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			5c. PROGRAM ELEMENT NUMBER		
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14. ABSTRACT Goal: Use high resolution ex-situ TEM imaging and diffraction and in-situ LCTEM video to understand the MOF structures and their fundamental mechanisms of their growth on the different ALD substrates. Link the TEM results with the porosity and gas sorption properties published previously by the Parson/Peterson groups					
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a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	UU		Nathan Gianneschi
					19b. TELEPHONE NUMBER 858-246-0857

## Report Title

Final Report: Growth on Treated Surfaces and Degradation Under Various Conditions of Metal Organic Frameworks Captured by In Situ Liquid TEM

### ABSTRACT

Goal: Use high resolution ex-situ TEM imaging and diffraction and in-situ LCTEM video to understand the MOF structures and their fundamental mechanisms of their growth on the different ALD substrates. Link the TEM results with the porosity and gas sorption properties published previously by the Parson/Peterson groups

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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Number of Presentations: 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received      Paper

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**(d) Manuscripts**

Received      Paper

**TOTAL:**

Number of Manuscripts:

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**Books**

Received      Book

**TOTAL:**

Received

Book Chapter

**TOTAL:**

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**Patents Submitted**

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**Patents Awarded**

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**Awards**

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Lucas Parent	1.00
<b>FTE Equivalent:</b>	<b>1.00</b>
<b>Total Number:</b>	<b>1</b>

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Nathan Gianneschi	0.10	
<b>FTE Equivalent:</b>	<b>0.10</b>	
<b>Total Number:</b>	<b>1</b>	

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**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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**Names of Personnel receiving masters degrees**

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**Total Number:**

**Names of personnel receiving PHDs**

NAME  
**Total Number:**

**Names of other research staff**

NAME                      PERCENT SUPPORTED  
**FTE Equivalent:**  
**Total Number:**

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

PDF Attached

**Technology Transfer**

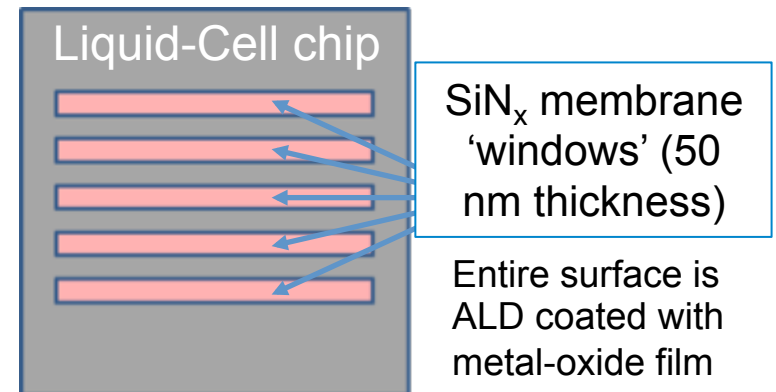
# ZIF-8 MOF Growth on ALD Metal-Oxide Thin-Film Substrates

(Collaboration between Gianneschi group, Parson group, and Peterson group)

**Goal:** Use high resolution *ex-situ* TEM imaging and diffraction and *in-situ* LCTEM video to understand the MOF structures and their fundamental mechanisms of their growth on the different ALD substrates → Link the TEM results with the porosity and gas sorption properties published previously by the Parson/Peterson groups

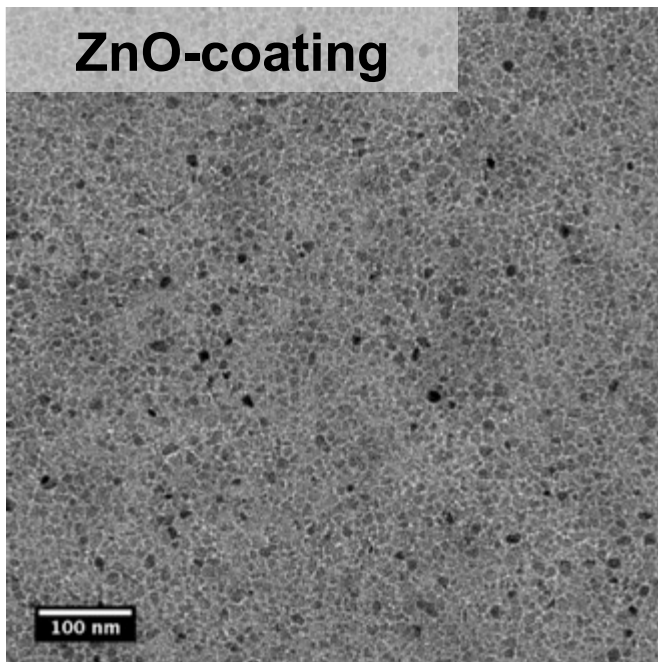
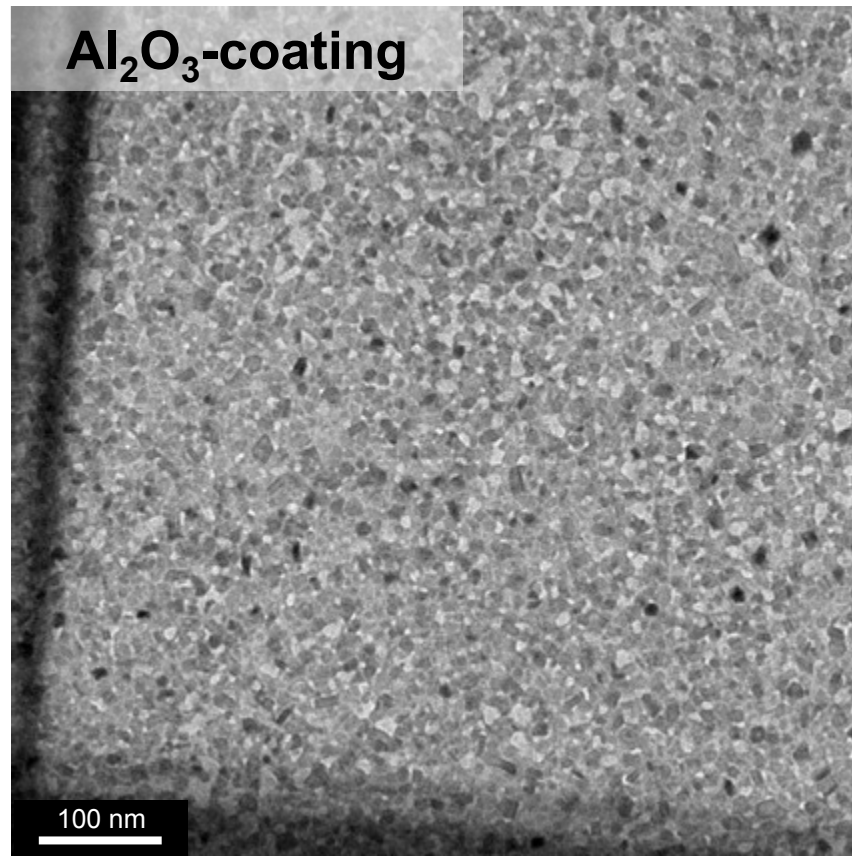
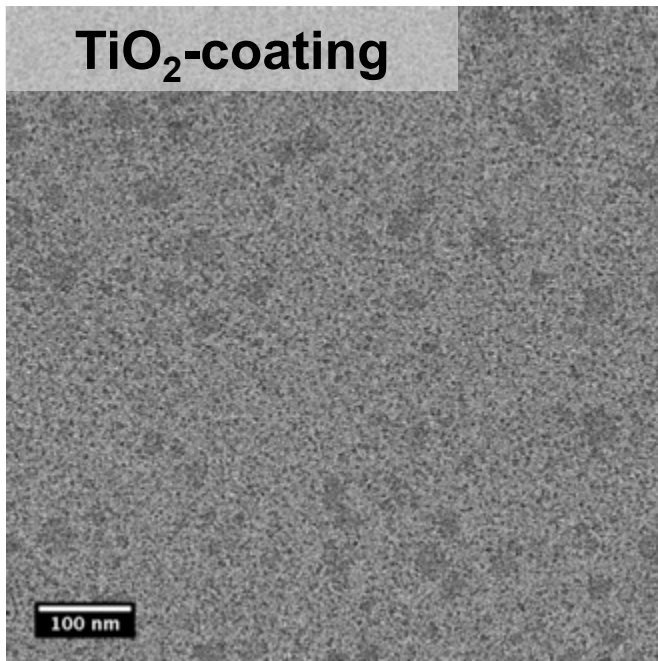
## Experimental Protocol:

- ALD Coating of the liquid-cell chips with chips with three different metal-oxide thin-films ( $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ ) → Parson group (NC State)
- 1. Ex-situ TEM: ALD coated chips are submerged in ZIF-8 precursor growth solution for several days → ZIF-8 nucleates and grows on ALD film
  - Image and diffraction patterns of MOF structures
- 2. In-situ LCTEM: Assemble the liquid-stage with ALD coated chips and flow in the ZIF-8 growth solution
  - Acquire live TEM video of MOF nucleation and growth
- For both types of experiments, compare the different metal-oxide surfaces



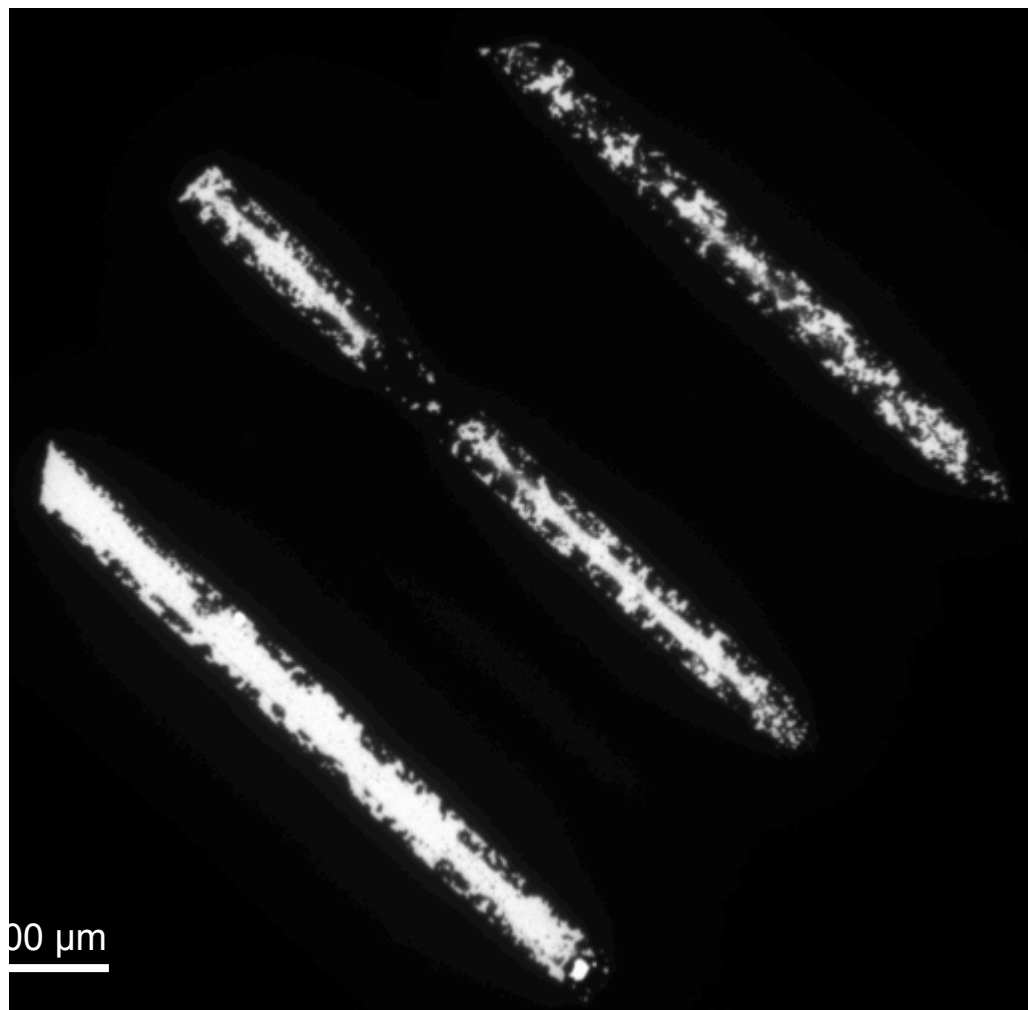
(ZIF-8 growth solution: Zinc-nitrate mixed with methylimidazole in methanol)

# ALD coatings on $\text{SiN}_x$ membrane prior to ZIF-8 growth

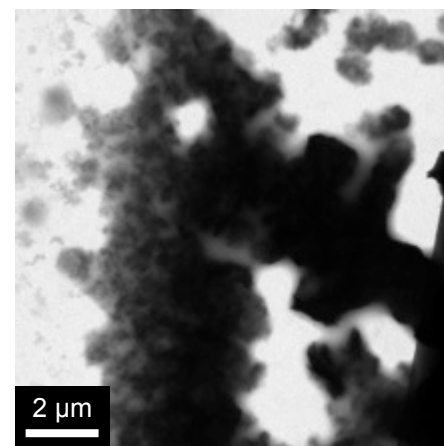
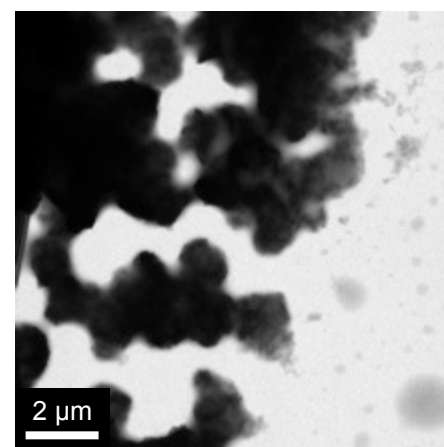
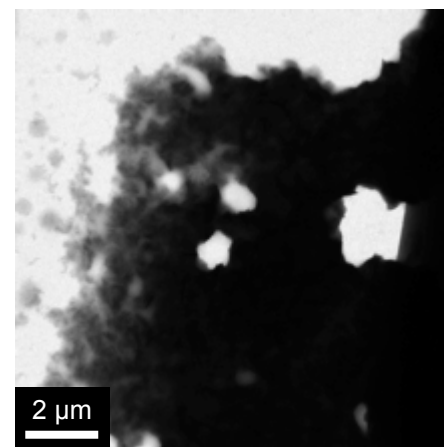


- All three different ALD metal-oxide coatings have polycrystalline (inhomogeneous) structures → this grain structure is most evident in the ZnO and Al<sub>2</sub>O<sub>3</sub> coatings
- We hypothesize that certain defect sites or grains with preferential orientation may serve as MOF nucleation locations
- The differences in the metal-oxide coatings atomic structure and grain structure could be a major factor in the differences in MOF structures that grow on their respective surfaces

## $\text{Al}_2\text{O}_3$ coated chips – *ex situ* MOF growth

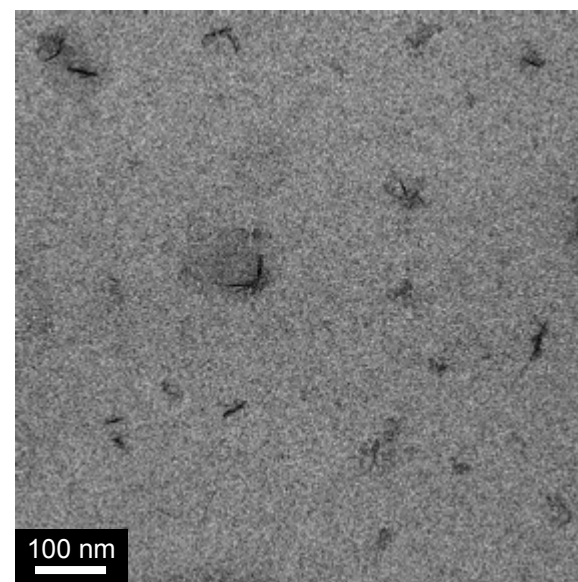
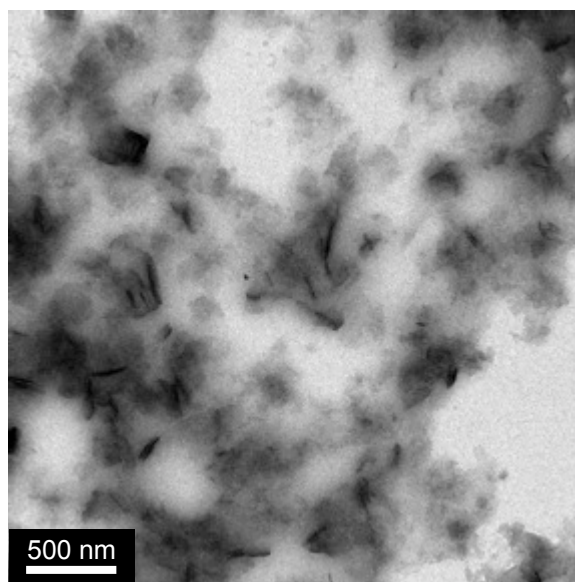
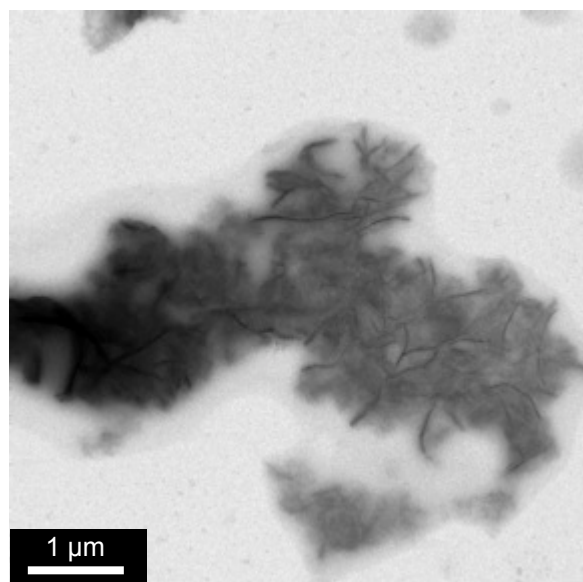
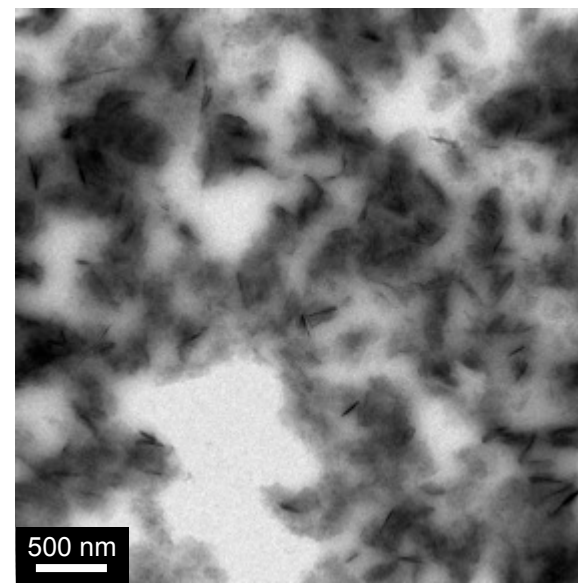
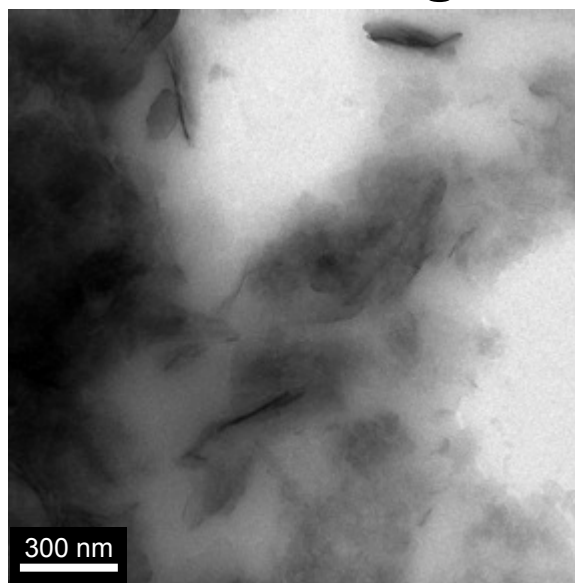
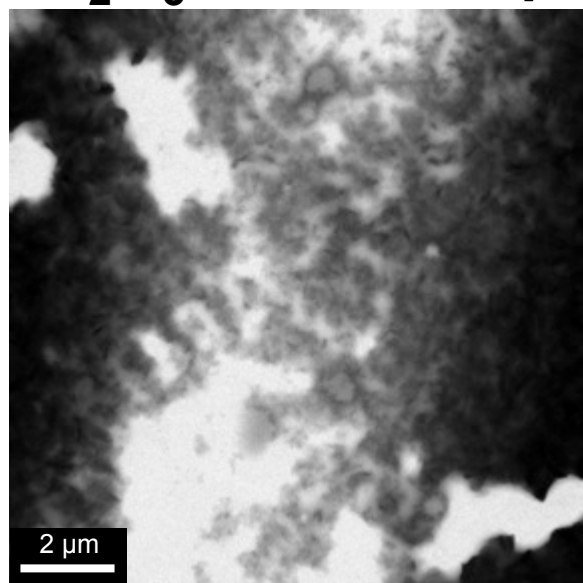


**ZIF-8** grown on  $\text{Al}_2\text{O}_3$  ALD coated chip has good coverage with large/thick MOF structures, composed of sub-crystallites



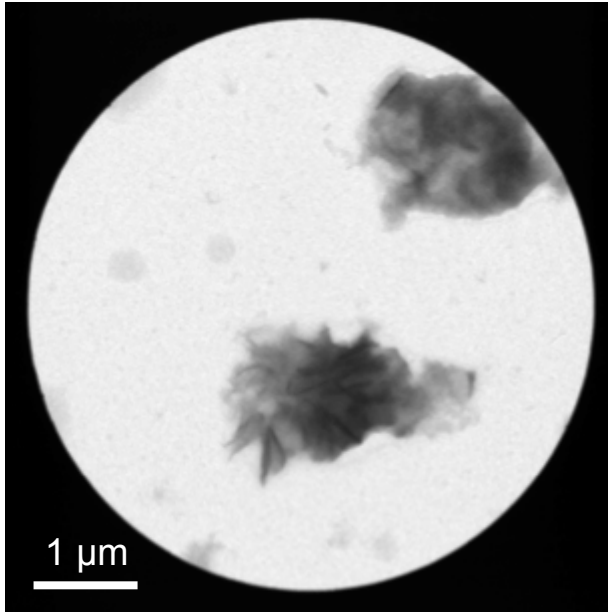


## $\text{Al}_2\text{O}_3$ coated chips – *ex situ* MOF growth

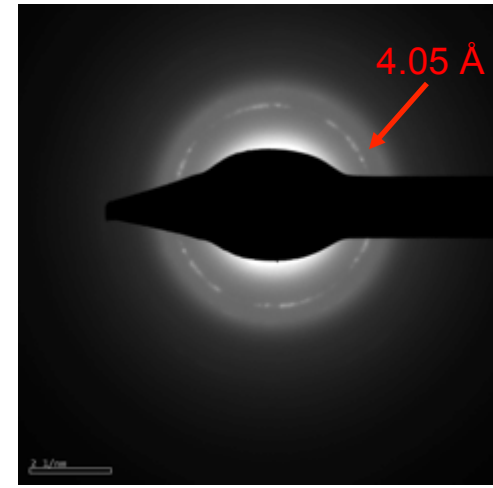
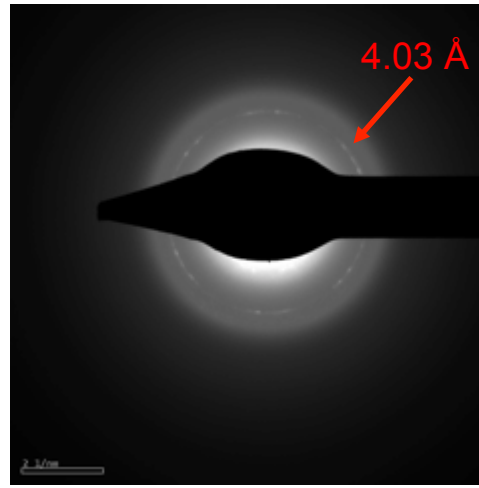
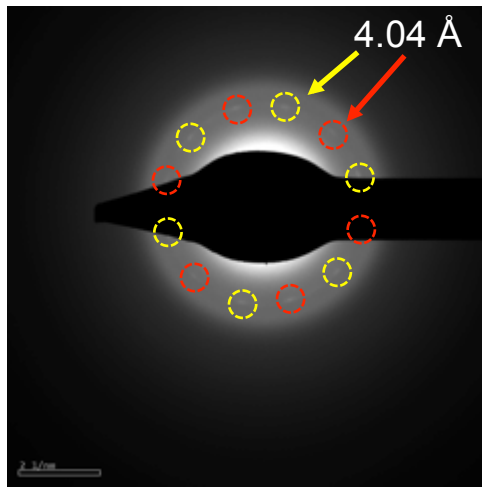


**ZIF-8** grown on  $\text{Al}_2\text{O}_3$  ALD coated chip: Sub-crystallites have rod-like morphologies that cluster to form the large, macroscale MOFs. Individual, isolated rod MOFs crystallite are also found (lower right image).

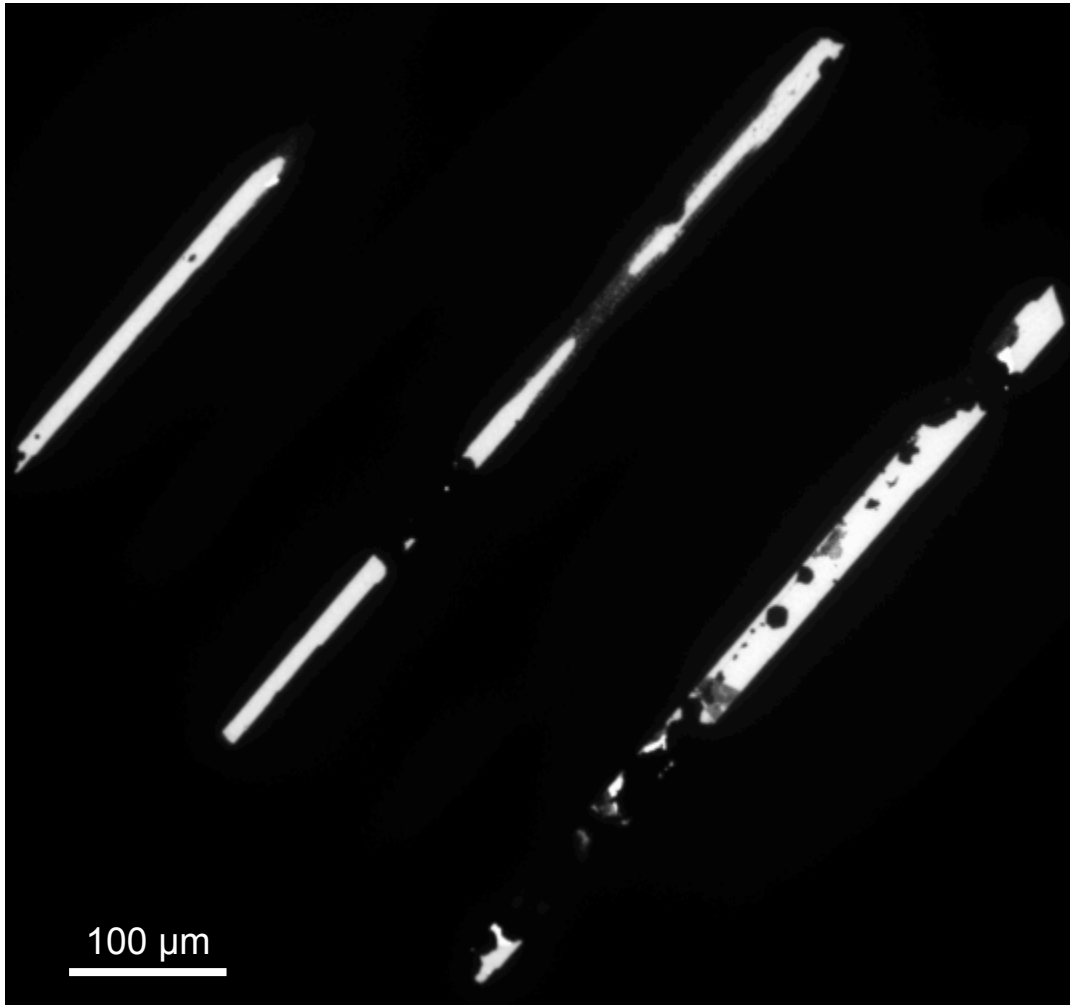
# $\text{Al}_2\text{O}_3$ coated chips – *ex situ* MOF growth



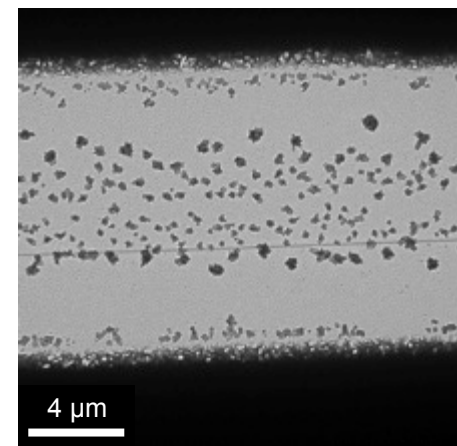
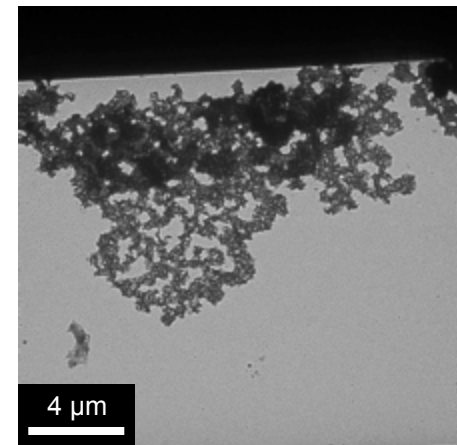
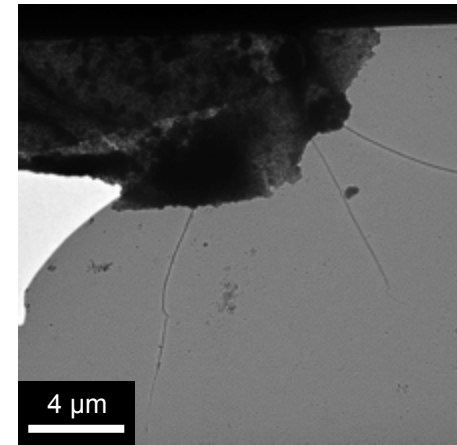
ZIF-8 grown on  $\text{Al}_2\text{O}_3$  ALD coated chip has an **hexagonal** crystalline nanostructure with a predominate lattice spacing of  **$\sim 4.04 \text{ \AA}$**



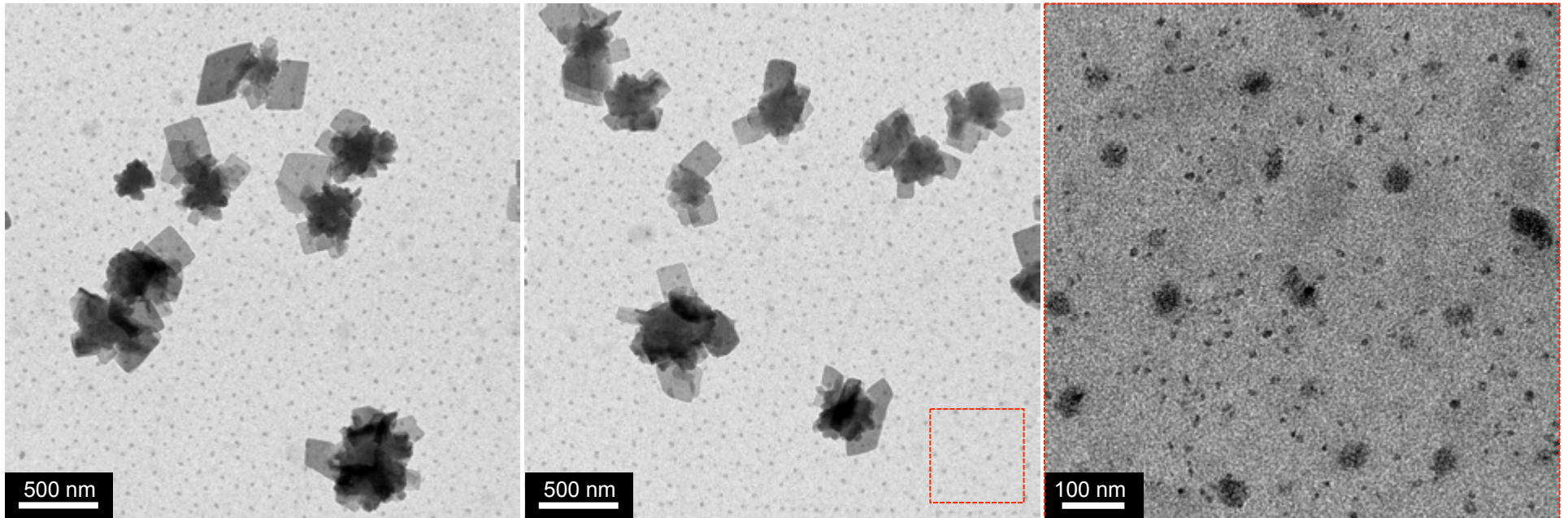
## ZnO coated chips – *ex situ* MOF growth



**ZIF-8** grown on **ZnO** ALD coated chip has moderate/patchy coverage with some large/thick and some smaller MOF structures, composed of sub-crystallites

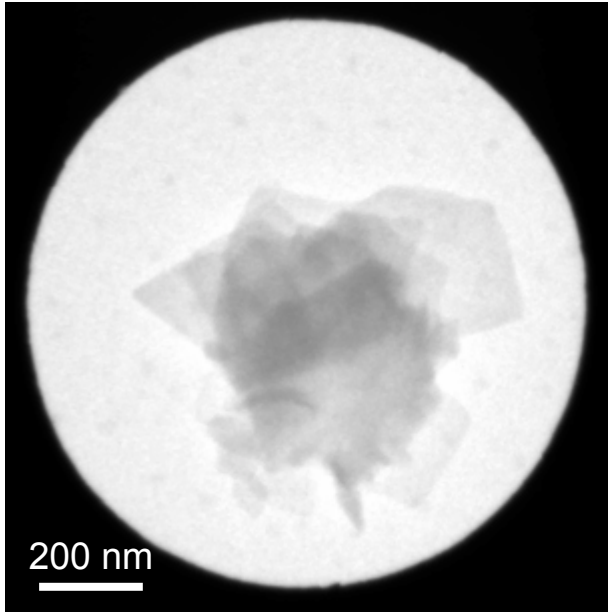


## ZnO coated chips – *ex situ* MOF growth

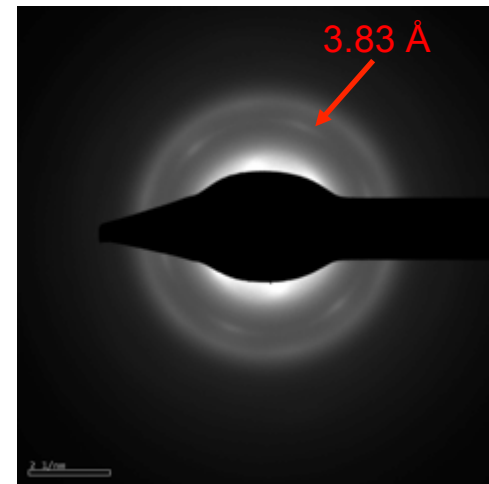
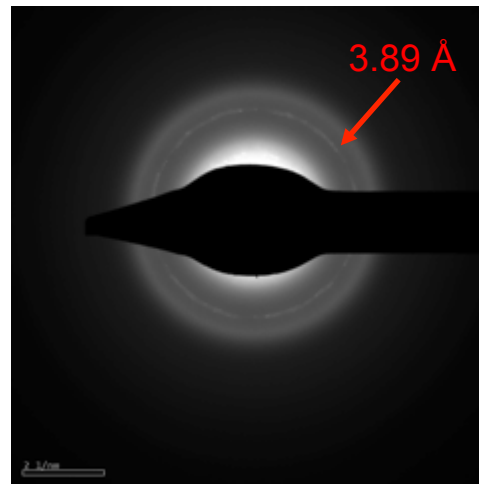
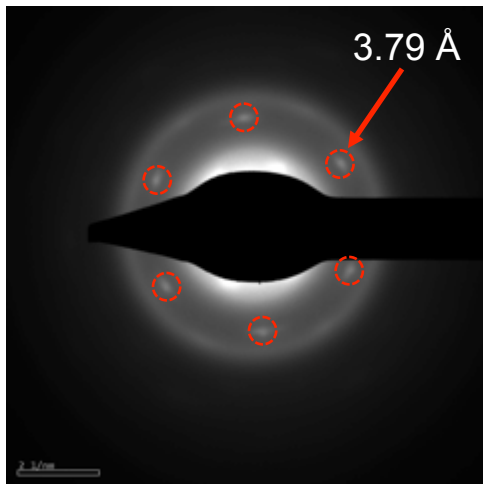


**ZIF-8** grown on **ZnO** ALD coated chip: Sub-crystallites have faceted, sheet-like morphologies that appear to grow in flower-like geometries as smaller isolated structures. We are currently unable to identify the speckled material in the background, red box (is it small MOF seeds or simply free metal that precipitated from the precursor solution upon drying the chip?).

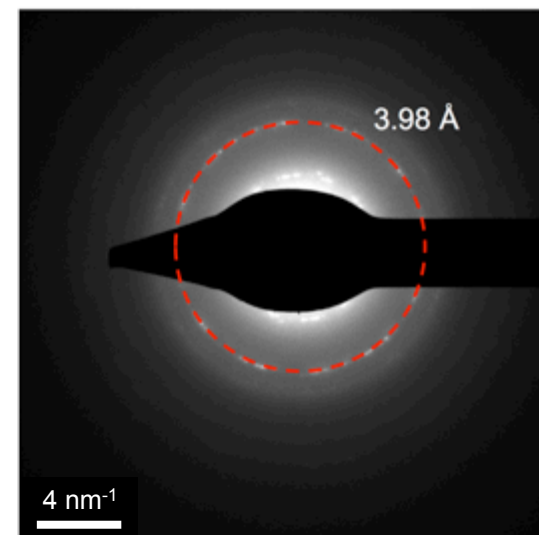
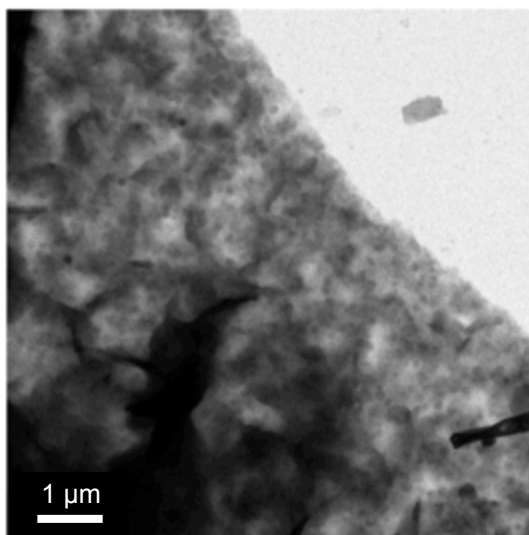
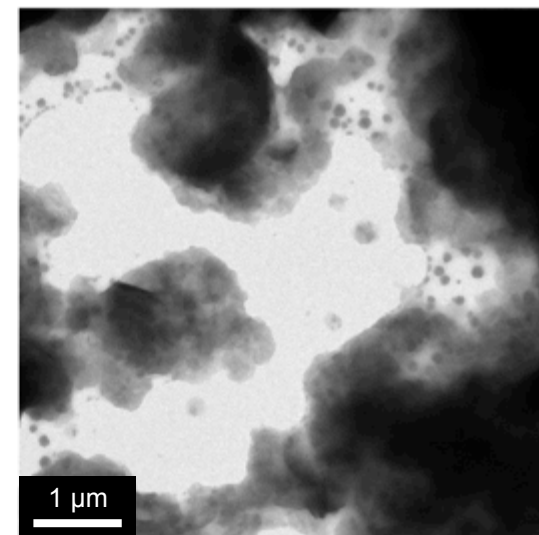
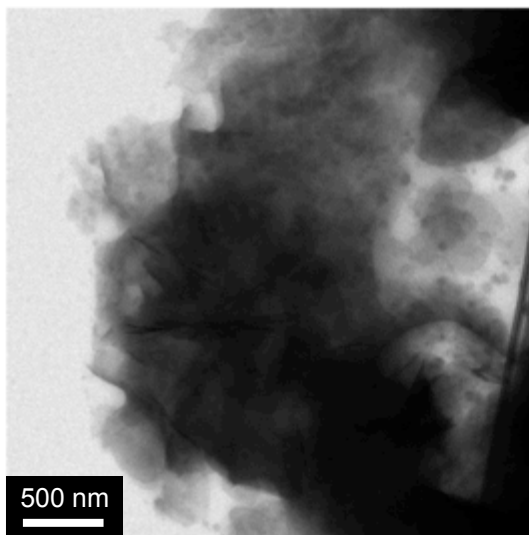
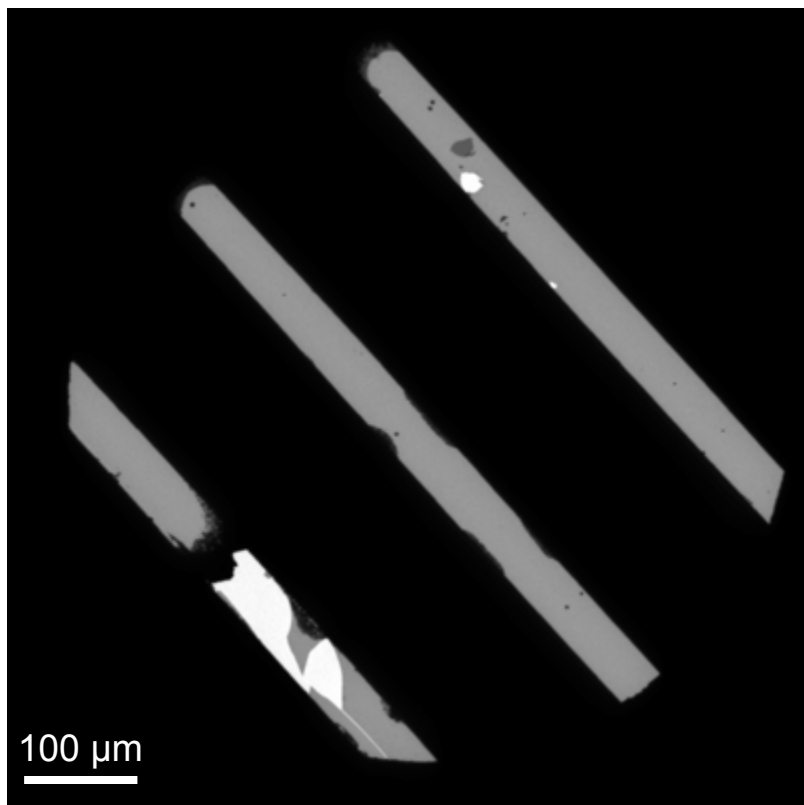
# ZnO coated chips – *ex situ* MOF growth



ZIF-8 grown on ZnO ALD coated chip has an **hexagonal** crystalline nanostructure with a predominate lattice spacing of **~3.85 Å**



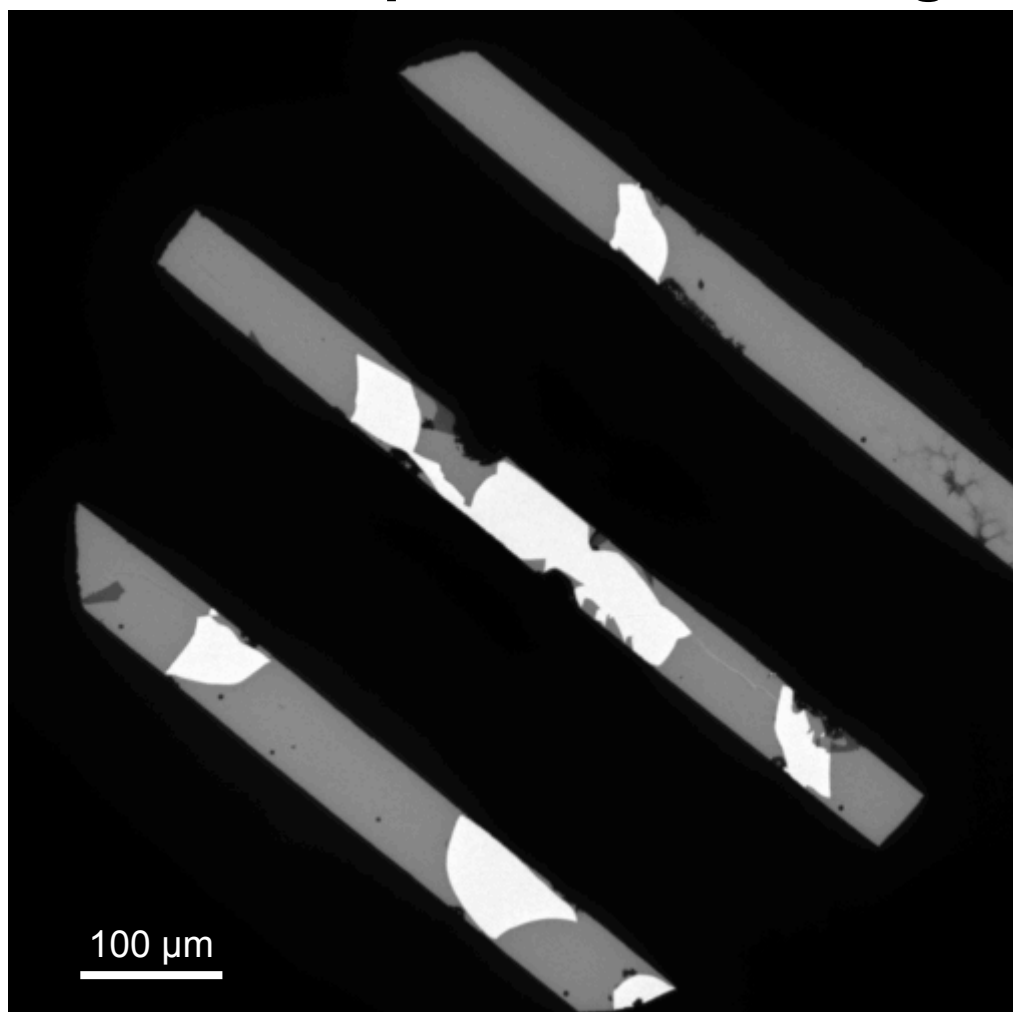
## TiO<sub>2</sub> coated chips – *ex situ* MOF growth



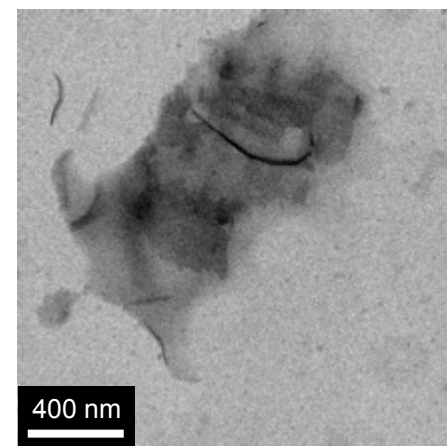
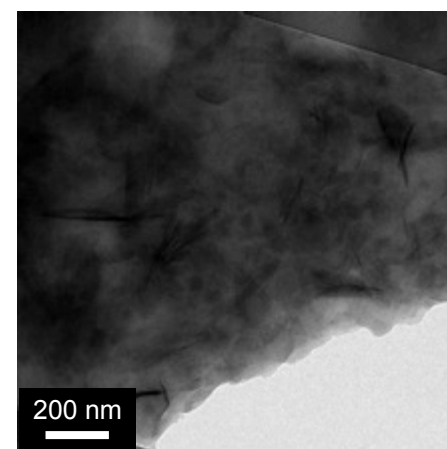
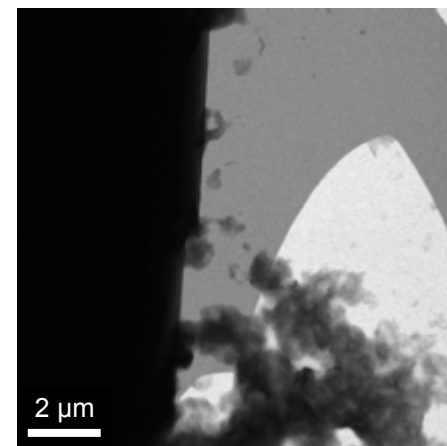
**ZIF-8** grown on **TiO<sub>2</sub>** ALD coated chip has low-moderate/patchy coverage with some large/thick and some smaller MOF structures, composed of sub-crystallites of particle-like or sheet-like morphologies

**ZIF-8** grown on **TiO<sub>2</sub>** ALD coated chip has crystalline nanostructure with a predominate lattice spacing of **~3.98 Å**

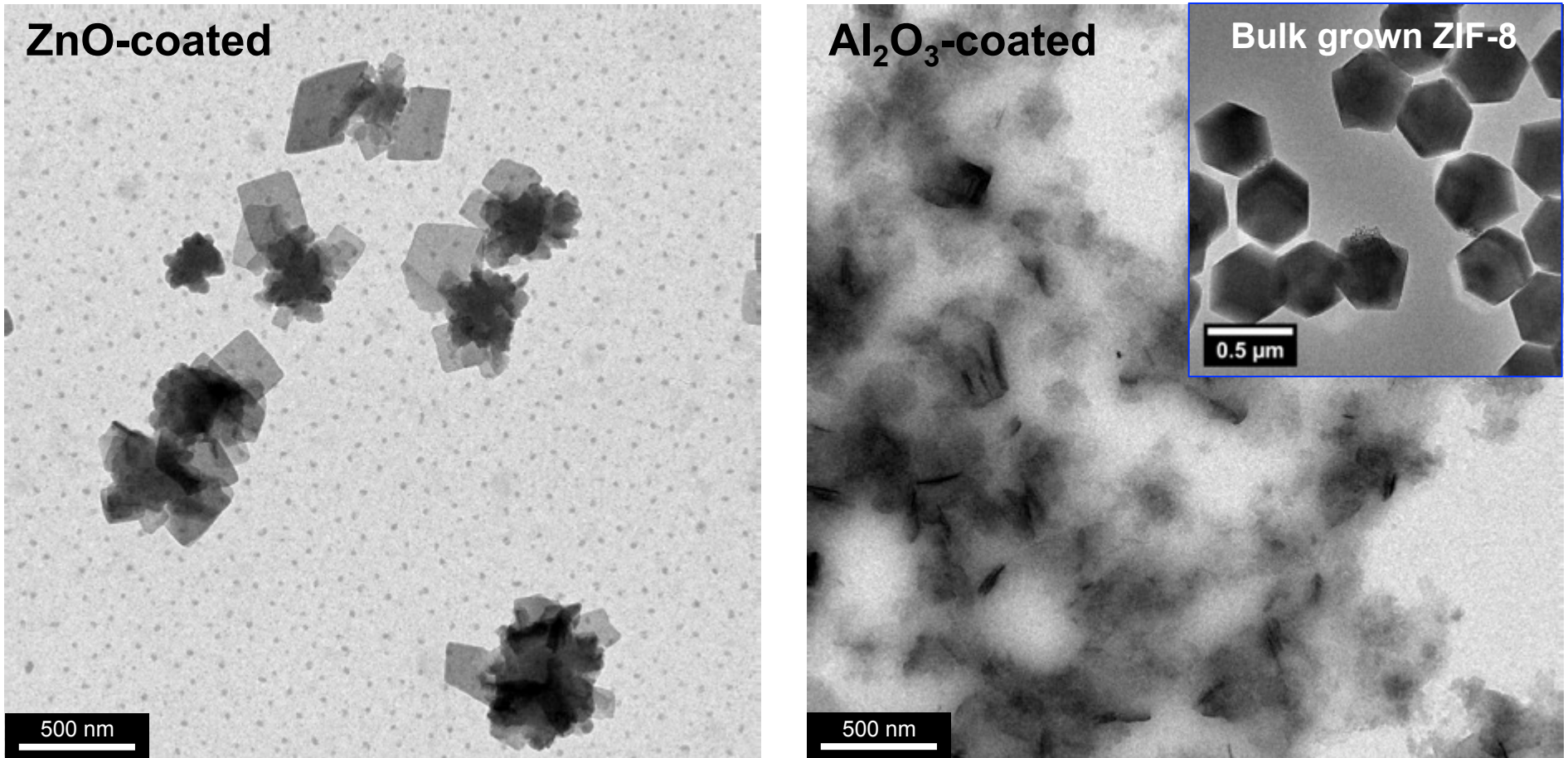
## Non-coated chips – *ex situ* MOF growth



**ZIF-8** grown on **non-coated** chip has little coverage with some large/thick MOFs but mostly smaller MOF structures, composed of sub-crystallites in rod-like or particle-like morphologies (similar to  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  surfaces). No morphologies similar to those on ZnO chip.



## Summary – *ex situ* MOF growth



- ZIF-8 grown on **ZnO** has lower coverage, generally smaller structures and sheet-like sub-crystallite morphologies. Predominant lattice spacing is  $\sim 3.85$  Å and is hexagonal.
- ZIF-8 grown on **Al<sub>2</sub>O<sub>3</sub>** has very high coverage, large structures and rod-like sub-crystallite morphologies. Predominant lattice spacing is  $\sim 4.04$  Å and is hexagonal.
- Oxide-substrate clearly influences the bulk MOF morphology and its crystal structure during growth.
- ZIF-8 does not adhere as well to the **TiO<sub>2</sub>** substrate (predominant lattice spacing  $\sim 3.98$  Å), and very poorly adheres to uncoated SiN<sub>x</sub> membranes.



# *In situ* LCTEM Experiments (Summary of Results, Failed Experiments)

- First set of experiments using the ALD-coated chips was done mimicking Joe's JACS LCTEM MOF growth paper → pre-mix the the two precursor solutions, and using a syringe pump and the inlet line of the liquid stage to flow the mixture into the liquid-cell
  - The problem with this method is that MOF nucleation and growth is initiated before the solution reaches the ALD-coated windows
  - During the *in situ* LCTEM experiments run in this manner (using each of the three different metal-oxides), we did not observe any growth of MOF nanostructures in the viewing area of the liquid-cell (on the ALD-coated windows)
- The growth solution is methanol-based, which evaporates extremely quickly if small volumes are pipetted directly on the ALD-coated LCTEM chip surface (the typical preparation method for LCTEM experiments using aqueous solutions)
  - We tried working in the 4°C cold room, and rapidly pipetting the the first and then second MOF precursor solution directly on the ALD-coated chip surface, and then assembling the liquid-cell
  - In several attempts we were unable to maintain a hydrated liquid-cell by using this preparation method
  - The LCTEM growth experiments on the ALD-substrates will require a novel preparation method...

# Potential Future Work: ALD-Substrate MOF Growth Project

- Dry-state TEM imaging and diffraction characterization of the MOF structures formed when grown in bulk on the ALD-coated fibers (materials that have been published by Peterson group)
  - Using ZIF-8 MOF as comparison with the MOF structures we have grown on the ALD thin-film coated LCTEM chips
  - Using other MOFs of interest → understand differences in MOF nanostructure formation for different MOF chemistries and metal-oxide substrates
- Continue to pursue *in situ* LCTEM MOF growth experiments using the ALD-coated chips → MOF growth solution must be mixed directly on LCTEM chip surface (we are developing a picoliter sample deposition system for on-chip mixing that prevents evaporation for the LCTEM chips to enable the preparation of volatile solvent solution that are otherwise extremely difficult to load and maintain a hydrated liquid-cell)

# Gas-sorption and “Breathing” Behavior of MOFs Studied by *in situ* Environmental-TEM

(Collaboration between Gianneschi group and Cohen group → UCSD)

\*ETEM experiments conducted at PNNL EMSL user facility

**Goal:** Use nano-scale *in situ* ETEM imaging and diffraction in the presence of various gases ( $N_2+H_2O$ , CO and  $H_2$ ,  $CH_4$ ,  $CO_2$ ,  $N_2$ ...) to directly observe the fundamental mechanisms of molecular adsorption in individual MIL-53 MOF nanocrystals and the resulting transformations (“breathing” behavior) in the MOF lattice structure and overall nanocrystal morphology in real-time.

## Experimental Protocol:

- MIL-53 MOF samples are synthesized in nanoscale morphologies (sub-300 nm thick crystals) and prepared on standard copper/carbon TEM grids
- At vacuum/room temp in ETEM → selected MIL-53 MOF nanocrystals are imaged at high resolution and diffraction patterns (DPs) acquired
- Gas of choice is flown into the ETEM column (contacting MOF grid) at low pressure (<5 mbar), and selected MOF crystals are imaged/DP periodically over time to monitor and characterize any changes in nanostructure or morphology.
  - Temperature ramping (heating holder) can also be employed depending on the gas sorption or “breathing” behavior of interest

# Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or $\text{Cr}^{\text{III}}(\text{OH}) \cdot \{\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\} \cdot \{\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}\}_x \cdot \text{H}_2\text{O}_y$

Christian Serre,<sup>\*,†</sup> Franck Millange,<sup>†</sup> Christelle Thouvenot,<sup>†</sup> Marc Noguès,<sup>†</sup> Gérard Marsolier,<sup>‡</sup> Daniel Louër,<sup>‡</sup> and Gérard Férey<sup>\*,†</sup>

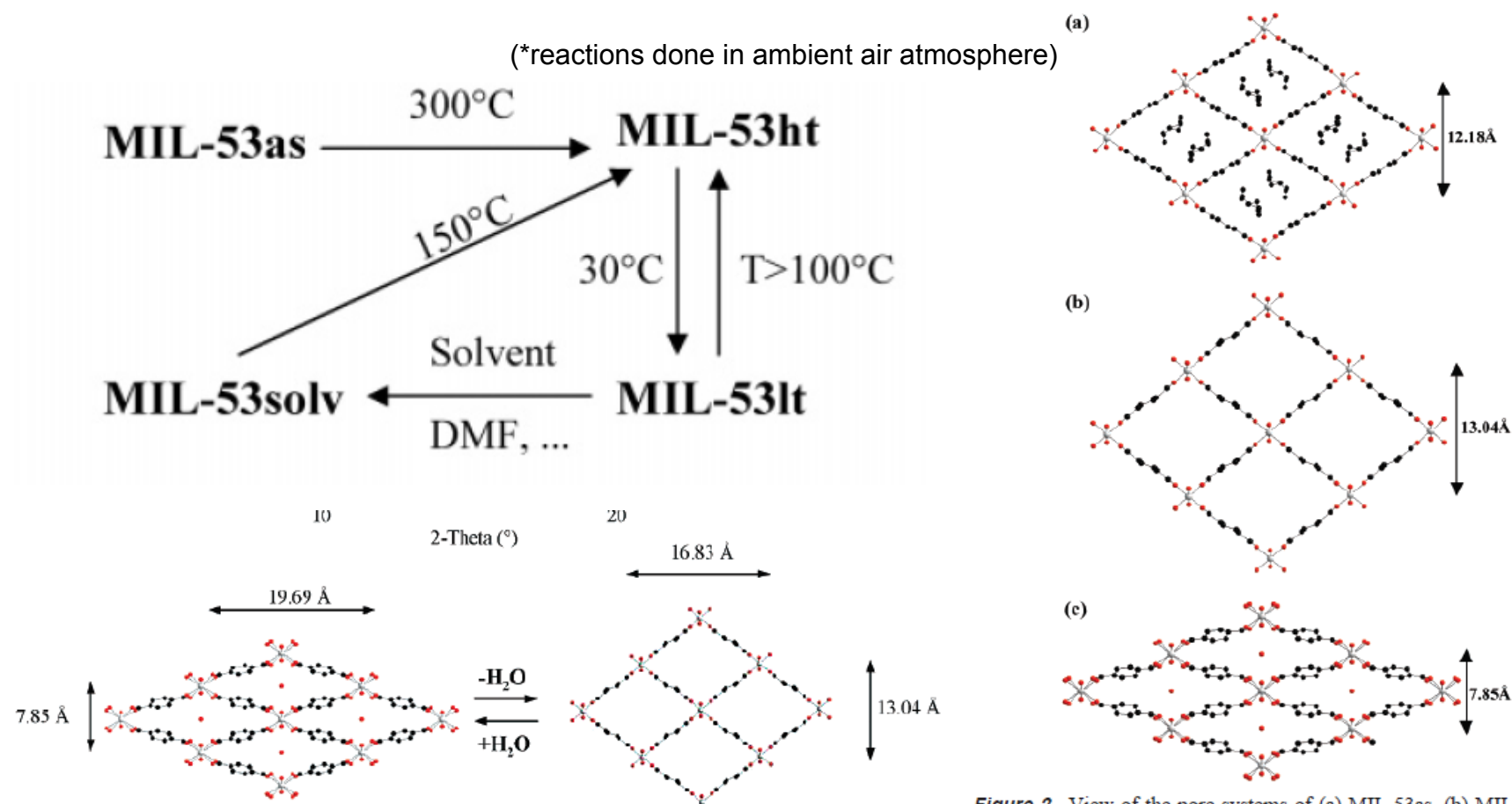


Figure 2. View of the pore systems of (a) MIL-53as, (b) MIL-53ht, and (c) MIL-53lt.

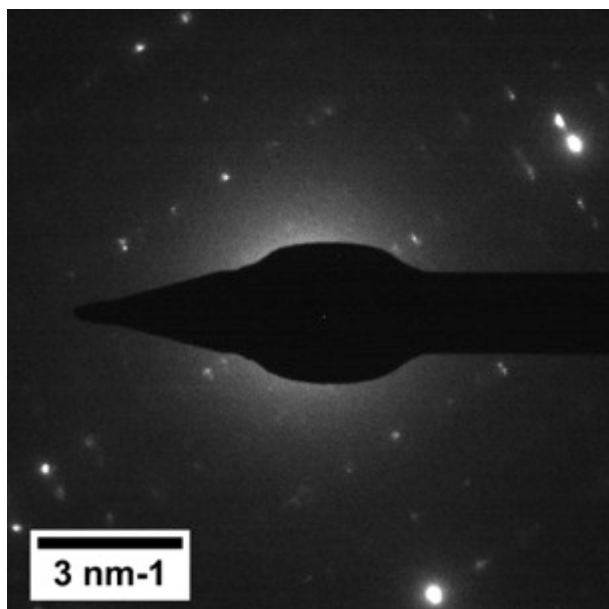
# Cr MIL-53 ETEM exp 1

(Based on JACS paper on previous slide)

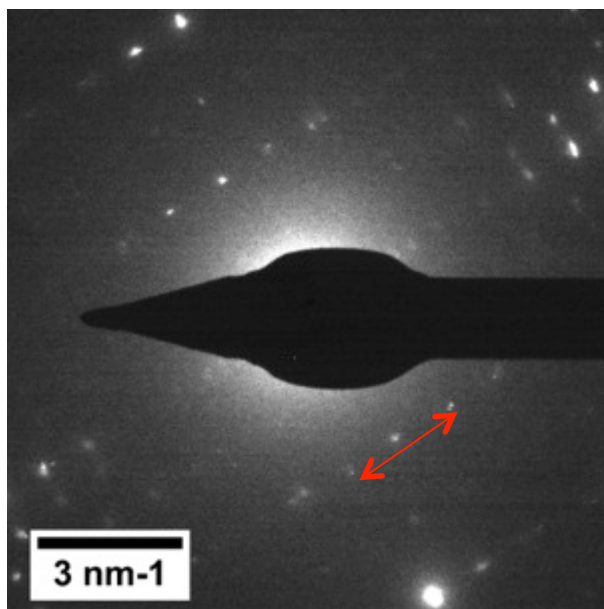
1. High vacuum, room temp (*Im19, DP20*)
2. 3 mbar H<sub>2</sub>O, 30 mins, room temp (*Im21, DP22*)
3. Heat to 300°C, 20 mins, 2.6 mbar, (*Im23, DP24*)
4. Cool to room temp quickly, 5 mins (*Im25, DP26/27*)
5. Heat to 120°C, 5 mins (*Im28, DP29*)
6. Heat to 300°C, 20 mins (*Im30, DP31/32*)
7. Cool to room temp and left over night (14 hours) at pressure (*Im63, DP64*)

This was then followed by:

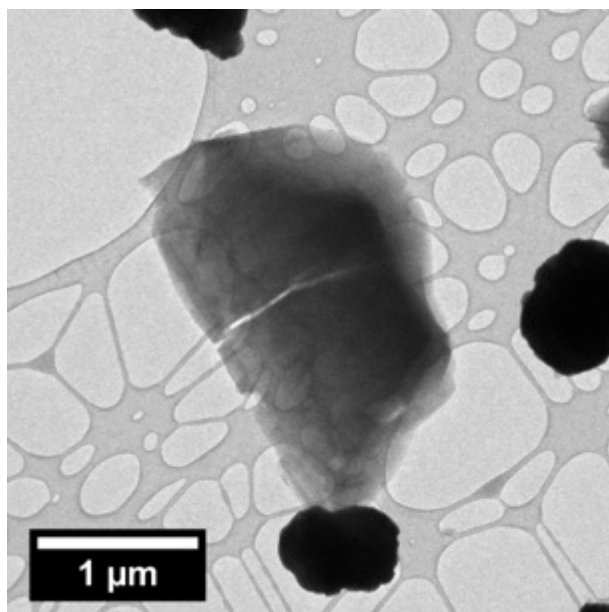
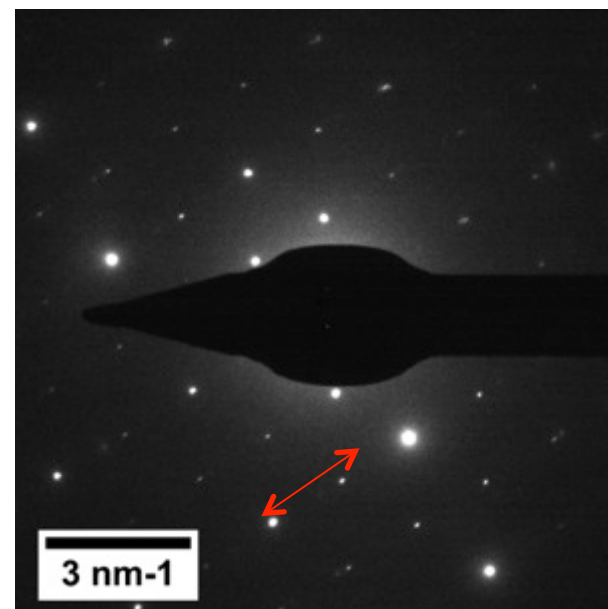
1. 3°C per min heating patterns from 30° – 300°C starting *Im65-92* held at 300°C *Im93* (+5mins) *Im94* (+ 10 mins)
2. Cool to r.t. *Im95/96/97* (few mins) *Im102* (+2 hours)
3. Removed holder, outside for 15 mins *Im104, DP103*



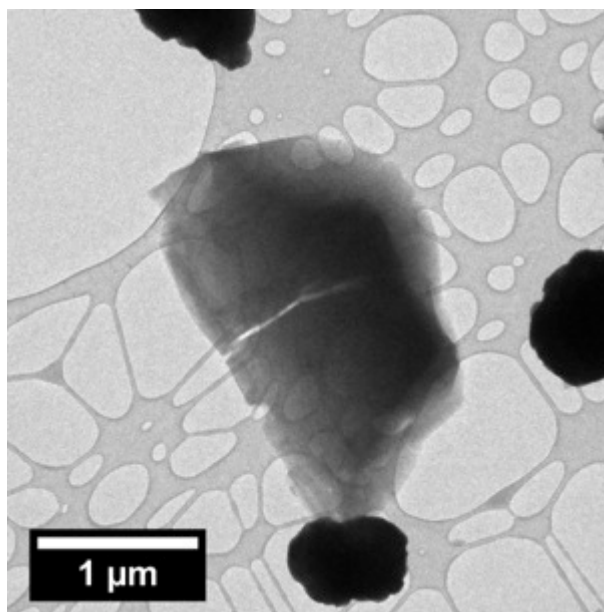
0.77 nm



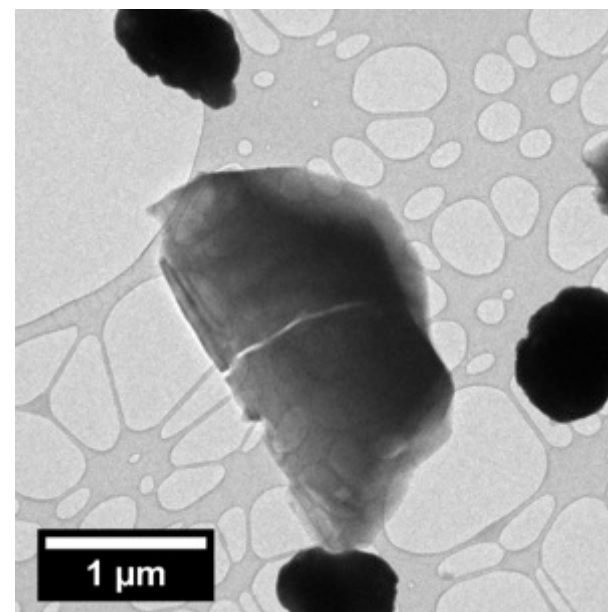
0.59 nm



r.t, vac

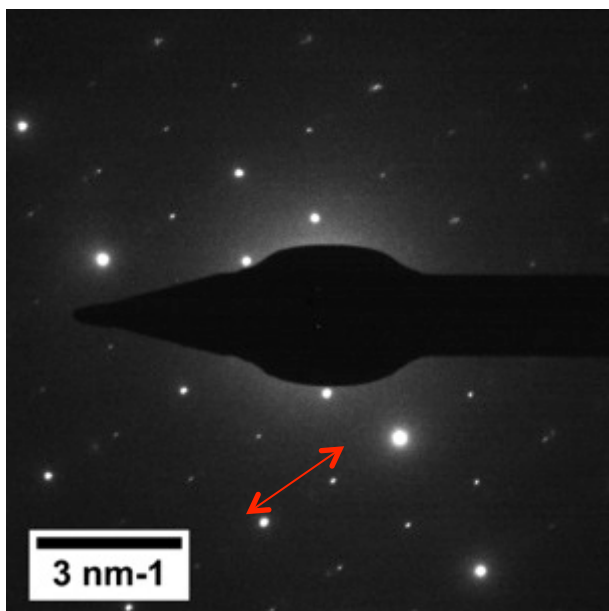


r.t, 3mbar H<sub>2</sub>O

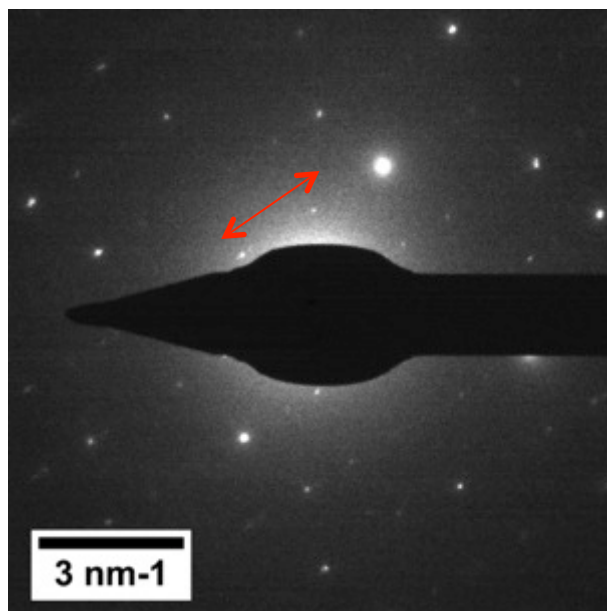


300°C, 3mbar H<sub>2</sub>O

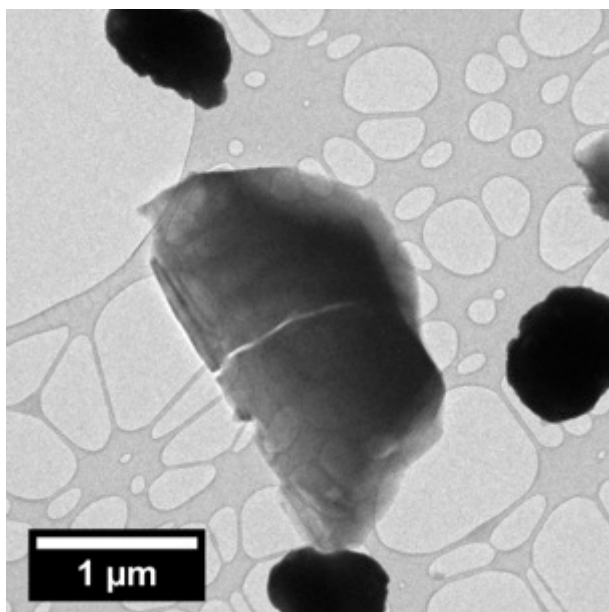
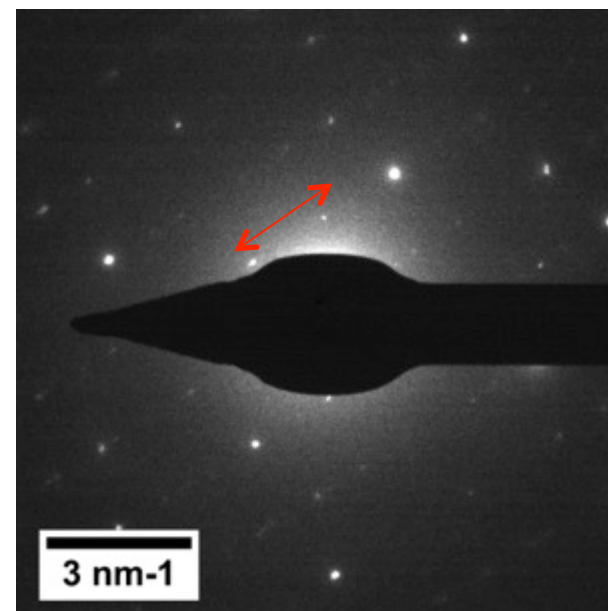
0.59 nm



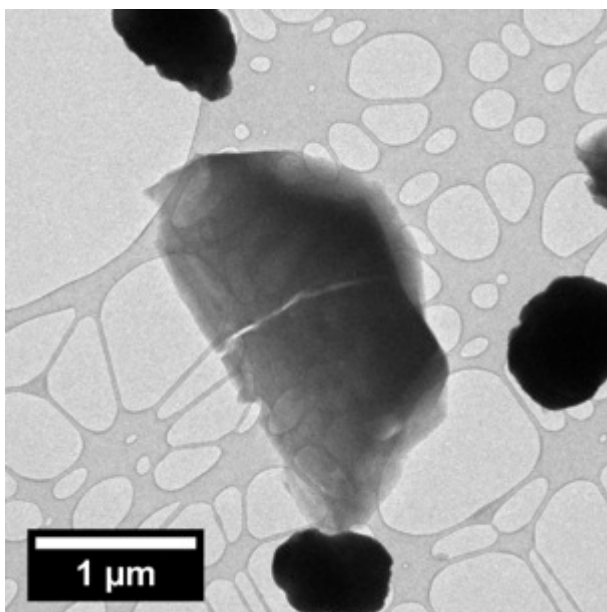
0.59 nm



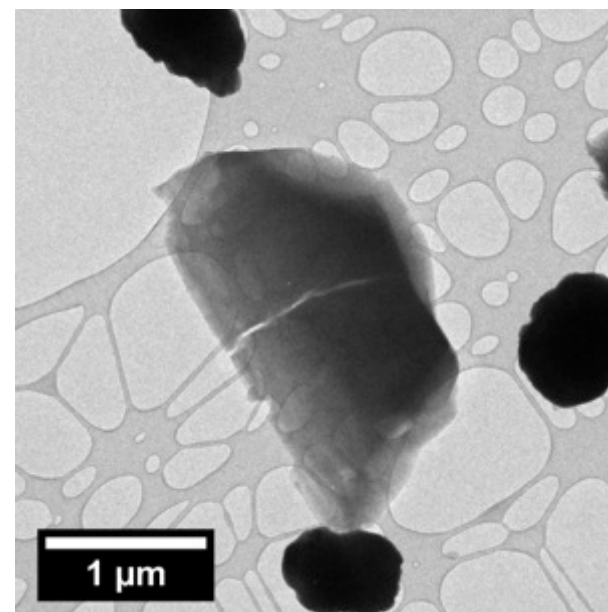
0.59 nm



300°C, 3mbar H<sub>2</sub>O

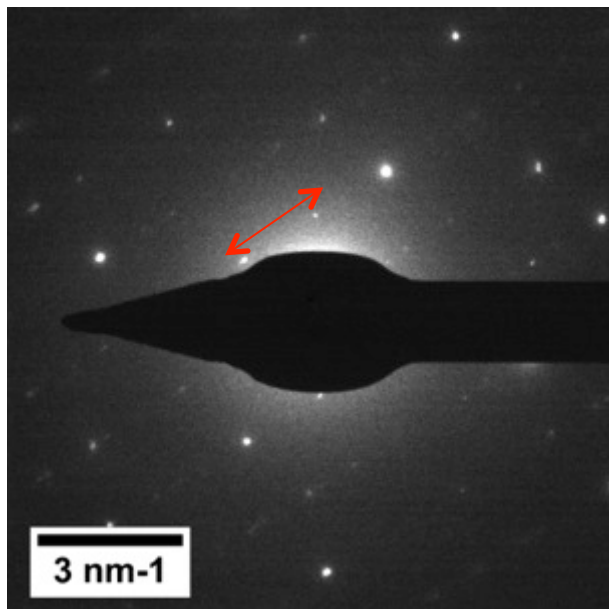


r.t, 3mbar H<sub>2</sub>O (post cooling)

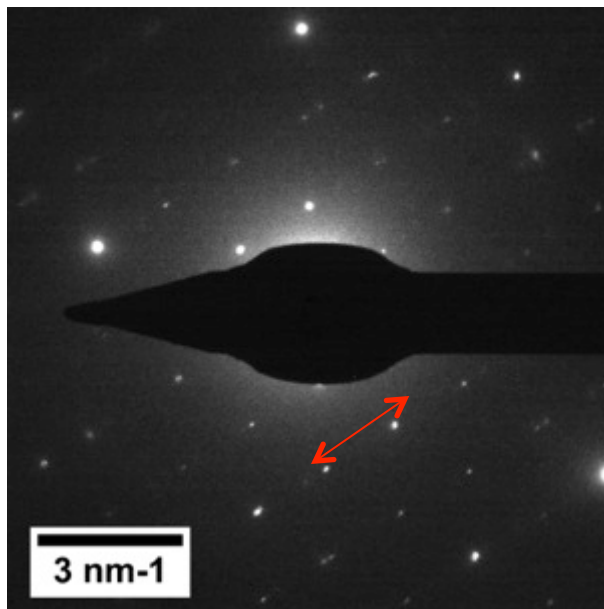


120°C, 3mbar H<sub>2</sub>O

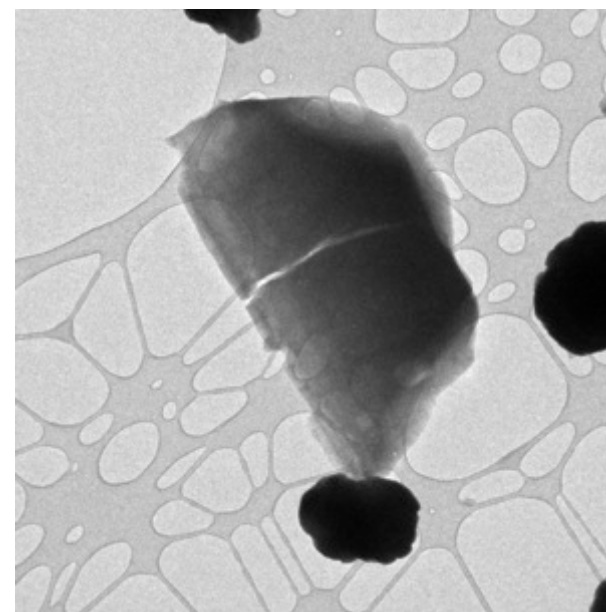
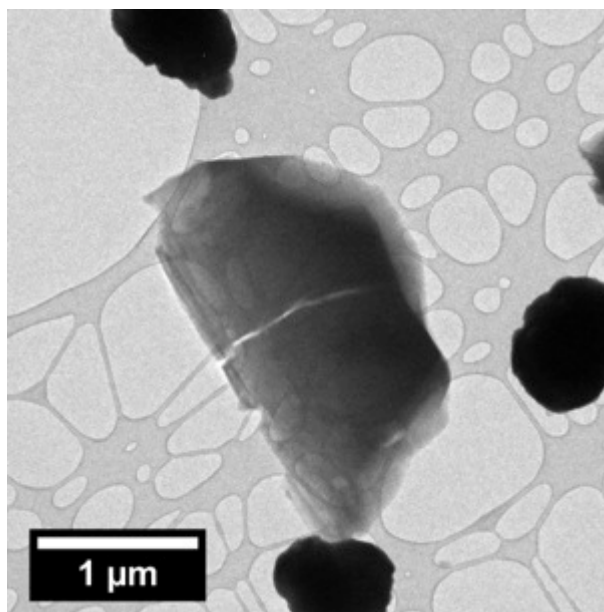
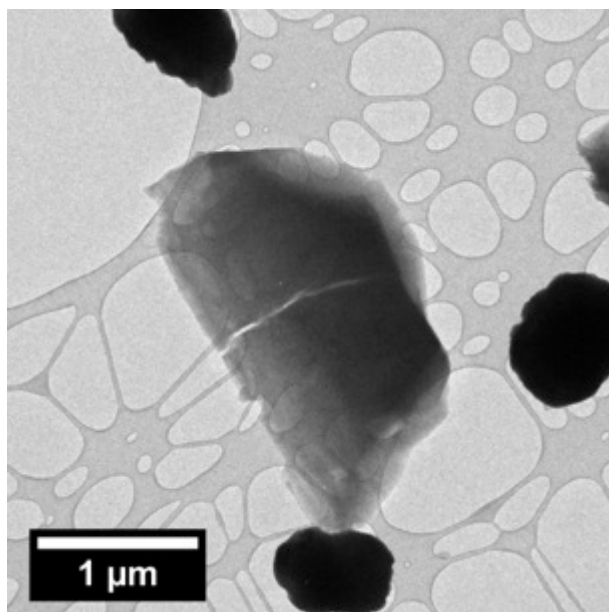
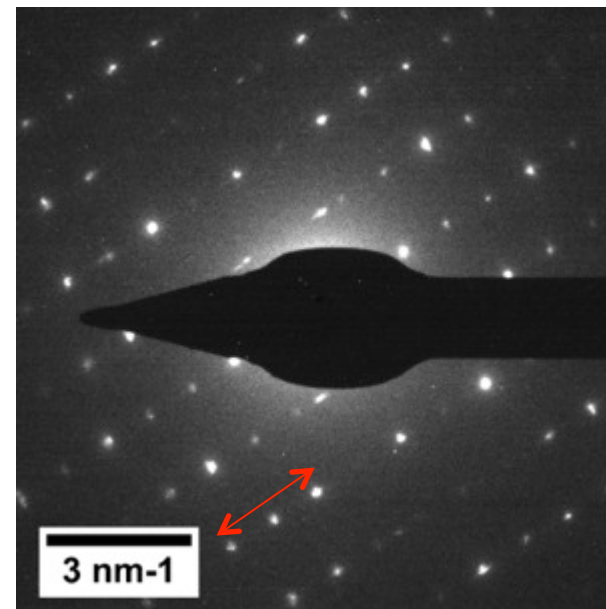
0.59 nm



0.59 nm



0.96 nm



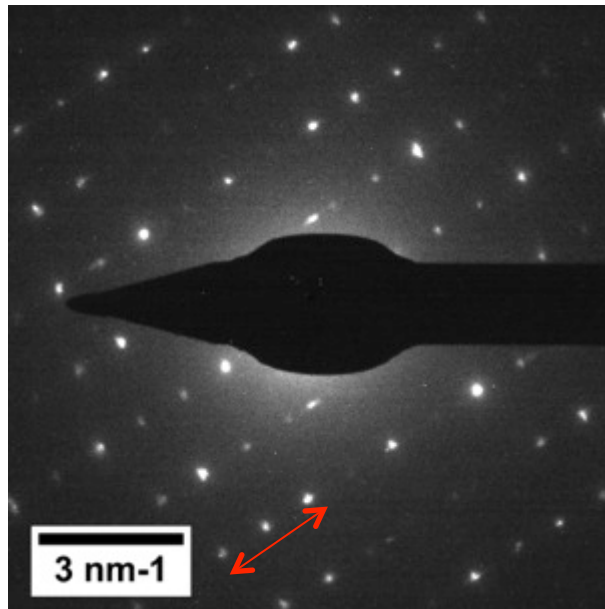
120°C, 3mbar H<sub>2</sub>O

300°C, 3mbar H<sub>2</sub>O

r.t (over night), 3mbar H<sub>2</sub>O

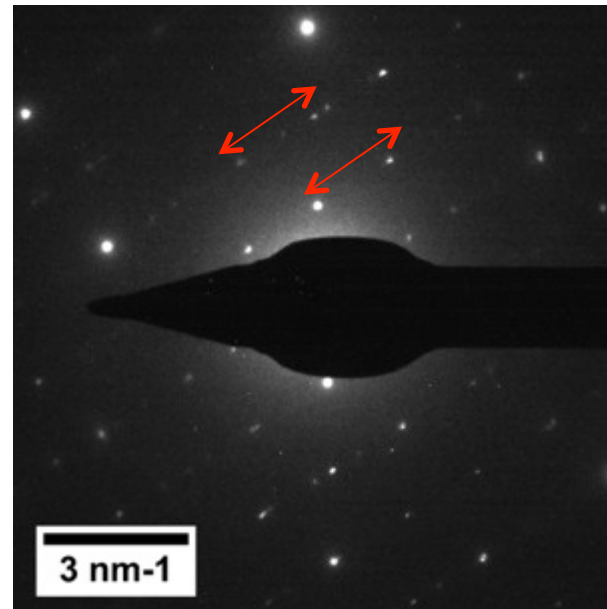


0.96 nm



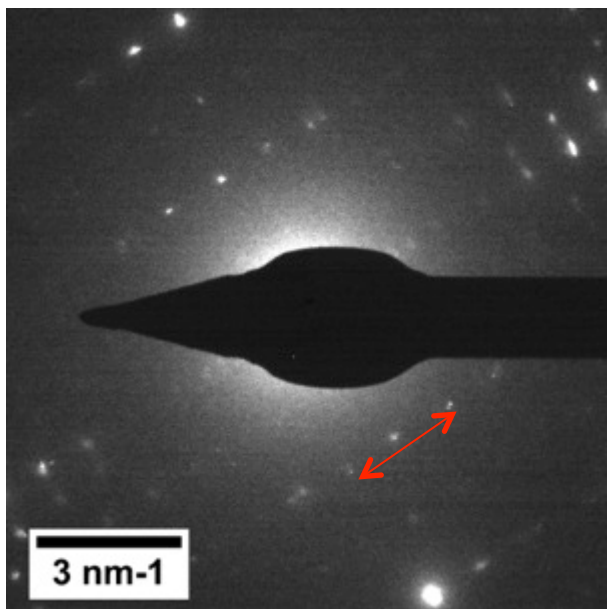
r.t (over night), 3mbar H<sub>2</sub>O

0.57 nm

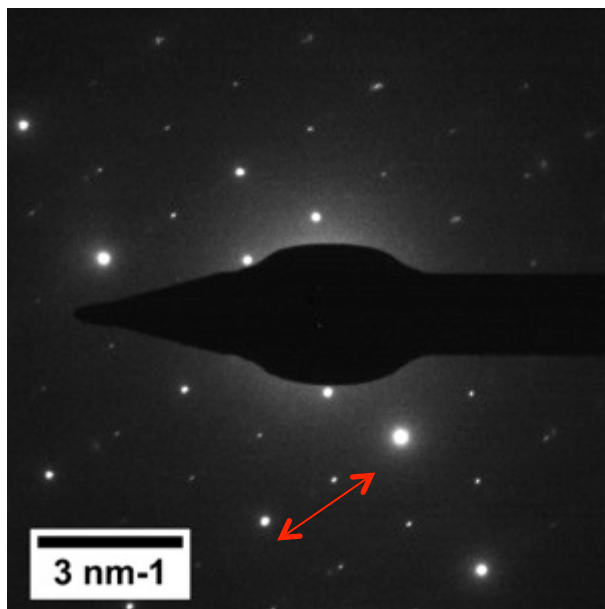


300°C, 3mbar H<sub>2</sub>O

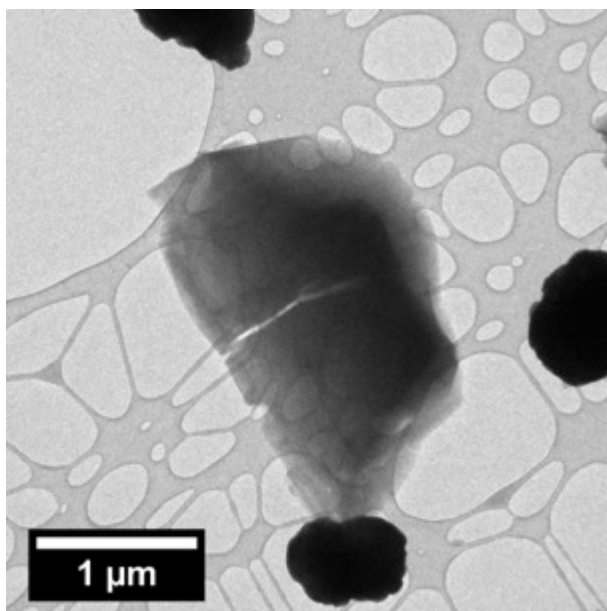
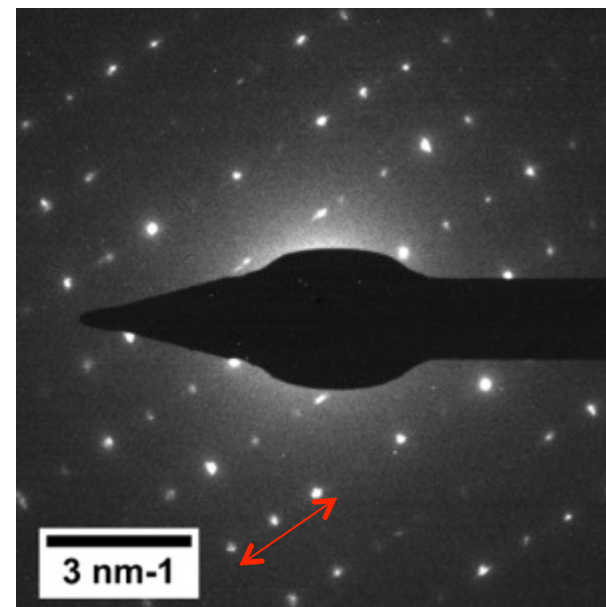
0.77 nm



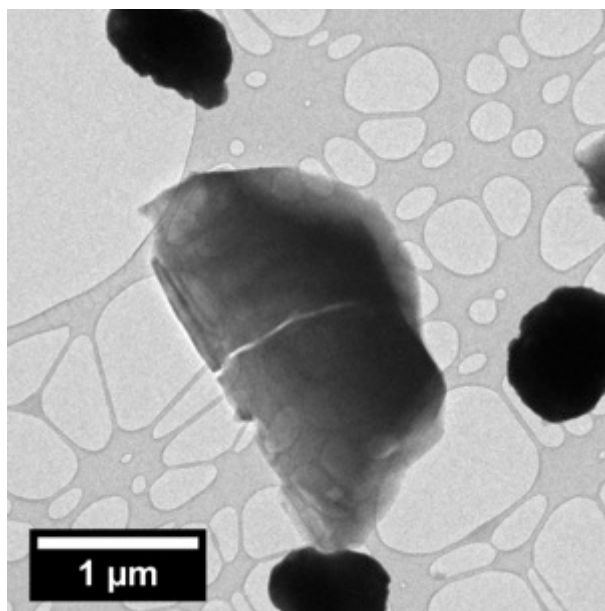
0.59 nm



0.96 nm



r.t, 3mbar H<sub>2</sub>O



300°C, 3mbar H<sub>2</sub>O

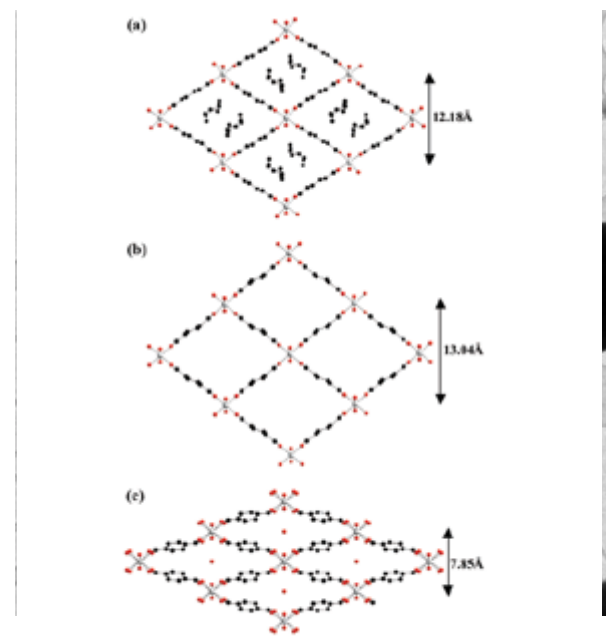


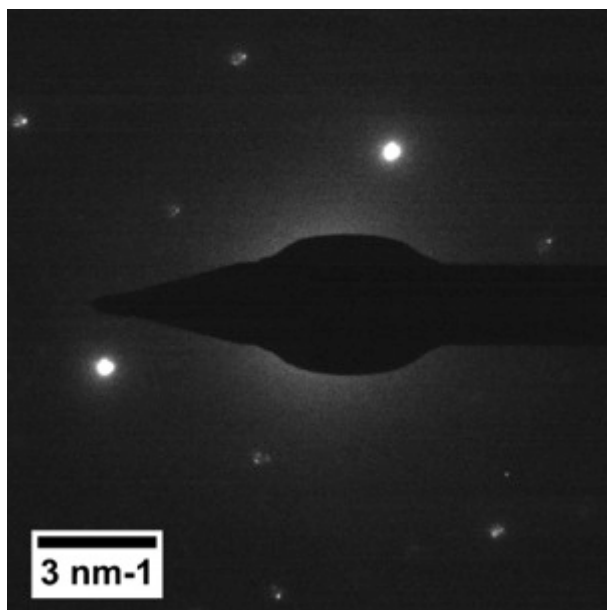
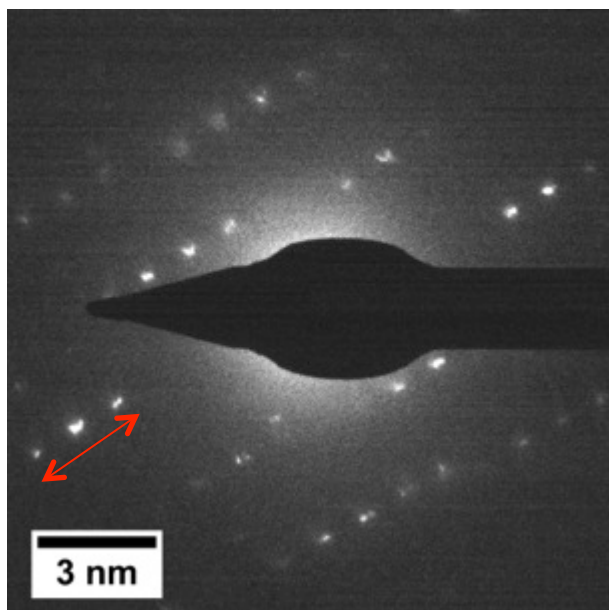
Figure 2. View of the pore systems of (a) MIL-53as, (b) MIL-53ht, and (c) MIL-53lt.

# Cr MIL-53 ETEM exp 2

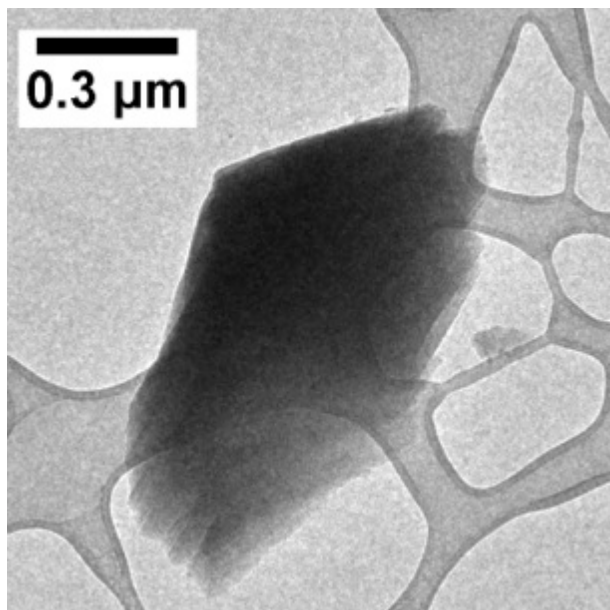
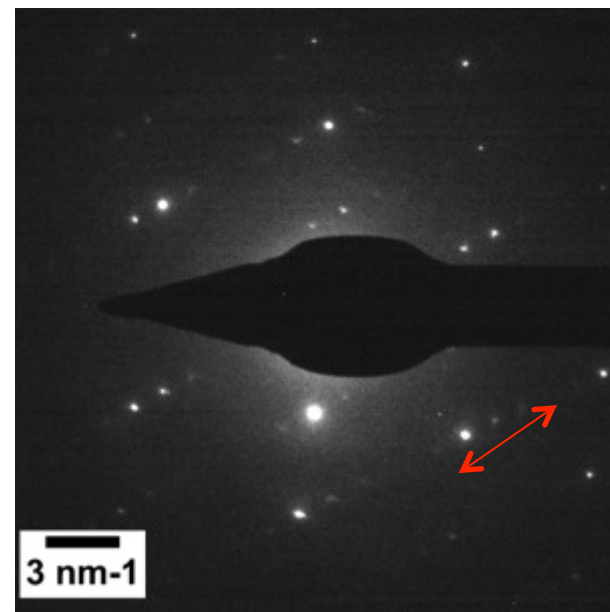
(Same breathing concept studied as exp 1)

1. 2.2 mbar H<sub>2</sub>O, room temp (*Im2, DP5*)
2. Heating at 3° C from 30°-300° C (*Im6-39*)
3. Hold for +55 min at 300° C (*Im46*), +85 min (*Im31*)
4. Cool to room temp (*Im52/53*)
5. Remove from ETEM column at room temp and reinsert into column (2.2 mbar H<sub>2</sub>O) at room temp after 1hr at atmospheric pressure (*Im54/55/56*)
6. Heating ramp 30°-300° C at 5° C/min (2 mbar H<sub>2</sub>O) (*Im57-89*)
7. Left at 300° C for +20 min (*Im91*)
8. Cool to RT (*Im93/92*)

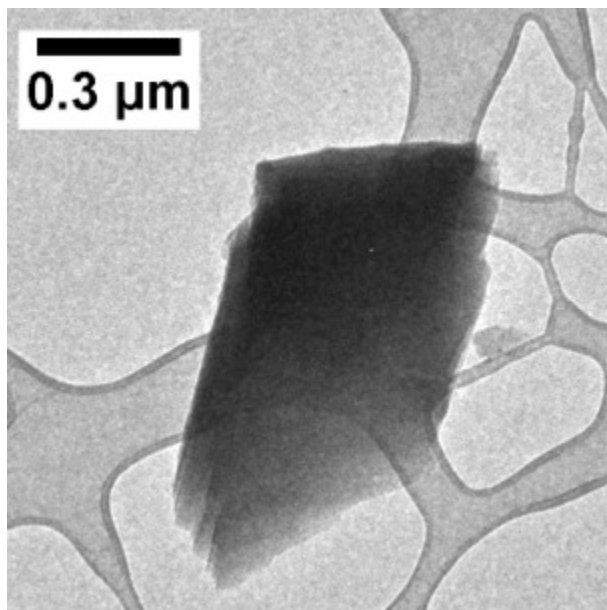
0.84 nm



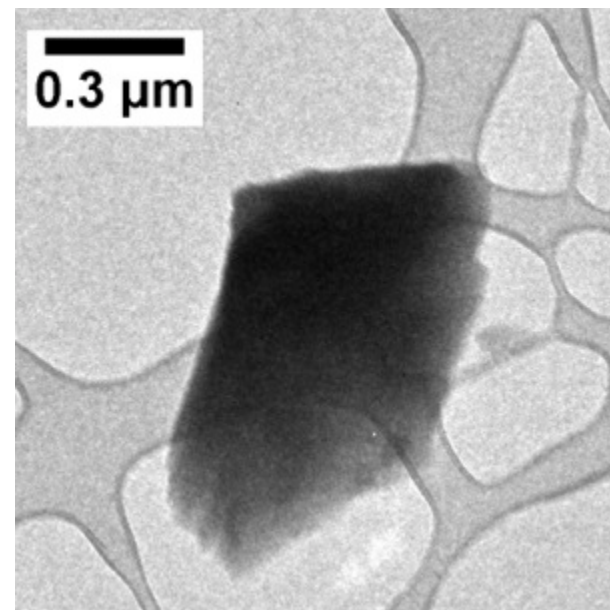
0.72 nm



r.t, 2mbar H<sub>2</sub>O (as synth)



300°C, 2mbar H<sub>2</sub>O



r.t, 2mbar H<sub>2</sub>O (re insert)

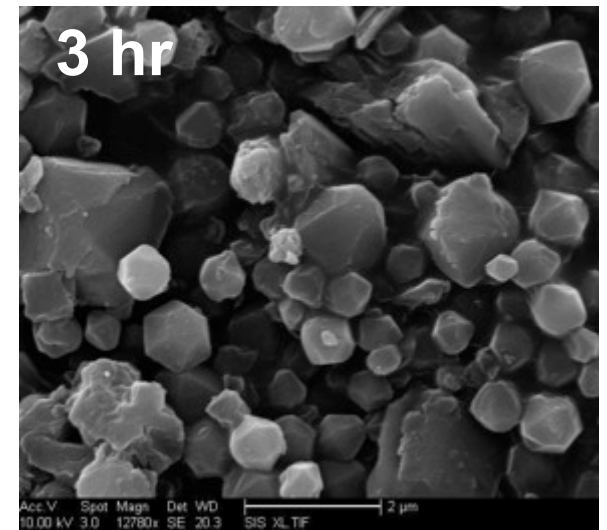
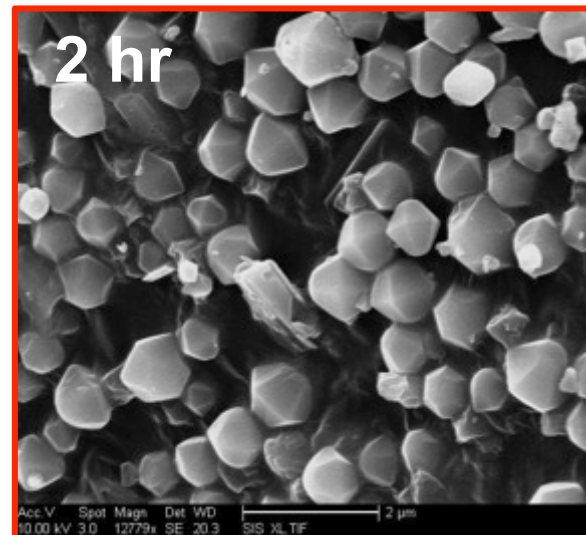
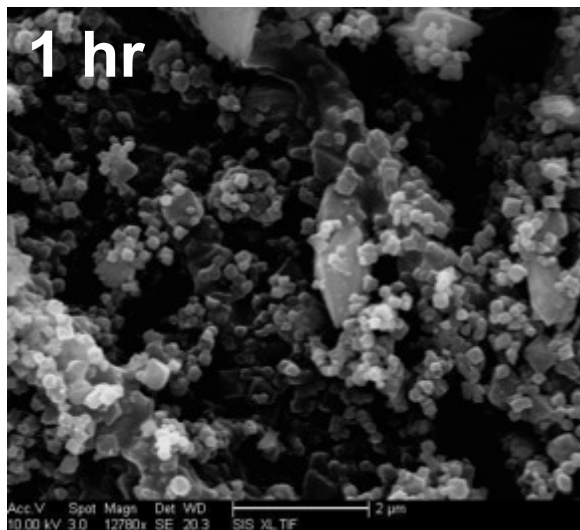
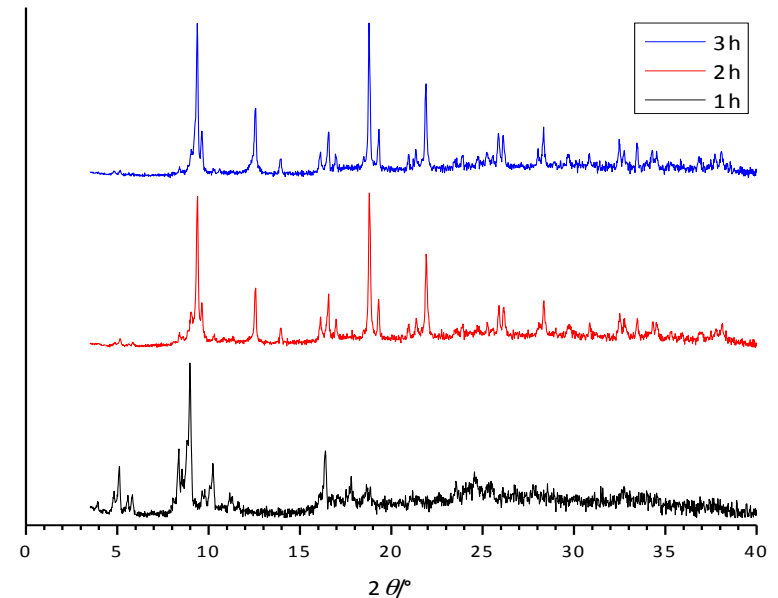
# Fe MIL-53 ETEM experiments – Not as Successful (negligible changes induced in particles)

\*ETEM experiments for the Fe MIL-53 were based on bulk gas-sorption studies done in the Cohen lab (shown in following slides, which found structural changes in the Fe MOF in CO<sub>2</sub> or N<sub>2</sub> gases (done at higher gas pressures than is possible in the ETEM))\*

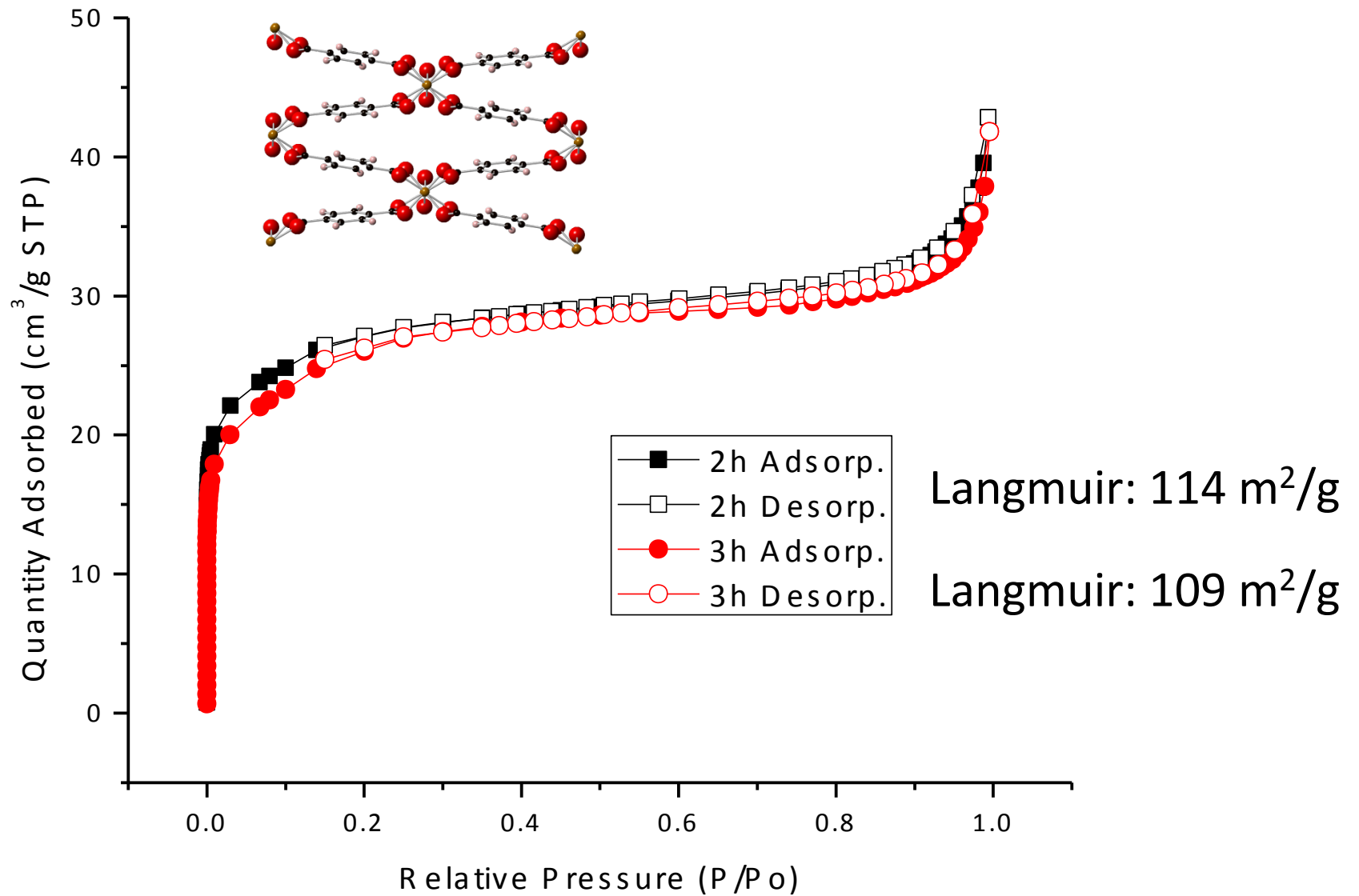
- Fe Exp 1 – no heating holder, CO<sub>2</sub>, N<sub>2</sub>, 10 mbar, no change
- Fe Exp 2 – CO<sub>2</sub>, heated r.t. 200°C 10 mbar
  - Look at images
  - Switch to N<sub>2</sub> at temperature
  - Pumped to Vacuum and cooled down
  - Fe Exp 3 – heated at vacuum, then flowed CO<sub>2</sub> at temp, stopped CO<sub>2</sub>, pumped to high vac (DP25/27/29),

# Sub- $\mu\text{m}$ Fe MIL-53 for ETEM Experiments: Developing New Synthesis Conditions for small MOF NPs

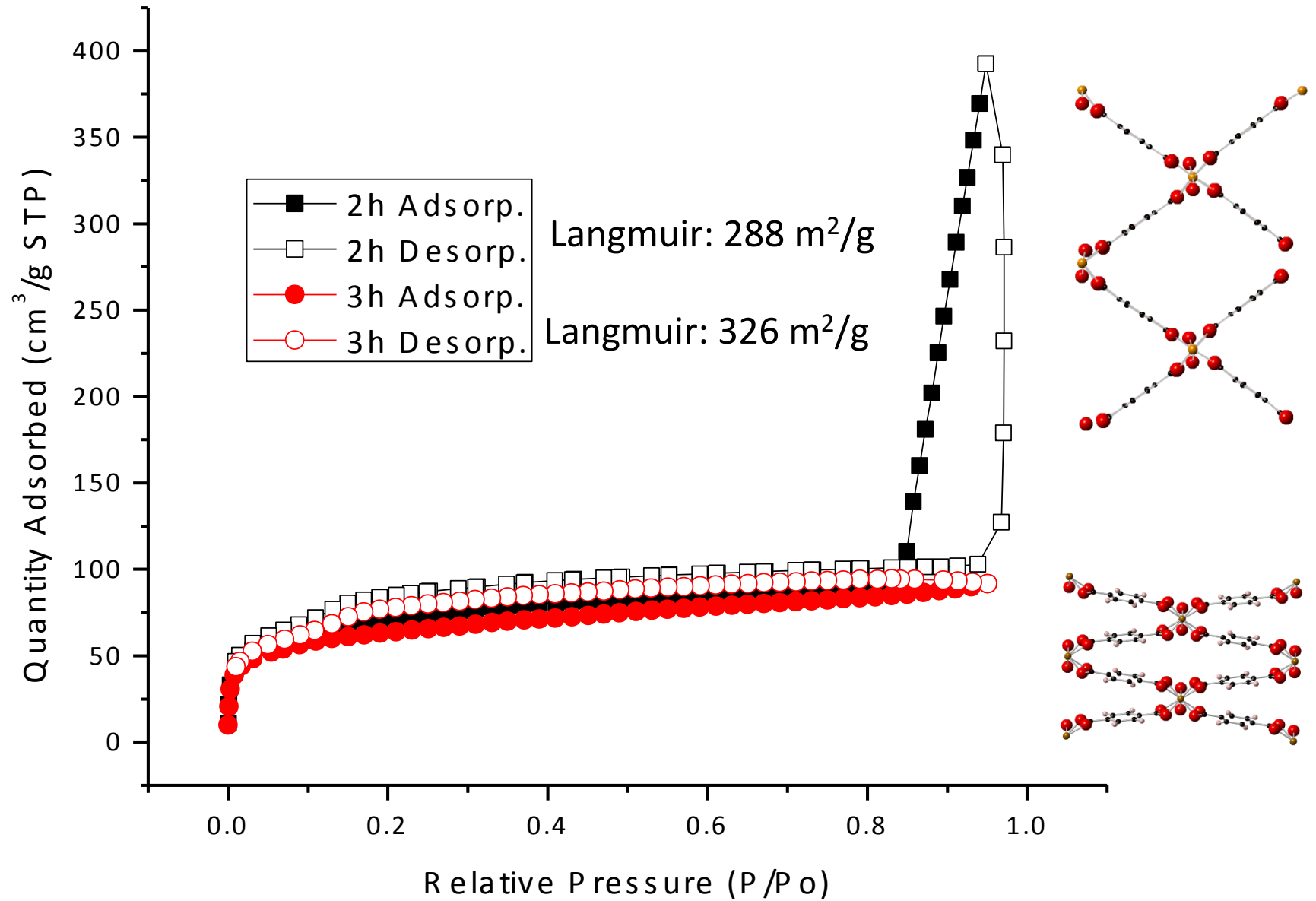
- 0.54 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.332 g  $\text{H}_2\text{bdc}$  were dissolved in 10 mL DMF
- Solution was transferred to a Teflon lined bomb placed in a  $150^\circ\text{C}$  oven for 1, 2, or 3 hrs.
- Collected by centrifuge and washed with MeOH.



# N<sub>2</sub> Sorption Isotherms

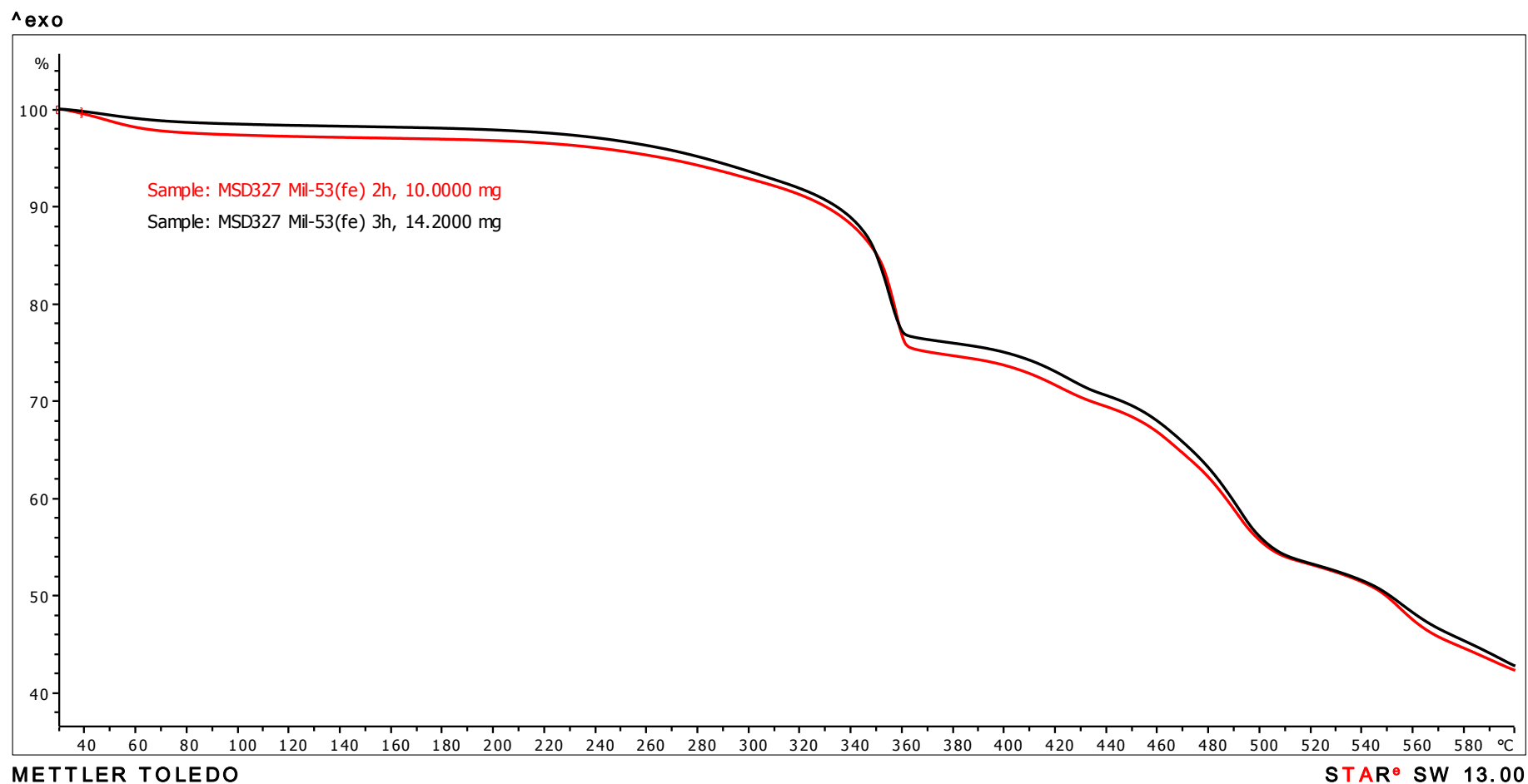


# CO<sub>2</sub> Sorption Isotherms





# MIL-53(Fe) TGA Curves



# Summary Potential Future Work: MIL-53 “Breathing” and Gas-Sorption

- Water vapor ETEM experiments with temperature ramping were successful in producing structural transformations in Cr MIL-53 particles:
  - Nanostructure changes were recorded over time as the temperature was increased/decreased through diffraction patterns
  - Interestingly, little changes in overall particle morphology → unable to take lattice resolution magnification images or elemental spectroscopic measurements due to MOF beam damage
- Due to the complexity of the electron diffraction patterns of these MOF, it is challenging to match our ETEM results with the breathing results published in *JACS*, **2002**, *124*, 13519 by XRD
  - This is in progress, and we also plan to mimic out ETEM experiments in bulk powder and run XRD analysis at the various transformation steps to help in this process
- The Cohen lab has succeeded in developing a new synthetic route to obtain smaller Fe MIL-53 particles (sub-500 nm diameters) that are ideal for TEM analysis → however, N<sub>2</sub>- and CO<sub>2</sub>-sorption ETEM experiments did not work as planned, likely due to the low pressure constraint of the ETEM.

# Post-Synthetic Modification Processes in MOFs: Metal Exchange in Zr UiO-66

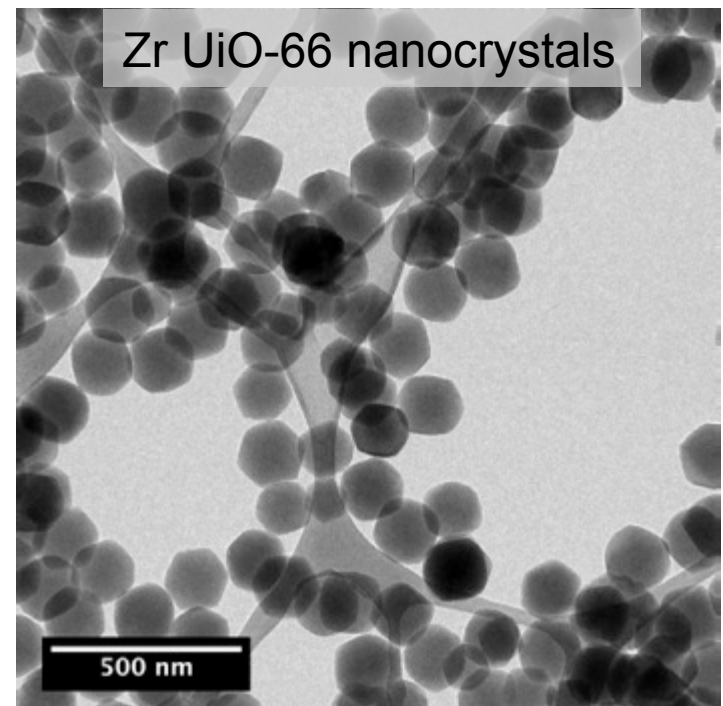
(Collaboration between Gianneschi group and Cohen group)

**Goal:** Use high resolution *ex-situ* TEM imaging, diffraction, and spectroscopic elemental analysis to understand the process of metal exchange in UiO-66 nanocrystals → The Cohen lab has many recent publications on metal exchange in this system (monitored by PXRD), but little is known about the mechanisms involved or the extent of exchange in individual MOF nanoparticles.

→ Try to use LCTEM to observe metal exchange mechanism *in situ*

## Experimental Protocol:

- The Cohen Lab synthesizes Zr UiO-66 MOF particles, following published literature conditions
  - Metal exchange reactions are carried out on the bulk samples in solution for both Hf and Ti metals (following literature procedure)
  - Bulk MOF powders are analyzed by PXRD
- The 3 MOF samples (pristine, Hf, and Ti) are analyzed by electron microscope
  - High-resolution imaging of overall morphology and nanostructure
  - STEM EELS spectral mapping for elemental location analysis



# Metal Exchange in Zr UiO-66:

## Literature Conditions Used to Prepare TEM Samples (Titanium and Hafnium exchange)

- **TiCp<sub>2</sub>Cl<sub>2</sub> Exchange:**
  - 28 mg Zr UiO-66
  - 25 mg TiCp<sub>2</sub>Cl<sub>2</sub> (1 eq.)
  - 2 mL DMF

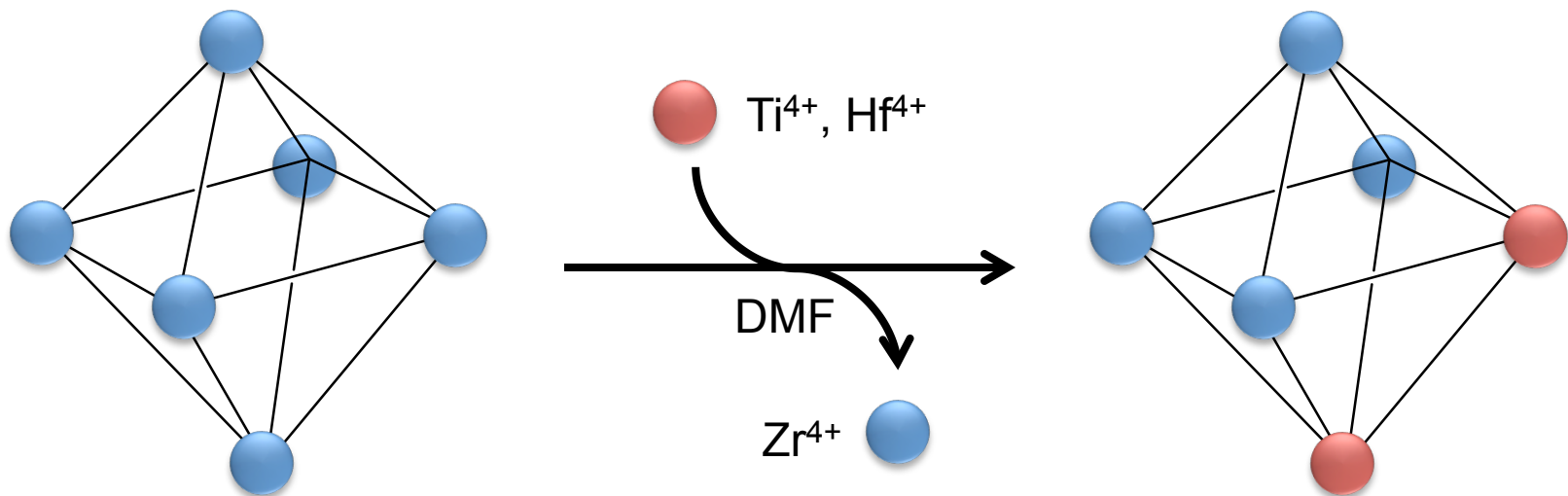
Temperature	Time		
Room Temp.	1 day	3 days	5 days
85°C	1 day	3 days	5 days

- **HfCl<sub>4</sub> Exchange:**
  - 28 mg UiO-66
  - 32 mg HfCl<sub>4</sub> (1 eq.)
  - 2 mL DMF

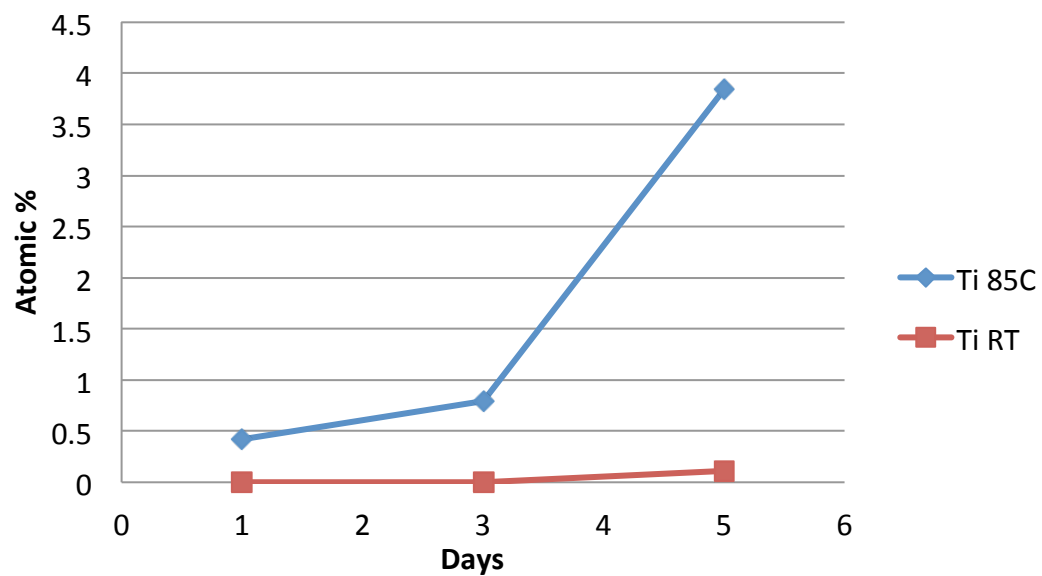
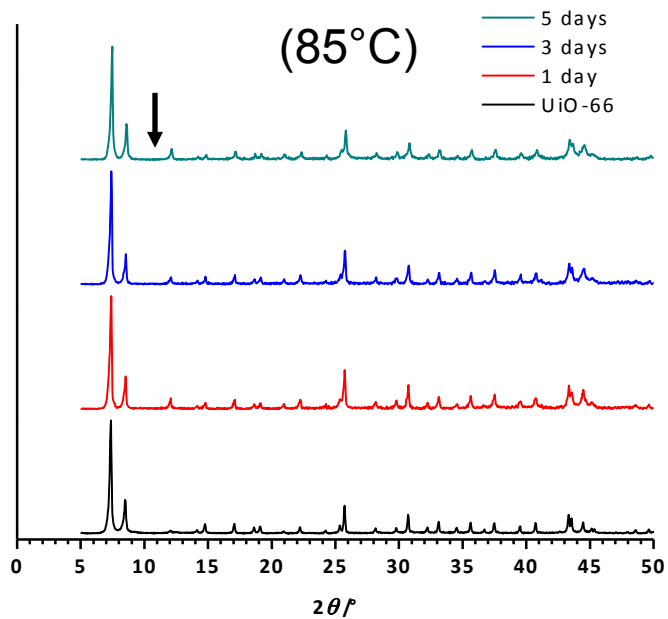
Temperature	Time		
Room Temp.	1 day	3 days	5 days
85°C	1 day	3 days	5 days

(DMF is not compatible with *in situ* Liquid-Cell holder, so an alternate solvent system must be developed for *in situ* LCTEM experiments to observe metal exchange processes)

# Zr UiO-66 Metal Exchange

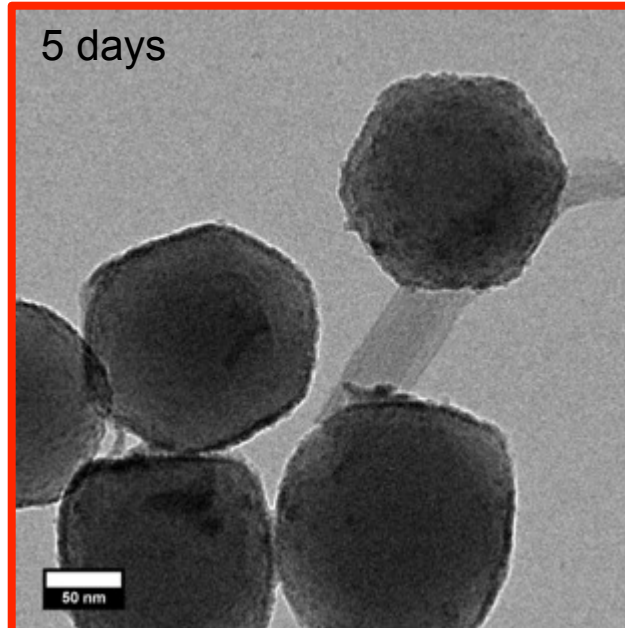
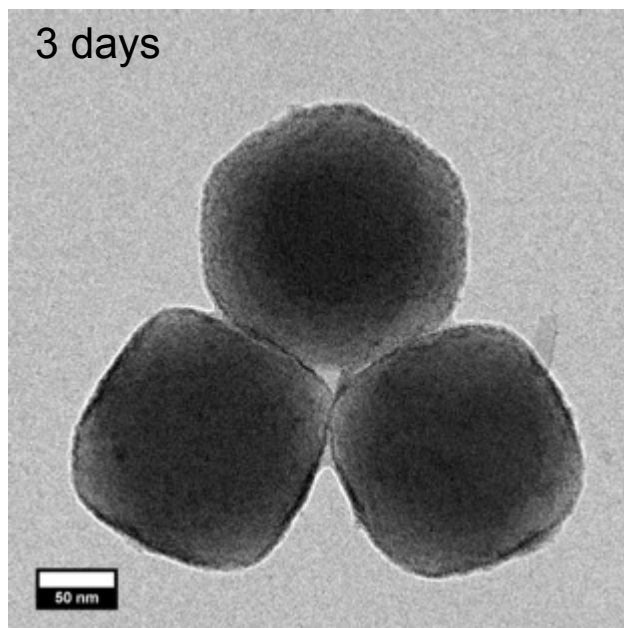
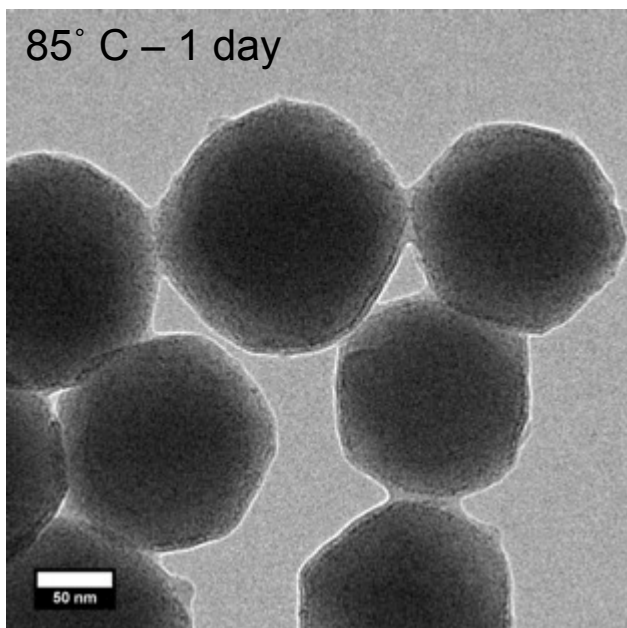
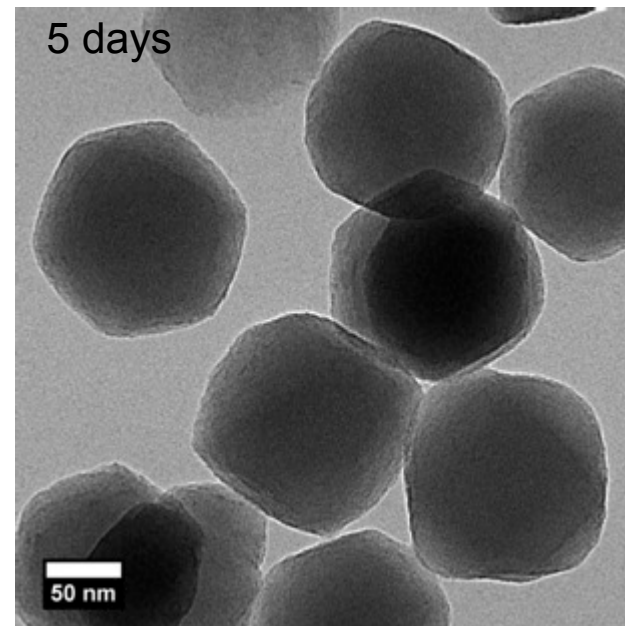
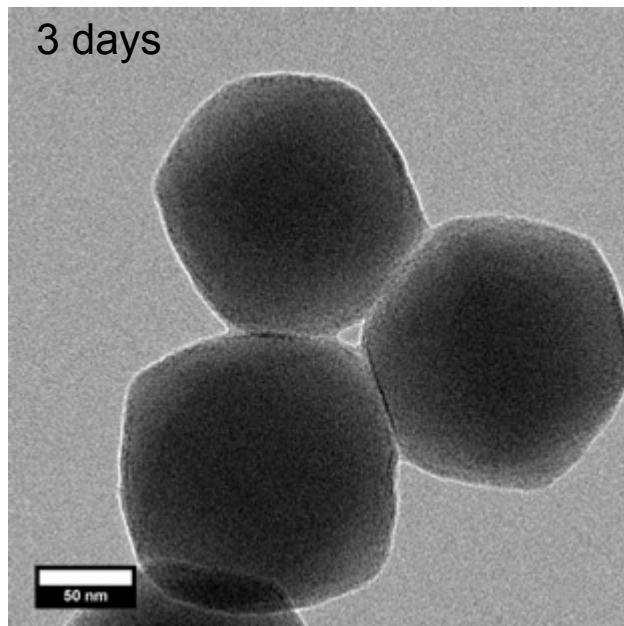
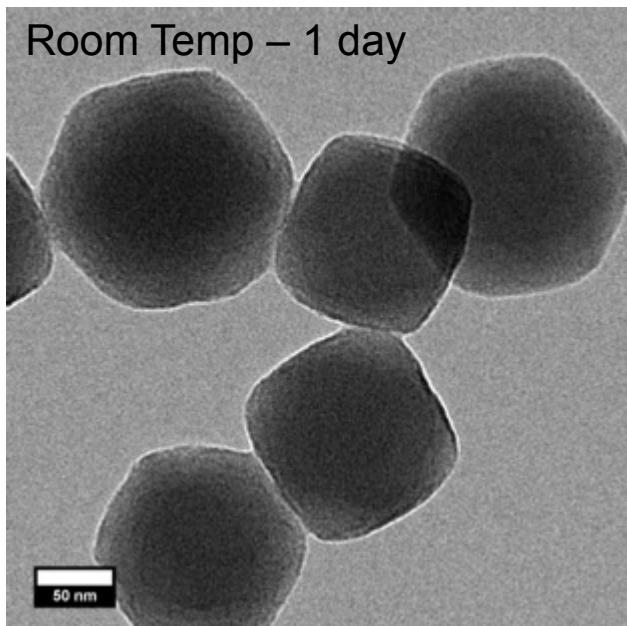


## Ti Exchange (bulk analysis)



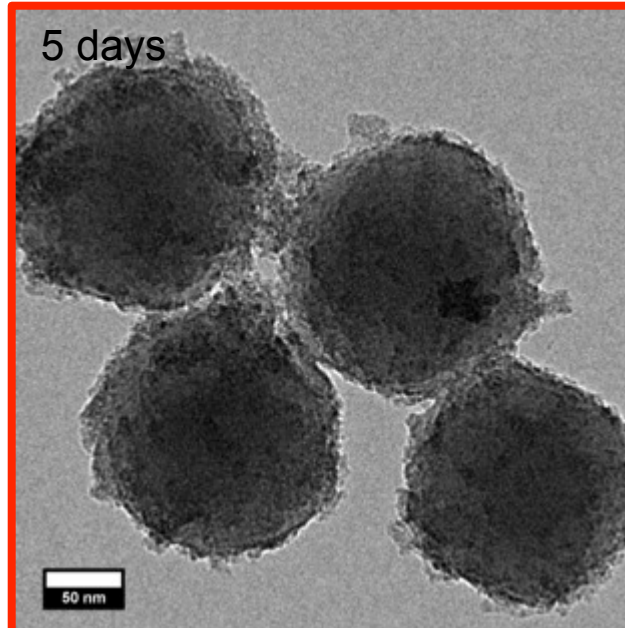
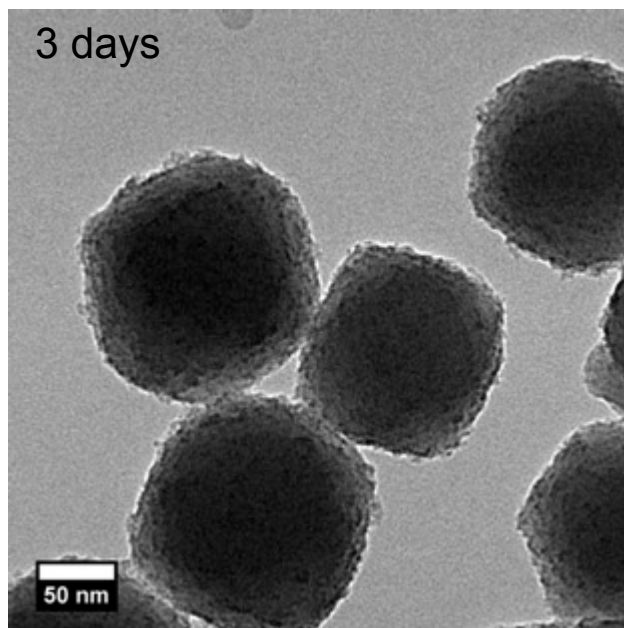
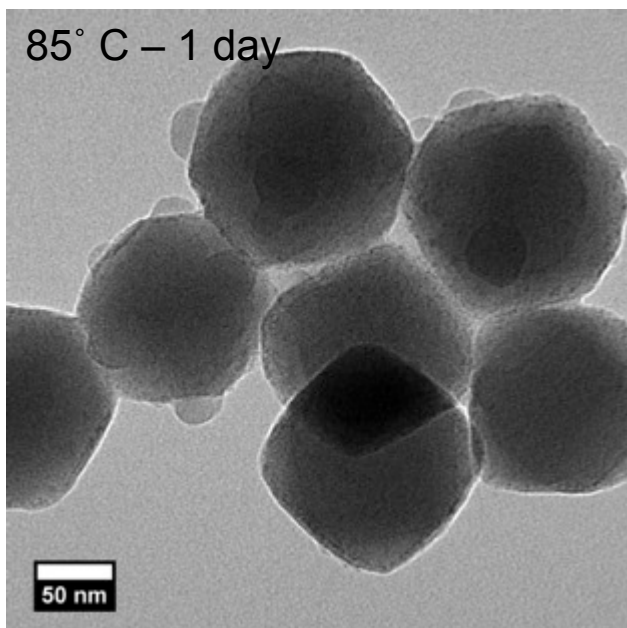
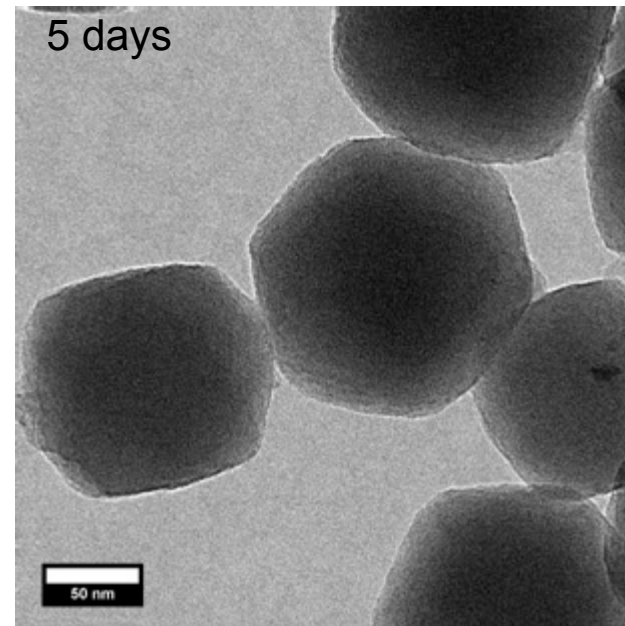
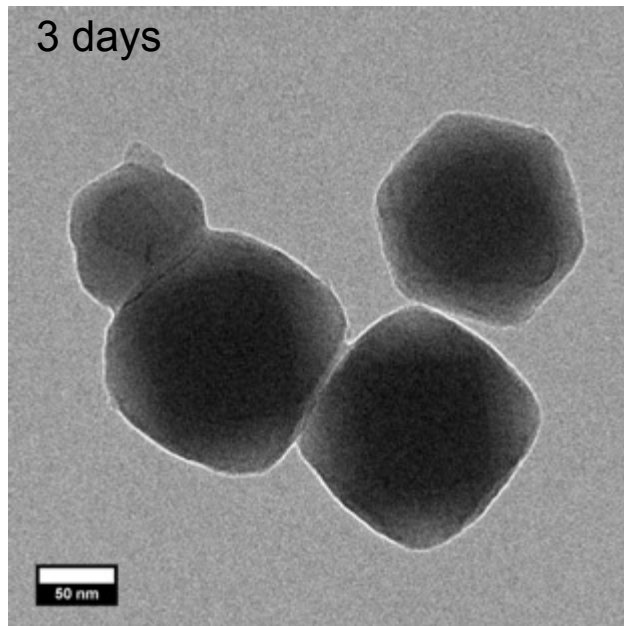
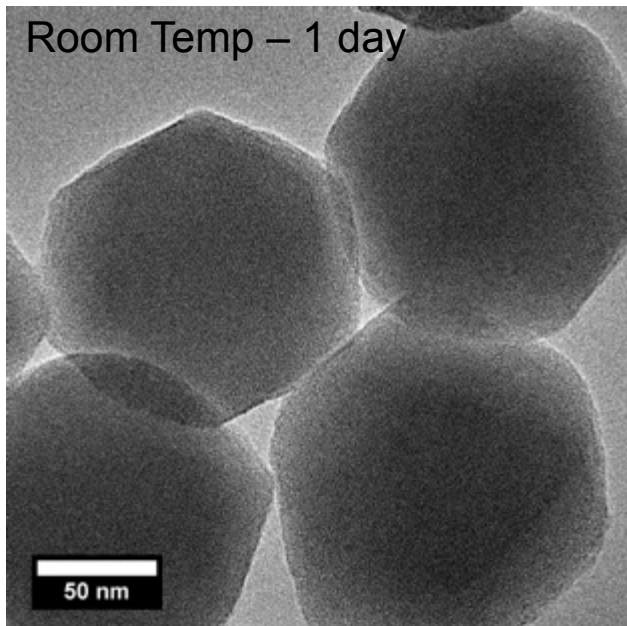
Literature exchange conditions  
(DMF)

# Hf exchange into Zr UiO-66



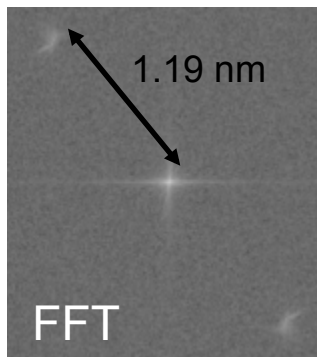
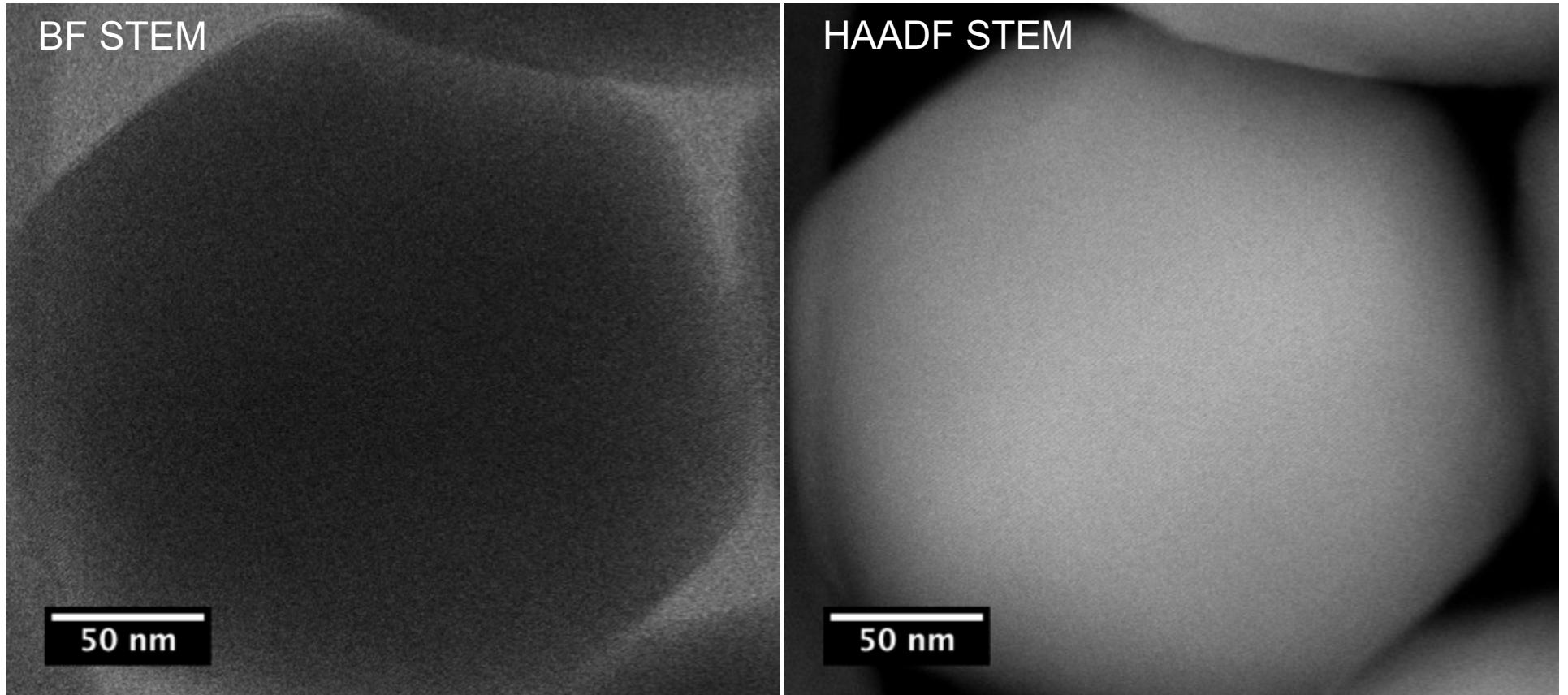
Literature exchange conditions  
(DMF)

# Ti exchange into Zr UiO-66



# Zr UiO-66 (no exchange)

\*SuperSTEM (UK) characterization

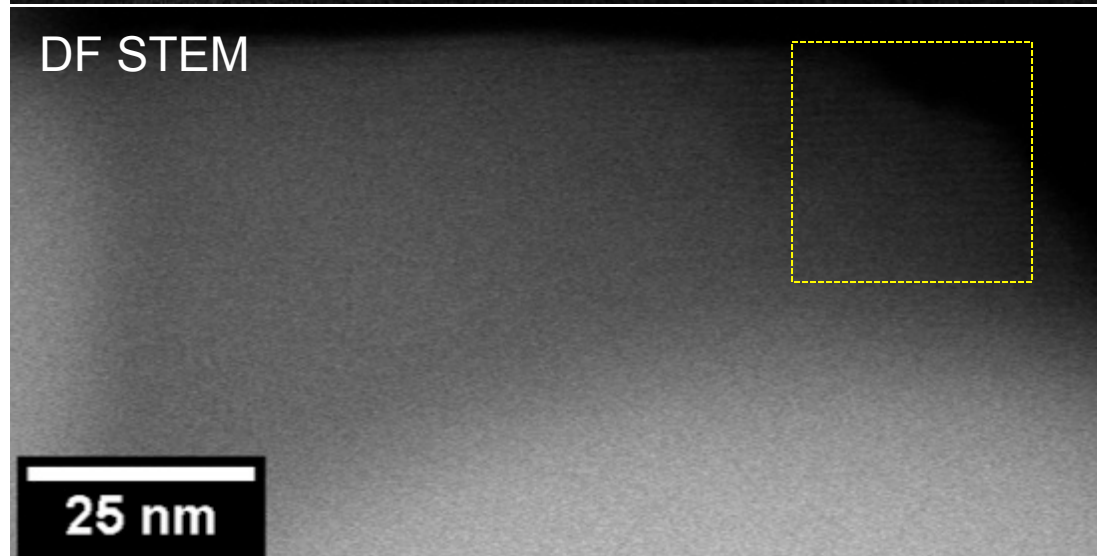
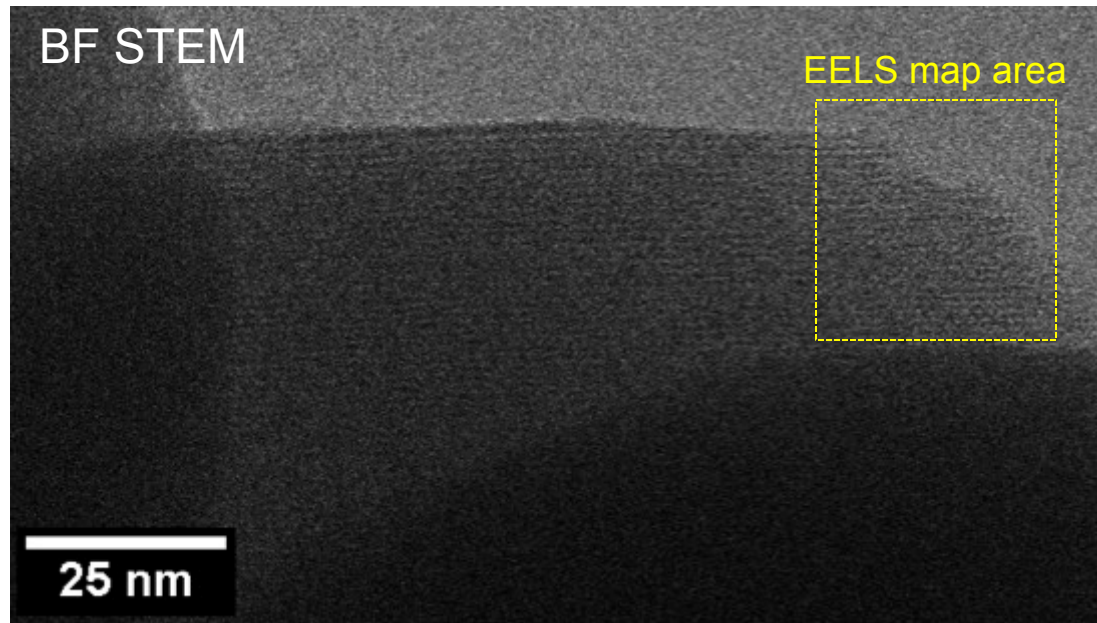


- Crystal structure (pore channels) extend to surface of single-crystal Zr UiO-66 nanoparticles
- Measured pore spacings of **~1.19 nm** and **~1.06 nm**



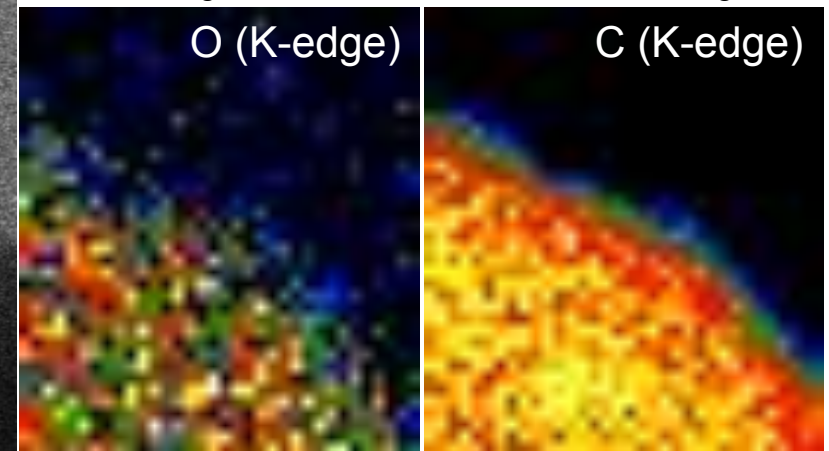
# Zr UiO-66 (no exchange)

\*SuperSTEM (UK) characterization



## STEM EELS Elemental Maps

Yellow → highest element signal, red then green → lower signal, blue/black → lowest element signal



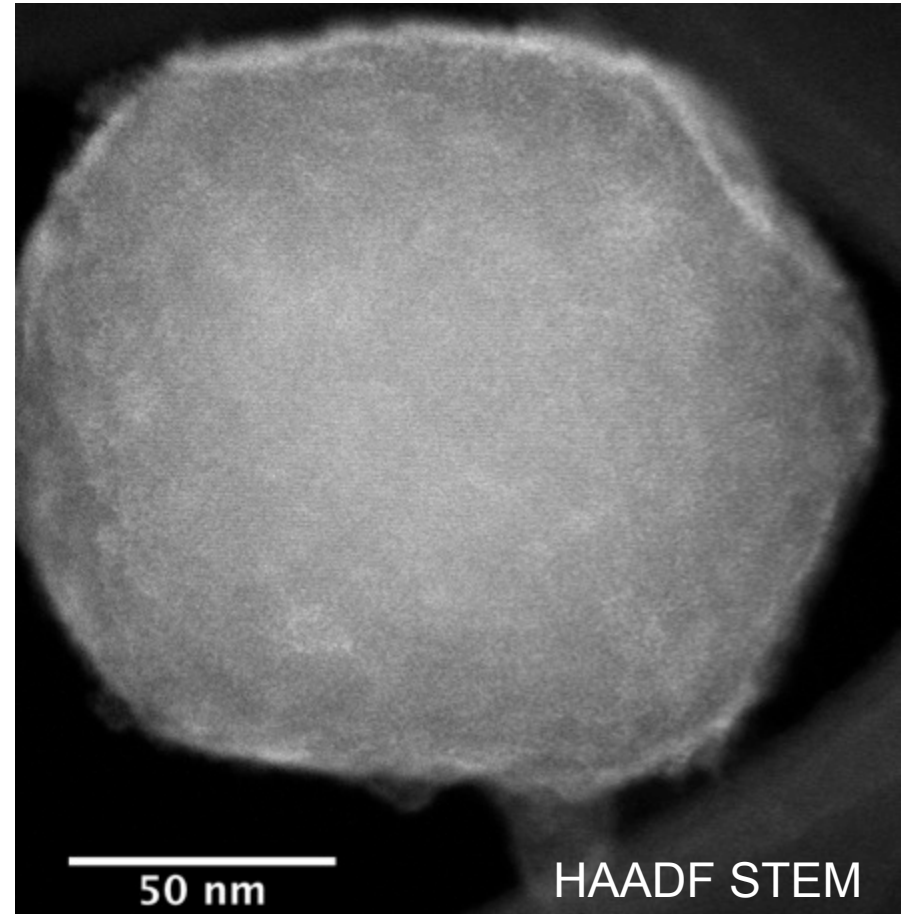
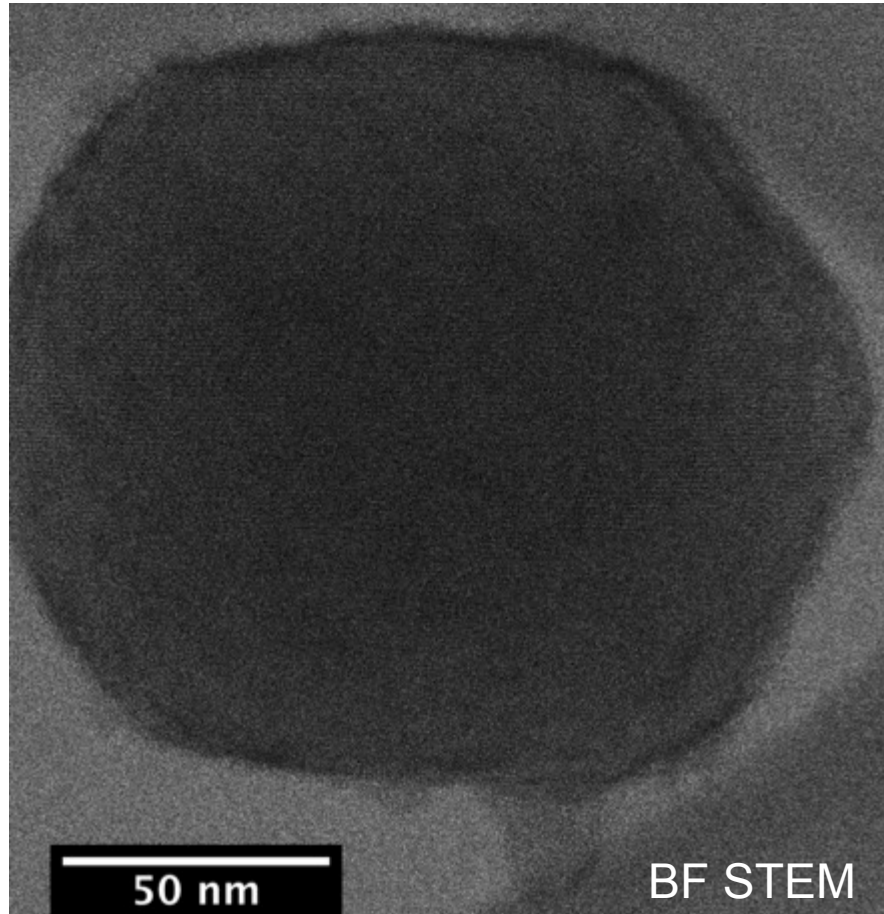
-Generally uniform distribution of both O and C in the crystal, that appears to scale well with particle thickness

-**O and C extend to particle edge**, no oxide surface layer

-Due to Zr EELS peak locations, it is very difficult to generate EELS maps for Zr

# Hf exchange in Zr UiO-66

\*SuperSTEM (UK) characterization

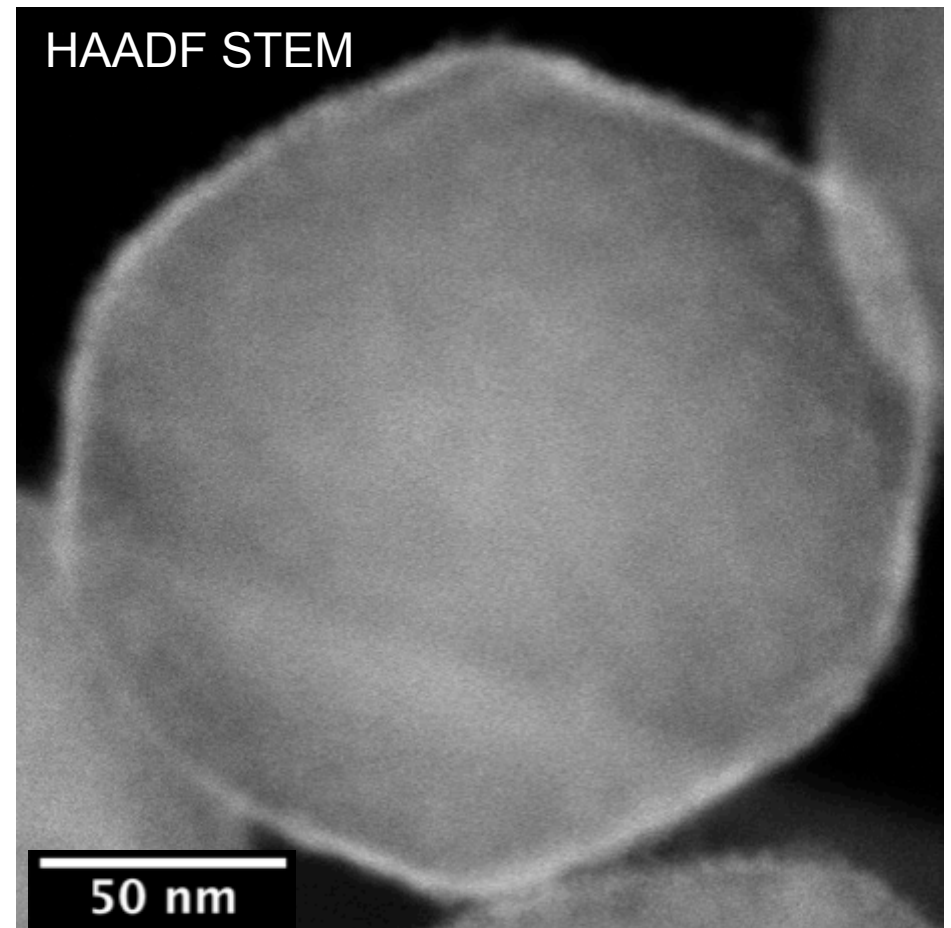
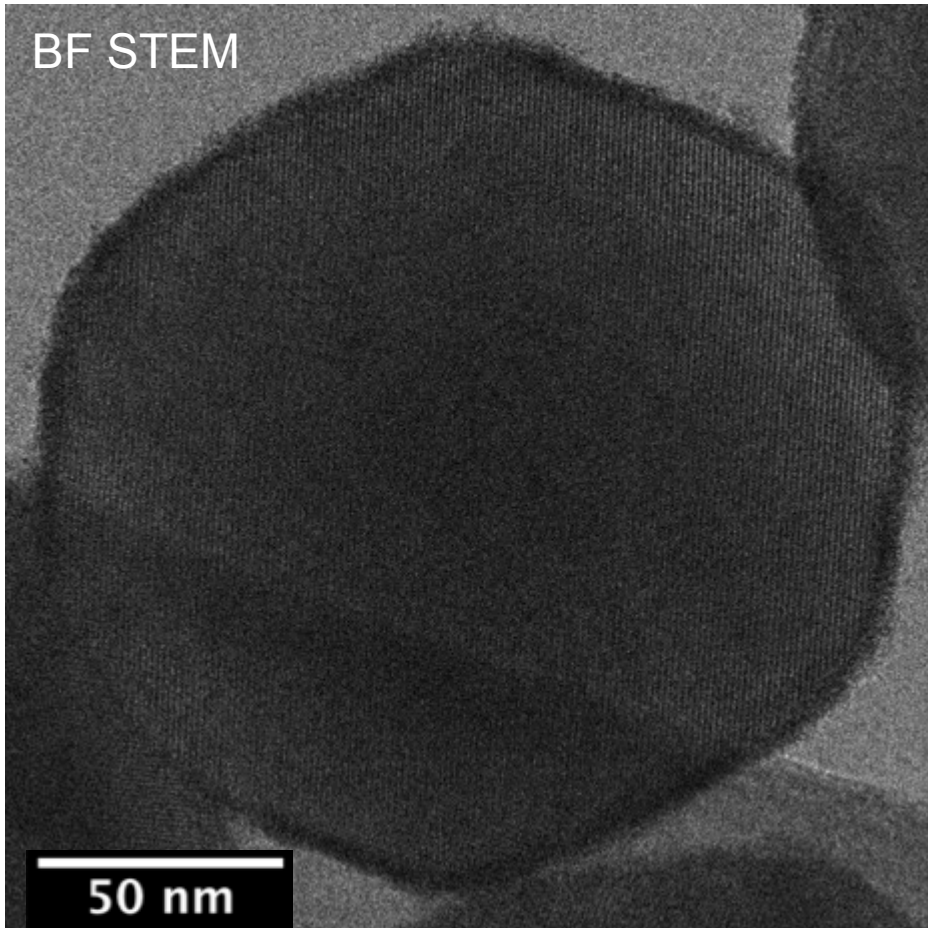


-Crystal structure (pore channels) **does not extend to surface** of nanoparticles → instead there is a high Z-number (or very thick) patchy **surface layer that is amorphous** in structure (**likely Hf rich**) → it is unclear by imaging alone if the Hf has replaced Zr atoms, or if the Hf layer is simply coating the the Zr UiO-66 particles

-Measured pore spacings of **~1.2 nm** and **~1.06 nm** (matching no exchange sample)

# Hf exchange in Zr UiO-66

\*SuperSTEM (UK) characterization

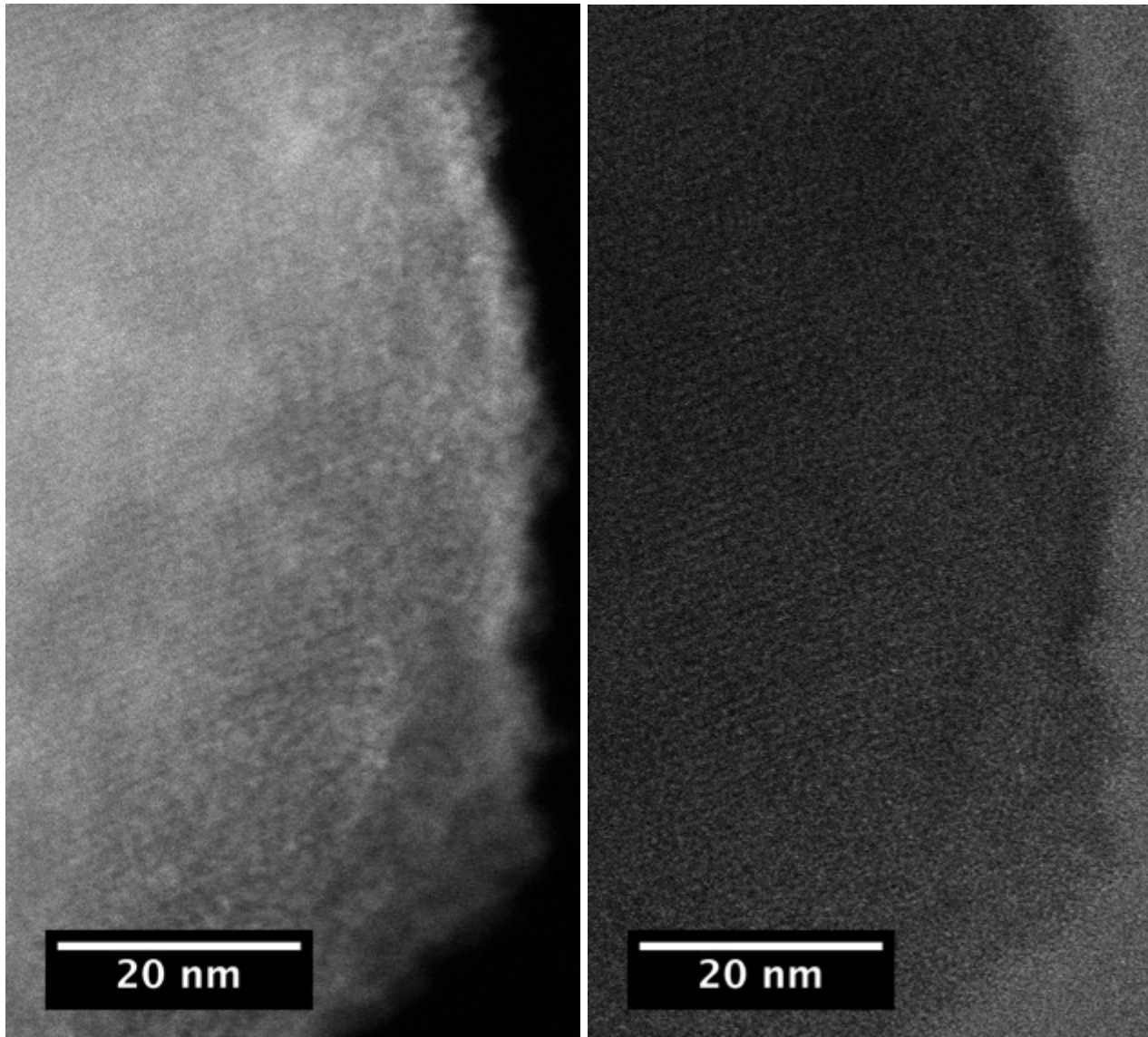


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-Measured pore spacings of **~1.2 nm** and **~1.06 nm** (matching no exchange sample)

# Hf exchange in Zr UiO-66

\*SuperSTEM (UK) characterization



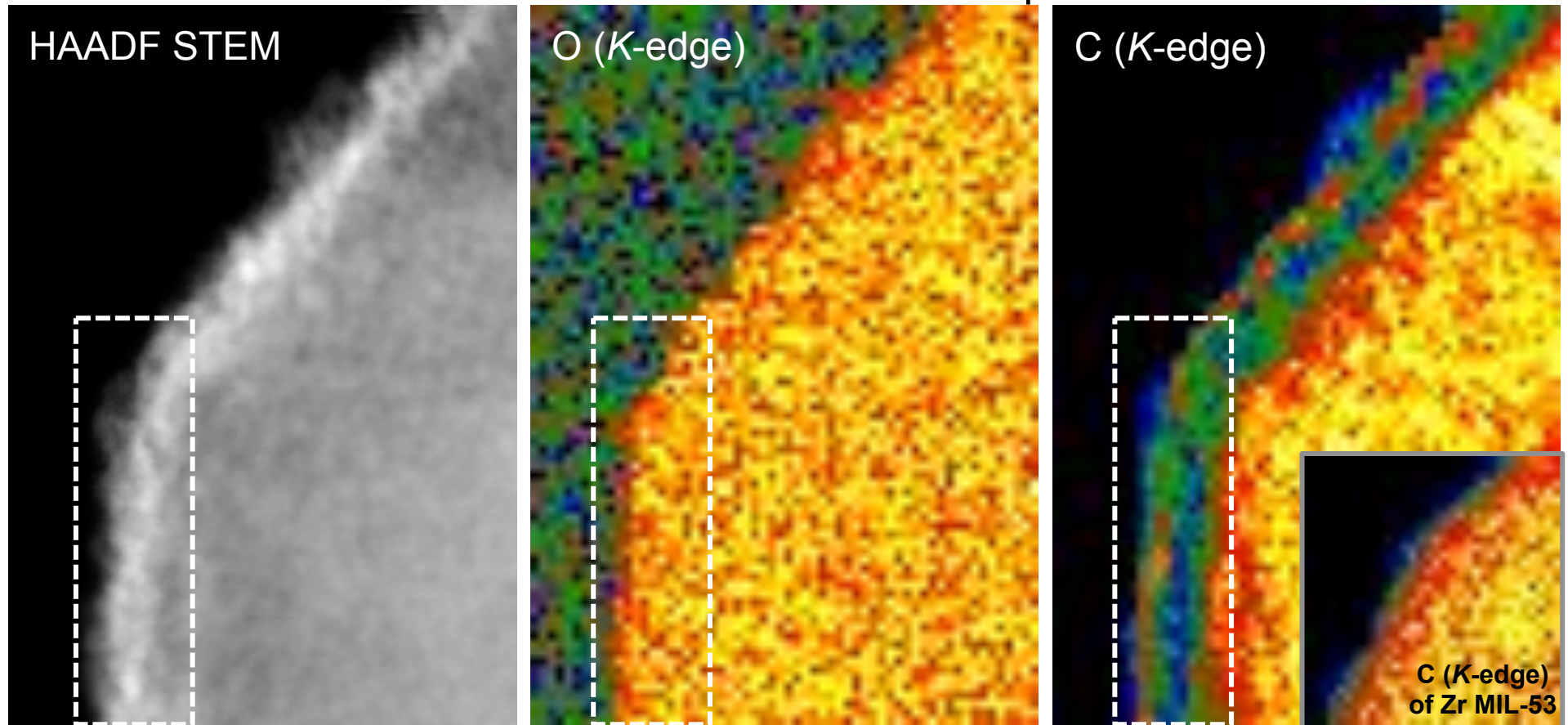
-Patchy, non-crystalline and high Z-number surface layer is found coating all bulk particles, which otherwise have pore spacing consistent with the pristine Zr UiO-66 particles

-It is unclear from imaging alone if the surface layer is simply a coating that is added on the initial particles, or if some replacement or exchange has occurred at the surface between Hf and Zr, but that this exchange process does not maintain the original MOF structure...

# Hf exchange in Zr UiO-66

\*SuperSTEM (UK) characterization

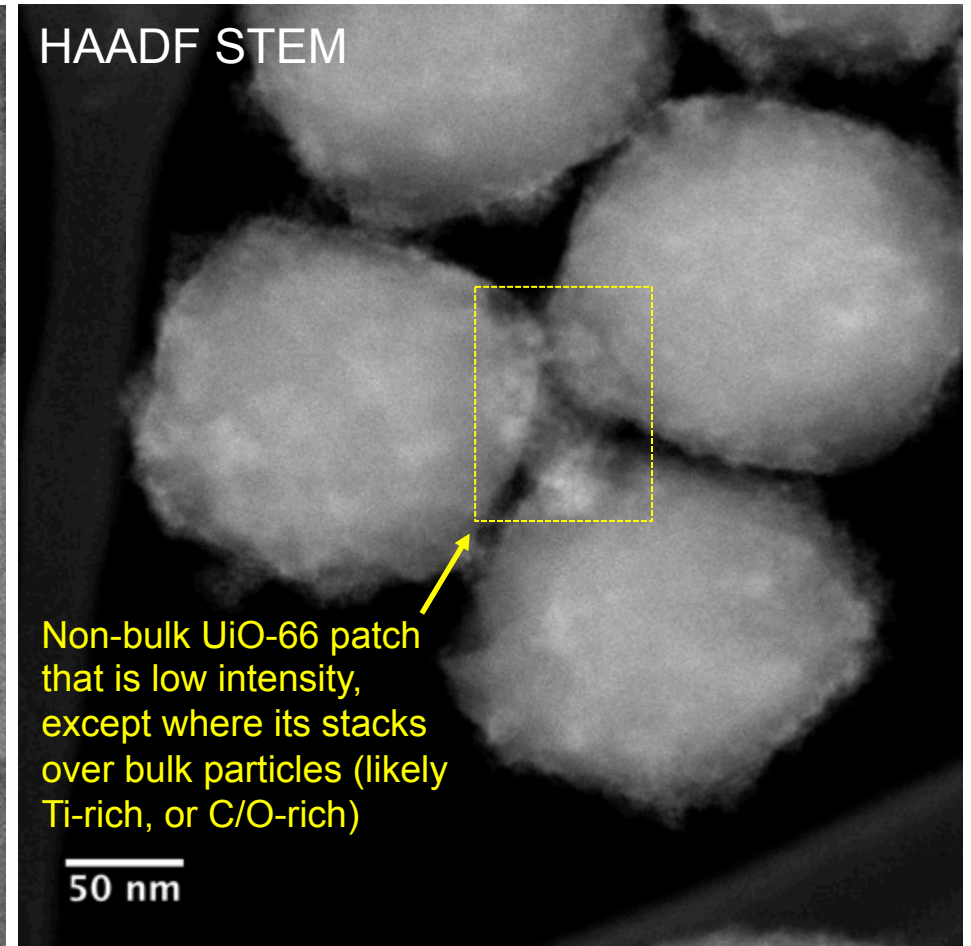
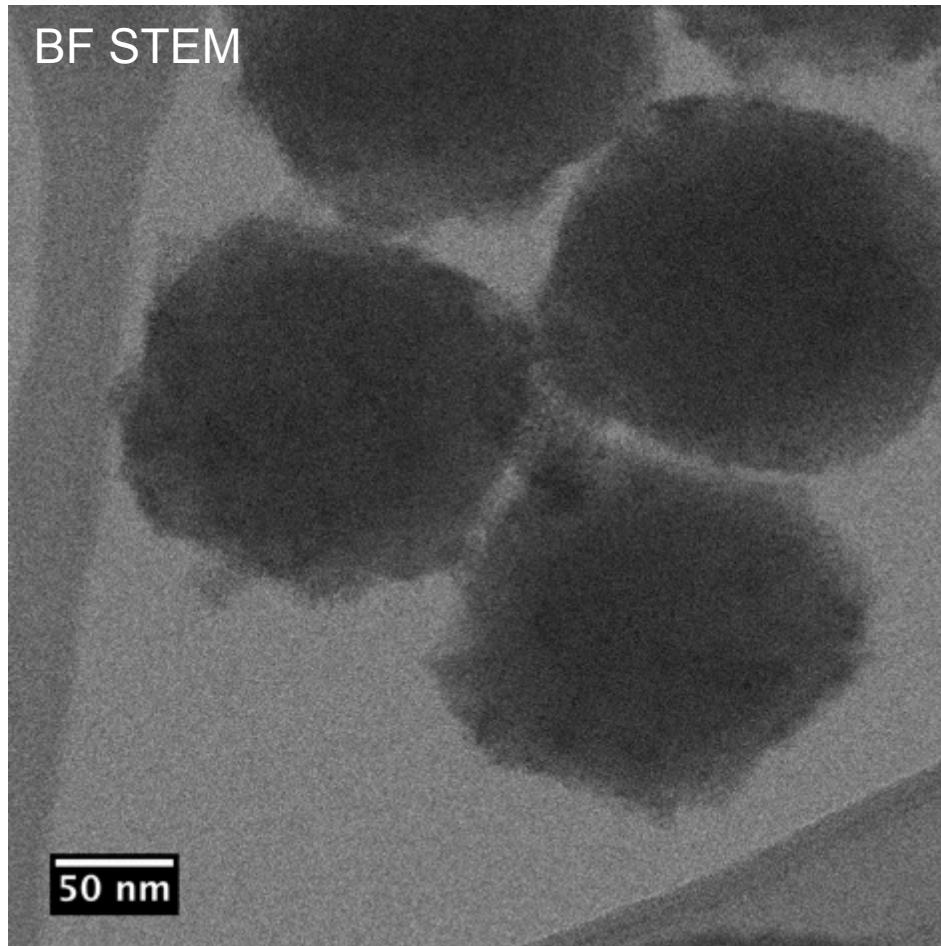
STEM EELS Elemental Maps



The surface layer that is clearly composed of higher Z-number atoms (Hf, rather than Zr), is also very carbon deficient relative to the bulk UiO-66 particle → this might suggest that the **surface layer is not MOF-like**, but more likely an **amorphous Hf-oxide** (the surface layer is not oxygen deficient) → **no evidence that Hf enters the bulk of the particles or has undergone any exchange with Zr** → the lack of C in the Hf layer would suggest a surface coating over the pristine particles

# Ti exchange in Zr UiO-66

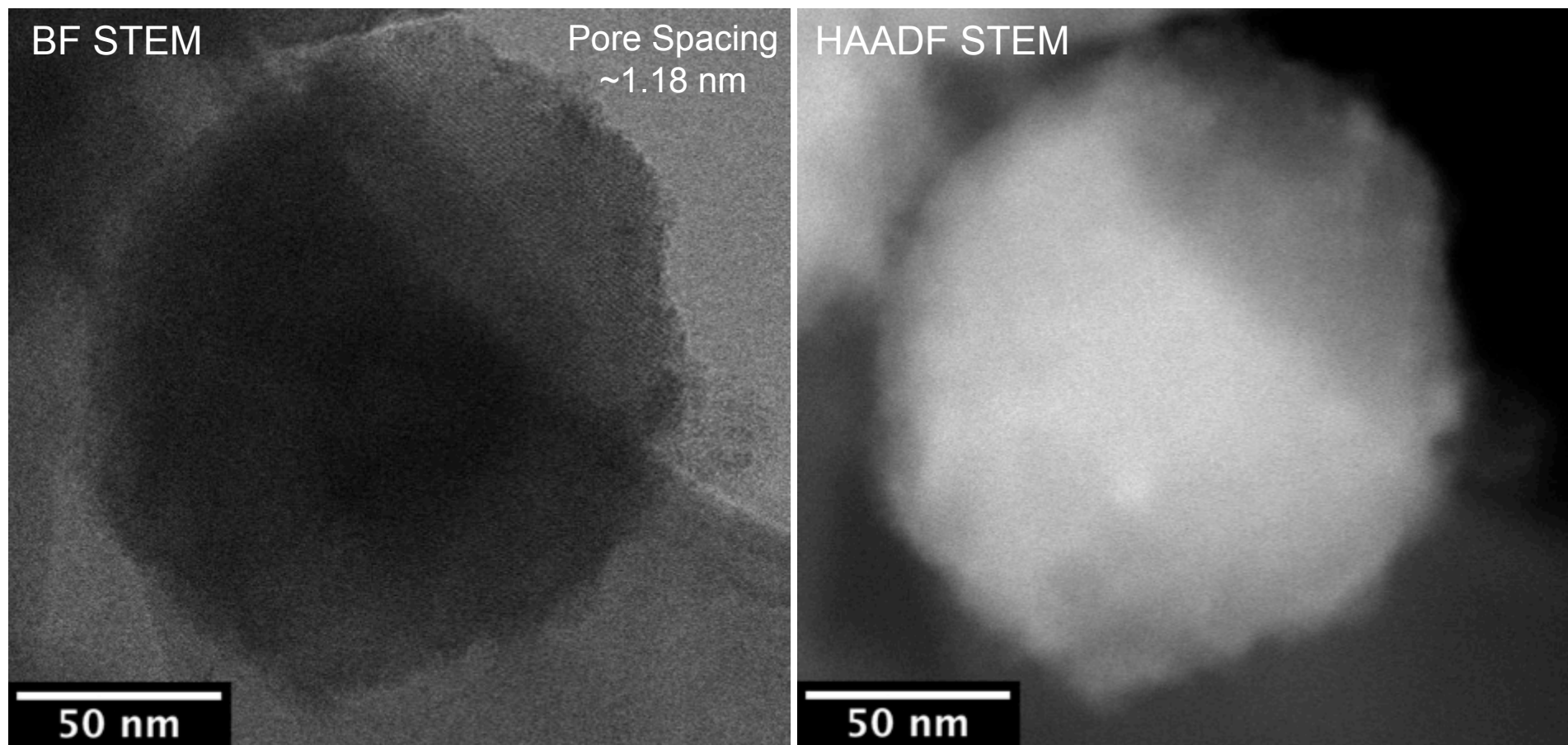
\*SuperSTEM (UK) characterization



HAADF STEM images do not show a uniform low Z-number surface layer, which might be expected if the sample was similar to the Hf-exchange sample (Ti is lower-Z than Zr) → instead, there are surface patches that are low Z (or very thin) except where they stack over the bulk particle, where they add thickness and high pixel intensity in HAADF STEM

# Ti exchange in Zr UiO-66

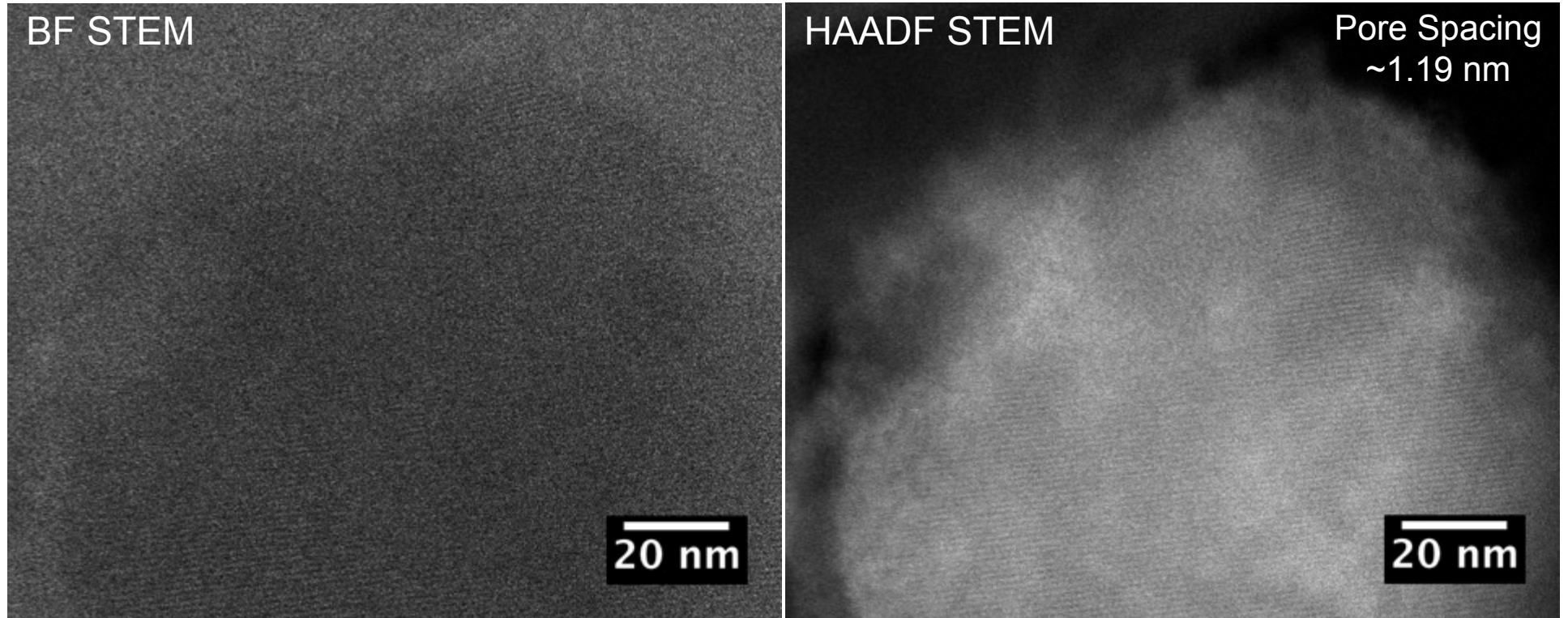
\*SuperSTEM (UK) characterization



HAADF STEM images do not show a uniform low Z-number surface layer on the bulk MOF particles, which might be expected if the sample was similar to the Hf-exchange sample (Ti is lower-Z than Zr) → instead, there are surface patches that are low Z (or very thin) except where they stack over the bulk particle, where they add thickness and high pixel intensity in HAADF STEM → Bulk MOF spacing is consistent with Zr UiO-66 spacing

# Ti exchange in Zr UiO-66

\*SuperSTEM (UK) characterization

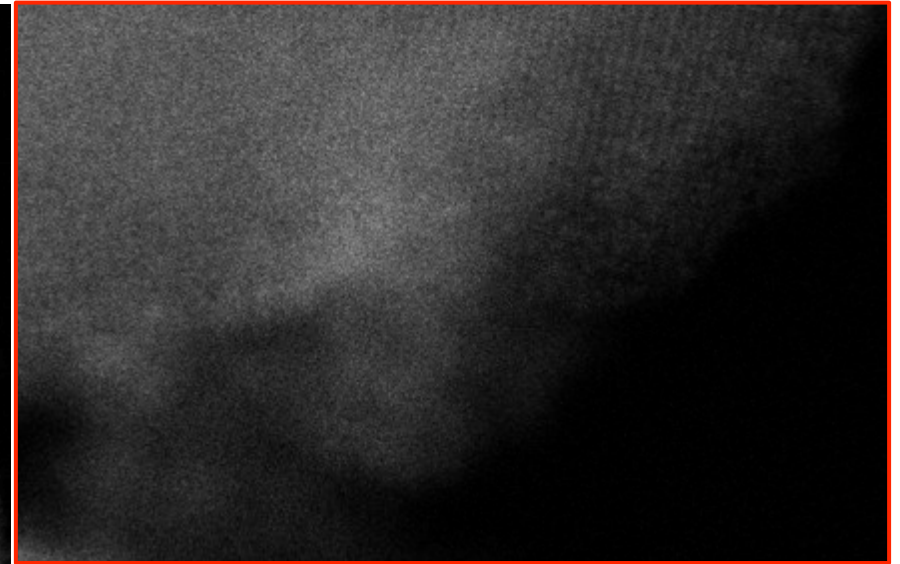
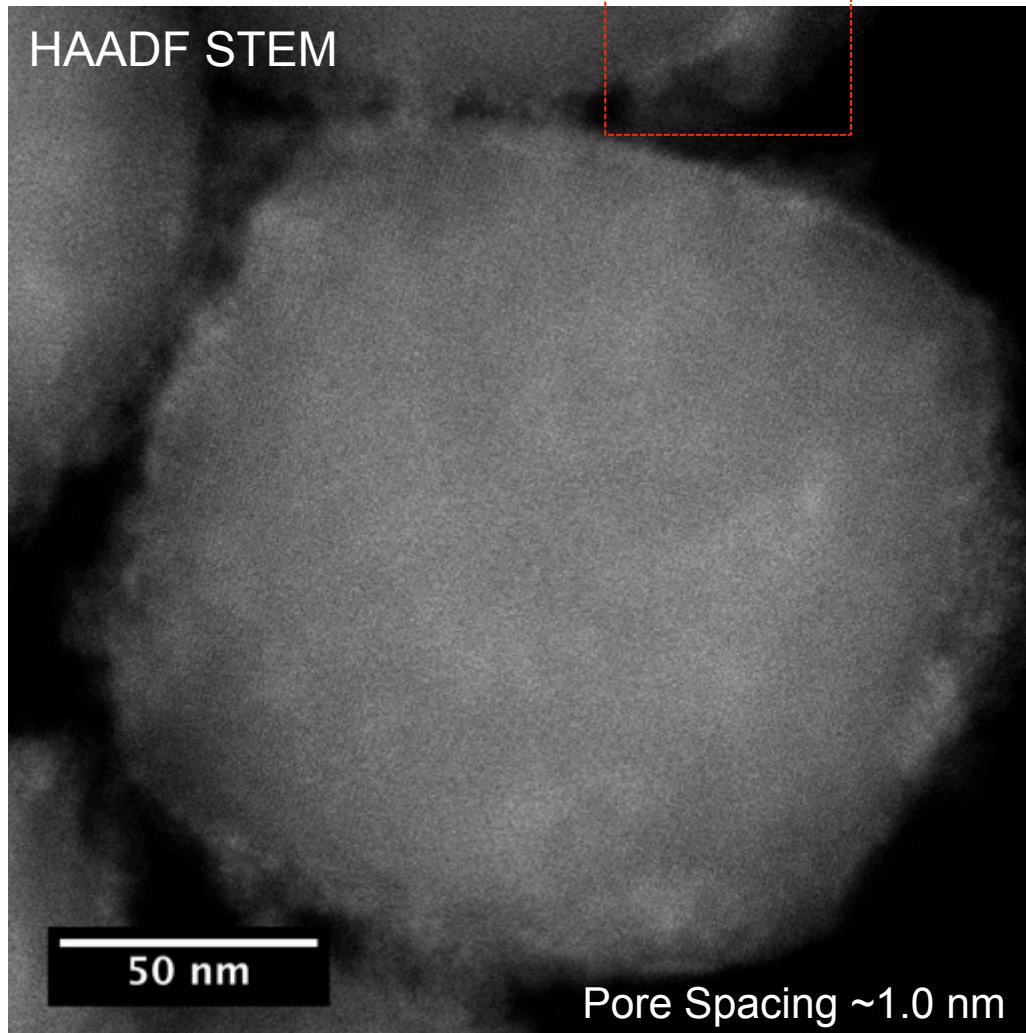


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# Ti exchange in Zr UiO-66

\*SuperSTEM (UK) characterization

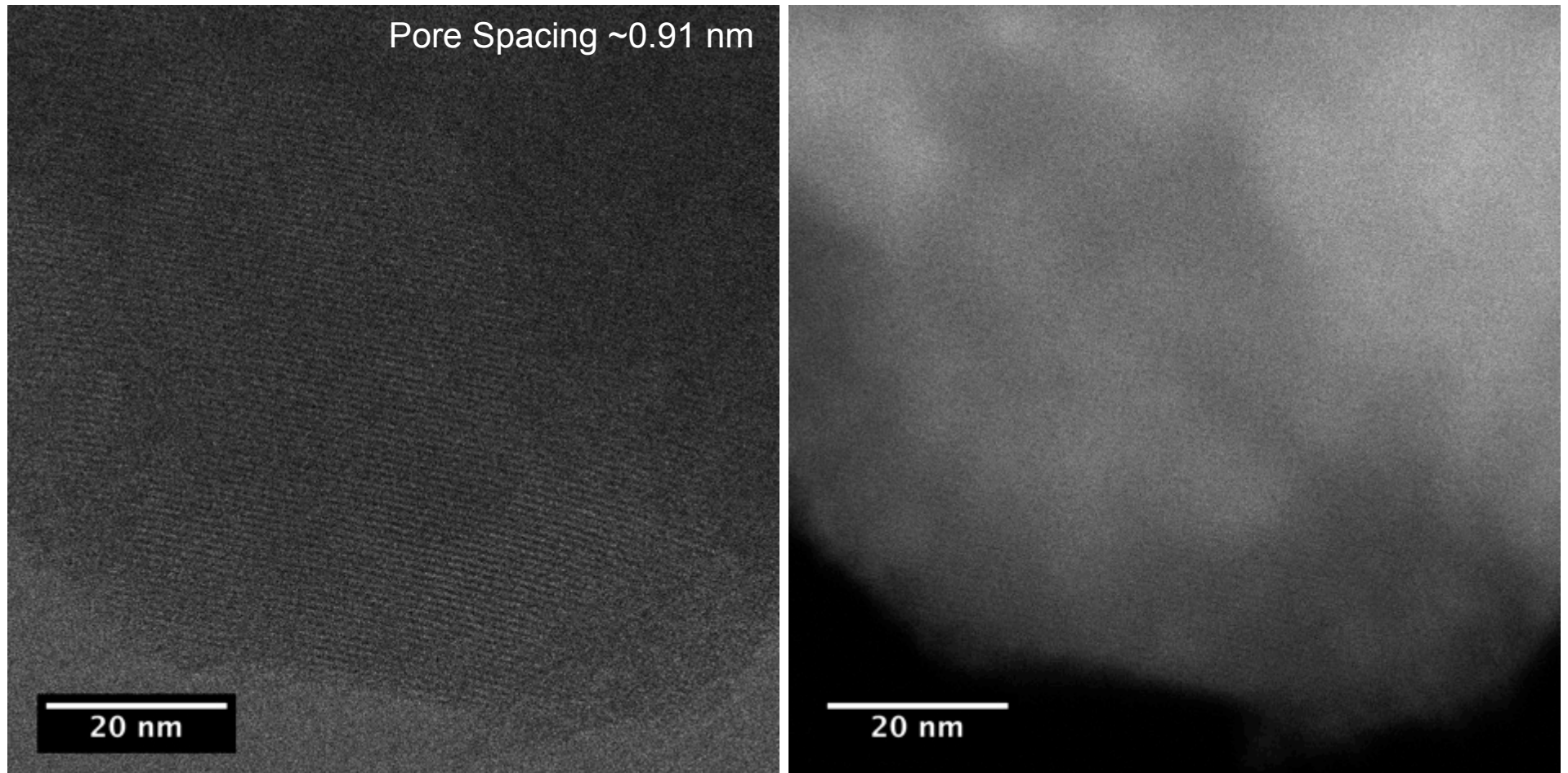


-Pore-channel fringes do appear to extend all the way to the edge/surface in some particles → however, there is also significantly thinner or lower Z-atoms (Ti exchange?) regions

-Patchy nanostructures over bulk particle surface are found coating all bulk particles

# Ti exchange in Zr UiO-66

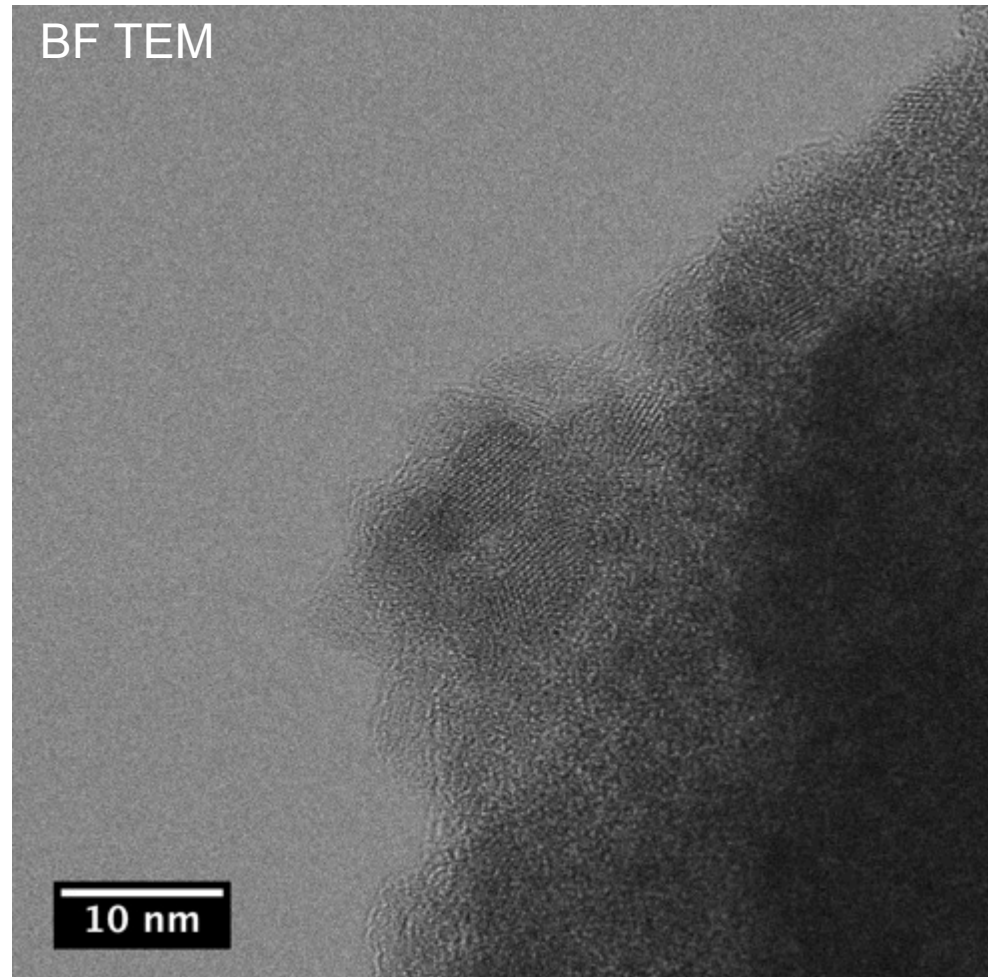
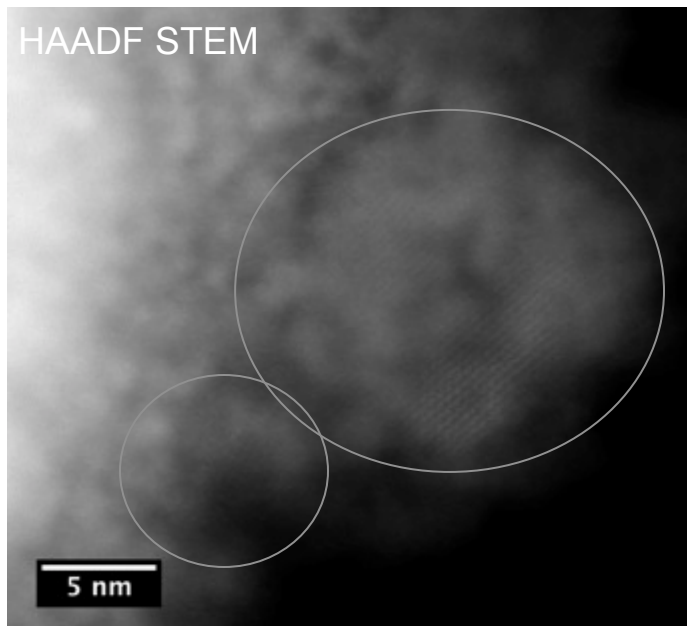
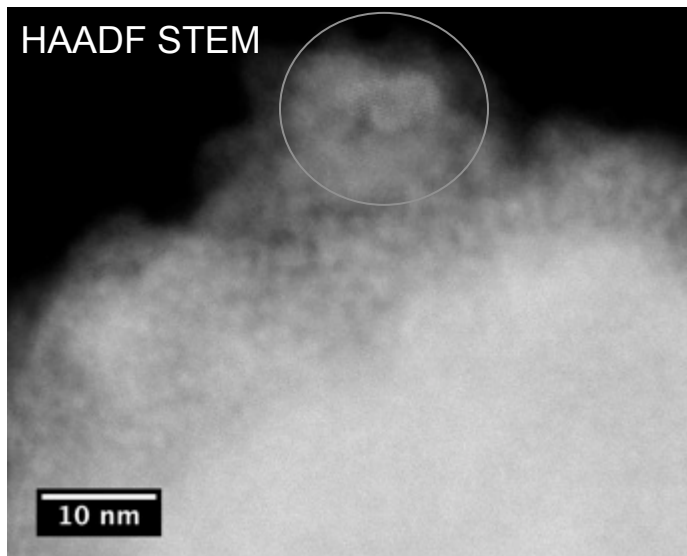
\*SuperSTEM (UK) characterization



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# Ti exchange in Zr UiO-66

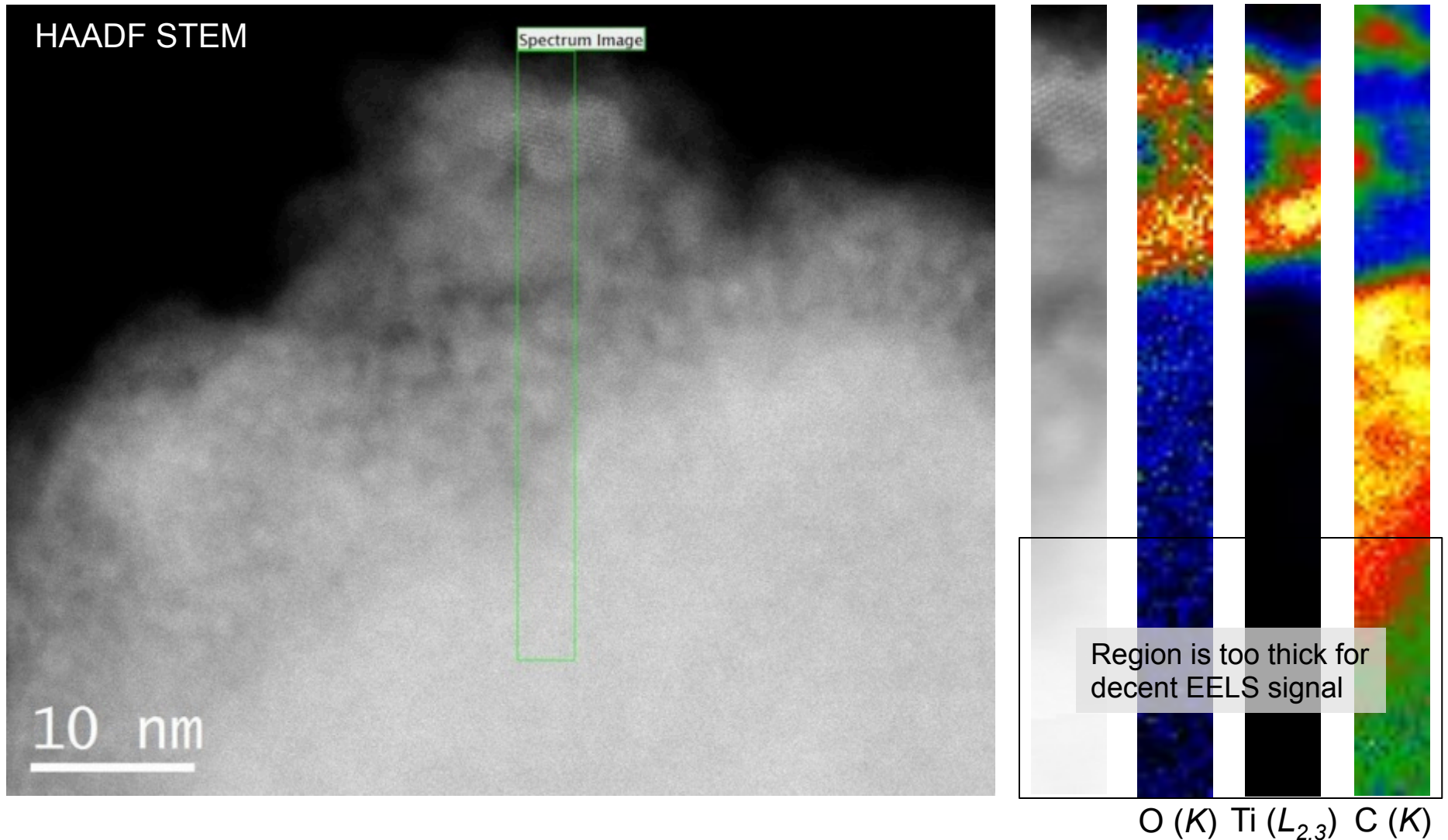
\*SuperSTEM (UK) characterization



Surface nanostructures are often **crystalline**, with lattice spacing that resemble those of **Anatase** and possibly Rutile ( $\text{TiO}_2$  nanostructures) → Possible that some Ti/O rich regions are also amorphous

# Ti exchange in Zr UiO-66

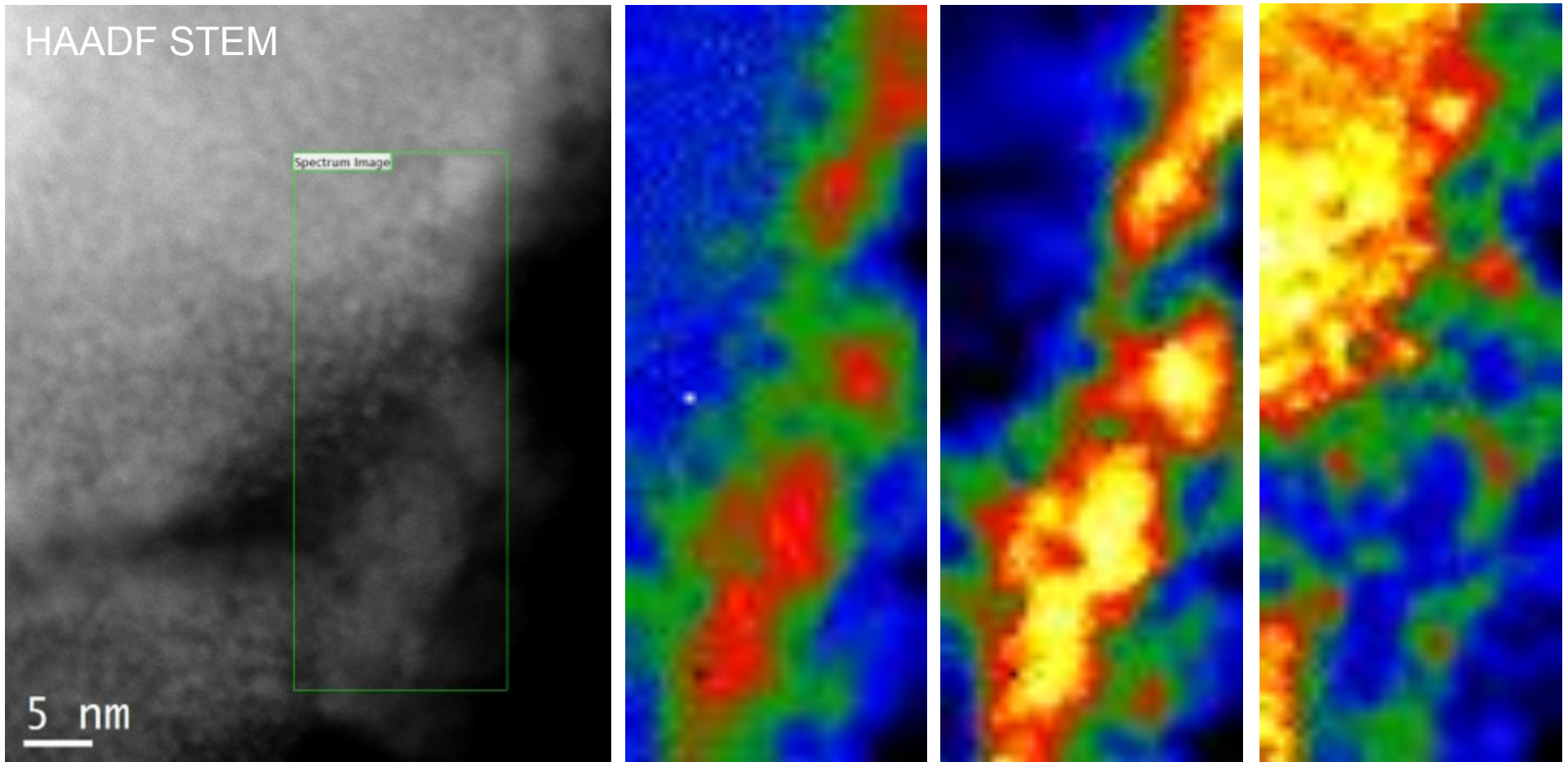
\*SuperSTEM (UK) characterization



Surface nanostructures (generally crystalline) are Titanium/Oxygen rich, Carbon deficient  
→ This clearly suggests these structures are **not MOFs and are likely Titania crystallites**

# Ti exchange in Zr UiO-66

\*SuperSTEM (UK) characterization



O (K)

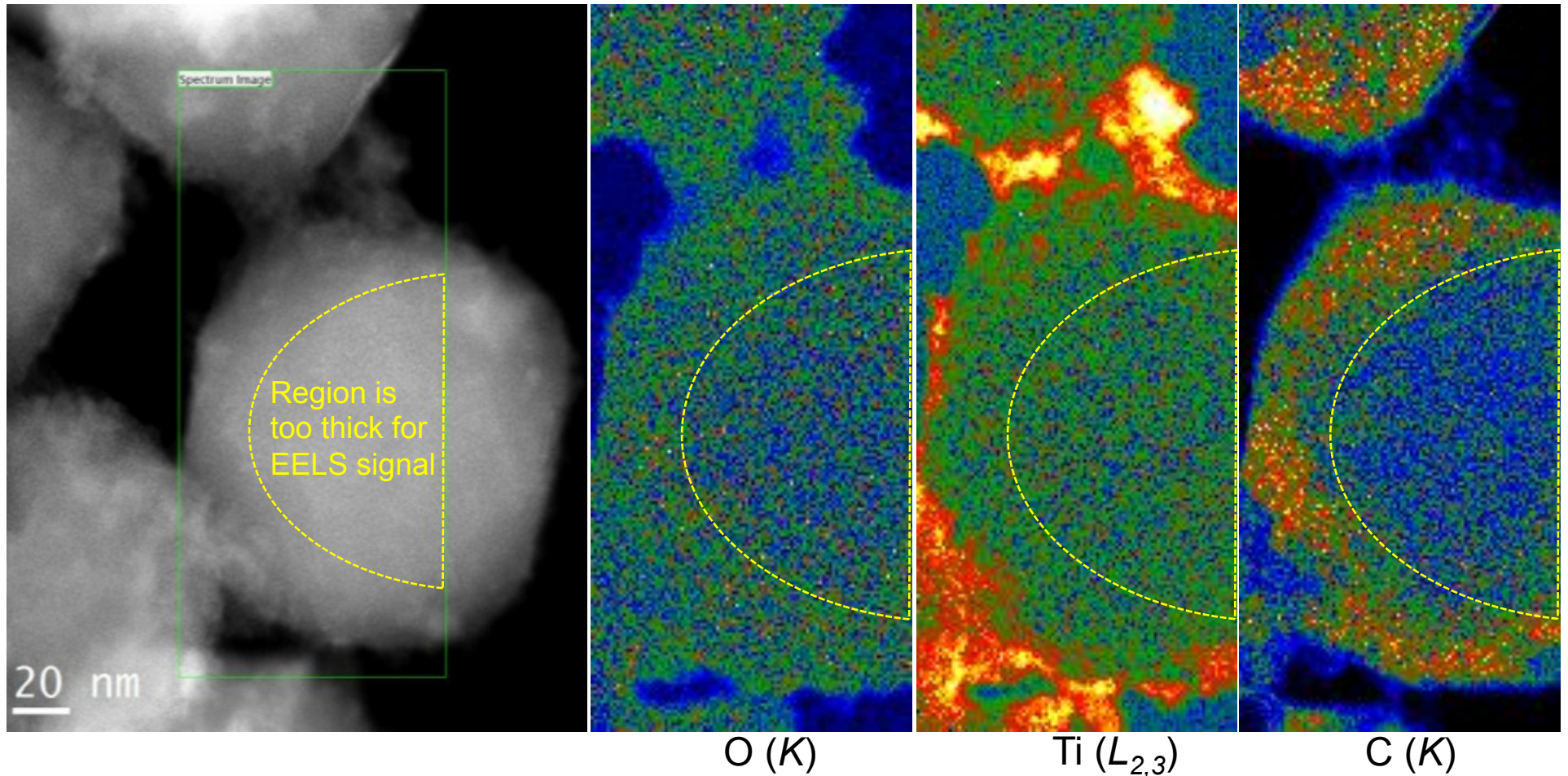
Ti (L<sub>2,3</sub>)

C (K)

Surface nanostructures (generally crystalline) are Titanium and Oxygen rich and Carbon deficient → This clearly suggests these structures are **not MOFs** and are likely **Titania crystallites**

# Ti exchange in Zr UiO-66

\*SuperSTEM (UK) characterization



The bulk MOF particles have fairly complete coverage (though it is patchy in thickness) of the Titanium/Oxygen rich nanomaterial

# Summary Potential Future Work: Metal Exchange in MOFs

- High-resolution TEM/STEM imaging combined with analytical STEM EELS spectral mapping has revealed significant new insight into the field of post synthetic modification of MOFs
  - These new electron microscopy results suggest that metal exchange in the Zr UiO-66 MOF might not actually be occurring...
    - Instead, it seems that for Hf “exchange”, an amorphous Hf-oxide coating forms over the Zr UiO-66 particles
    - And for Ti “exchange”, small TiO<sub>2</sub> (anatase) nanocrystals nucleate and grow at the surface of the Zr UiO-66 particles (possibly amorphous Ti/O nanostructures too)
  - Due to the limitations of generating EELS signal for Zr, the analysis done thus far lacks information about the remaining Zr content
    - STEM EDS elemental mapping is ideal for quantifying Zr, and also Hf and Ti
      - We will access a national user facility (PNNL or LBL) with analytical STEM EDS capabilities to complete our understanding of the Zr UiO-66 metal exchange system
- The results from this work highlight the need to similar electron microscopy studies of all post synthetic modification systems (metal exchange and possibly ligand exchange) → We will investigate other systems of interest of the Cohen Lab

# Metal Exchange in Zr UiO-66 Developed for Potential LCTEM Metal Exchange Experiments (ethanol, which is LCTEM compatible)

*Work in Progress*

Ti - UiO-66 (85° C)

Zr - UiO66

Hf - UiO66 (60° C)

