

Aspects of Crystal Growth and Atomic-Scale Characterization of Uranium Oxide Micro-Particles

Darrell Mayberry
Pacific Northwest
National Laboratory

Riane Stene
Pacific Northwest
National Laboratory

Katherine Koh
Pacific Northwest
National Laboratory

Corlisa Awino
Pacific Northwest
National Laboratory

Alan Albrecht
Pacific Northwest
National Laboratory

Tim Pope
Pacific Northwest
National Laboratory

ABSTRACT

To ensure the highest quality of analytical measurements, the IAEA's network of analytical laboratories (NWAL) must manage robust internal quality assurance and control (QA/QC) plans. The International Atomic Energy Agency (IAEA) routinely distributes well-characterized quality control (QC) samples to the NWAL and conducts Interlaboratory Comparison (ILC) studies to periodically assess their analytical performance. Although certified reference materials are available for bulk analytical techniques, the selection of available materials for the QA/QC of analytical methods for particle analysis is limited. As the IAEA needs micrometer-sized nuclear materials (e.g., uranium oxide) with well-characterized properties such as size, density, homogeneity, and elemental and isotopic composition for its NWAL particle analysis laboratories' QA/QC program, the Pacific Northwest National Laboratory (PNNL), Savannah River National Laboratory (SRNL), and Forshungszentrum Jülich are producing bespoke working reference materials which are useful for a range of QA/QC measurements to meet this need. PNNL's efforts are focused on hydrothermal synthesis methods for producing particulate uranium oxides and, more recently, mixed actinide oxides (i.e., $U_{1-x}Th_xO_2$). Herein, the details of PNNL's particle synthesis control of particle morphology.

INTRODUCTION

Trace analysis of particulate material collected on environmental swipe samples continues to be one of the cornerstones of the IAEA's process for verifying member States' reports and declarations as part of the Non-Proliferation Treaty. The IAEA's Network of Analytical Laboratories (NWAL) must manage robust internal quality assurance and control plans to ensure the highest quality of analytical measurements. To assess NWAL analytical performance, the IAEA periodically distributes well-characterized quality control samples for interlaboratory comparison studies. Certified reference materials and well-characterized working reference materials are readily available for bulk analytical techniques and commercially available from organizations such as the US Department of Energy New Brunswick Laboratory, the US National Institute for Standards and Technology, and the European Commission's Joint Research Centre G2 in Geel, Belgium. However, the selection of available particulate materials for quality assurance and control of analytical methods is limited.

Consequently, the expansion of well-characterized, micrometer-sized nuclear materials, such as uranium oxide particles, is integral. To meet this need, the Pacific Northwest National Laboratory (PNNL) is formulating a range of uranium working reference materials that address changing criteria.

This work includes a summary of PNNL's particle synthesis strategy, characterization methods, and recent advances toward particle morphology control.

As part of the nuclear fuel cycle, uranium dioxide (UO_2) is of particular interest as a working reference material. The Pacific Northwest National Laboratory (PNNL) is formulating a range of uranium oxide working reference materials that address changing criteria [1]. Our approach is via a hydrothermal synthesis route that affords milligram-scale, phase-controlled synthesis of crystalline UO_2 particles [2]. The reaction is performed at high temperature and pressure within the confinement of a Teflon-lined, stainless steel pressure vessel. We employ organic amines as both reducing agents and structure-directing ligands, as uranyl ions are readily complexed with ethylenediamine, inducing the thermolysis reaction that triggers the nucleation and growth of UO_2 crystals [3].

Particles synthesized from the uranyl nitrate precursor show varied morphologies. Some particles were individual, well-defined single-crystal octahedra, while others had less-defined edges and appeared as two or more octahedra fused together. The proposed reason for the formation of the fused octahedral particles rather than single octahedral particles was insufficient ethylenediamine in the solution. An appropriate amount of ethylenediamine is necessary for it to effectively function as a structure-directing ligand in addition to a reducing agent. A higher concentration of ethylenediamine would likely enhance its structure-directing ligand function and increase the occurrence of individual single-crystal octahedral particles by properly guiding UO_2 into the crystal lattice of the growing nucleated particle.

Additionally, increasing the ethylenediamine concentration would lower the pH of the reaction solution and lead to increased protonation (and loss of lone pairs) on both amine moieties. This eliminates ethylenediamine's ability for dative bonding with nucleated UO_2 particles and "free" UO_2 molecules, leaving hydrogen bonding as the only mechanism for coordination. The much weaker hydrogen bonding may render the ethylenediamine less effective as a structure-directing ligand and result in morphological changes to particles.

In addition to pure UO_2 , a protocol for U/Th reference particles was developed, which can serve as a point of comparison for age-dating individual uranium particles [4]. A process to artificially age particles was incorporated into the particle synthesis protocol to expand the range of obtainable "ages" of U/Th reference particles. Purified U feedstock material was doped with varied quantities of Th through the addition of a Th stock solution during synthesis. Electron dispersive spectroscopy (EDS) was used to verify that Th was uniformly distributed with U in the synthesized particles. A method to effectively reset the age of feedstock materials to zero years by removing the Th contamination was also developed [5]. It was concluded from studies utilizing commercially available UTEVA and TEVA separation columns that a TEVA-TEVA double stack (two TEVA columns joined vertically) was the most effective method of separating the Th content (greater than 95% separation).

Herein, we describe continued research and development to tailor the size, shape, and morphology of UO_2 particles by altering the synthetic conditions during the hydrothermal process. A multi-parametric study was performed to evaluate the impact of uranium precursor materials and reaction conditions on the size, shape, and morphology of the resulting UO_2 particles.

RESULTS & DISCUSSION

Effect of Uranium Precursor

The impact of the uranium precursor on the resulting UO_2 particle morphology and size was assessed by comparing UO_2 particles produced from two readily available precursors: $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (uranyl acetate) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (uranyl nitrate). The developed hydrothermal synthetic route was chosen to synthesize UO_2 from the uranium precursors.[1] After reaction completion (48 hours at 160°C), the Teflon-lined stainless-steel autoclave was allowed to cool to room temperature and opened to reveal a black precipitate at the bottom of the Teflon liner, which was identified as UO_2 particles. The UO_2 particles were transferred to a centrifuge tube, filled with 12 mL of deionized water, and centrifuged at 4000 rpm for 15 minutes. The deionized water was pipetted off of the precipitated particles after centrifugation, and another 12 mL of fresh deionized water was added to the tube, followed by another 15-minute centrifugation. This centrifugation process was repeated using 1:1 (v/v) water:isopropanol, isopropanol, and finally, Vertrel XF. After the centrifugation process, an aliquot of UO_2 particles was deposited on a silicon planchet for microscopy of the particles.

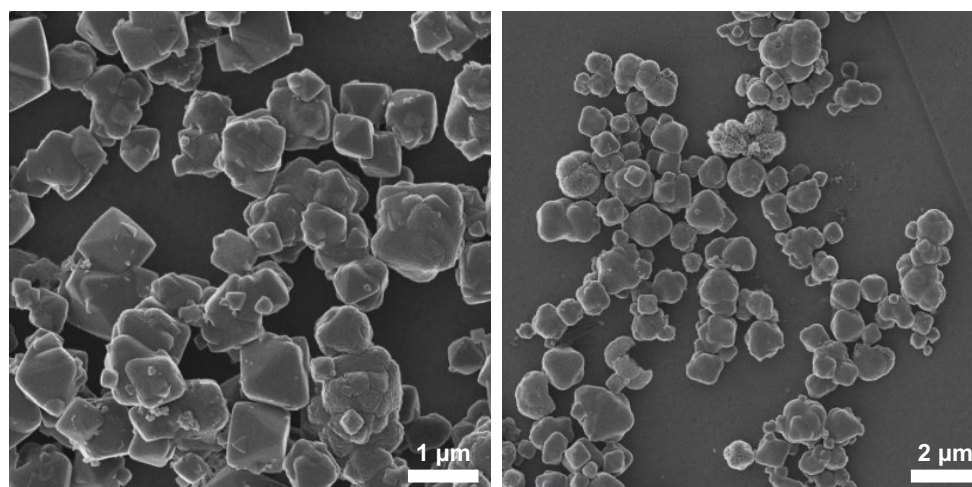


Figure 1. Microscopy images of UO_2 particles produced from uranyl nitrate (left image) and uranyl acetate (right image).

Imaging was conducted to assess the morphology and size of the UO_2 particles produced from uranyl acetate and uranyl nitrate precursors (images are displayed above in Figure 1). The particles obtained from the uranyl nitrate precursor displayed a mostly octahedral shape with relatively smooth faces and sharp edges. These UO_2 particles also displayed a mixture of single-crystal octahedral particles and polycrystalline spherical particles with multiple fused octahedra that grew into a single particle. The size of single-crystal octahedral particles predominantly ranged from $0.7\text{--}1.5\ \mu\text{m}$, while that of the polycrystalline particles ranged from $1.3\text{--}2.0\ \mu\text{m}$. The UO_2 particles obtained from the uranyl acetate precursor displayed a mixture of octahedral-shaped particles along with agglomerated particles that were amorphous. The octahedral particles produced from the uranyl acetate precursor had smooth surface textures and rounded edges; they were single-crystal and polycrystalline. The size of the octahedral particles from the uranyl acetate precursors ranged from $0.3\text{--}1.1\ \mu\text{m}$, while that of the amorphous particles ranged from $1\text{--}2.5\ \mu\text{m}$. In general, the uranyl nitrate precursor particles

produced a more homogenous batch of particles in terms of shapes and sizes than the uranyl acetate precursor particles.

We hypothesize that the inhomogeneous morphology of particles produced from the uranyl acetate and the more homogeneous morphology of the particles from uranyl nitrate result from the difference in ligand binding of the acetate ligand versus the nitrate ligand. The acetate ligand has a stronger binding affinity for the uranyl ion than the nitrate ligand [6,7]. The ability of the acetate or nitrate ligand to dissociate from the uranyl ion is central to the reduction of U(VI) to U(IV), as ethylenediamine likely coordinates to the uranyl ion prior to reduction. The acetate being relatively strongly bound to the uranyl ion blocks potential coordination sites needed for ethylene diamine to coordinate with the uranyl ion. Uranyl ions from uranyl nitrate are more easily reduced by ethylenediamine than uranyl acetate due to the nitrate ligand's weaker binding affinity; this creates less competition for the coordination of ethylenediamine to the uranyl ion.

Ethylenediamine also plays a potential role as a structure-directing ligand, which can coordinate to the surface of UO_2 nucleated particles with one amine moiety and a solution-phase "free" UO_2 molecule with the second amine moiety [8]. The amine moiety helps guide the "free" UO_2 molecule to the surface of the nucleated particle, where it can then incorporate itself into the crystal lattice of the particle. The relatively high strength of the U-acetate bond also impacts particle formation by competing with ethylenediamine as a structure-directing ligand. Acetate can also act as a structure-directing ligand, but ethylenediamine is the better-directing ligand of the two. Ethylenediamine has a much weaker binding affinity for UO_2 than acetate because ethylenediamine is a neutral N-donor ligand versus the charged O-donor ligand of acetate [6]. Ethylenediamine can bind to the UO_2 particle surface, direct a "free" UO_2 molecule into the crystal lattice, and dissociate from the surface more easily than the acetate, which doesn't dissociate as easily. The facile dissociation of ethylenediamine allows it to migrate across the particle's surface and direct incoming molecules. The acetate will bind more strongly to UO_2 in the lattice, thus inhibiting its movement and directing-ability over the surface of the particle. This competitive directing ligand effect of the acetate causes the octahedral particles to have rounded edges and more amorphous particles to be present compared with particles produced using the nitrate, which does not compete as much with ethylenediamine as a directing ligand.

Effect of pH

While the uranyl nitrate precursor produced mostly octahedral particles with smooth surfaces and sharp edges, some particles appeared to be composed of two or more fused octahedra that grew together to form one larger particle. We hypothesize that the fused octahedra particles, as opposed to the exclusive formation of single octahedral particles, result from a dearth of ethylenediamine in the solution. Because ethylenediamine acts as a reducing agent and structure-directing ligand, excess is needed to serve both functions. Additional ethylenediamine should suppress the growth of multiple octahedra into a single particle by properly guiding the UO_2 in solution into the crystal lattice of a nucleated particle. It is also important to have a profusion of unprotonated ethylenediamine in solution so that it can coordinate (via lone pair electrons) to nucleated particle surfaces. If the pH of the reaction solution is too low, then both amine moieties of ethylenediamine will be protonated, eliminating any coordination to the nucleated particle or to "free" UO_2 in the solution through lone pair electrons. Full protonation of ethylenediamine leaves hydrogen bonding – which is much weaker than dative bonding through lone pair electrons – as the only mode by which to attach to a nucleated

particle surface or to UO_2 in solution. This may render it a less effective structure-directing ligand and could induce morphological changes. To examine the influence of pH on morphology, we conducted particle syntheses at varied pH with uranyl nitrate as the uranium precursor.

For this test, the reaction above was completed as dictated in reference [1], however during the last stirring stage, prior to pouring the reaction solution into the Teflon-lined stainless-steel autoclave, the pH was checked with a pH probe, and acetic acid or ethylenediamine was added to the solution to reach the desired pH. The reaction solution was then transferred to a Teflon-lined, stainless-steel autoclave and heated in an oven at $160\text{ }^\circ\text{C}$ for 48 hours. The autoclave was then allowed to cool to room temperature and opened to reveal a black precipitate at the bottom of the Teflon liner, which was identified as UO_2 particles. The particles were centrifuged using the same procedure described in the previous section.

Microscopy was conducted to assess morphological changes in the UO_2 particles produced at various pH (Figure 2). The particles show a distinct change in morphology as the pH changes. At pH 7.4, the particles are mostly spherical, 1–1.5 μm in diameter. The particles produced at pH 6.81 were 90–95% octahedrally shaped with an average diameter of 1 μm . The particles produced at pH 6.71 were composed of 50–60% octahedrally shaped particles with a similar 1 μm diameter. At pH 6.54, the morphology was uncontrolled, and amorphous particles that tended to agglomerate were produced. The amorphous particles produced at pH 6.54 confirm our hypothesis that low pH reduces the functionality of ethylenediamine as a structure-directing ligand. These results also demonstrate the fact that particle morphology can be changed from spherical to octahedral to amorphous by relatively small changes in pH.

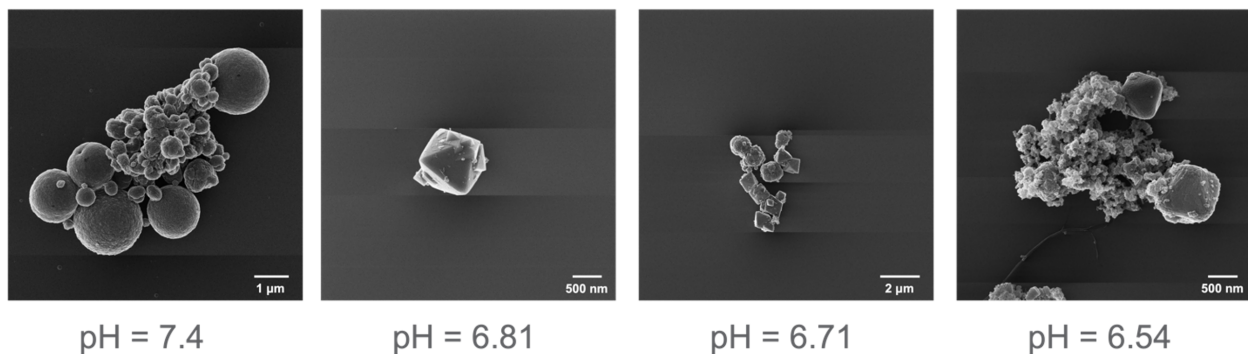


Figure 2. Microscopy images showing morphological changes in UO_2 particles synthesized at various pH using uranyl nitrate as the uranium precursor.

Table 1. Particle Morphology and Diameter Produced at Varied Reaction pH

Reaction pH	Morphology	Diameter
6.54	Very few, poorly defined octahedra; amorphous	Agglomerated particles
6.71	50–60% octahedra	1 μm (average)
6.81	90–95% well-defined octahedra	1 μm (average)
7.4	Spherical particles; no octahedra	1–1.5 μm

CONCLUSIONS

UO₂ particles were prepared using PNNL's previously established hydrothermal particle synthesis protocol. We investigated the impact of the uranium precursor and reaction solution pH on the morphology of the yielded particles. Uranyl nitrate was found to produce more homogenous particles in terms of both shape and size than a uranyl acetate precursor with the previously established protocol. Ethylenediamine was found to act as both a reducing agent and structure-directing ligand, but these properties are susceptible to the pH of the reaction solution. At high pH (7.4), the reaction produced spherical particles. The highest incidence of well-defined octahedral particles was obtained at pH 6.81. Further decreases in pH led to fewer octahedral particles and more amorphous, agglomerated particles. Because ethylenediamine serves as both a reducing agent and structure-directing ligand in the UO₂ particle synthesis process, the presence of numerous amorphous particles produced at the lowest pH examined (6.54) validates the hypothesis that lower reaction pH diminishes the efficacy of ethylenediamine's structure-directing functionality. We also show that relatively small changes in pH can modify particle morphology.

ACKNOWLEDGMENTS

The authors wish to thank the IAEA Environmental Sample Laboratory team for their expert advice and critical feedback throughout this work. The Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830. This work was sponsored by the US Department of Energy, National Nuclear Security Administration, Office of International Nuclear Safeguards.

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