Designing Silicon Nanostructures for High Energy Lithium Ion Battery Anodes

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May 14, 2012

Project ID #ES148

Overview

Timeline

- Start: Jan 1, 2011
- End: Dec. 31, 2014
- Percent complete: 30%

Budget

- Total project funding
  $1,200k from DOE
- Funding received in FY11
  $300k
- Funding for FY12
  $300k

Barriers

Barriers of batteries

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

Targets: high energy materials and cells

Partners

- BATT program PI's around the country

Project Objective and Relevance

Overall objective

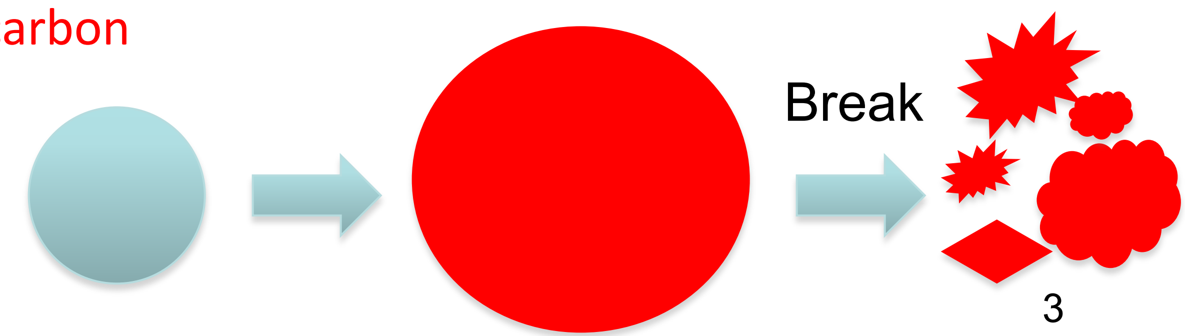
We seek to overcome the charge capacity limitation of conventional carbon anodes by designing and understanding a nano silicon electrode. This anode can address the issues caused by the volumetric expansion of the materials and provide a good cycle life. The overall goal is highly relevant to the VT battery program.

FY 11 objective

Understanding silicon expansion and fracture during lithium reaction and developing promising nanostructures.

Si: 4200 mAh/g, 10X of carbon

$Si \longleftrightarrow Li_{4.4}Si$



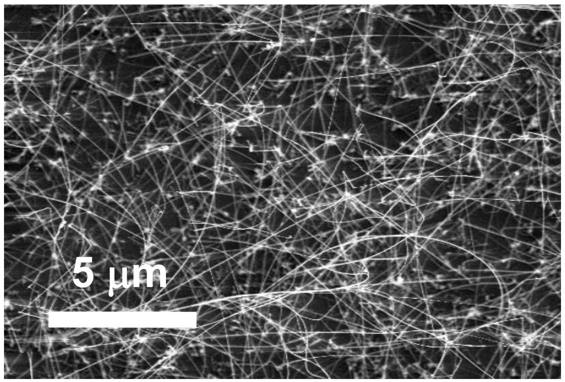
For Si: volume expansion by 4 times

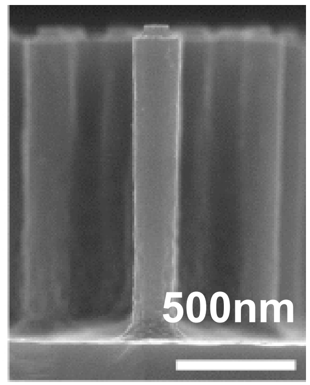
Milestones for FY11 and 12

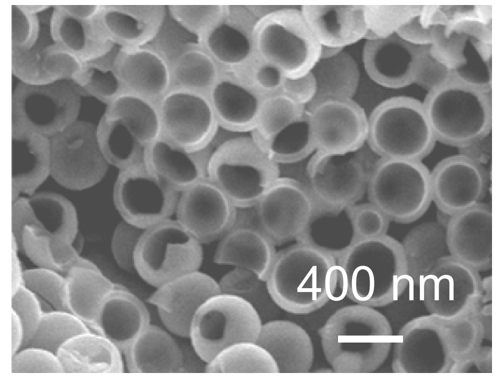
Month/year	Milestones
6/2011	Identify the method to connect Si nanoparticles electrically (completed)
9/2011	Find out the relationship of critical breaking size versus capacity for deep lithiation . Identify a method to produce hollow silicon structure. (completed)
2/2012	Obtain detailed information 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 (on schedule)
10/2012	Optimize nanostructured Si for long cycle life (>1000 cycles). (on schedule)
1/2013	Develop fundamental understanding of the features that control volume expansion/contraction in Si nanostructures . (on schedule)

Approach/Strategy

Advanced nanostructured Si materials design and synthesis



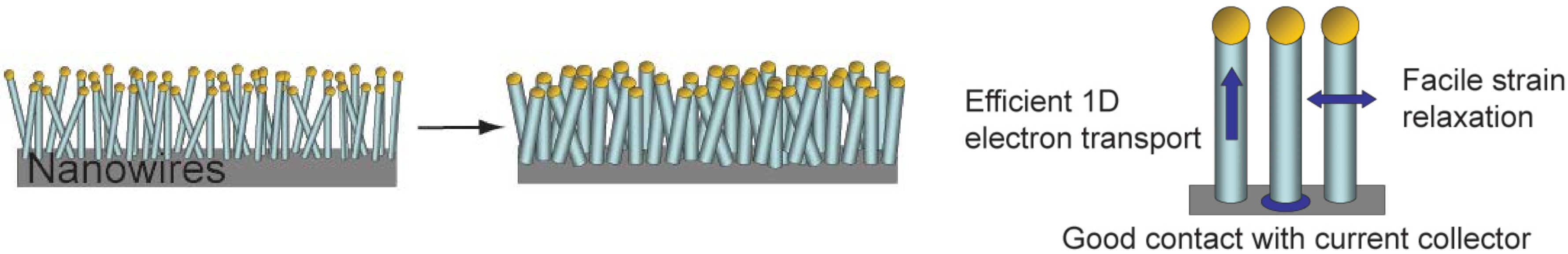




Structure and property characterization
- Ex-situ transmission electron microscopy
- In-situ transmission electron microscopy
- Ex-situ scanning electron microscopy

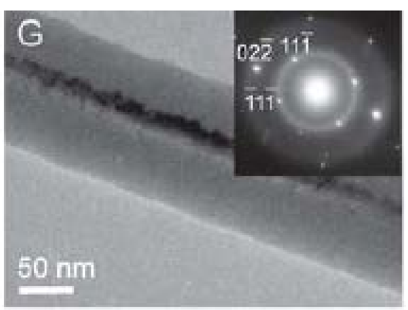
Electrochemical testing
- Coin cells and pouch cells.
- A set of electrochemical techniques.

Previous Results on Silicon Nanowire Anodes



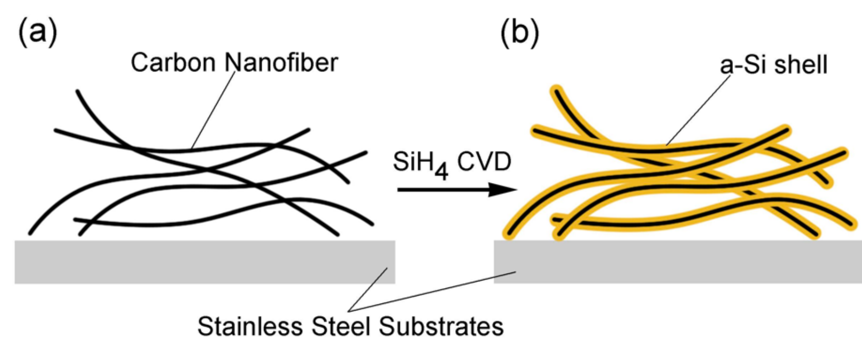
Cui group, Nature Nanotechnology 3, 31 (2008).

Crystal-amorphous Si core-shell nanowires



Cui group
Nano Letters 9, 491 (2009).

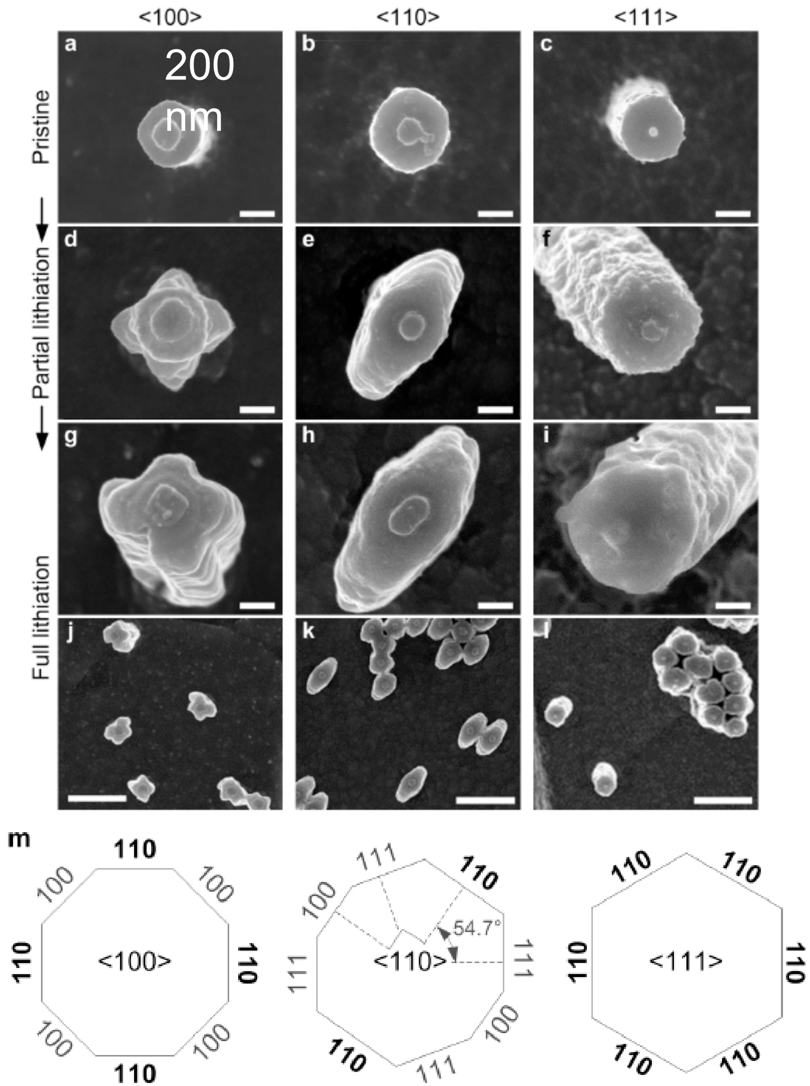
Carbon-silicon core-shell nanowires

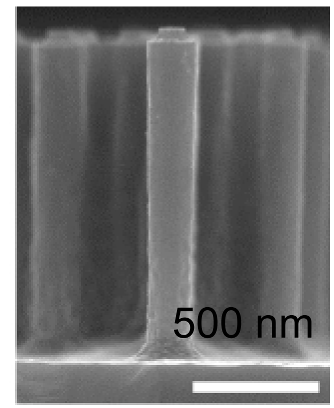


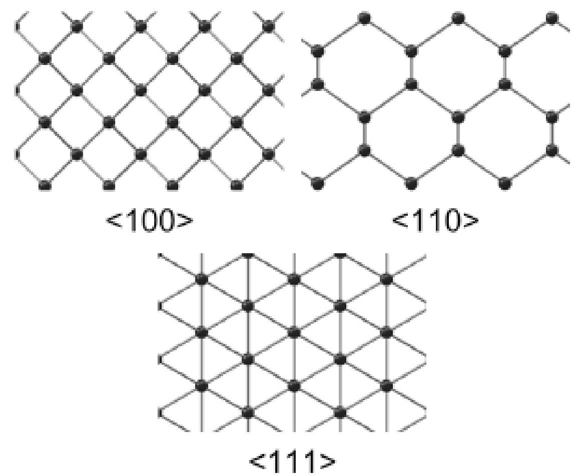
Cui group
Nano Letters 9, 3370 (2009).

Accomplishment

Discovering anisotropic expansion of crystalline Si upon lithiation



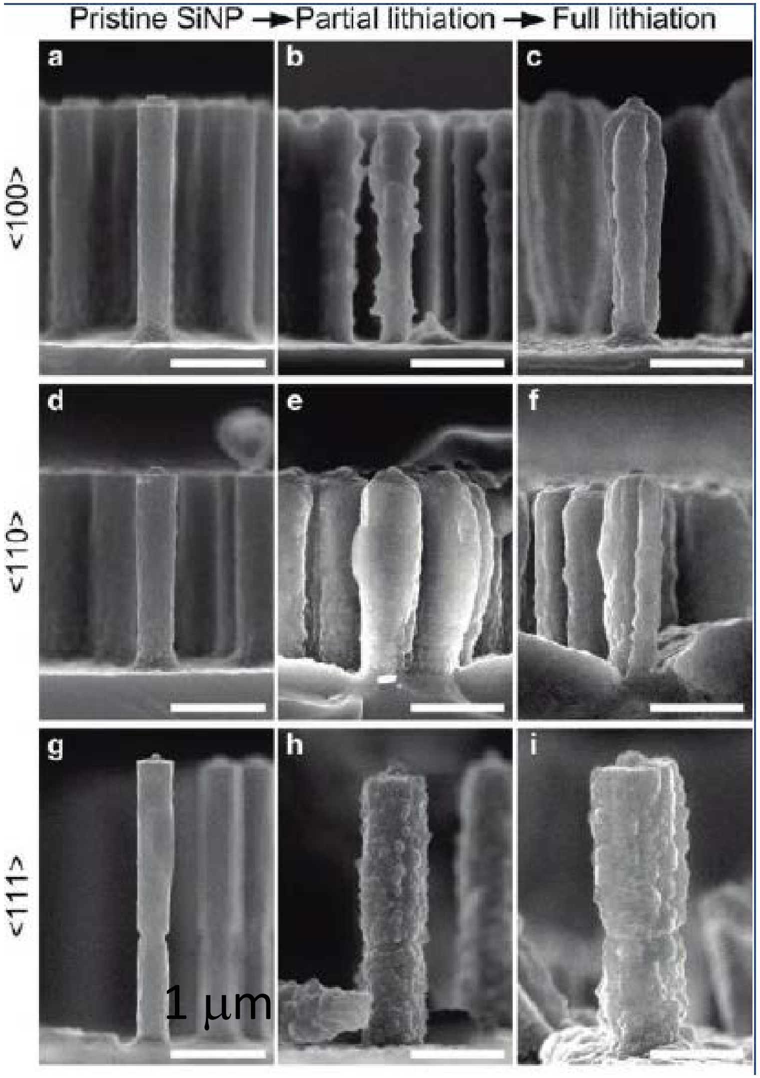




(Cui group,
Nano Letters 11, 3034 (2011))

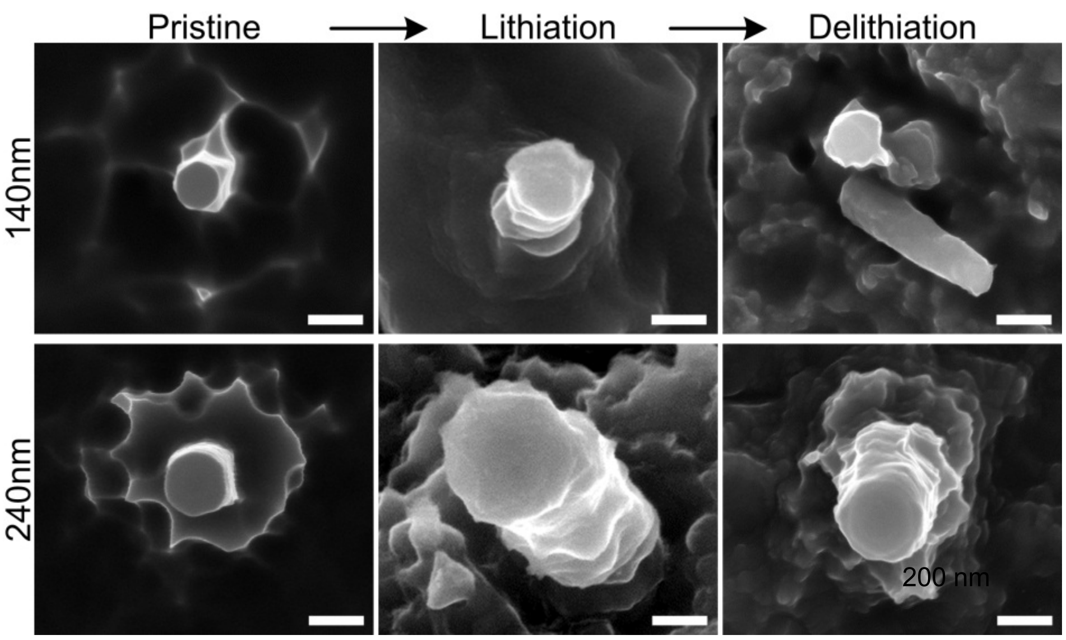
Accomplishment

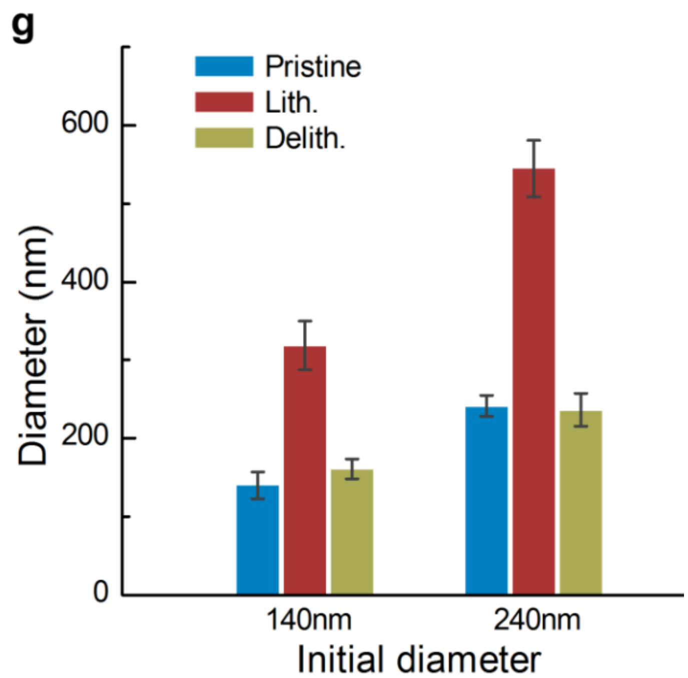
The length of nanopillar changes very little.



Accomplishment

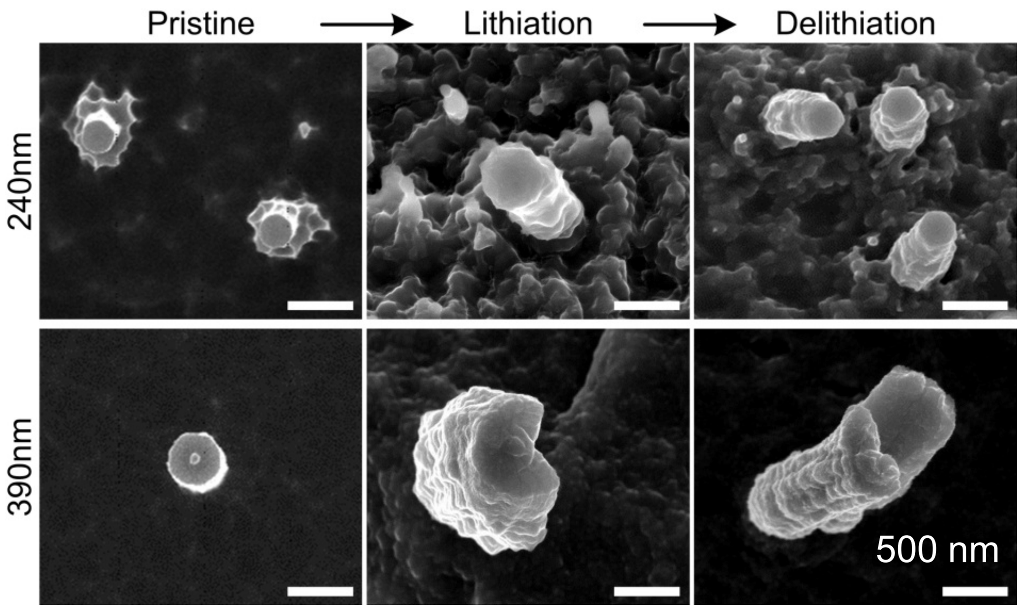
Expansion and Contraction of Si Nanostructures

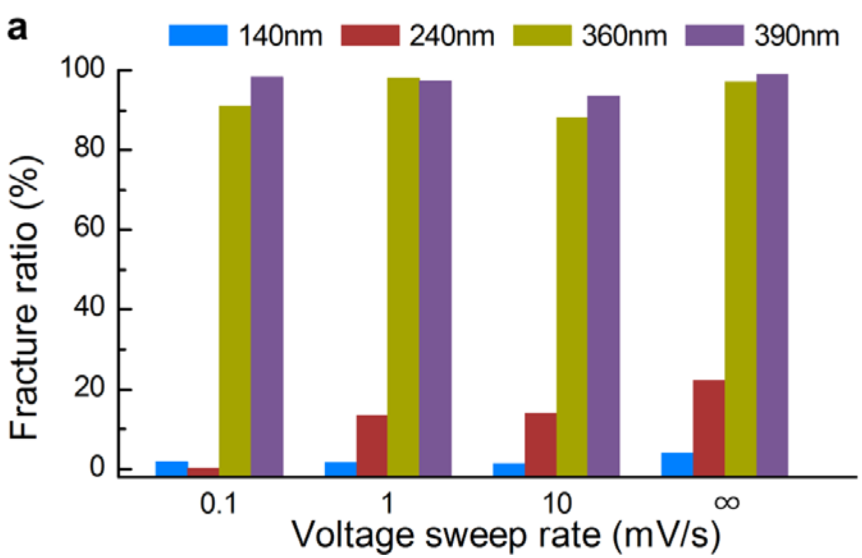




Lithiation: ~200% expansion ***Delithiation: shrinks back***

Accomplishment





Large Si nanopillar is easy to break.

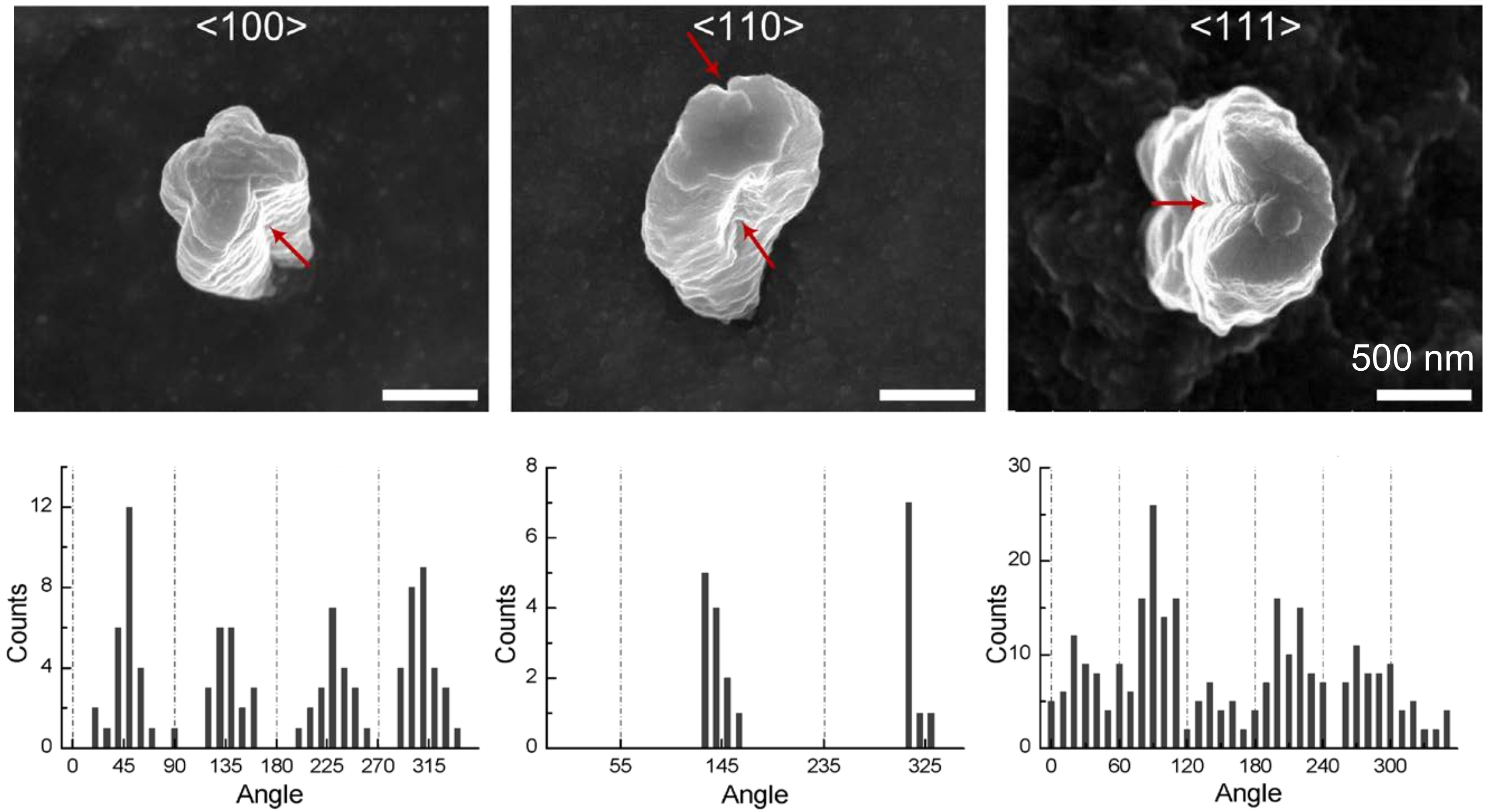
Transition size: 240 ~ 360 nm

Fast reaction enhances fracture

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

Accomplishment

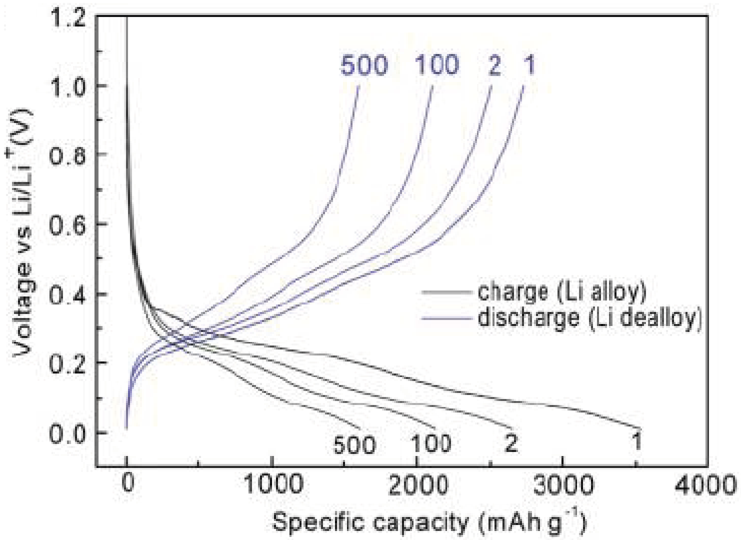
Discovering anisotropic fracture

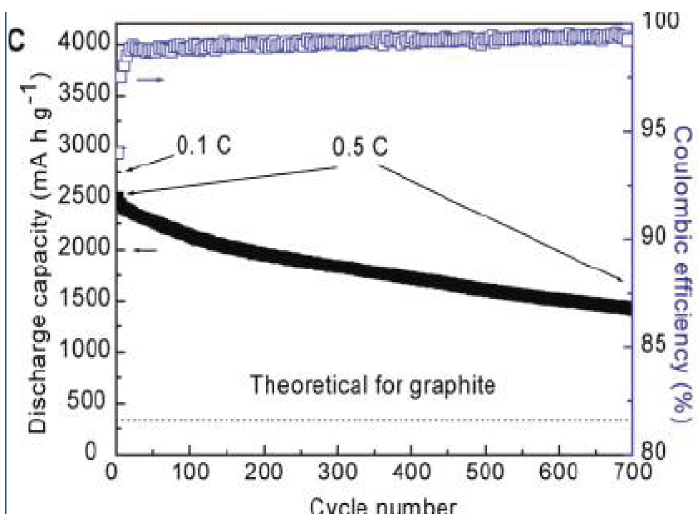


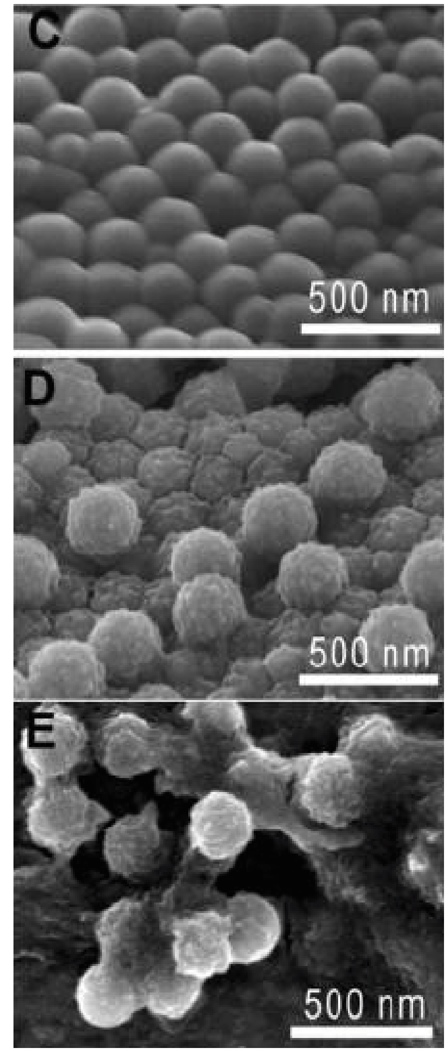
Cui group, Proc. Natl. Acad. Sci. U.S.A., 109, 4080 (2012).

Accomplishment

Hollow Si nanophere anodes







0 cycle

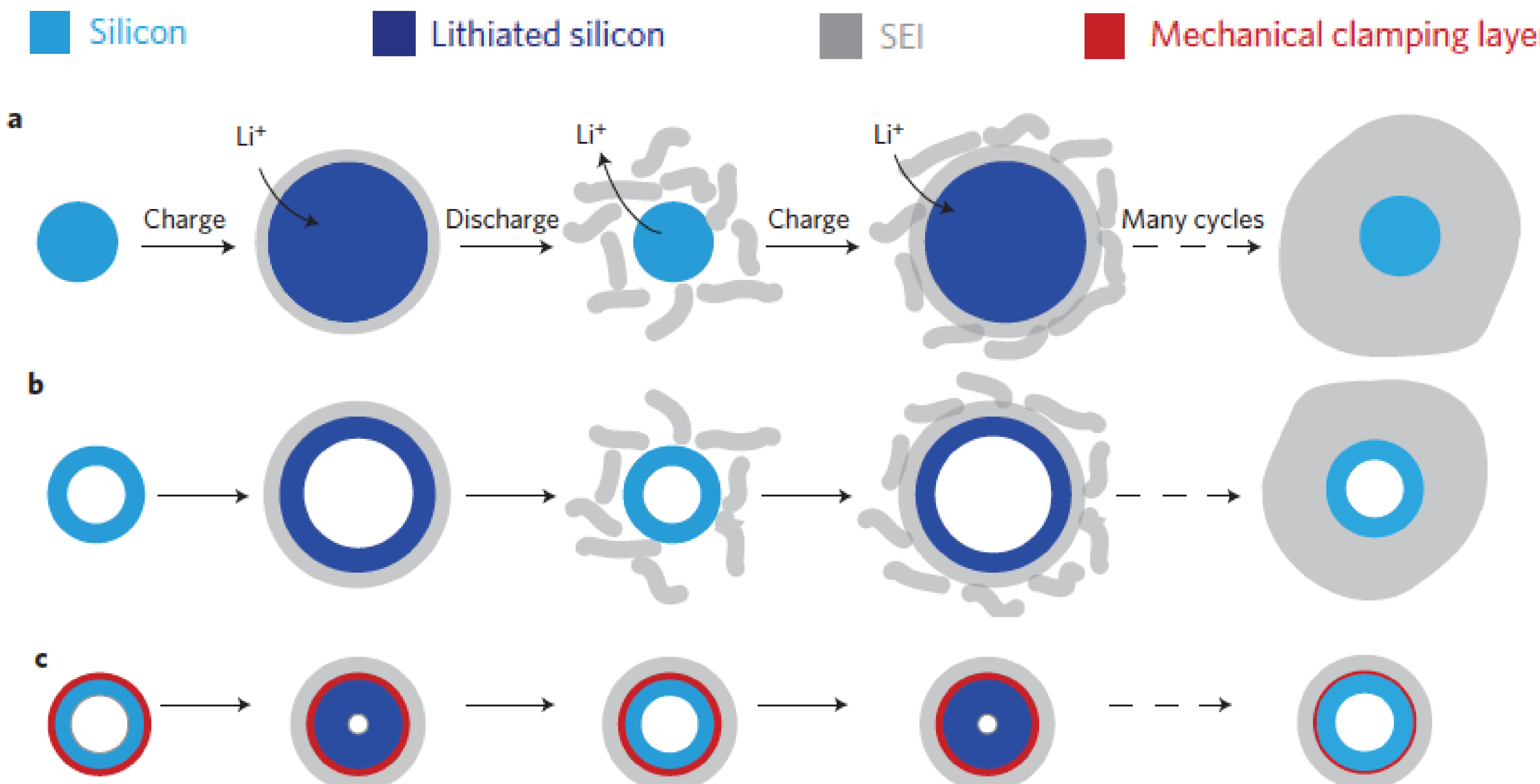
40 cycle

700 cycles

8% decay per 100 cycles

Accomplishment

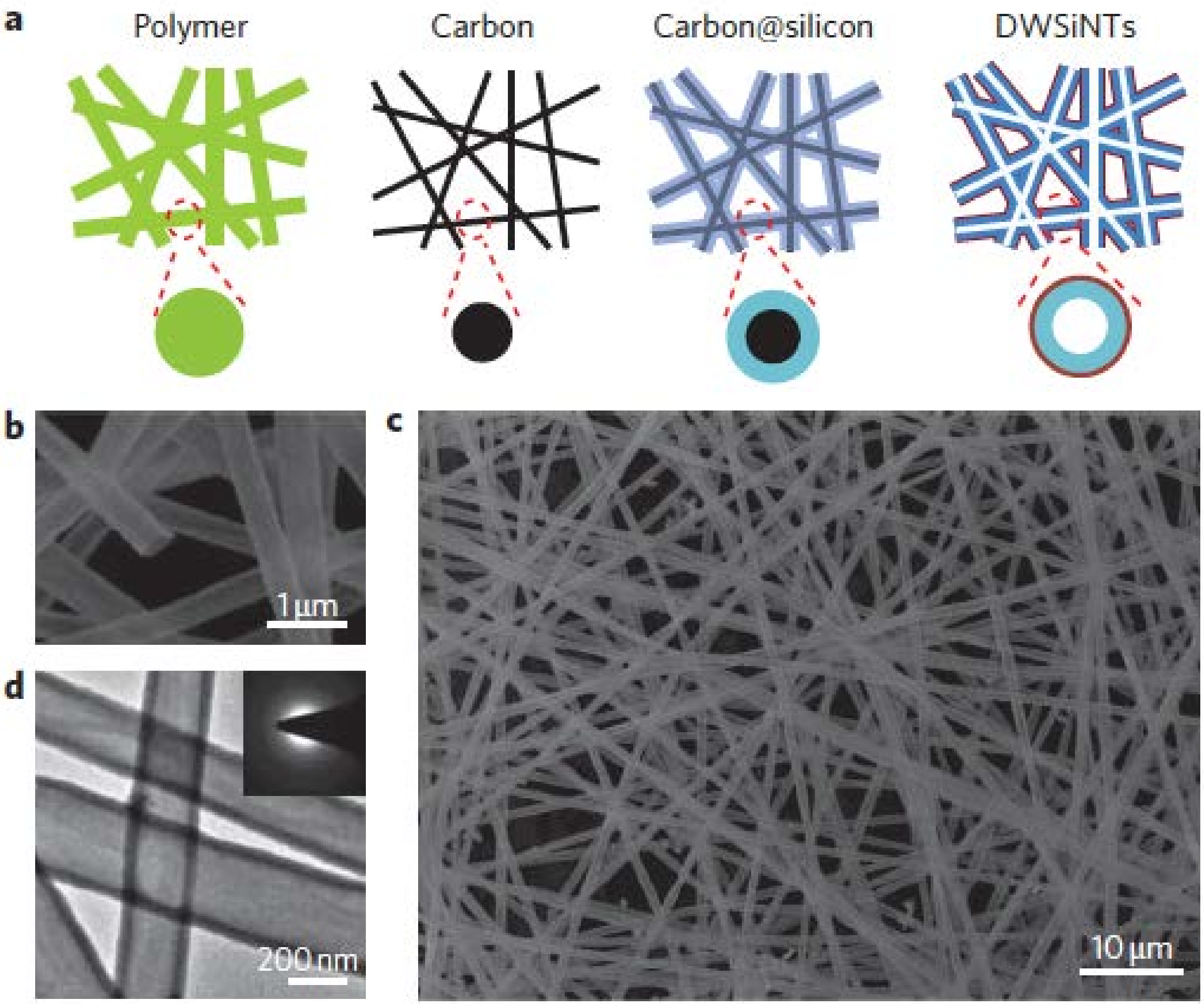
Designing double walled hollow Si structures to address
- Mechanical breaking
- Solid Electrolyte Interphase (SEI)



(Yi Cui Group *Nature Nanotech* (2012, in press))

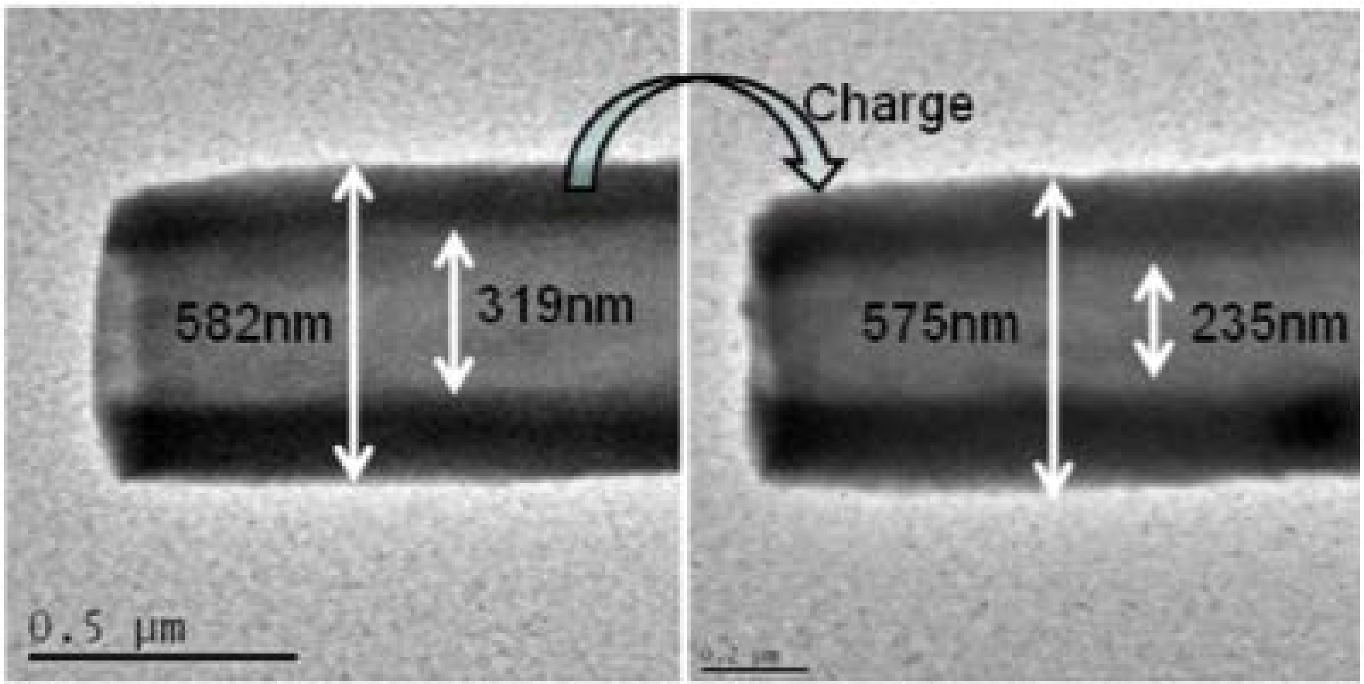
Accomplishment

Synthesis and Characterization of Double-Walled Si Nanotubes



Accomplishment

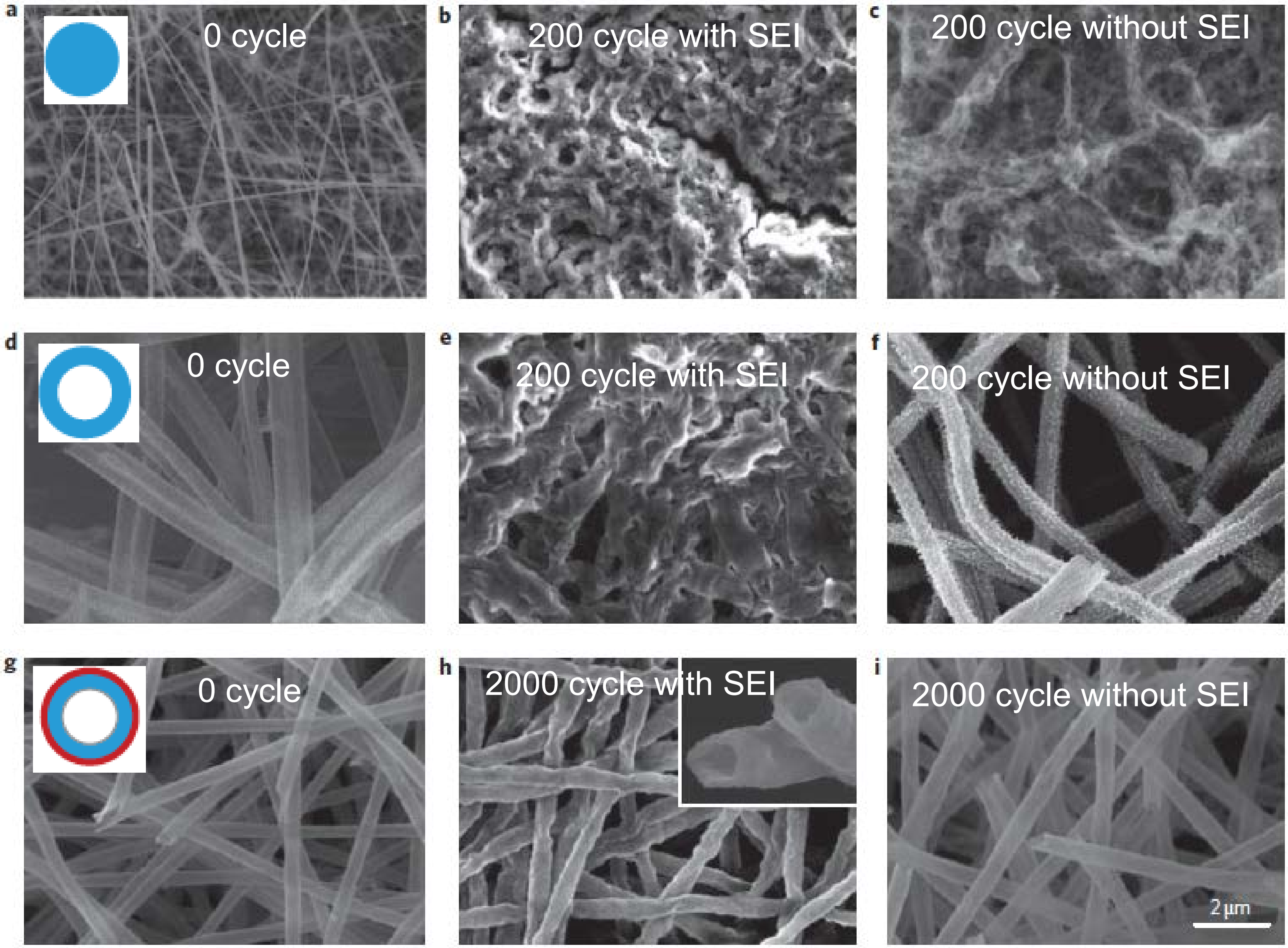
Characterization of Double-Walled Si Nanotubes by ex-situ transmission electron microscopy



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

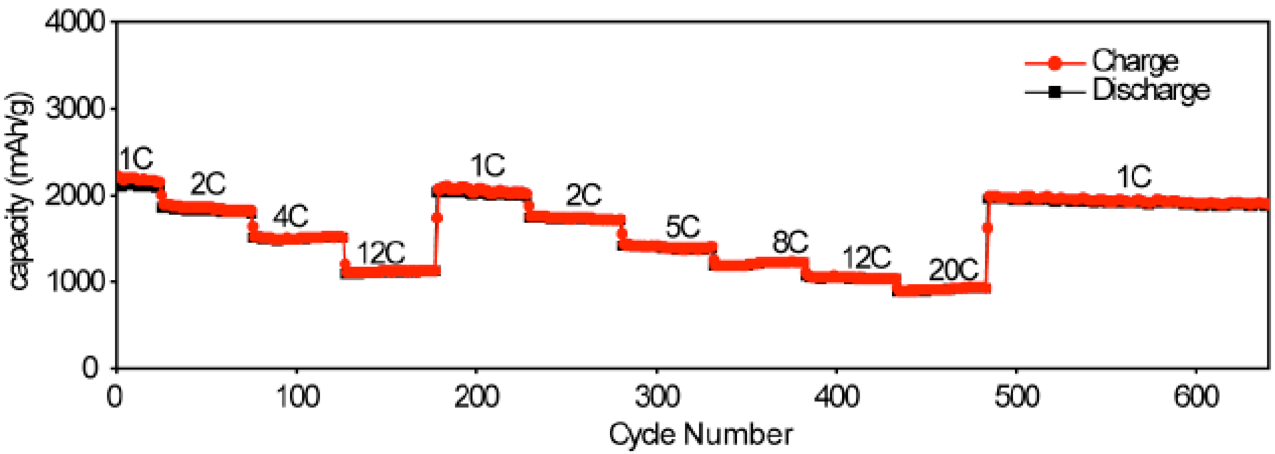
(Yi Cui Group *Nature Nanotech* (2012, in press))

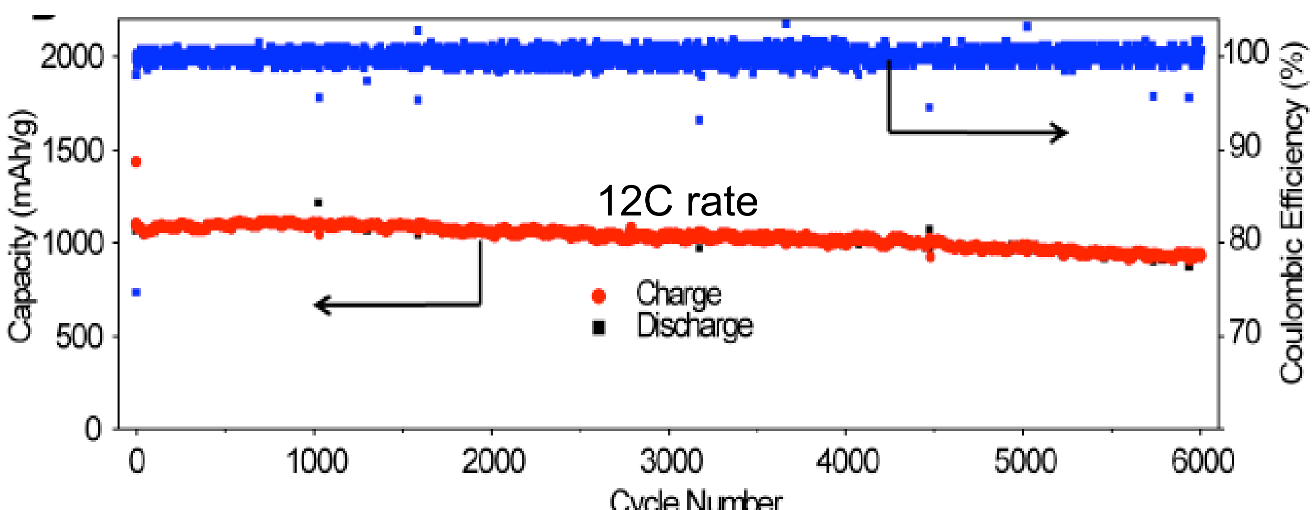
Accomplishment: Comparison Study



Accomplishment

High performance double-walled Si nanotubes





(Yi Cui Group *Nature Nanotech* (2012, in press))

Collaboration and Coordination

- Collaborate with a large number of PI's within DOE BATT Si anode program.

- Help leading the diagnostics thrust of Si anodes.

- Coordinate with a number of universities and national labs to identify key needs of Si anode development.

- Collaborate with battery company (Amprius) to speed up their development

Proposed Future Work

- Using in-situ transmission electron microscopy to watch Li-Si structure and volume change in real time and discover the key fundamental mechanism hidden in other techniques.
- Further understand the nanoscale design to optimize Si anodes, for example, the ratio of Si material dimension vs porosity/hollow space .
- Develop synthesis method to produce the designed Si anode structure.
-Test the Si anode structure with high areal mass loading.
- Develop surface modification to increase the coulombic efficiency.

Summary

- **Relevance:** The goal of this project is to develop high capacity Si anodes with nanomaterials design, 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. 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 been playing very active role in building collaboration and coordination.
- **Proposed Future Work:** Rational and exciting future has been planned.