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Low Temperature Synthesis and Sintering of d-UO_2, d-U and d-U/La Alloy Nanoparticles

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Low Temperature Synthesis and Sintering of U Based Nanoparticles

U compound studies are of interest for nuclear energy applications; Goal of recycling and reusing dissolved uranium oxide from spent nuclear fuels

NP Synthesis

Ongoing studies consider the conditions of spent nuclear fuels for long term stability under radiation.

We report on several d-U based nanoparticles formed under γ-radiation with goals of recovering and reusing.

NP Sintering

Industrial practices use high temperatures (1700 °C) to sinter uranium oxide containing materials such as fuel pellets and shielding.

We report on d-UO_2 sintering temperatures in the range of 500°C - 700°C; more than 700°C below the lowest reported sintering temperatures.

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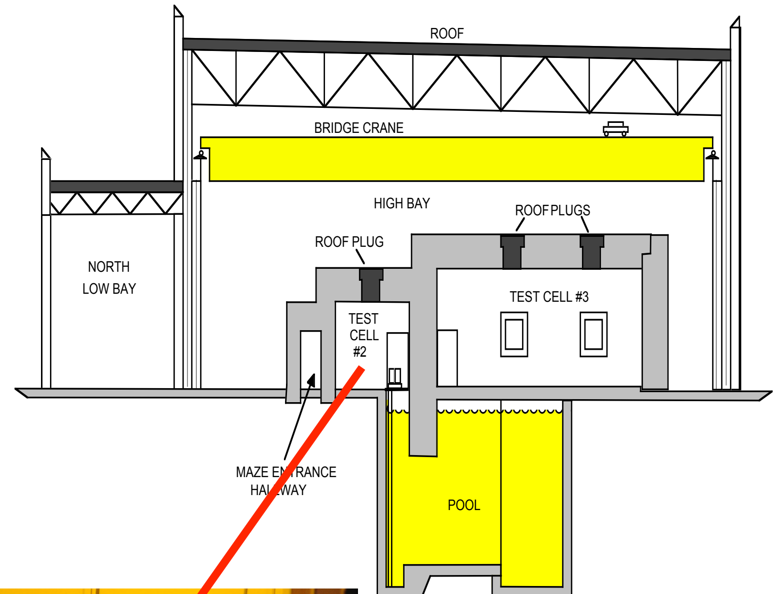
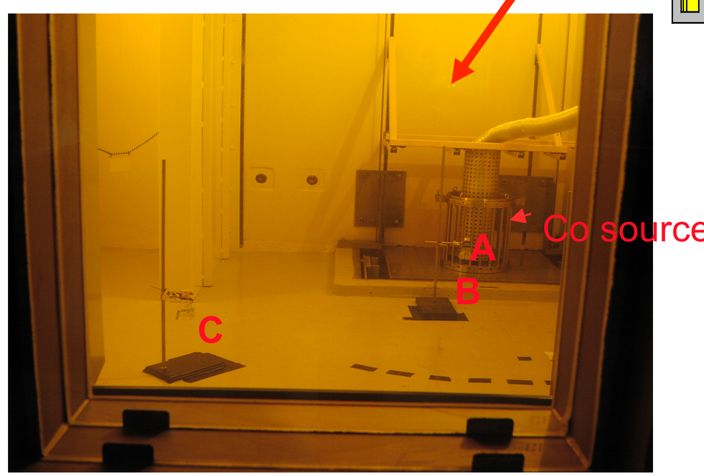
Room Temp Radiolysis at Sandia (SNL) GIF Facility

Sandia Gamma Irradiation Facility (GIF) is a
^{60}Co source : 1.345 x 10^5 Ci, ≈ 300K rad/hr.





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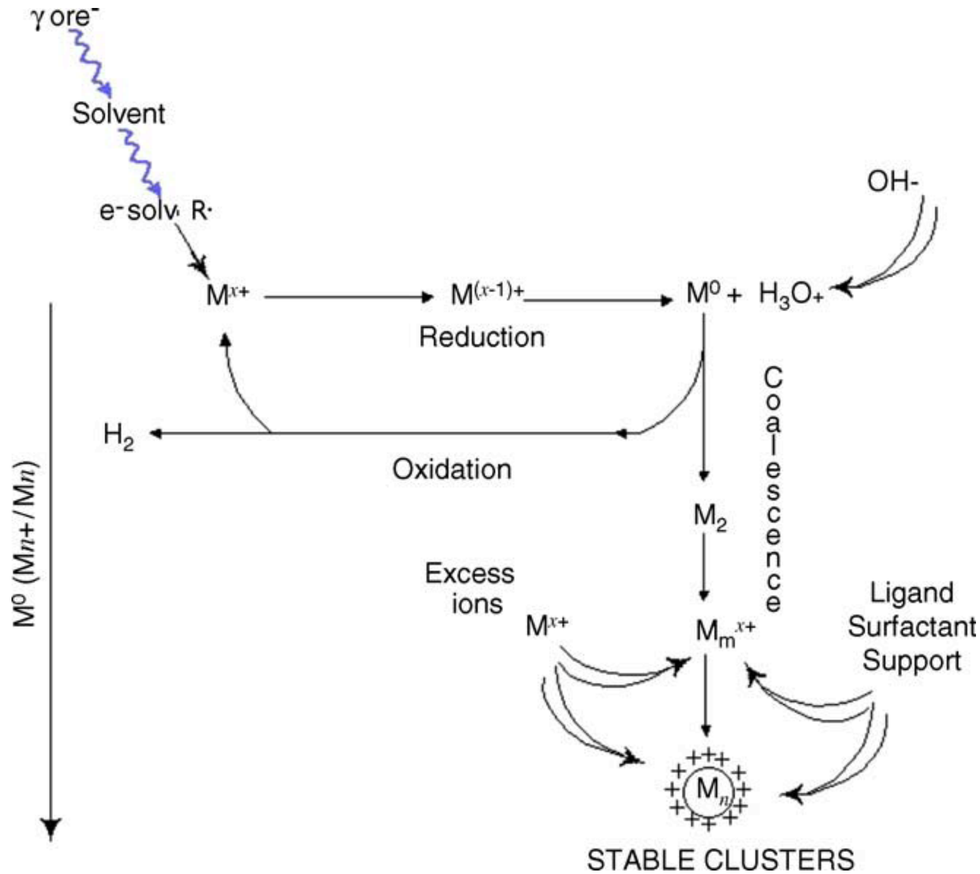
Radiolysis Pathway for Nanoparticle Formation

Ion reduction by ionizing radiation:
Dose rate dictates [e$^-$] in reaction solution thereby affecting the chemistry of the NP formation

$H_2O \Rightarrow e^-_{aq}, H_2, OH^\bullet, H^\bullet, H_3O^+, H_2O_2, HO_2^\bullet$



Belloni, *Catalysis Today*, **2006**,*113*,141

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Reaction Mechanism for d-UO_2 Nanoparticles

Ion reduction by ionizing radiation:
Dose rate dictates [e^-] in reaction solution thereby affecting the chemistry of the NP formation

$H_2O \Rightarrow e^-_{aq}, H_2, OH^\bullet, H^\bullet, H_3O^+, H_2O_2, HO_2^\bullet$

Particle formation via radiolysis (γ-irradiation)

$^{\cdot}OH(^{\cdot}H) + e_{aq}^- + CH_3OH \rightarrow e_{aq}^-/\ ^{\cdot}CH_2OH + H_2O(H_2)$

$e_{aq}^-/\ ^{\cdot}CH_2OH + UO_2^{2+} \rightarrow UO_2^0 + ^{\cdot}CH_2OH$

Particle growth

$x^{\cdot}CH_2OH + (UO_2)_n \rightarrow (UO_2)_n^{x-} + xCH_2O + xH^+$

Aqueous room temperature synthesis to form NPs

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Nanoparticle (NP) Synthesis & Analysis

Experimental NP Synthesis:

- 25ml dilute $UO_2(NO_3)_2$ aqueous solutions containing alcohol (MeOH)
- Purged solution with argon
- Exposed solutions to γ-irradiation

NP Analysis:

- UV-vis: Varian Cary 300 Scan UV-visible Spectrophotometer
- Transmission Electron Microscopy (TEM): JEOL 1200EX (120 kV) bright-field
- High Resolution TEM and scanning TEM: FEI Tecnai G(2) F30 S-Twin (300 kV) TEM at Sandia's Center for Integrated Nanotechnologies (SNL CINT)
  - 0.14 nm resolution in high-angle annular dark-field (HAADF) mode
  - Equipped with energy-dispersive X-ray (EDX) & electron energy-loss spectrometer (EELS)

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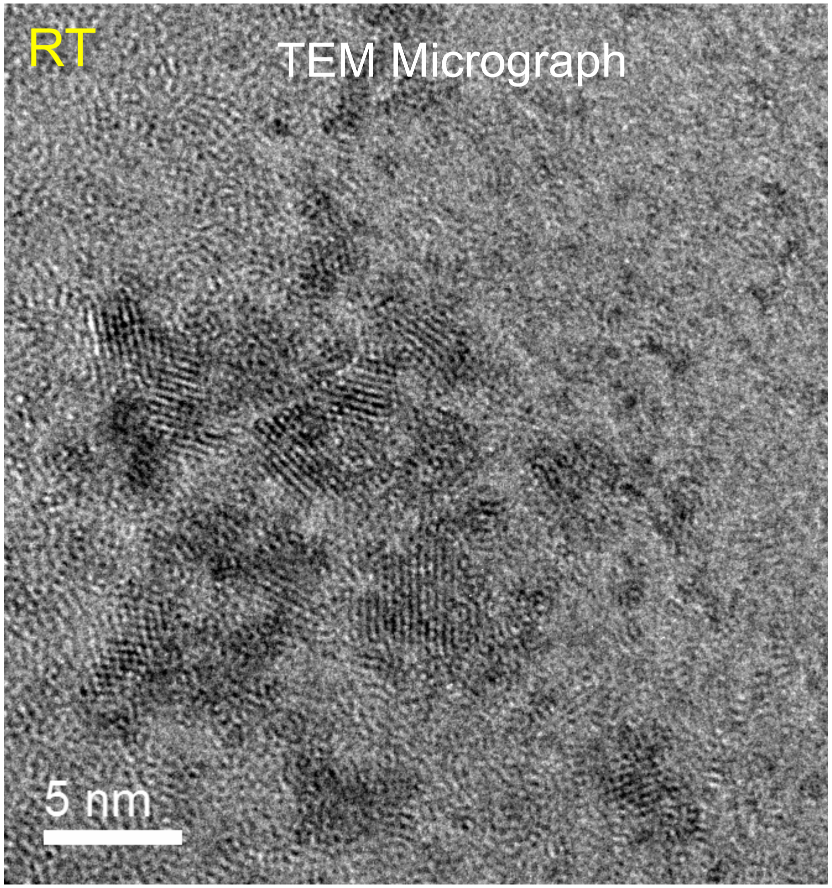
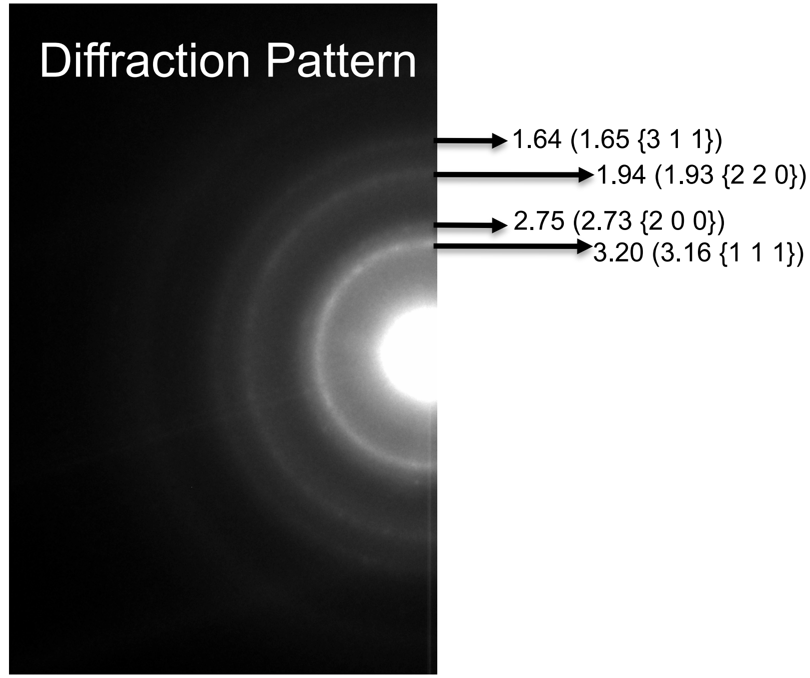
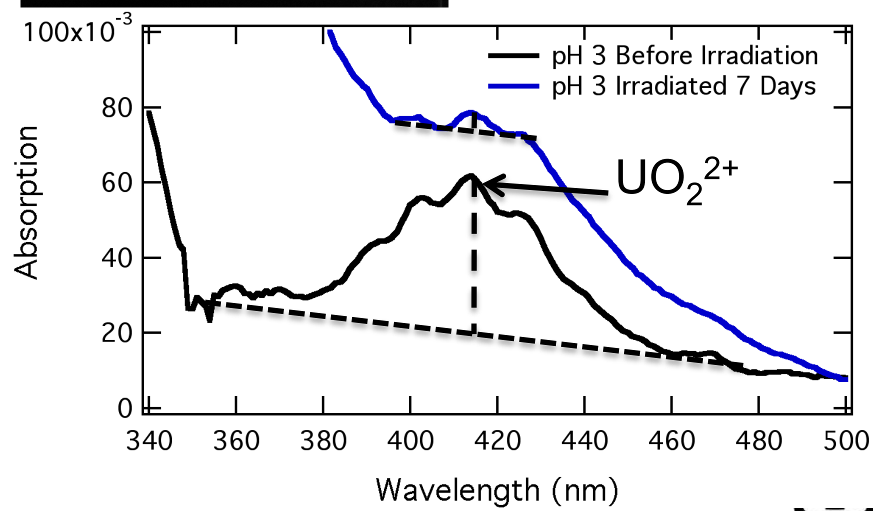
Characterization of UO_2 NPs Formed at pH 3







UO_2 NP formation confirmed by UV-vis, bright-field TEM and diffraction

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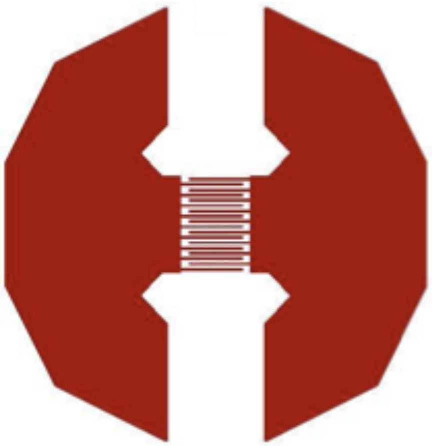
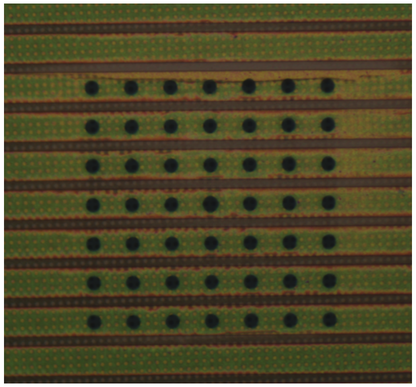
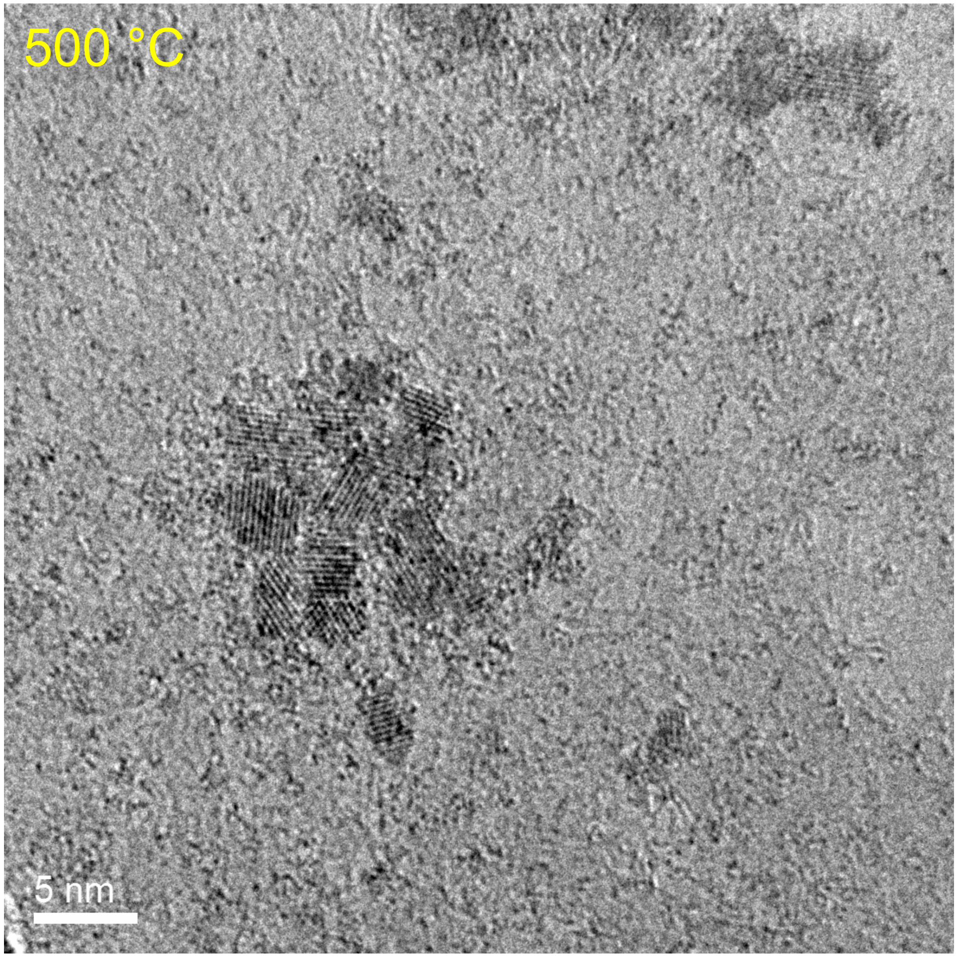
In-Situ TEM UO_2 NP Sintering

Protochips Aduro™ holder







In-situ TEM sintering achieved with low drift and fast T response

T stepped from room temperature (RT) to:
200 °C, 300 °C, 400 °C, 500 °C, and 600 °C
and back to RT successively
Less than 1 ms response; accurate to 0.5 - 3°C

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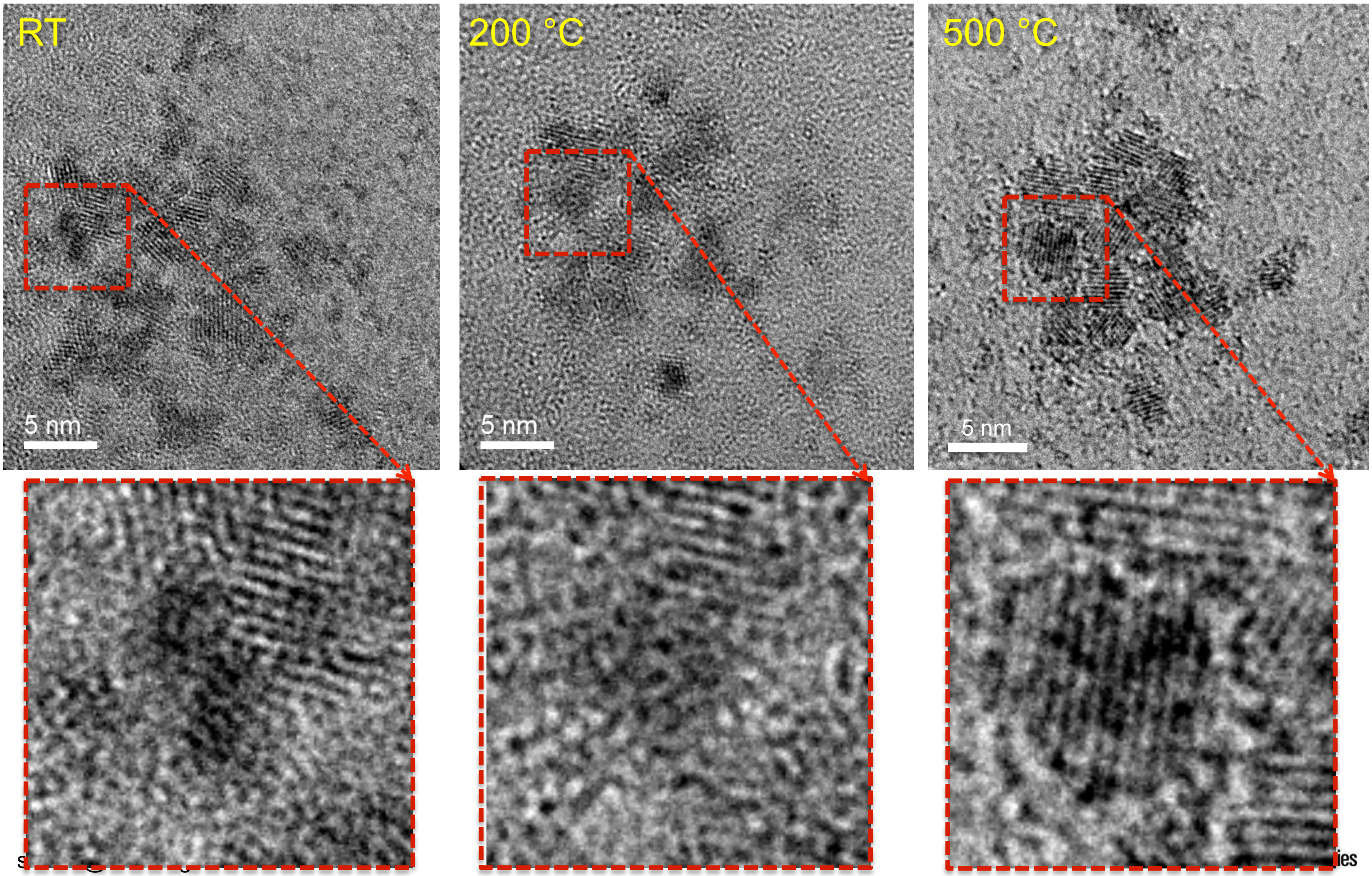
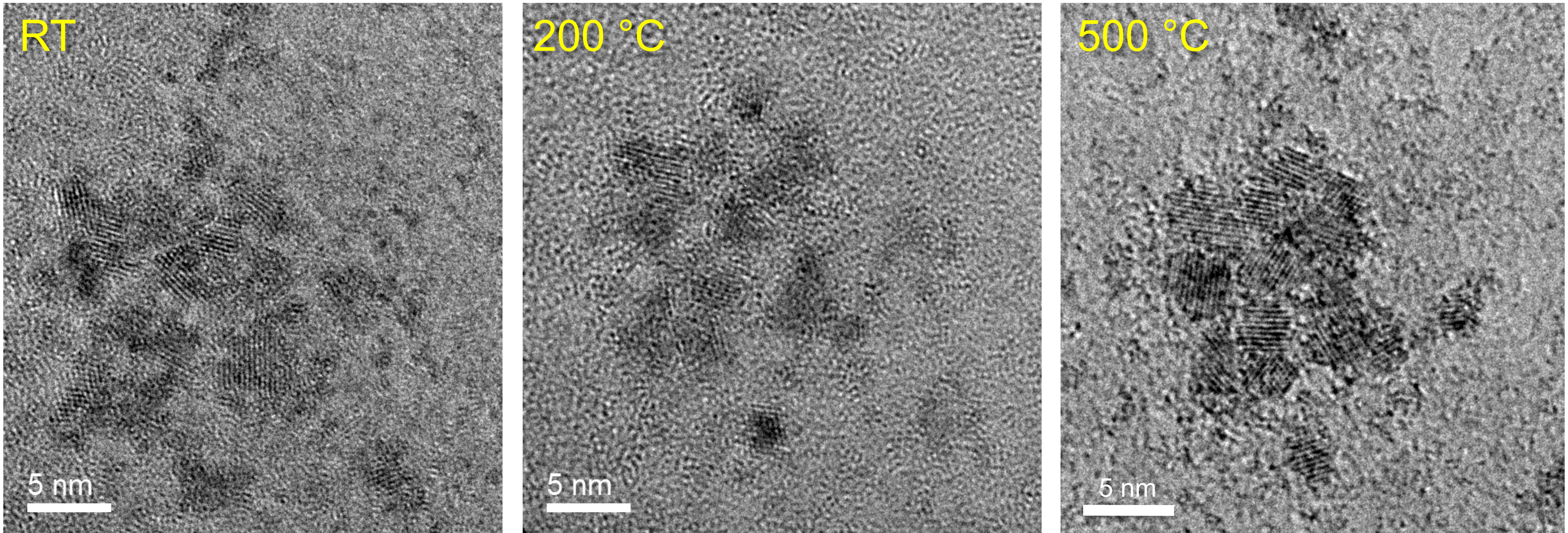
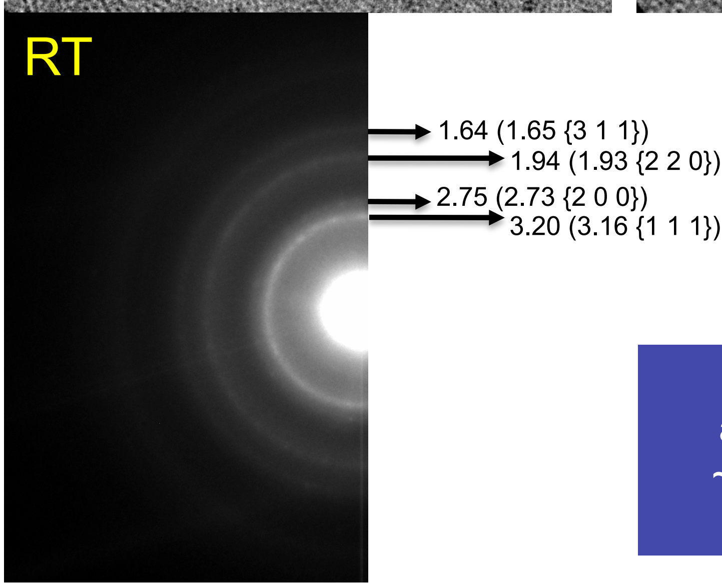
UO_2 NP Sintering at 500 °C

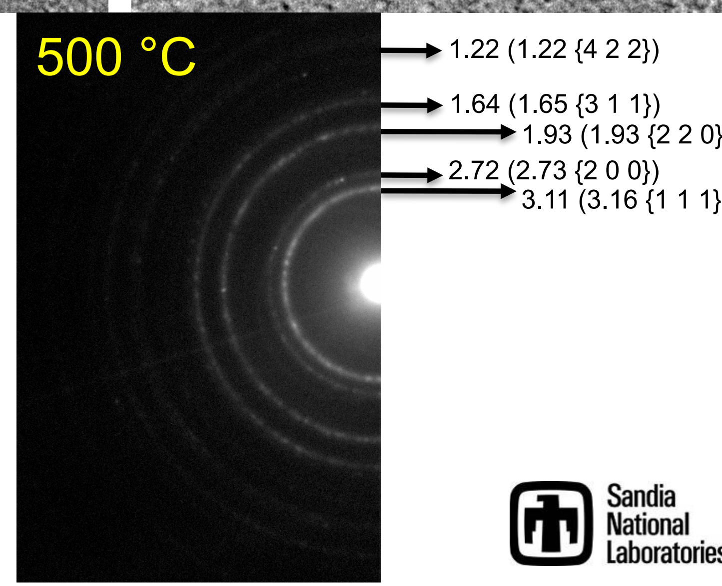


UO_2 NP Sintering at 500 °C





Low T NP sintering achieved at 500 °C; ~1000 °C lower than previously reported



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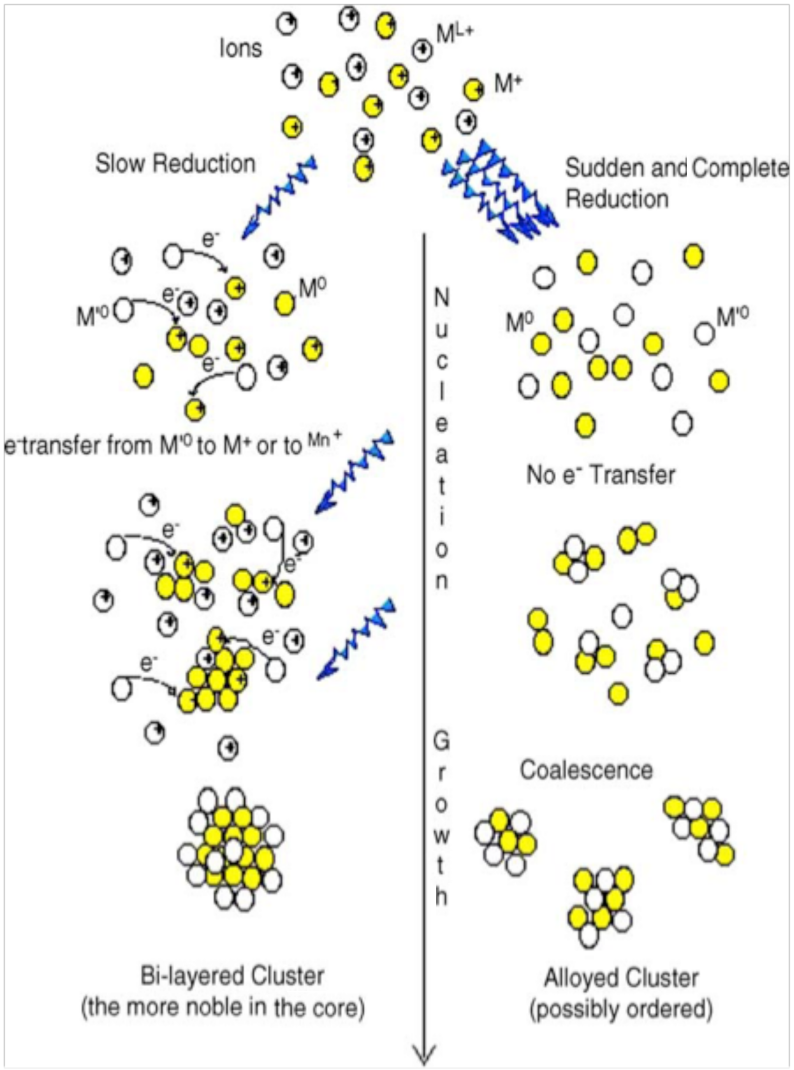
Methodology to Access and Control Alloy Phase Spaces

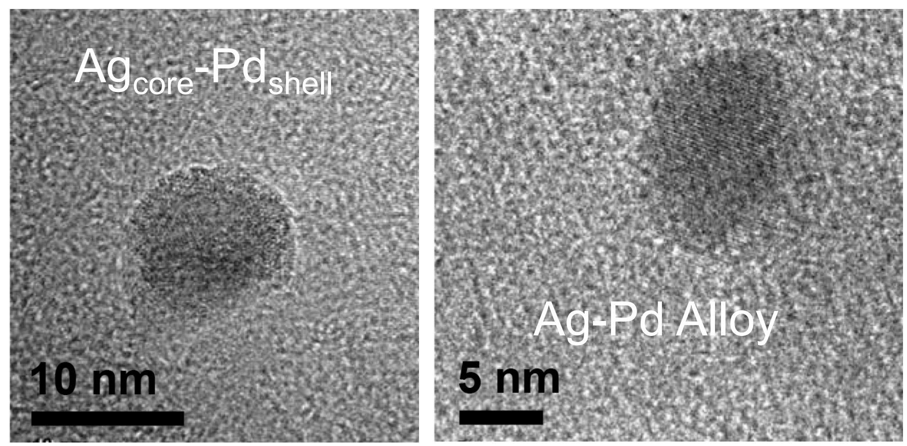


Belloni, *Catalysis Today*, **2006**,*113*,141

Alloys: Possibility to access different phase space than with traditional melting

Using high radiation dose and high dose rate, we pursue nanoparticle alloy formation

Slow Reduction | Sudden Reduction



Redjala, T. et al. *Oil Gas Sci. Technol.* ***2006***

$AgNO_3$, $HAuCl_4$, $Pd(NO_3)_2$ and poly (vinyl alcohol) (PVA, 99% hydrolysed, MW = 86000); Dose rate of 1.75 $Gy.s^{-1}$

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Experimental Methods: d-U d-U-alloy Nanoparticle (NP) Synthesis

Experimental NP synthesis:

0.004 M total salts:

50% UCl_4, (50% $La(NO_3)_3 \cdot 6(H_2O)$ or $EuCl_3 \cdot 6H_2O$)

alcohol (MeOH), organic polymer (PVA) in DI H_2O

Sealed and purged solution with argon

γ-irradiated at 300 rad/sec for 30 min.

Particle formation via radiolysis (γ-irradiation)

$$^{\cdot}OH(^{\cdot}H) + e_{aq}^{-} + CH_3OH \rightarrow e_{aq}^{-}/\,^{\cdot}CH_2OH + H_2O(H_2)$$

$$e_{aq}^{-}/\,^{\cdot}CH_2OH + U^{4+} \rightarrow U^0 + \,^{\cdot}CH_2OH$$

Particle growth

$$x\,^{\cdot}CH_2OH + (U)_n \rightarrow (U)_n^{x-} + xCH_2O + xH^+$$

Aqueous room temperature synthesis to form NPs

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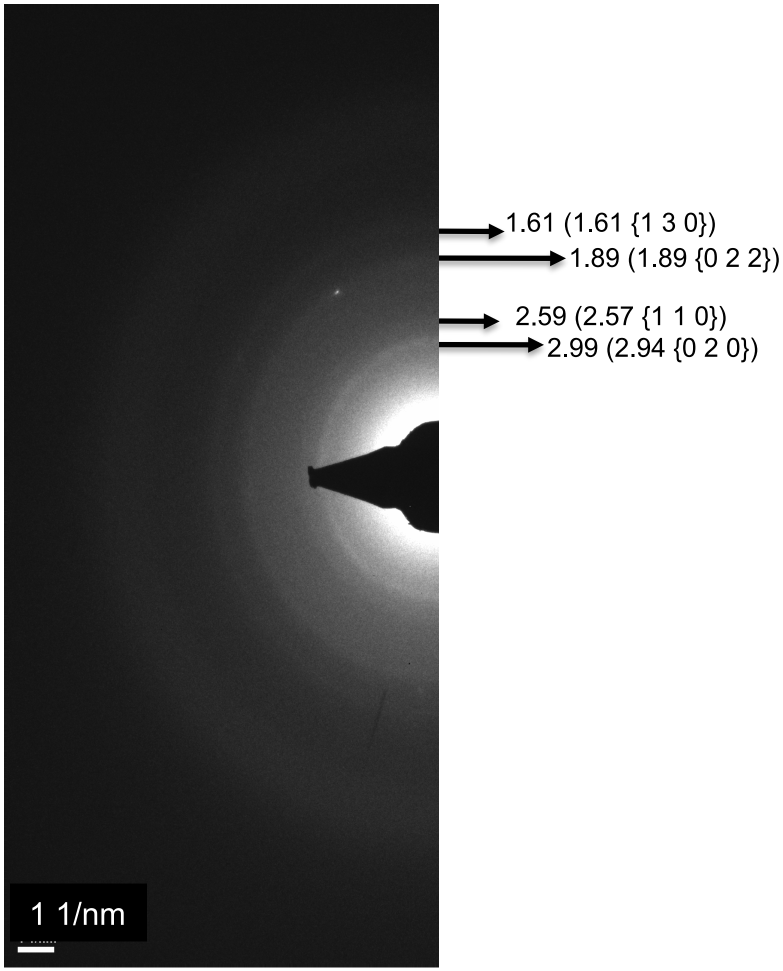
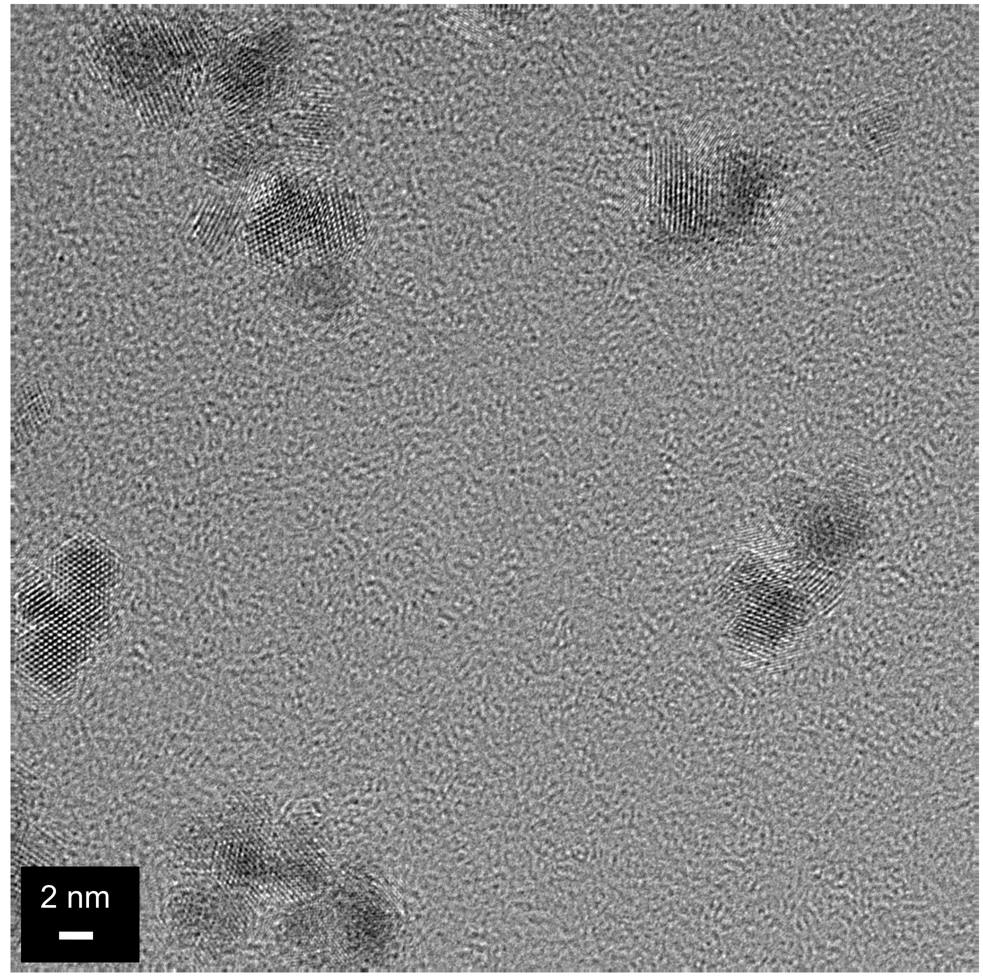
Possible Evidence of U NP Formation





Indication of alpha-U NP formation from lattice spacings determined from diffraction

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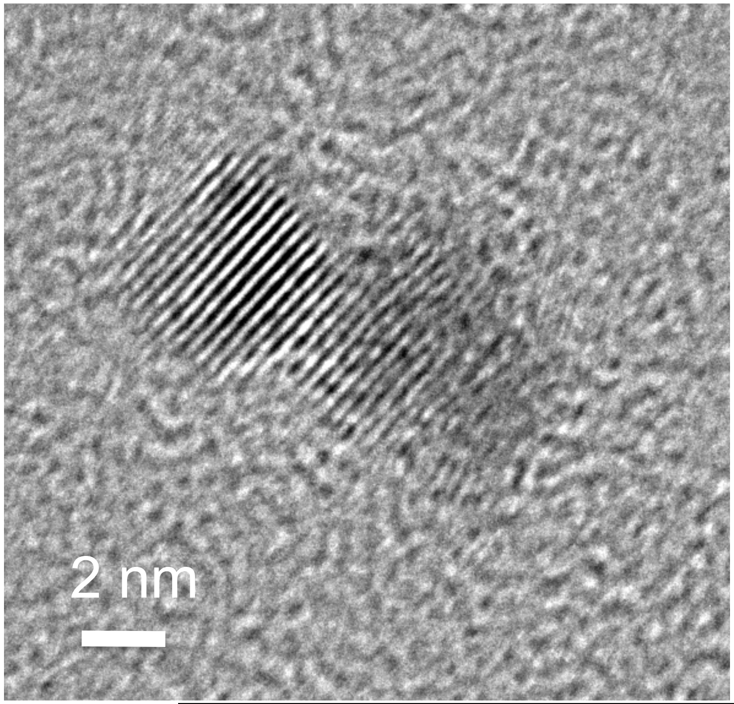
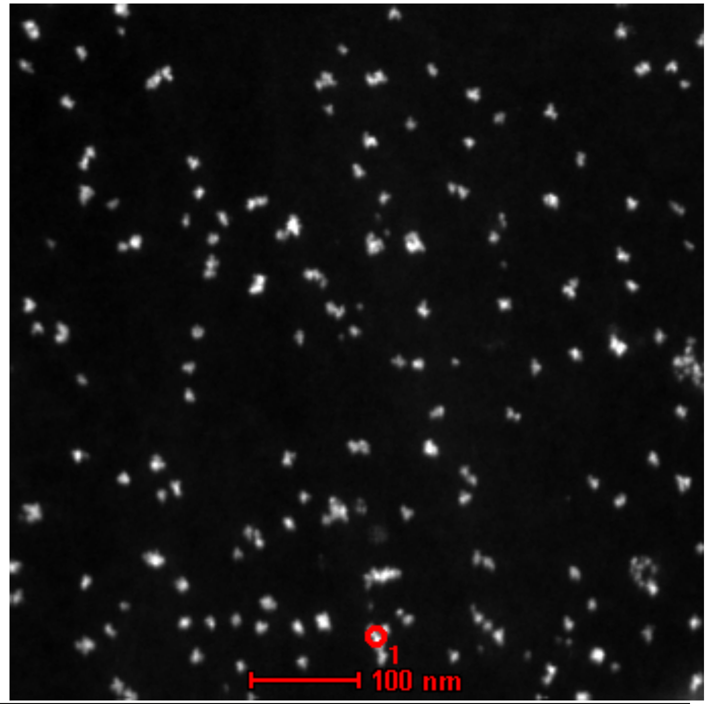
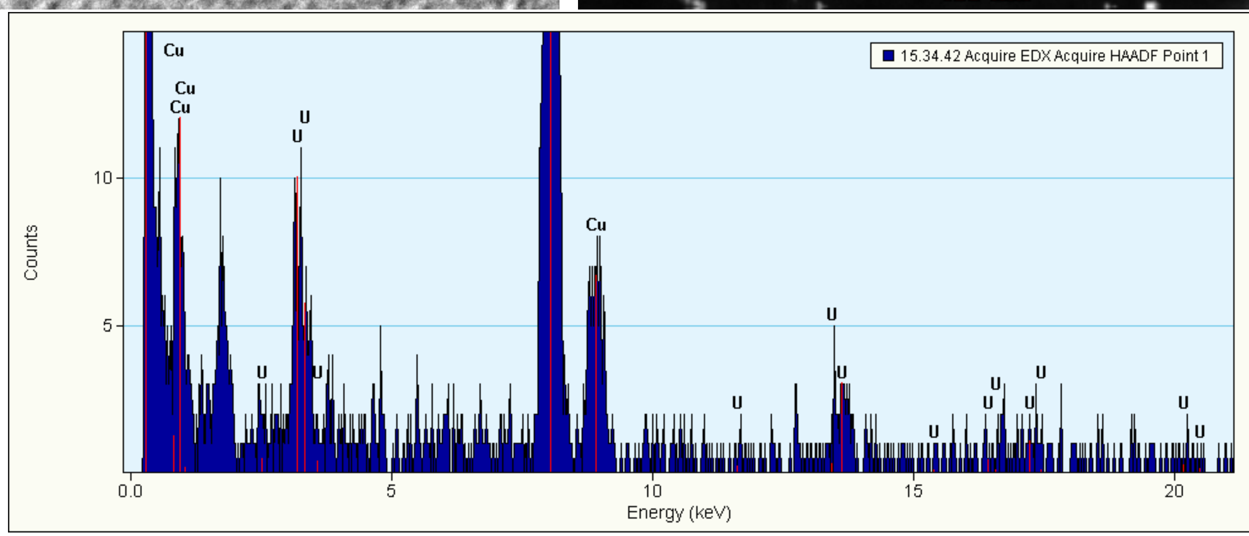
Evidence of d-U NP Formation with Single Particle EDX







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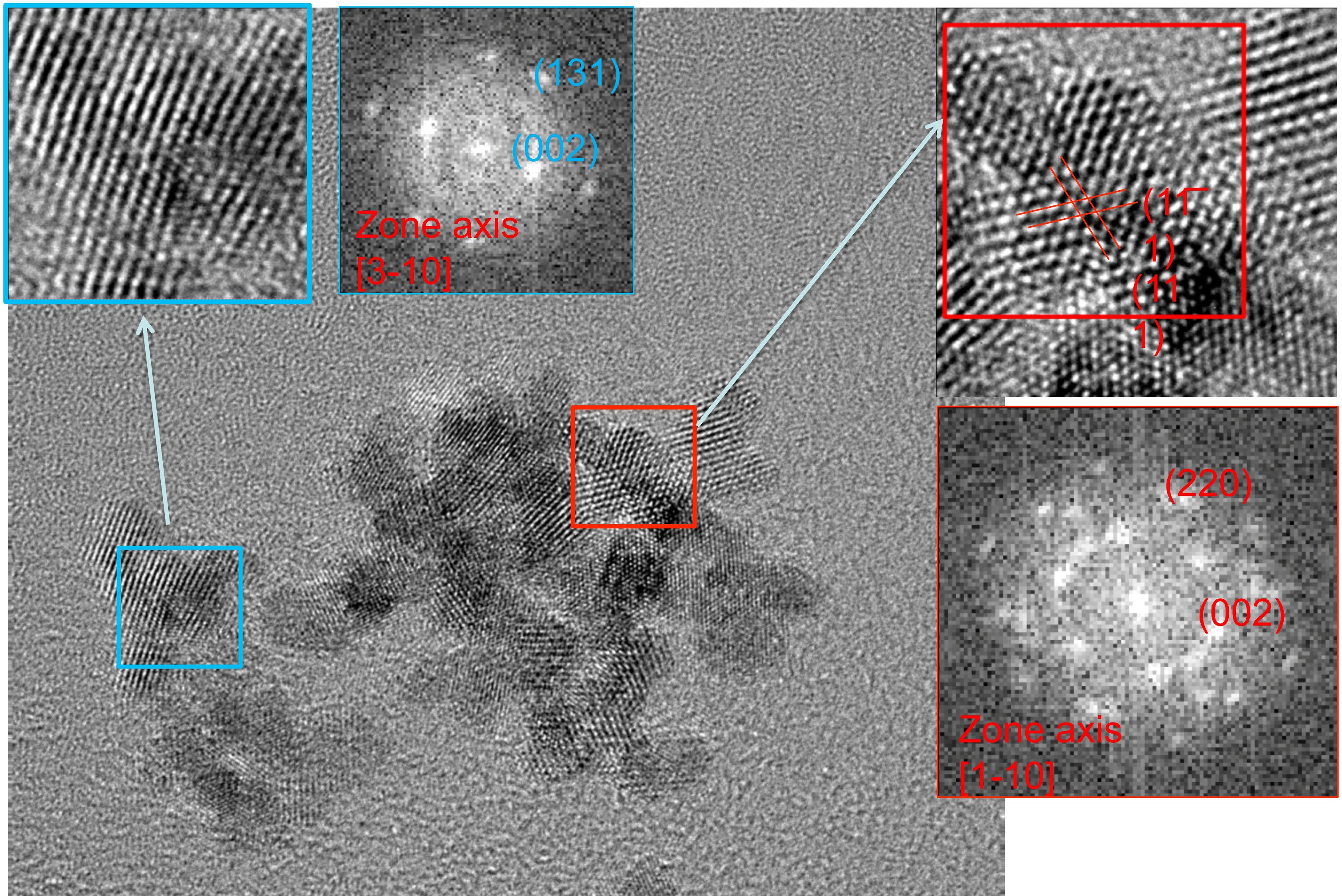
d-U NP Form d-UO_2 When Exposed to Air for on TEM Grids



UO_2 highly stable, and NPs convert quickly

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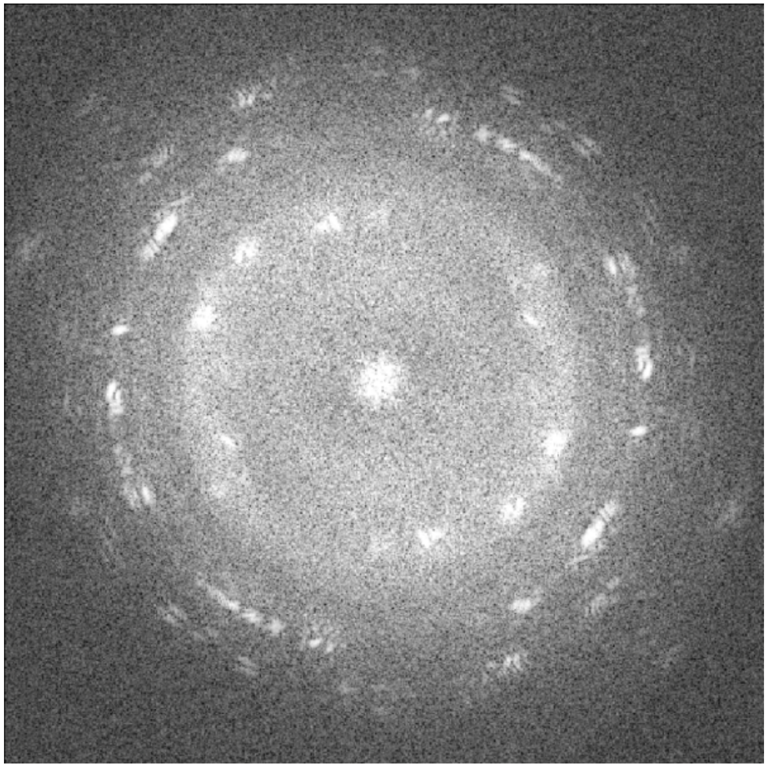
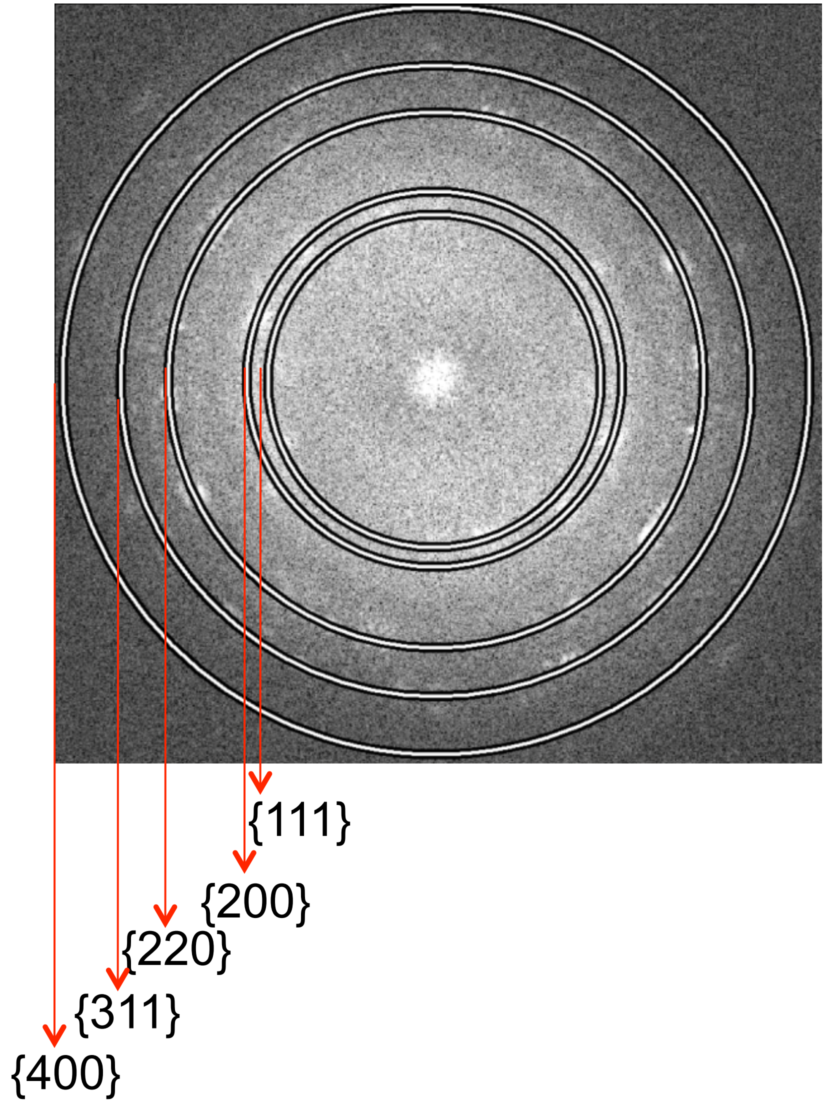
FFT of TEM Support Evidence of Conversion to d-UO_2



Fast Fourier Transform (FFT)



Diffraction agrees with fcc-UO_2 phase

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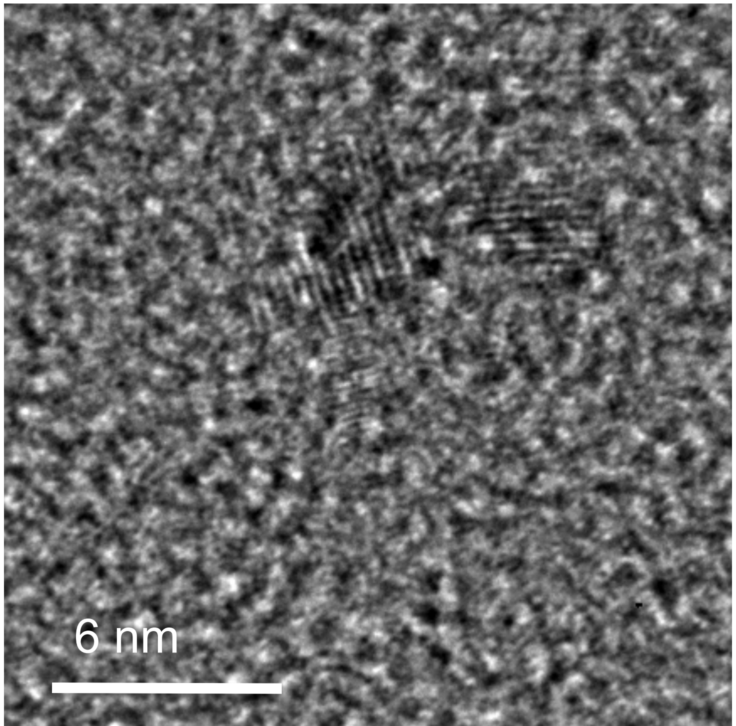
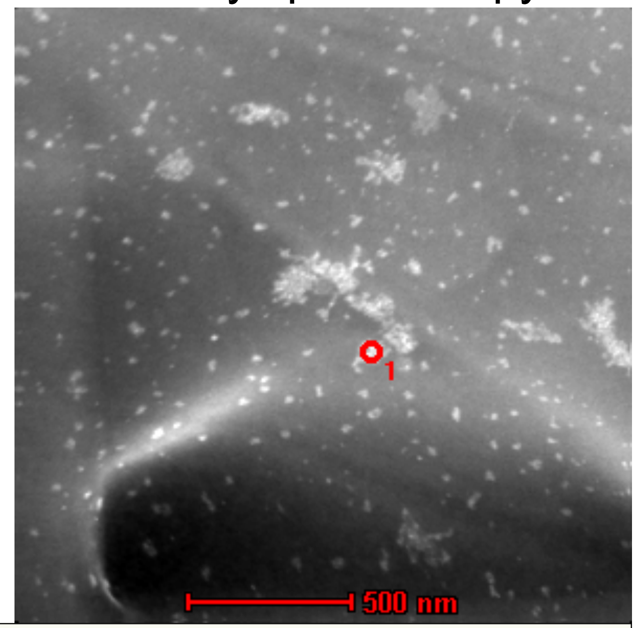
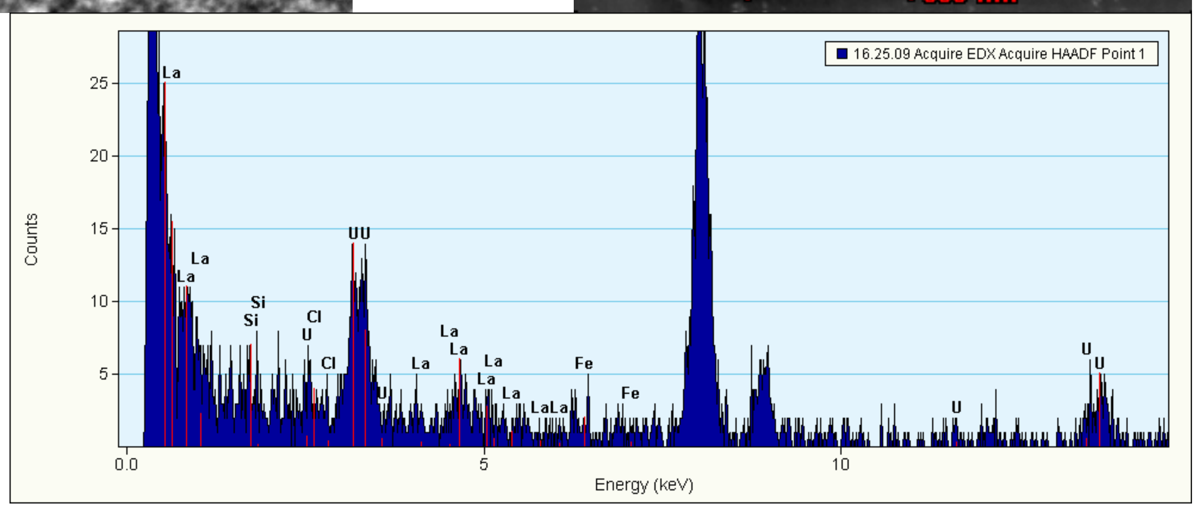
Preliminary Evidence of Alloyed d-U-La NPs by Radiolysis



HAADF Energy-dispersive X-ray spectroscopy





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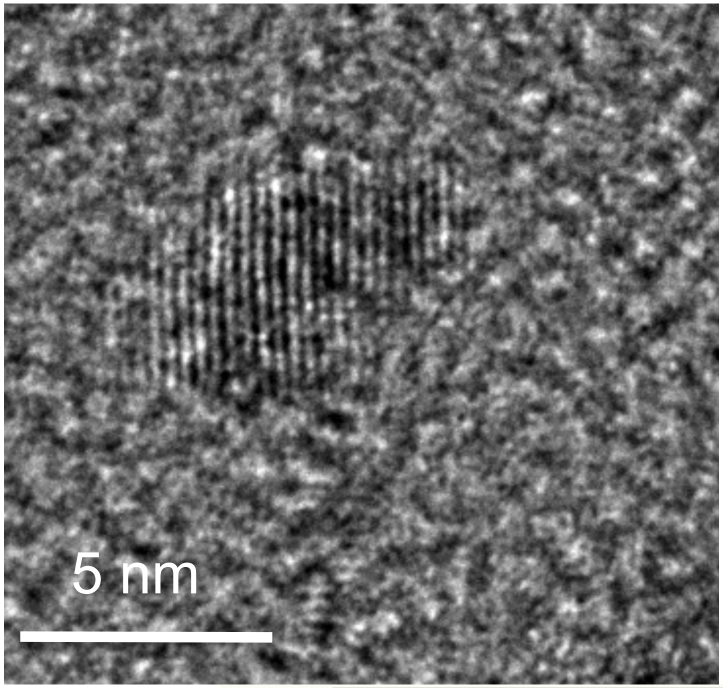
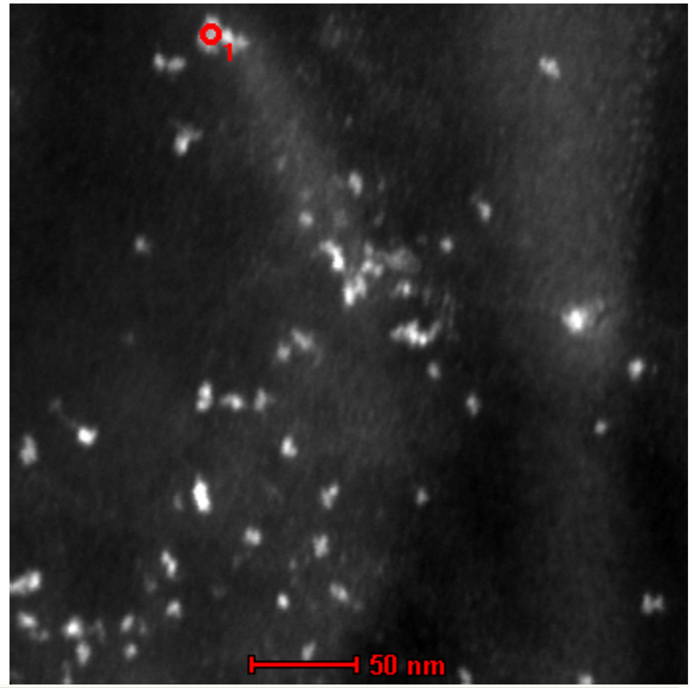
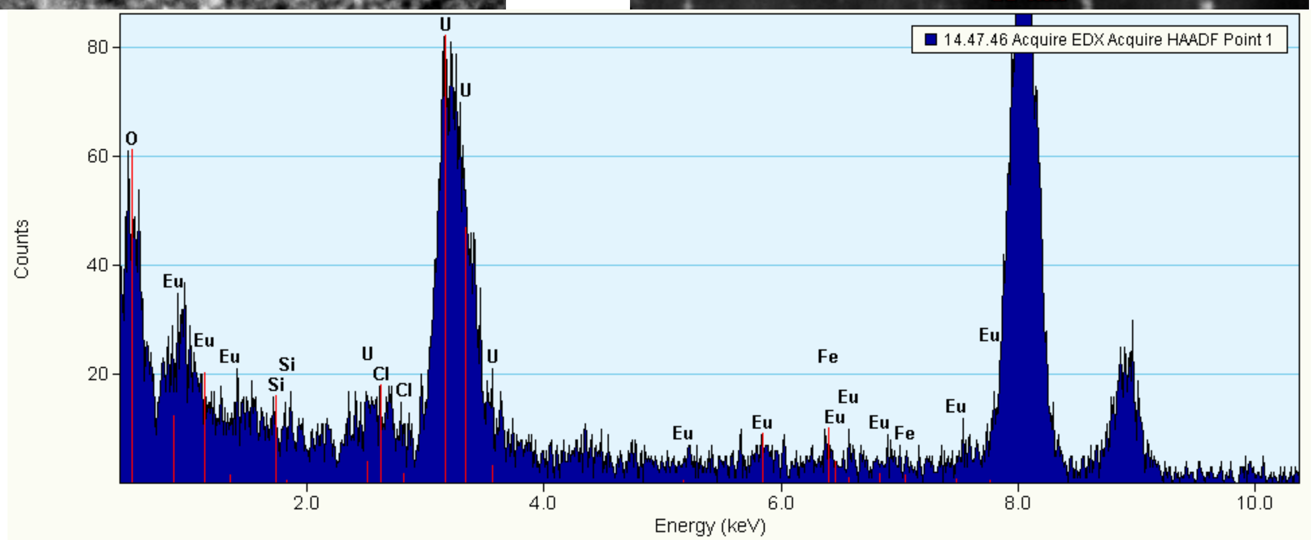
Preliminary Evidence of U-Eu Alloyed NPs







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Conclusions

γ-irradiation allows for room temperature synthesis of U containing NPs.

Successfully optimized pH conditions for d-UO_2 NP formation. UO_2 NPs formed by γ-irradiation at 5 rad/s and 300 rad/s from $UO_2((NO_3)_2)$ and UCl_4.

Sintering of d-UO_2 ≈ 2-5nm NPs. NP sintering occurs at 500 to 700°C.

Preliminary evidence of U metal NP formation and U-Lanthanide alloying NPs.

However, data shows lack of stability against oxidation for U metal which, by extension is expected in alloys.

Work in Progress:

Stabilization of U metal and alloy NPs needed.

Investigate NP stability in sealed vessels without exposure to air.

Sintering of metals and alloys to determine sintering temperature.

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Acknowledgement

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TEM: Xiaohua Liu, Jianyu Huang, Paula Provencio, Yang Liu
NP Sintering/Heated Stage TEM: David Robinson, Benjamin Jacobs

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