Nuclear Science and Security Consortium
Virtual Scholar Showcase 2020

New Precursors for Actinide Nanomaterials

06/03/2020
Mark Straub
UC Berkeley
Introduction

Mark Straub

Advisors: John Arnold, Stefan Minasian

Focus Area: Radiochemistry and Forensics
Relevance to the NNSA Mission

- Microscopic particles are released during processing, transport, and burnup of nuclear materials\(^1\)
  - Can be analyzed for age, chemical form, and enrichment\(^2\)

- Certified reference materials (CRMs) of actinide nanomaterials: needed as controls for forensic assignments\(^{3,4}\)

- Developing synthetic routes to nanostructured CRMs:
  - Composition and morphology can be controlled with a detailed understanding of chemical bonding

**Project Overview**

- **Goal:** develop methods to access new uranium nanomaterials

<table>
<thead>
<tr>
<th>Isotropic nanomaterials</th>
<th>Anisotropic nanomaterials</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0D</strong></td>
<td><strong>1D</strong></td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>Nanorods, wires</td>
</tr>
<tr>
<td><strong>2D</strong></td>
<td><strong>3D</strong></td>
</tr>
<tr>
<td>Thin films, plates</td>
<td>Frameworks</td>
</tr>
</tbody>
</table>

- Many accessible compositions of $U_xO_y$
  - Controlling structure is challenging
  - Phase-pure nanomaterials are rare

Chemical vapor deposition (CVD) from uranium precursors:

![CVD process diagram]

Solution synthesis of UO₂ nanoparticles (NPs):

![Solution synthesis process diagram]

Routes to oxide nanomaterials

- **Synthesizing new uranium nanomaterials:**
  - Tunable precursors
  - Well-defined decomposition
  - Nucleation and growth control
Requirements for molecular precursors

- Decompose to form uranium oxide
  - Single pathway ideal

- Volatile (gas-phase methods) or soluble (solution methods)

\[ \text{Amidates} \]

Amidate ligand overview

- Metal oxide precursors
- Highly tunable
- Thermal properties can be controlled by changing R_1 and R_2
Synthesis of uranium amidate precursors

• Goal: new molecular precursors for UO$_2$ nanomaterials

\[ \text{UO}_4(1,4\text{-dioxane})_2 + 4 \rightarrow \text{U(TPTA)}_4 \]

light green crystals

• Characterized using nuclear magnetic resonance (NMR) spectroscopy and x-ray crystallography
Volatile uranium amidates

- Bis(alkyl)-substituted amidates may offer higher volatility
  - Advantageous for CVD precursors

\[ \text{U}^{4+}(1,4\text{-dioxane})_2 + 4 \quad \text{THF, 25 °C} \]

\[ 3 \text{ d} \quad - 4 \text{ KI} \]
\[ - 4 \text{ 18-crown-6} \]

emerald green crystals

- Significantly more volatile
**Proposed mechanism:**

- 1. Alkene elimination
- 2. Protonolysis
- 3. Nitrile elimination

**U(amidate)_4 decomposition**

\[
\text{U(amidate)
}_4 \xrightarrow{300 \, ^\circ C} \text{U(amidate)
}_3 \xrightarrow{-\text{Alkene}} \text{U(amidate)
}_2 \xrightarrow{-\text{Protonolysis}} \text{UO}_2
\]
• Proposed mechanism:
  - 1. Alkene elimination
  - 2. Protonolysis
  - 3. Nitrile elimination
U(ITA)$_4$ decomposition

300 °C
16 h

* = Amide
* = Nitrile
* = Isobutylene
Collaboration for uranium oxide CVD

- Established a collaboration with Dr. Sanjay Mathur at the University of Cologne for chemical vapor deposition (CVD) of UO$_2$ films

- Shipped precursors to Cologne, worked together to design deposition experiments

CVD of UO$_2$ from amidate precursor

- Precursor temp: 160 °C
- Si substrate temp: 500 °C
- Pressure: $7.5 \times 10^{-7}$ torr

With Dr. Sanjay Mathur and coworkers
• Custom precursor design → new UO₂ nanostructures!

With Dr. Sanjay Mathur and coworkers
• Custom precursor design $\rightarrow$ new UO$_2$ nanostructures!

With Dr. Sanjay Mathur and coworkers
Powder x-ray diffraction (PXRD)

- Preferred growth along \{111\} planes

With Dr. Sanjay Mathur and coworkers
• What other high surface area UO₂ nanomaterials can we access using a molecular precursor approach?

With Dr. Sanjay Mathur and coworkers
Templated actinide dioxide particles

• Ultra-small (< 3 nm) actinide dioxide (AnO$_2$) particles can be released during burnup and reprocessing of nuclear fuels$^1$

• Models for these AnO$_2$ NPs are difficult to isolate
  – Aggregation is common at small sizes

• Solution: use a template to control particle size!

Formation of an inclusion compound

- Molecular precursors can be loaded into a porous framework, then decomposed *in situ* to $\text{AnO}_2$ NPs

$\text{An} = \text{U}, \text{Th}$

- COF-5 absorbs up to 50 wt% $\text{An(hfa)}_4$

$10^{-4}$ torr (static vacuum) 2 d
AnO$_2$@COF-5 nanoparticle synthesis

- AnO$_2$ particles confined to the pore size of the COF
Mechanistic control of products

• Hydrolysis of An(hfa)$_4$@COF-5 with water vapor gives AnO$_2$:

\[
\text{H}_2\text{O vapor} \quad 200 \, ^\circ\text{C} \quad \text{AnO$_2$@COF-5}
\]

\[
\text{An} = \text{U, Th}
\]

• Pyrolysis instead gives AnF$_4$ via fluoride abstraction:

\[
\text{Argon} \quad 300 \, ^\circ\text{C} \quad \text{AnF$_4$@COF-5}
\]

\[
\text{An} = \text{U, Th}
\]
Conclusions

• Custom molecular precursors → new actinide materials!
  – UO$_2$ thin films (2-D)
  – UO$_2$ nanotrees (3-D)
  – Templated UO$_2$ and ThO$_2$ nanoparticles (0-D)

• These methods could be used to produce nanostructured UO$_2$ CRMs with any desired $^{238}$U/$^{235}$U ratio
NSSC experience

NSSC-LANL Keepin Nonproliferation Summer Program (2017)

• **Mentors:** Jackie Kiplinger and Julianna Fessenden
• **Project:** review article on modern pre- and post-detonation nuclear forensics

Radiochemistry and Nuclear Forensics Course (TA)

• Hands-on lab course introducing students to radiochemical methods
Beyond the PhD

• Seeking job opportunities at national labs!
  – Graduating this year

• Interests:
  – Inorganic chemistry and materials science
  – Nuclear energy and waste
  – Renewable energy technologies
Acknowledgements

**UC Berkeley:**
Prof. John Arnold
Michael Boreen
Jade Fostvedt
Joe Brackbill
Erik Ouellette
Christopher Ye
Anukta Jain

**LBNL:**
Dr. Stefan Minasian
Dr. Liane Moreau
Dr. Yusen Qiao
Dominic Russo
Jacob Branson
Ziad Shafi
Acknowledgements

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003180.

Disclaimer: This presentation was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.