SAND2011-9168 C

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Nanobatteries: Science Revealed in Small

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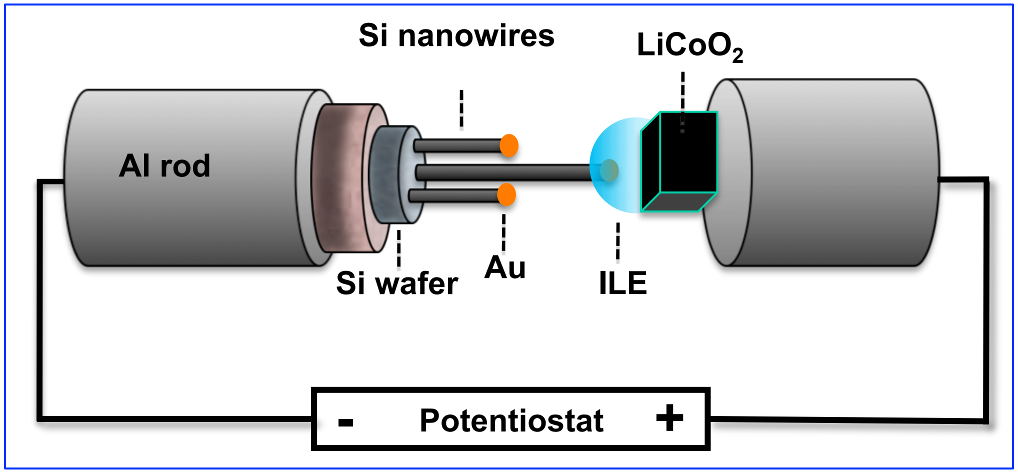
[1]SNL, [2]U. of Pitts., [3]GIT, [4]MIT, [5]LANL, [6]UMD



DEPARTMENT OF ENERGY
NEES
NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

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Sandia National Laboratories

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 of high energy density anodes due to large volume expansion**

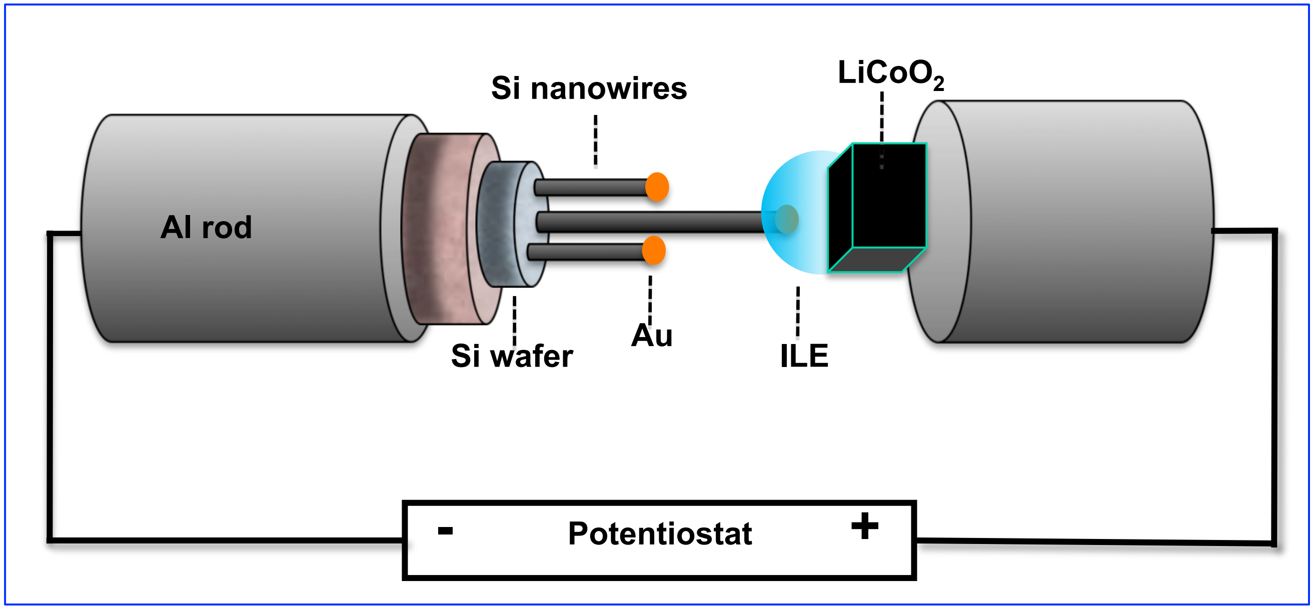
- **Lithium ion transport kinetics as a function of nanoscale structure dimension**

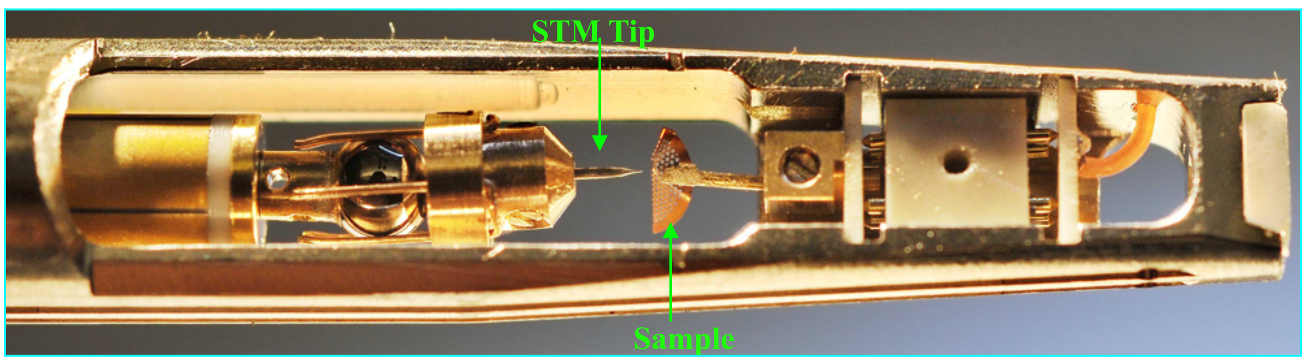
- **Electrode and electrolyte interface (e.g. SEI), how SEI forms, how does it evolve during cycling, and how does it lead to battery degradation?**

We need new capabilities to address these challenges!

The first nanobattery inside TEM!

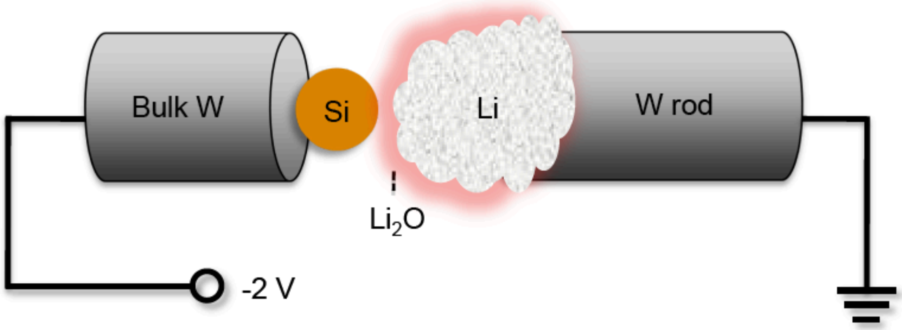
Our approach: A single nanowire Li-ion battery (Open Cell)

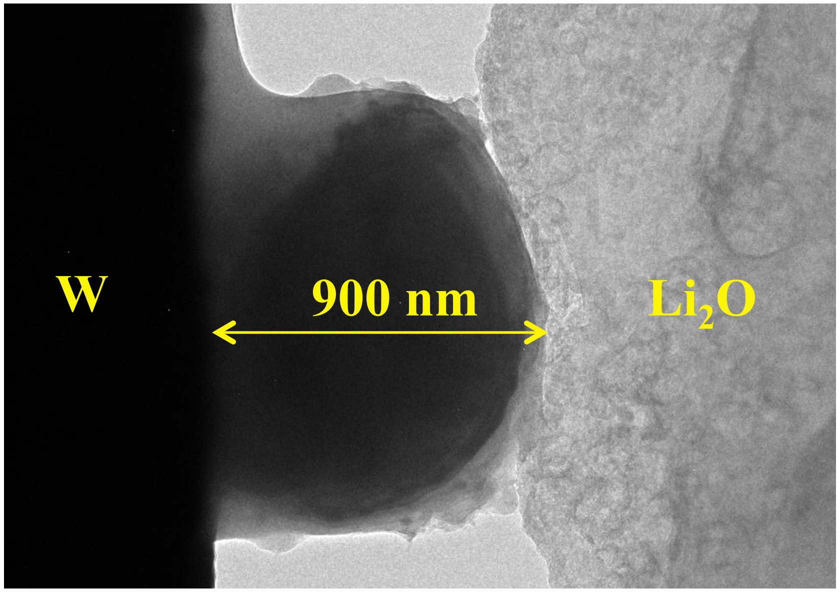




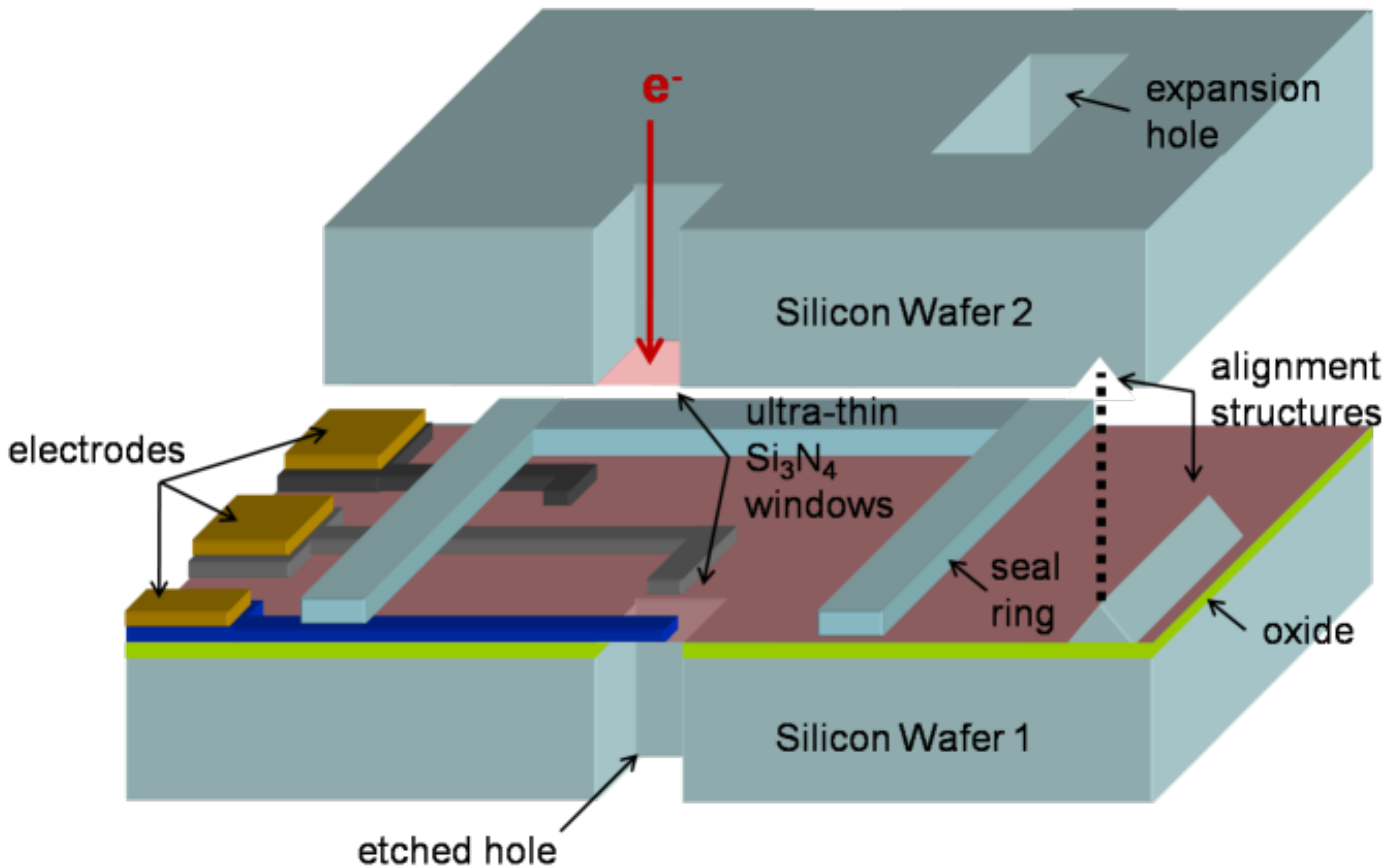
Smallest battery; very clean system, no binder

An all solid electrochemical cell

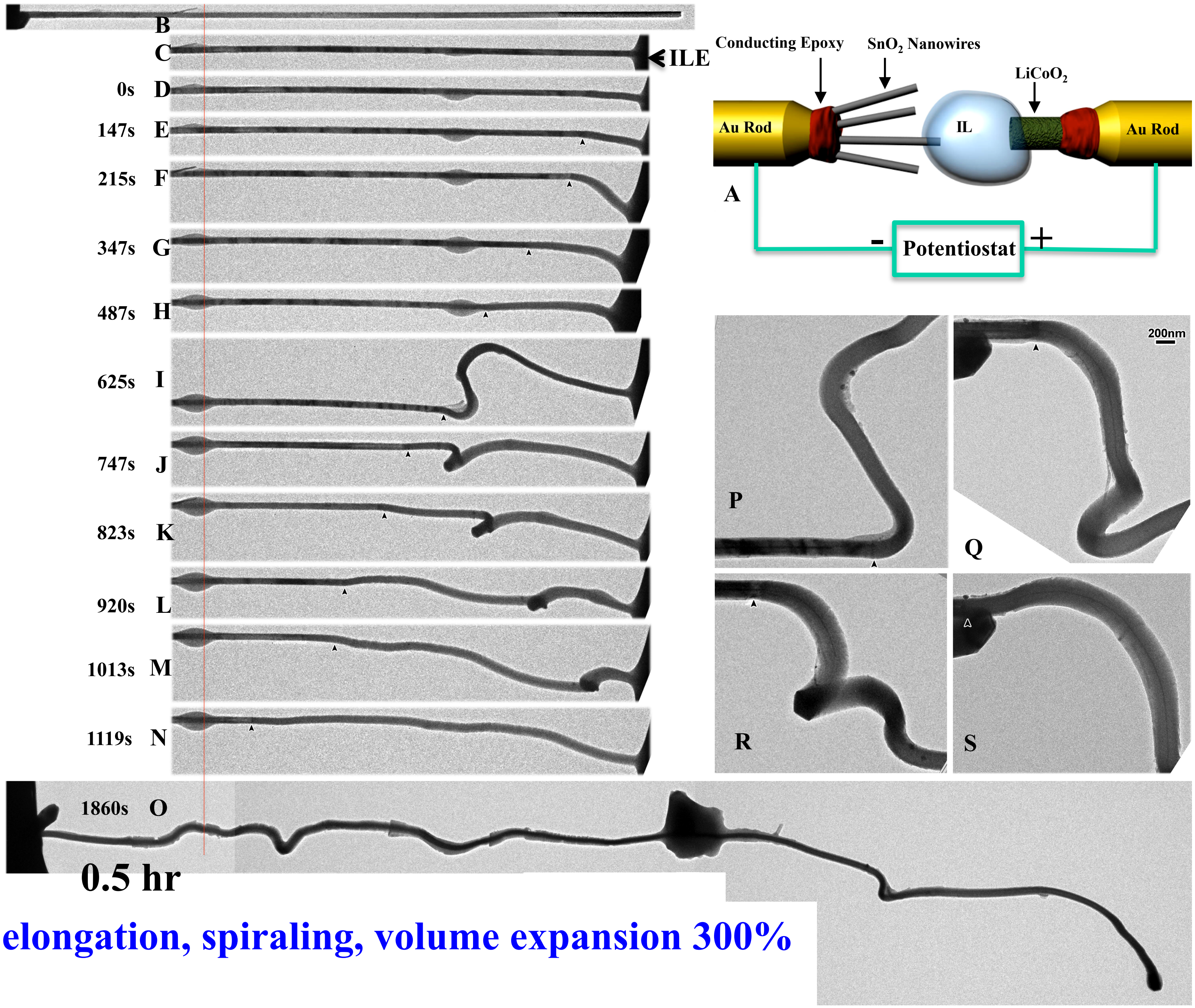




Future work: liquid electrochemical cell

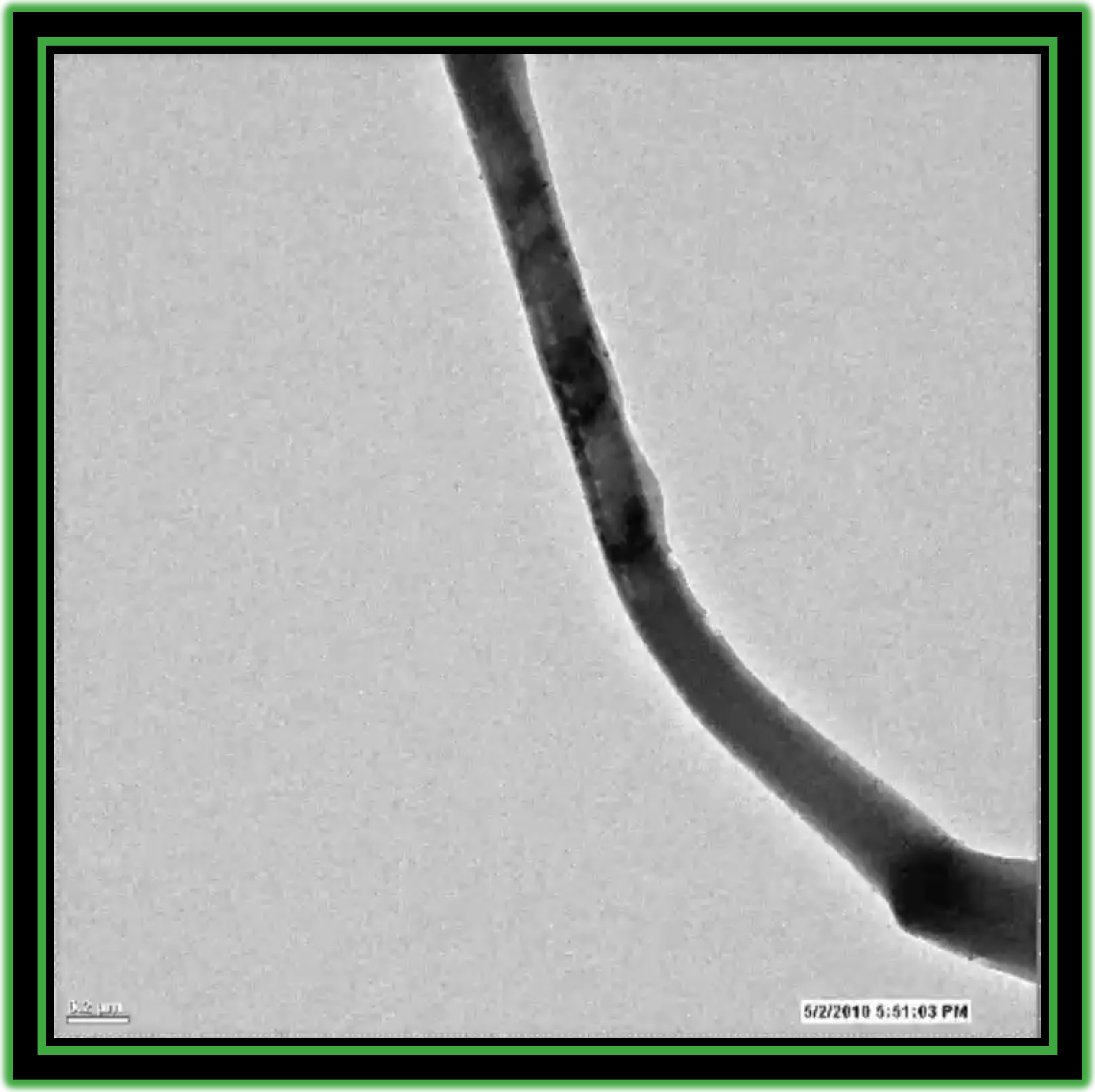


Huang *et al.*, Science Dec. 10, 2010; Phys Rev. Lett. 106, 248302 (2011)

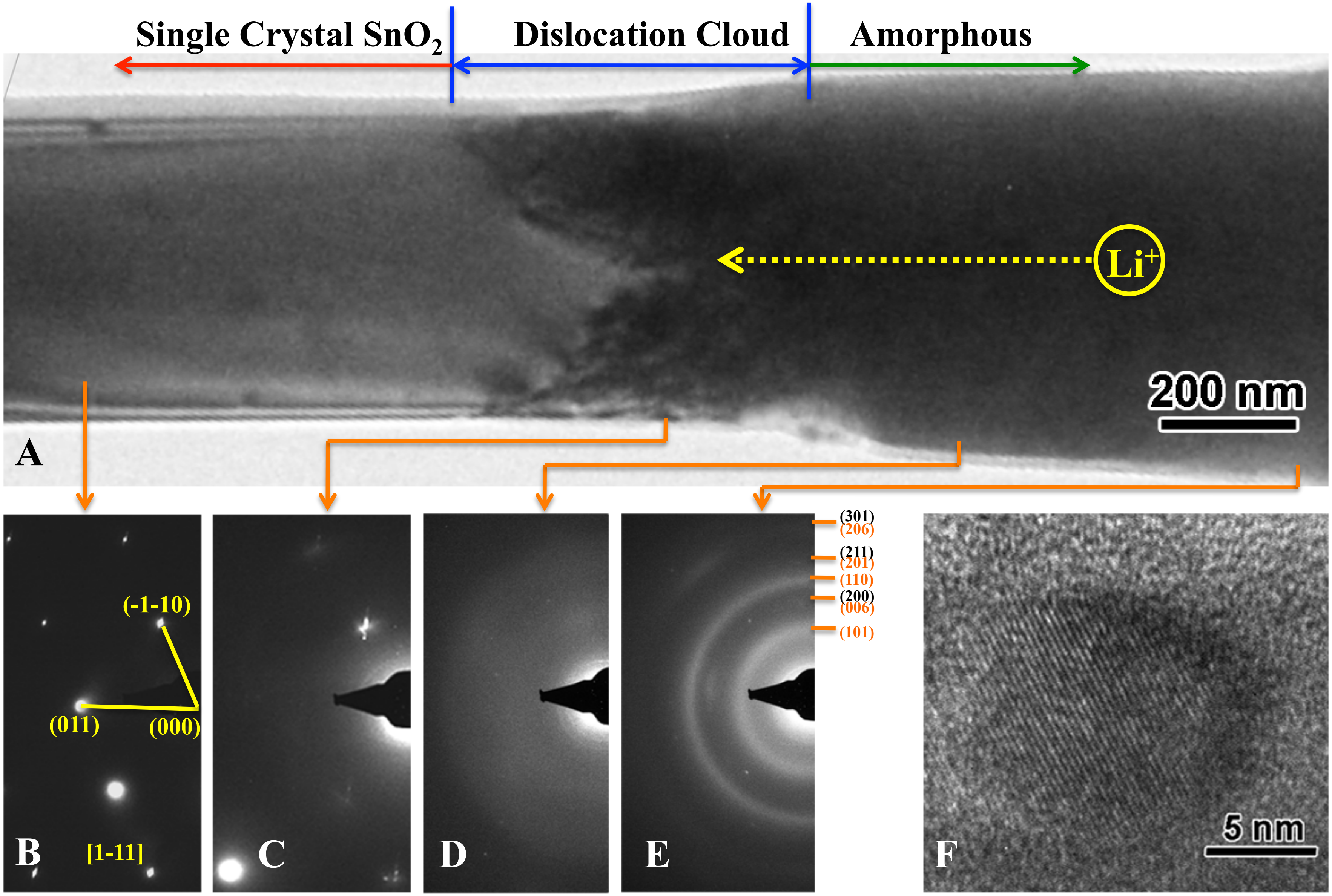


90% elongation, spiraling, volume expansion 300%

In-situ TEM charging of a single SnO_2 NW

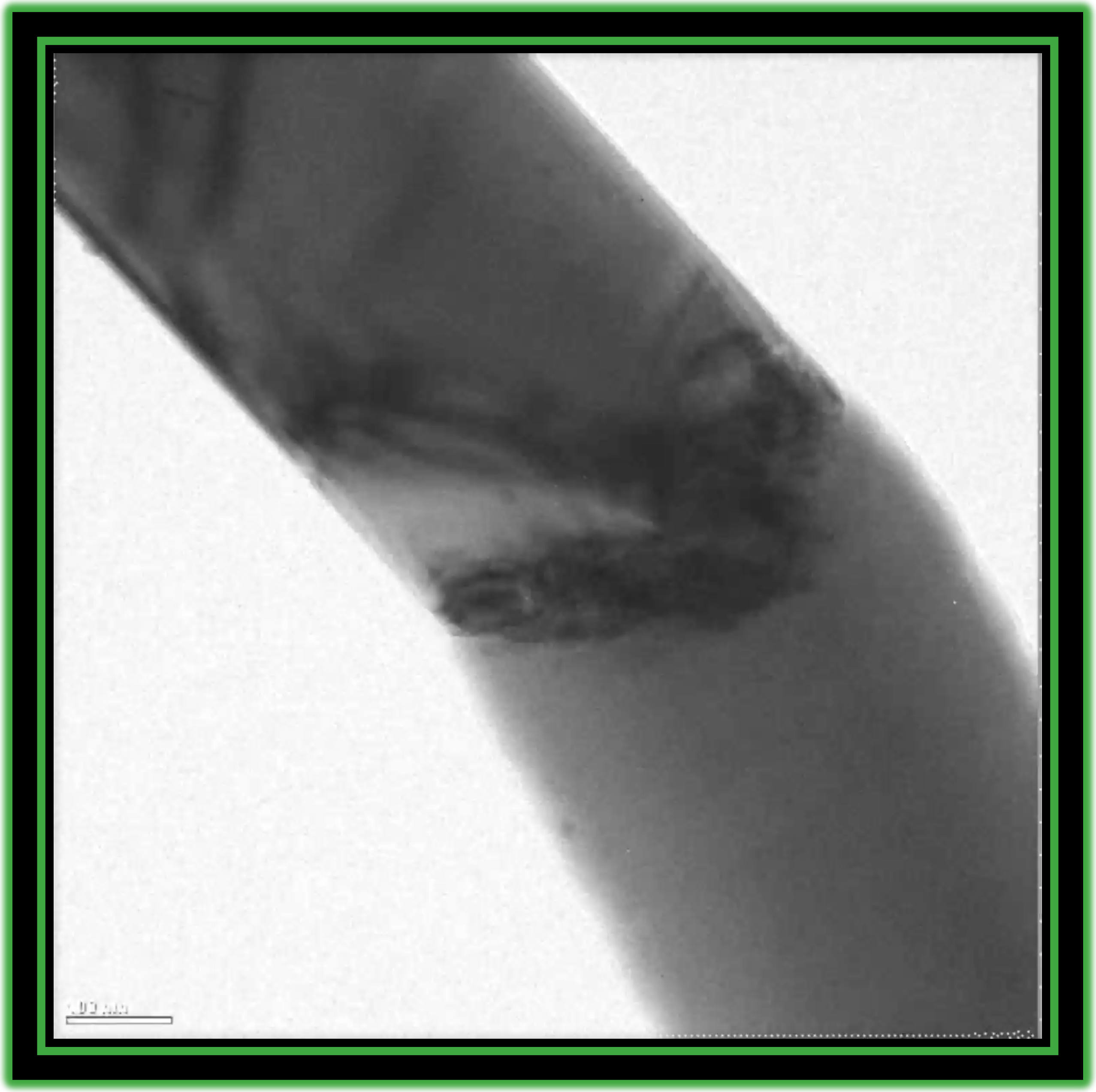


Forest of dislocations in the reaction front

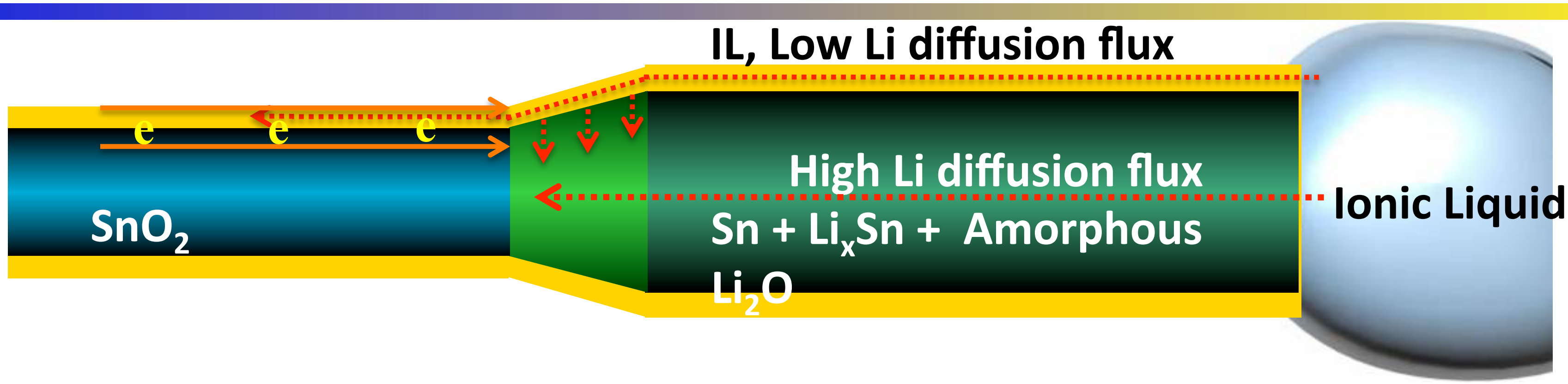


Dislocation cloud; diameter expansion, phase transformation: amorphization

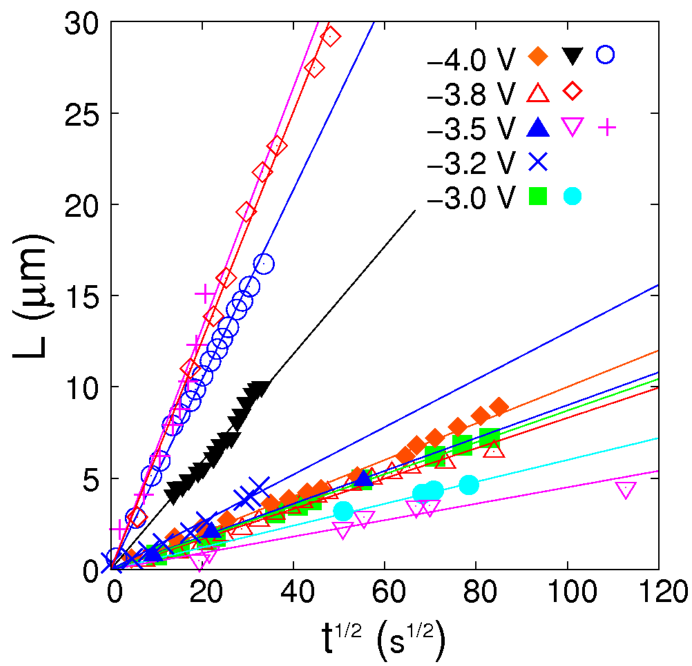
Dislocation dynamics in the reaction front



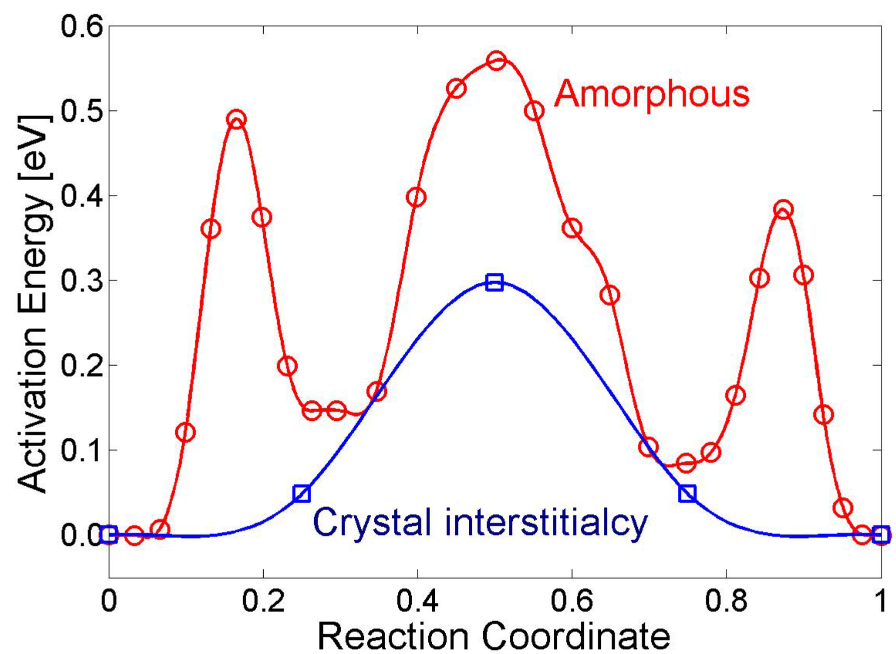
How does the SnO_2 NW battery work?



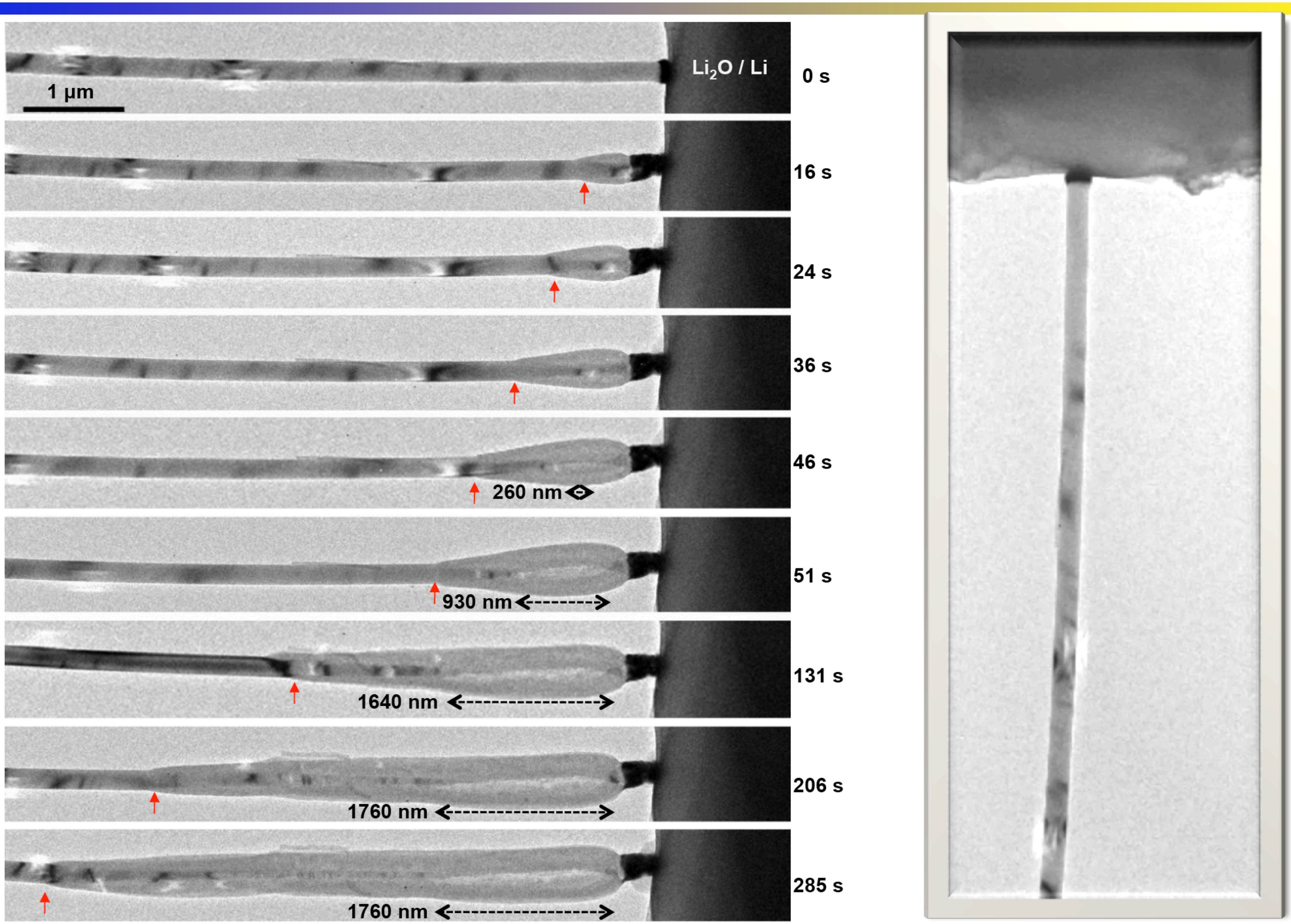
$$4Li^+ + SnO_2 + 4e^- \rightarrow 2Li_2O + Sn$$
$$Sn + x\,Li^+ + x\,e^- \leftrightarrow Li_xSn\ (0 \leq x \leq 4.4)$$



$D = 10^{-10}\ cm^2/s$

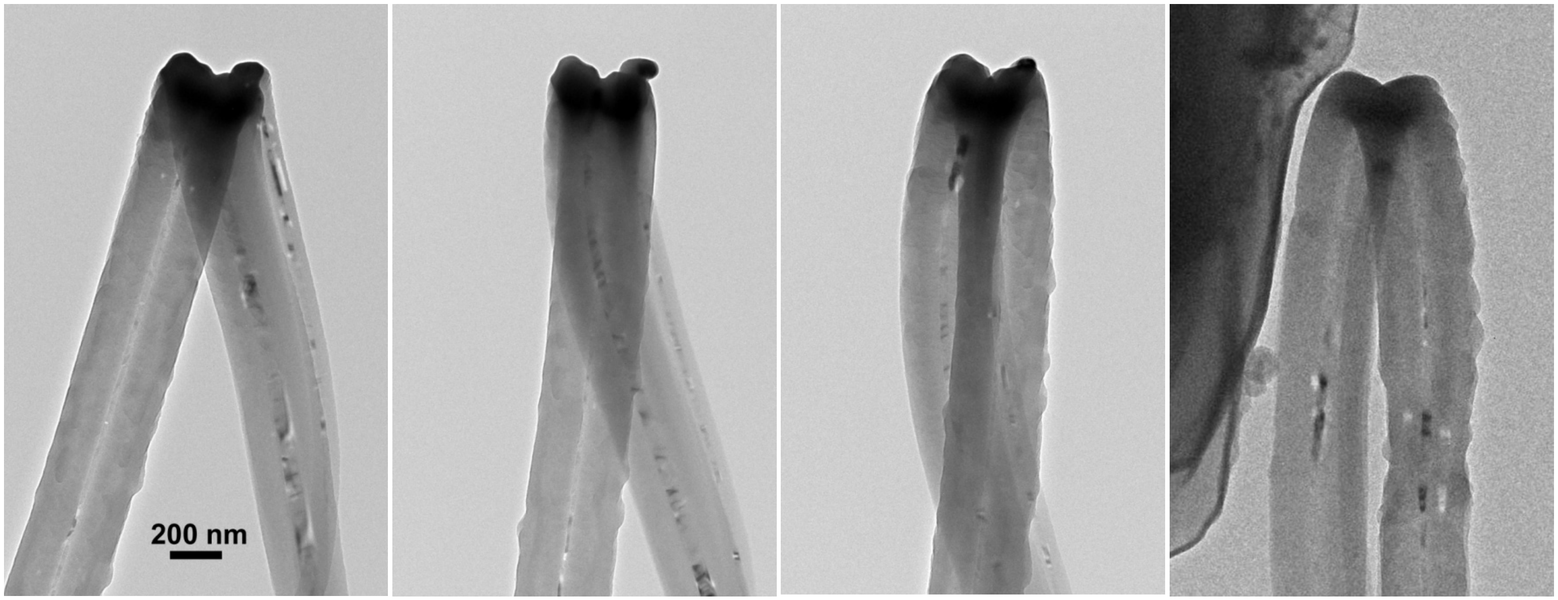


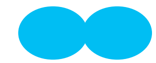
1: Anisotropic expansion and crack in Si

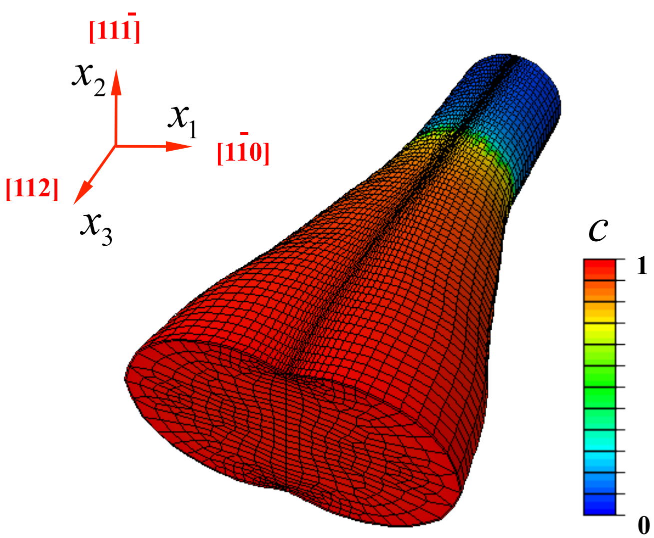


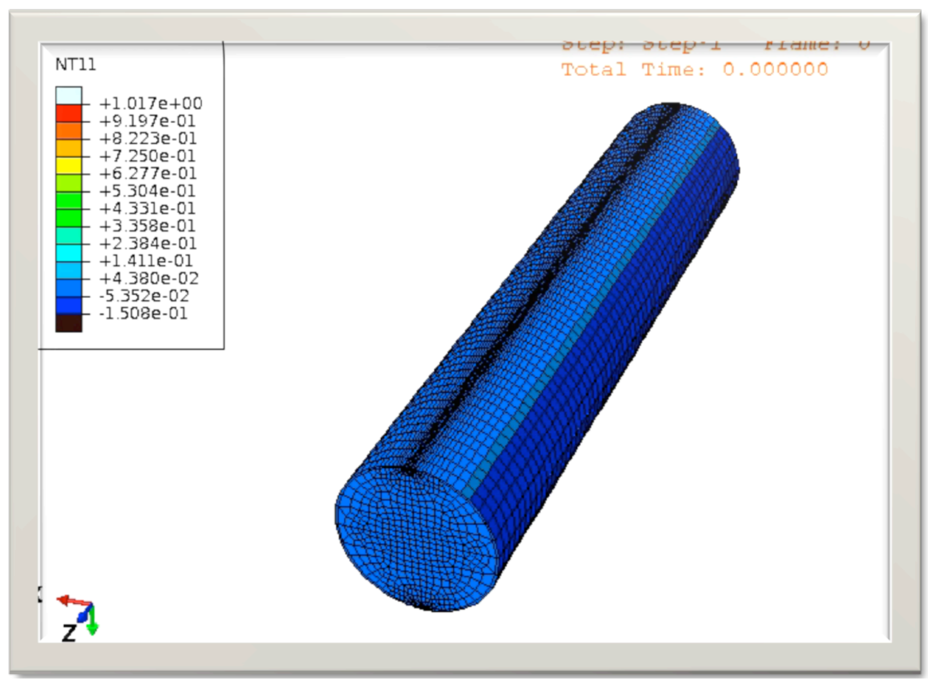
Anisotropic volume expansion in Si NWs

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



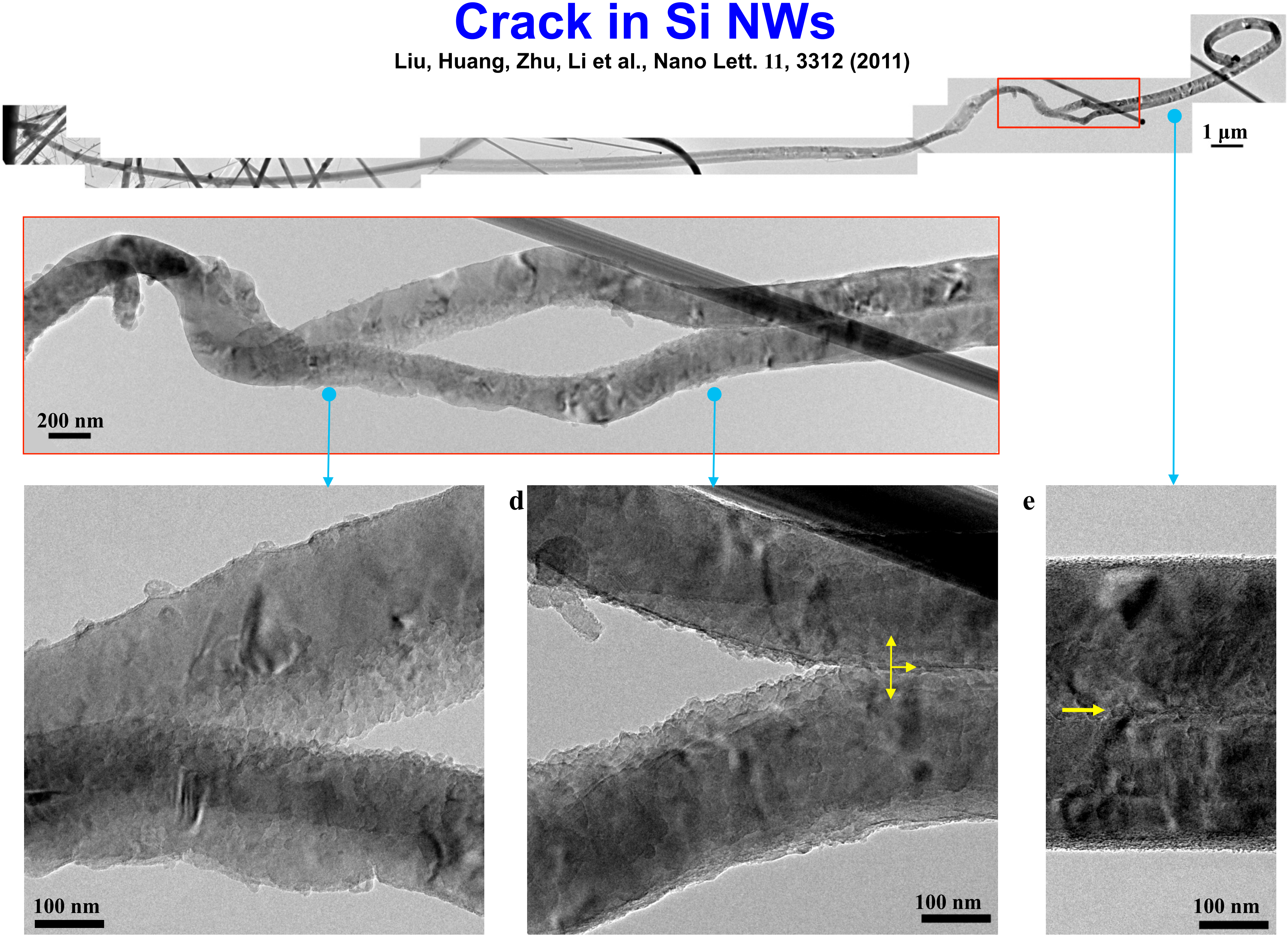




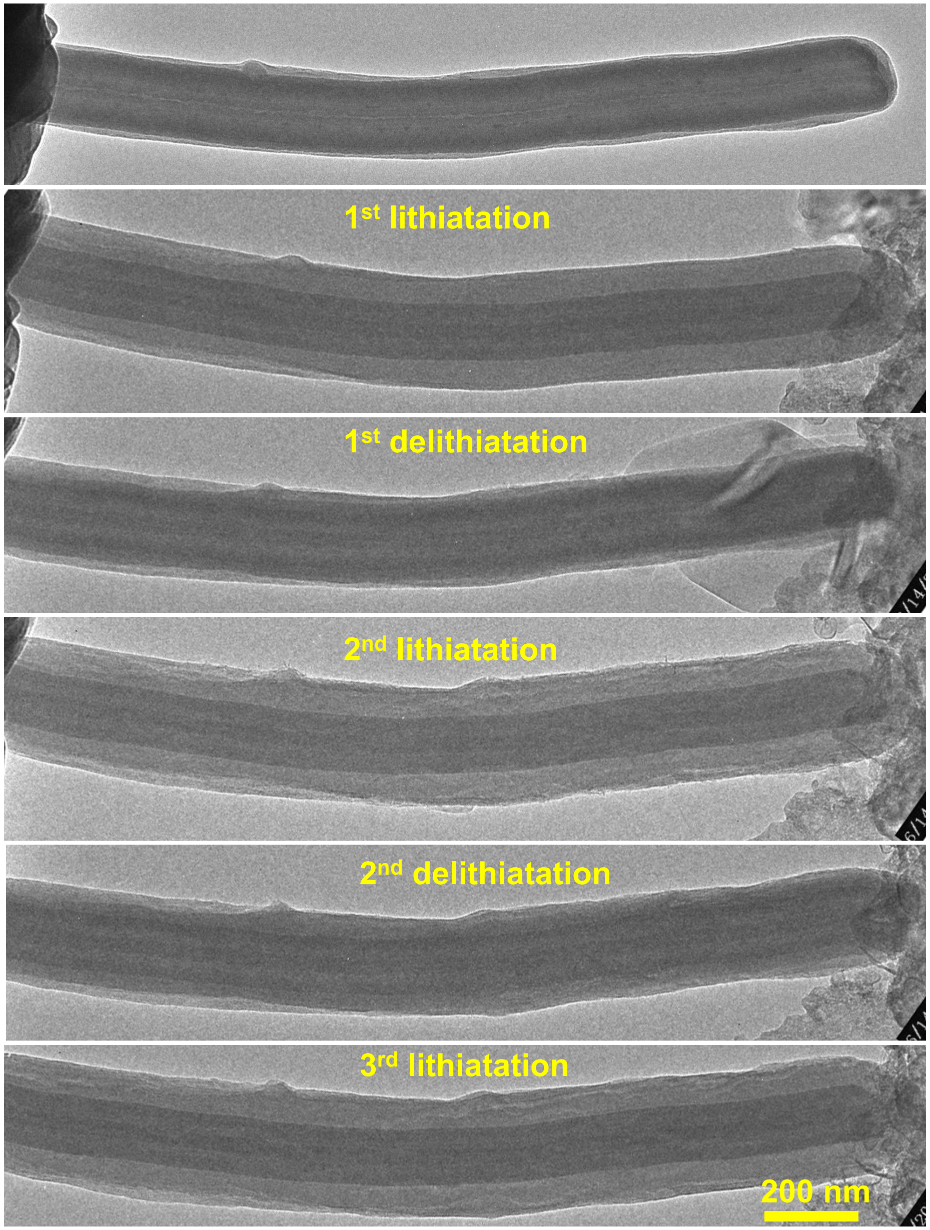


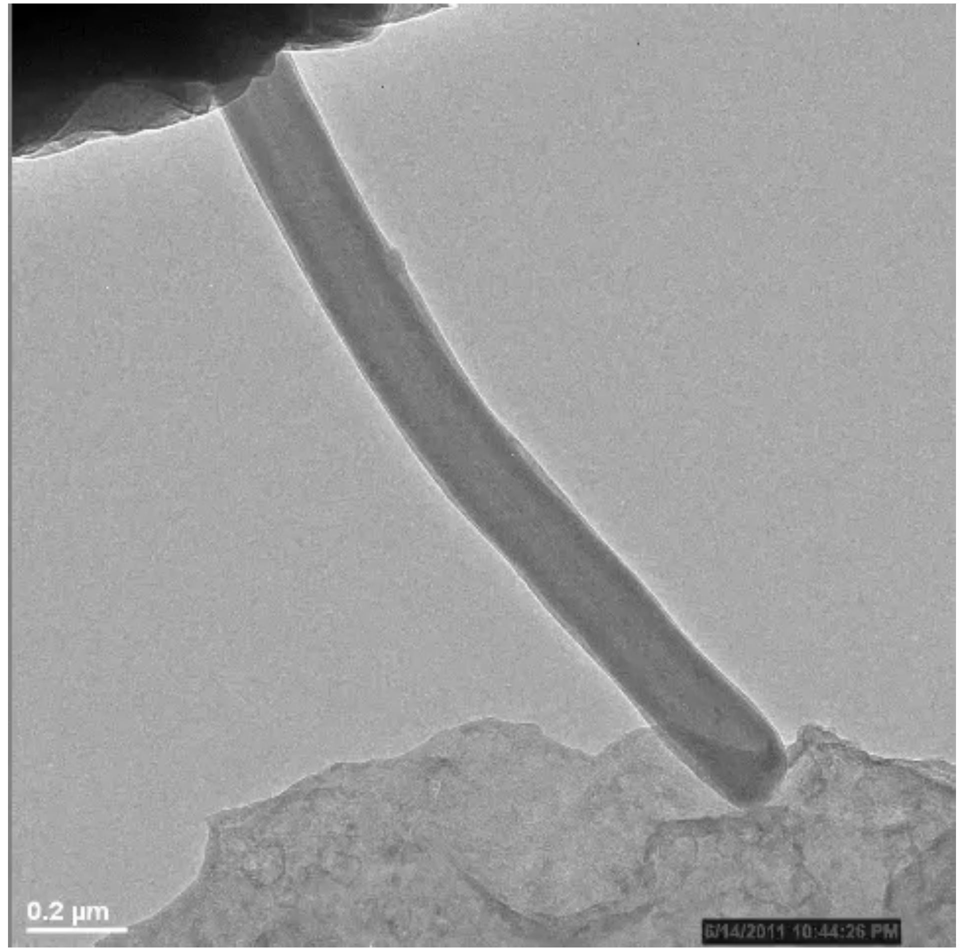
Crack in Si NWs

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



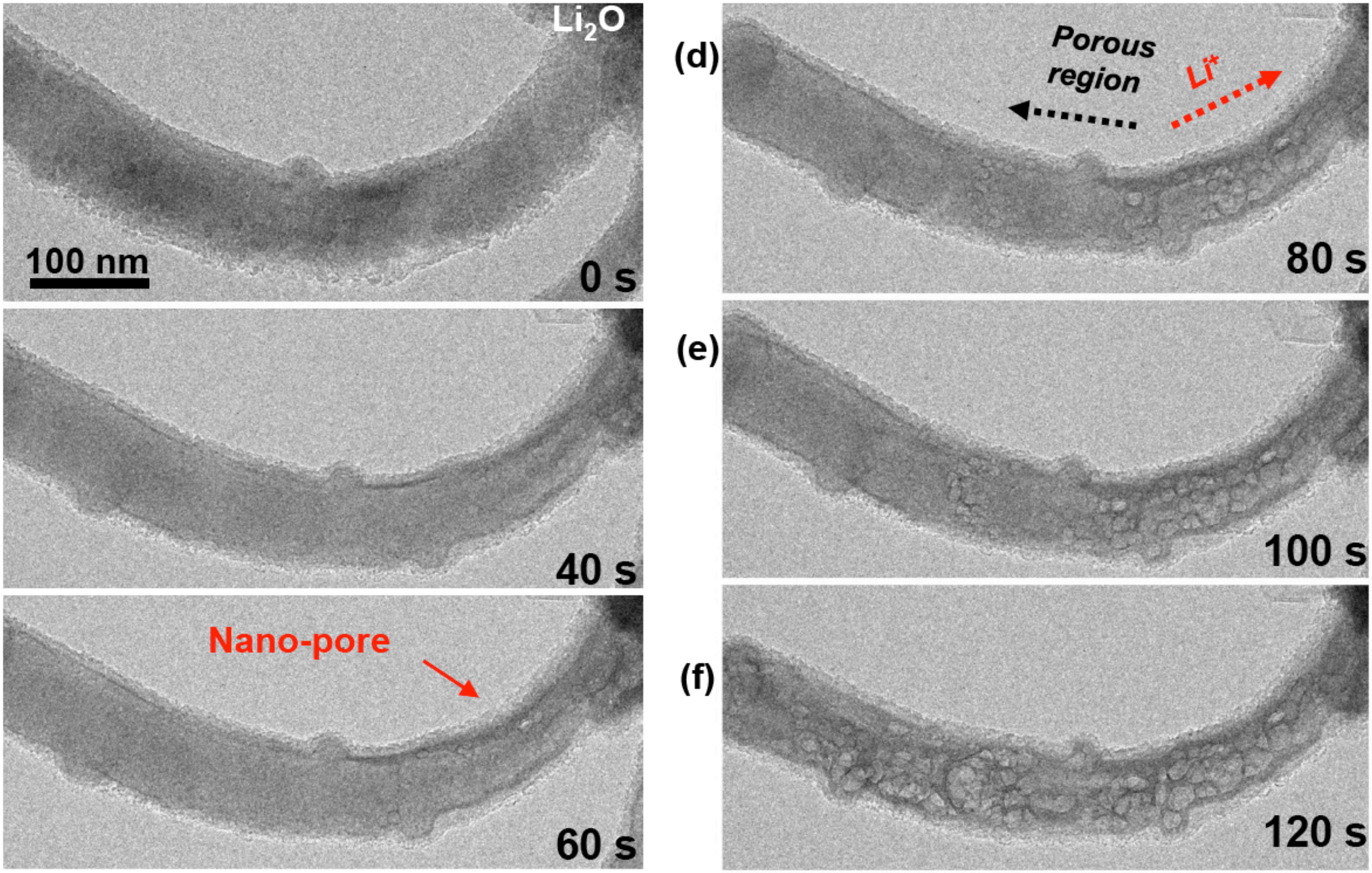
2: In-situ cycling of a-Si/CNT electrode (ASI)





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

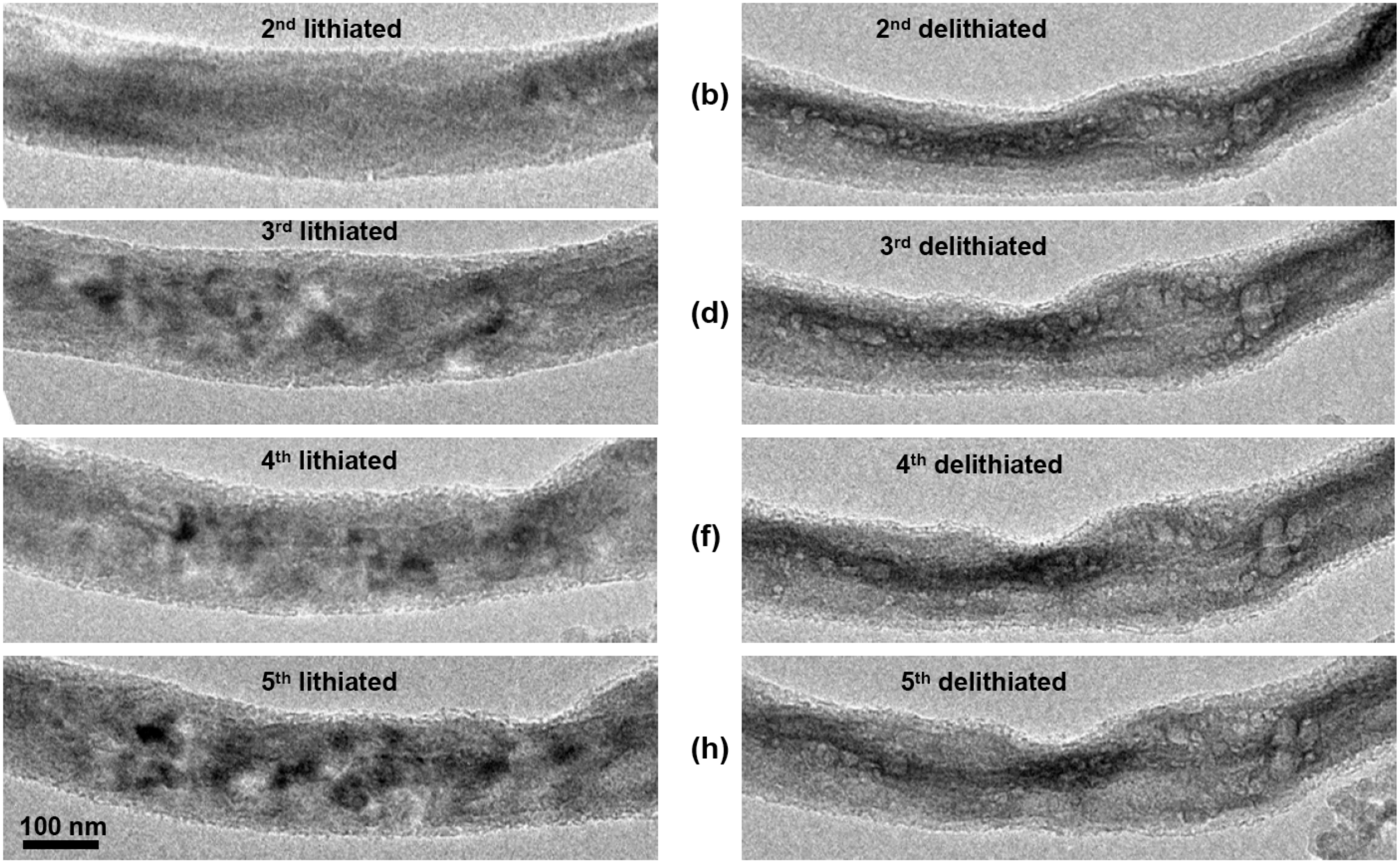
3: Reversible nano-pore formation in Ge NWs



Ge: 1384 mA h/g, Graphite: 372, Si: 3579. Electric conductivity 10000 times of Si

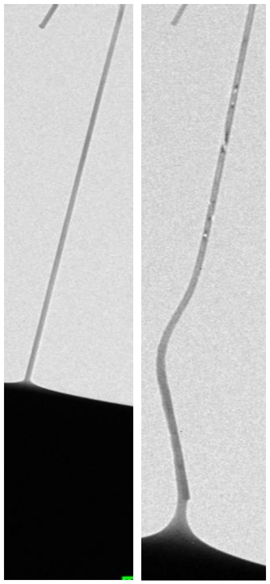
Xiao Hua Liu, Shan Huang, S. Tom Picraux, Ju Li, Ting Zhu, and Jian Yu Huang, Nano Lett. 11, 3991 (2011)

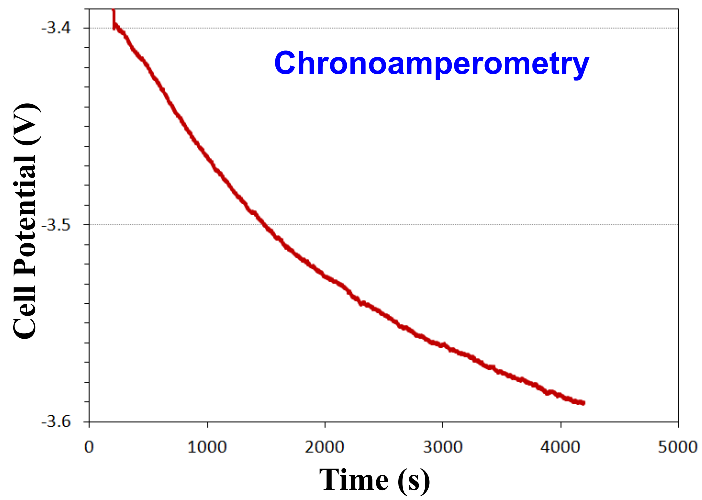
3: Reversible nano-pore formation in Ge NWs



Ge: long cycle lifetime

Quantitative control and measurement in nanoscale electrochemistry



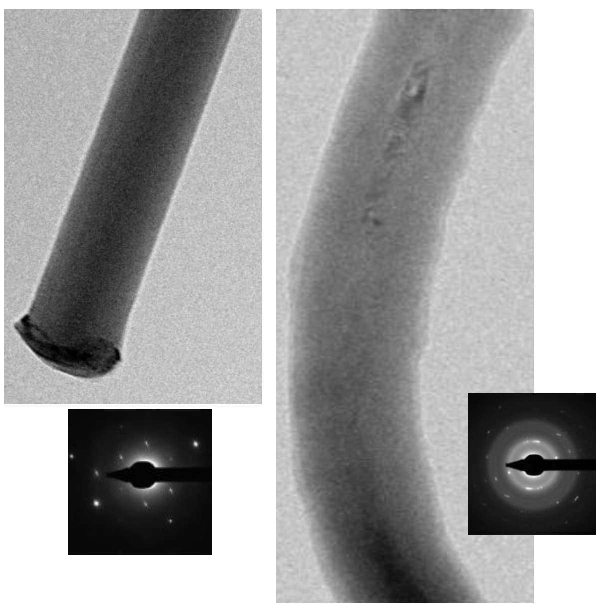


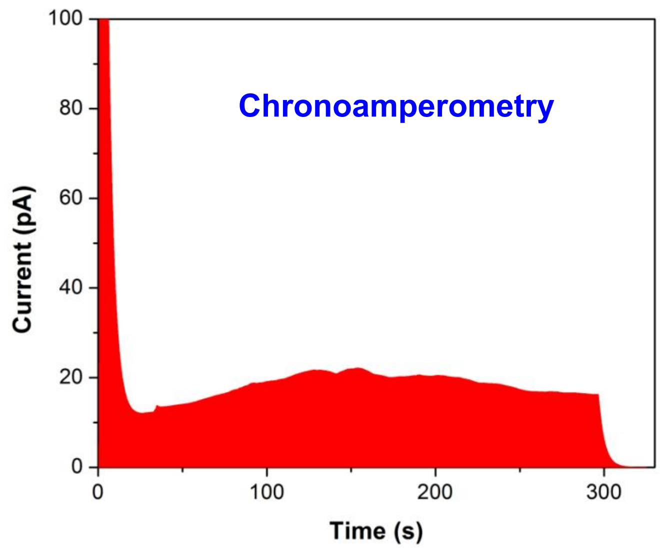
Q_{app} = 7.9 nC

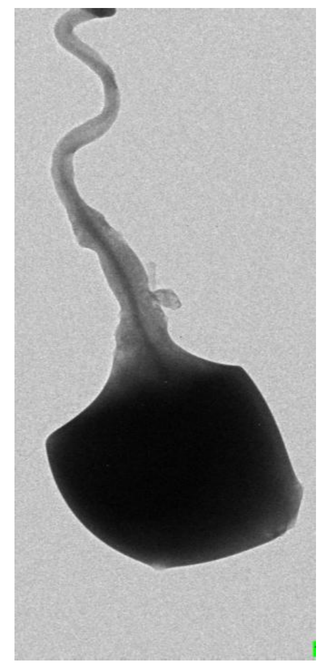
$Q_{Li_{3.75}Si}$ = 11.5 nC

68%

A subset of wires exhibit efficiencies of 60 – 130%
- Li content
- Competing red. rxns

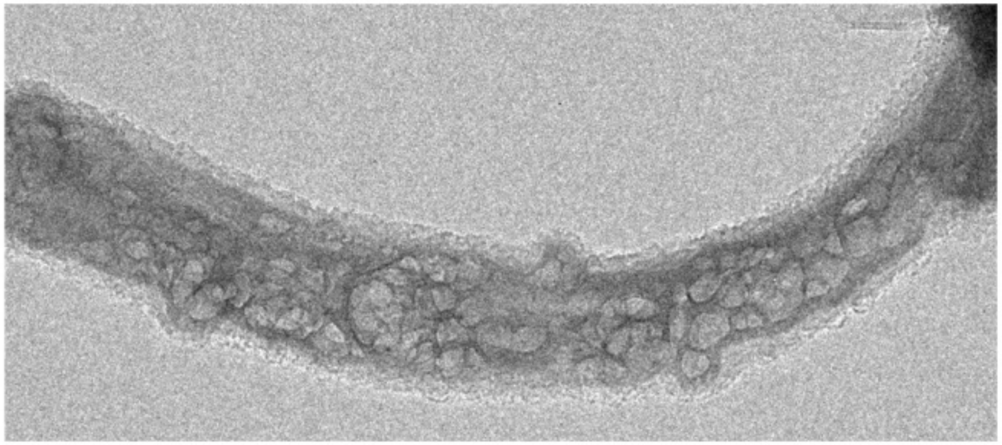






Kevin Zavadil, Xiaohua Liu, Yang Liu, Jianyu Huang et al., unpublished

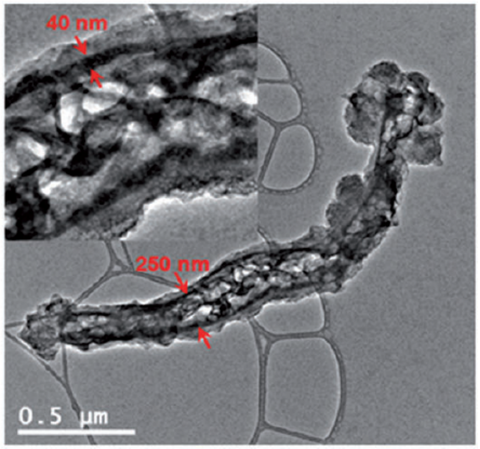
Relevance of in-situ battery to conventional electrochemical cell



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)

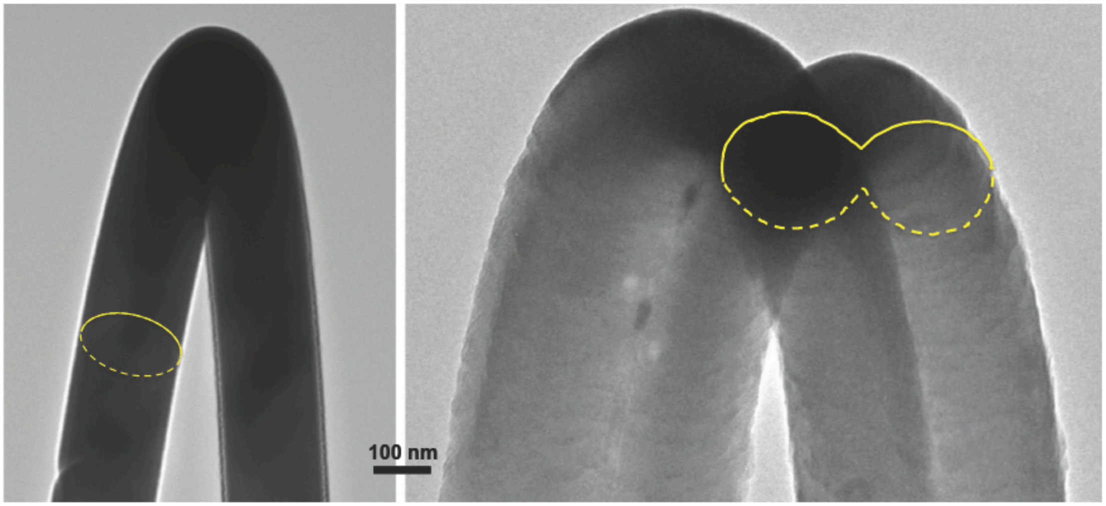


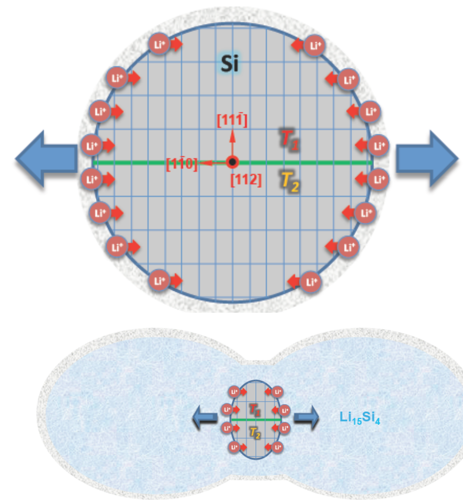
Conventional Electrochemical Result

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.

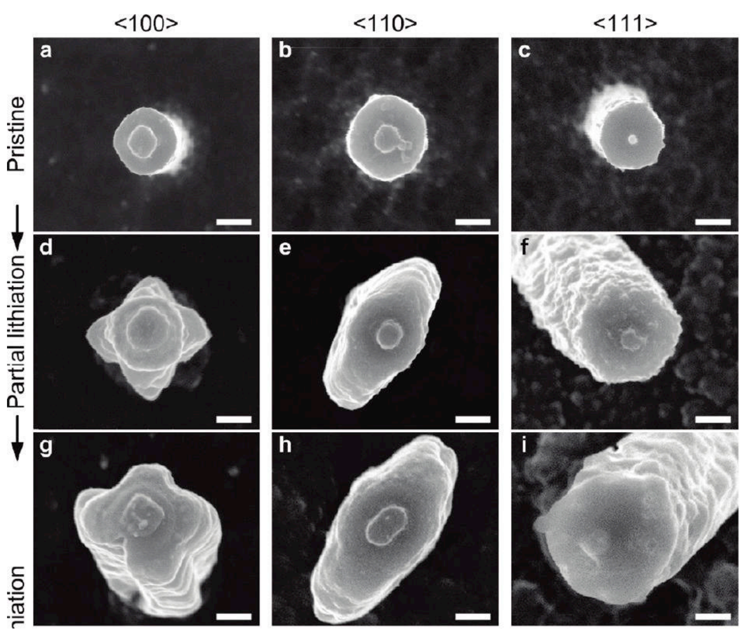
Cho et al., **Angew. Chem.** 10.1002/anie. 201103062

Relevance of in-situ battery to conventional electrochemical cell

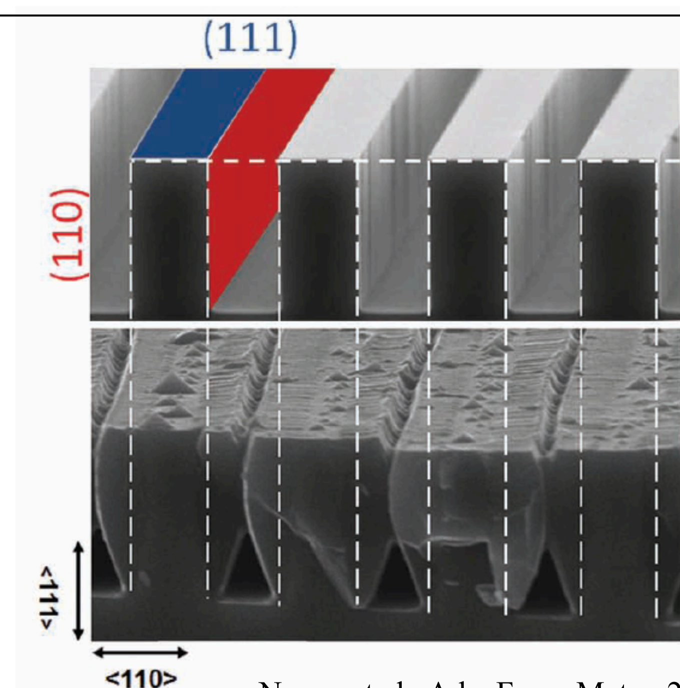




Liu & Huang et al., Nano Lett. 11, 3312 (2011)



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



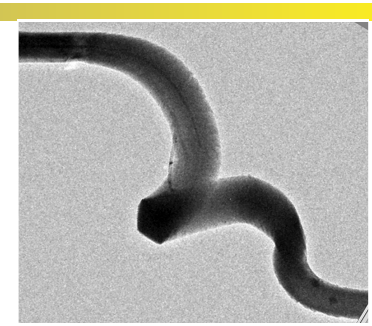
Nuzzo et al., Adv. Func. Mater. 21, 2412 (2011)

Nanowires studied and publications

Science
Vol. 330, 1515 (2010)

In Situ Observation of the Electrochemical Lithiation of a Single SnO_2 Nanowire Electrode

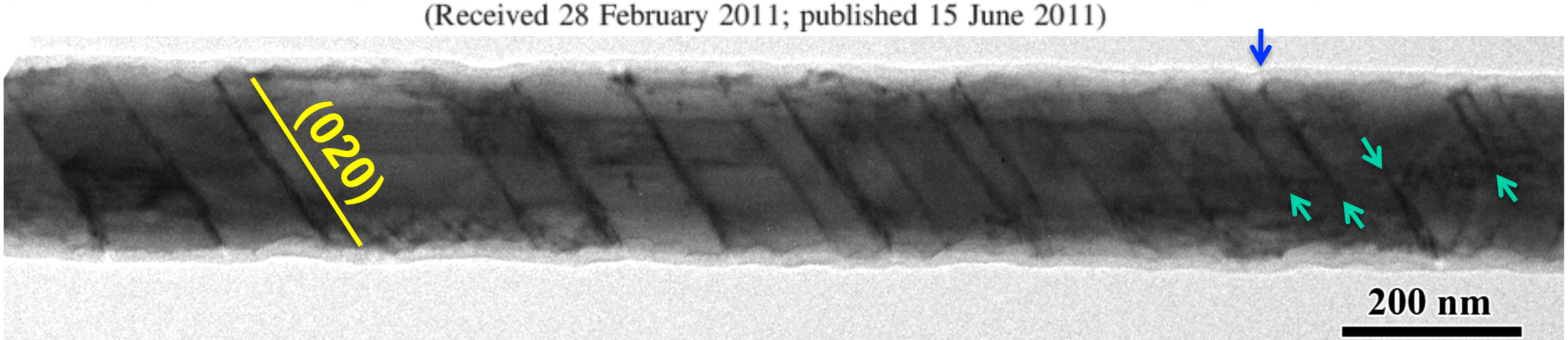
Jian Yu Huang,[1*] Li Zhong,[2] Chong Min Wang,[3*] John P. Sullivan,[1*] Wu Xu,[4] Li Qiang Zhang,[2] Scott X. Mao,[2*] Nicholas S. Hudak,[1] Xiao Hua Liu,[1] Arunkumar Subramanian,[1] Hongyou Fan,[5] Liang Qi,[6,7] Akihiro Kushima,[7] Ju Li[6,7*]



PRL 106, 248302 (2011) PHYSICAL REVIEW LETTERS week ending 17 JUNE 2011

Multiple-Stripe Lithiation Mechanism of Individual SnO_2 Nanowires in a Flooding Geometry

Li Zhong,[2] Xiao Hua Liu,[1] Guo Feng Wang,[2] Scott X. Mao,[2] and Jian Yu Huang[1,*]
[1]*Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*
[2]*Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, USA*
(Received 28 February 2011; published 15 June 2011)

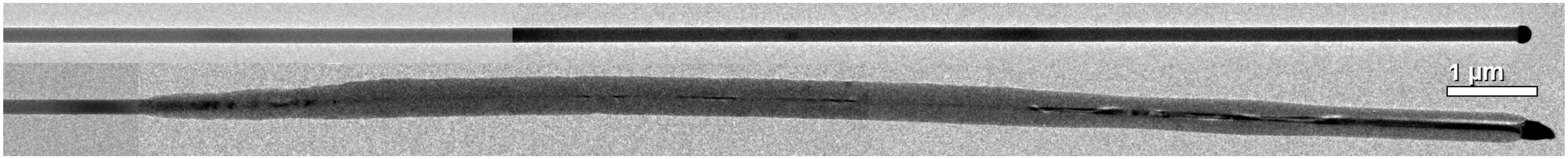


Nanowires studied and publications

NANO LETTERS 11, 2251 (2011)

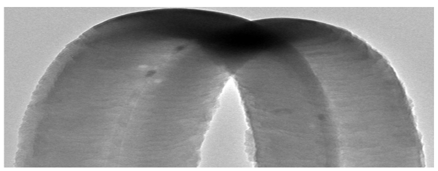
Ultrafast Electrochemical Lithiation of Individual Si Nanowire Anodes

Xiao Hua Liu,[†] Li Qiang Zhang,[‡,∥] Li Zhong,[‡] Yang Liu,[†] He Zheng,[‡,¶] Jiang Wei Wang,[‡] Jeong-Hyun Cho,[§] Shadi A. Dayeh,[§] S. Tom Picraux,[§] John P. Sullivan,[†] Scott X. Mao,[‡] Zhi Zhen Ye,[∥] and Jian Yu Huang[*,†]



NANO LETTERS 11, 3312 (2011)

Anisotropic Swelling and Fracture of Silicon Nanowires during Lithiation

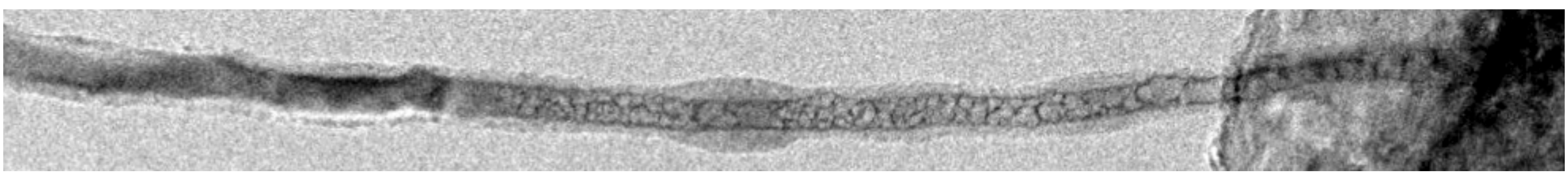


Xiao Hua Liu,[†] He Zheng,[‡,∠] Li Zhong,[‡] Shan Huang,[§] Khim Karki,[∥] Li Qiang Zhang,[‡,¶] Yang Liu,[†] Akihiro Kushima,[⊥] Wen Tao Liang,[#] Jiang Wei Wang,[‡] Jeong-Hyun Cho,[∇] Eric Epstein,[∥] Shadi A. Dayeh,[∇] S. Tom Picraux,[∇] Ting Zhu,[*,§] Ju Li,[*,⊥,○] John P. Sullivan,[†] John Cumings,[∥] Chunsheng Wang,[◆] Scott X. Mao,[‡] Zhi Zhen Ye,[¶] Sulin Zhang,[#] and Jian Yu Huang[*,†]

NANO LETTERS 11, 3991 (2011)

Reversible Nanopore Formation in Ge Nanowires during Lithiation–Delithiation Cycling: An In Situ Transmission Electron Microscopy Study

Xiao Hua Liu,[†] Shan Huang,[‡] S. Tom Picraux,[§] Ju Li,[∥,⊥] Ting Zhu,[*,‡] and Jian Yu Huang[*,†]

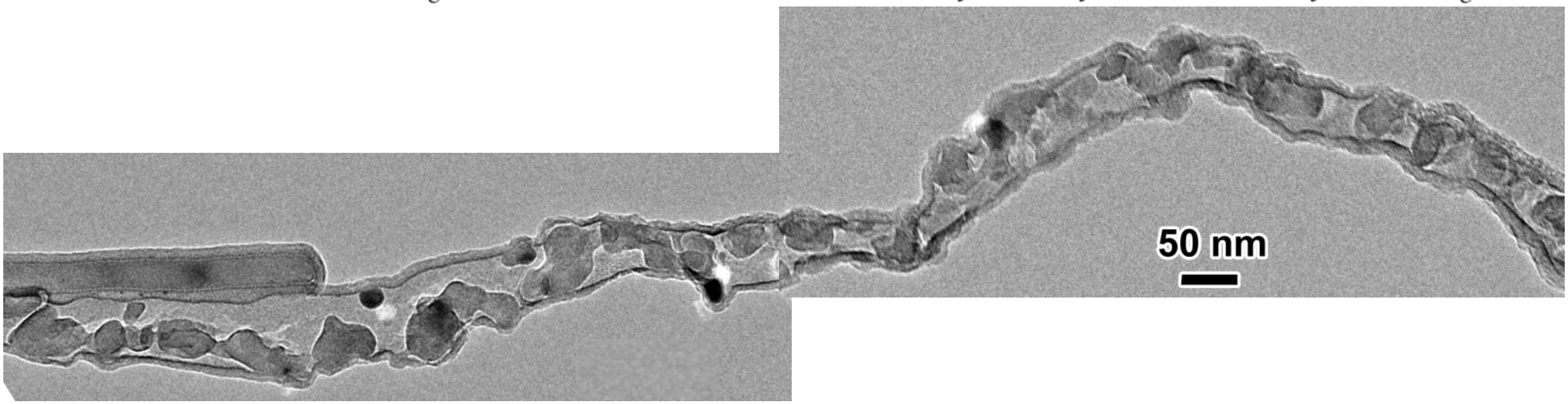


Nanowires studied and publications

NANO LETTERS 11, 4188 (2011)

In Situ Transmission Electron Microscopy Observation of Pulverization of Aluminum Nanowires and Evolution of the Thin Surface Al_2O_3 Layers during Lithiation–Delithiation Cycles

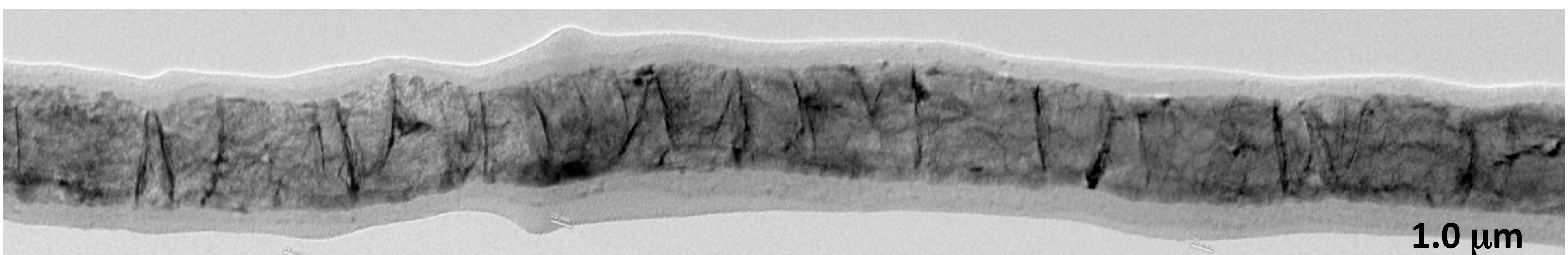
Yang Liu, Nicholas S. Hudak, Dale L. Huber, Steven J. Limmer, John P. Sullivan, and Jian Yu Huang*



NANO LETTERS 10.1021/nl201376j

Leapfrog Cracking and Nanoamorphization of ZnO Nanowires during In Situ Electrochemical Lithiation

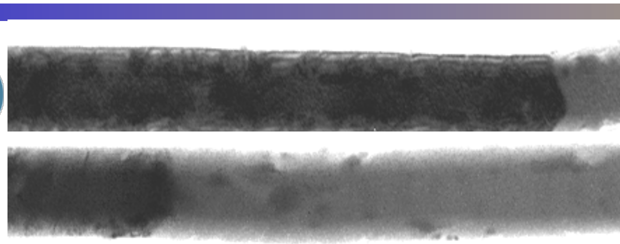
Akihiro Kushima,[†] Xiao Hua Liu,[‡] Guang Zhu,[§] Zhong Lin Wang,[§] Jian Yu Huang,[*,‡] and Ju Li[*,†,||]



Nanowires studied and publications

ACS NANO

5, 4800 (2011)

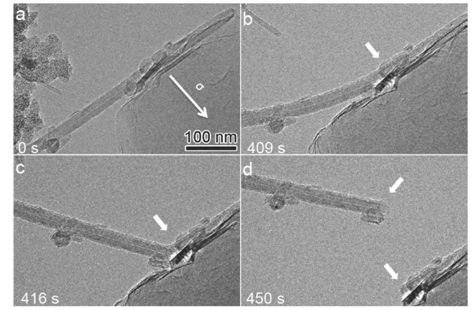


Controlling the Lithiation-Induced Strain and Charging Rate in Nanowire Electrodes by Coating

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, 7245 (2011)



Lithiation-Induced Embrittlement of Multiwalled Carbon Nanotubes

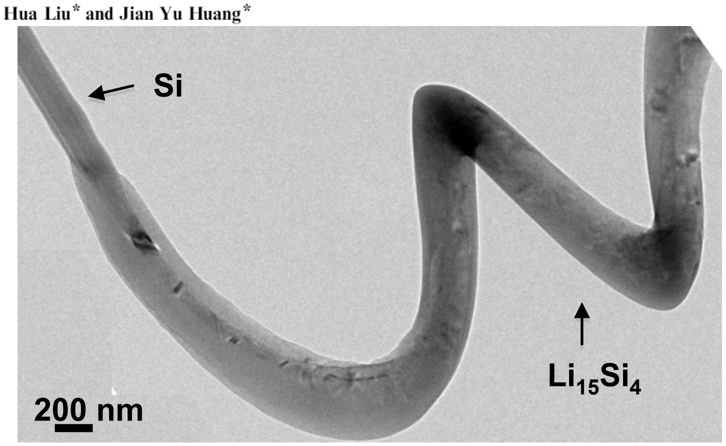
Yang Liu,[†] He Zheng,[‡,#] Xiao Hua Liu,[†] Shan Huang,[§] Ting Zhu,[§,*] Jiangwei Wang,[‡] Akihiro Kushima,[⊥] Nicholas S. Hudak,[†] Xu Huang,[∥] Sulin Zhang,[∥] Scott X. Mao,[‡] Xiaofeng Qian,[¶] Ju Li,[⊥] and Jian Yu Huang[†,*]

Energy & Environmental Science 4, 3844 (2011)

www.rsc.org/ees PERSPECTIVE

In situ TEM electrochemistry of anode materials in lithium ion batteries

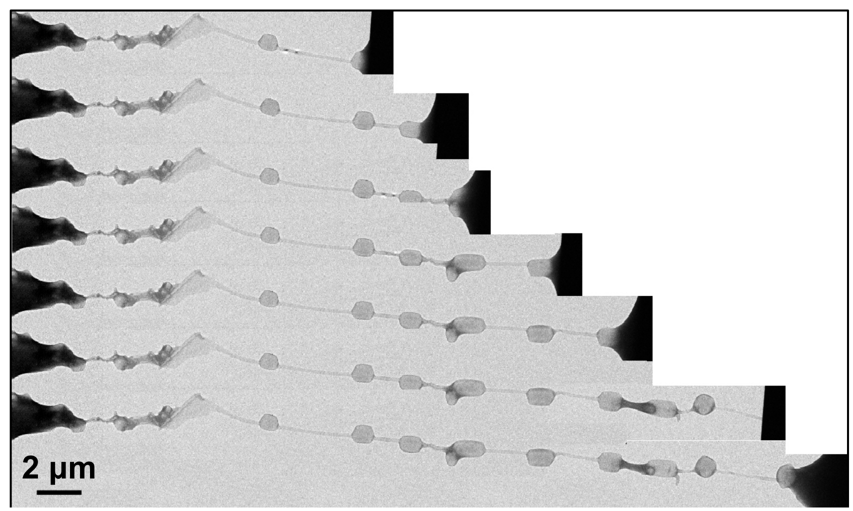
Xiao Hua Liu* and Jian Yu Huang*



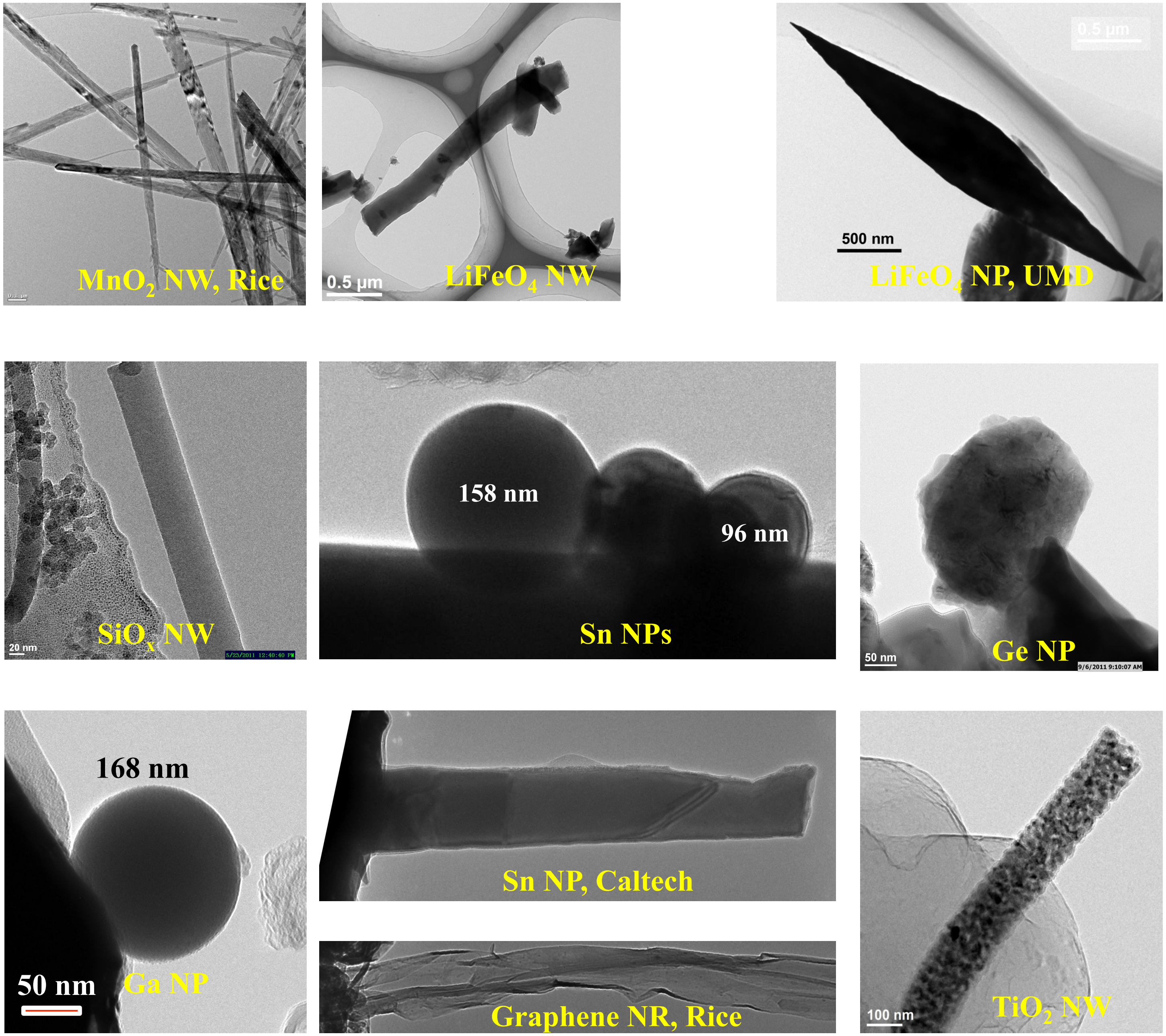
APPLIED PHYSICS LETTERS 98, 183107 (2011)

Lithium fiber growth on the anode in a nanowire lithium ion battery during charging

Xiao Hua Liu,[1] Li Zhong,[2] Li Qiang Zhang,[2,4] Akihiro Kushima,[3] Scott X. Mao,[2] Ju Li,[3] Zhi Zhen Ye,[4] John P. Sullivan,[1] and Jian Yu Huang[1,a)]



Nanowires and nanoparticles to be studied in the future



Summary and Perspective

- The first working nano battery 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