Wiring Up Silicon Nanostructures for High Energy Lithium Ion Battery Anodes

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Project ID #ES148

Overview

Timeline

- Start: Jan 1, 2011
- End: Dec. 31, 2014
- Percent complete: 60%

Budget

- Total project funding
  $1,200k from DOE
- Funding received in FY12
  $300k
- Funding for FY13
  $300k

Barriers

Barriers of batteries

- Low energy density
- High cost
- Cycle and calendar life

Targets: high energy electrode materials and cells

Partners

- Collaboration
  - BATT program PI's
  - PNNL: In-situ TEM
  - SLAC: In-situ X-ray
  - UT Austin: Prof. Korgel,materials
  - Stanford: Prof. Nix, mechanics; Prof. Bao, materials.
  - Amprius Inc.

Project Objective and Relevance

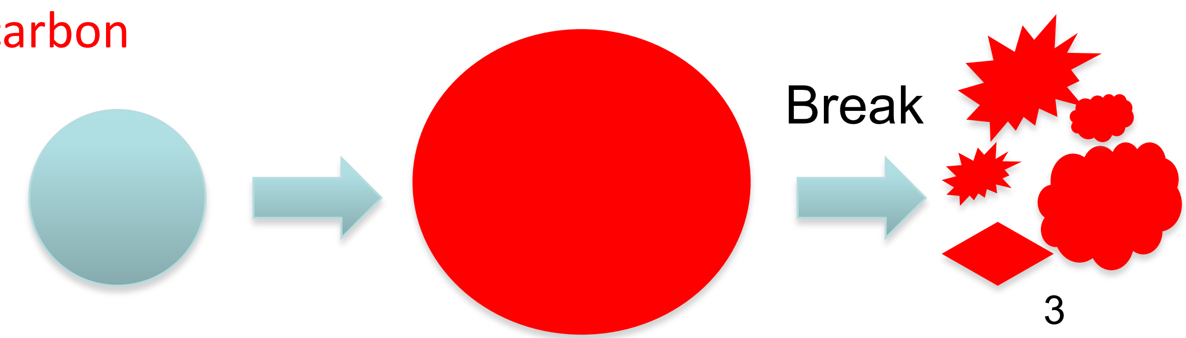
Objective

- To develop Si anodes with 10x specific charge capacity to replace the existing C anodes for high energy Li ion batteries for transportation, relevant to VT Program.
- To Understand and design nanostructure Si can address the challenging issues caused by the large volumetric expansion and provide a good cycle life.
- To Develop scalable low-cost methods for nanostructured Si anodes.

For Si: volume expansion by 4 times

Si: 4200 mAh/g, 10X of carbon

$Si \longleftrightarrow Li_{4.4}Si$

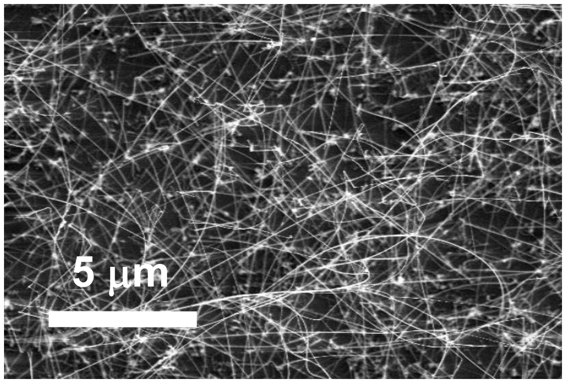


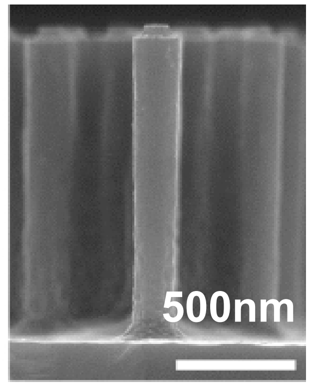
Milestones for FY12 and 13

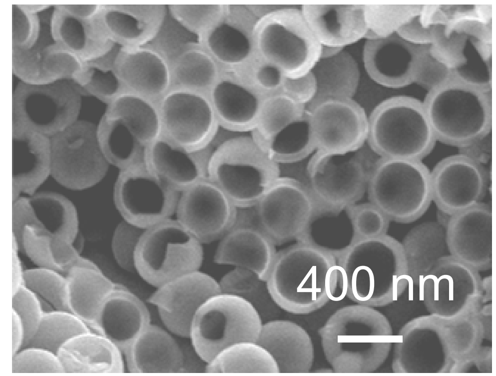
Month/year	Milestones
9/2011	Find out the relationship of critical breaking size versus capacity for deep lithiation . Identify a method to produce hollow silicon structure. (completed)
3/2012	Obtain detailed information on the volume expansion and contraction of Si. Fabricate hollow anodes with high reversible capacity and high Coulombic efficiency (Completed)
6/2012	Determine effect of hollow structure on volume expansion, compared to non-hollow nanostructures (completed)
10/2012	Optimize nanostructured Si for long cycle life (>1000 cycles). (completed)
12/2012 Go-no go	Start to develop scalable and low-cost nano-Si with the identified materials design rules. (completed)
3/2013	Develop low cost and scalable Si yolk-shell nanostructures with stable cycle life (completed)
5/2013	Develop low-cost synthesis of Si nanoparticles from renewable sources (on-schedule)

Approach/Strategy

Advanced nanostructured Si materials design and synthesis



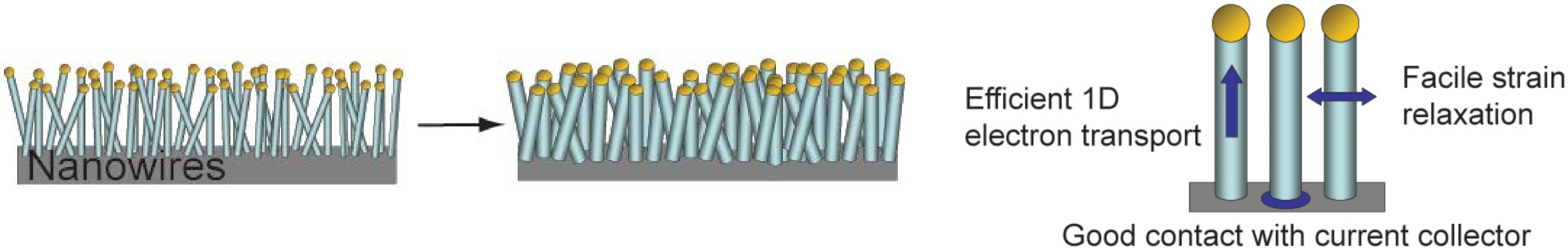




Structure and property characterization
- Ex-situ transmission electron microscopy
- In-situ transmission electron microscopy
- Ex-situ scanning electron microscopy

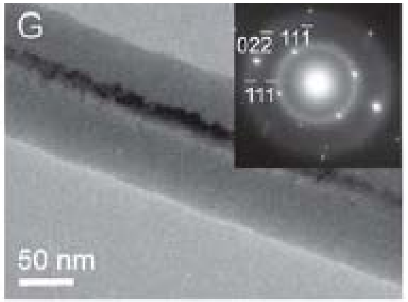
Electrochemical testing
- Coin cells and pouch cells.
- A set of electrochemical techniques.

Previous Results on Silicon Nanowire Anodes



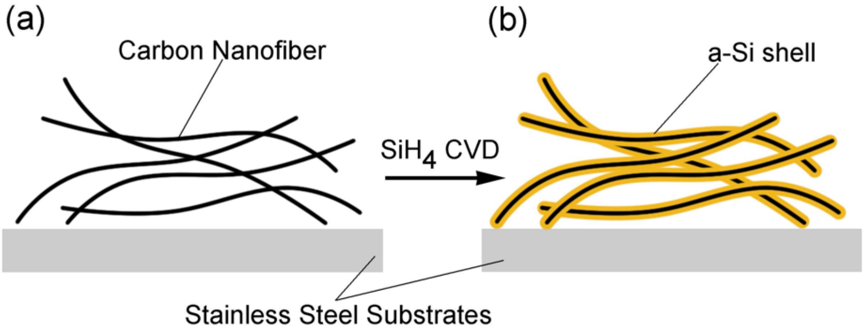
Cui group, Nature Nanotechnology 3, 31 (2008).

Crystal-amorphous Si core-shell nanowires



Cui group
Nano Letters 9, 491 (2009).

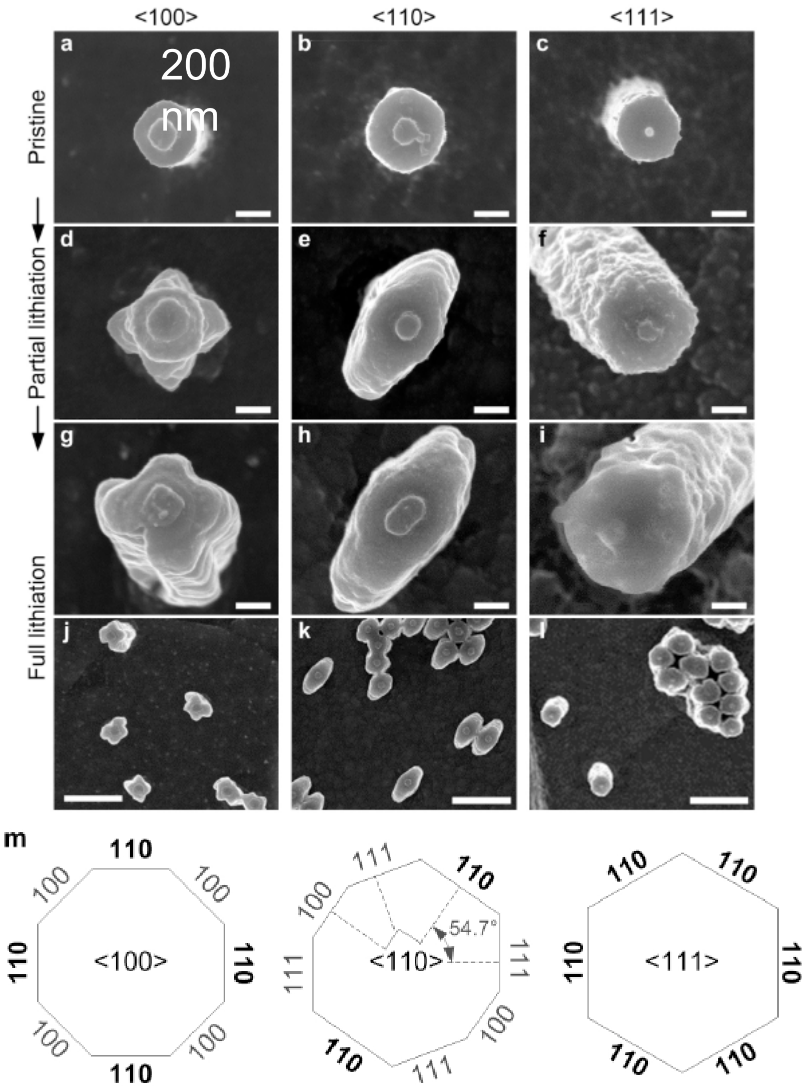
Carbon-silicon core-shell nanowires

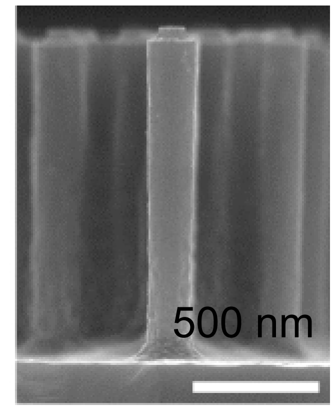


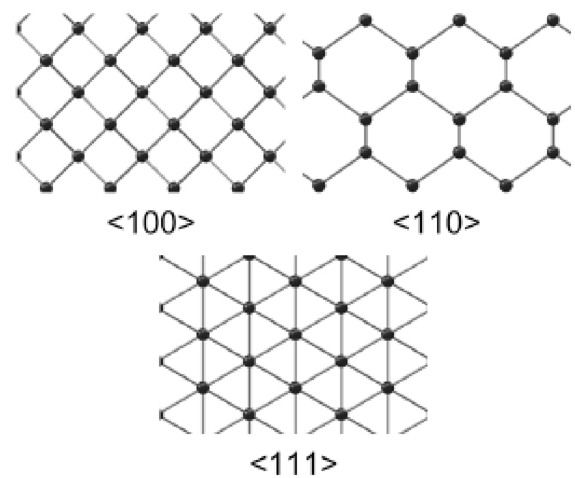
Cui group
Nano Letters 9, 3370 (2009).

Accomplishment

Discovering anisotropic expansion of crystalline Si upon lithiation

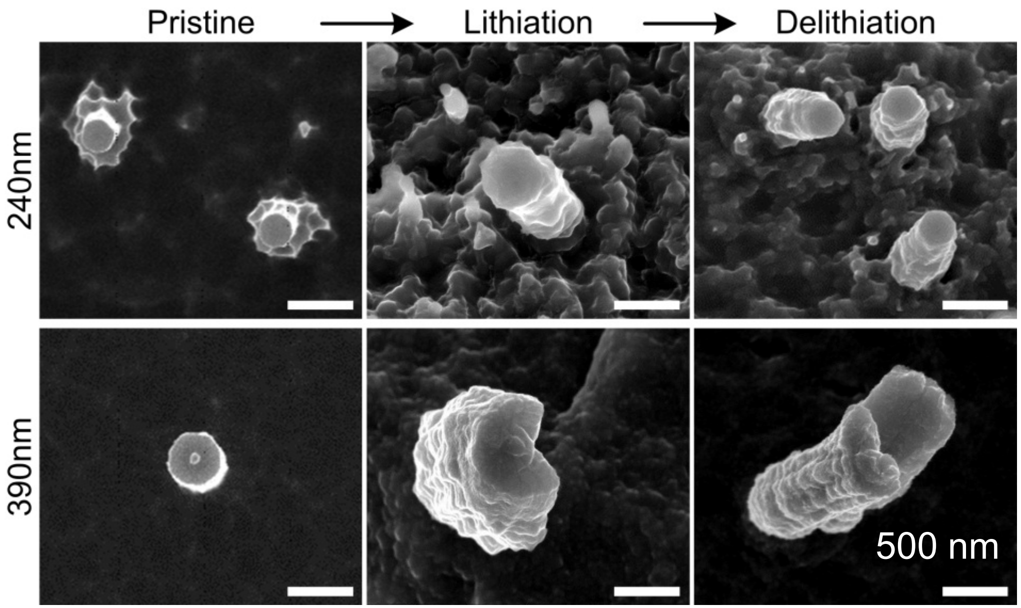




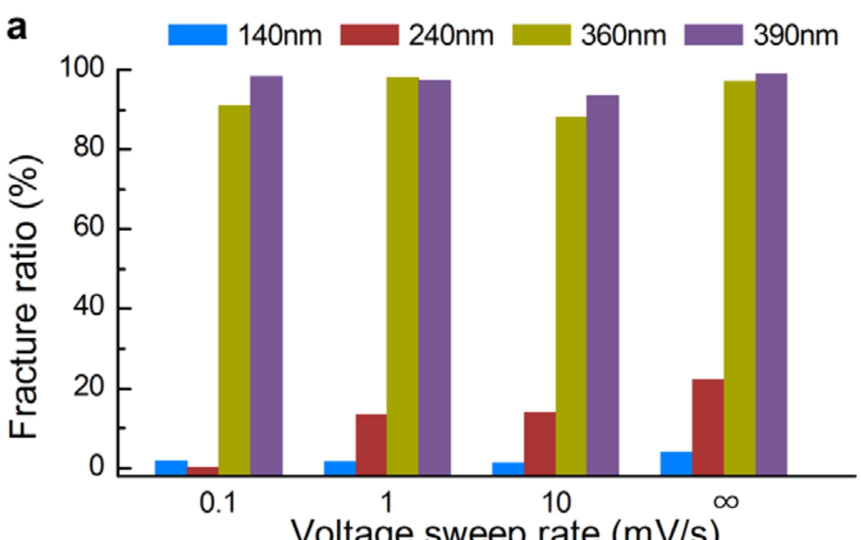


(Cui group,
Nano Letters 11, 3034 (2011))

Accomplishment



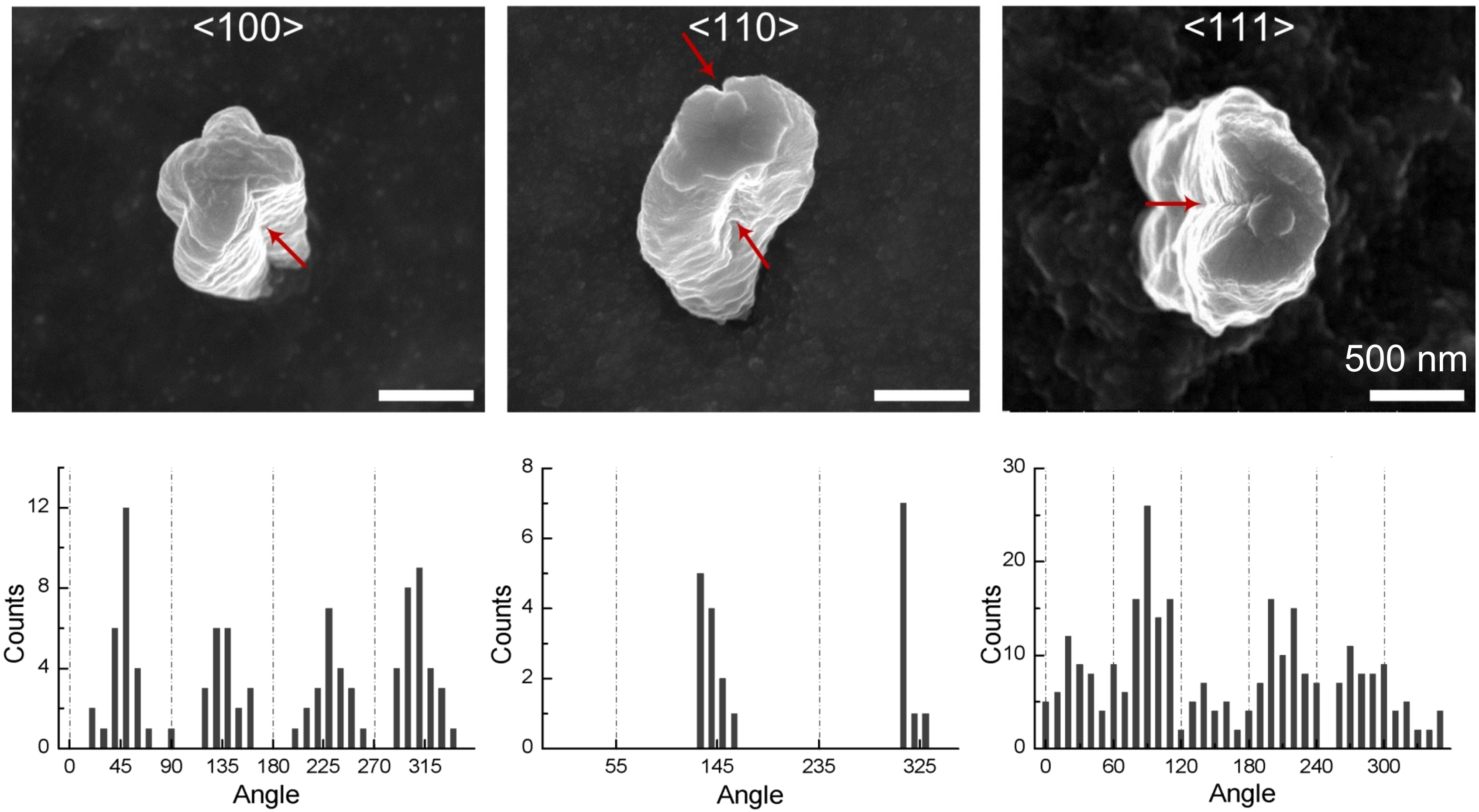
- Identified critical breaking size: 240 ~ 360 nm
- Discovered fast charging enhances fracture



Cui group, Proc. Natl. Acad. Sci. U.S.A., 109, 4080 (2012).

Accomplishment

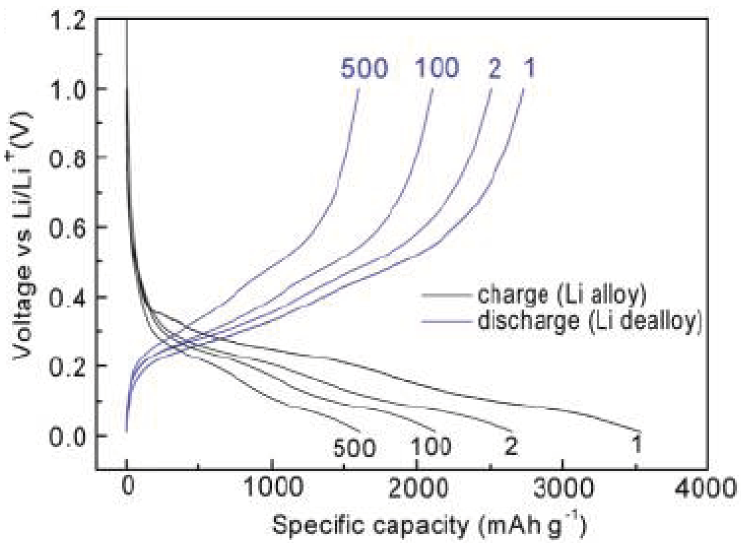
Discovering anisotropic fracture of crystalline Si

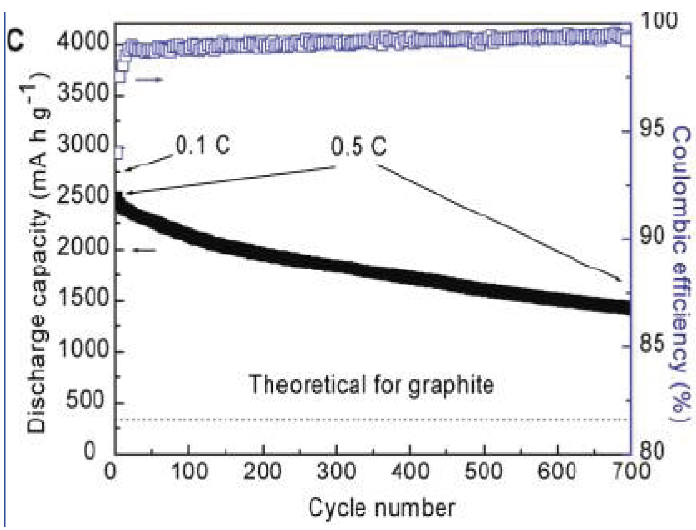


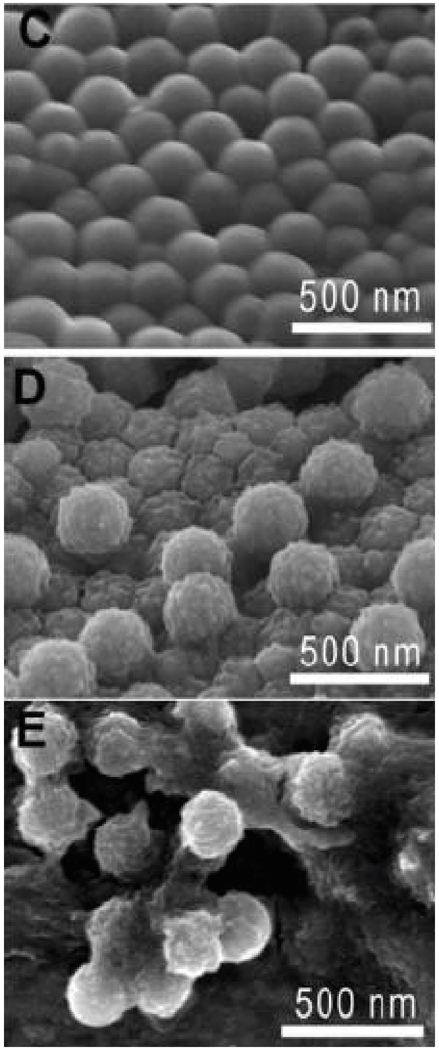
Cui group, Proc. Natl. Acad. Sci. U.S.A., 109, 4080 (2012).

Accomplishment

Developed hollow Si nanophere anodes







0 cycle

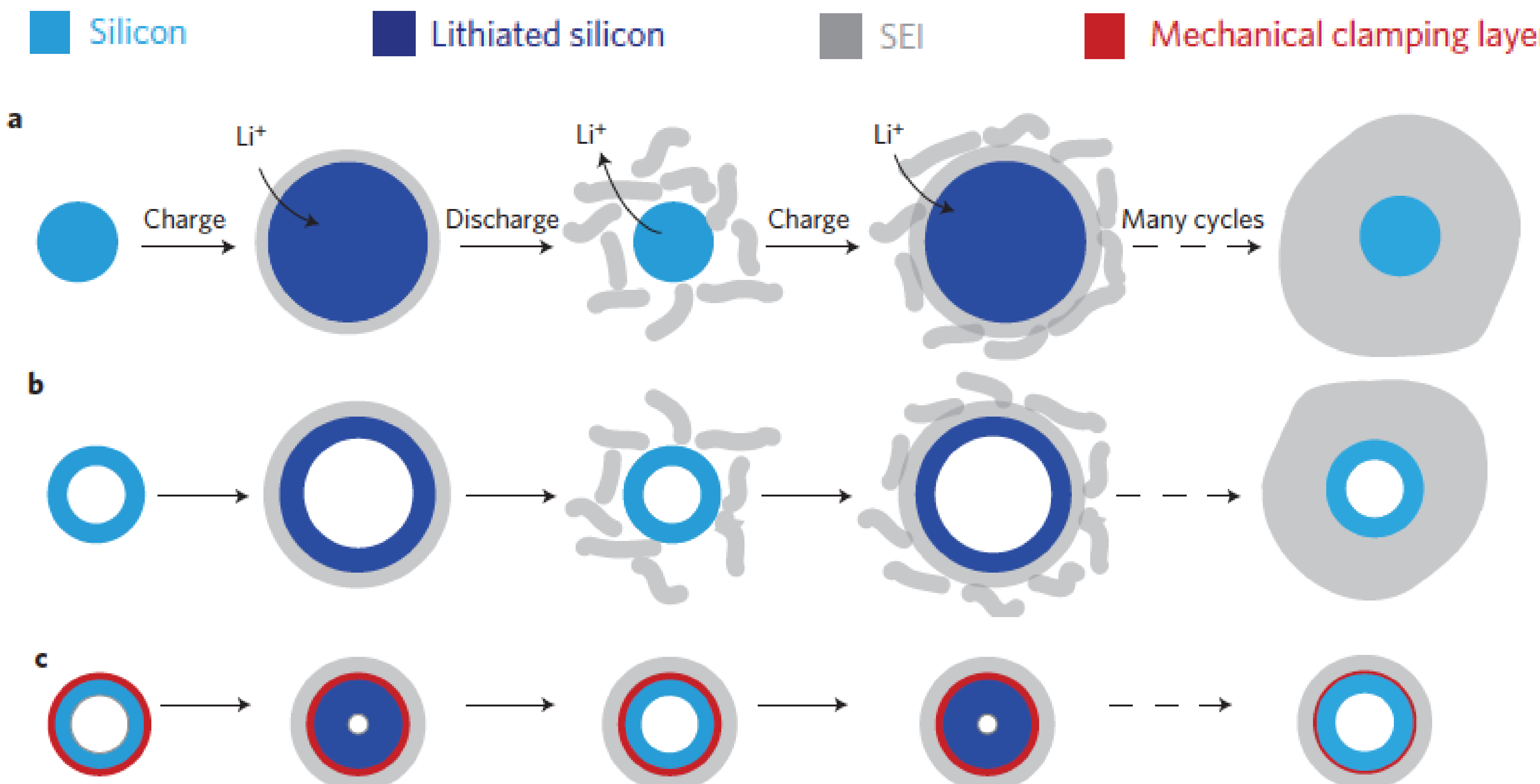
40 cycle

700 cycles

8% decay per 100 cycles

Accomplishment

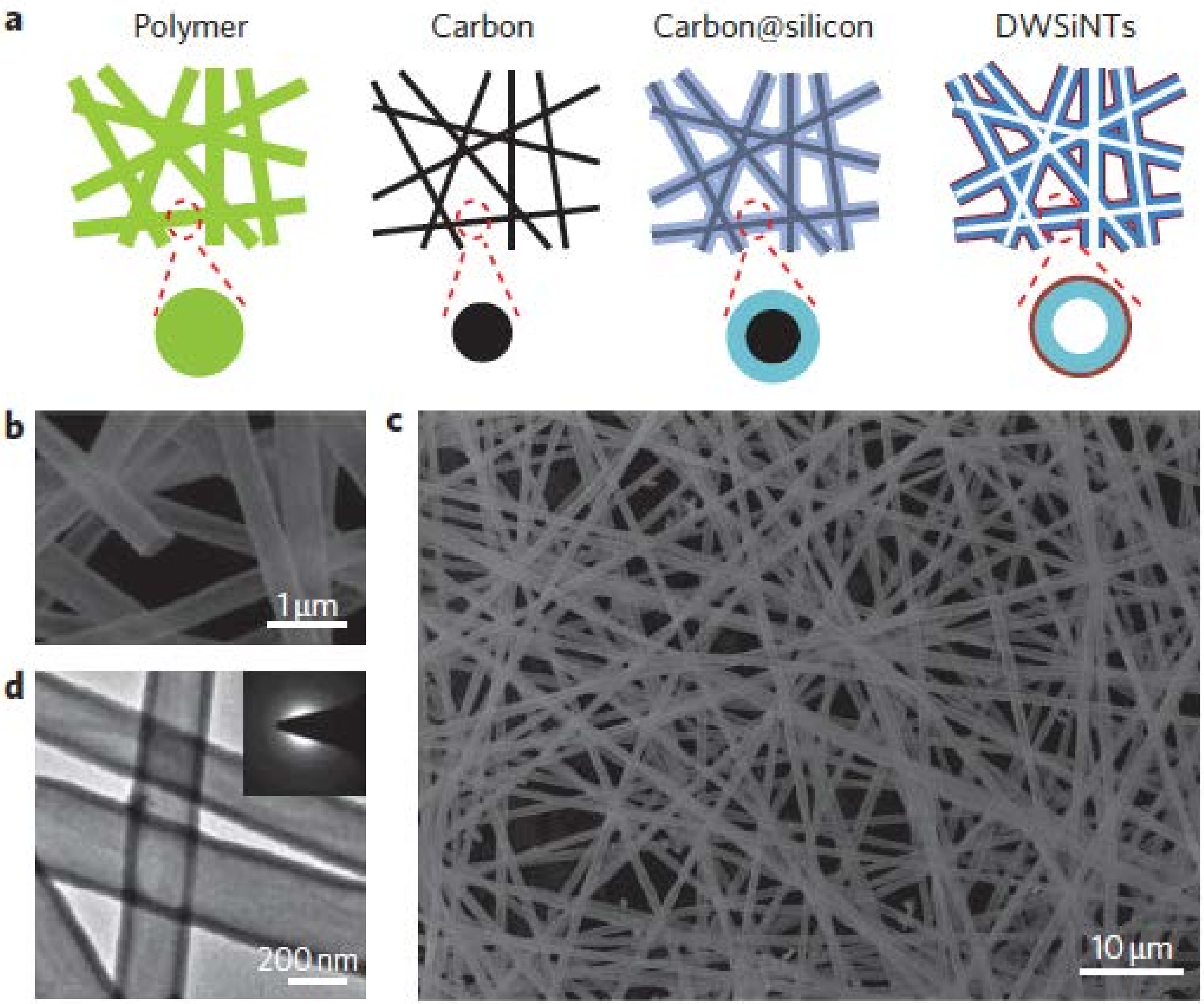
Designing double walled hollow Si structures to address
- Mechanical breaking
- Solid Electrolyte Interphase (SEI)



(Hui Wu, Yi Cui *Nature Nanotech* 7, 310 (2012))

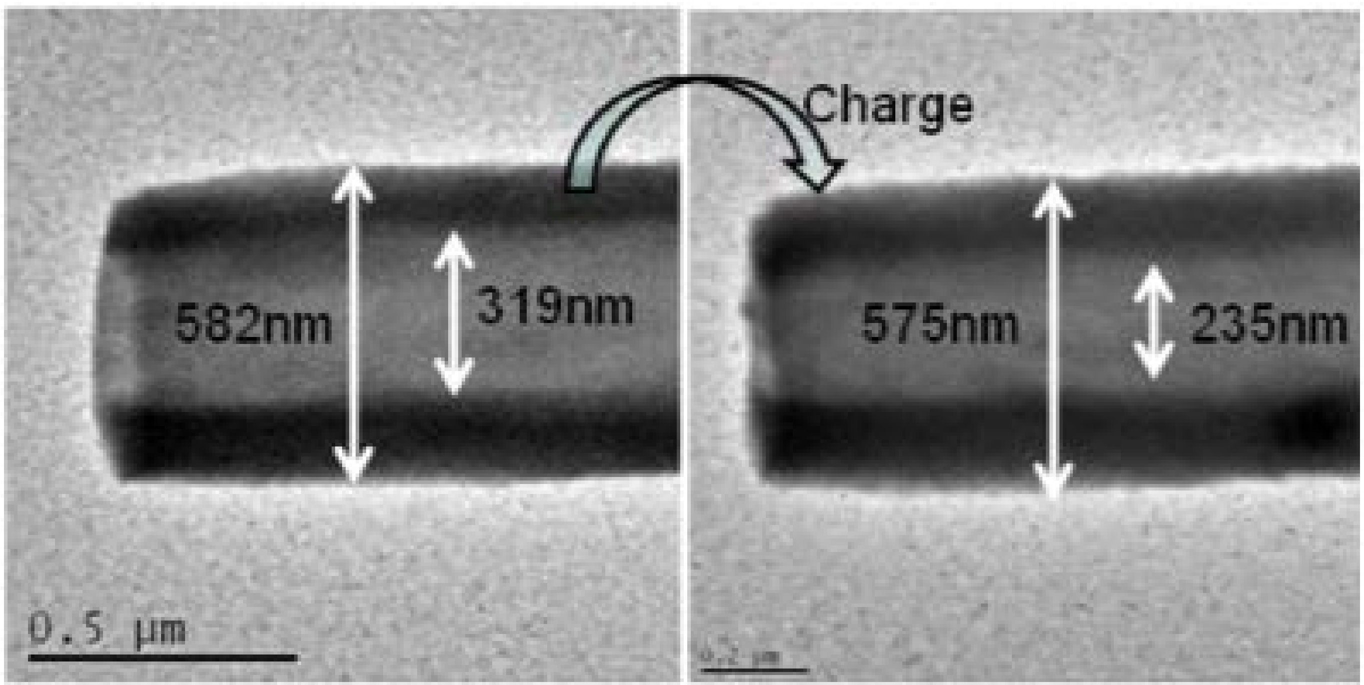
Accomplishment

Synthesis and Characterization of Double-Walled Si Nanotubes



Accomplishment

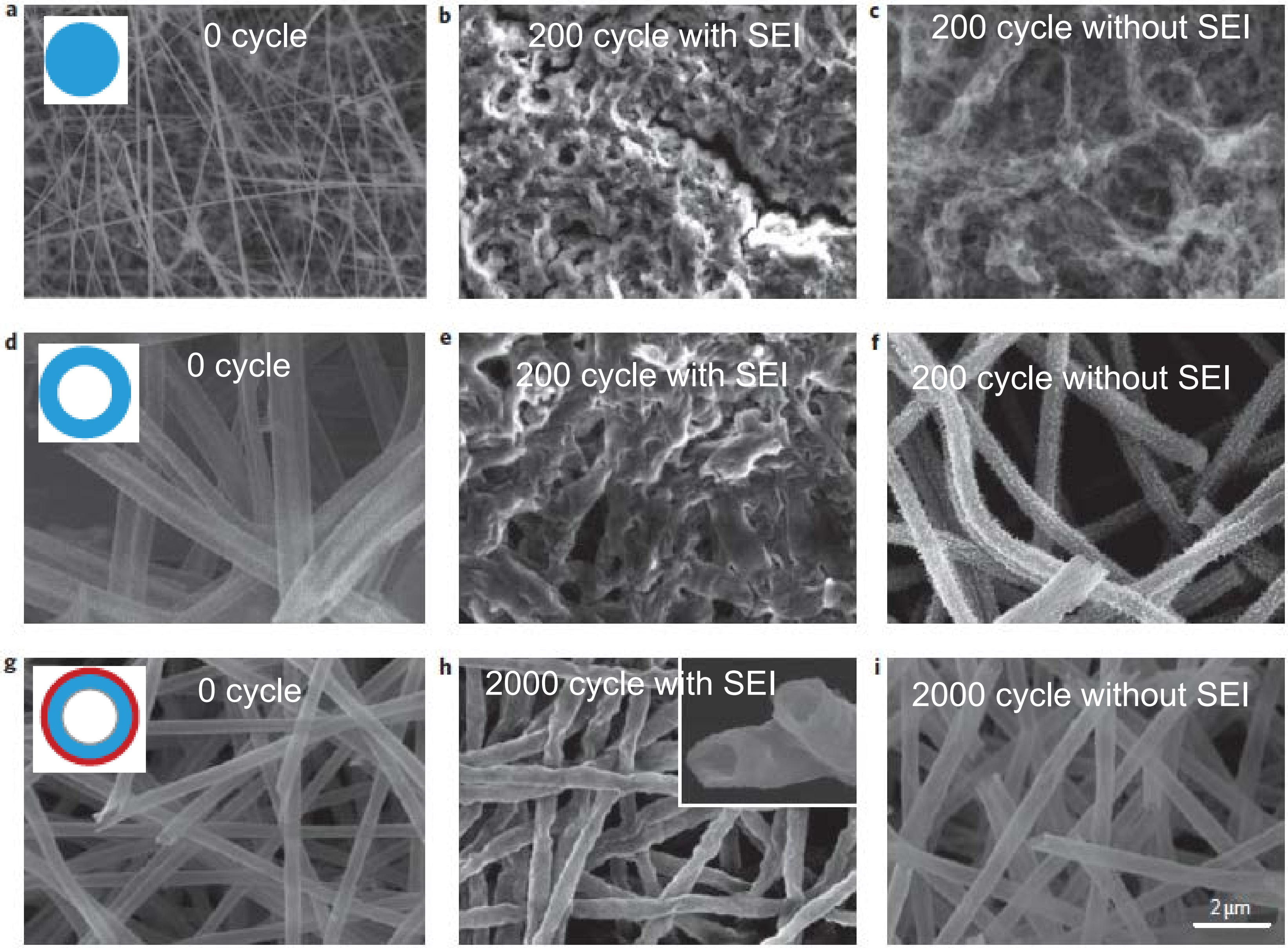
Characterization of Double-Walled Si Nanotubes by ex-situ transmission electron microscopy



- Outer diameter has no change.
- Inner diameter changes.

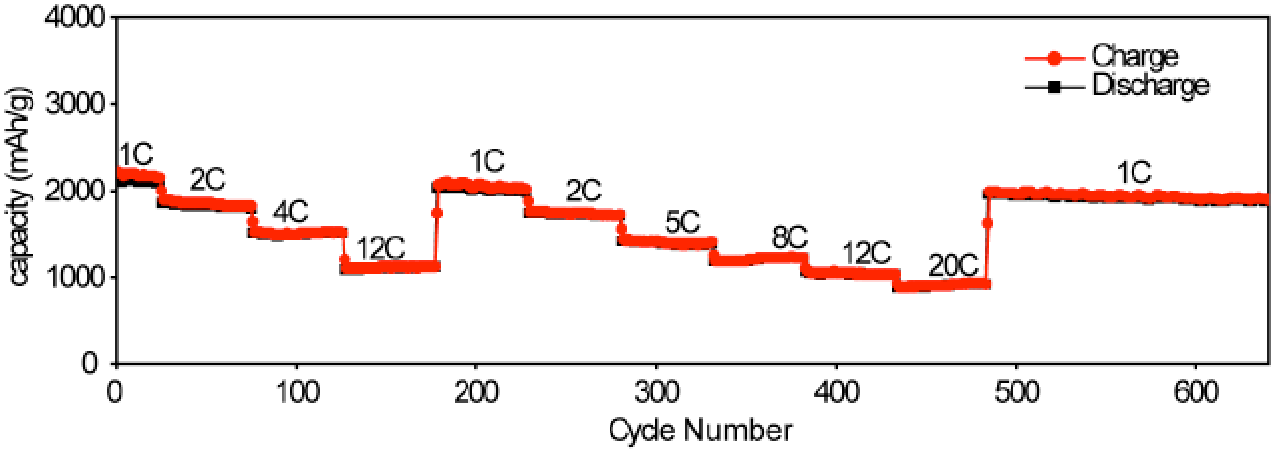
(Hui Wu, Yi Cui *Nature Nanotech* 7, 310 (2012))

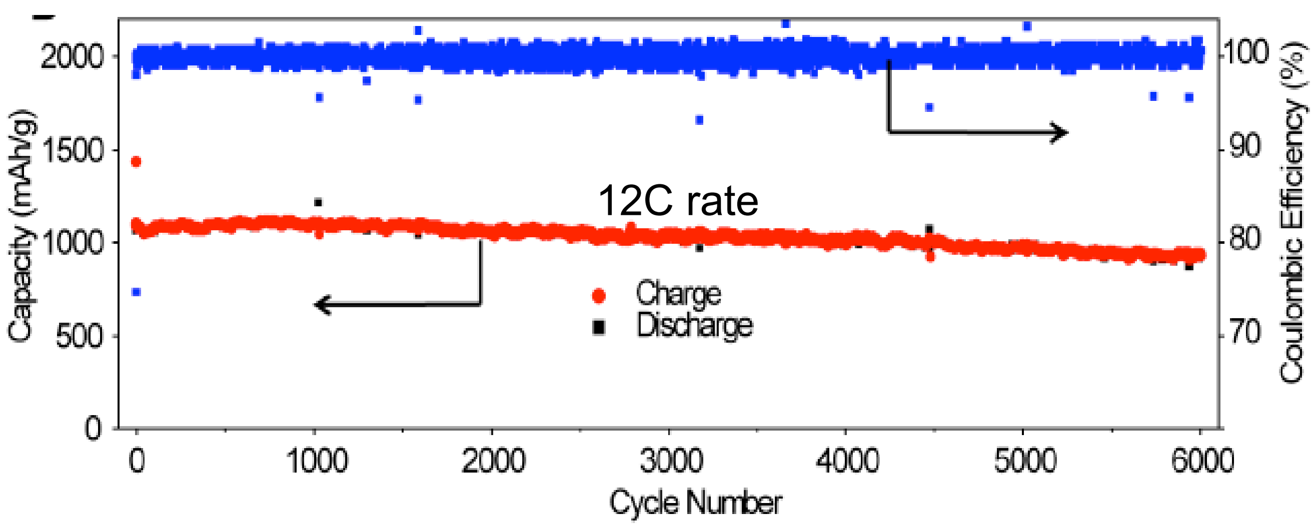
Accomplishment: Comparison Study



Accomplishment

High performance double-walled Si nanotubes

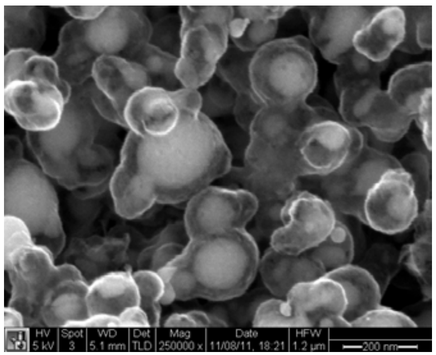


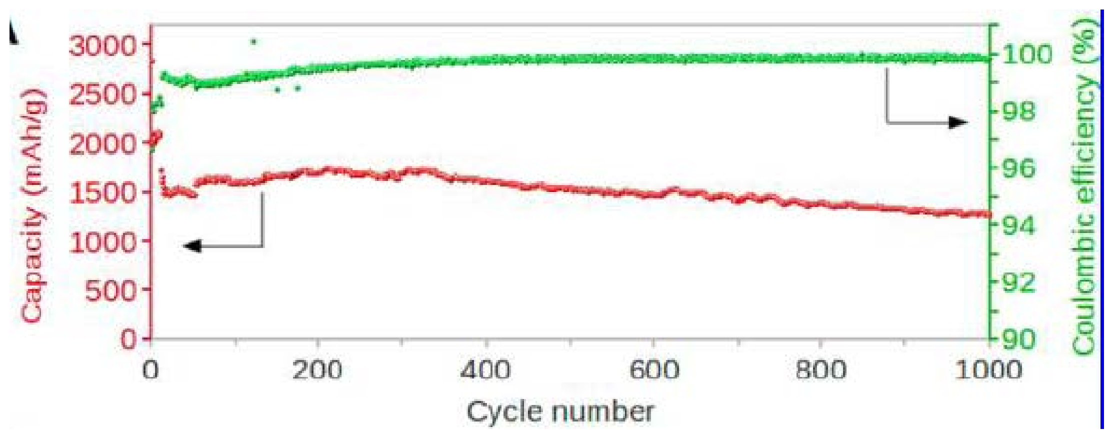


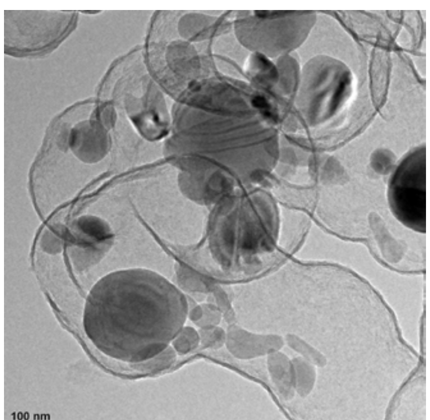
(Hui Wu, Yi Cui *Nature Nanotech* 7, 310 (2012))

Accomplishment

Successfully designed and synthesized Si yolk-shell structure with long cycle life for low-cost and scalable anodes.



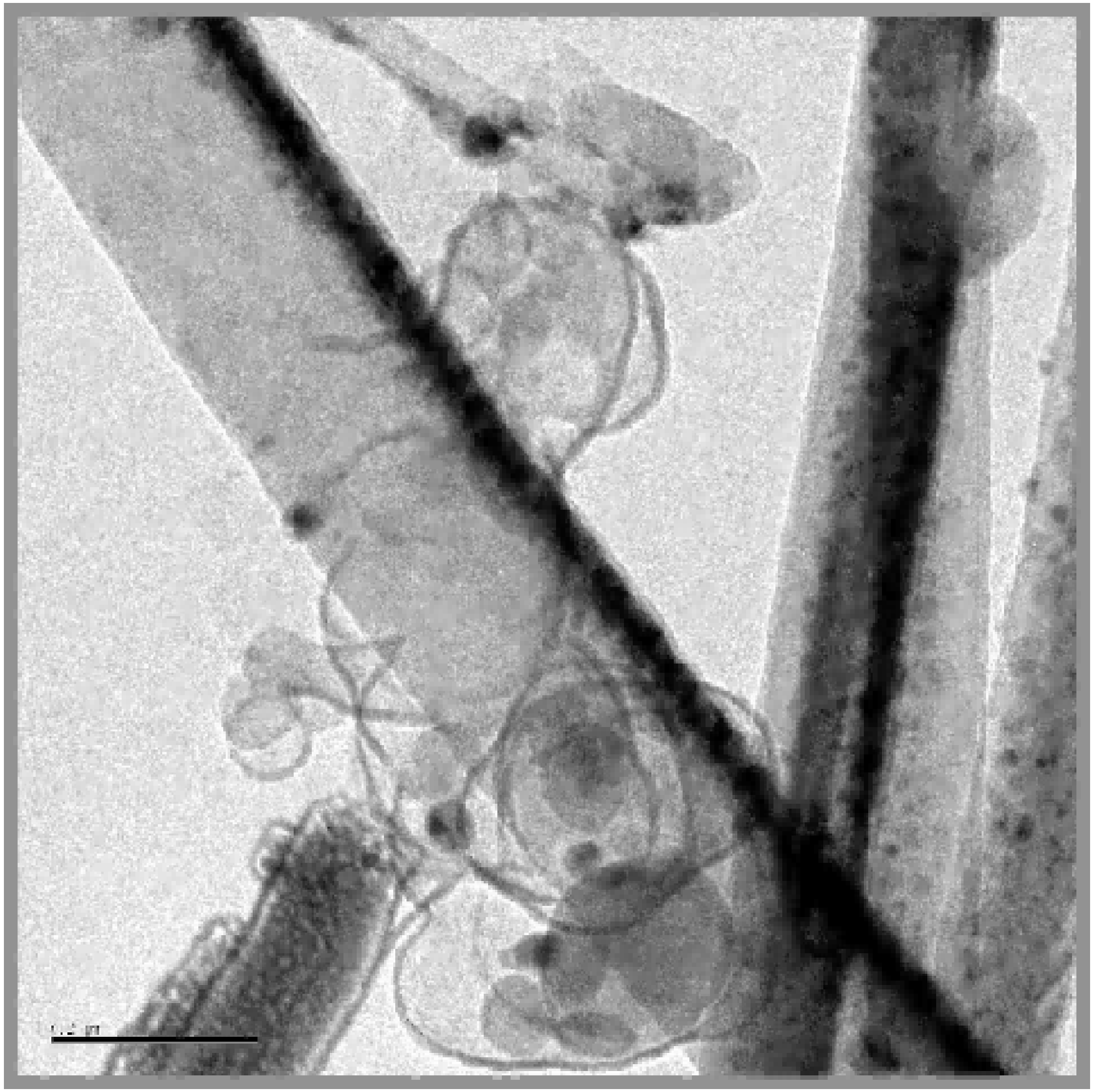




C/10 for 1st cycle, C/3 for 10 cycles, 1C for the rest)

N. Liu, M. McDowell, Yi Cui, Nano Letters 12, 3315 (2012).

Video of In-situ TEM



N. Liu, M. McDowell, Yi Cui, Nano Letters 12, 3315 (2012).

Collaboration and Coordination

- PNNL: In-situ TEM, Dr. C. Wang
- SLAC: In-situ X-ray, Dr. M. Toney
- UT Austin: Prof. Korgel, a-Si materials
- Stanford: Prof. Nix, mechanics; Prof. Bao, polymer materials
- Companies: Amprius Inc.

Proposed Future Work

- Further understand the nanoscale design to optimize Si anodes, for example, the ratio of Si material dimension vs porosity/hollow space .
- Further develop scalable and low-cost method for synthesizing nano-Si with desired performance.
- Test the Si electrodes with high areal mass loading up to 2-3mg/cm^2.
- Develop surface modification to increase the first cycle coulombic efficiency >90% and improve the later cycle coulombic efficiency.

Summary

- **Objective and Relevance:** The goal of this project is to develop high capacity Si anodes with nanomaterials design to enable high energy batteries, highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanosynthesis, characterization and battery testing, which has been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** The project has produced many significant results, meeting milestones. They include identifying the fundamental materials design principles, synthesizing and testing, and developing low-cost and scalable methods. The results have been published in top scientific journal. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaboration.
- **Proposed Future Work:** Rational and exciting future has been planned.