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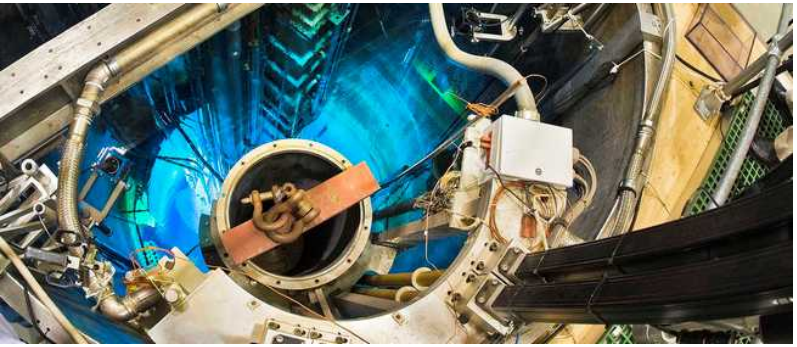
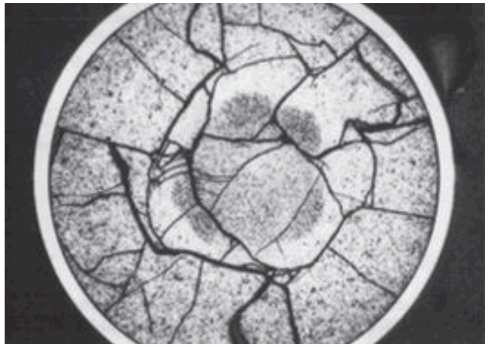
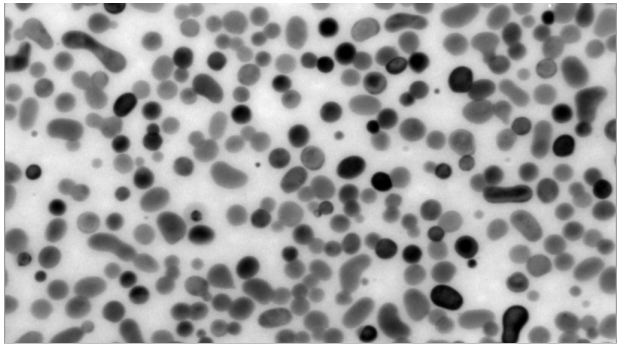

Synthesis and characterization of d-UO_2 nanoparticles for nuclear fuel microanalysis

Presented by:

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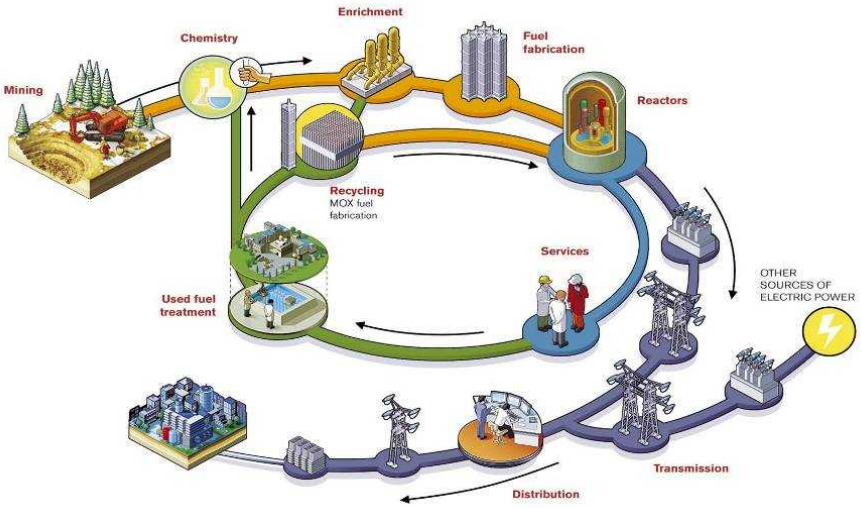
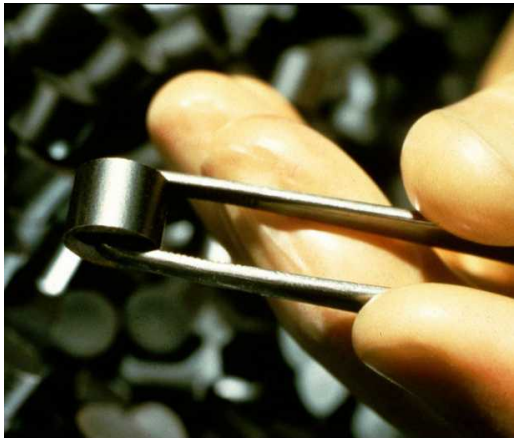
Motivation

- Uranium dioxide (UO_2) has been used as a commercial LWR fuel since the inception of nuclear power
- UO_2 processing route has remained the same for the past 60+ years
  - Ore > U_3O_8 > UF_6 > Enrichment > UO_2
- Other novel synthesis routes and potential applications of different forms of UO_2 are yet to be explored
  - UO_2 in nanoparticle or thin film forms may have both research and industrial applications



Yellowcake Uranium (U_3O_8)
Photo: Ivan Pierre Aguirre/Texas Tribune

Uranium Hexafluoride (UF_6)
Photo: AREVA

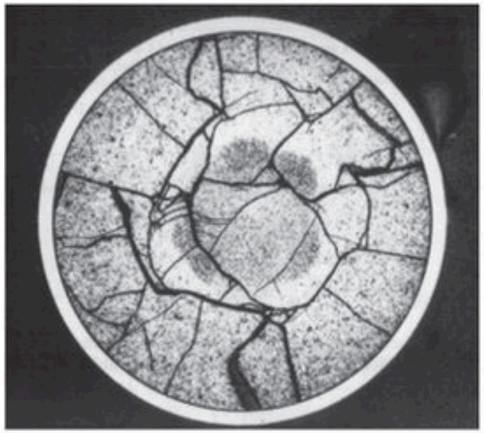


Uranium Dioxide (UO_2)
Photo: NRC

Why UO_2 Nanoparticles & Films?

- Small quantities of depleted uranium are more easily handled in lab environments
  - Allow for fundamental studies of materials properties/behavior for nuclear fuel applications
- Can deposit more easily on substrates (sputter or grow single crystals)
  - Likely necessary for semiconductor applications[1]
  - Also potentially useful for studies of interfaces
- Eliminates need for involved sample preparation for TEM investigation
  - Can deposit directly on lacey carbon or Si_3N_4 grids
- Greater control over microstructure and stoichiometry via different processing routes

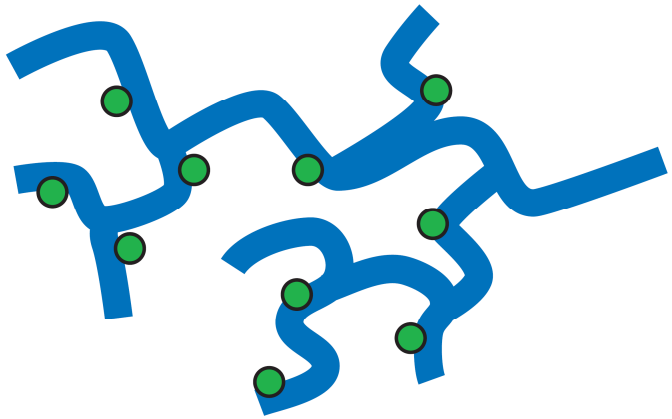
	UO_2	GaAs	Si
Band Gap	1.30 eV	1.39 eV	1.14 eV
Dielectric constant	22	12.9	11.7
Max Temperature	2600 K	470 K	470 K



[1] T. T. Meek & B. von Roedern, *Semiconductor devices fabricated from actinide oxides.* Vacuum **83** (2008) pp. 226-228.
[2] R.C. Ewing, *Long-term storage of spent nuclear fuel.* Nature Materials **14** (2015) pp. 252-257.

UO_2 Nanoparticle Synthesis

- Polymer assisted deposition (PAD)
  - Binding to polymers homogeneously distributes metal in solution
  - Air- and water-stable precursors
  - Flexible application to substrate – spin, dip, spray-coat, drop-cast, etc
  - Thermal decomposition of metal polymer leads to high density films and/or particles



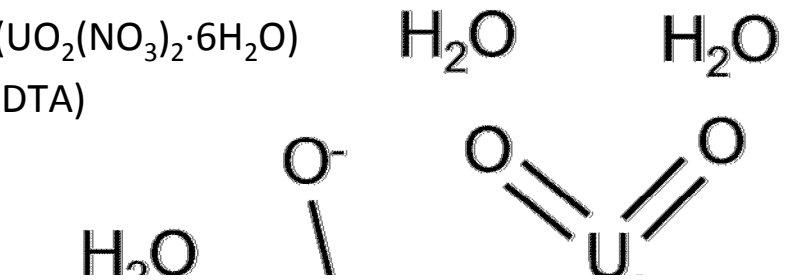
Metals evenly spaced on polymer

Polyethylenimine (PEI)

[1] Jia, Q.X., et al. Polymer-assisted deposition of metal-oxide films. *Nature Materials.* **3** (2004) 529-532.
[2] Burrell, A.K., et al. Polymer assisted deposition. *Chemical Communications.* (2008) 1271-1277.

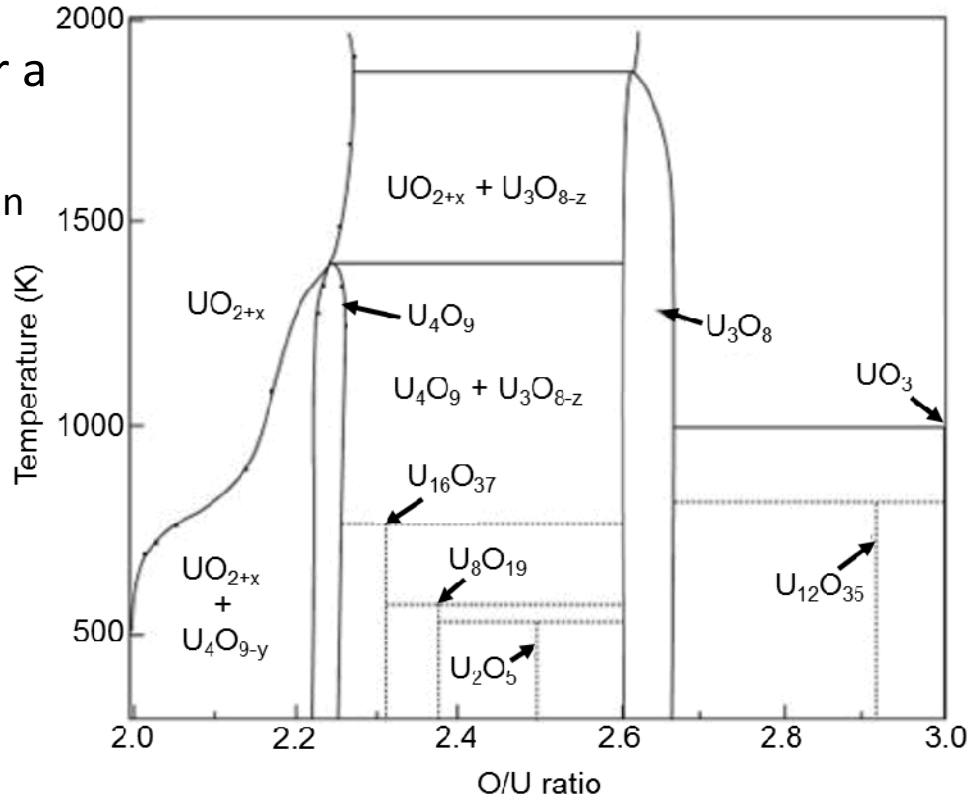
UO_2 Nanoparticle Synthesis

- Reagents, in aqueous solution with DI H_2O
  - 0.1 M depleted uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$)
  - 0.125 M ethylenediaminetetraacetic acid (EDTA)
  - 0.125 M polyethylenimine (PEI)
  - Nitric acid (HNO_3, to adjust pH to 7.5)



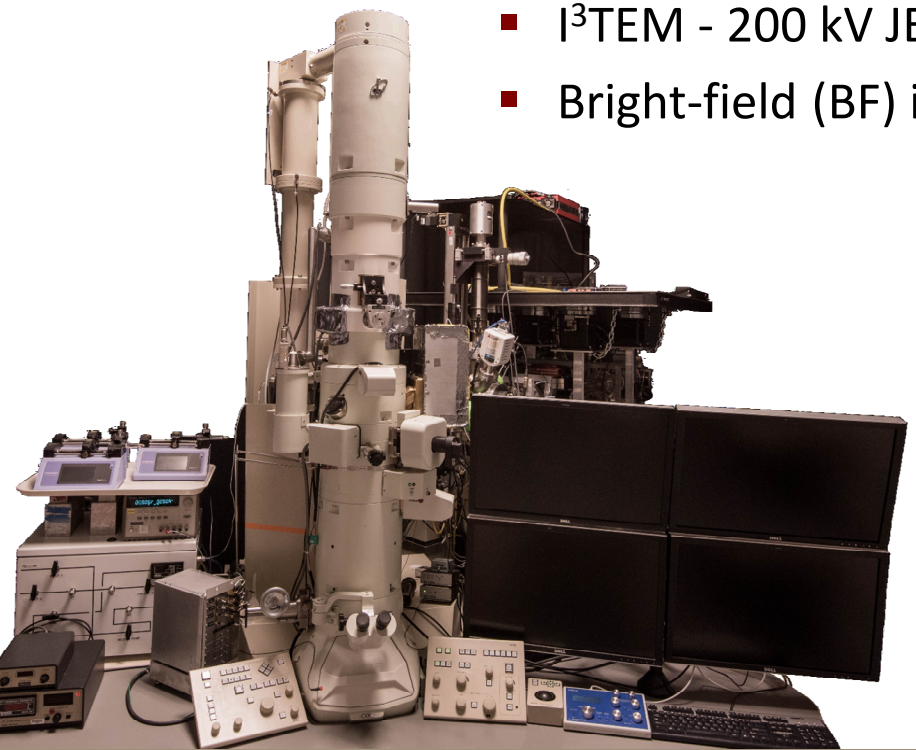
- Drop cast on either Si_3N_4 TEM grids or a Zircaloy-4 substrate
  - Zr-4 was heated to 150 °C for 30 s between additions

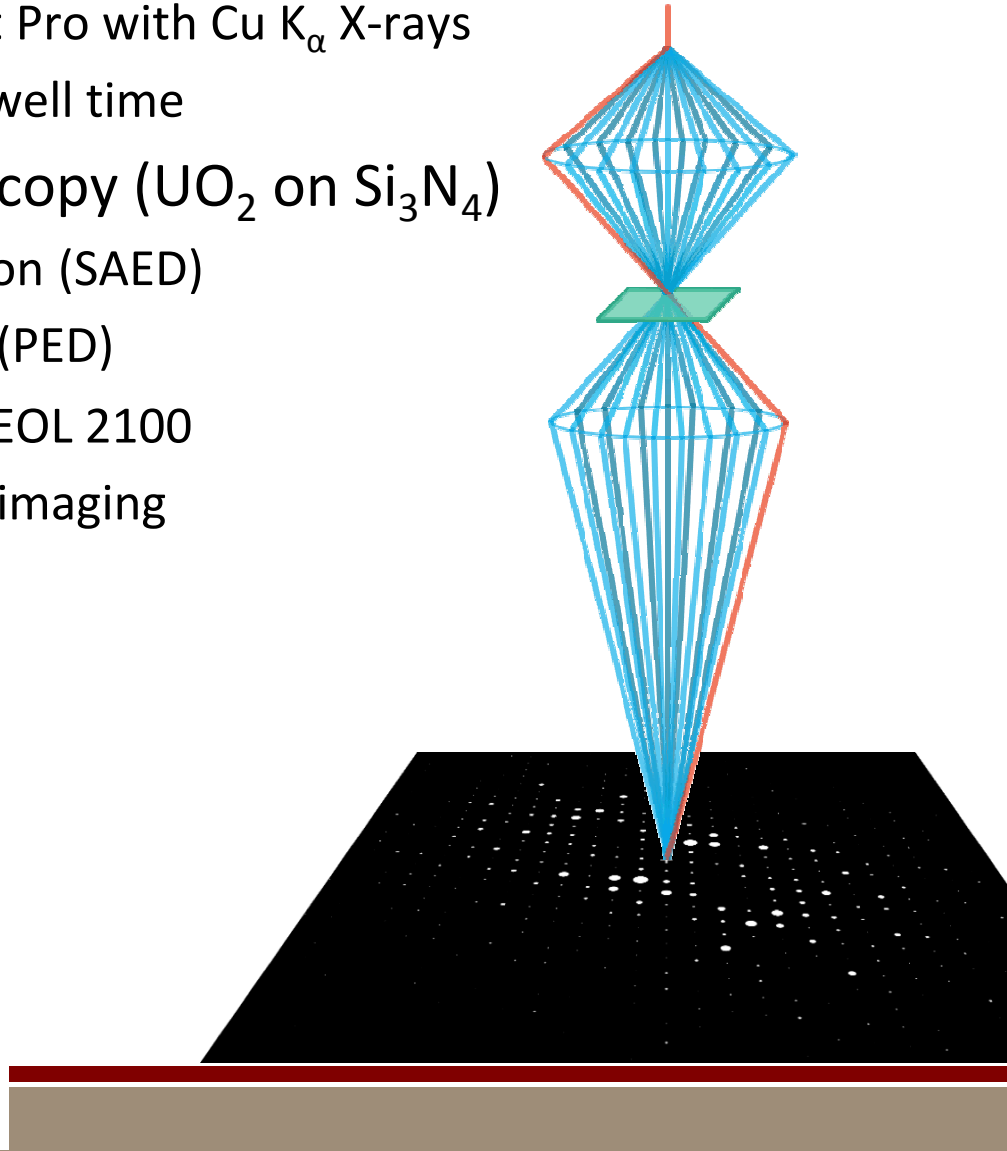
- Sintered at 1000 °C under varied atmospheric conditions
  - Atmospheric air (oxidizing)
  - Ultra-pure argon (inert)
  - Argon-hydrogen (reducing)*



Experimental Characterization

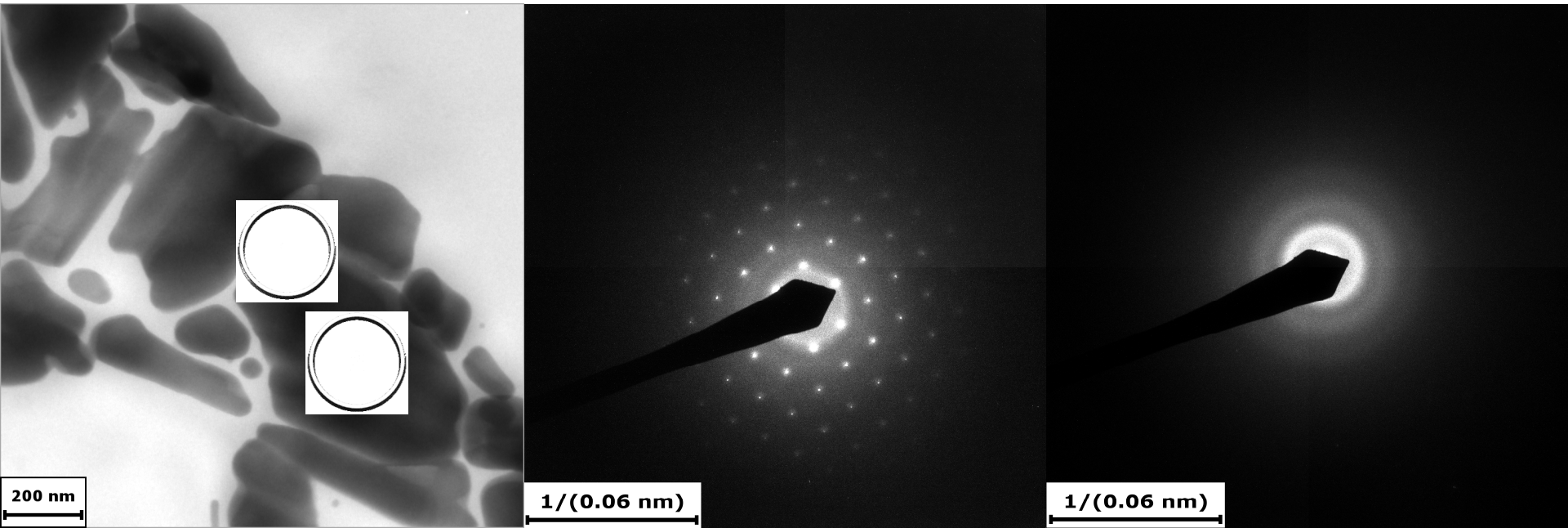
- Powder X-Ray Diffraction (UO_2 on Zr-4, Ar sintered)
  - θ/2θ scan on PANalytical X'Pert Pro with Cu K_α X-rays
  - 0.0167° step size, 0.152°/sec dwell time
- Transmission electron microscopy (UO_2 on Si_3N_4)
  - Selected area electron diffraction (SAED)
  - Precession electron diffraction (PED)
    - I^3TEM - 200 kV JEOL 2100
    - Bright-field (BF) imaging





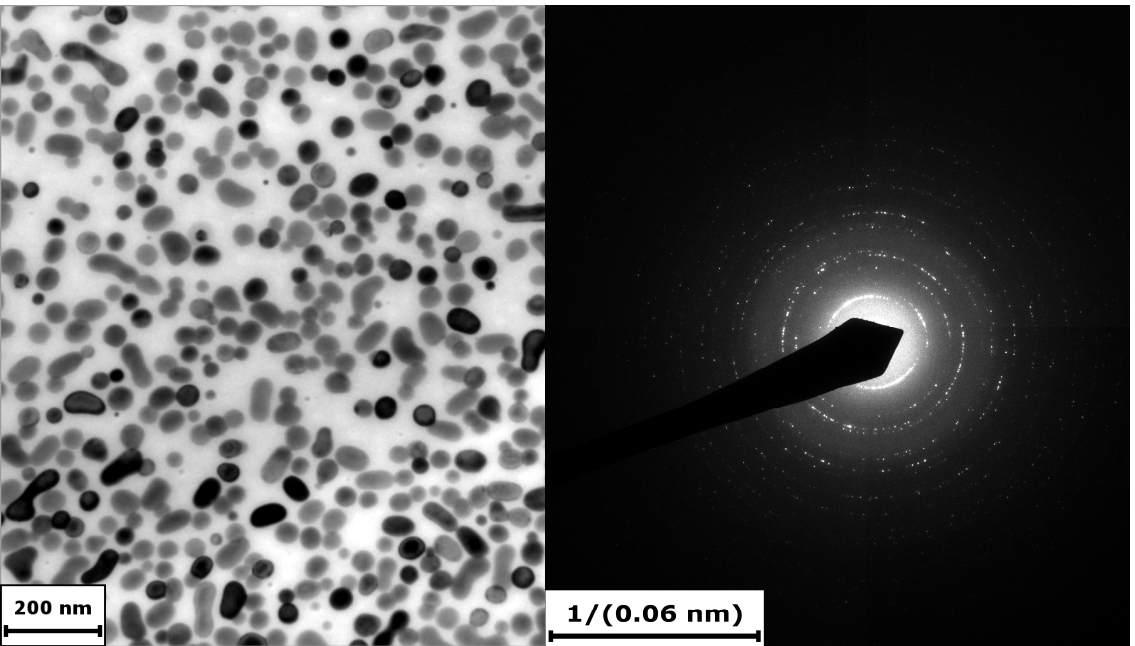
Atm-sintered UO_2 – TEM Analysis

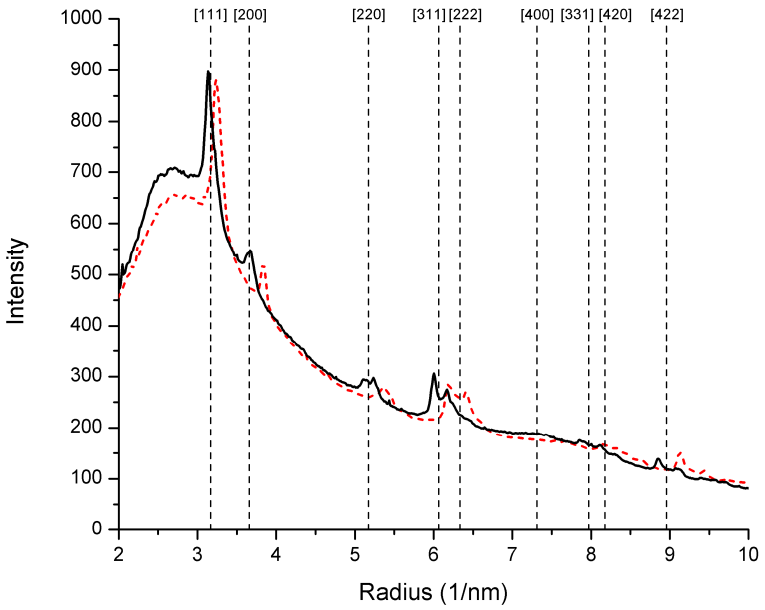
- "Particles" appeared as large, irregulary-shaped grains
- SAED for smaller, isolated, crystalline grains indicated fcc/fluorite structure consistent with $UO_{2\pm x}$ phase
- SAED for majority of particles indicate amorphous rings



Ar-sintered UO_2 – TEM Analysis

- Specimens appeared as small, spheroidal particles
- SAED ring pattern spacings appear to be consistent with a $UO_{2\pm x}$ phase

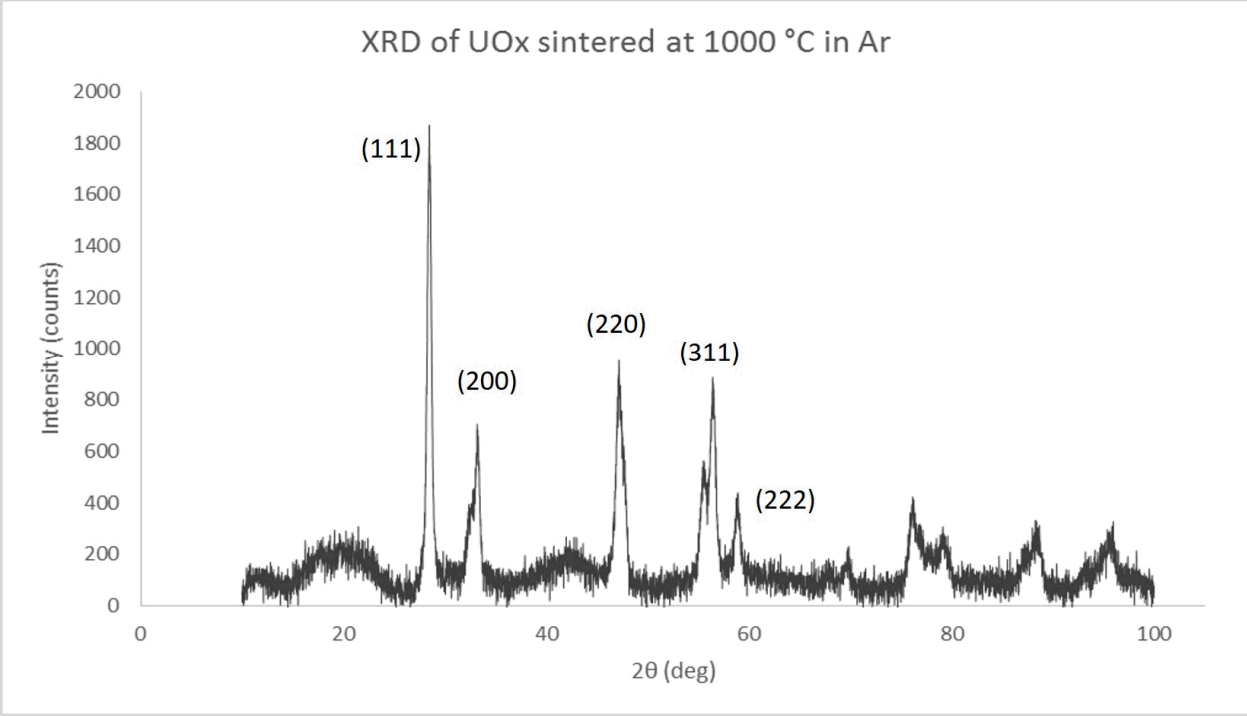




Ar-sintered UO_2 – PXRD Analysis

- PXRD results show good agreement with SAED analysis

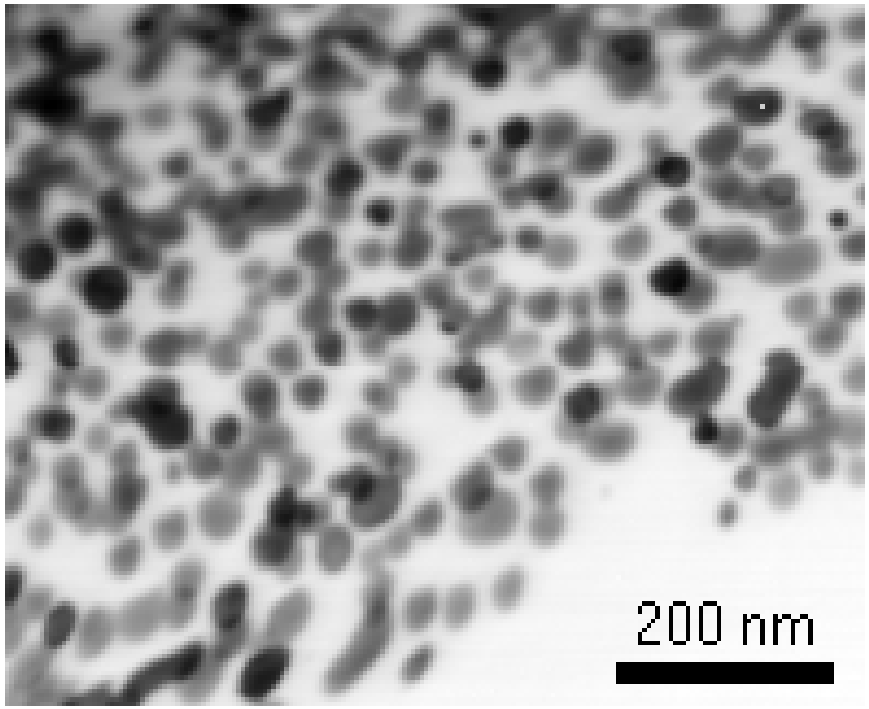
- Peaks consistent with fcc/fluorite structure of $UO_{2\pm x}$

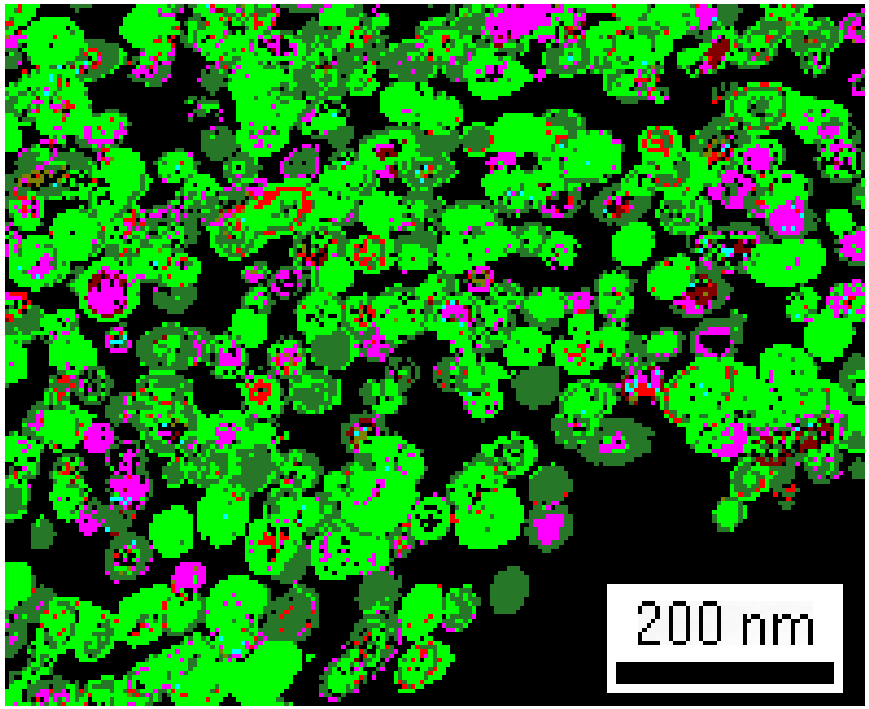


Ar-sintered UO_2 – PED Analysis

- PED not useful for determining exact $UO_{2\pm x}$ stoichiometry

- Does appear to confirm that primarily $UO_{2\pm x}$ phase is present as opposed to other O-rich phases





Next Steps

- Synthesize and characterize UO_2 particles following sintering in reducing (Ar-H) environment
- Attempt in-situ sintering in vacuum
- Grow epitaxial UO_2 thin films using the PAD technique
- Explore properties and behavior of these particles and thin films in various environments
  - Radiation Tolerance
  - Electrical properties
  - Environmental effects

Summary & Conclusions

- d-$UO_{2\pm x}$ nanoparticles have been synthesized using PAD with subsequent 1000 °C sintering in different environments
- Resulting particle phases and structure has been characterized with PXRD and diffraction-based TEM techniques
- Sintering in an oxidizing, aerobic environment results in large (200+ nm), mostly amorphous structures with isolated $UO_{2\pm x}$ grains
- Sintering in an inert Ar environment results in a fine dispersion of small (~60 nm) spheroidal particles that all appear to be a $UO_{2\pm x}$ phase
- Future efforts seek to investigate the effect of reducing (Ar-H) sintering environments and attempt epitaxial thin-film growth

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Thank you for your attention.
Questions?