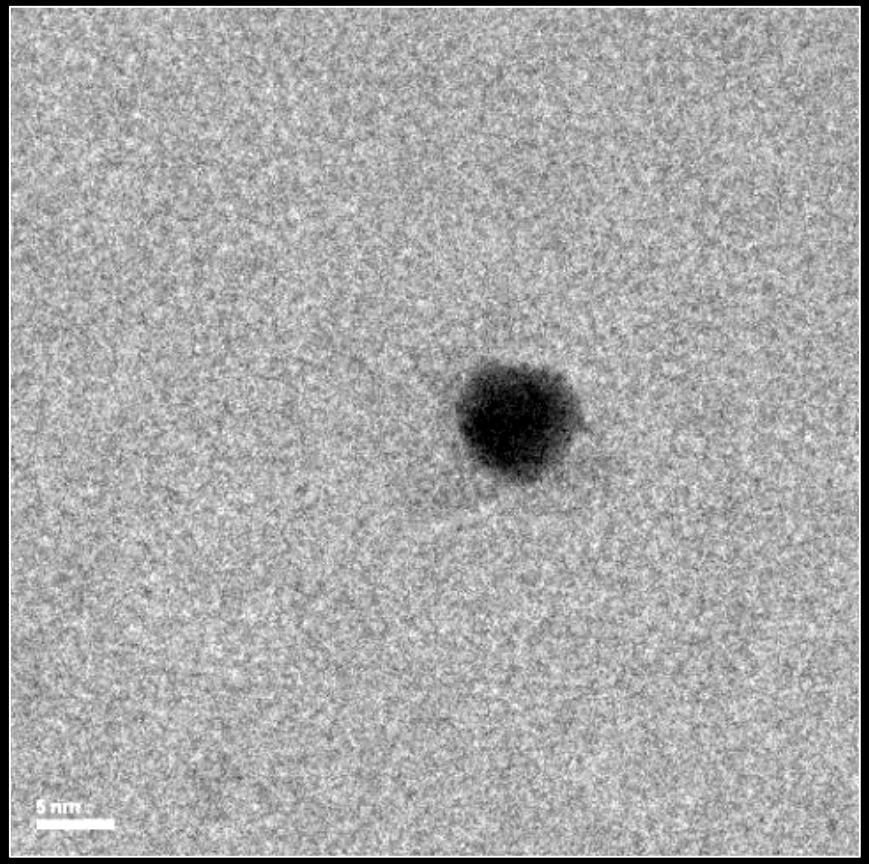
The T = 0 problem

Focused beam induced coarsening at (>300 pA)

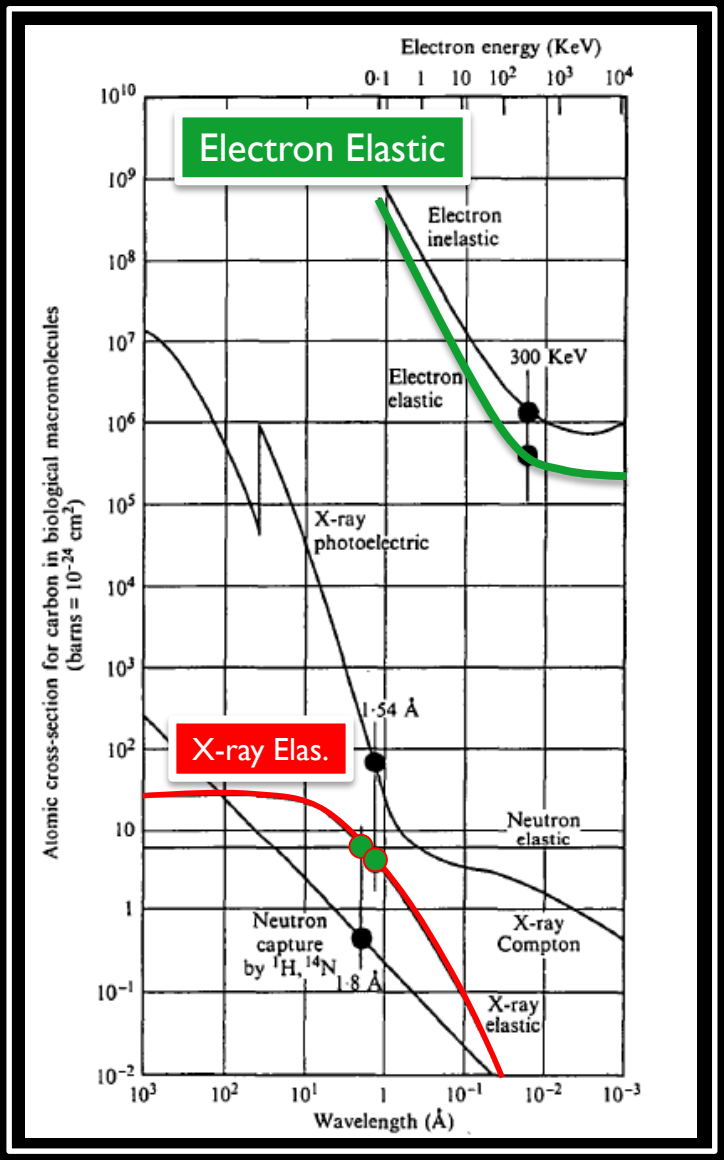


High-dose imaging in gas

4500/Ang.^{2}/sec



Fast Electron vs. X-ray



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

How many damaging events per useful imaging event.

Least Damage

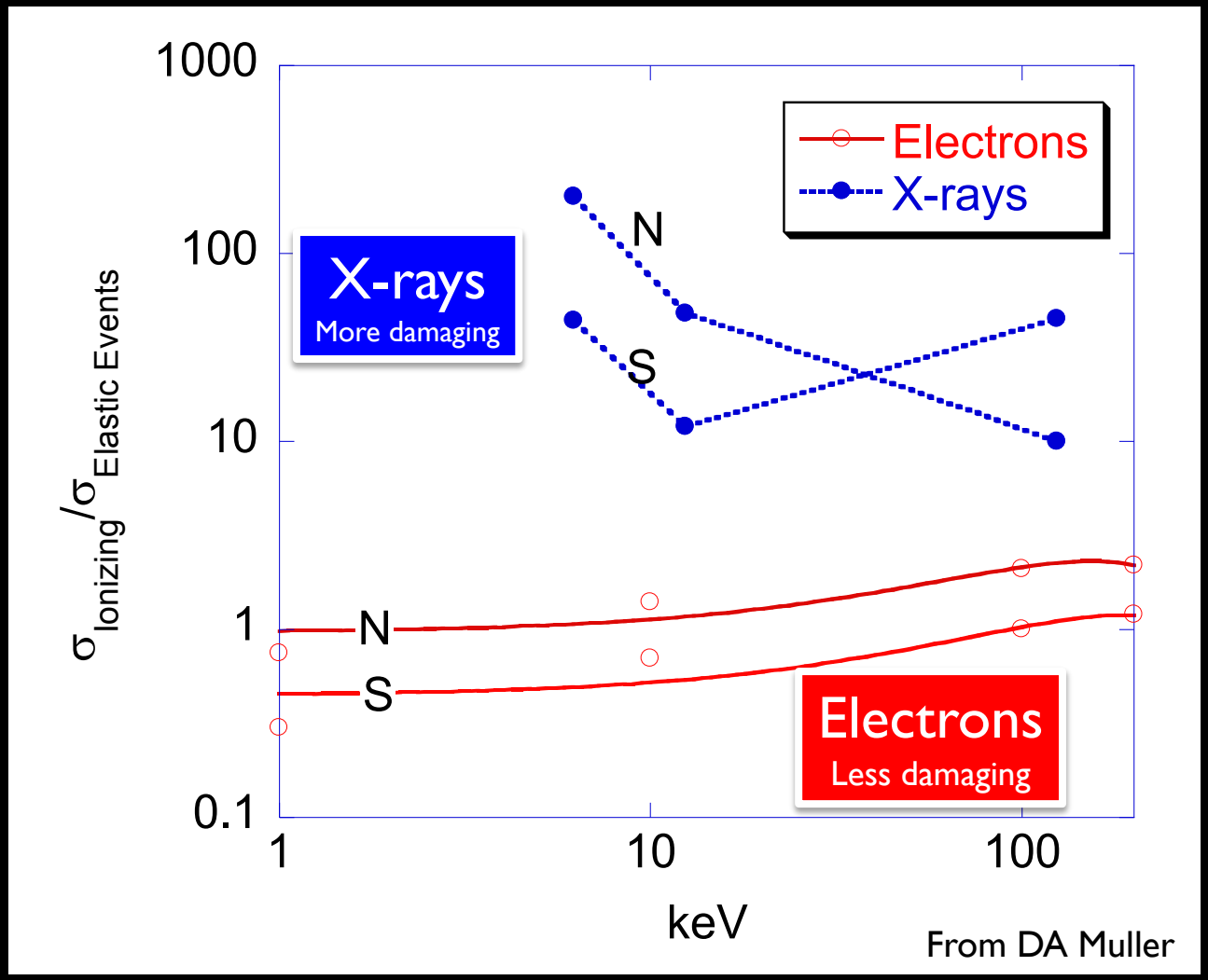
Elastic Imaging – Electrons win

Inelastic imaging – Soft X-rays win

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

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

Damaging / Useful



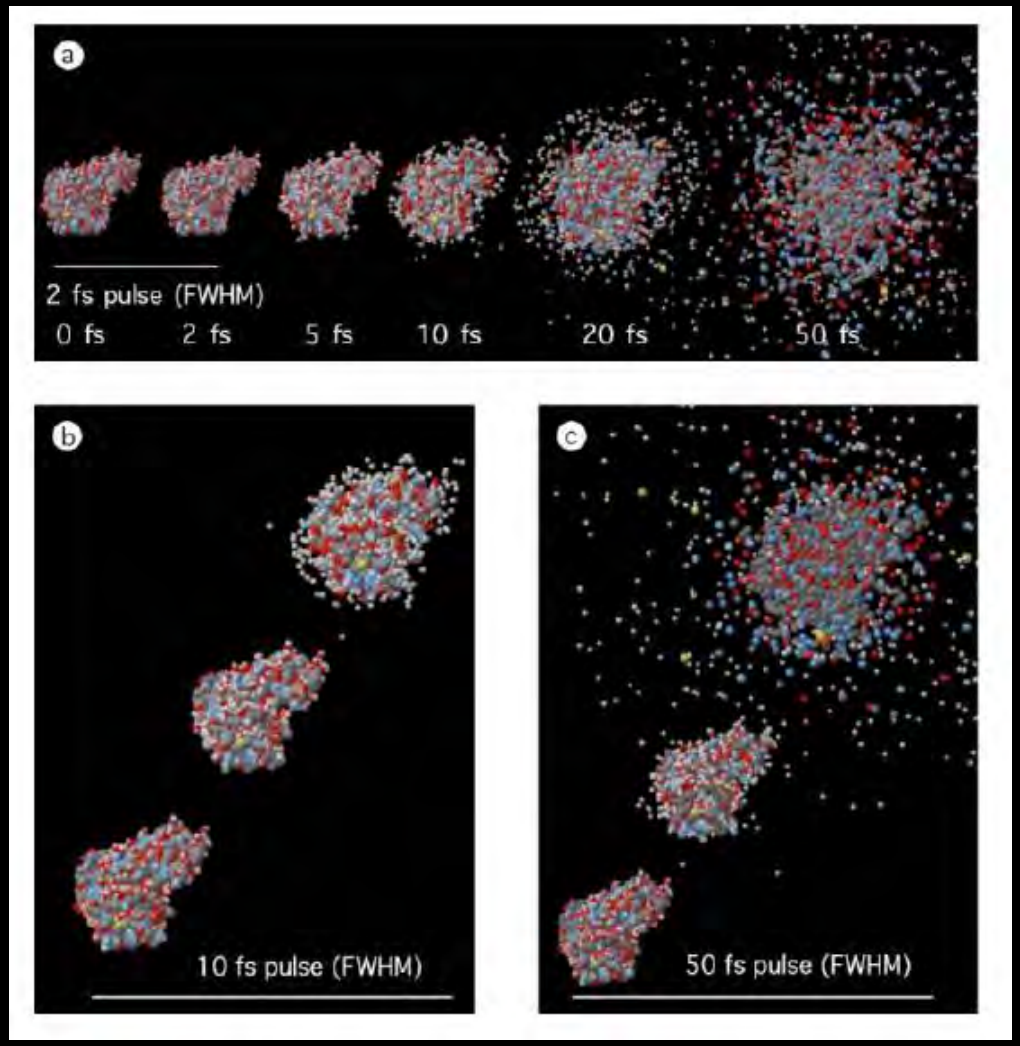
More elastic info per damaging event

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

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

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

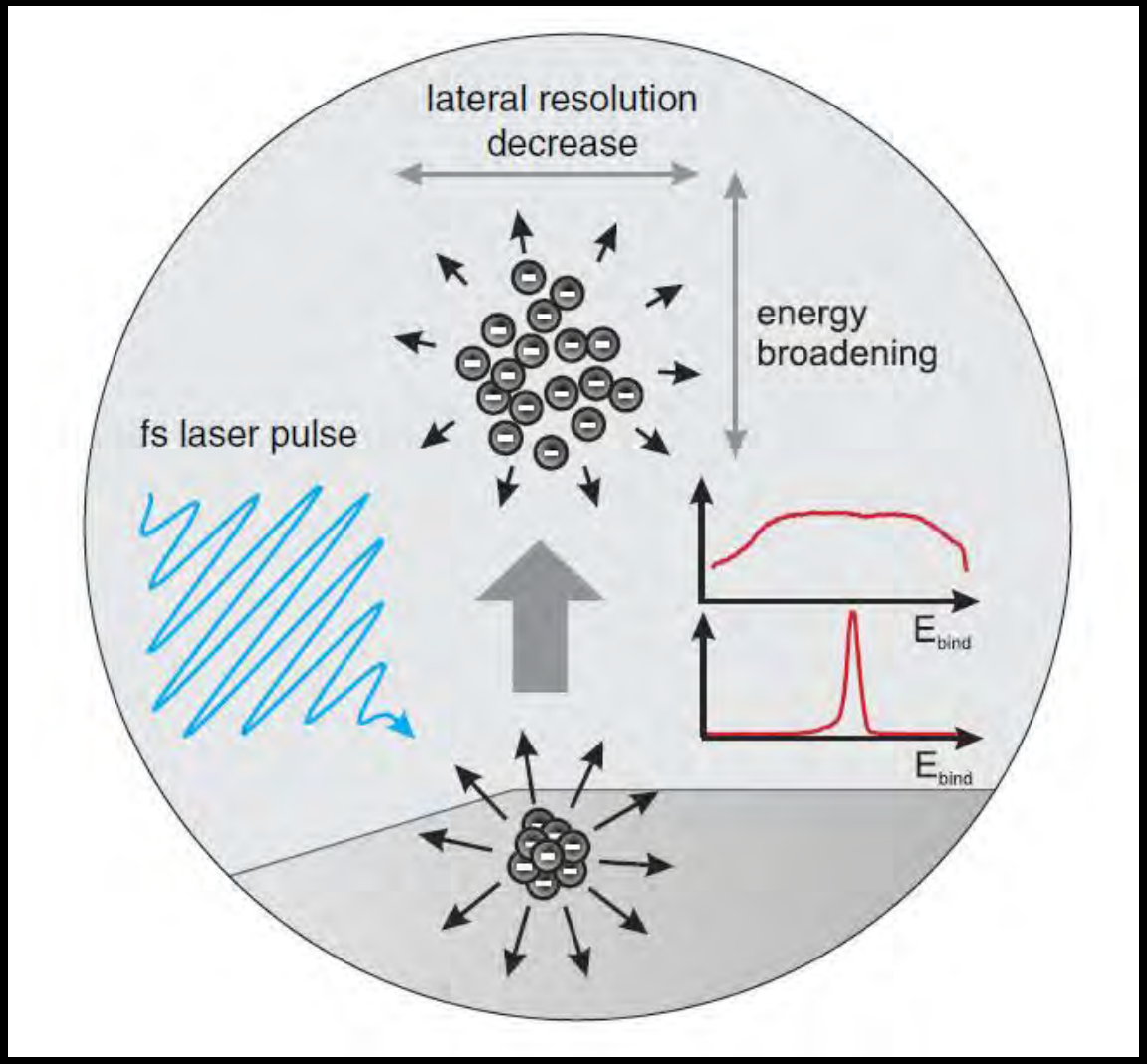
Can we do Free Electron Laser-type of protein crystallography with short electron pulses?



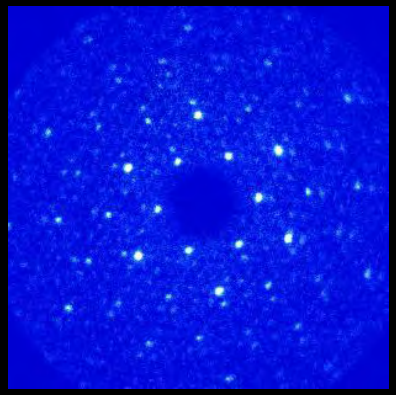
- We have really good lateral and longitudinal **coherence** with electrons
- What are the limitations?

Proceedings of FEL 2006, BESSY, Berlin, Germany

Diffract and Destroy is Difficult Using Electron Pluses due to the Space Charge Effect



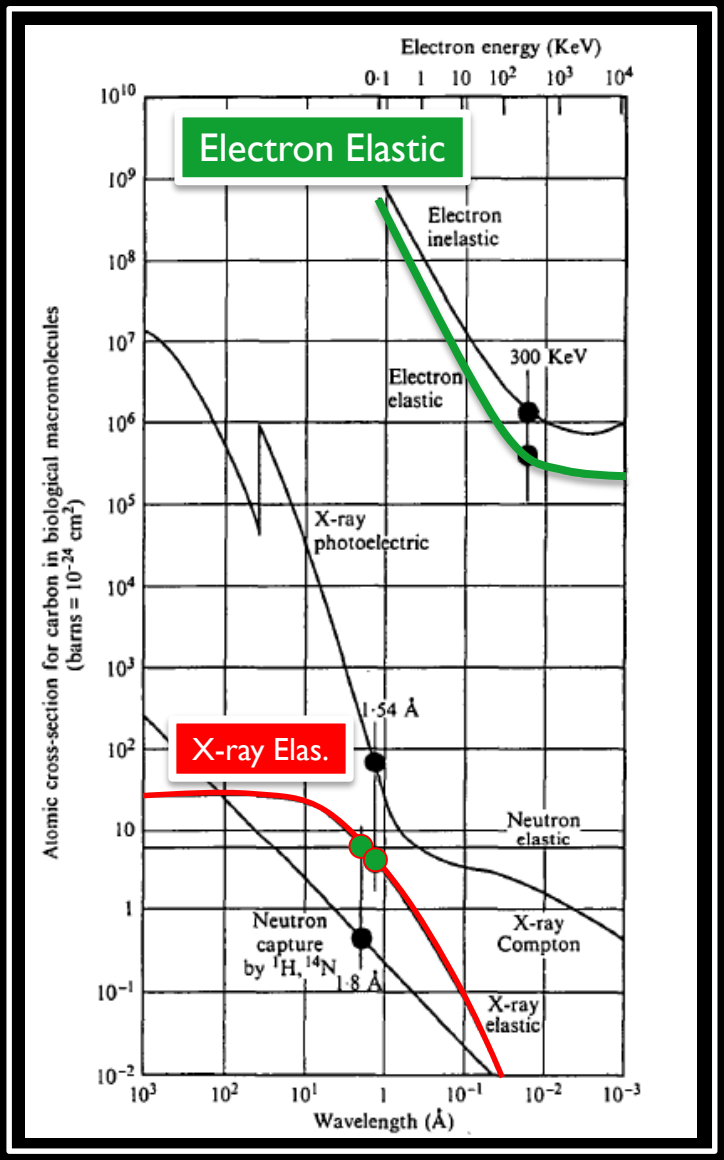
- The temporal width of the electron pulses decreases quickly with the number of electrons



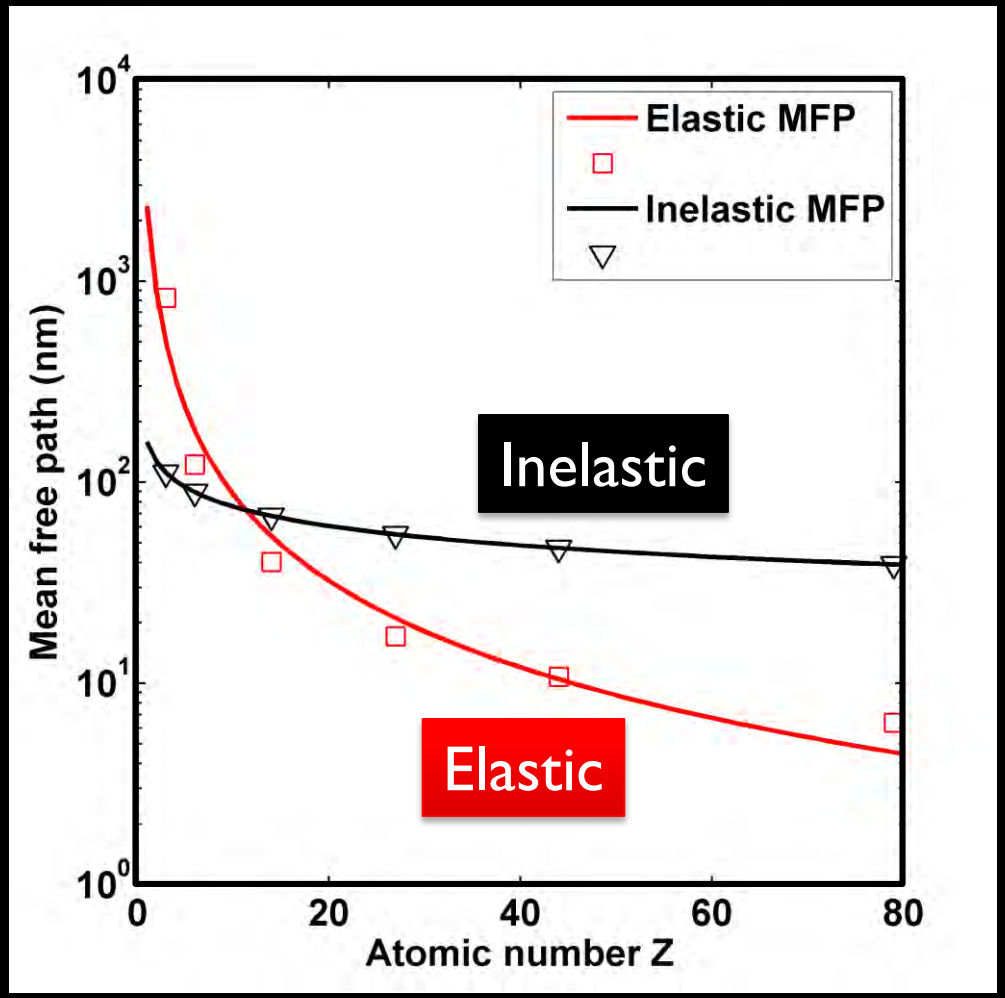
XJ Wang, J. Hill, and Y. Zhu et al, arXiv:1304.5176
Diffraction Patter of 1T-TaS2
40-120 fs single pulse of 3x10^4 2.8 MeV electrons

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

Electron Mean Free Path

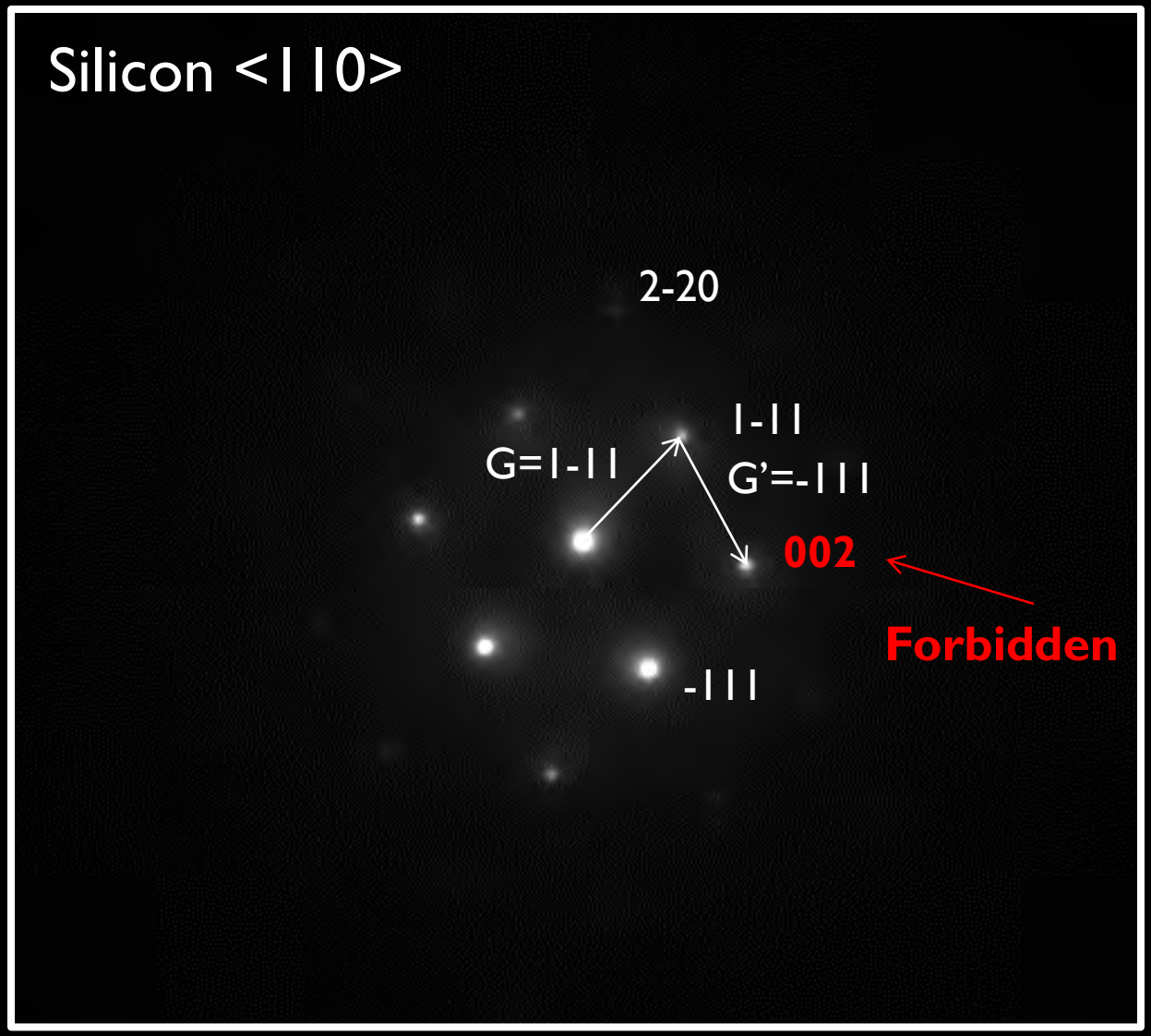


Mean free path for 100 keV electrons



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

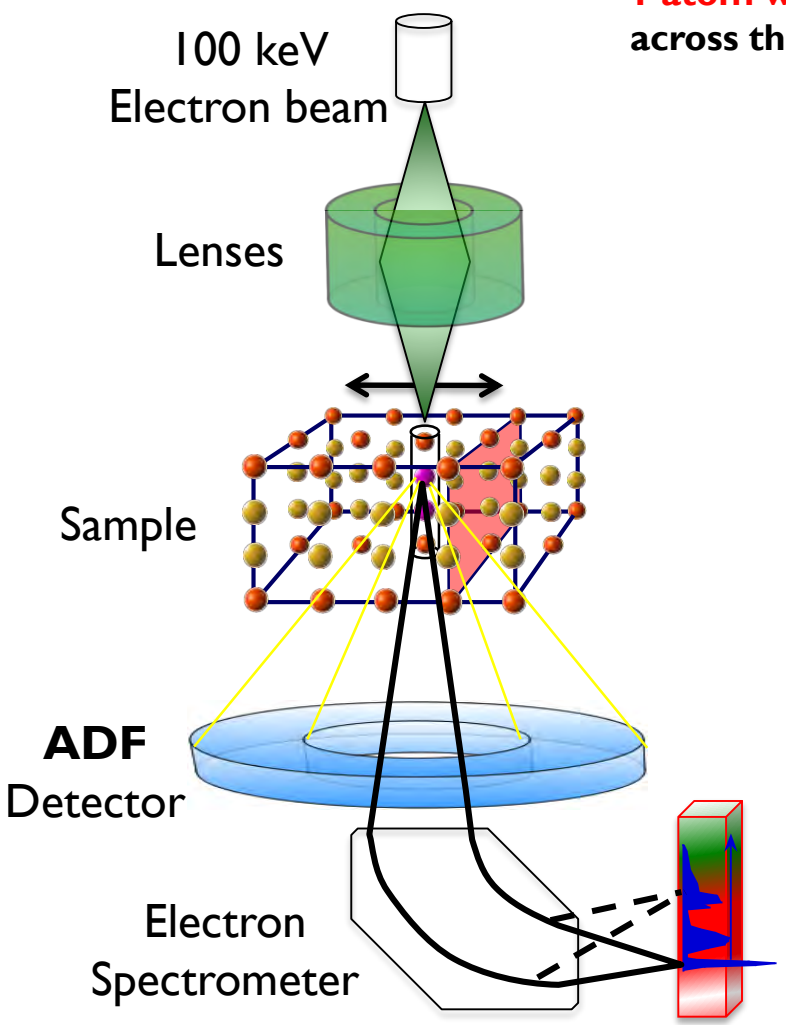
Electron Diffraction is Highly Dynamical

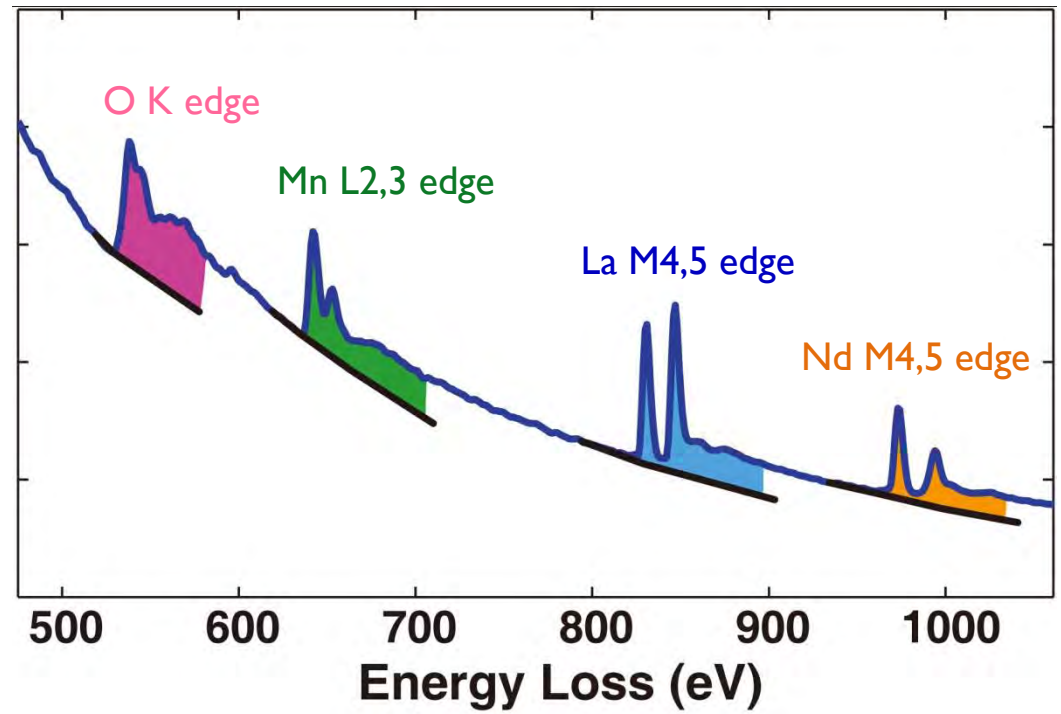


- It is nontrivial to do crystallography with electron diffraction

Scanning Transmission Electron Microscopy

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



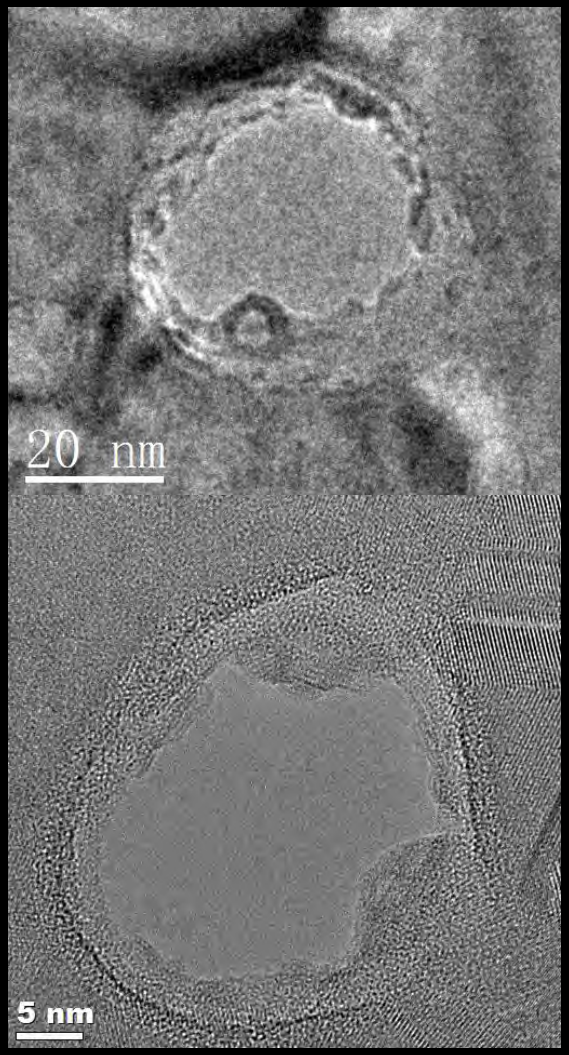


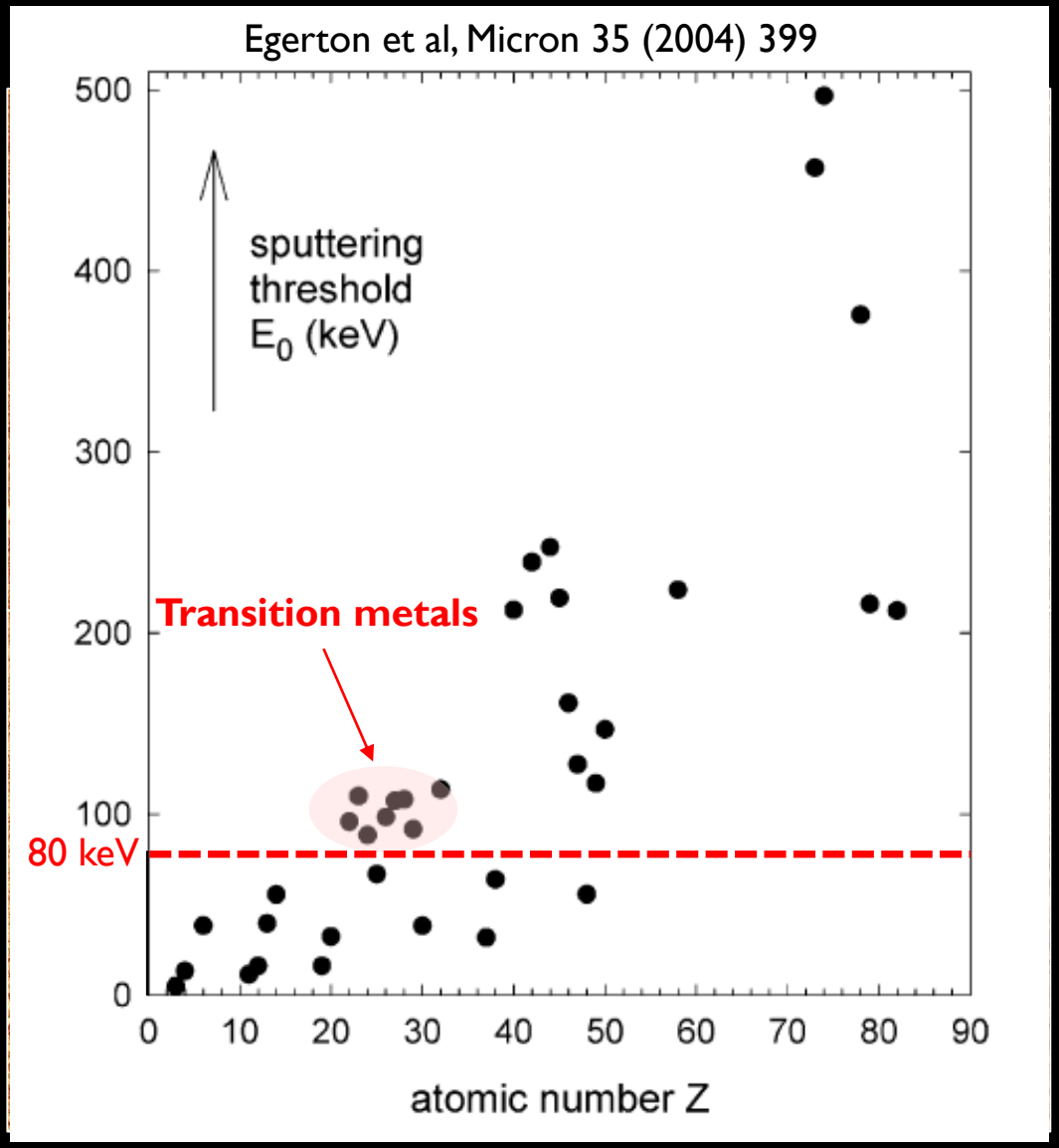
Inelastic Scattering

EELS: Chemical Imaging

300 keV Beam Effect

After beam illumination

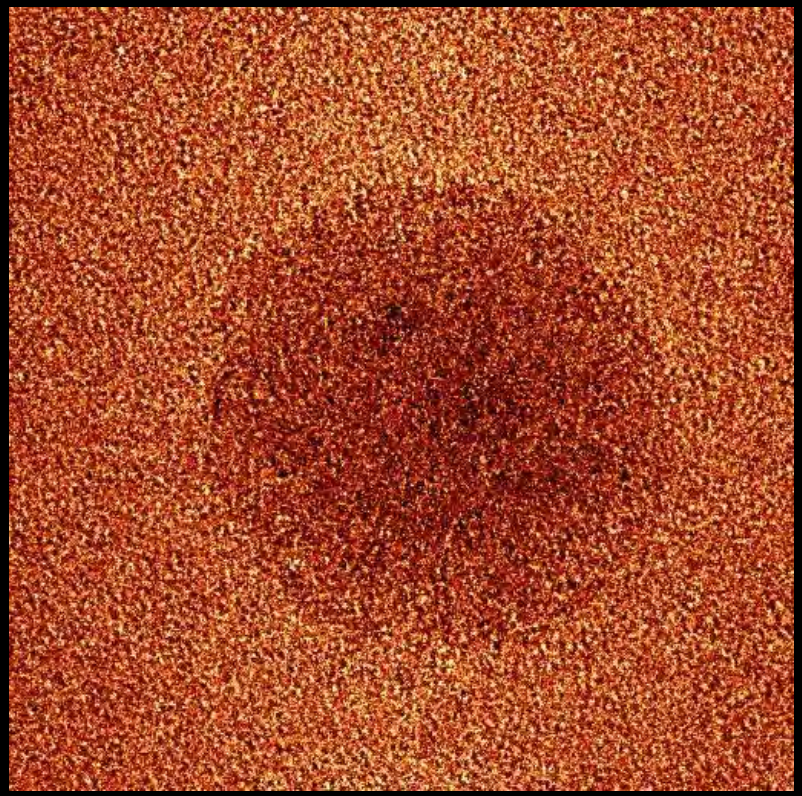




- Sputtering threshold for Co is 120 kV
- 300 keV electron beam induces particle morphology change and the Kirkendall effects

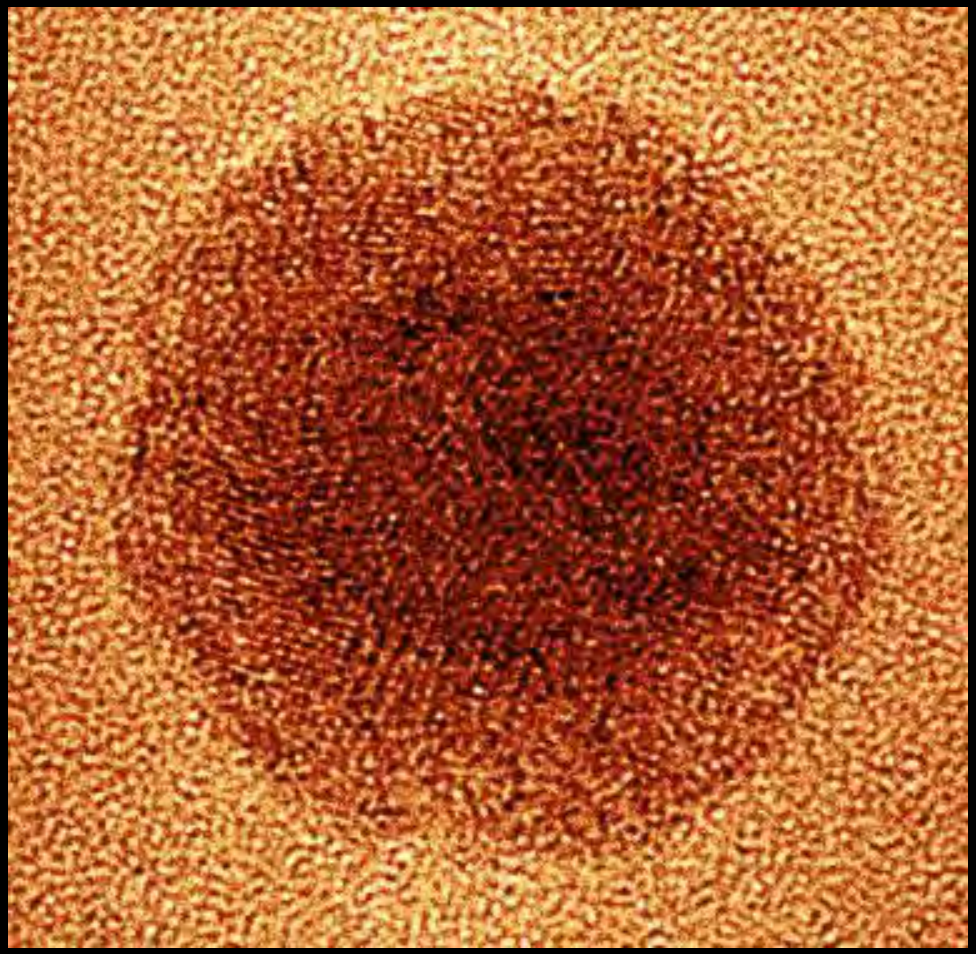
80 keV and Low-Dose Imaging

1 min continuous acquisition



38 electrons/Ang.^{2}/sec

Summed Over 30 Drift-Corrected Images



~1000 electrons/Ang.^2

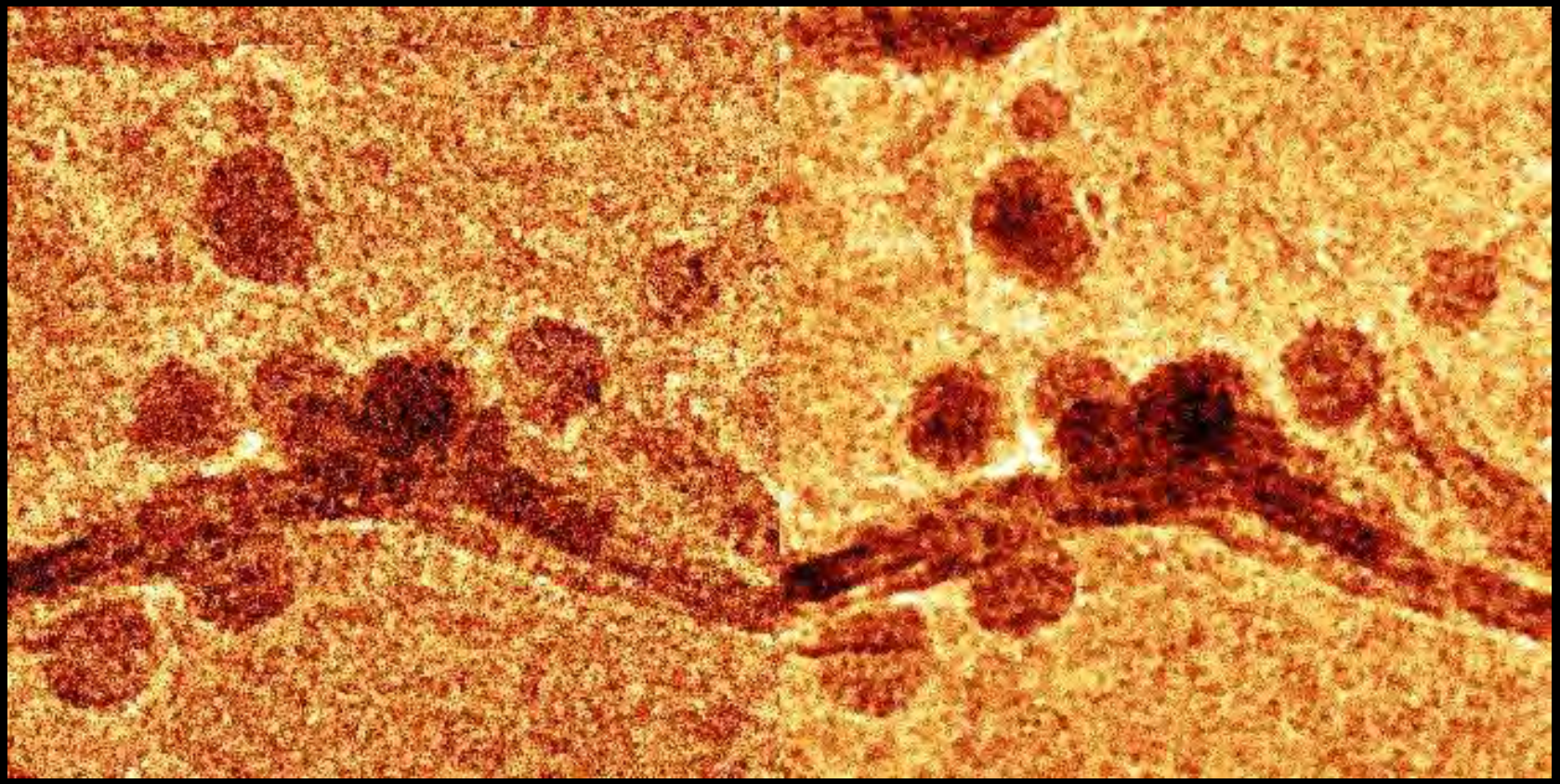
- Low-dose averaging

80 keV and Low-Dose Imaging Cobalt Particles in Hydrogen

400C H2 3.9 mbar, 100 sec

2.7 electrons/Ang.^2/sec

7.5 electrons/Ang.^2/sec



10 nm

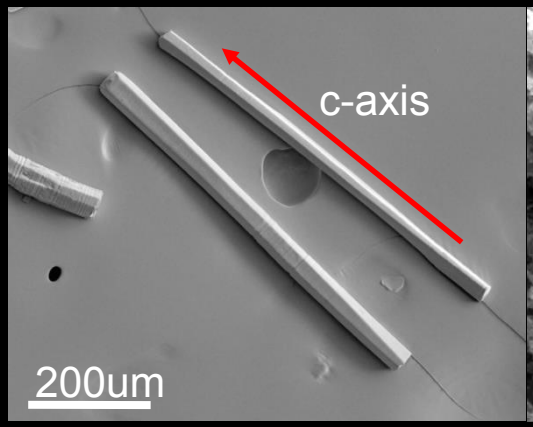
Ultralow dose vs. low dose

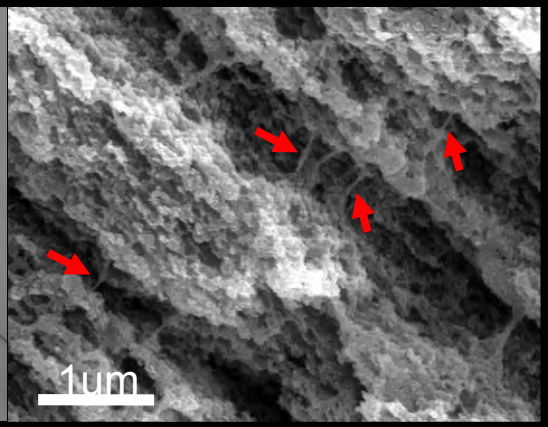
- Surface oxide layers are removed at 400C H2 reduction

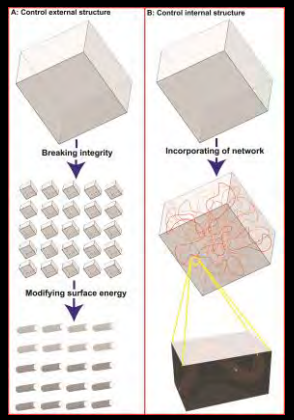
Biogenic Porous/fiber-incorporated Calcite Single Crystals

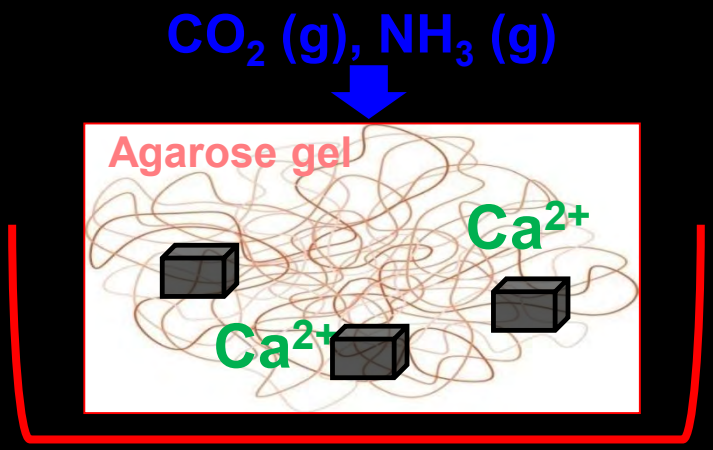
Calcite = $CaCO_3$ with a rhombohedral unit cell

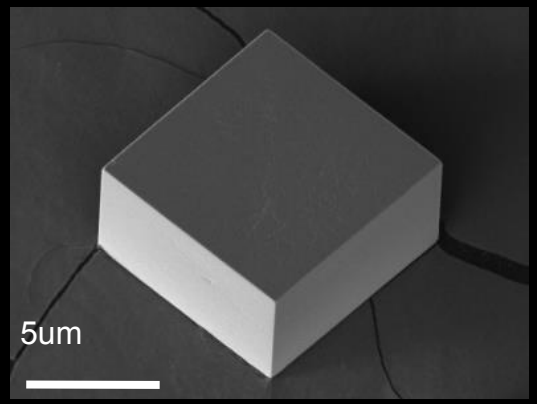
Mollusk shell







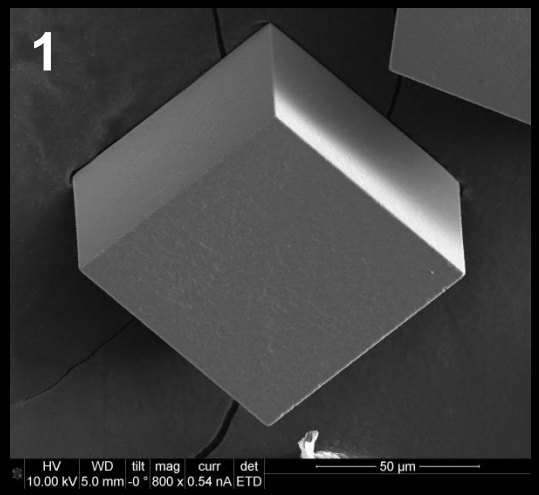


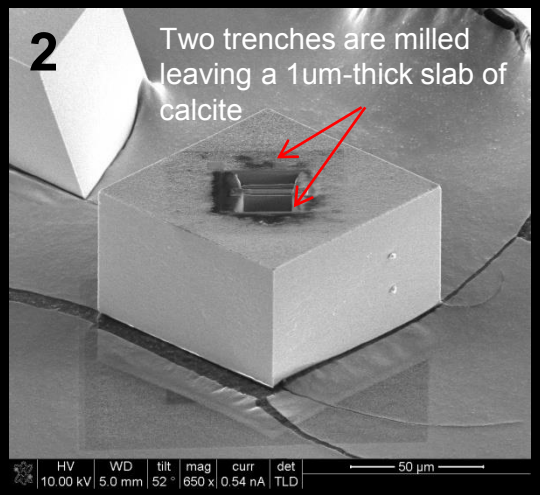


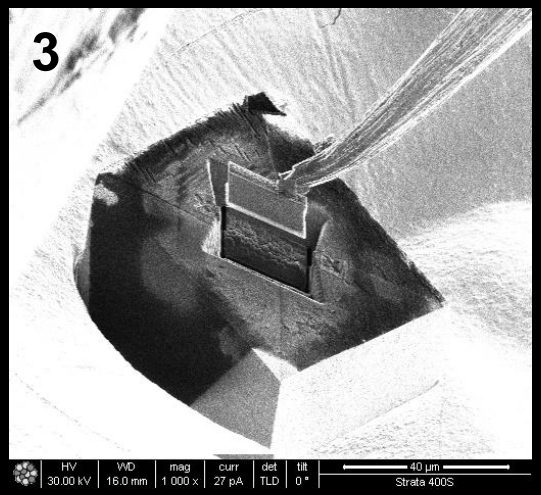
H. Li*, H. L. Xin*, et al, *Advanced Functional Materials*, 2011, **21**, 2028-2034.

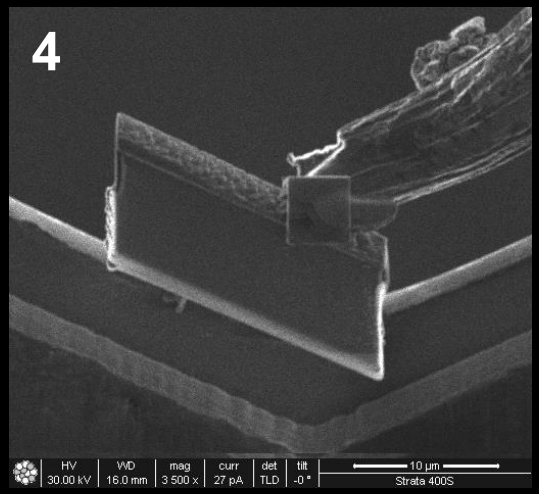
The high toughness of biogenic single crystal calcite inspire us to create a bi-phase mesoporous single crystals using calcite and polymer fibers.

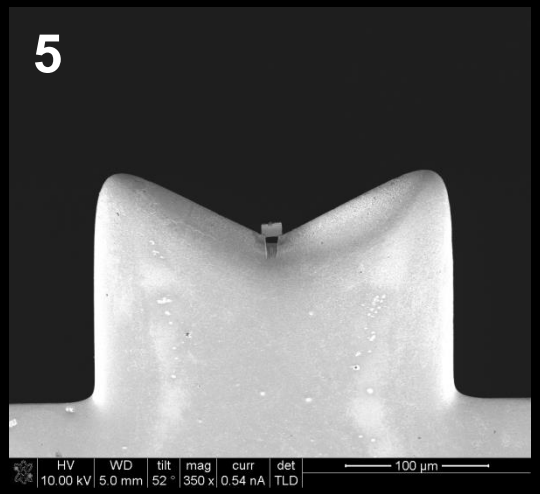
Focused Ion Beam Lift-out Method

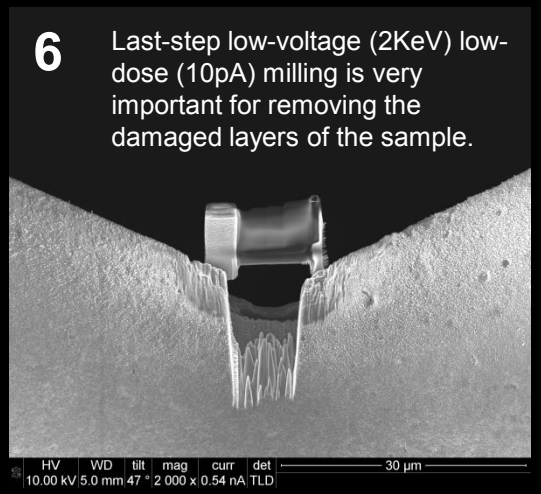












An electron transparent sample with only ~3nm-thick surface damaged layer can be prepared by the FIB lift-out method.

Reducing Surface Amorphous Layer is Critical for Imaging Radiation Sensitive Materials

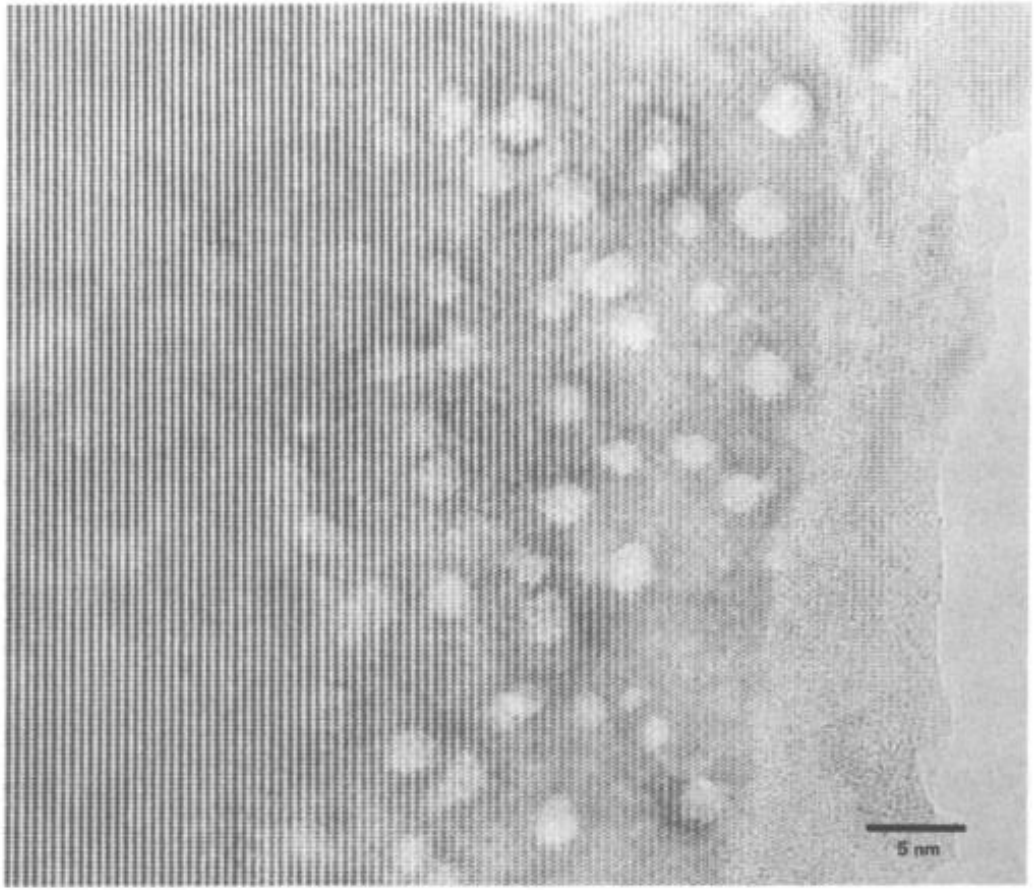
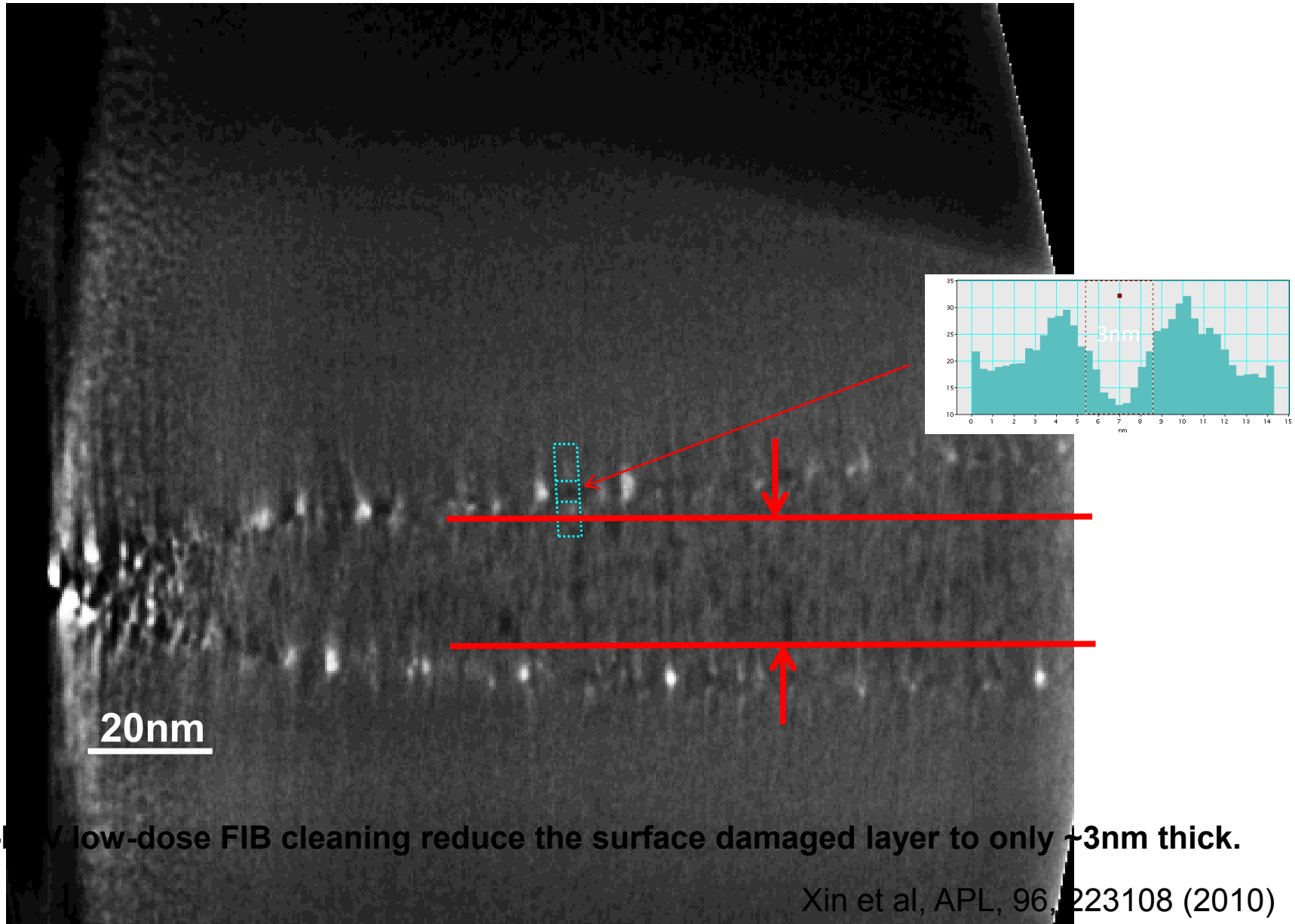


Fig. 2. TiO_2 irradiated under high flux conditions along along the ⟨101⟩ zone. Beam damage resulted in a defective surface layer and void formation.

MI Buckett et al, Electron Irradiation Damage in Oxides, Ultramicroscopy 29 (1989) 217

- Nucleation of vacancies from interfaces

Porous Low-k (SiCOH) in Cross-section



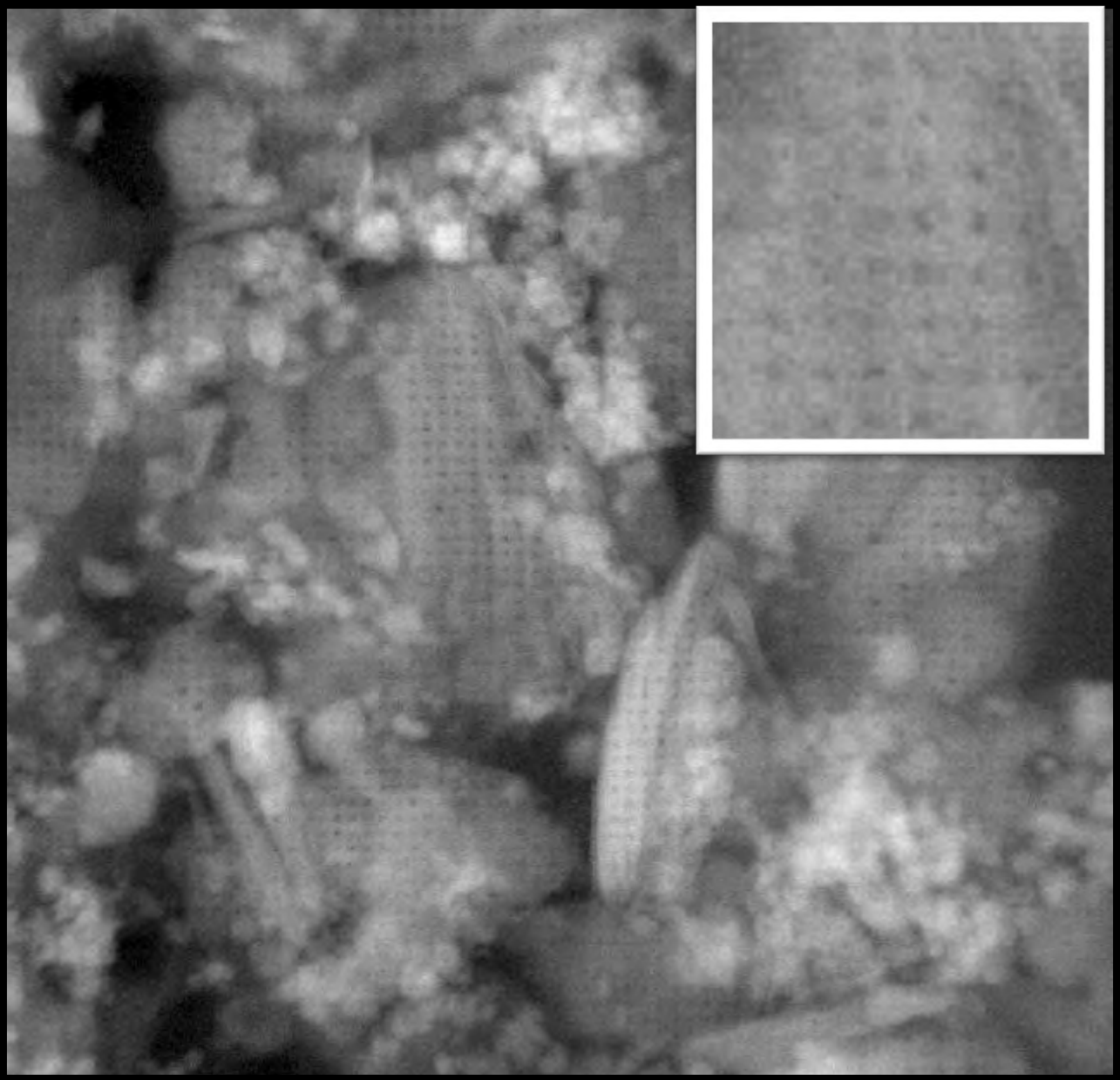
Low-k, UV low-dose FIB cleaning reduce the surface damaged layer to only ~3nm thick.

Xin et al, APL, 96, 223108 (2010)

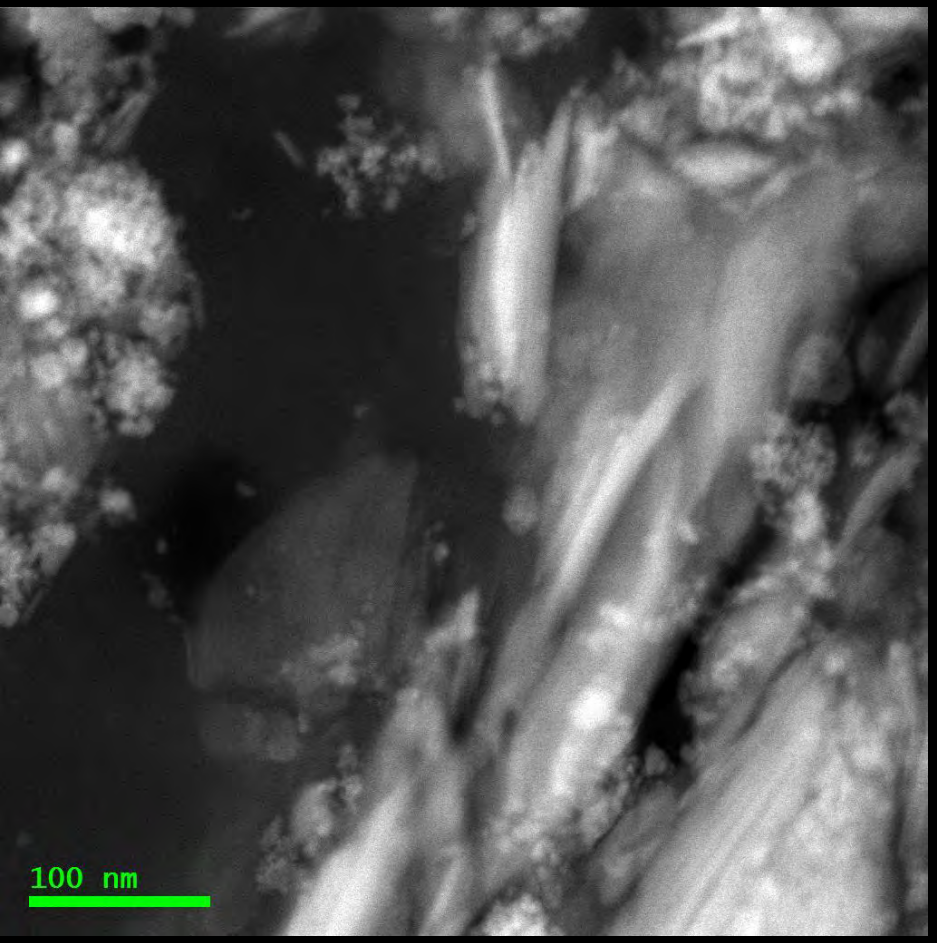
You need to keep your beam scanning

- 60 pA
- 1 Angstrom
- 0.2 sec/pixel
- 7×10^7 e^-/A^2

- Critical dose of clay
- 1×10^5 e^-/A^2

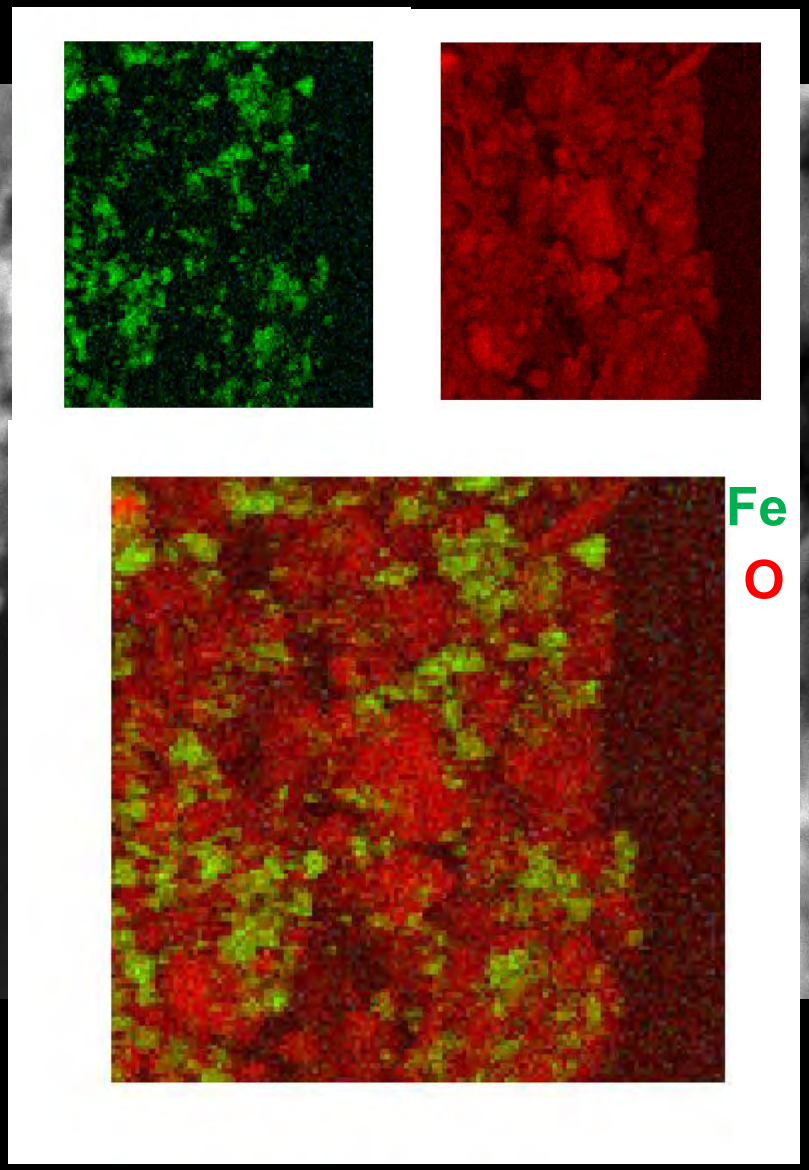


After Spreading Dose Into Each Pixels



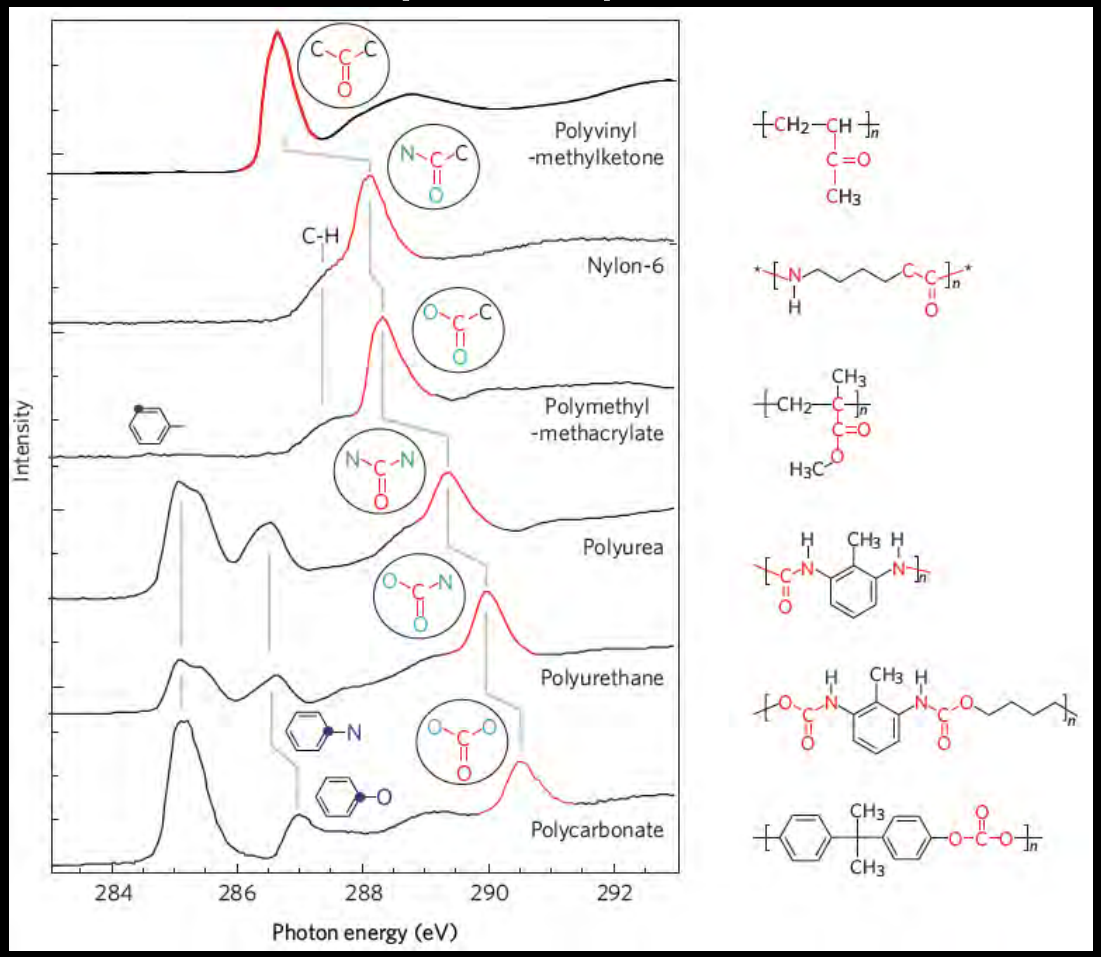
Before

- 1x10^5 electrons/A^2/pixel



Spectroscopy: What's the True Carbon K edge?

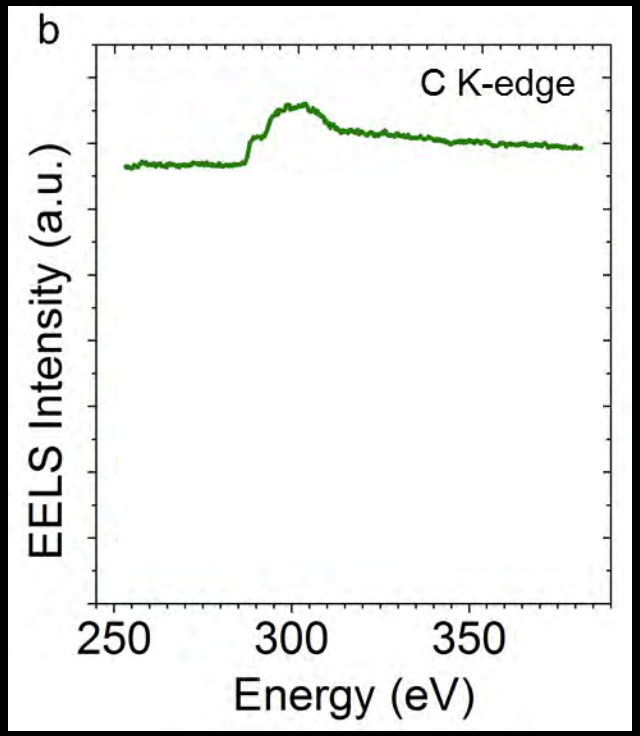
X-ray Absorption

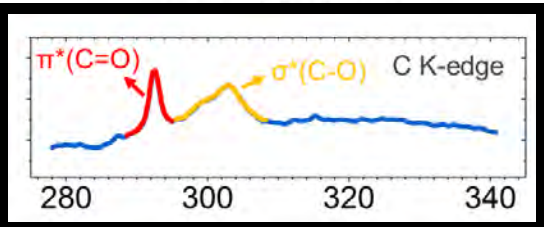


Ade and Stoll, Nature Mats, 8 (2009) 281
Ade and Hitchcock, Polymer 49 (2008) 643

EELS of Li_2CO_3

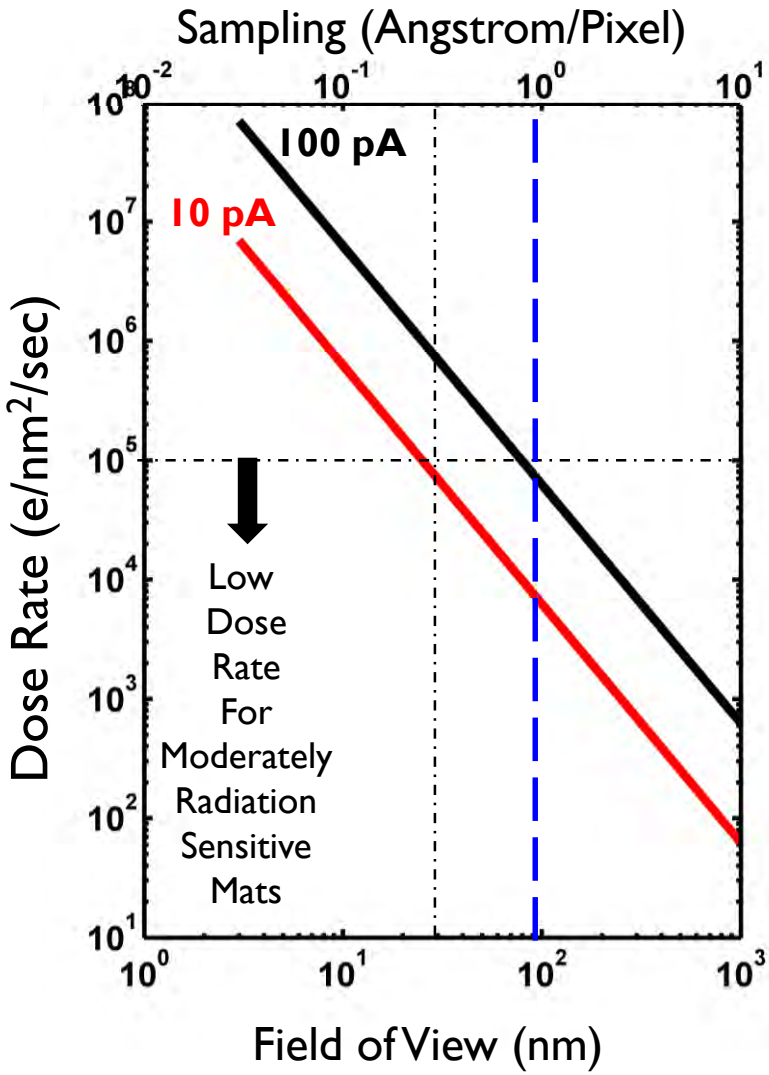
500 electrons/Å^2/spectrum





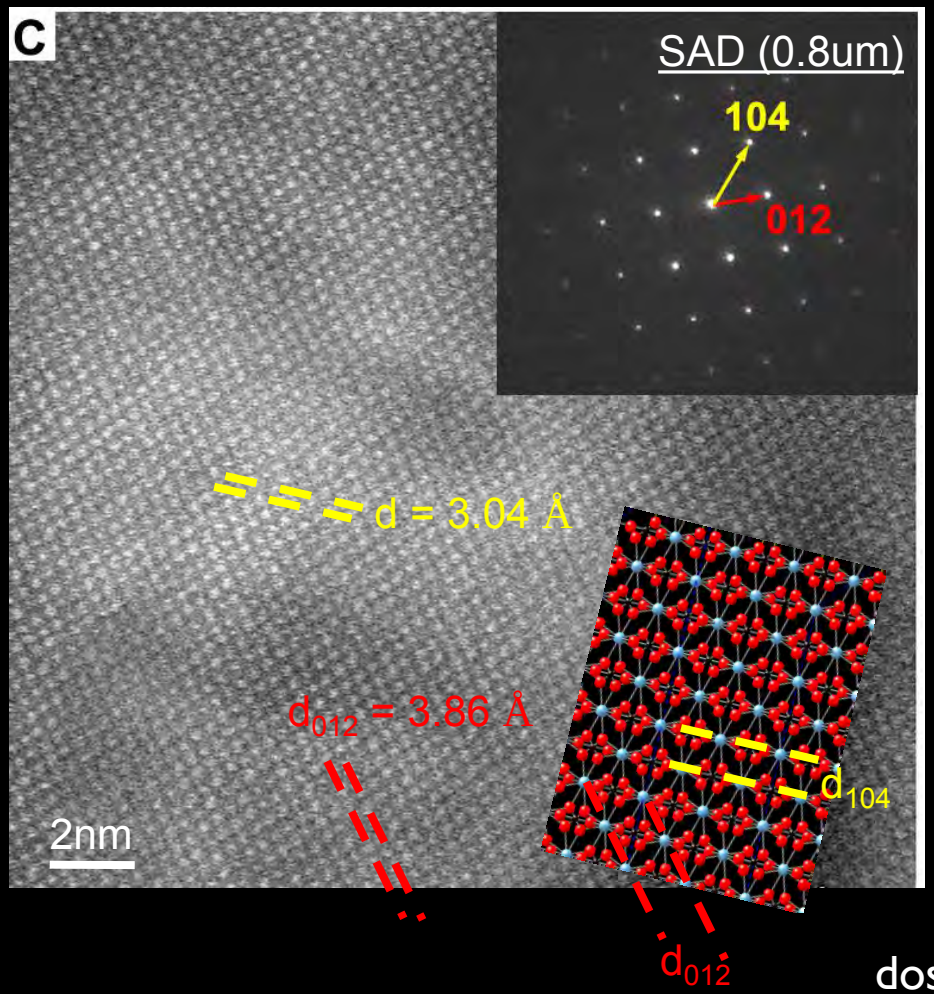
L. Feng *et al* Xin, Nat. Comm. 2015

Low Dose Rate Imaging in STEM



- 1×10^7 e/nm^2 is the critical dose of moderately radiation sensitive materials such as clay and FeO(OH)
- Focusing and final image requires 40 sec. To avoid seeing damage in the image, the dose rate should be 1/100sec of the critical dose, i.e. 1×10^5 e/nm^2/sec
- Uncorrected machine: >20nm field of view
- Corrected machine: >100nm field of view

Polymer-incorporated Calcite in Scanning Transmission Electron Microscope

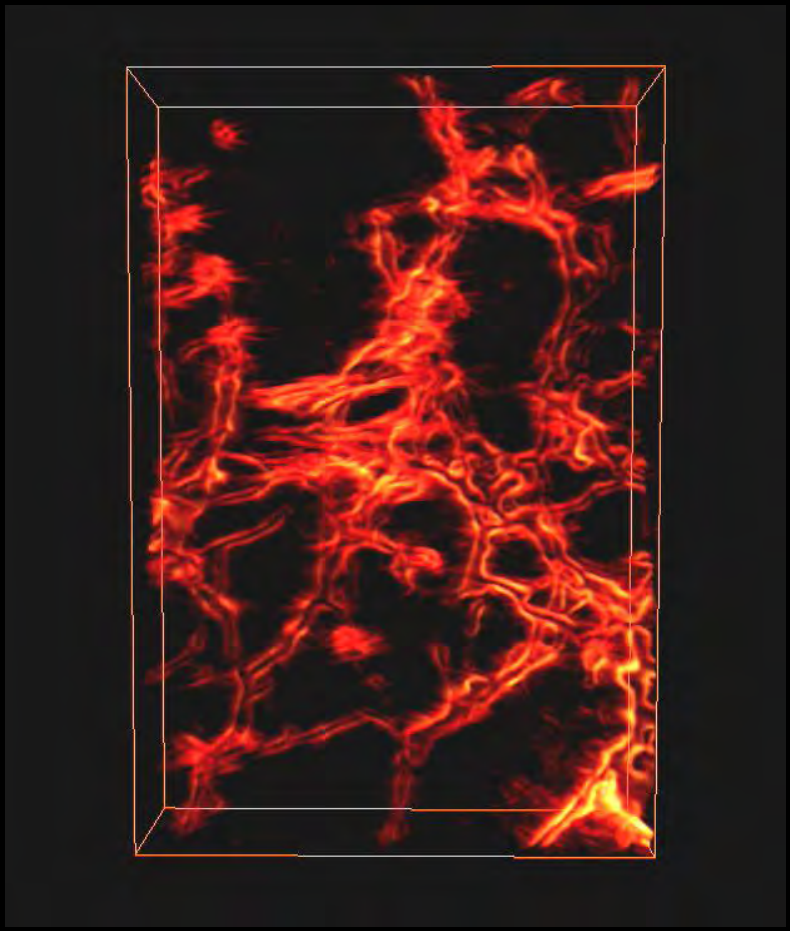


Fiber average diameter: 13 ± 5 nm
dose rate: 22 $e^-/nm^2/sec$, total dose: 8×10^4 e^-/nm^2

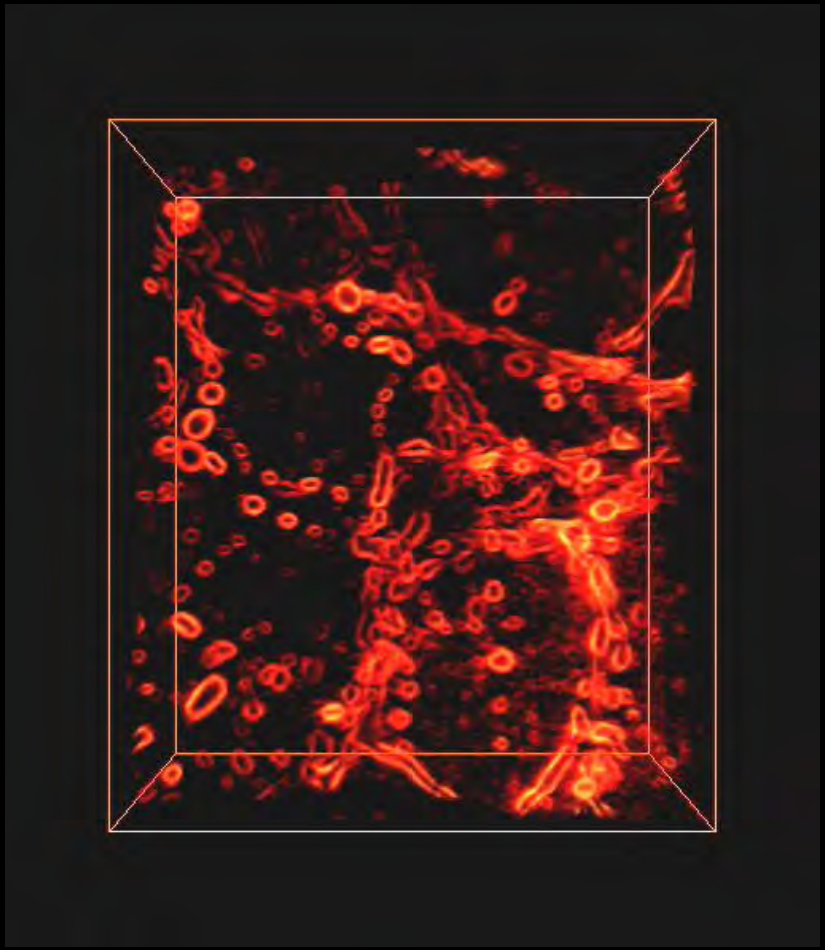
The host calcite is single crystalline and the engulfed fiber networks are orientated and connected fairly randomly.

Li (1), Xin (1) et al, Science (2009)

3-D Reconstruction of the Calcite Incorporated Agarose Fibers

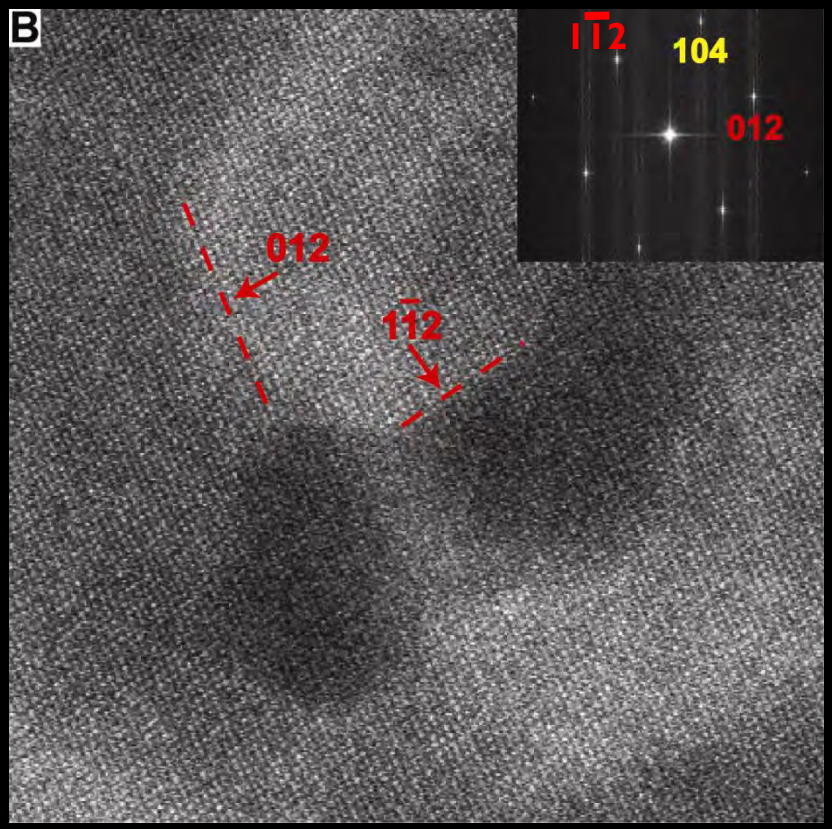


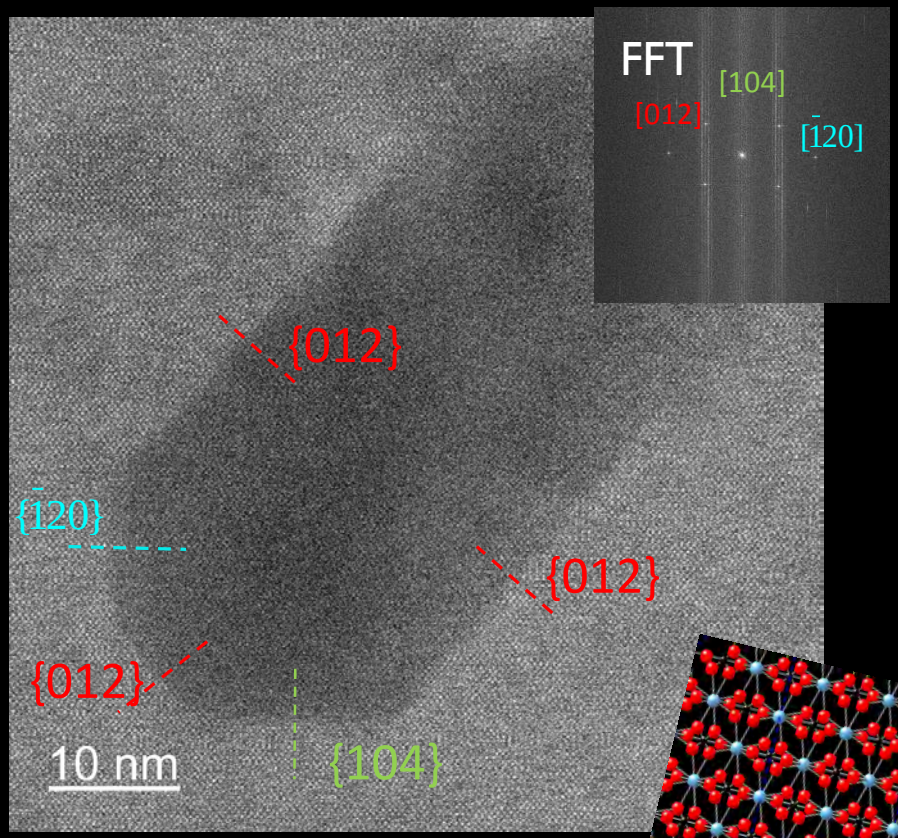
200 nm

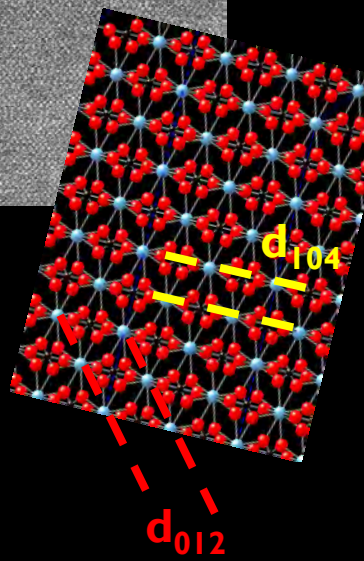


Li (1), Xin (1) et al, Science (2009)

Existence of {012} Polar Surfaces







{104} are neutral planes – lower energy
{012} are homocharged planes – higher energy

Direct observation of facets at the calcite/fiber interfaces and {012} polar surfaces (higher energy) are observed.

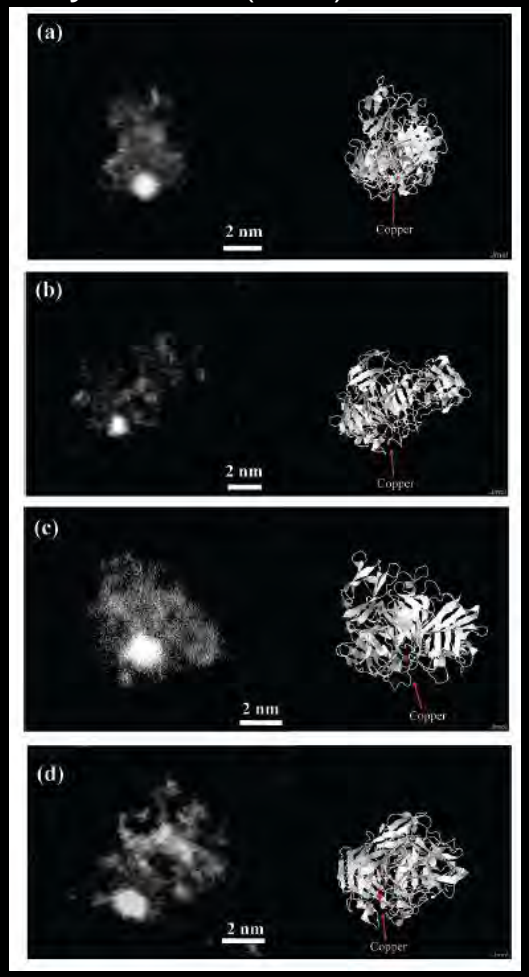
Future Directions

CFN K2 Direction Electron Detection
Ultrahigh sensitivity
Ultrahigh contrast transfer
Ultrahigh DQE

removed

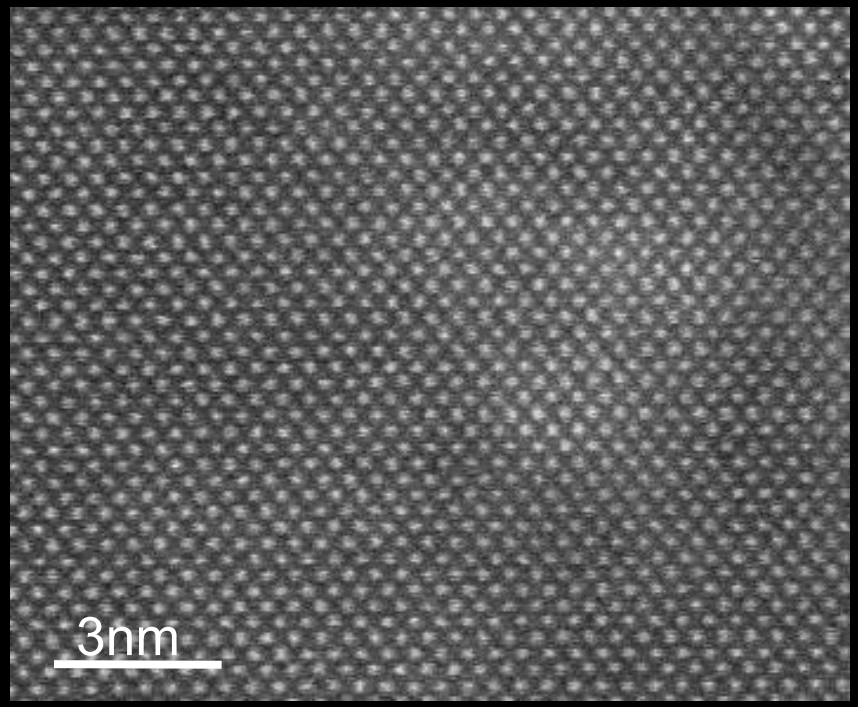
Image from Gatan

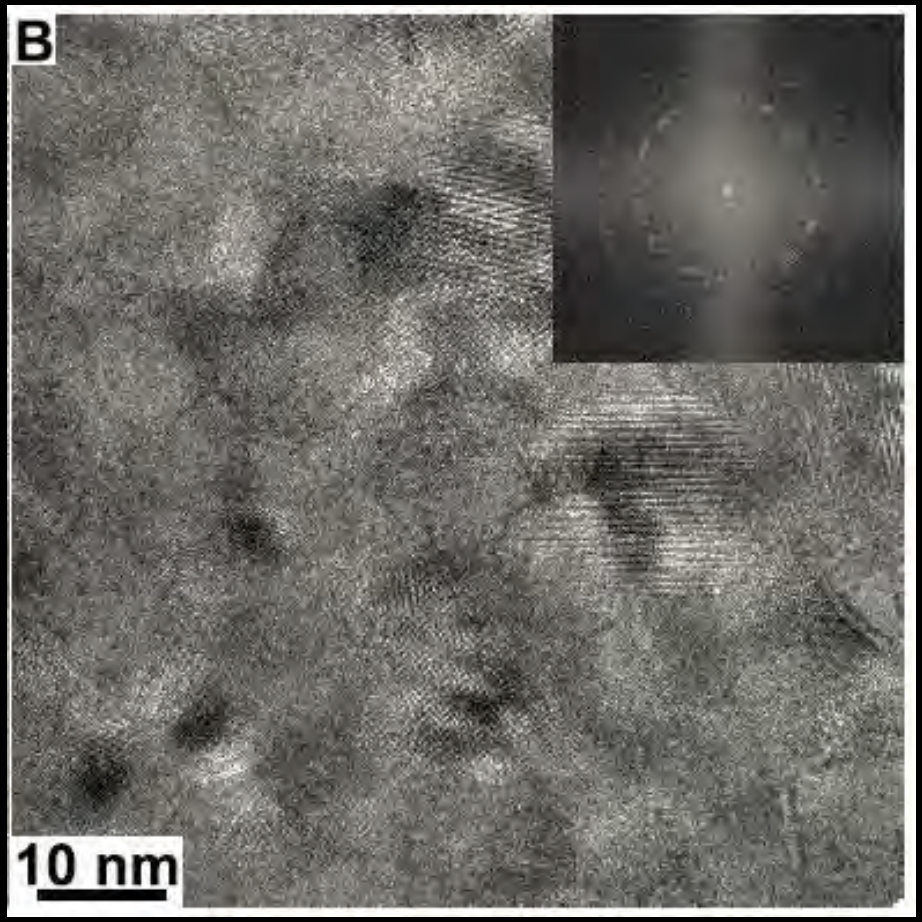
JACS, 131 (2009) 10231



Acknowledgements

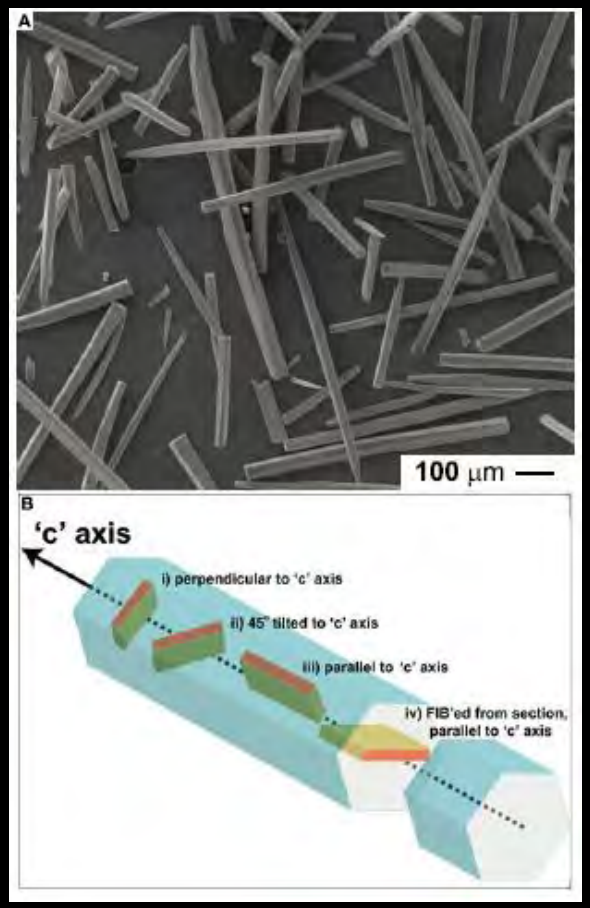
STEM vs. TEM

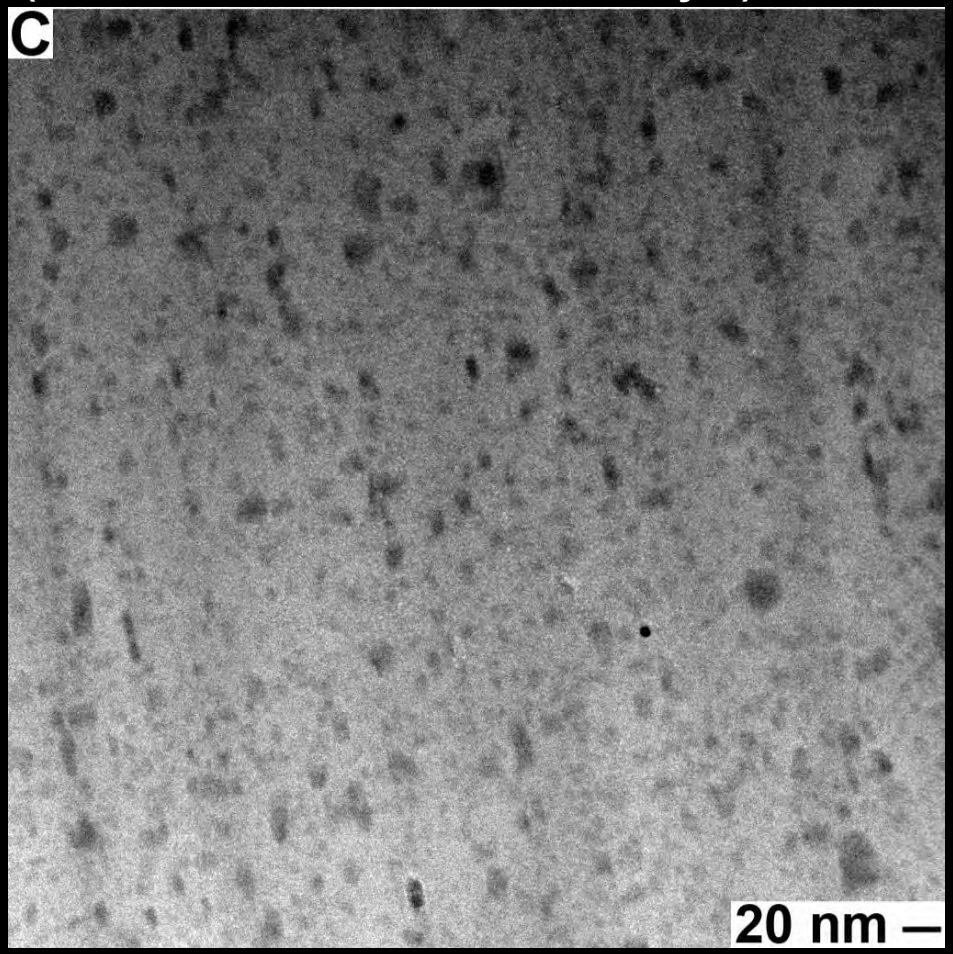




What About Charged Macromolecules ?

(Mollusk Shell - the Prismatic Layer)





- Projection images seem to suggest a random distribution …

Li*, Xin*, et al, *Advanced Functional Materials*, 2011, **21**, 2028-2034.

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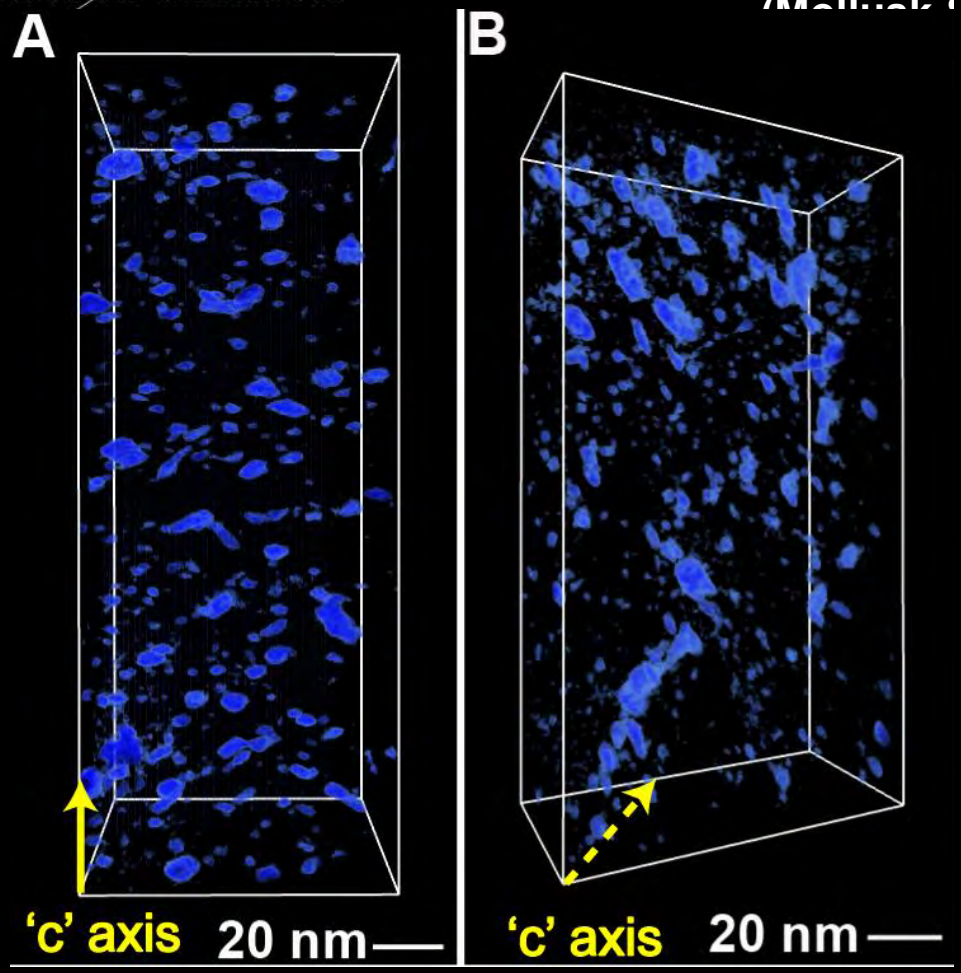

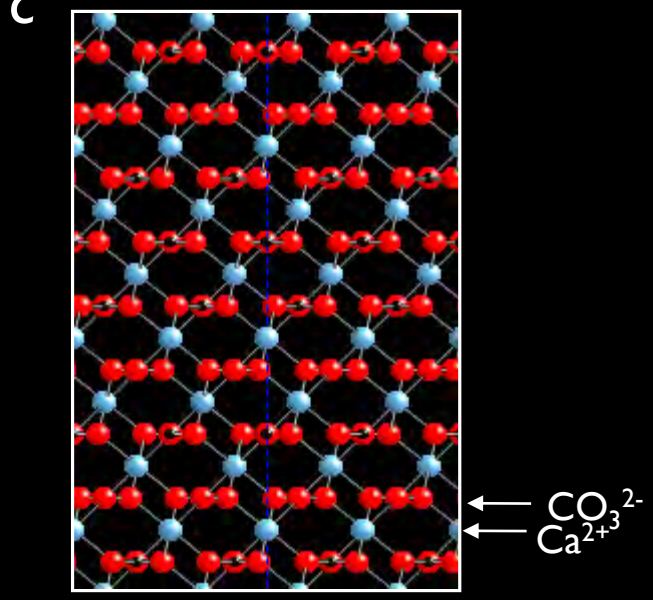

- Reconstruction reveals the disk like features aligned perpendicular to the c-axis (polar planes)

Li*, Xin*, et al, *Advanced Functional Materials*, 2011, **21**, 2028-2034.

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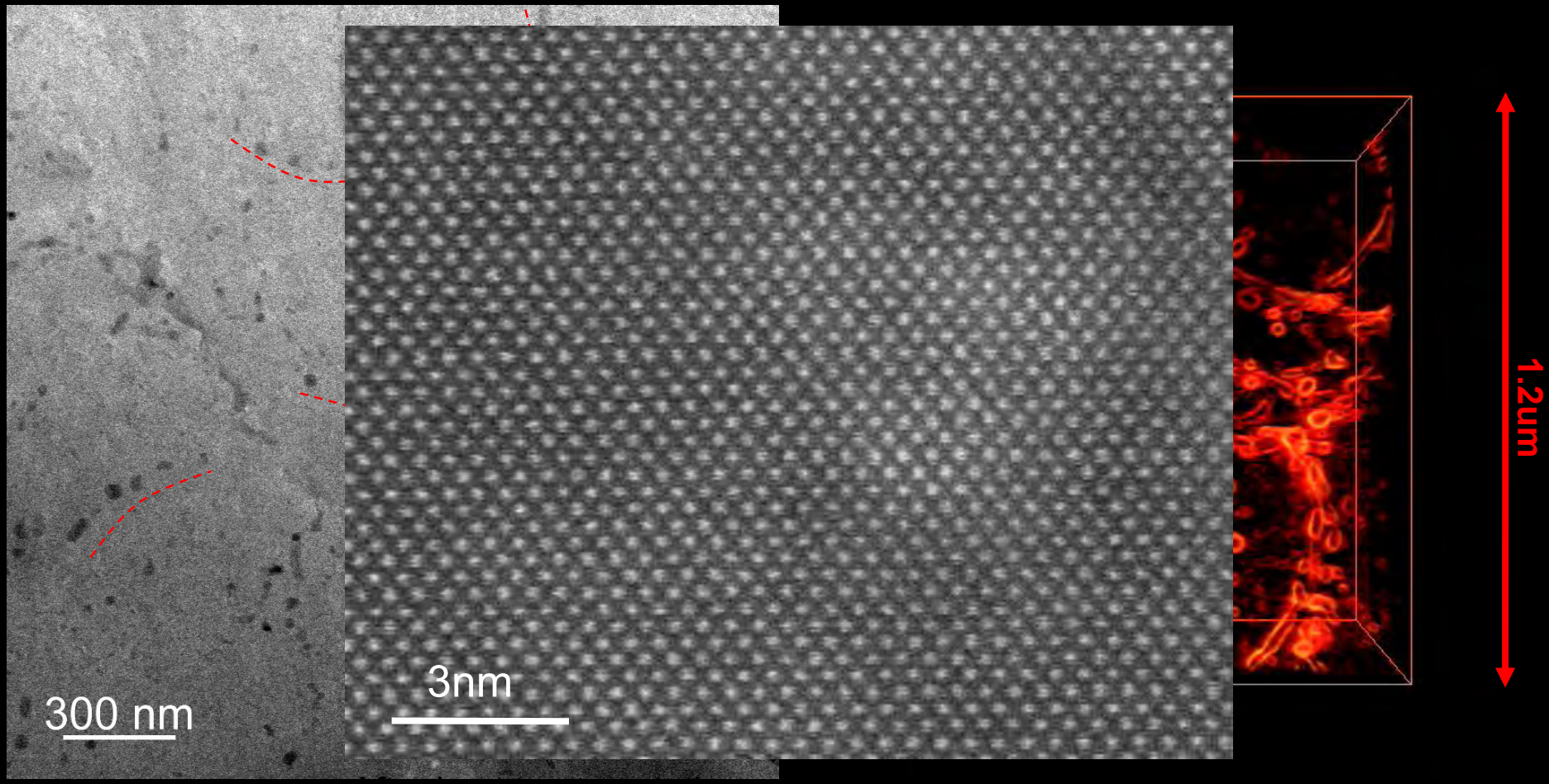
After 400°C Heat Treatment