Tech Talk

Sample Preparations for High Quality TEM Analyses

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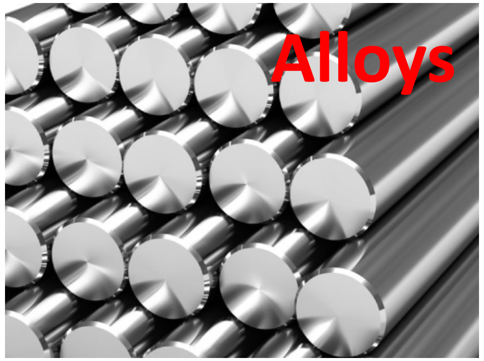
Outline

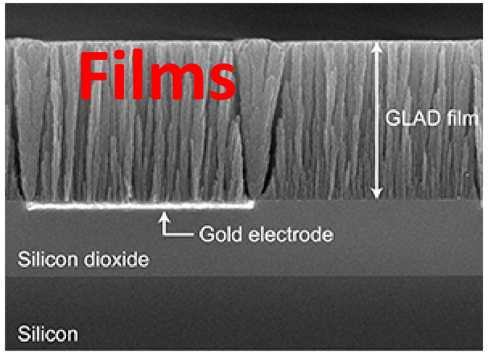
- How to choose the suitable methods to make TEM samples?
- Crush Method
- Ar Ion Milling Method
- Electrochemical Methods
- Microtome
- Focus Ion Beam Milling
- Replica → Only the duplication of the morphological features. Many other structural/chemical details are lost. Not covered here.
- Some specific complicated cases
- Cryo sample preparation → Not covered here.

High Quality Electron Transparent Sample:

- ✓ Very thin (less than 100 nm);
- ✓ Large flat electron transparent regions;
- ✓ No additional/foreign artifact;
- ✓ No contamination;

How to choose the suitable methods to make TEM samples?





Everything which is in solid state can be prepared as TEM samples.

Crush Method

Some representative applications:

- ❑ Conventional powders samples with different sizes;
- ❑ Very brittle bulk samples (intermetallic, quasicrystals…)
- ❑ ……

Advantages

- ✓ Very robust/efficient/economical;
- ✓ No ion beam damage

Disadvantages

- ✓ May change the original morphological features;

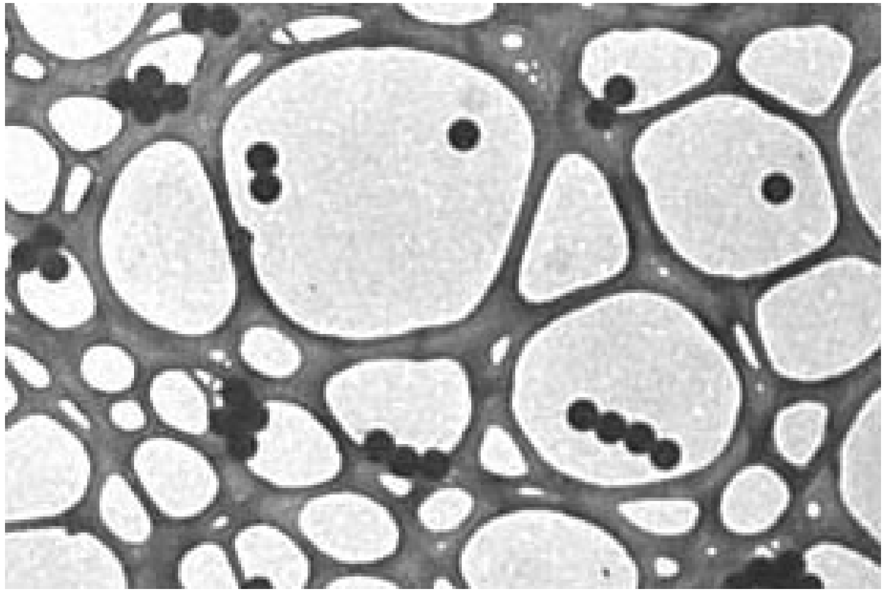
General steps:

1. If pristine powder size is in micrometer size, use the pestle and mortal to crush the powders;
2. Dispersed powders into alcohol;
3. Using ultrasonic method to distribute the original powders uniformly;
4. Transfer several drops on suitable TEM grids;

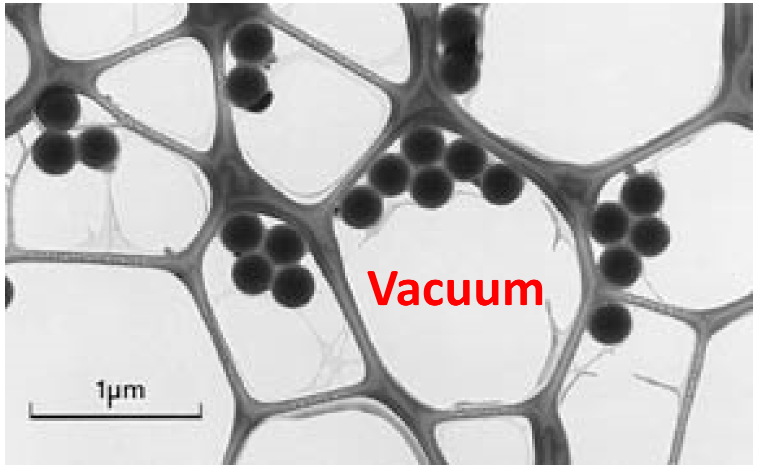
How to keep the internal boundaries of the microsphere powders?

How to choose the TEM grids?

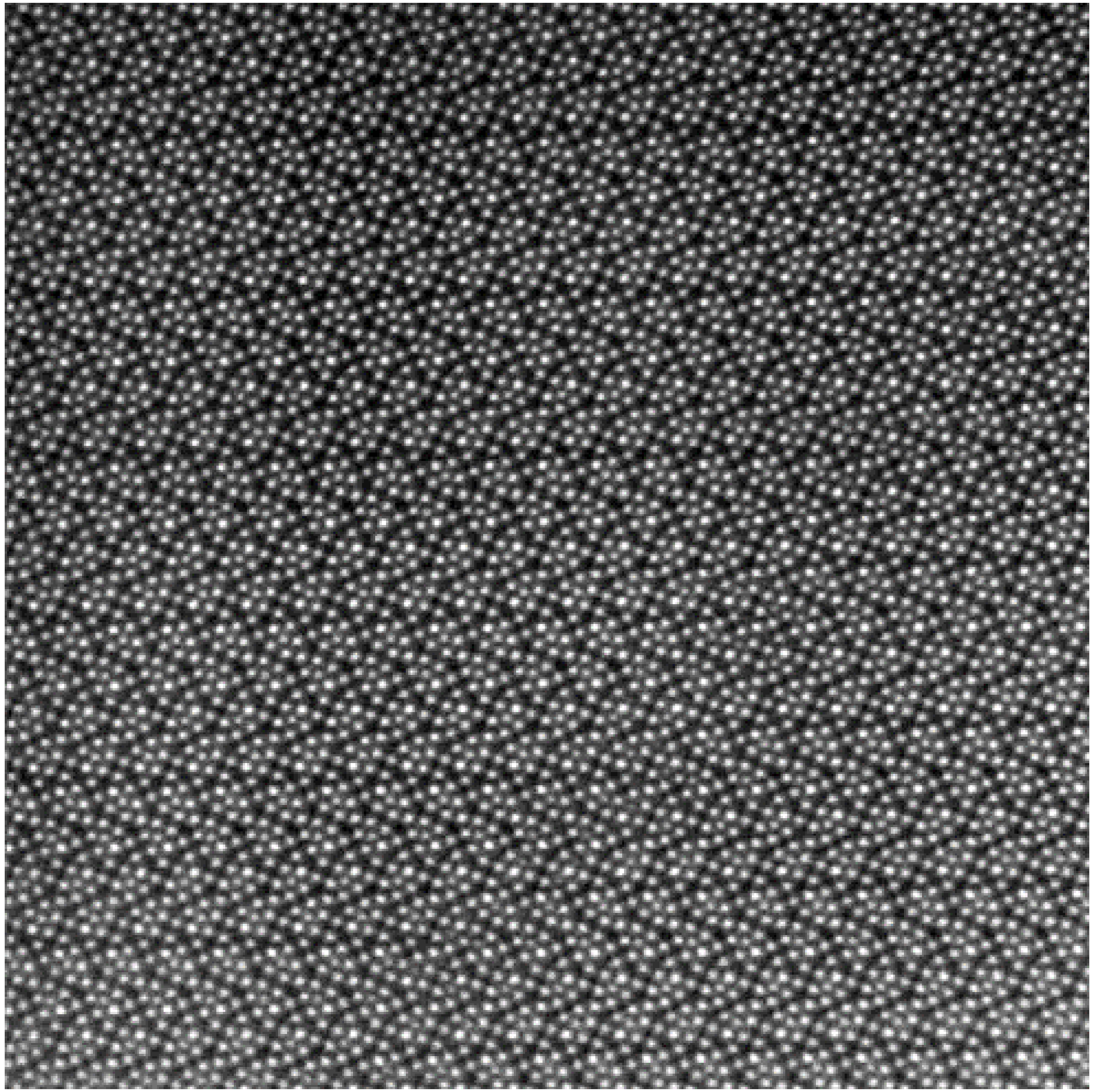
- ❑ Particle size less than 10 nm
- ❑ Particle size larger than 10 nm
- ❑ ......

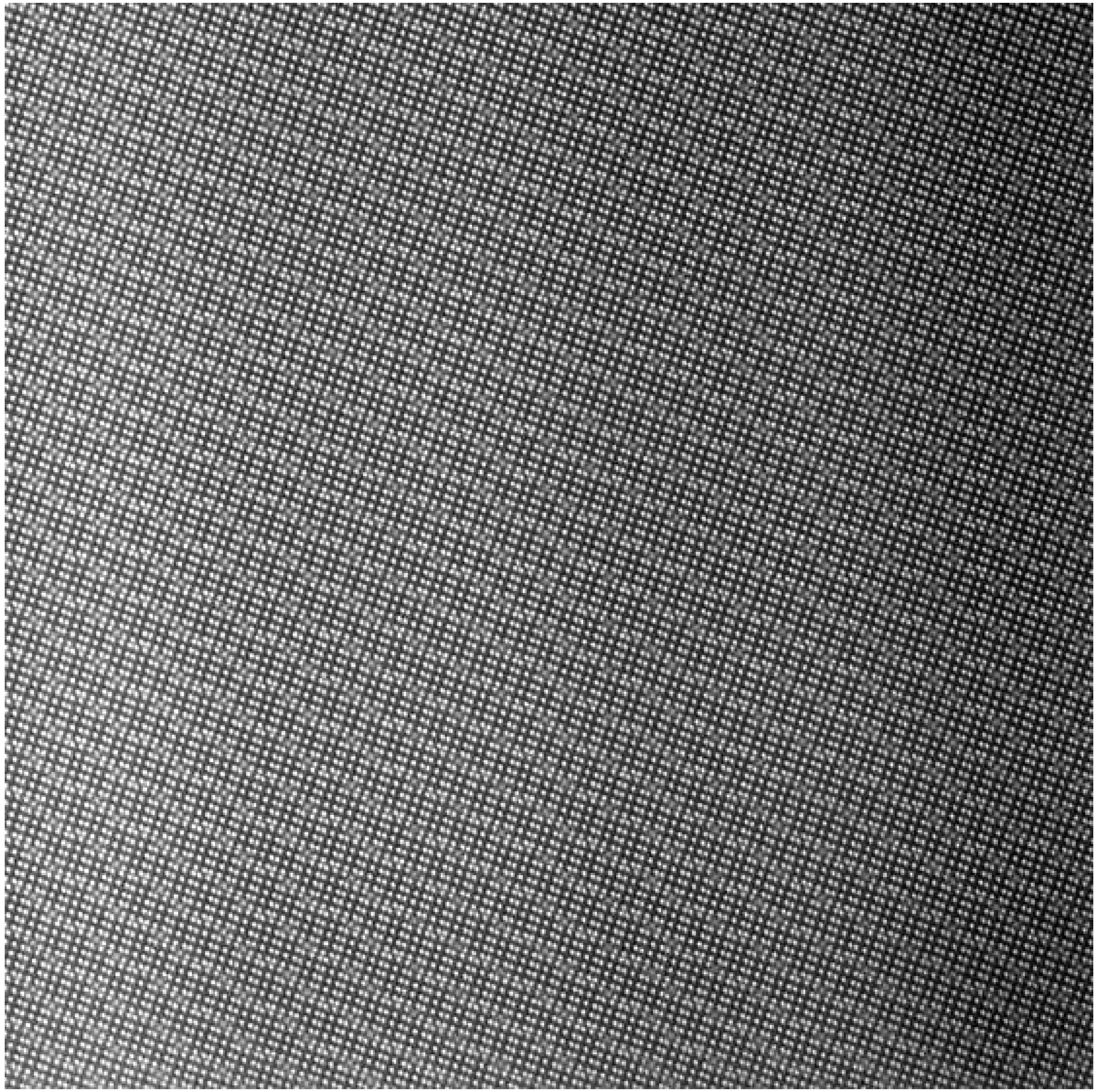


Ultrathin Carbon Film on Lacey Support Films



Lacey Support Films





Microstructural features of the W-Nb-O oxide.

Unpublished work

Ar Ion Milling Method

Fischione 1050 TEM Mill

- From -150 °C to room temperature
- 0.1 V to 6 kV
- Beam size: 1.5 mm at 5 kV
- Milling angle range from 0 to 10 degree

Advantages

✓ Very robust;

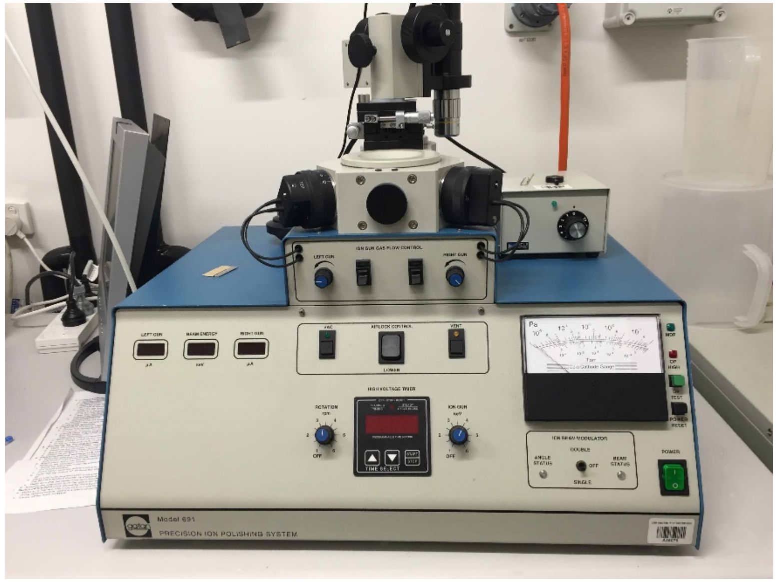
✓ Applicable to almost all the materials

Disadvantages

✓ Not found yet

Some representative applications:

- ❑ Various kinds of engineering alloys and compounds;
- ❑ Various kinds of thin film system which are not sensitive to air/water
- ❑ Powder samples with the size of micrometers;
- ❑ Samples with irregular shape with the size of micrometers (e.g. hair, copper wire….)
- ❑ ……



Gatan 691 PIPS

Leica RES101

PIPS^{TM} II

- Room temperature (No cold stage)
- 1.5 kV to 6 kV
- Beam diameter: 350μm to 800 μm FWHM at 5 kV
- Milling angle range from 0 to 10 degree

Advantages of PIPS^{TM} II

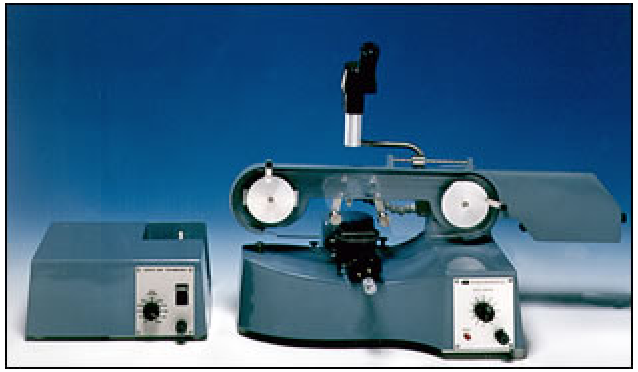
- X,Y stage permits alignment of argon beams to region of interest on the sample (**Very precise location**)
- Improved collimated beam provides useable voltages as low as 100 volts for rapid and damage free preparation of FIB lamella

General steps:

1. Cut thin slices (less than 1 mm) from the bulk sample;
2. Polish the slices down to around 100 μm;
3. Punch into standard size (3 mm diameter);
4. Continually polishing down to 30-50 μm by hand;
5. Dimpling down to around 10 μm;
6. Perforation by Ar^+ milling;

OptiPrep™ Polishing System

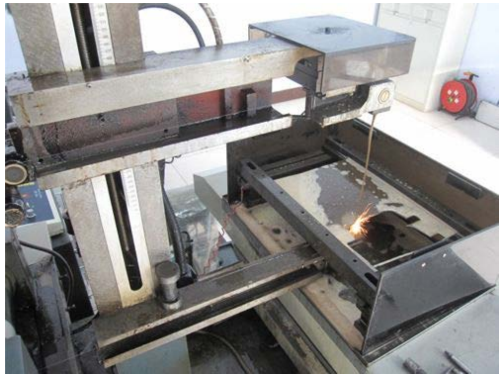
*Desired sample angles are obtained based on geometric orientation built into the fixture.



Abrasive Slurry Saw

Low Speed Saw

Linear Precision Saws

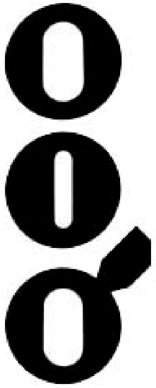


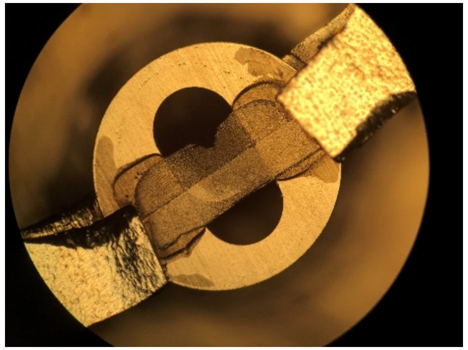
Wire-Electrode Cutting

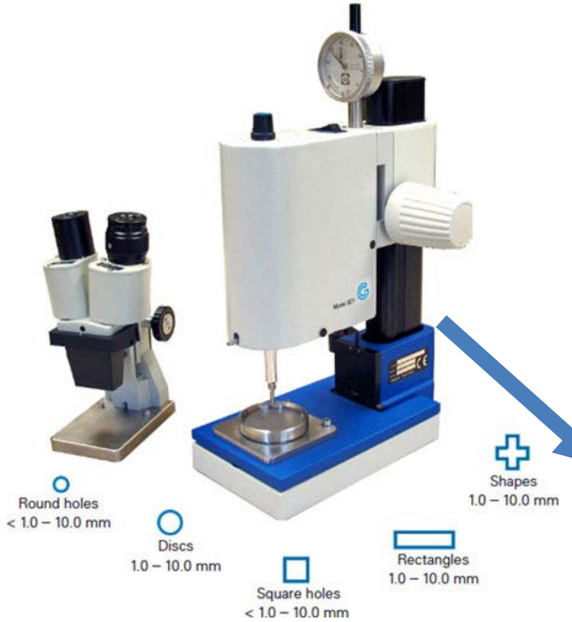
General steps:

1. **Cut thin slices (less than 1 mm) from the bulk sample;**
2. **Polish the slices down to around 100 µm;**
3. **Punch into standard disk (3 mm diameter)*;**
4. **Continually polishing down to 30-50 µm by hand;**
5. **Dimpling down to around 10 µm;**
6. **Perforation by Ar^+ milling;**

* If your slice is not in standard size, you need to use grids.







Ultrasonic Cutter

Both Brittle and Ductility Materials

Punch Equipment

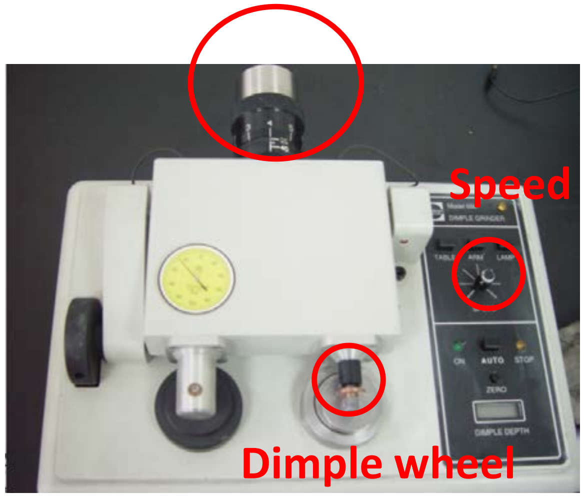
Ductility Materials

Disk Grinder System

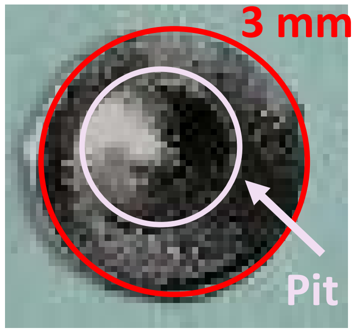
General steps:

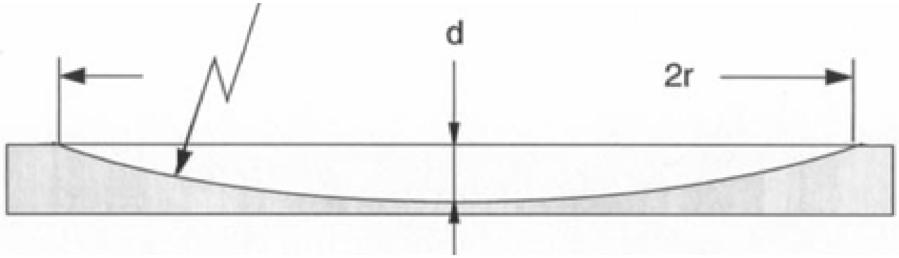
1. **Cut thin slices (less than 1 mm) from the bulk sample;**
2. **Polish the slices down to around 100 μm;**
3. **Punch into standard disk (3 mm diameter)*;**
4. **Continually polishing down to 30-50 μm by hand;**
5. **Dimpling down to around 10 μm;**
6. **Perforation by Ar^+ milling;**

*** If your slice is not in standard size, you need to use grids.**



Gatan 656 Dimple Grinder





Diameter of dimple wheel, **D**
Diameter of the pit, **2r**
Depth of the pit, **d**

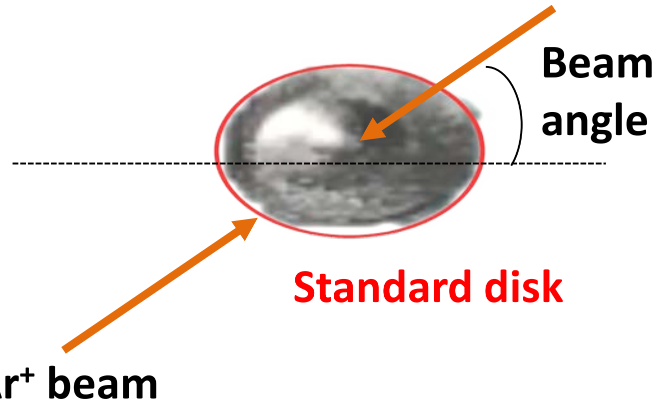
$d=r^2/D$

D can be 10, 15, 20, 25 mm;

General steps:

1. **Cut thin slices (less than 1 mm) from the bulk sample;**
2. **Polish the slices down to around 100 μm;**
3. **Punch into standard disk (3 mm diameter)*;**
4. **Continually polishing down to 30-50 μm by hand;**
5. **Dimpling down to around 10 μm;**
6. **Perforation by Ar^+ milling;**

*** If your slice is not in standard size, you need to use grids.**



Fischione 1050 TEM Mill

Model 1050 TEM Mill Milling Rates

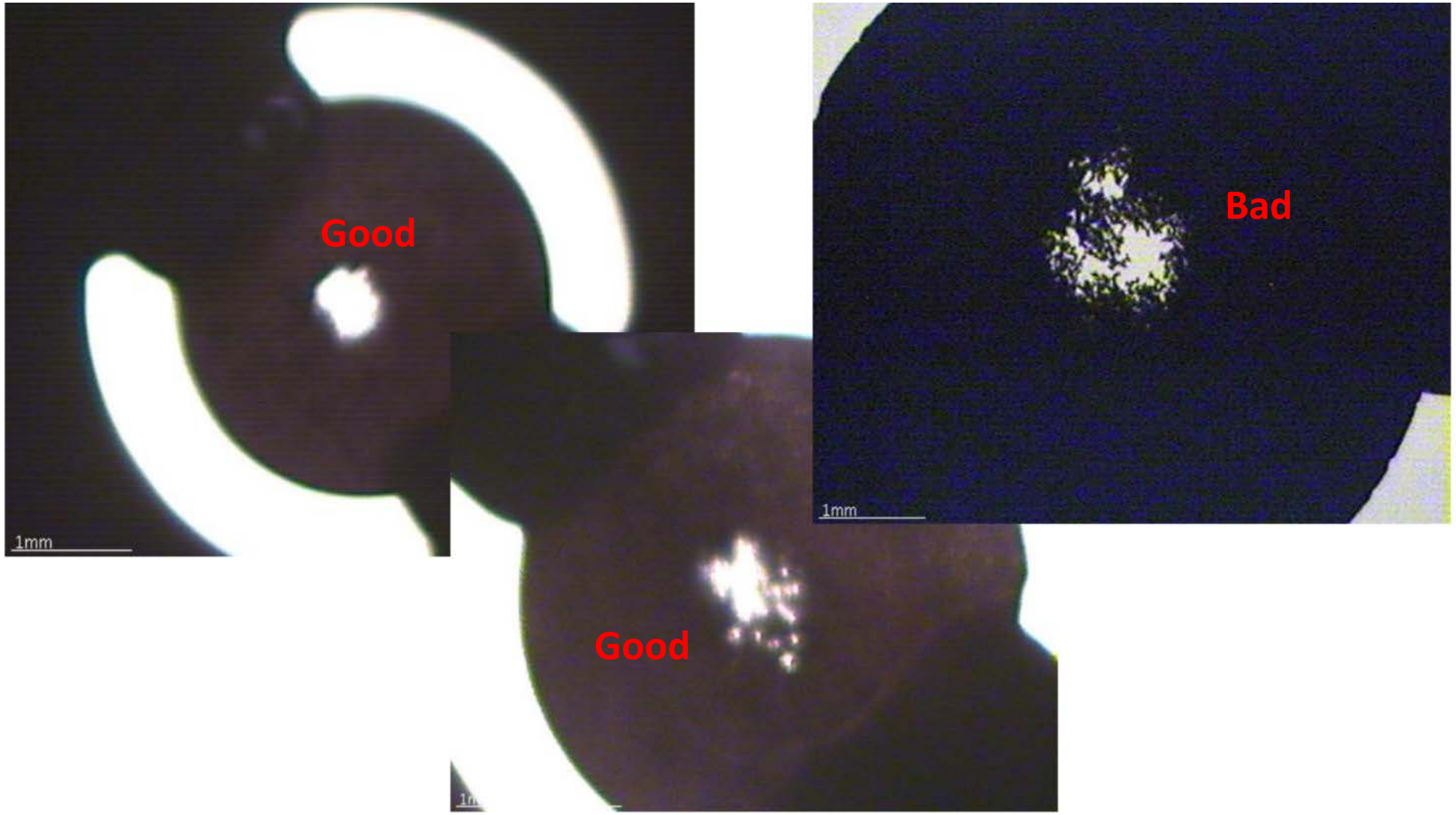
The milling rates are based on the following milling parameters:

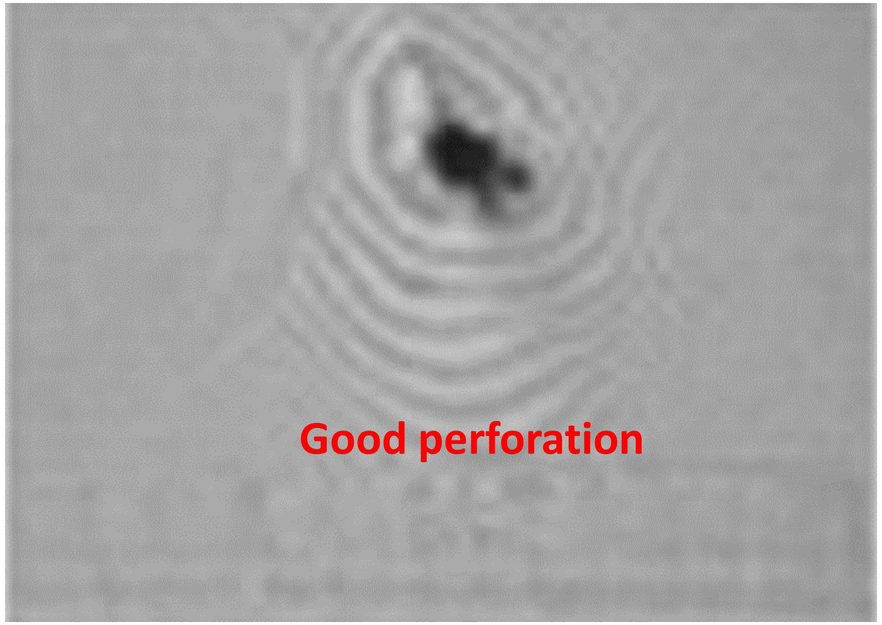
- Energy: 5 kV
- Number of ion sources: 2
- Beam size: 1.5 mm
- Beam angle: ± 10°
- Laser sensitivity: 15%

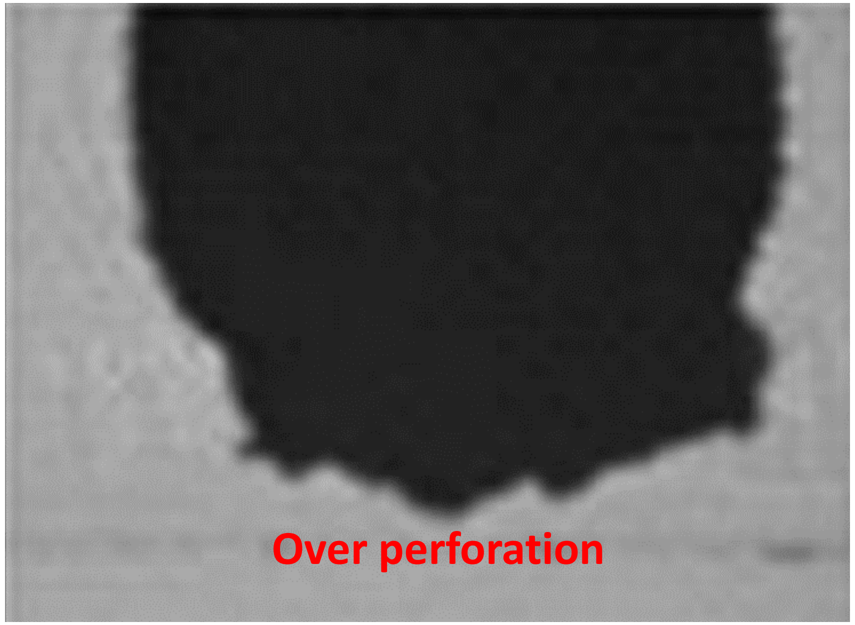
Material	μm/hour
Nickel	12.1
Tantalum	7.9
Aluminum	23.3
Titanium	15.7
Tungsten	7.1
Molybdenum	7.6
Stainless steel	11.3
Silicon	10.6

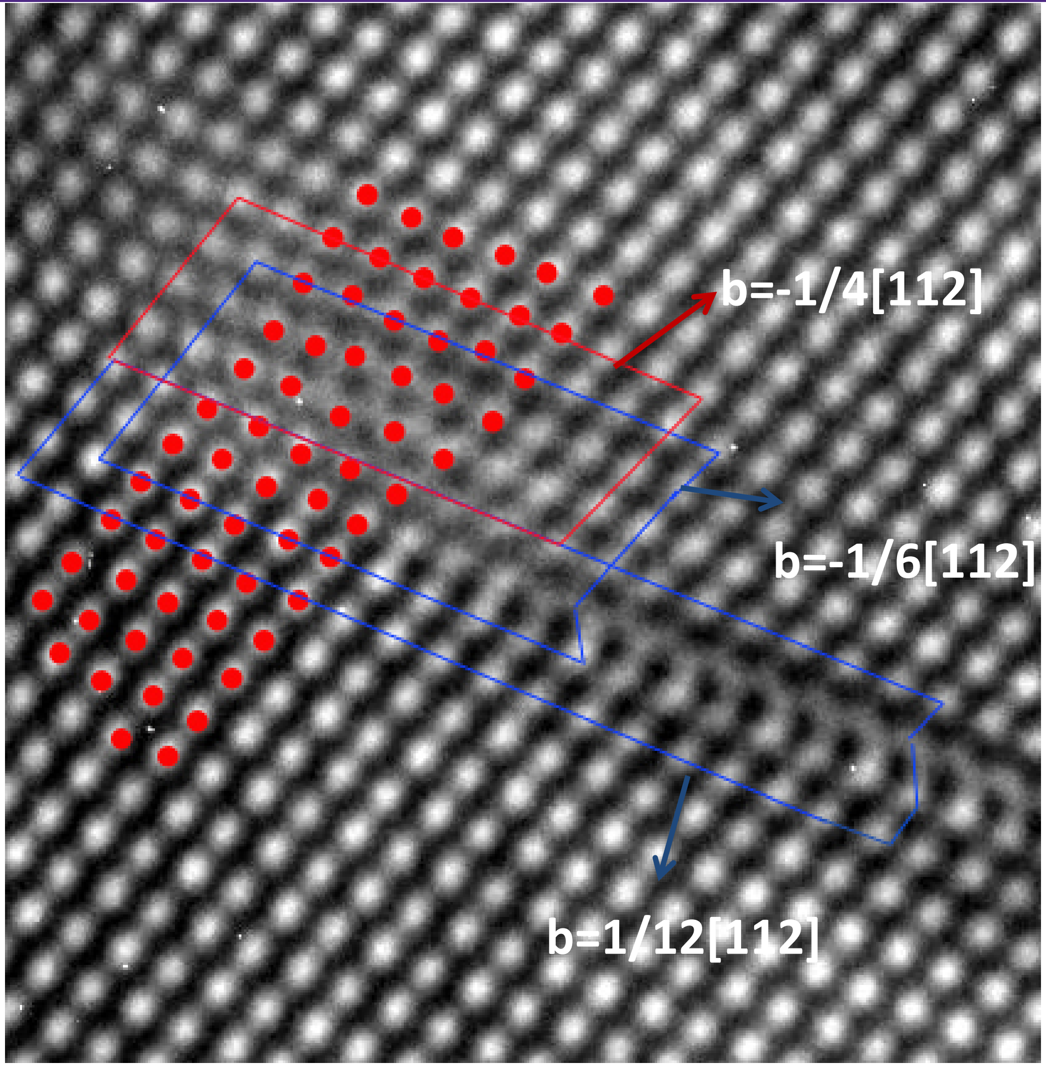
Main adjustable parameters：

- **Voltage (0-6 kV);**
- **Beam angles (0-10 degree);**
- **Temperature (-150 ℃ to room temperature);**


Good
Bad
Good
1mm
1mm

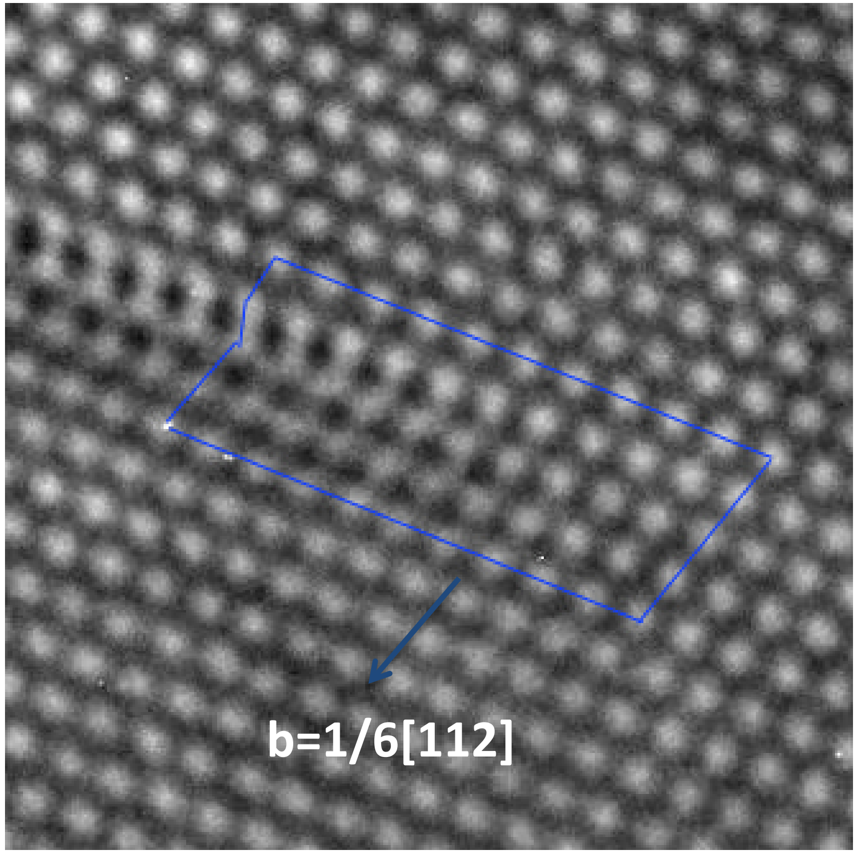

Good perforation


Over perforation



Dislocation dipole ?
Two 60° dislocation?

Ni_3Al foils



Two edges of the former SF

b1=1/2<110>=1/6<211>+SF+ 1/6<12-1>
60° dislocation=30° dislocation+90° dislocation+SF
b2=1/2<110> 60° dislocation

Atomic scale revealing the dissociation of dislocations and the interactions among dislocations.

Unpublished work

Electrochemical Method

Struers TenuPol-5

Critical parameters:

- Low temperature (Liquid N2);
- Suitable electrolyte;
- Suitable voltage and current;

General steps:

1. Cut thin slices (less than 1 mm) from the bulk sample;
2. Polish the slices down to around 100 µm;
3. Punch into standard disk (3 mm diameter);
4. Continually polishing down to 30-50 µm by hand;
5. Perforation using the electrochemical method;

Advantages

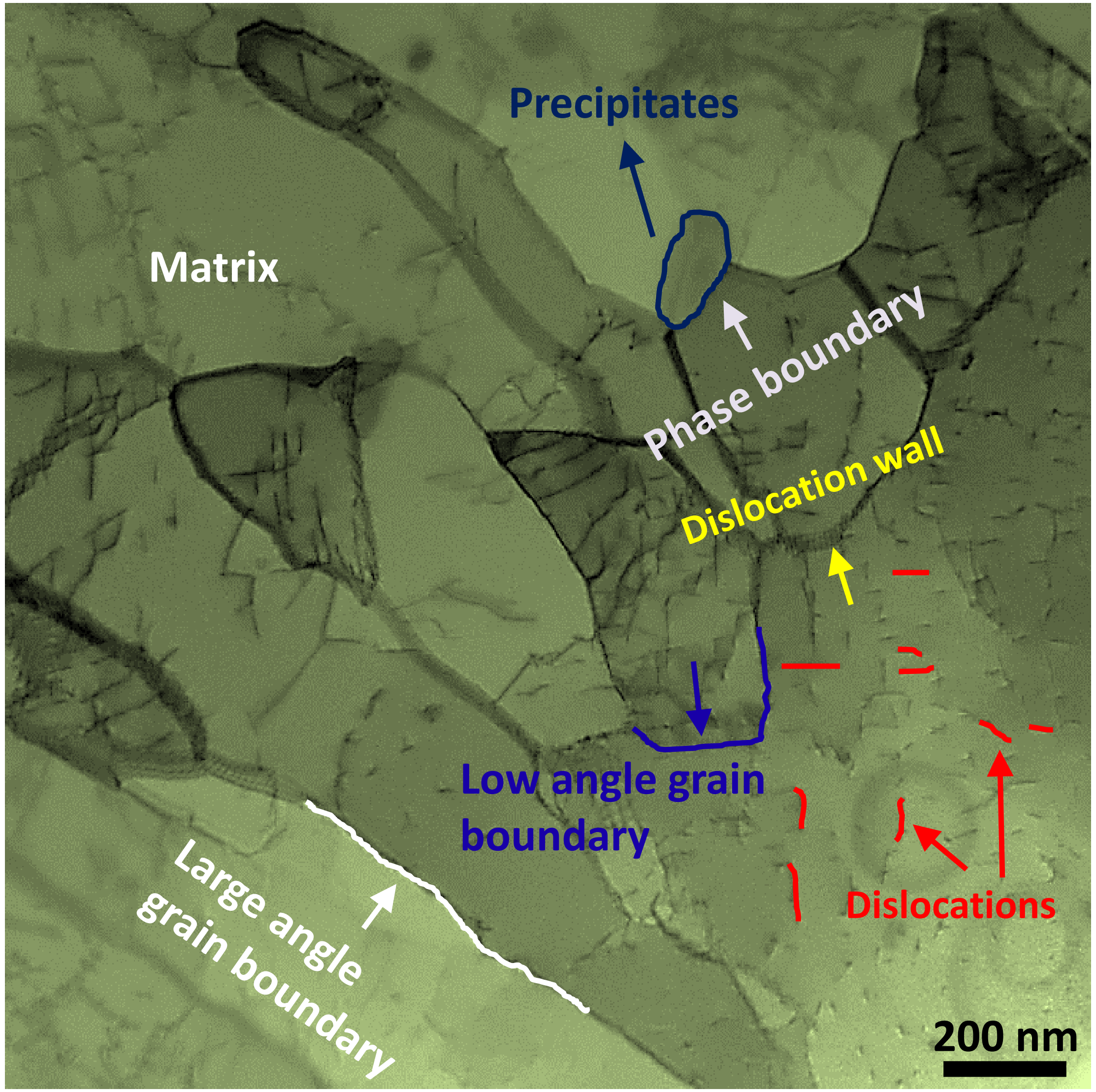
- ✓ Relatively fast/efficient;
- ✓ No additional ion beam damage;

Disadvantages

- ✓ Only samples having conductivity;
- ✓ Poor controllability;
- ✓ May lose the secondary phases;
- ✓ Low success rate;
- ✓ May introduce contamination;

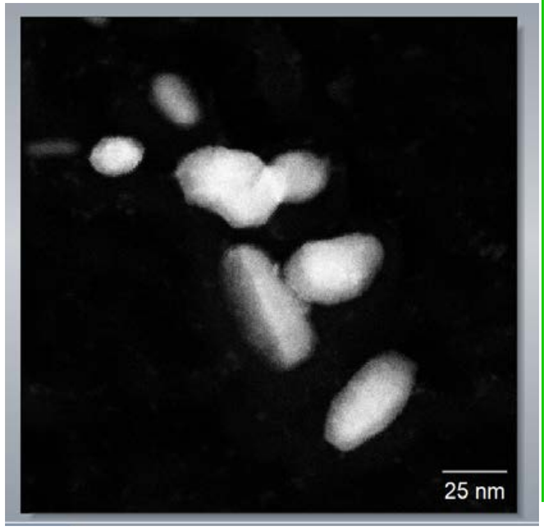
Some representative applications:

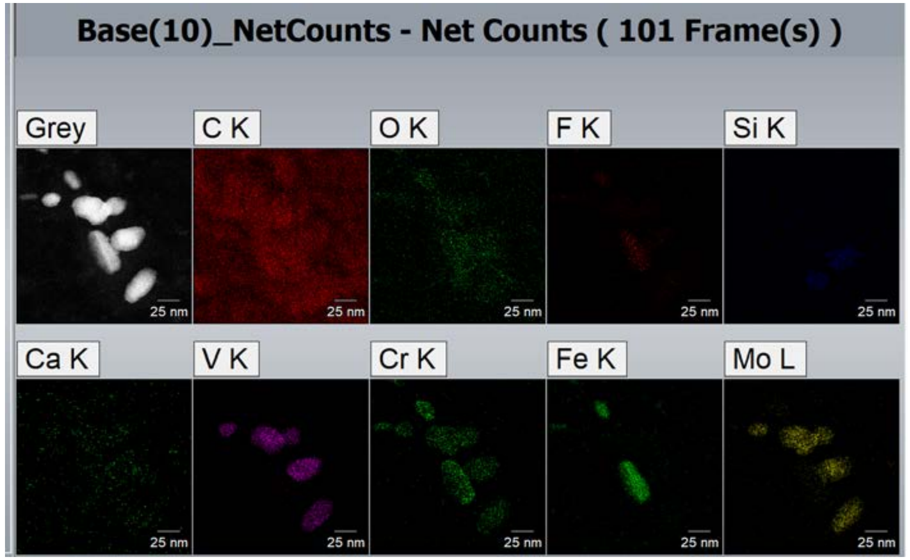
❑ Various kinds of engineering alloys;



Electrochemical twin-jet method

Extraction of secondary phases





Advantages

- ✓ Relatively accurate composition for smaller particles (less than 10 nm);

Disadvantages

- ✓ Not robust;
- ✓ Lose interfacial/orientation information;
- ✓ Poor controllability;
- ✓ Not good for high quality analyses;

In courtesy of Dr. Jeffery Lin

Microtome Method

- From -180 °C to room temperature
- Section thickness from several nanometers to 15 micrometers
- Glass knives and diamond knives

Leica UC7/FC7 Cryo-Ultramicrotome

Advantages

✓ **Very gentle/robust;**

Disadvantages

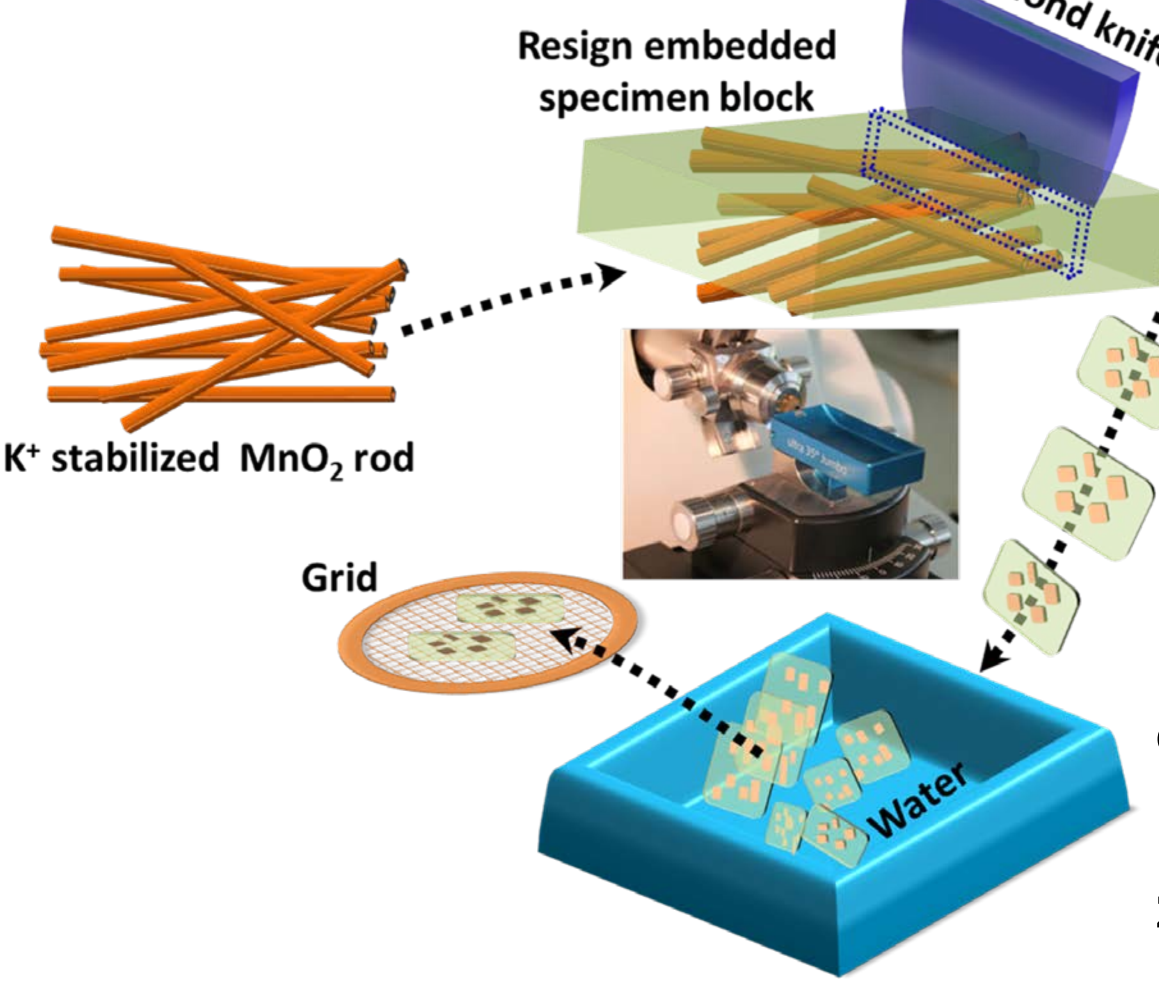
✓ **May introduce contamination within TEM columns;**

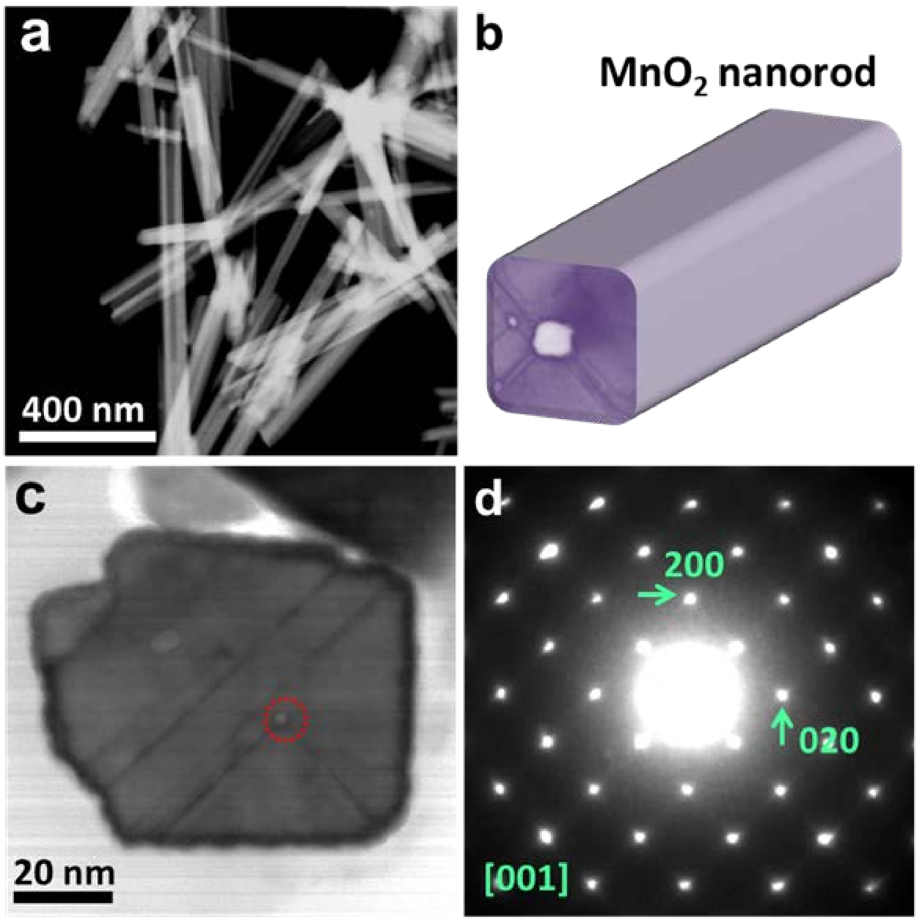
Some representative applications:

- ❑ **Observations from the cross-section of the nanorod;**
- ❑ **Powder samples with the size of micrometers;**
- ❑ **Samples with irregular shape with the size of micrometers (e.g. hair, copper wire….)**
- ❑ **Biological samples**
- ❑ **……**

Cross-section of Nanorod

Reasons: The occurrence of rod along cross-section probability in conventional preparation methods is too low.



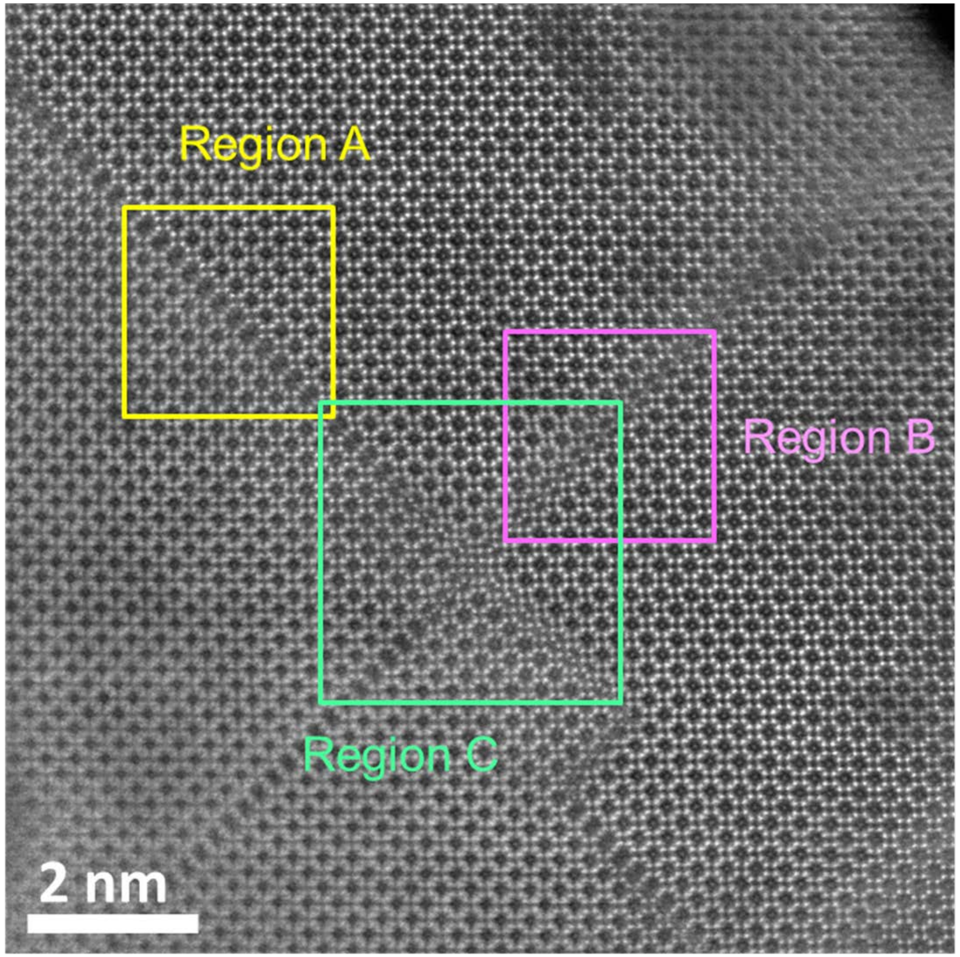


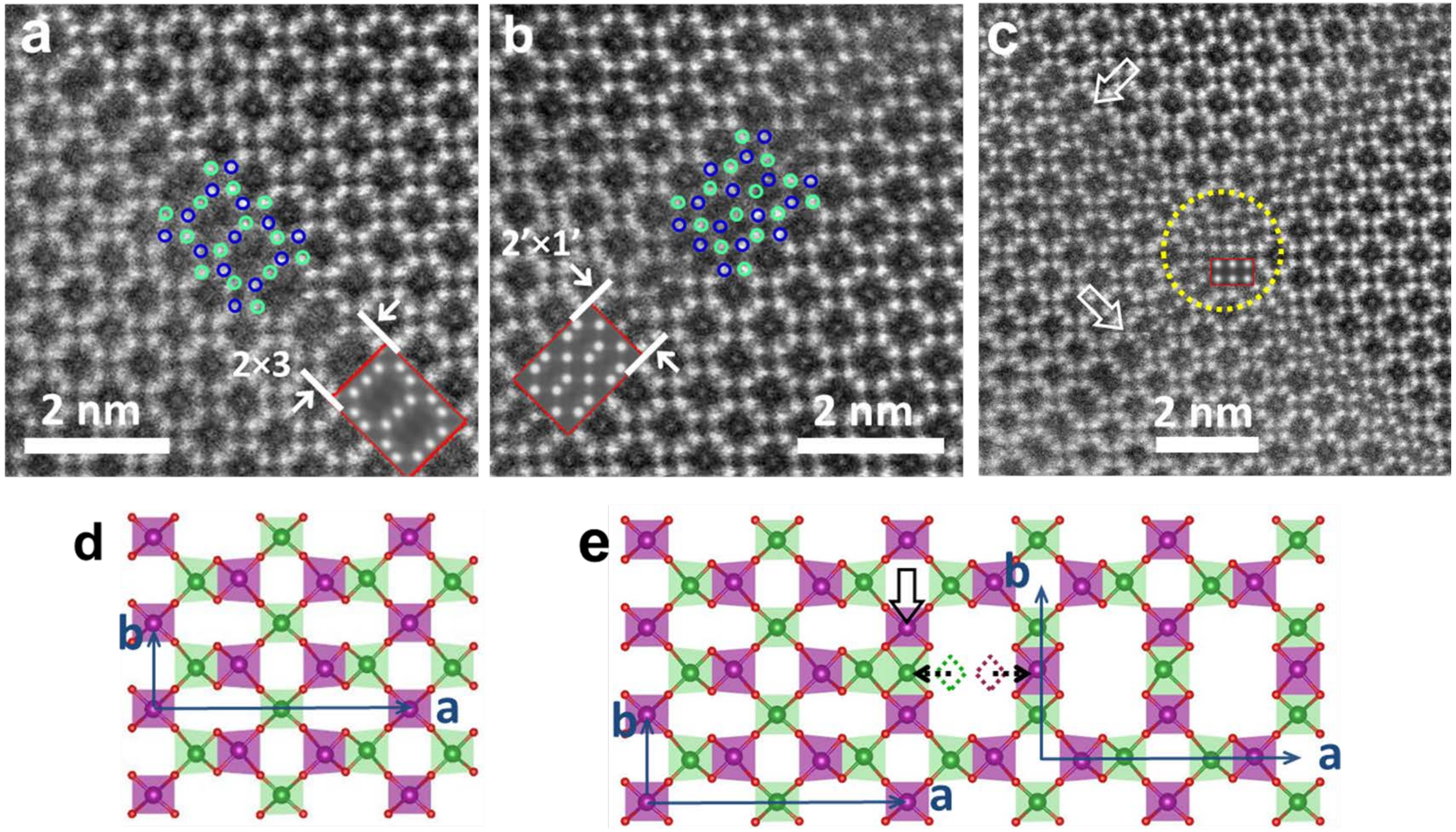
General steps:

1. Imbed the sample with resigns;
2. Cut the consolidated reigns using suitable settings;
3. Transfer the sections to TEM grid;

Unpublished work

Cross-sectional features of MnO_2 nanorod





2′ × 1′ tunnel

2′ × 1′ + 2′ × 1′ → 2 × 3 tunnel

Atomic scale nanostructual features within hollandite MnO_2 revealed along the cross section.

Unpublished work

FIB Method

Advantages

- ✓ Very precise;

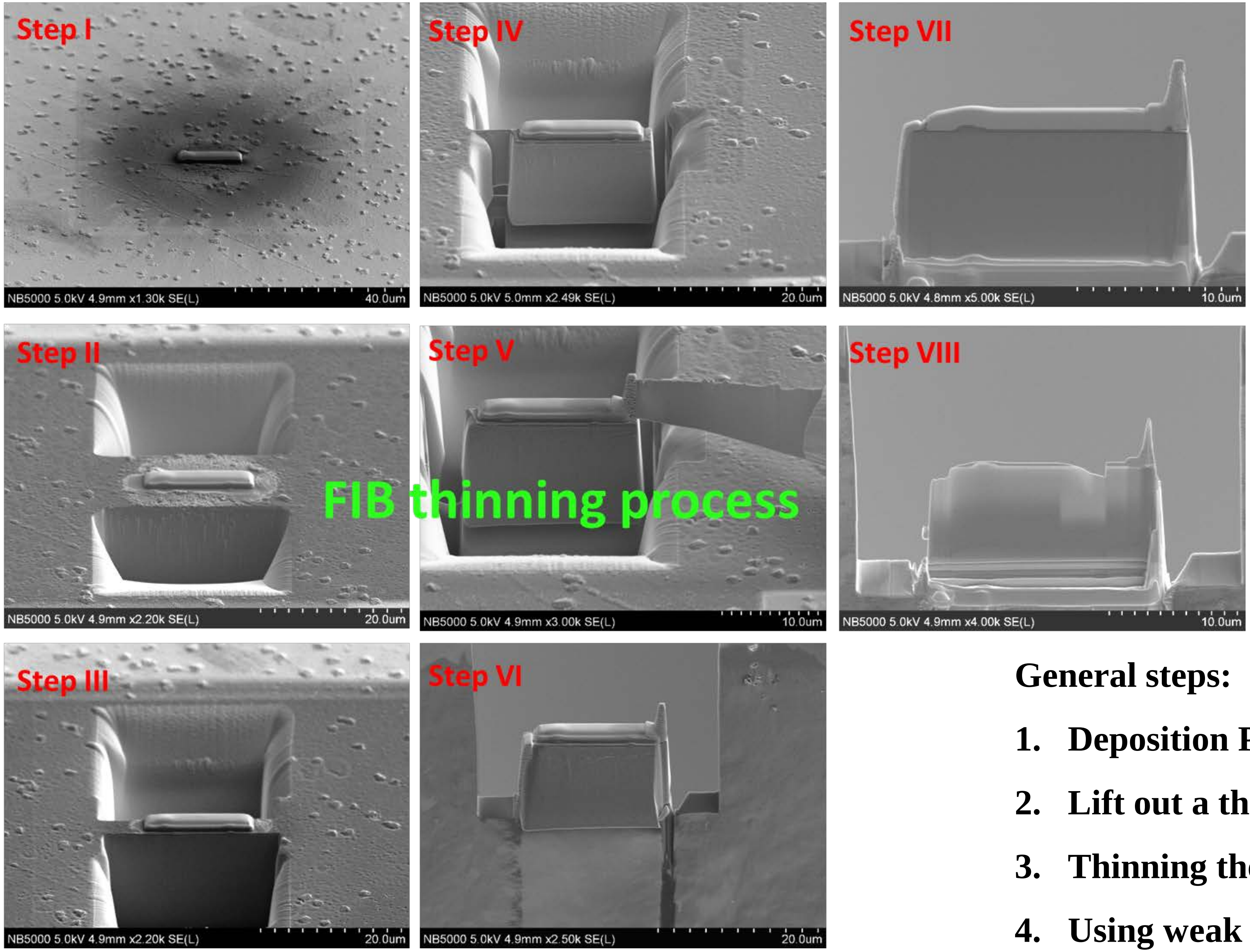
Disadvantages

- ✓ Ion beam damage may happen;
- ✓ Easily contaminated within the TEM columns;
- ✓ Not economical;

Some representative applications:

- ❑ Cross-section of thin films particularly the water/air sensitive films;
- ❑ Super hard materials and films (e.g. diamond, BN, SiC, Al_2O_3…)
- ❑ Very precious/small/irregular bulk samples
- ❑ Microsphere powder samples
- ❑ Precise locations pickup
- ❑ ……

- Five gas injection systems for etching/deposition
- Dual beam
- Bruker EDS
- Raith ELPHY ion beam lithography (IBL) capabilities
- Lift out tools for TEM and Atom Probe samples



Substrate: Solid electrolyte $La_{(1-x)/3}Li_xNbO_3$ (LLNbO)

Li content x=0.05, $(111)_p$

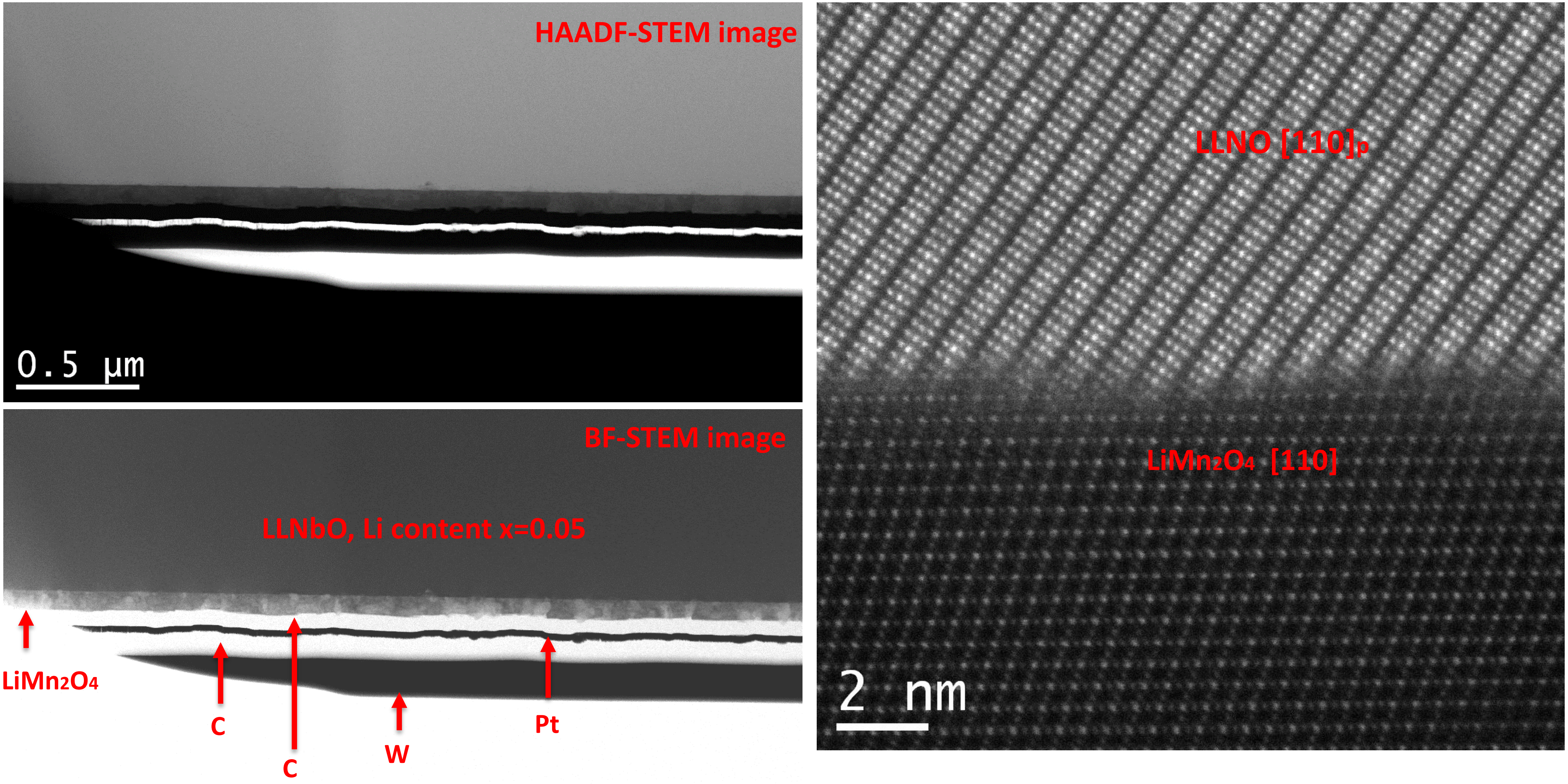
Thin film: Cathode material $LiMn_2O_4$; thickness 100nm

Used facility: HITACHI NB5000

Reasons: This thin film contains Li. It is better to avoid water/air.

General steps:

1. **Deposition Pt/C to protect the surface;**
2. **Lift out a thin slice;**
3. **Thinning the slice;**
4. **Using weak conditions to remove the beam damage;**

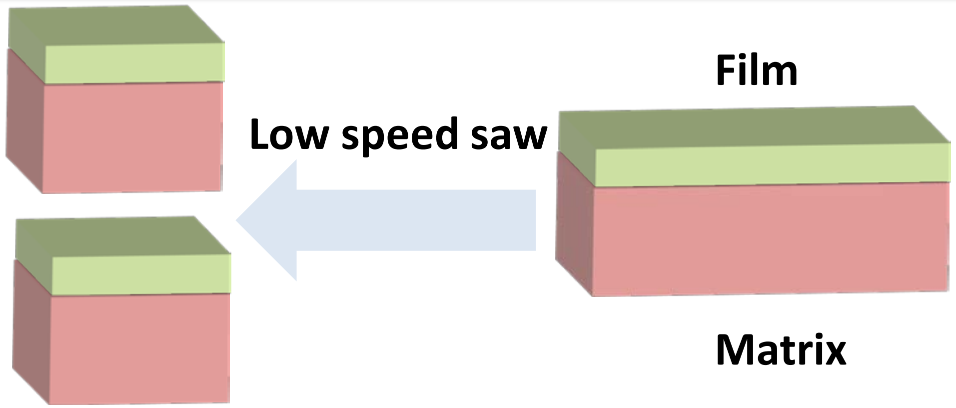


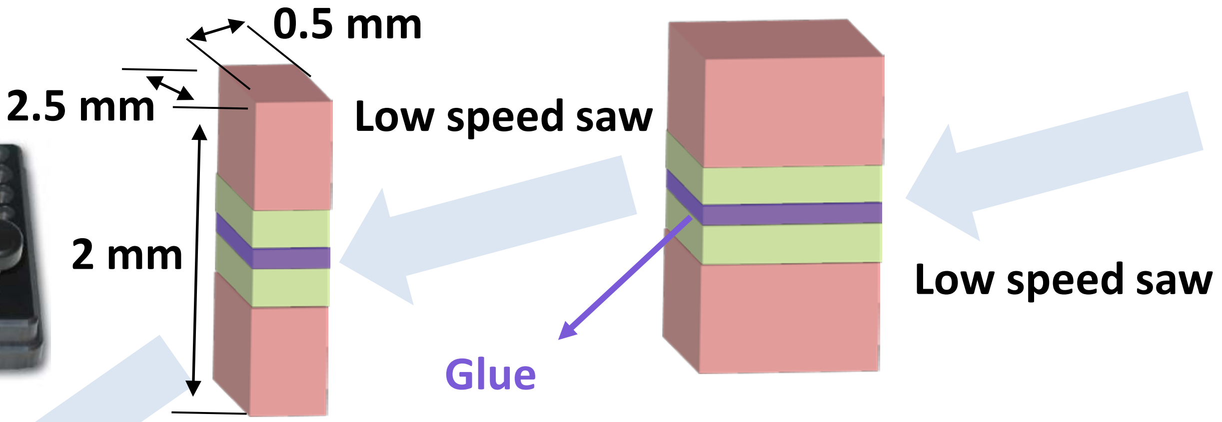
Atomic scale revealing the interfacial between solid electrolyte and cathode materials.

Unpublished work

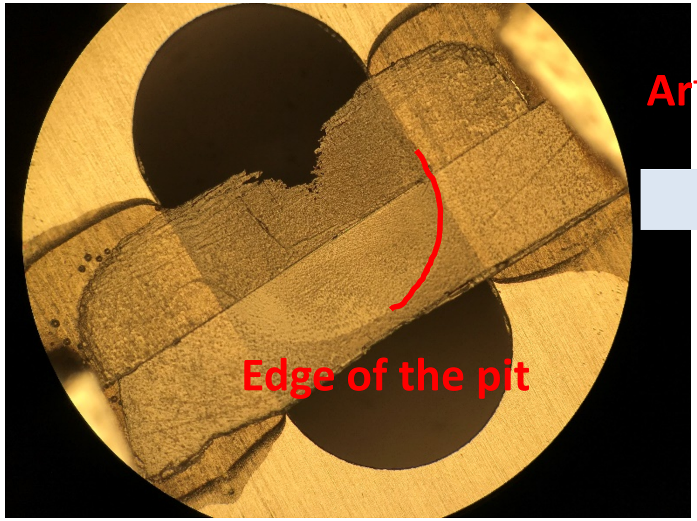
Some specific complicated cases

✓ **How to prepare the cross-section samples using PIPS?**

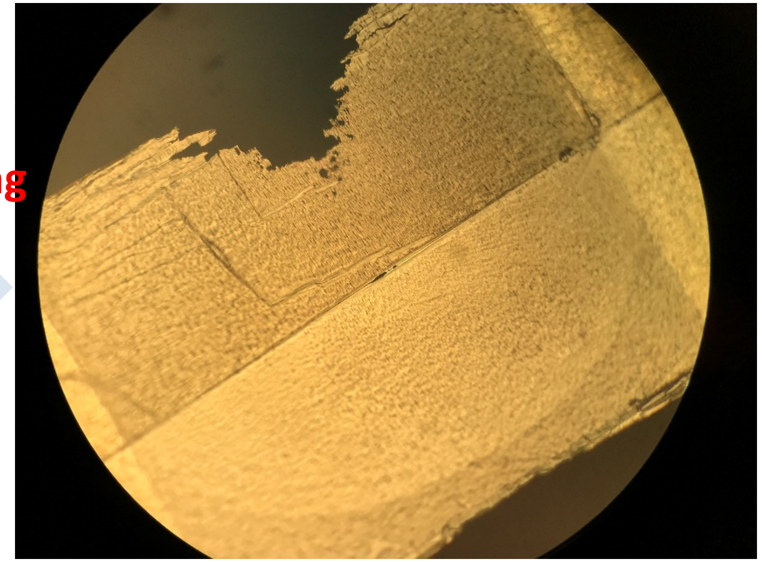


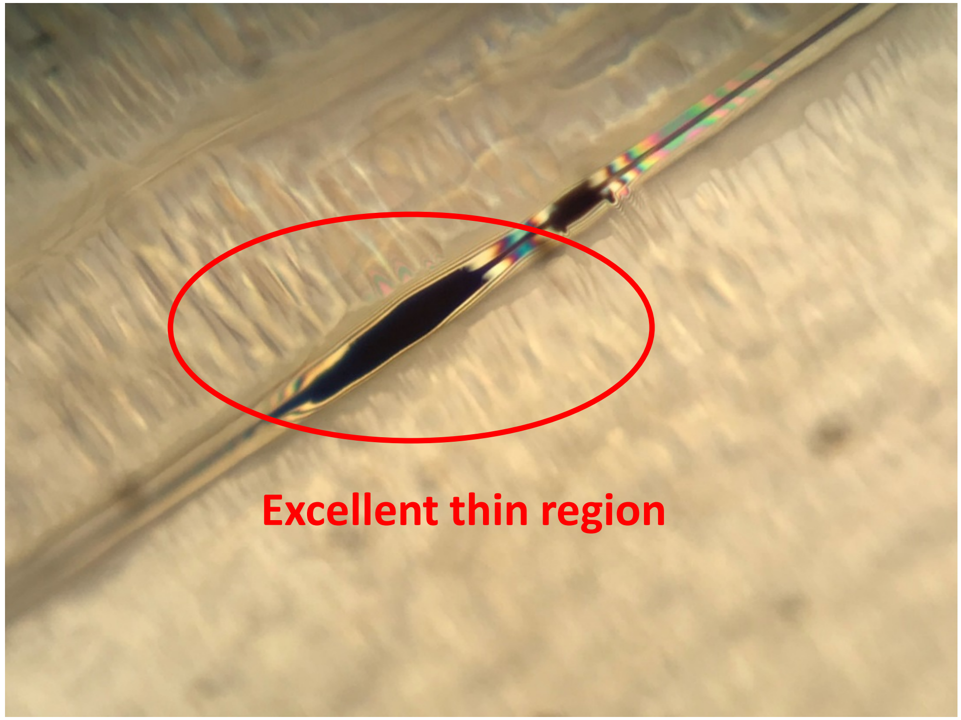


Mount slice on the Mo grid, polishing, and dimpling



Ar^+ Milling

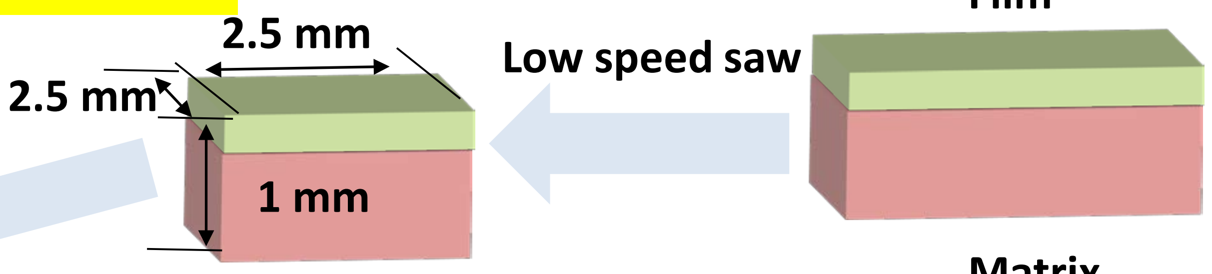




In courtesy of Dr. Yunlong Tang

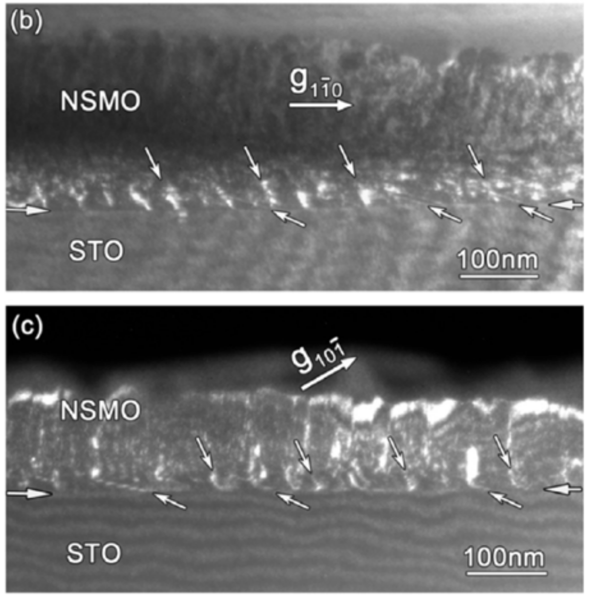
Some specific complicated cases

✓ How to prepare the plan-view samples of thin films using PIPS?



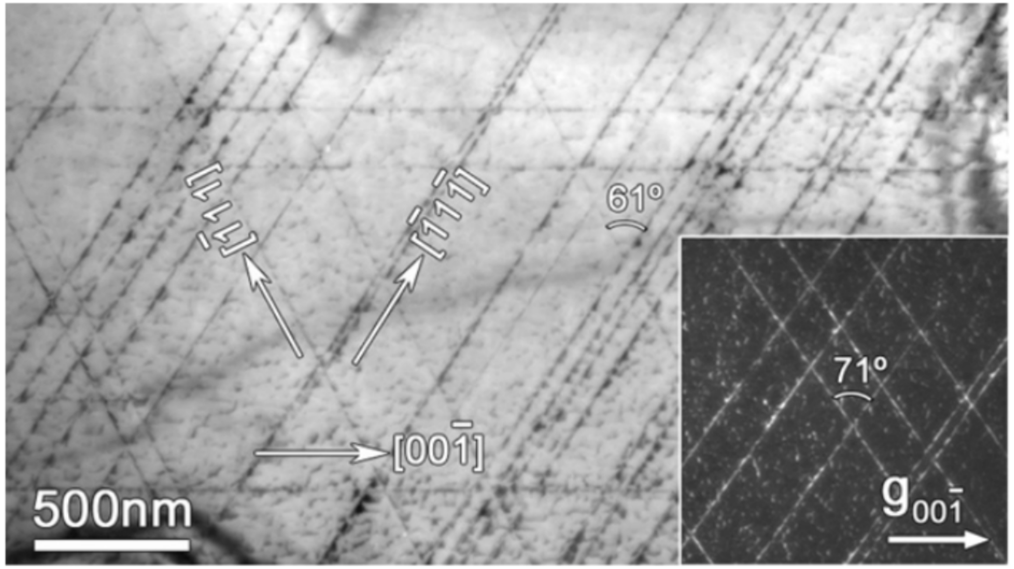
Mount slice on the Mo grid, polishing, and dimpling, ion milling*

*For ion milling, you need to make the two ion guns only mill the substrate. Also, you need to attach a filter paper to prevent the deposition.



Dislocations in cross-section

Dislocations in plan-view



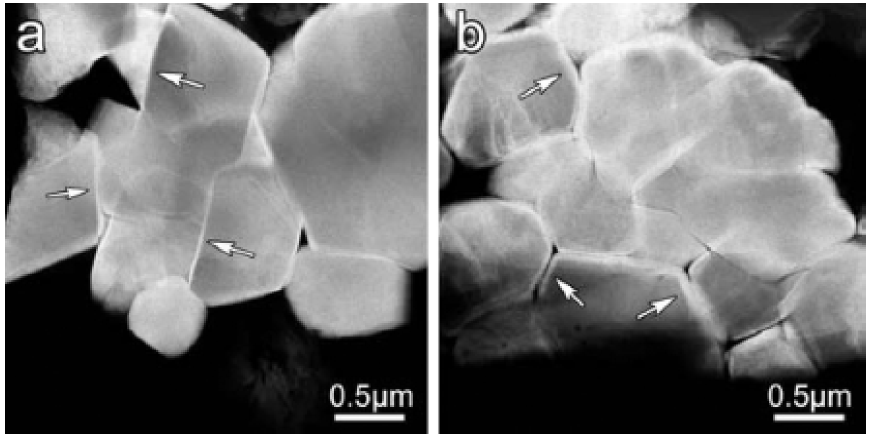
Tang, et al, *Acta Materialia* 60 (2012): 5975-5983

✓ Preparation of electron transparent sample for micrometer spherical powders using PIPS

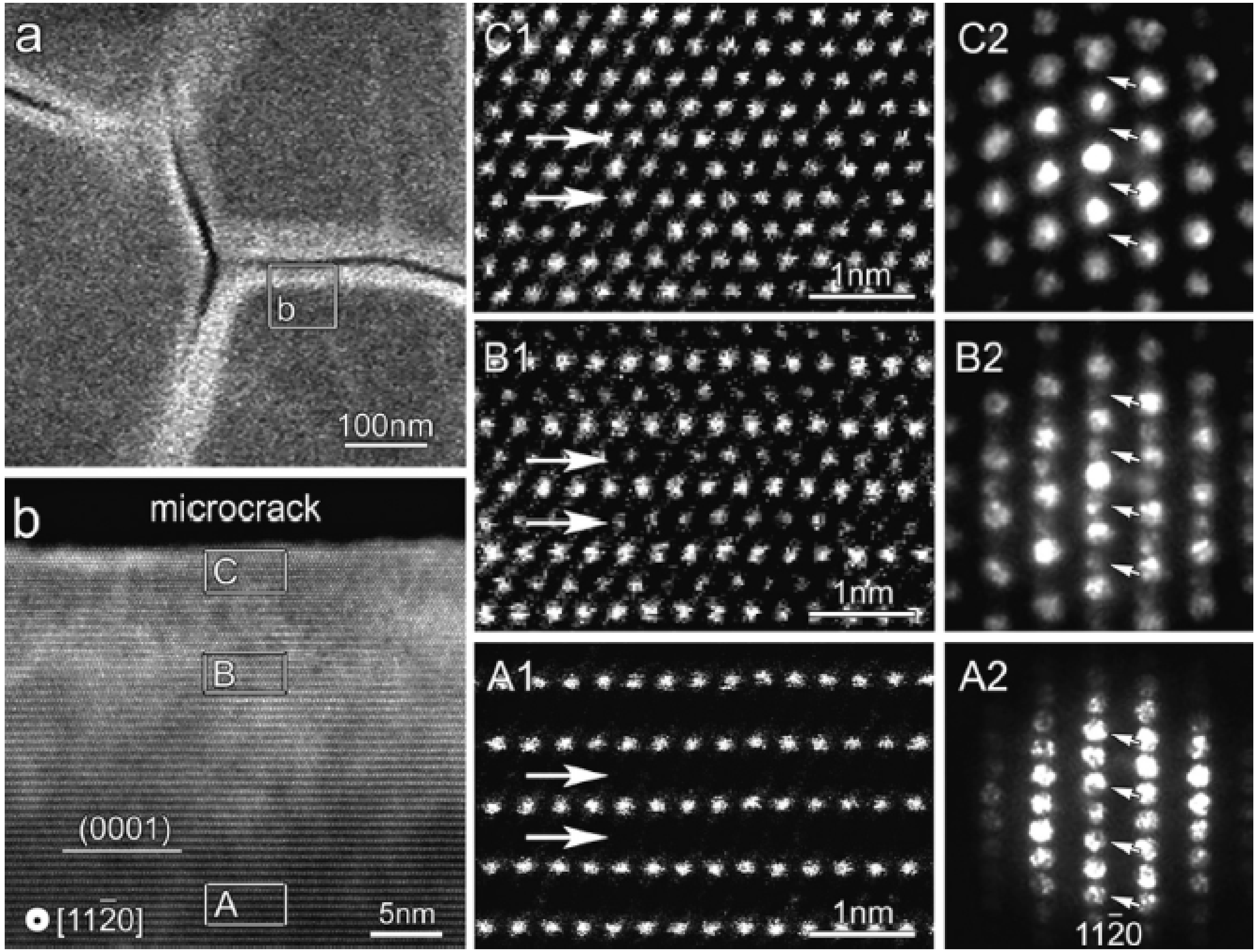
General steps:

1. Imbed the powders within resign;
2. Consolidation of the resign;
3. Cutting slices with the thickness of around 100 μm;
4. Punch into standard disk with a diameter of 3 mm;
5. Polishing, dimpling, ion milling

The boundary and interface information are kept.



Zheng, et al, *Journal of the Electrochemical Society* 158 (2011): A357-A362



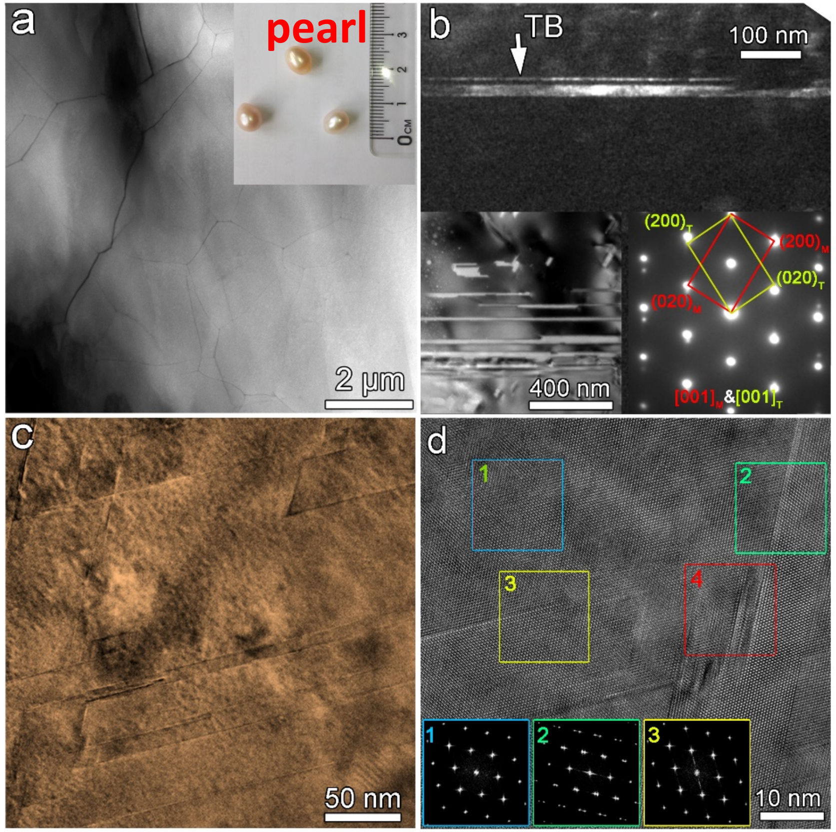
Atomic scale revealing the structural/chemical feature in the charged layer $LiCoO_2$ cathode materials.

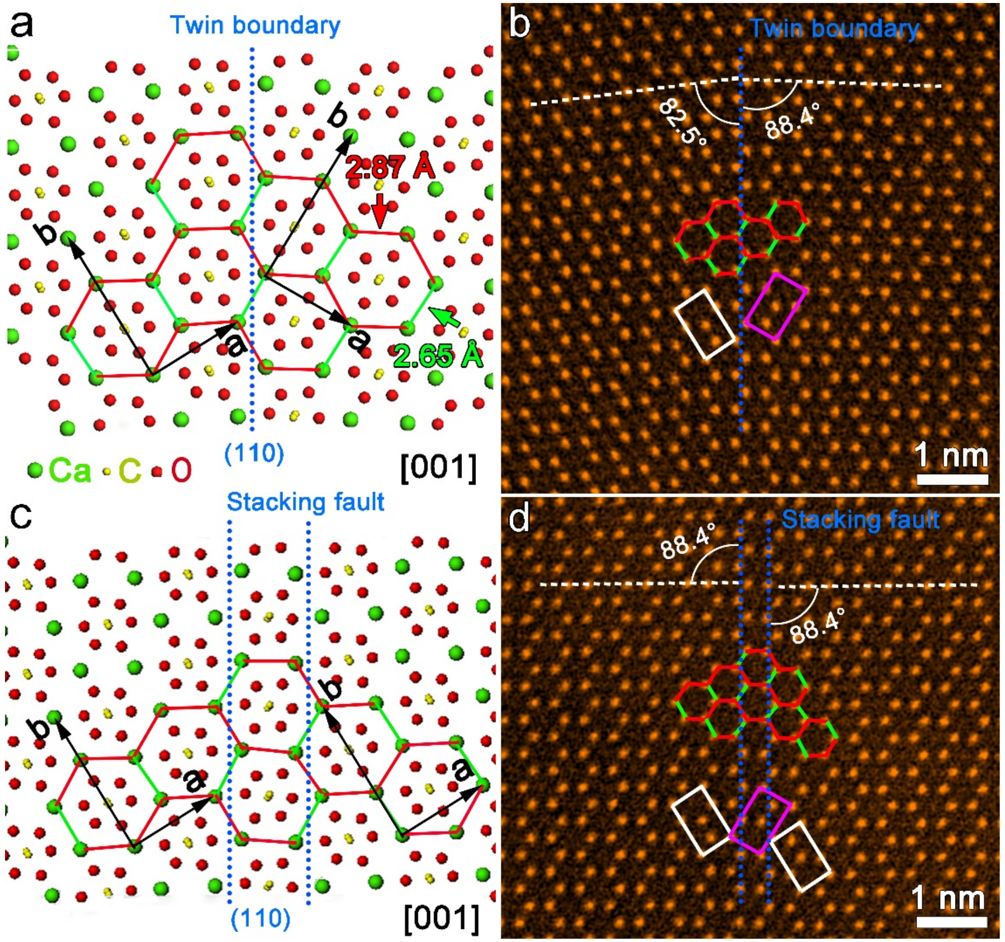
✓ How to make electron transparent samples for shells using PIPS?

General steps:

1. Crush the shells;
2. Pick up a small piece and make one flat surface;
3. Bond the flat surface with the Mo grid;
4. Gently plashing/dimpling;
5. Gentle ion milling;

CaCO3 (Calcite, Aragonite, Vaterite)





Atomic scale revealing the defect configurations within aragonite structure in "good" pearl.

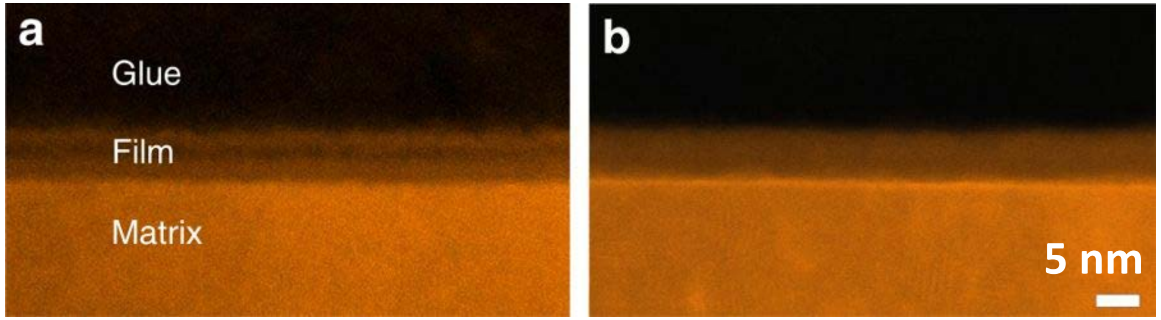
Unpublished work

✓ How to make electron transparent samples for the irregular items?

If carbon film is deposited on the Al foils, how to observe the interface between Al foil and carbon film?

Foils

How to observe the passive film on stainless steel?



Wire

Hair

Zhang, et al, *Nature Communications* 9 (2018): 2559

Acknowledgements

NUANCE
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Prof. Vinayak P. Dravid
Dr. Paul Smeets
Dr. Roberto Dos Reis

Thank you for your attention!

Q.&A.