SAND2011-9128C

Synthesis and Low Temperature In Situ Sintering of UO_2 Nanoparticles

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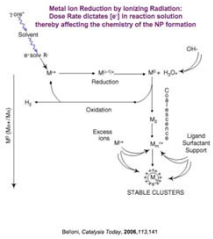
Introduction: UO_2 NPs via Radiolysis

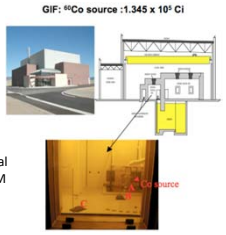
The recycling and reuse of uranyl salt solutions produced from the acid dissolution of spent nuclear fuels is of interest for the reprocessing of nuclear fuels. The ability to utilize these dissolved salts as a precursor for bulk UO_2 defines a materials pathway for the reduction of nuclear waste.

This study focuses on the thermal stability and sintering behavior of the d-UO2 NPs by TEM with an in situ heating stage from Protochips, Inc. The d-UO2 NPs exhibit sintering temperatures in the range of 500°C-600°C, which is between 700-1000° lower than reported bulk UO_2 sintering temperatures. Detailed characterization results from UV-vis, TEM, and in situ heating stage TEM are presented for the reaction solutions , the RT NPs products and the sintered NPs.

NP Synthesis and Characterization

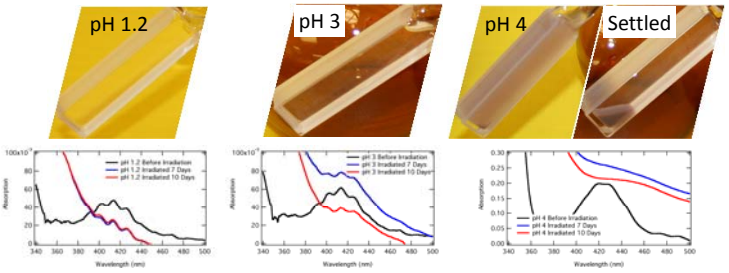


Nanoparticle formation process using gamma rays as a reductant



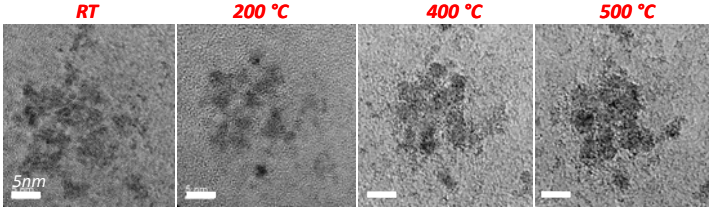
Gamma Irradiation Facility at Sandia National Labs in Albuquerque, NM

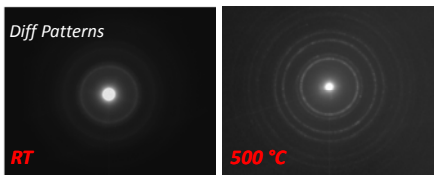
- 10 mM uranyl nitrate in solution with water and 10% IPA is sealed in a quartz vessel and bubbled with N_2 for 20 min.
- Irradiation carried out at 5 Rad/sec for 7 to 10 days.
- Suspensions are imaged and characterized with UV-Vis spectroscopy.



In-Situ Sintering of NPs, from reaction at pH = 3.0

TEM characterization with JEOL 2010F field emission microscope operating at 200 kV in bright field mode (BF). EDS using Oxford Inca X-Sight system. In-situ heating with Protochips Aduro™ holder. Temperatures were stepped from room temperature (RT) to the predetermined temperature, held for 30 seconds, and stepped back to RT. High resolution TEM analysis is carried out between heat treatments.

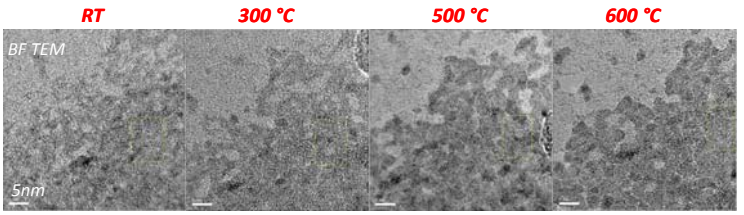


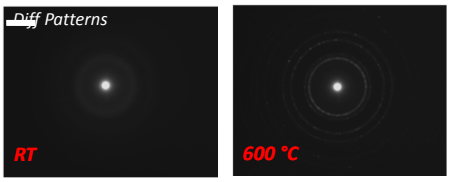


Diffraction Data in Angstroms

RT	500° C
3.20	3.11
2.75	2.72
1.94	1.93
1.65	1.64

Incomplete Reaction at Low pH (1.5)

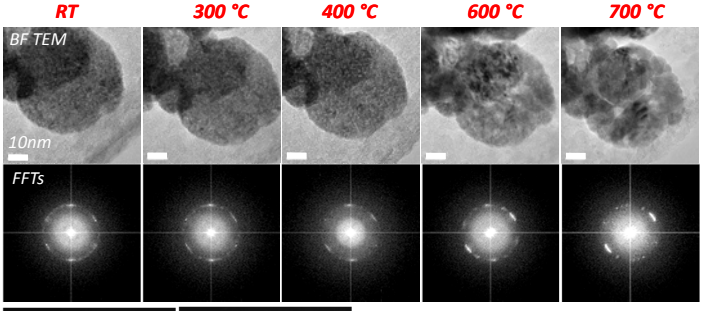


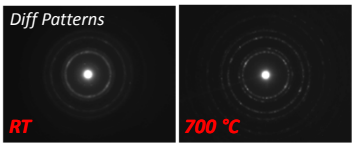


Diffraction Data in Angstroms

RT	700° C
3.17	3.12
	2.75
1.83	1.93
	1.65
	1.35
	1.25
	1.21
	1.11
	1.04
	0.91
	0.84

Optimal Synthesis at pH = 4; Near Complete Reduction of Salt to NP





Diffraction Data in Angstroms

RT	700° C	Lit. Values UO_2 41-1422	Lit. Values UO_2 36-89
6.51			
3.23	3.15	3.15	3.15
2.78	2.72	2.73	2.70
1.97	1.93	1.93	1.94
1.69	1.64		
	1.58		
	1.35		
	1.24		

Conclusion

Uranyl nitrate forms uranium oxide (UO_2) NPs under irradiation. pH adustment affects the resulting nanoparticle structure and degree of completion during synthesis. At low pH, there is evidence that the reaction does not proceed far from the ionic precursor to form UO_2 NPs. When the pH is not adjusted, the pH is still relatively low and at equilibrium, even after 10 days of reaction, UV-Vis indicates that a large fraction of UO_2^{2+} ions remain. Only at elevated pH is there evidence that the reaction has proceeded to completion by UV-Vis spectroscopy.

TEM evidence concurs with the formation of UO_2 over the full pH range investigated. Diffraction indicates that UO_2 is formed by radiolysis, before heating. Upon heating we observe sintering as low as 400 °C – 500 °C and the UO_2 phase remains.

***For complete data, see: Chem. Mater.* 2011, in press, DOI: 10.1021/cm2020669.**

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