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Tying the nanoscale science to bulk scale energy and environment applications

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Technical Focus

- Technical Focus:
  Chemical study of confinement and reactivity of ions and molecules
  - capture by zeolites, metal-organic frameworks (MOFs), clays and amorphous silicas
  - capture by reduction (γ-radiolysis, electron beam)

- The study of Structure-Property Relationships on the nanoscale enabling the informed testing of the materials for a wide range of interests.

- Structure analysis of host-guest systems on the nanoscale has led to strong collaborations with staff scientists at the APS/ANL for synchrotron & Pair Distribution Function (PDF) analysis, SNS/ORNL for Inelastic Neutron Scattering

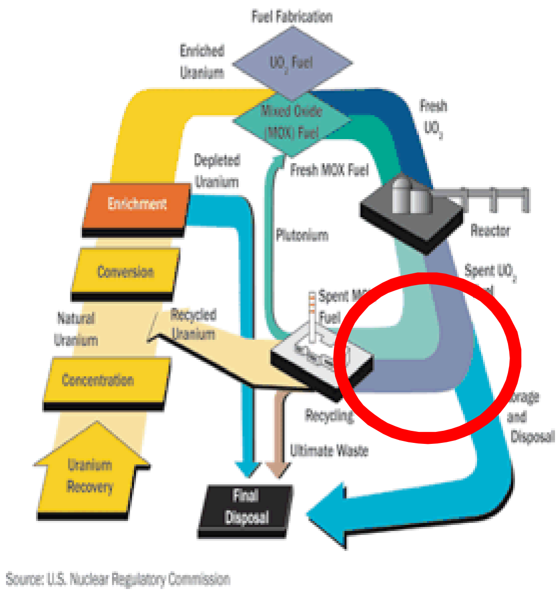
- Structure analysis by microscopy, Ion Beam Lab (BES funded) at Sandia

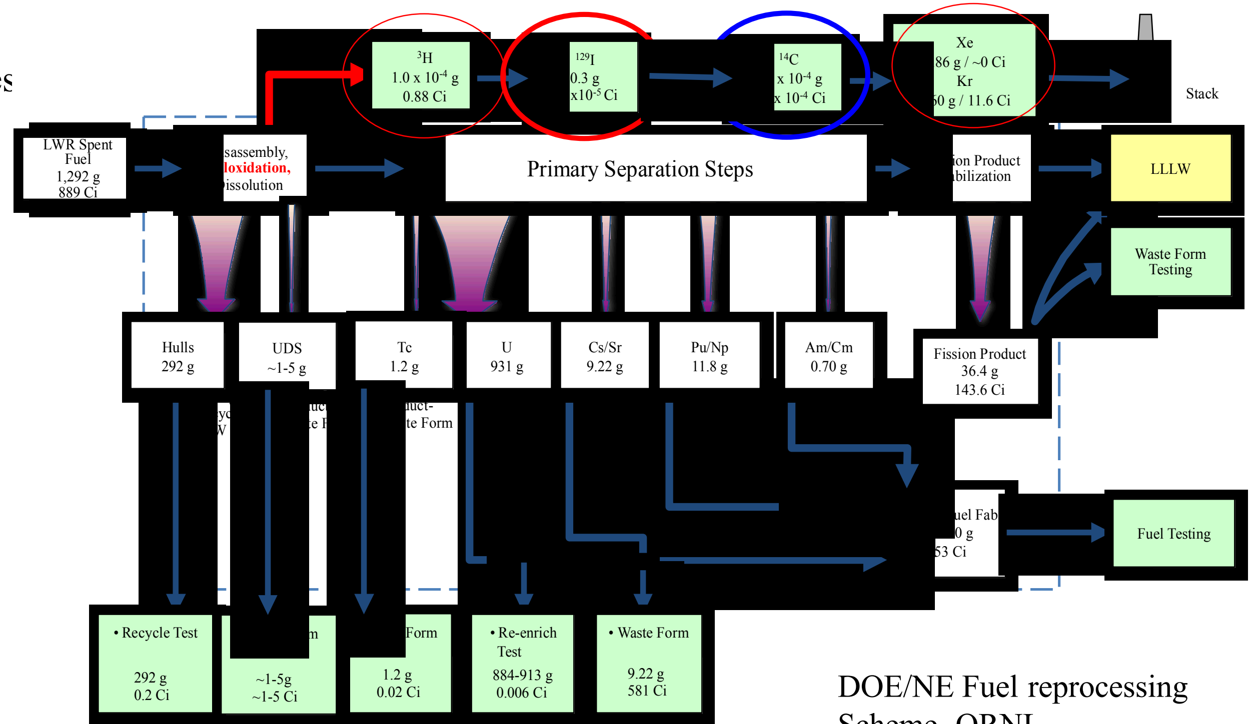
- Strong Interdisciplinary Teams working in concert.
  diverse programs require diverse teams
  chemists, engineers, computational modelers, national labs, universities and industry

- Mentoring: postdocs, young staff and collaborating young professors,
  strong support of women and minorities into the sciences

Applications: Recovery of fission gases, Daughter products, and Dissolved fuel metals and oxides

Reprocessing: capture on nonburnable volatile fission products and lesser actinides

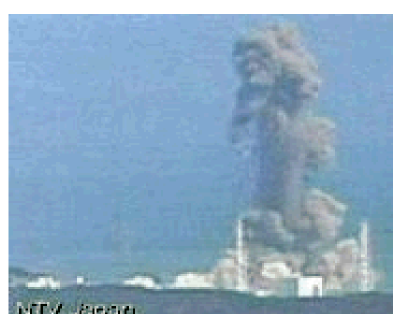




DOE/NE Fuel reprocessing Scheme, ORNL

Legacy, Accident or Produced rad aqueous waste requiring highly specific ion capture

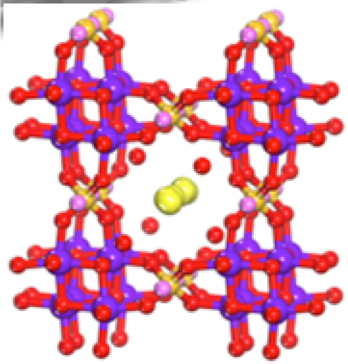
Fukashima Daiichi Nuclear Power Plant explosion 2011 I^{129}, I^{131} volatile gas released; Cs^{135}, Cs^{137} & Sr^{90} aqueous released *(www.IAEA.org)*

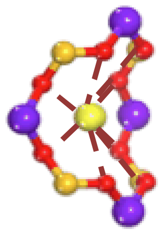


Hanford Tank Farm

Elements, Dec 2006

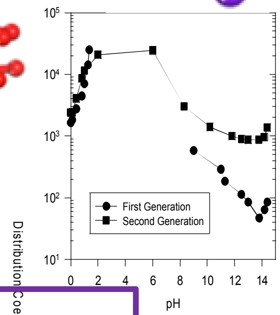
Example 1: Nanoporous Materials
Highly Selective Ion and Gas Capture

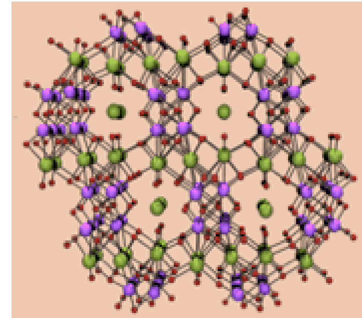




CST, Molecular Sieve:
R&D100 1996
JACerS, 2009, *92(9)*, 2144
JACerS, 2011, *94(9)*, 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

CST, Cs^+ removal from water to Pollucite Waste Form
US Patents *6,479,427; 6,110,378*

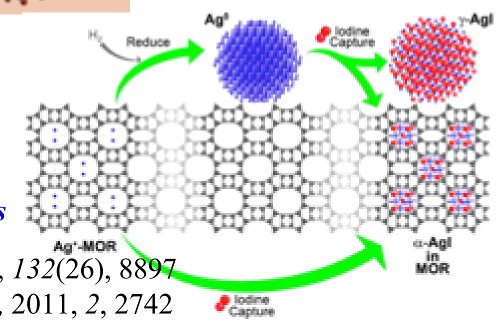




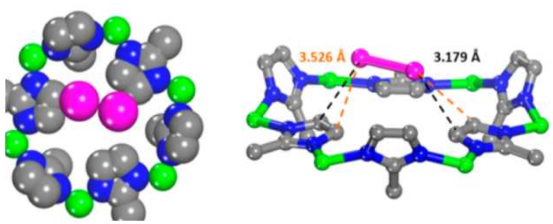
SOMS Molecular Sieve,
Sr^{2+} getter,
1-step to Perovskite WF
JACS, 2002,*124(3),* 1704
US Patent *7,122,164;* 2006

Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

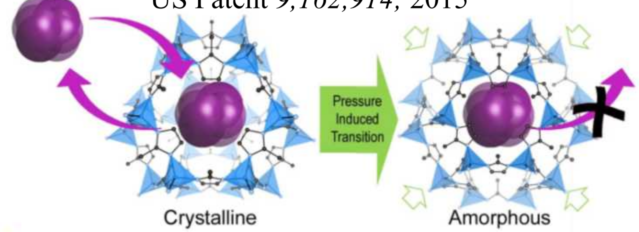
Ag-MOR Zeolite,
$I_2(g)$ capture & mechanisms
JACS, 2010, *132*(26), 8897
JPC Letters, 2011, *2*, 2742

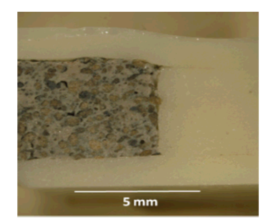


I_2/ZIF-8 MOF,
Encapsulation to Waste Form
JACS, 2011,*133(32)*,12398
JACS 2013, *135*, 16256



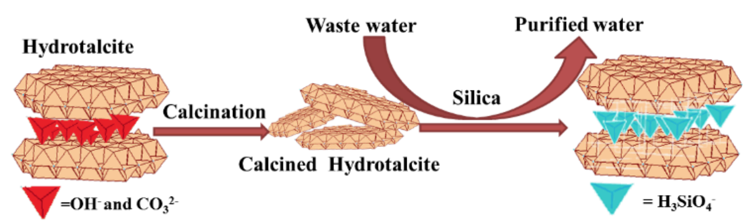
MOF *Amorphization for Gas Storage*
JACS, 2011,*133*(46),18583
US Patent *9,162,914;* 2015





Glass Composite Waste Form:
JACerS, 2011, *94*(8), 2412
US Patent *8,262,950*; 2012

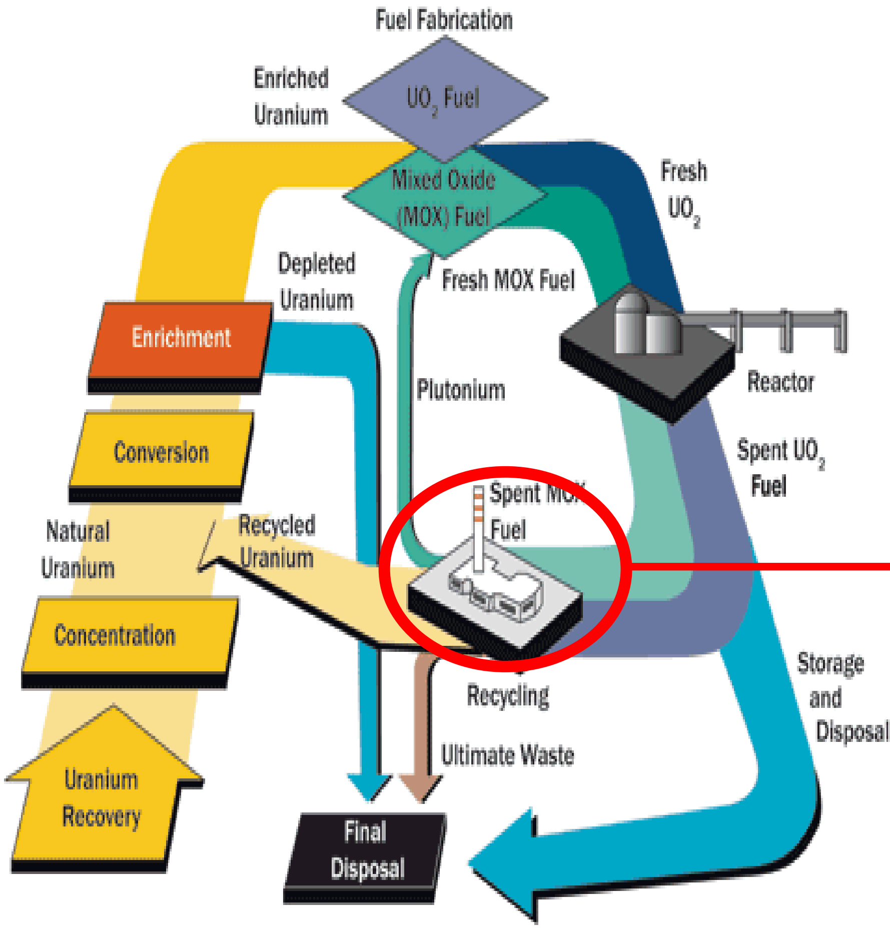
MOF Cu-BTC*:*
I_2 from Humid Gas Stream
Chem. Mater. 2013, *25*(13), 2591



Water Purification/ Silica Ion Exchange:
J. Water Proc. Eng. **2017**, *17*, 117; **2017**, *20*, 187

Capture and Storage of Volatile Fission Gases from Nuclear Fuel Reprocessing and/or Nuclear Accidents

Nuclear Fuel Reprocessing (NE)



Source: U.S. Nuclear Regulatory Commission

Separations of non-burnable volatile fission products and lesser actinides

Fundamental materials studies into
- Why known materials work well

and

- Synthesis and Development of new and improved separations materials

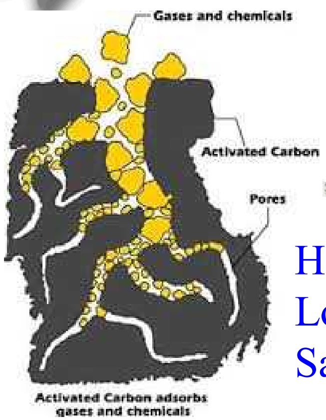
Utilizing state-of-the-art

Predictive modeling
Synthesis methods
Characterization methods
On-line testing in complex streams

May 2012, Jan 2013
Participated in joint JNFL, Areva, and DOE/labs for Iodine sorption and waste forms (at Rokkasho, La Hague & CEA)

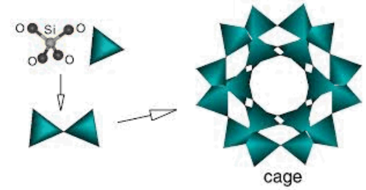
US Regulatory Conditions Indicate Capture of Volatile Fission Gases: orders of magnitude ***Greater*** *than current standards world wide.*

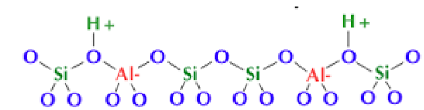
Nanoporous Gas Adsorption Materials



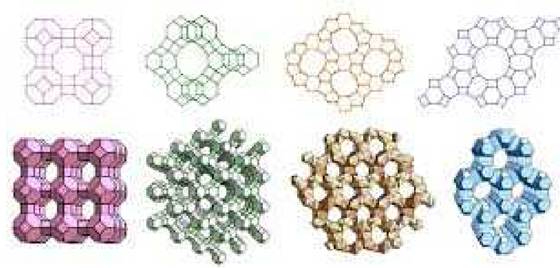
Higher sorption capacity
Lower Selectivity
Saturation from background gases

Activated Carbon/Charcoal > 500 m^2/g



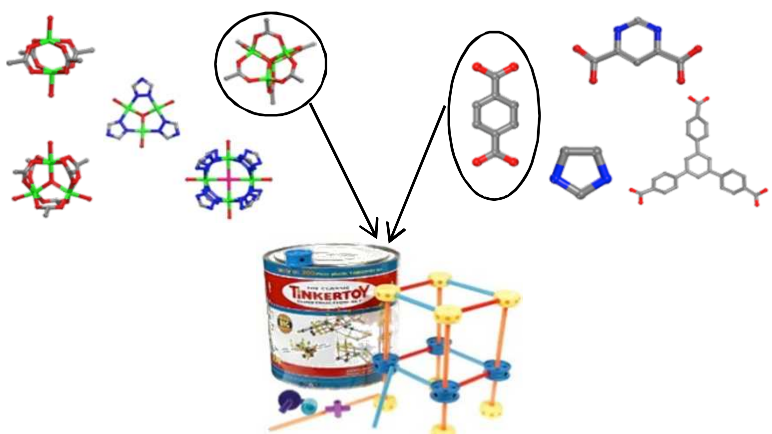


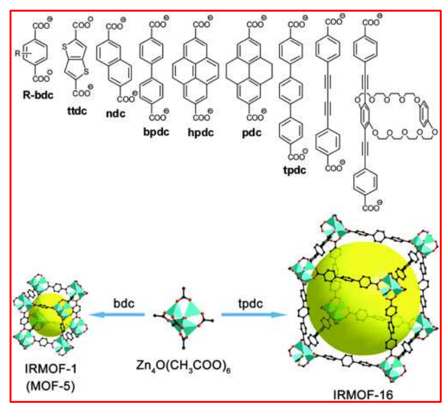
Lower Sorption Capacity
Size & Chem Selectivity (?)



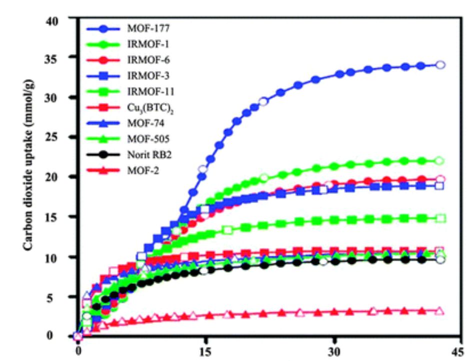
Zeolite~100 m^2/g

Metal-Organic Frameworks (MOFs) >1000m^2/g





Target: Extremely High Selectivity & High Capacity



Yaghi, JACS, 2005,127, 17998

Ag-MOR zeolite, Traditional Iodine Capture Material

- While I^{129} is only found in small concentrations in nuclear effluent, the effective capture and storage of iodine is critically important to public safety due to its involvement in human metabolic processes and its long half-life (~10^7 years).

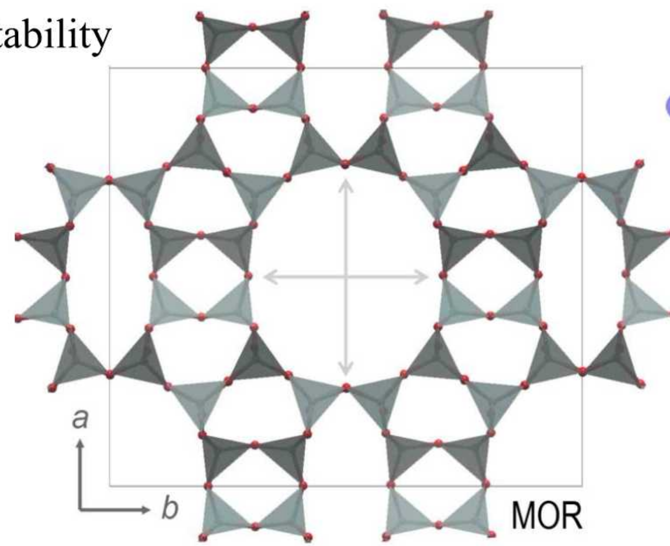
- Silver Mordenite (MOR) is a standard iodine-getter, although the iodine binding mechanism remains poorly defined. Presumably an iodide forms within the zeolite's pores

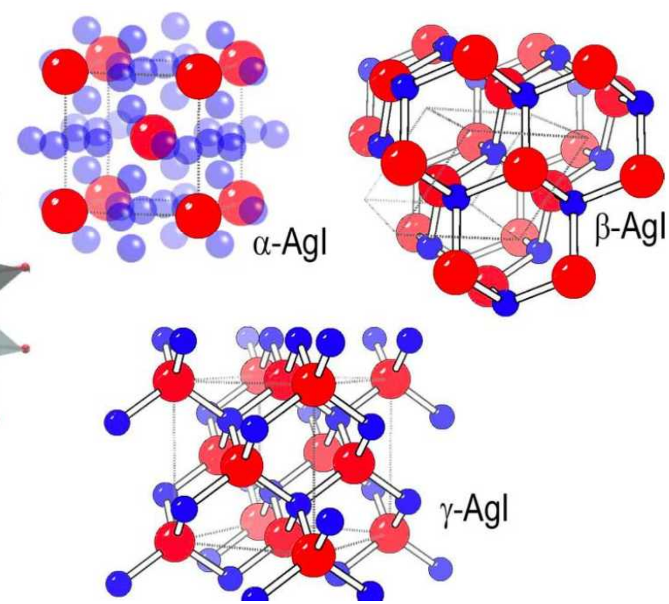
- Understanding **Structure-Property Relationship between Nanoscale and Bulk effects**
  - To optimize capture
  - Impacts processing for long term storage
  - To predict long term stability

MOR, Mordenite

$X_2Al_2Si_{10}O_{24} \cdot 7(H_2O)$

12 MR, 7.0 x 6.5Å

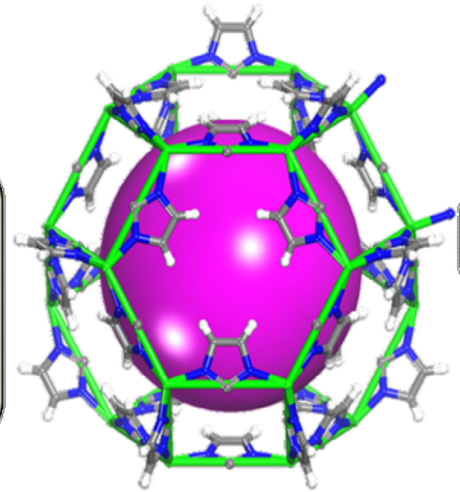




Judicious Selection of "Ideal" MOF Candidate

Traditionally zeolites/molecular sieves are used as baseline materials for selectivity and sorption. materials are tuned for high selectivity and high capacity.

Basolite Z1200, ZIF-8
Constricted Pore Opening (≈ 3.4Å)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O



I_2@ZIF-8 ~ 125 wt.% I_2

JACS, **2011**, *133*(32),12398

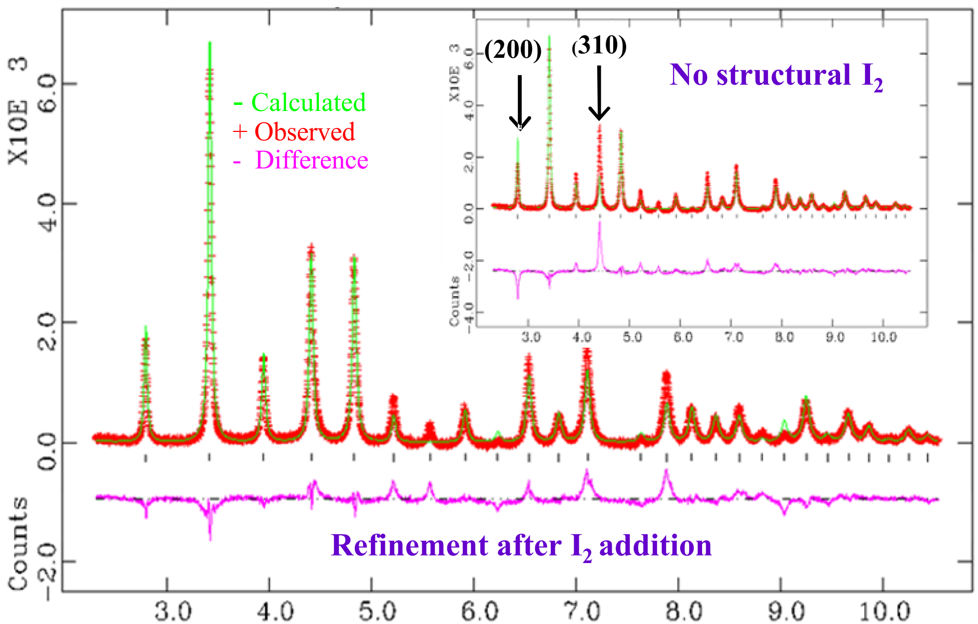
Pre-requisites

- Restrictive pore apertures to impart molecular selectivity for a directional diffusion of iodine (~3.35 Å)
- Large surface area and pore volume
- High *chemical*, *thermal*, and *moisture* stability

ZIF-8 Park, K.S. et.al *PNAS* **2006**, *103,* 10186.

- ✓ The β-cages, 11.6 Å in diameter, are connected via six-member ring (6 MR) apertures of ~3.4 Å
- ✓ Surface area ZIF-8 = 1,947 m^2 g^{-1} and Pore volume= 0.663 cc g^{-1}
- ✓ Chemically stable in boiling solvents (including water), and thermally stable up to 550°C

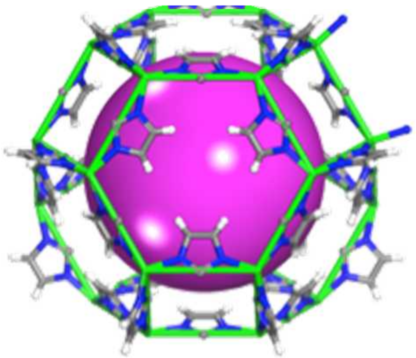
High-Resolution Synchrotron-based XRD



Calculated, observed and difference spectrum of 0.4 I/Zn loading of I_2@ZIF-8 after I_2 inclusion in structure refinement by Rietveld analysis (inset: before I_2 inclusion).

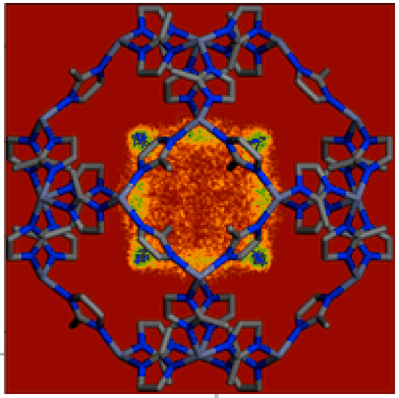
- Sample crystallinity is maintained up to ~1.3 I/Zn loadings
- Bragg reflections broaden significantly > 1.3 I/Zn
- difficult to distinguish from the pronounced diffuse features in the "background"
- MOF lattice contracts to accommodate increased I_2 loadings
- Not enough structural resolution obtainable from XRD

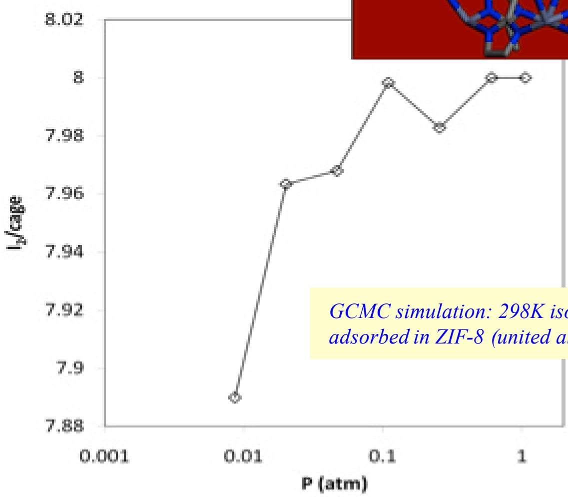
Integration of Experiment & Modeling to Identify Chemical Reasons for I_2 Sorption



Molecular modeling

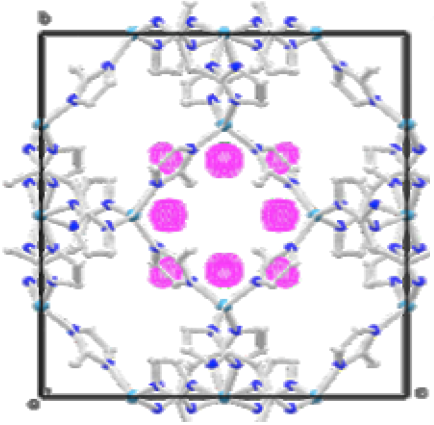
MD Simulation:
Electron density determined



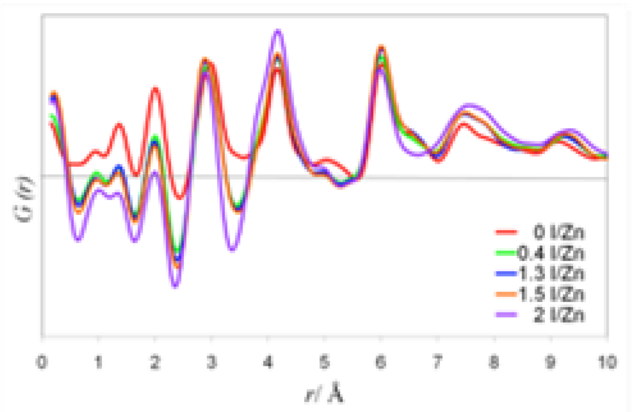


GCMC simulation: 298K isotherm of I_2 adsorbed in ZIF-8 (united atom model)

Complementary local and long-range structural probes



Difference-Fourier analysis map

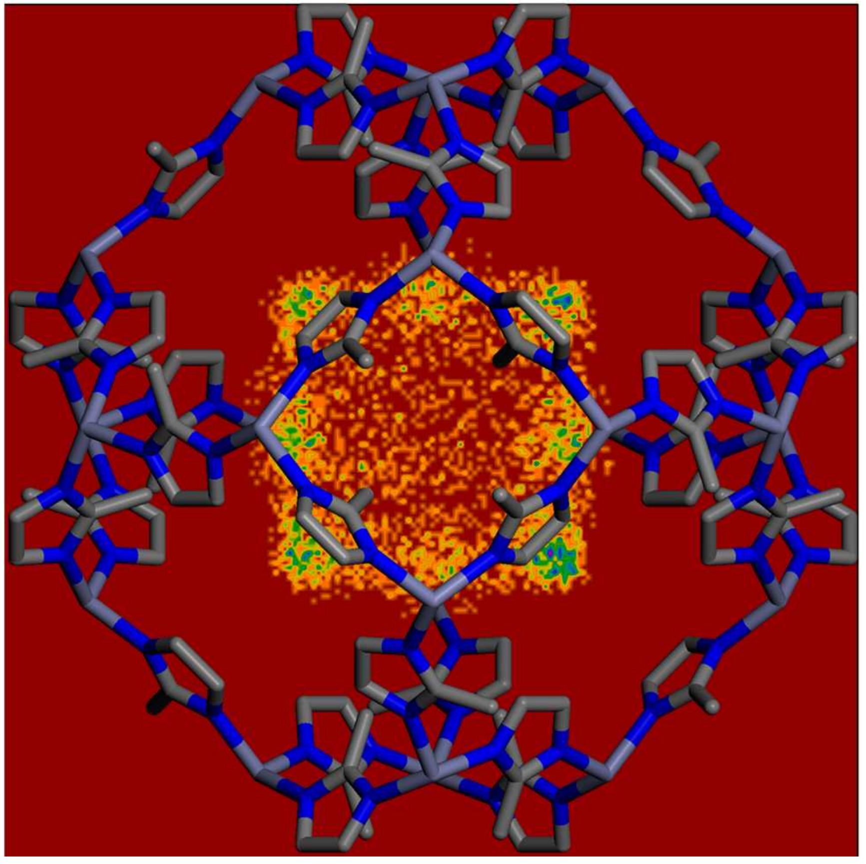


Pair Distribution Function analysis – ANL/APS synchrotron

J. Amer. Chem. Soc., **2011**, *133* (32), 12398.

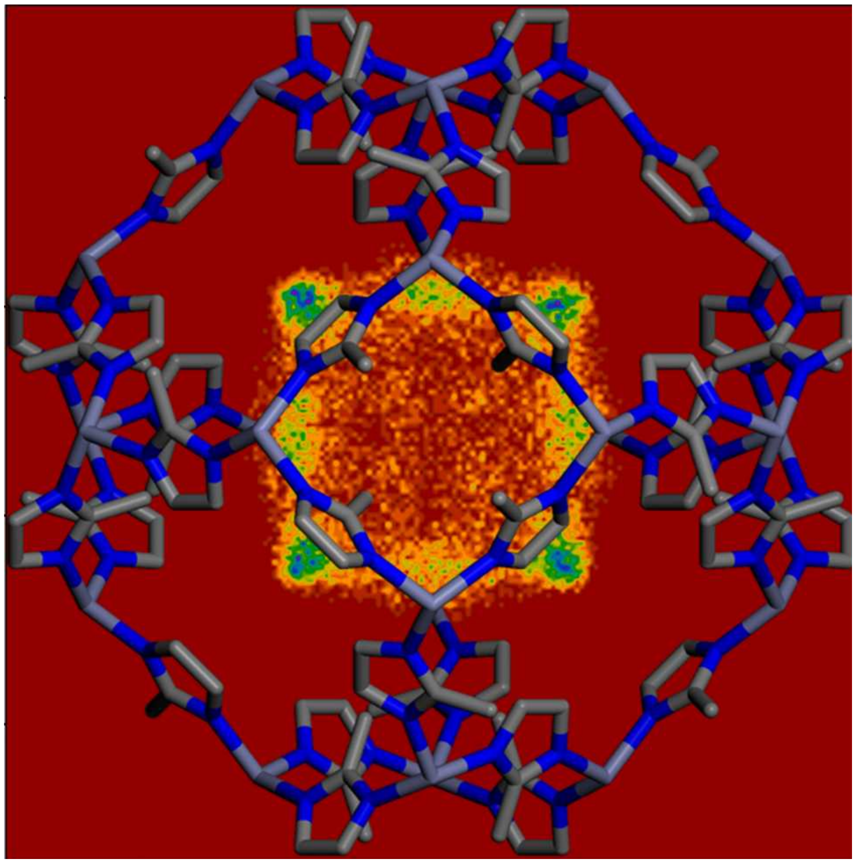
MD simulations Predict I_2 Location and Loading Capacities Per Cage

0.5 I/Zn (~1.5 I_2 per cage)

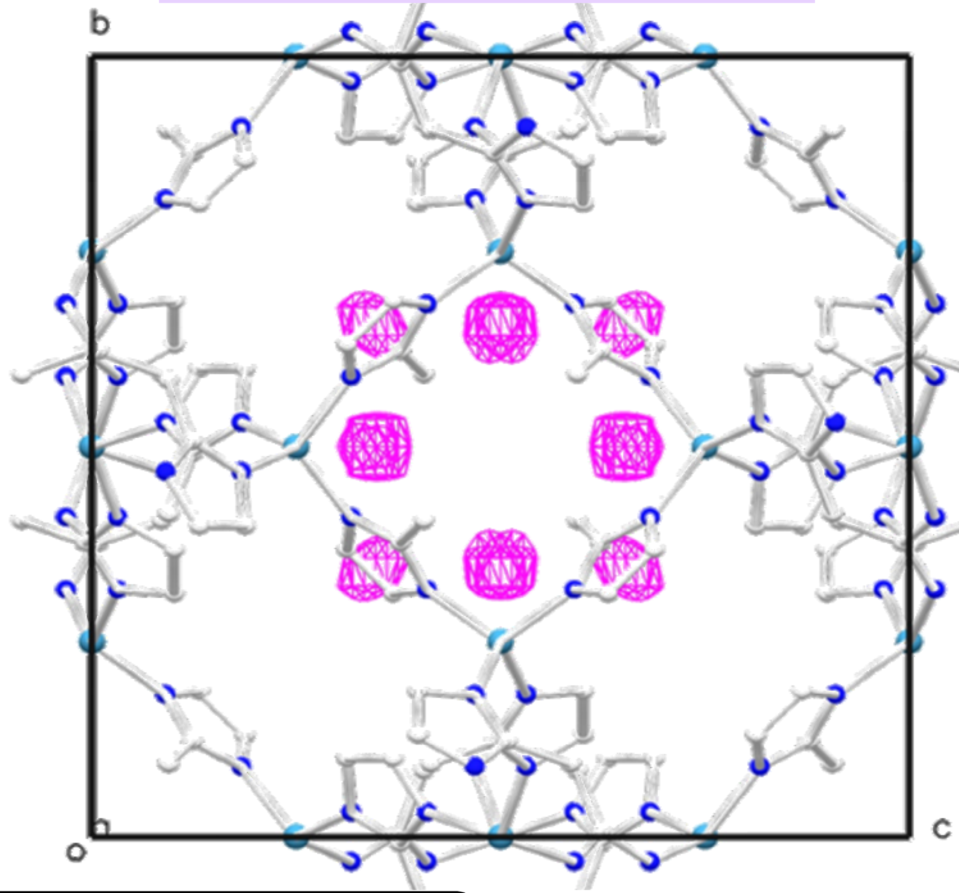


MD Simulations Closely Match Modeling Predictions of I_2 Electron Density

MD Simulation Analysis



Crystallographic Data: Difference-Fourier analysis map



2 I/Zn (~6 I_2 per cage)

To Date, *Pair Distribution Function* (PDF) Analysis

Use of high energy X-rays and large area detectors key to <u>structure resolution of heavier elements such as *Silver*</u>

*The PDF, **G(r)***, is related to the ***probability*** of finding an atom at a distance ***r*** from a reference atom. It is the Fourier transform of the total structure factor, ***S(Q)***.

$$\boldsymbol{G(r)} = 4\pi r\,\rho_0[\underbrace{\boldsymbol{g(r)}-1}_{\text{probability}}] = (2/\pi)\int Q[\underbrace{\boldsymbol{S(Q)}-1}_{\text{structure factor}}]\sin(Qr)\,dQ$$

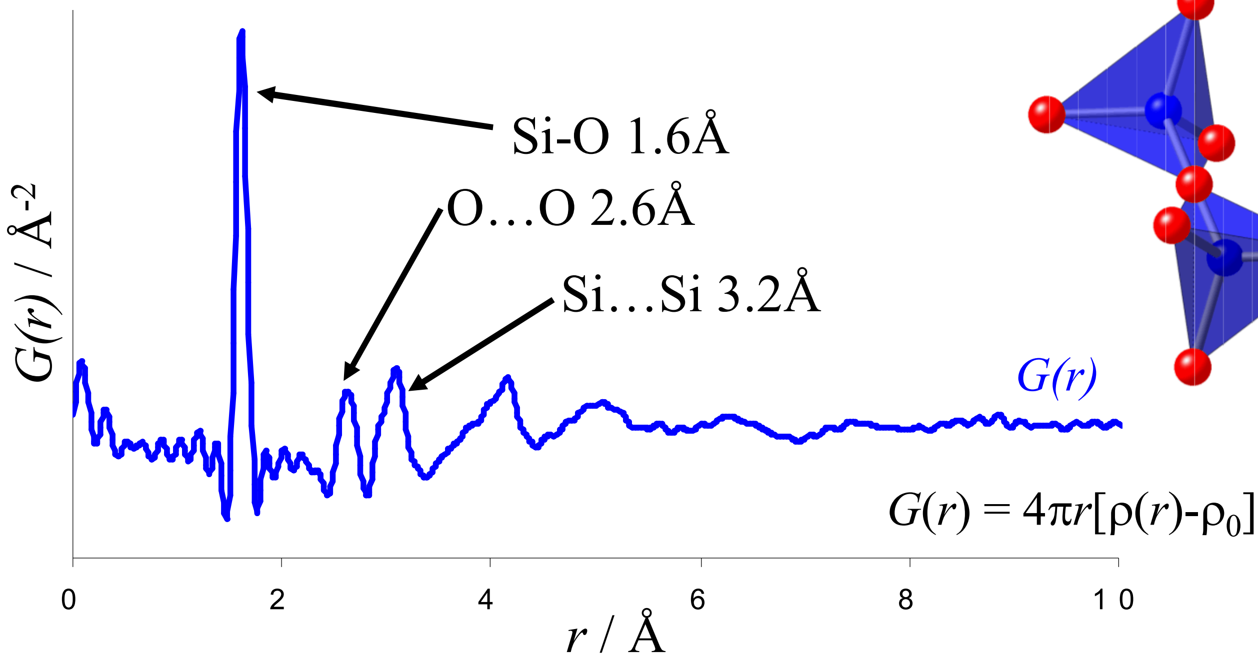
The structure factor, ***S(Q)***, is related to coherent part of the diffraction intensity

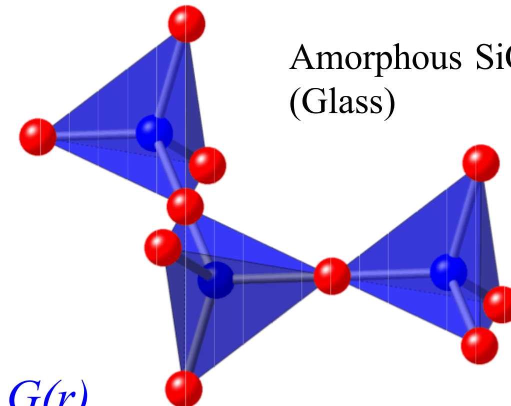
$$\boldsymbol{S(Q)} = 1 + [\underbrace{\boldsymbol{I^{coh}(Q)}}_{\text{diffraction intensity (corrected)}} - \sum c_i|f_i(Q)|^2] / |\sum c_i f_i(Q)|^2$$

Apply corrections for background, absorption, Compton & multiple scattering

PDF Provides Insight Into Short Range Structural Order

- a weighted histogram of ALL atom-atom distances





Amorphous SiO_2 (Glass)

Peak position ⟷ Bond length / distance

Peak area ⟷ Coordination #, scattering intensity

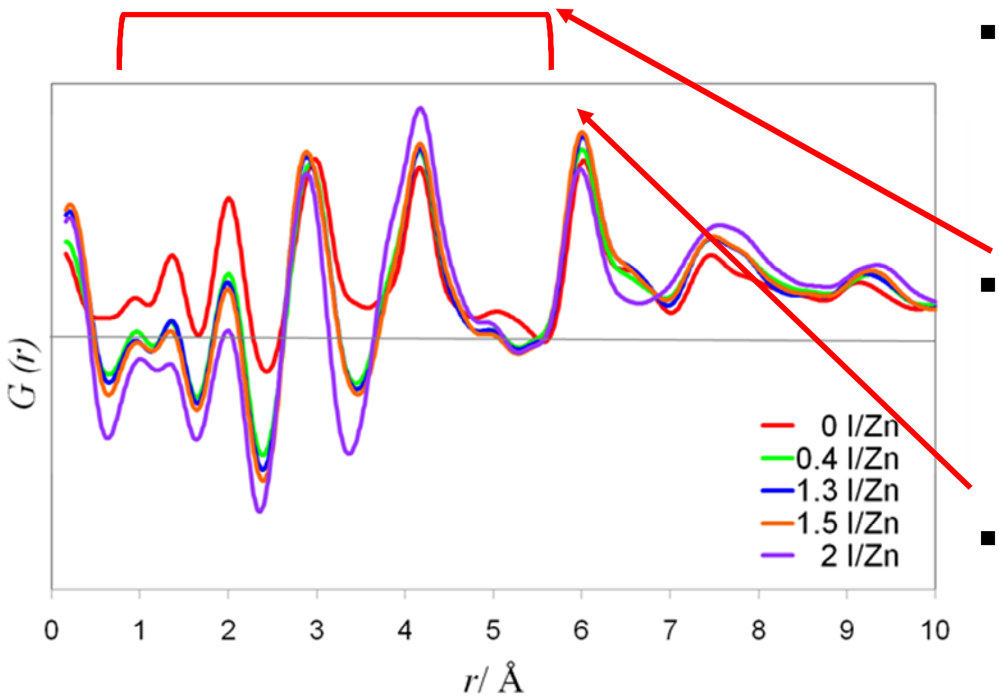
Peak width ⟷ Disorder, bond angle distribution

Peak r_{max} ⟷ Particle size, coherence

→ **Structural Modeling**

Application to Zeolites to Examine Short Range Interactions of Guests in Pores

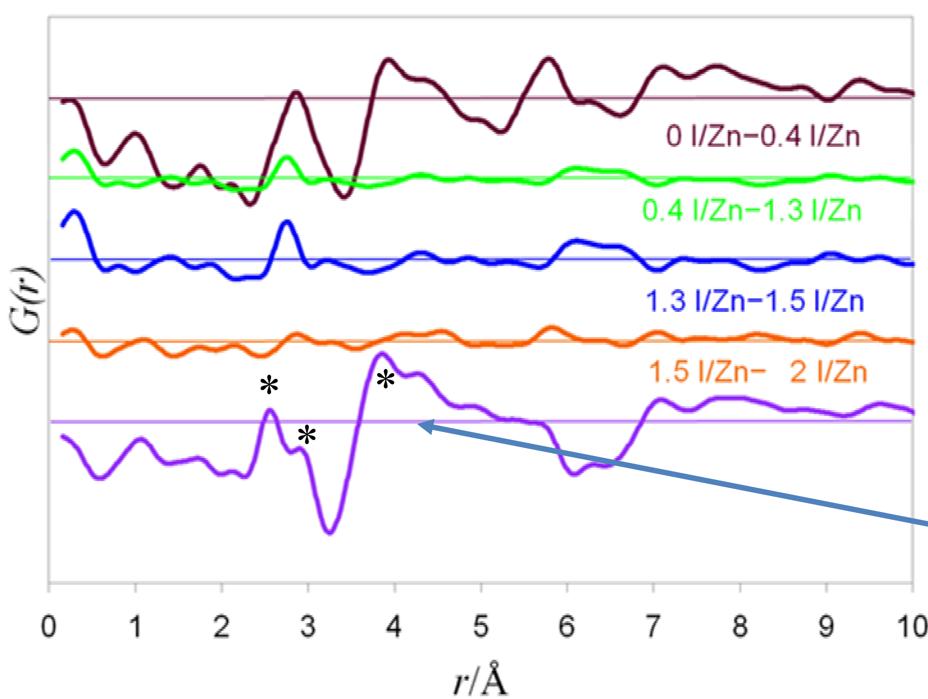
PDF of I2@ZIF-8



short-range order and framework connectivity are maintained at all loading levels

- The PDF method- a weighted histogram of the atomic distances, independent of sample crystallinity
- Below ~6 Å, the *MOF cage features are retained in the PDF at all I_2 loading levels*
- The persistence of the peak at ~6 Å, corresponding to the Zn-(MeIM)-Zn' distance
- >1.3 I/Zn lose long range structural information though individual cages maintain crystalline integrity

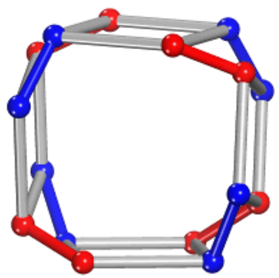
Differential PDF Analysis (d-PDF) subtraction of framework for only I_2 information

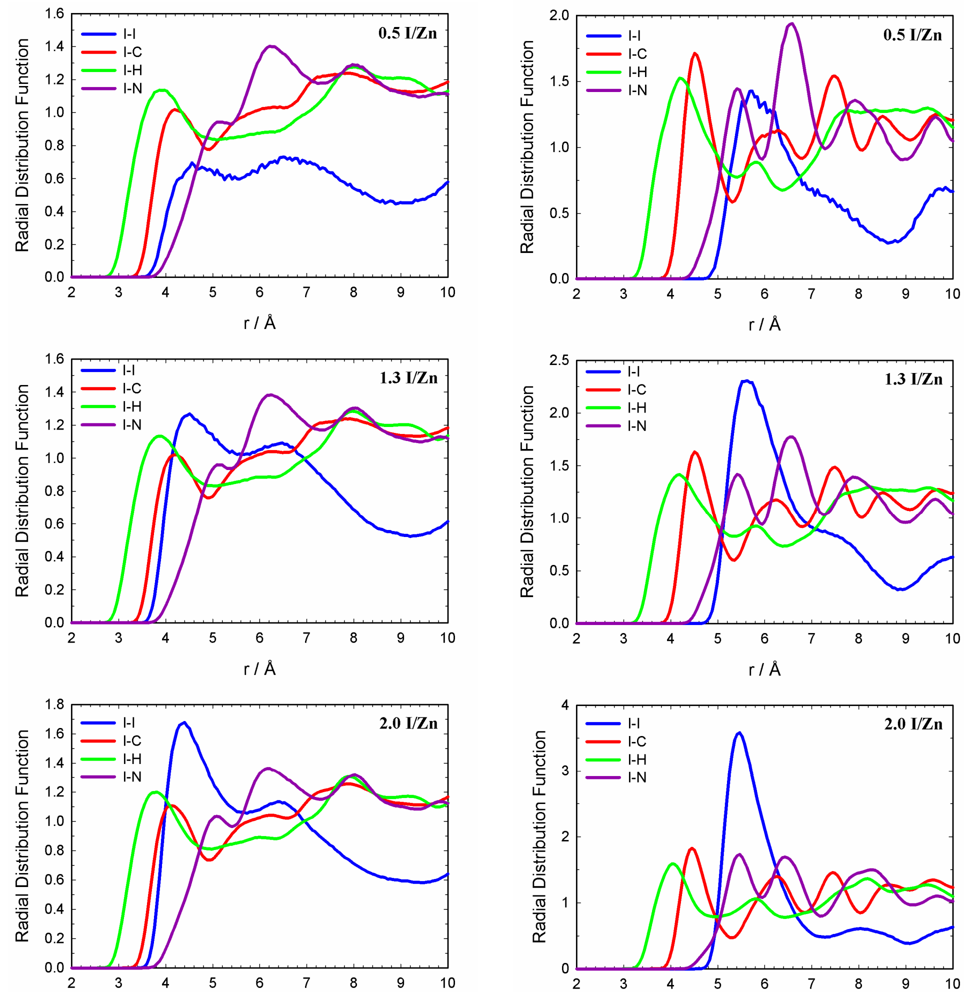


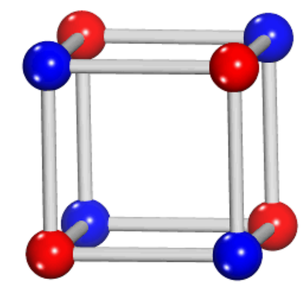
- Differential analysis applied to isolate I_2 guest molecules contributions
- Incremental I_2 loading up to 1.3 I/Zn peaks at 2.75 Å, 3.23 Å, 4.29 Å, 4.91 Å, 5.46 Å, 6.01 Å, and 6.61 Å
- I_2 loading >1.3 I/Zn: changes observed to MOF cage structure
  - new peaks 2.56 Å, 2.94 Å, and 3.79 Å
  - intensity changes for peaks 4.29 Å. 4.91 Å, and 3.23 Å

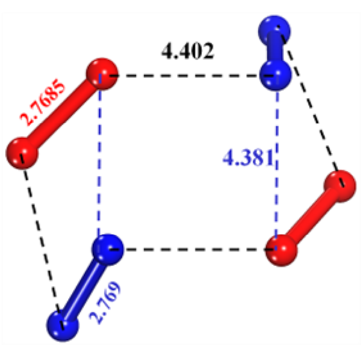
At loadings above 1.3 I/Zn, rearrangement of I_2 molecules required inside cage

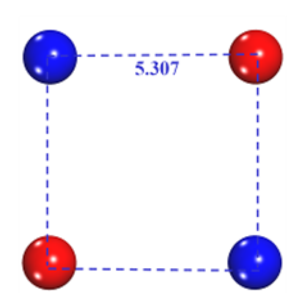
Experimental−Modeling Agreement Radial Distribution Functions (RDFs) for Diatomic and United-Atom Models





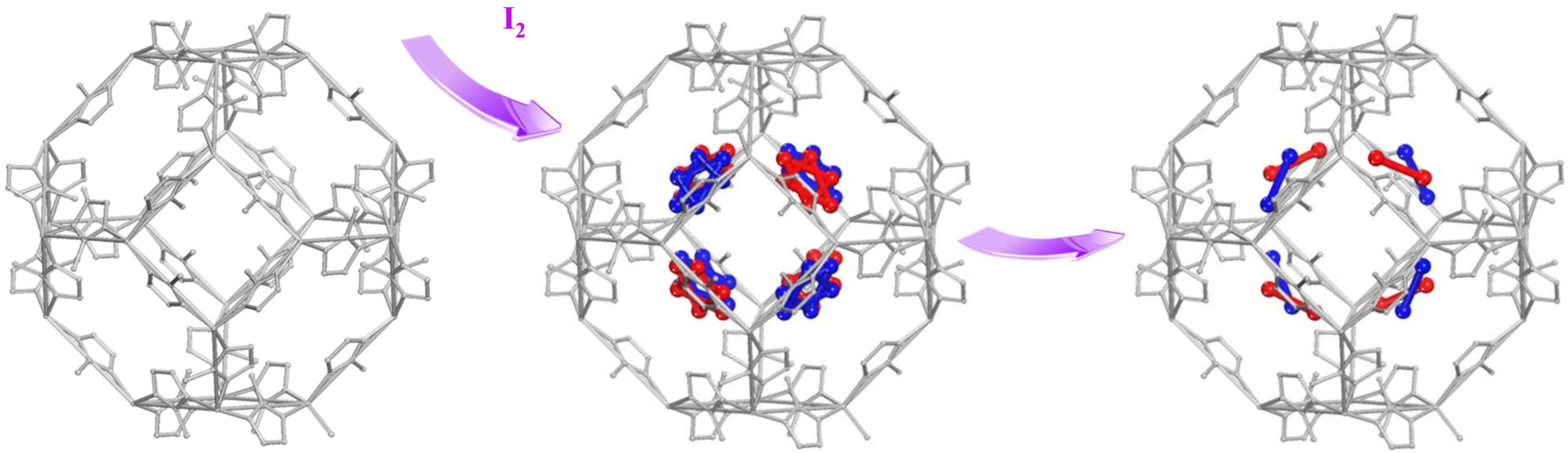






Good agreement between crystallography, PDF and modeling regarding nearest neighbors distances

Combined Analyses:
Determination of I_2 Binding Locations inside ZIF-8 Pore



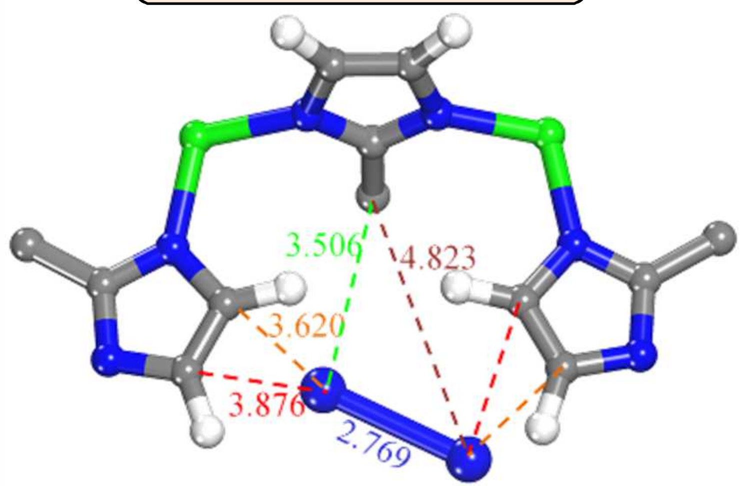
Activated β-cage

Dynamically disordered I_2 molecules

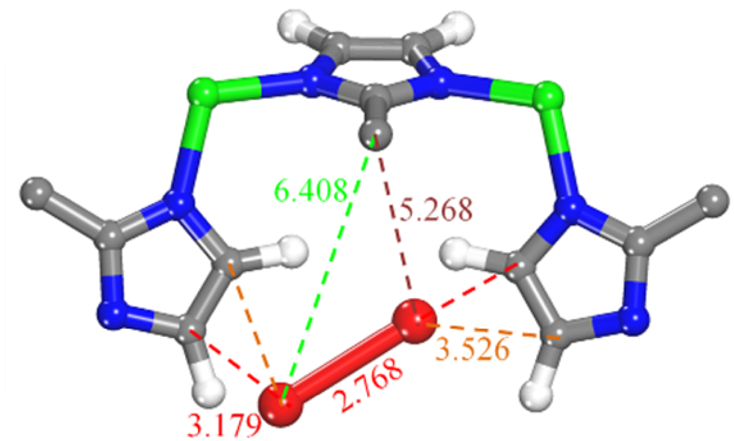
Refined I_2 sites:
I_a (blue) and I_b (red)

Two distinct I_2 binding site: I_a and I_b Appears site I_a has preferential binding, more thermodyamically stable?

I_a site



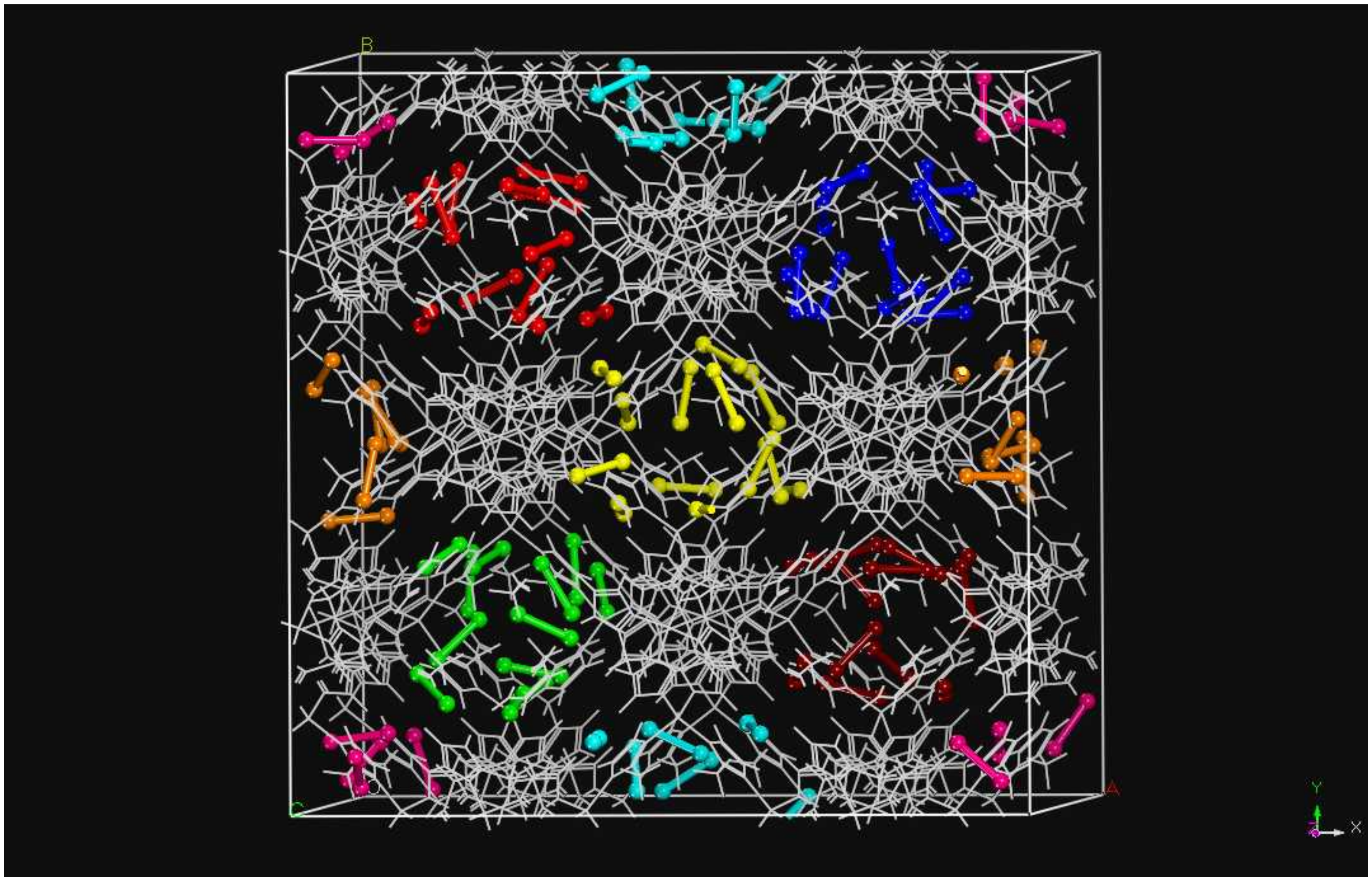
I_b site



I_2 site occupancy and $I_2 \cdots$MeIM close contacts in I_2@ZIF-8

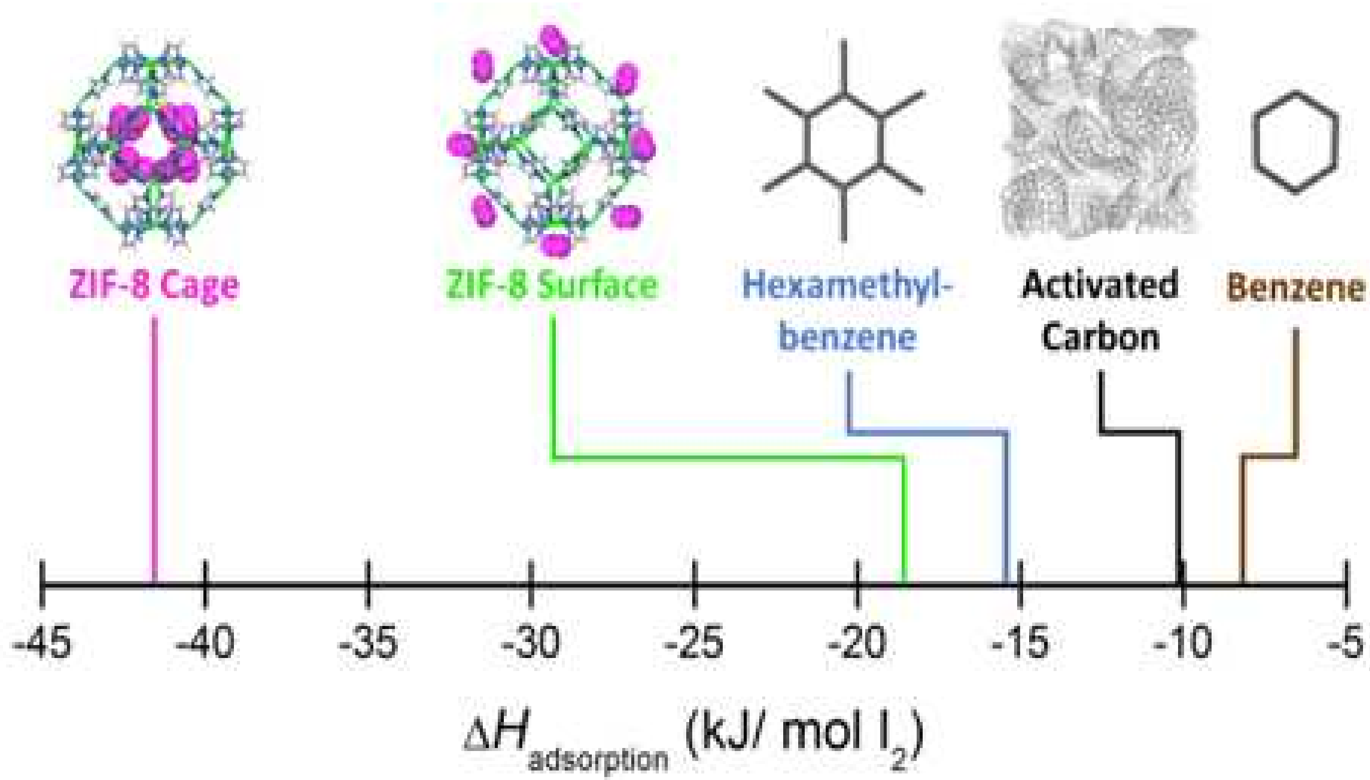
I_2 site	Site occupancy		Contacts with MeIM	
	0.4 I/Zn	1.3 I/ Zn	C (CH_3)	C(H=CH)
I_a	0.28	0.88	3.506 Å; 4.823 Å	3.620 Å; 3.876 Å
I_b	0.14	0.38	5.268 Å; 6.408 Å	3.179 Å; 3.526 Å

Dynamics of I_2 Within Cages: No Predicted Mobility of Gas Molecules In/Out of Individual Cages



Metal Organic Frameworks (MOFs) for fission gas adsorption: iodine (I_2)

In collaboration with J. Hughes and A. Navrotsky, UCDavis

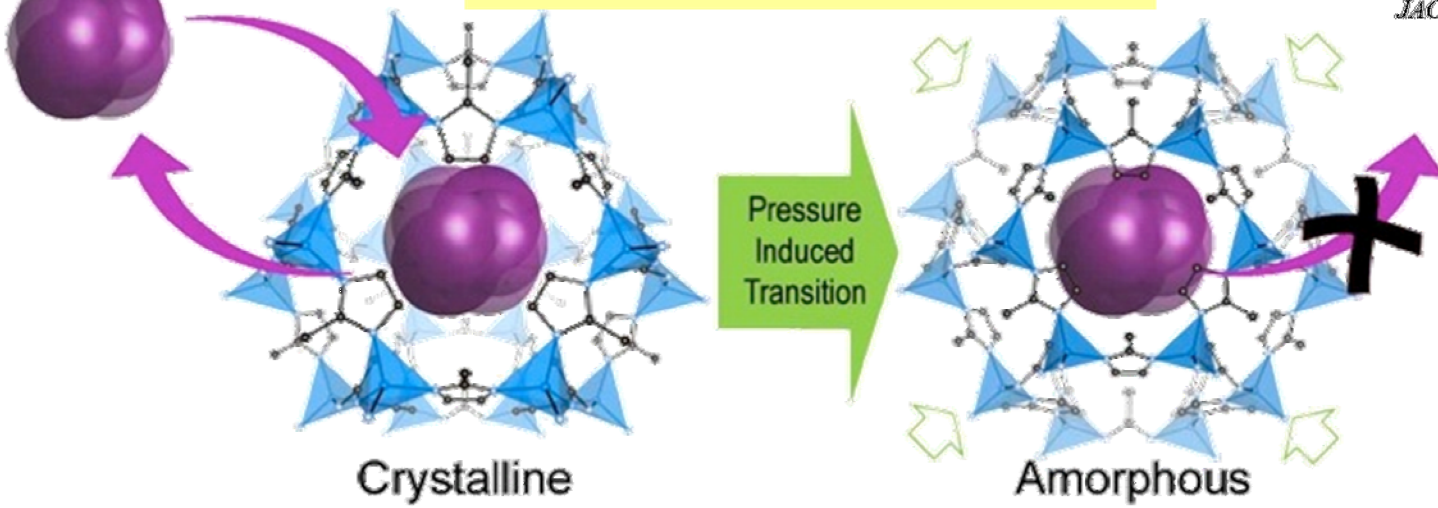


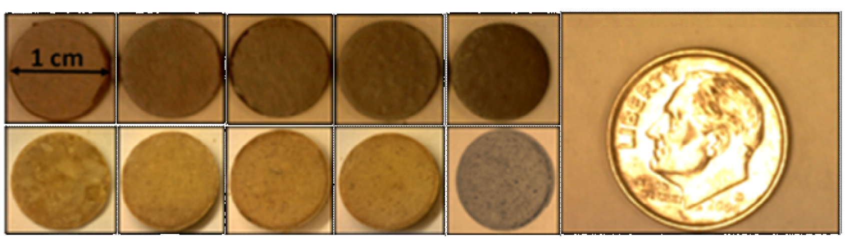
JACS, **2013,** 135(44), 16256

I_2@ZIF-8 Pressure-Induced Amorphization of Trapped Gases: Enhanced Retention

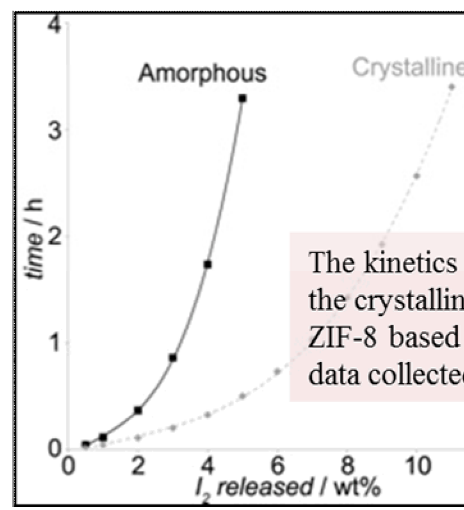
Secure consolidated interim storage before incorporation into a long term waste form.

Chapman, Nenoff, et al., *JACS* **2011**, *133*(46), 18583.





Crack free pellets of iodine loaded ZIF-8 powders were obtained by applying uniaxial mechanical pressure.

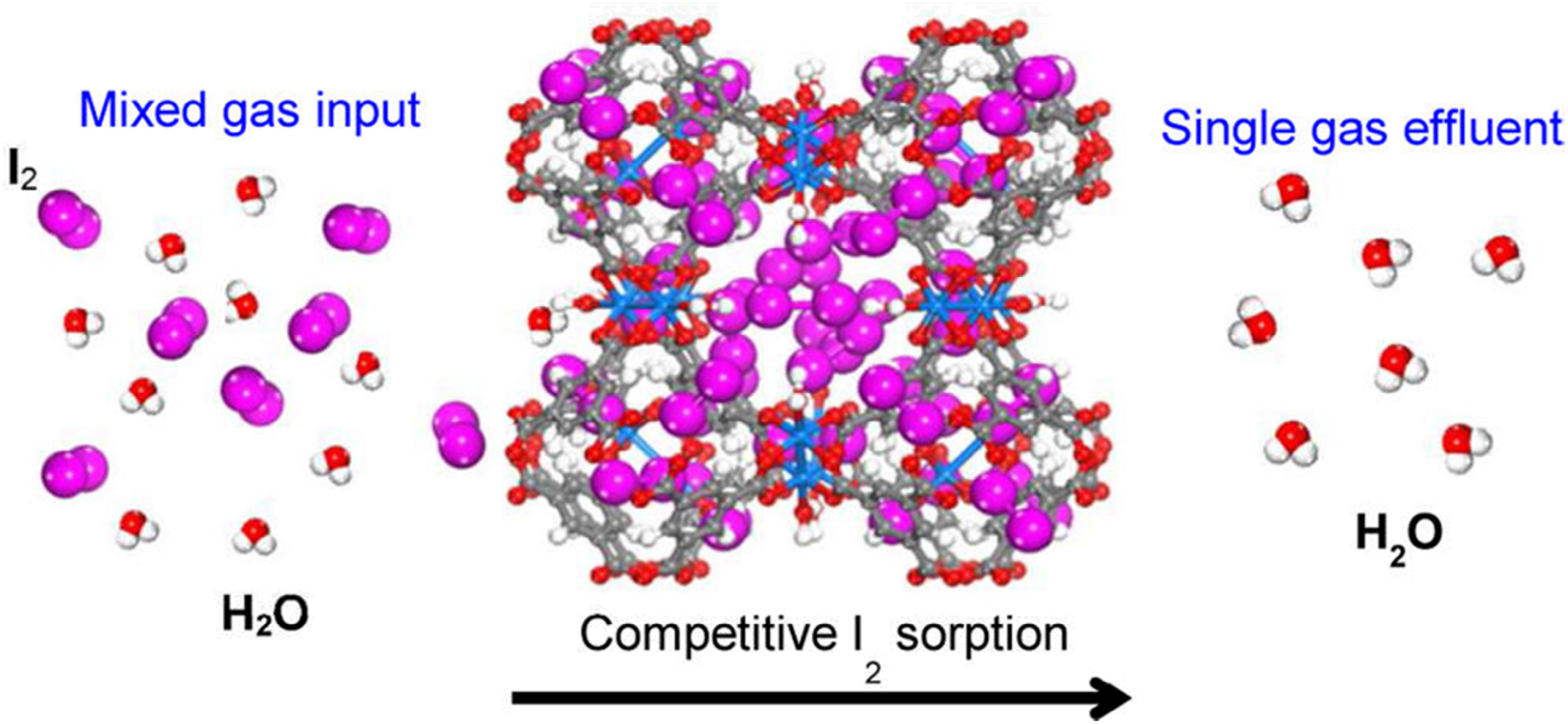


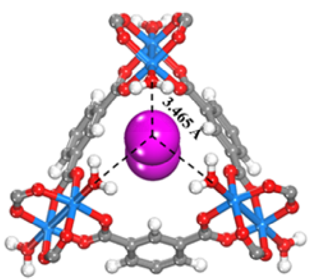
The kinetics of I_2 release from the crystalline and amorphized ZIF-8 based on isothermal TGA data collected at 200°C, 4hours

Crystal Structure of I_2@HKUST-1, selectivity of I_2 over H_2O

I_2/HKUST-1 **3.3 I/Cu**

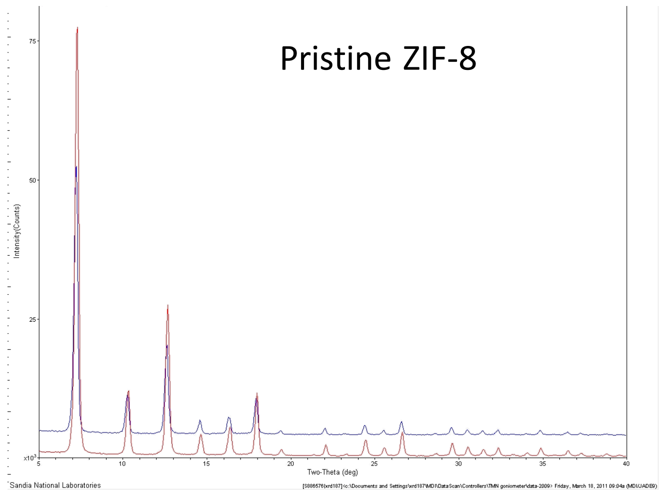
Sava Gallis, Nenoff, et.al., *Chem. Mater.*, **2013**, *25* (13), 2591

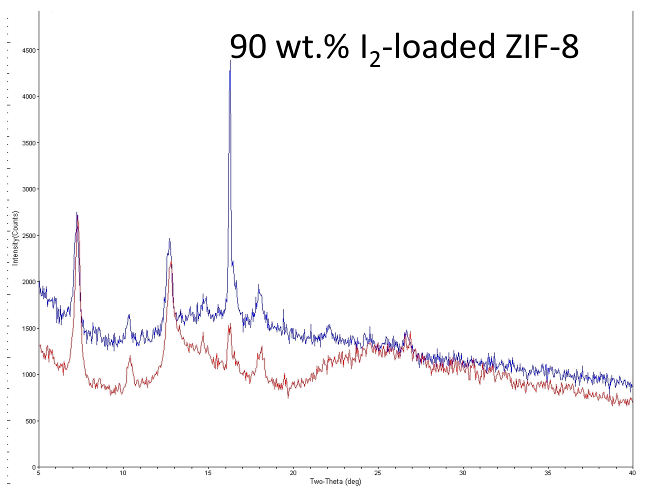




Iodine – Metal center (Cu) strongly bound
High Selectivity!
Trumps hydrophilicity of MOF

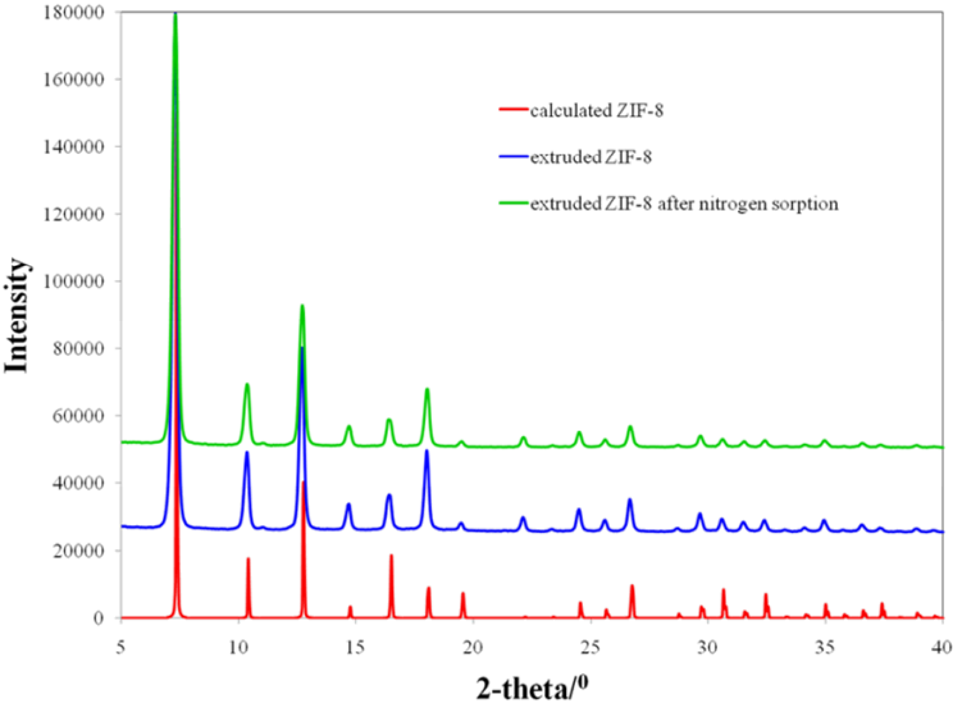
Irradiation studies at the Sandia Gamma Irradiation Facility (GIF)

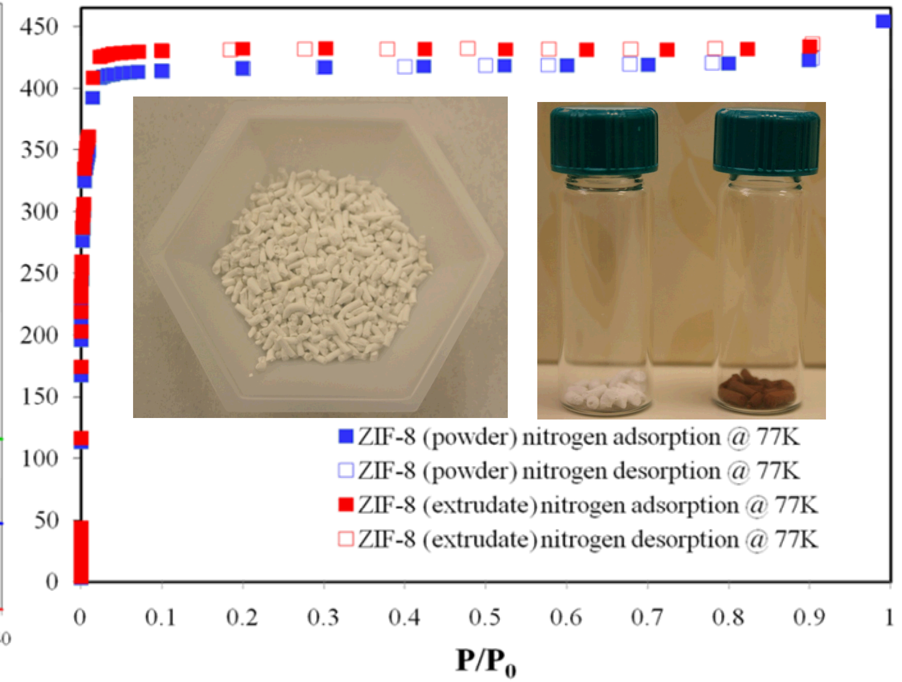




- Pristine and I_2-loaded ZIF-8 sample were exposed to Co-60 gamma irradiation at the Sandia Gamma Irradiation Facility (GIF)
- Dose rate= 0.1 Rads/sec; total dose= 2.59 x 10^5 Rads (2218 Gy); *samples maintain crystallinity*
- This irradiation study is a good approximation of an adequately shielded long-term disposal environment

Sample Pelletizing For Industrial Applications





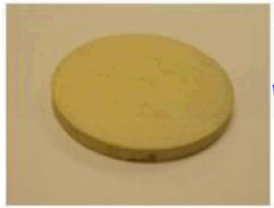
Binder-Free, No Loss of Accessible Surface Area or Sorption Properties

Sandia GCM: "Universal" Waste Form Material

US Patent 8,262,950; Sept 2012

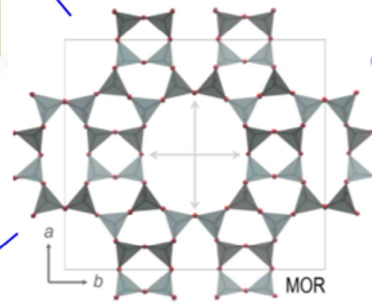
Homogenous Glass GCM: for
AgI or AgI-MOR off-gas capture and storage

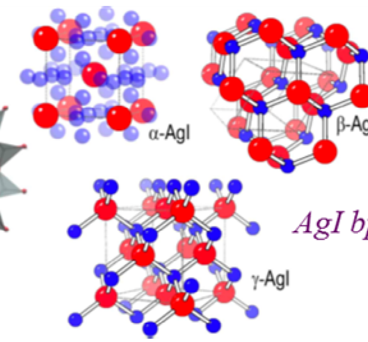
50 wt% AgI/50 wt% Glass
500°C for 3 hr



50 wt% AgI/50 wt% Glass,
500°C for 3 hr

"Universal" Low Temperature Glass Waste Form
Durabilty studies show that SNL GCM can successfully incorporate and store a wide variety of "fission gas – loaded" oxide based *getters*

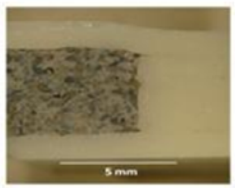




AgI bp ***556° C***

Core-Shell GCM Glass Waste Forms

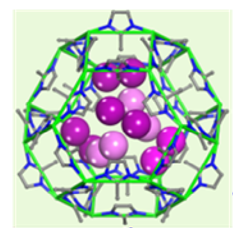
Glass shell, AgI/glass core,
75/25

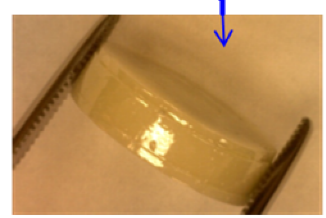


Glass shell,
AgI-MOR/Ag/Glass core 80/20/5

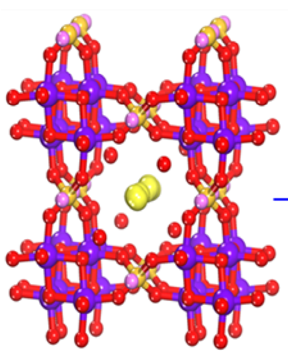
JACerS, **2011**, *94*(8), 2412

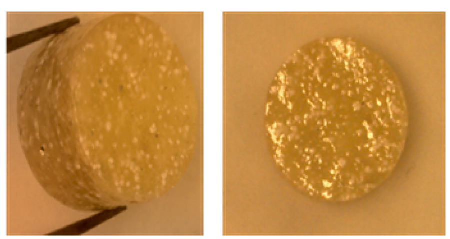
I_2/MOF, Isolation to Waste Form
JACS, **2011**, *133*(32), 12398
Ind. Eng. Chem. Res (Invited Article) **2012**, *51*(2), 614





Cs-CST Low Temp Glass Waste Form, No Cs Loss in Sintering





T. M. Nenoff, tmnenof@sandia.gov

Summary and Future directions

- I_2 adsorption in ZIF-8 is mainly due to *favorable interactions with the 2-MeIM linker*
- Up to *6 I_2 molecules are captured* (2 I/Zn) inside each cage; complementary MD simulations confirm I_2 mobility is restricted within individual cages
- PDF analyses confirm that the *framework structure is retained beyond the loss of the long-range crystalline symmetry*
- High-adsorptive capacity is maintained in extruded pellet form
- Current studies focus on achieving selective adsorption capabilities from complex, multicomponent off-gas streams

Use of High MOF selectivity to Iodine to Make Direct Electrical Readout Sensors

Enable the safety of first responders, Real-time accident warnings

The ability to sense and identify *individual gases* from the complexity of the environment requires highly selective materials.

- Current conductivity-based devices generally fall into two categories:,
  - Solid state - (oxide based) require higher temperatures (>200°C) for interaction of the gas with the surface oxides; heating devices are needed.
  - Fuel cell – room temperature liquid electrolyte, easily fouled, short lifetime
- Utilization of *MOFs with impedance spectroscopy*[1] to develop novel sensing technologies
- Exceptionally high selectivity of polarizable gases of interest (eg., I_2) under ambient conditions

[1]*Sensors*, **2009**, *9*, 1574

Iodine Sensors with High Selectivity in Environmental Conditions

Impedance spectroscopy,

polarizable molecules increase the capacitance and thereby decrease the impedance.

The selectivity of MOFs for I_2 under mild conditions paired with the **polarizability of the I_2** molecules, enables real-time electrical sensing (direct electrical readout) via impedance spectroscopy.
Common air component gas molecules such as Ar, O_2 and N_2 are not/not-highly polarizable molecules

Modular platform:

able to test MOFs of different configurations, metal centers and charge transfer capabilities

Real-Time sensing by impedance spectroscopy (IS):

All measurements to date are simple single sine measurements.
The electrical test equipment generates a single sine voltage wave at a given frequency,
& measures the returned current in terms of its:
- **magnitude** (this relates to the impedance, |Z| on the plots) and
- **phase angle** compared to the original voltage wave

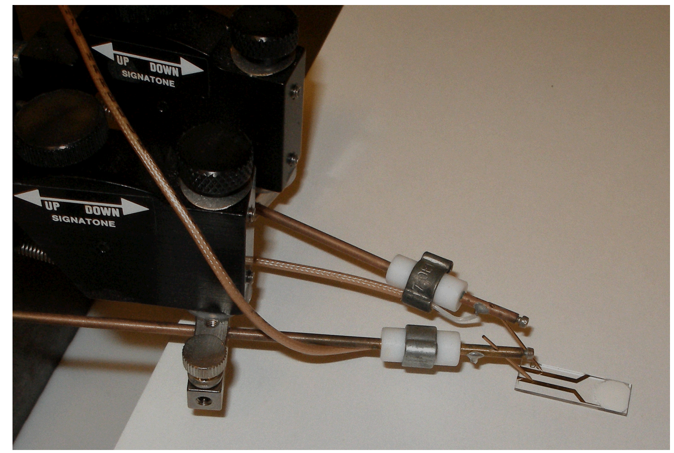
In fast fourier transform (FFT), a voltage pulse is sent out.
The pulse is the FFT of 20+ frequencies.
The measurement time is limited by the lowest frequency.
High Efficient Method: can collect ~ 20 data points in nearly the same time as the 1 lowest frequency data point.

This is all contained in commercial equipment and software.

Iodine Sensors with High Selectivity in Environmental Conditions

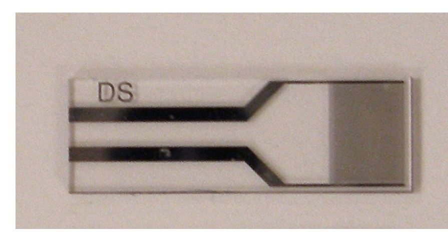
Solartron 1296 dielectric interface in series with a Solartron 1260 frequency response analyzer.
All sensor testing in a faraday cage to minimize electrical noise.

Samples are contacted with tungsten probes.



The dielectric interface allows us to **measure impedances as large as 10^{14} Ohms and frequencies 1 mHz – 1 MHz**.
Unique SNL specific: specialized high impedance, low frequency test equipment
(Common electrical test equipment has a lower input impedance than these coatings)

- Inter Digitated Electrodes (IDE's):
  10 µm wide platinum lines (125 pairs), 10 µm spacing on glass substrate
- MOF film: MOF + binder
- Film: screen printed onto platinum interdigitated electrodes
- Iodine adsorption studies: in air and humidity at 25, 40, 70 ˚C
- Test response over a broad electrical frequency response (1 MHz – 1 mHz)

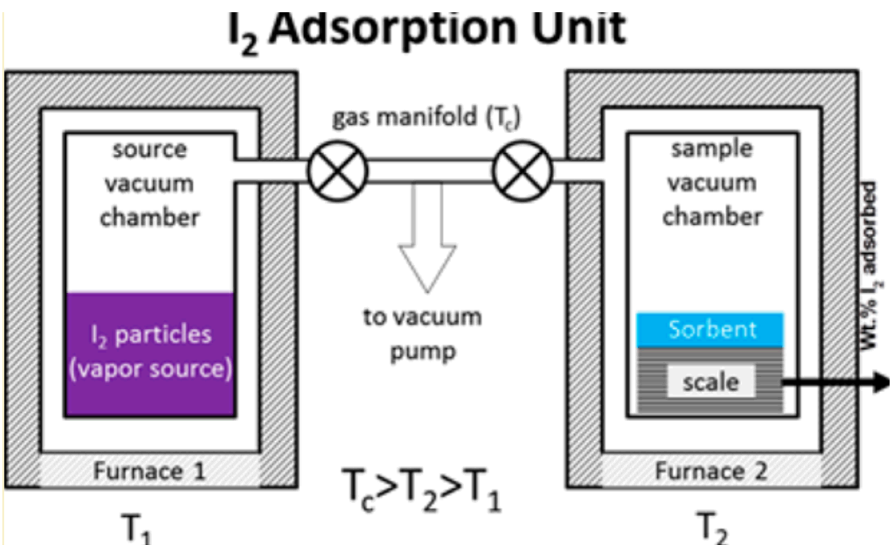


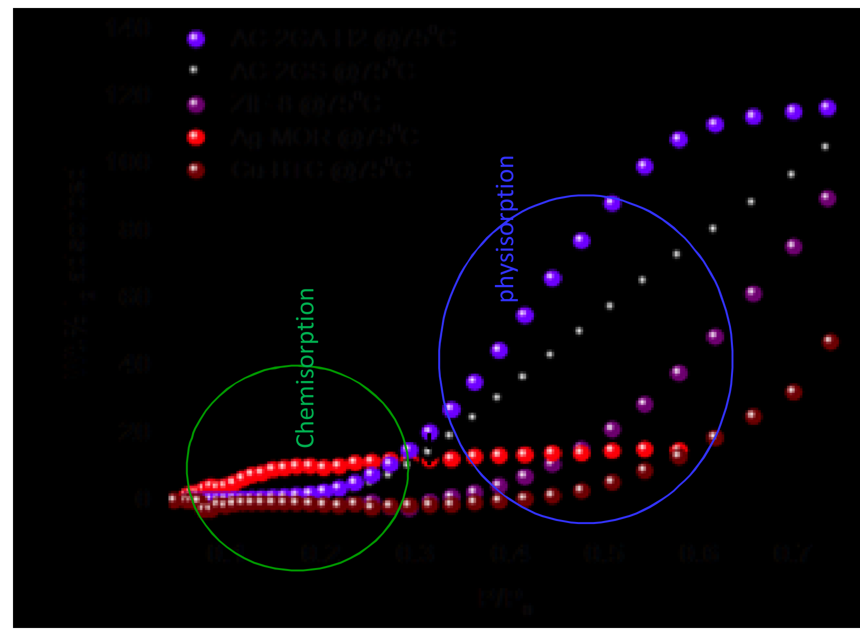
1 cm

Comparison studies of I_2 adsorption on Various Nanoporous Materials

Using a combination of Modeling (GCMC) and Iodine (I_2) Adsorption Studies to compare various nanoporous phases for iodine adsorption

MOFs, Zeolites/Molecular Sieves, Activated Carbons/Charcoals





P/P$_o$ <0.3: I_2 adsorption occurs in **small pores** & **strong chemisorption interactions** with framework or extra framework

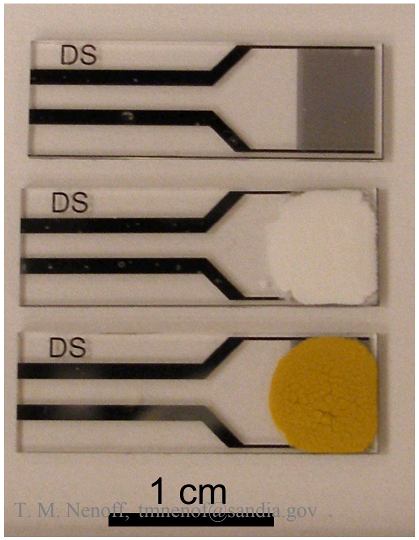
Ind. Eng. Chem. Res., **2017**, 56(8), 2331

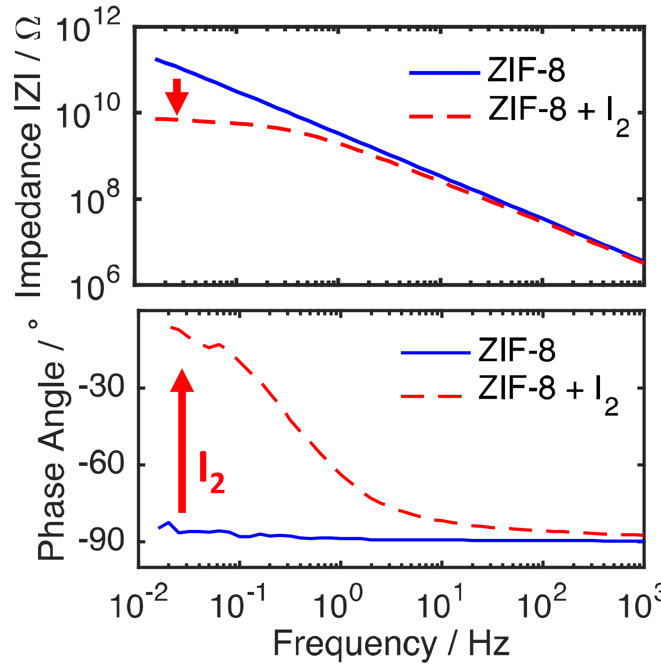
Iodine (I_2) Sensor with ZIF-8

as-received

ZIF-8

ZIF-8 + I_2 70 °C





>1 order magnitude decrease in impedance 70 °C, 30 min I_2 exposure

Sensor changes from ideal capacitor to nearly ideal resistor at low frequency after I_2 sorption.

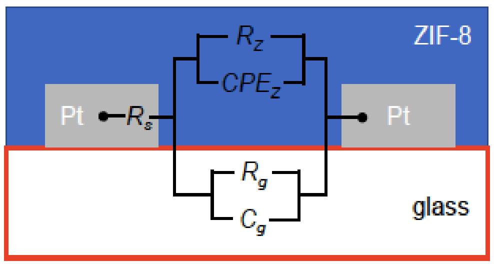
Loading Temperature (˚C)	"Empty MOF" Device impedance (GΩ)	"I_2-Loaded MOF" Device impedance (GΩ)	% Change
Room temp.	171	121	-29%
40	182	20.7	-89%
70	182	7.22	-96%

|Z| recorded at 15 mHz. 10 mV AC. 0 V DC.

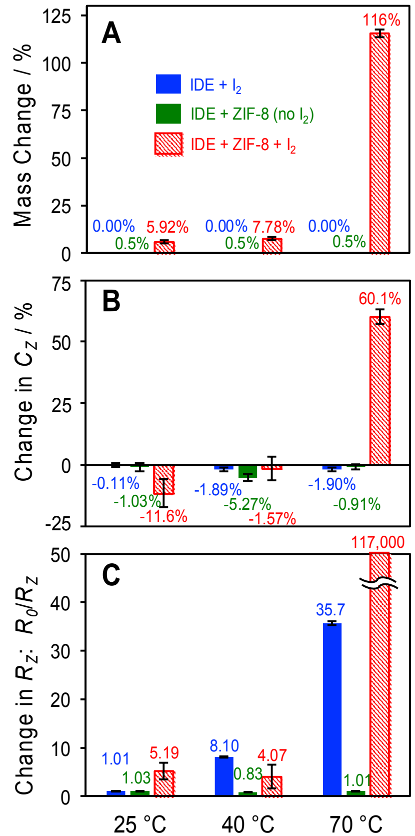
Small & Nenoff, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 44649

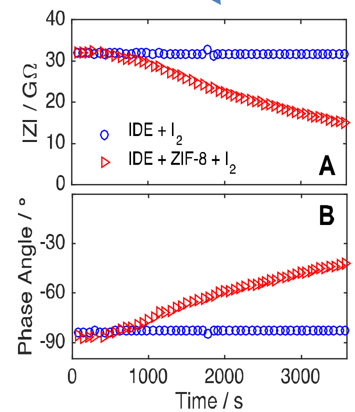
Effects of Temperature, Time and Competing gases

Equivalent circuit used to model impedance data

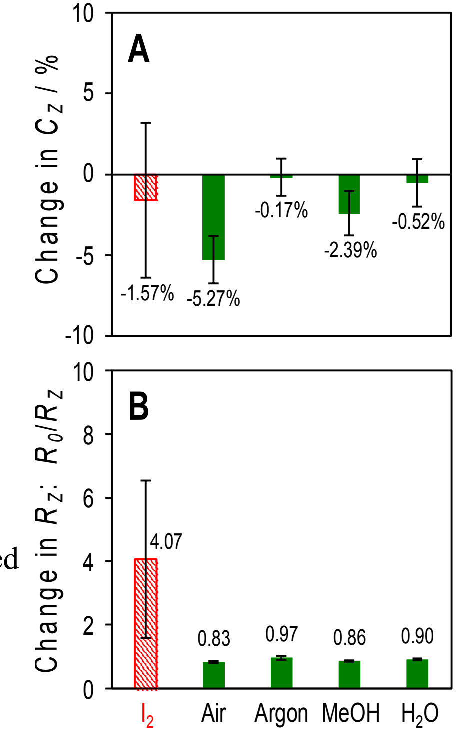


Cross sectional drawing of the sensor, (s=series, g=glass, z=ZIF-8) showing how the circuit elements *Rs*, R_Z, CPE_Z, *Rg*, and *Cg* spatially relate to the materials used.





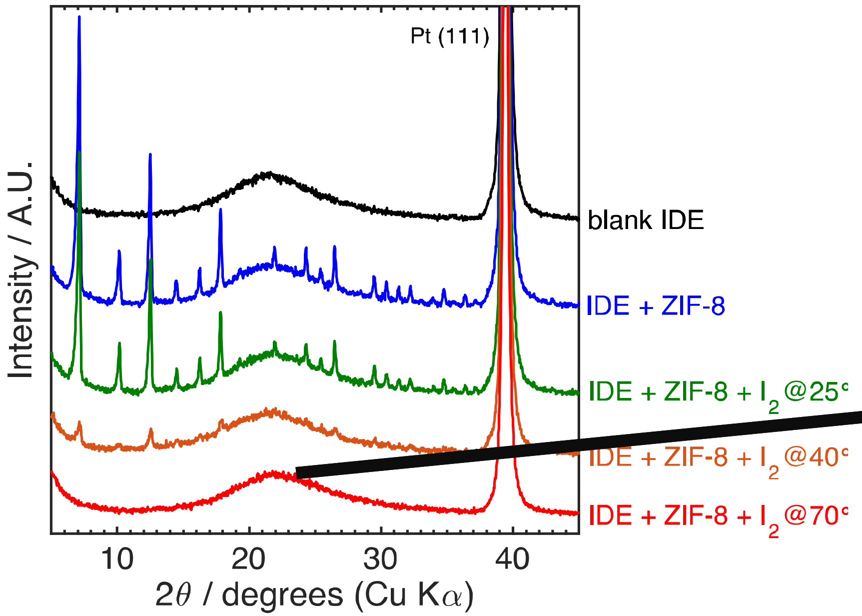
100 mHz for uncoated & ZIF-8-coated IDEs exposed to gaseous I_2 at 25 °C.



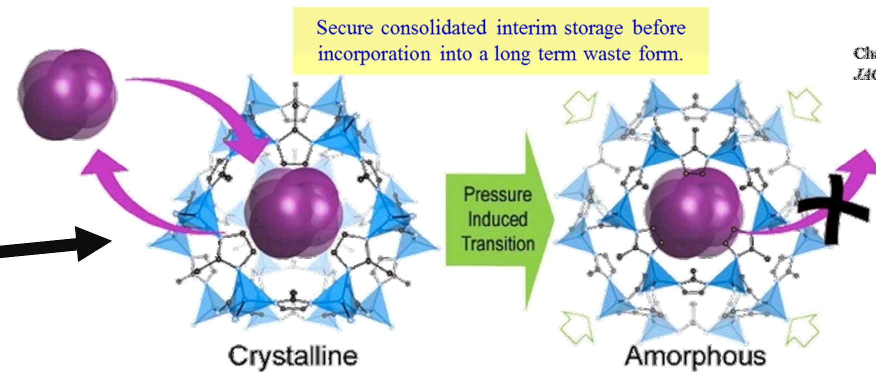
Responses evident for IDE+ I_2 gas.
However, IED+ ZIF-8 + I_2 indicates *response plus gas selectivity*
At 70°C, highest Rz >10^5 x response

MOF/Sensor Temperature Dependence

ZIF-8@sensor



Retention of Iodine in MOF due to SHORT range crystallinity



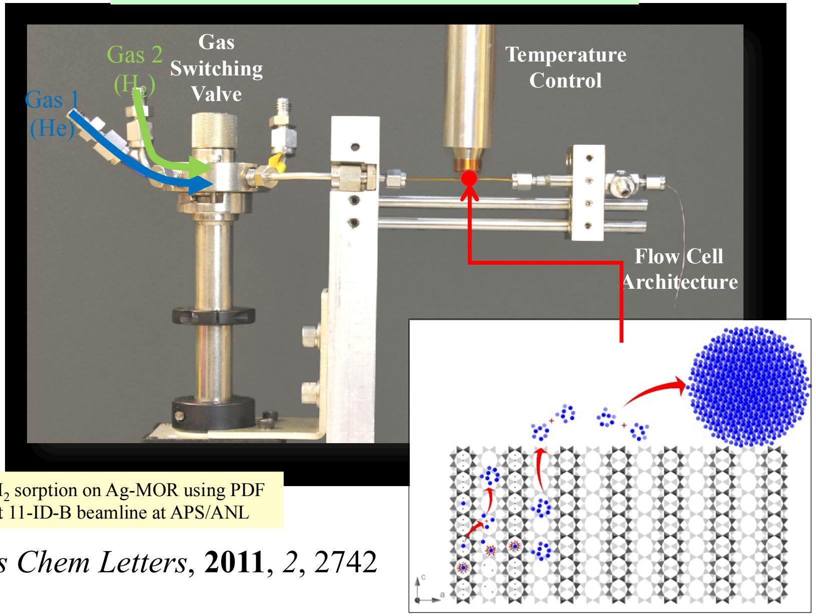
Chapman, Nenoff, et.al., *JACS* **2011**, *133*(46), 18583

Next steps:

- does framework chemistry / I_2 adsorption mechanisms translate into improved sensor
- what does an optimized sensor design look like
- sensor response to other fission gases
- sensor response to industrial gases (eg., hydrocarbons)

Nanoparticle Formation for Heterogenous Catalysis, Gas Capture

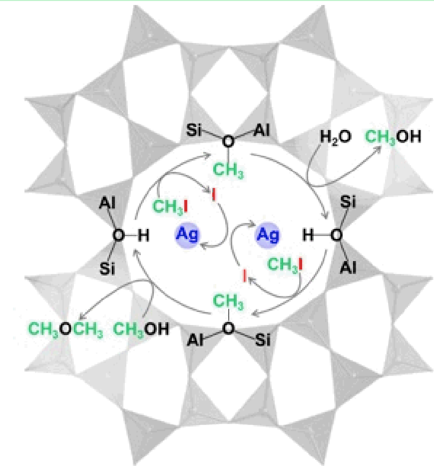
Determine Mechanism of Ag^+ to Ag° NPs in MOR



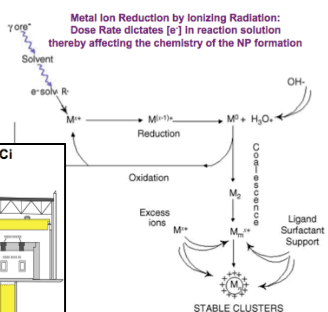
In situ I_2 sorption on Ag-MOR using PDF setup at 11-ID-B beamline at APS/ANL

J Phys Chem Letters, **2011**, *2*, 2742

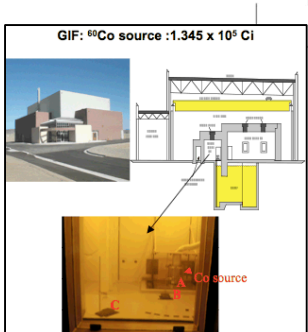
Mechanism of Iodine Capture on Ag-MOR from Acidic Humid CH_3-I Stream: Catalytic Cleaving of CH_3-I and I Capture
Micro. Meso. Mater., **2014**, *200*, 297 (invited)

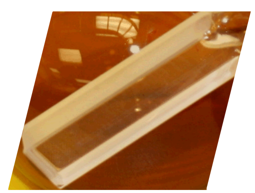


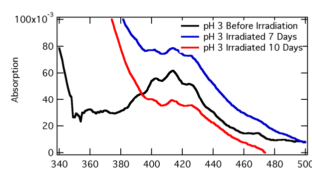
γ-irradiation NP formation and growth via sintering

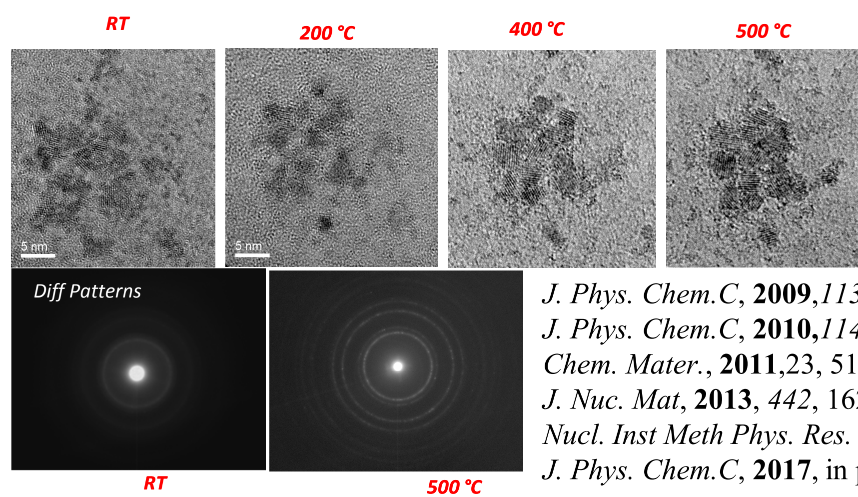


Belloni, *Catalysis Today*, 2006,113,141









J. Phys. Chem.C, **2009**, *113*, 1155
J. Phys. Chem.C, **2010**, *114*, 14309
Chem. Mater., **2011**, 23, 5185
J. Nuc. Mat, **2013**, *442*, 162
Nucl. Inst Meth Phys. Res. B; ***2017***
J. Phys. Chem.C, **2017**, in prep.

T. M. Nenoff, tmnenof@sandia.gov

Formation of metallic or alloy Nanoparticles By Radiolysis

- Radiolysis by γ-radiation is used as synthetic method to *access new phases:*
  Invited Review article, Nenoff, et.al., *J. Phys. Chem C*, **2018**, in review

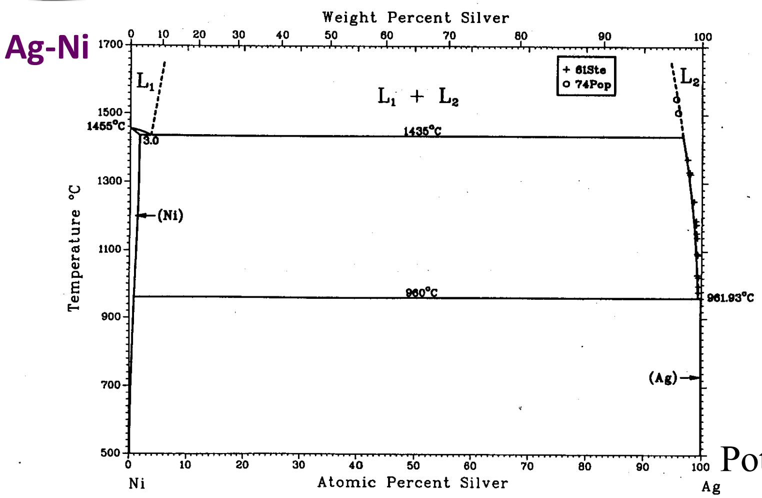
- By varying the dose rate, we vary the structure of nanoparticle growth in solution over a wide composition range in alloys

- Reactions occur at room temperature

- *Allows for the formation of non-thermodynamically predicted phases*

- Use of Radiolysis to drop reaction temperature to ≈25°C
  thereby dramatically decreasing the temperature of oxide or alloy formation

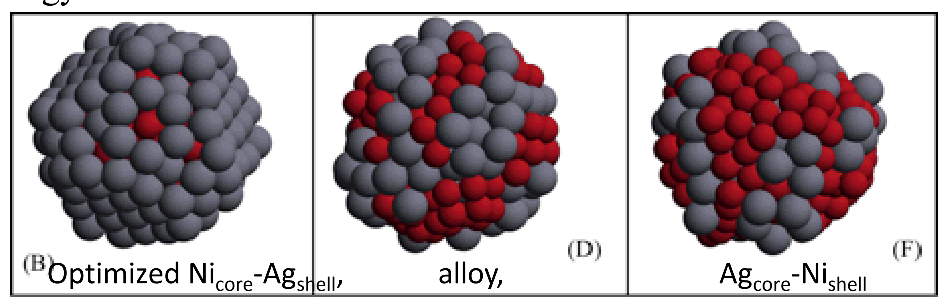
Non thermodynamically predicted Ag-Ni alloy NPs by γ-irradiation

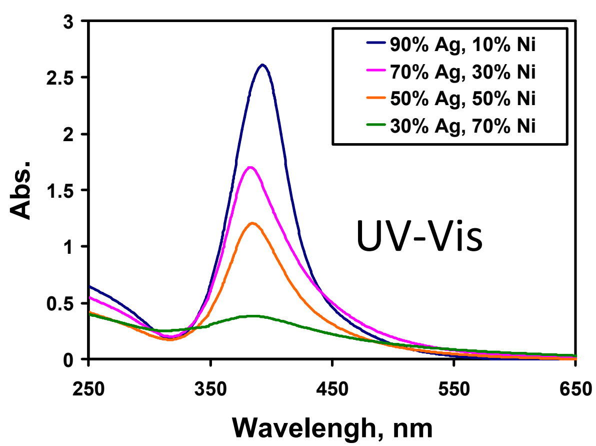


T. B. Massalski, *ASM International*, 2nd Ed., **1990**

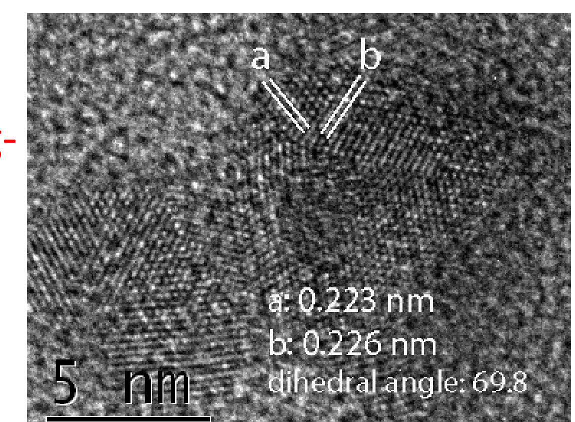
	Ag	$Ag_{0.9}$-$Ni_{0.1}$	$Ag_{0.7}$-$Ni_{0.3}$	$Ag_{0.5}$-$Ni_{0.5}$	$Ag_{0.3}$-$Ni_{0.7}$	Ni
$[Ag^+]$, × 10^{-4} M	2	1.8	1.4	1	0.6	0
$[Ni^{2+}]$, × 10^{-4} M	0	0.2	0.6	1	1.4	2
$[Ag^+] + [Ni^{2+}]$, × 10^{-4} M	2	2	2	2	2	2
$[Ag^+]:[Ni^{2+}]$	Ag NPs	9:1	7:3	5:5	3:7	Ni NPs

Potential Energy = 0eV 43.7eV 57.2eV





50%Ag-50%Ni



J. Phys. Chem.C, **2009**, *113*, 1155 ; *J. Phys. Chem.C*, **2010**, *114,* 14309; *J. Chem. Theory Comput.*, **2011**, *7*, 485

Low Temperature Synthesis and Sintering of U Based Nanoparticles

U metals or alloys:
- Advanced nuclear fuel compositions (mixed metals, mixed metal oxides)
- Recycling and reusing dissolved uranium oxide from spent nuclear fuels
- Recovery of dissolved fuels from accident pools

Traditional Methods of synthesizing and Fabricating nuclear fuels involves traditional alloy and mixed metal oxide processing (high temperature melts).
Volatilization of fuel components is major issue.

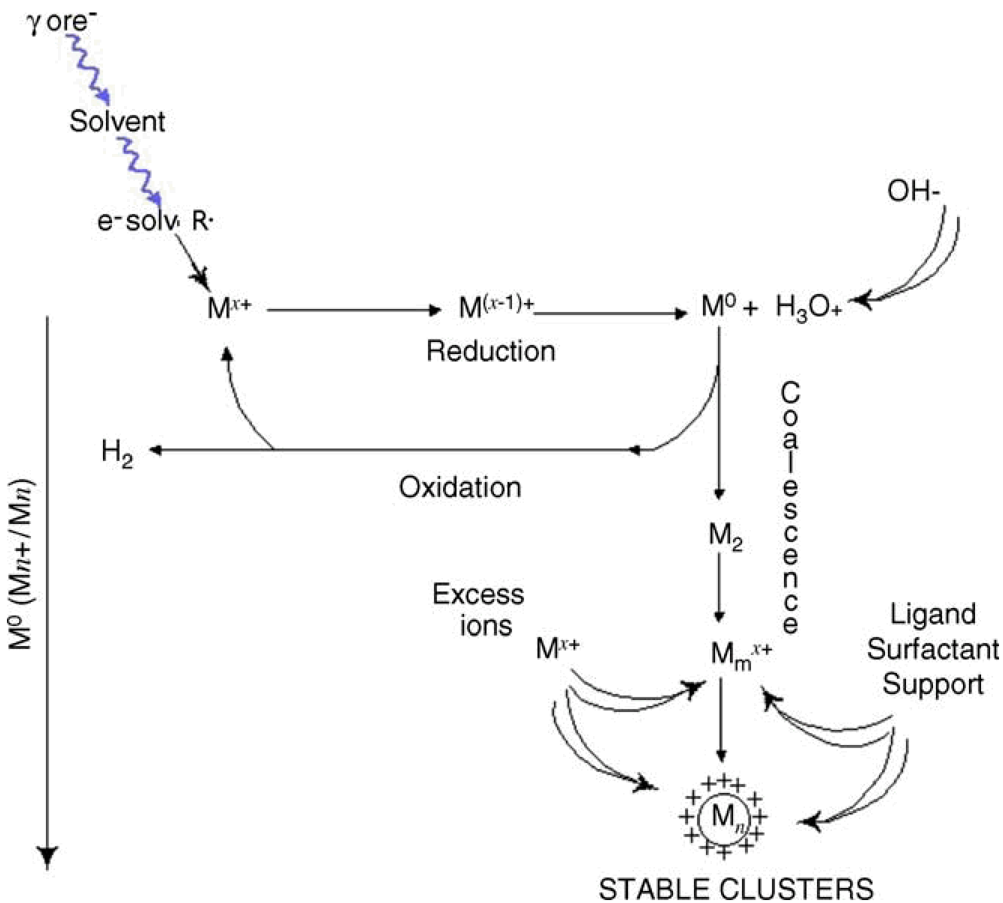
$(U_{0.75}Pu_{0.20}Np_{0.02}Am_{0.03})O_{2\pm x}$ where x ~ 0.05 to 0.03
(K. McClellan, DOE/NE Oxide Fuel Fabrication Lead, LANL)

Sintering of nanoparticles is also dramatically dropped due to the high surface to volume ratio

Radiolysis for Nanoparticle Formation

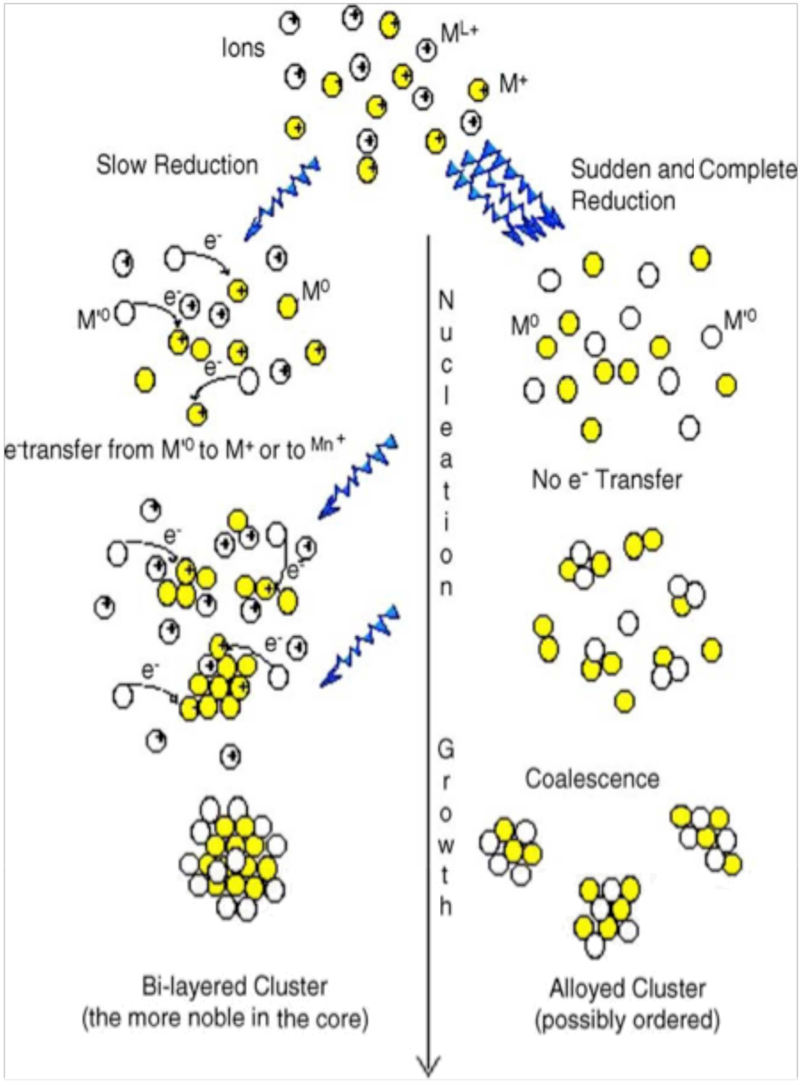
Metal ion reduction by ionizing radiation:
Dose rate dictates [e⁻] in reaction solution thereby affecting the chemistry of the NP formation

$$H_2O \Rightarrow e^-_{aq}, H_2, OH^\bullet, H^\bullet, H_3O^+, H_2O_2, HO_2^\bullet$$



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

Methodology to Access Ni-based Alloy Phase Spaces

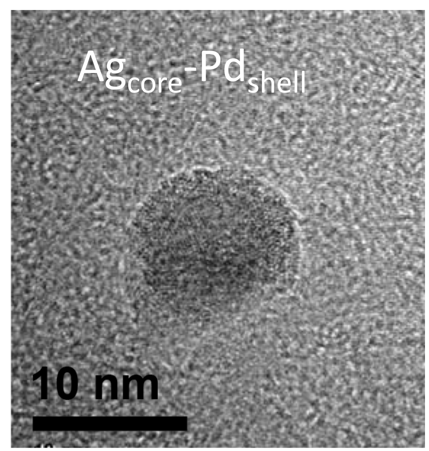


Belloni, *Catalysis Today*, **2006**,*113*,141

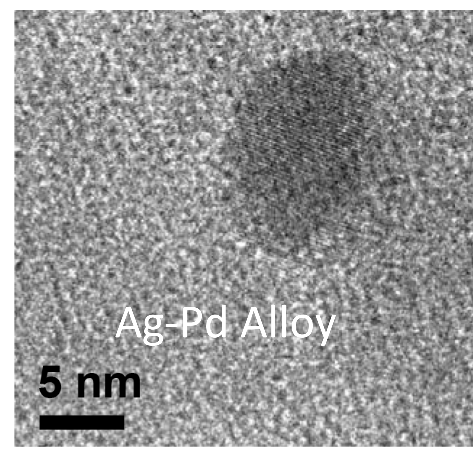
Alloys: Possibility to access different phase space than with traditional melting

Using high radiation dose and High dose rate, we pursue nanoparticle alloy formation

Slow Reduction



Sudden Reduction



Redjala, T. et al. *Oil Gas Sci. Technol.* ***2006***

$AgNO_3$, $HAuCl_4$, $Pd(NO_3)_2$ and poly (vinyl alcohol) (PVA, 99% hydrolysed, MW = 86000); Dose rate of 1.75 $Gy.s^{-1}$

Room Temp Radiolysis at Sandia (SNL) GIF Facility

Sandia Gamma Irradiation Facility (GIF) is a ^{60}Co source : 1.345 x 10^5 Ci, ≈ 300K rad/hr.

Nanoparticle (NP) Synthesis & Analysis

Experimental NP Synthesis:

Into 25ml solutions in 100ml vials add dilute metal salt solutions, alcohol (MeOH), organic polymer (PVA) and DI H_2O.

Purged solution with N_2, sealed and stored in dark.

Exposed solutions to γ-irradiation.

NP Analysis:

(1) UV-vis: Varian Cary 300 Scan UV-visible Spectrophotometer

(2) Transmission Electron Microscopy (TEM): JEOL 1200EX (120 kV) bright-field

(3) High Resolution TEM and scanning TEM: FEI Tecnai G(2) F30 S-Twin (300 kV) TEM at Sandia's Center for Integrated Nanotechnologies (SNL CINT)
- 0.14 nm resolution in high-angle annular dark-field (HAADF) mode
- equipped with energy-dispersive X-ray (EDX) & electron energy-loss spectrometer (EELS)

action Mechanism for d-UO_2 Nanoparticles

Particle formation via radiolysis (γ-irradiation)

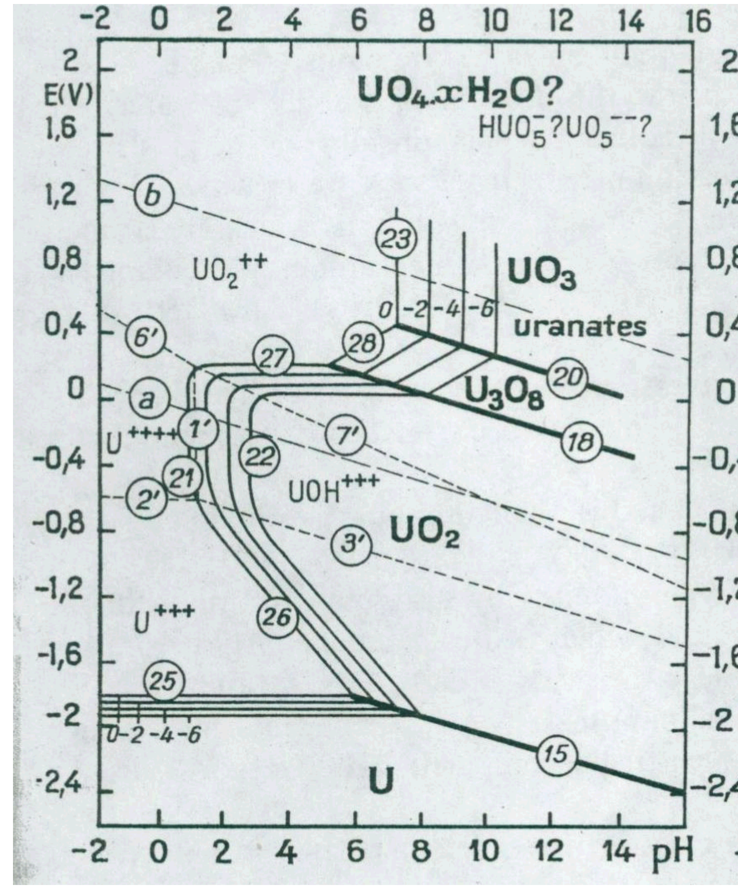
$$^{\cdot}OH(^{\cdot}H) + e_{aq}^{-} + CH_3OH \rightarrow e_{aq}^{-}/\,^{\cdot}CH_2OH + H_2O(H_2)$$

$$e_{aq}^{-}/\,^{\cdot}CH_2OH + UO_2^{2+} \rightarrow UO_2^{0} + \,^{\cdot}CH_2OH$$

Particle growth

$$x\,^{\cdot}CH_2OH + (UO_2)_n \rightarrow (UO_2)_n^{x-} + xCH_2O + xH^{+}$$

Pourbaix Diagram



Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions; 1974.*

Aqueous room temperature synthesis to form NPs

Nanoparticle (NP) Synthesis & Analysis

Experimental NP Synthesis:

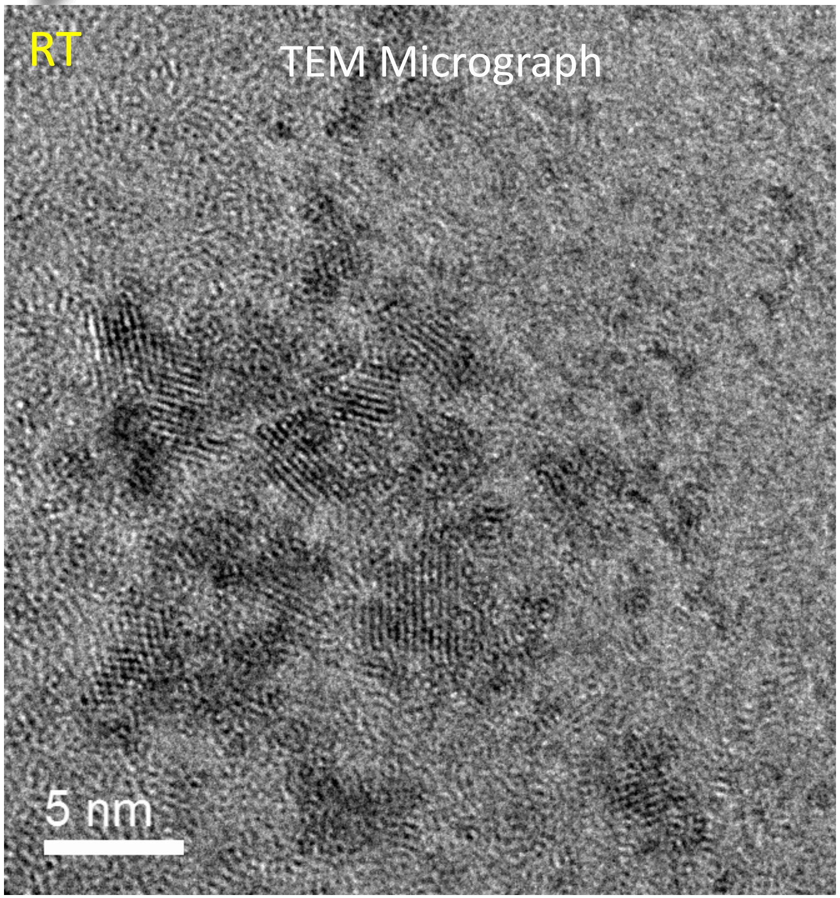
- 25ml dilute $UO_2(NO_3)_2$ aqueous solutions containing alcohol (MeOH)
- Purged solution with argon
- Exposed solutions to γ-irradiation

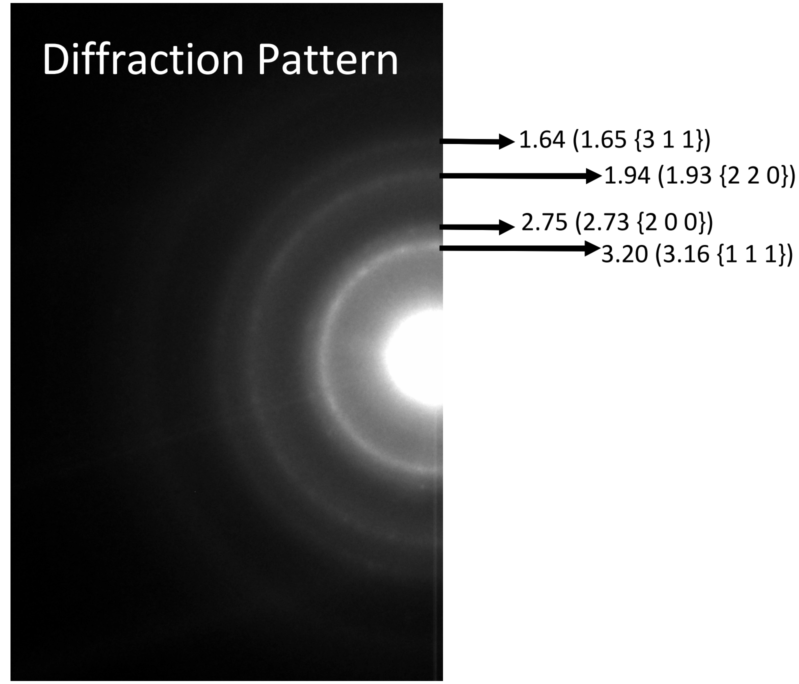
NP Analysis:

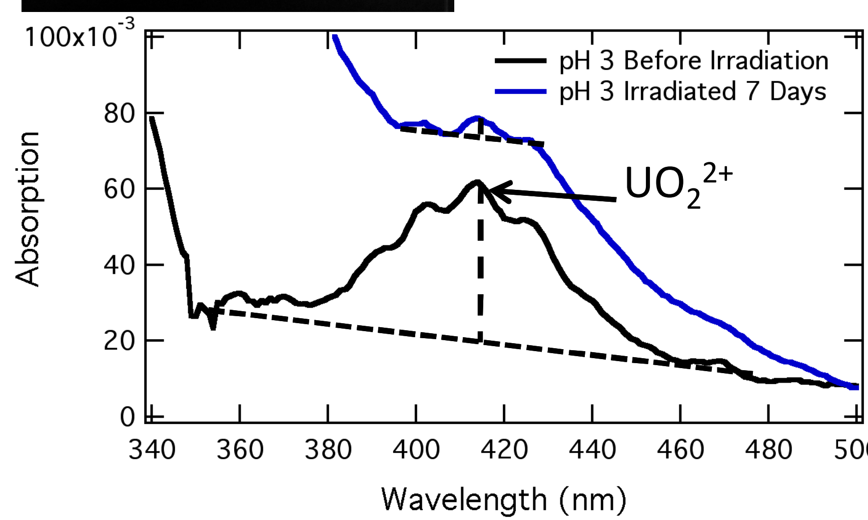
- UV-vis: Varian Cary 300 Scan UV-visible Spectrophotometer
- Transmission Electron Microscopy (TEM): JEOL 1200EX (120 kV) bright-field
- High Resolution TEM and scanning TEM: FEI Tecnai G(2) F30 S-Twin (300 kV) TEM at Sandia's Center for Integrated Nanotechnologies (SNL CINT)
  - 0.14 nm resolution in high-angle annular dark-field (HAADF) mode
  - Equipped with energy-dispersive X-ray (EDX) & electron energy-loss spectrometer (EELS)
- Concurrent *ab initio* molecular dynamics simulations for the hydration energies of U(III) and U(IV) guided the experiments
  J. Chemical Physics, **2012**, *137*(7), 074502

Characterization of UO_2 NPs Formed at pH 3

Chem. Mater., **2011**,23, 5185



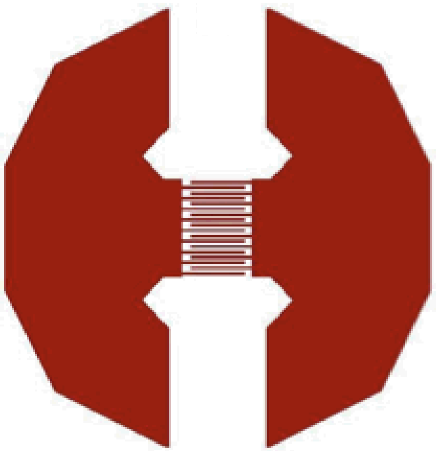


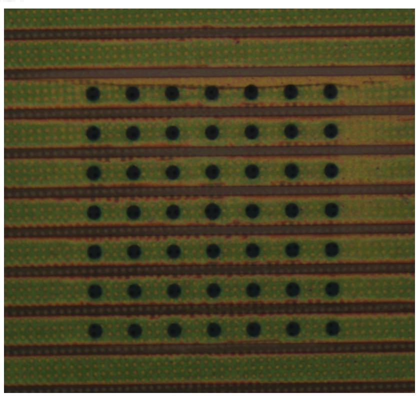


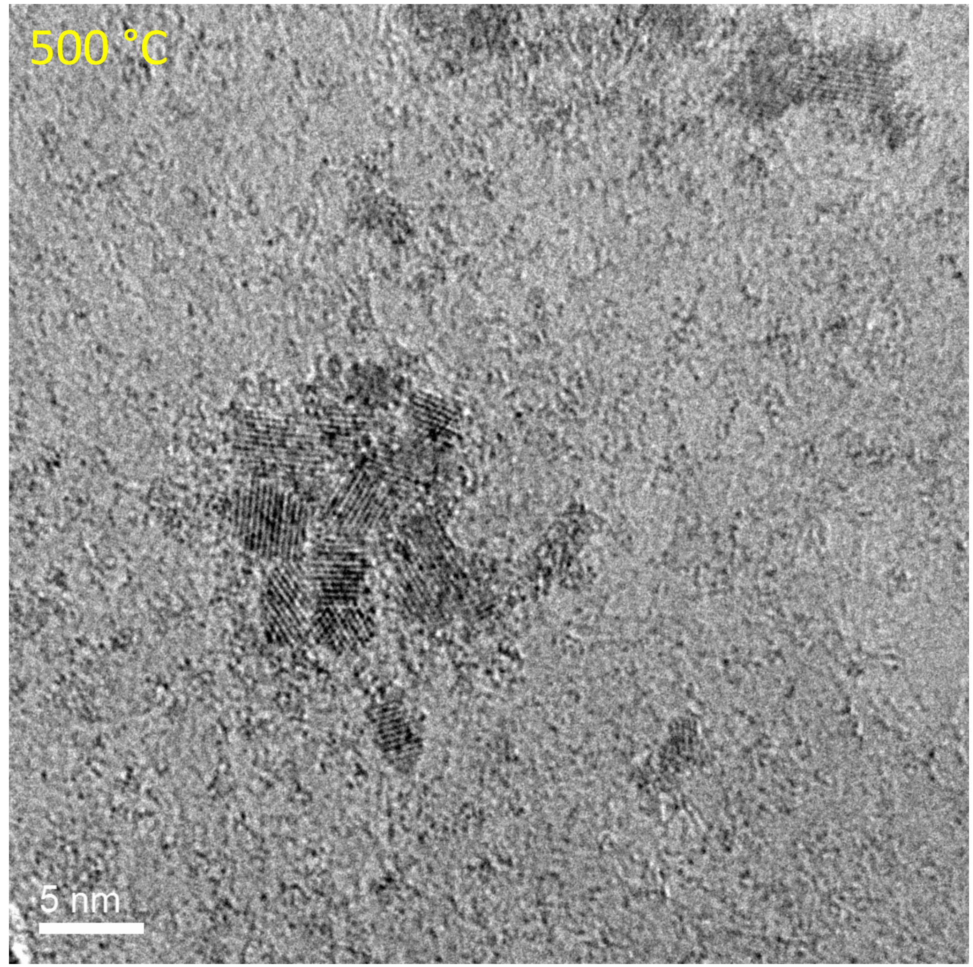
UO_2 NP formation confirmed by UV-vis, bright-field TEM and diffraction

In-Situ TEM UO_2 NP Sintering

Protochips Aduro™ holder



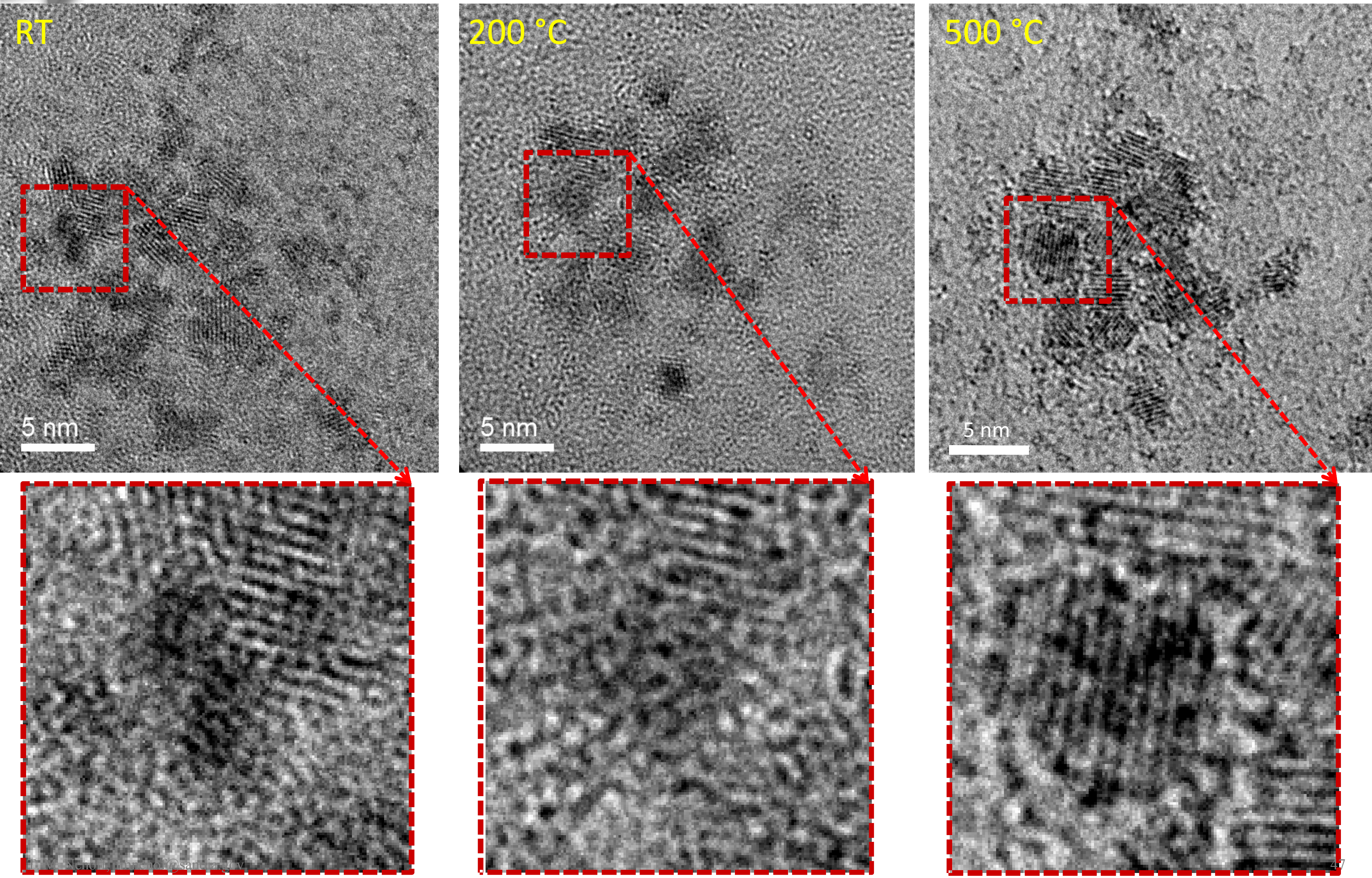




In-situ TEM sintering achieved with low drift and fast T response

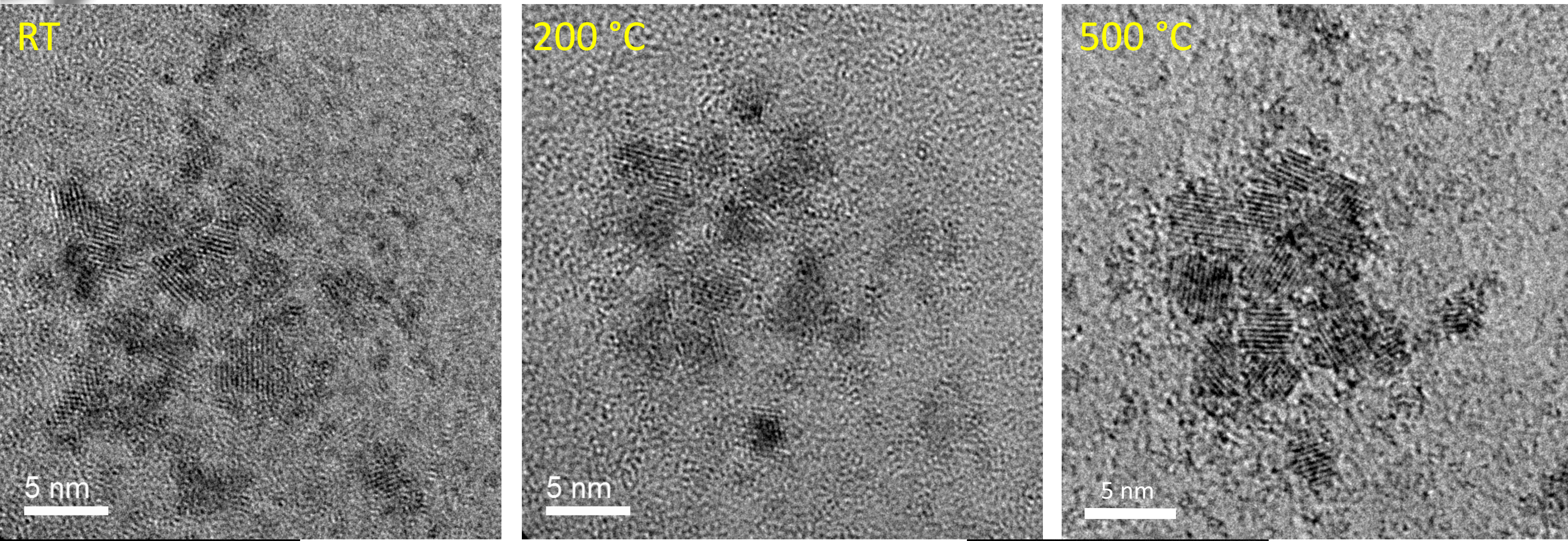
T stepped from room temperature (RT) to:
200 °C, 300 °C, 400 °C, 500 °C, and 600 °C
and back to RT successively
Less than 1 ms response; accurate to 0.5 - 3°C

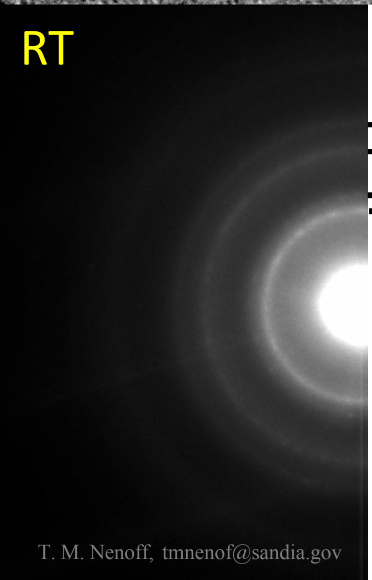
UO_2 NP Sintering at 500 °C



UO_2 NP Sintering at 500 °C

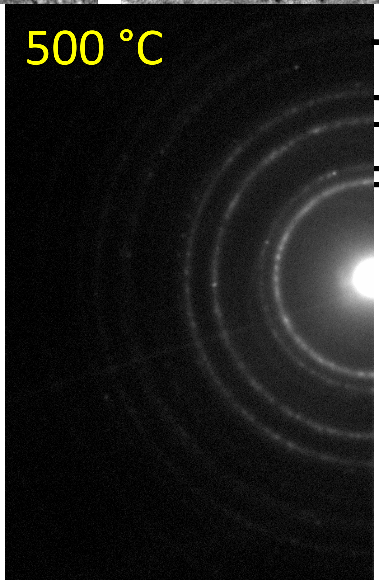
Chem. Mater., **2011**,23, 5185





1.64 (1.65 {3 1 1})
1.94 (1.93 {2 2 0})
2.75 (2.73 {2 0 0})
3.20 (3.16 {1 1 1})

Low T NP sintering achieved at 500 °C; ~1000 °C lower than previously reported



1.22 (1.22 {4 2 2})
1.64 (1.65 {3 1 1})
1.93 (1.93 {2 2 0})
2.72 (2.73 {2 0 0})
3.11 (3.16 {1 1 1})

Experimental Methods:
d-U d-U-alloy Nanoparticle (NP) Synthesis

Experimental NP synthesis:

0.004 M total salts:

50% UCl_4, (50% $La(NO_3)_3 \cdot 6(H_2O)$ or $EuCl_3 \cdot 6H_2O$)

alcohol (MeOH), organic polymer (PVA) in DI H_2O

Sealed and purged solution with argon

γ-irradiated at 300 rad/sec for 30 min.

Particle formation via radiolysis (γ-irradiation)

$$^{\cdot}OH(^{\cdot}H) + e_{aq}^{-} + CH_3OH \;\; -> \;\; e_{aq}^{-}/\,^{\cdot}CH_2OH + H_2O(H_2)$$

$$e_{aq}^{-}/\,^{\cdot}CH_2OH + UO_2^{2+} \;\; -> \;\; UO_2^{0} + \,^{\cdot}CH_2OH$$

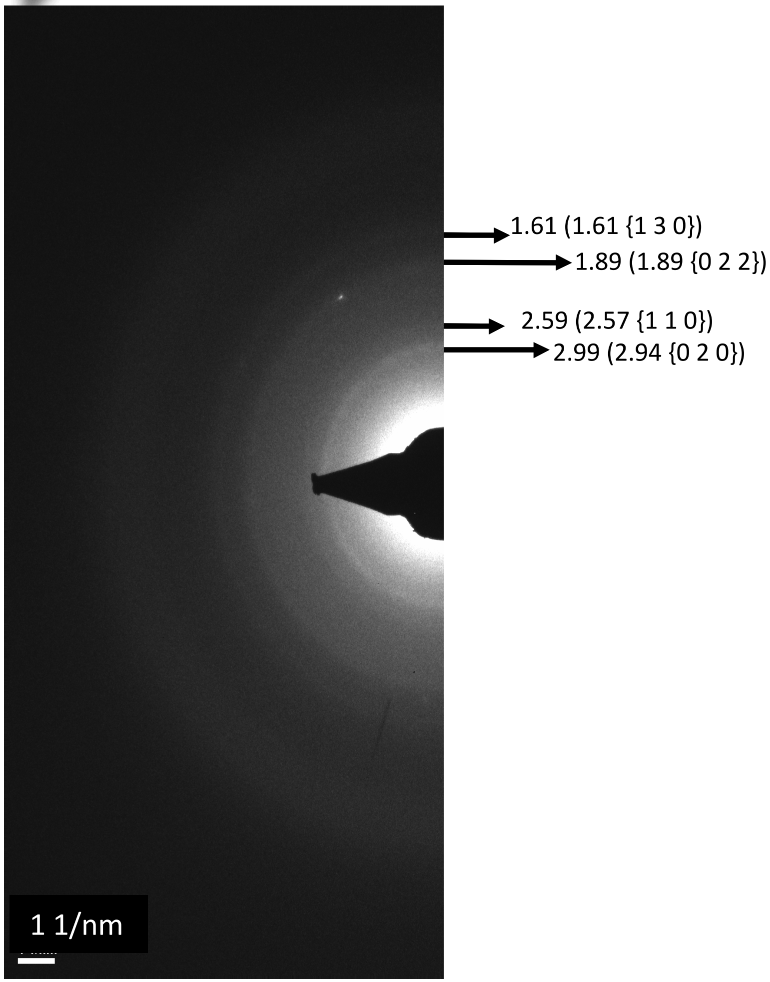
Particle growth

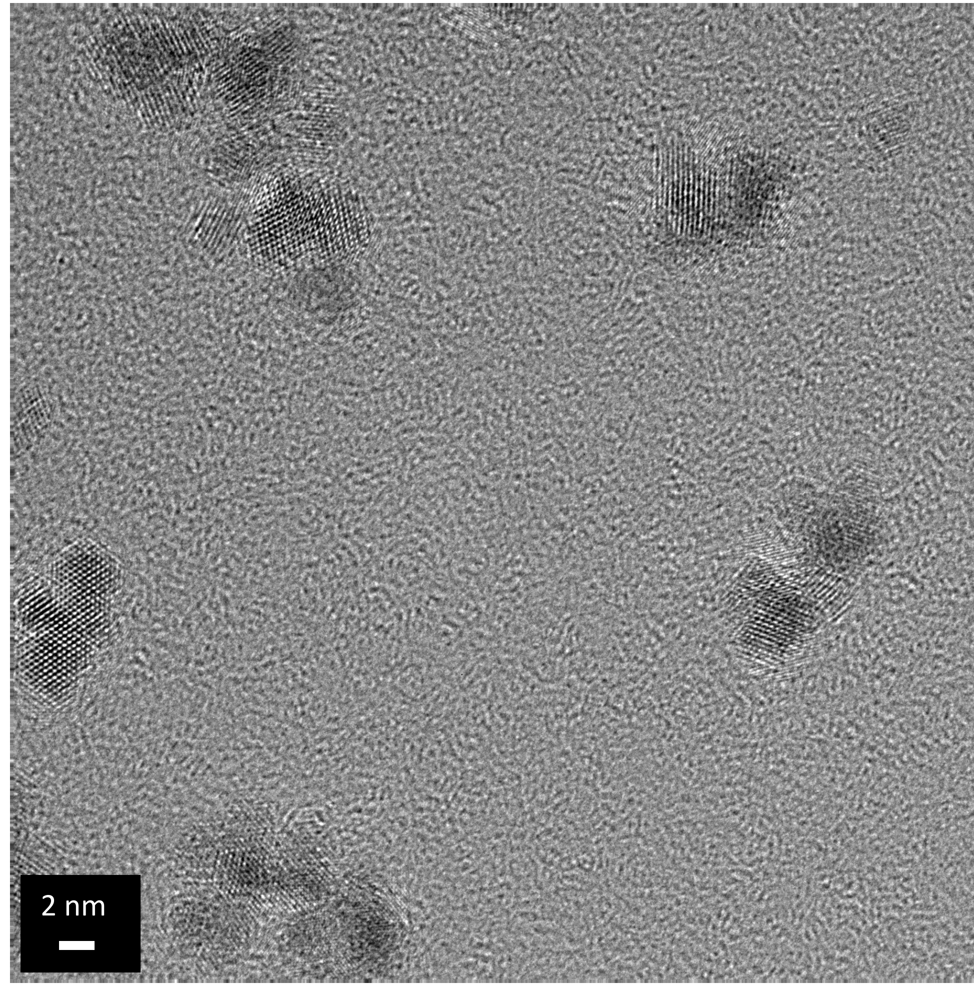
$$x\,^{\cdot}CH_2OH + (UO_2)_n \;\; -> \;\; (UO_2)_n^{x-} + xCH_2O + xH^{+}$$

Aqueous room temperature synthesis to form NPs

Evidence of U NP Formation

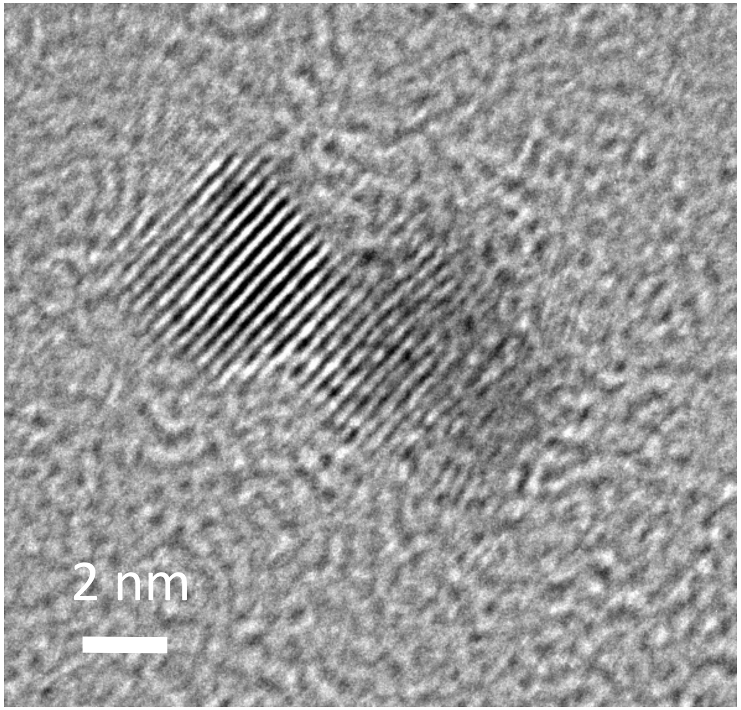
J. Nuc. Mat, **2013**, *442*, 162

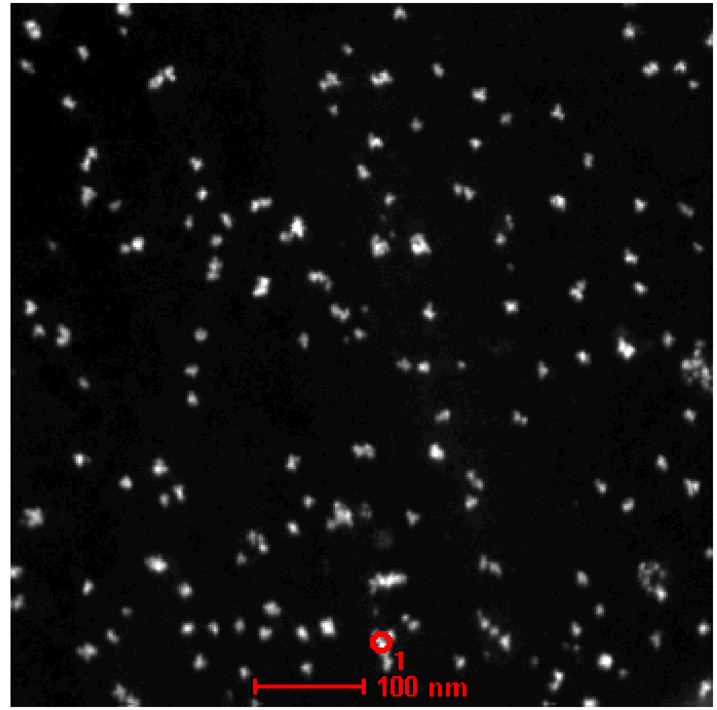


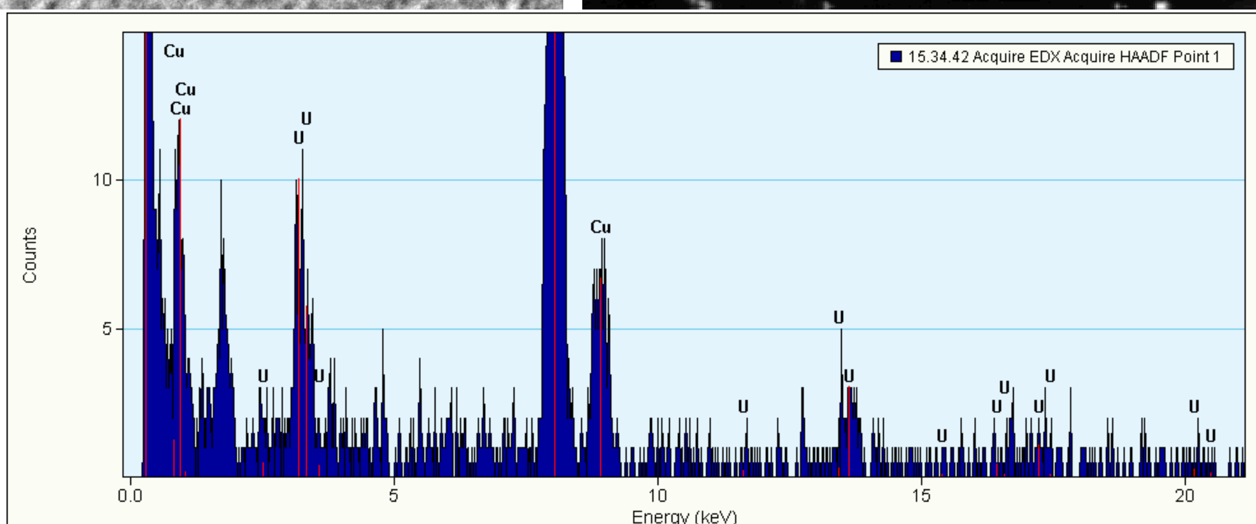


Indication of alpha-U NP formation from lattice spacings determined from diffraction

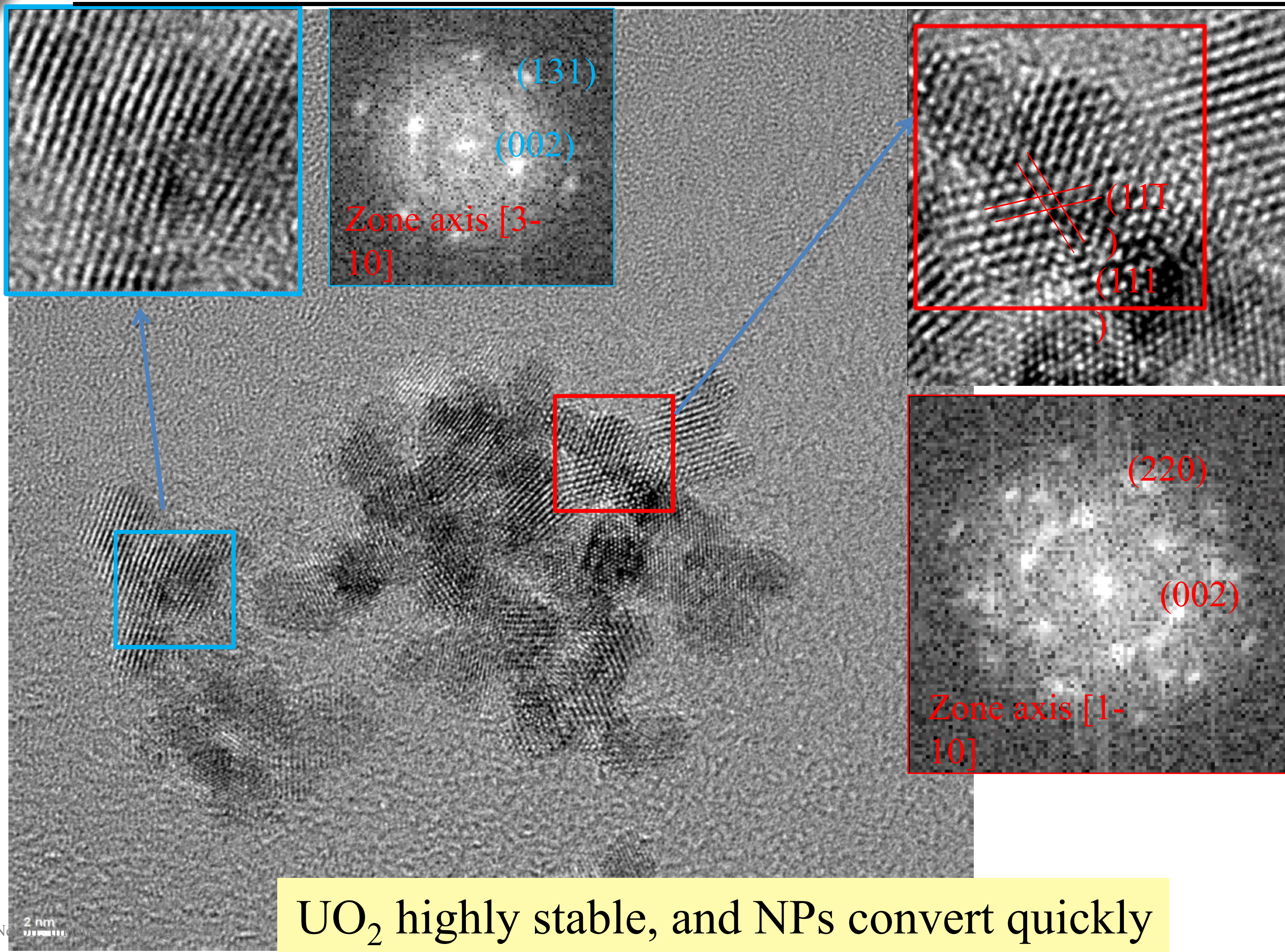
Evidence of d-U NP Formation, Single Particle EDX





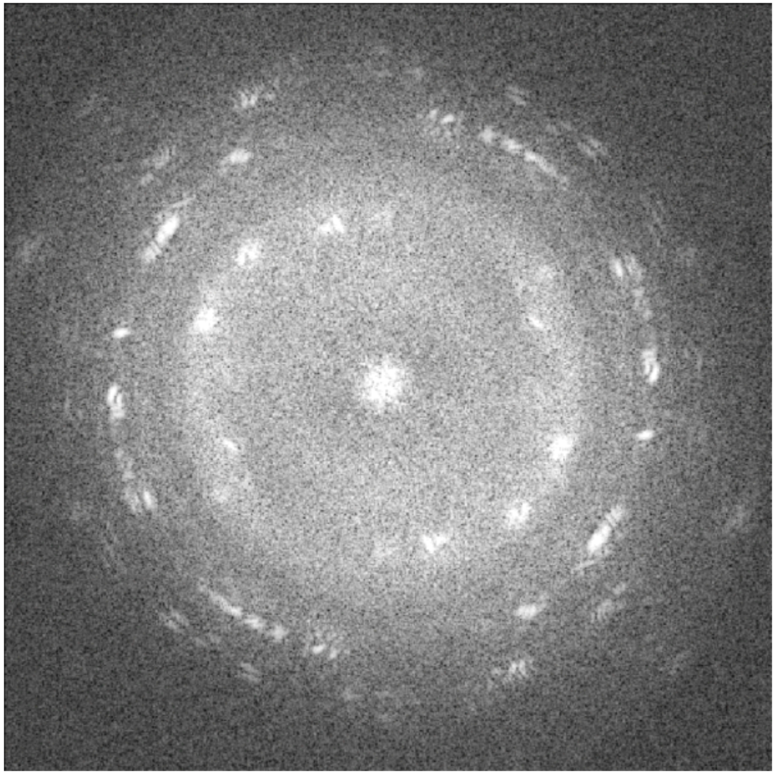


Exposure to air: d-U NP Form d-UO_2 (on TEM Grid)

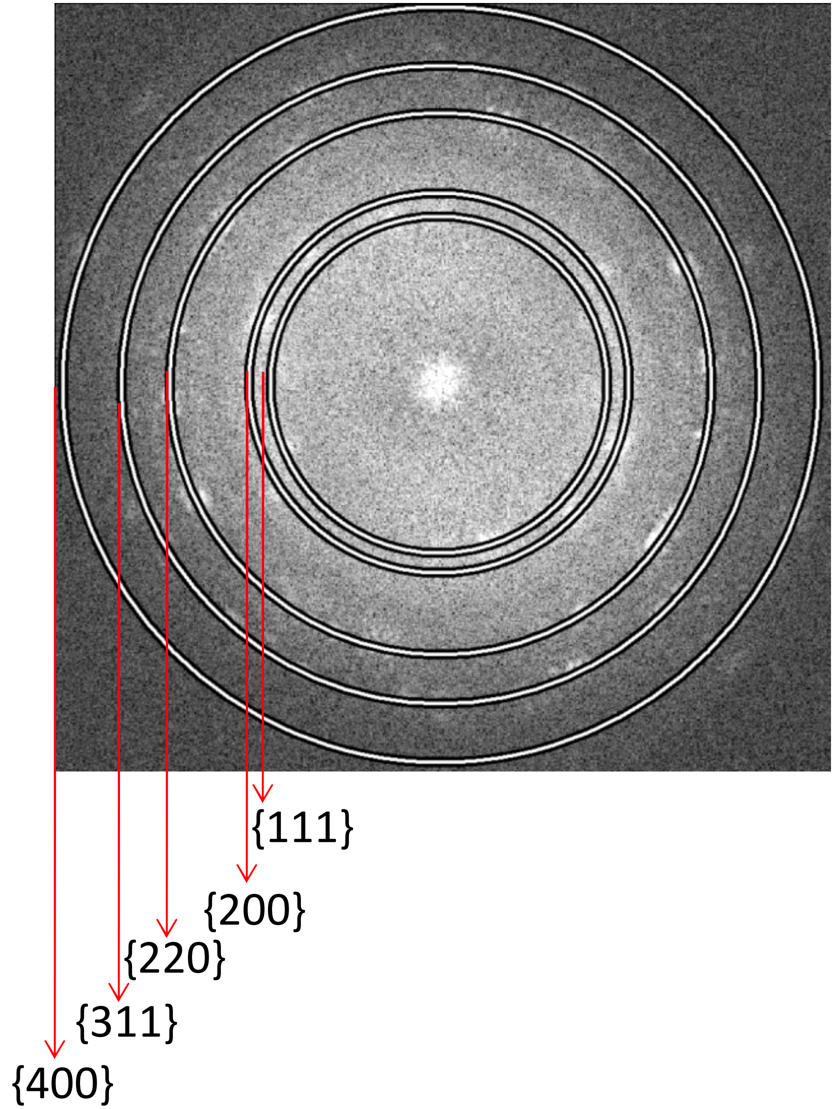


UO_2 highly stable, and NPs convert quickly

FFT of TEM Support Evidence of Conversion to d-UO_2

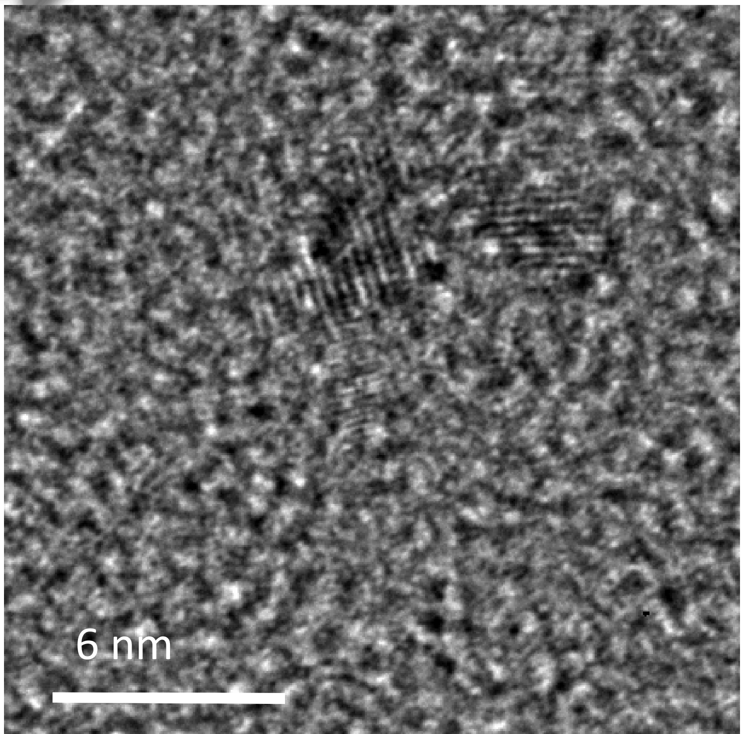


Fast Fourier Transform (FFT)

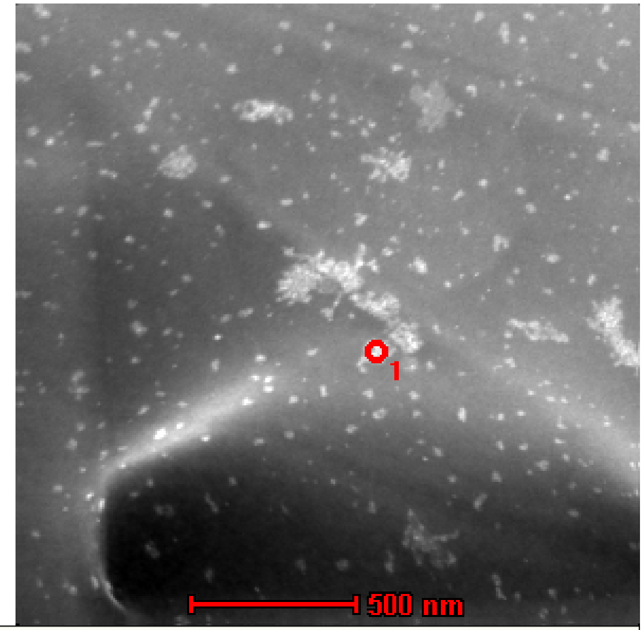


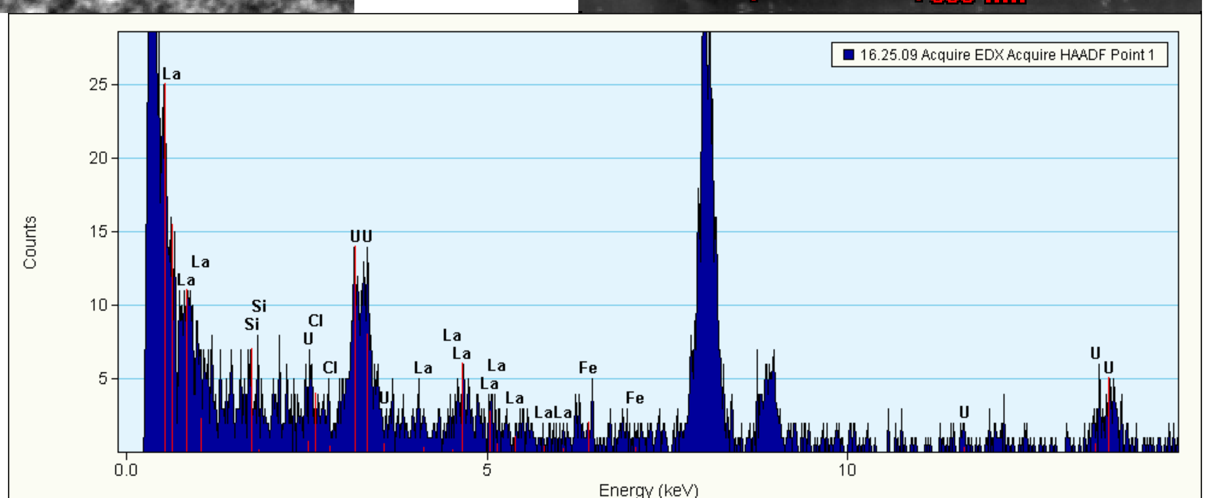
Diffraction indicates fcc-UO_2 phase

Alloyed d-U-La NPs by Radiolysis

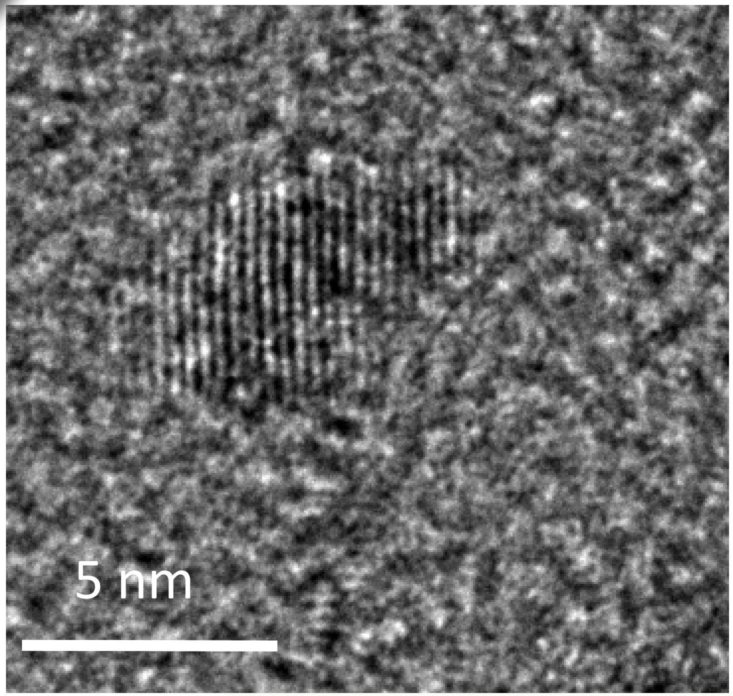


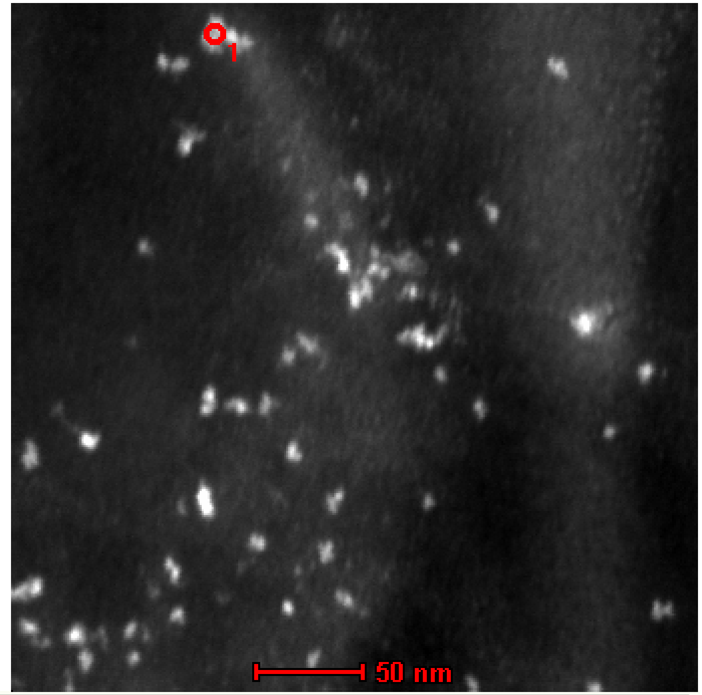
HAADF Energy-dispersive X-ray spectroscopy

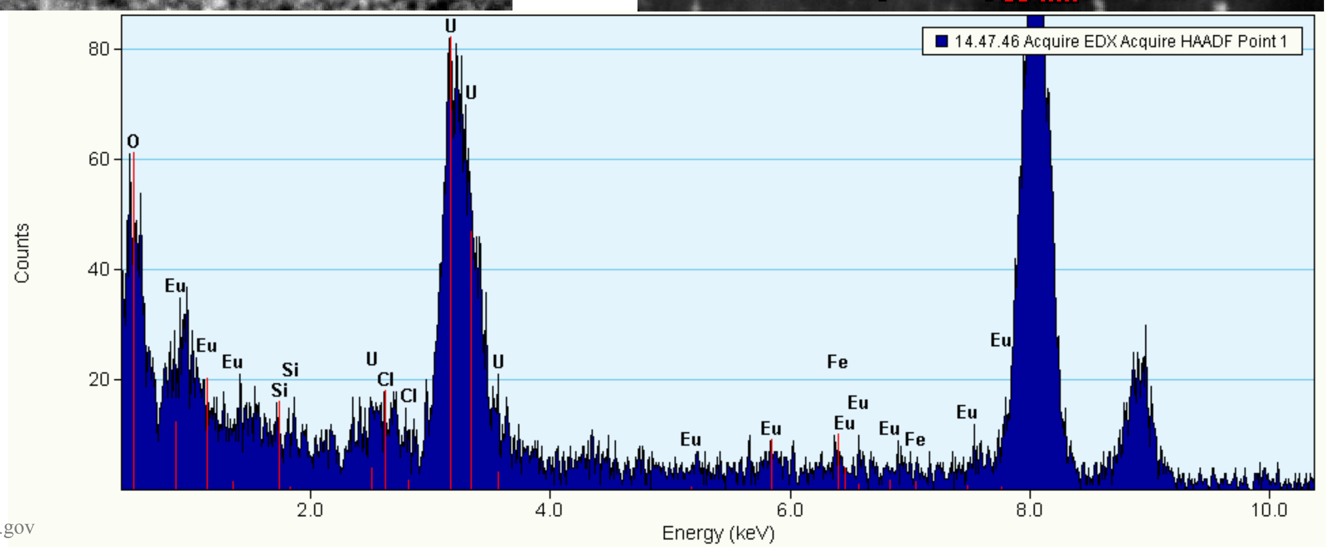




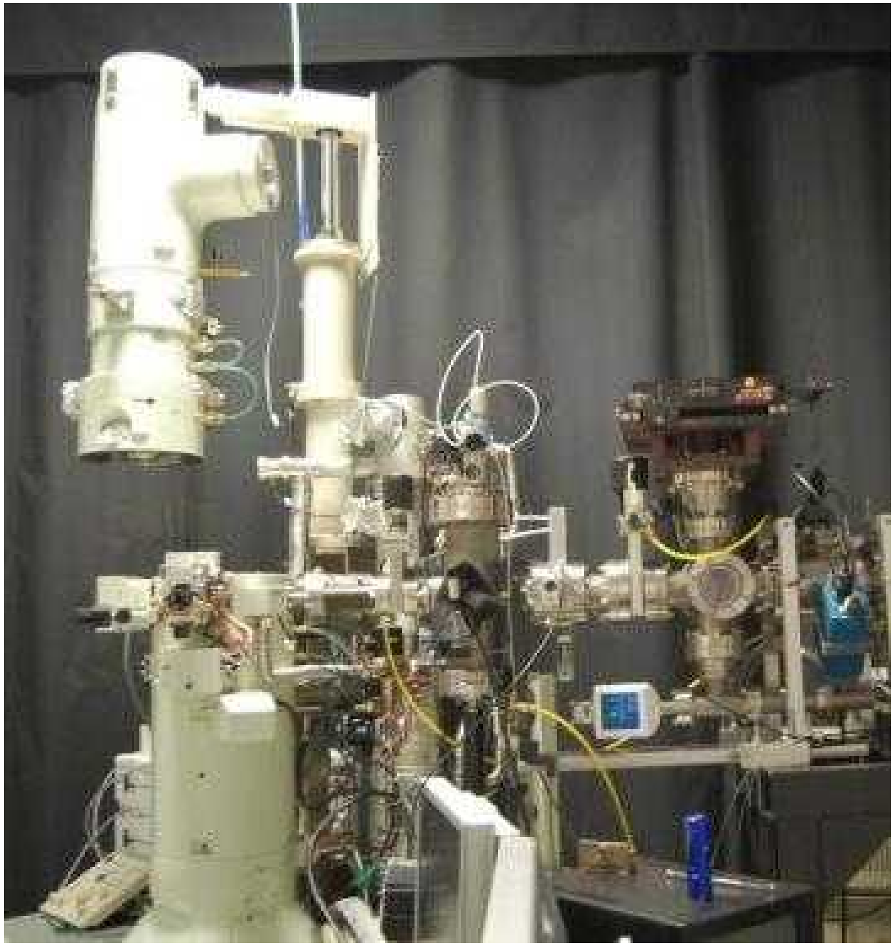
U-Eu Alloyed NPs







Sandia's IBL and I^3TEM (BES funded)



Knowledge of room temp oxide synthesis pathways:
- important for to the field of nuclear waste where high temp synthesis methods may result in volatilization of component oxides

La Oxide nanostructures sysnthesis
From salt solutions
Exposure to 200kV TEM electron beam

Solutions flowed through a microfluidic
TEM statge

Nucleation and growth process ,

Nanostructure formation pathways
Monitored

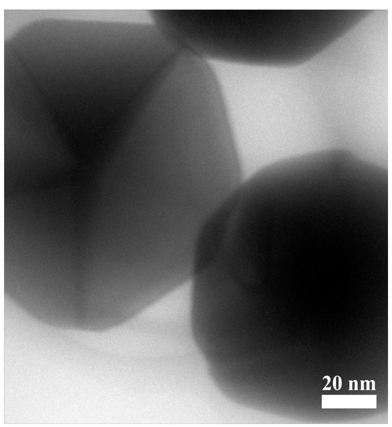
Solution concentration and flow ragte
Conditions greatly influence the
Resulting nanostructure

In Situ Environmental Stages: Mixing Liquid

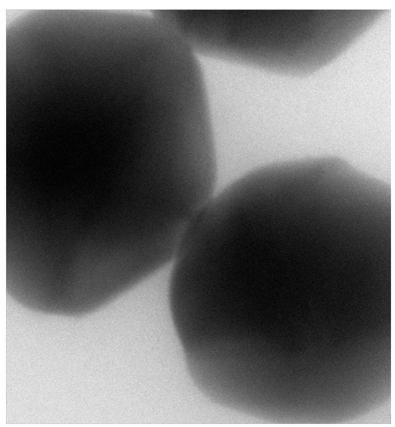
- 200 kV JEOL JEM 2100 TEM
at the Sandia National Laboratories Ion Beam Laboratory, and a Poseidon in situ microfluidic TEM stage developed by Protochips, Inc.
- two Si chips with 50 nm thick SiN
windows, each 400 x 50 □m in dimension. Two O-rings sealed the liquid cell and a metal plate (with a small hole for the electron beam to enter) was screwed on top.

Microfluidic Stage

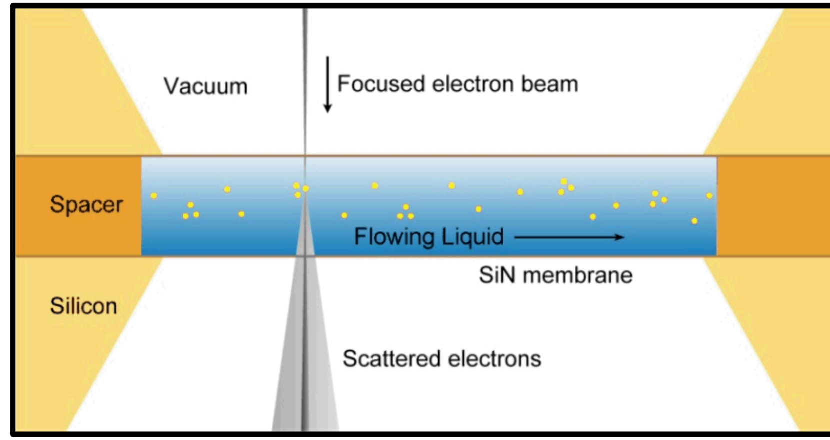
- Mixing of two channels
- *In situ* resistive heating
- Continuous observation of the reaction channel
- Chamber dimensions are controllable

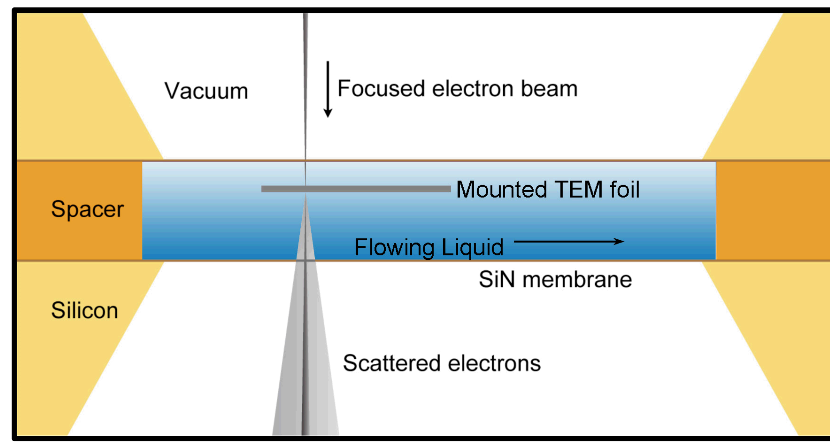


Au, Without Water



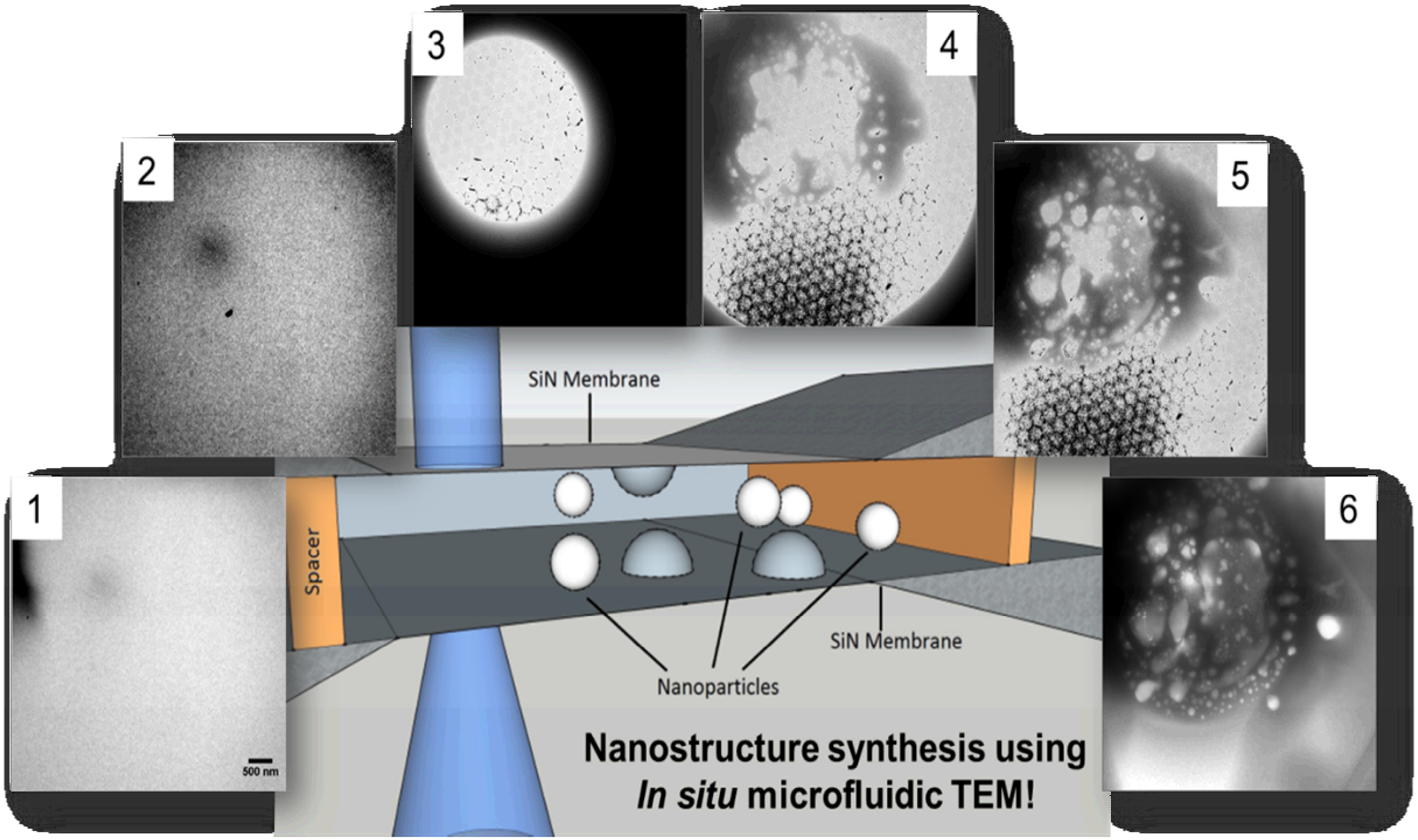
Au, Water Flow 100 μL/hr



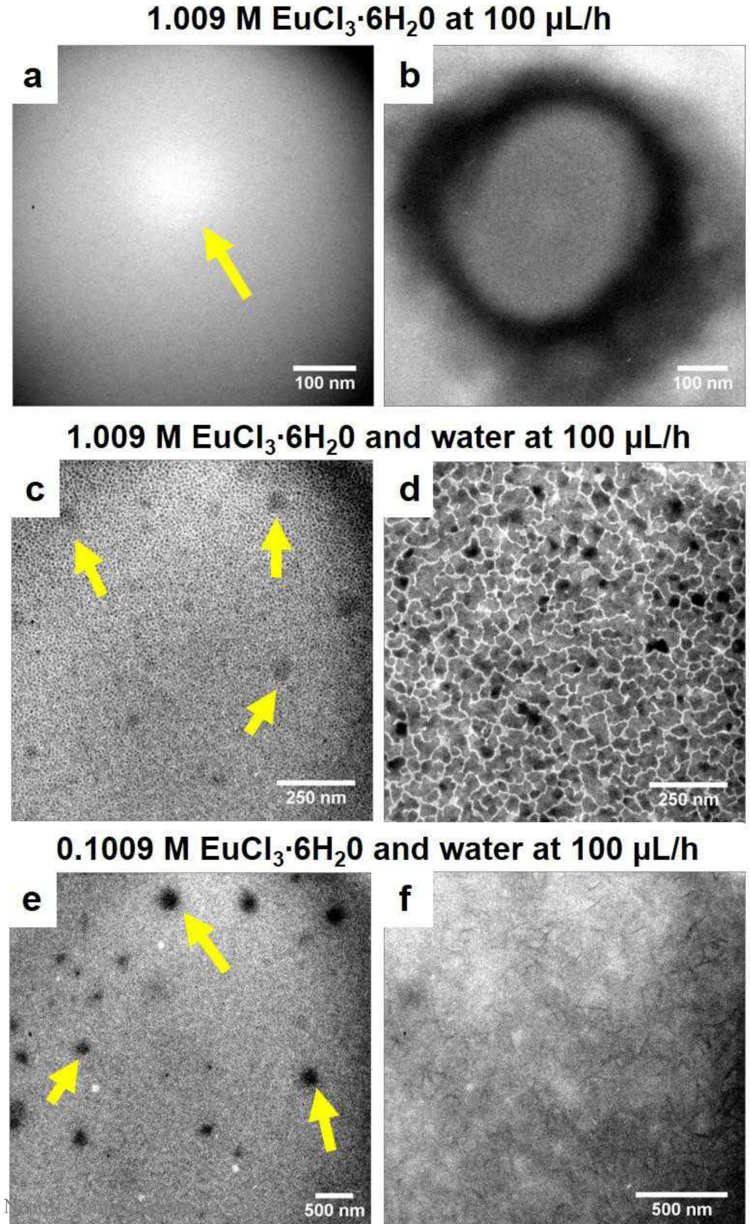


Cross-sectional schematic of liquid cell

Microfluidic TEM studies of La, Eu, and Y NP growth



Eu NP growth, affect of concentration and flow rates



Images showing nanostructure evolution in $Eu(NO_3)_3 \cdot 6H_20$ solution at the various concentrations and flow conditions explored in this study before and after focusing the electron beam to form the final structure.

Yellow arrows: ppts

Left before focusing the beam, right after focusing the beam
Different concentrations and flow rates.

Conclusions

γ-irradiation allows for room temperature synthesis of U containing NPs.

Successfully optimized pH conditions for d-UO_2 NP formation. UO_2 NPs formed by g-irradiation at 5 rad/s and 300 rad/s from $UO_2((NO_3)_2)$ and UCl_4.

Sintering of d-UO_2 ≈ 2-5nm NPs. NP sintering occurs at 500 to 700°C.

Preliminary evidence of U metal NP formation and U-Lanthanide alloying NPs.

However, data shows lack of stability against oxidation for U metal which, by extension is expected in alloys.

Work in Progress:

Stabilization of U metal and alloy NPs needed.

Investigate NP stability in sealed vessels without exposure to air.

Sintering of metals and alloys to determine sintering temperature.

Sandia National Laboratories

Albuquerque, New Mexico

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Engineers and Scientists
Fiscal year Oct 1 – Sept 30
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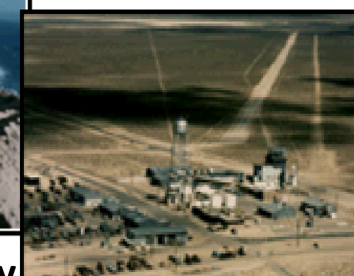
Kauai Test Facility
Hawaii

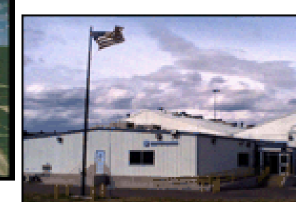


Tonopah Test
Range, Nevada

Livermore, CA

Yucca Mountain,
Nevada

WIPP,
New Mexico



Pantex, Texas

Sandia Truman Fellowship FY19

Seeking Applicants!

Sandia National Laboratories is seeking applicants for the **President Harry S. Truman Fellowship** (in National Security Science and Engineering).

Candidates for this position are expected to have solved a major scientific or engineering problem in their thesis work or have provided a new approach or insight to a major problem, as evidenced by a recognized in

The Fellowship provides the opportunity for new Ph.D. scientists and engineers to pursue independent research of their own choosing that supports Sandia's national security mission.

The appointee is expected to foster creativity and to stimulate exploration of forefront S&T and high-risk, potentially high-value research and development.

Sandia's research focus areas are: bioscience, computing and information science, engineering science, materials science, nanodevices and microsystems, radiation effects and high energy density physics, and geosciences.

The Truman Fellowship is a three-year appointment. The salary is $111,200 plus benefits and research funding for the proposal.

The deadline is November 1 of each year and normally begins on October 1 the following year.

Requirements:

Candidates must meet the following requirements:

- Ph.D. awarded within the past three years at the time of application or completed Ph.D. requirements; with strong academic achievement and evidence of exceptional technical accomplishment, leadership, and ability to team effectively
- Candidates must be seeking their first national laboratory appointment (no previous postdoc at a national laboratory)
- Ability to obtain a DOE "Q" clearance, which requires US citizenship

Visit http://sandia.gov/careers/students_postdocs/fellowships/truman_fellowship.html

Jill Hruby Fellowship FY19

Seeking Applicants!

Sandia National Laboratories is seeking applicants for the **Jill Hruby Fellowship** in National Security Science and Engineering.

This fellowship aims to develop **women** in the engineering and science fields who are interested in technical leadership careers in national security.

Applicants must display excellent abilities in scientific and/or engineering research and show clear promise of becoming outstanding leaders.

Jill Hruby Fellows have the opportunity to pursue independent research that supports Sandia's purpose: to develop advanced technologies to ensure global peace. **In addition to receiving technical mentorship, Jill Hruby Fellows participate in a unique, prestigious leadership development program.**

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- Ability to obtain a DOE security clearance, which requires US citizenship

Visit http://www.sandia.gov/careers/students_postdocs/fellowships/hruby_fellowship.html

Questions? / Thank you

Extra Slides