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In-situ Transmission Electron Microscopy (TEM) Study on the Lithium Ion Transport in Si-Ge heterostructured Nanowires

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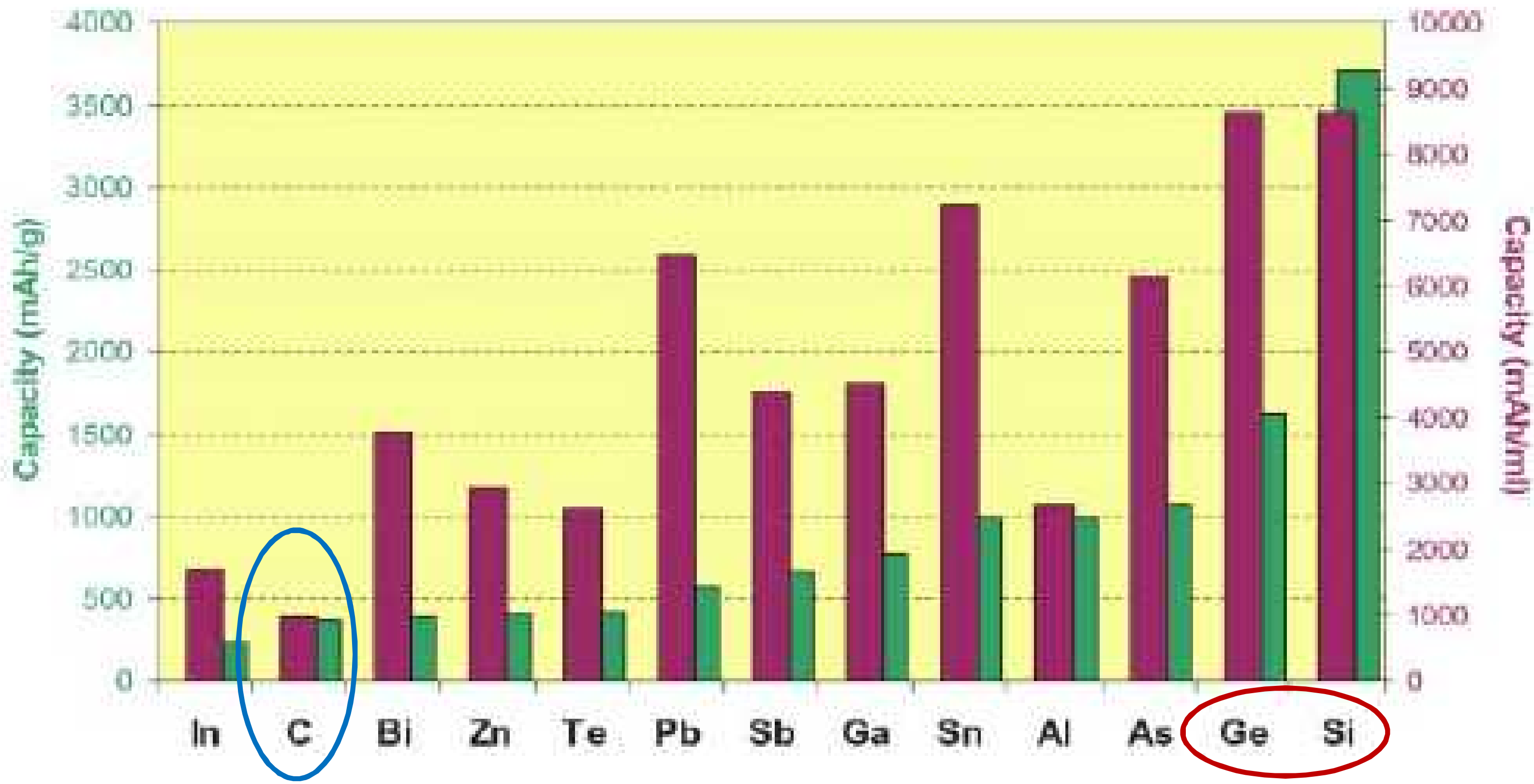
Why Ge-Si heterostructures?
----having a balanced high capacity and high charging/discharging rate

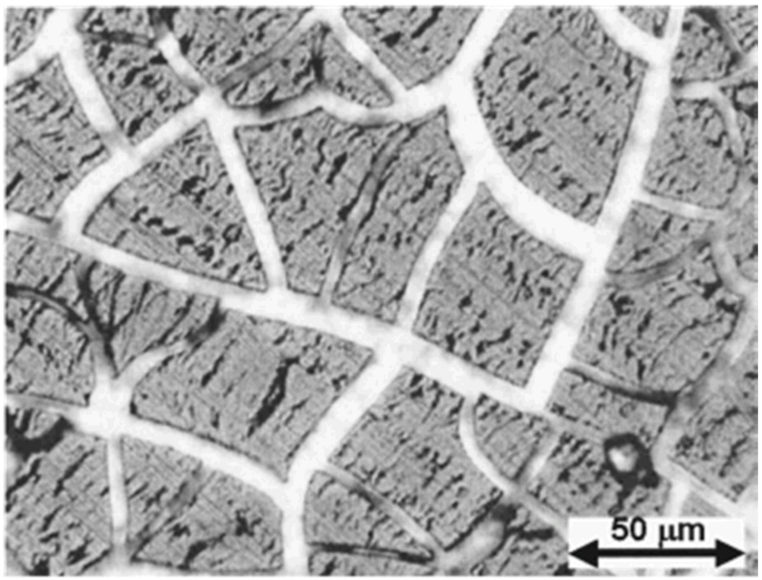


Si possesses the largest theoretical gravimetric capacity in the anode materials.
Ge also has large capacity (both gravimetric and volumetric), second only to silicon.
In addition, Ge has high intrinsic electronic conductivity and lithium ion diffusivity.

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

Severe mechanical problem due to the large volume expansion

New anode materials such as Si, Ge, Sn, SnO_2 usually experience 100% ~ 300% volume expansion upon lithiation, which is hard to control and causes fracture of the electrodes.



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

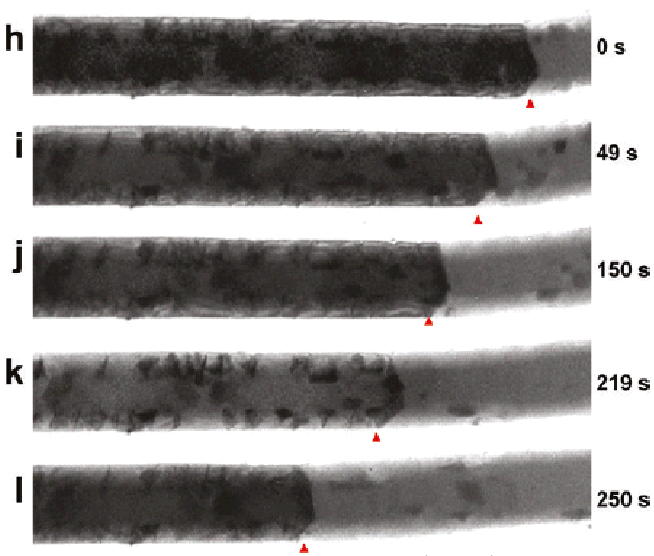
A dry lake bed

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

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

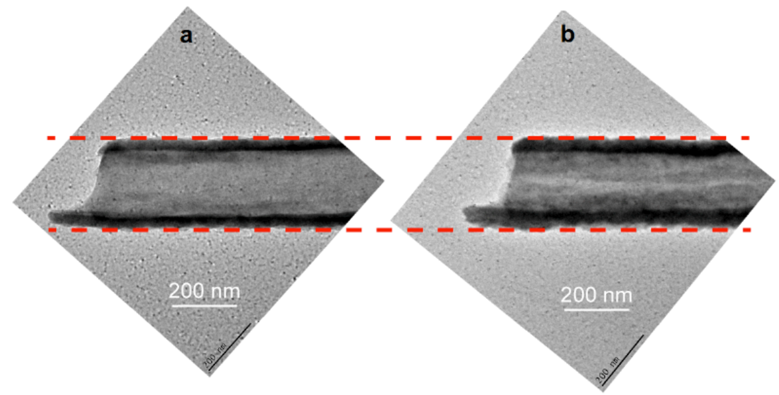
The normally used method:
External mechanical confinement

Example #1: carbon-coated SnO_2 nanowire



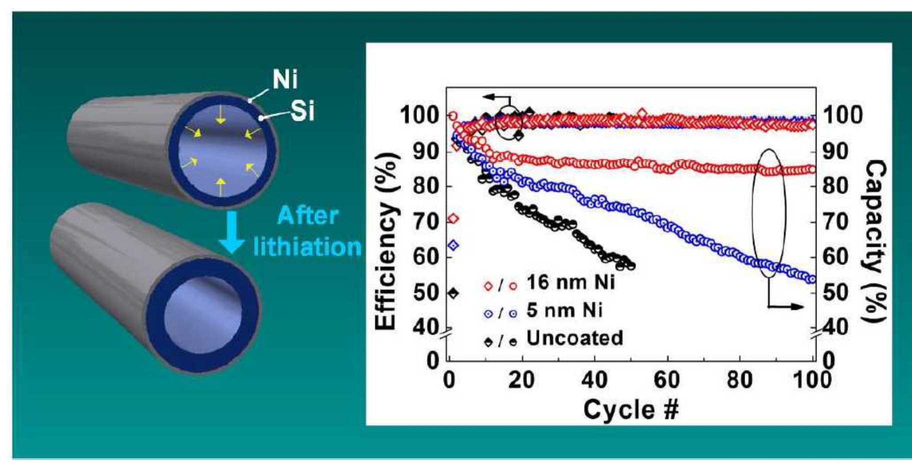
L. Zhang et al, ***ACS Nano***, 5, 4800 (2011)

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)

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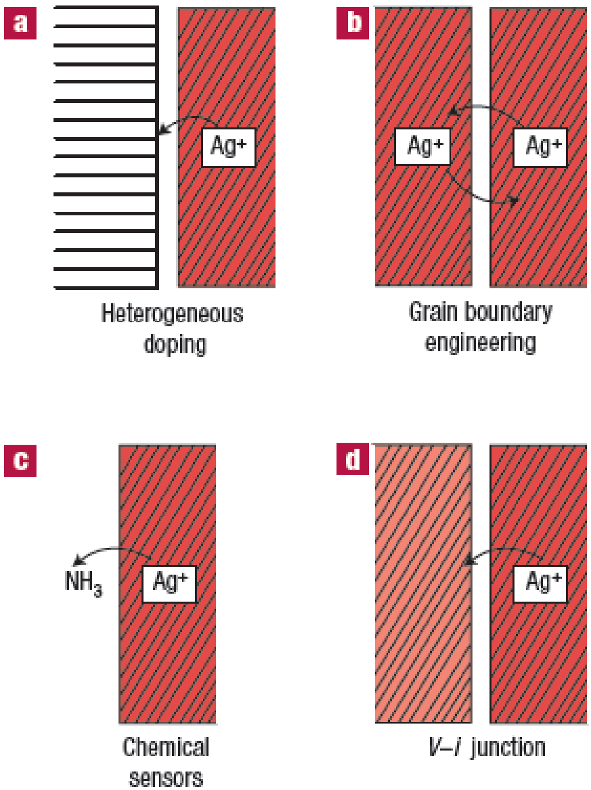
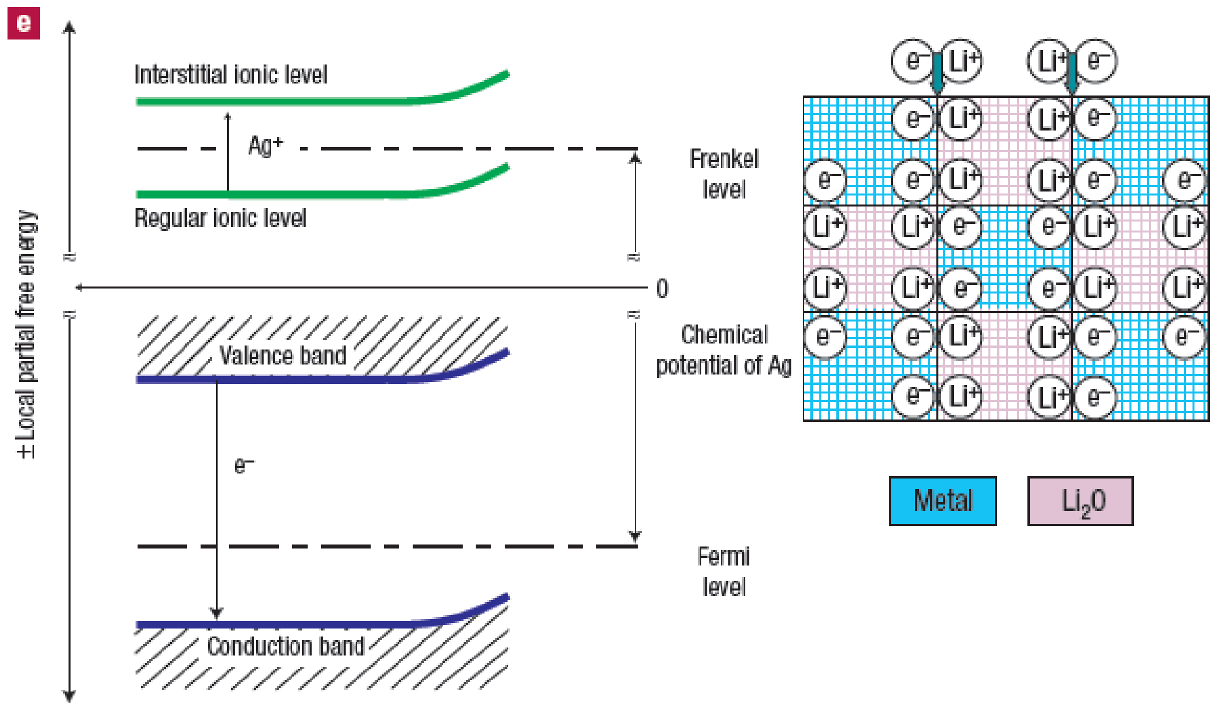
Interface and nanosize effects on nano-ionics

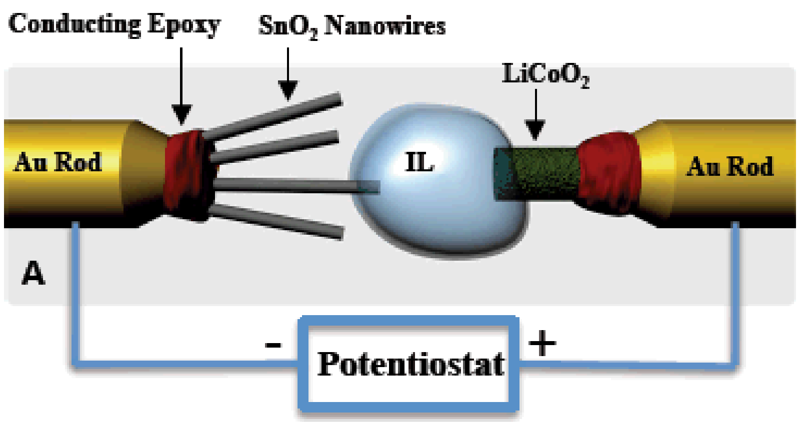


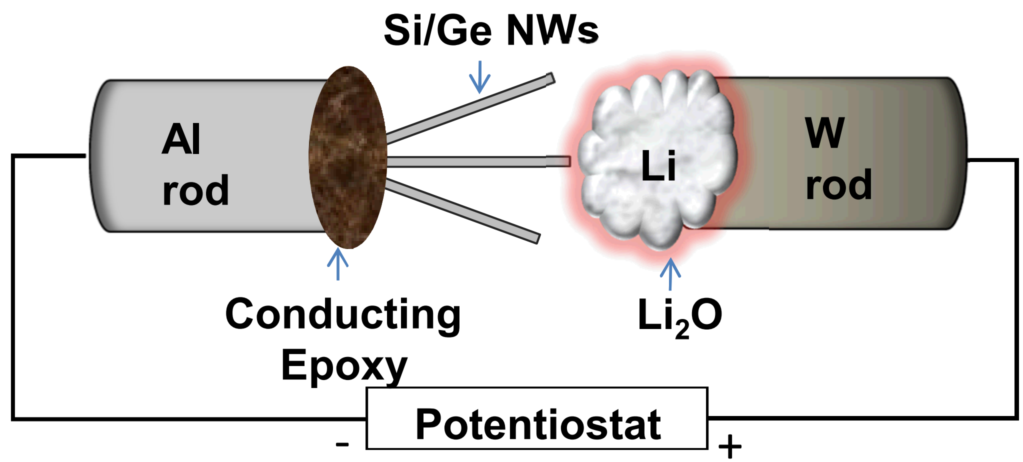


In the past two decades, it has been shown that ionic transport properties can be dominated by interfaces at the nanoscale, which provides the possibility to control the Li diffusion pathways and to modify the volume expansion direction by introducing heterojunctions (namely chemical and structural discontinuities).

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

Experimental setup of in-situ TEM battery test





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

Liu *et al.*, ***Adv. Energy Mater.*** 2, 722 (2012)

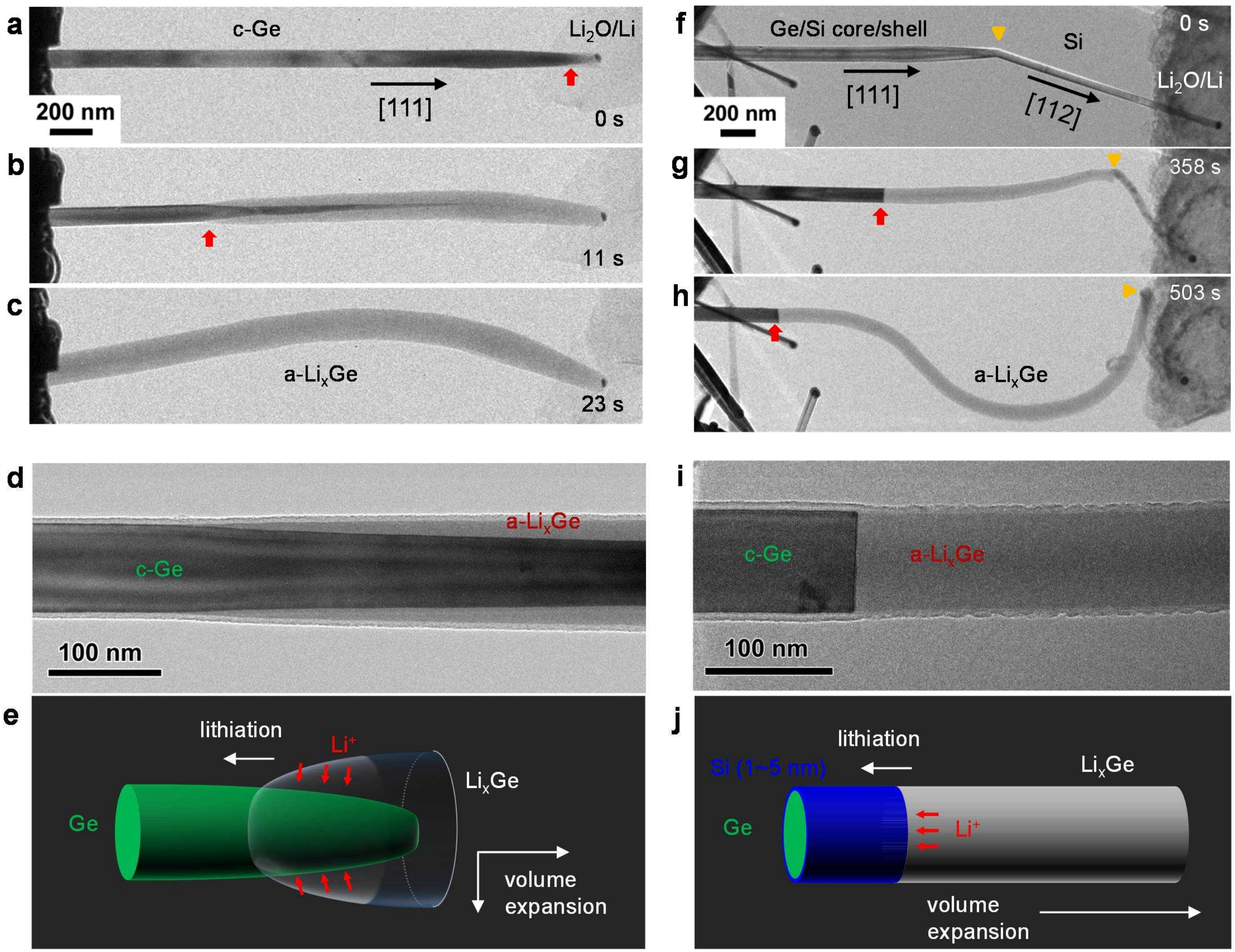
Introduce a vacuum-compatible electrolyte.

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 LiAlSiO.

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

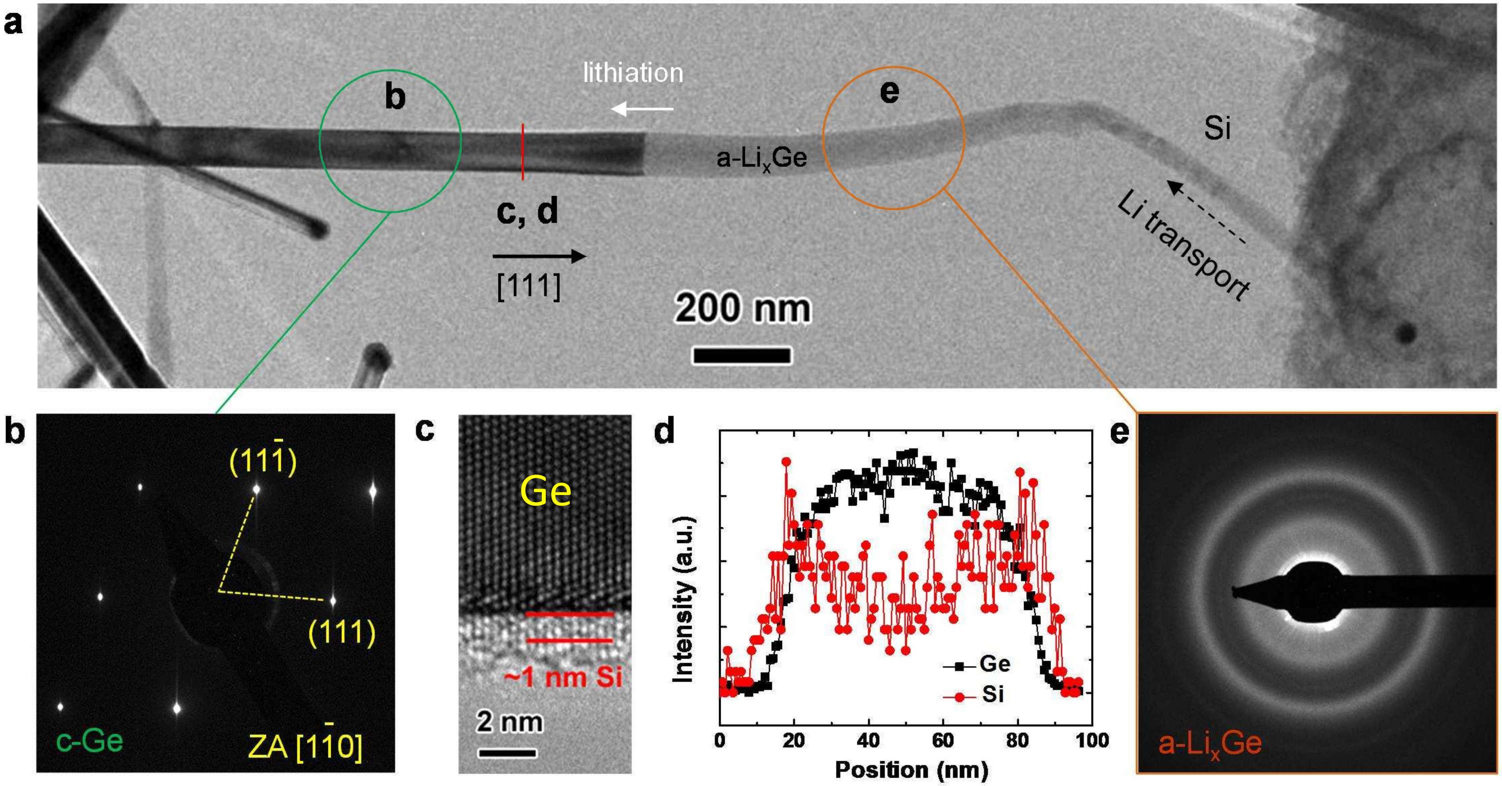
Distinct Lithiation Behavior in Hetero-nanowires

Pure Ge nanowire
Core-shell lithiation
Both swelling and elongation

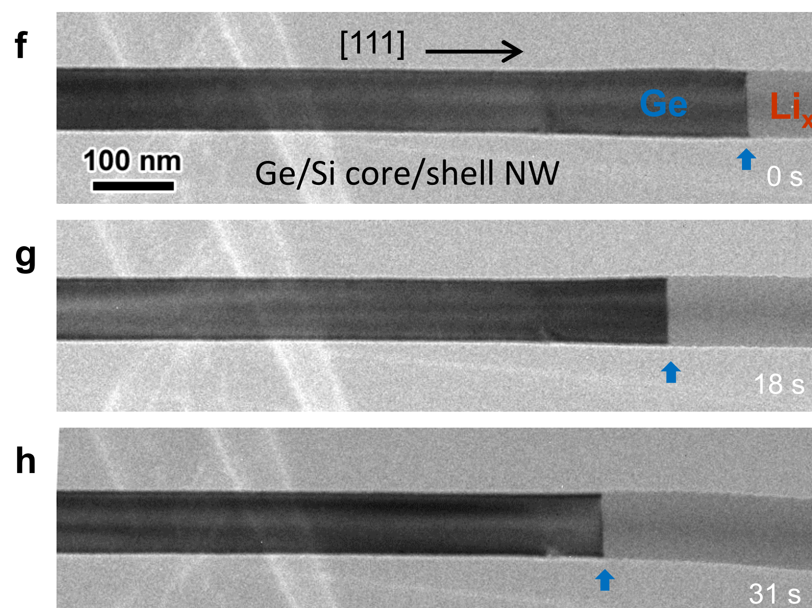


Ge/Si core/shell nanowire
Pure axial lithiation
Only elongation

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

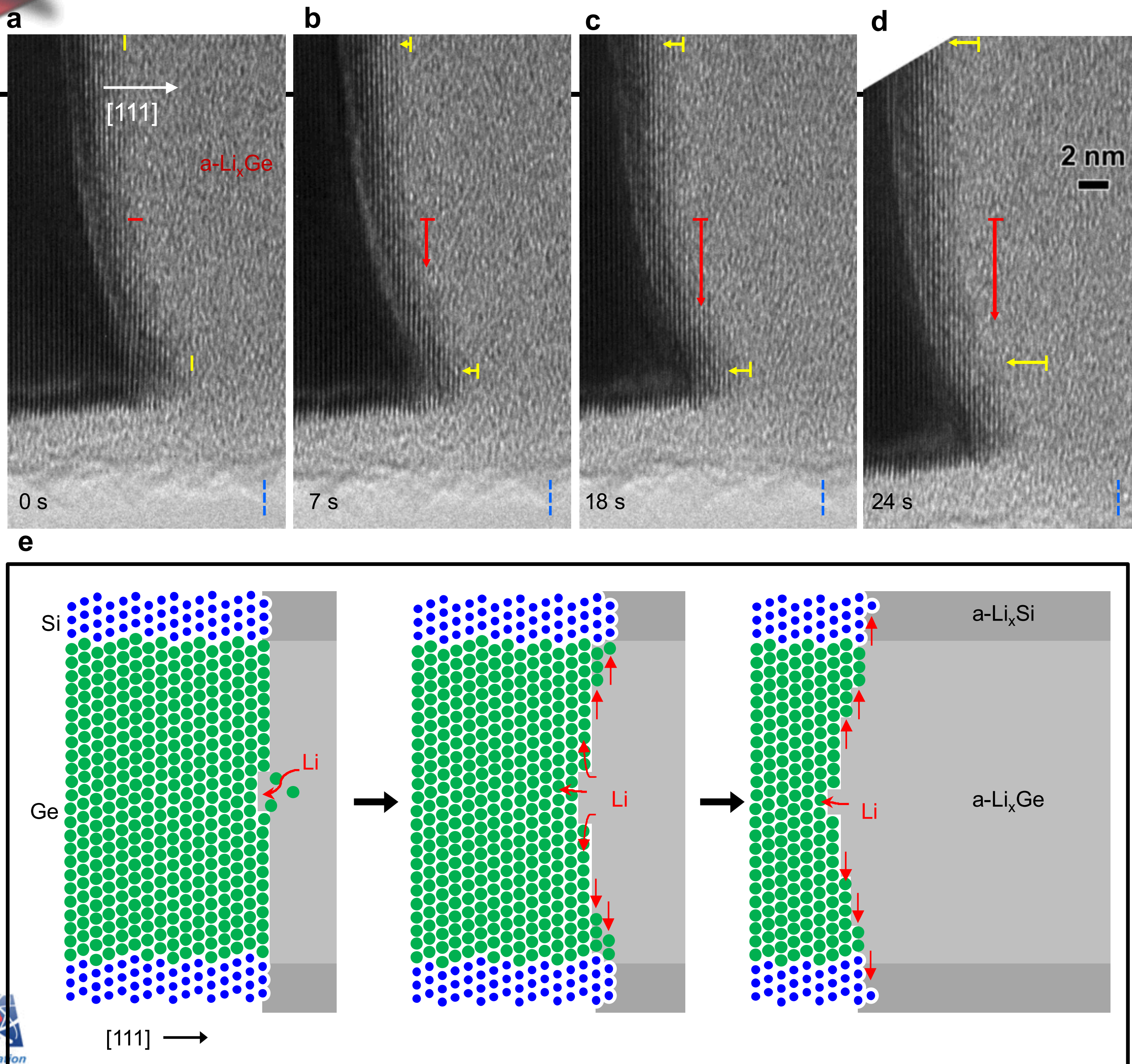


Introducing an ultrathin (down to ~1 nm) and epitaxially-grown Si surface layer can dramatically change the volume expansion direction!!!

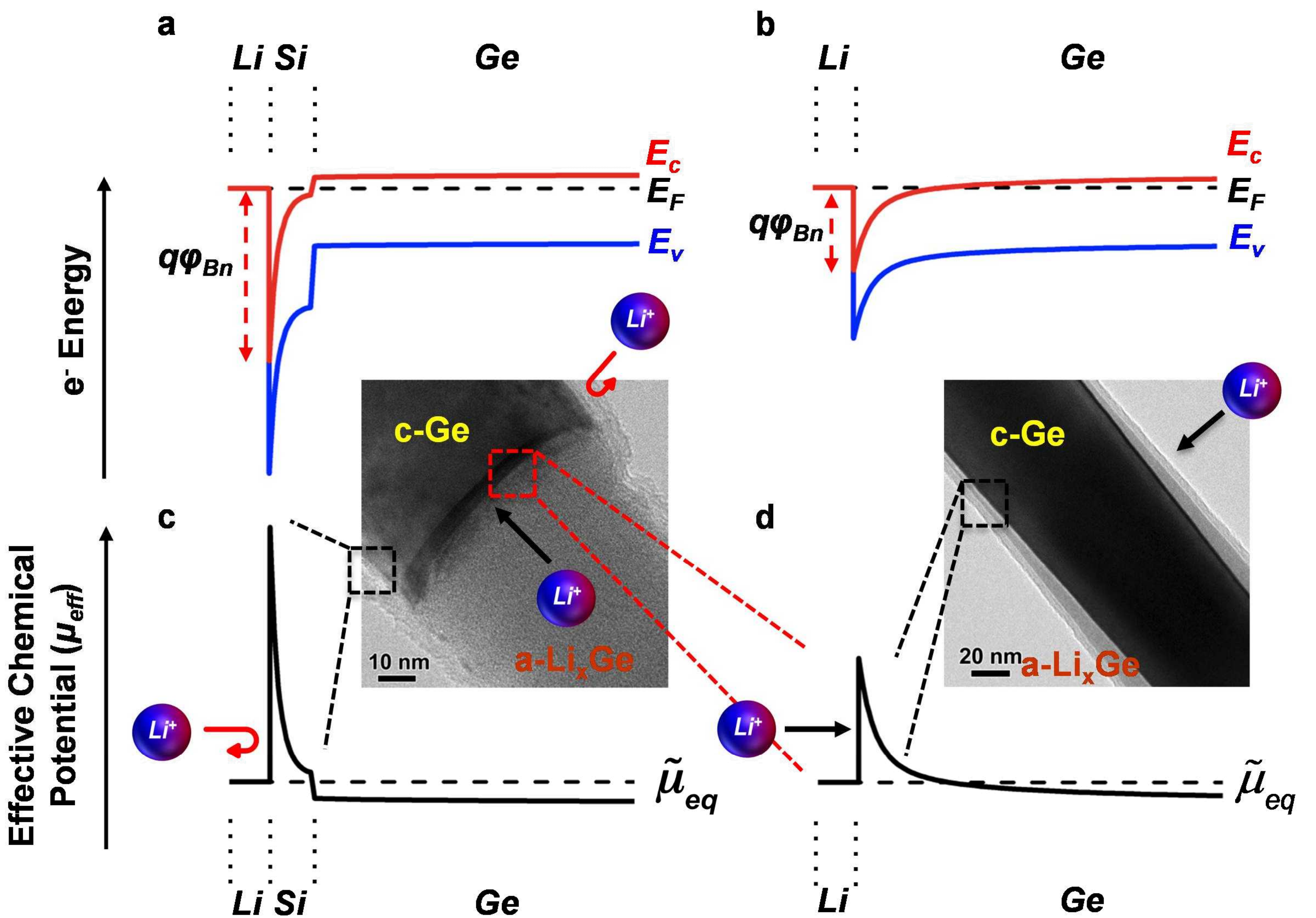


Y. Liu et al., ***Nano Letters***, 13, 4876 (2013)

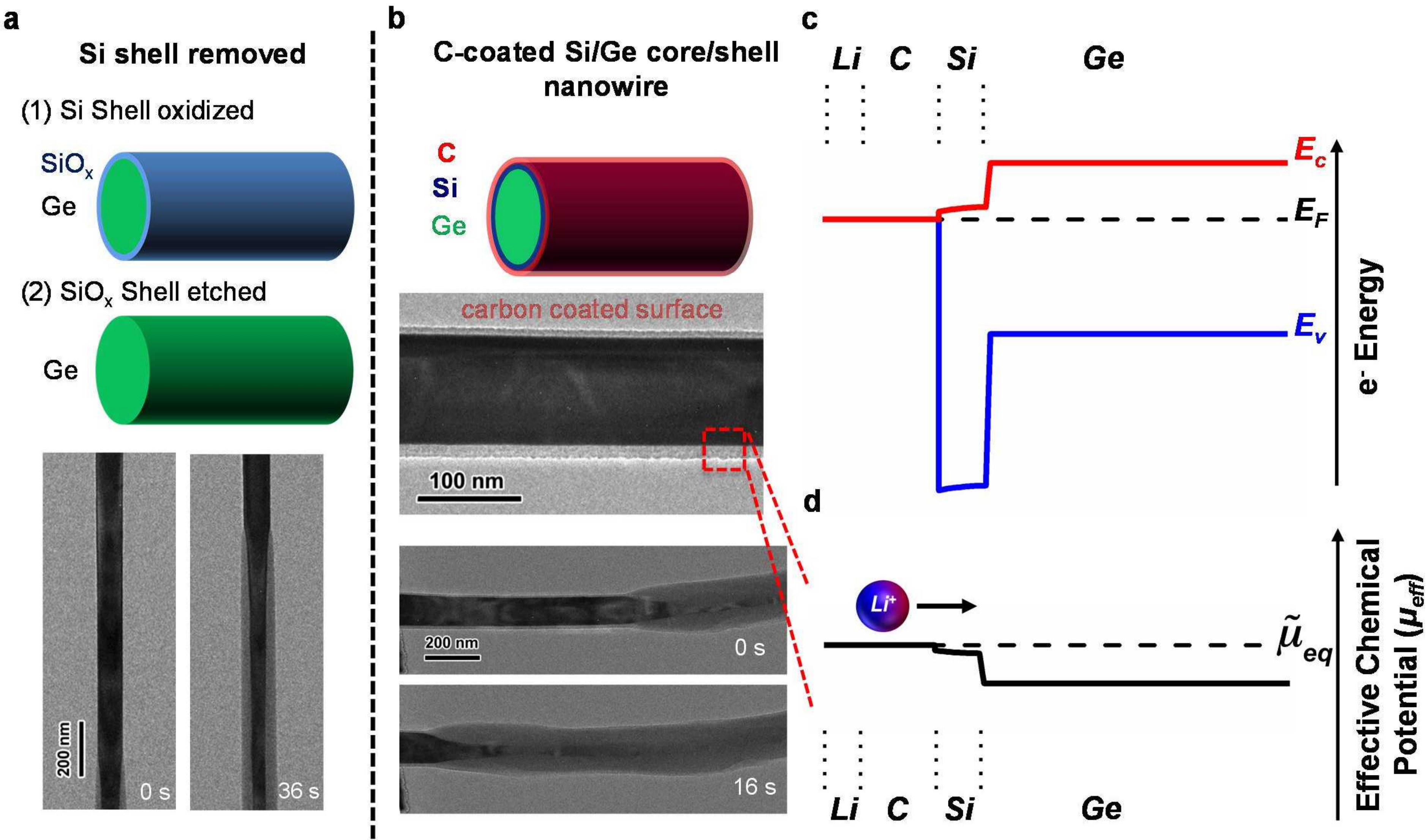
Atomic Layer by Layer Lithiation Reaction



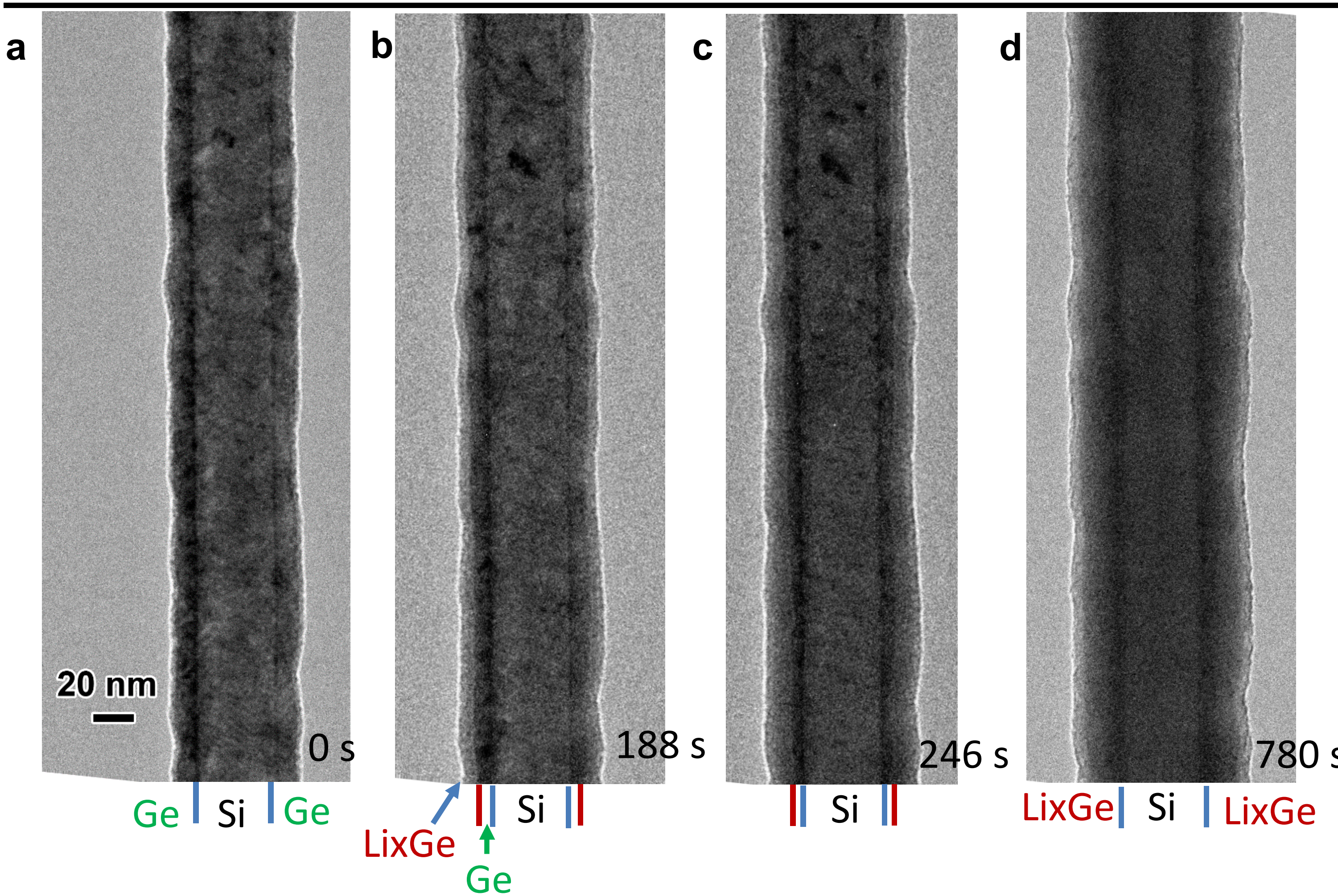
A larger chemical potential for Si surface than for Ge surface



Control experiments under different scenarios



Lithium ion transport in Si-core and Ge-shell nanowire



Si core-Ge shell nanowire shows radial lithiation, not axial lithiation! Si core was not lithiated, the lithium ion stopped at the Si/Ge interface.

Conclusions and Perspective

- Two different lithiation behaviors with sharp contrast, i.e., core/shell lithiation in pure Ge nanowires, in Si-core/Ge-shell nanowires *versus* axial lithiation in Ge/Si core/shell nanowires, were observed, which indicate two different Li ion transport mechanisms.
- The presence of the Si shell slows down the lithiation reaction at the surface and forms a chemical potential barrier that blocks Li ion diffusion through the shell, resulting in the axial lithiation of the Ge/Si core/shell nanowires.
- The first direct observation of the dramatic interfacial effect on ionic transport at the nanoscale.
- Also the first demonstration that the lithiation behavior of a nanostructure can be controlled by interface and band-gap engineering.
- This work highlights the potential importance of materials design of lithium ion battery electrodes, and proves a new and effective way to control the volume expansion of high-energy anode materials.

ACKNOWLEDGMENTS

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Thank you very much for your attention!

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