Physical Response of Gold Nanoparticles to Ion Beam Modification

SAND2014-3296C

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Sandia National Laboratories

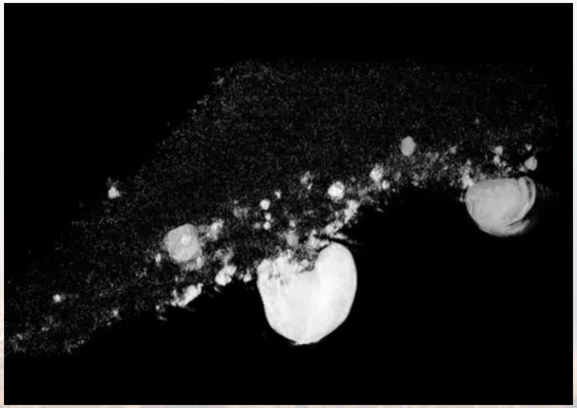
April 23, 2014

Sandia's Ion Beam Lab

***In situ* Ion Irradiation TEM**

Unirradiated Au NP model

Irradiated Au NP model



Outline

- Importance of understanding the structural evolution of nanoparticles
- A new *in situ* TEM capability to characterize radiation damage
- *In situ* and 4D irradiation of Au NP with Cu, Au, and He ions
- Production of new far-from-equilibrium nanostructures

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This work was partially supported by DOE, Office of Science, Office of Basic Energy Sciences.

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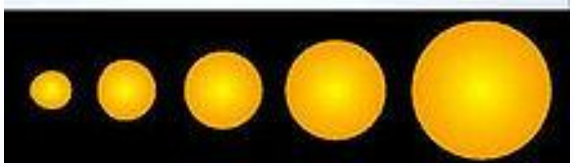
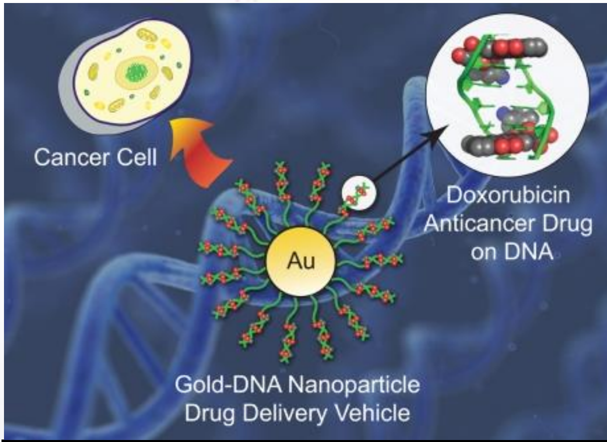
Nanoparticles in Extreme Environments

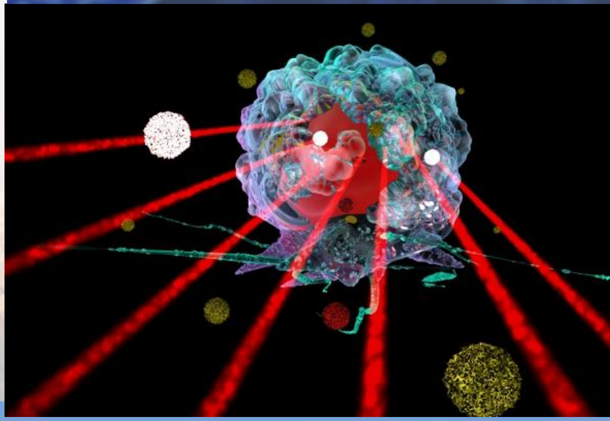


Au nanoparticles (Au NP) are of interest due to their unique optical, electronic, molecular-recognition, and catalytic properties

- **Photothermal and laser ablation cancer therapies – concentrate IR into heat**
- **Tumor targeting and drug carriers – enhance dose delivery**
- **Catalysts for air-pollution control**

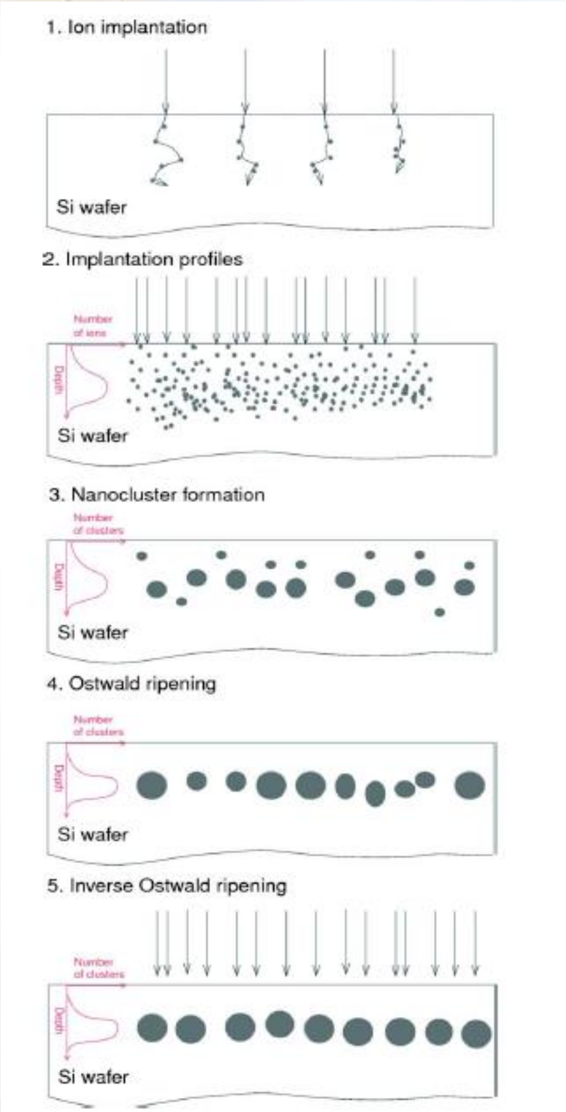
Do the unique properties of the NP withstand extreme radiation?

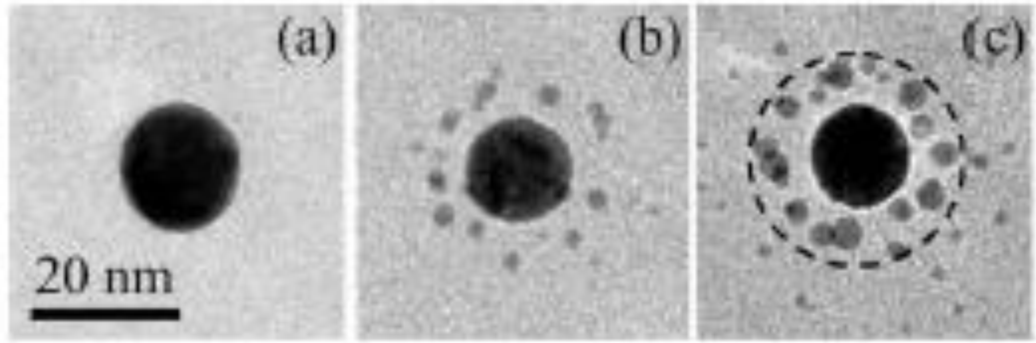




Nenoff et. al. *SNL News Release* (2007).

Previous Studies Investigated Embedded Particles

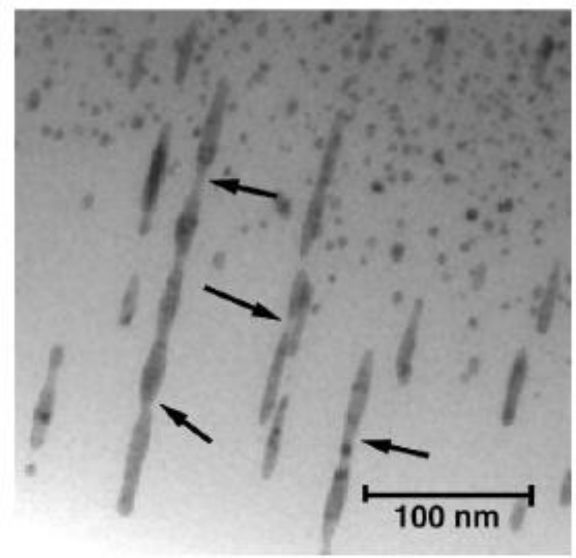




G. Rizza et. al. *Phys. Rev. B 76* (2007) 245414.

Au NCs in SiO_2 matrix irradiated at increasing fluences with 4 MeV Au ions at room temperature. Two generations of satellites observed.

Ion tracks can be formed in SiO_2 matrices and nanoparticle elongation and nanowire formation has been observed. Pt NP are shown, irradiated with 185 MeV Au ions. Arrows point to nanorod fragments.

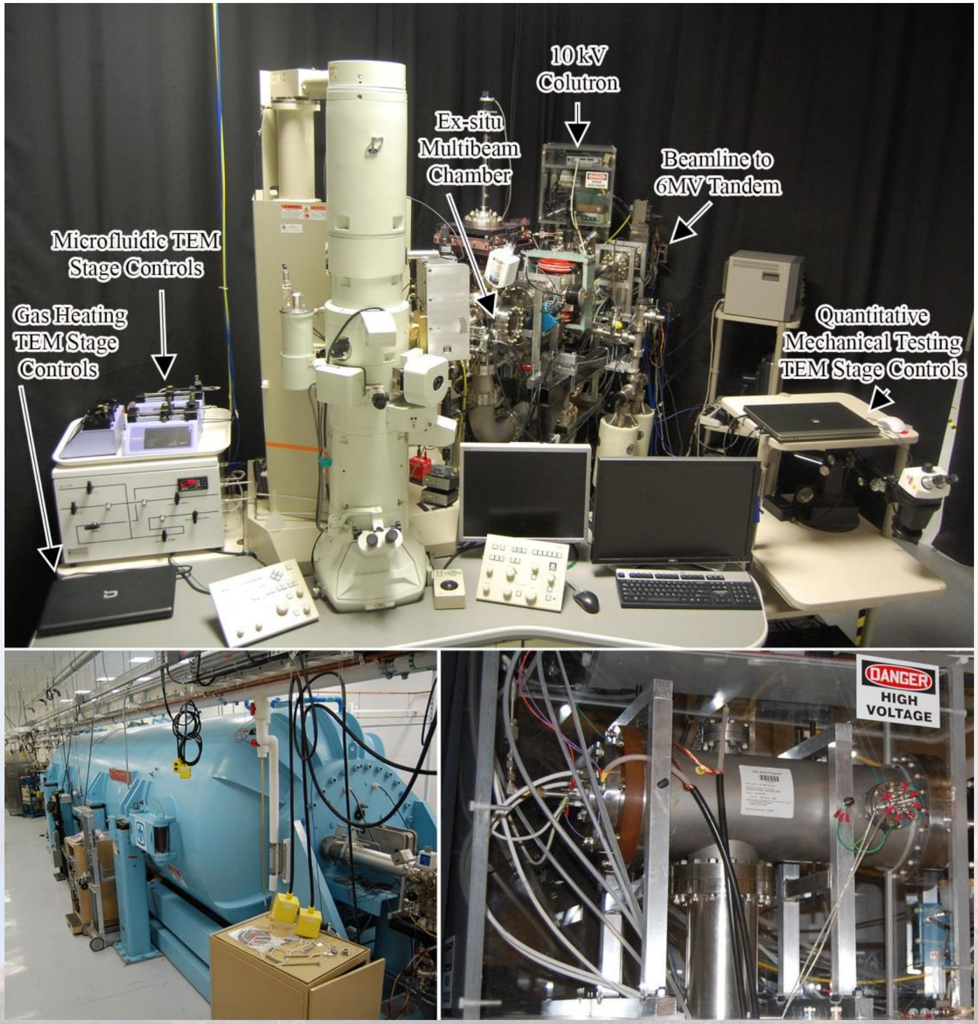


M.C. Ridgway et. al. *NIM B 267* (2009) 931.

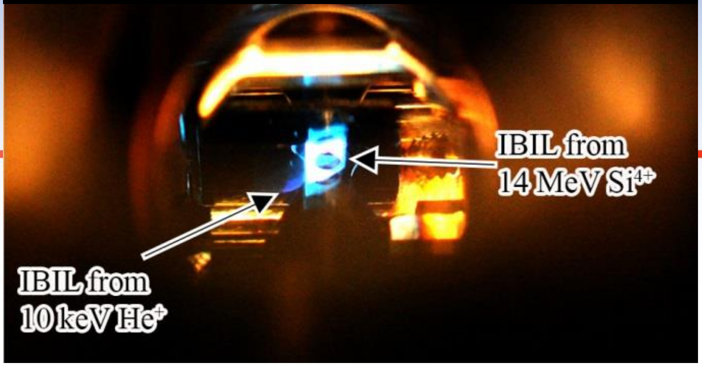
A.V. Krasheninnikov and K. Nordlund. *J. Appl. Phys.* 107 (2012) 071301.

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

10 kV Colutron - 200 kV TEM - 6 MV Tandem

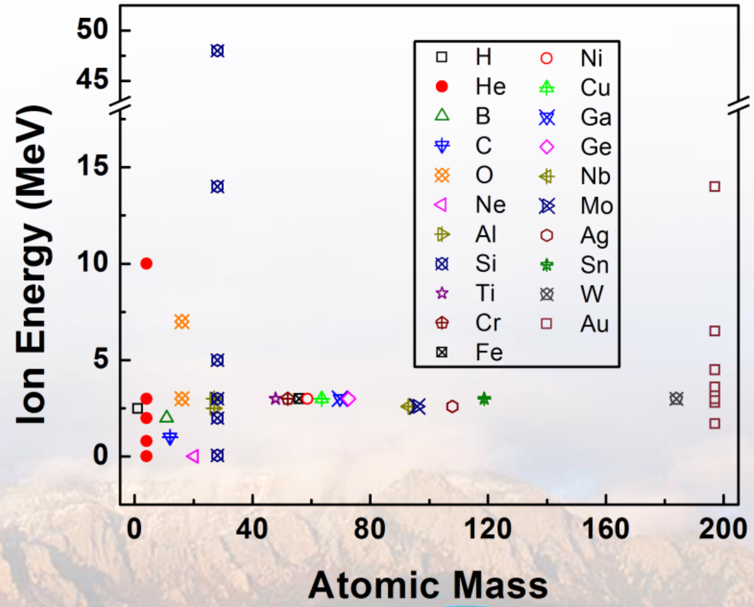


IBIL from a quartz stage inside the TEM



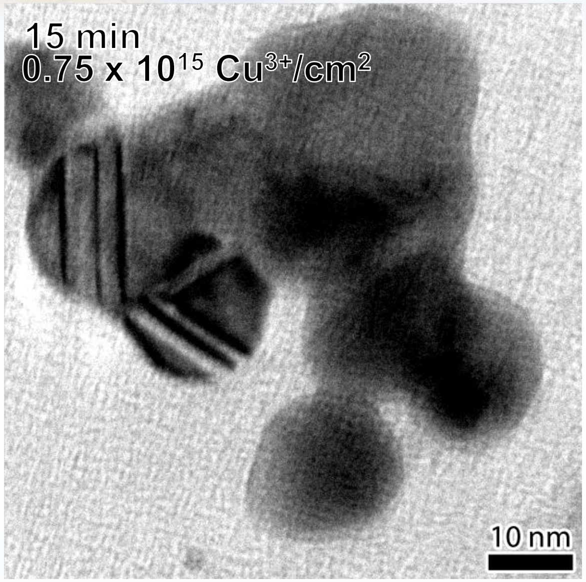
Direct real time observation of ion irradiation, ion implantation, or both with nanometer resolution

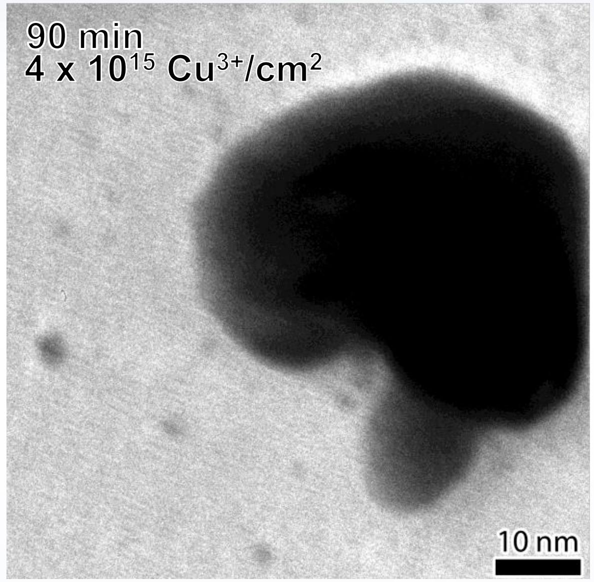
Ion species & energy introduced into the TEM

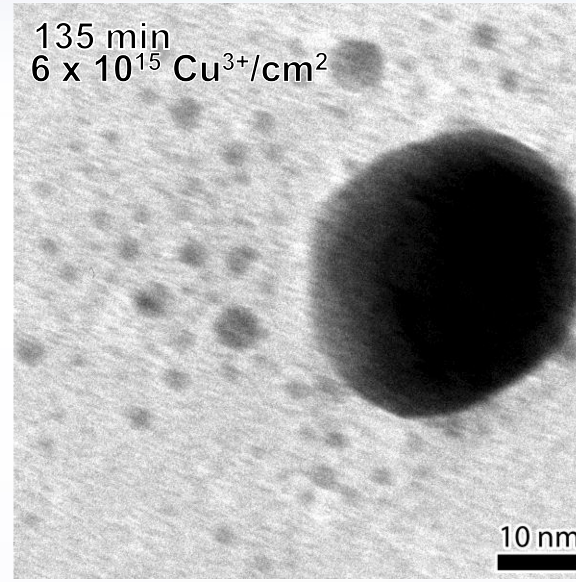


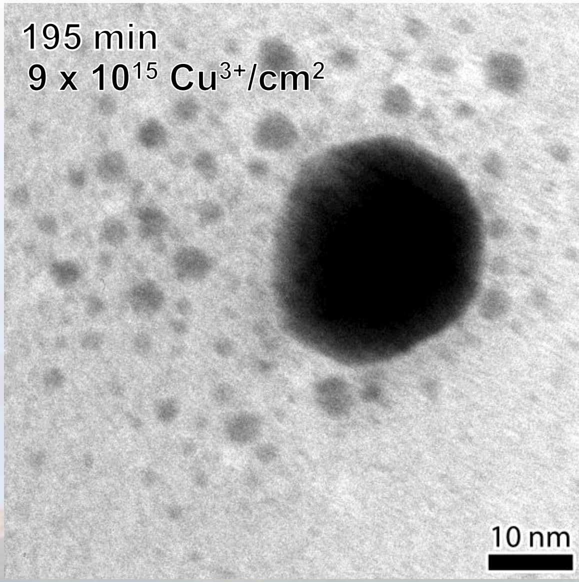
Au NP Irradiated with 100 nA of 3 MeV Cu^{3+}

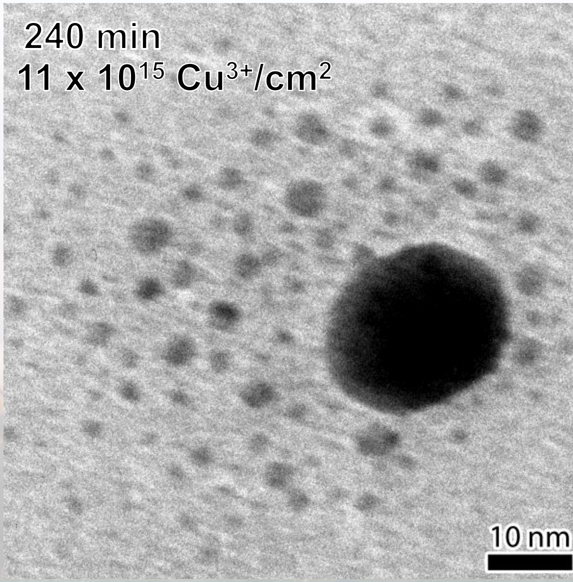
Collaborators: S.M. Hoppe











Over 4 h, group of Au NP coalesced and smaller particles sputtered off, then grew

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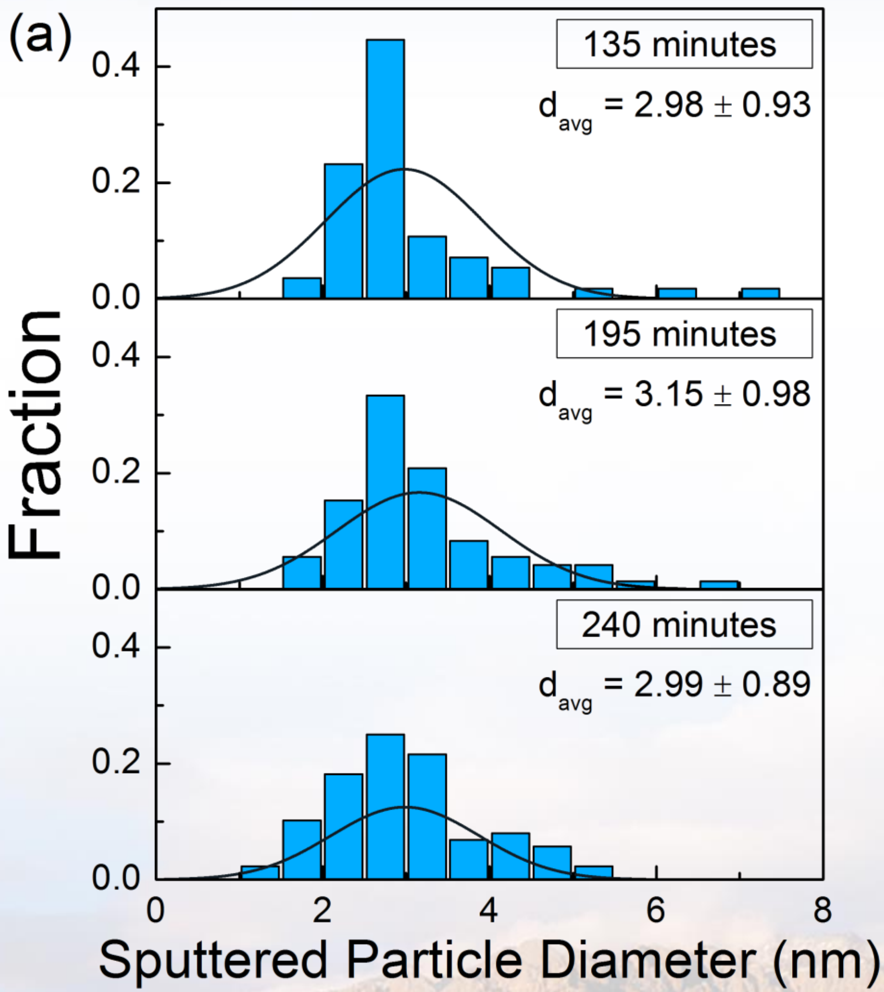
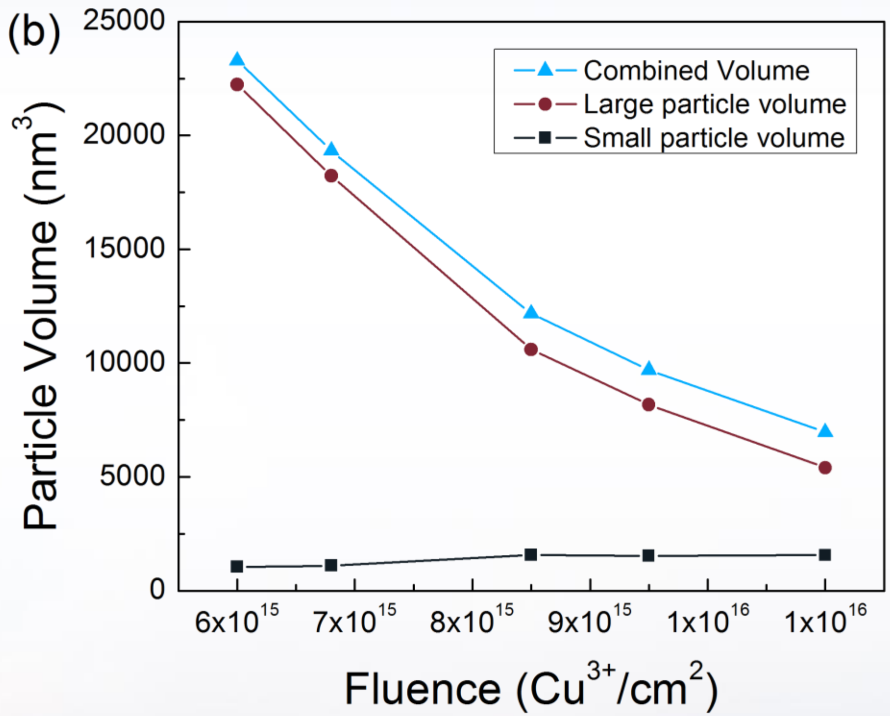
Analysis of Au NP Irradiated with 100 nA of 3 MeV Cu^{3+}

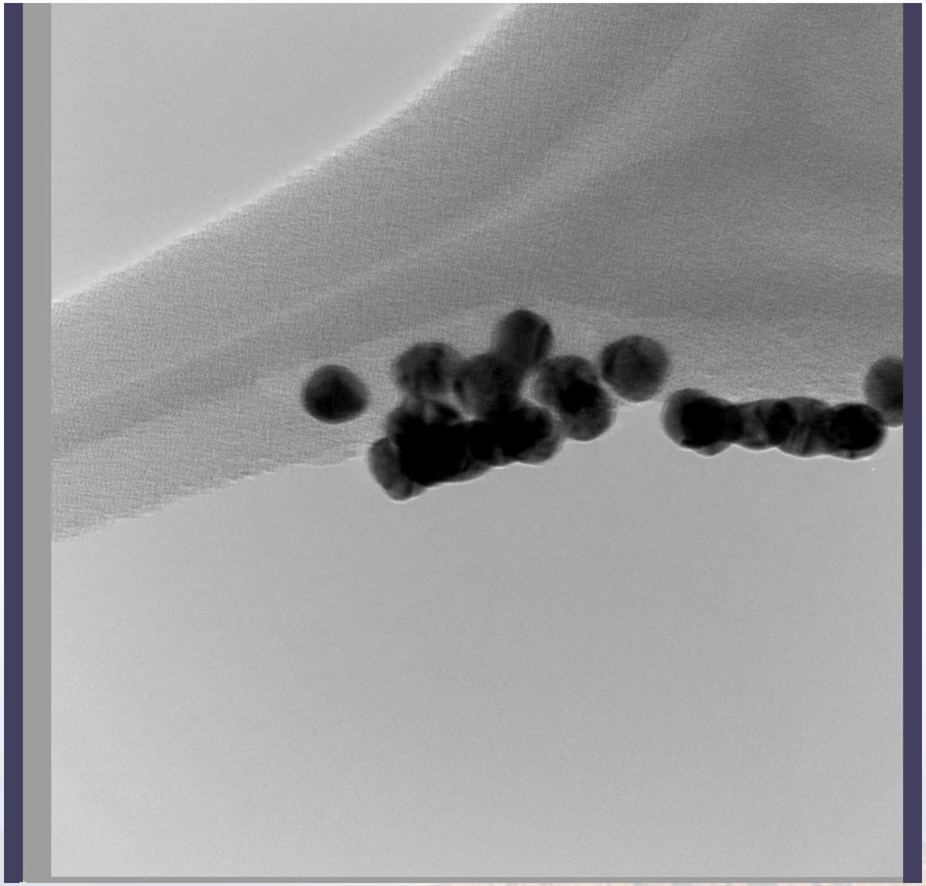




Diameter of sputtered particles did not change substantially. A good deal of material was dispersed outside the nearby halo.

Tomographic Reconstruction of Au NP

Aligned tilt series of unirradiated Au NP



Tomography reconstruction of Au NP

Recent advancements in TEM control and reconstruction software permit collection and production of 3D model of the “transmission” micrograph.

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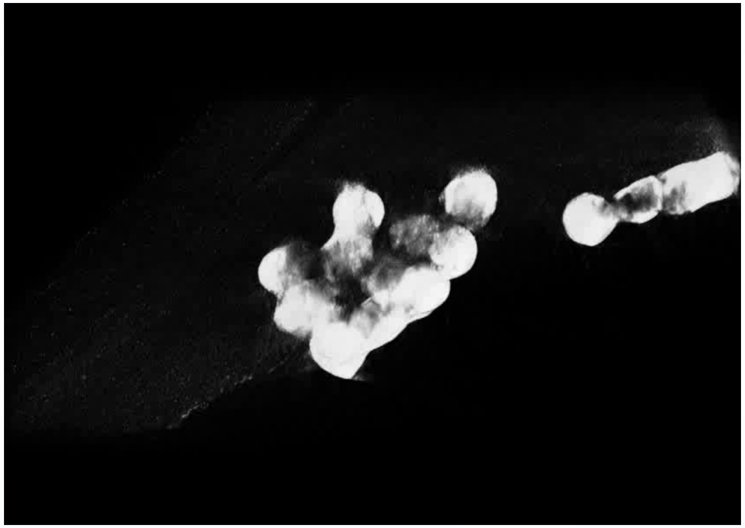
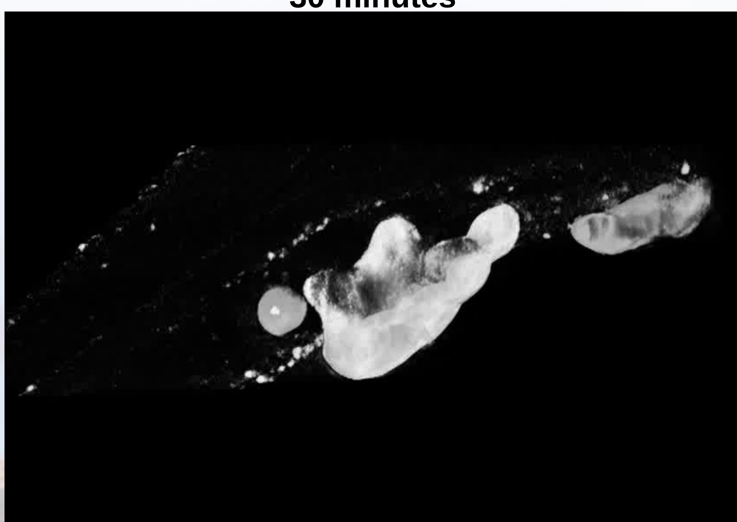
Tomography of Au NP Irradiated due to 3 MeV Cu^{3+}

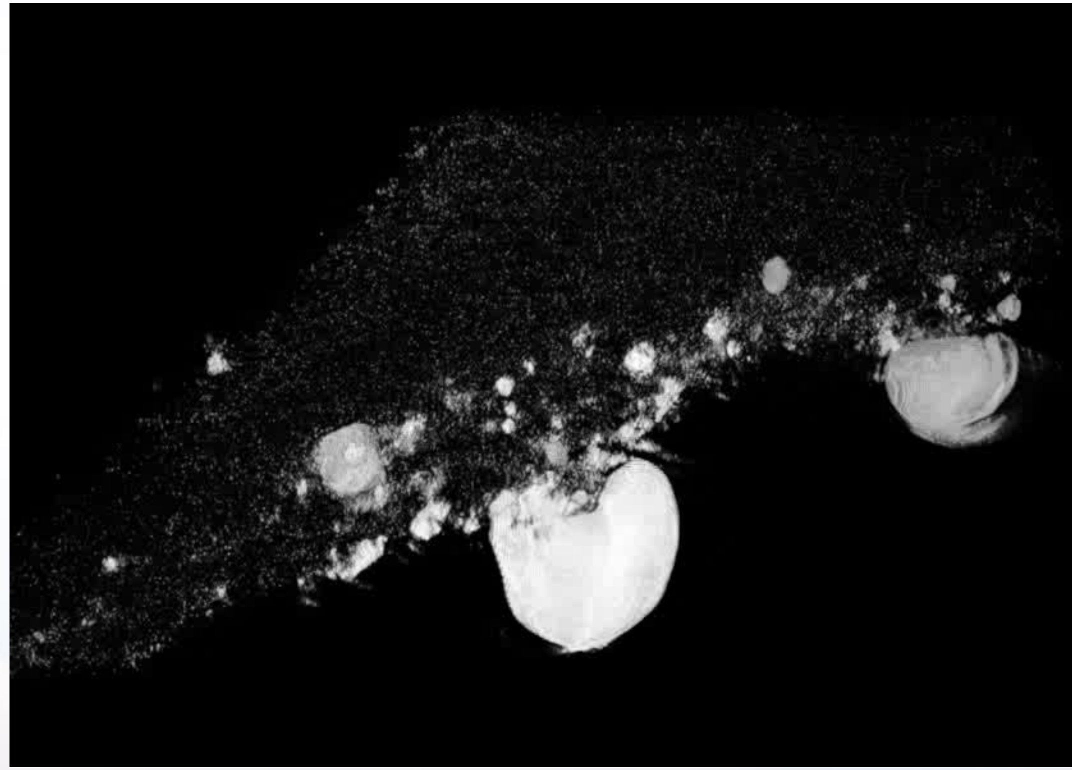
Unirradiated



30 minutes

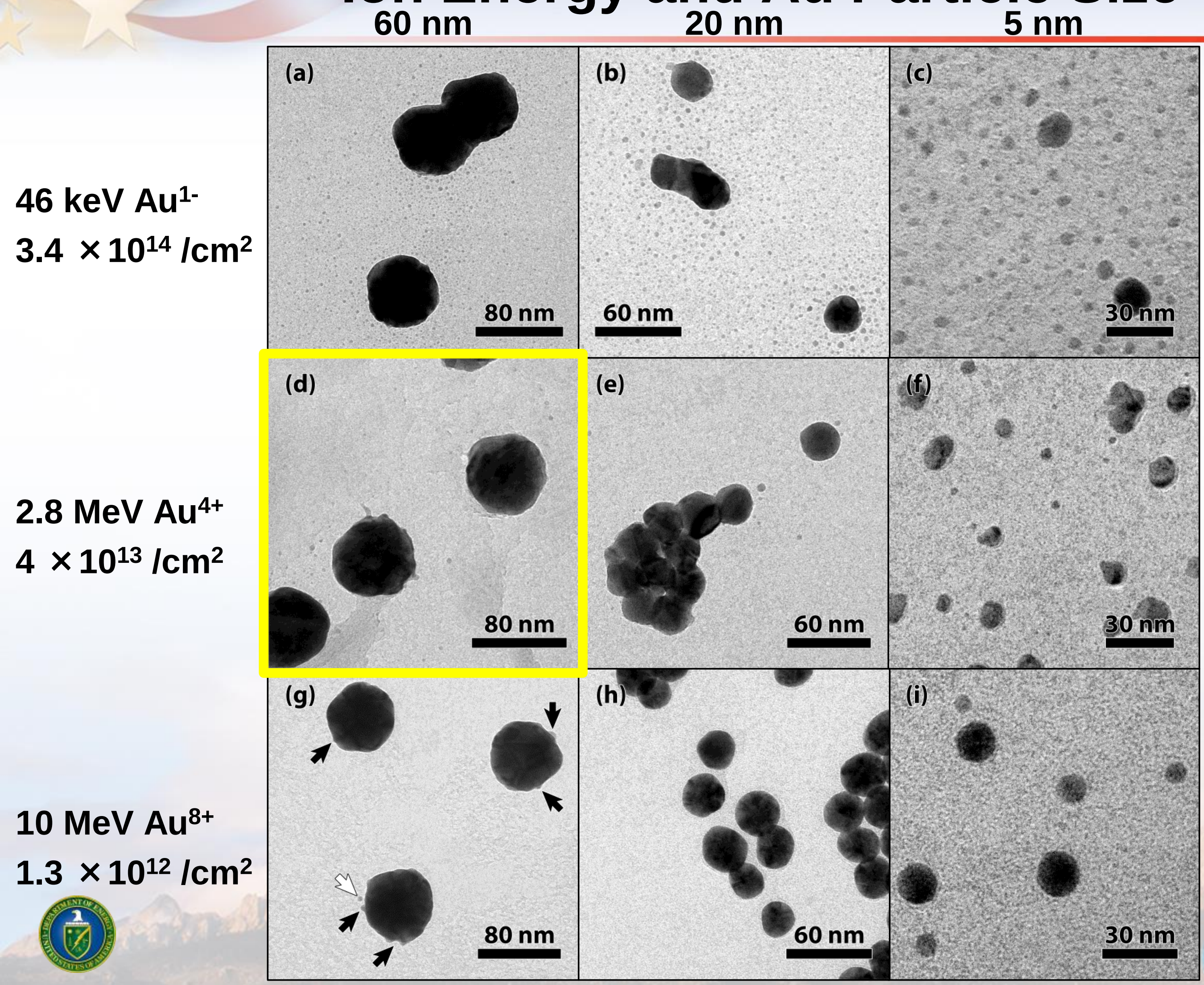


60 minutes



Tilt series were collected after each dose of irradiation resulting in 4D tomography with 3D reconstructions showing radiation damage over time.

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



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

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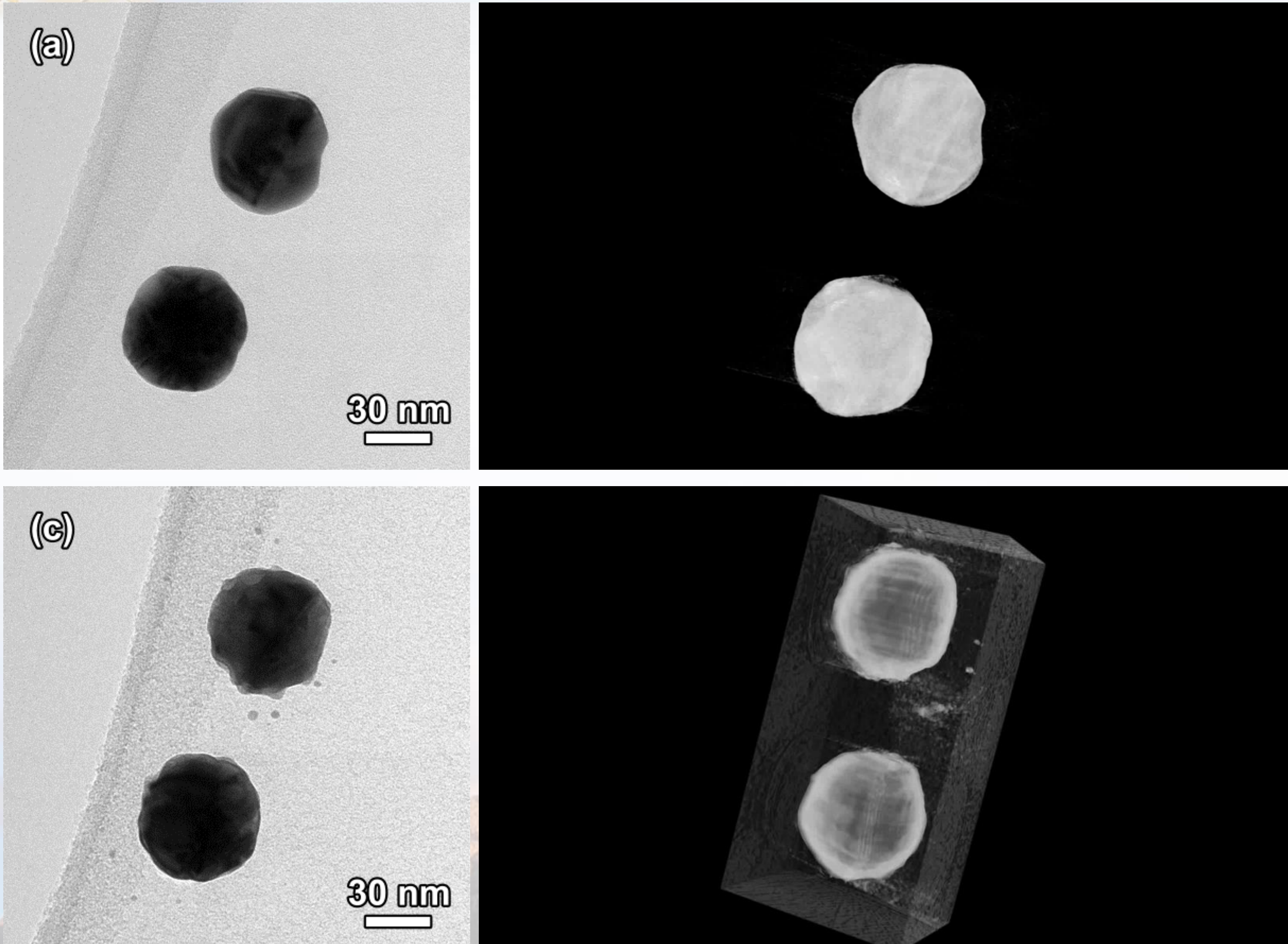
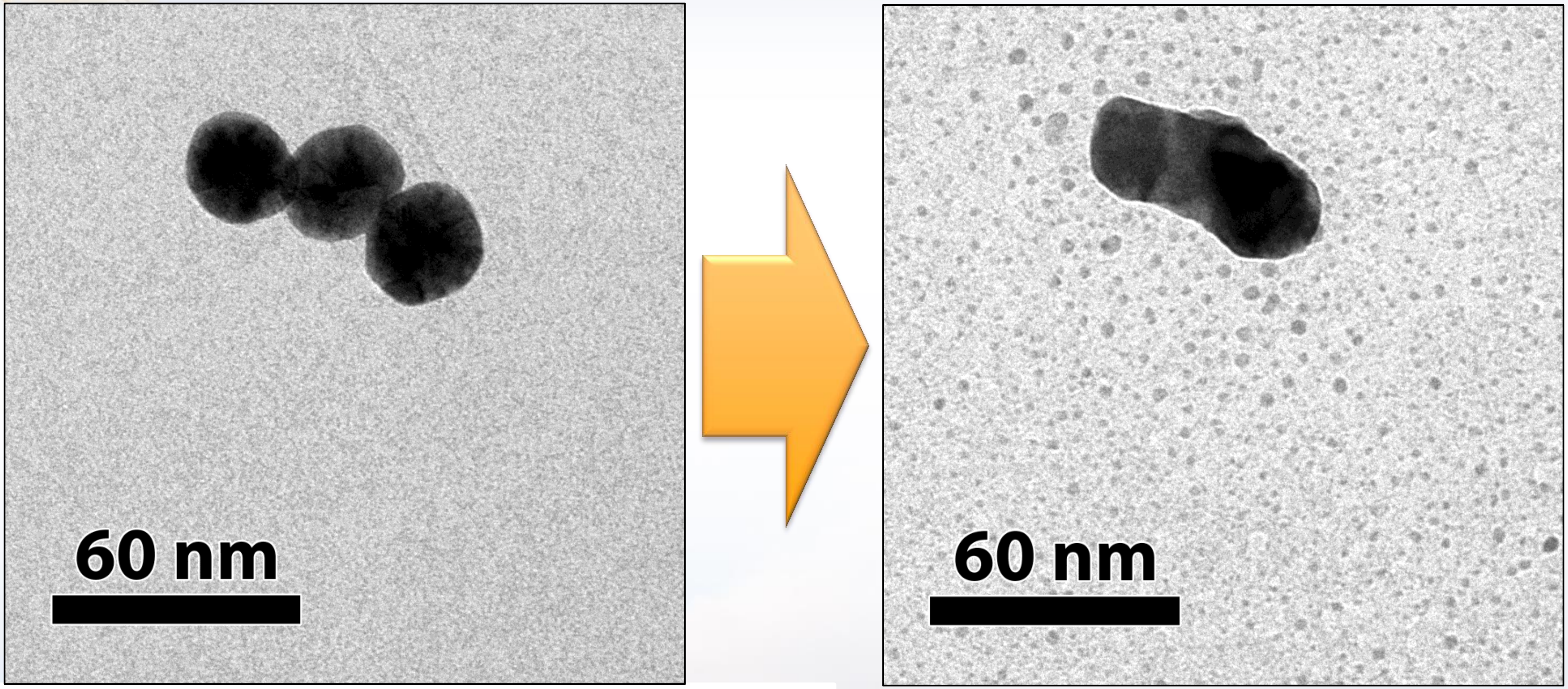
Surface effects of heavy ions



60 nm Au NPs before and after 2.0 × 10^{14} ions/cm^2 of 2.8 MeV Au^{4+}

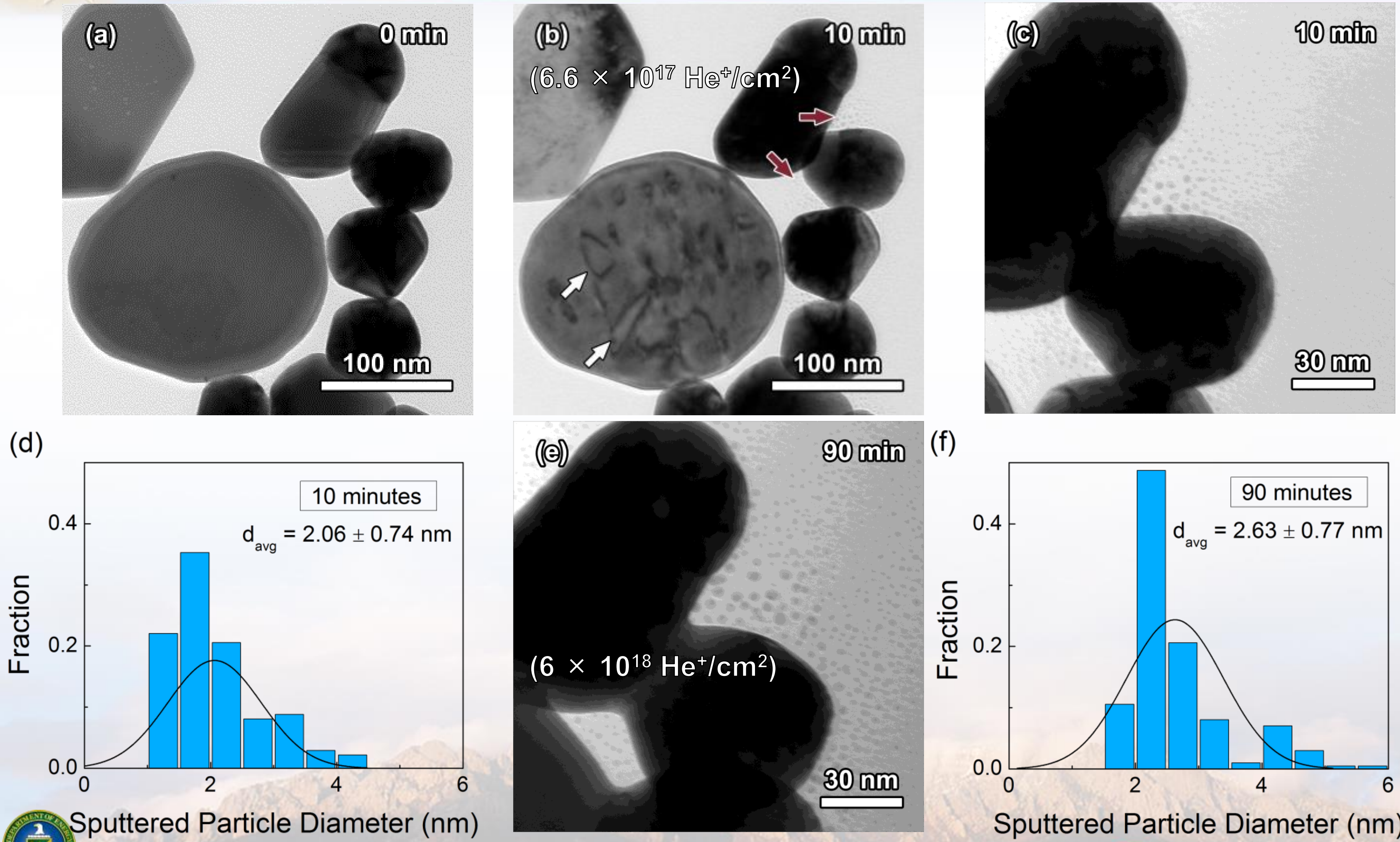
Initial Quantification of the Observed Structural Evolutions



- Heating is expected to be significant
  - Single 3 MeV Cu^{3+} ion
  - 20 nm diameter Au NP
  - Electronic stopping only
- Calculated temperature increase of 400 ºC per ion
- Melting point of Au NP ~900°(5 nm)
- Melting point of bulk Au 1064°

Ion irradiation causes both coalescence and sputtering of Au NP and appears to be related to the ratio of electronic and nuclear stopping power

Formation of Dislocation Loops & Sputtered Particles due to He implantation



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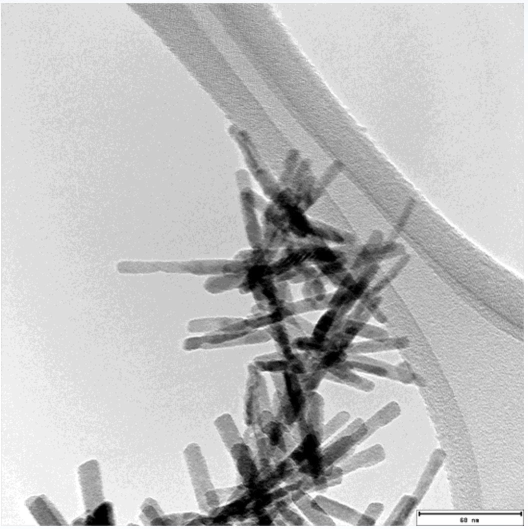
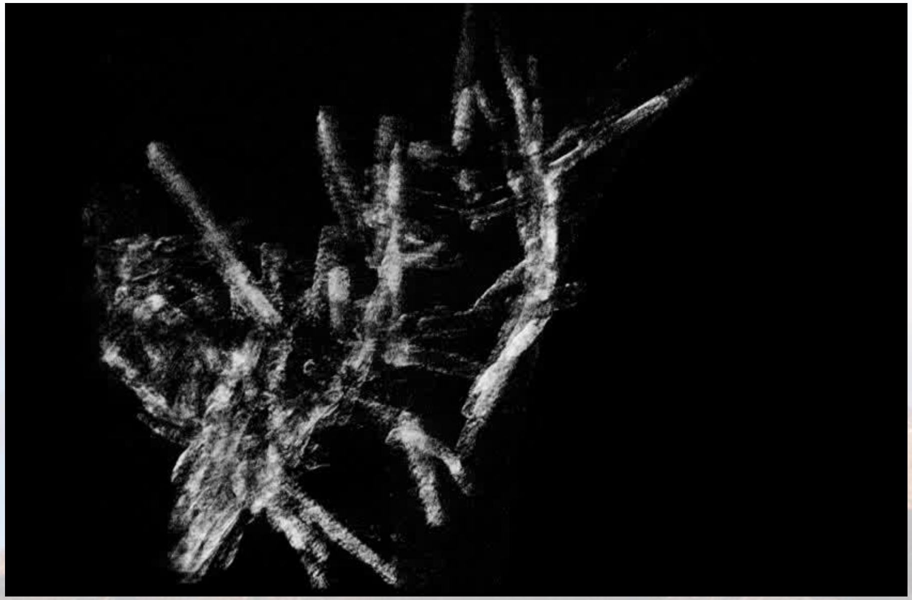
Capability Extends to Other NP Systems

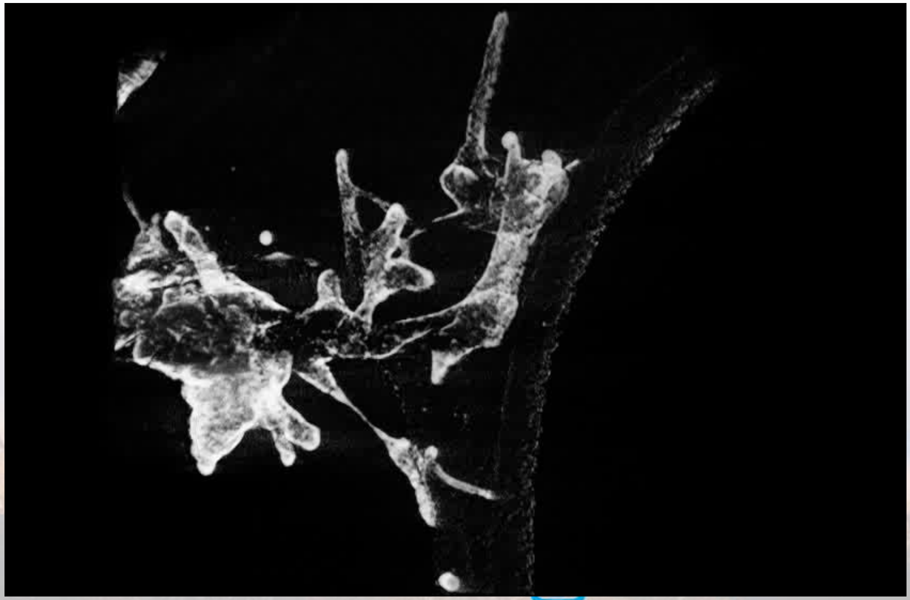


$CdWO_4$ has been irradiated with Cu^{3+} and H^+ to characterize its radiation hardness for nanorod-composite scintillator applications.

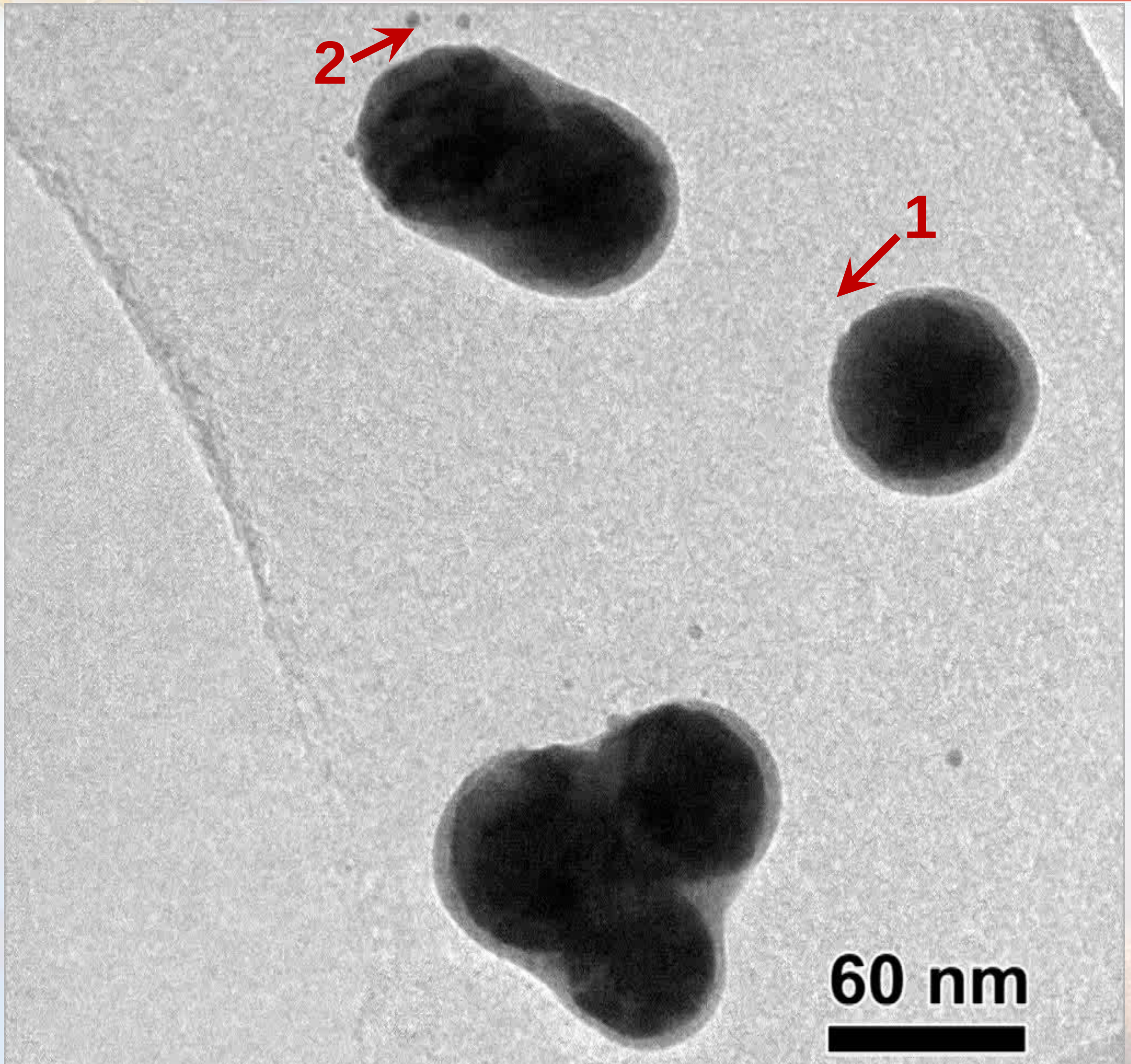
Unirradiated



5 minutes



Single Ion Strikes

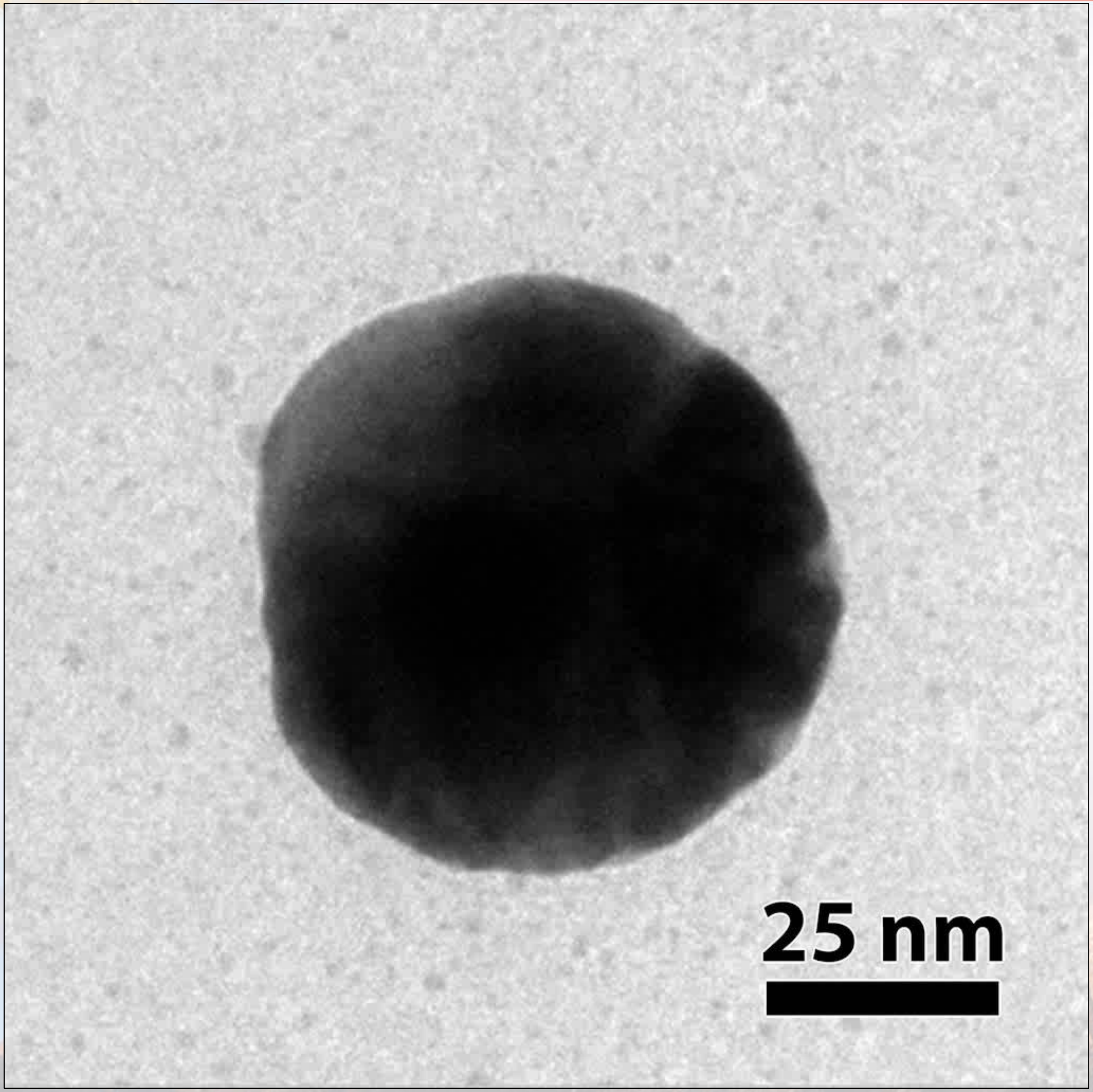


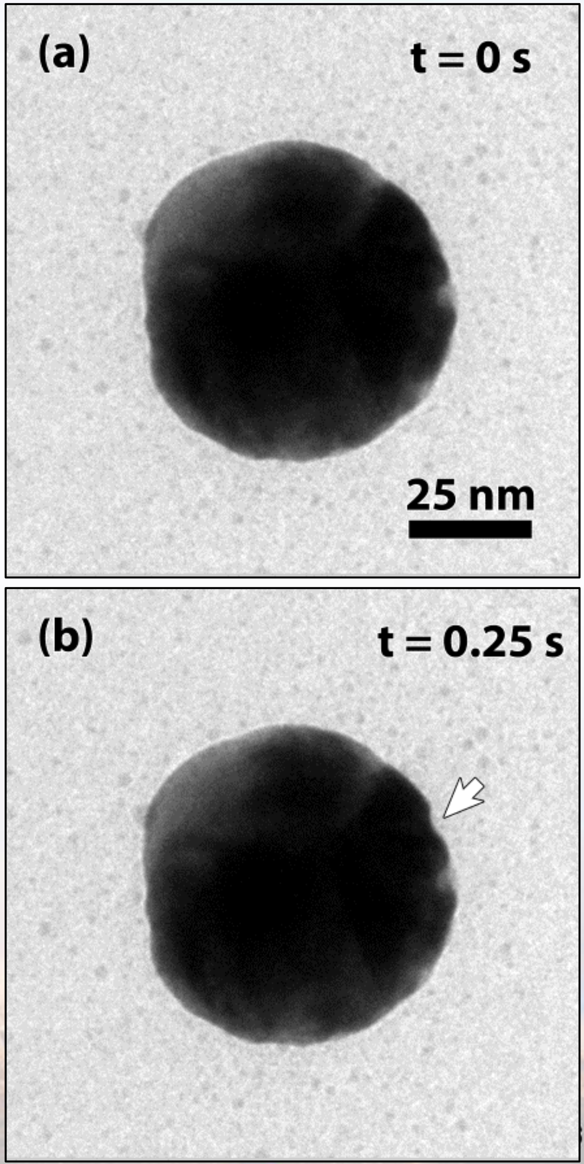
Video playback at 2x real time.

- 2.8 MeV Au^{4+} ions into 60 nm diameter Au nanoparticles
- 100 kx magnification
- Nanoscale filaments created by individual ions

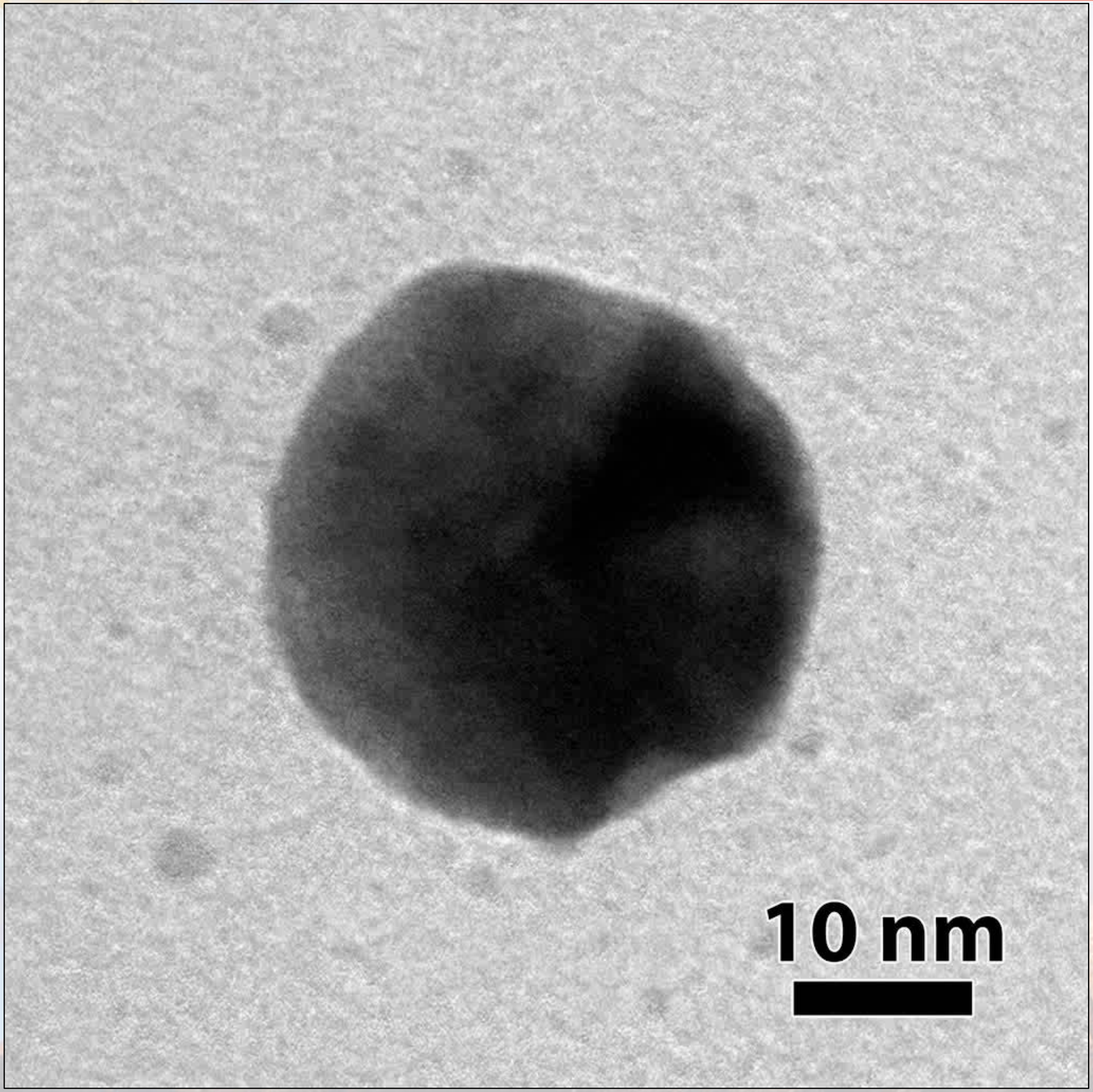
The permanent and transient structures resulting from single ion strikes can be directly observed

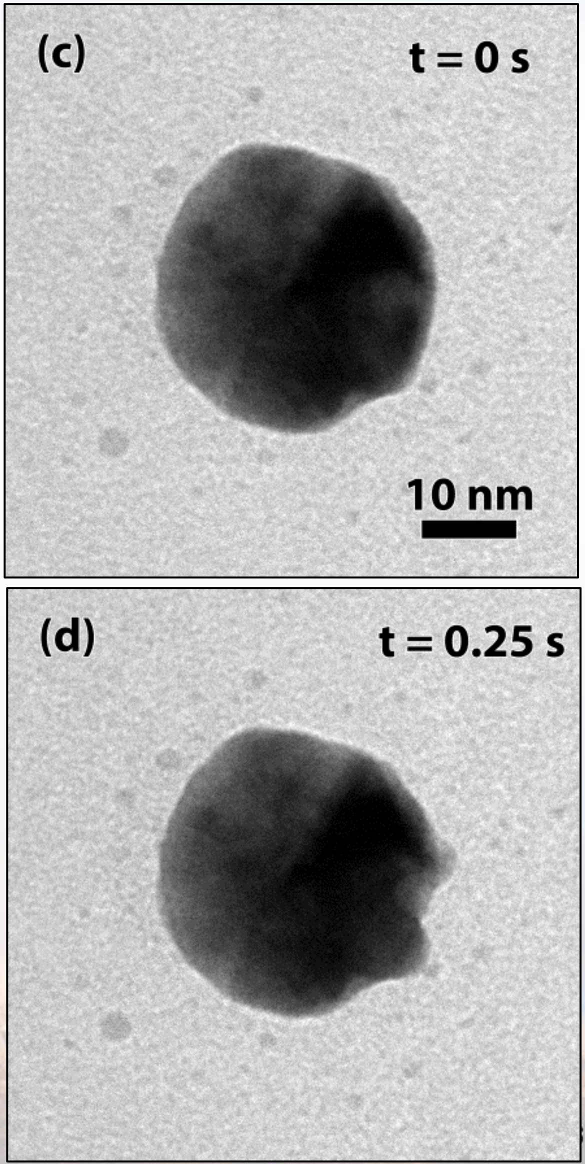
Single Ion Effects with 46 keV Au^{1-} ions: 60 nm



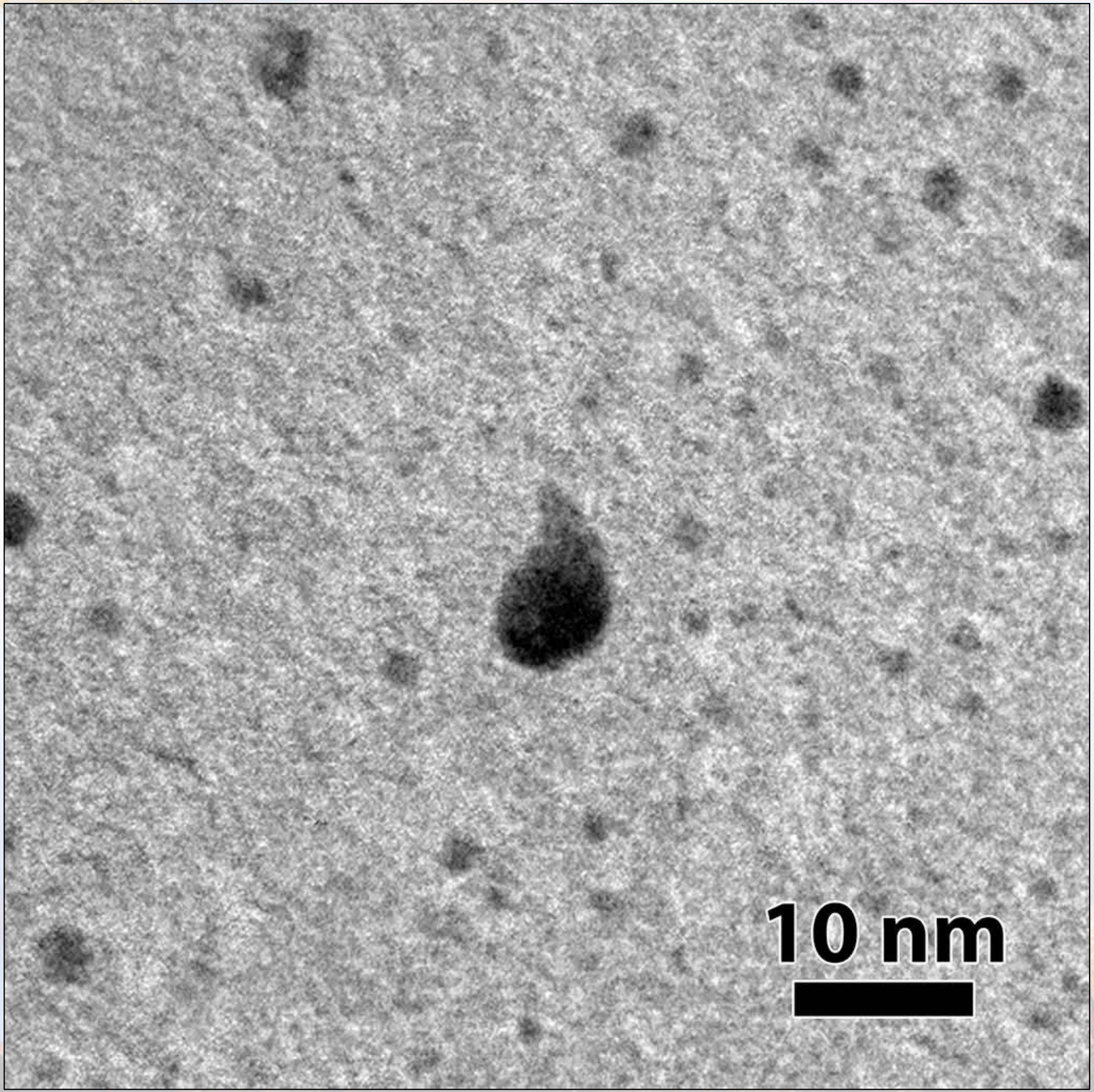


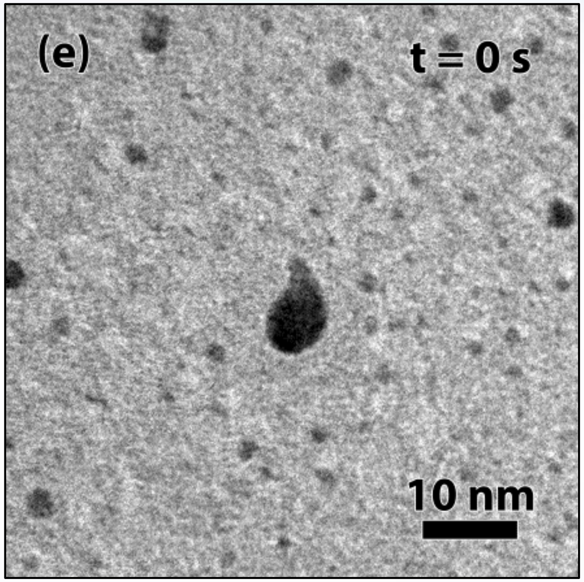
Single Ion Effects with 46 keV Au^{1-} ions: 20 nm

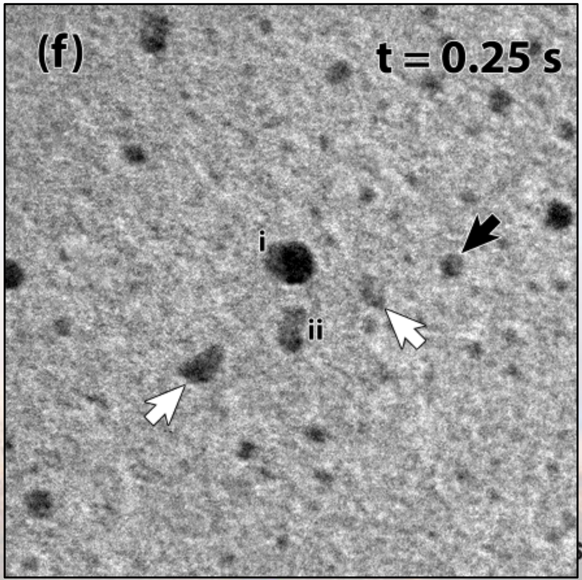




Single Ion Effects with 46 keV Au^{1-} ions: 5 nm

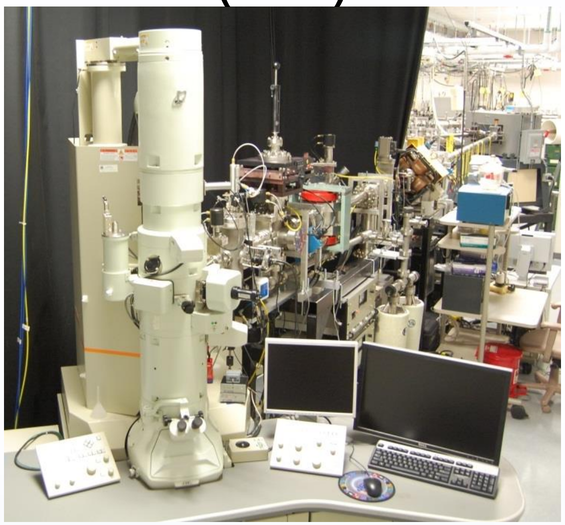






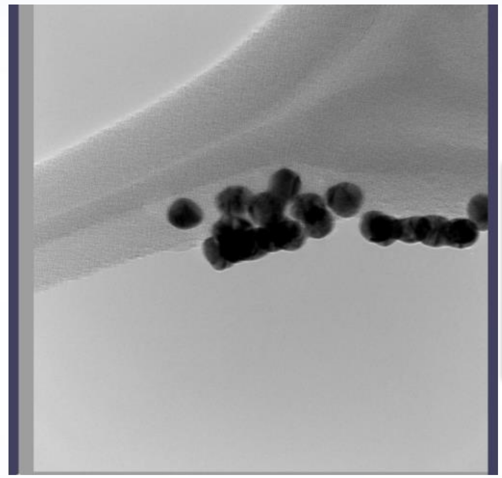
Conclusions: Advanced Microscopy Techniques Applied to Nanoparticles in Radiation Environments

***In situ* Ion Irradiation TEM (I^3TEM)**

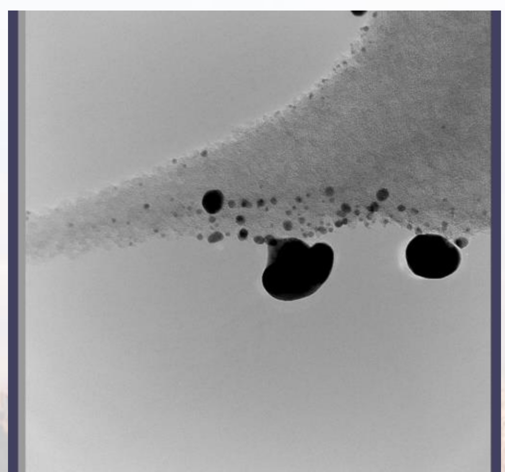


Hummingbird tomography stage

Aligned Au NP tilt series - unirradiated

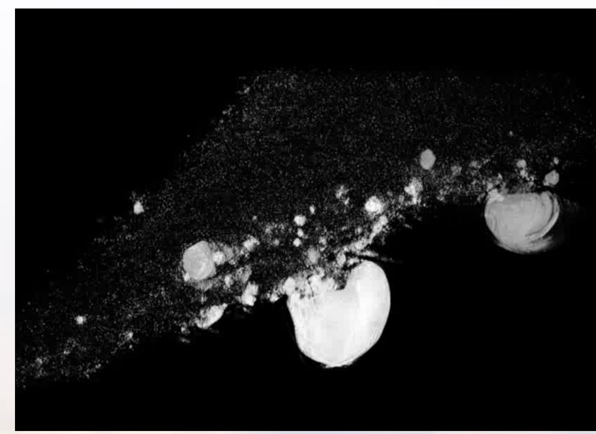


Aligned Au NP tilt series - irradiated



Unirradiated Au NP model

Irradiated Au NP model



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

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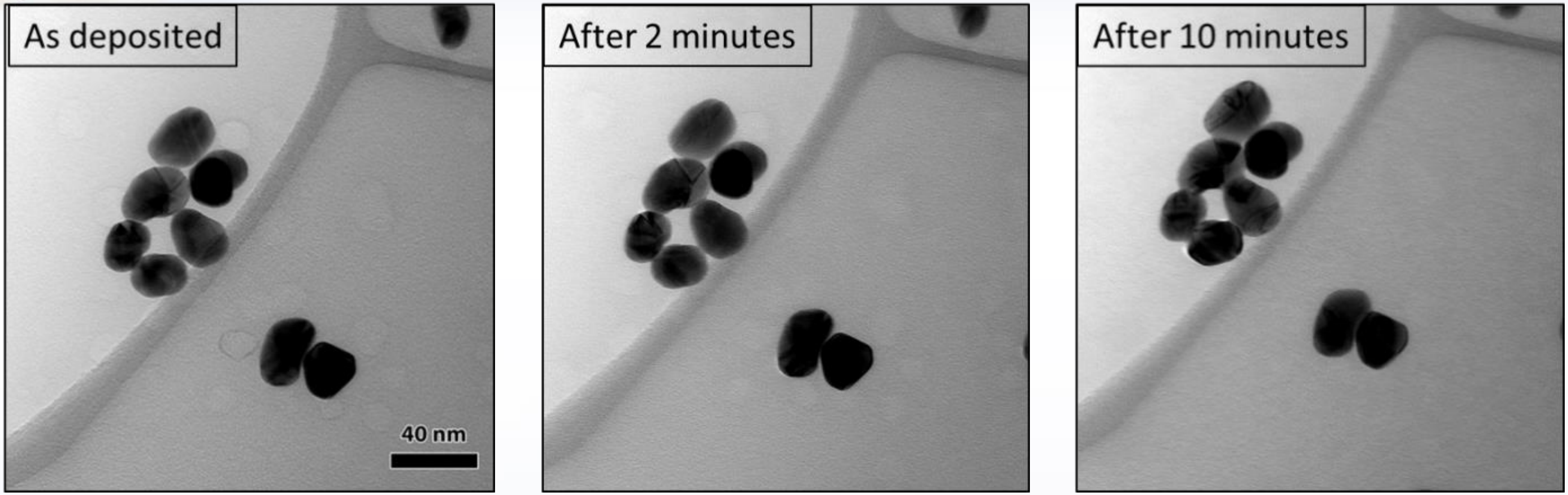
Electron Beam Effect



Example of electron beam-induced sintering of Au NPs over a 10 minute time period. The beam was incident at typical imaging intensity (200 kV, ≤100 pa/cm^2), and no ion beam was present.

Electron beam effect results in some local sintering, but no sputtering or major rearrangement.