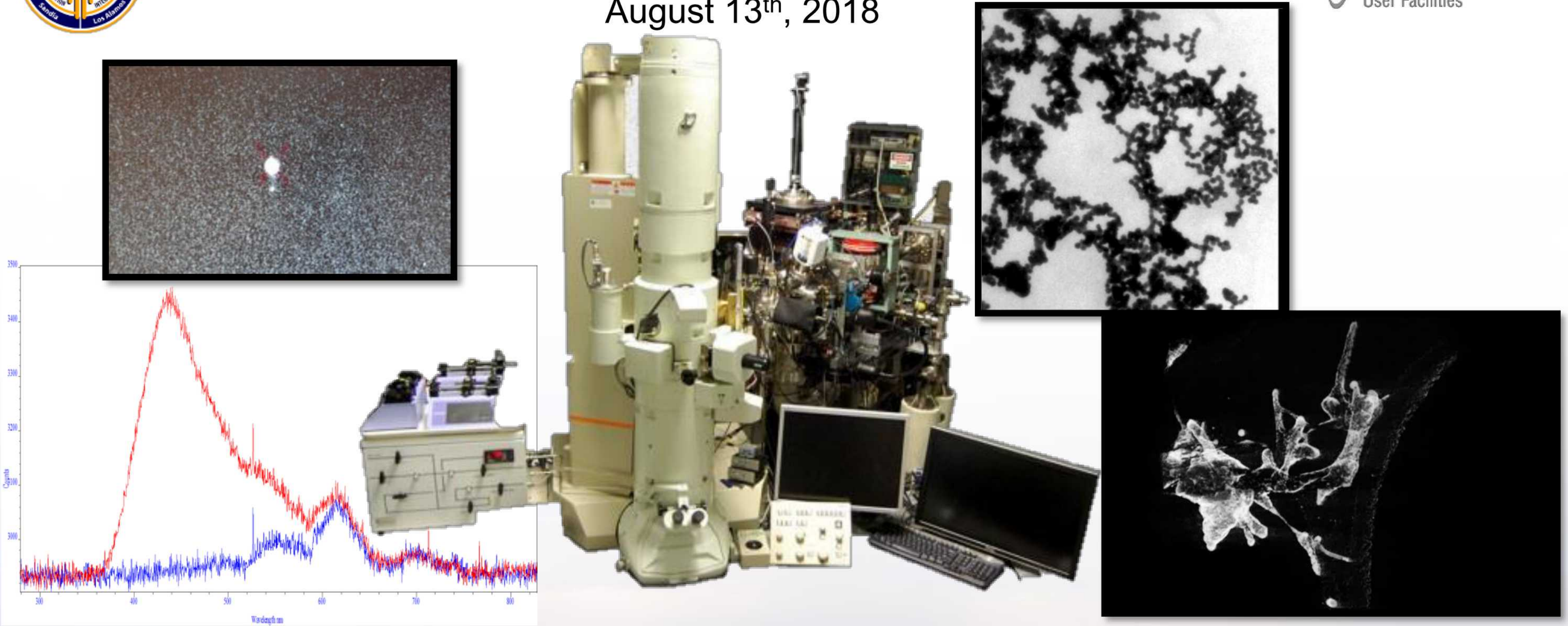
SAND2018-9395C

Progress in Coupling Electron Microscopy and Ion Beam Induced Luminescence

K. Hattar

Ion Beam Lab at Sandia National Laboratories

August 13th, 2018

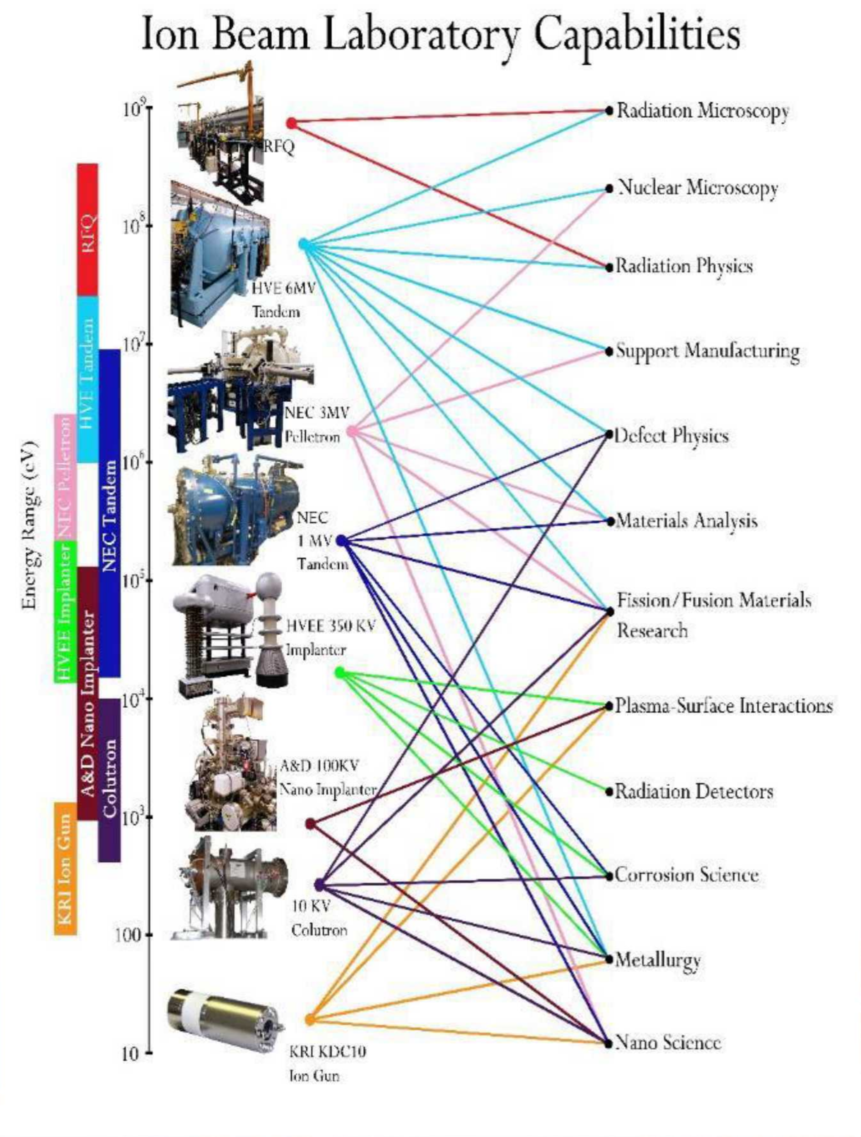


Collaborators:

- P. Price, C.M. Barr, A. Monterrosa, J. Kolar-Gutierrez, M. Marshall, P. Price, M. Abere, D. Adams, IDES Inc., S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, P. Yang, P. Feng, F.P. Doty, M.D. Allendorf, J.V. Branson, C.J. Powell, G. Vizkelethy, P. Rossi, B.L. Doyle, D.L. Buller, D.C. Bufford, N. Heckman, B. Boyce, J. Carroll, C. Taylor, B. Muntifering, & S. Briggs

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

Sandia’s Ion Beam Laboratory

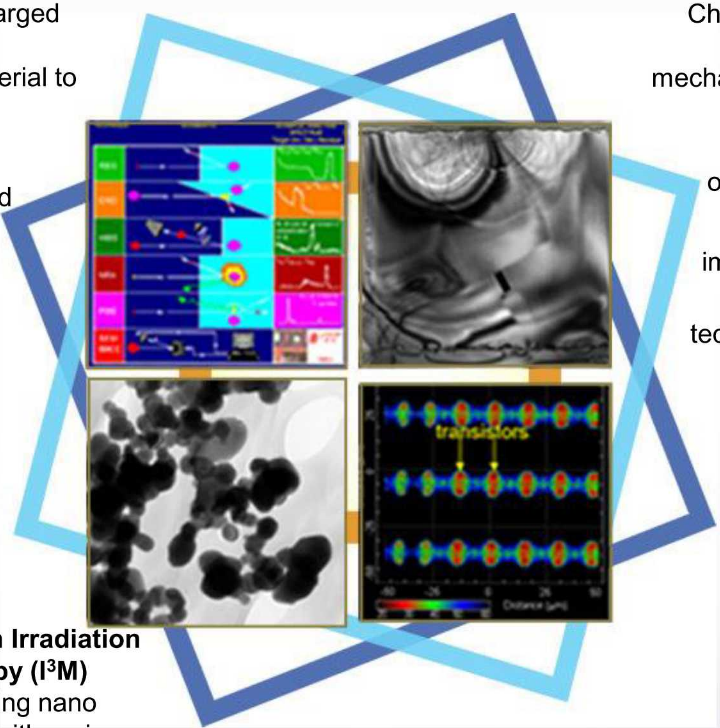


Ion Beam Analysis (IBA)

Shooting a charged particle at an unknown material to determine it’s identity, local chemistry, and structure.

Ion Beam Modification (IBM)

Changing the optical, mechanical, and chemical properties of materials via ion implantation to meet technological needs



***In Situ* Ion Irradiation Microscopy (I^{3}M)**

Bombarding nano samples with various particles and observing the changes in real time to understand how materials will behave in extreme environments.

Radiation Effects Microscopy (REM)

Using ion emissions to determine the Radiation hardness of microelectronics, identifying potential weaknesses.

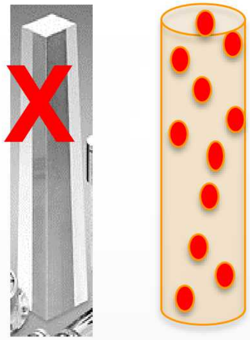
The IBL has a unique and comprehensive ion beam capability set including and *In situ* Ion Irradiation Transmission Electron Microscopy.

Need for Advanced Scintillators

New scintillating materials are critically needed to protect the United States.

Goal: determine the utility of size-selected high Z transition metal tungstates (MWO_4) as novel scintillating materials

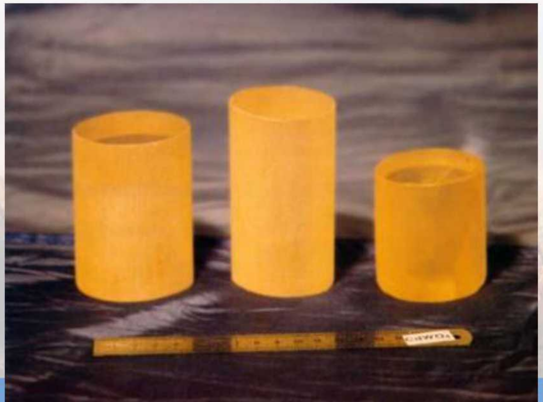
- Characterize novel nanotungstates and their radiation hardness
- Investigate size effects on radiation interaction
- Elucidate radiation interaction mechanisms



High Z Nanocomposite

Single crystal scintillators suffer from : low luminosity, volume restrictions, mechanical ruggedness, and chemical instability

$CdWO_4$ single crystal scintillators



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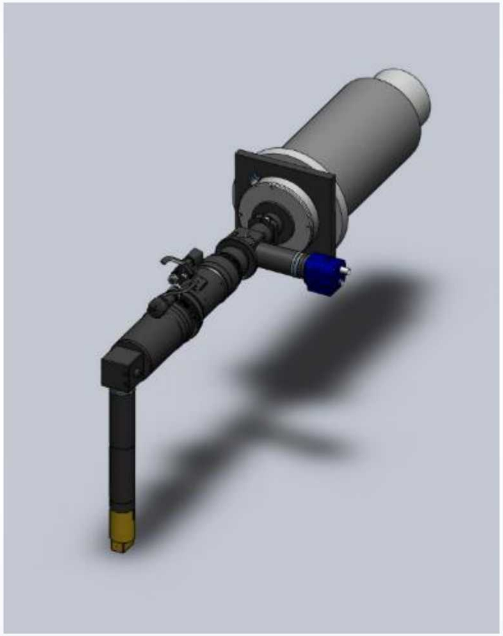
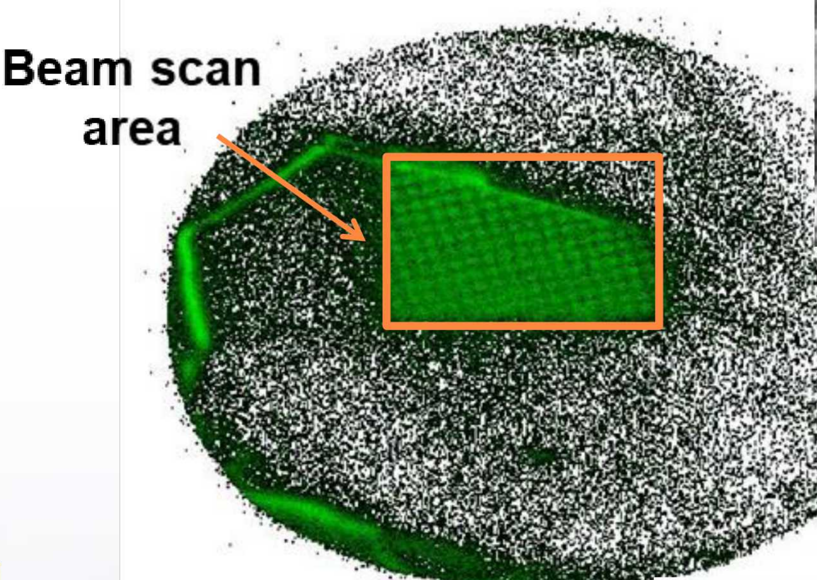
Nanorods of $CdWO_4$

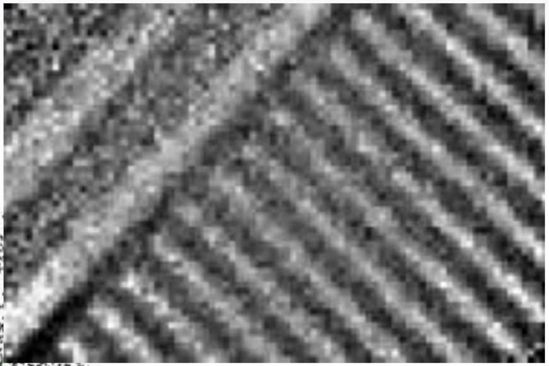
Improvement in scintillation properties?

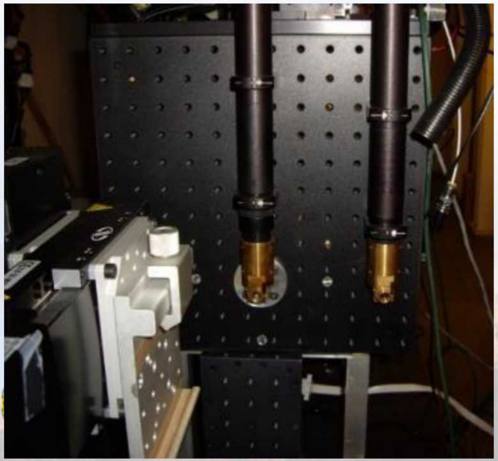
Imaging Penetrating Radiation through Ion Photon Emission Microscopy

Collaborators: J.V. Branson, C.J. Powell, G. Vizkelethy, P. Rossi, and B.L. Doyle

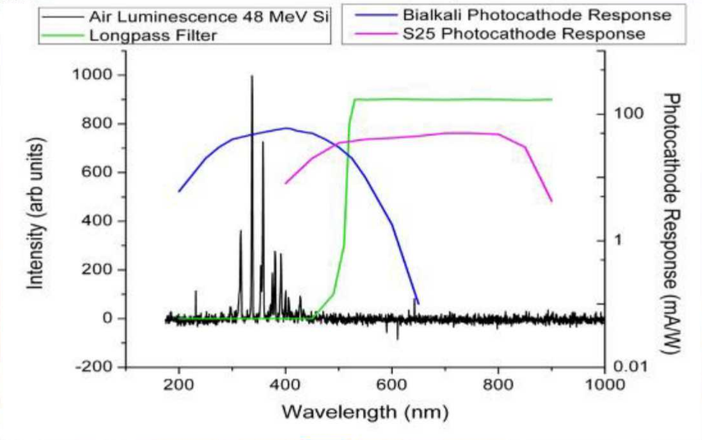








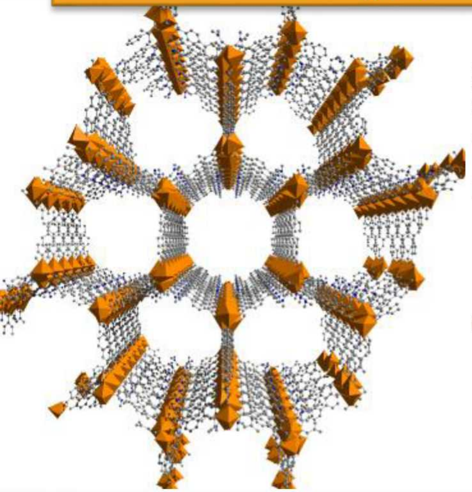
IPEM utilizes advanced phosphors in order to explore radiation effects. So phosphor stability and radiation tolerance is essential.

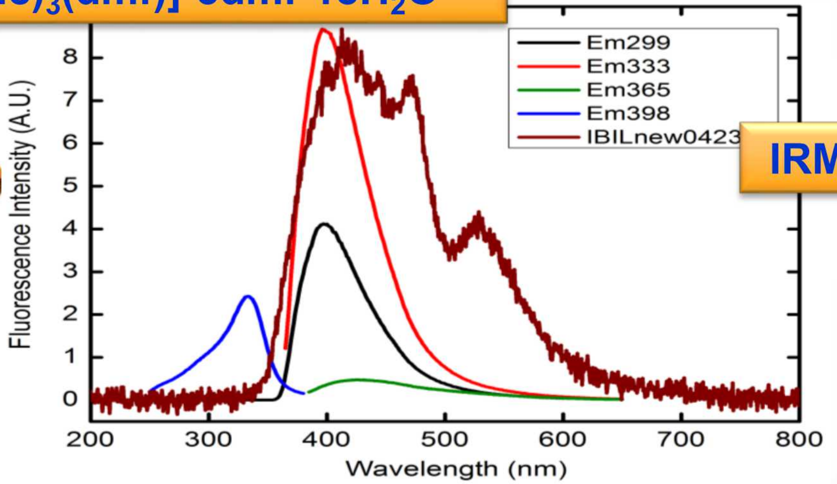


Metal Organic Frameworks Provide Interesting and Tailorable IBIL

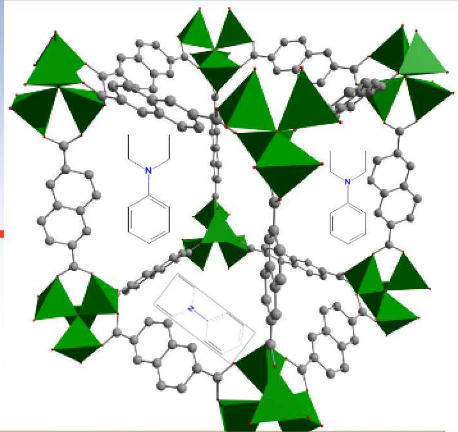
Collaborator: J.V. Branson, P. Feng, F.P. Doty, and M.D. Allendorf

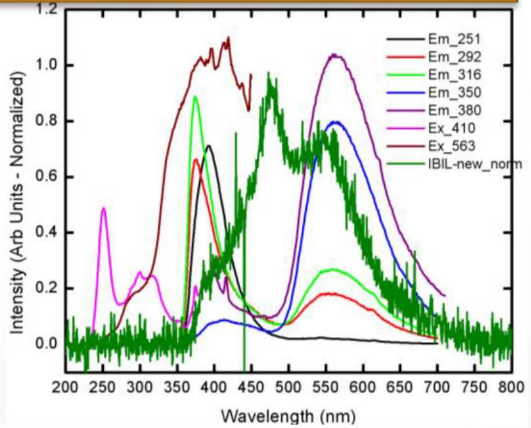
JUC-48: $[Cd_3(bpdc)_3(dmf)]\cdot 5dmf\cdot 18H_2O$



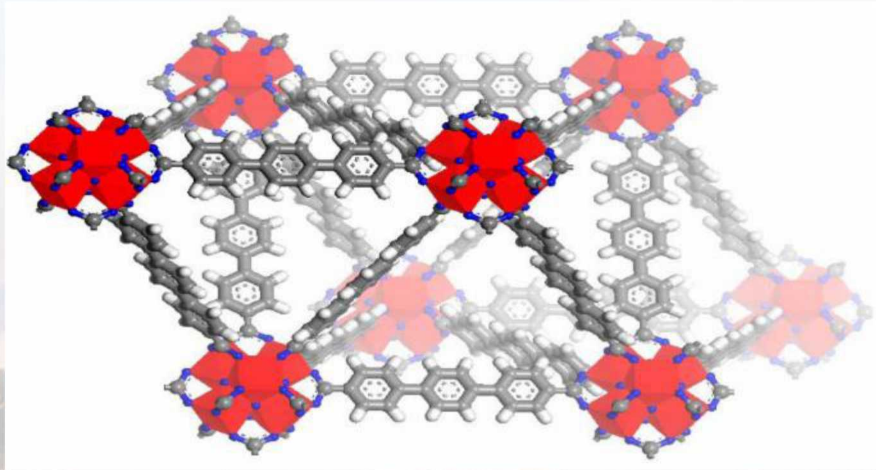


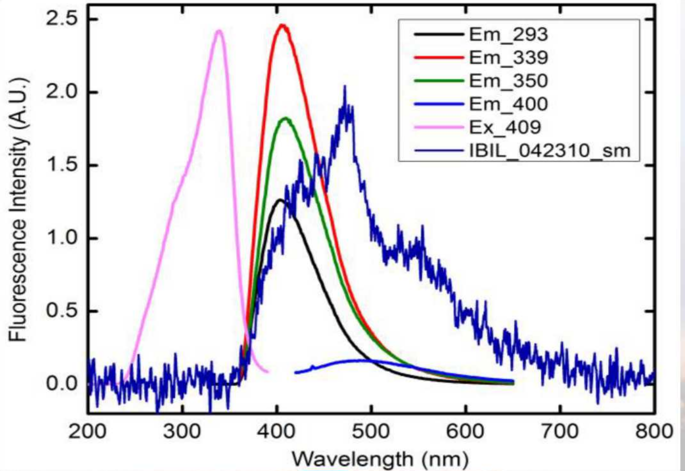
IRMOF-8 with N,N-diethylaniline





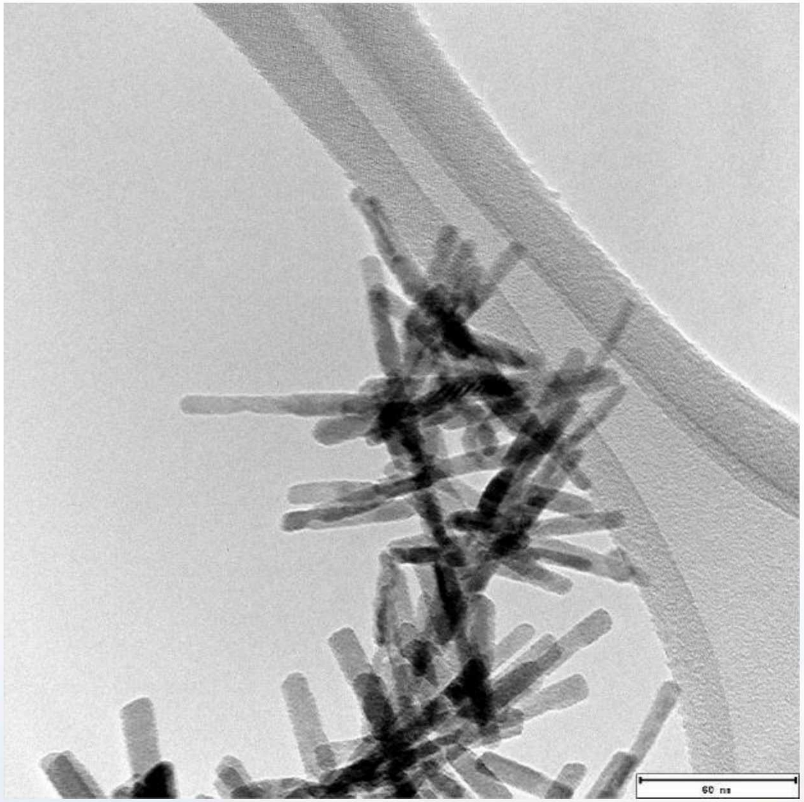
$[Zr_6O_4(OH)_4(CO_2)_{12}]$-BPDC based MOF

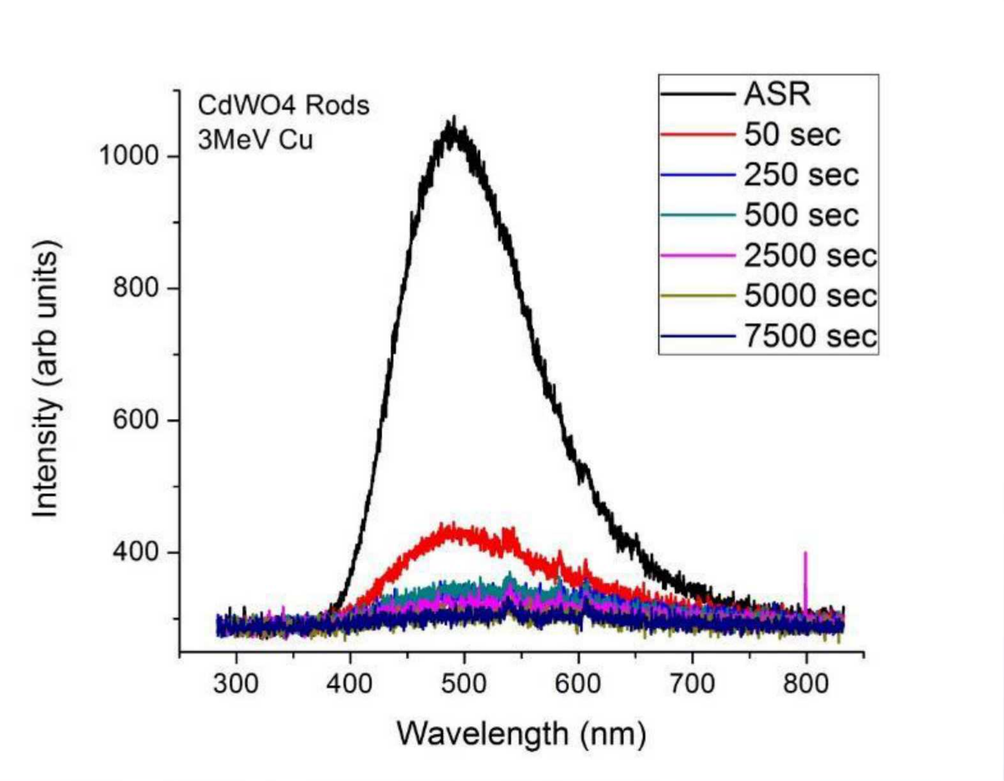




Degradation of Tungstate Nanoparticles Luminescence Properties

Collaborator: S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, and F.P. Doty





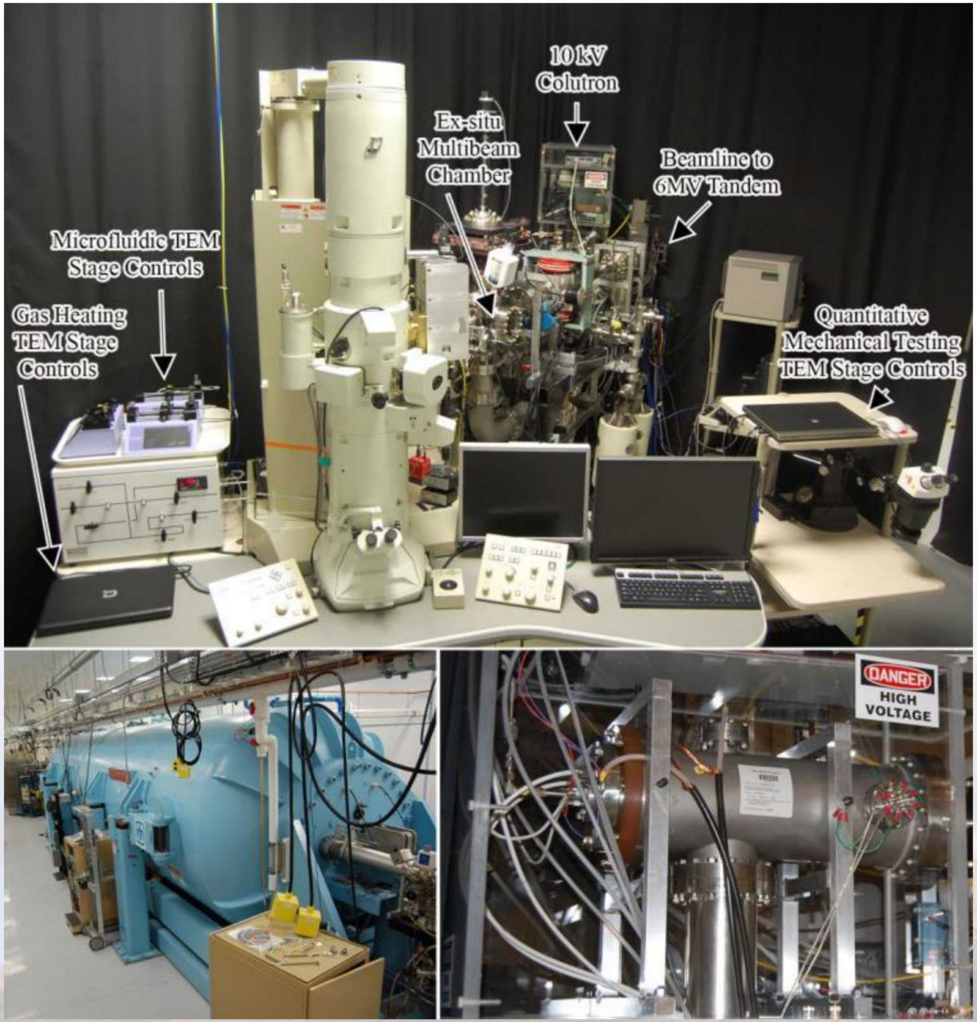
Increasing radiation dose → Decrease in intensity & Sometimes a shift in peaks

What structural change causes this effect?

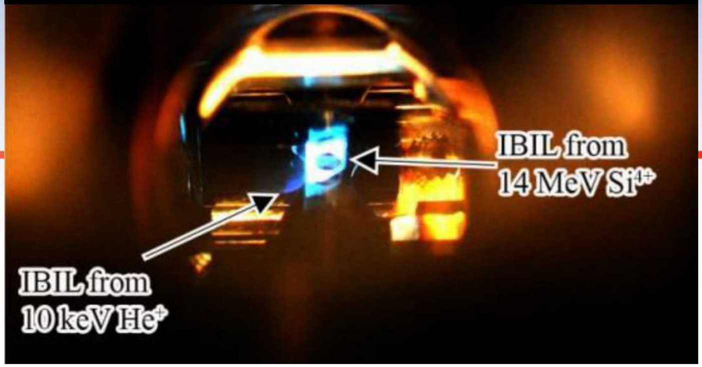
Sandia's Concurrent *In situ* Ion Irradiation TEM Facility

Collaborator: D.L. Buller

10 kV Colutron - 200 kV TEM - 6 MV Tandem

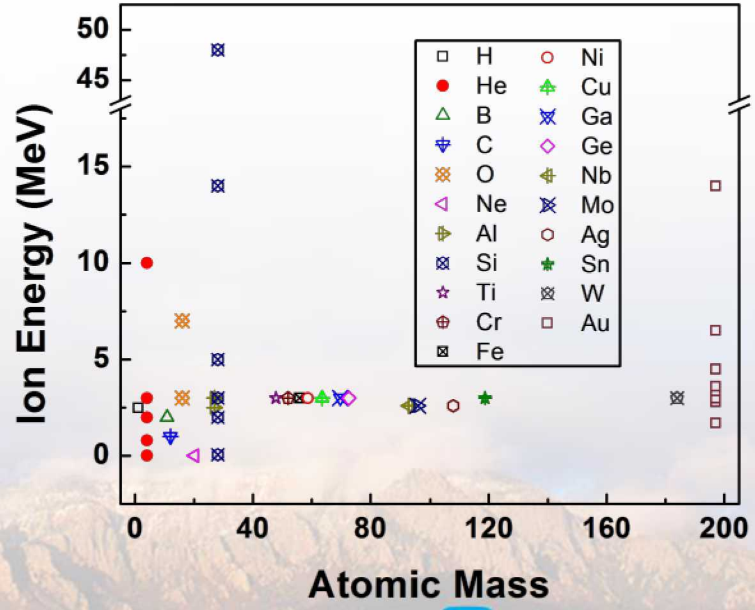


IBIL from a quartz stage inside the TEM



Direct real time observation of ion irradiation, ion implantation, or both with nanometer resolution

Ion species & energy introduced into the TEM



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Cumulative Effects of Ion Irradiation as a Function of Ion Energy and Au Particle Size

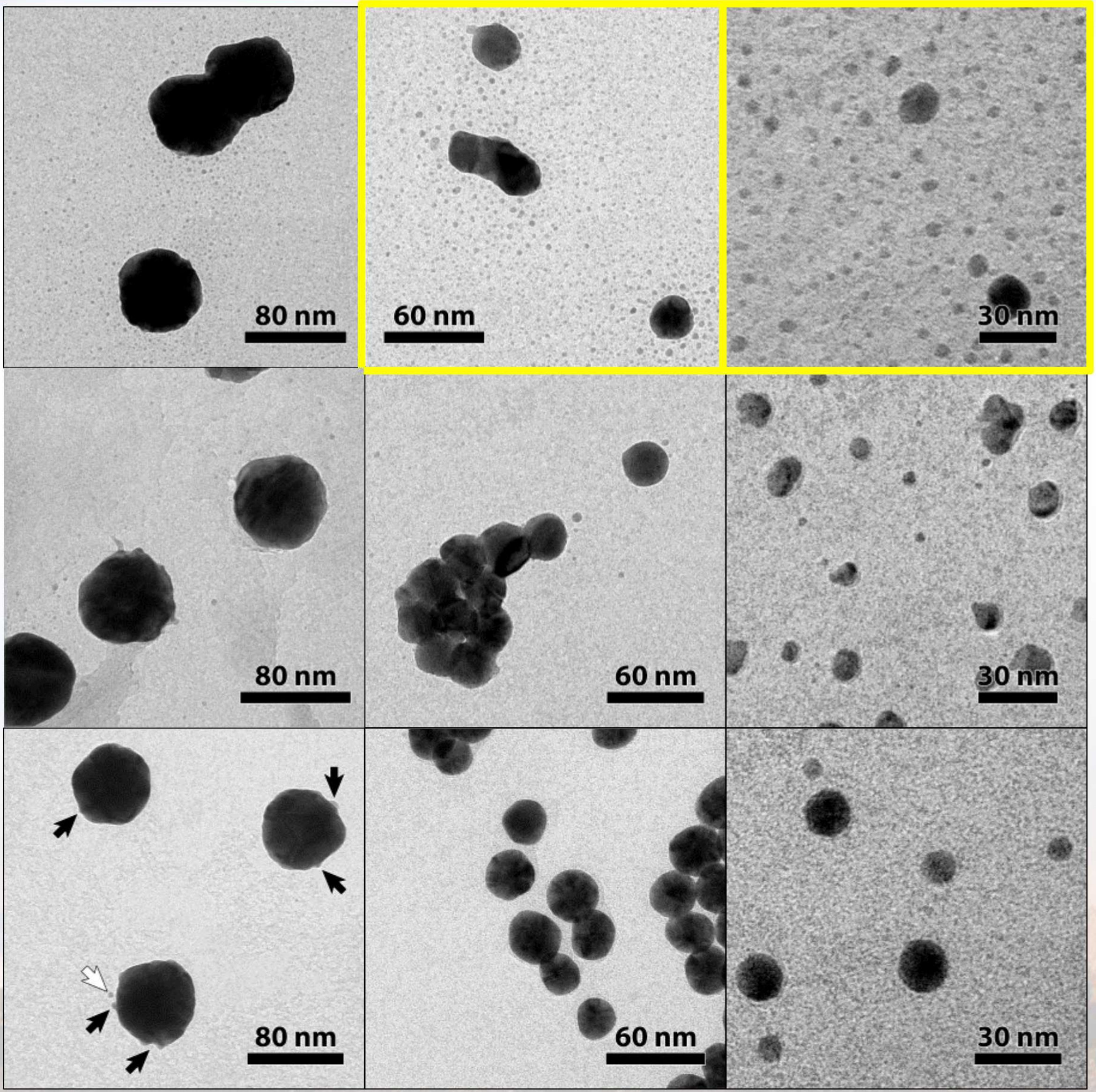
Collaborator: D.C. Bufford

60 nm | 20 nm | 5 nm

46 keV Au^{1-}
3.4 × 10^{14} /cm^2

2.8 MeV Au^{4+}
4 × 10^{13} /cm^2

10 MeV Au^{8+}
1.3 × 10^{12} /cm^2



Particle and ion energy dictate the ratio of sputtering, particle motion, particle agglomeration, and other active mechanisms

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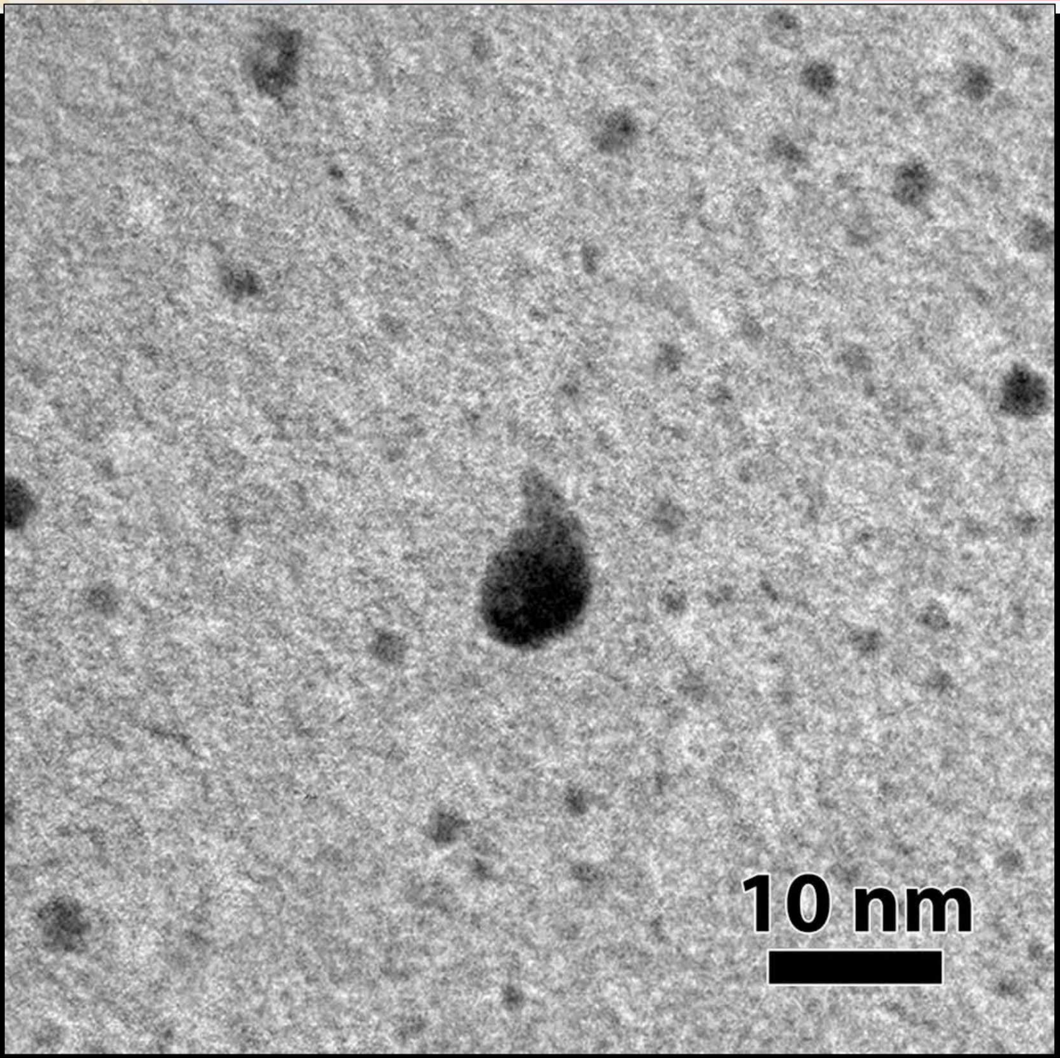
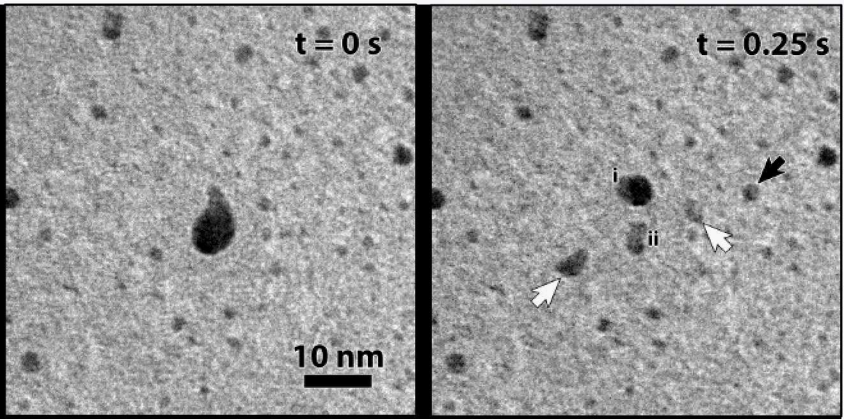
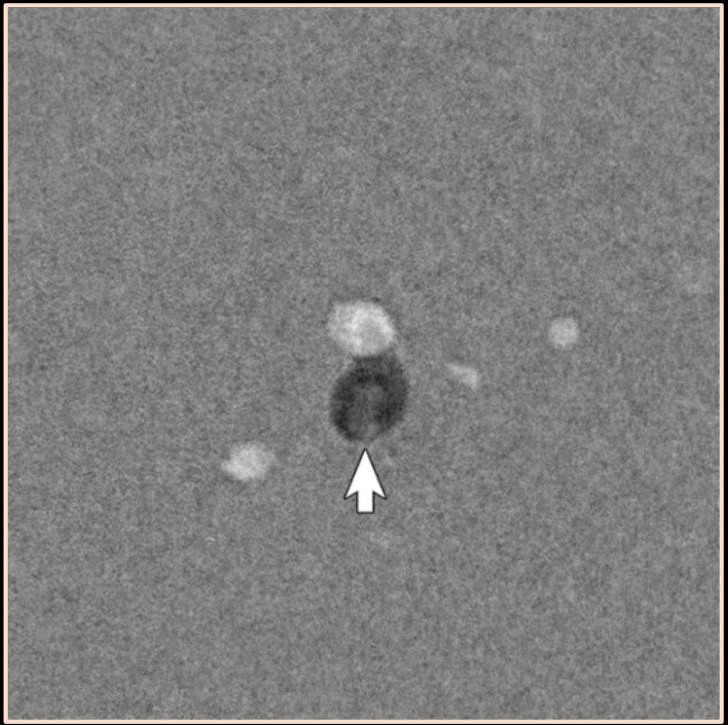
Single Ion Strikes:
46 keV Au^{1-} ions into 5 nm Au nanoparticles

Collaborator: D.C. Bufford

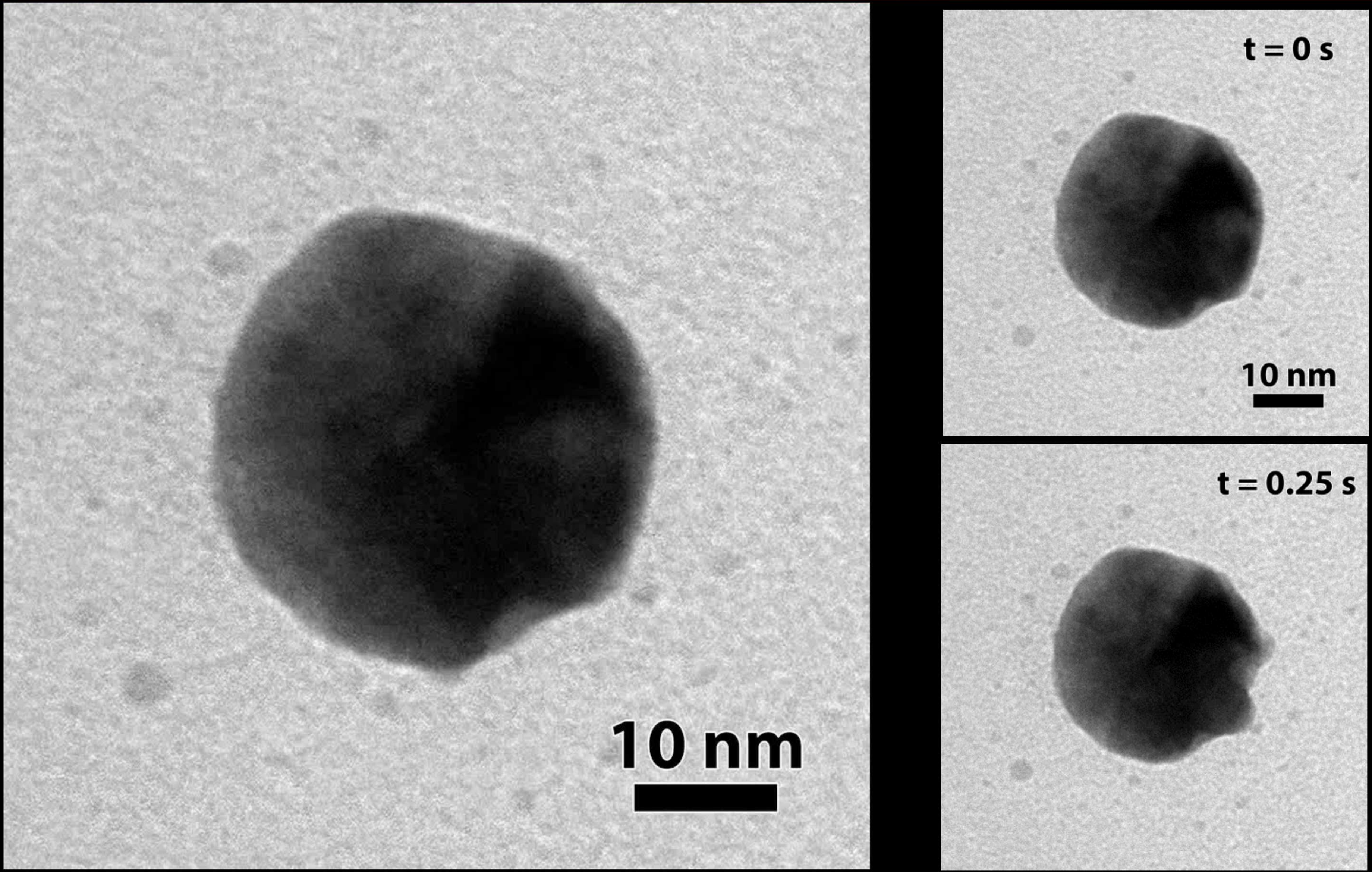






Single Ion Strikes: 46 keV Au^{1-} ions into 20 nm NPs

Collaborator: D.C. Bufford



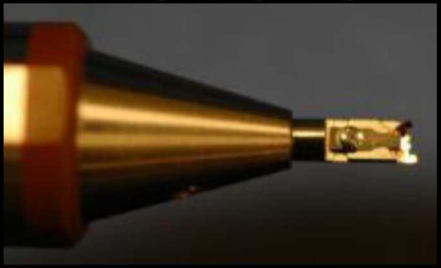
Electron Tomography Provides 3D Insight

Collaborators: S.H. Pratt & T.J. Boyle

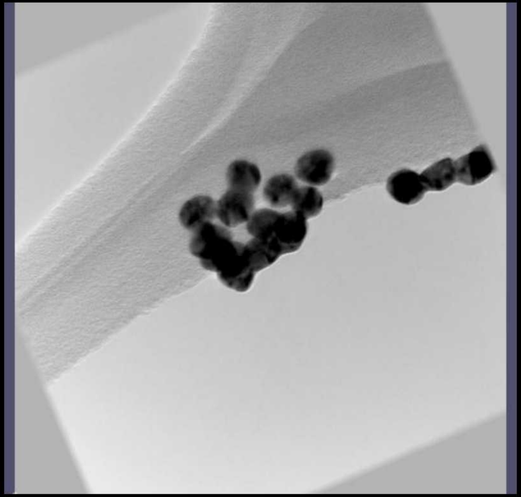
In situ Ion Irradiation TEM (I^{3}TEM)

+

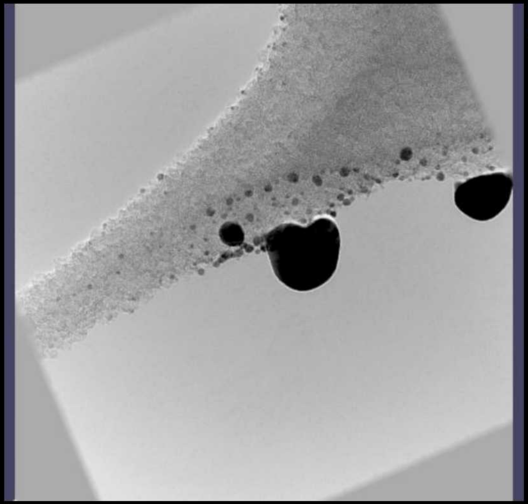
Hummingbird tomography stage



Aligned Au NP tilt series - unirradiated

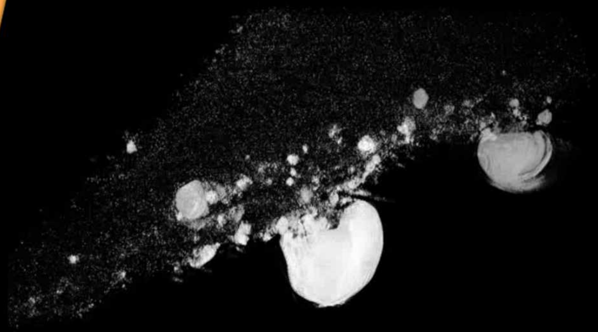


Aligned Au NP tilt series - irradiated



Unirradiated Au NP model

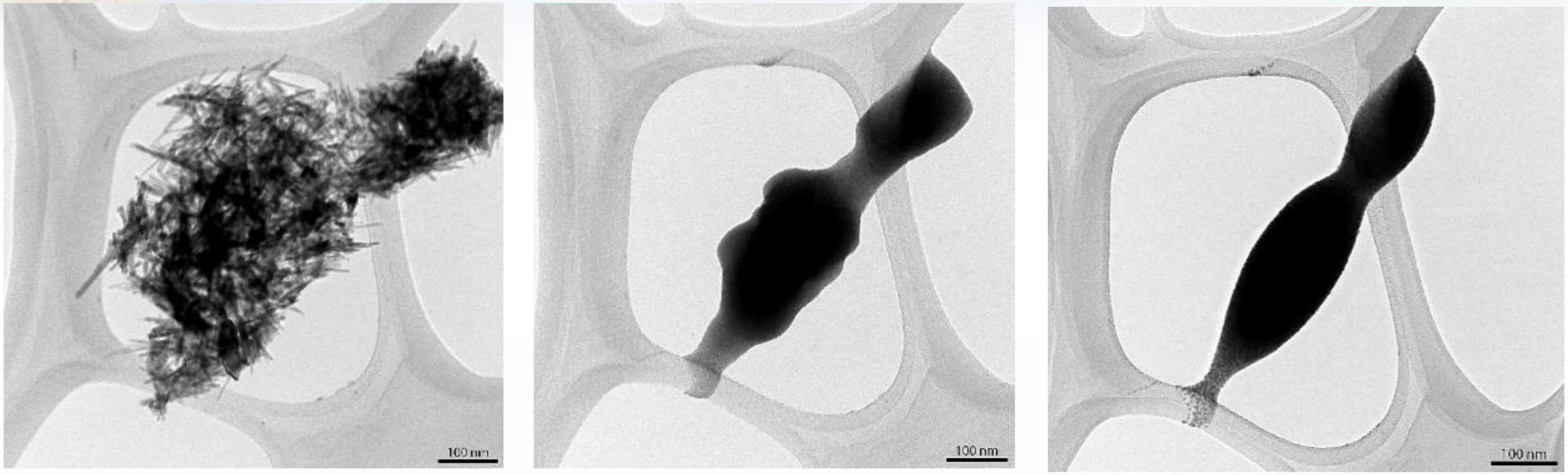
Irradiated Au NP model

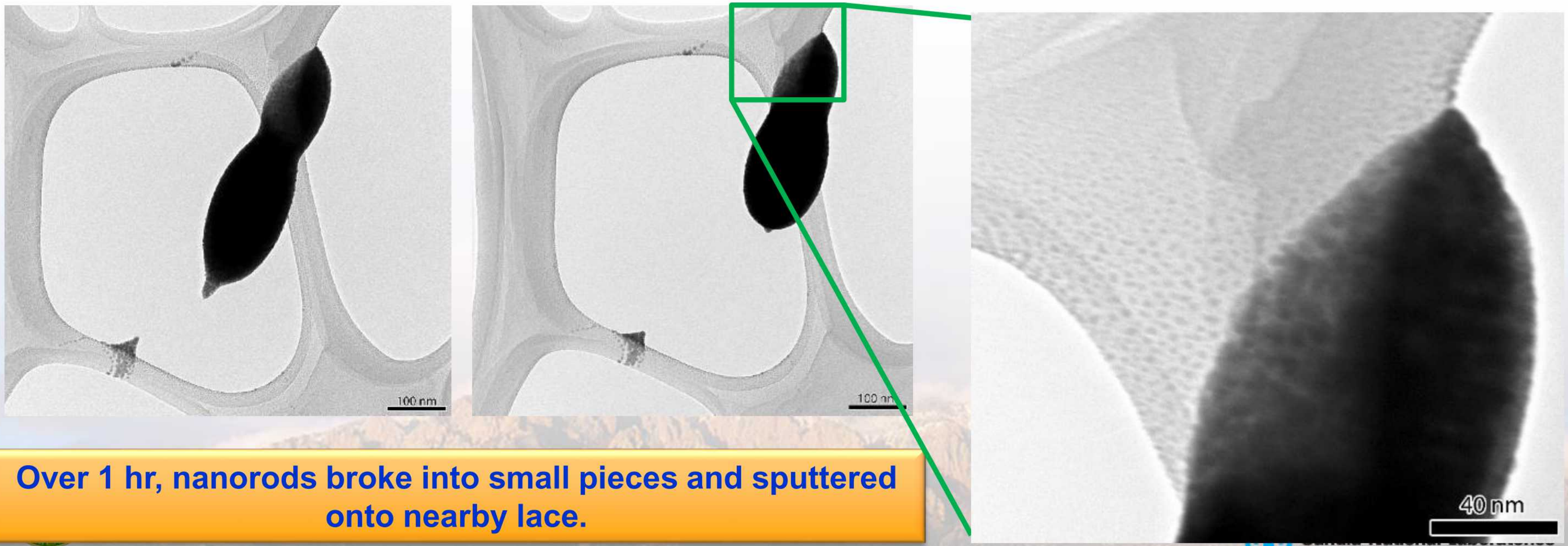


The application of advanced microscopy techniques to extreme environments provides exciting new research directions

$CdWO_4$ irradiated with 50 nA of 3 MeV Cu^{3+}

Collaborator: S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, and F.P. Doty





Over 1 hr, nanorods broke into small pieces and sputtered onto nearby lace.

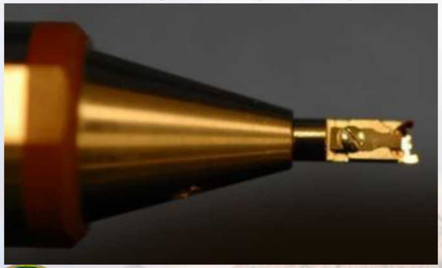
Advanced Microscopy Techniques Applied to Radiation Environments

Collaborator: S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, and F.P. Doty

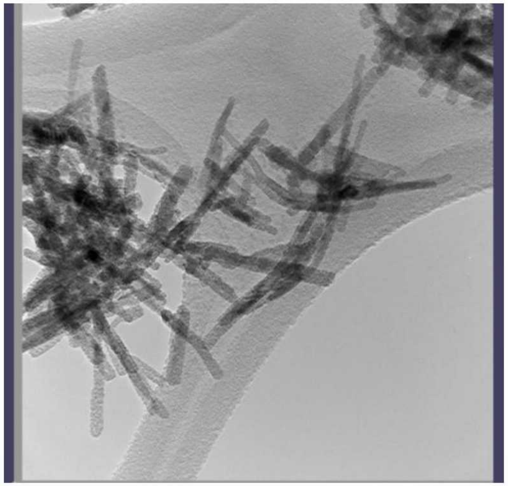
In situ Ion Irradiation TEM (I^3TEM)

+

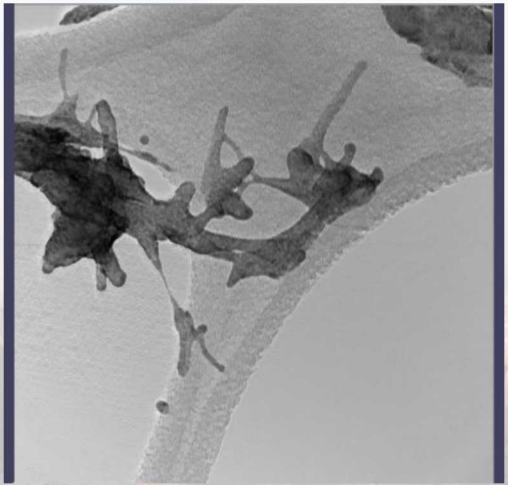
Hummingbird tomography stage



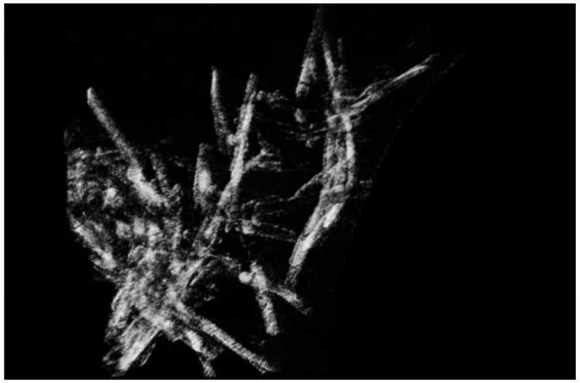
Aligned $CdWO_4$ tilt series Unirradiated



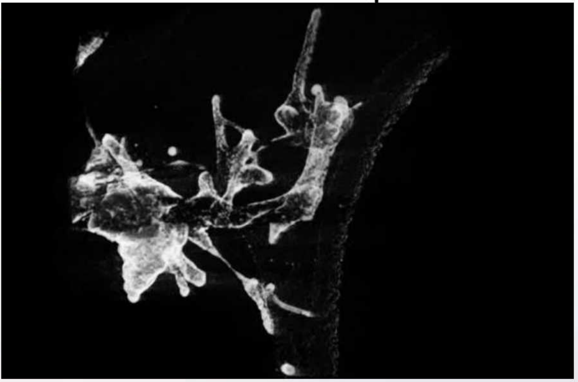
Irradiated



Unirradiated $CdWO_4$ model



Irradiated $CdWO_4$ model



The application of advanced microscopy techniques to extreme environments provides exciting new research directions

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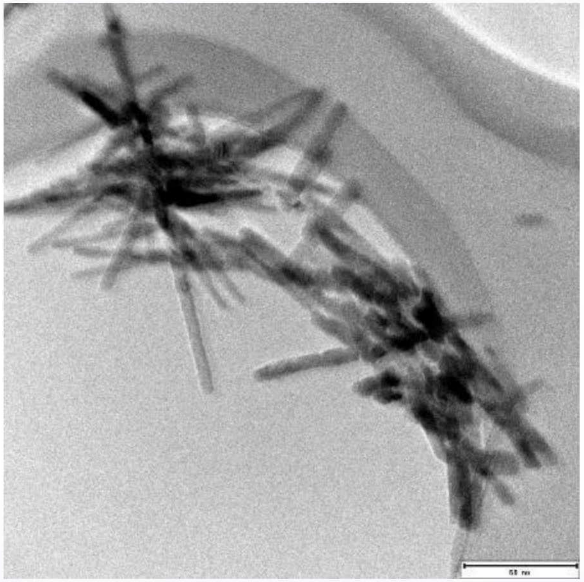
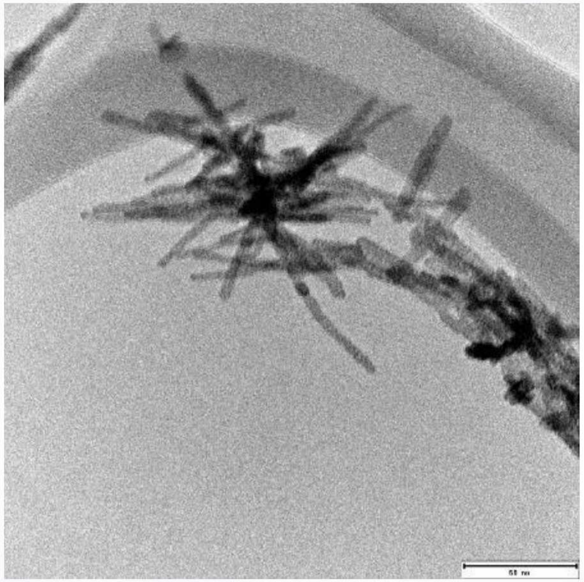
In situ Proton Irradiation as First Order Simulation of Neutrons

Collaborator: S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, and F.P. Doty

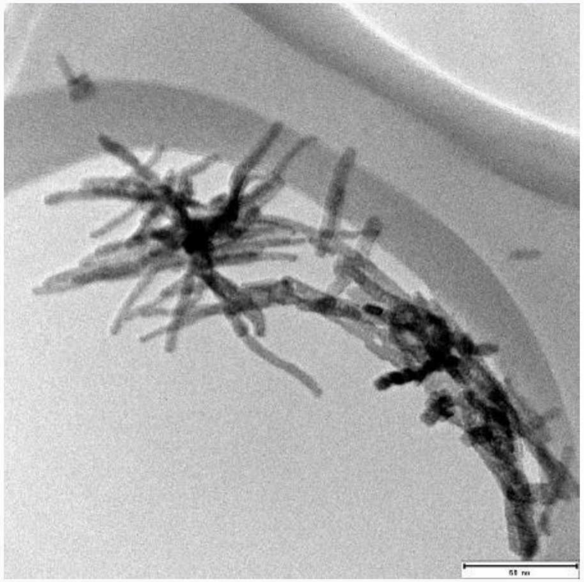
Unirradiated

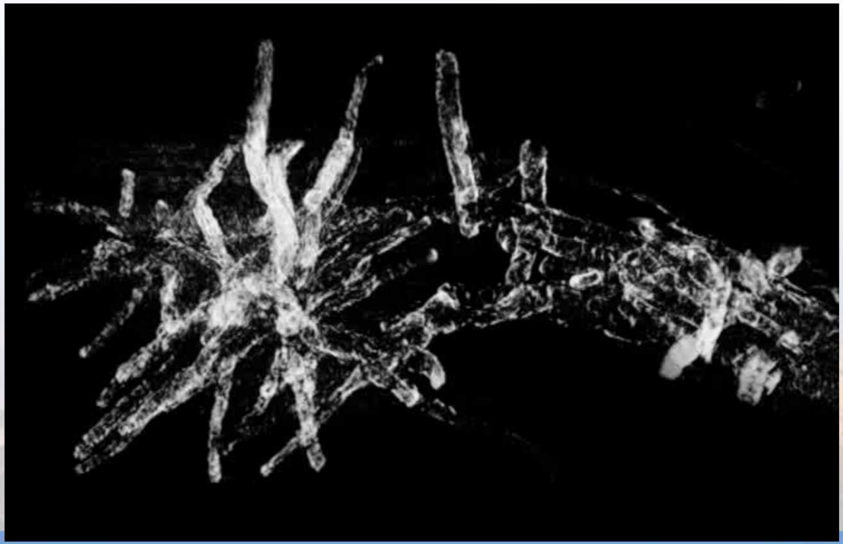


15 minutes



60 minutes





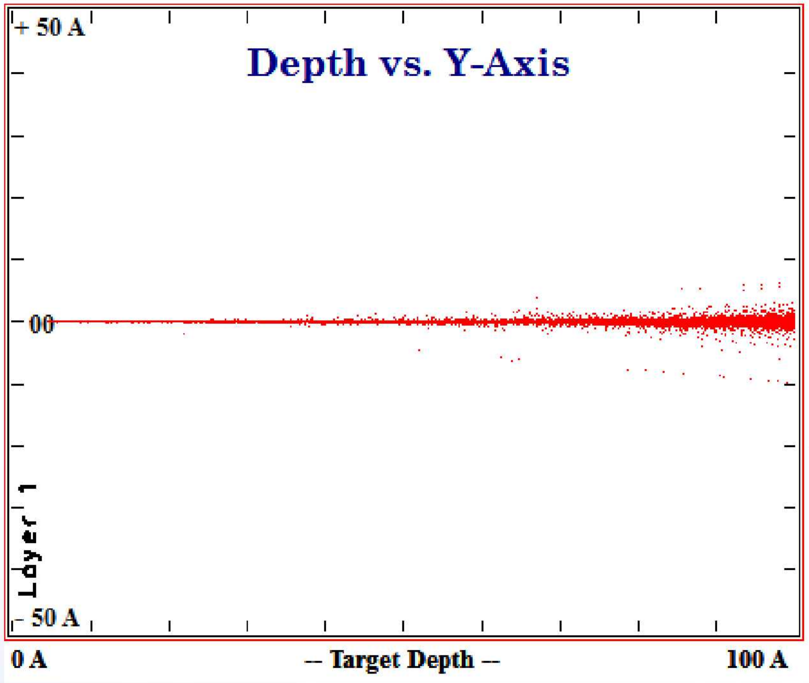
160 nA of 2.5 MeV H^+ used to simulate neutron radiation shows less change. Results suggest good radiation hardness for tungstate nanorod-composite scintillators.

Comparison of Proton and Copper Irradiation

Theoretical Comparison

Collaborator: S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, J. Villone, P. Yang, and F.P. Doty

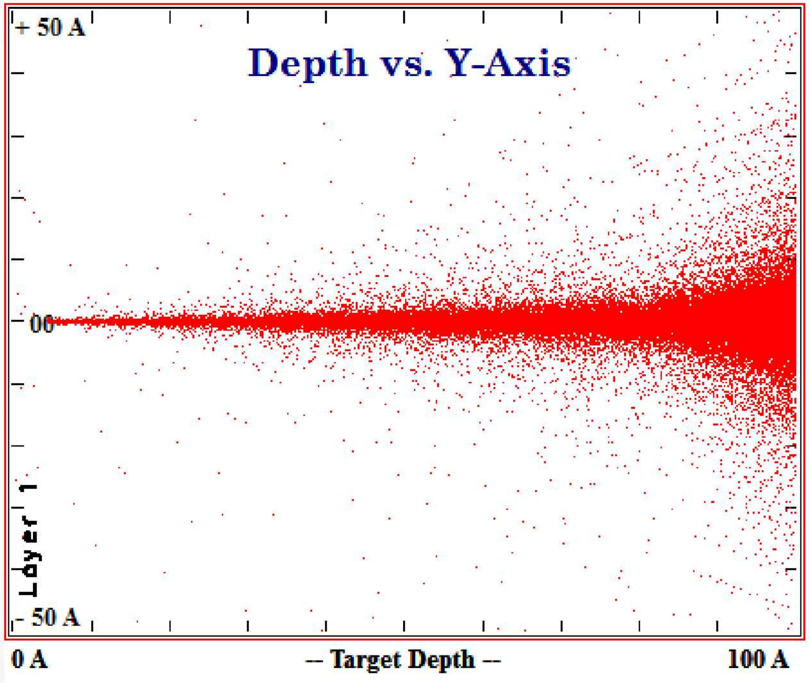
Displacement Damage from 2.5 MeV H



SRIM simulation of the Frenkel pairs created by the ion irradiation conditions used in 10 nm thick $CdWO_4$ noparticle.

Note the large number of pairs over the same simulation set, as well as the two order magnitude dE/dx elec. and four dE/dx Nuc.

Displacement Damage from 3 MeV Cu



Sample	Density (g/cm3)	Species	Energy (MeV)	Current (nA)	**dE/dx Elec.**	**dE/dx Nuc**	Proj. Range (um)	Long. Straggle (um)	Lat. Struggle (um)
CdWO4	7.9	H	2.5	~100-200	**5.97E-02**	**3.80E-05**	33.62	2.2	3.59
PbWO4	8.235	H	2.5	~100-200	**5.18E-02**	**3.39E-05**	37.22	2.8	4.63
CdWO4	7.9	Cu	3	~10-30	**2.19E+00**	**5.31E-01**	1.25	0.4581	0.4096
PbWO4	8.235	Cu	3	~10-30	**2.67E+00**	**6.11E-01**	1.16	0.3632	0.3328

In contrast to heavy ion irradiation, Proton irradiation produces IBIL, but minimal damage in the high-Z tungstates.

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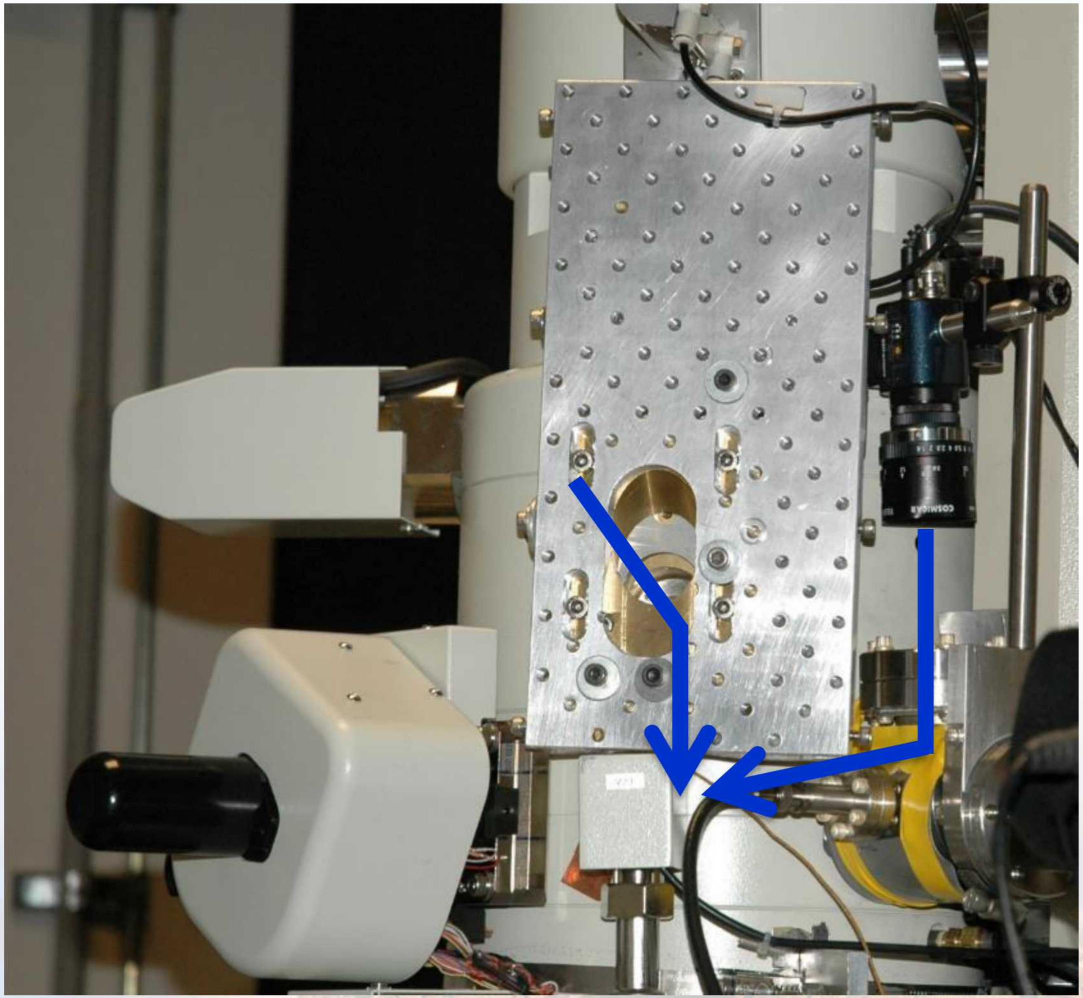
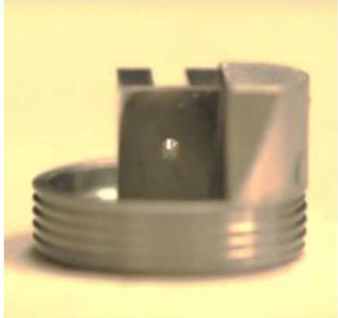
Optical View inside TEM

Collaborators: M. Marshall, P. Price, M. Abere, D. Adams, and IDES Inc.

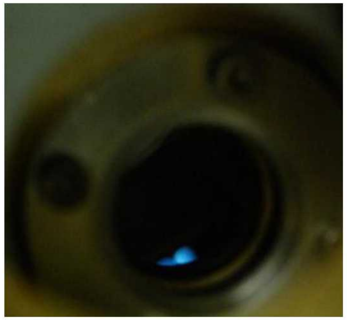


Two optical pathways were added to the I^{3}TEM, which permits *in situ* TEM luminescence studies and laser beam access

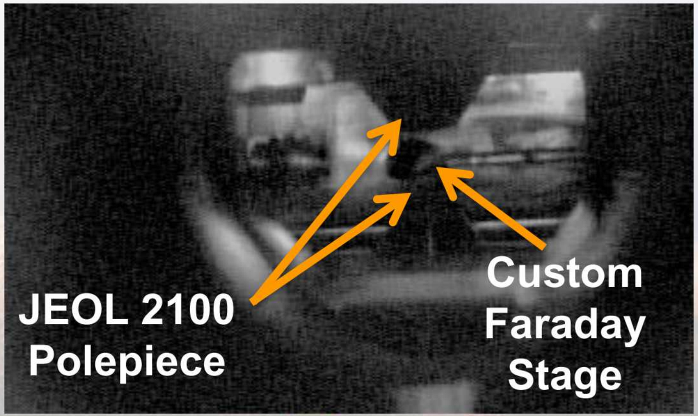
Optical Mirror in TEM



First IBIL in TEM

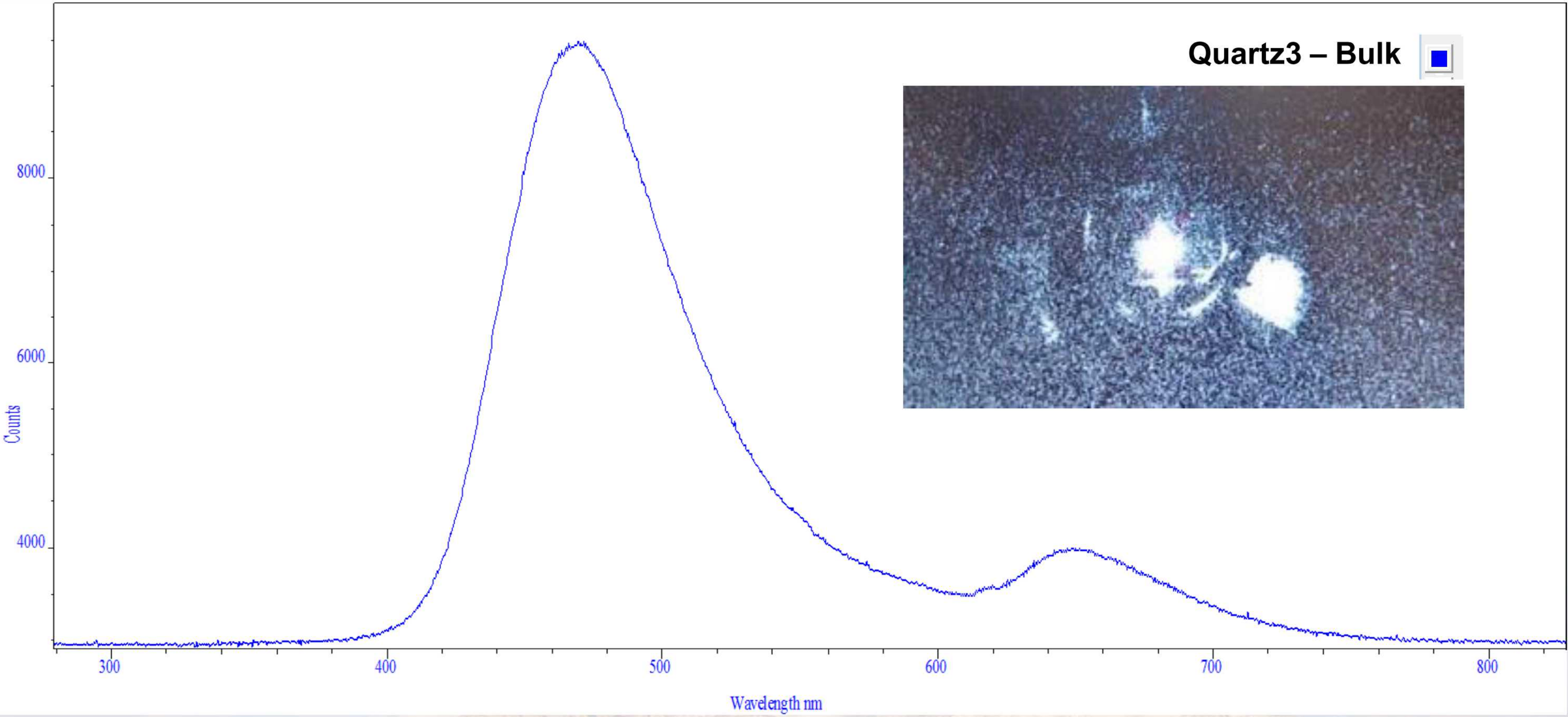


- Angled mirror on top of the objective polepiece with bore hole for the electron path was installed.
- Mirror in the top of the beamline port
- Designed to permit *in situ* observation of laser pulses



Demonstration of Cathodoluminescent in the TEM

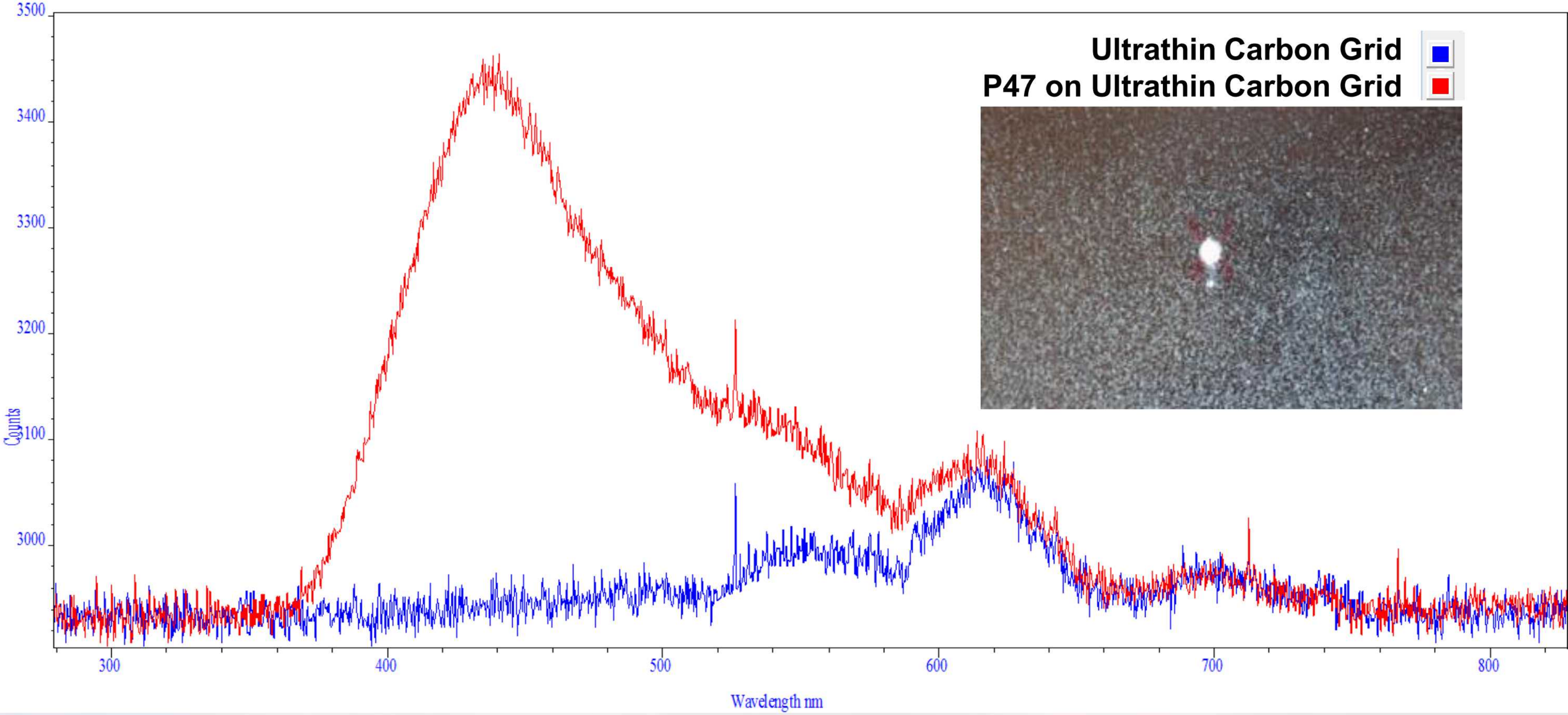
Collaborators: J. Kolar-Gutierrez, D. Buller



5 minutes of 200 keV electron on a quartz cover slide

Demonstration of *In situ* TEM Cathodoluminescent

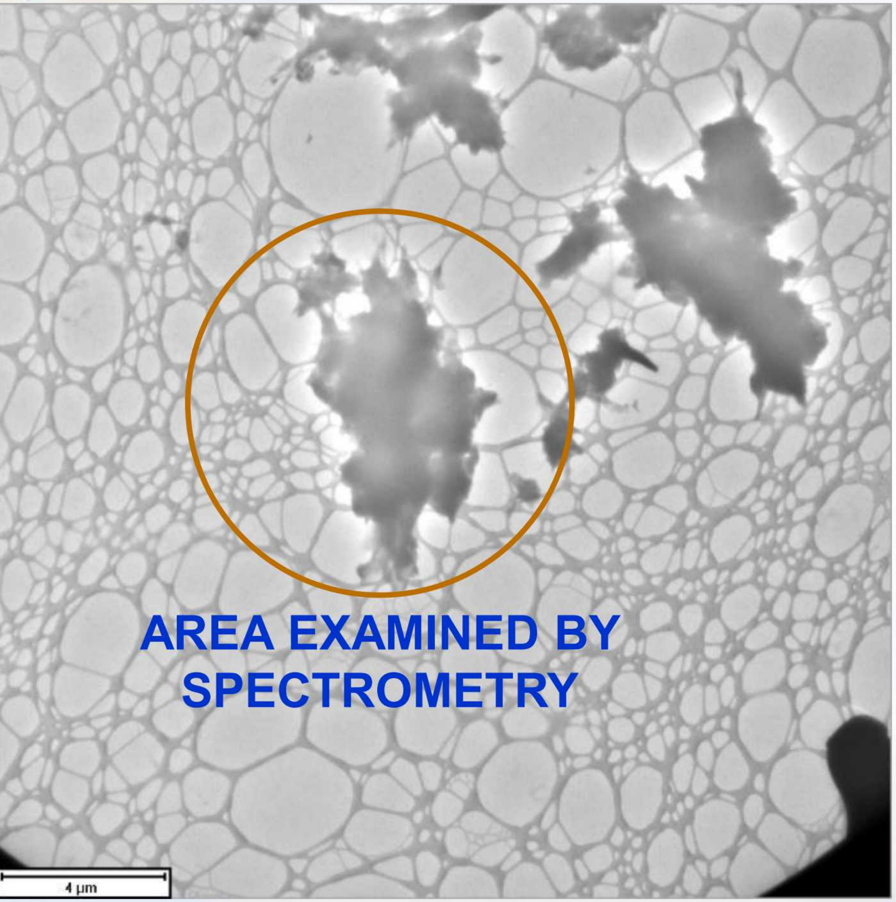
Collaborators: J. Kolar-Gutierrez, D. Buller

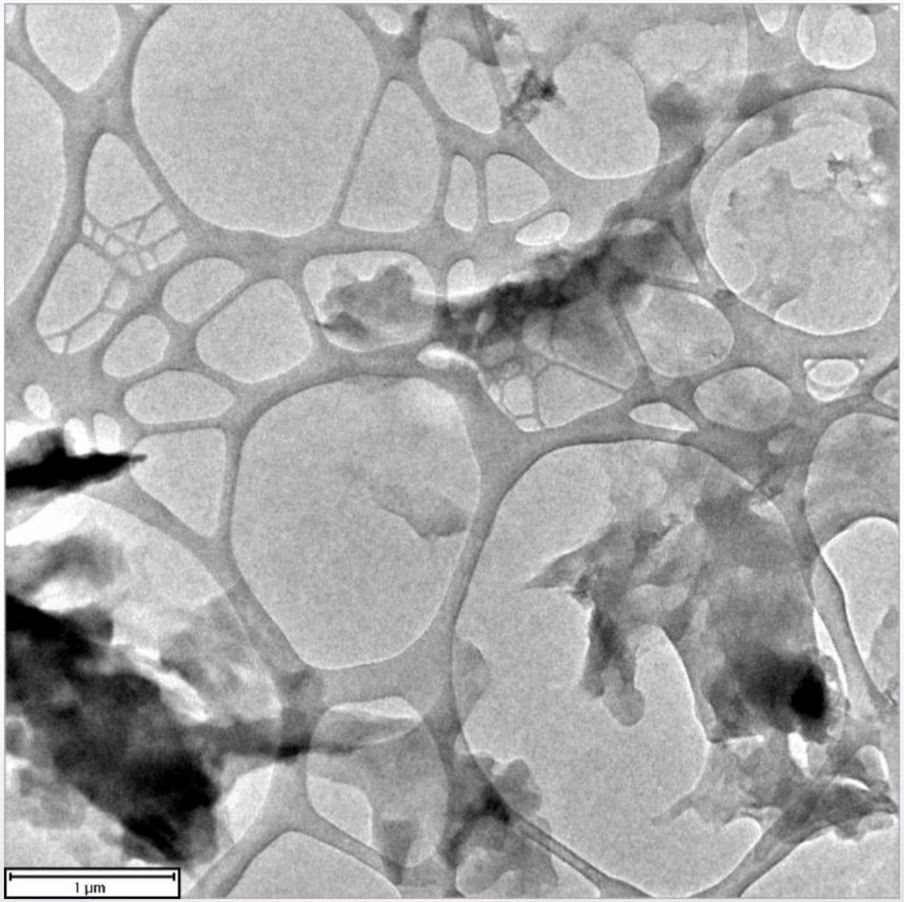


The CL from TEM sample (P47) and lacy-carbon copper TEM grid can be delineated and directly tied to the observed area

Demonstration of *In situ* TEM Cathodoluminescent

Collaborators: J. Kolar-Gutierrez, D. Buller

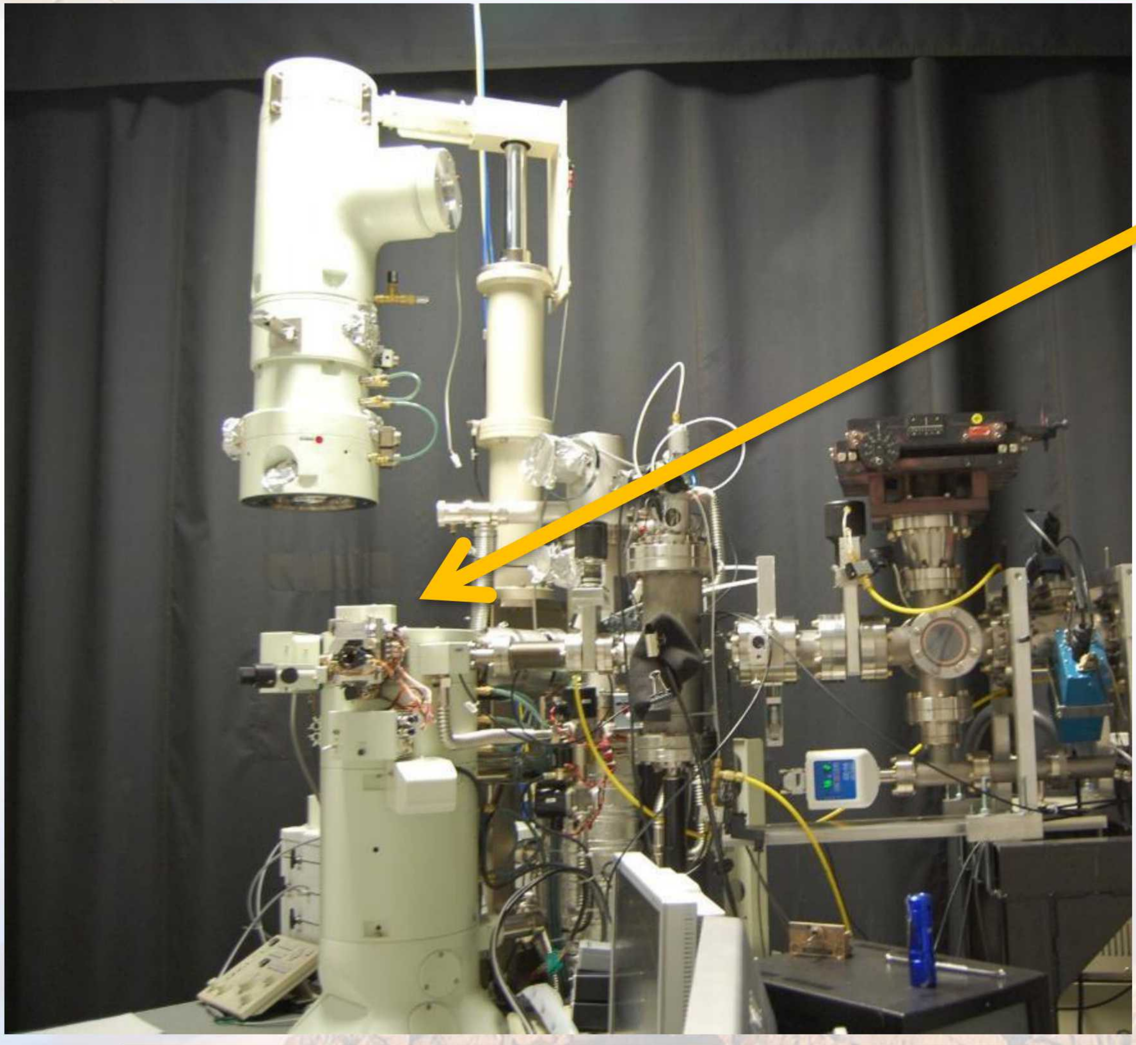




The respective TEM images of the area analyzed by spectrometry

In situ TEM Laser Exposure towards *in situ* Photoluminescence

Collaborators: D.L. Buller, P. Price, A. Monterrosa, D. Adams, M. Abere



Optical Pathway in an I^{3}TEM

- **Angled mirror with bore hole for the electron path was installed.**
- **Mirror is located on top of the objective polepiece "heart of the TEM"**
- **Port is being constructed with thick leaded glass to permit light through, but not x-rays created by ion or electron beams.**
- **Should permit *in situ* IBIL and CL.**

An optical port is currently being added to the I^{3}TEM, which, if successful, will permit *in situ* TEM luminescence studies (CL and IBIL)

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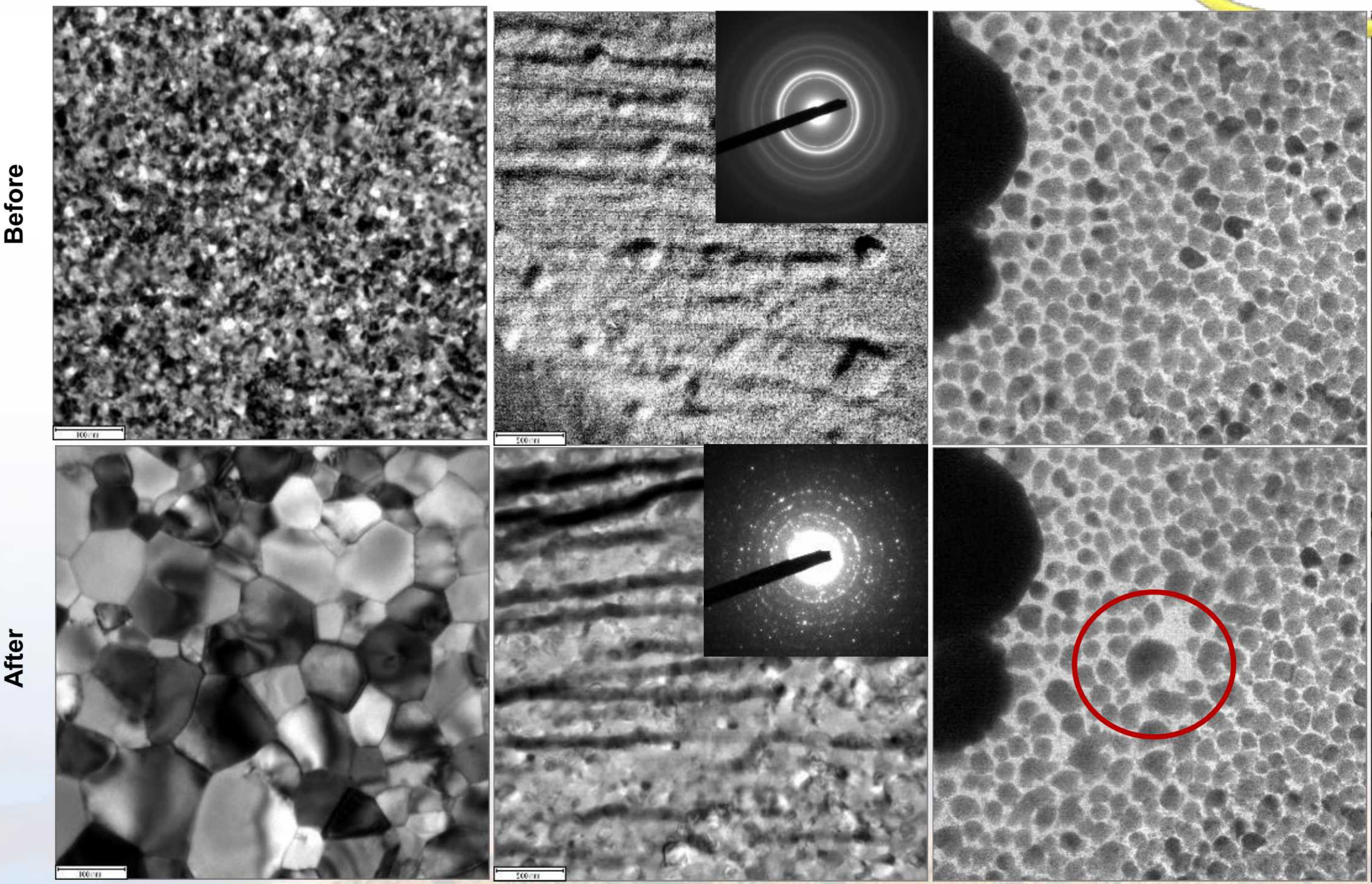
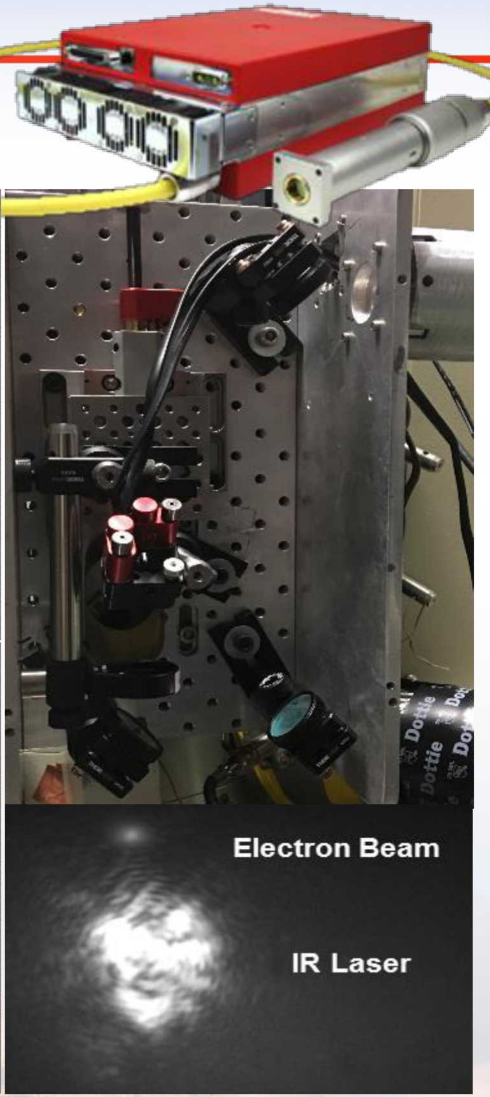
Initial Laser Heating Observatios

Collaborator: P. Price, A. Monterrosa, C.M. Barr, D. Adams, M. Abere

Pt Grain Growth **Reactive Multilayer Films** **Nanoparticle Sintering**

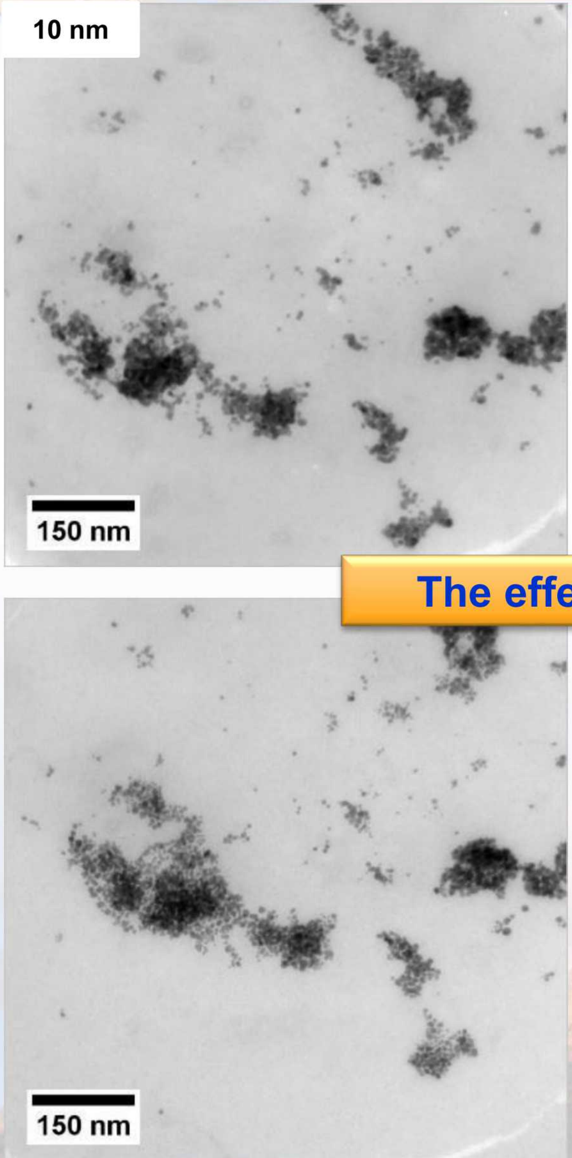


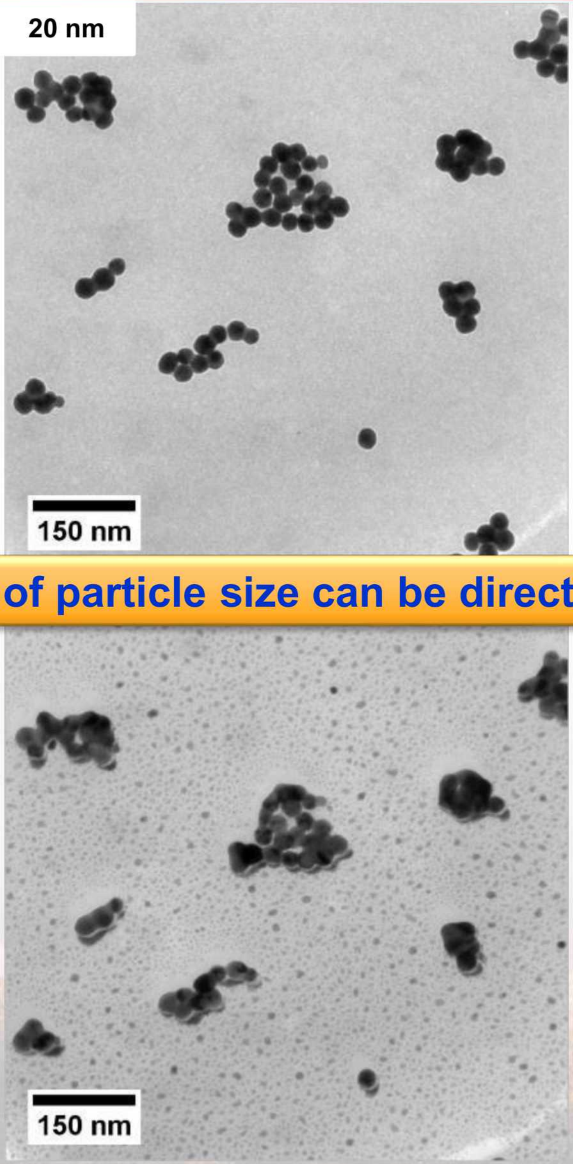


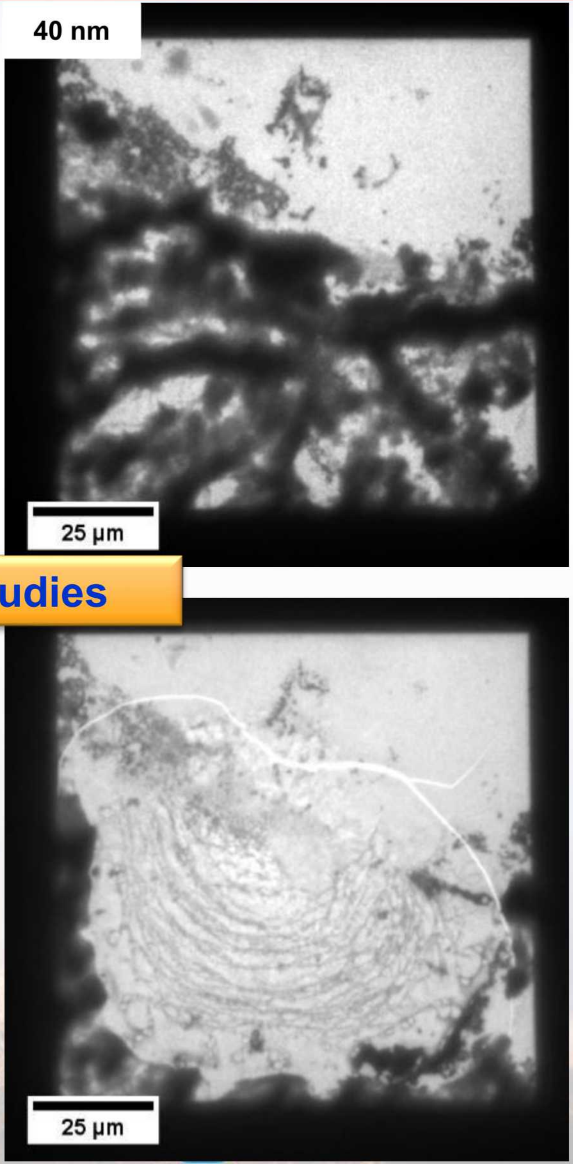
We can now introduce rapid thermal heating with any TEM stage or ion beam conditions

Comparison of 10, 20, and 40 nm Au Nanoparticle Laser Sintering

Collaborator: P. Price, A. Monterrosa, C.M. Barr, D. Adams, M. Abere



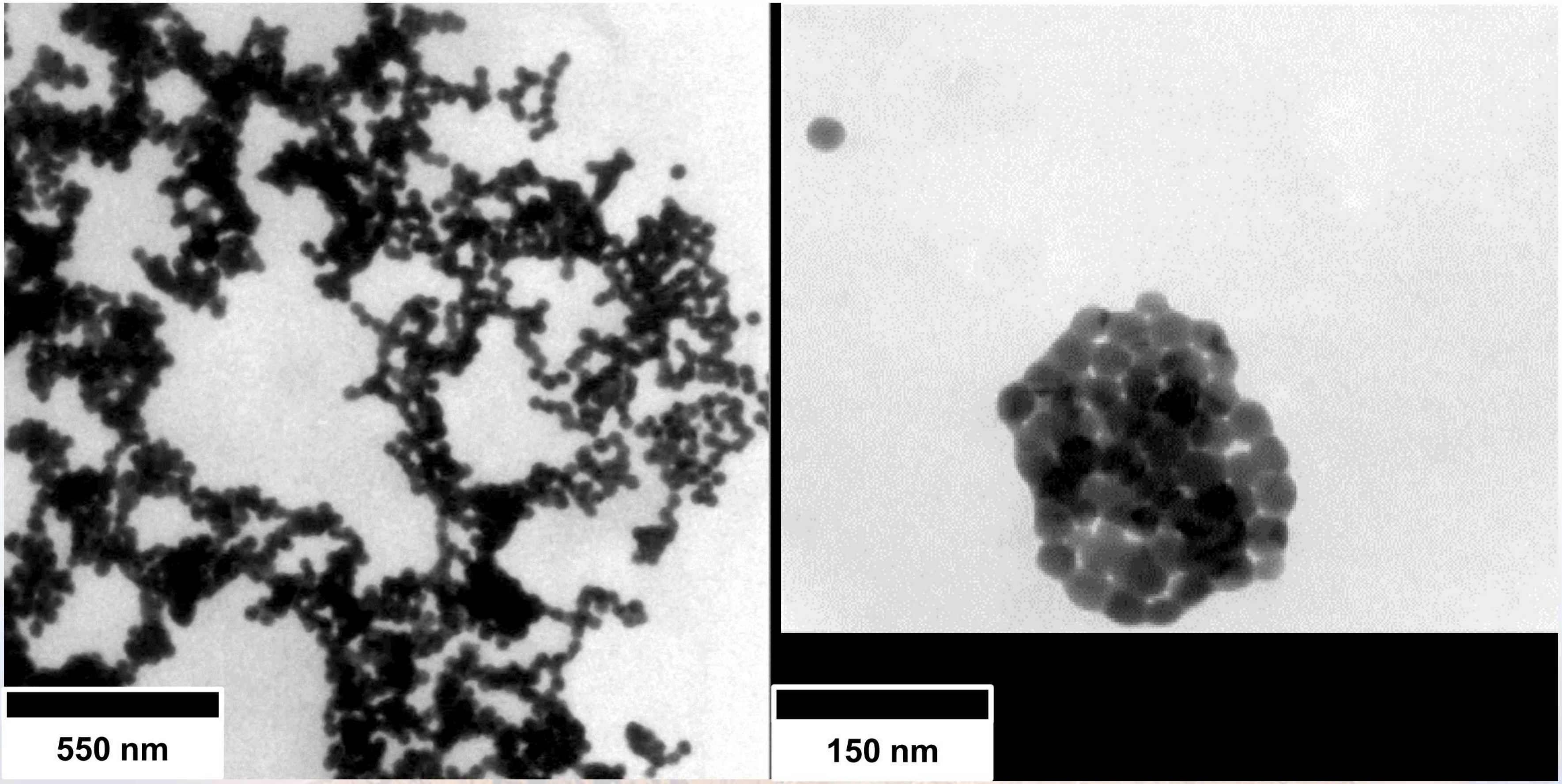




The effect of particle size can be directly studies

Complex Interaction Au NPs Exposed to Laser Irradiation

Collaborator: P. Price, A. Monterrosa, C.M. Barr, D. Adams, M. Abere



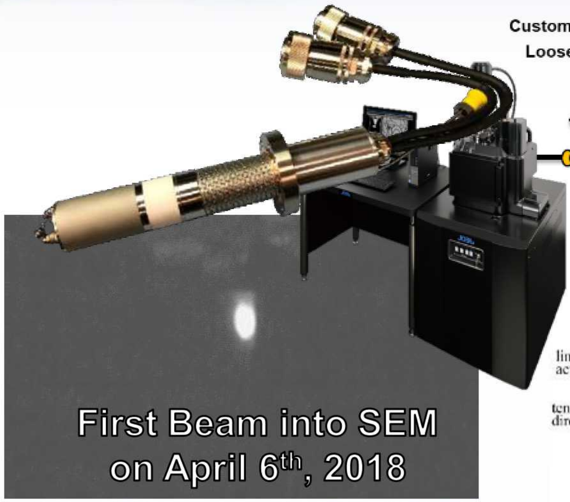
Speed = 2.5x

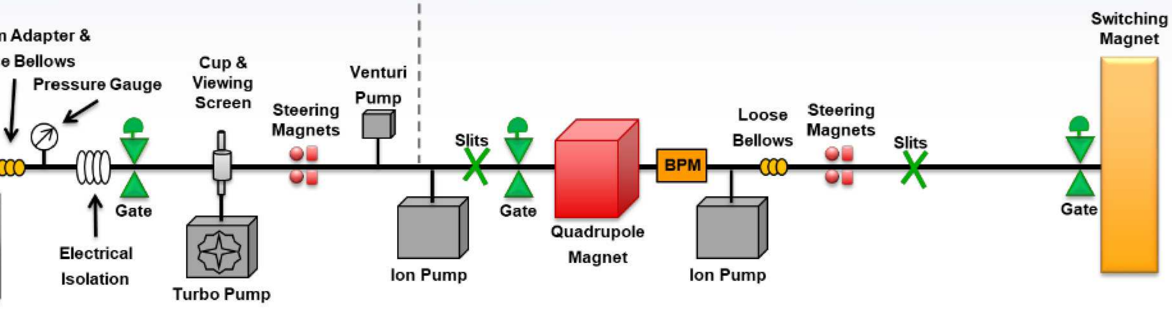
A Complex Combination of Sintering, Reactions, and Ablation Occurs

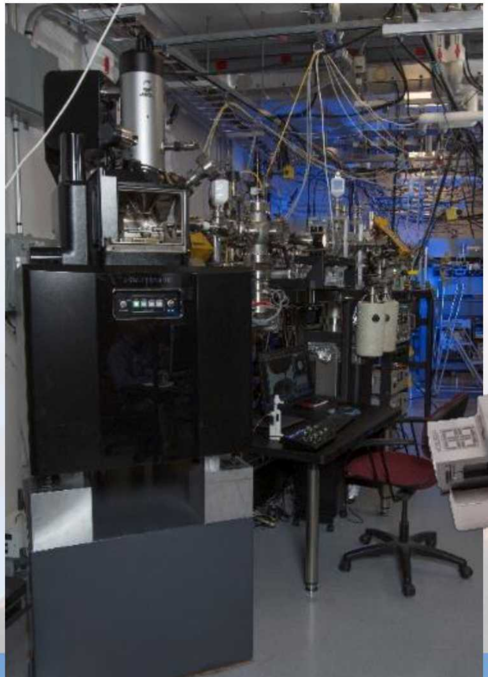
In situ Ion Irradiation SEM (I^{3}SEM)

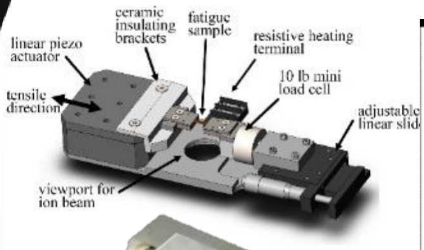
1st Generation 0th Generation

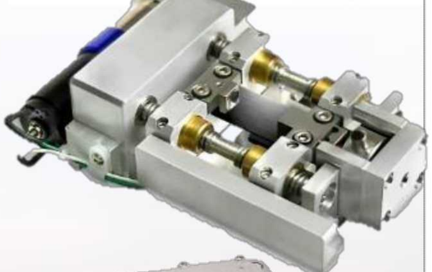
Collaborators: N. Heckman, D. Buller, B. Boyce, J. Carroll, C. Taylor, B. Muntifering, & S. Briggs

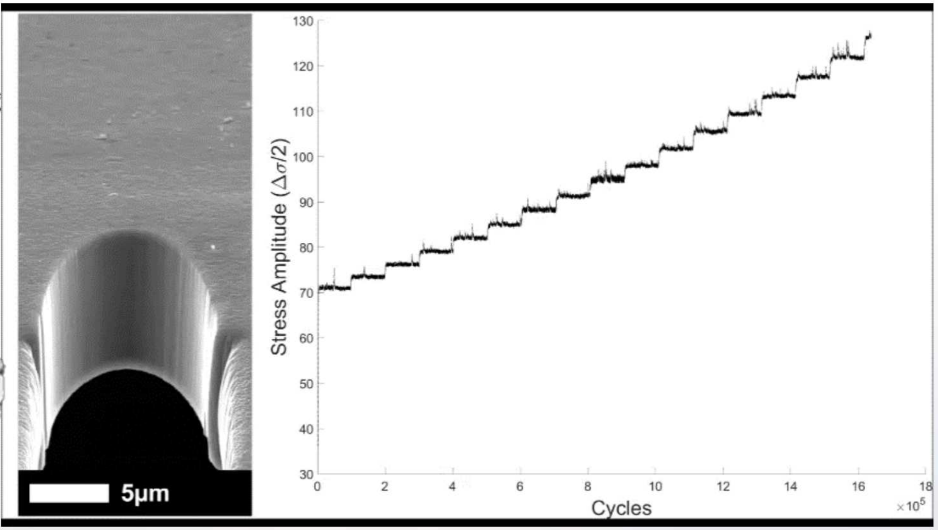

First Beam into SEM on April 6th, 2018











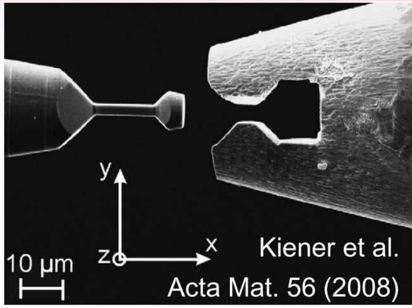
S.A. Briggs

Coupling a 6 MV Tandem and Ion Gun to a SEM Tuesday

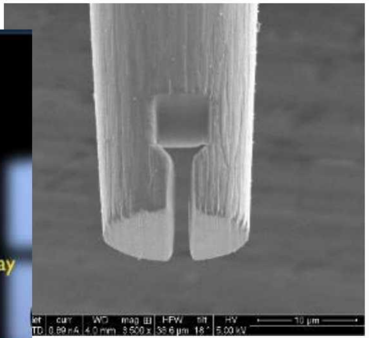
August 14, 4:45 PM in Room Ft. Worth 6-7

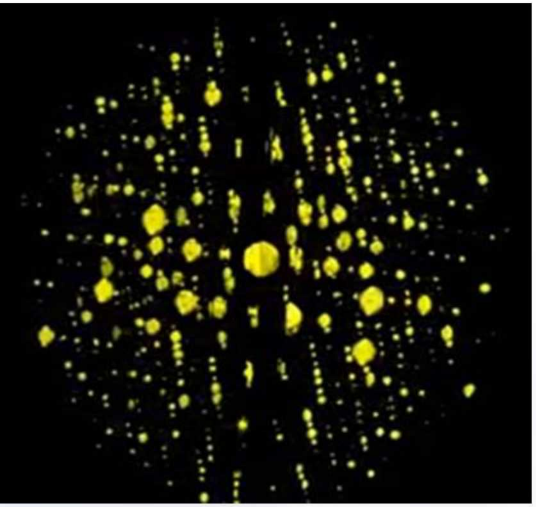
Future Directions Under Pursuit

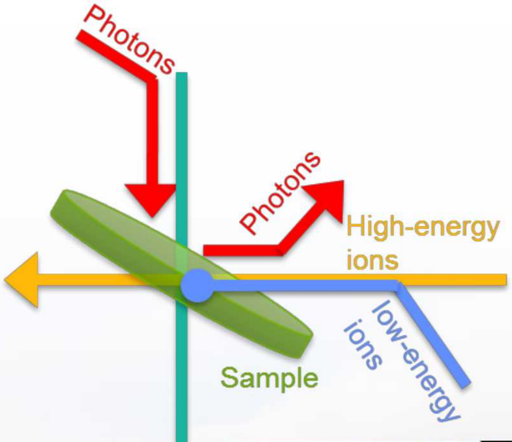
1. **In-situ TEM CL, IBIL (currently capable)**
2. ***In situ* ion irradiation TEM in liquid or gas (currently capable)**
3. **PED: Local texture characterization (currently capable)**
4. **Quantitative in-situ tensile/creep experiments (currently capable)**
5. **DTEM: Nanosecond resolution (laser optics needed)**

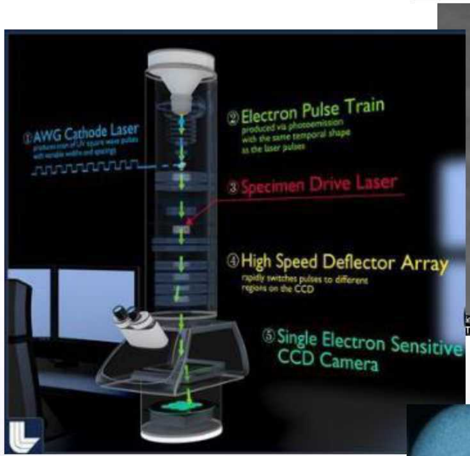


Kiener et al. Acta Mat. 56 (2008)

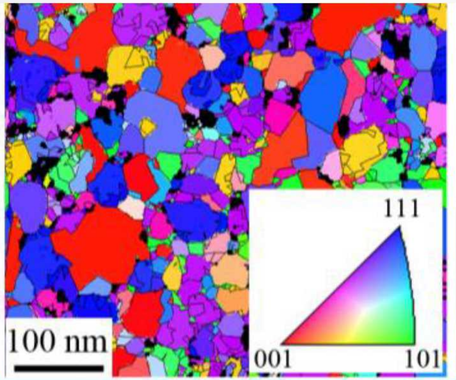


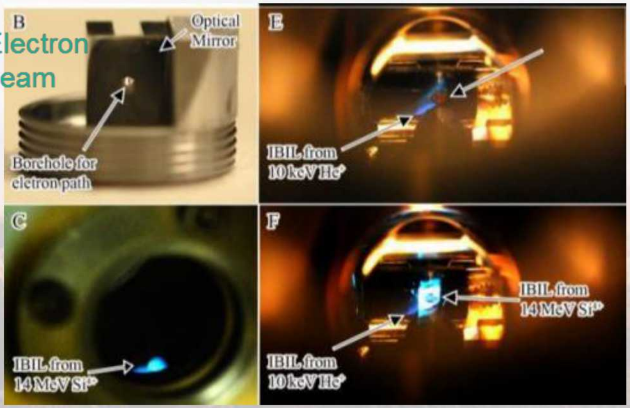


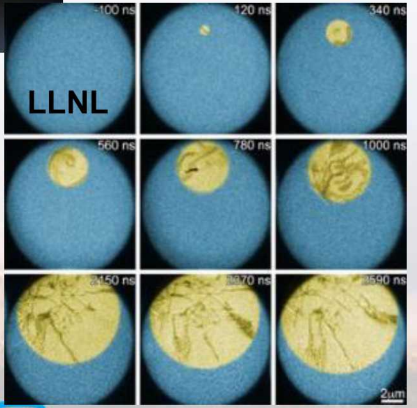




AppFive NanoMegas







LLNL

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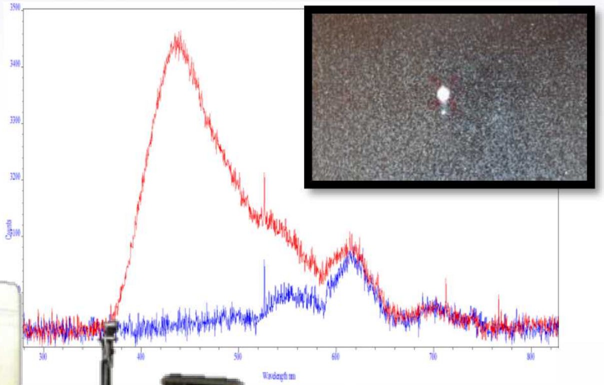
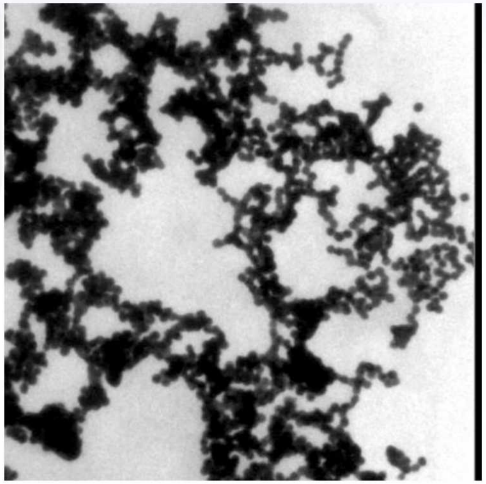
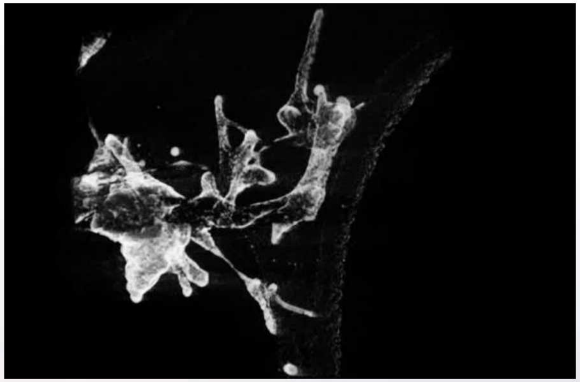
Summary

- Sandia's I^{3}TEM is a unique facility for understanding mechanisms at the nanoscale
  - Only facility in the world with a wealth of overlapping *in situ ion irradiation* capabilities including PL, CL, and IBIL
  - *In situ* high energy ion irradiation from H to Au
  - *In situ* gas implantation
  - 18 TEM stages with various capabilities







Sandia's I^{3}TEM although still under development is providing a wealth of possibility to explore the interplay of PL, CL, and IBIL

Collaborators:

- P. Price, C.M. Barr, A. Monterrosa, J. Kolar-Gutierrez, M. Marshall, P. Price, M. Abere, D. Adams, IDES Inc., S.M. Hoppe, B.A. Hernandez-Sanchez, T.J. Boyle, P. Yang, P. Feng, F.P. Doty, M.D. Allendorf, J.V. Branson, C.J. Powell, G. Vizkelethy, P. Rossi, B.L. Doyle, D.L. Buller, D.C. Bufford, N. Heckman, B. Boyce, J. Carroll, C. Taylor, B. Muntifering, & S. Briggs

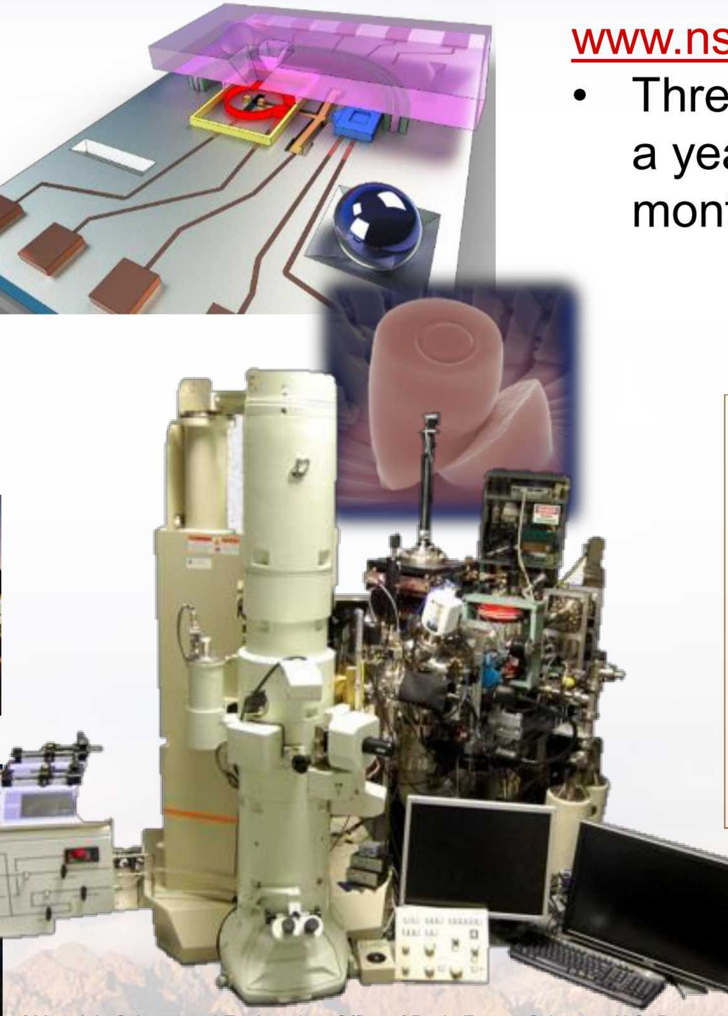
This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

Sandia's <u>USER</u> Capabilities

D. Hanson, W. Martin, M. Wasiolek

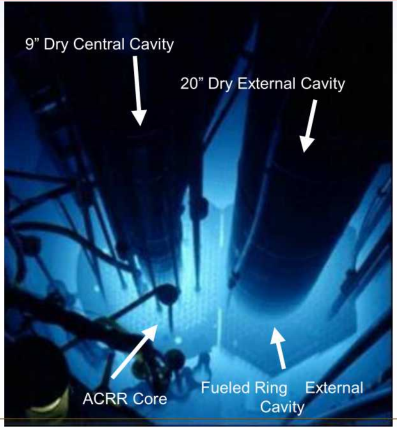
www.cint.lanl.gov

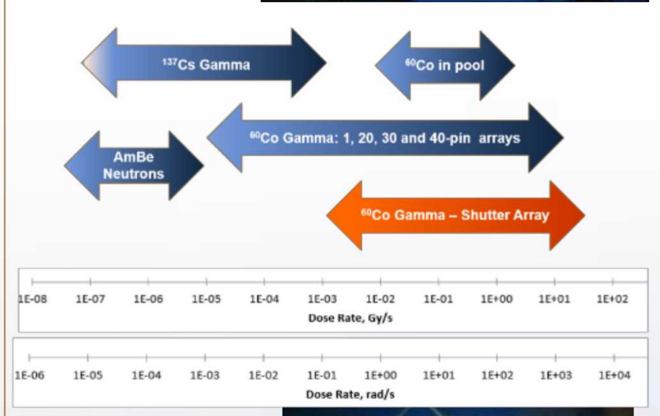
- Spring and Fall proposals for 18 months
- Rapid Access proposal anytime for 3 months



www.nsuf.inl.gov

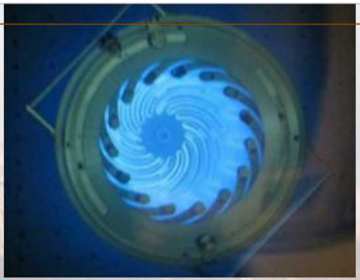
- Three proposal a year for 9 months





Core Facility - SNL

Gateway Facility - LANL



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