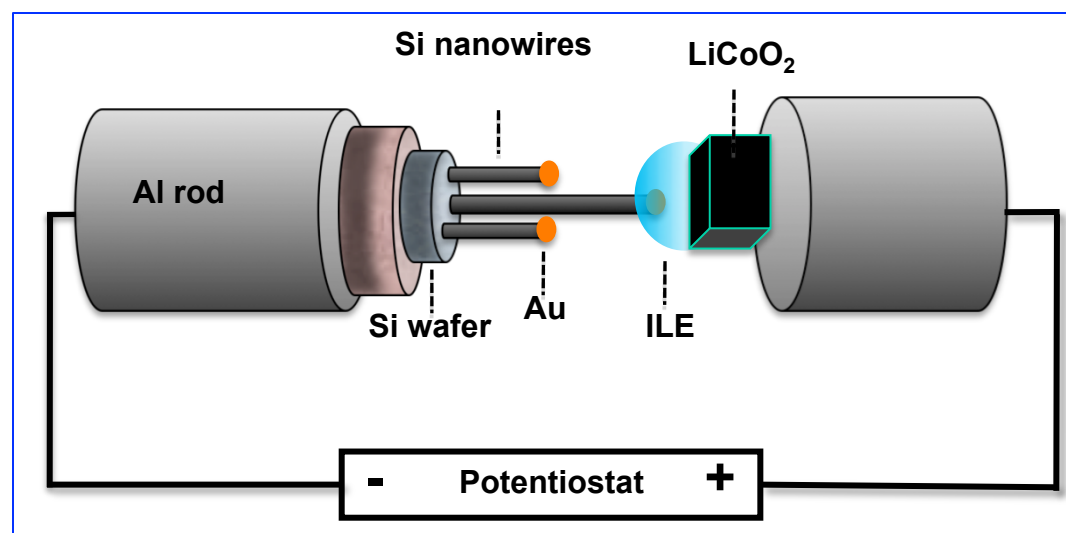


In-Situ TEM Electrochemistry of Individual Nanowire and Nanoparticle Electrodes

Jianyu Huang

Sandia National Laboratories
Center for Integrated Nanotechnology
Albuquerque, NM 87123



Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



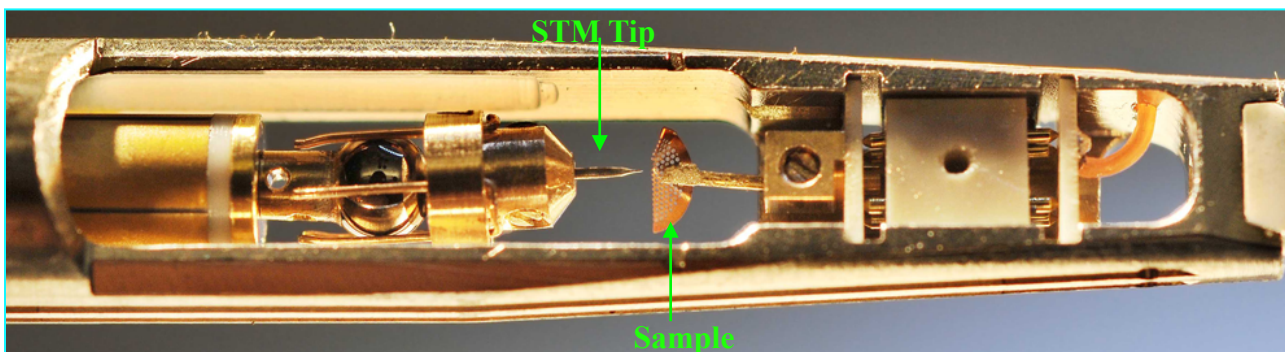
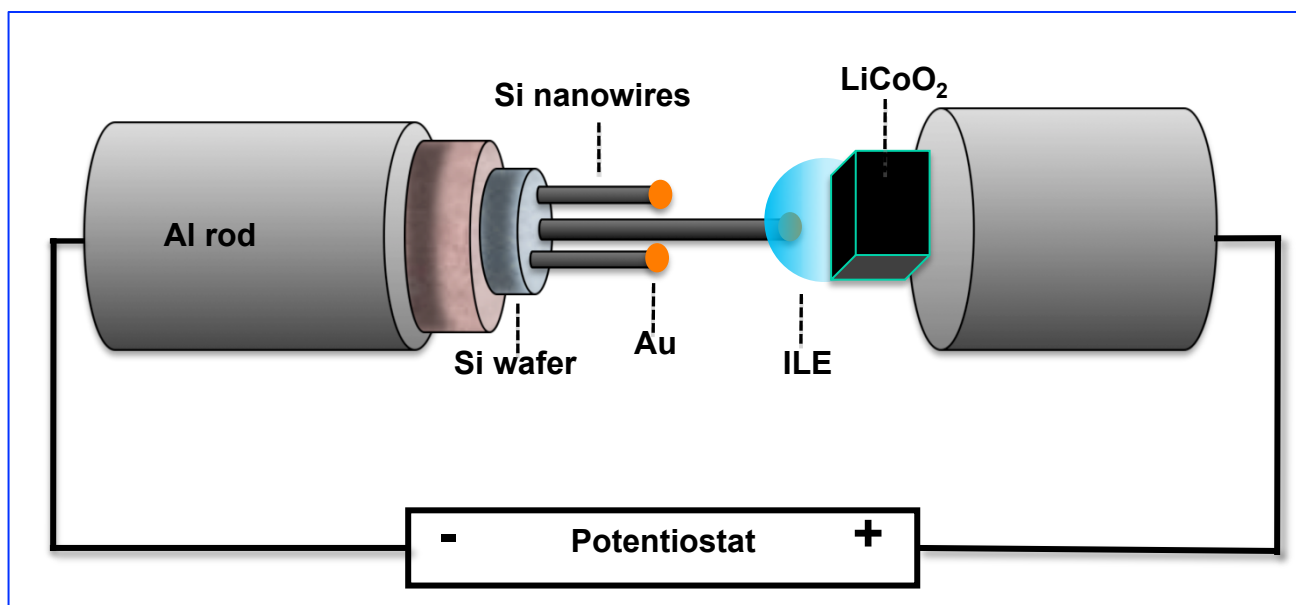
Challenges facing lithium ion batteries

- Lithium ion batteries (LIBs) are broadly used in portable electronics, but we still face many challenging issues in developing powerful LIBs for electrical vehicle and power backup applications.
- Mechanical failure of high energy density anodes due to large volume expansion
- How can structural stability during cycling be achieved?
- Lithium ion transport kinetics as a function of nanoscale structure dimension
- Electrode and electrolyte interface (e.g. SEI), how SEI forms, how does it evolve during cycling, and how does it lead to battery degradation?

We need new capabilities to address these challenges!

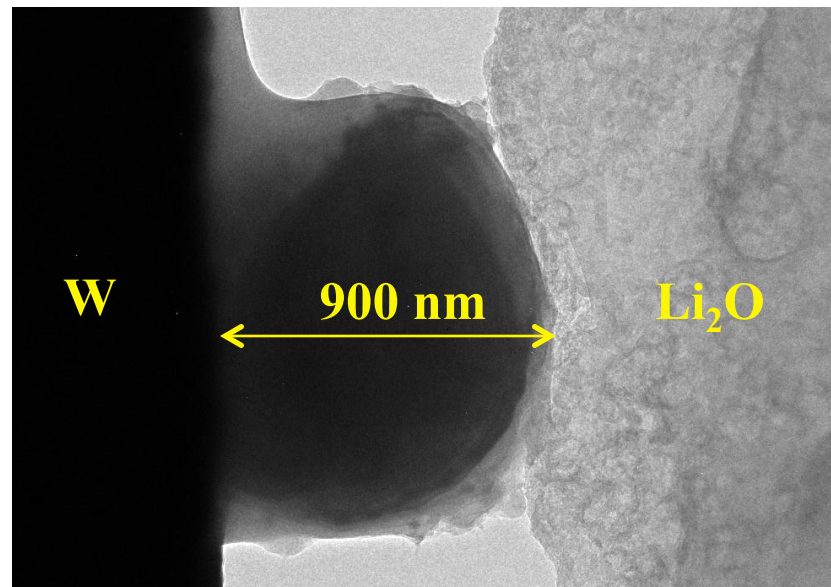
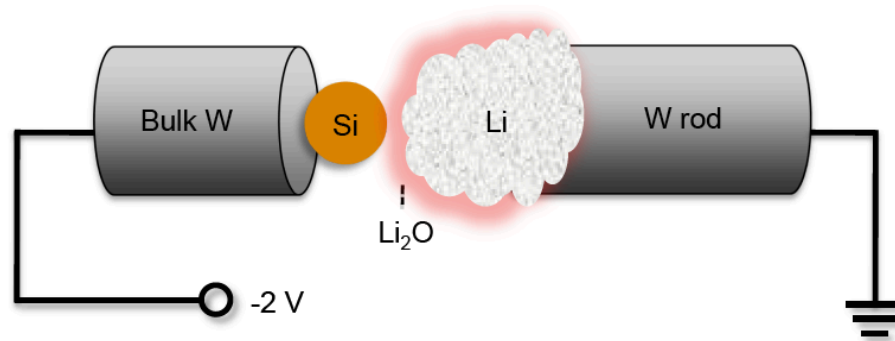
Created a working nano Li-ion cell inside a TEM!

Our approach: A single nanowire Li-ion cell (open cell)



Very clean system, no binder

An all solid electrochemical cell

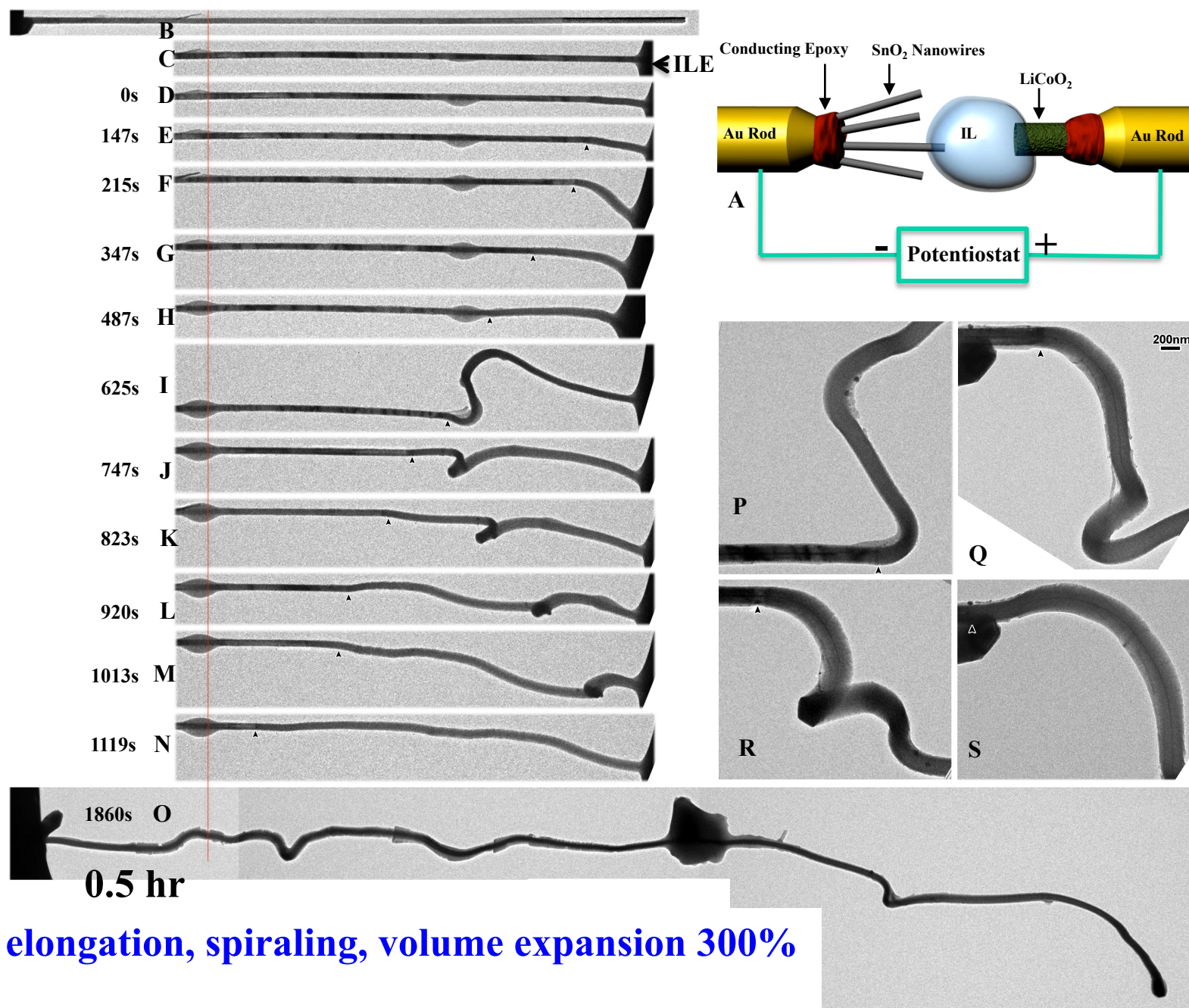


Ionic liquid flow along a Si NW in TEM

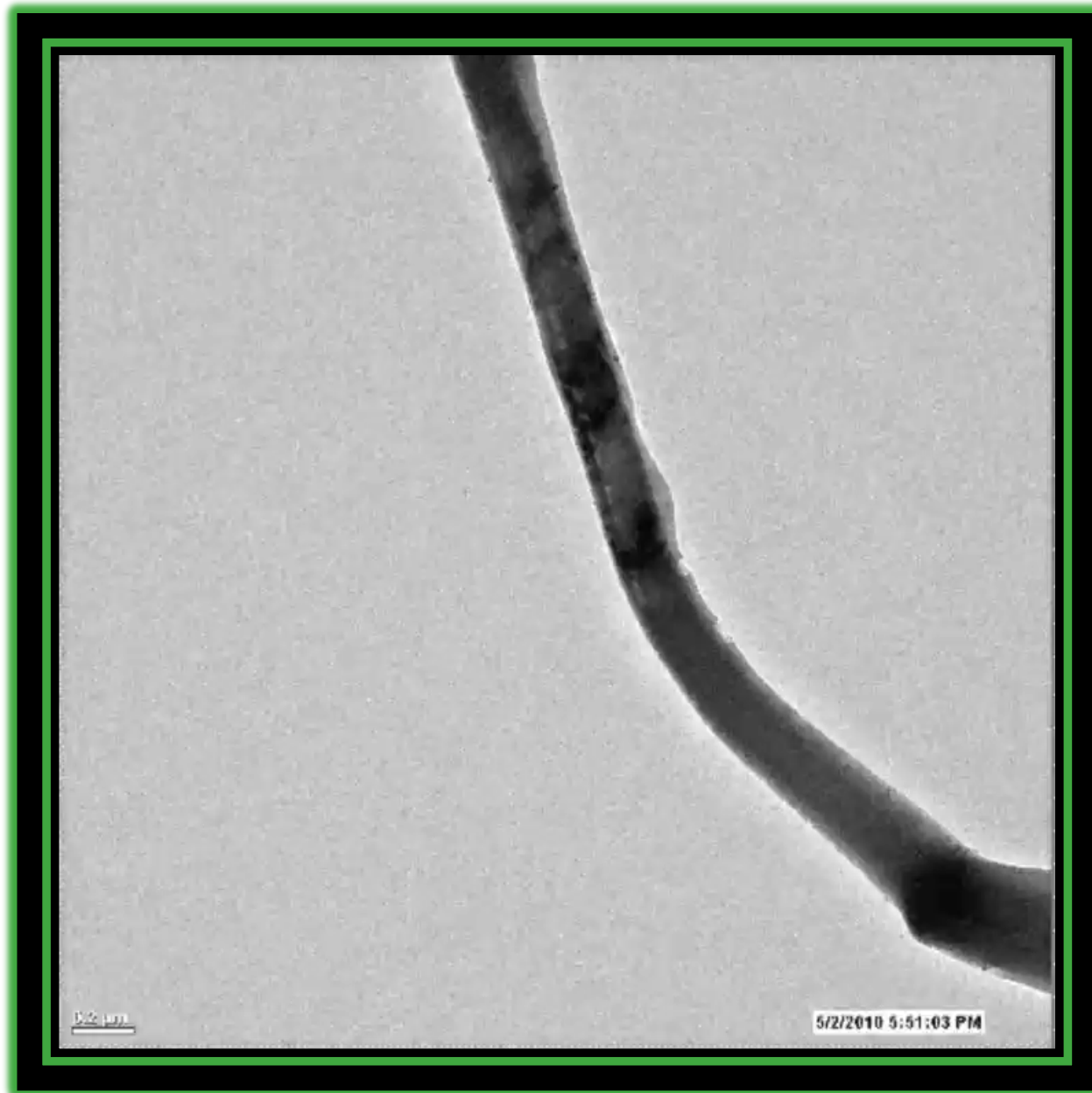


Jian Yu Huang, Li Zhong, Yu-Chieh Lo, S.X. Mao, Ju Li, submitted

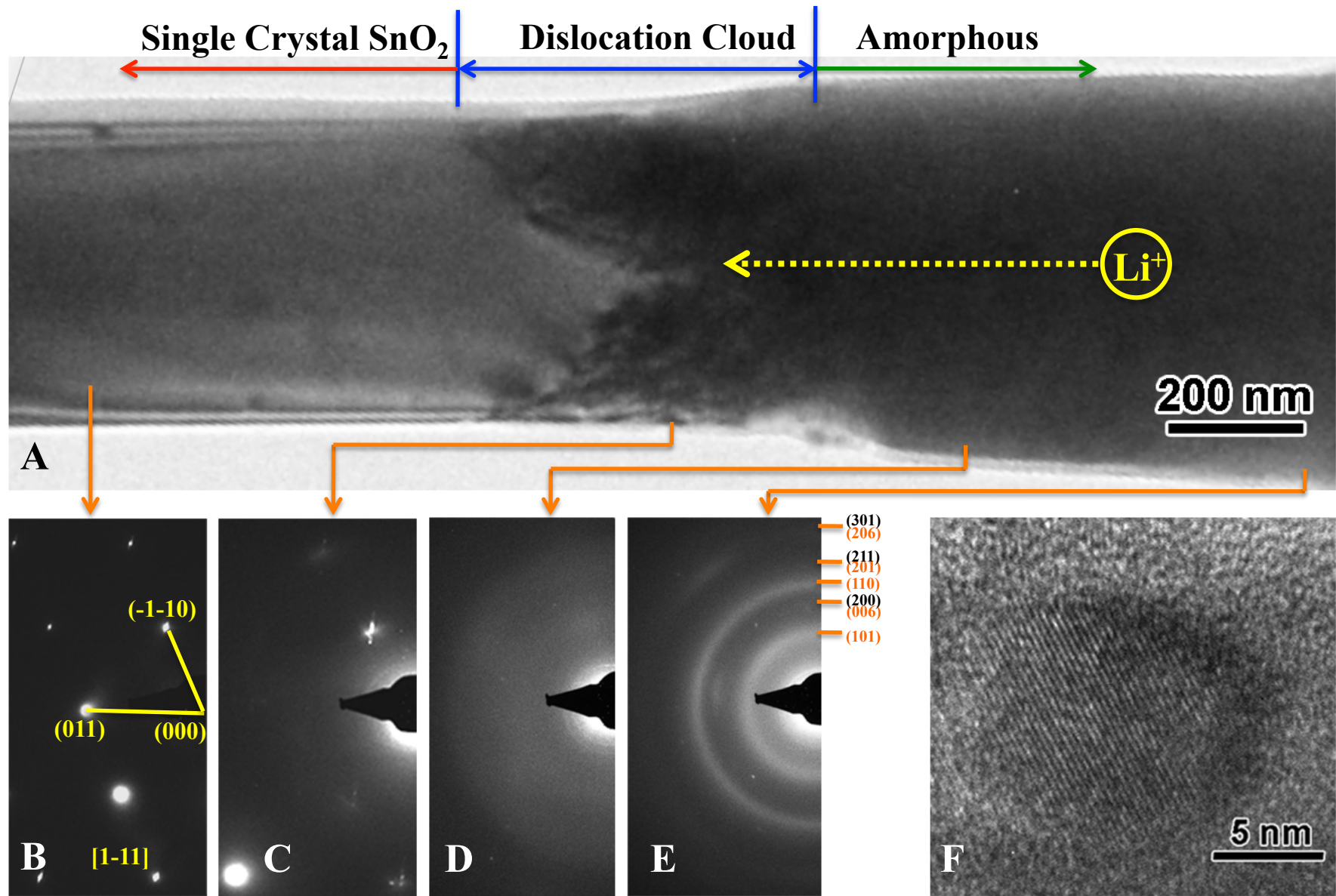
Huang *et al.*, **Science** Dec. 10, 2010



In-situ TEM charging of a single SnO₂ NW

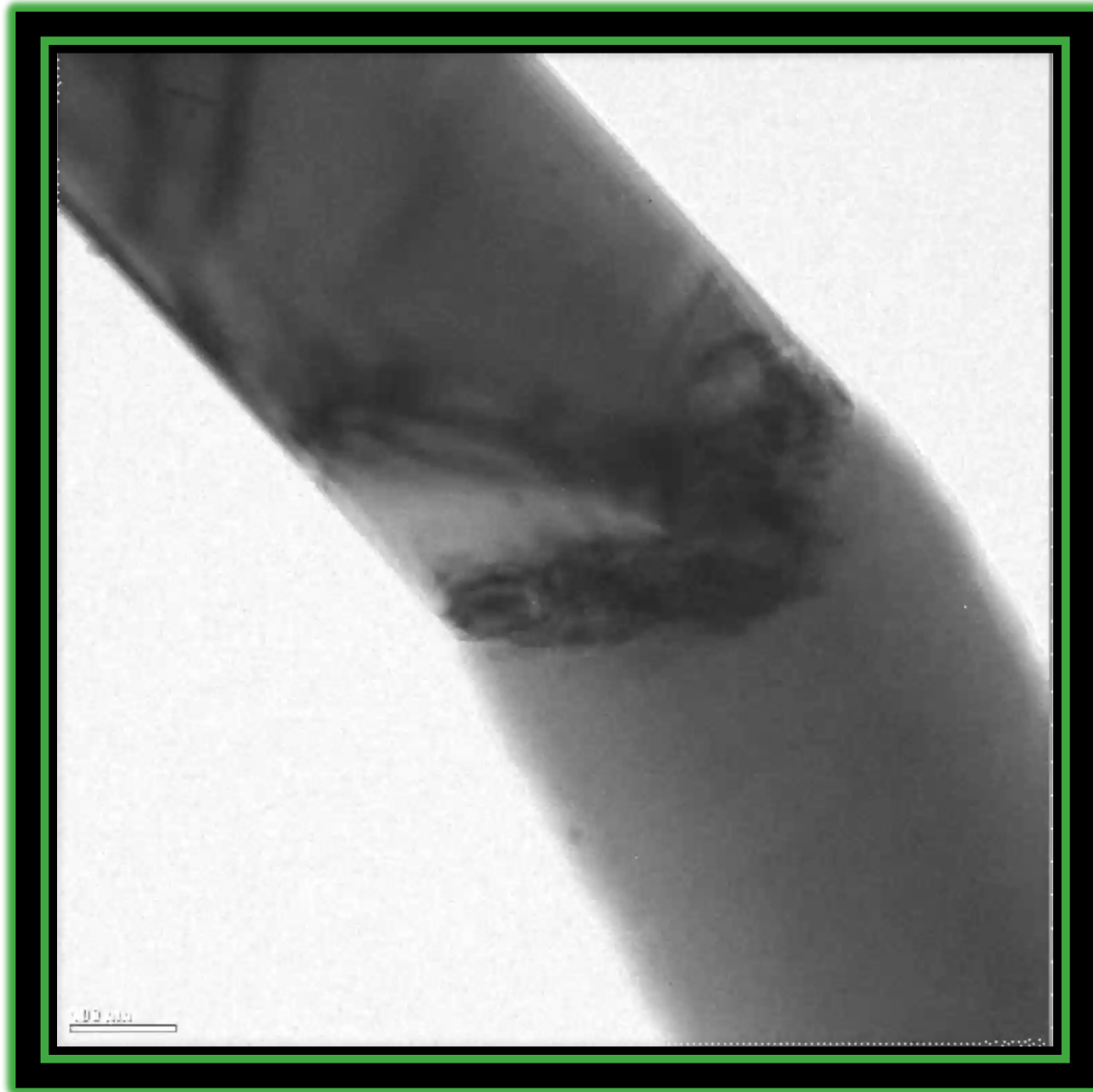


Forest of dislocations in the reaction front

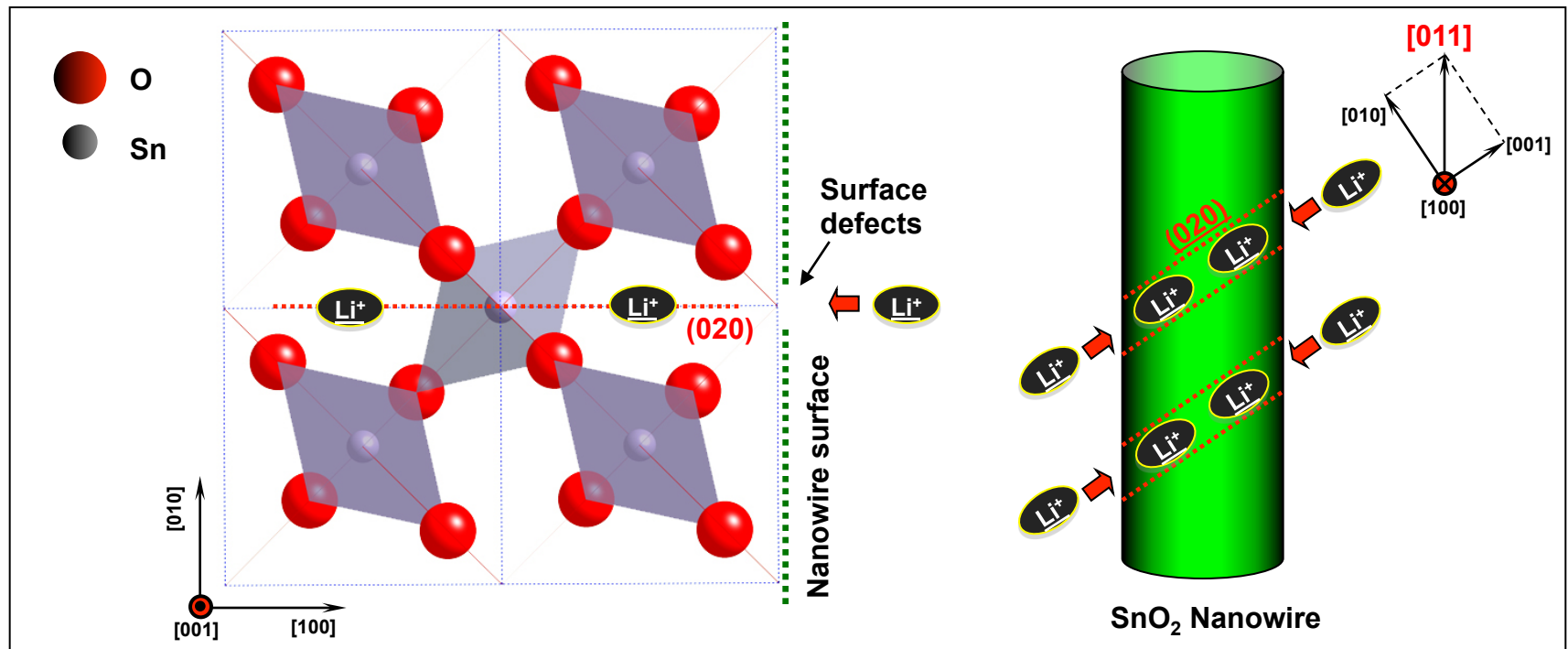
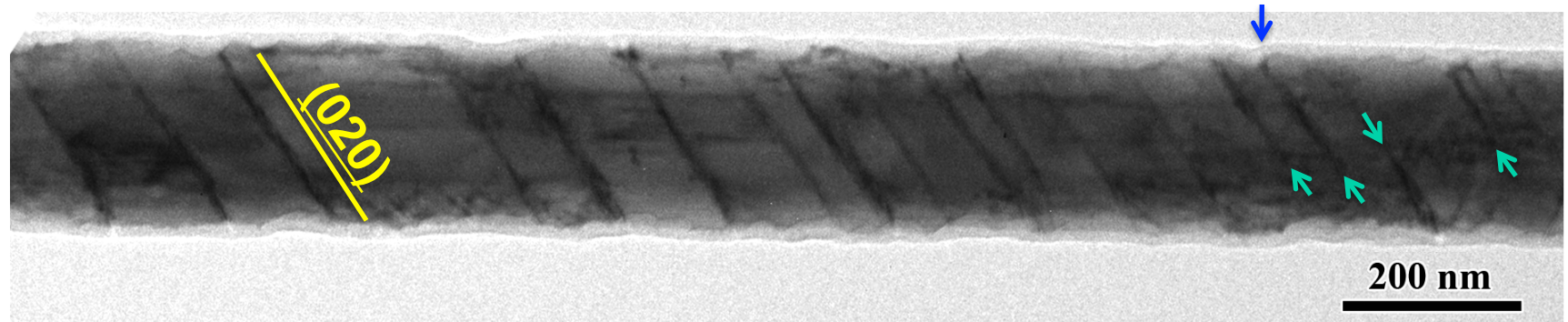


Dislocation cloud; diameter expansion, phase transformation: amorphization

Dislocation dynamics in the reaction front

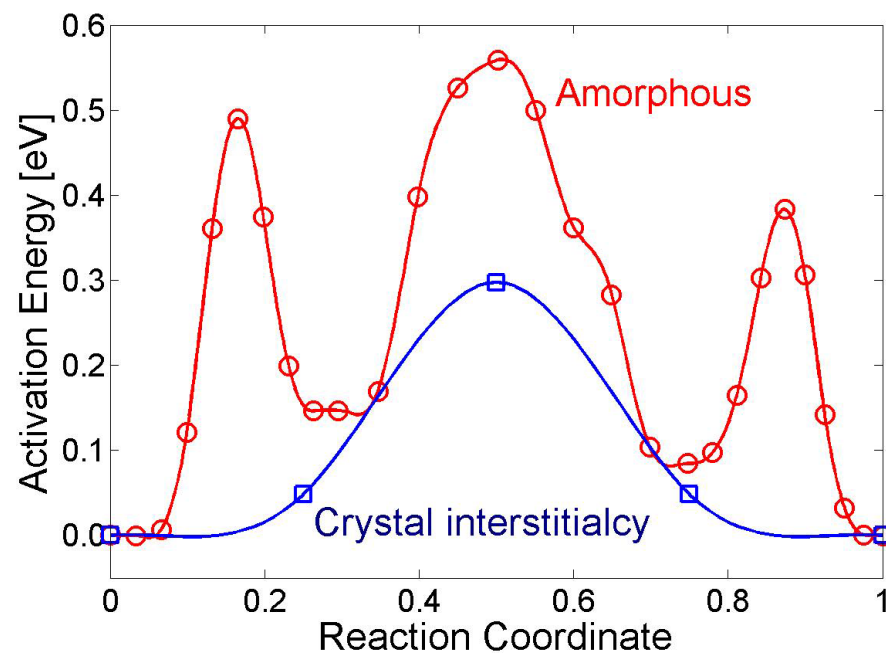
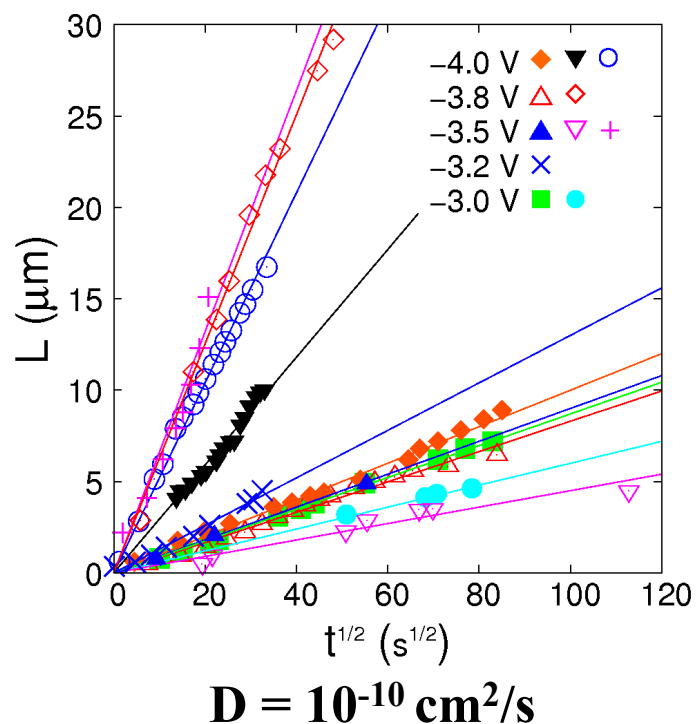
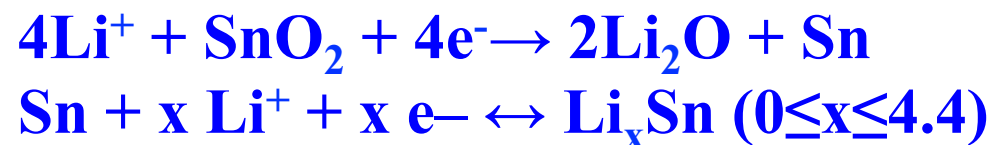
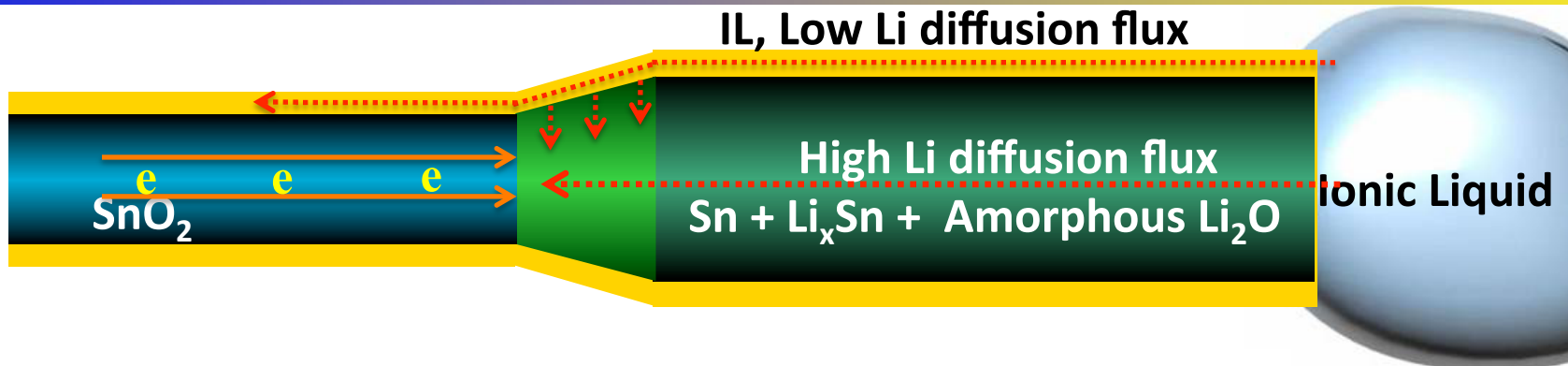


Multiple strip lithiation mechanism in a flooding geometry

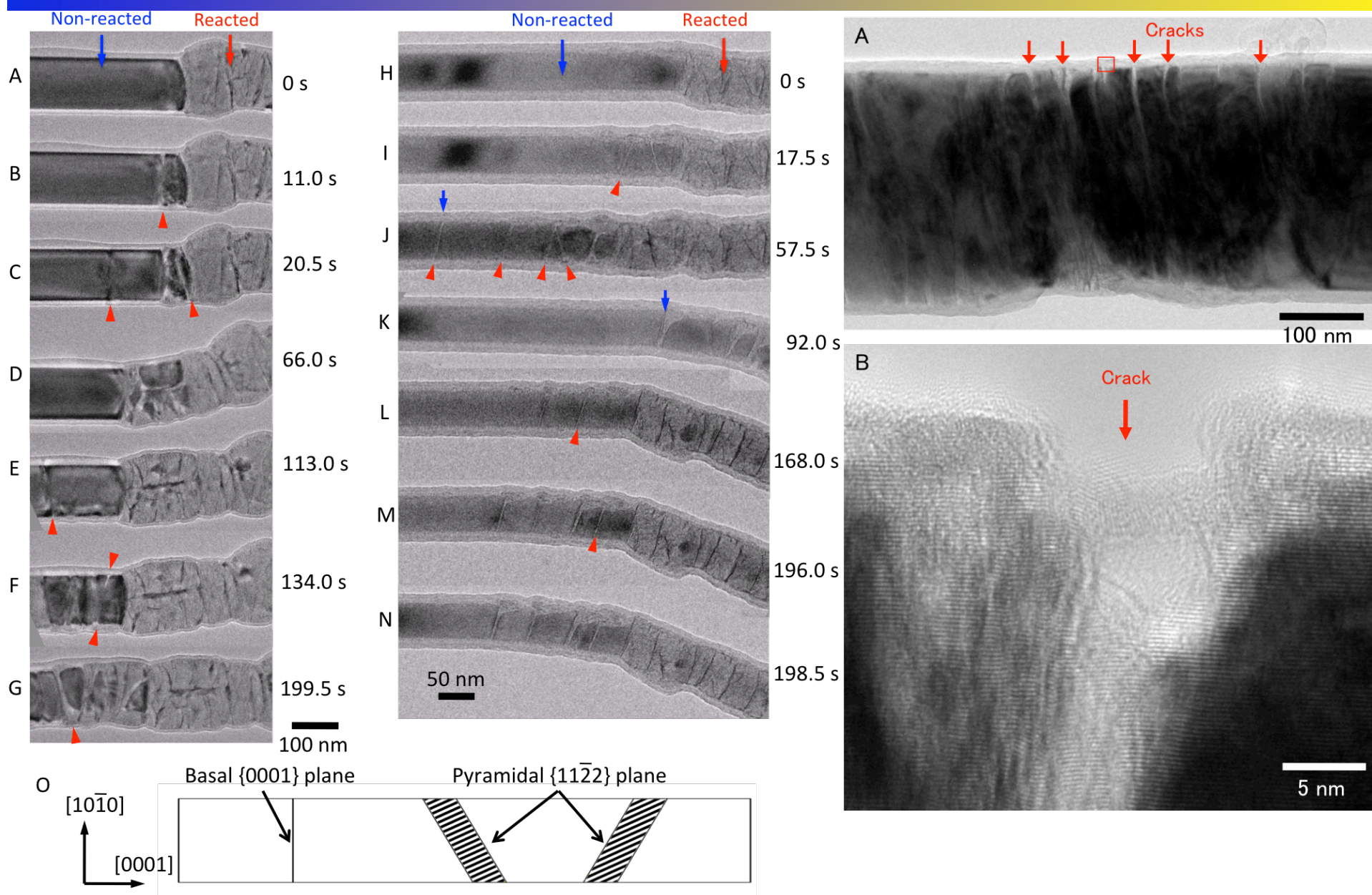


Zhong, Liu, Mao, Huang, **Phys. Rev. Lett.** 106, 248302 (2011)

How does the SnO_2 NW electrode work?

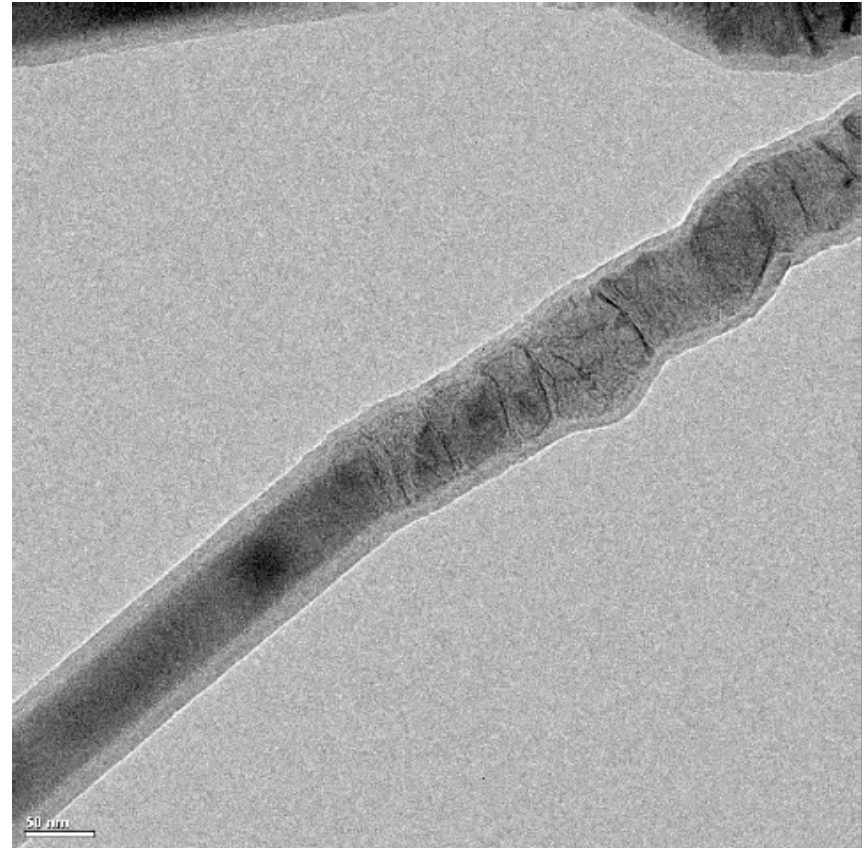
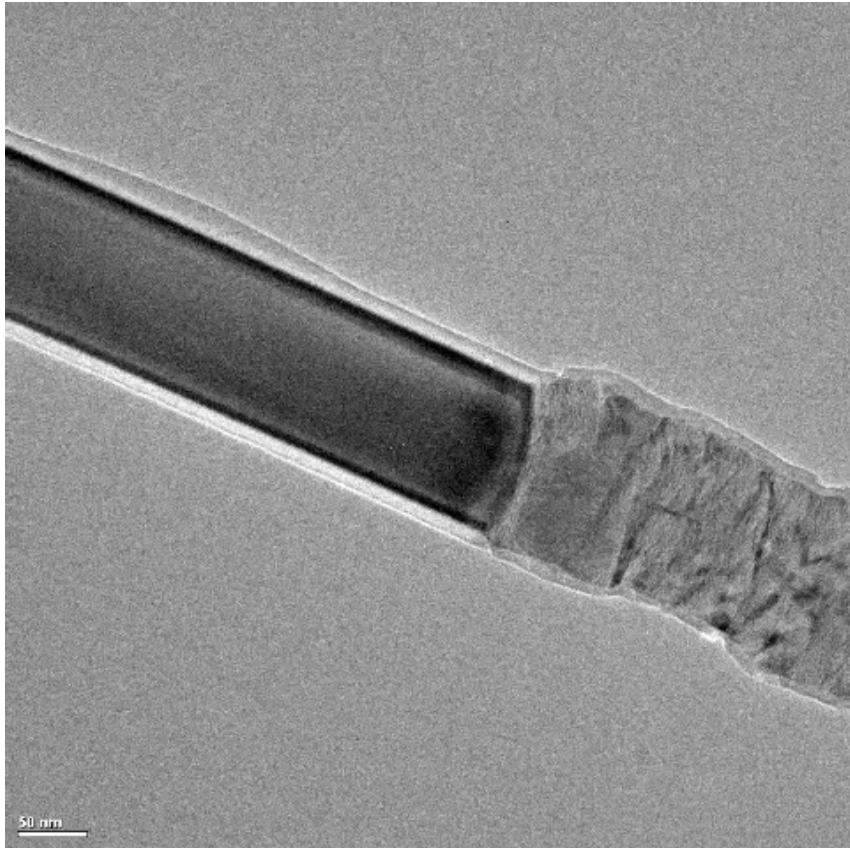


Case study 1: Discrete cracking in ZnO nanowire during lithiation

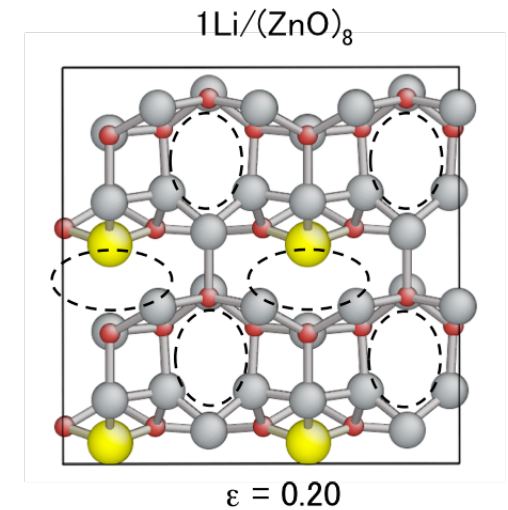
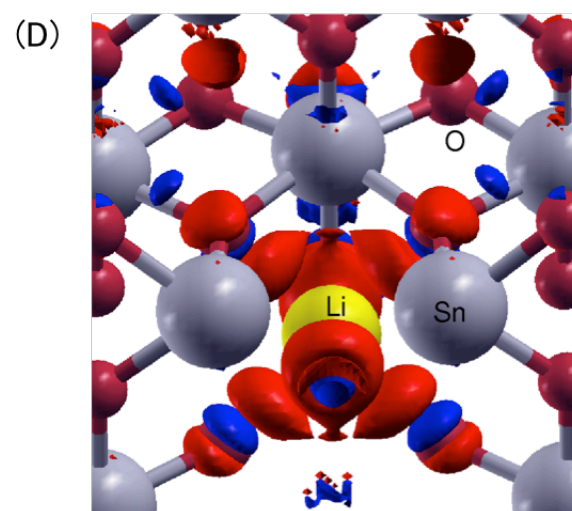
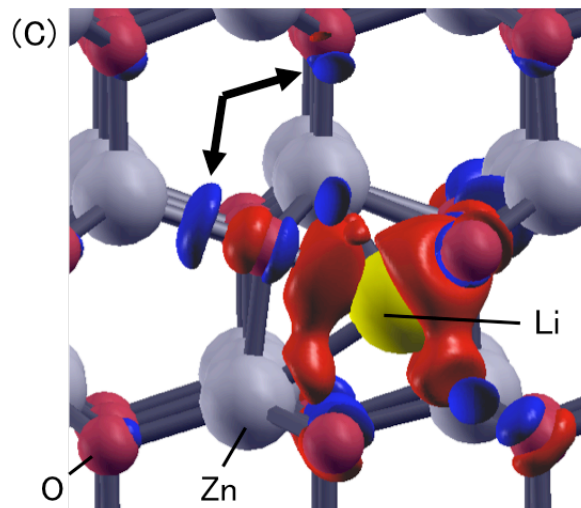
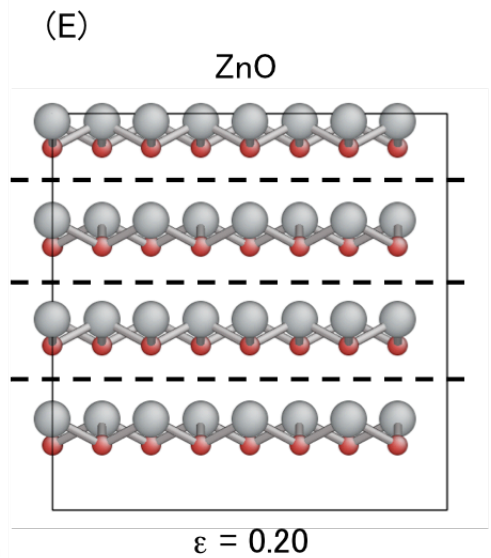
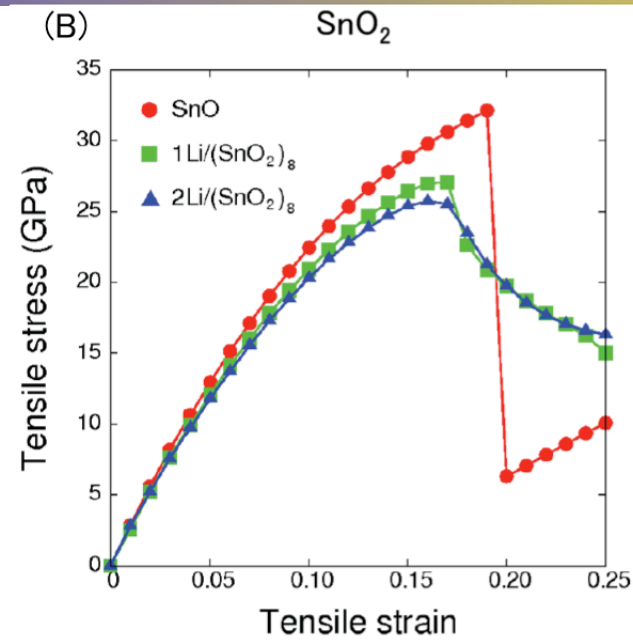
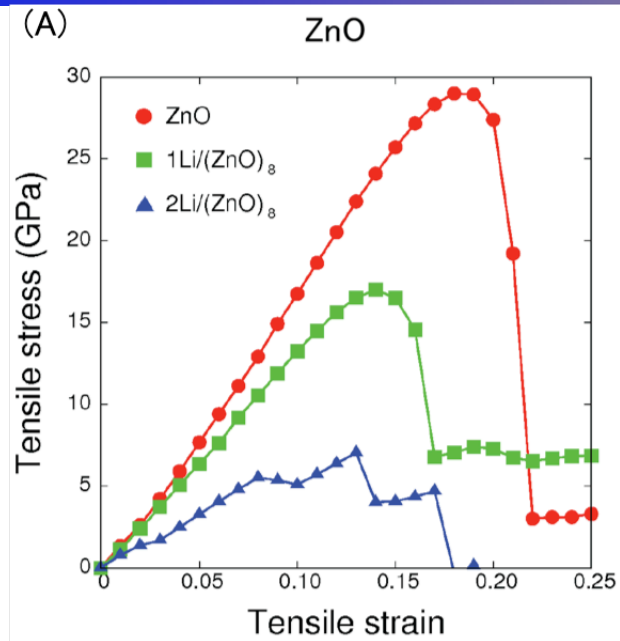


Akihiro Kushima, Xiao Hua Liu, Guang Zhu, Zhong Lin Wang, Jian Yu Huang, and Ju Li, Nano Lett., DOI: 10.1021/nl201376j

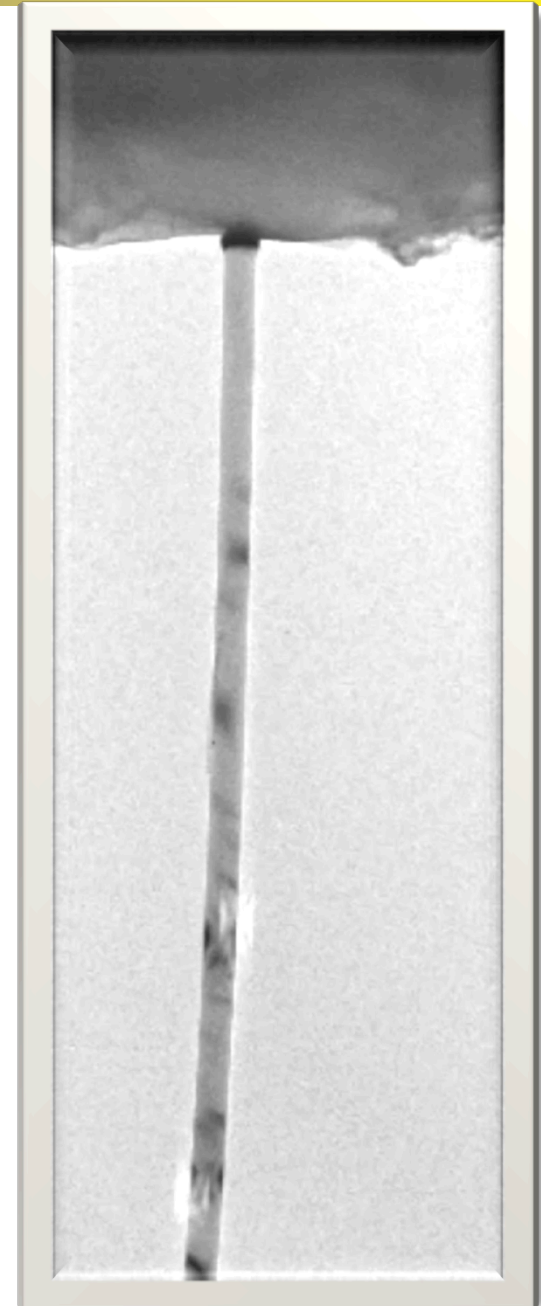
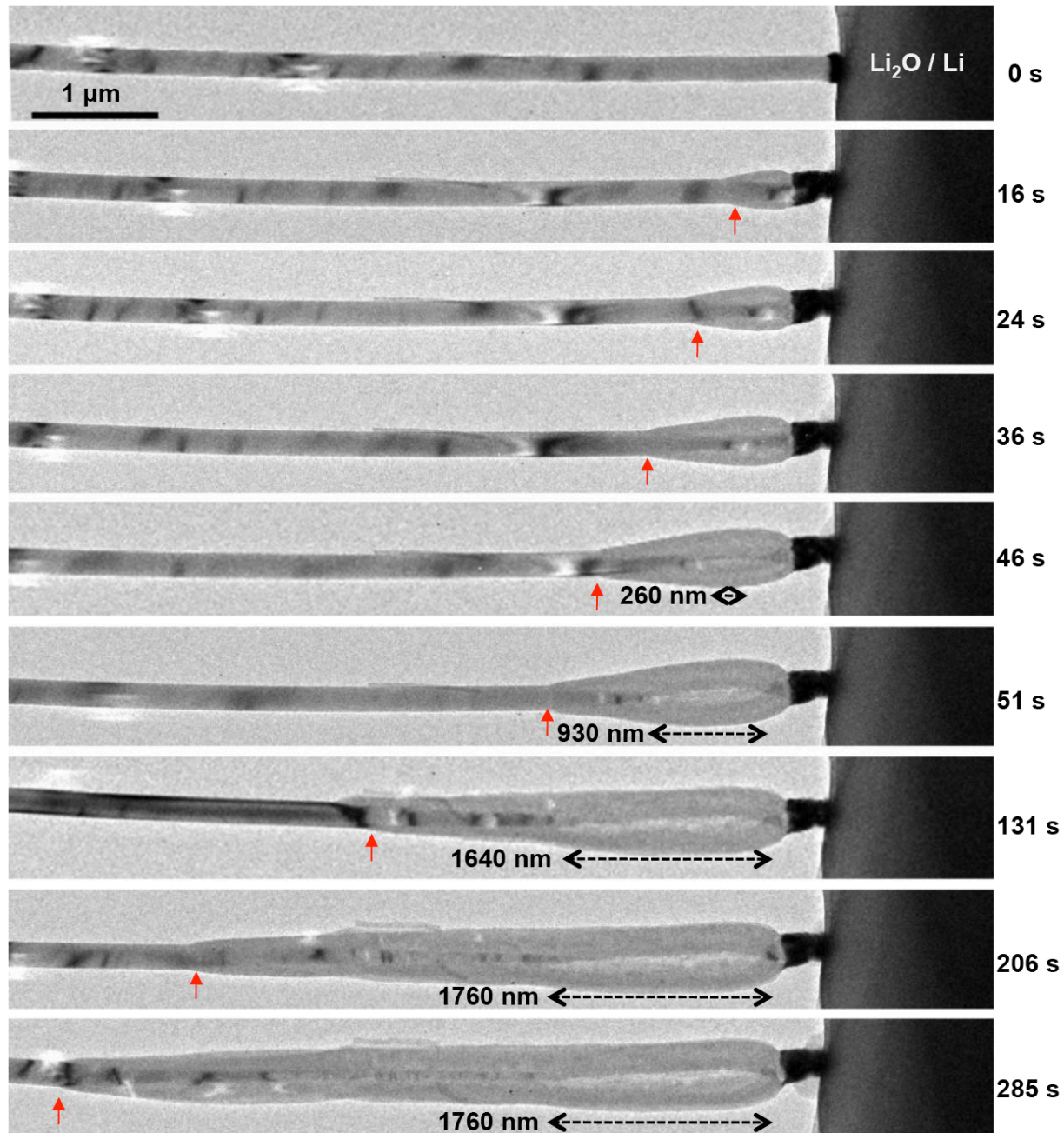
Discrete cracking in ZnO nanowire during lithiation



Lithiation embrittlement of ZnO NWs

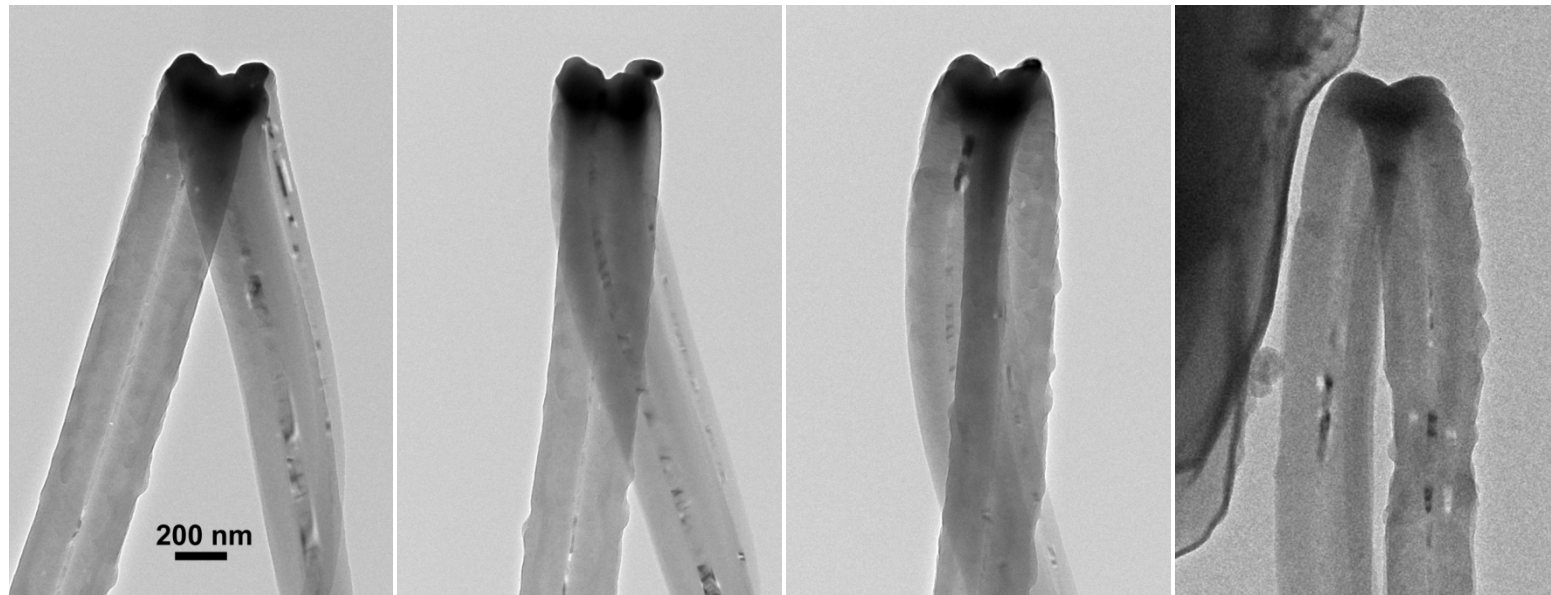


2: Anisotropic expansion and crack in Si

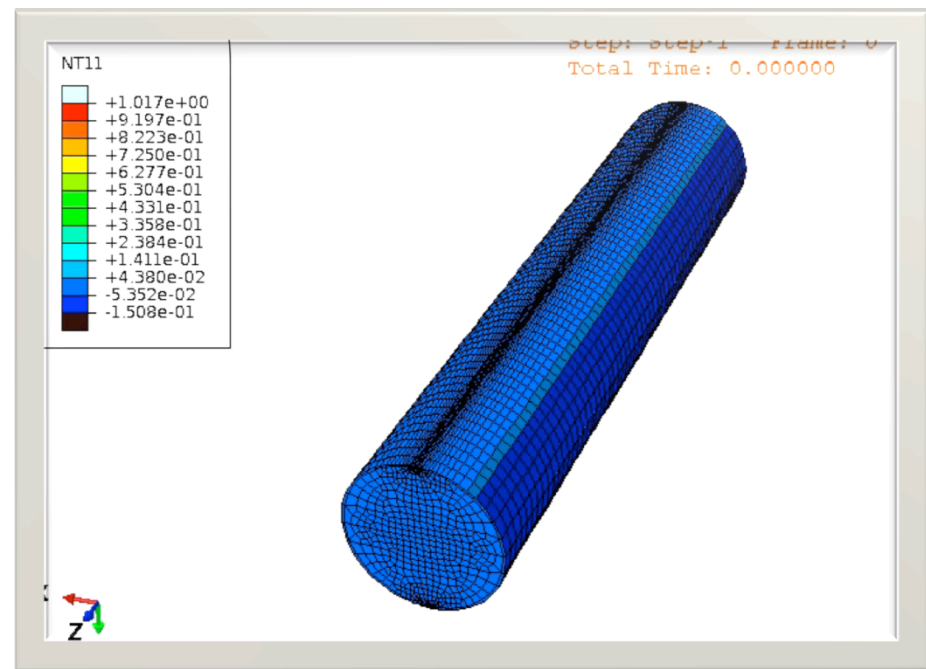
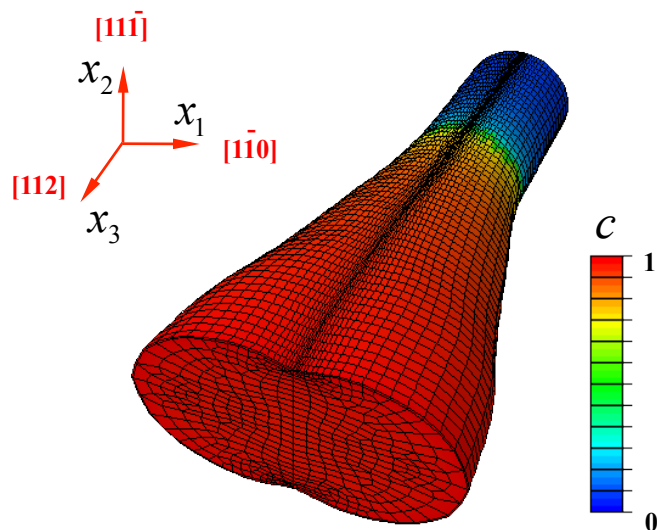


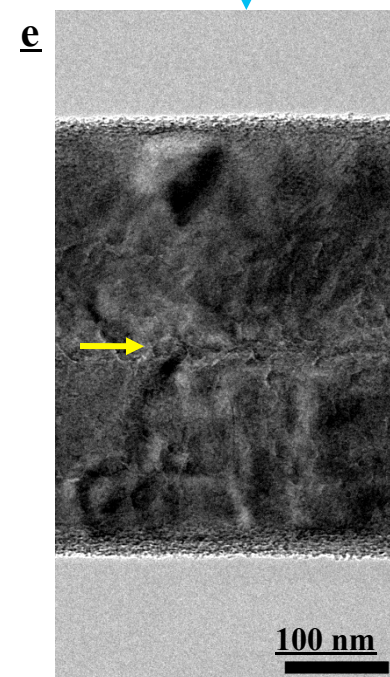
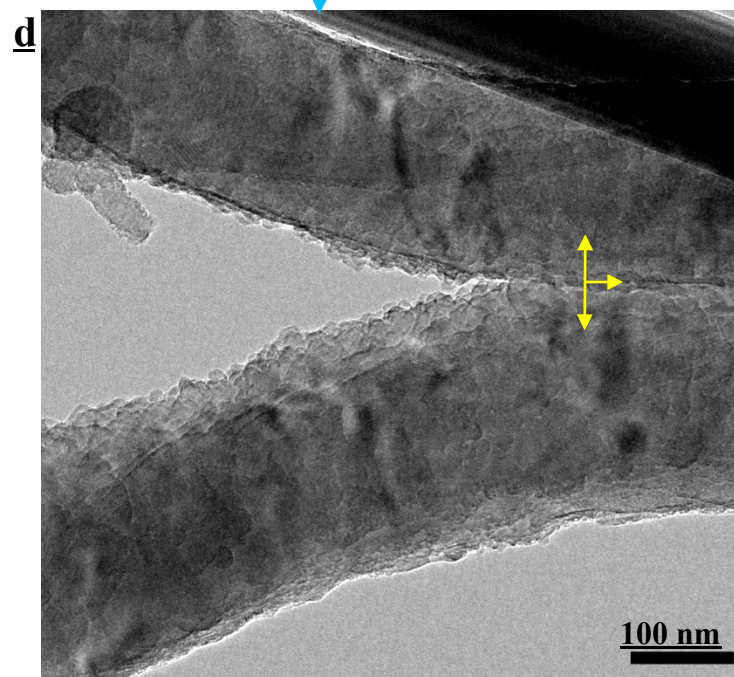
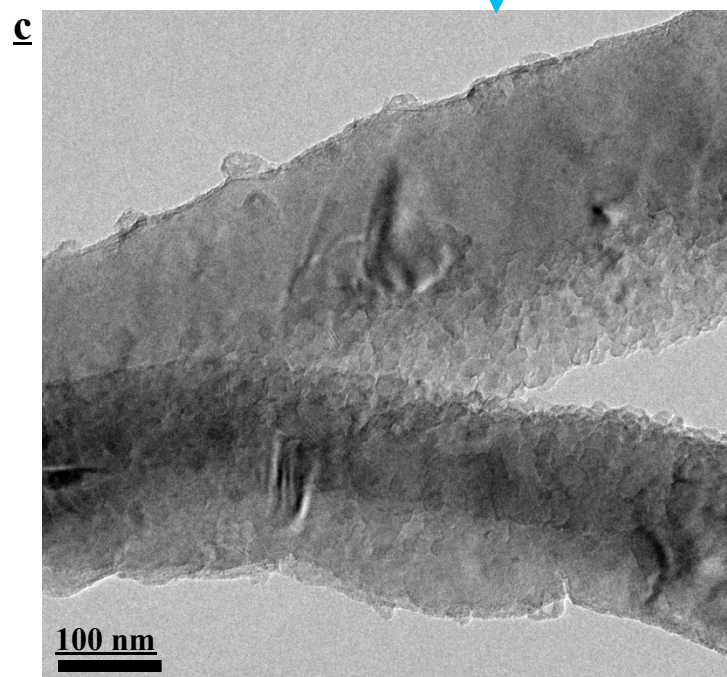
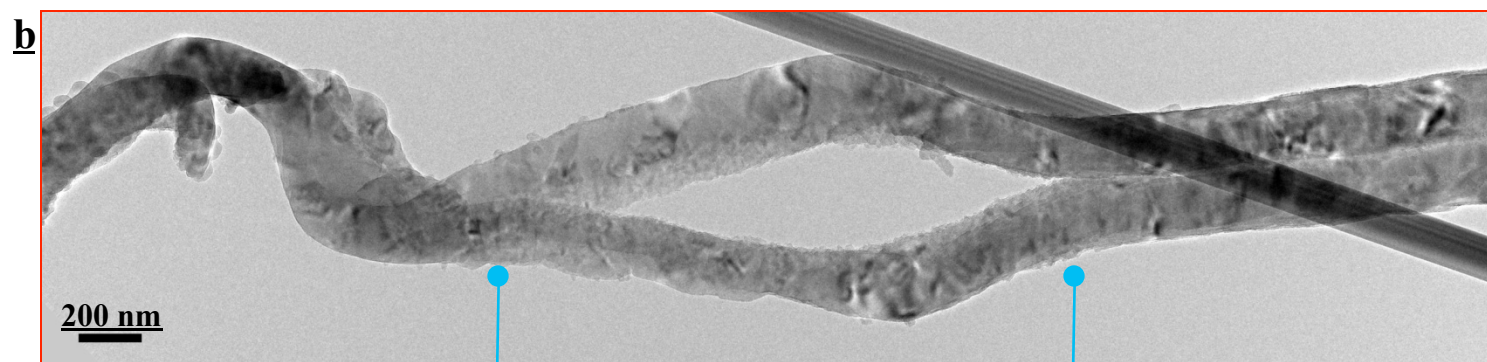
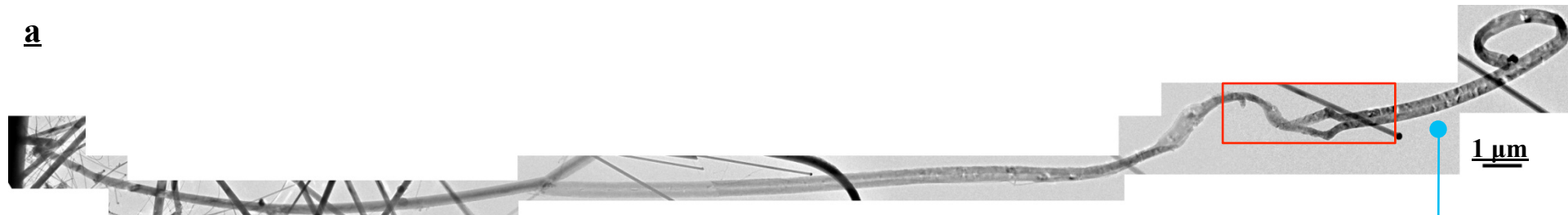
Anisotropic volume expansion in Si NWs

Liu, Huang, Zhu, Li et al., Nano Lett. 11, 3312 (2011)

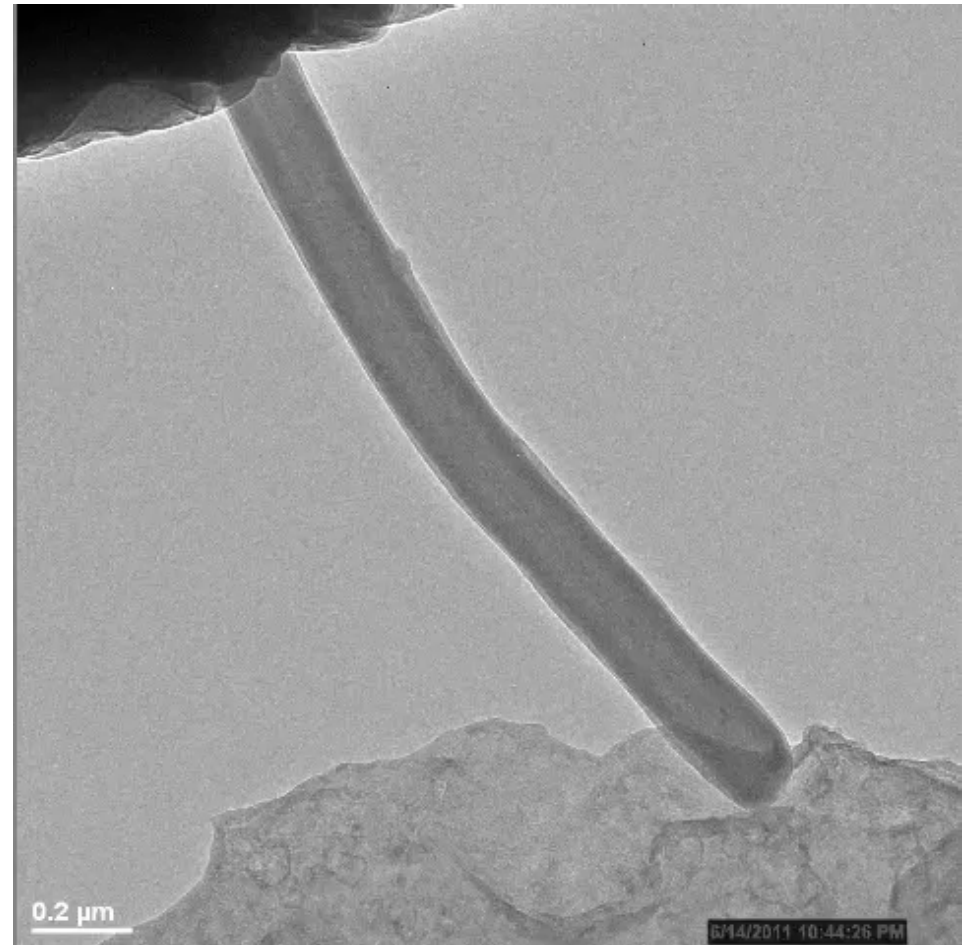
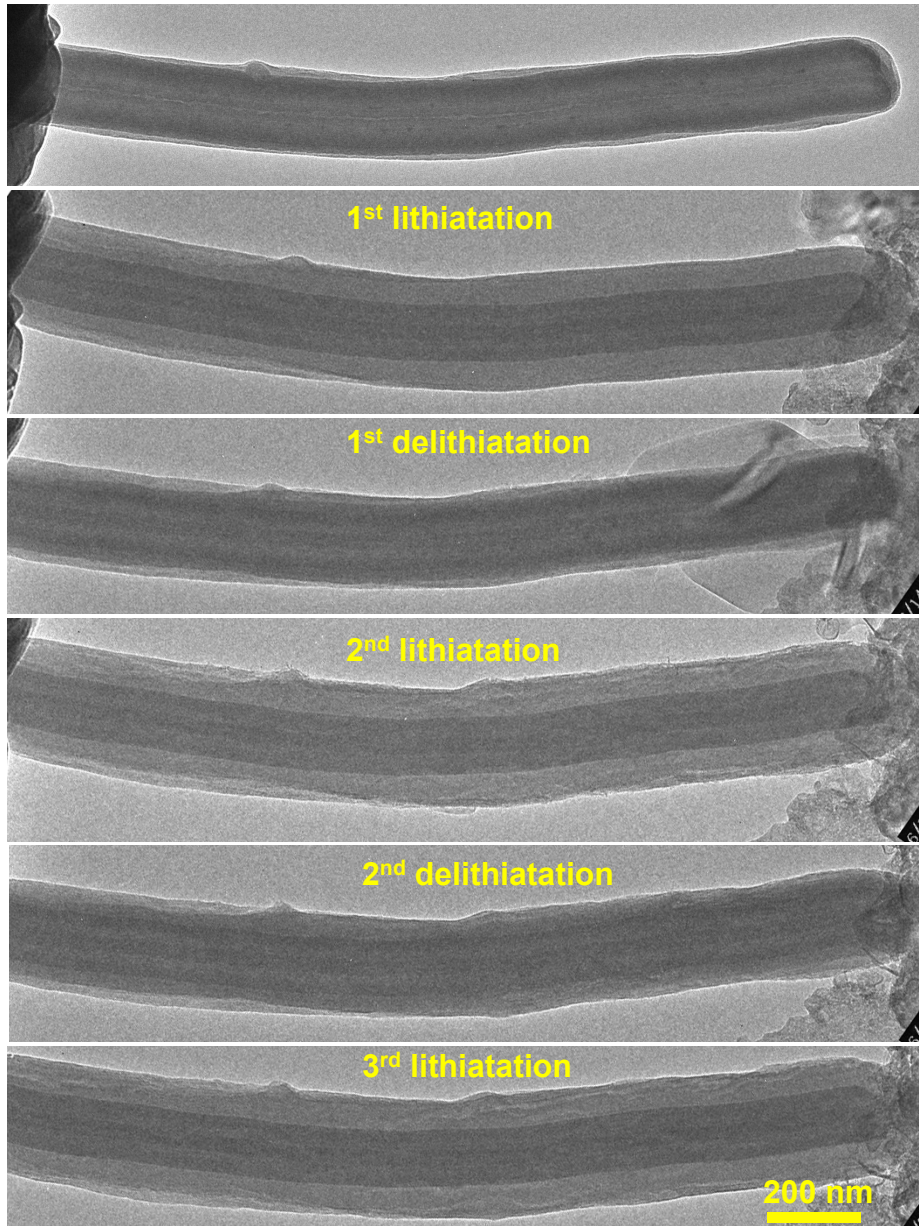


Peanut cross section

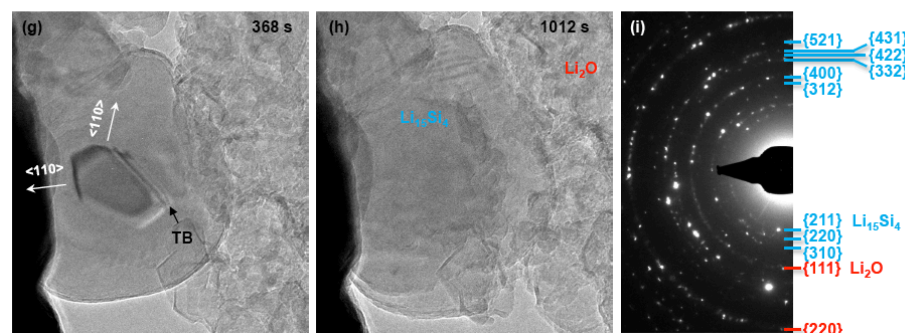
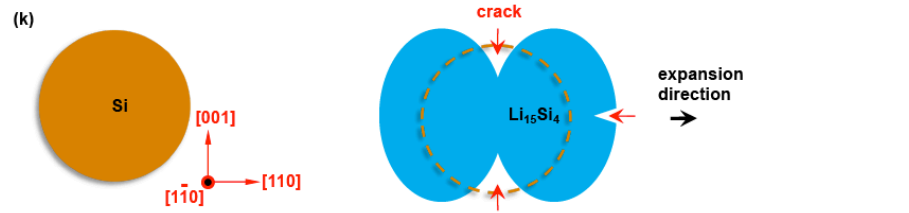




In-situ cycling of a-Si/CNT electrode (ASI, GM)

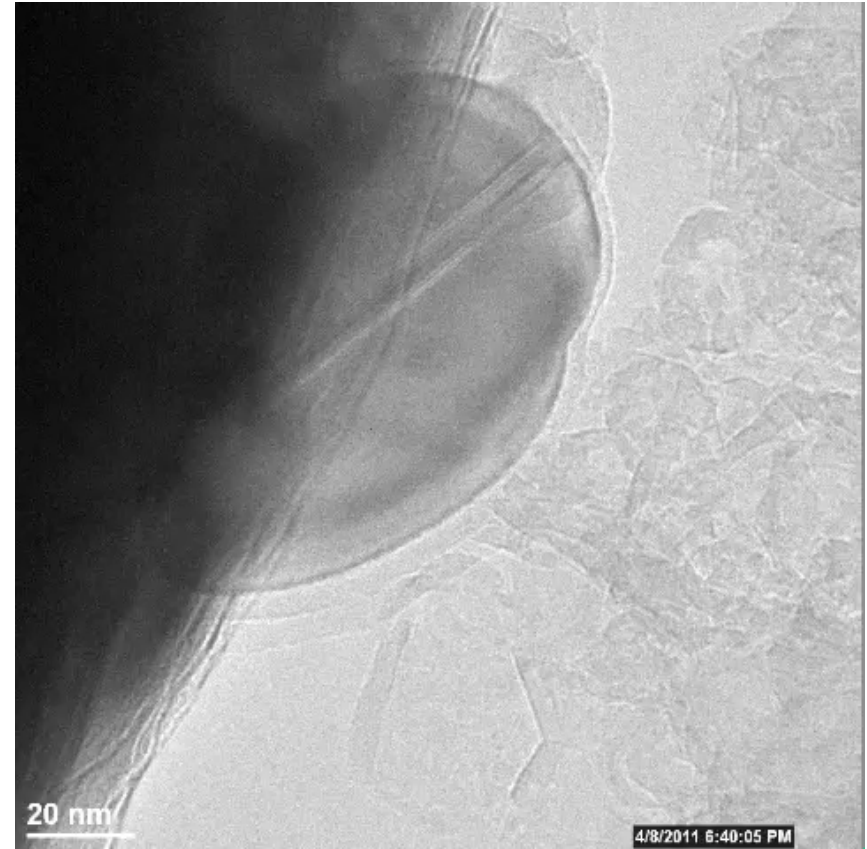
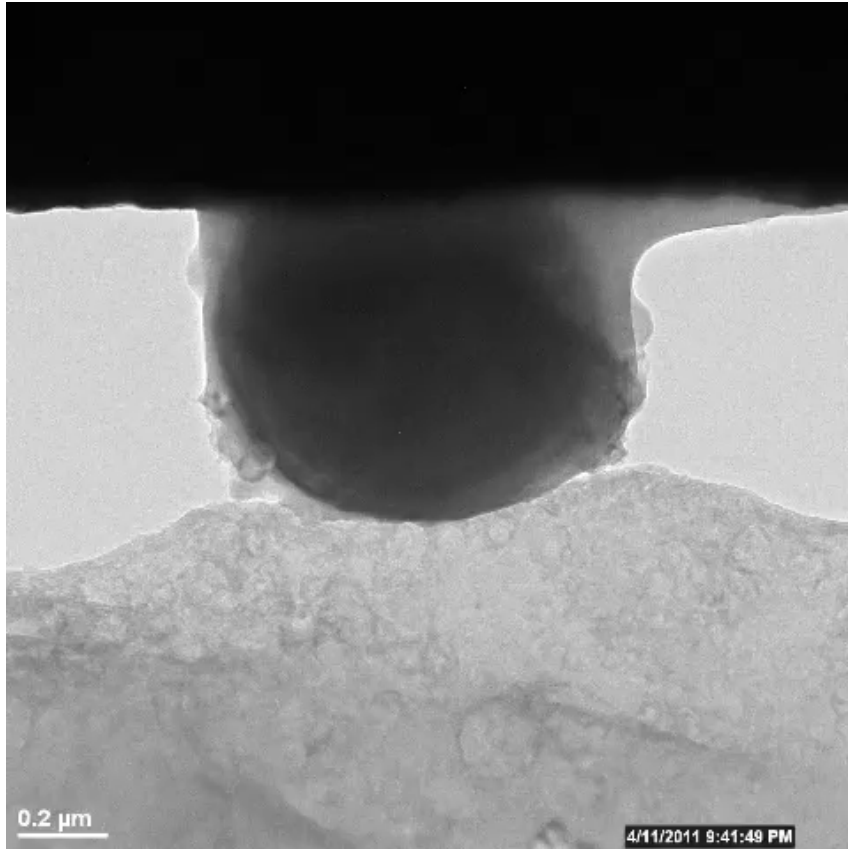


J.W. Wang, S.X. Mao, D. Burton, J.Y. Huang, Unpublished

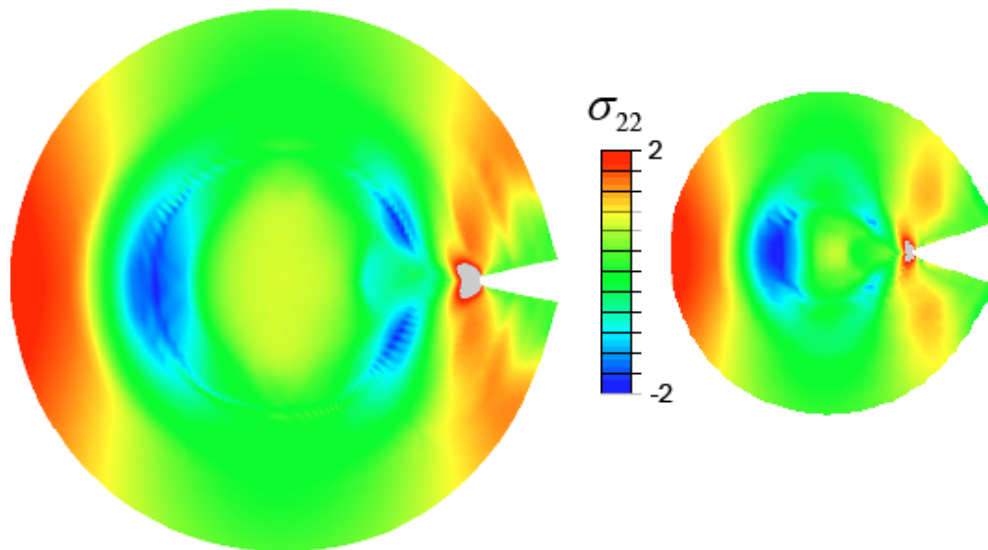
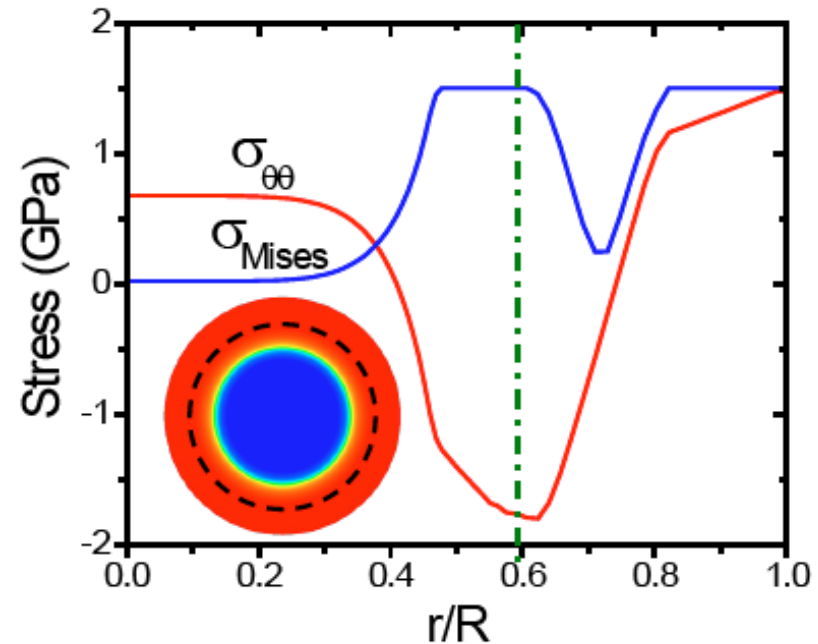
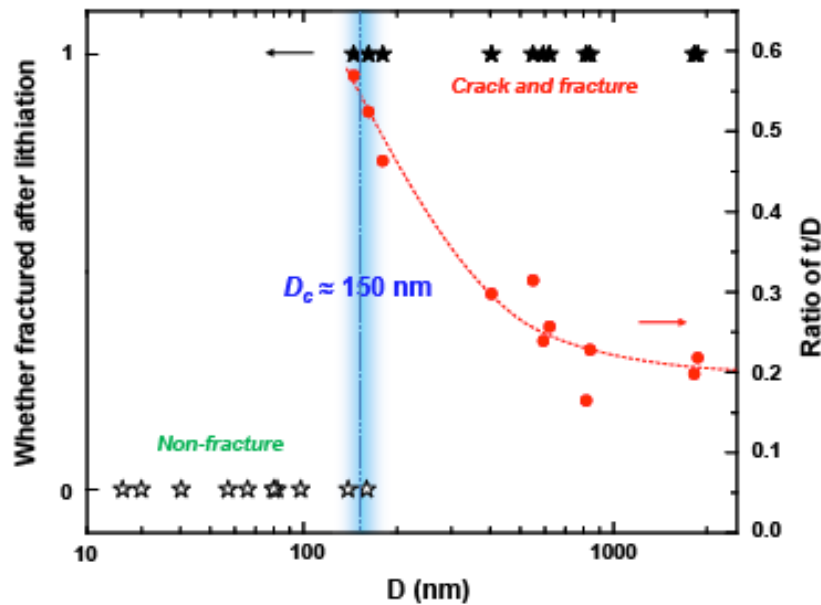


Xiao Hua Liu, Li Zhong, Shan Huang, Scott X. Mao, Ting Zhu, and Jian Yu Huang
submitted

Size dependent fracture of Si nanoparticles



Size dependent fracture of Si nanoparticles

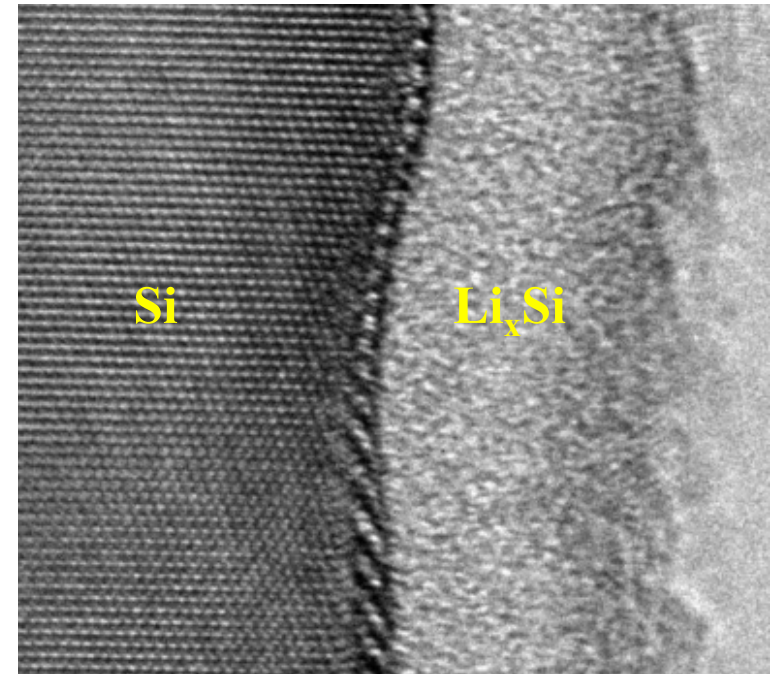
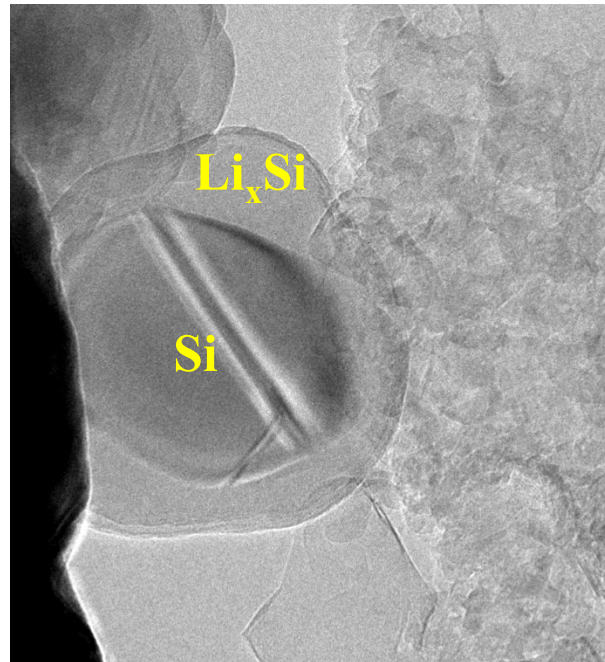
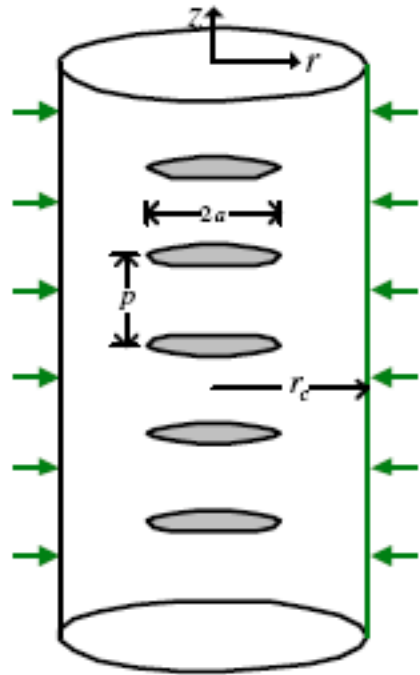


T. Zhu , X.H. Liu, J.Y. Huang *et al.*, submitted

K.J. Zhao, Z.G. Suo *et al.*, Journal of Power Sources 2011

S.L. Zhang, T. Zhu, J. Li, J.Y. Huang *et al.*, in preparation

Size dependent fracture of Si nanoparticles



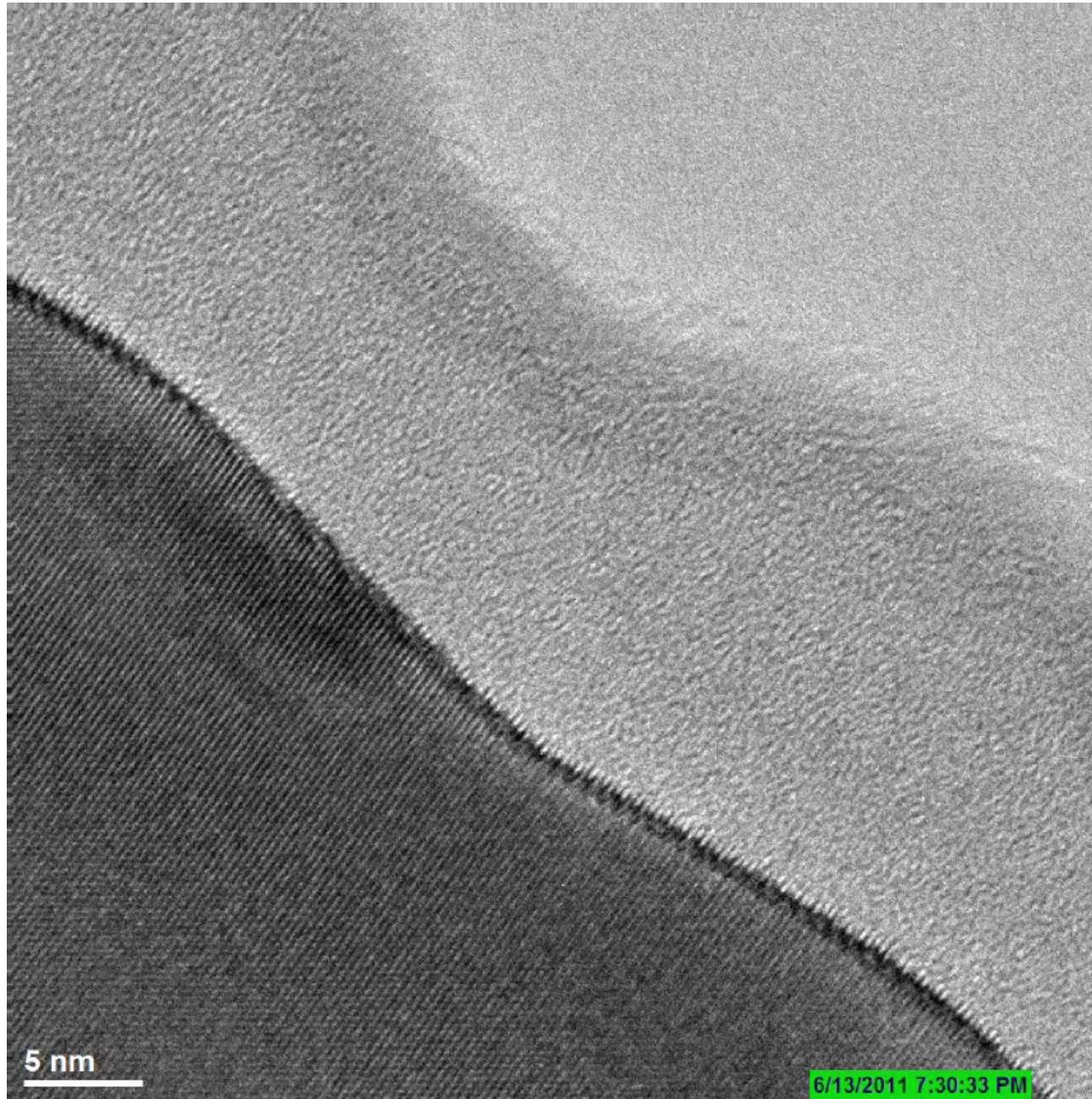
- **Single-phase model**
- **Surface stress always compression**
- **Cracks nucleate from center**

- **Two-phase model**
- **Surface stress is tensile**
- **Cracks nucleate from surface**

Y. T. Cheng, M.W. Verbrugge, J. Power Sources 190 (2009) 453
T.K. Bhandakkar, H.J. Gao, Int. J. Sol. Struc. 48 (2011) 2304
K.J. Zhao, M. Pharr, J.J. Vlassak, Z.G. Suo, J. Appl. Phys **109**,
016110, 2011

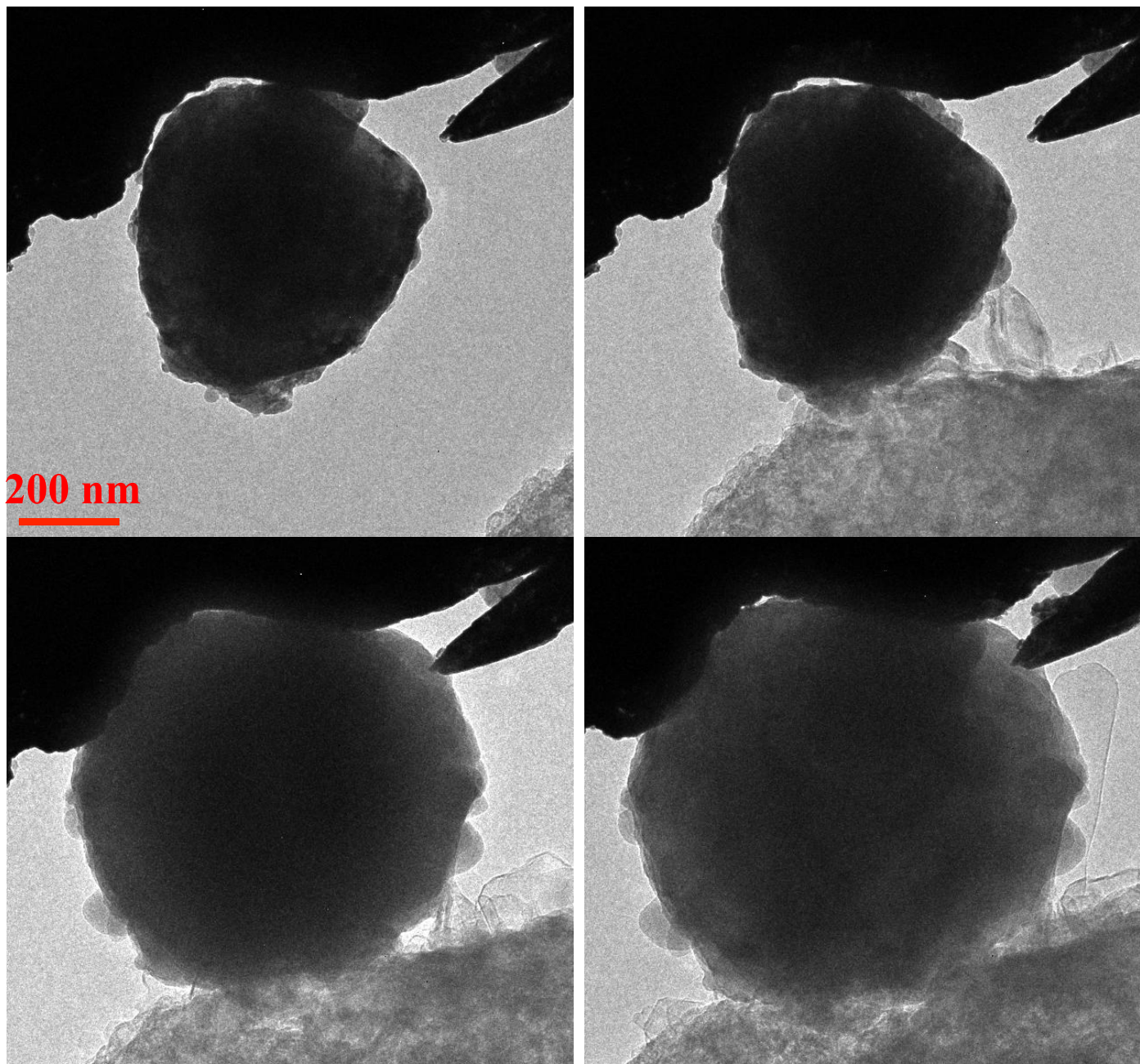
Chon et al., PRL 2011
Zhao et al., J. Power Source, 2011
Zhu, Liu, Huang *et al.*, submitted

Atomically sharp interface during lithiation Si



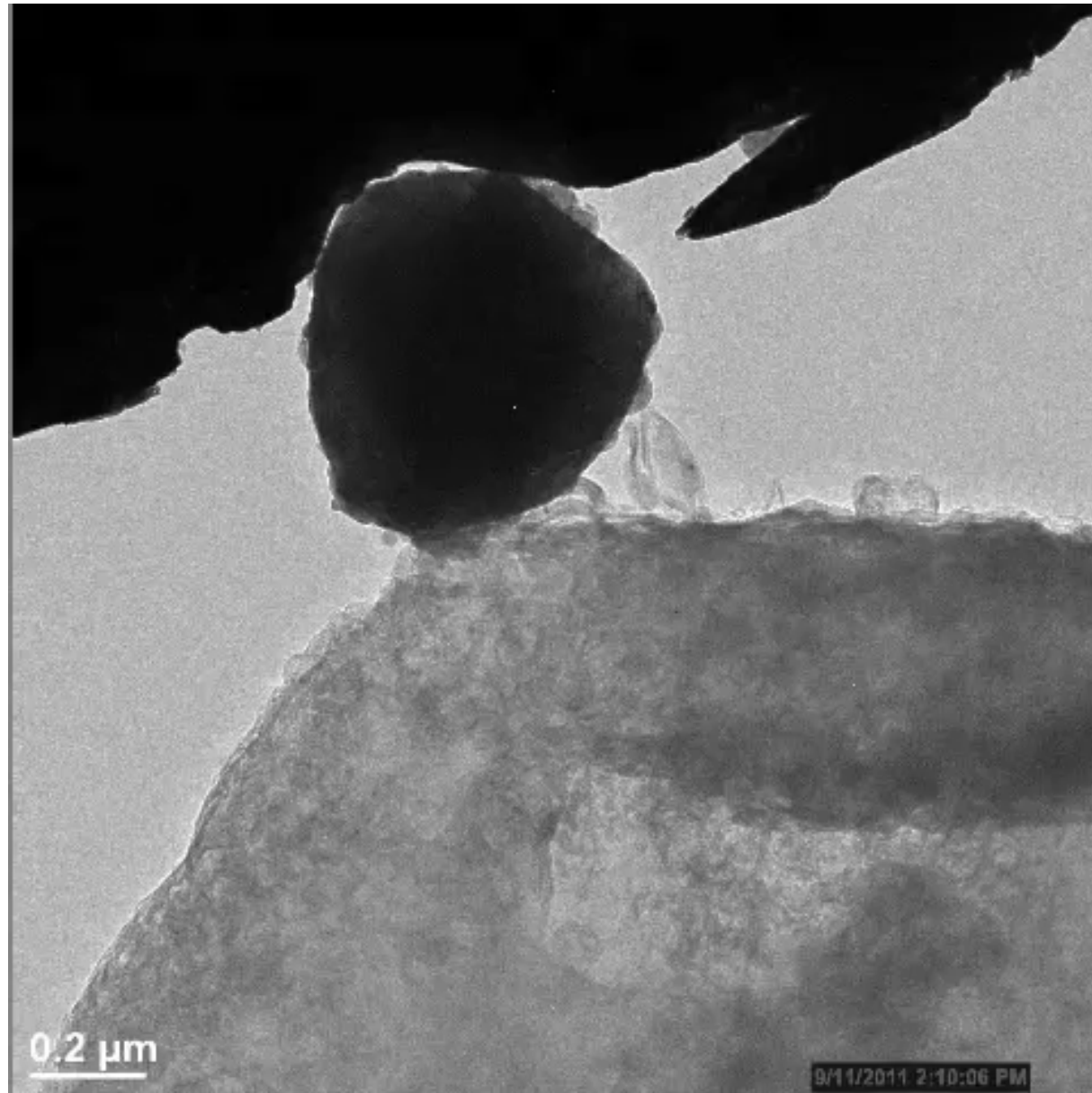
X.H. Liu
J.Y. Huang
unpubsished

Lithiation of Ge nanoparticles



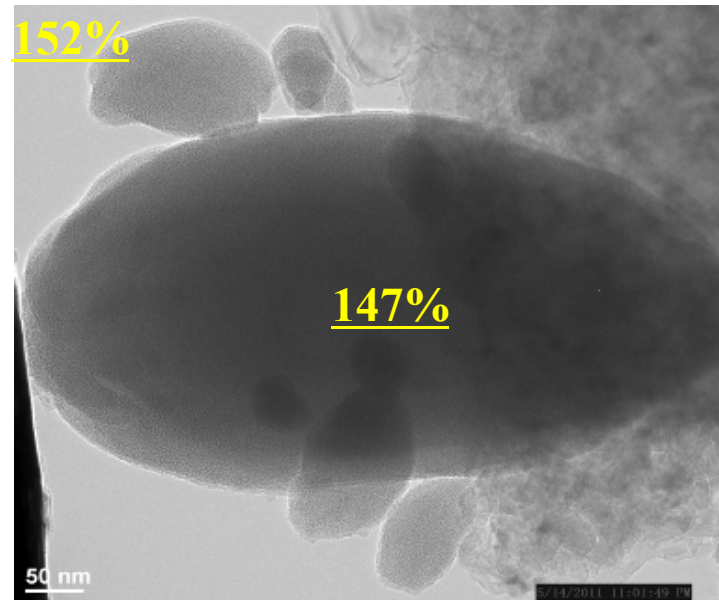
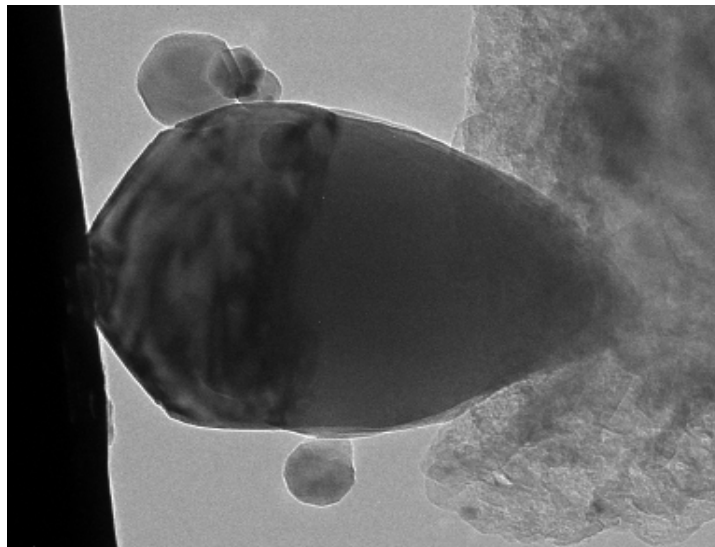
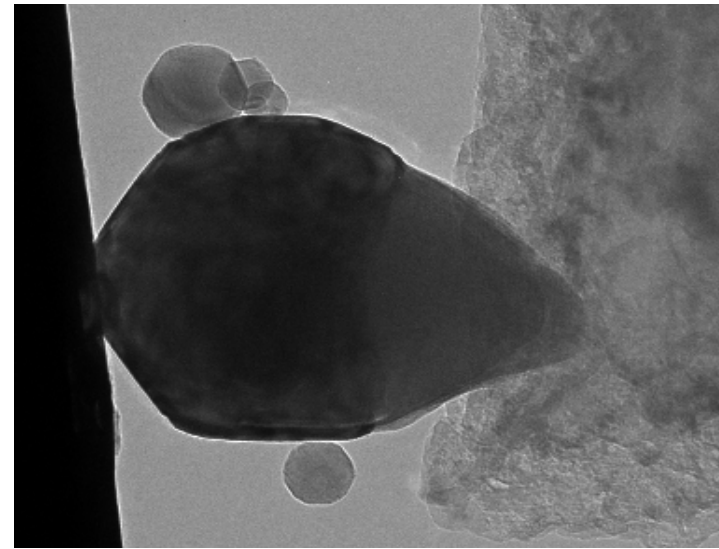
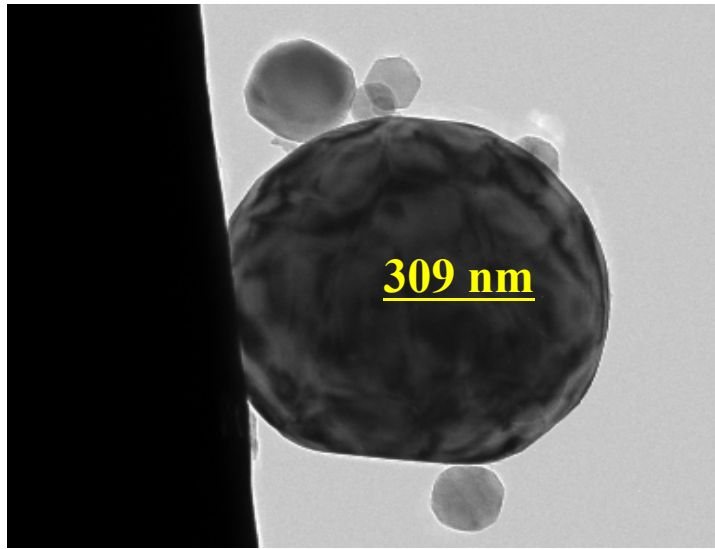
W.T. Liang,
S.L. Zhang,
J.Y. Huang
unpublished

Lithiation of Ge nanoparticles



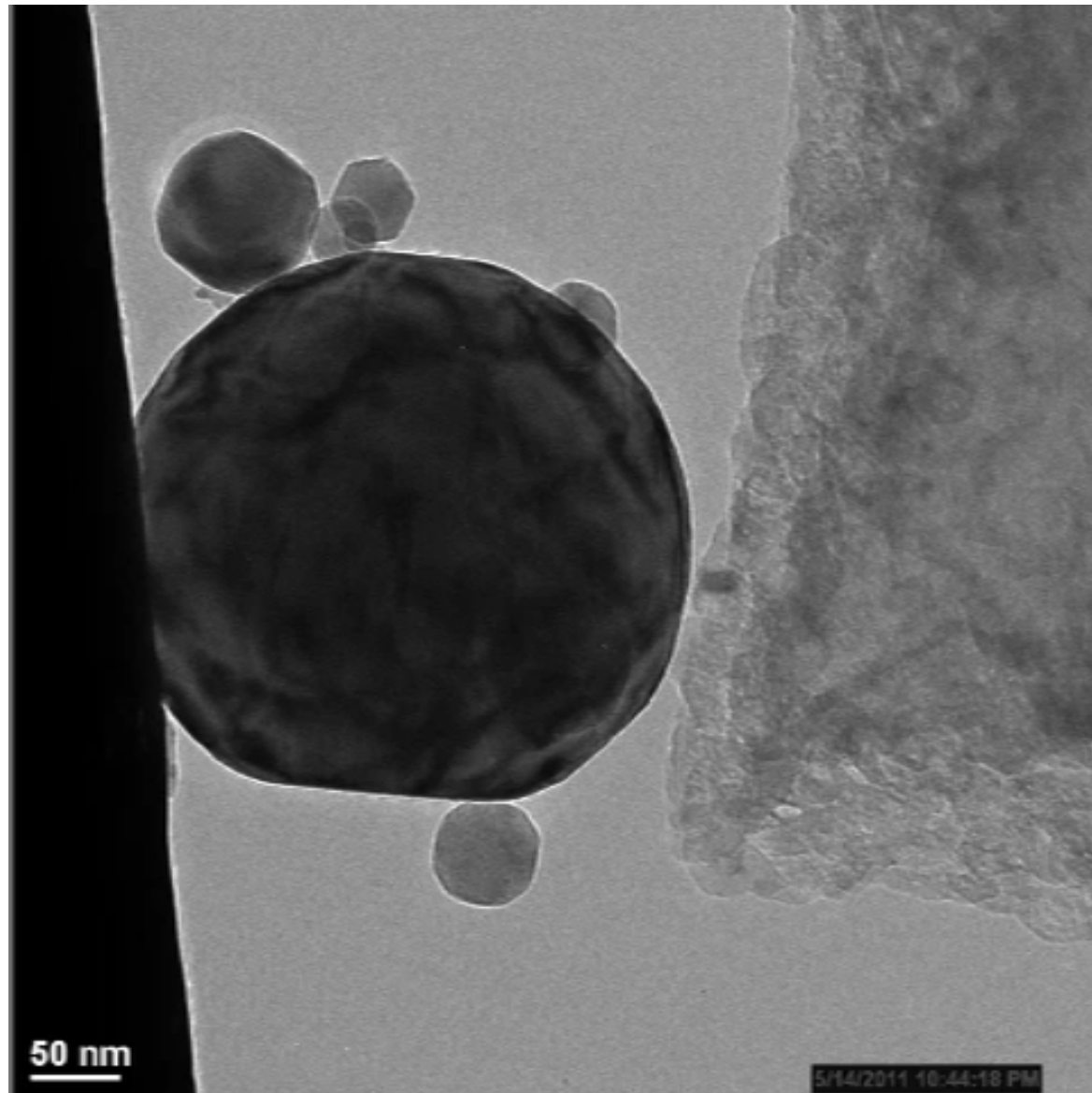
W.T. Liang,
S.L. Zhang,
J.Y. Huang
unpublished

Lithiation of Sn nanoparticles



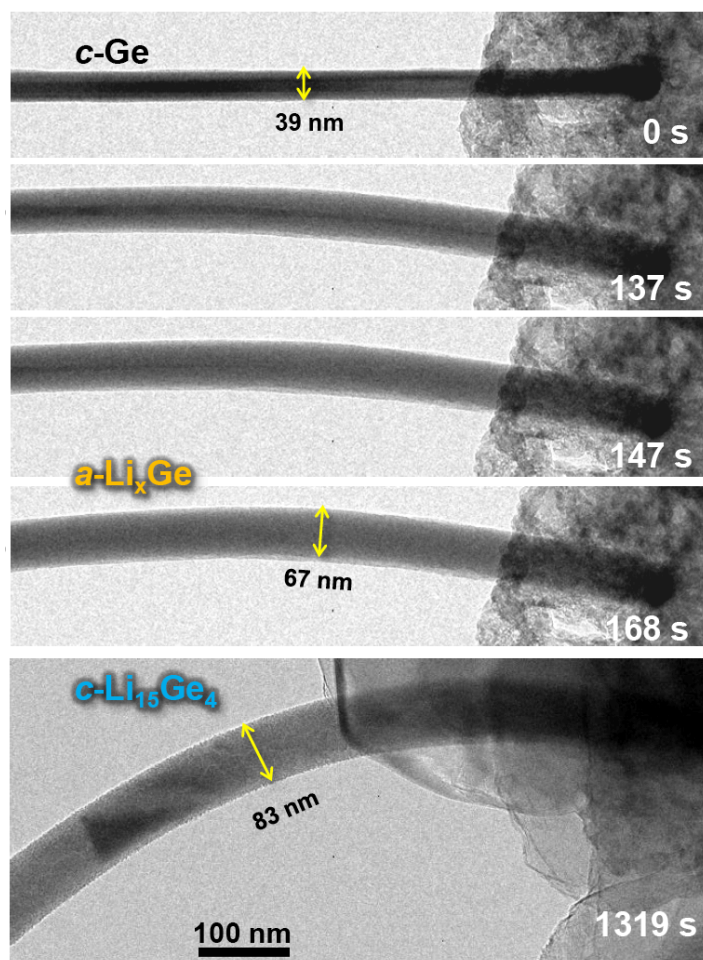
J.W. Wang, S. Mao, J.Y. Huang, unpublished

Lithiation of Sn nanoparticles

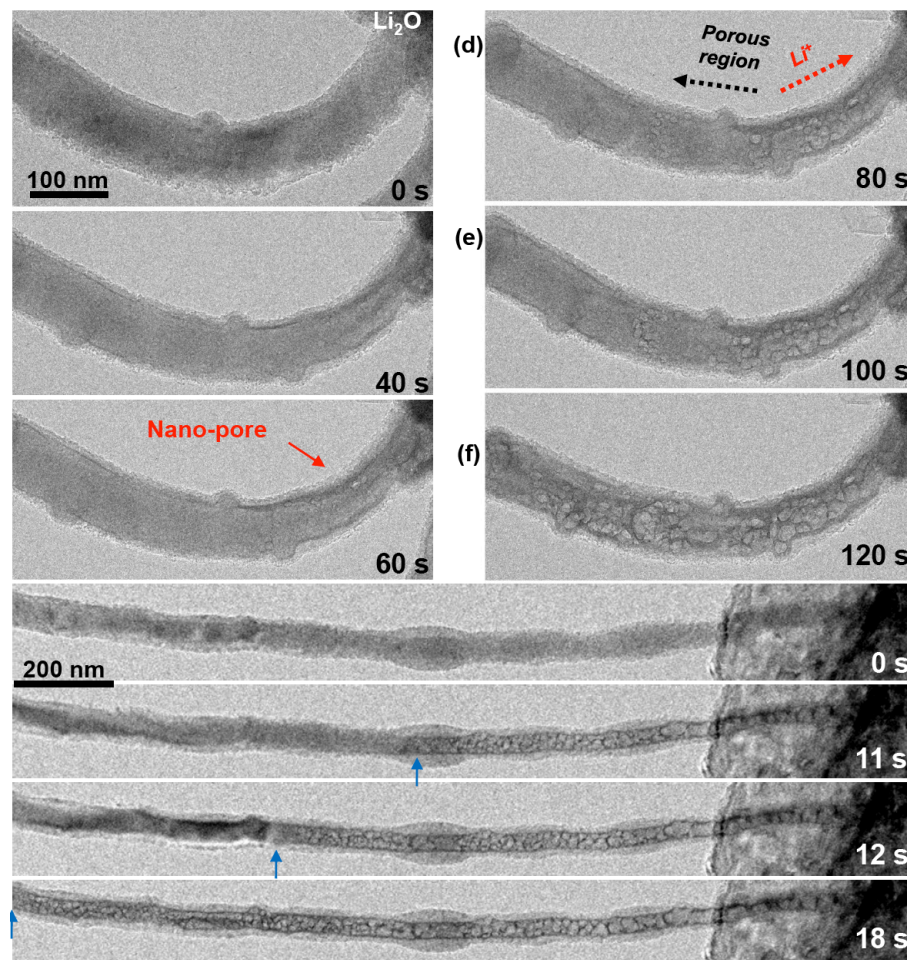


J.W. Wang, S. Mao, J.Y. Huang, unpublished

4: reversible nano-pore formation in Ge NWs



Lithiation

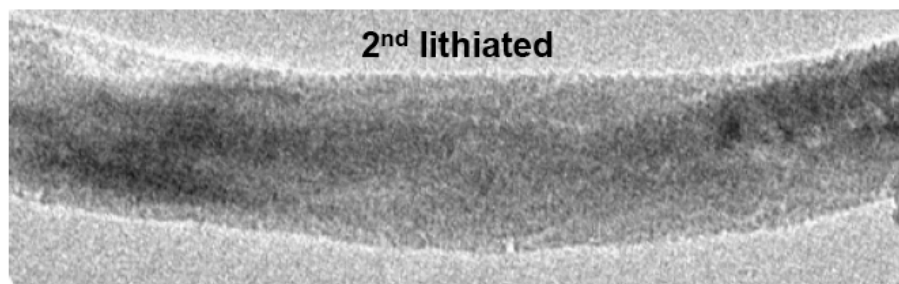


De-Lithiation

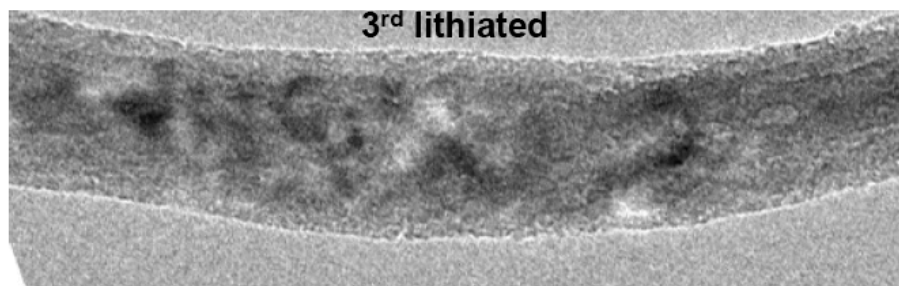
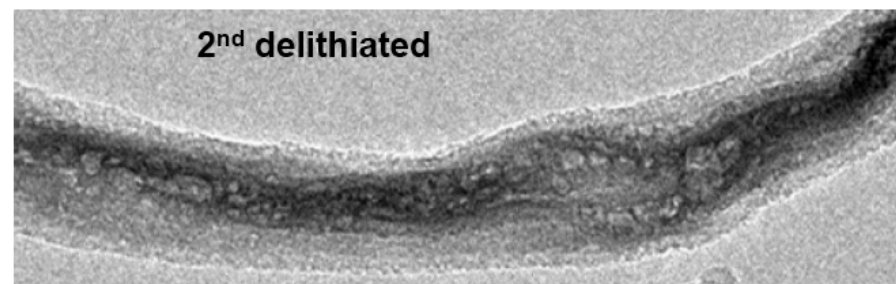
Ge: 1384 mA h/g, Graphite: 372, Si: 3579. Electric conductivity 1000 times of Si

Xiao Hua Liu, Shan Huang, S. Tom Picraux, Ju Li, Ting Zhu, and Jian Yu Huang, Nano Lett. 11, 3991 (2011)

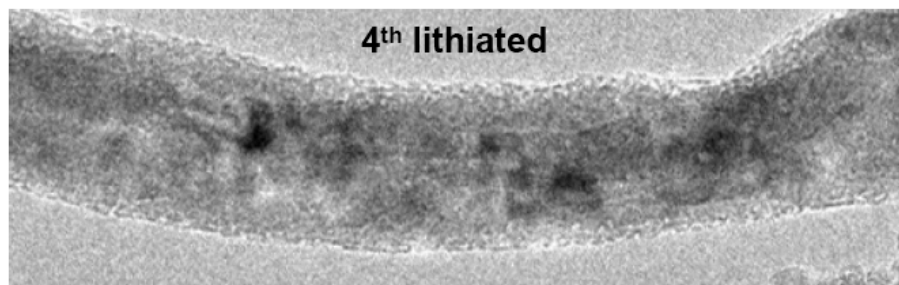
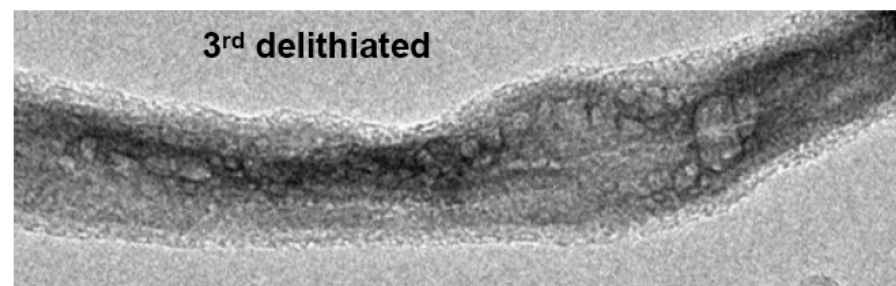
Reversible nano-pore formation in Ge NWs



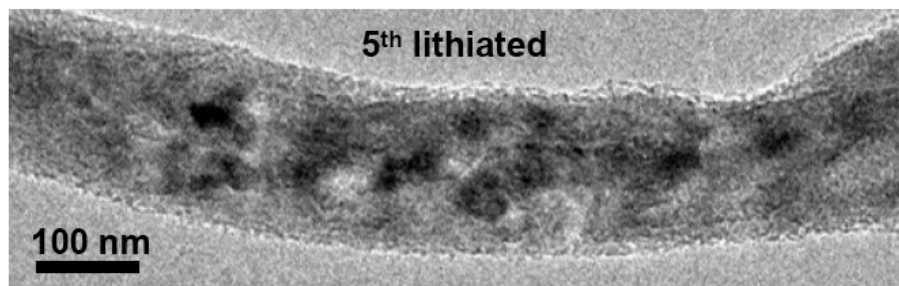
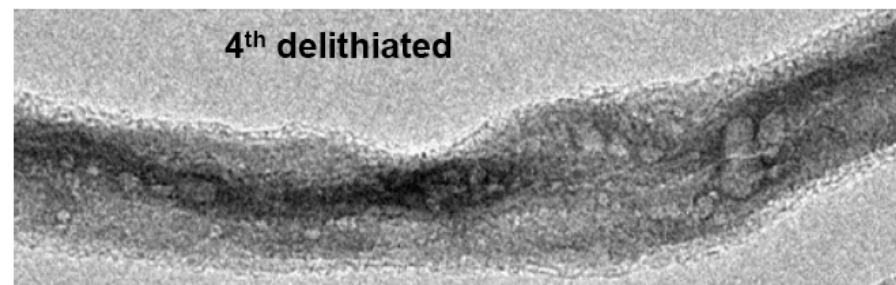
(b)



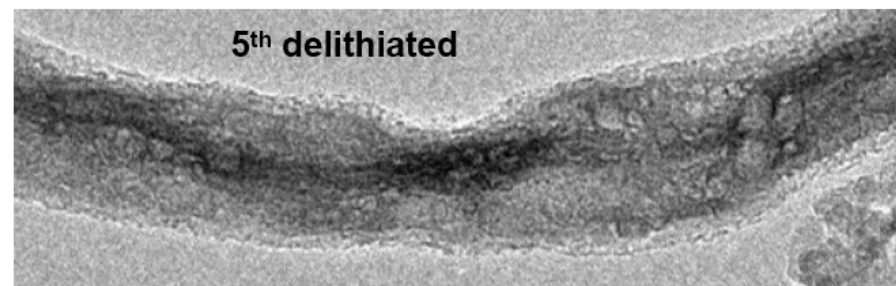
(d)



(f)

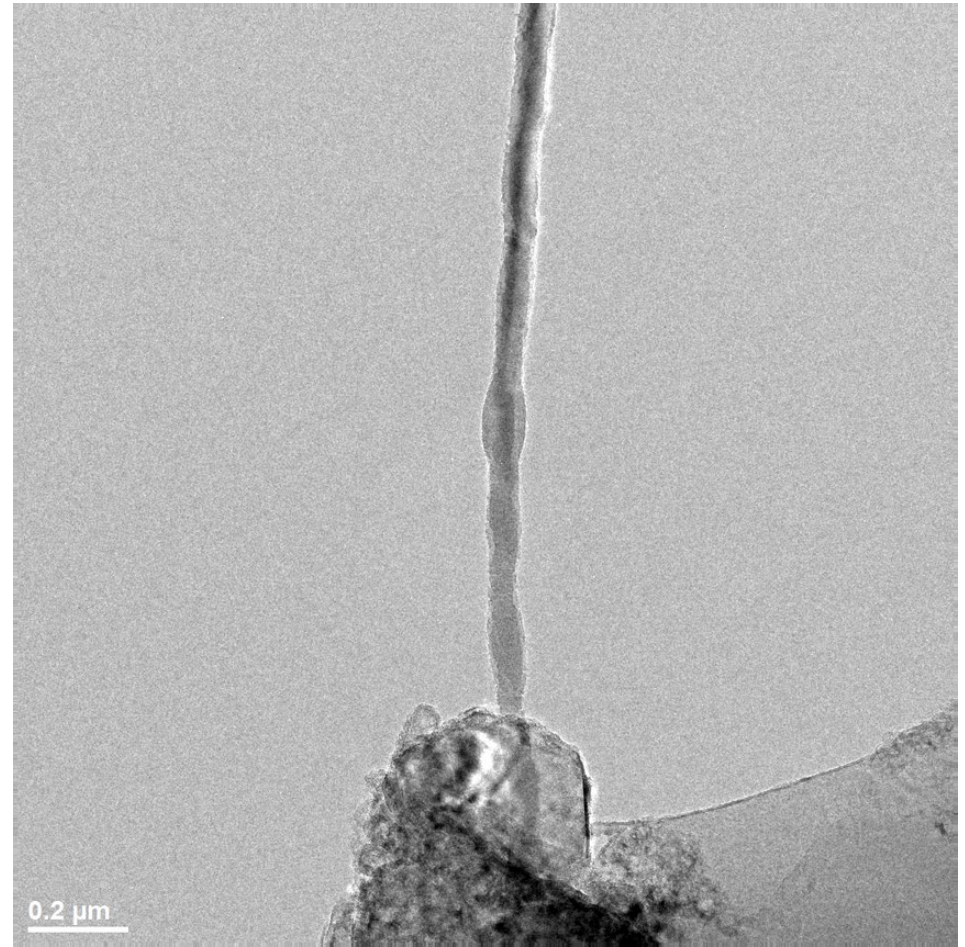
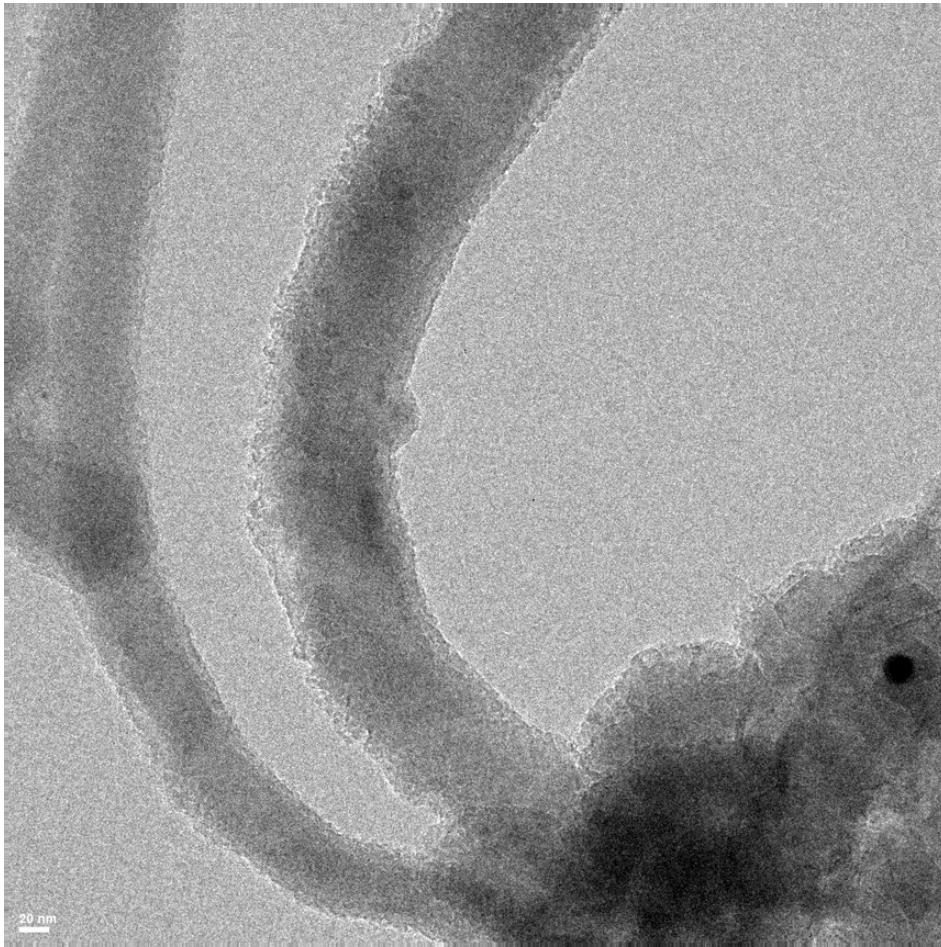


(h)

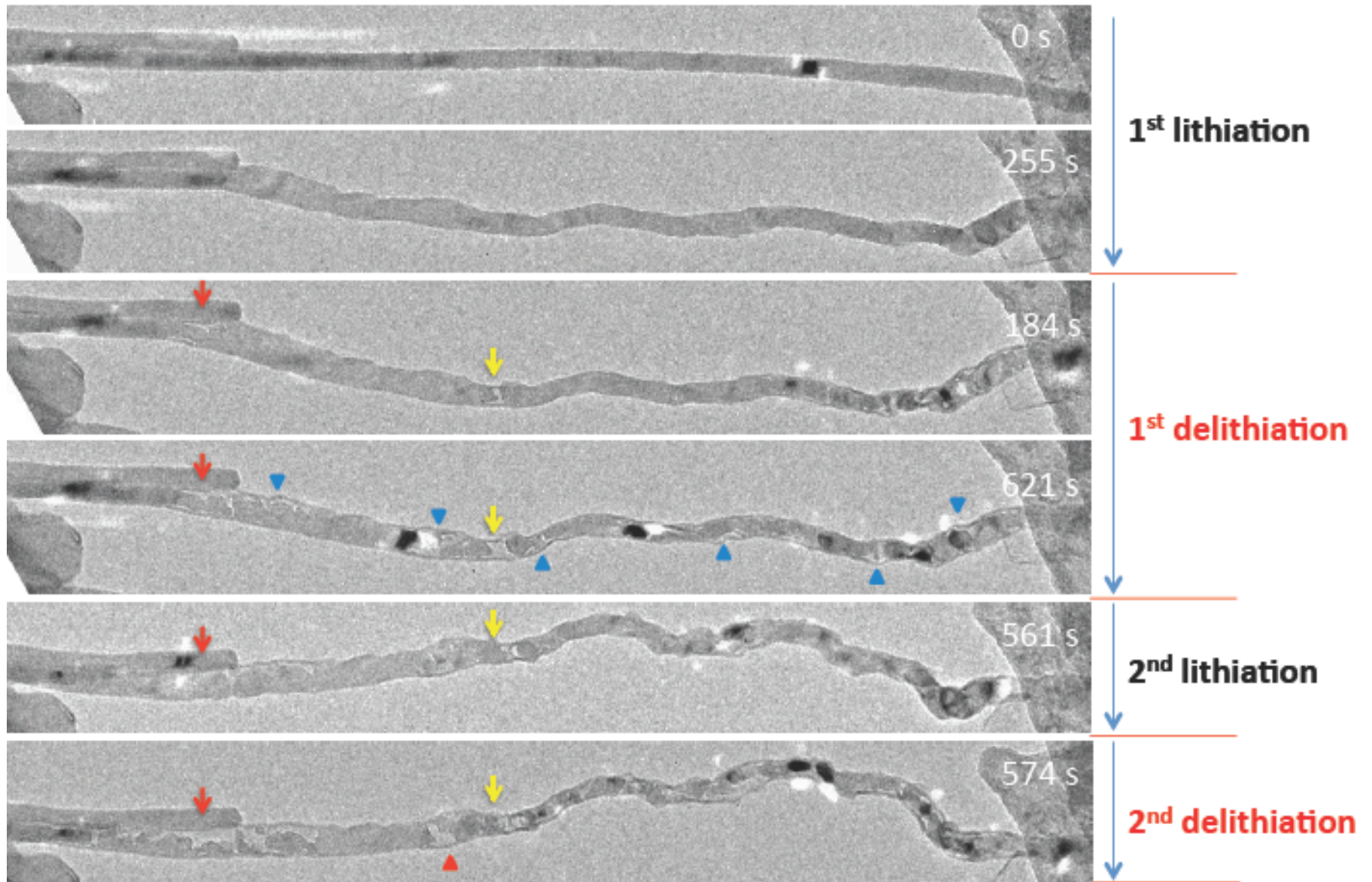


Ge: long cycle lifetime

Case study 4: reversible nano-pore formation in Ge NWs

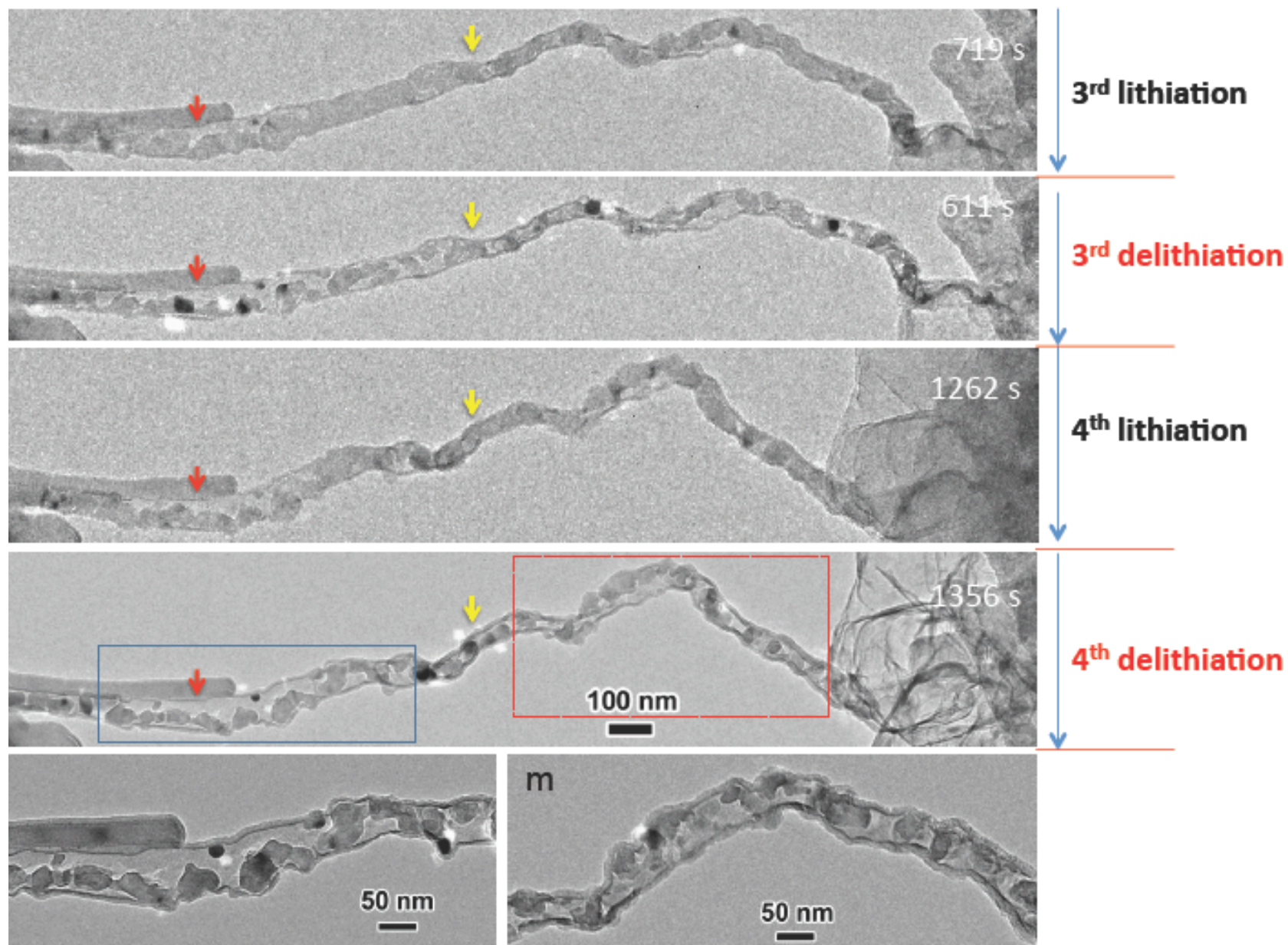


5: Pulverization of Al NWs

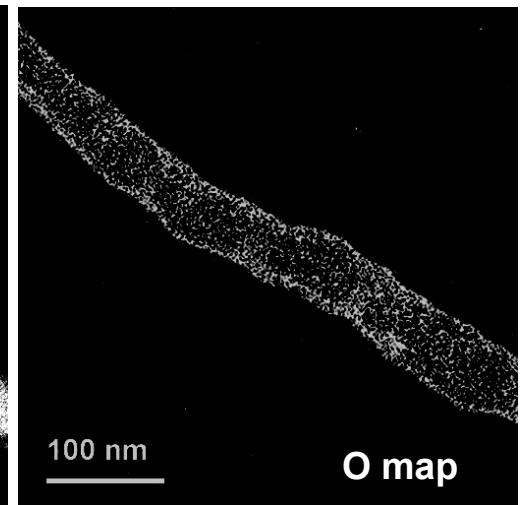
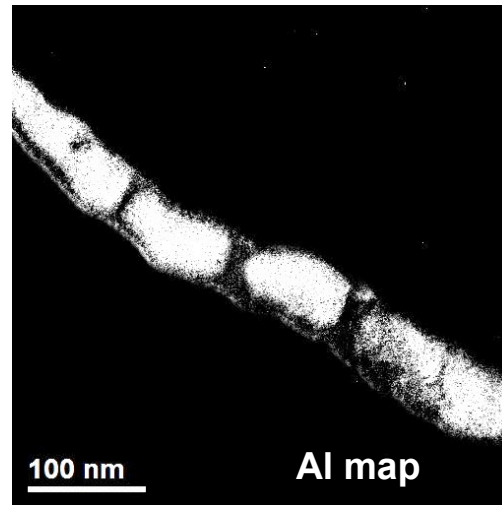
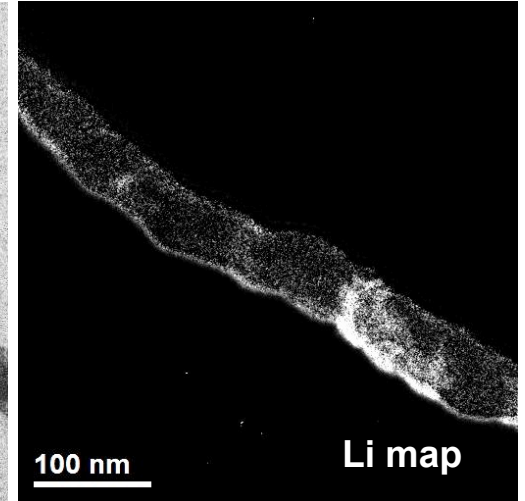
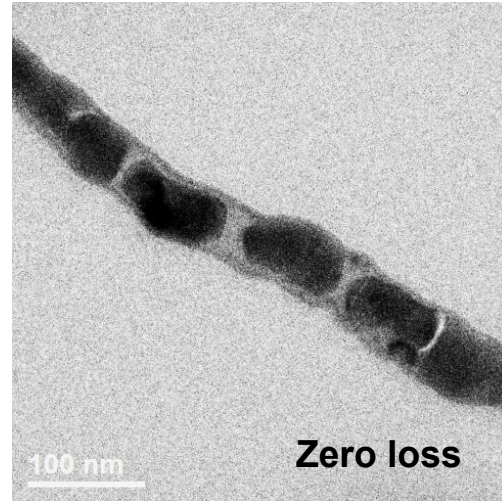
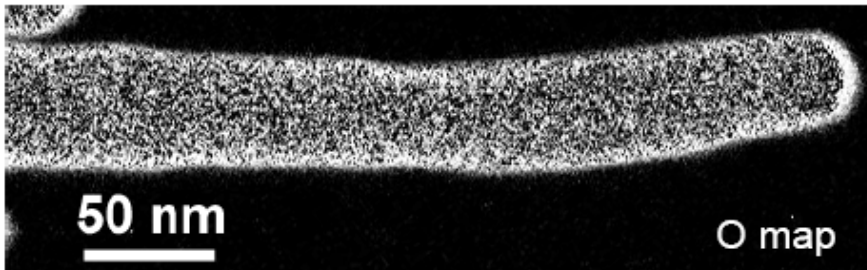
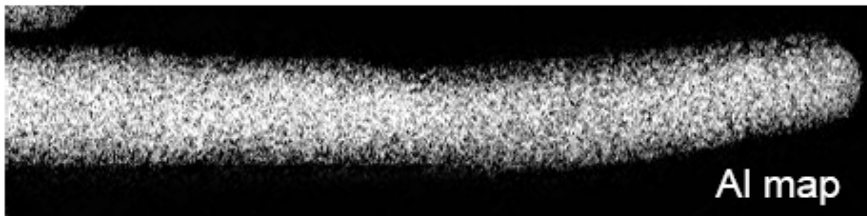
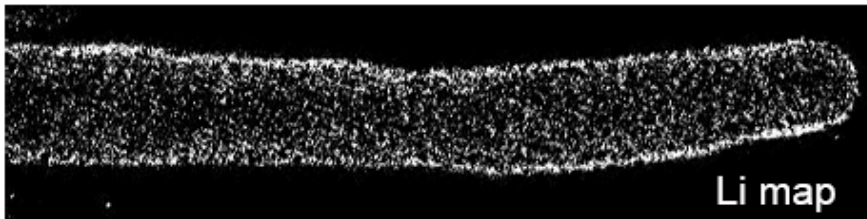
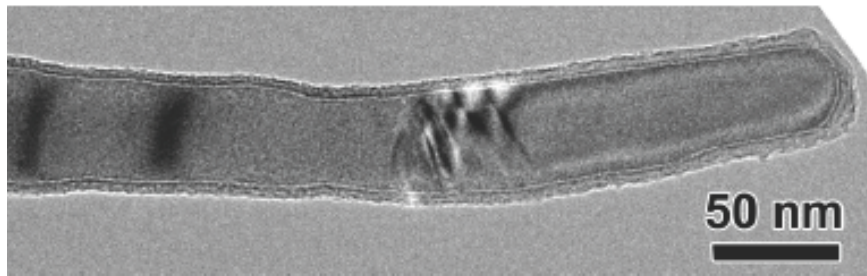


Yang Liu, Jian Yu Huang et al., Nano Lett. Doi: 10.1021/ nl202088h

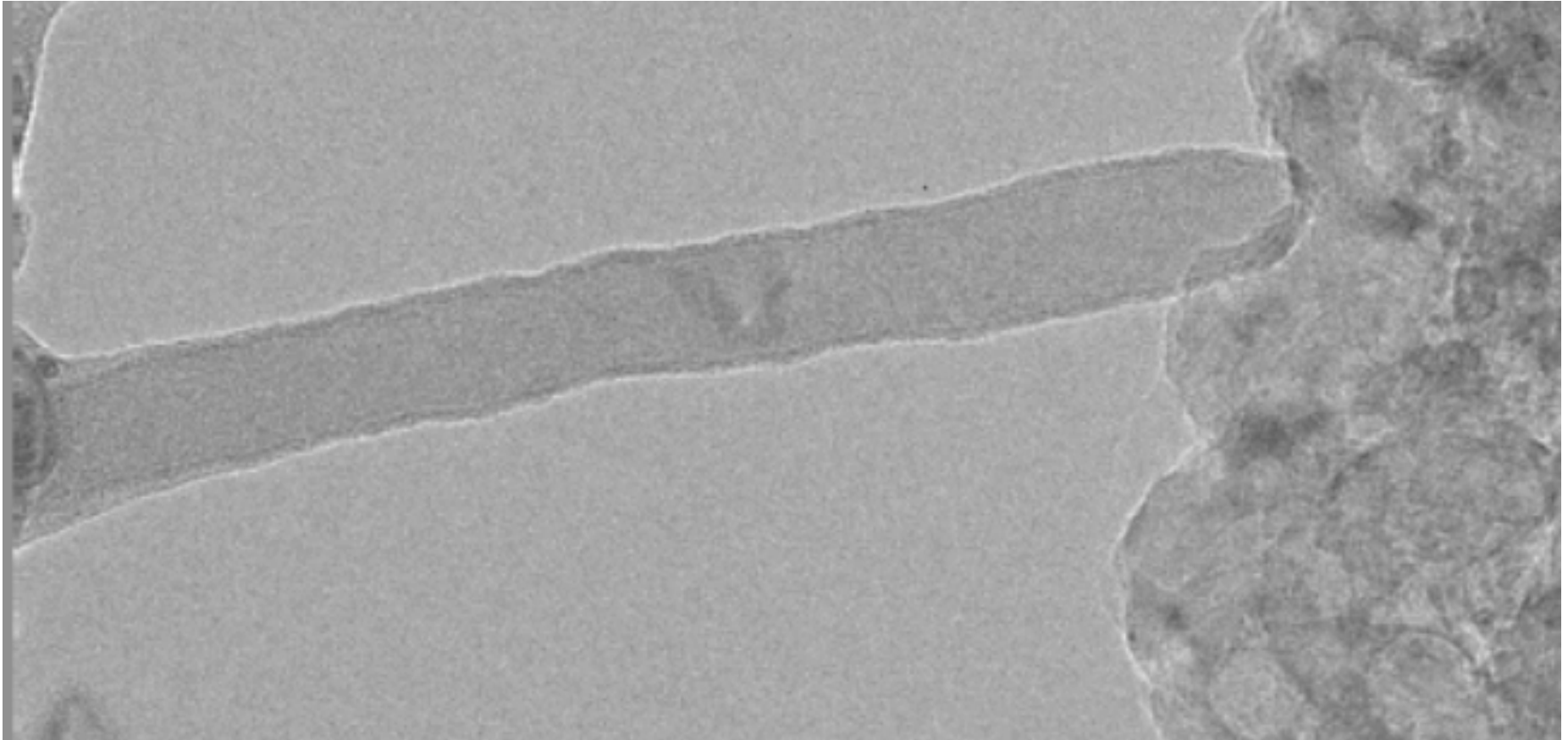
Pulverization of Al NWs



Pulverization of Al NWs

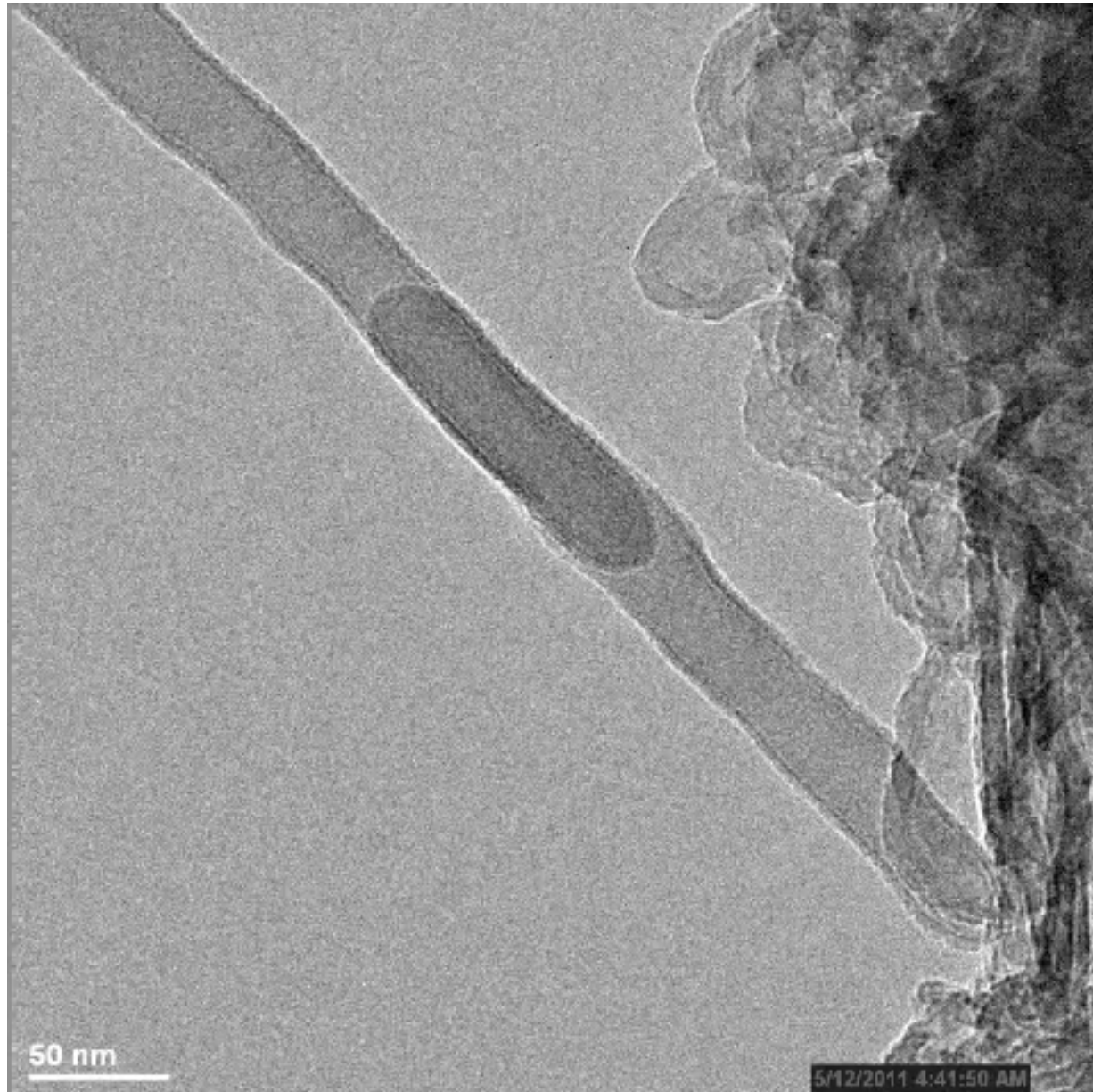


Pulverization of Al NWs

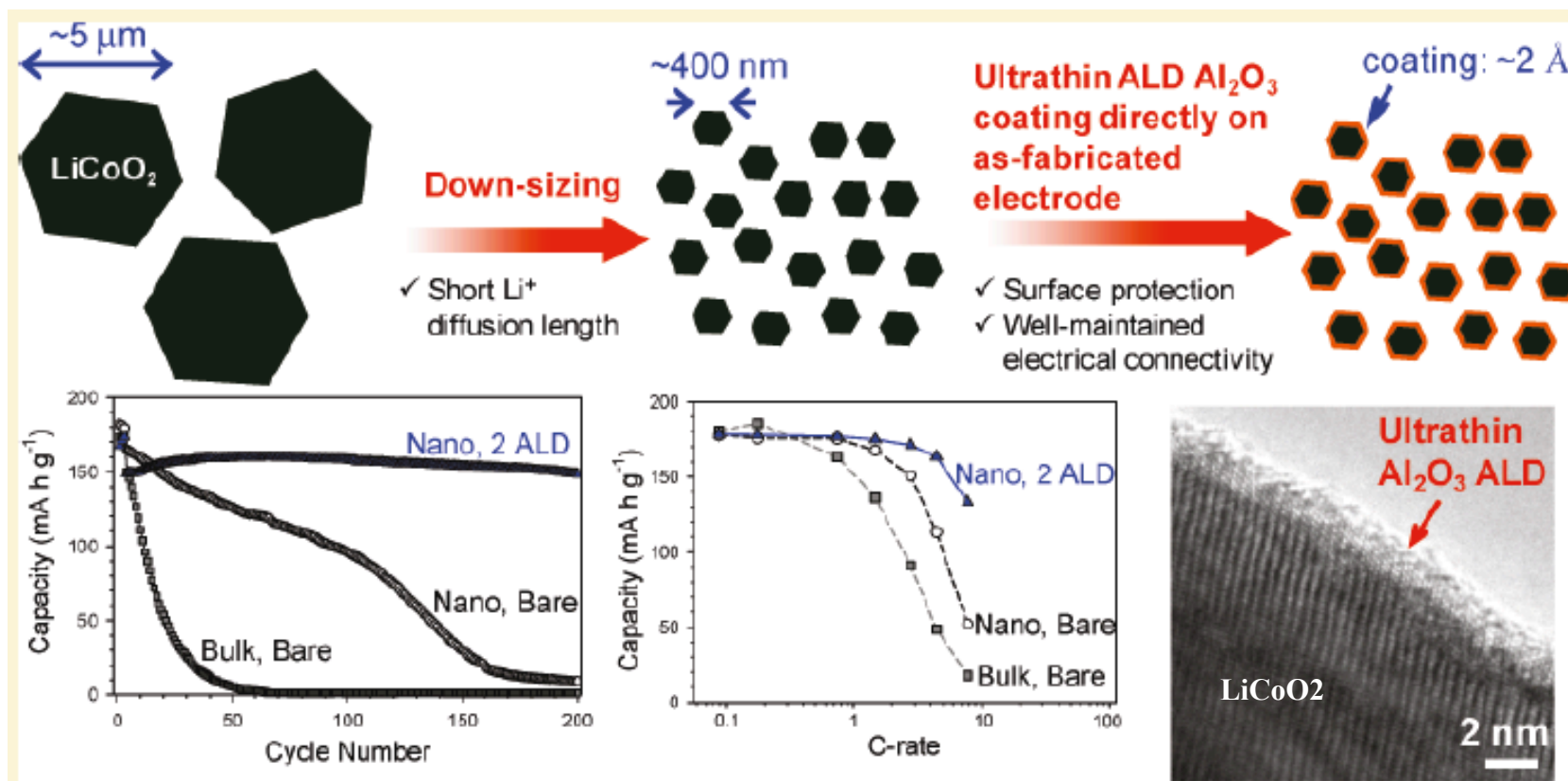


- **Surface Al_2O_3 lithiated first, forming Li-Al-O glass**
- **Solid electrolyte with good ion conductivity**
- **Mechanical robust**

Pulverization of Al NWs

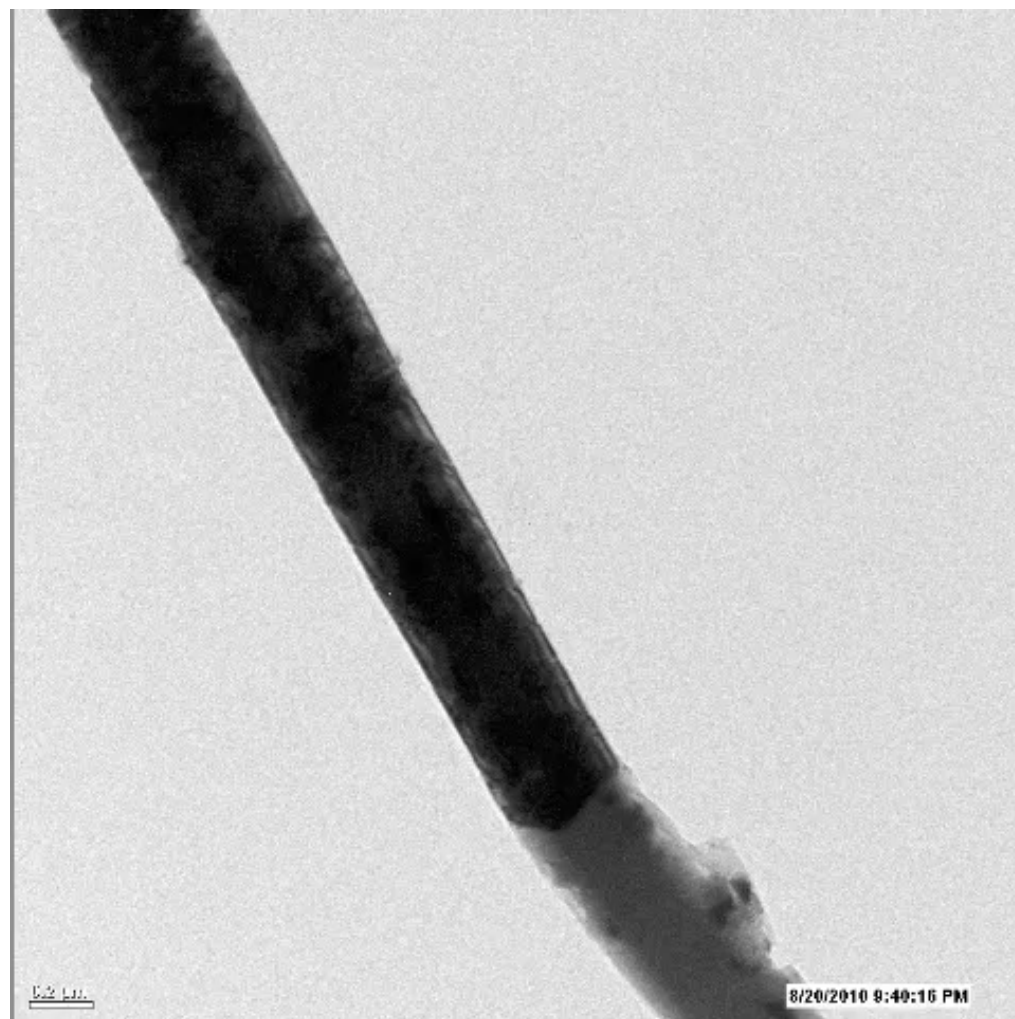
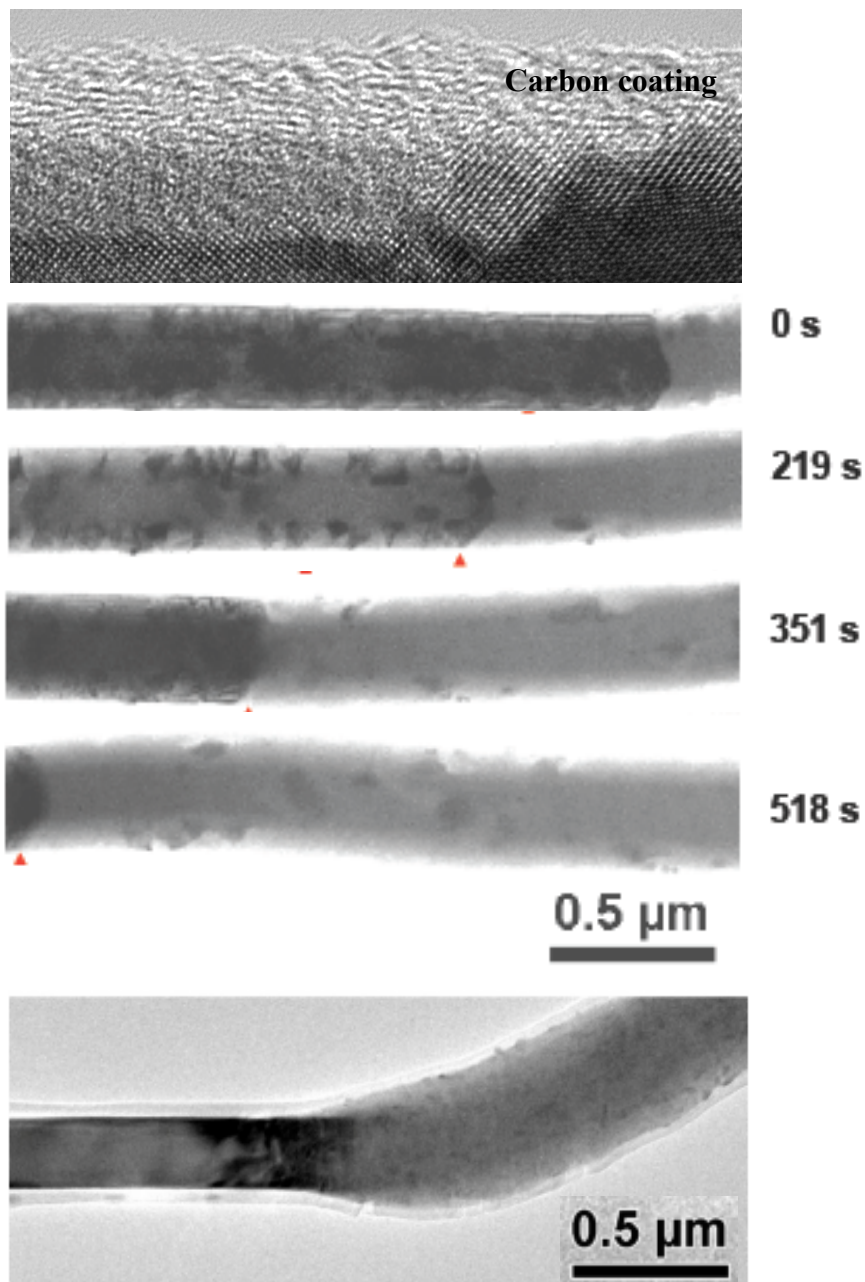


Implication to ALD



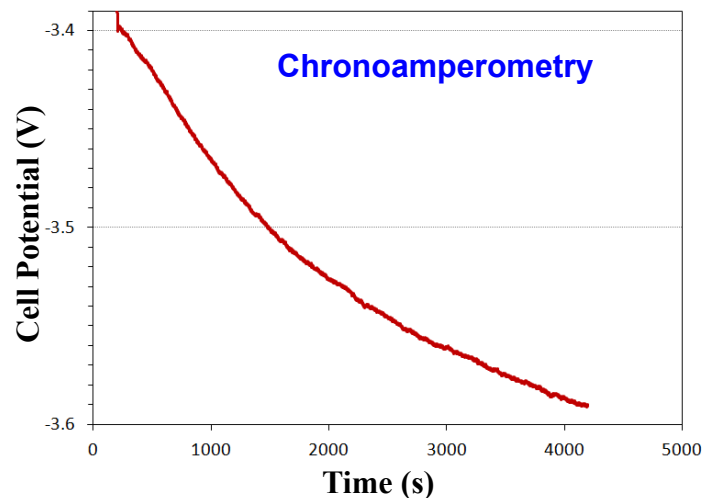
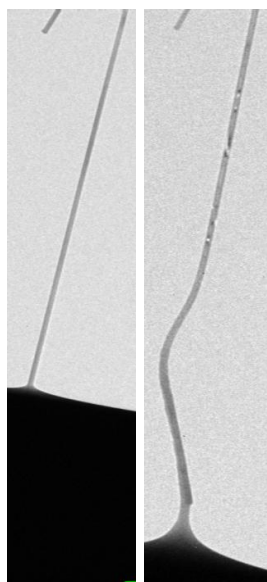
Scott, Dillon *et al.*, Nano Lett. 10.1021/nl1030198

6: Controlling lithiation induced strain by coating



Li Qiang Zhang, Xiao Hua Liu, Yang Liu, Shan Huang, Ting Zhu, Liangjin Gui, Scott X. Mao, Zhi Zhen Ye, Chong Min Wang, John P. Sullivan, and Jian Yu Huang
ACS Nano 5, 4800–4809 (2011)

Quantitative control and measurement in nanoscale electrochemistry



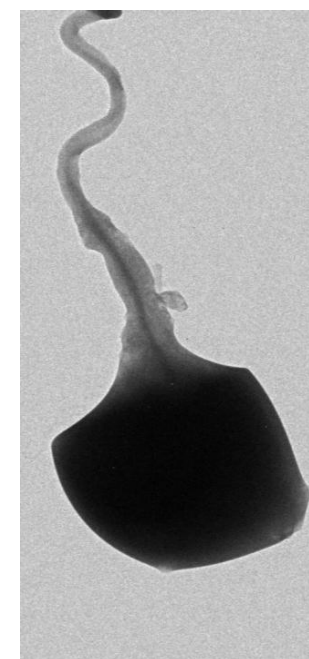
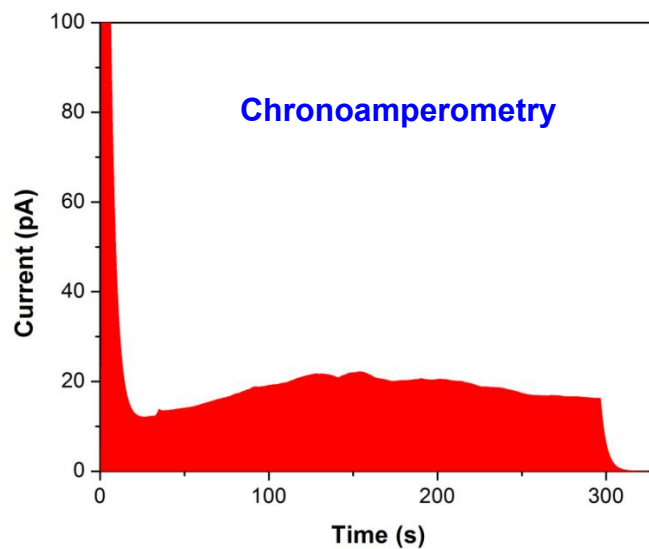
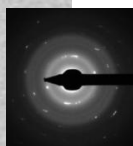
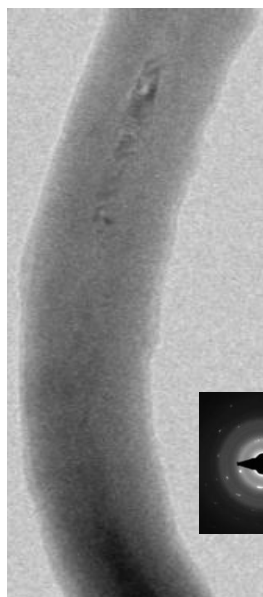
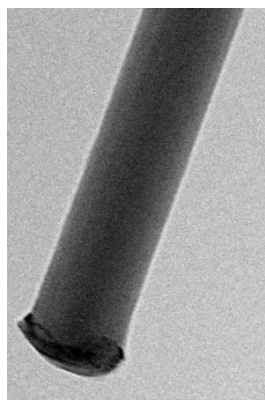
$$Q_{\text{app}} = 7.9 \text{ nC}$$

$$Q_{\text{Li}_{3.75}\text{Si}} = 11.5 \text{ nC}$$

68%

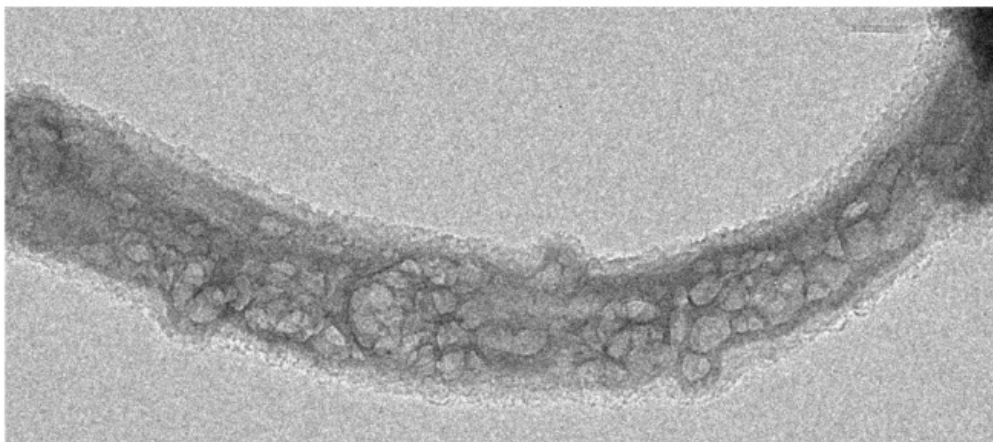
A subset of wires exhibit efficiencies of 60 – 130%

- Li content
- Competing red. rxns



Kevin Zavadil, Xiaohua Liu, Yang Liu, Jianyu Huang et al., unpublished

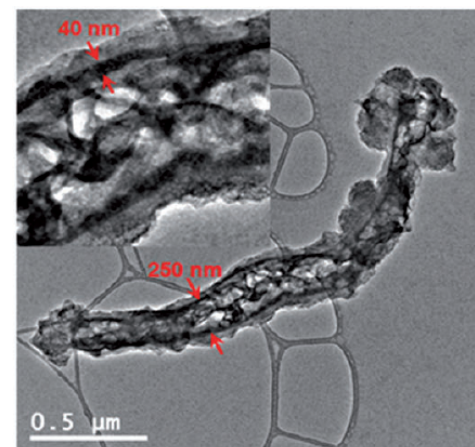
Relevance of in-situ battery to conventional electrochemical cell



In-Situ Result

structure for facile stress relaxation, respectively. These results suggest that Ge, which can develop a reversible nanoporous network structure, is a promising anode material for lithium ion batteries with superior energy capacity, rate performance, and cycle stability.

Xiao Hua Liu, Shan Huang, S. Tom Picraux, Ju Li, Ting Zhu, and Jian Yu Huang
Nano Lett. 11, 3991 (2011)

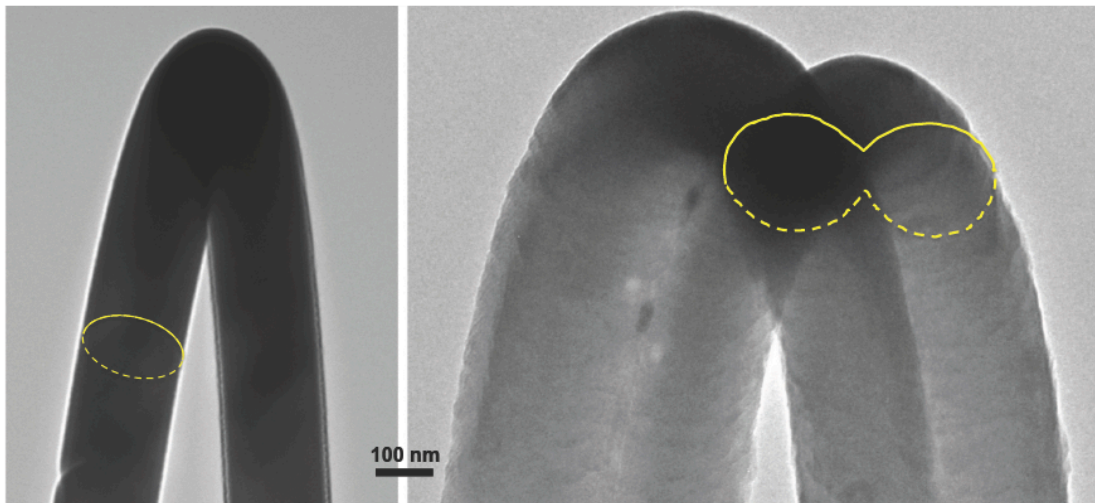


**Conventional
Electrochemical Result**

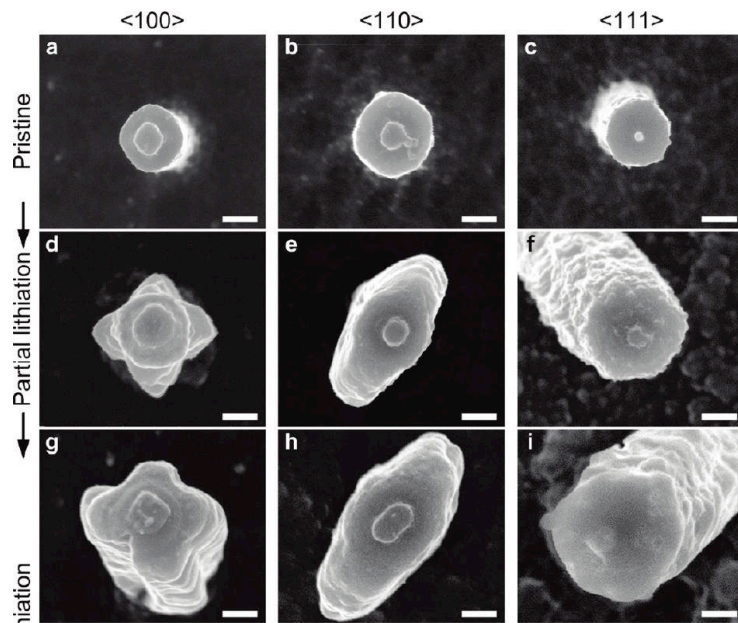
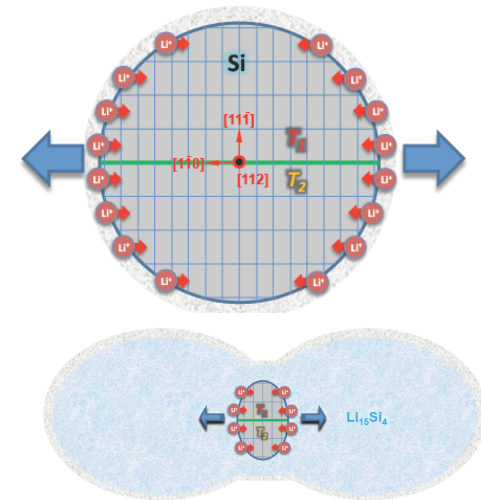
In conclusion, Ge NTs have been synthesized using a high-yield method. The Ge NTs demonstrated exceptionally high rate capability with excellent capacity retention and stability over 400 cycles, suggesting that Ge NTs are ideally suited as anodes for a new generation of high-power lithium-ion batteries for a wide range of applications.

Cho et al., **Angew. Chem.** 10.1002/anie.
201103062

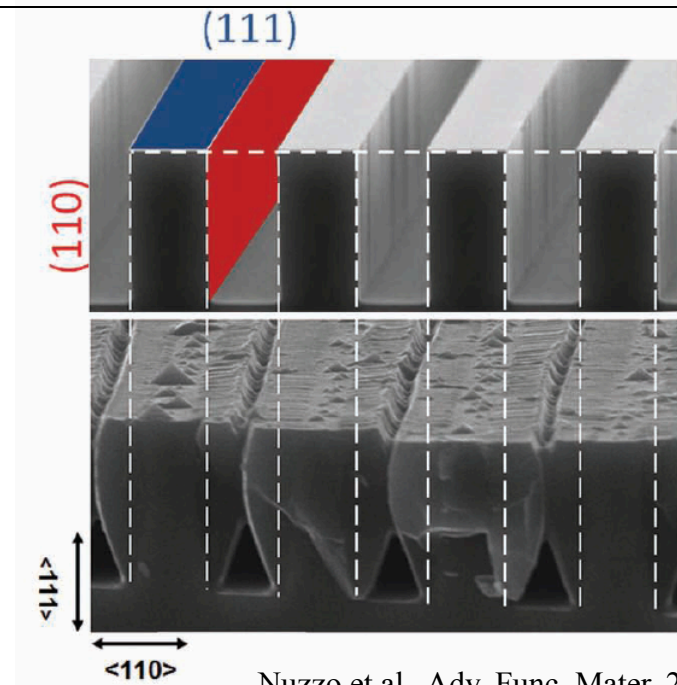
Relevance of in-situ battery to conventional electrochemical cell



Liu & Huang et al., Nano Lett. 11, 3312 (2011)



Yi Cui et al., Nano Lett. 11, 3034 (2011)



Nuzzo et al., Adv. Func. Mater. 21, 2412 (2011)

Summary and Perspective

- Created an in-situ electrochemical cell inside a TEM.
- “See” the effect of ion and electron transport, and how electrode function in real time and high spatial resolution, provide fundamental understandings of LIBs.
- Material, size, crystallographic orientation dependent
- Results directly tied into the design of high energy density and high power density LIBs.
- Can be extended to many other material system, cathode/anode, different electrolyte
- How the ALD coating retaining the capacity? In-situ SEI formation
- Advance science of LIBs, providing important guidance in designing high energy density, high power density LIBs

Collaborators

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S. T. Picraux, *CINT, Los Alamos National Laboratory*

C.M. Wang, W. Xu, *PNL*

Chunsheng Wang, J. Cumings, G. Rubloff, *UMD*

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