SAND2011-5886C

Low Temperature Synthesis and Sintering of UO_2 Nanoparticles

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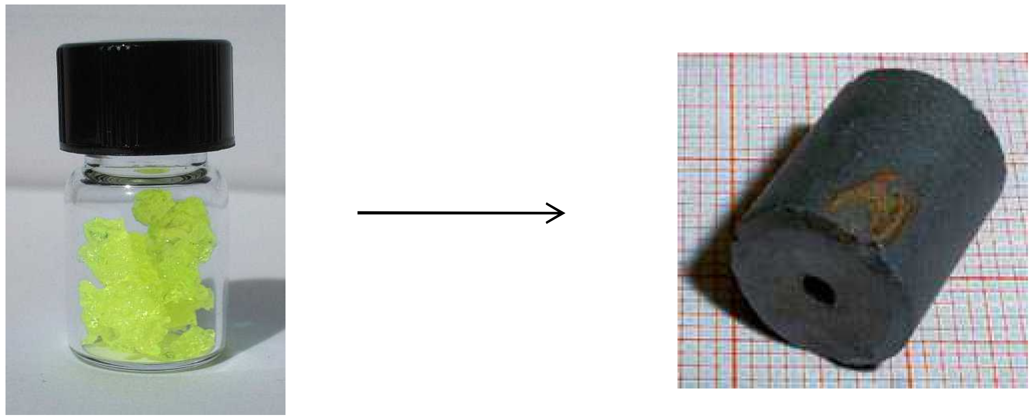
Jeju Island, Korea

David B. Robinson
Sandia National Laboratories
Livermore, CA, USA

UO_2 processing



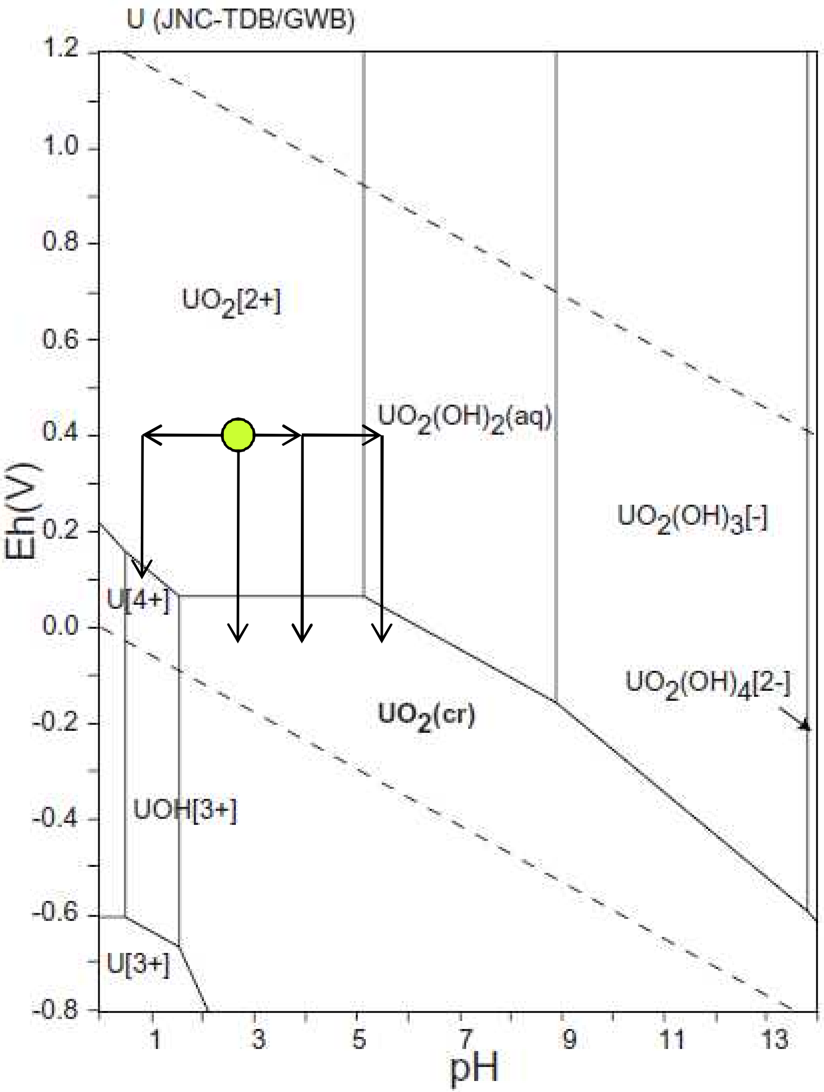
$UO_2(NO_3)_2$ UO_2

Goals

- Understand how UO_2^{2+} becomes UO_2
- Develop more efficient processing with fewer high-temperature steps
- Minimize volatilization of actinides

Images from Wikipedia articles on the compounds.

U Pourbaix diagram



We use pH adjustment and gamma irradiation to find a convenient, high-yield path to UO_2

Then use heated-stage TEM to observe initial stages of sintering

Geological Survey of Japan
Open File Report #419

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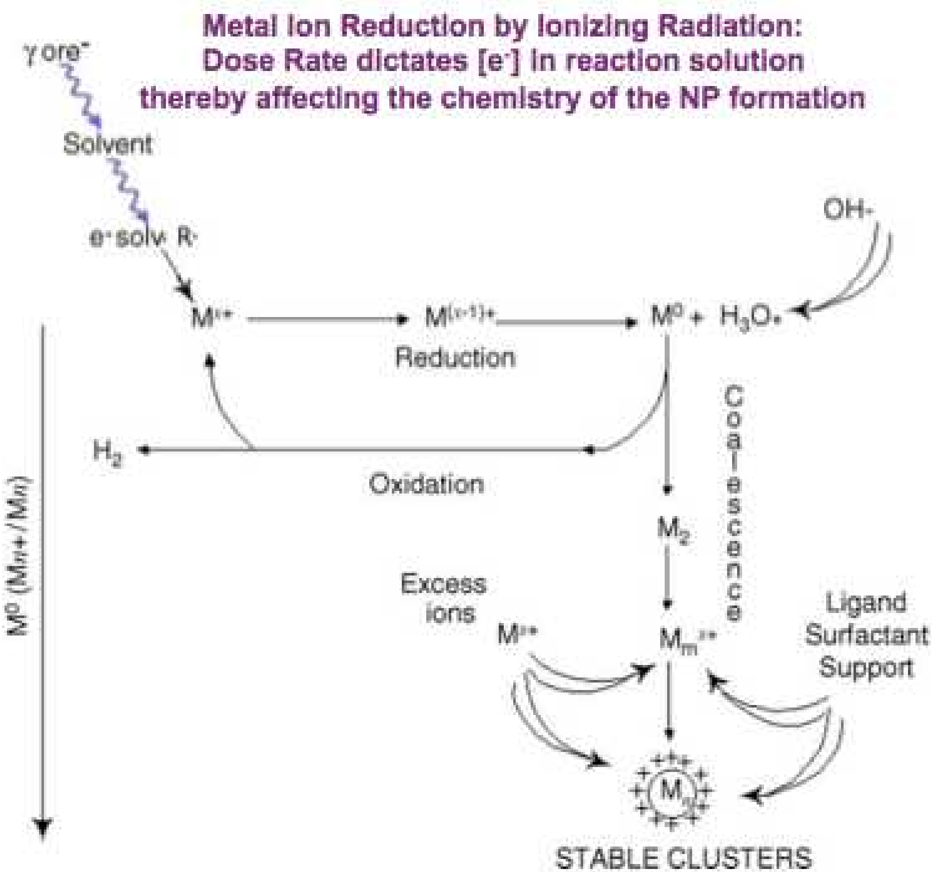
Radiochemistry of Nanoparticles



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

Gamma produces strong oxidizers and reductants (nonequilibrium)

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

$M^{n+} + n\ e^-_{aq} \Rightarrow M^0$

$UO_2^{2+} + 2\ e^-_{aq} \Rightarrow UO_2\ (s)$

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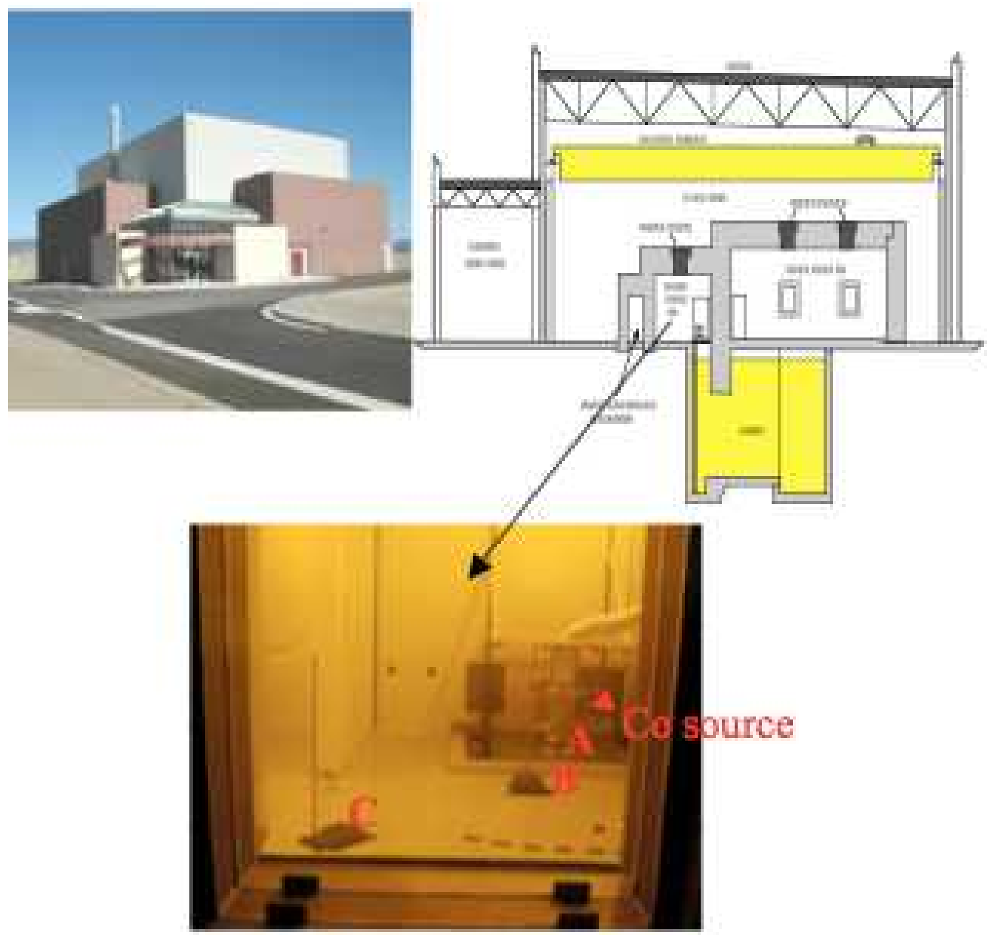
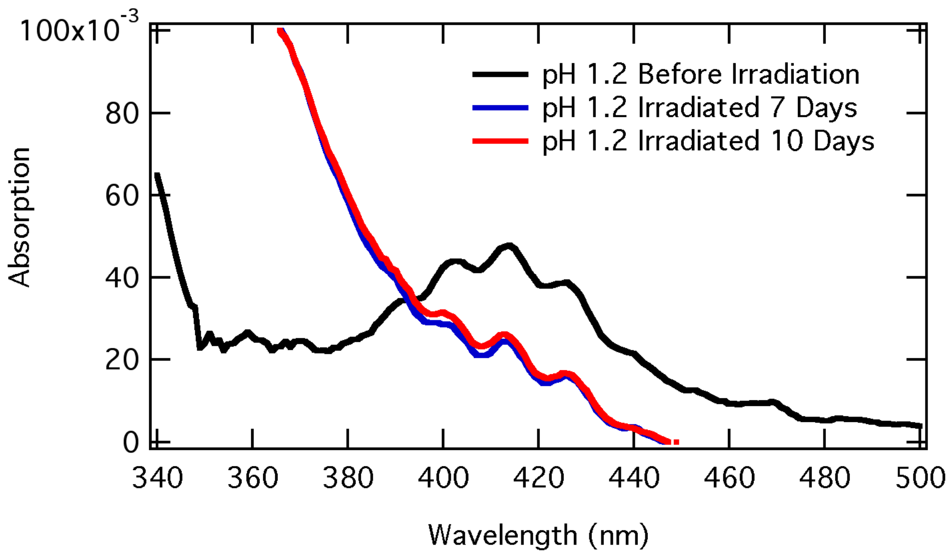
Sandia’s Gamma Irradiation Facility

GIF: ^{60}Co source :1.345×10^5 Ci



Strongly acidic conditions



Incomplete reaction

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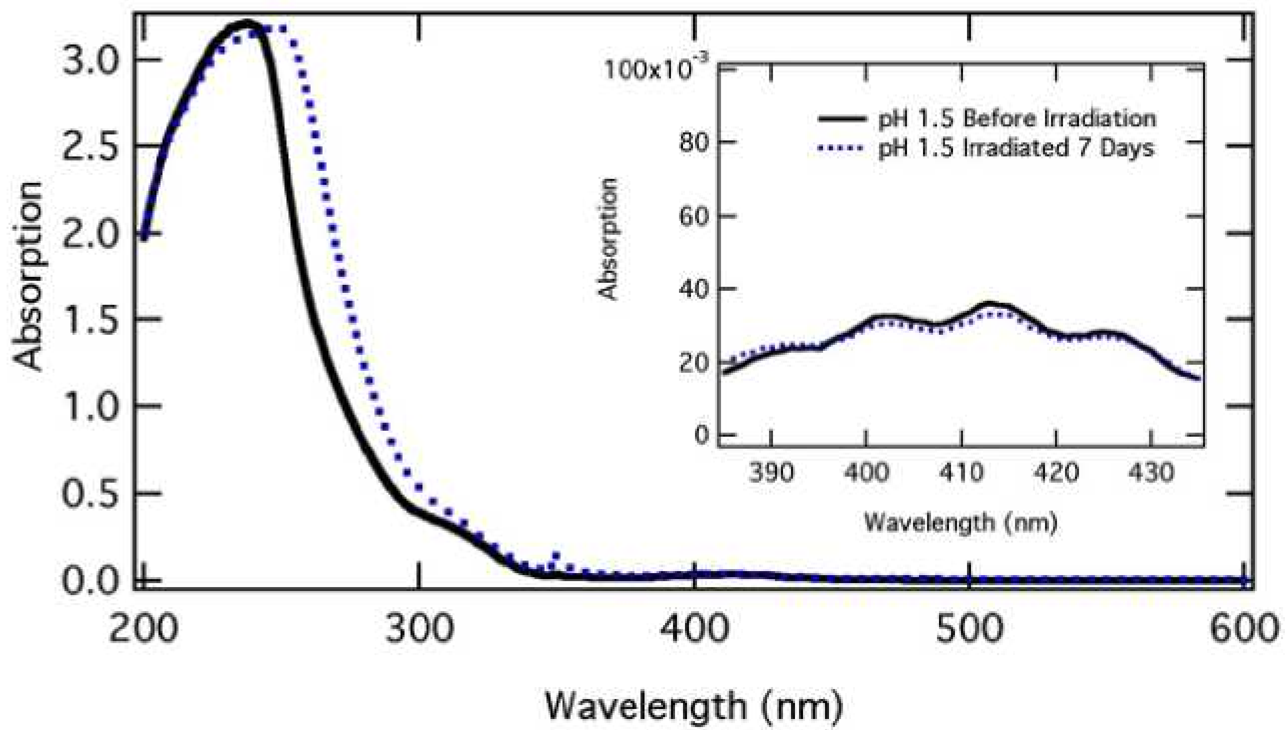
Chloride vs. nitrate



Chloride interacts differently with reactants

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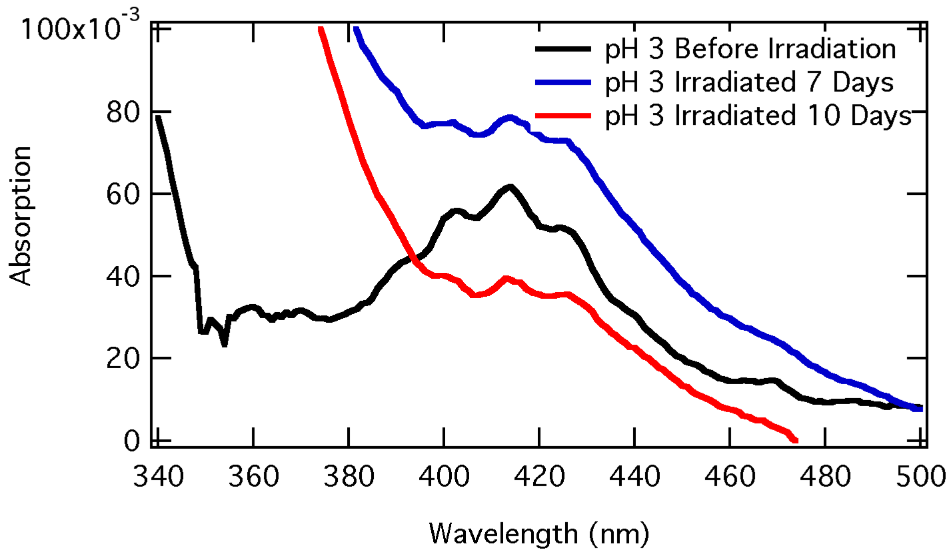
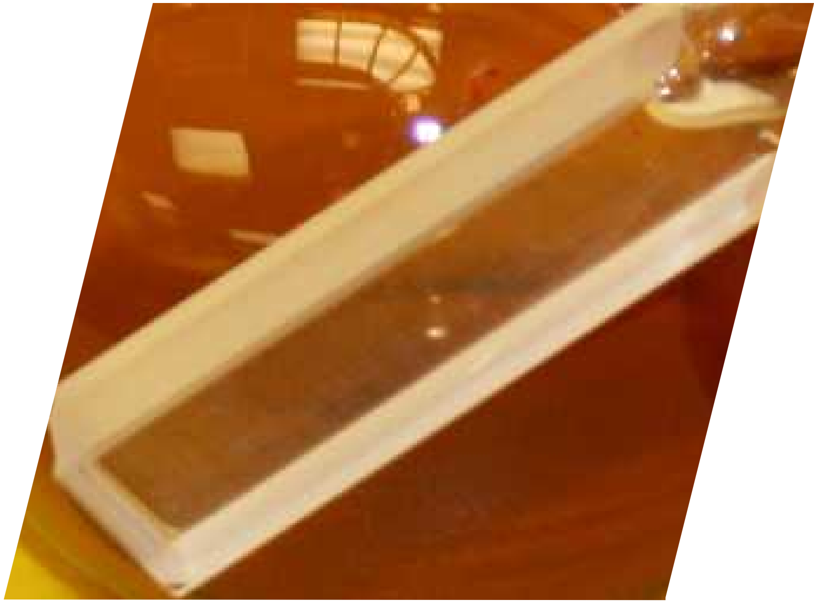
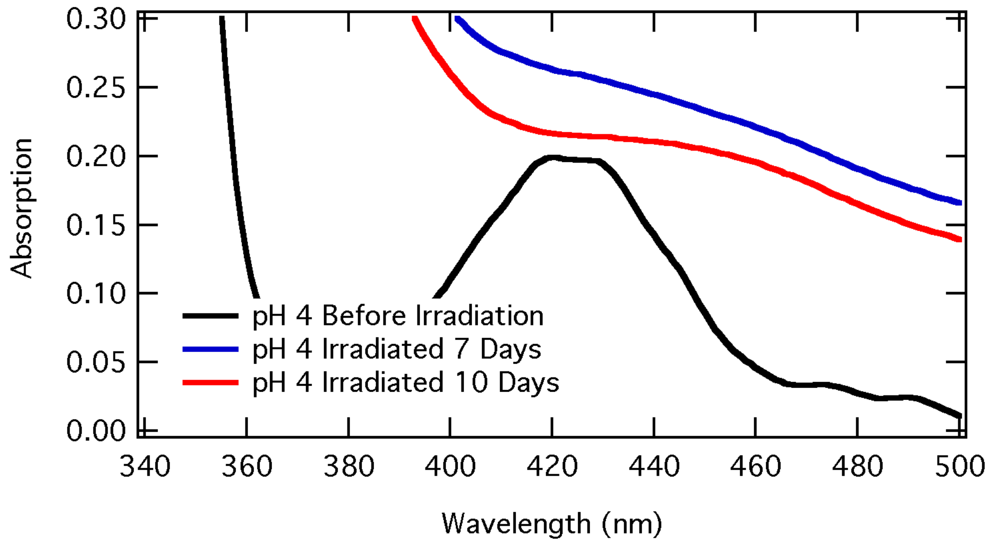
Acidic conditions

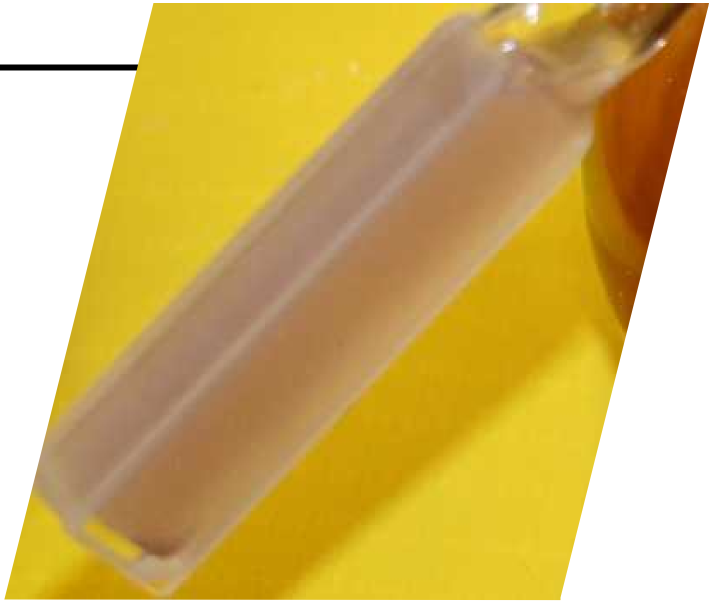


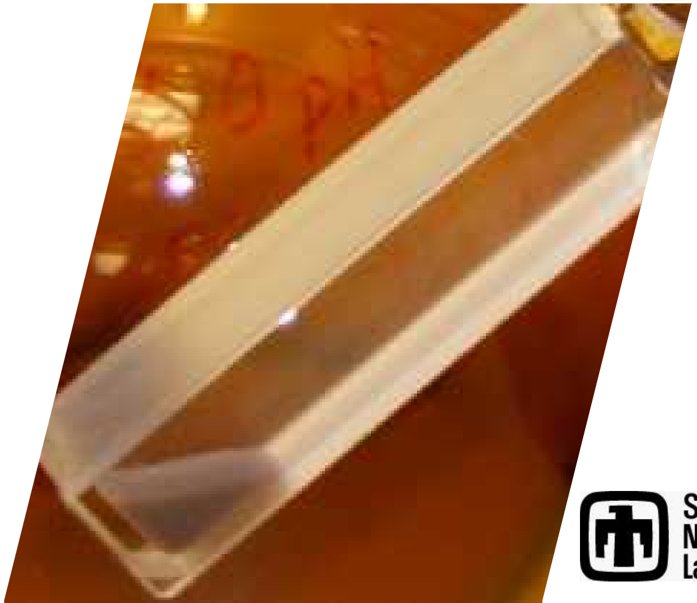


Cloudier product

Weakly acidic







Precipitate forms

Different reactant species are present

Protochips heated TEM stage

Old approach: resistive heating of entire stage
- Requires cooling water, which frequently clogs
- Severe drift
- Noise/oscillation problems
- Slow ramp rates and settling

Protochips:
- Heat only a microfabricated grid
- Ramps 1000 C / ms, RT – 1200 C
- Also permits electrical measurement

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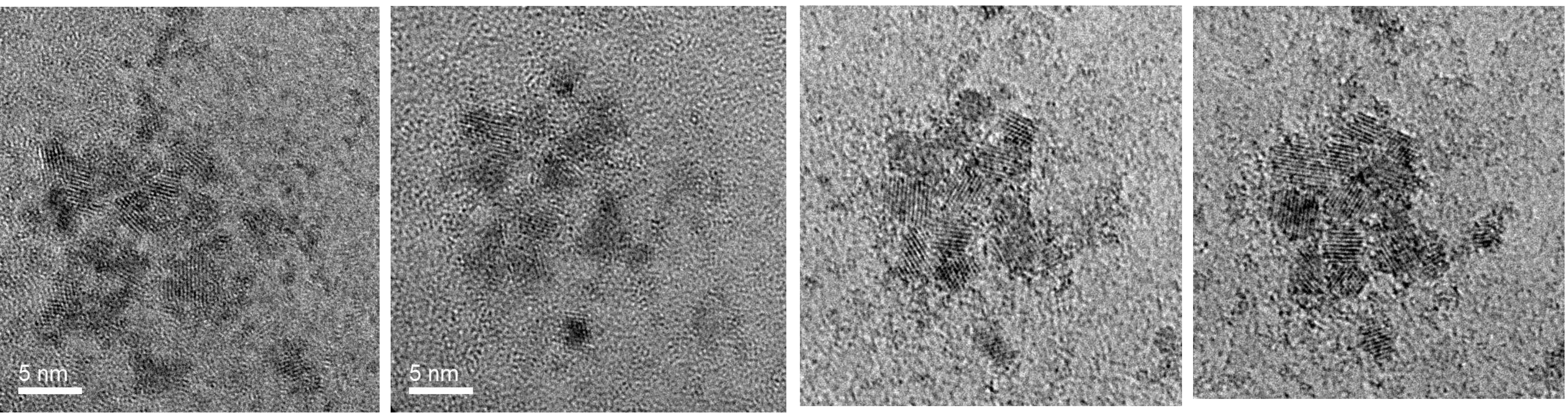
pH 3 heating

RT 200 °C 400 °C 500 °C



Consolidation is observed on TEM grid

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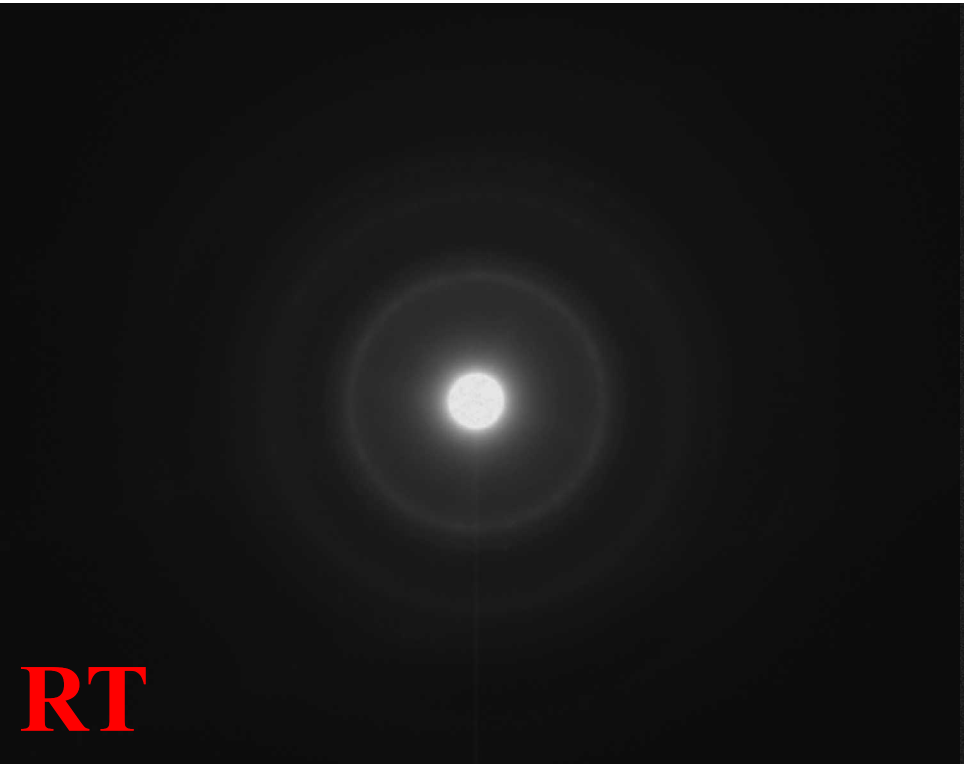
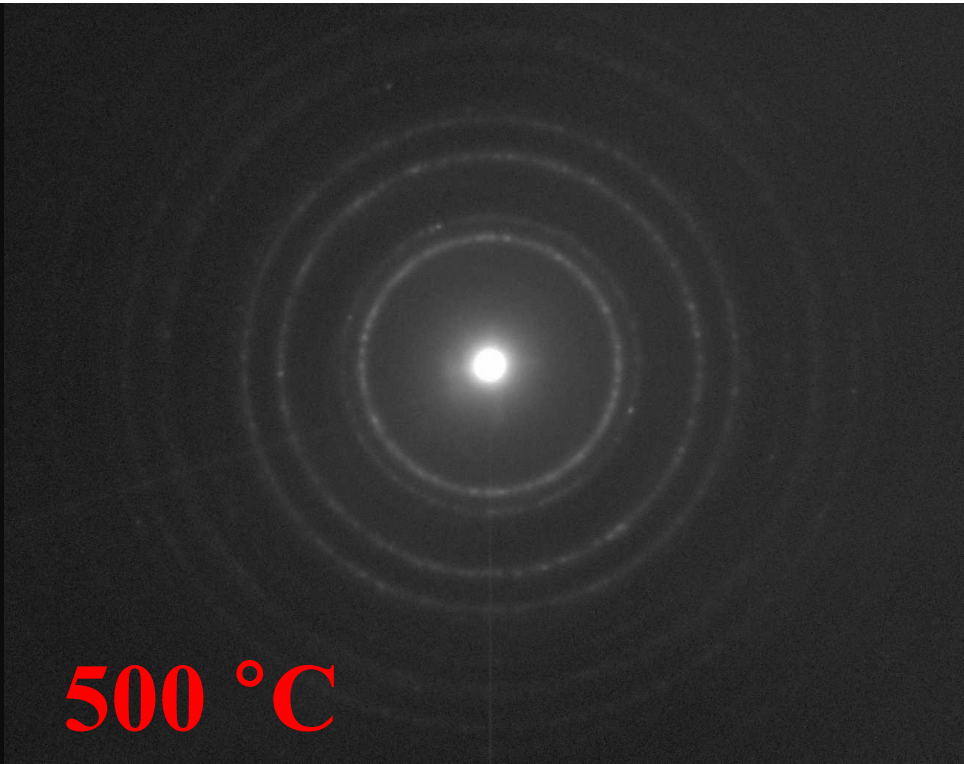
Electron diffraction patterns (pH 3)

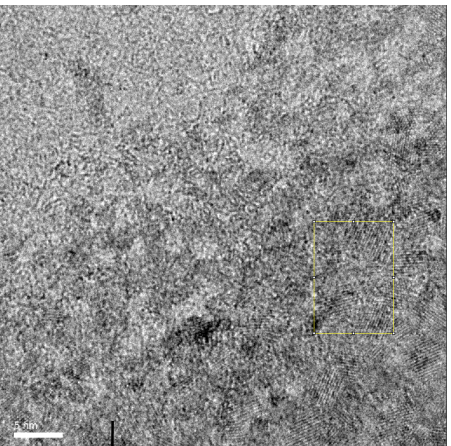
Sharper lines indicate grain growth



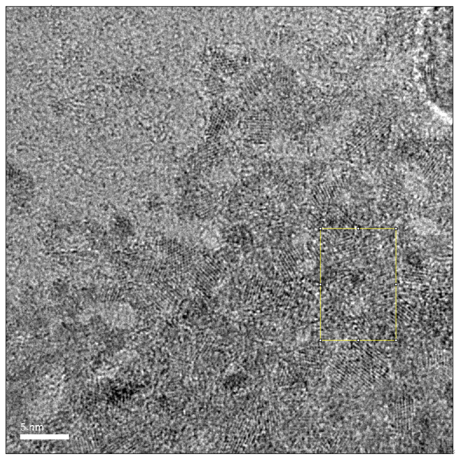


pH 1.5 heating (with chloride)

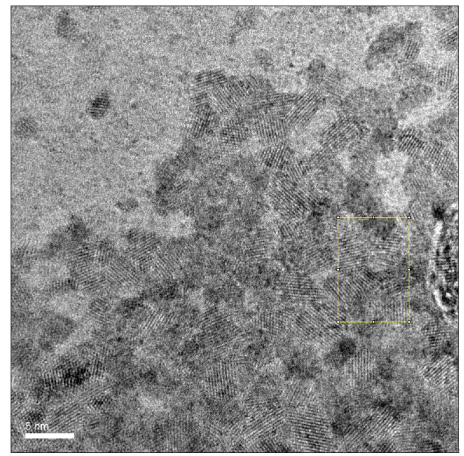
RT



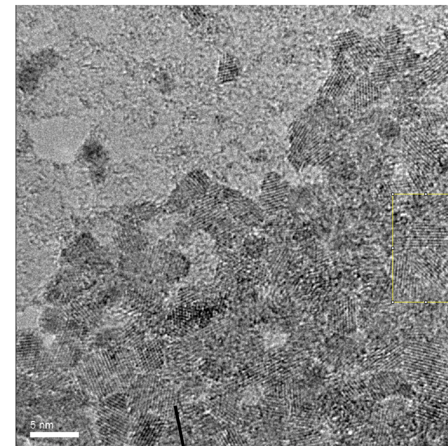
300 °C

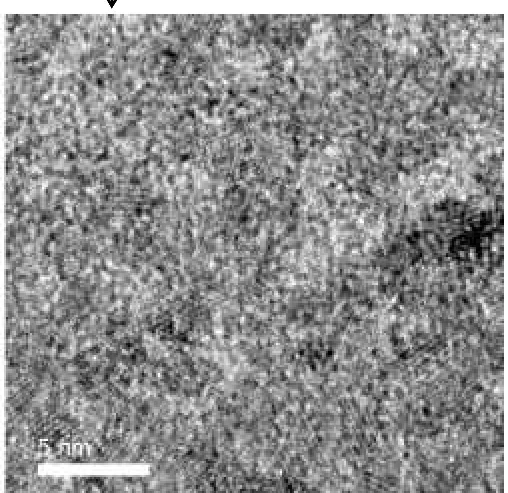


500 °C

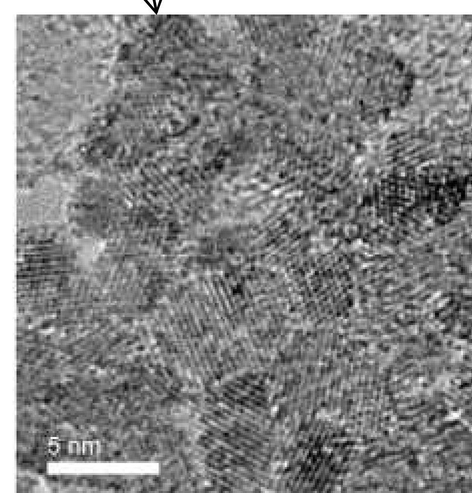


600 °C



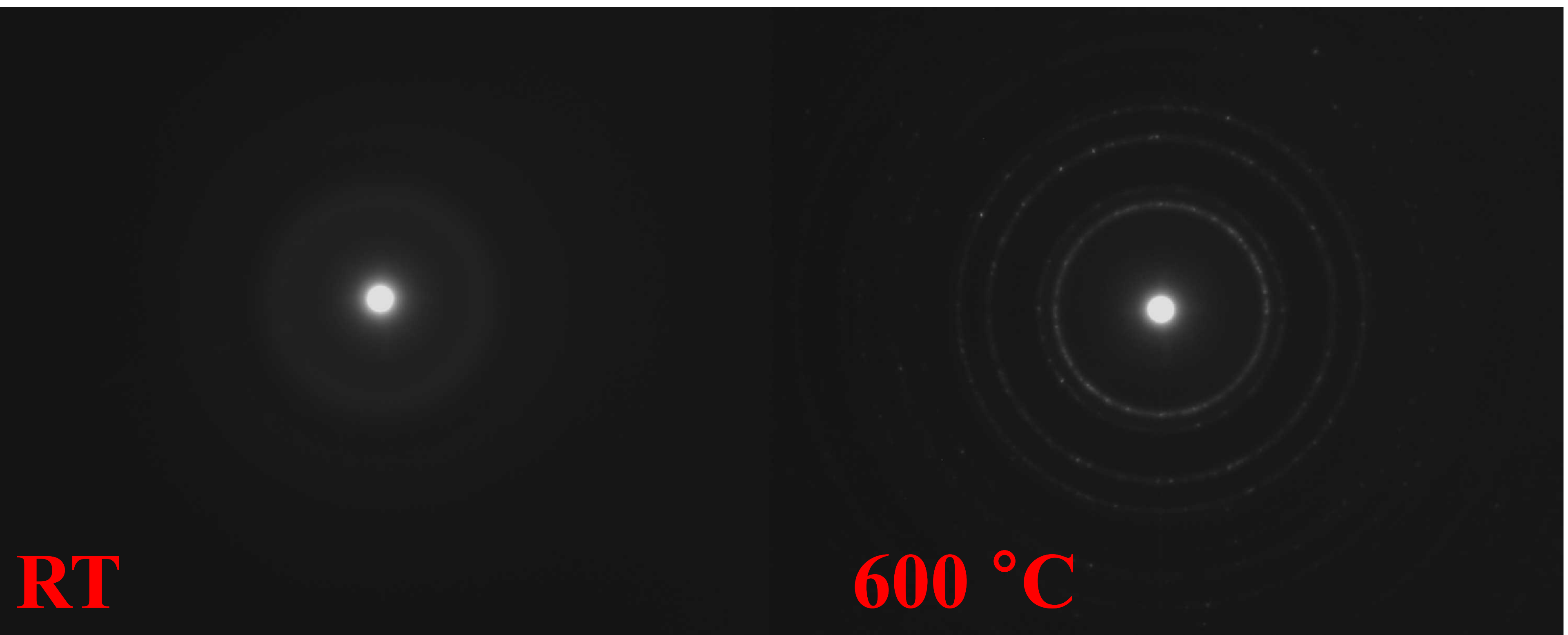


Likely a mixture of UO_2 and dried reactant
- still consolidates

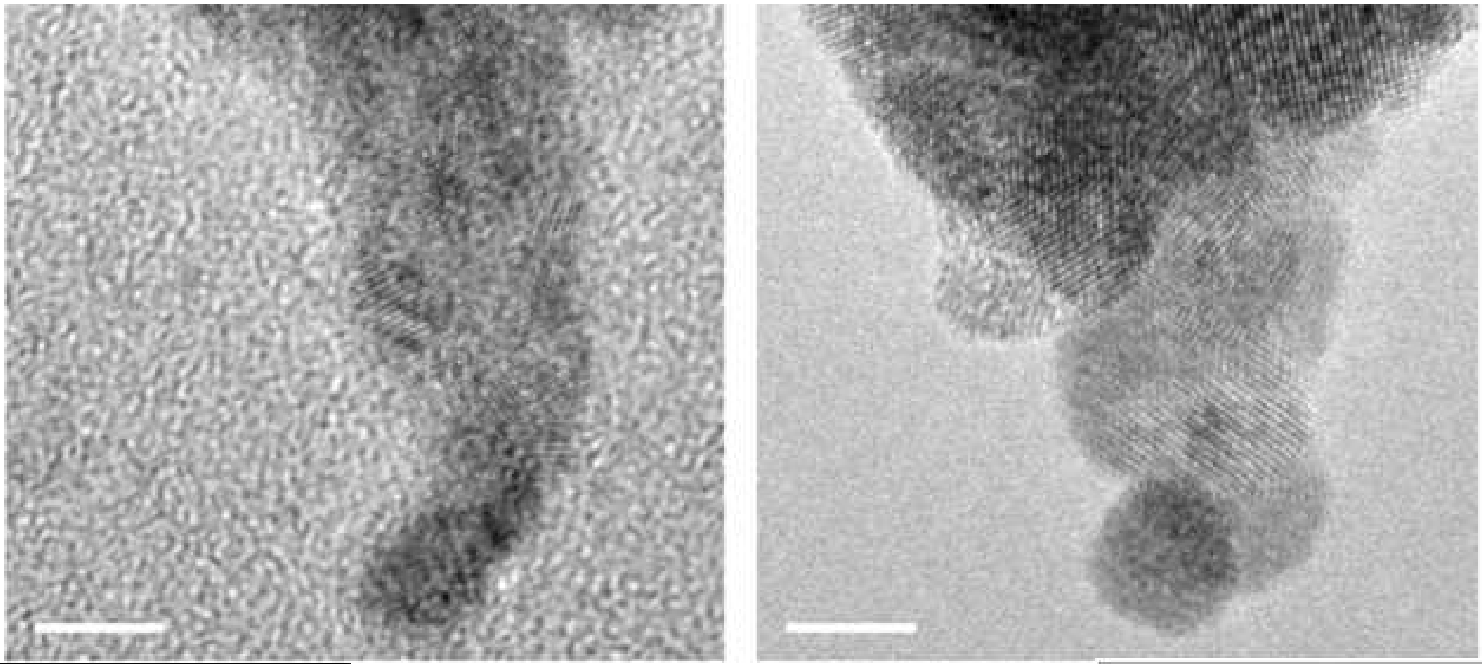


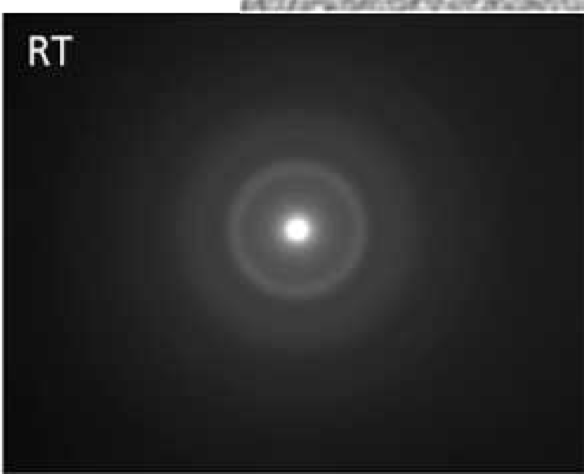
Electron diffraction (pH 1.5, chloride)

Grain growth is also observed, but less crystalline starting (and ending) point



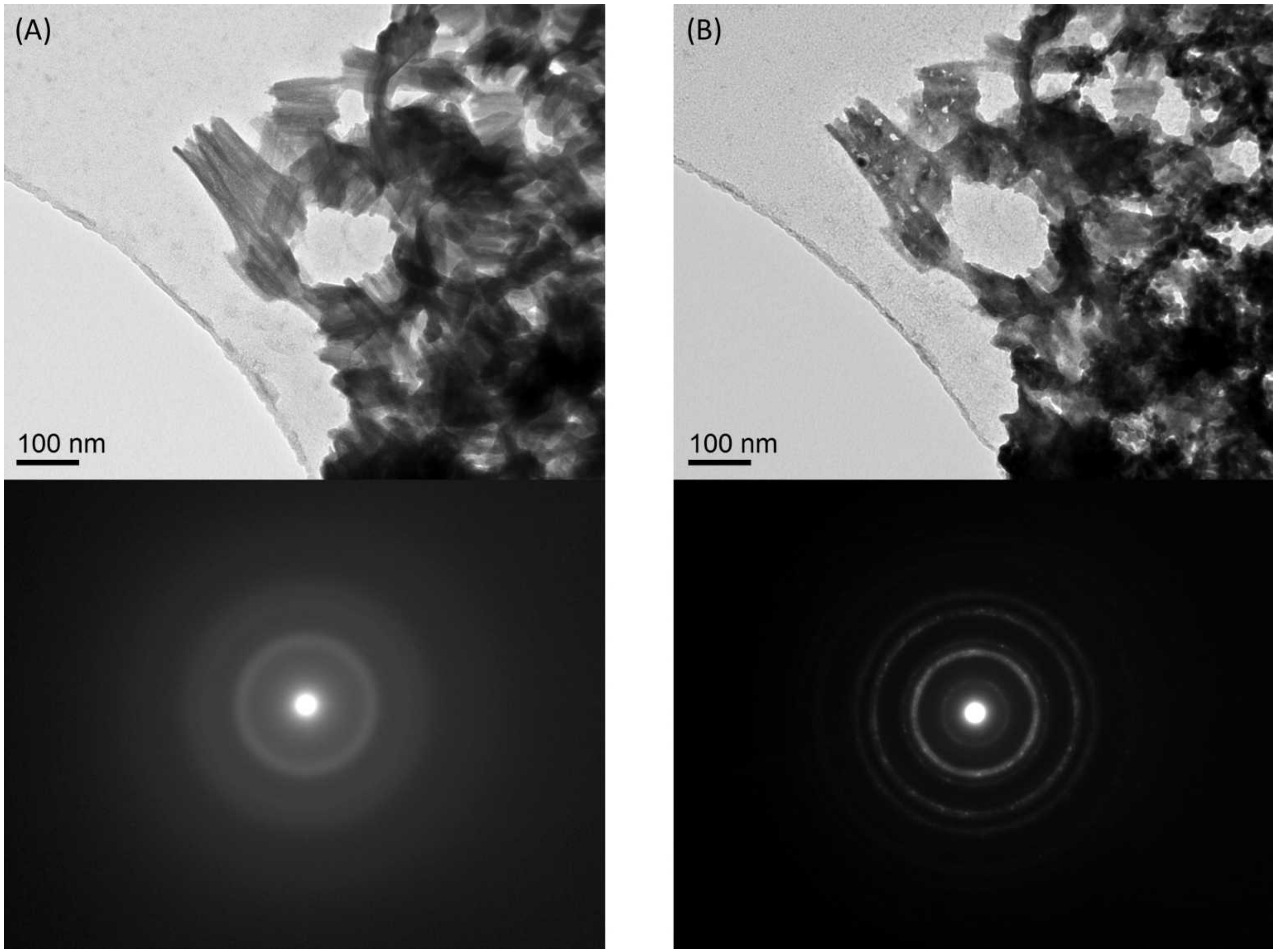
pH 4





Clear grain growth

pH 4: Condensation

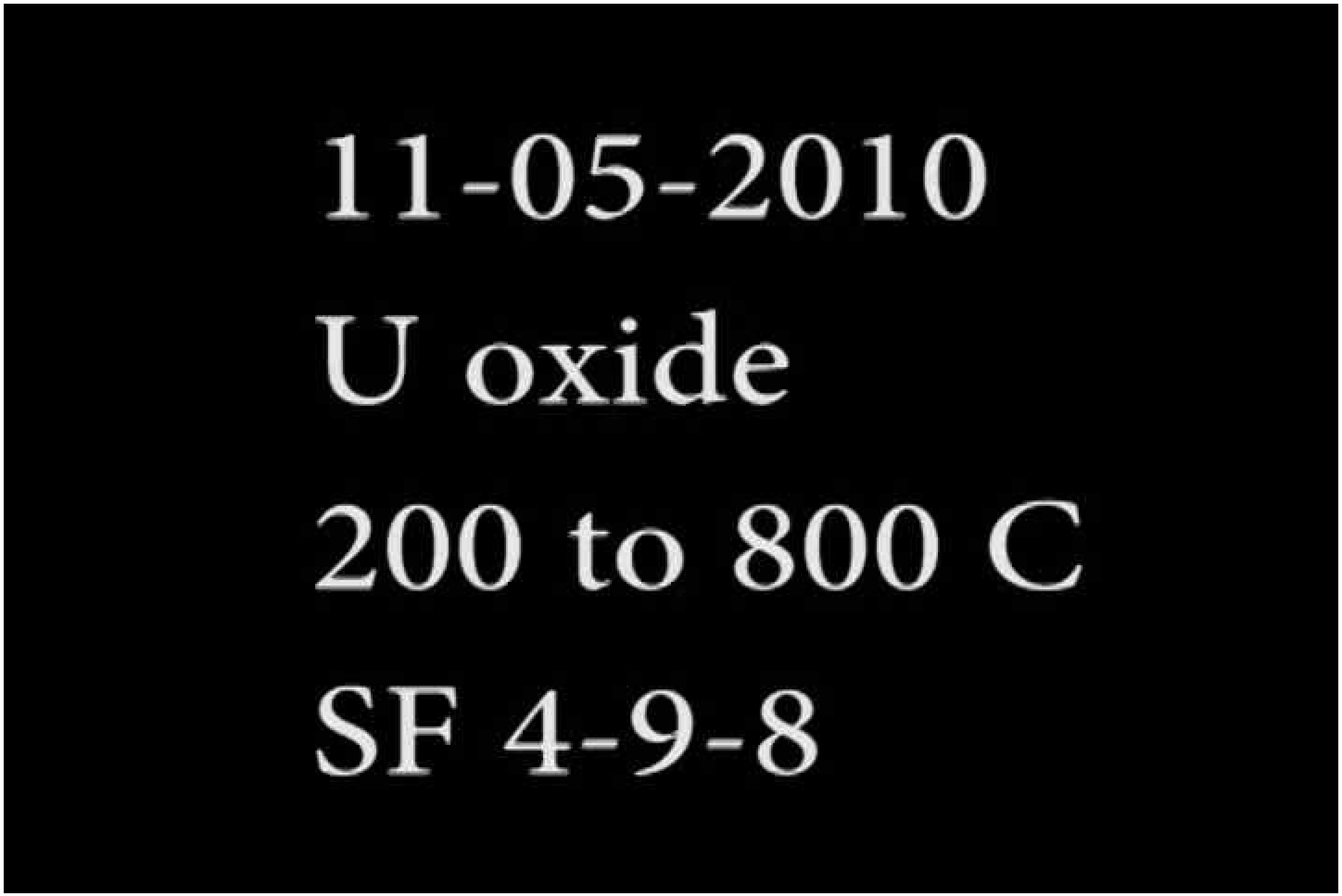


Holes form

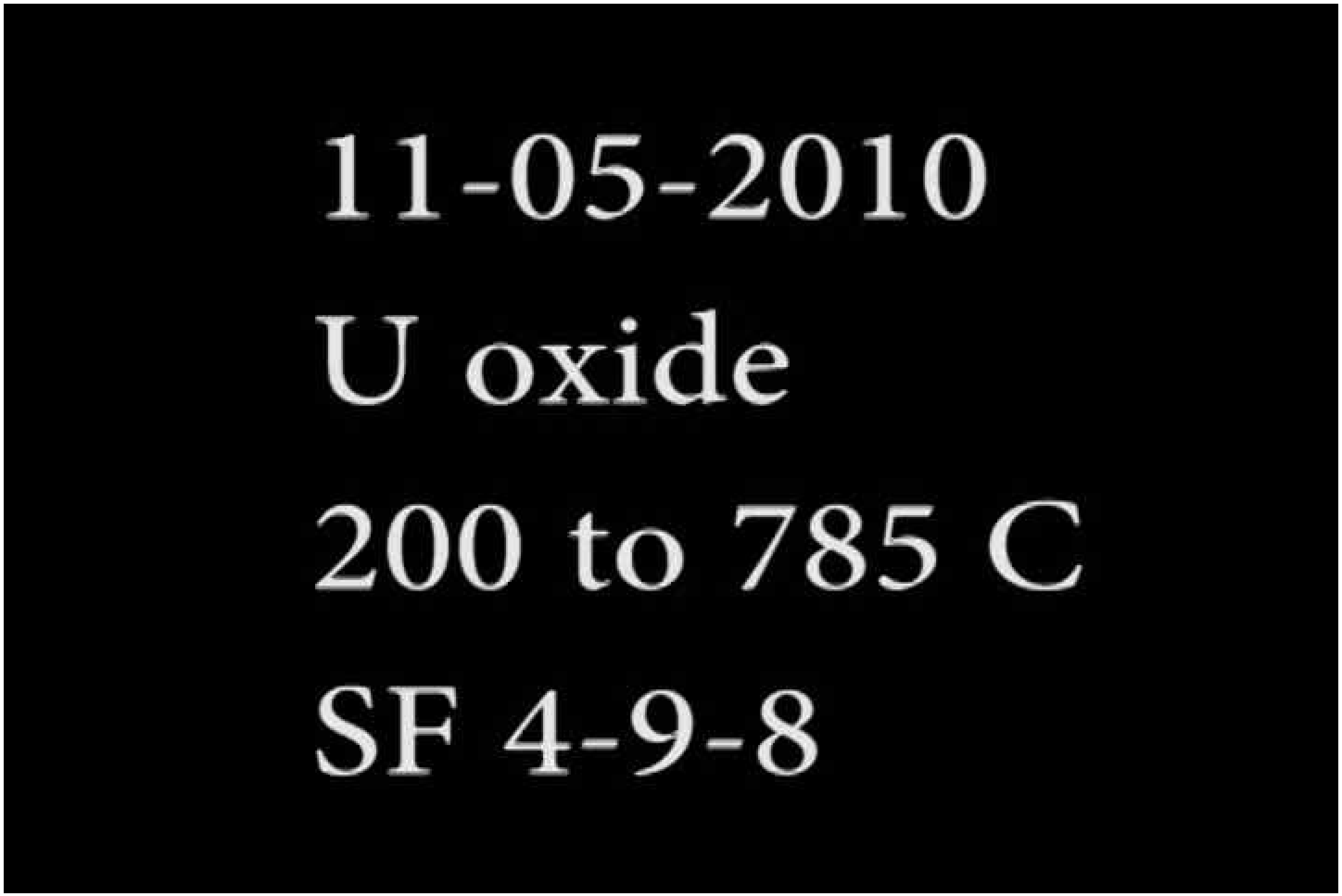
$2\ UO_2(OH)_2 \rightarrow 2\ UO_3 + 2H_2O$

Partial reactant precipitation at higher pH

pH 4 sintering movie

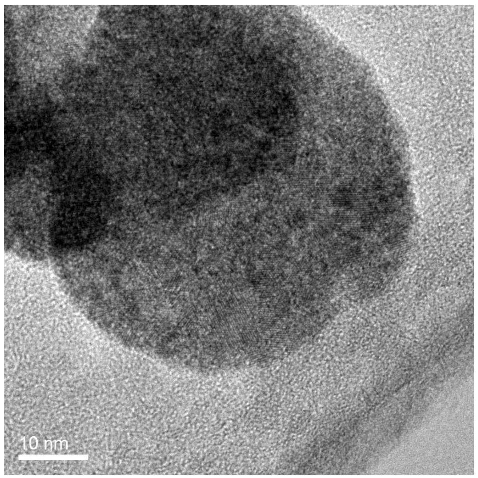


pH 4 condensation movie

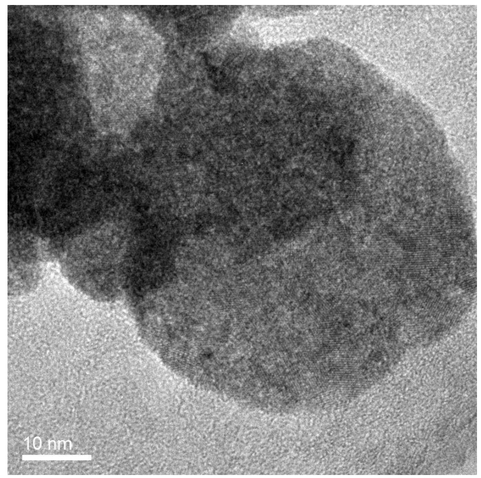


pH 5

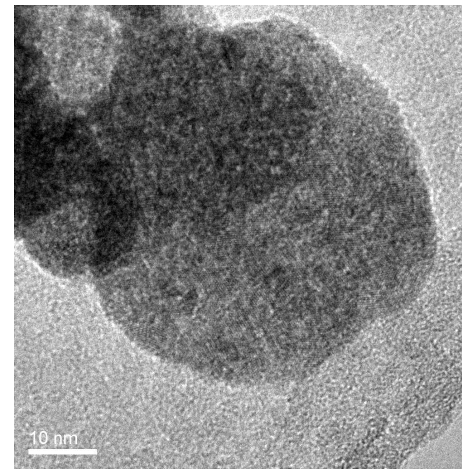
RT



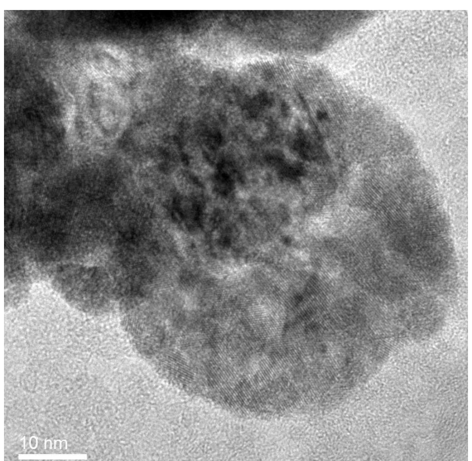
300 °C



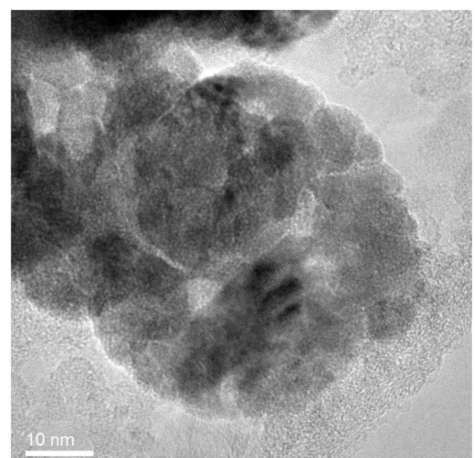
400 °C



600 °C

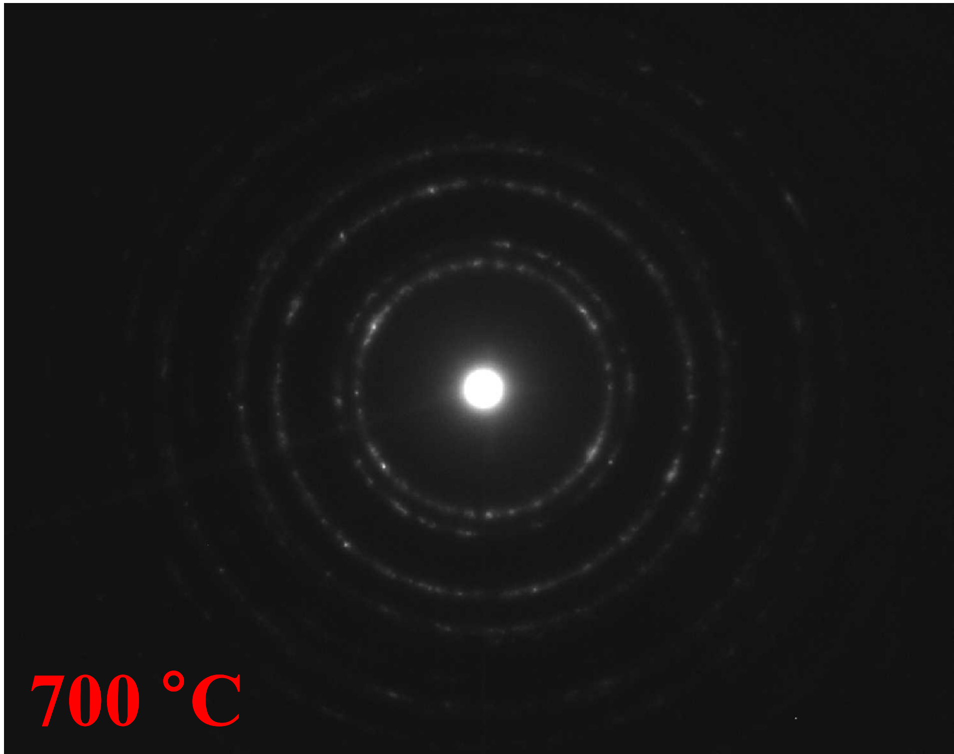


700 °C



Electron diffraction, pH 5

Similar sintering (and not just condensation) occurs at pH 5



Summary and conclusions

Sandia (Albuquerque, NM, USA)

- UO_2 precipitation requires a balance between pH and reduction
  - Preferably avoid UO_2^{2+} precipitation, soluble U^{4+}, reoxidation
- UO_2 consolidates, UO_2^{2+} condenses upon heating
- Initial sintering processes occur well below bulk sintering temperatures (~ 1700 C)
- Product yield at low temperature can be optimized
- Initial low-temperature treatment may prove useful

Acknowledgements

Sandia (Albuquerque, NM, USA) drobins@sandia.gov

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Protochips

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