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Revealing the Working and Degradation Mechanisms in Lithium-Ion Batteries via In-situ Transmission Electron Microscopy

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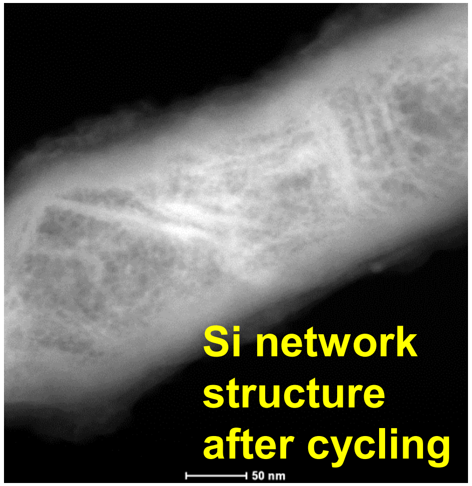
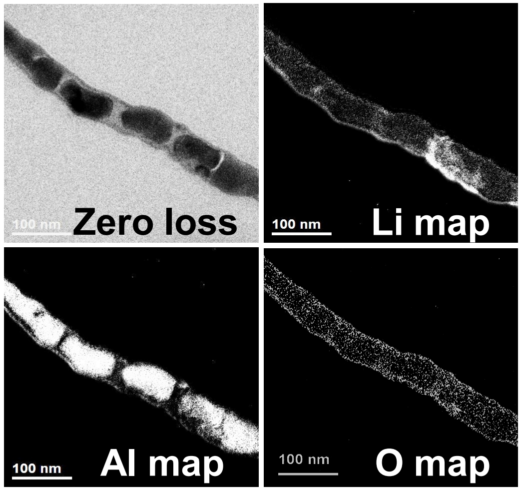
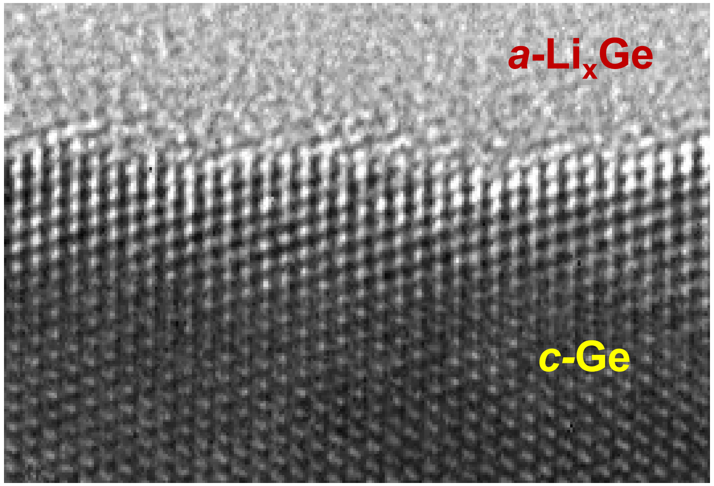


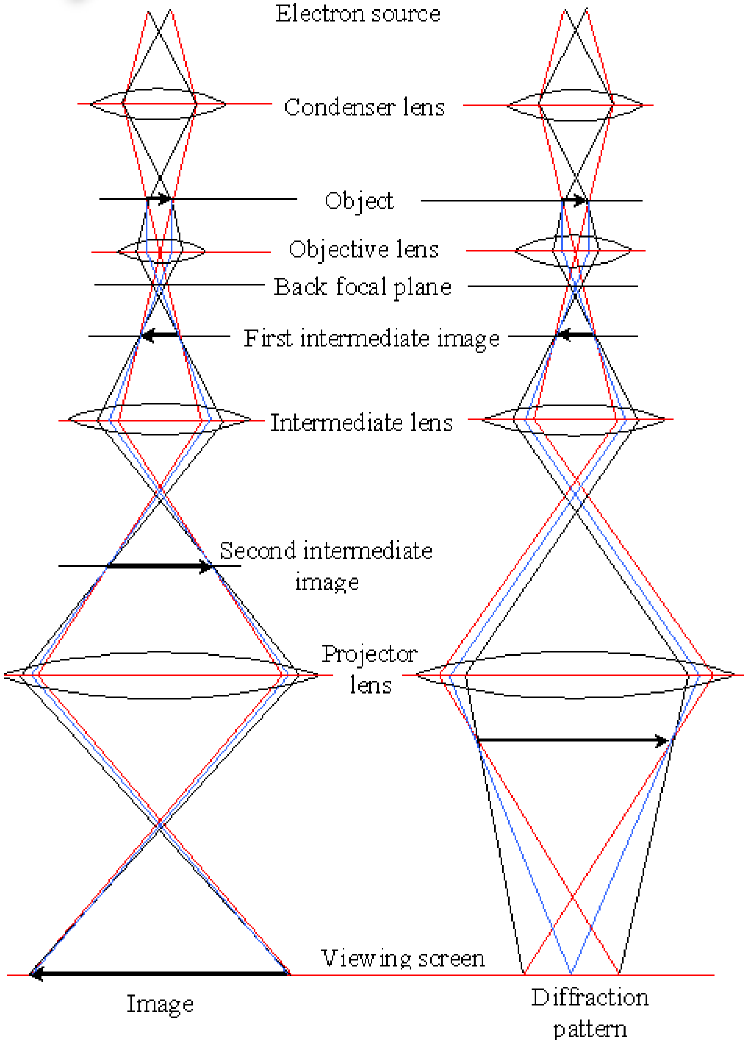




Outline

- Why Transmission Electron Microscopy (TEM)?
- Why in-situ TEM?
- Research Experience
- In-situ TEM Electrochemistry
  - ✓ Motivation
  - ✓ Methods
  - ✓ Li-ion batteries
  - ✓ Quantitative electrochemistry on individual nanostructure
  - ✓ Beyond Li-ion batteries (such as, Na-ion batteries, Li-O_2 battery)
- Conclusions and Perspective

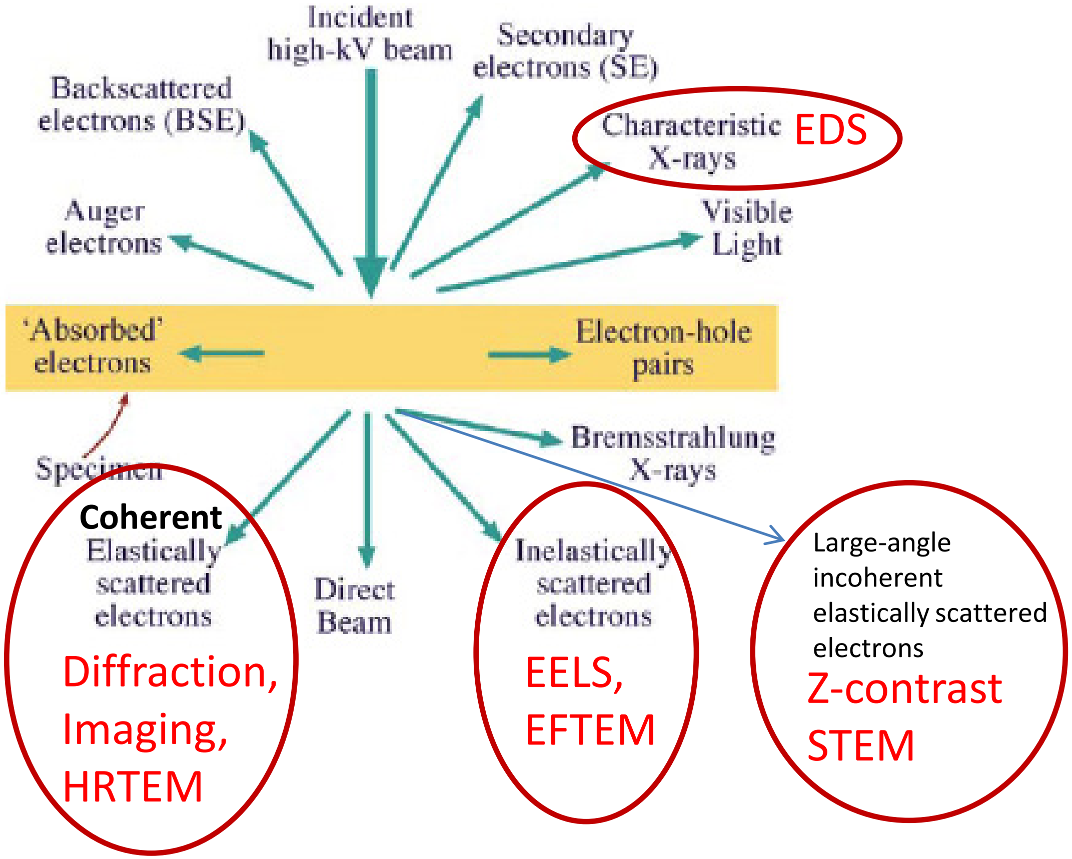
Why Transmission Electron Microscopy (TEM)?



Ray diagram

labs.mete.metu.edu.tr/tem/TEMtext/TEMtext.html

Electron-specimen interaction



EDS

Coherent

Diffraction,
Imaging,
HRTEM

EELS,
EFTEM

Large-angle incoherent elastically scattered electrons

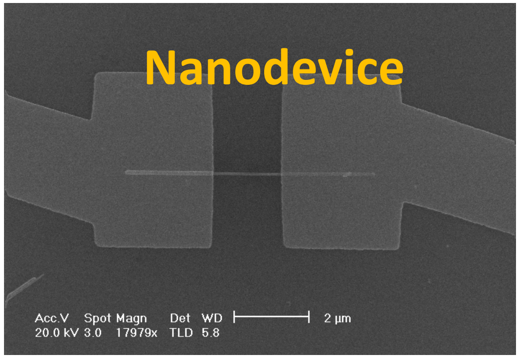
Z-contrast
STEM

Williams & Carter, TEM textbook, Springer (2009)

TEM techniques

- **Imaging** [diffraction contrast, phase contrast (High resolution TEM, HRTEM), Z-contrast (Scanning TEM, STEM), energy-filtered (EFTEM),…]
- **Diffraction** (select-area, convergent beam, nano-area,…)
- **Spectrometry** [EDS, Electron energy loss spectroscopy (EELS)]
- **Cryo-EM**
- **3D tomography**
- **Simulations**
- **…**

Why in-situ TEM?

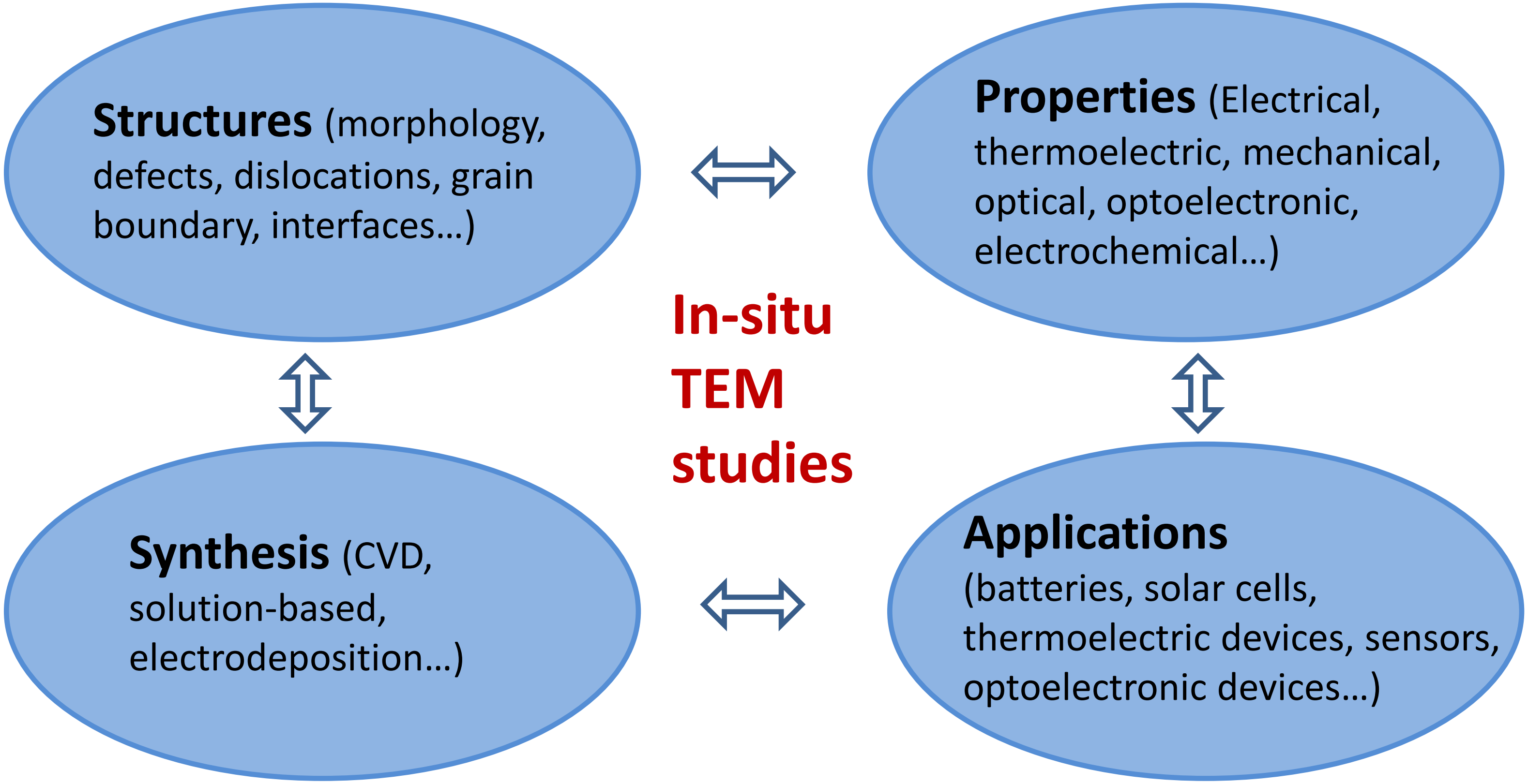


Using the advanced TEM techniques:
TEM/STEM, HRTEM, EDS, EELS, EFTEM, Diffraction…
We can get these information:
Structure, phase, defects, crystal orientation, chemical composition and distribution, chemical state information…

Using the advanced device fabrication and characterization,
We can get these information:
Electrical properties, thermal transport properties, mechanical and optical properties, and the electrochemical performance…

However, there exists a gap between the structures and physical properties studies of nano- or micro-structured materials, i.e. studying the structures without knowing the properties, and *vice versa*.

Why in-situ TEM?



Structures (morphology, defects, dislocations, grain boundary, interfaces…)

Properties (Electrical, thermoelectric, mechanical, optical, optoelectronic, electrochemical…)

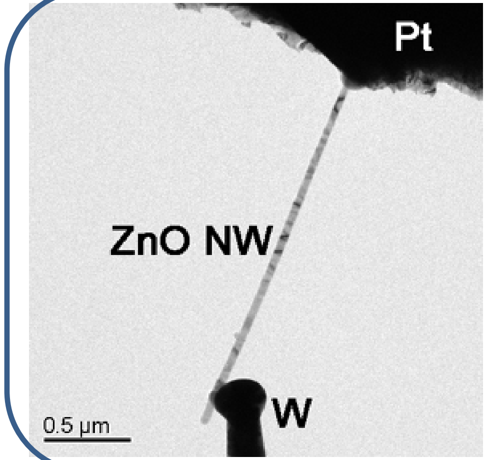
In-situ TEM studies

Synthesis (CVD, solution-based, electrodeposition…)

Applications (batteries, solar cells, thermoelectric devices, sensors, optoelectronic devices…)

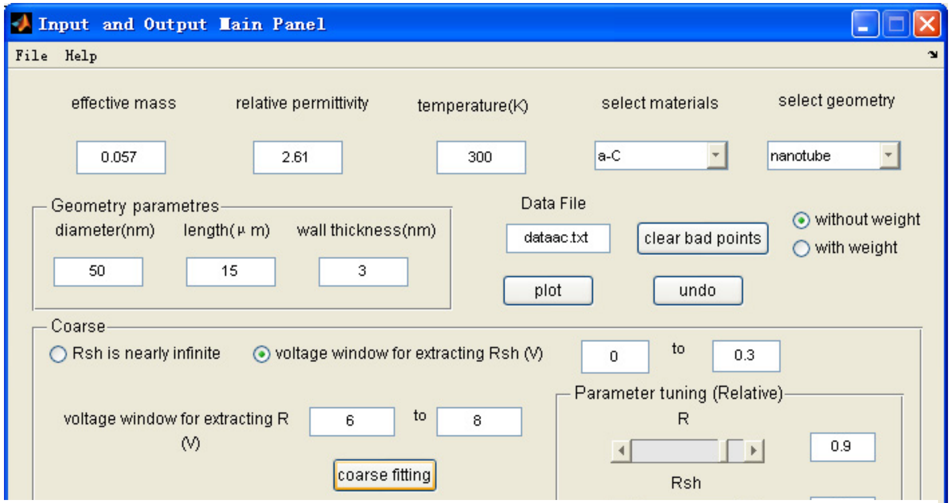
We can deeply understand their relationships by conducting simultaneous structures characterizations and properties measurements, through developing advanced in-situ TEM techniques. It can provide detailed directions/insights on how to synthesize materials and design novel architectures to realize powerful applications.

Research Experience



In-situ measurement of the electrical and thermal transport properties of individual nanostructures

Metal-Semiconductor-Metal (MSM) model



effective mass: 0.057
relative permittivity: 2.61
temperature(K): 300
select materials: a-C
select geometry: nanotube

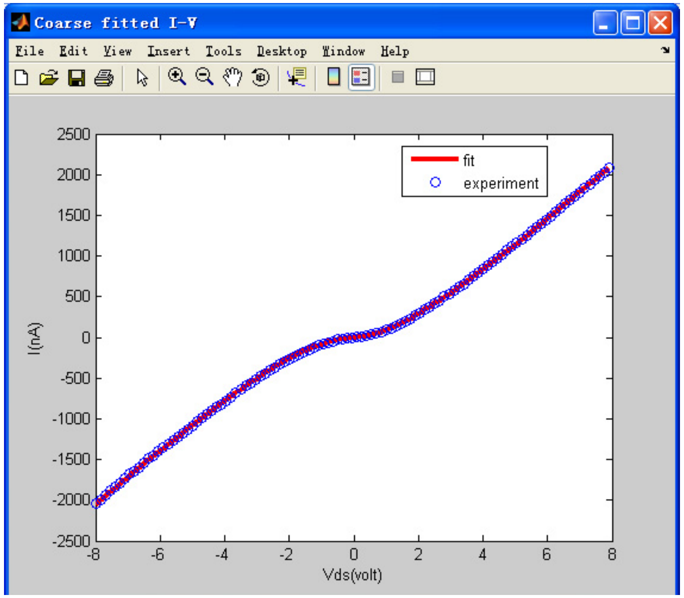
Geometry parametres
diameter(nm): 50
length(µ m): 15
wall thickness(nm): 3

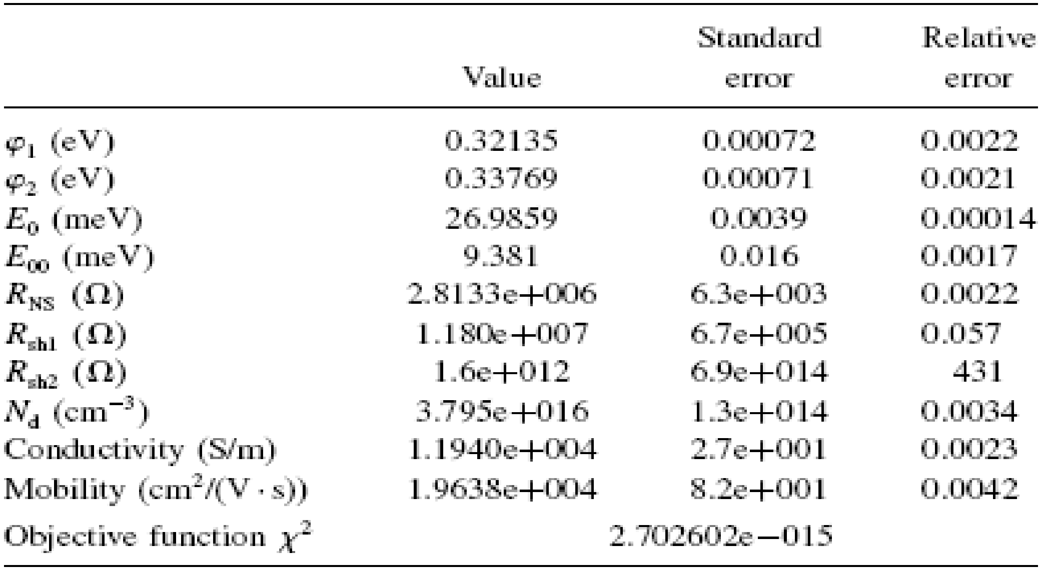
Data File: dataac.txt

● without weight
○ with weight

Coarse
○ Rsh is nearly infinite
● voltage window for extracting Rsh (V): 0 to 0.3
voltage window for extracting R (V): 6 to 8

Parameter tuning (Relative)
R: 0.9
Rsh



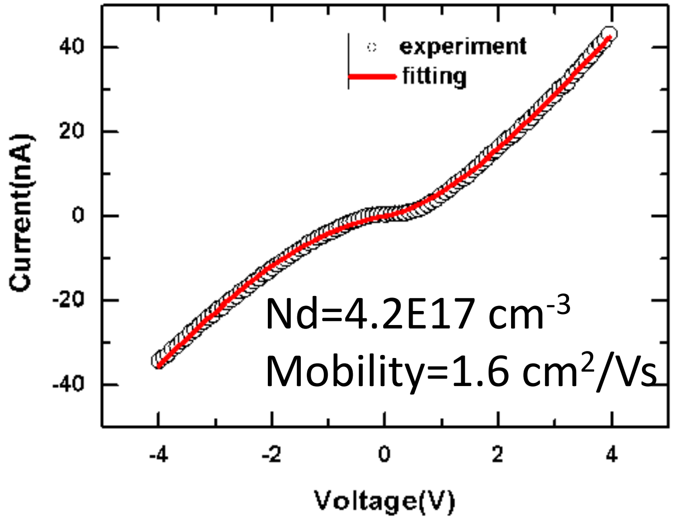


	Value	Standard error	Relative error
φ_1 (eV)	0.32135	0.00072	0.0022
φ_2 (eV)	0.33769	0.00071	0.0021
E_0 (meV)	26.9859	0.0039	0.00014
E_{00} (meV)	9.381	0.016	0.0017
R_{NS} (Ω)	2.8133e+006	6.3e+003	0.0022
R_{sh1} (Ω)	1.180e+007	6.7e+005	0.057
R_{sh2} (Ω)	1.6e+012	6.9e+014	431
N_d (cm^{-3})	3.795e+016	1.3e+014	0.0034
Conductivity (S/m)	1.1940e+004	2.7e+001	0.0023
Mobility ($cm^2/(V \cdot s)$)	1.9638e+004	8.2e+001	0.0042
Objective function χ^2	2.702602e−015		

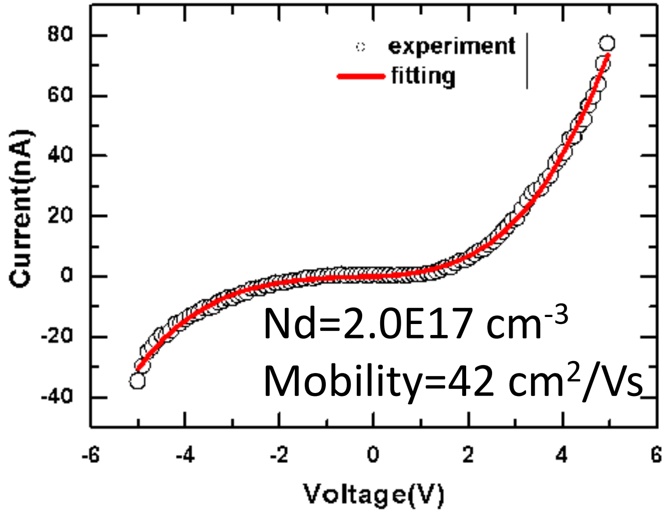
Z.Y. Zhang, **Y. Liu** et al., ***Adv. Func. Mater***. 17, 2478 (2007)
Y. Liu et al, ***J. Nanosci. Nanotechno***. 8, 252 (2008)

Research Experience

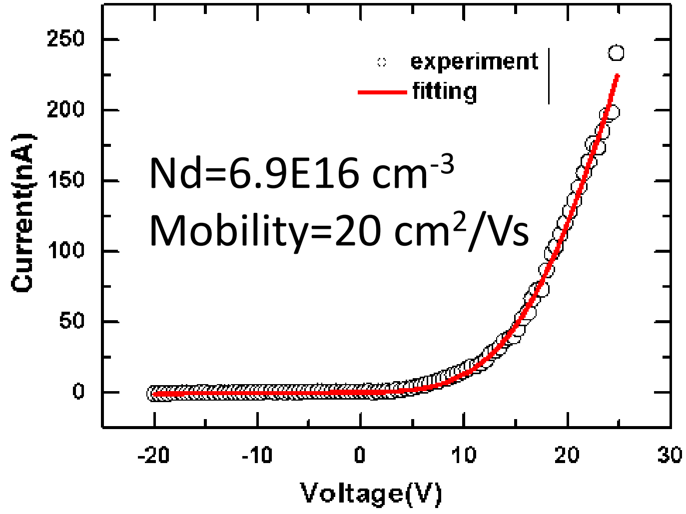
Applications



Nd=4.2E17 cm^{-3}
Mobility=1.6 cm^2/Vs



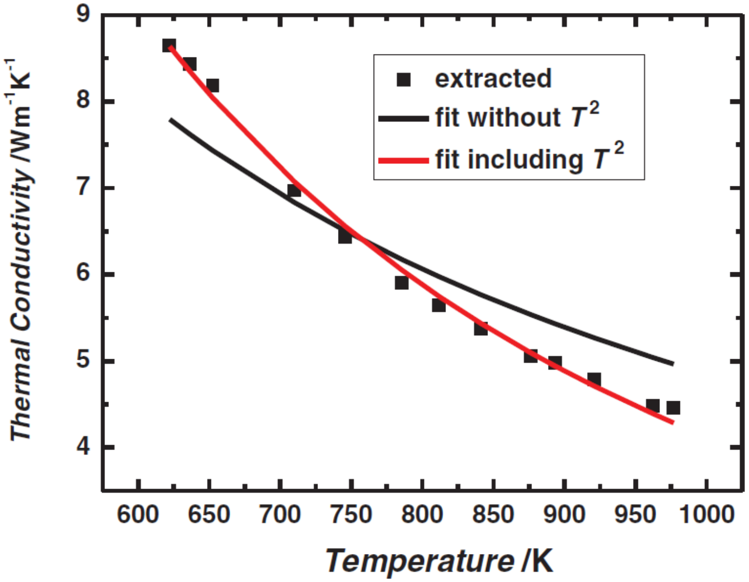
Nd=2.0E17 cm^{-3}
Mobility=42 cm^2/Vs

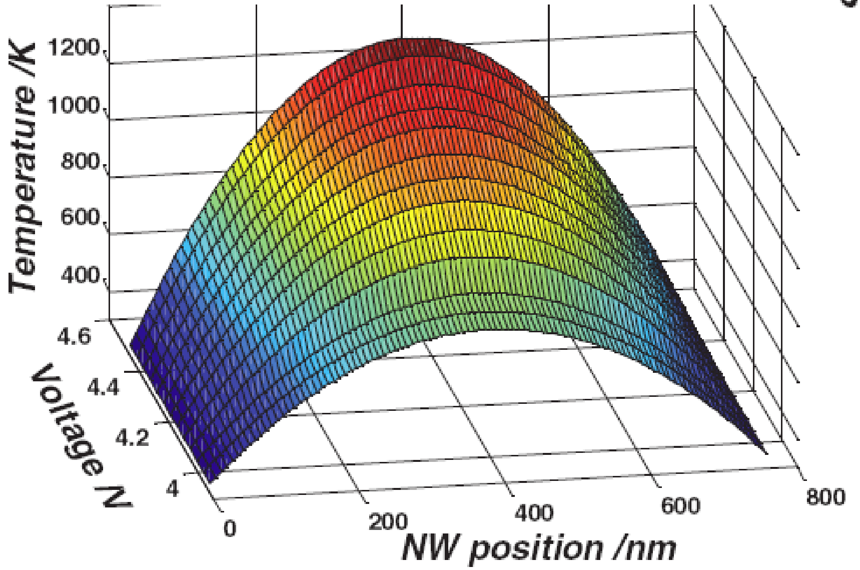


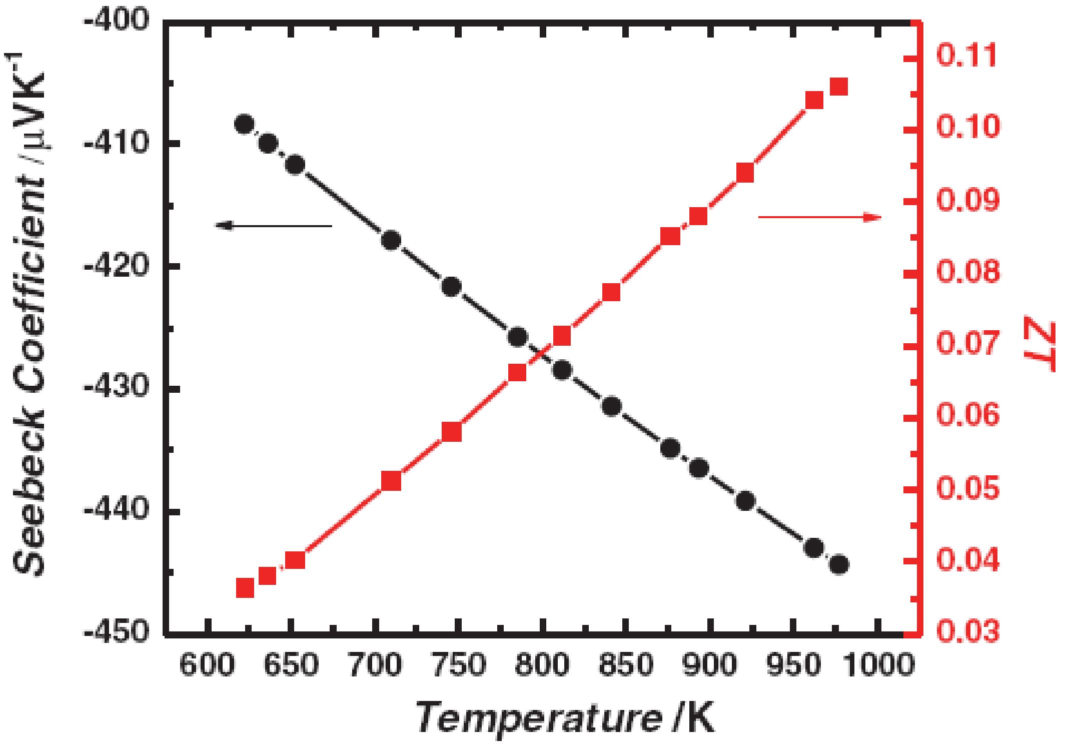
Nd=6.9E16 cm^{-3}
Mobility=20 cm^2/Vs

This model and software provides us a tool for quantitatively analyzing electrical transport properties of semiconducting nanomaterials from two terminal measurements.

Research Experience

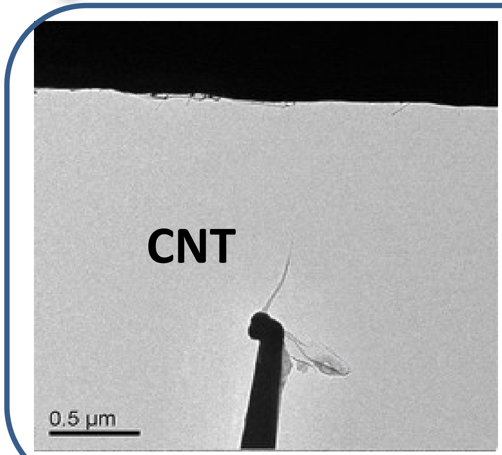




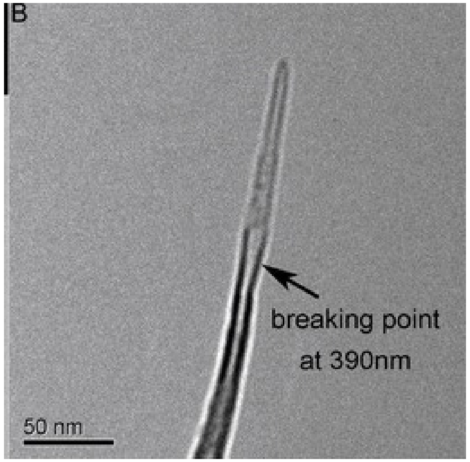


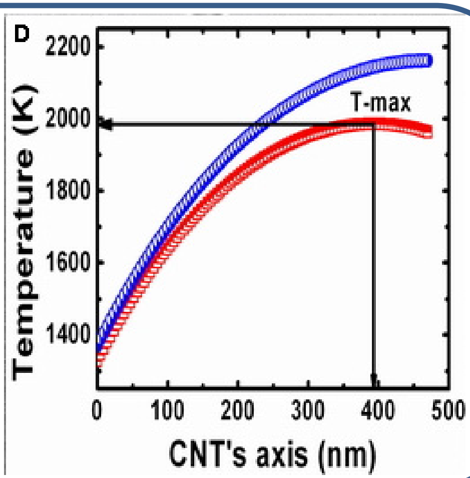
<u>**Y. Liu**</u> et al., ***Adv. Func. Mater***. 21, 3900 (2011)

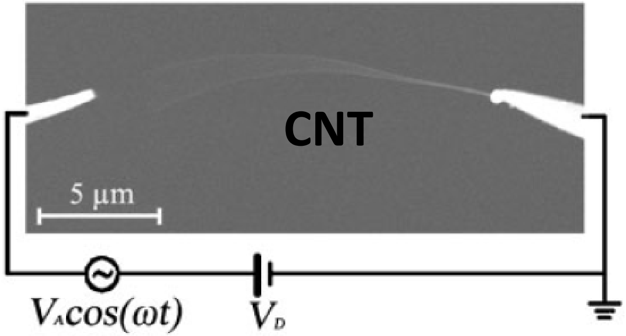
Research Experience



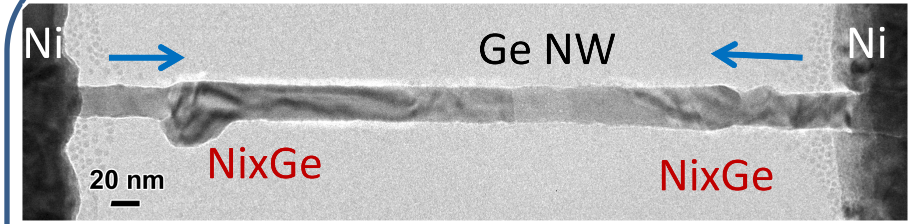
In-situ study of field emission mechanism of carbon nanotubes





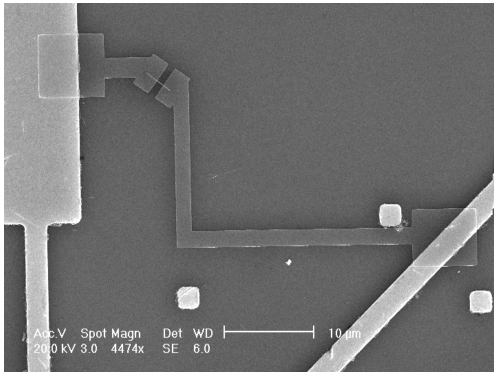


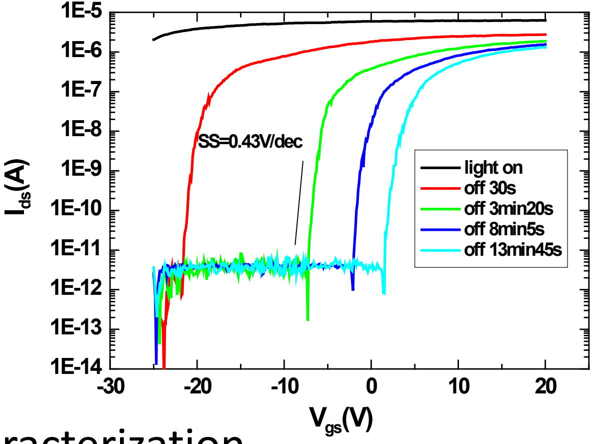
In-situ study of mechanical properties of carbon nanotubes



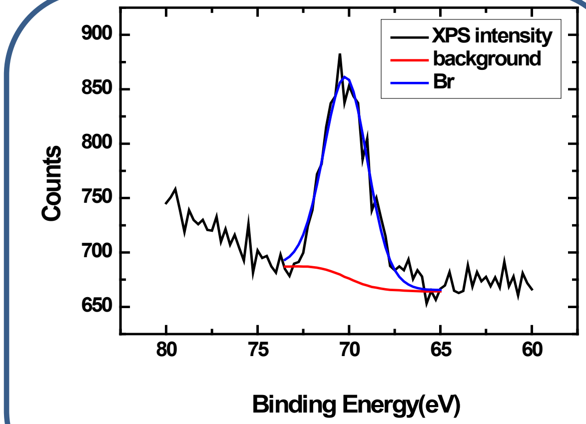
In-situ heating experiments on nickel reaction with Ge nanowires.

Research Experience

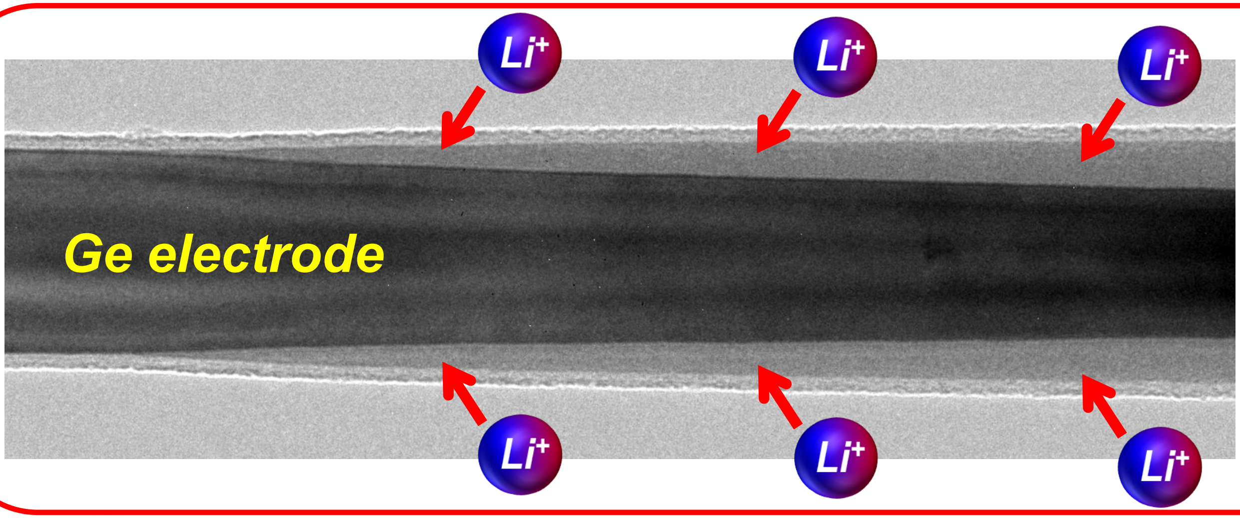




Device fabrication and characterization

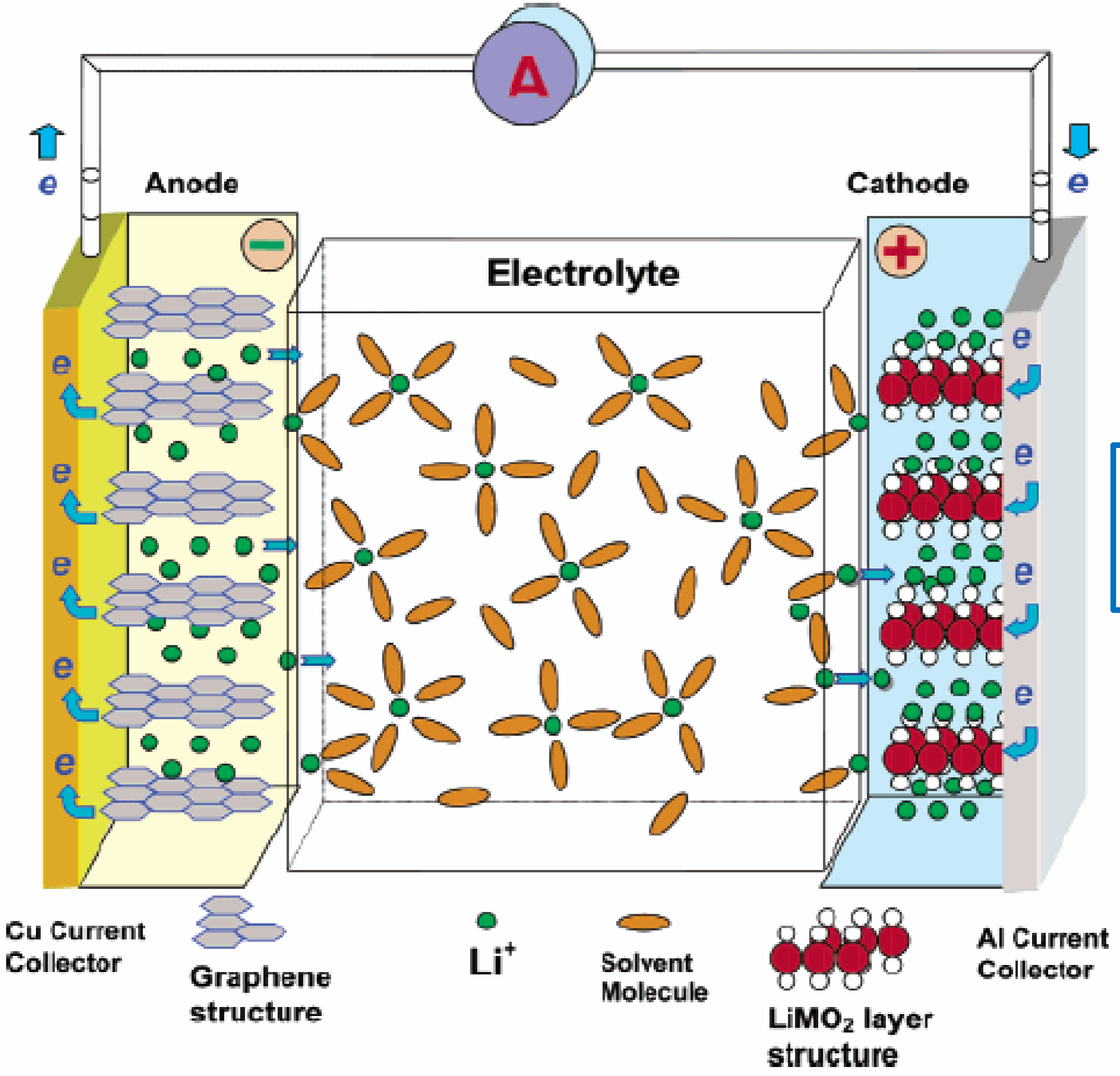


Surface functionalization



In-situ TEM **electrochemistry study** on the working and degradation mechanisms in batteries

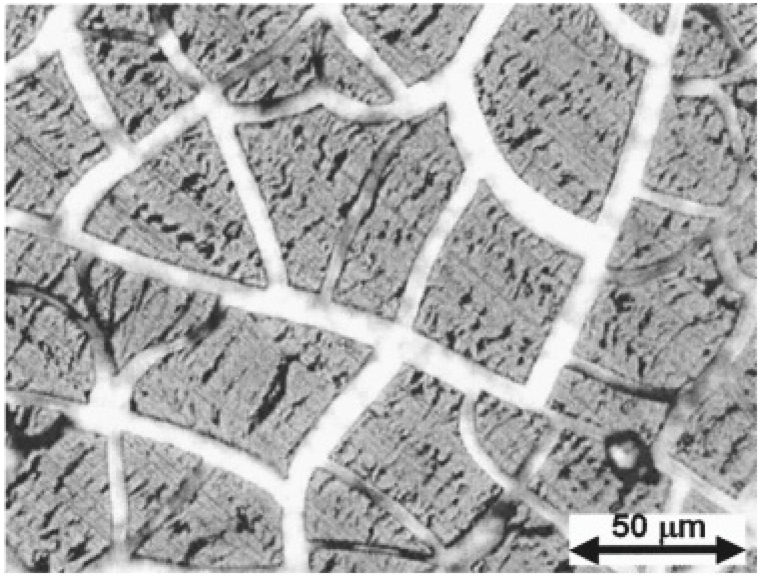
Motivation



- ✓High energy and power density
- ✓Good cyclability
- ✓Low cost

Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 2-4, 2007

Motivation



Optical micrograph of a Li-alloy film after expansion and contraction

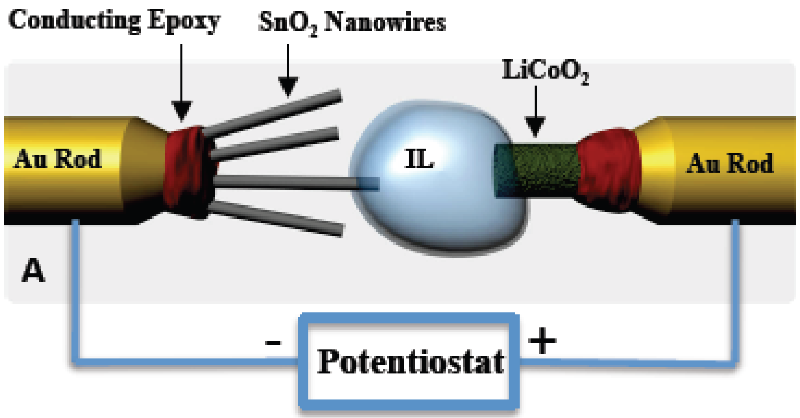
A dry lake bed

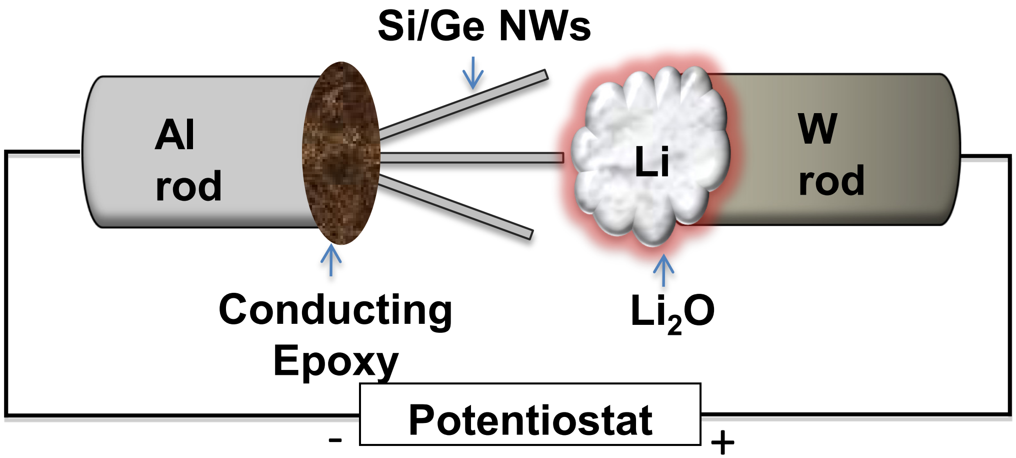
Dahn et al., ***Electrochem. Solid-State Lett.*** 4, A137 (2001)

- A fundamental understanding of the microstructural change of the electrodes and solid electrolyte interphase (SEI) layer during battery operation.
- Li-ion batteries (LIB) generally use liquid electrolyte, which is not compatible with the high vacuum of a TEM.
- How to create a working nano-LIB inside a TEM?
- Understanding the fundamental nano-electrochemistry.

Methods

Experimental setup of *in situ* TEM battery test





J.Y. Huang *et al.*, ***Science*** 330, 1515 (2010)

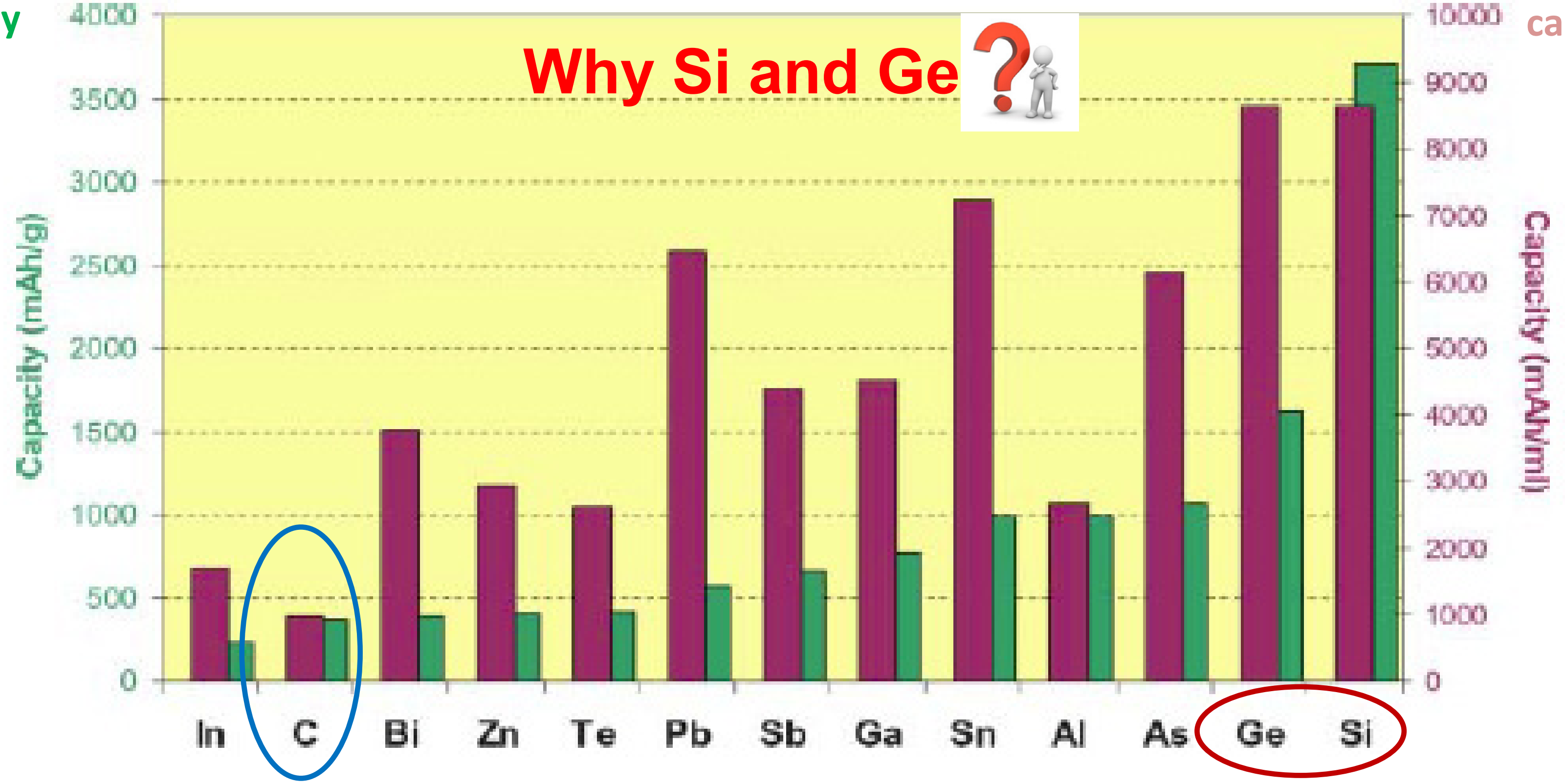
X.H. Liu and **Y. Liu** *et al.*, ***Adv. Energy Mater.*** 2, 722 (2012)

Introduce a vacuum-compatible electrolyte.

Using the naturally oxidized Li_2O layer on Li metal as the solid electrolyte.
The Li_2O here can be replaced by other kinds of solid electrolytes, such as LiPON and LiAlSiOx.

Building a nano-battery in a TEM, allowing for real time and atomic scale observations of battery charging and discharging processes.

1. Different lithiation behavior in c-Si and c-Ge



Gravimetric capacity

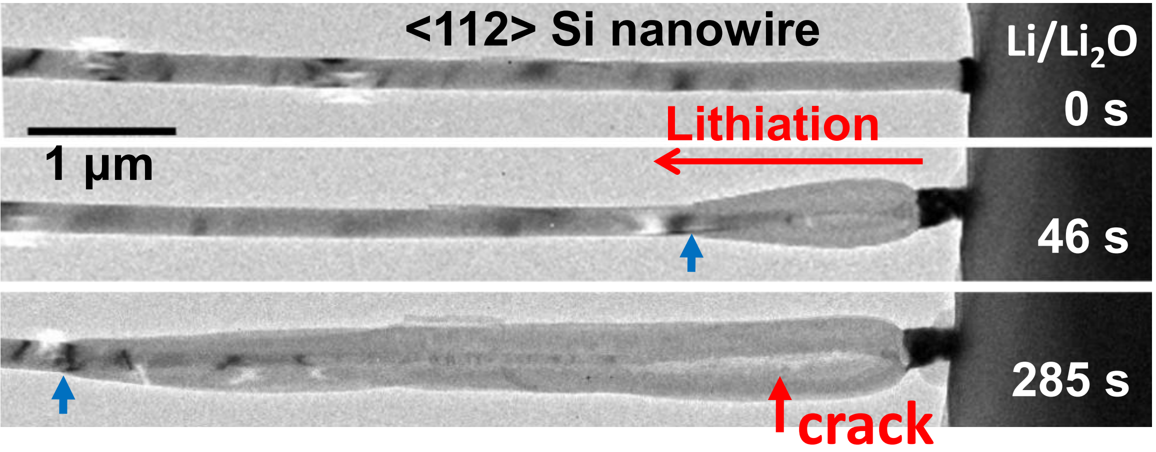
Volumetric capacity

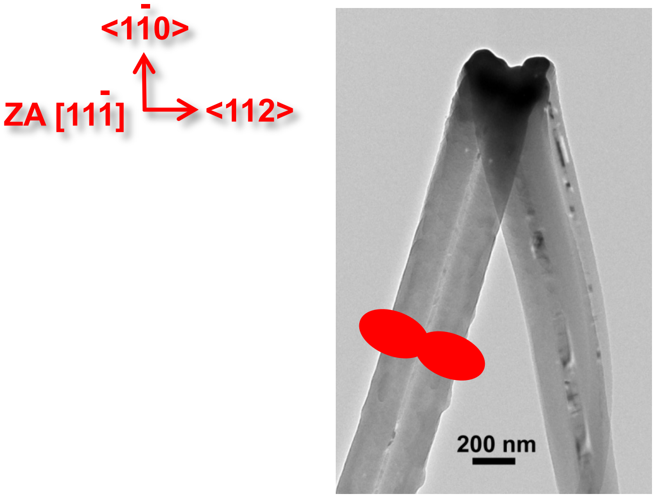
Why Si and Ge?

Si possesses the largest theoretical gravimetric capacity in the anode materials.
Ge also has large capacity (both gravimetric and volumetric), second only to silicon.
In addition, Ge has high intrinsic electronic conductivity and lithium ion diffusivity.

D. Larcher et al., ***J. Mater. Chem.***, 2007, 17, 3759–3772

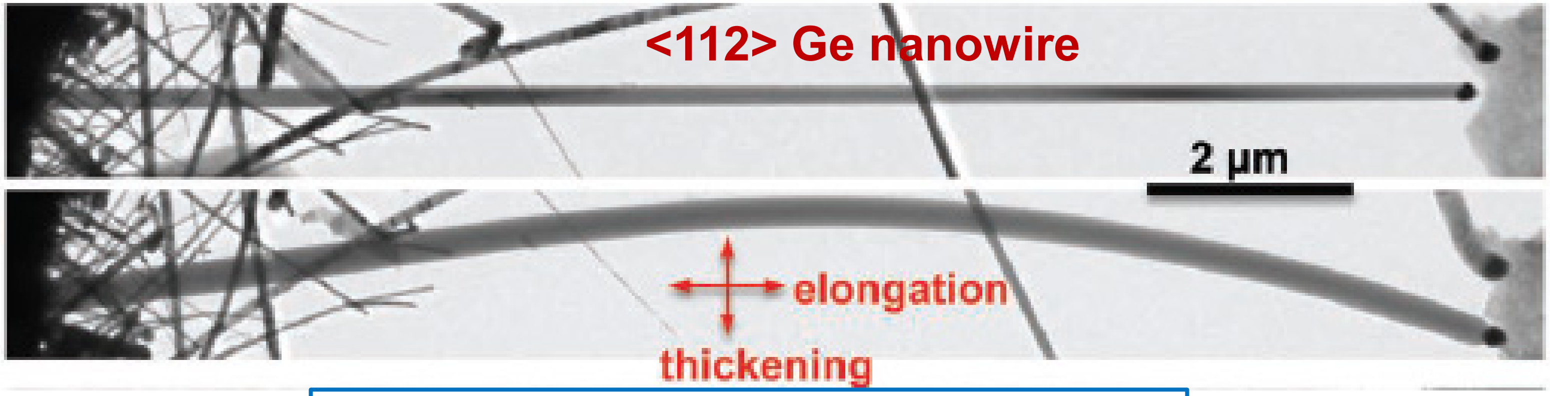
Anisotropic expansion in c-Si *versus* isotropic expansion in c-Ge





Highly anisotropic volume expansion in c-Si

X. H. Liu, …, **Y. Liu**, et al. ***Nano Letters,*** 11, 3312, (2011)



Almost isotropic volume expansion in c-Ge

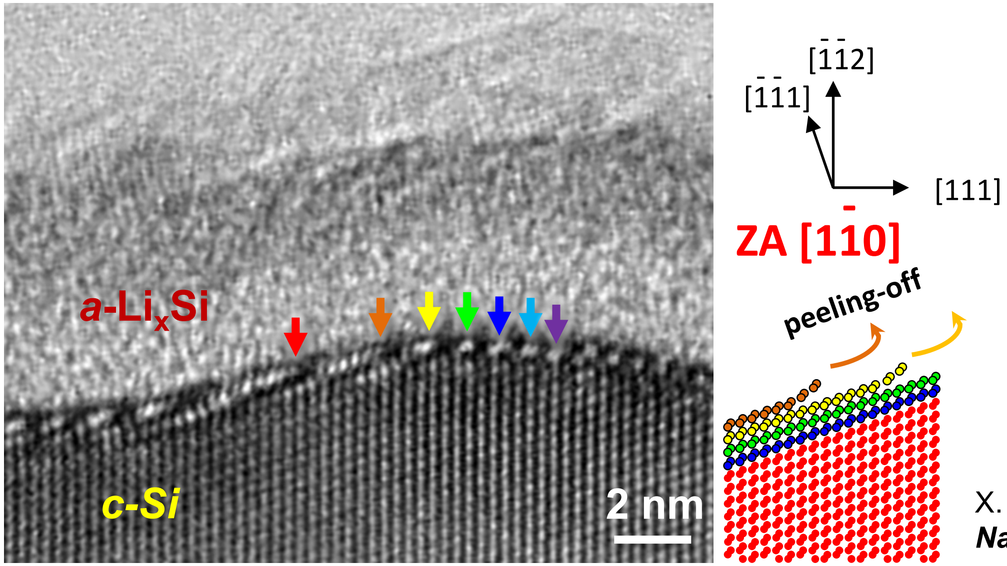
X.H. Liu and **Y. Liu** *et al*., ***Adv. Energy Mater.*** 2, 722 (2012)

Atomic scale imaging of lithiation process in Si and Ge nanowires

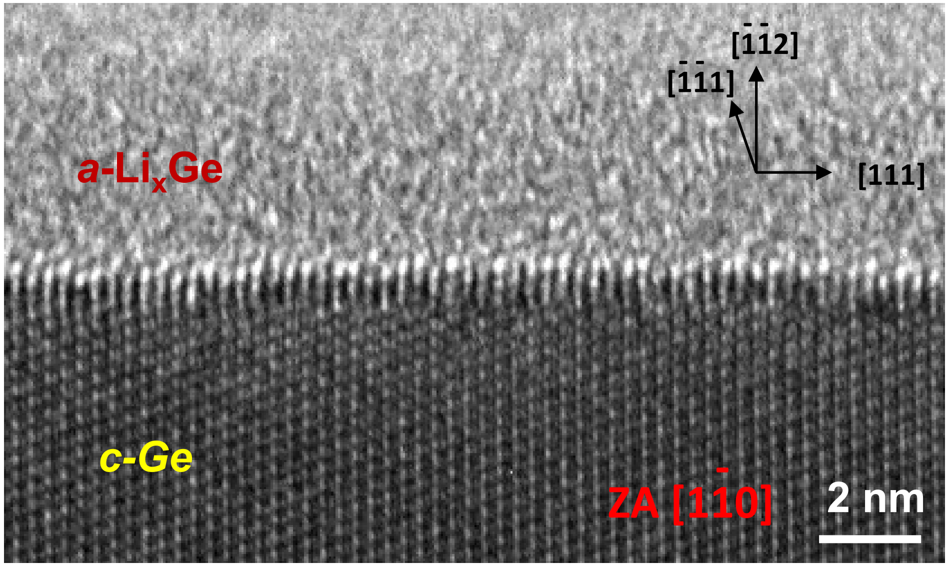
Summary:
Li ions can hardly penetrate the {111} close-packed Si planes, but can penetrate the {111} close-packed planes in Ge.

The peeling-off effect of each (111) plane is not obvious in Ge.

This observation from the microscopic view can provide the root cause for the anisotropic expansion in Si upon first lithiation and the almost isotropic expansion in Ge.



X. H. Liu, …, **Y. Liu** et al. ***Nature Nanotechnology***, 7, 749, (2012)



Y. Liu et al. ***Chemelectrochem***, 2014 in press

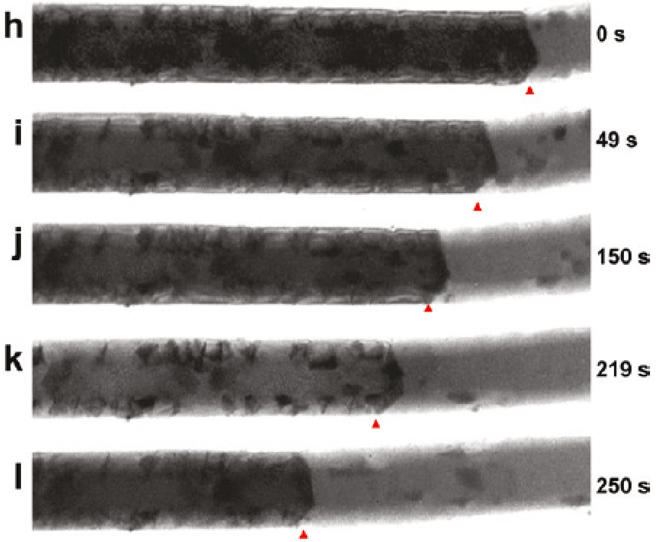
Y. Liu et al. in preparation

2. Tailoring Lithiation Behavior by Interface and Bandgap Engineering

How to control the lithiation behavior and thus the volume expansion?

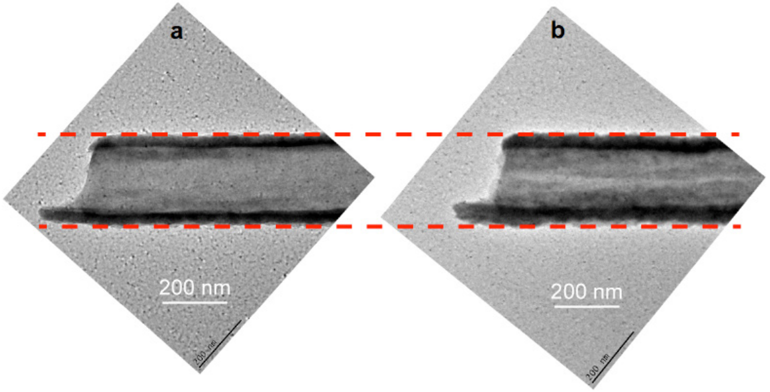
The normally used method:
External mechanical confinement

Example #1: carbon-coated SnO_2 nanowire



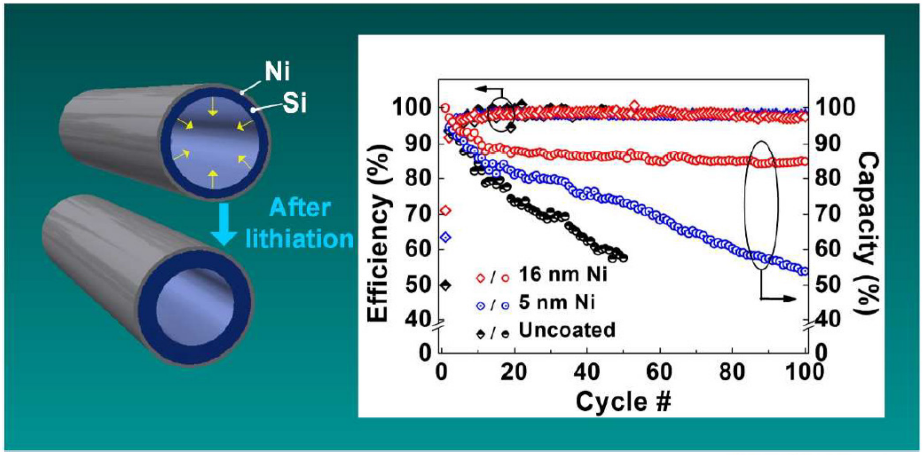
L. Zhang, X.H. Liu and **Y. Liu** et al, ***ACS Nano***, 5, 4800 (2011)

Example #2: SiO_2-coated Si nanotube



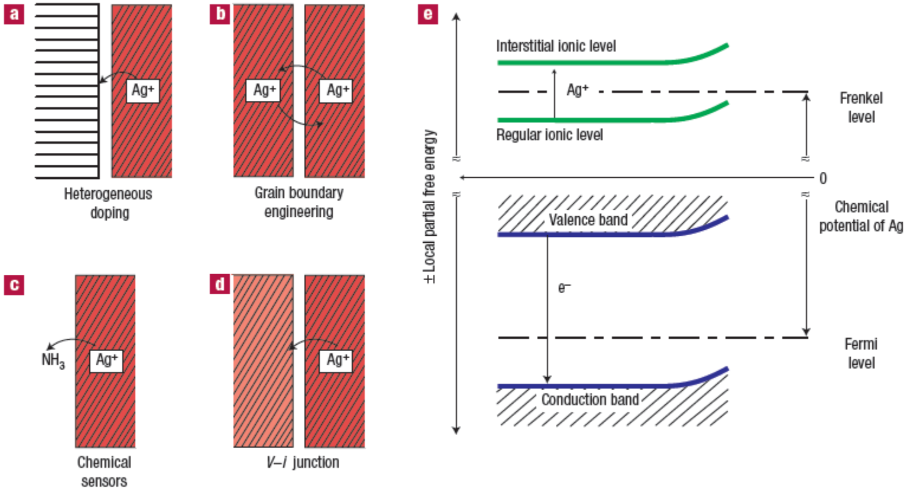
H. Wu et al, ***Nature Nanotechnology***, 7, 310 (2012)

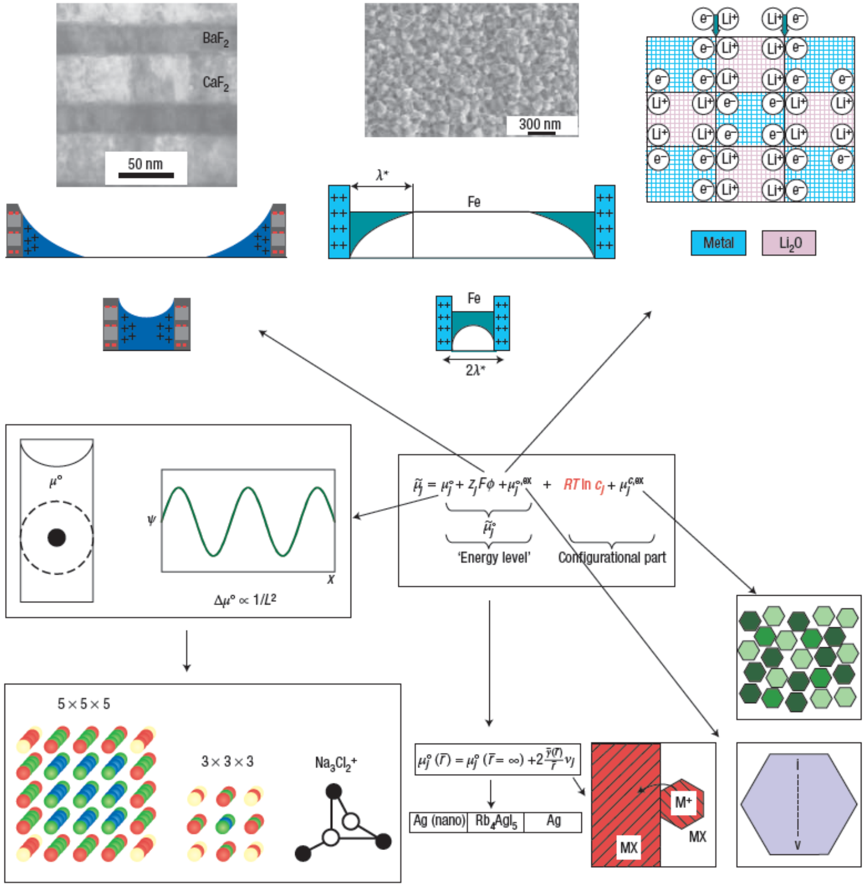
Example #3: Ni-coated Si nanotube



K. Karki et al, ***ACS Nano***, 7, 8295-8302, (2013)

Interface and nanosize effects on nano-ionics





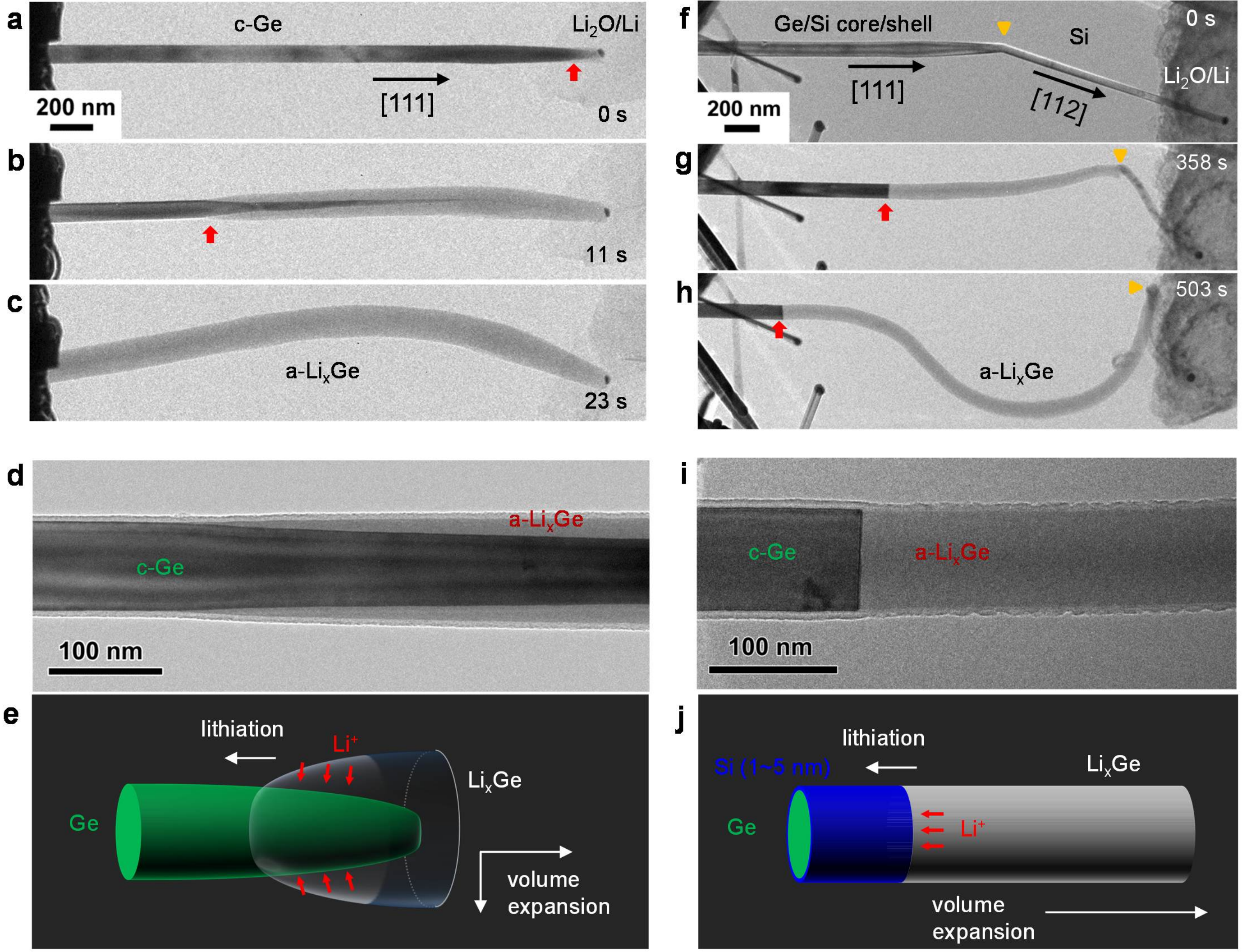
In the past two decades, it has been shown that ionic transport properties can be dominated by interfaces at the nanoscale, which provides the possibility to control the Li diffusion pathways and to modify the volume expansion direction by introducing heterojunctions (namely chemical and structural discontinuities).

J. Maier et al, ***Nature Materials*** 4, 805 (2005)

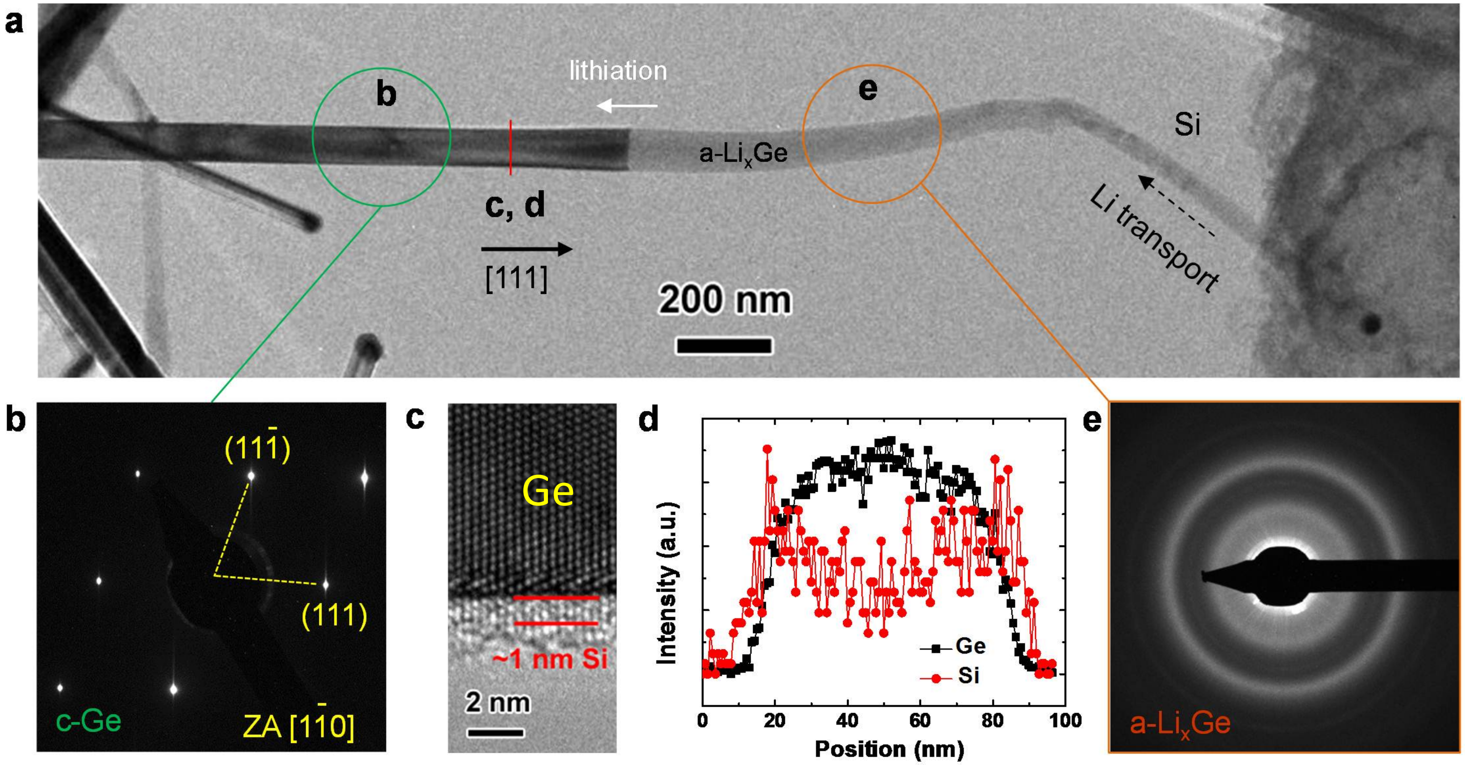
The sharp contrast in the lithiation behavior between pure Ge NW and Ge/Si core/shell NW

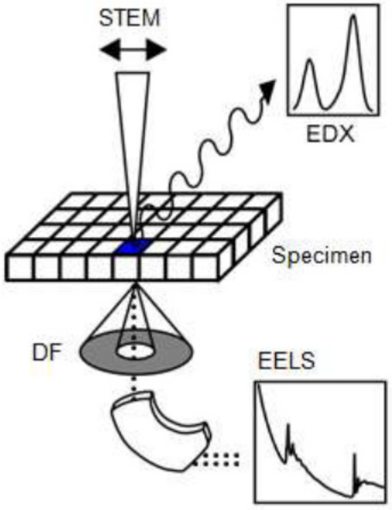
Pure Ge nanowire : Core-shell lithiation
Both swelling and elongation

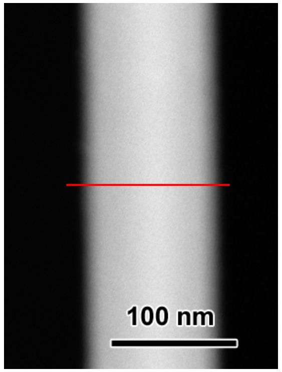
Ge/Si core/shell nanowire: Pure axial lithiation
Only elongation



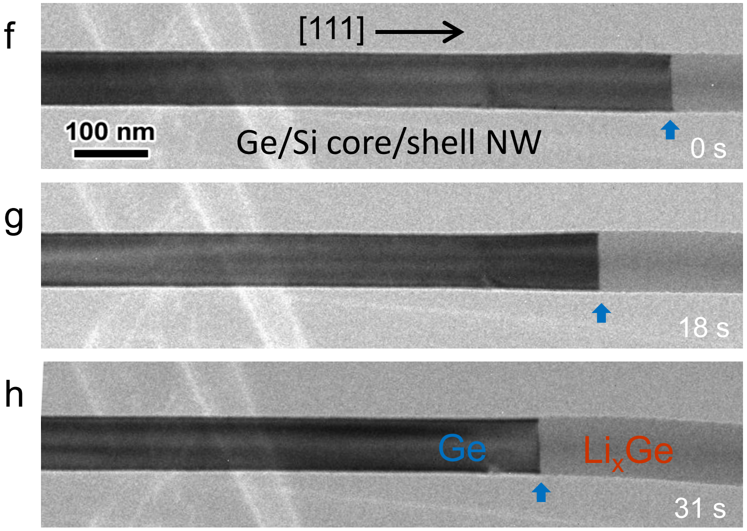
Y. Liu et al., ***Nano Letters***, 13, 4876 (2013)





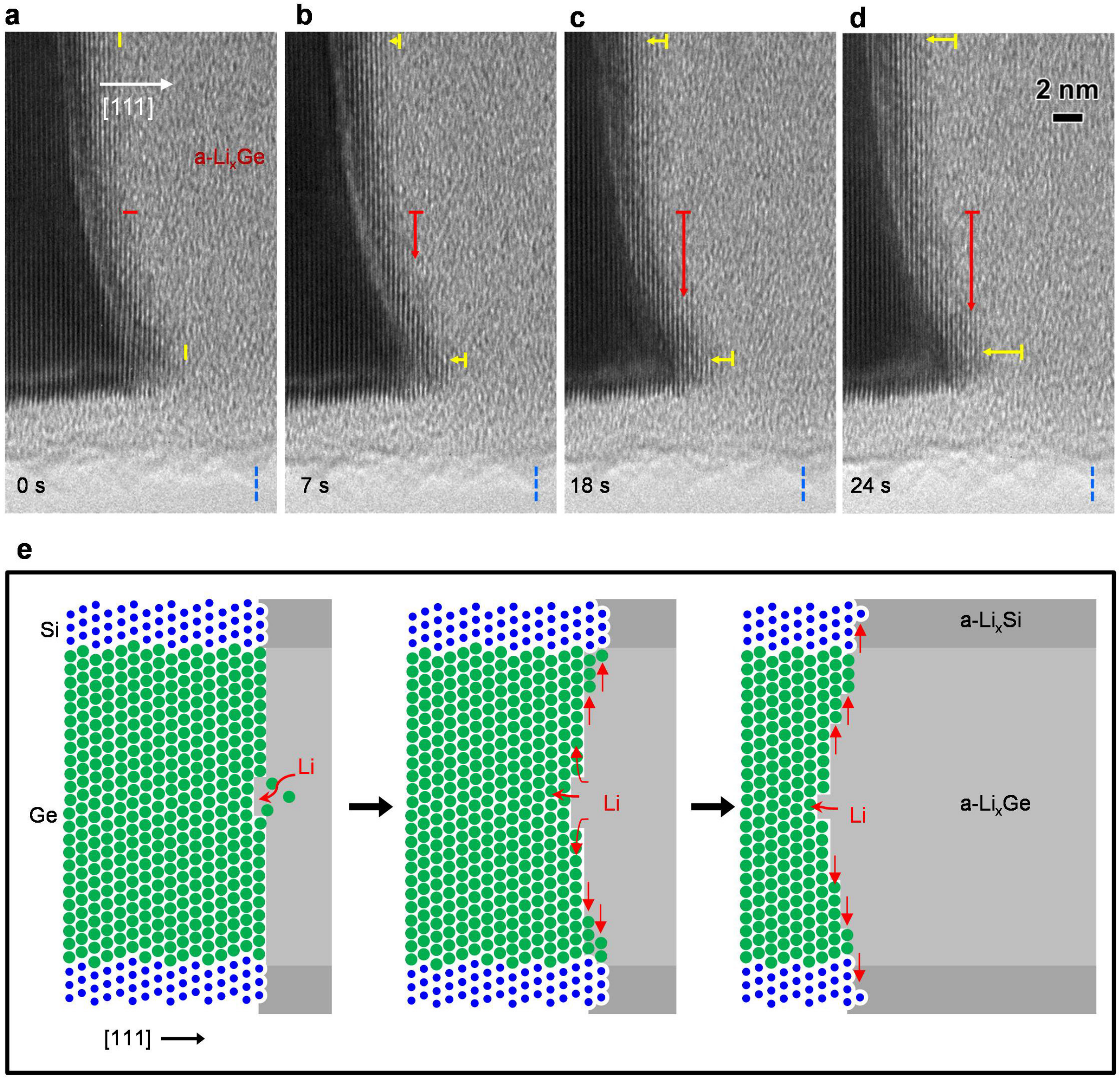


Introducing an ultrathin (down to ~1 nm) and epitaxially-grown Si surface layer can dramatically change the volume expansion direction!!!



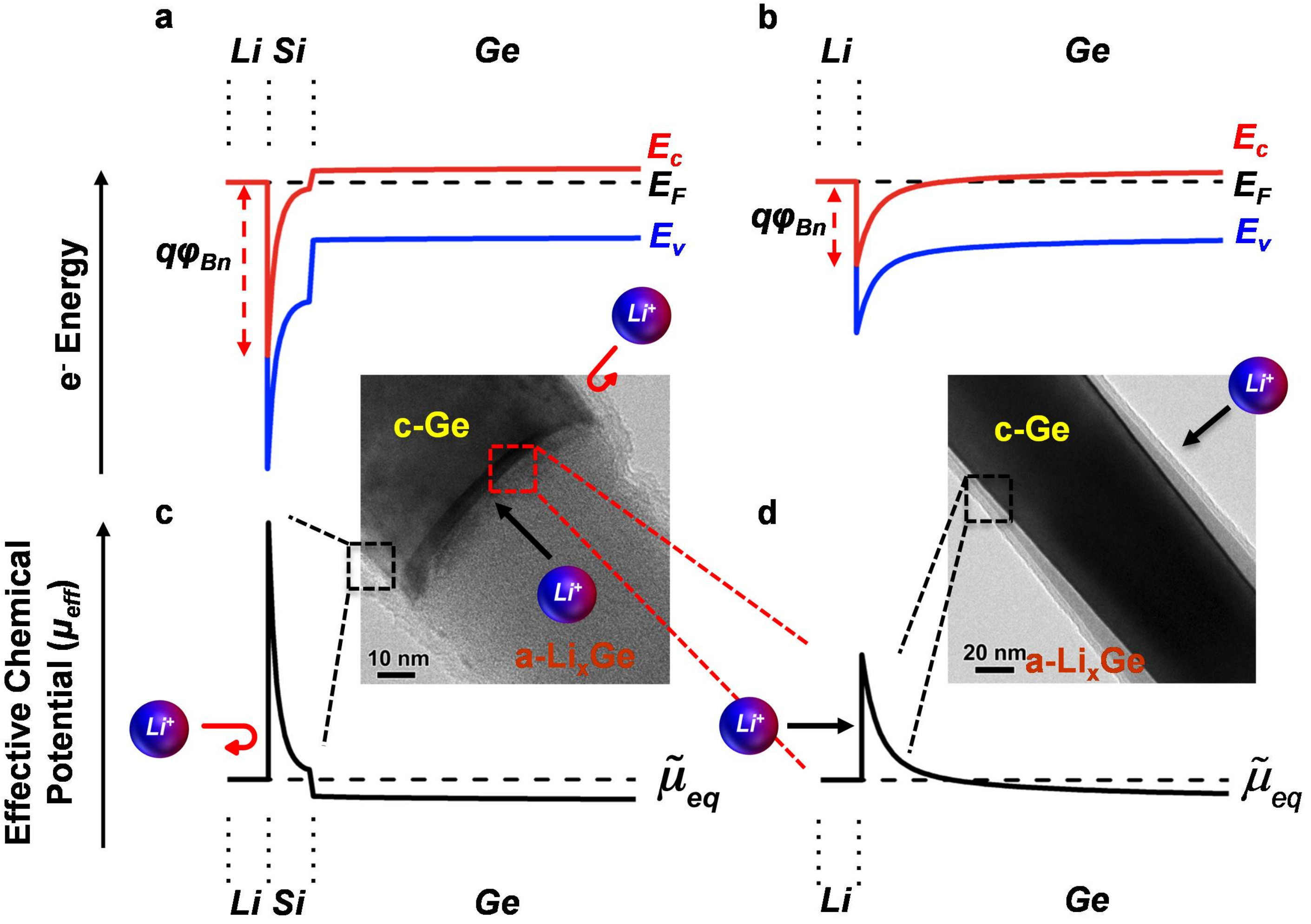
Y. Liu et al., ***Nano Letters***, 13, 4876 (2013)

Atomic scale imaging of lithiation process in Ge/Si core/shell nanowire



Y. Liu et al., ***Nano Letters***, 13, 4876 (2013)

A larger chemical potential for Si surface than for Ge surface



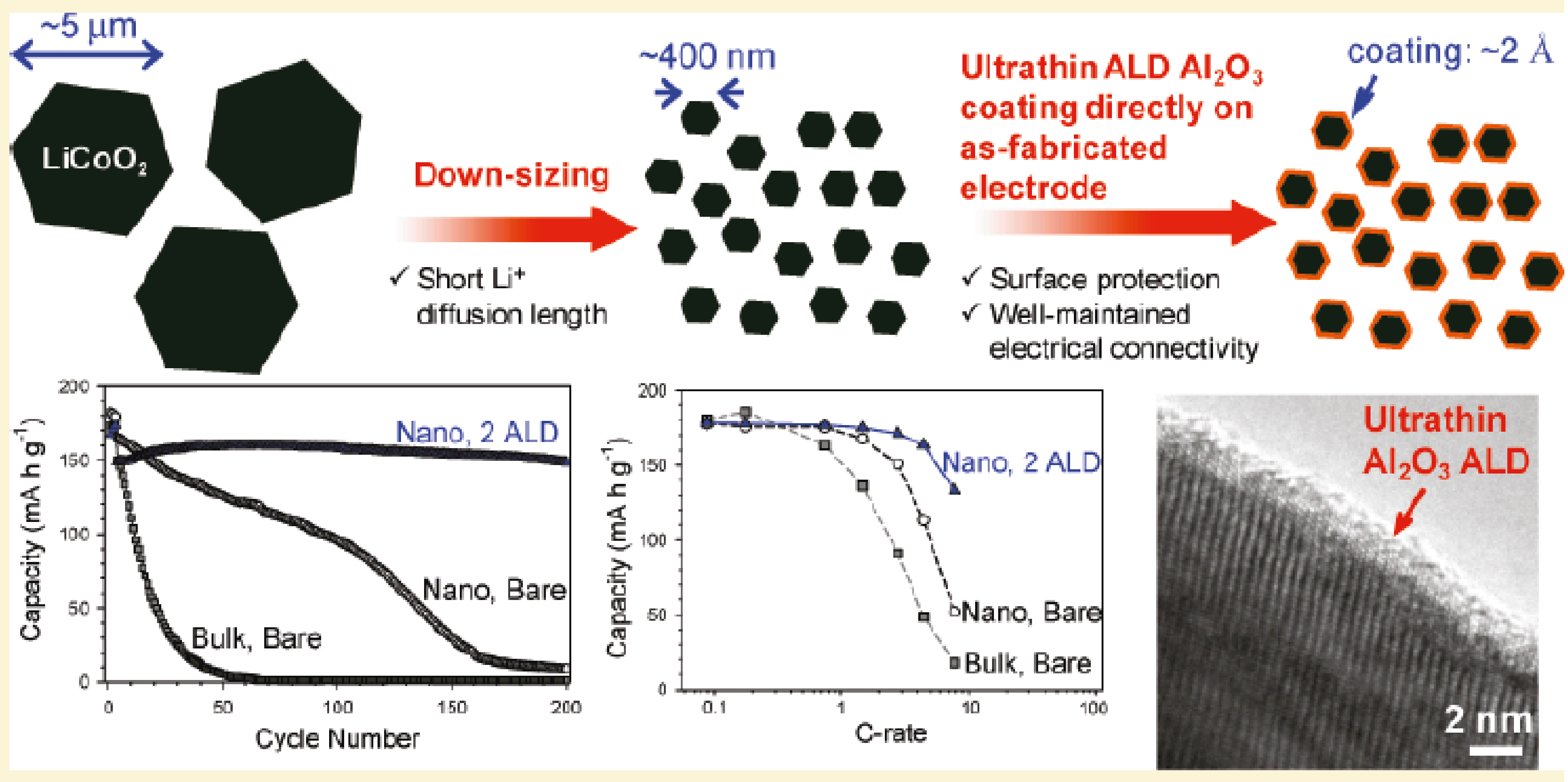
Summary:
This is the first direct observation of the dramatic interfacial effect on ionic transport at the nanoscale.

It provides a powerful additional degree of freedom to define the electrochemical reactions in Li-ion batteries.

Y. Liu et al., *Nano Letters*, 13, 4876 (2013)

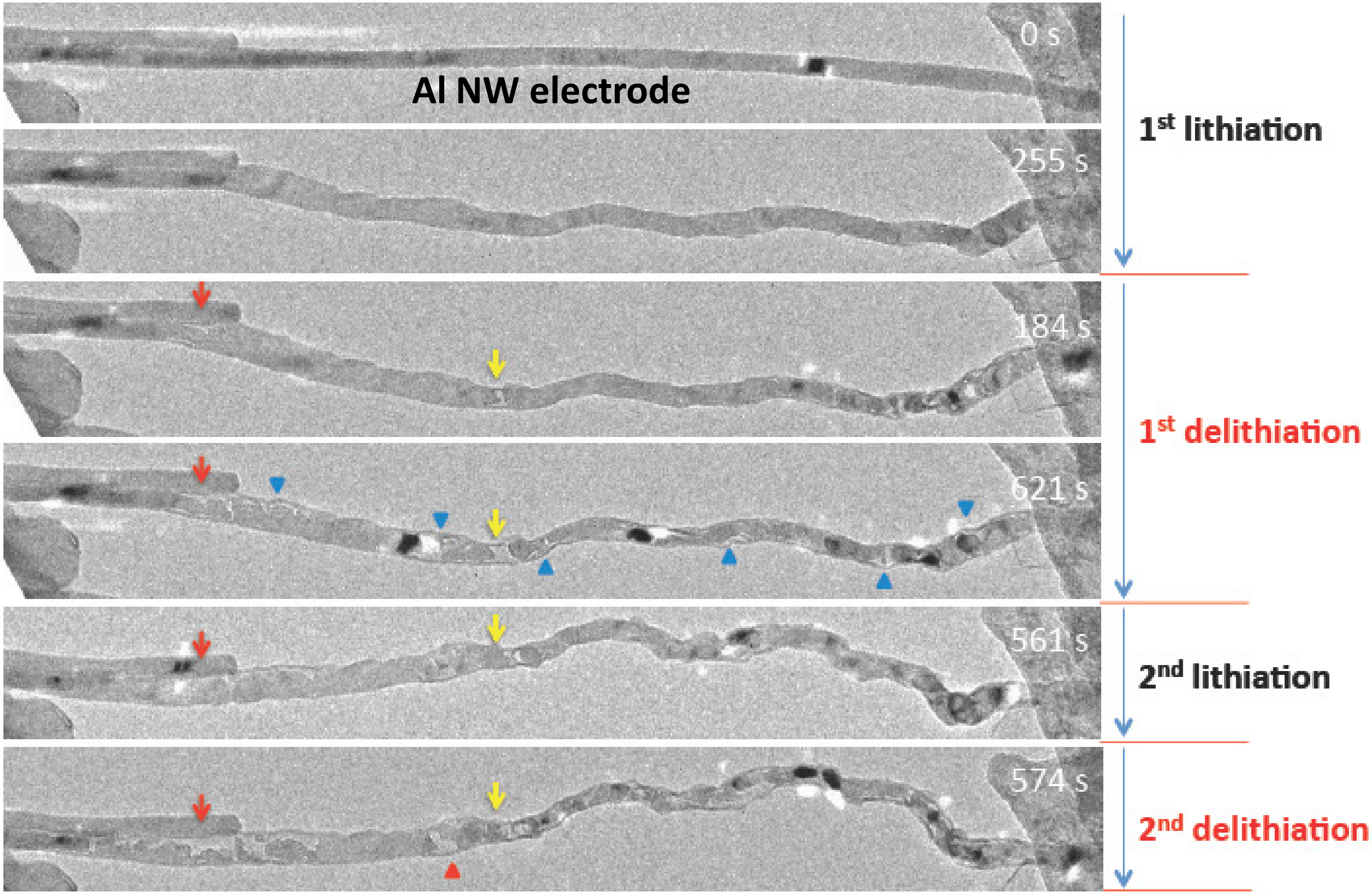
3. Pulverization of Al electrode and the function of ALD-Al_2O_3 coating

The evolution and function of these surface coatings of Al_2O_3 during cycling were not understood.



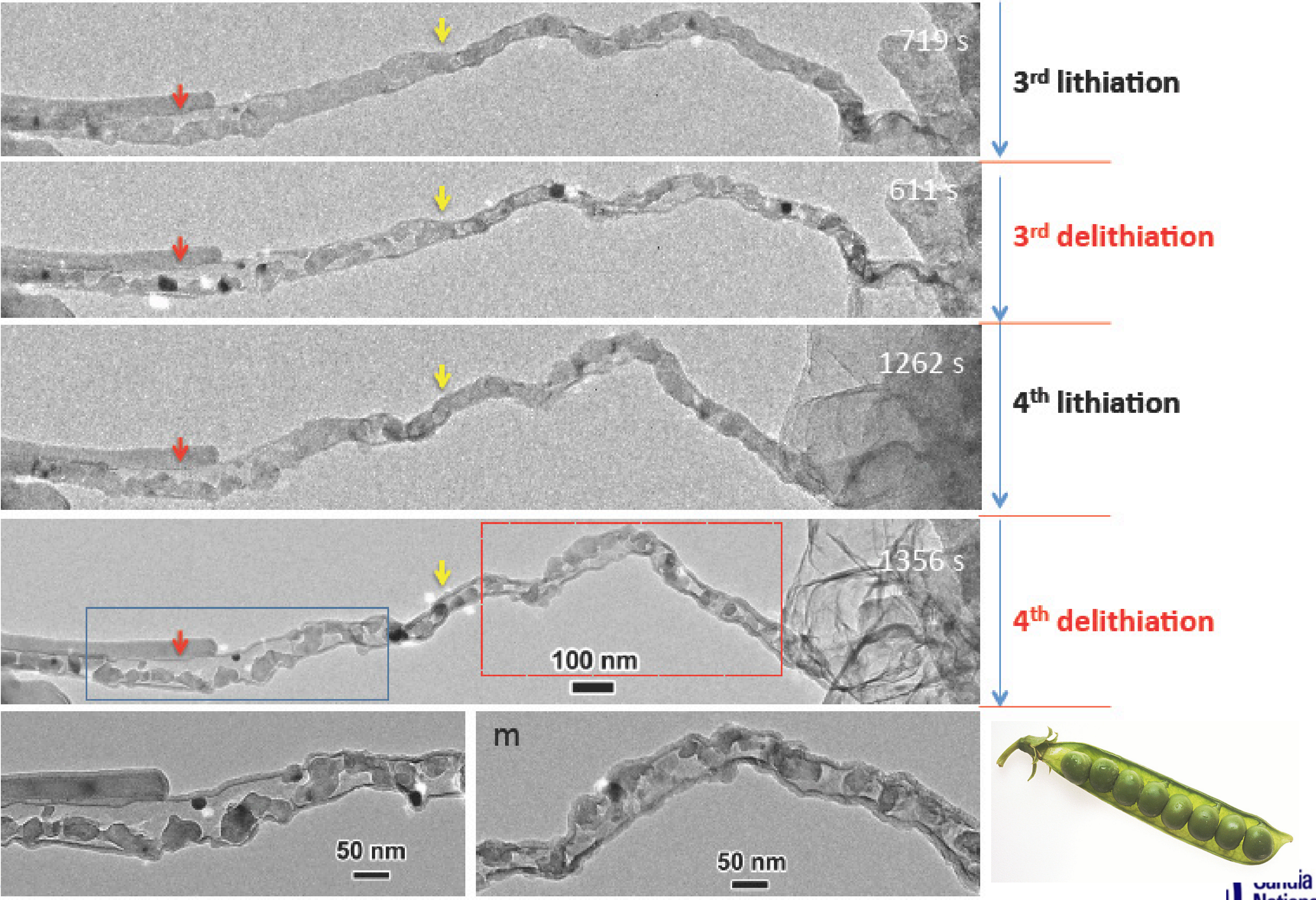
I. Scott et al., ***Nano Letters***, 11, 414 (2011)

Pulverization process of Al electrode



Y. Liu et al., ***Nano Letters***, 11, 4188 (2011)

Pulverization process of Al electrode



3rd lithiation

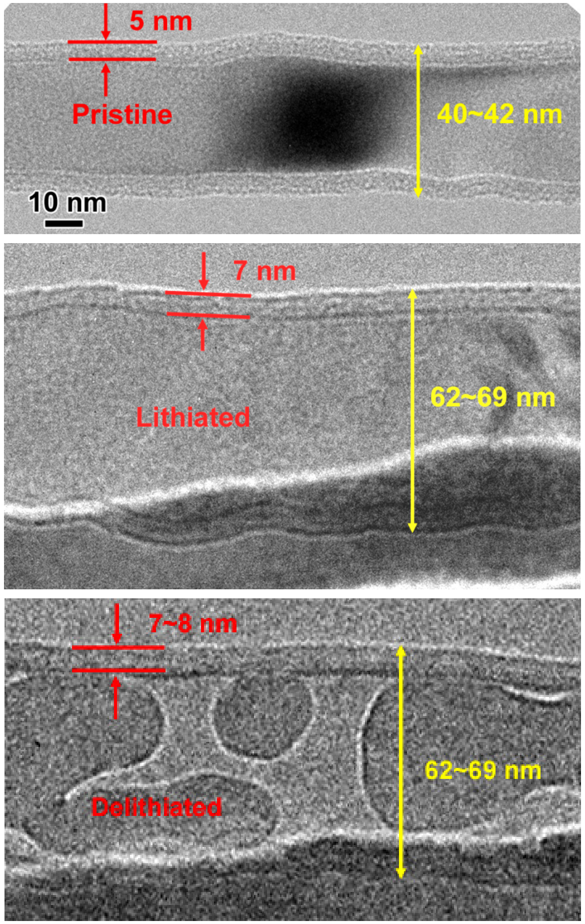
3rd delithiation

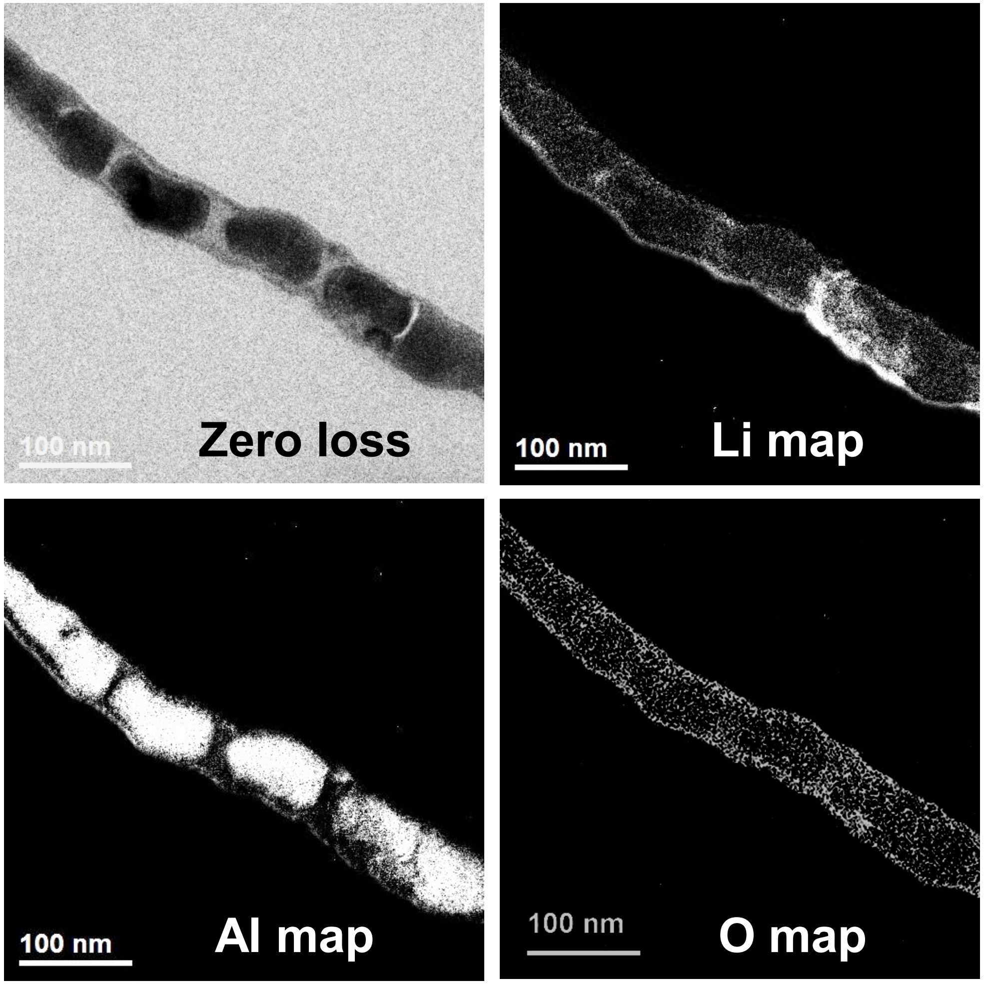
4th lithiation

4th delithiation

Y. Liu et al., ***Nano Letters***, 11, 4188 (2011)

Evolution of surface Al_2O_3 layer

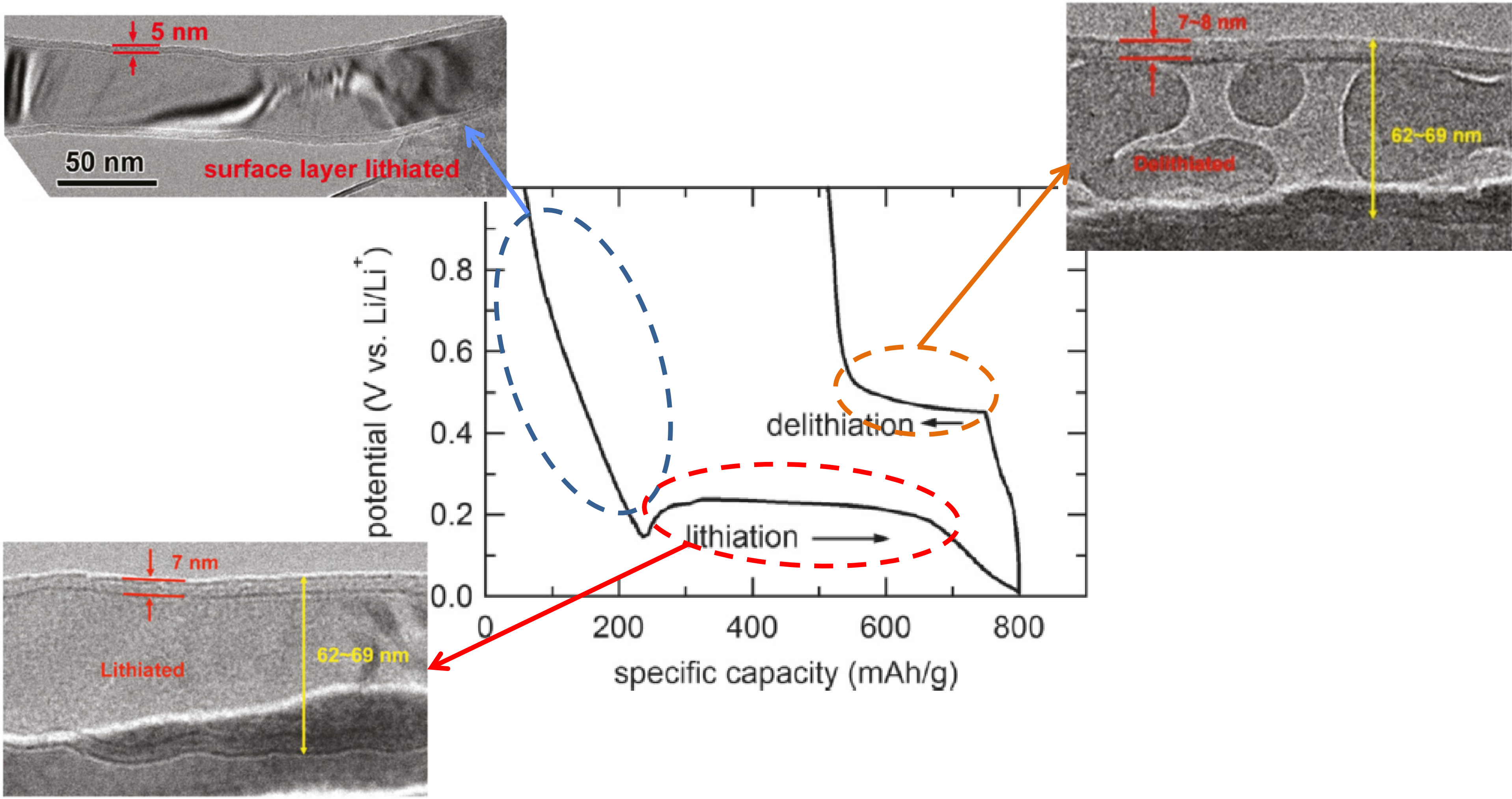




Al_2O_3 Layer was changed into Li-Al-O glass, wrapping the pulverized Al nanoparticles.

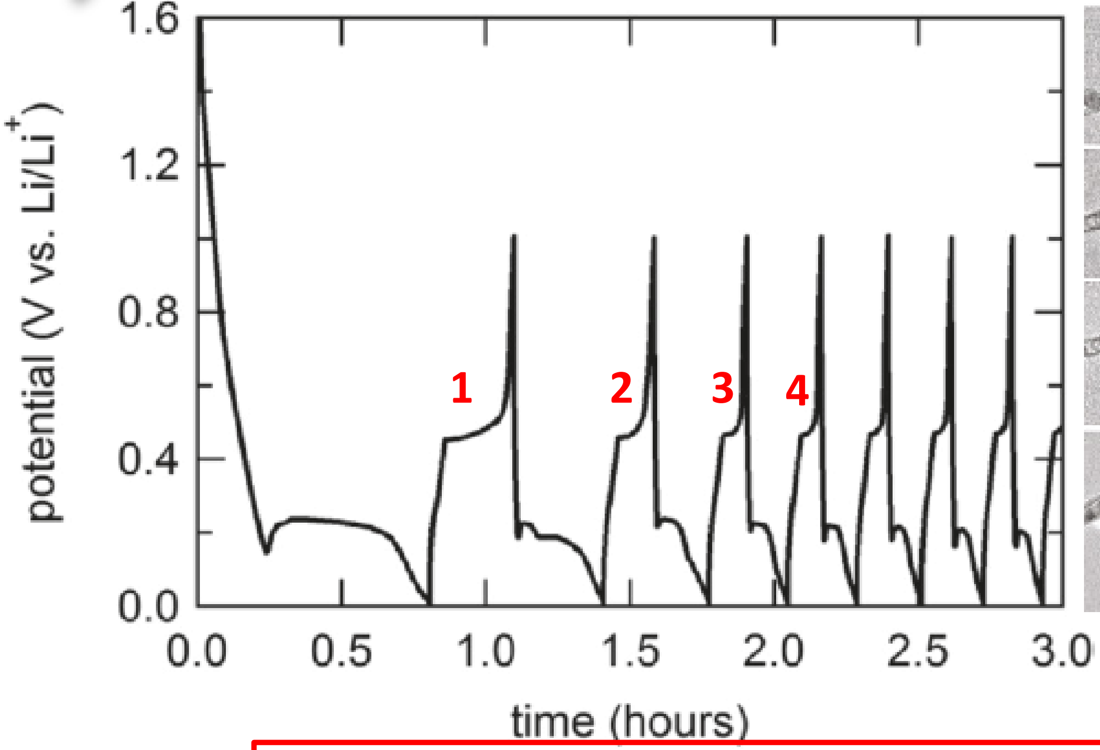
<u>**Y. Liu**</u> et al., ***Nano Letters***, 11, 4188 (2011)

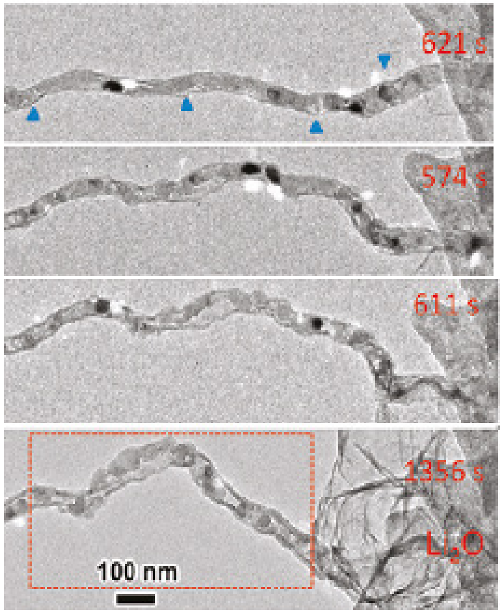
Correlation with the ex-situ coin cell results



Y. Liu et al., ***Nano Letters***, 11, 4188 (2011)

Correlation with the ex-situ coin cell results





1st delithiation

2nd delithiation

3rd delithiation

4th delithiation

Summary--The function of the thin surface Al_2O_3 coatings:

- The improvement of the performance of LIBs using Al_2O_3 coatings on active materials is attributed to the formation of the Li-Al-O glass layer.
- The Li-Al-O glass layer can provide a facile Li-ion transport path, relative to that in the usually formed solid electrolyte interface (SEI). (like artificial SEI)
- The mechanically robust Li-Al-O glass layer can mitigate mechanical degradation of the active materials to prevent them from breaking off the electrodes.

Y. Liu et al., ***Nano Letters***, 11, 4188 (2011)

4. Phase evolution of conversion anode RuO_2

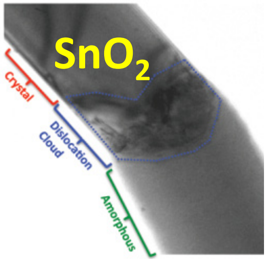
Metal oxide-based anodes can be classified into three groups depending on the reaction mechanisms:

Large irreversible capacity loss in the first cycle.

1. Li-alloy reaction mechanism:

$$M_xO_y + 2yLi^+ + 2ye^- \rightarrow xM + yLi_2O$$

$$M + zLi^+ + ze^- \leftrightarrow Li_zM$$

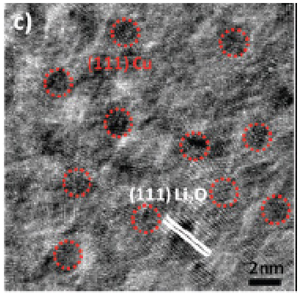


J.Y. Huang *et al.*, ***Science*** 330, 1515 (2010)

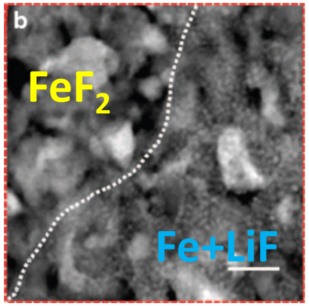
2. Conversion reaction mechanism:

$$M_xO_y + 2yLi^+ + 2ye^- \leftrightarrow xM + yLi_2O$$

CuO



X. Wang *et al.*, ***Chem. Commum.*** 48, 4812 (2012)



F. Wang *et al.*, ***Nature Commum.*** 3, 1201 (2012)

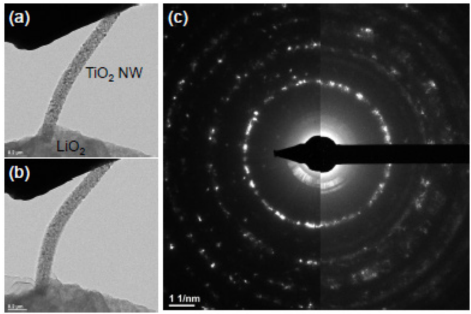
Li_2O can be converted to Li, and usually, the oxidation state can be fully utilized, more than one electron/Li ion are involved.

3. Insertion reaction mechanism:

$$MO_x + yLi^+ + ye^- \leftrightarrow Li_yMO_x$$

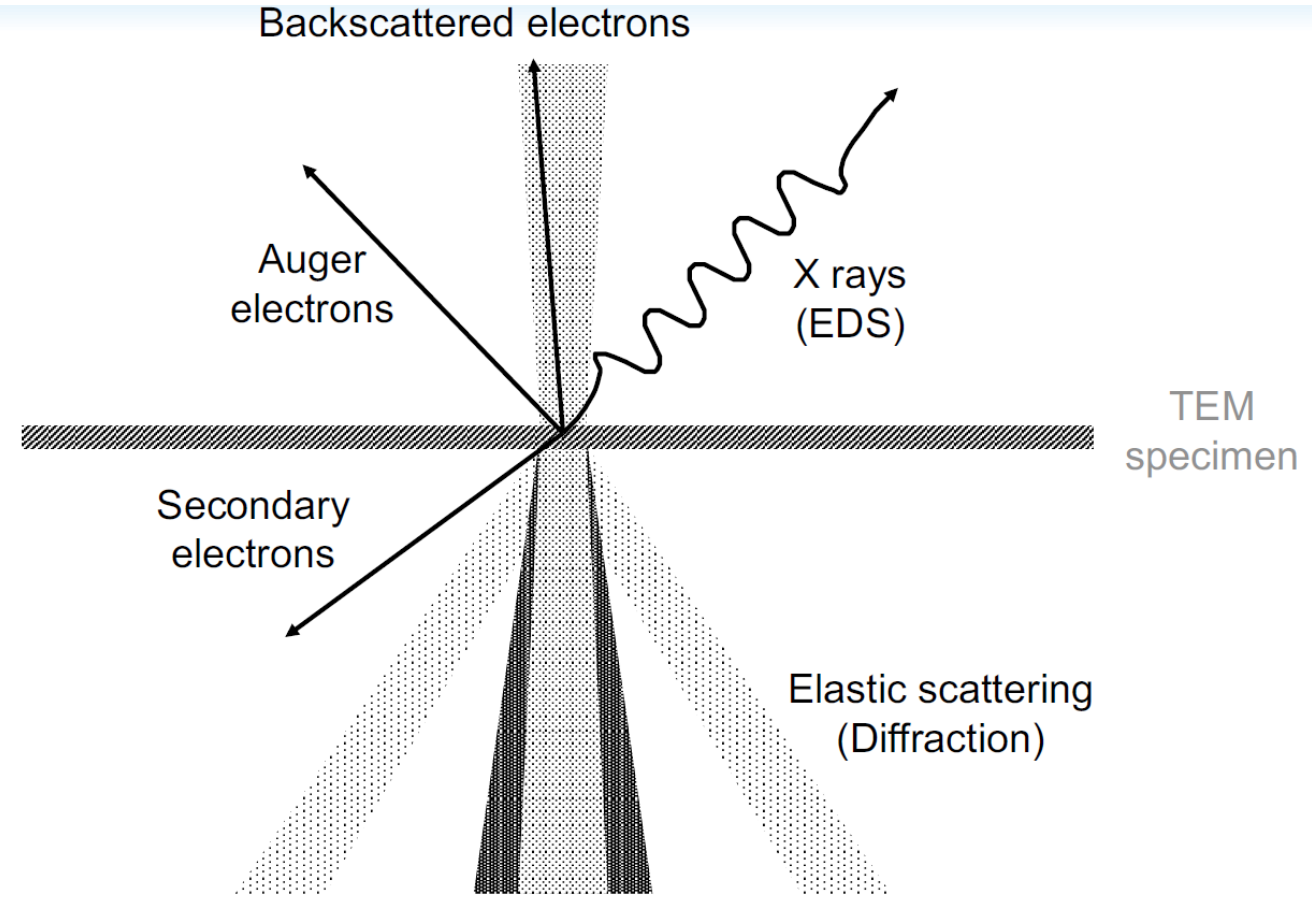
L. Ji and X. Zhang *et al.*, ***Energy Environ. Sci.*** 4, 2682 (2011)

TiO_2



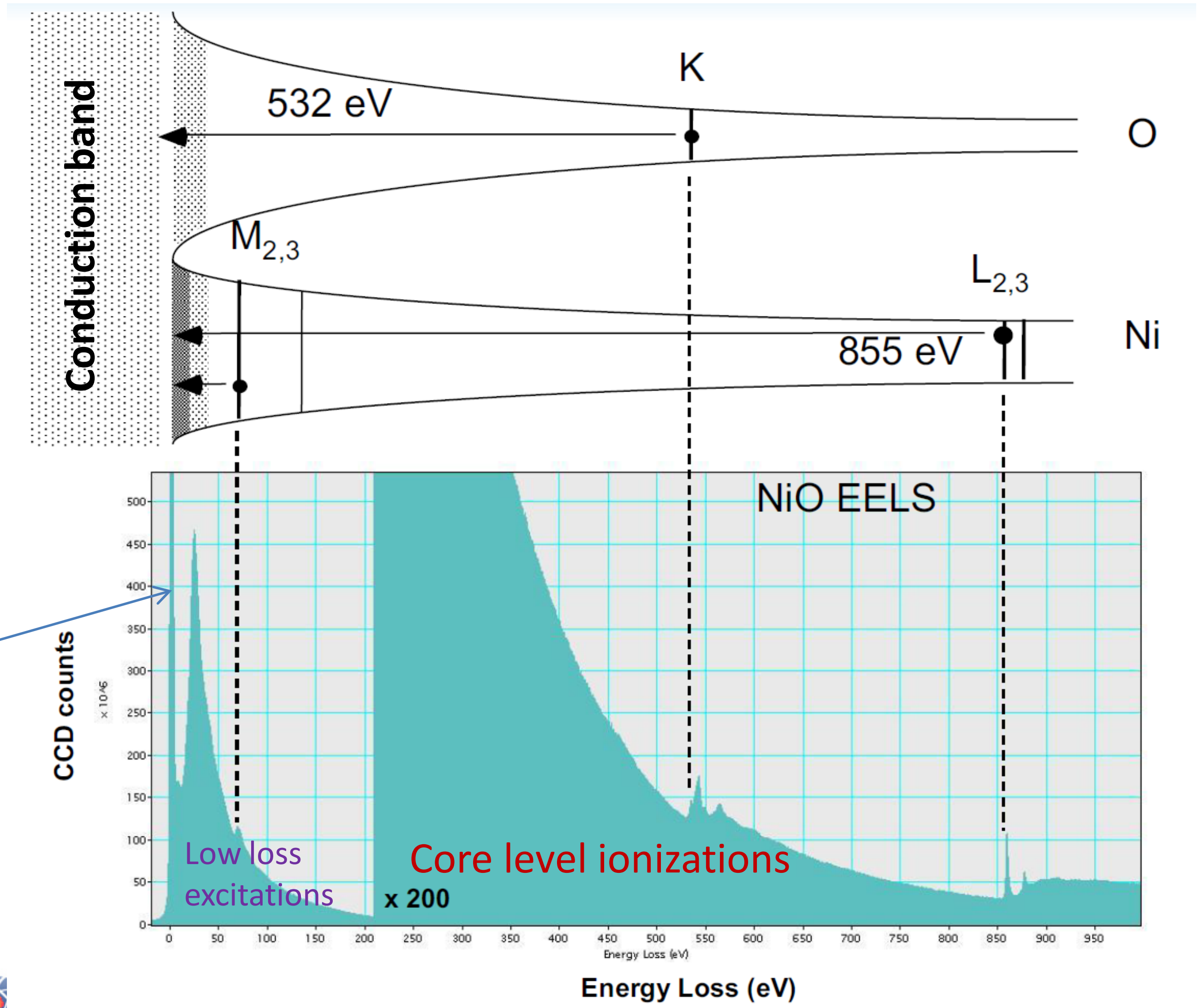
Y. Liu *et al.*, in preparation

Introduction to Electron energy loss spectroscopy (EELS)



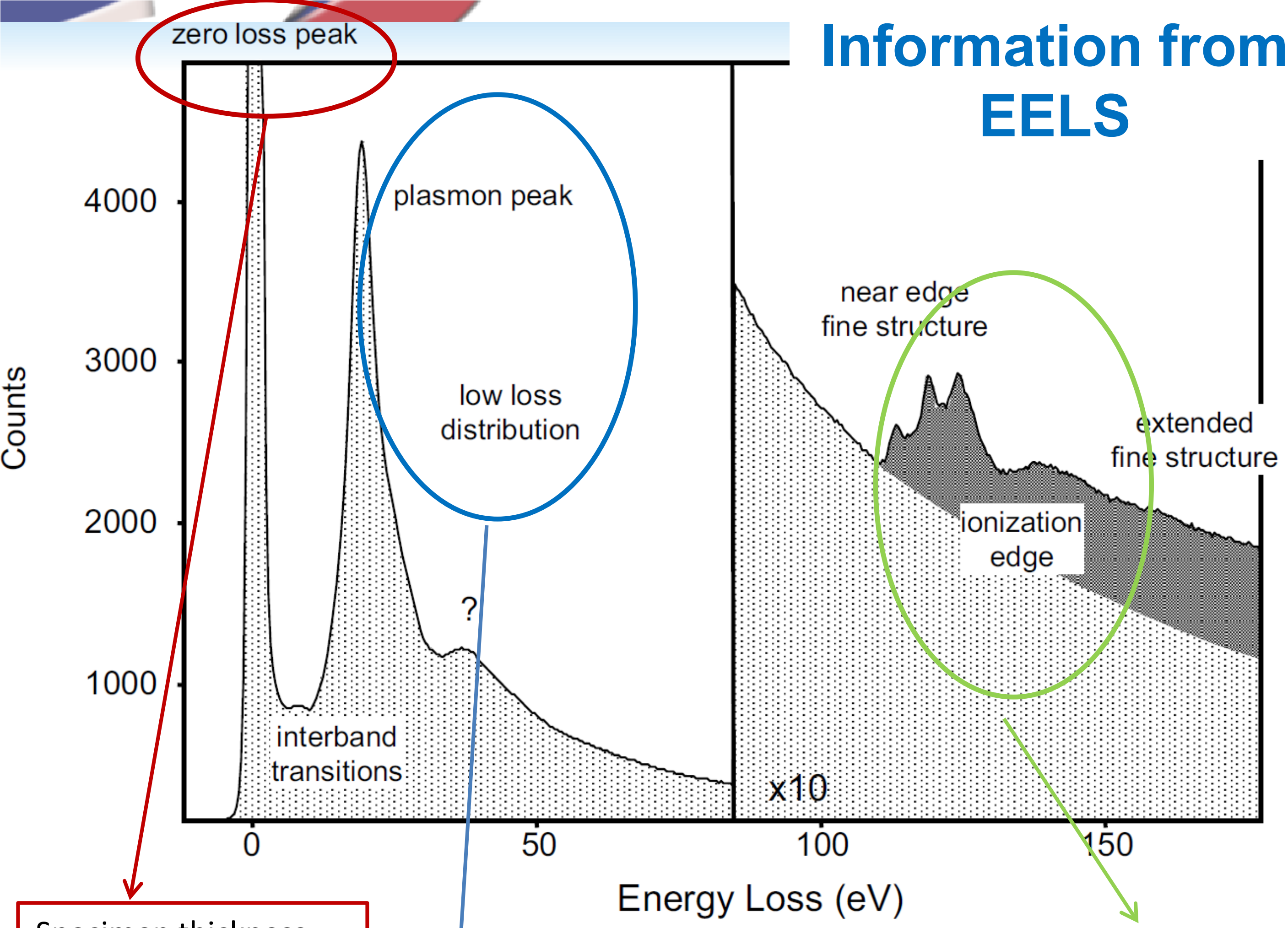
Inelastic scattering (EELS)

Correlation between EELS and specimen features



Zero loss

Information from EELS

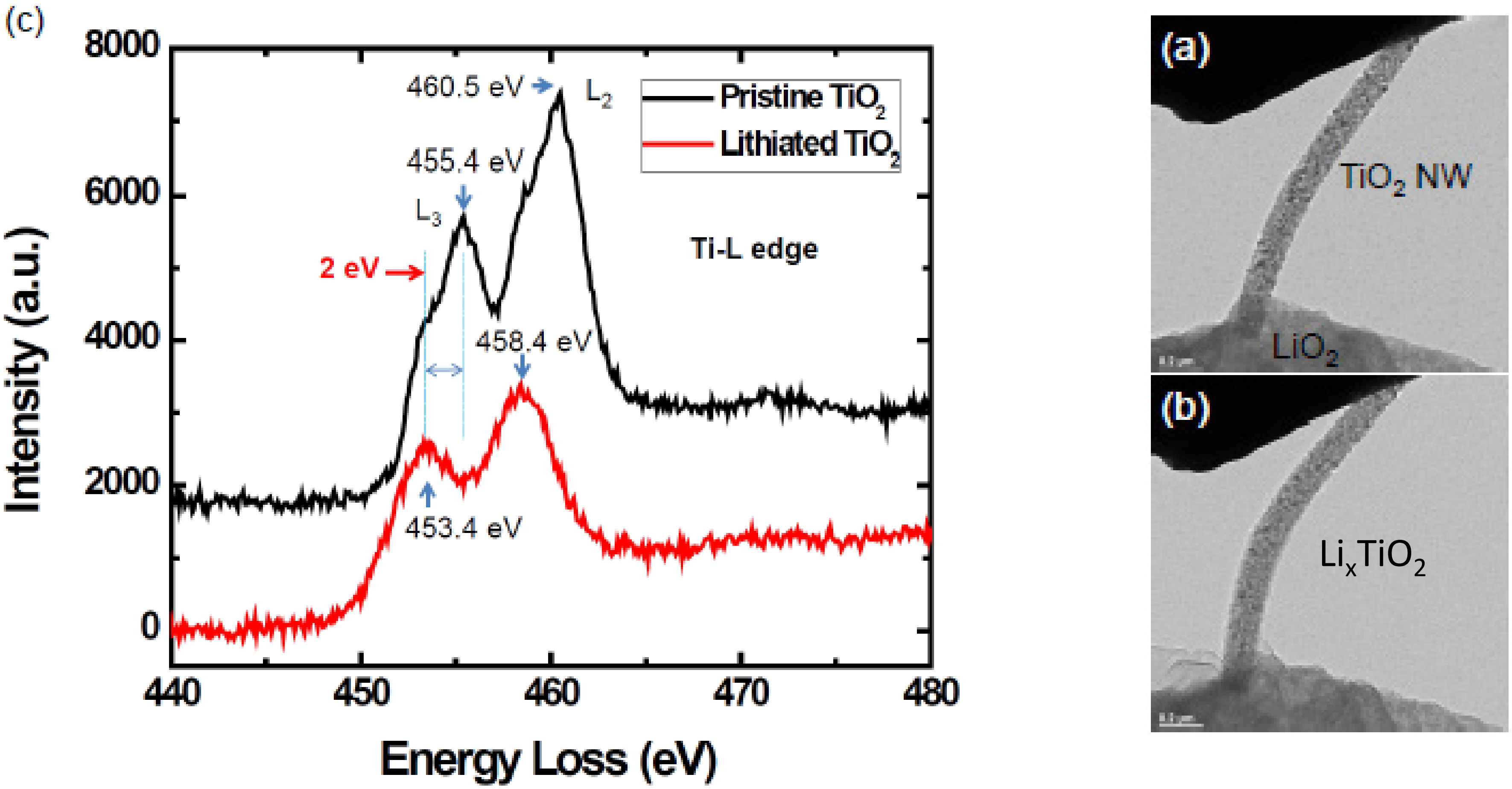


Specimen thickness,
Energy reference,
Intensity Reference

Valence/conduction electron density,
Phase location and identification,
Optical properties / dielectric function

Elemental composition and concentration,
ELNES (Energy Loss Near Edge Structure)
-Fingerprinting, unoccupied density of states,
EXELFS (EXtended Energy LossFine Structure)
-atom-specific radial distribution of near neighbors (RDF)

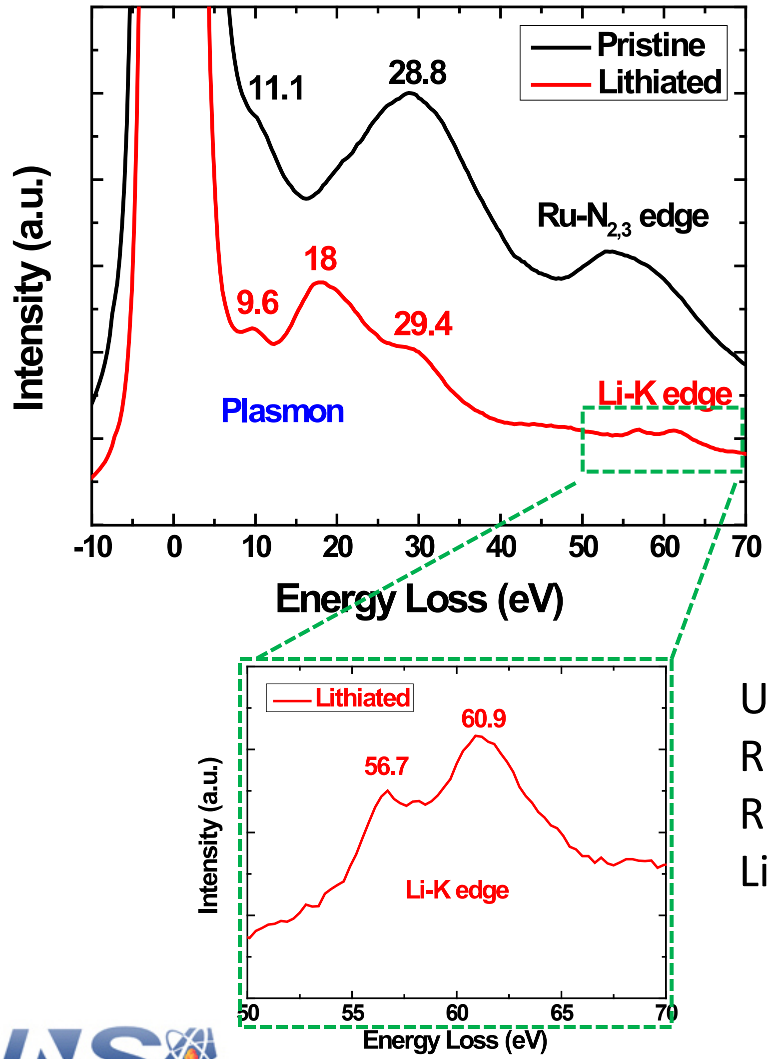
Example on lithiation in TiO_2

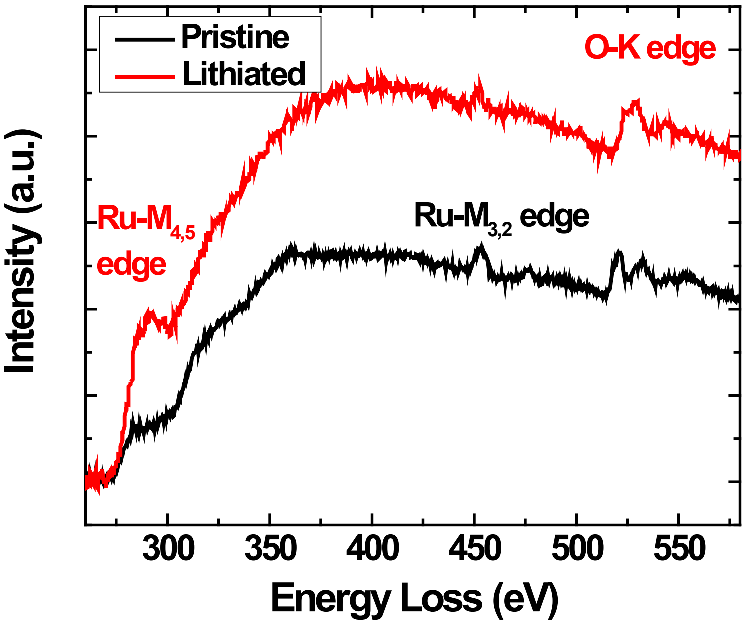


Chemical shift of Ti-L edge, indicating the transition from Ti^{4+} to Ti^{3+} upon lithiation.

Y. Liu *et al.*, in preparation

EELS data on RuO_2 before and after lithiation





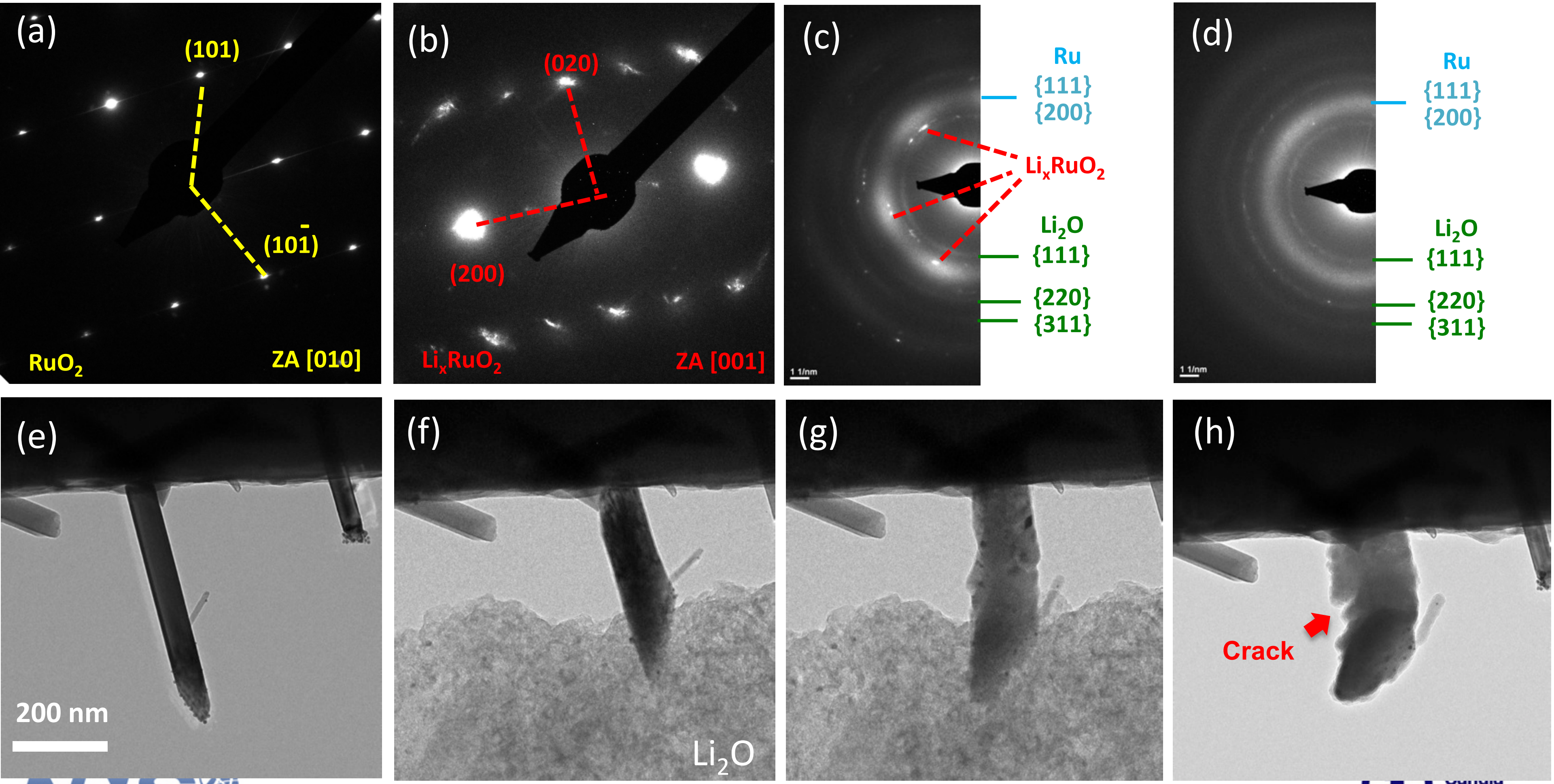
Upon lithiation,
Ru-$N_{2,3}$ edge significantly decreased,
Ru-$M_{4,5}$ edge increased, while Ru-$M_{3,2}$ edge decreased.
Li-K edge, assigned to Li_2O, showed up.

K.E. Gregorczyk and **Y. Liu** et al., ***ACS Nano***, 7, 6354 (2013)

Intermediate phases

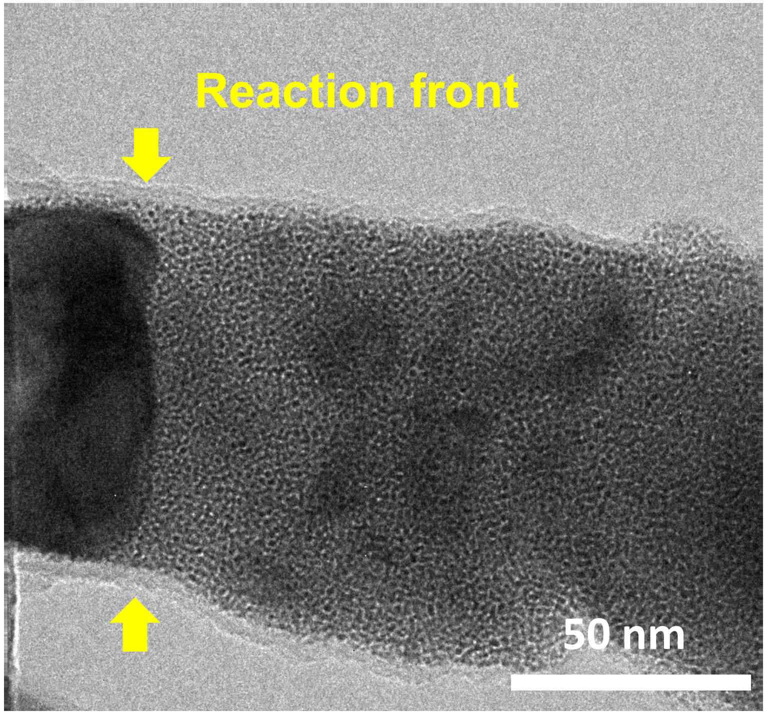
c-RuO_2 → c-Li_xRuO_2 (x~1) → Ru + c-Li_2O + Li_xRuO_2 → Ru + c-Li_2O

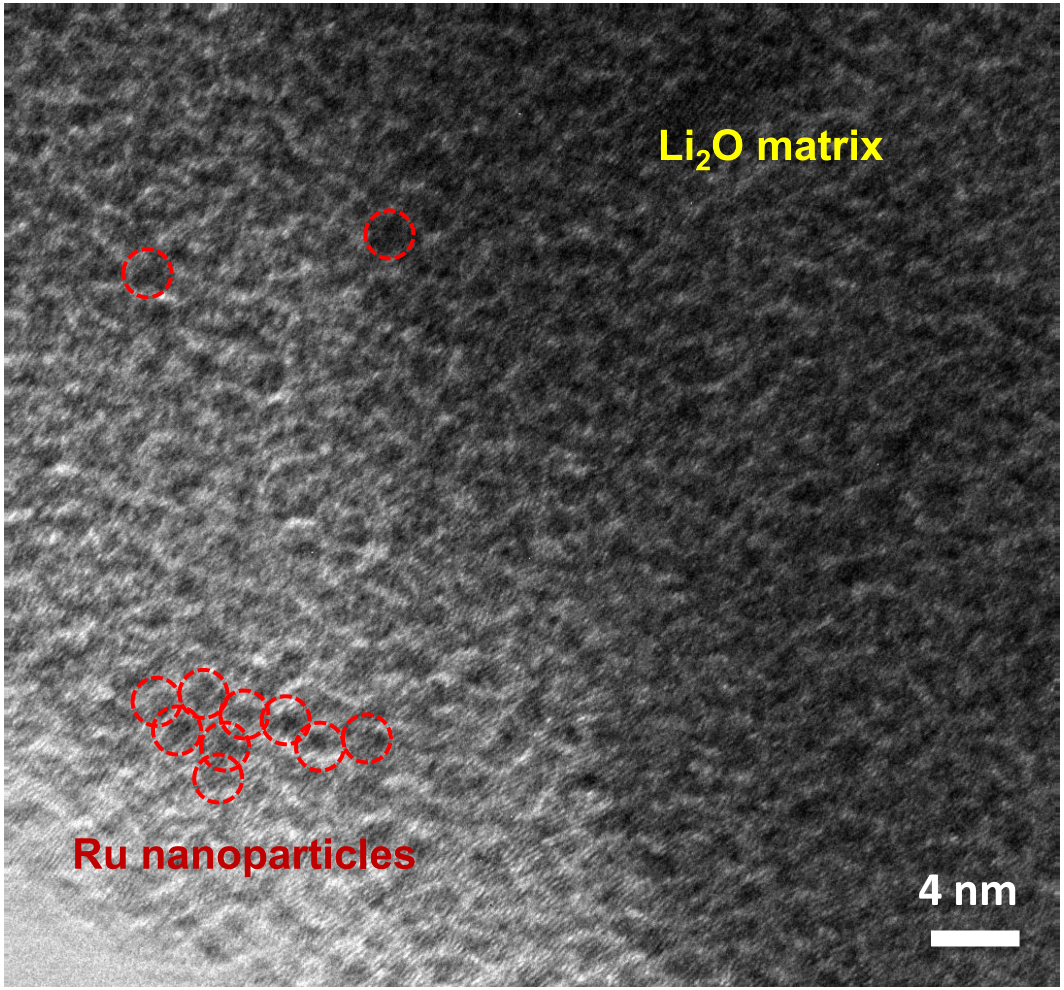
(Tetragonal, S.G.: $P4_2/mnm$) (Orthorhombic, S.G.: Pnnm)



K.E. Gregorczyk and **Y. Liu** et al., ***ACS Nano***, 7, 6354 (2013)

HRTEM after 1st lithiation



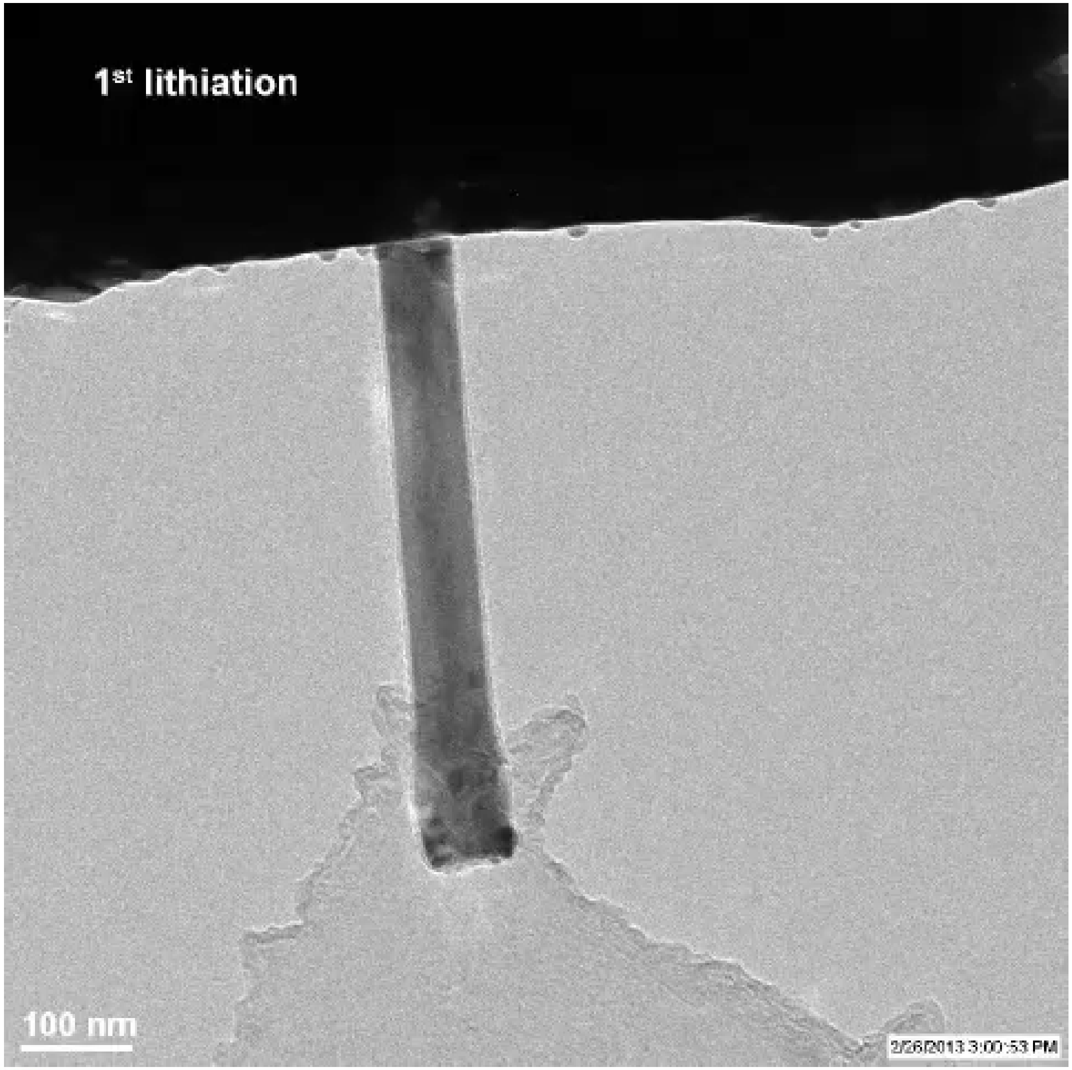


1~2 nm fine Ru nanoparticles formed connected network in the Li_2O matrix, serving as a facile conductive path for electrons, while the Li_2O provides a similar path for Li^+.

$RuO_2+4e^-+4Li^+ \rightarrow Ru^0+2Li_2O$

K.E. Gregorczyk and **Y. Liu** et al., ***ACS Nano***, 7, 6354 (2013)

Multiple cycling on individual nanowires

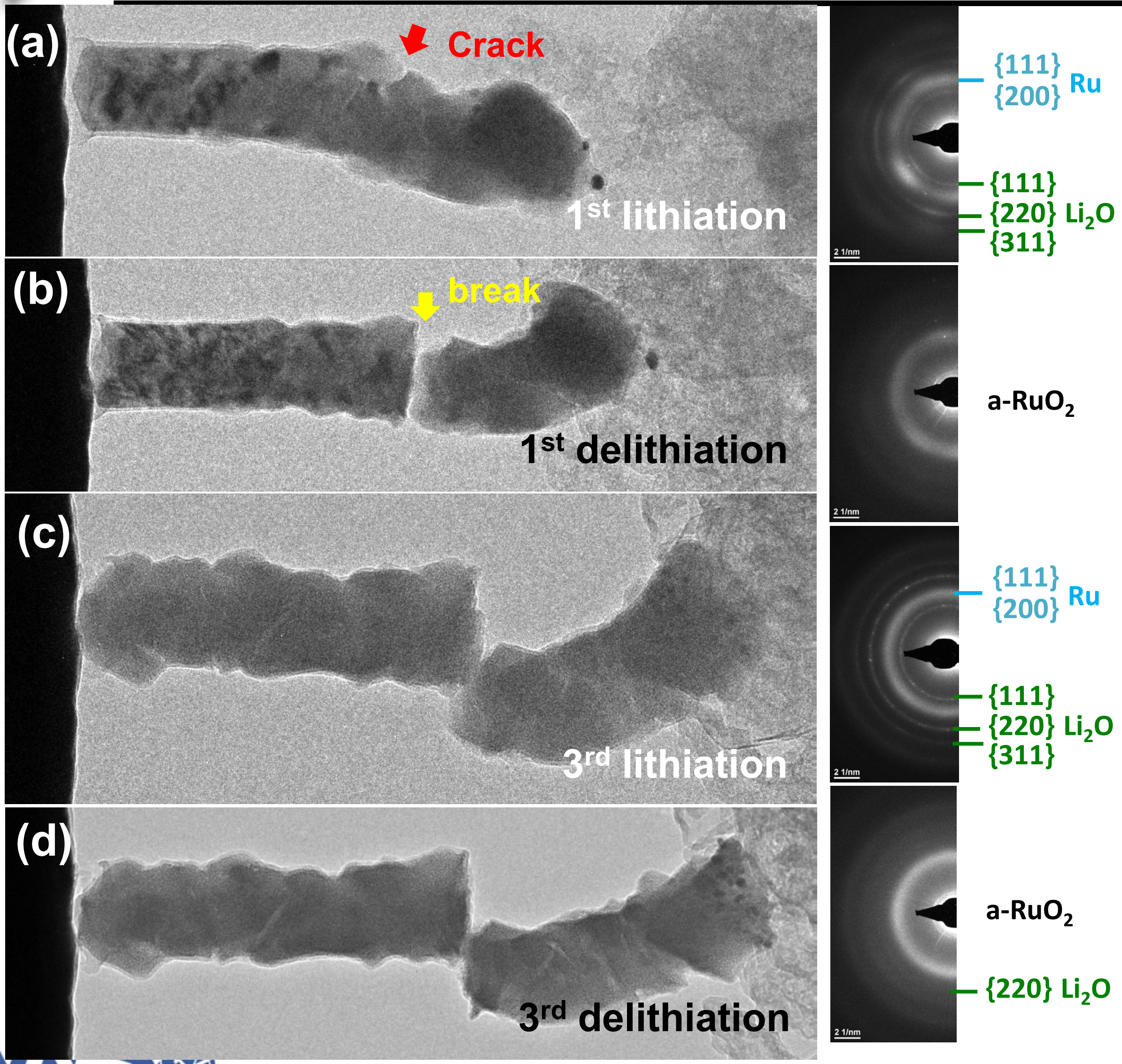


9 cycles

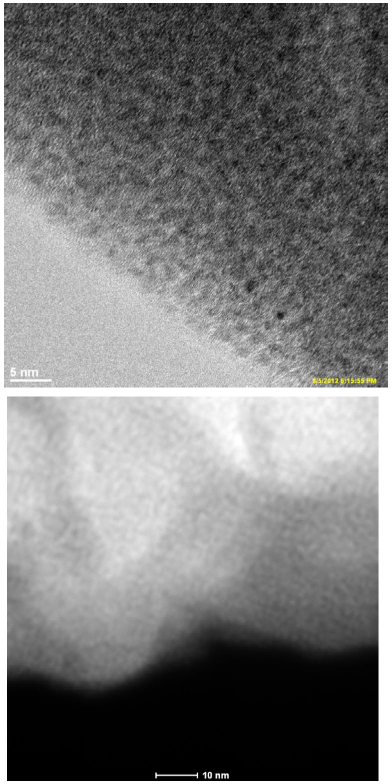
$RuO_2+4e^-+4Li^+\leftrightarrow Ru^0+2Li_2O$

K.E. Gregorczyk and **Y. Liu** et al., ***ACS Nano***, 7, 6354 (2013)

Multiple cycling on individual nanowires



After 3 cycles, HRTEM and HAADF-STEM images



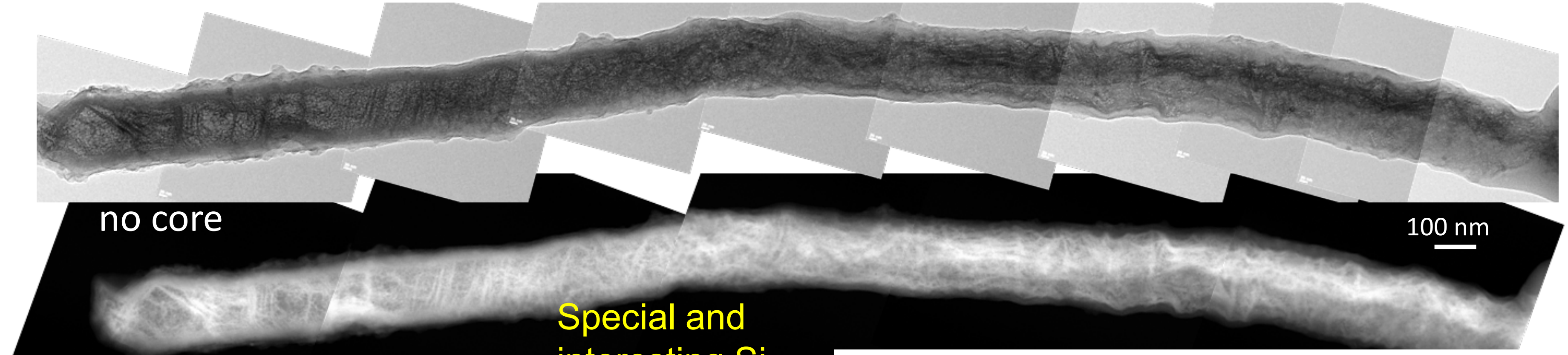
Some Ru nanoparticles embedded in a Li_2O matrix, indicating part of the reaction is irreversible.

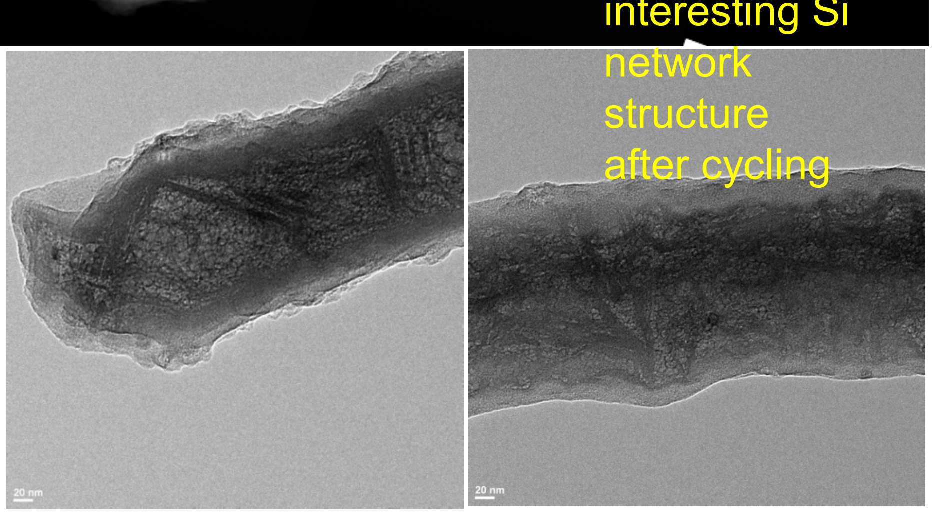
K.E. Gregorczyk and **Y. Liu** et al., ***ACS Nano***, 7, 6354 (2013)

5. Quantitative Electrochemistry inside TEM

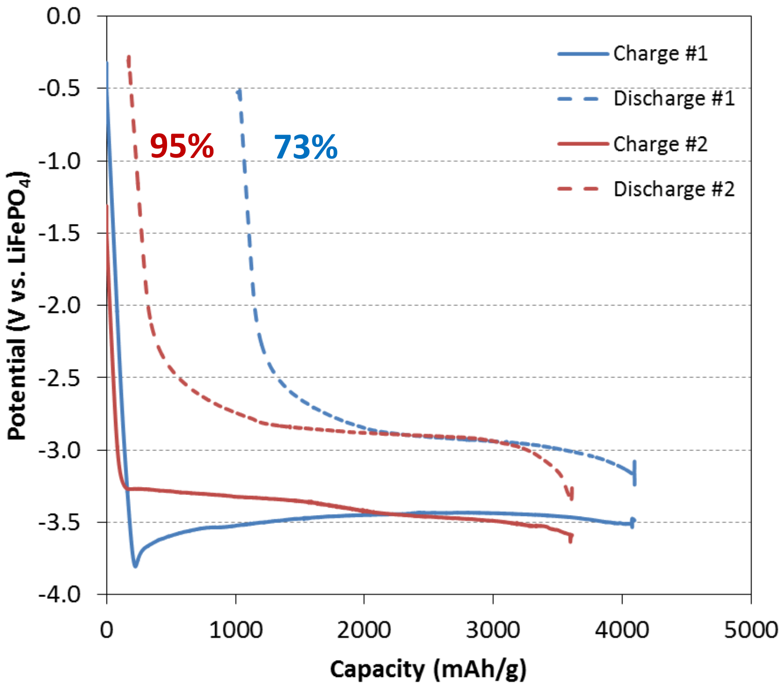
Si <111> 3 C rate

For a single Si nanowire with 100 nm diameter and 1 um length, 1 C rate = 65.5 fA current





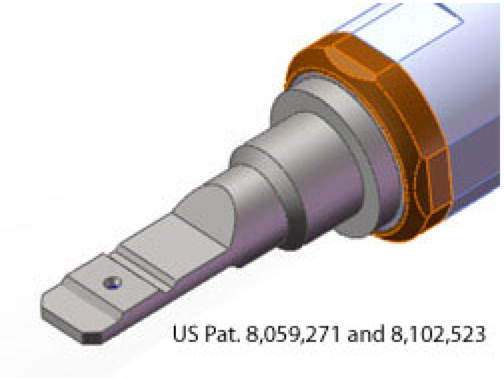
Special and interesting Si network structure after cycling

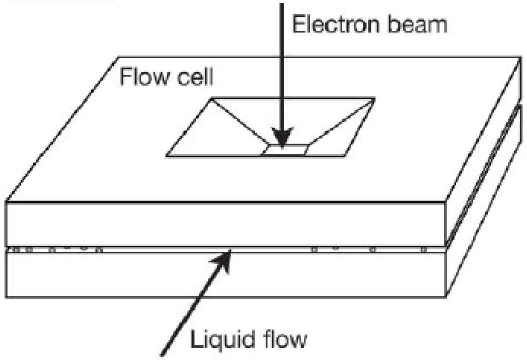


K. Zavadil and **Y. Liu** et al., in preparation

Flowing and TEM compatible liquid chips

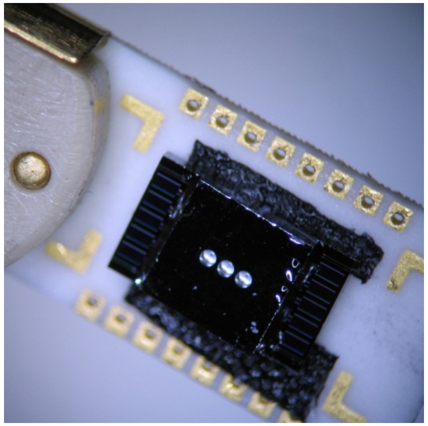
Commercialized
Hummingbird systems

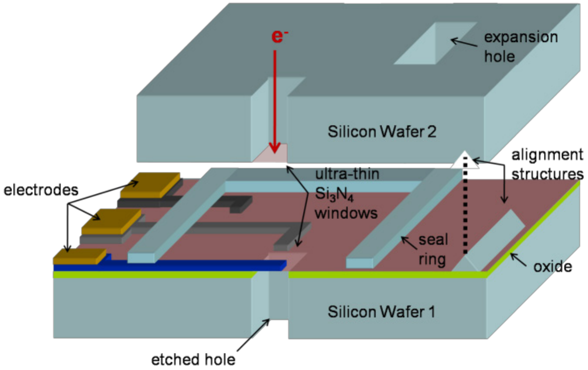


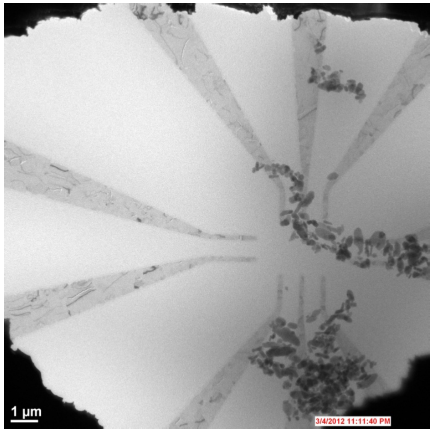


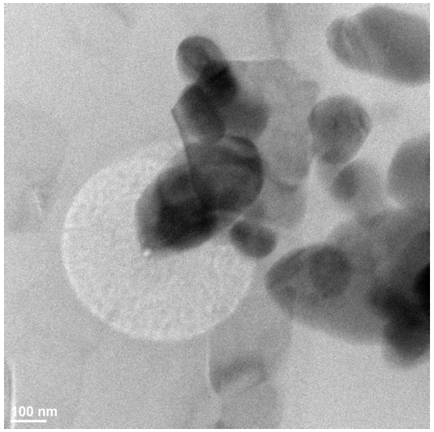
de Jonge et al., ***Proc. Natl. Acad. Sci.*** 106, 2159 (2009).

Our home designed liquid chip
And Nanofactory multiple-leads holder









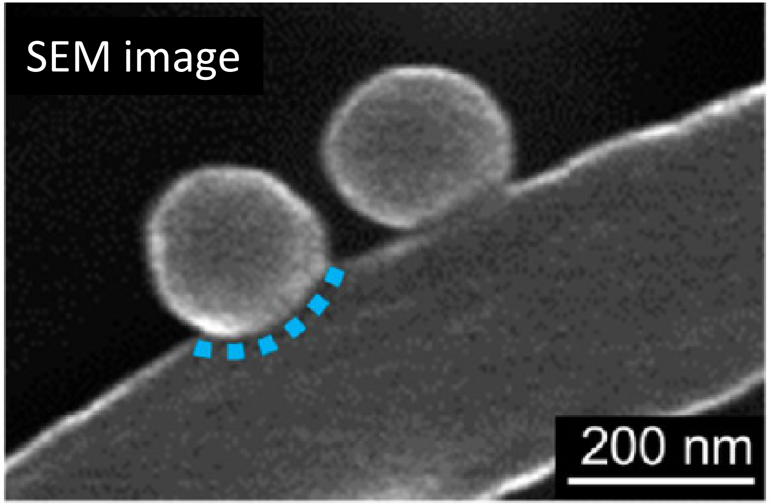
$LiFePO_4$ in EC/DEC electrolyte

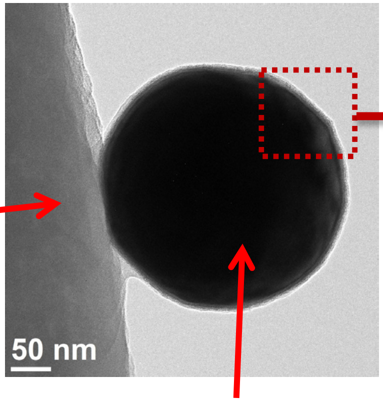
J. Sullivan and **Y. Liu**, *et al.*, in preparation.

Beyond Li-ion batteries

Na-ion batteries

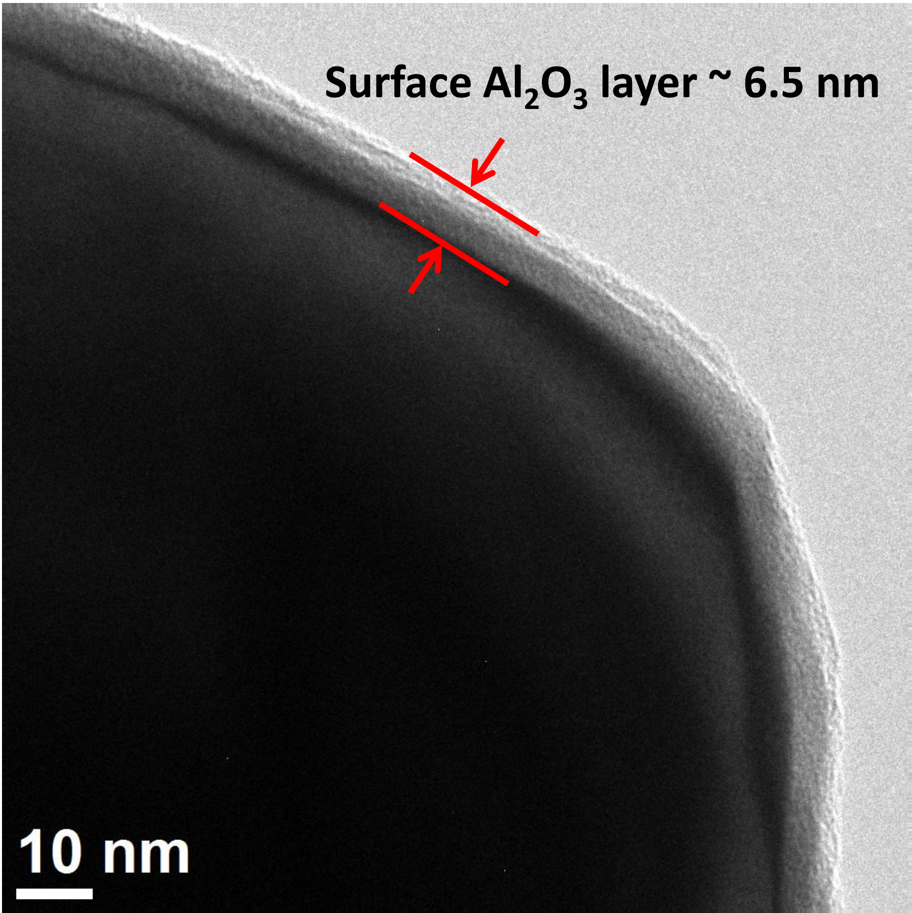
A promising anode material: Sn/ALD-Al_2O_3 on CNF





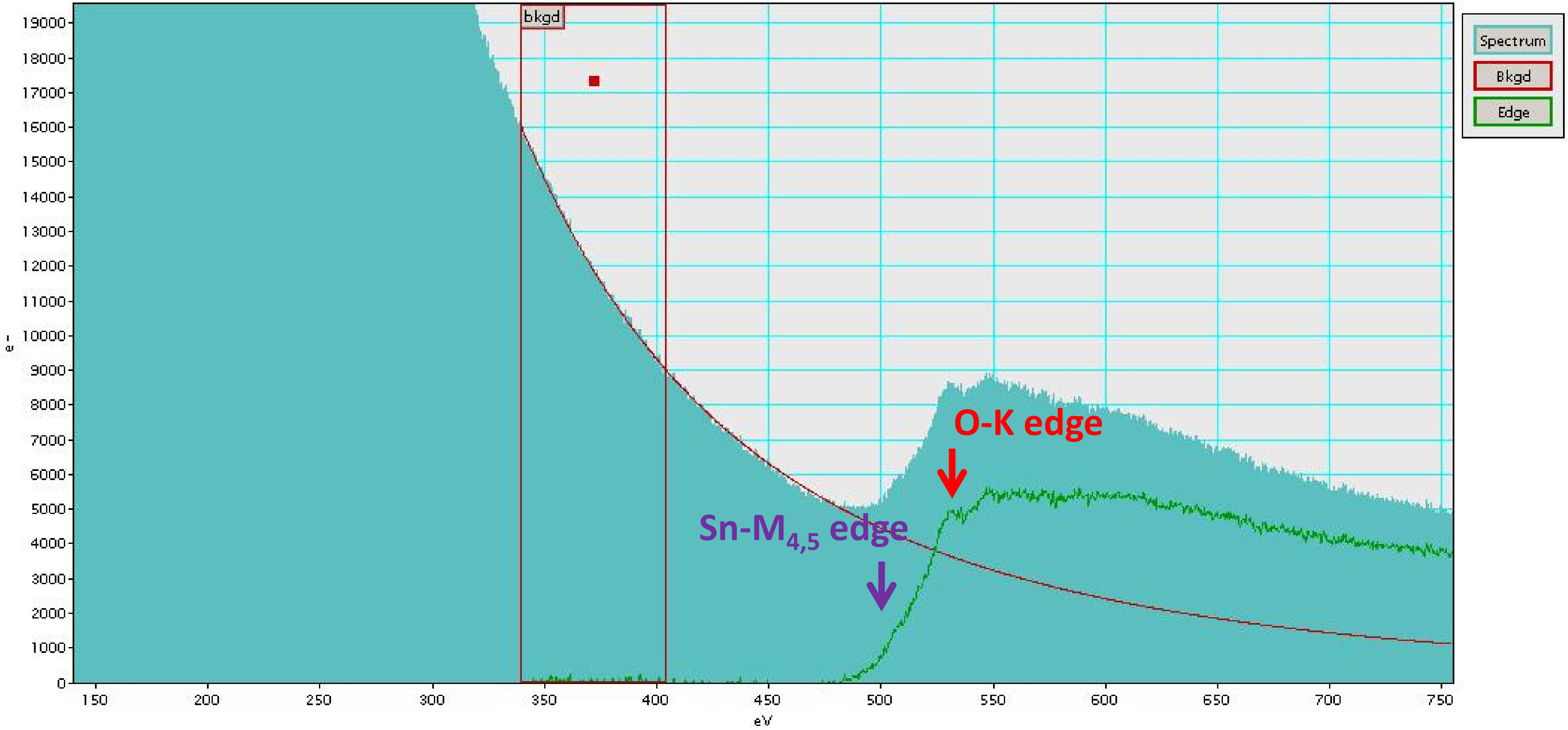
Carbon nanofiber

Sn nanoparticle with ALD-Al_2O_3 coating



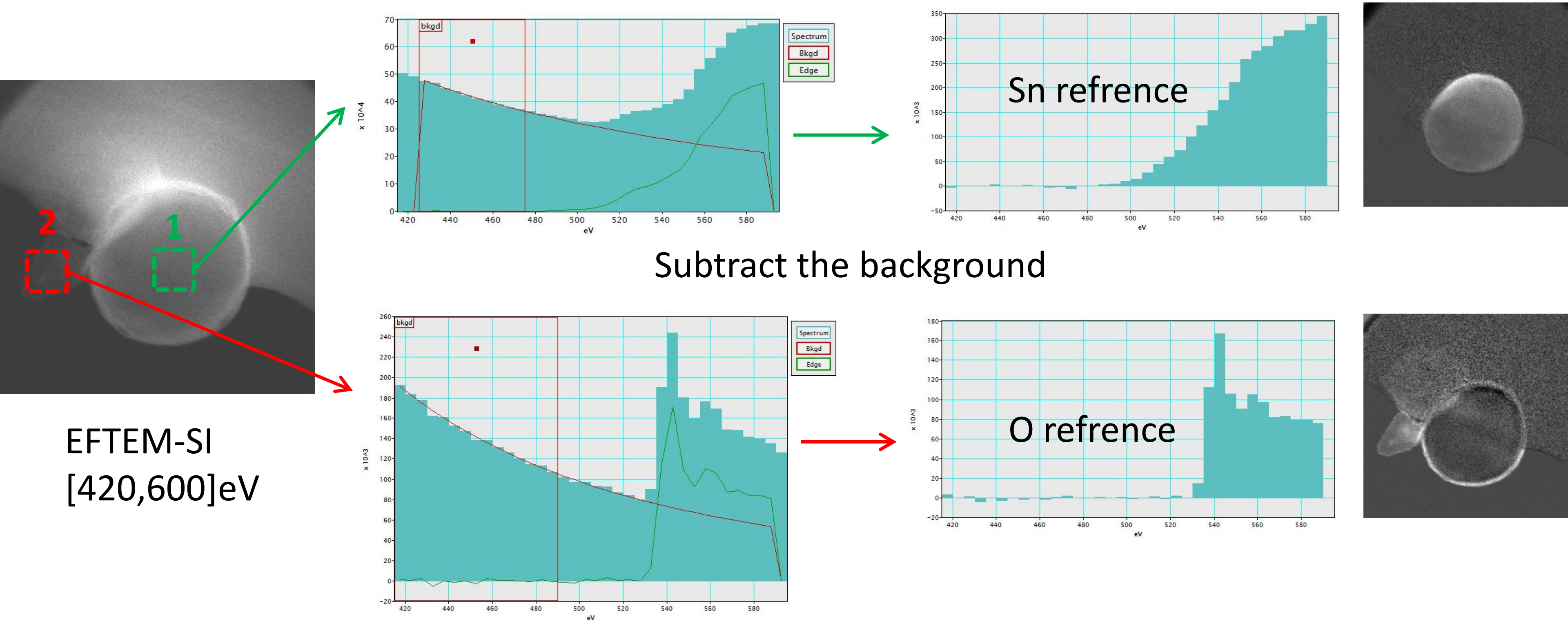
Difficulty in EFTEM mapping

O-K edge is overlapped with the broad Sn-M edge, thus, it is very difficult to do O mapping, due to the difficulty in subtracting the background correctly.



Advanced EELS technique—MLLS mapping

Multiple linear least-squares (MLLS) fitting can be used to fit a number of reference spectra to a spectrum, and thus can separate overlapping edges, do chemical state mapping and orientation mapping.



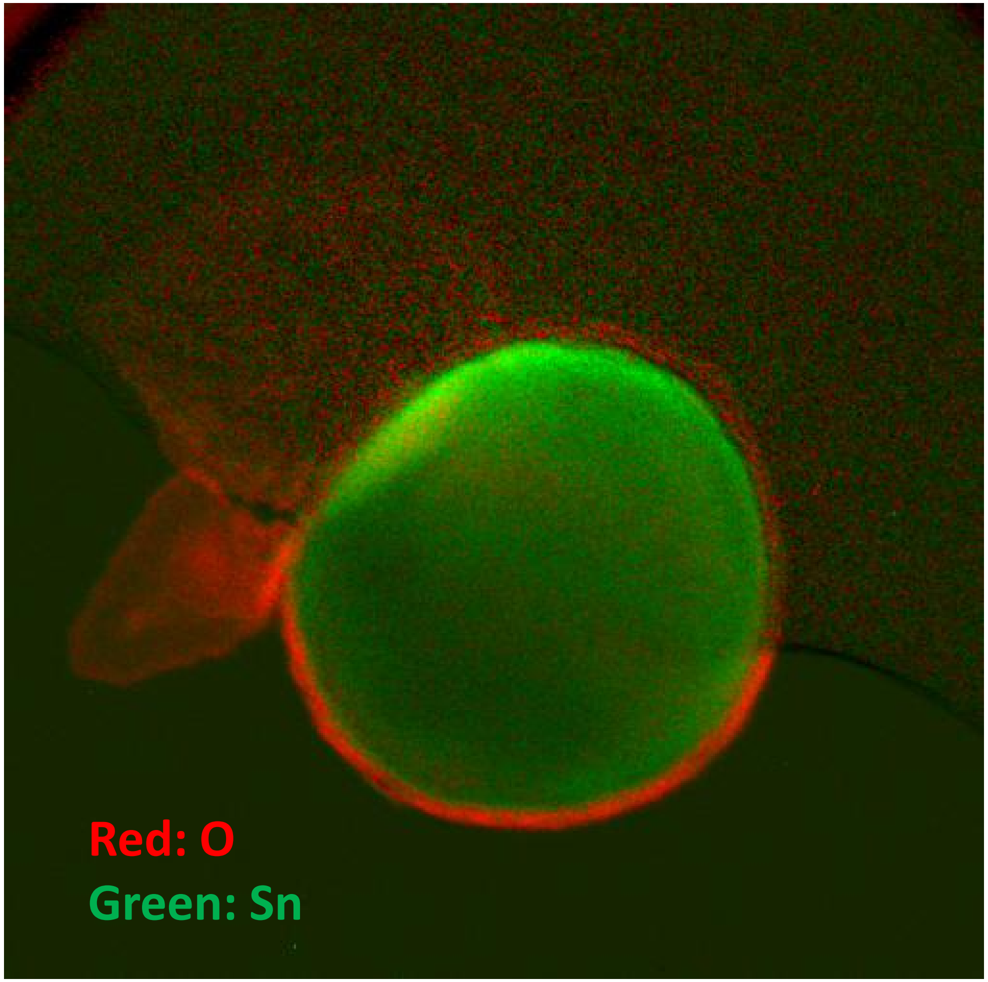
Sn refrence

Subtract the background

O refrence

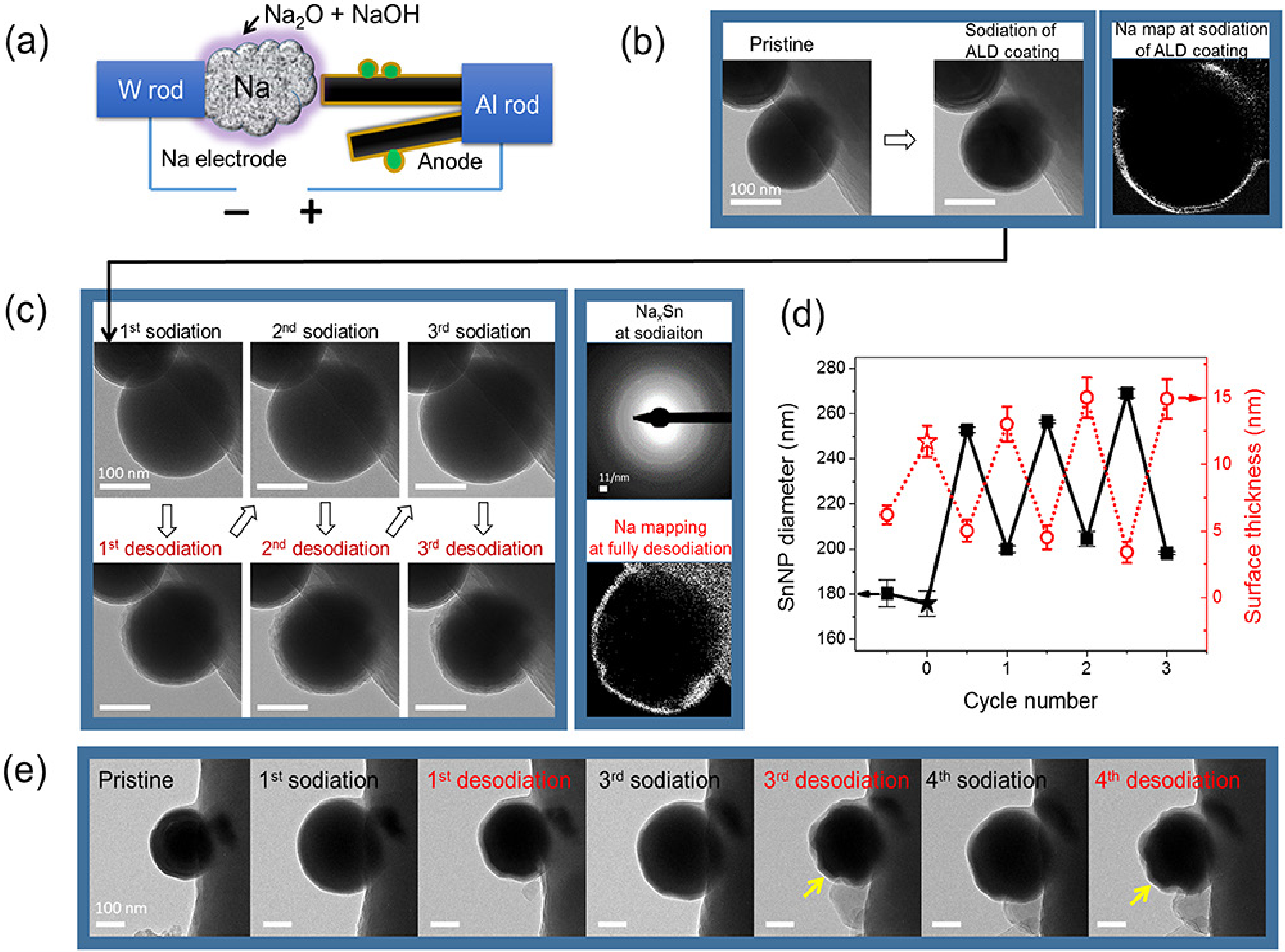
EFTEM-SI
[420,600]eV

MLLS mapping result



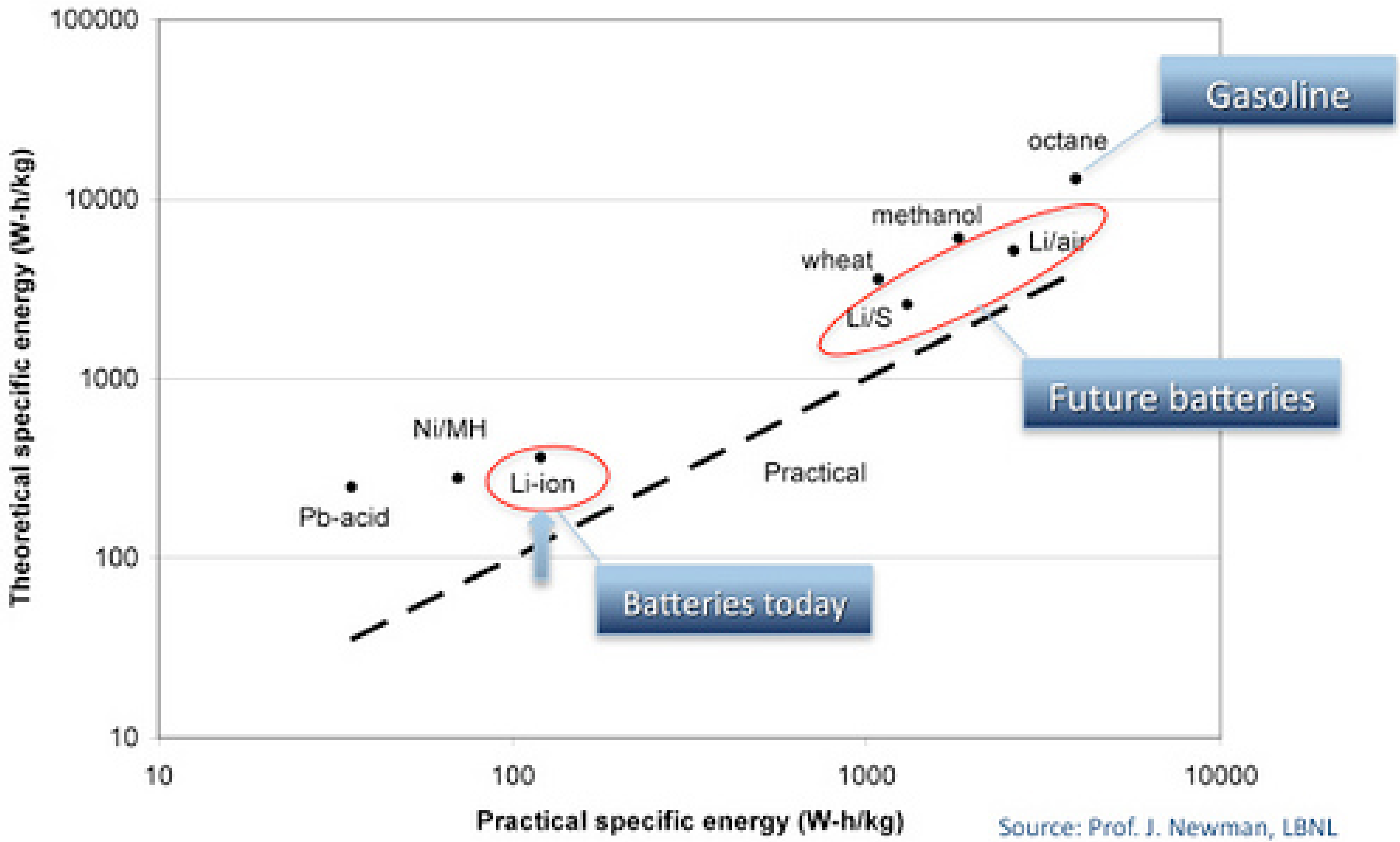
Particular acknowledgement goes to **Paolo Longo** @ Gatan, Inc. for assisting on the **GIF Quantum** when I was at Gatan EELS/EFTEM Training School.

Na-ion batteries



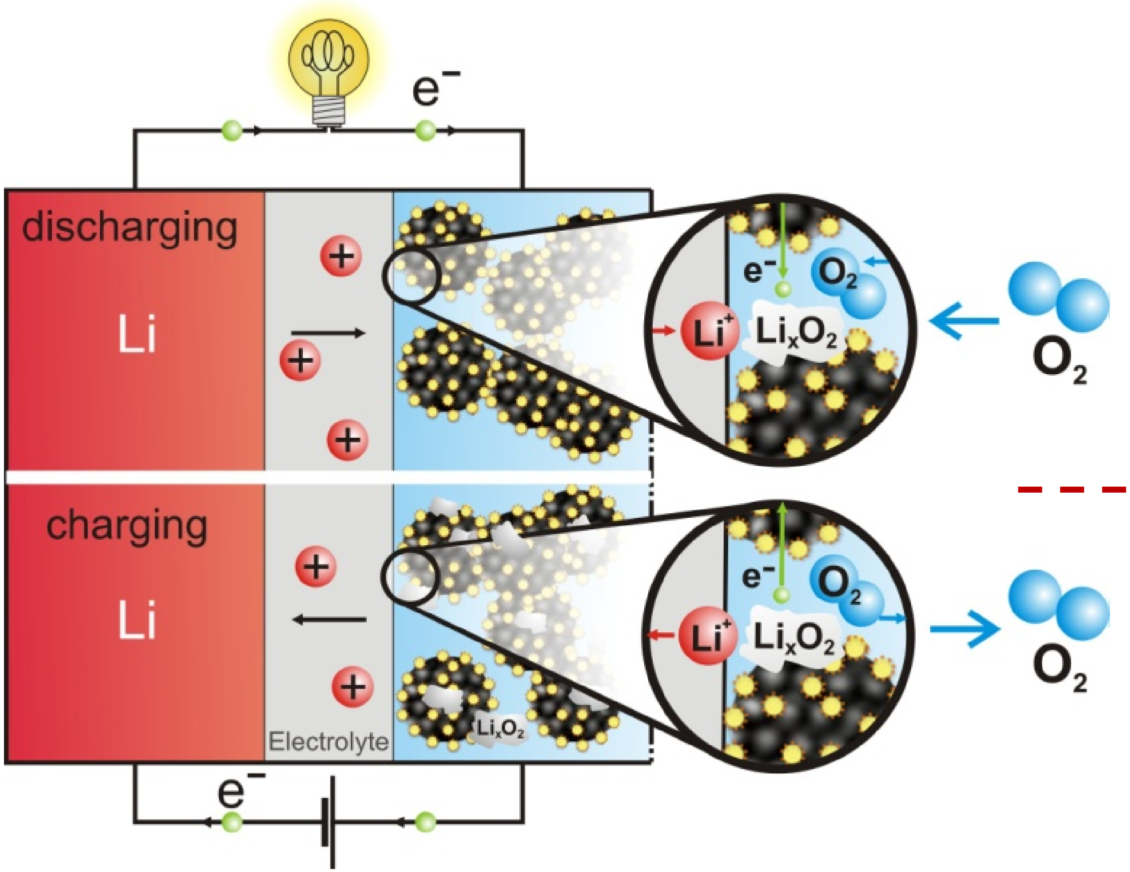
X. Han and **Y. Liu** et al., ***Nano Letters***, DOI: 10.1021/nl4035626

Li-air battery



Source: Prof. J. Newman, LBNL

Li-air battery: Working Principles



Negative electrode

$$2Li \rightarrow 2Li^+ + 2e^-$$

Positive electrode

$$2Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$$

Negative electrode

$$2Li^+ + 2e^- \rightarrow 2Li$$

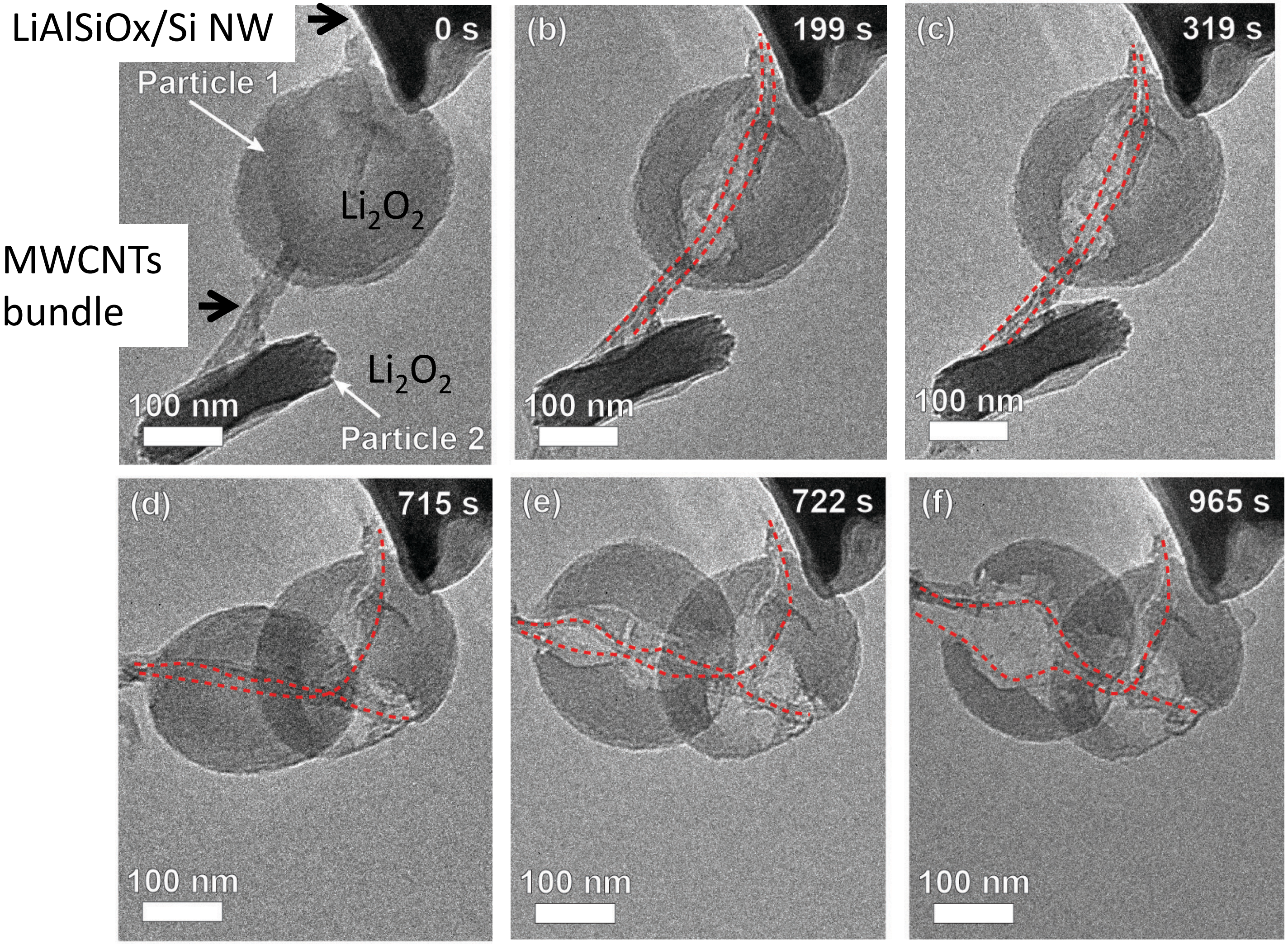
Positive electrode

$$Li_2O_2 \rightarrow 2Li^+ + 2e^- + O_2$$

Reverse electrochemical reaction at equilibrium potential of 2.96 V: $2Li + O_2 \leftrightarrow Li_2O_2$

Y.-C. Lu et al., ***Energy Environ. Sci.***, 6, 750 (2013)

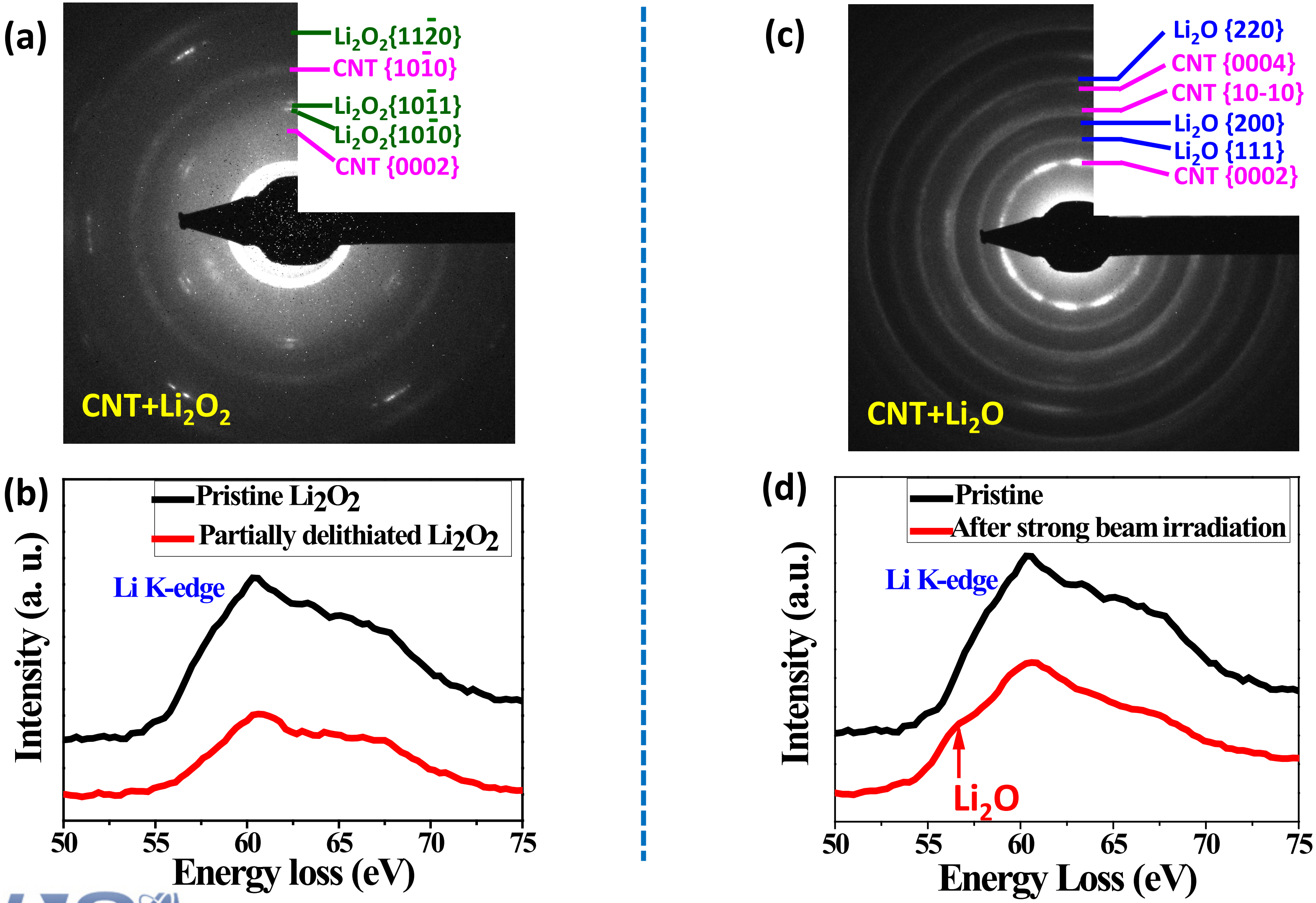
Electrochemical oxidation of Li_2O_2 on MWCNTs



Summary:
The oxidation of Li_2O_2 was found to occur preferentially at the MWCNT/ Li_2O_2 interface, which suggests that electron transport, not the transport of Li-ions, in Li_2O_2 ultimately limits the oxidation kinetics at high rate or overpotentials.

L. Zhong, R. Mitchell and **Y. Liu** et al., ***Nano Letters***, 13, 2209 (2013)

The first EELS reference for Li_2O_2



L. Zhong, R. Mitchell and **Y. Liu** et al., ***Nano Letters***, 13, 2209 (2013)

Conclusions and Perspective

- Constructed electrochemical cell inside a TEM, allowing for real time and atomic scale observations of battery electrode during operation.
- “Saw” the effect of ion and electron transport, provided fundamental understandings of the working and degradation mechanisms in LIBs.
- Controlled the ionic transport behavior in the nanoscale.
- Be able to study almost all kinds of material systems, anodes, cathodes, different electrolytes…
- How the ALD coating retains capacity? In-situ SEI formation.
- Quantitative electrochemistry on individual nanostructure.
- Beyond Li-ion batteries, such as Li-S, Li-air, Na-ion, Mg-ion systems.

Acknowledgments

I would like to offer my high appreciation to all my collaborators:

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Dr. Sergiy Krylyuk, Dr. Albert Davydov, **…** **National Institute of Standards and Technology**

Prof. Ting Zhu, Prof. Gleb Yushin, **…** **Georgia Institute of Technology**

Prof. Gary Rubloff, Prof. Chunsheng Wang, Prof. Liangbing Hu, Prof. YuHuang Wang, Prof. John Cumings,**…** **University of Maryland**

Dr. Akihiro Kushima, Prof. Ju Li, Prof. Yang Shao-Horn, **…** **MIT**

Prof. Sulin Zhang**…** **Pennsylvania State University**

Prof. Shadi Dayeh, **…** **UC-San Diego**

Prof. Jane Chang, **…** **UC-Los Angeles**

Prof. Scott Mao, **…** **University of Pittsburgh**

Prof. Wenzhi Li, **…** **Florida International University**

Prof. Ronggui Yang, **…** **University of Colorado Boulder**

Prof. Yoke-Khin Yap, **…** **Michigan technological university**

Prof. Barry Carter, **…** **University of Connecticut**

…

Acknowledgments

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY Office of Science

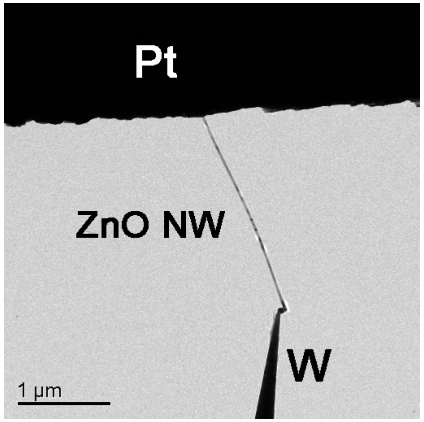
NEES
NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE

Center for Integrated Nanotechnologies
CINT
DISCOVERY PERFORMANCE EDUCATION INTEGRATION
Sandia Los Alamos

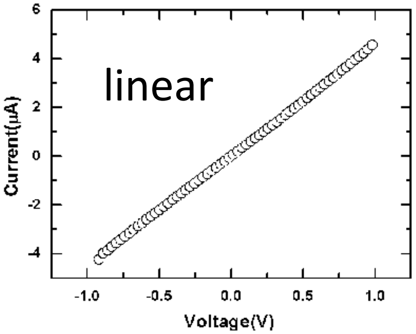
Thank you very much for your attention!

Back up slides

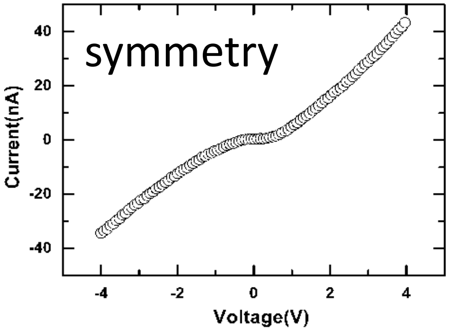
Model required

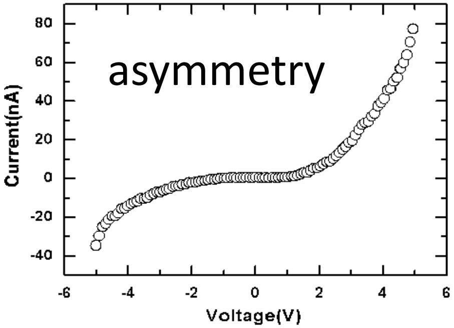


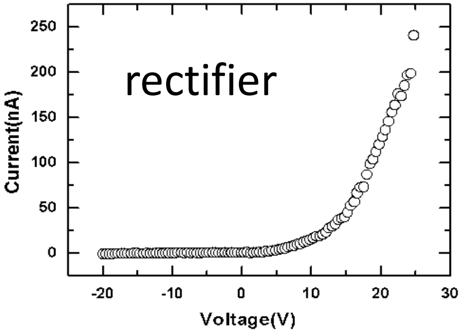
Two terminal
I-V curves



nonlinear

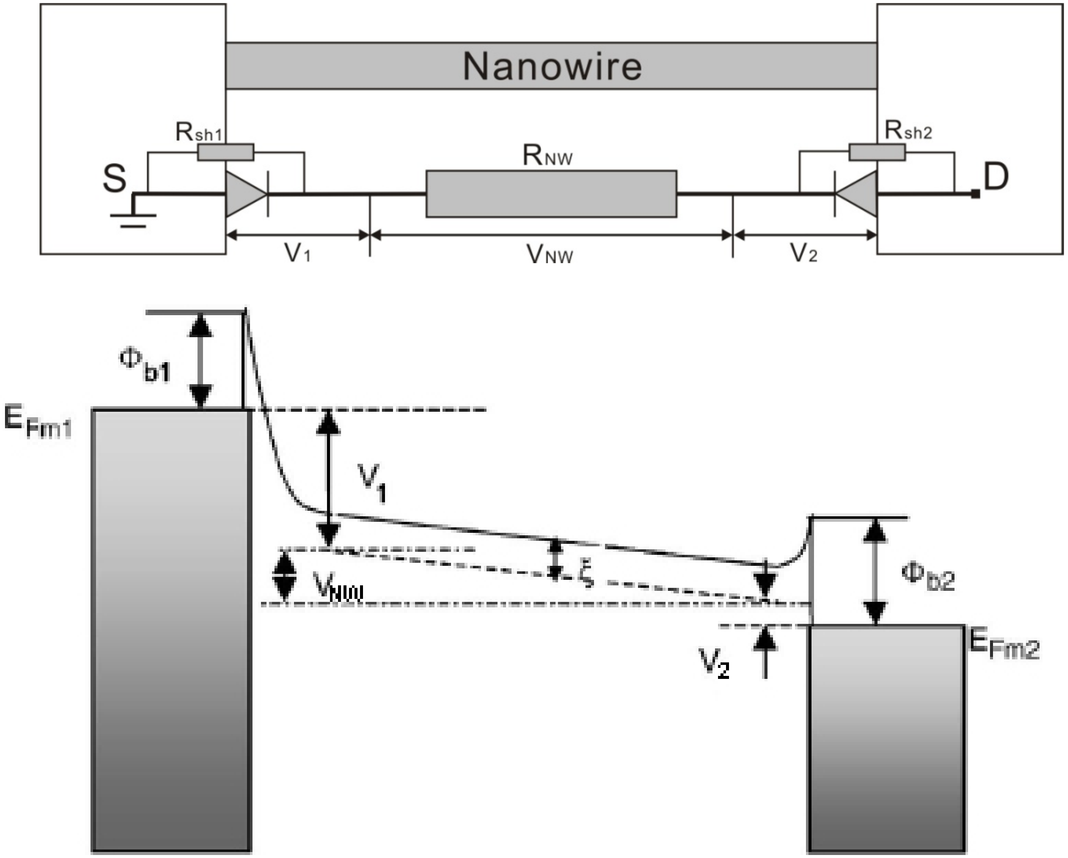






Decoupling the contact effect (Schottky barrier) and giving the intrinsic parameters (carrier concentration, mobility, conductivity) of the nanomaterials.

Metal-Semiconductor-Metal (MSM) model



$$I_1 = S_1 J_r(V_1) + V_1/R_{sh1}$$

$$I_2 = S_2 J_f(V_2) + V_2/R_{sh2}$$

$$I_{NW} = V_{NW} / R_{NW}$$

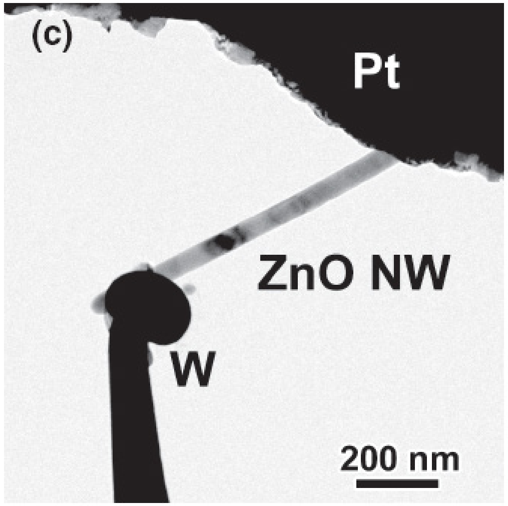
$$I_1 = I_2 = I_{NW}$$

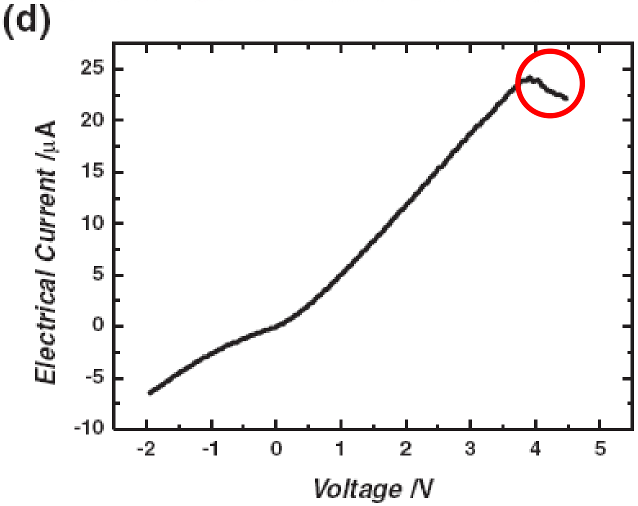
$$V = V_1 + V_2 + V_{NW}$$

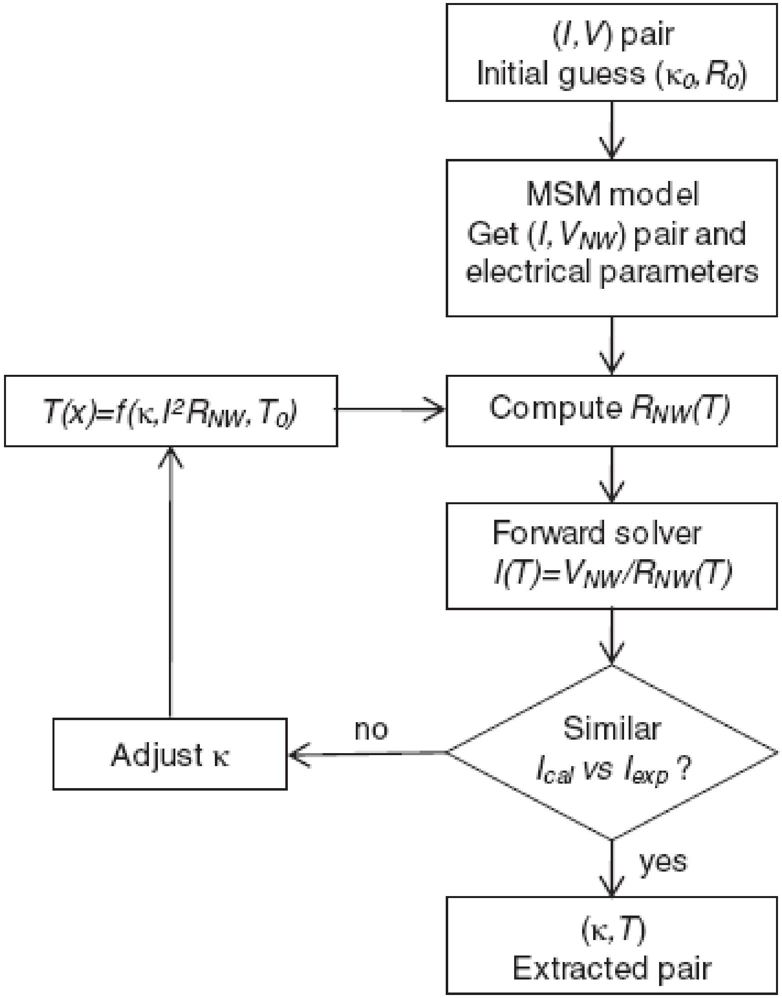
Given the parameters of nanowire and contacts, an unique current can be calculated under a bias.
Reversely, given the I-V curve, the parameters of nanowire and contacts can be obtained by fitting the I-V curve.

Z.Y. Zhang et al., ***Appl. Phys. Lett***. 88, 073102 (2006)
Z.Y. Zhang, **Y. Liu** et al., ***Adv. Func. Mater***. 17, 2478 (2007)

Thermoelectric properties of ZnO nanowire







(I, V) pair
Initial guess (κ_0, R_0)

MSM model
Get (I, V_{NW}) pair and electrical parameters

Compute $R_{NW}(T)$

$T(x)=f(\kappa, I^2R_{NW}, T_0)$

Forward solver
$I(T)=V_{NW}/R_{NW}(T)$

Similar
I_{cal} vs I_{exp} ?

no

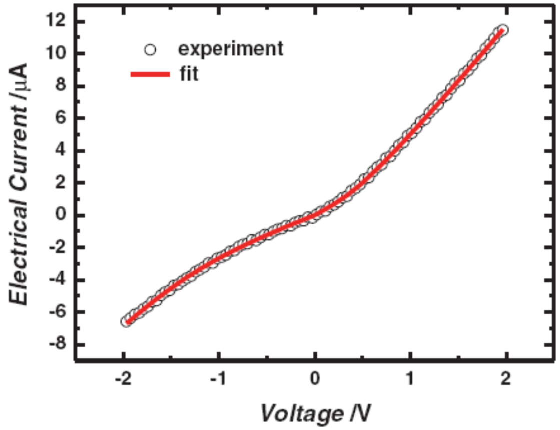
Adjust κ

yes

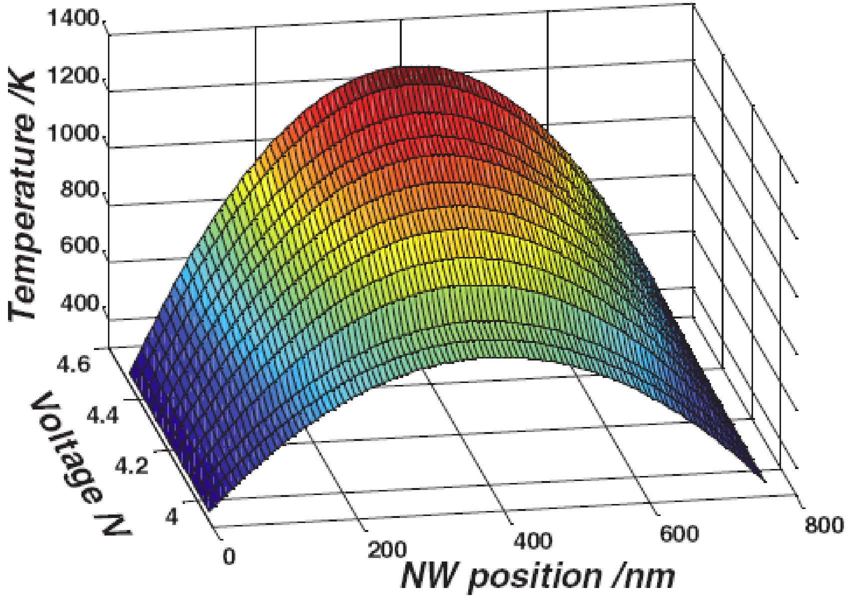
(κ, T)
Extracted pair

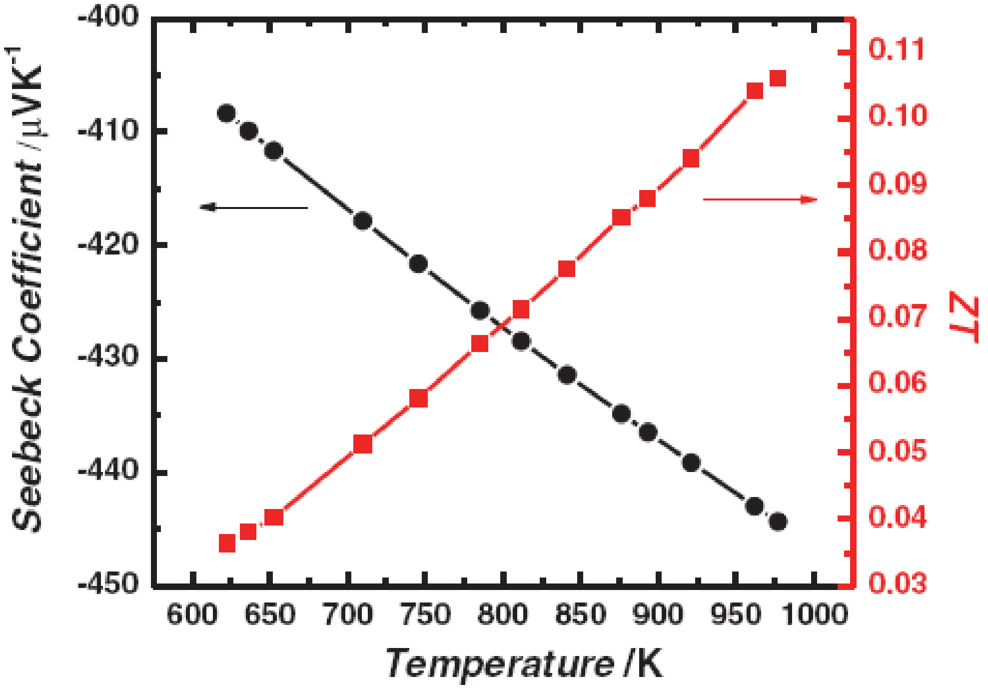
<u>Y. Liu</u> et al., ***Adv. Func. Mater***. 21, 3900 (2011)

Thermoelectric properties of ZnO nanowire



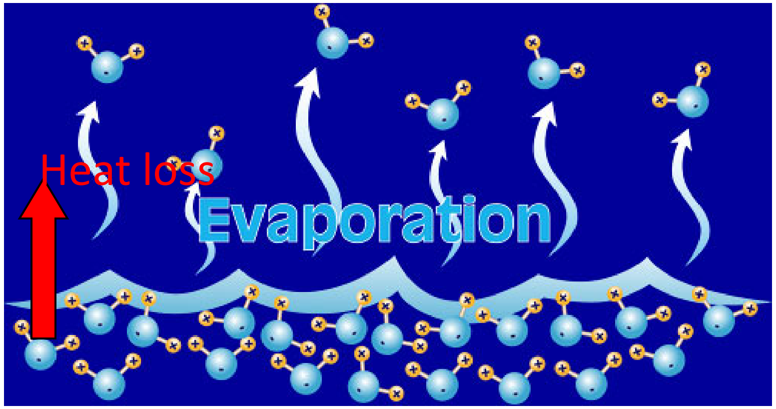
ϕ_1 [eV]	ϕ_2 [eV]	σ [Sm^{-1}]	N_d [cm^{-3}]	μ [$cm^2V^{-1}s^{-1}$]
0.19	0.36	3.19×10^3	1.27×10^{18}	157



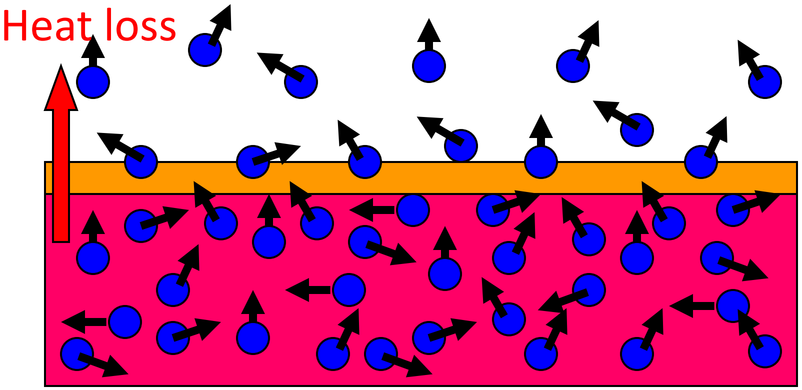


Y. Liu et al., ***Adv. Func. Mater***. 21, 3900 (2011)

Cooling Effect



Water evaporation



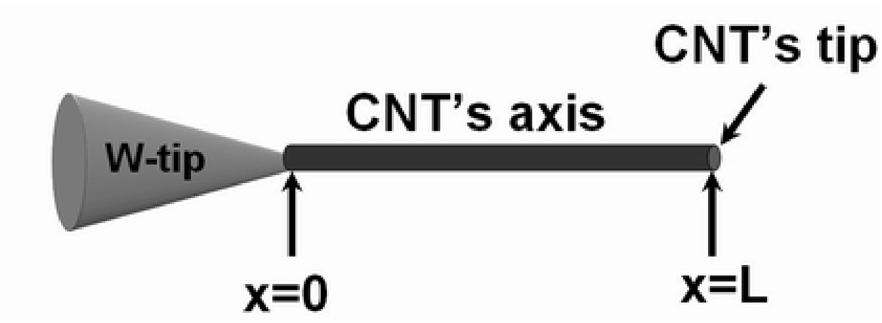
Thermionic emission

CNT field emission

$$E_0 = \frac{3}{2} k_B T$$

● electron

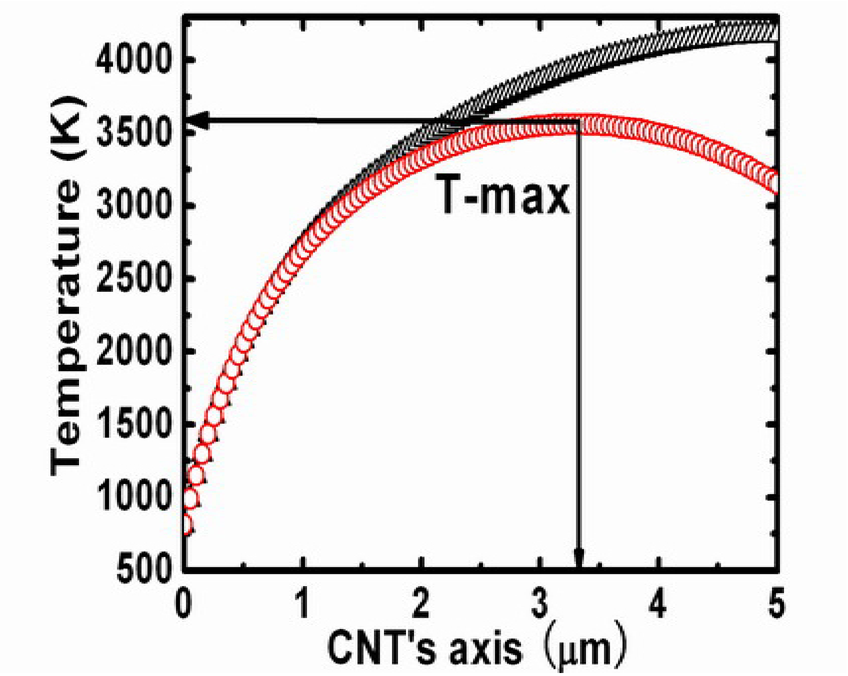
Model and Numerical calculation



$$\pi r^2 \kappa \frac{\partial^2 T_x}{\partial x^2}\,\mathrm{d}x - 2\pi r\,\mathrm{d}x\,\sigma(T_x{}^4 - T_0{}^4) + \frac{I^2\rho(T_x)}{\pi r^2}\,\mathrm{d}x = 0$$

$$T_{x=0} = \lambda \pi r^2 \kappa \left.\frac{\partial T_x}{\partial x}\right|_{x=0} + T_0$$

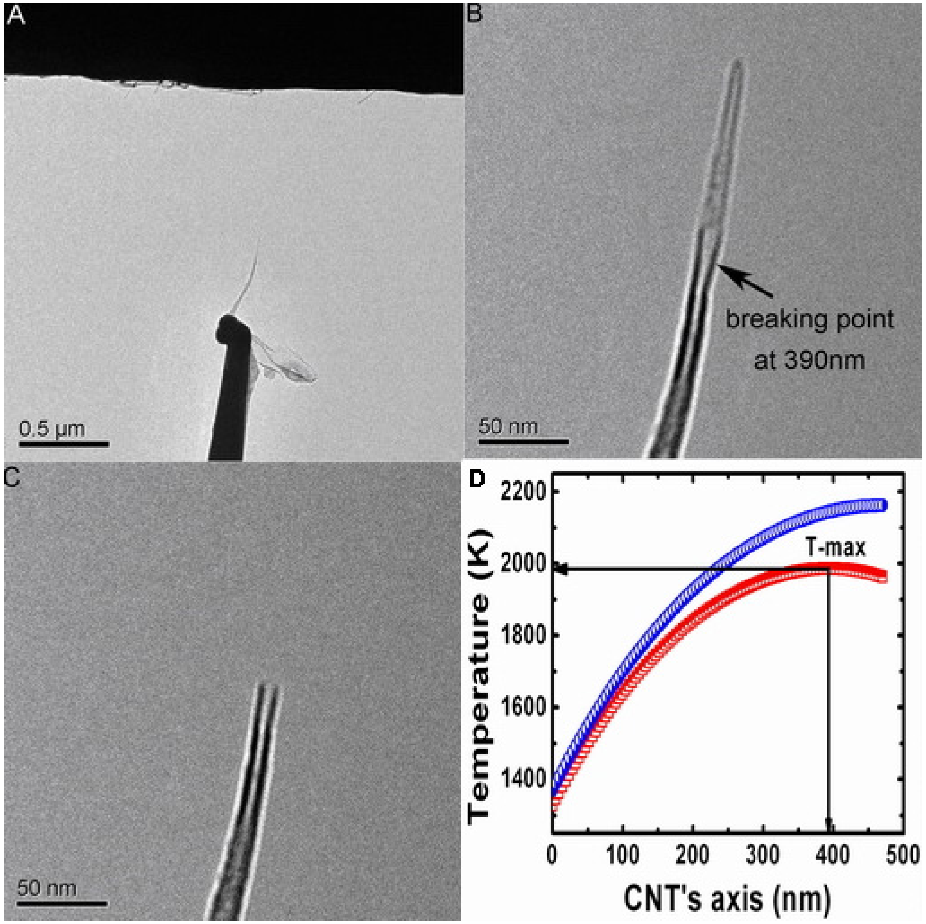
$$\left.\frac{\partial T_x}{\partial x}\right|_{x=L} = -\sigma\kappa^{-1}(T_{x=L}{}^4 - T_0{}^4) - \frac{3}{2}\kappa^{-1}\frac{k_B T_{x=L} I}{e\pi r^2}$$



L=5 μm D=10nm I=10 μA

The maximum temperature T_{max} point is not at the tip, but in the body!

Field emission mechanism of carbon nanotubes



$$I_{\max}(FE) \approx 35\mu A$$
$$< I_{\max}(TT) \approx 81\mu A$$

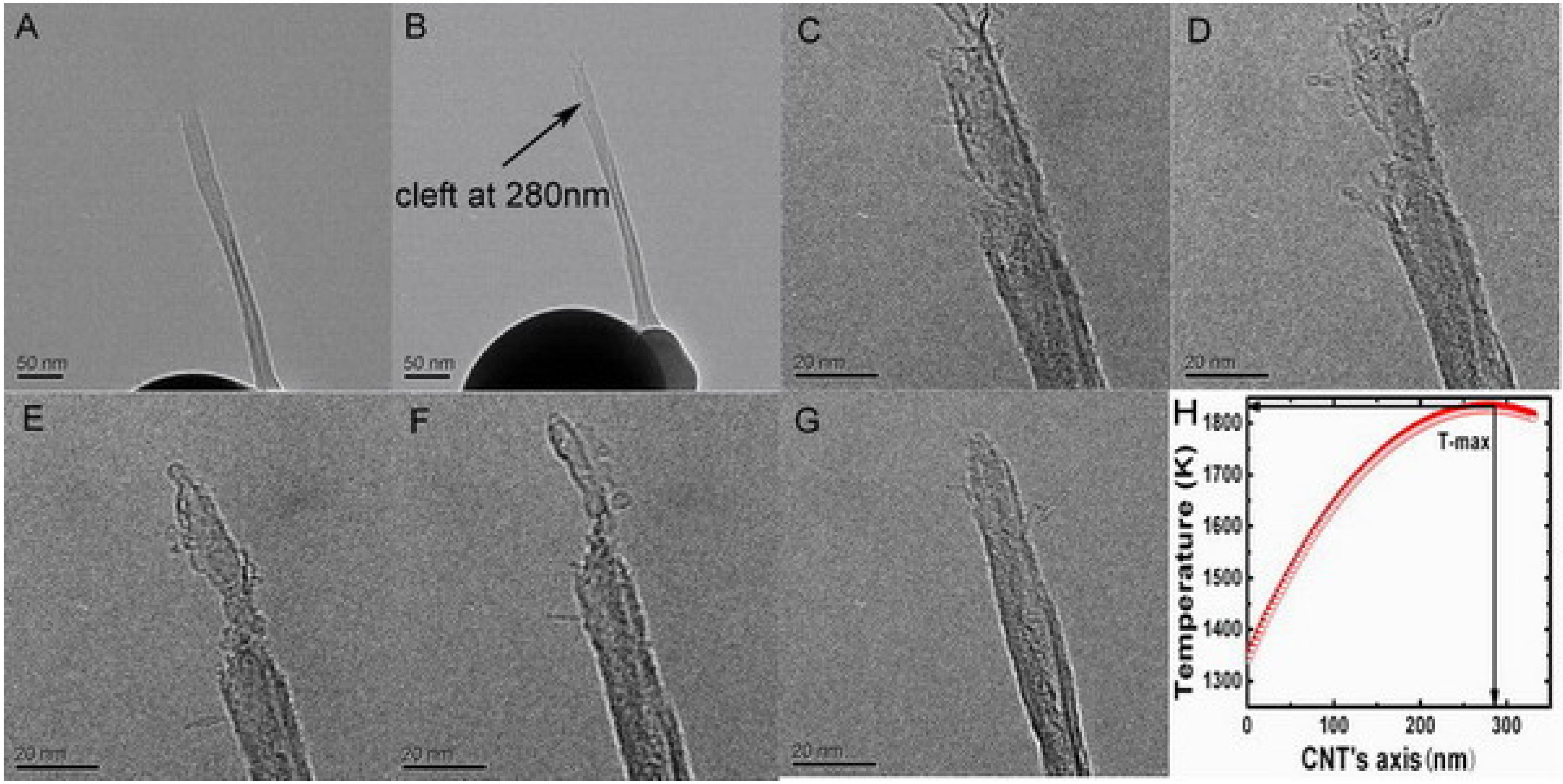
$$T_{\max}(FE) \approx 2000K$$
$$< T_{\max}(TT) \approx 3400K$$

Electrostatic Force Stress~ 3.9 GPa
< Tensile Stress ~ 11-63 GPa

Combination of Temperature-effect and Force-effect

Breaking point is at 390 nm
T_{max} point predicted by the model is at 394.8 nm

Field emission mechanism of carbon nanotubes



Breaking point is at 280 nm
T_{max} point predicted by the model is at 283.8 nm

W. Wei and **Y. Liu** et al., ***Nano Letters***, 7, 64 (2007)

The model used to estimate the chemical potential on Ge/Si nanowire

To rationalize the effects of the Si shell on Ge nanowire lithiation, we refer to the analogy of chemical potential barriers for impurity – Li ion – diffusion with that of chemical potential barriers for free charge carrier transport.

The effective potential for ions or defects at heterointerfaces is considered by moving the ion in the material by two steps: (1) moving the impurity across the interface, and (2) ionizing the impurity and returning the electron or hole to the starting position.

$$\mu_{eff} = H_M^0 + I_M - \left(E_M^c - \tilde{\mu}_M\right)$$

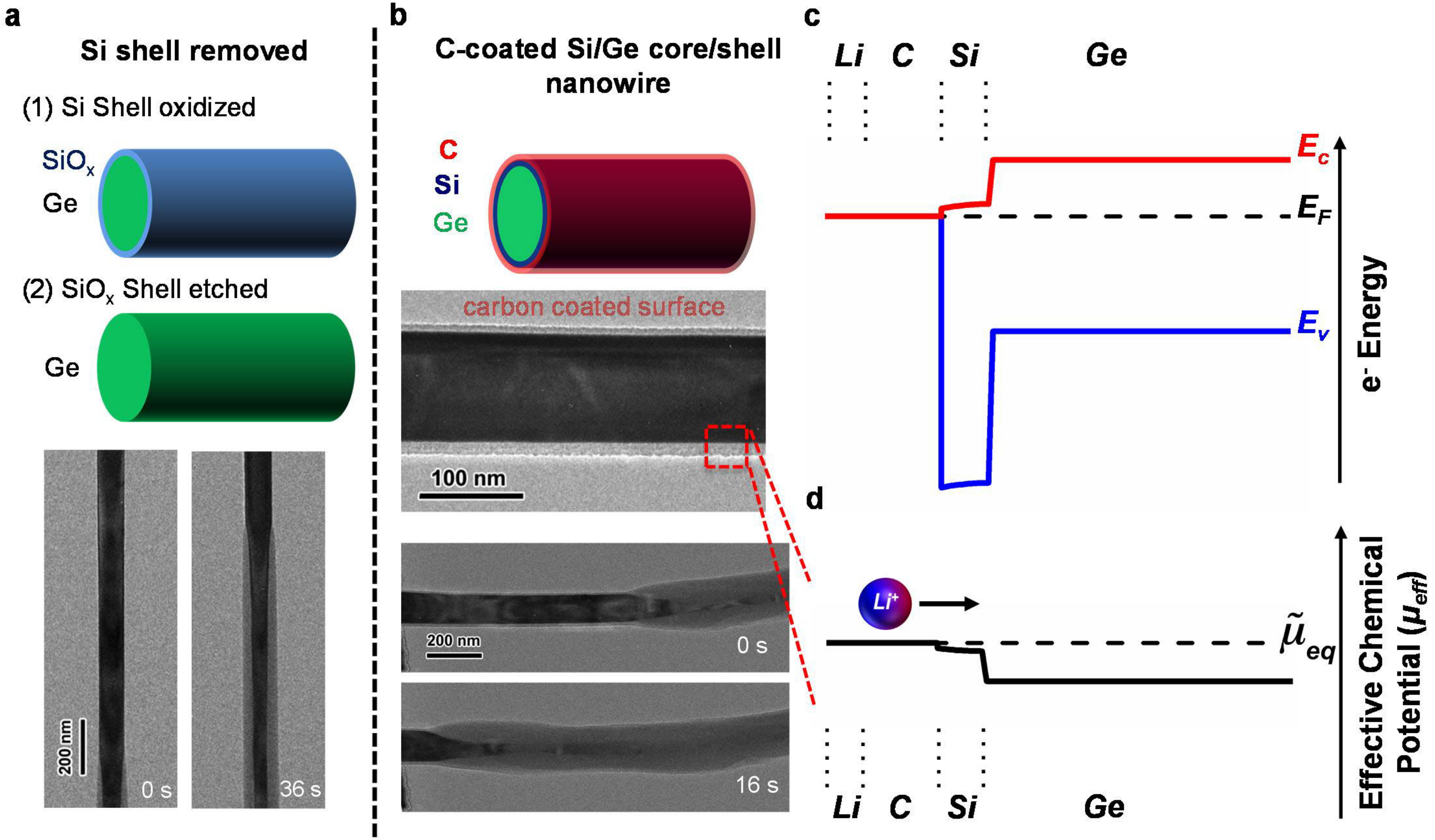
μ_{eff} is the corresponding effective potential for a Li ion,
M is either Si or Ge,
H_M^0 is the enthalpy of formation of the neutral Li defect site in M,
I_M is the ionization energy for Li ion in M,
E_M^c is the conduction band edge in M,
$\tilde{\mu}_M$ is the equilibrium electro-chemical potential across the whole structure.

J. Tersoff, J. ***Phys. Rev. Lett***. 65 (7), 887−890 (1990).

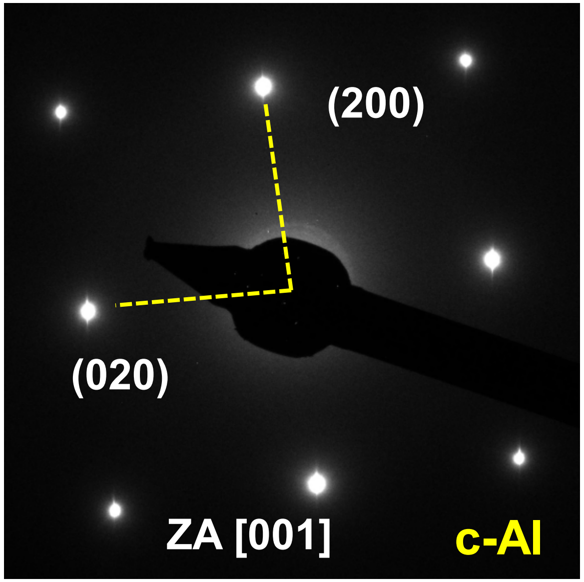
J. Maier et al, ***Nature Materials*** 4, 805 (2005)

Control experiments under different scenarios

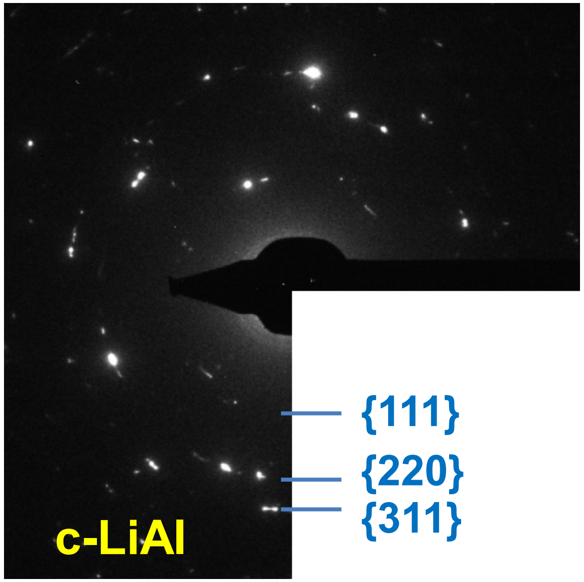
The equilibrium band-edge profiles across Ge/Si/C core/multi-shells nanowire, showing a chemical potential well for Li ions, which is therefore expected to accelerate the lithiation reaction at the surface of the nanowire, resulting in core-shell lithiation behavior, as shown in (b).



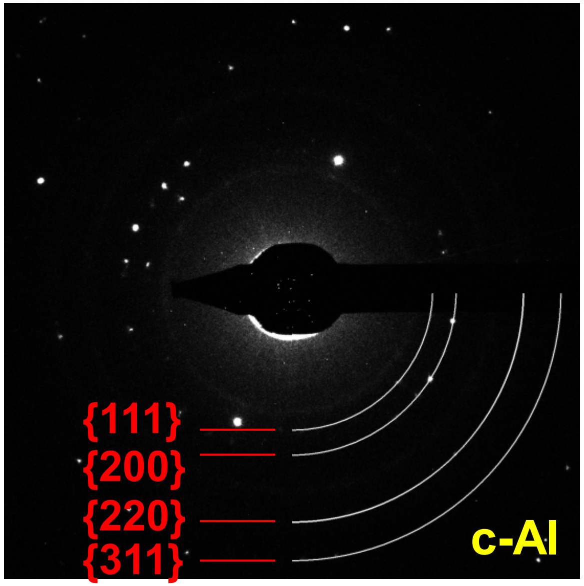
Lithiated phase of Aluminum Nanowires



Pristine Al NW



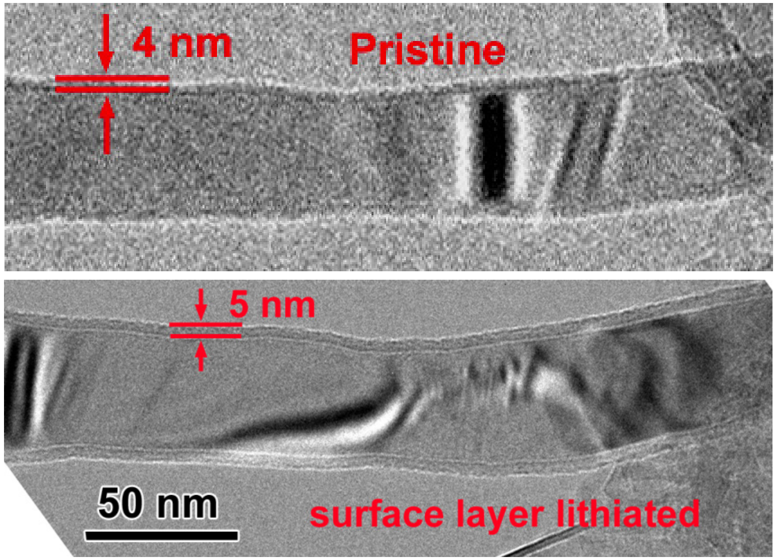
Lithiated Al NW

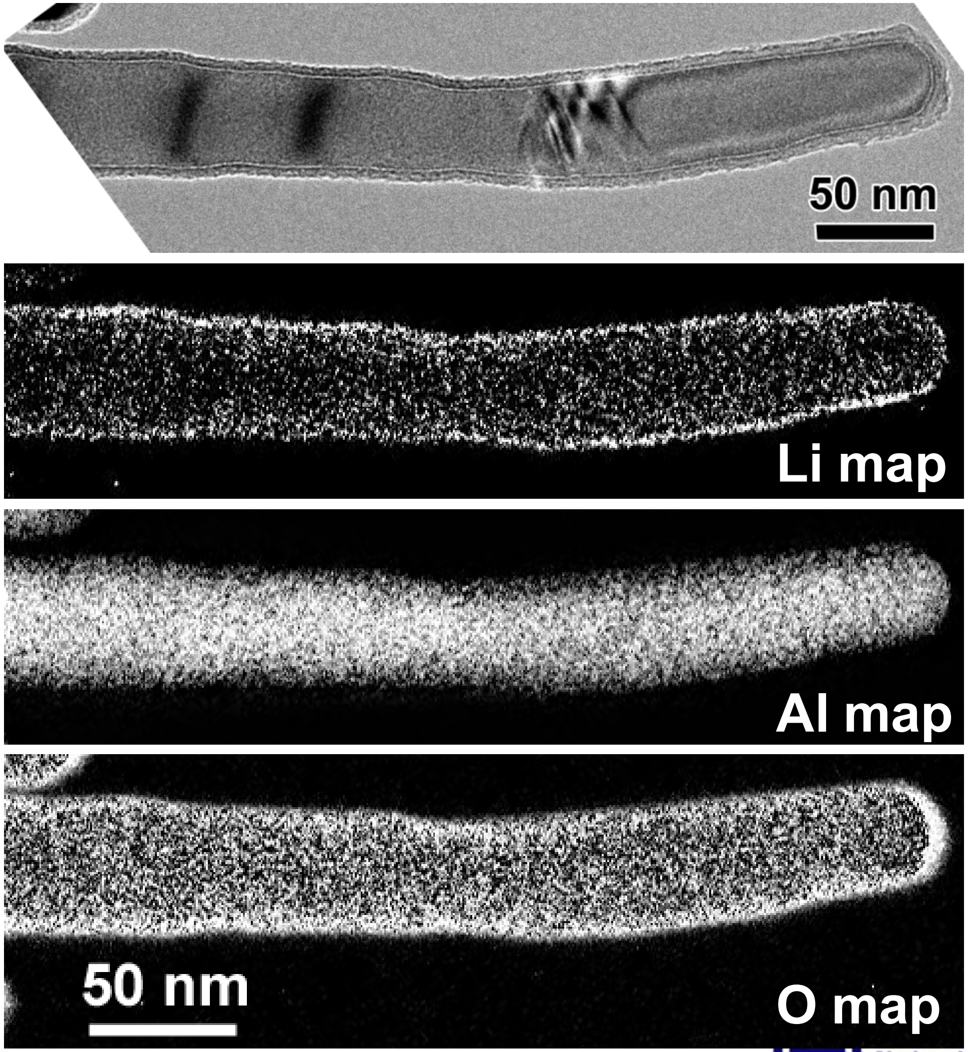


Delithiated Al NW

Electrochemically driven solid state amorphization (ESA) did not occur in the LiAl system.

Evolution of the Thin Surface Al_2O_3 Layers

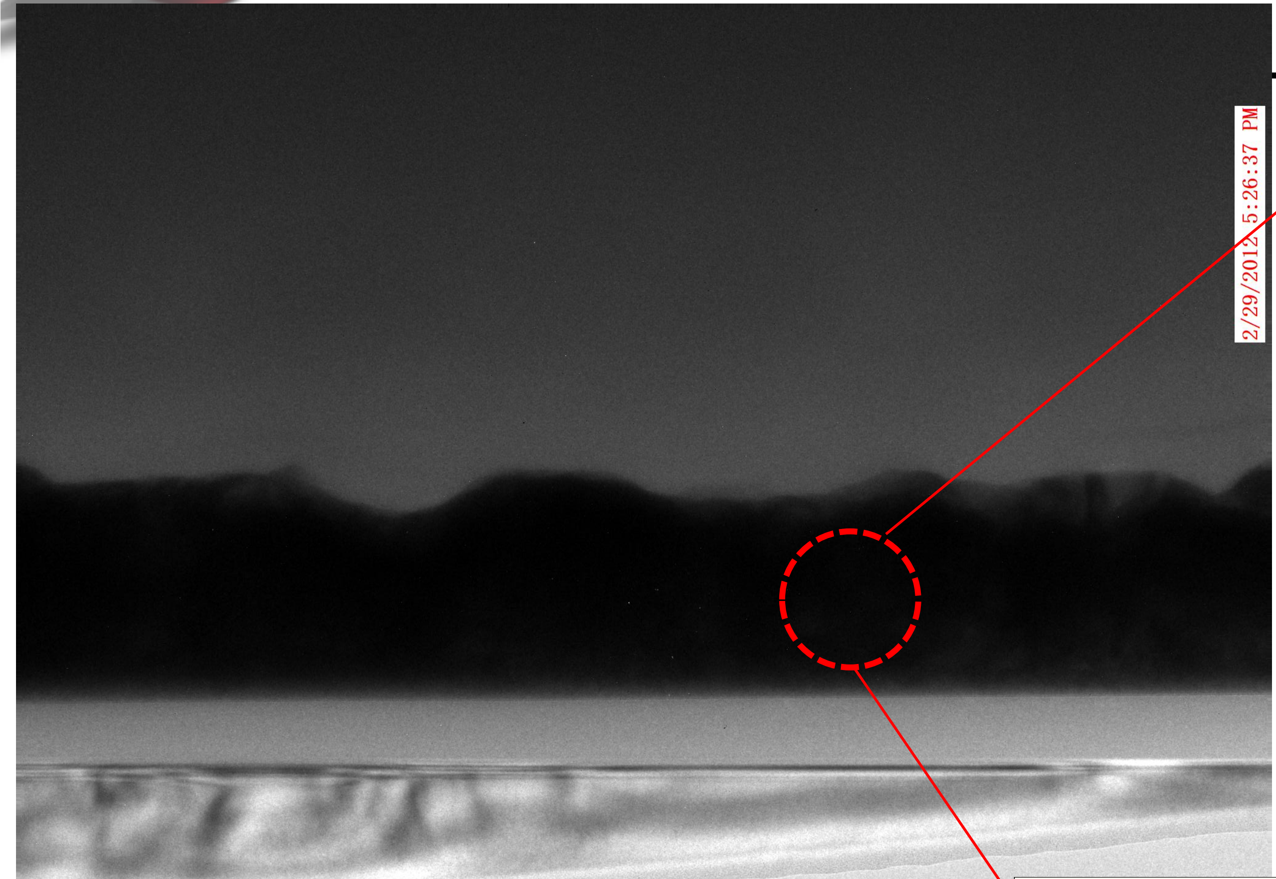


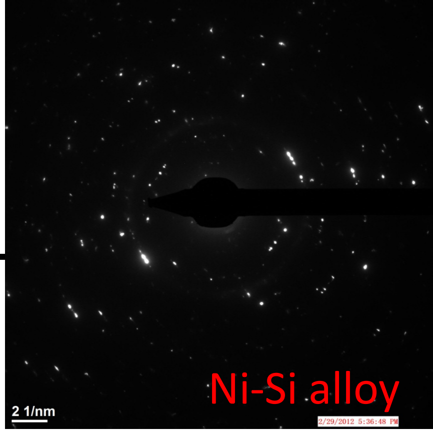


Controlled lithiation of the surface Al_2O_3 Layer

Al_2O_3 Layer was changed into Li-Al-O glass.

Cross-section on Ni-Si alloying





EDP

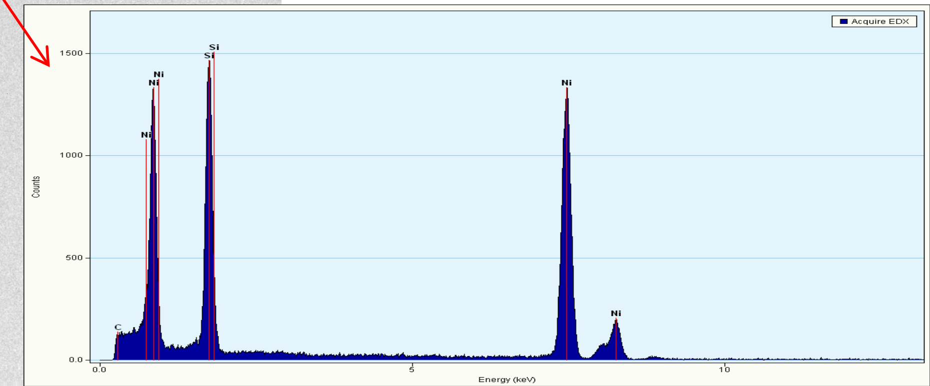
50 um Si

~400 nm Si-Ni alloy

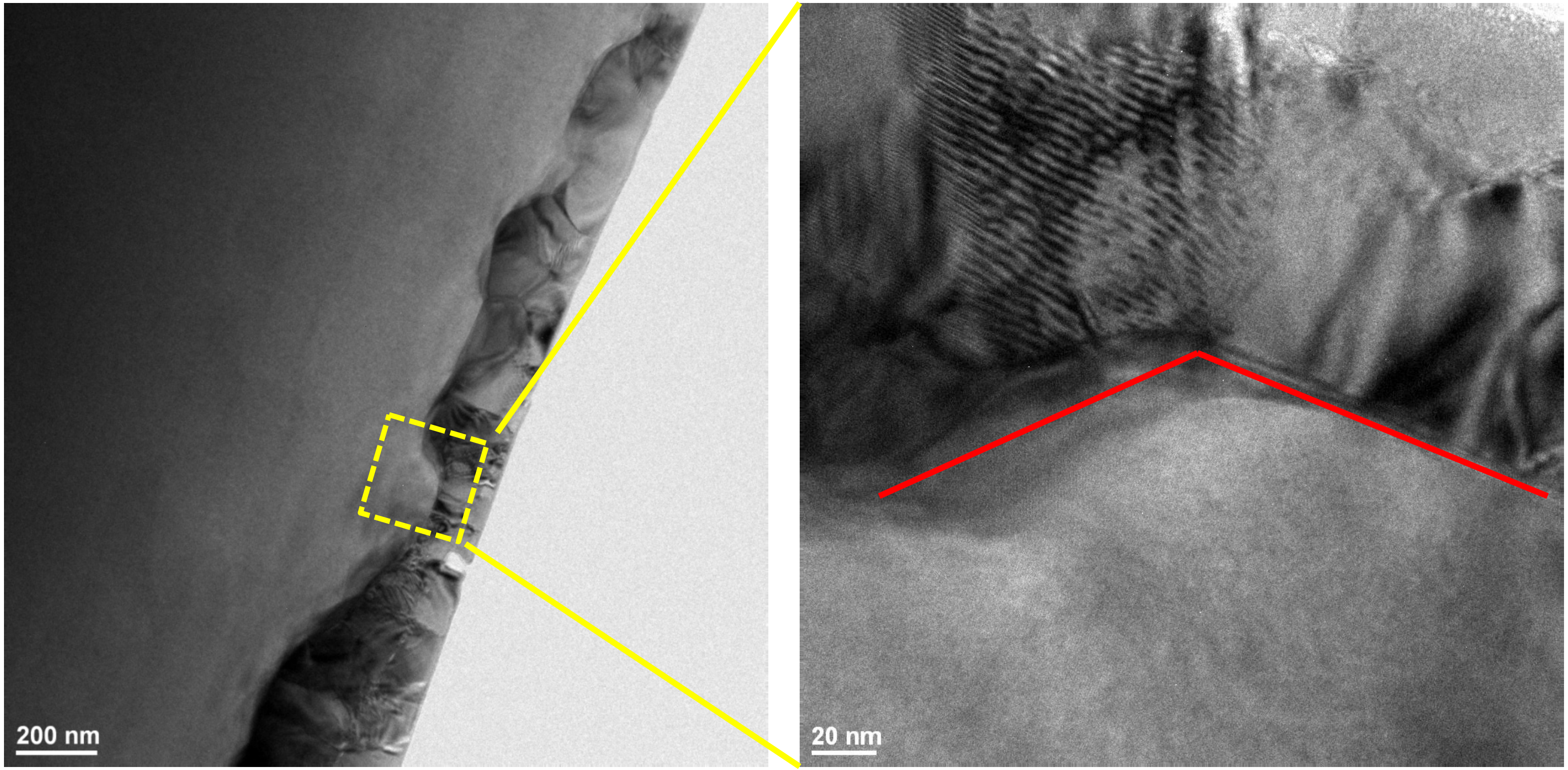
200 nm SiO_2

Bulk Si substrate

EDX

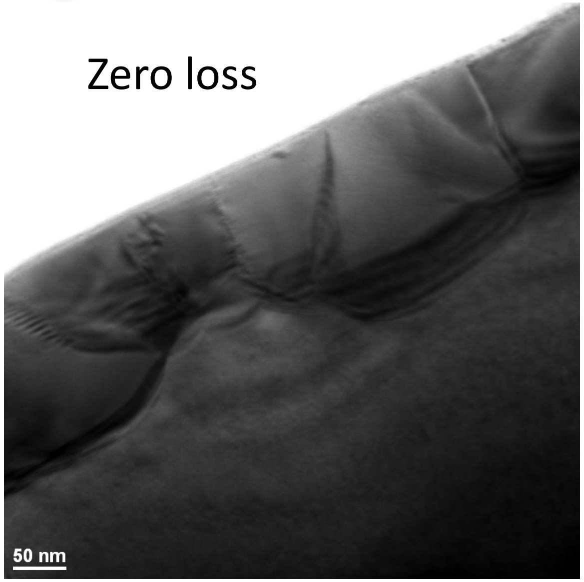


Cross-section on Ni-Si alloying

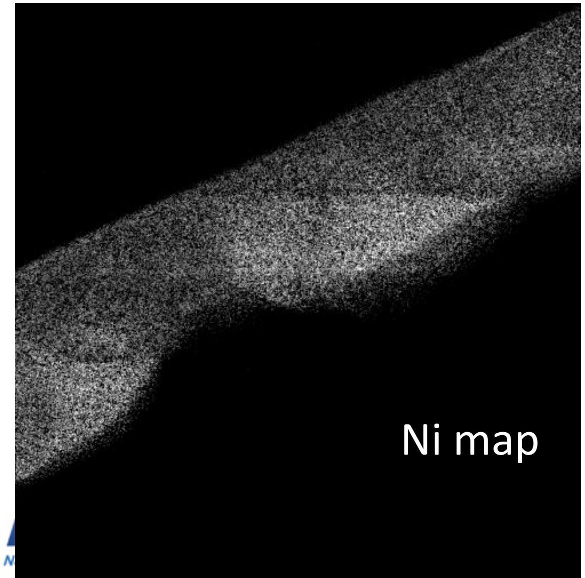


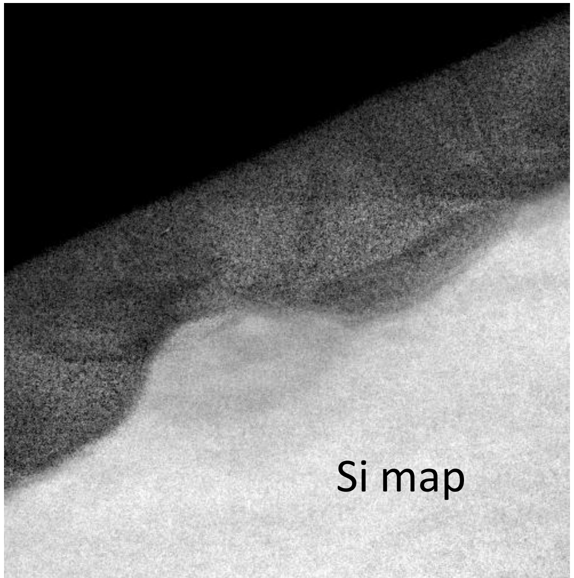
Collaborated with Prof. Shadi Dayeh @ UCSD

Cross-section on Ni-Si alloying


Zero loss

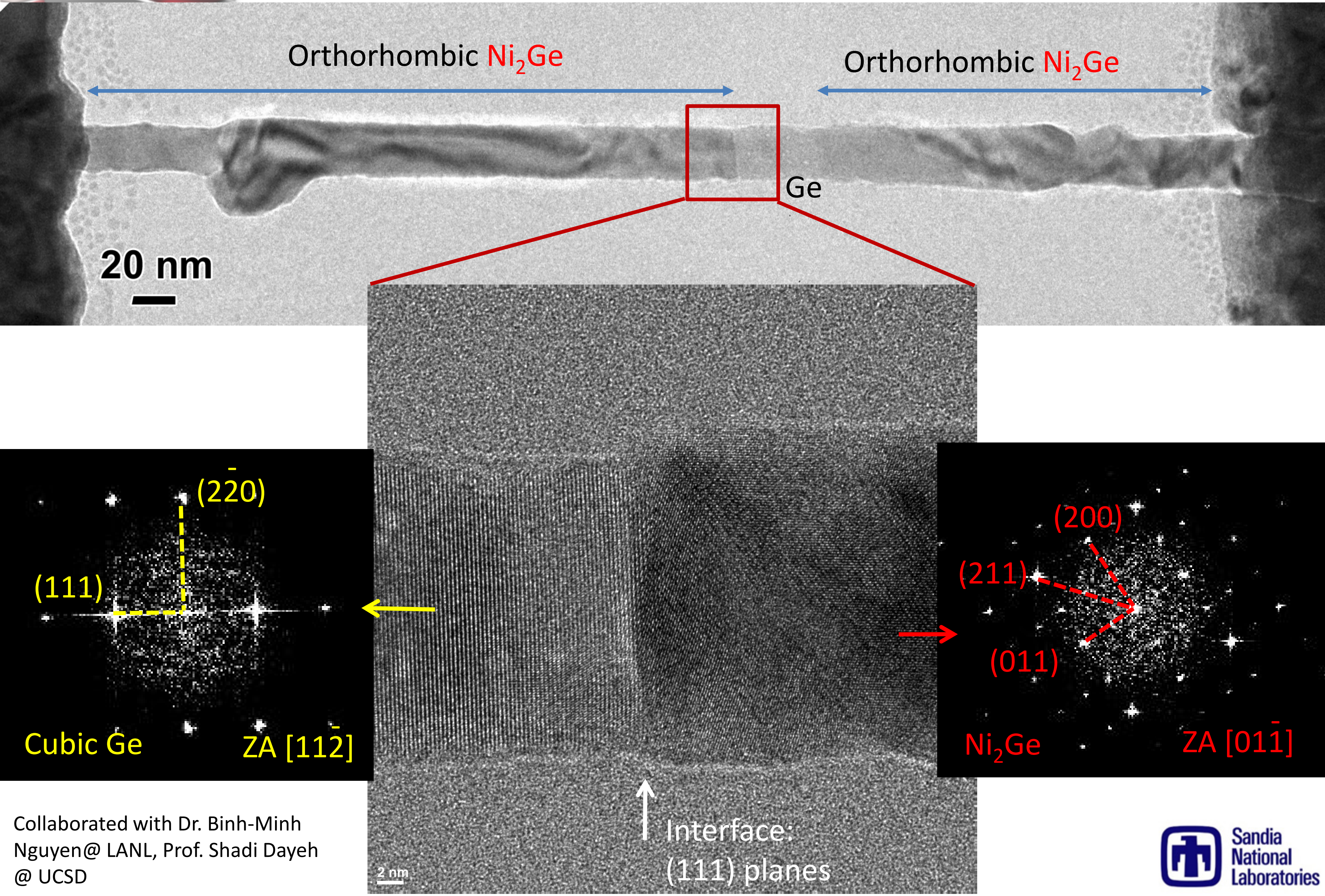
Mapping at the interface


Ni map


Si map

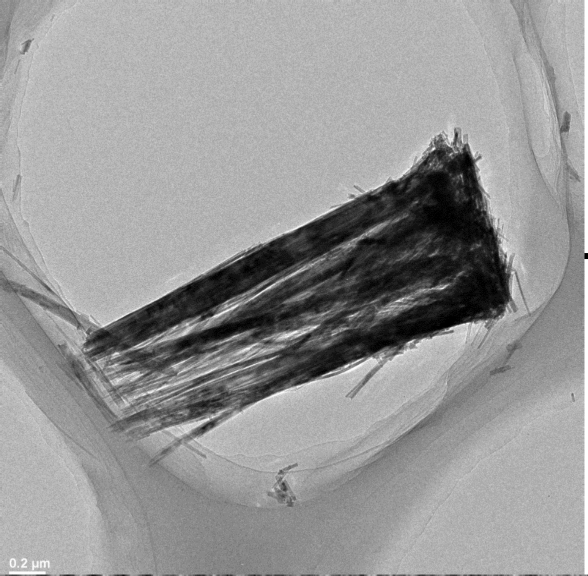
Collaborated with Prof. Shadi Dayeh @ UCSD

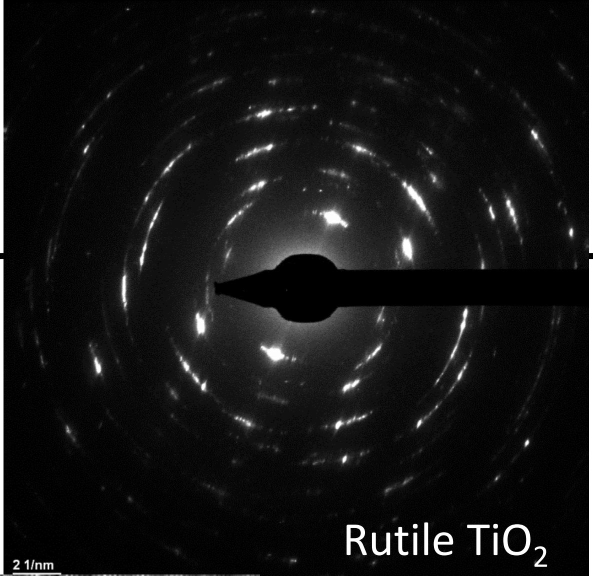
Heating experiment

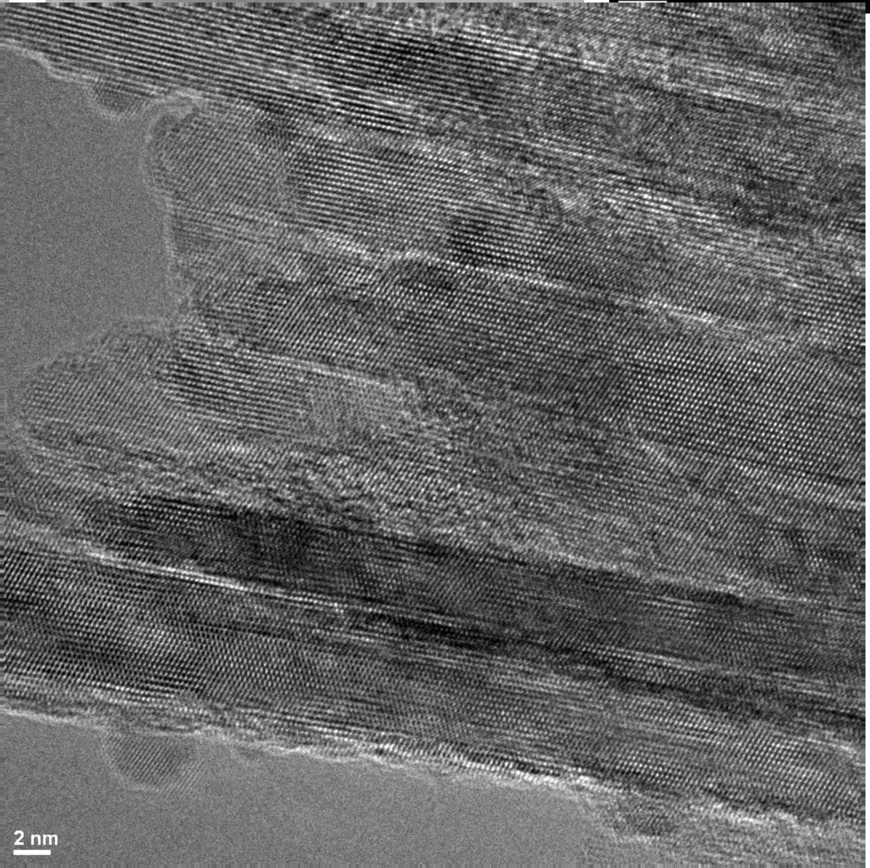


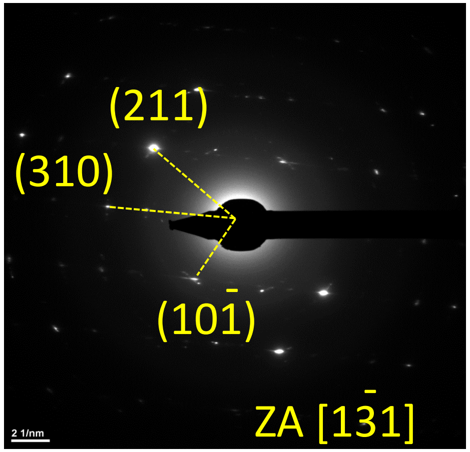
Collaborated with Dr. Binh-Minh Nguyen@ LANL, Prof. Shadi Dayeh @ UCSD

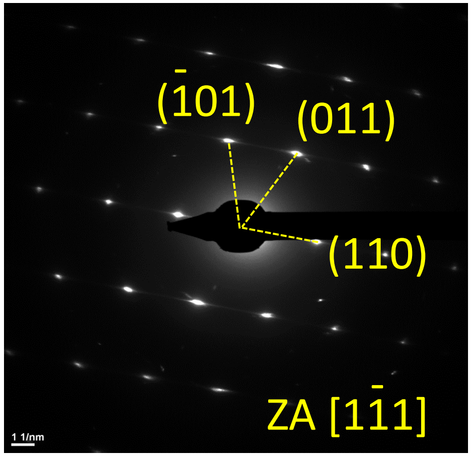
Growth-orientation determination







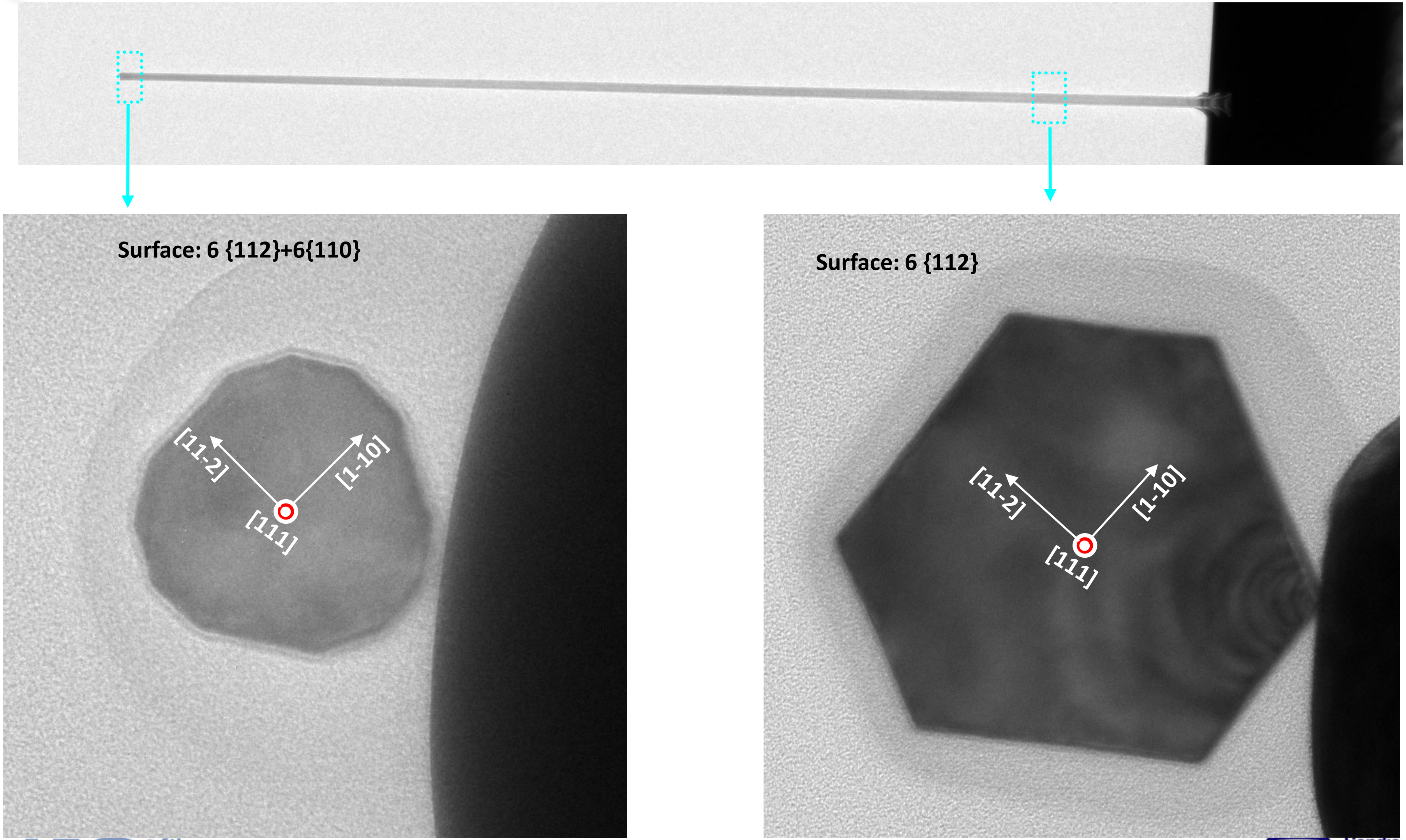




The growth direction is <310> X <110> = <001>

Collaborated with Prof. Wenzhi Li @ FIU

Cross section of <111> Si nanowires with position well-controlled



Collaborated with Dr. Sergiy Krylyuk, Dr. Albert Davydov @ NIST