Designing Nanomaterials for Energy Conversion and Storage

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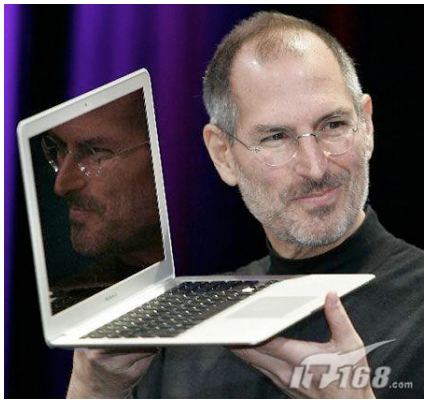
1. Nanowire Energy Storage

C. K. Chan and Y. Cui, *Nature Nanotechnology* 3, 31 (2008).
C. K. Chan and Y. Cui, *Nano Letters* 7, 490 (2007).
C. K. Chan and Y. Cui, *Nano Letters* 8, 307 (2007).
D.-K Kim, Y. Yang and Y. Cui, *Nano Letters* (ASAP,2008).
L. Cui and Y. Cui, *Nano Letter* (2009).
R. Ruffo, C. Wessels and Y. Cui *Electrochemistry Communication* (2009)

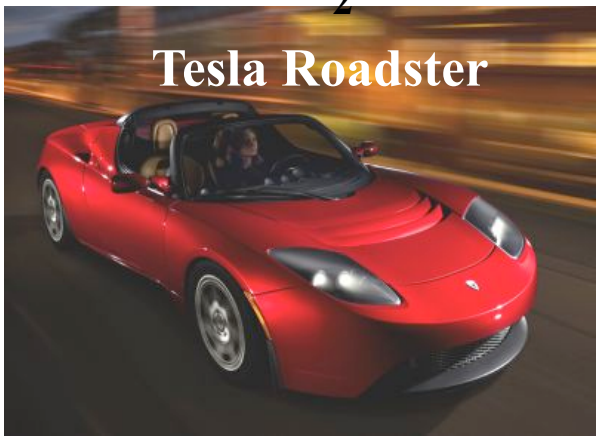
Energy Storage

Portable Electronics

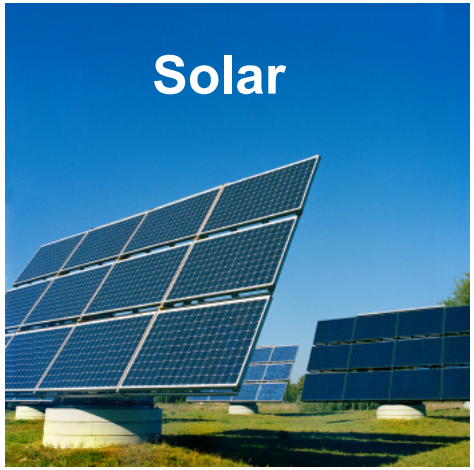


Hybrid, Plug-in, Electrical Vehicles

25-30% CO_2 emission

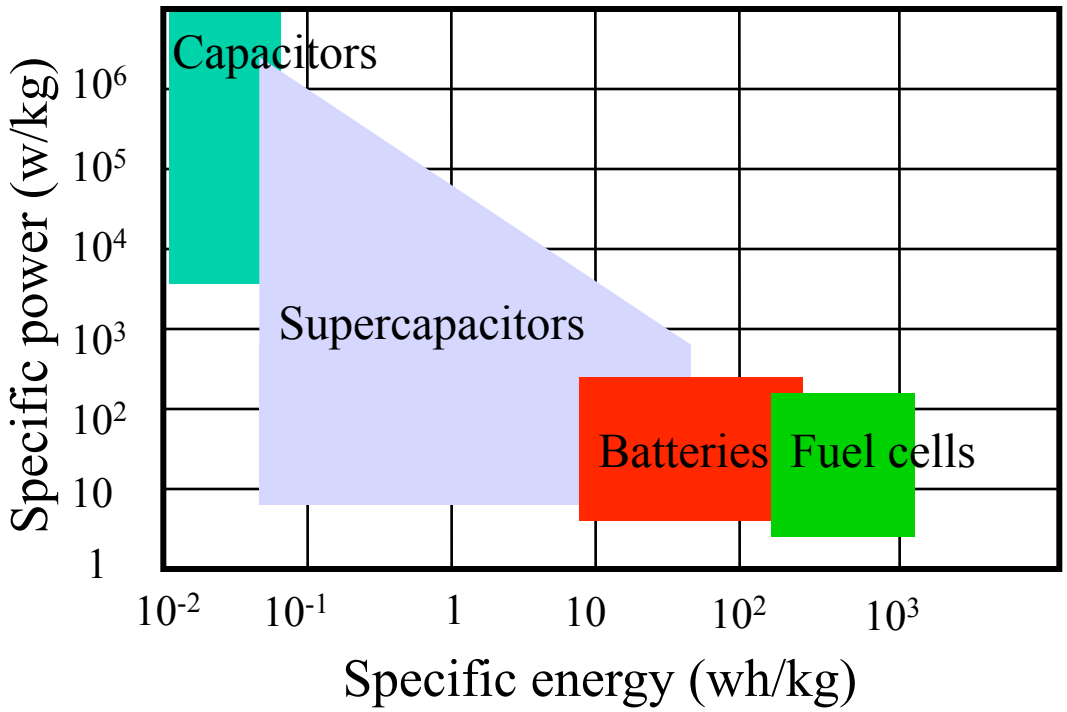


Renewable Energy and Electric Grid



Building Storage

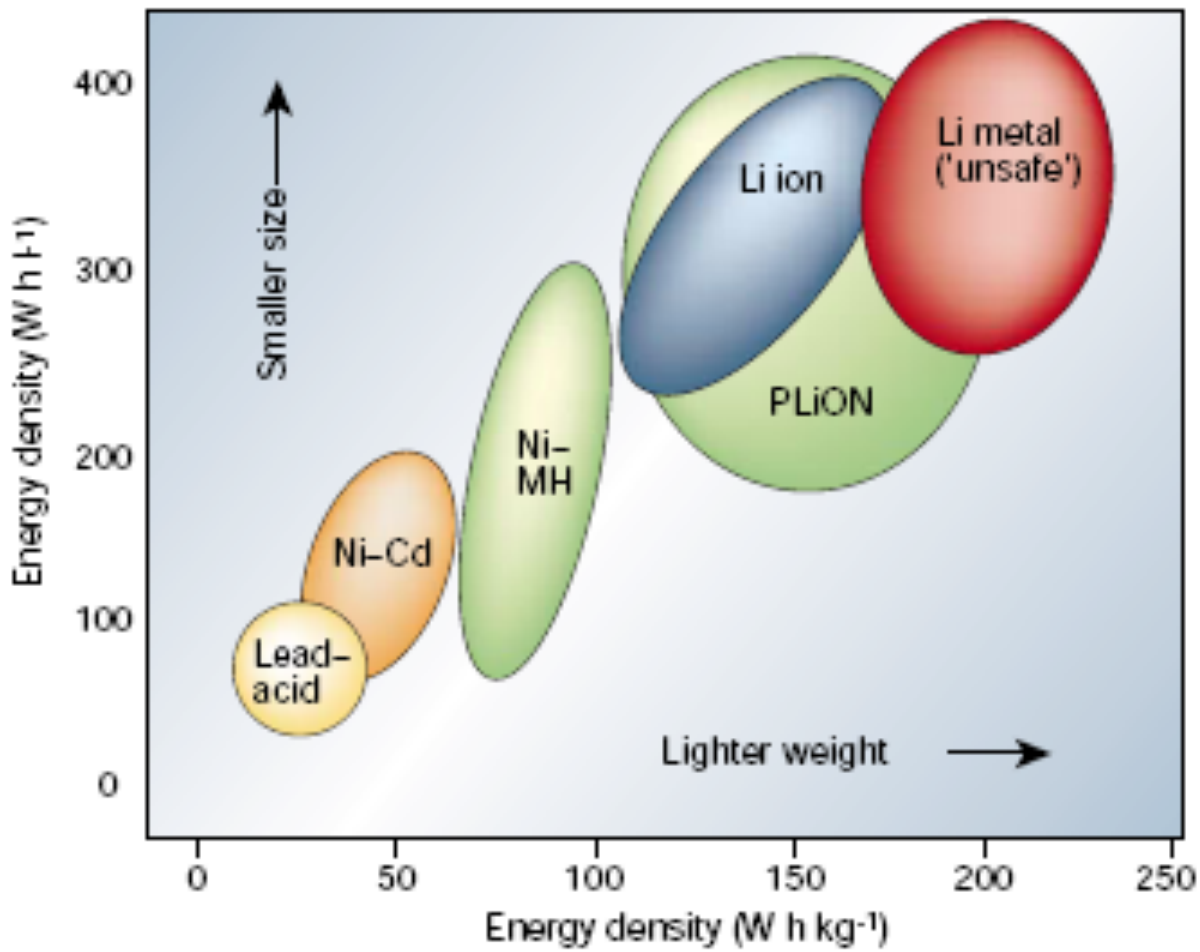
Comparison of Energy Storage Technologies



Important parameters:

- Energy density (Energy per weight or volume)
- Power density (Power per weight or volume)
- Cycle life and safety
- Cost

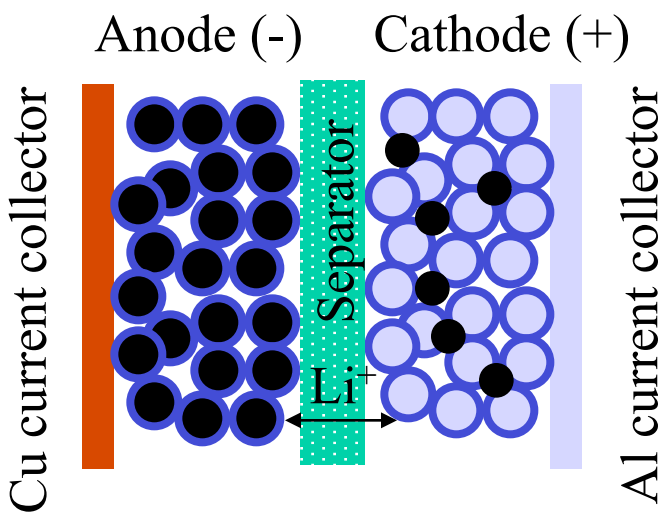
Why Li-Batteries?

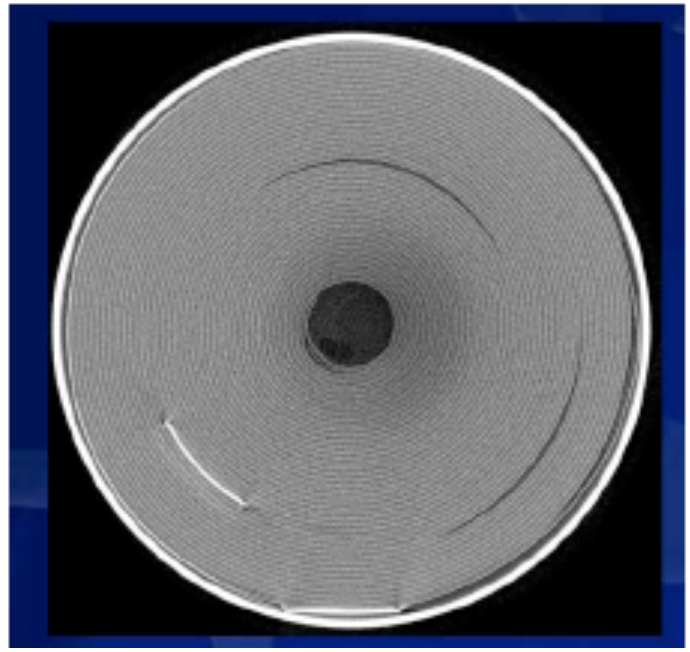


Lithium battery has the highest energy density among all the batteries.

J.-M. Tarascon & M. Armand. Nature. 414, 359 (2001).

Li Ion Battery 101





$$\textbf{Energy density} = \frac{\textbf{Voltage} \times \textbf{\# of movable Li ions in electrodes}}{\textbf{Total battery weight (or volume)}}$$

Electrode Materials in Existing Li Ion Batteries

Electrode materials determine the energy density.

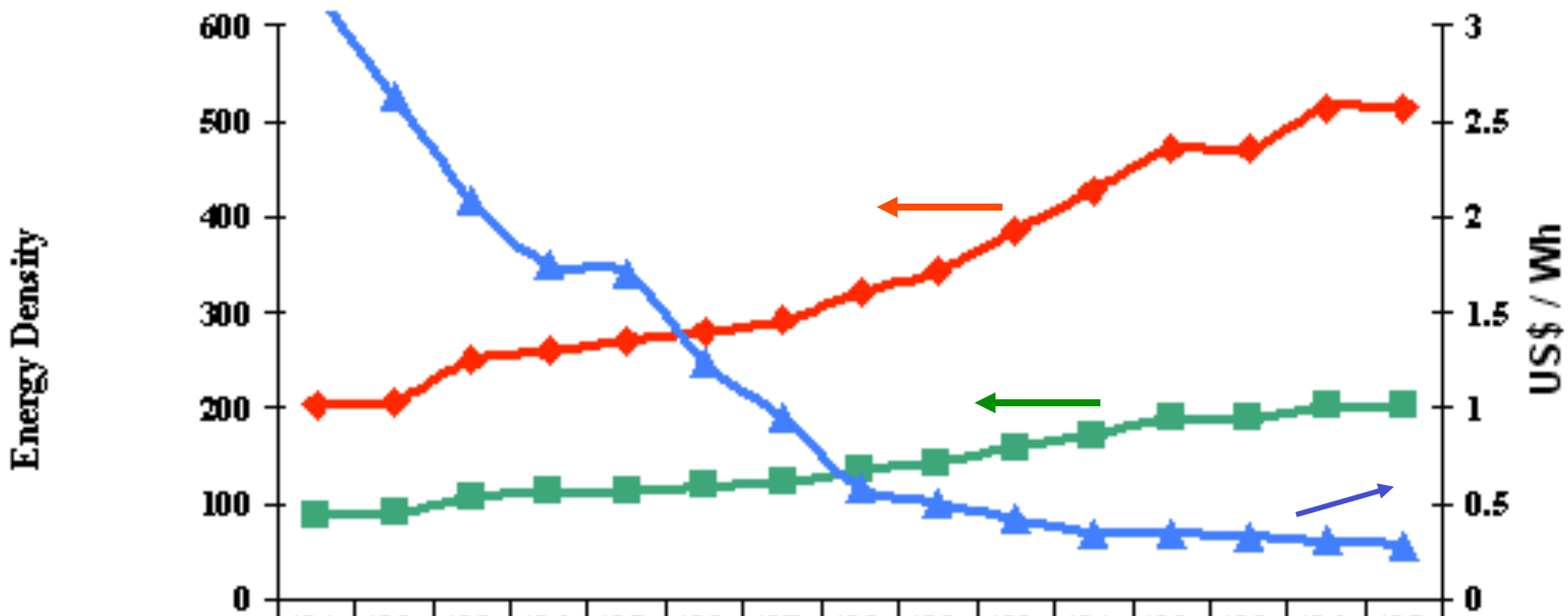
Anode materials

Graphite: 370 mAh/g

Cathode Materials

$LiCoO_2$	3.7 V	150 mAh/g	560 Wh/kg
$LiMn_2O_4$	4.0 V	140 mAh/g	560 Wh/kg
$LiFePO_4$	3.3 V	170 mAh/g	561 Wh/kg

Energy Density and Price of Li Ion Batteries



	'91	'92	'93	'94	'95	'96	'97	'98	'99	'00	'01	'02	'03	'04	'05
Wh/l	204	208	250	260	271	281	292	321	343	386	428	471	471	514	514
Wh/kg	88	90	108	113	114	119	123	135	143	159	172	189	189	202	202
US$/Wh	3.17	2.63	2.09	1.75	1.71	1.24	0.95	0.59	0.51	0.42	0.35	0.35	0.33	0.31	0.28

- Improvement only 8% per year, saturating now.
- New electrode materials are needed.

Two Types of Electrode Materials

Existing Technology:
Intercalation Materials

Advantages
- Li Intercalation mechanism
- Small structure change
- Fast Li moving rate

Disadvantages
-Small capacity

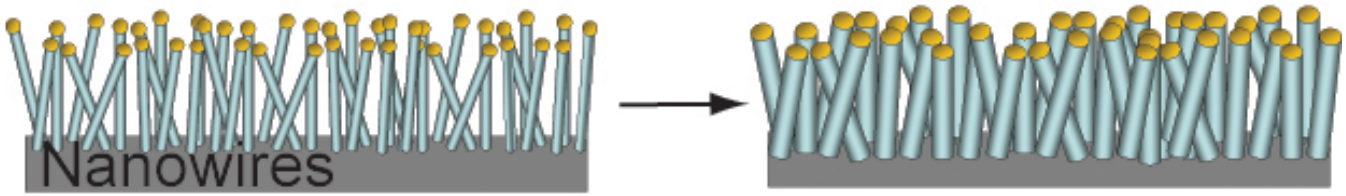
Future Technology:
New Materials

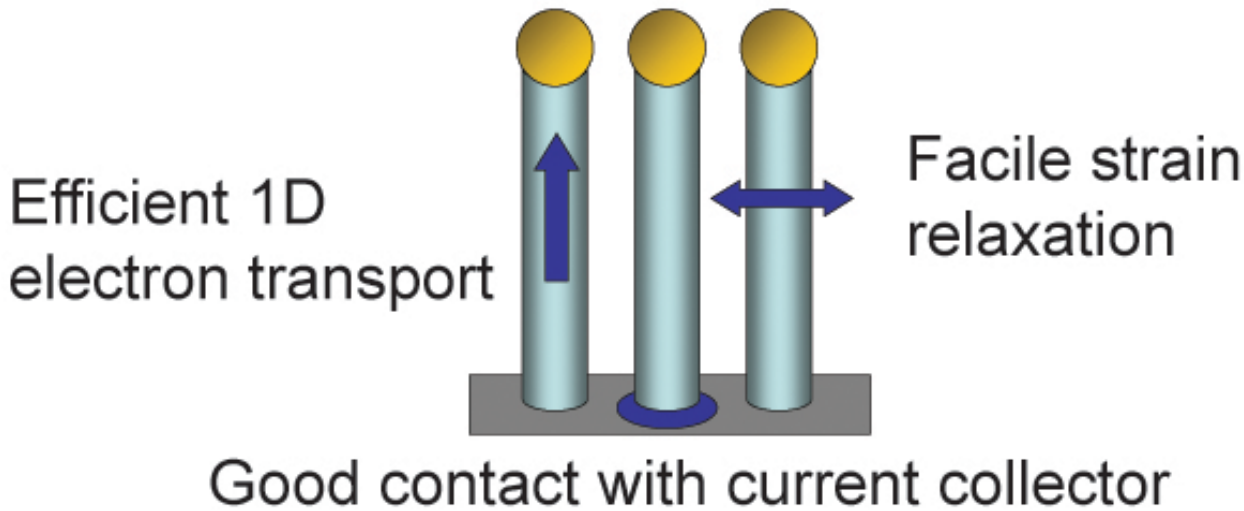
Advantages
- Li displacement/alloying reaction
- Large capacity

Disadvantages
- Large structure change
- Slower Li moving rate

Our Nanowire Battery Approach

Li insertion





Example: Si as Anode Materials

C anode: the existing anode technology.

$$C_6 \longleftrightarrow LiC_6$$

Theoretical capacity: 372 mA h/g
Less than 10% volume expansion.

Si anode

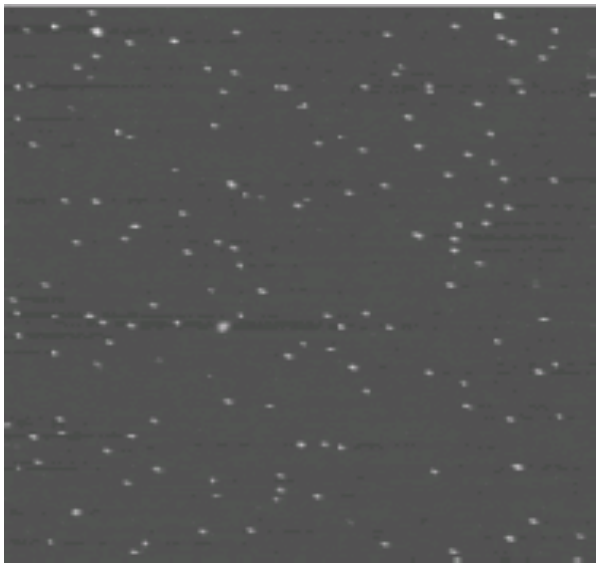
$$Si \longleftrightarrow Li_{4.4}Si$$

Theoretical capacity: 4200 mA h/g

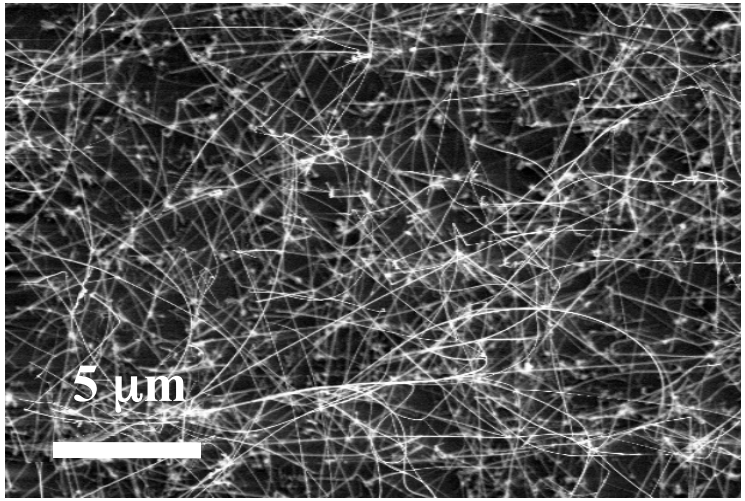
Problem for Si: 400% volume expansion.

Vapor-Liquid-Solid (VLS) Growth of Si Nanowires

Au Nanoparticles:
Scanning Electron Micrograph

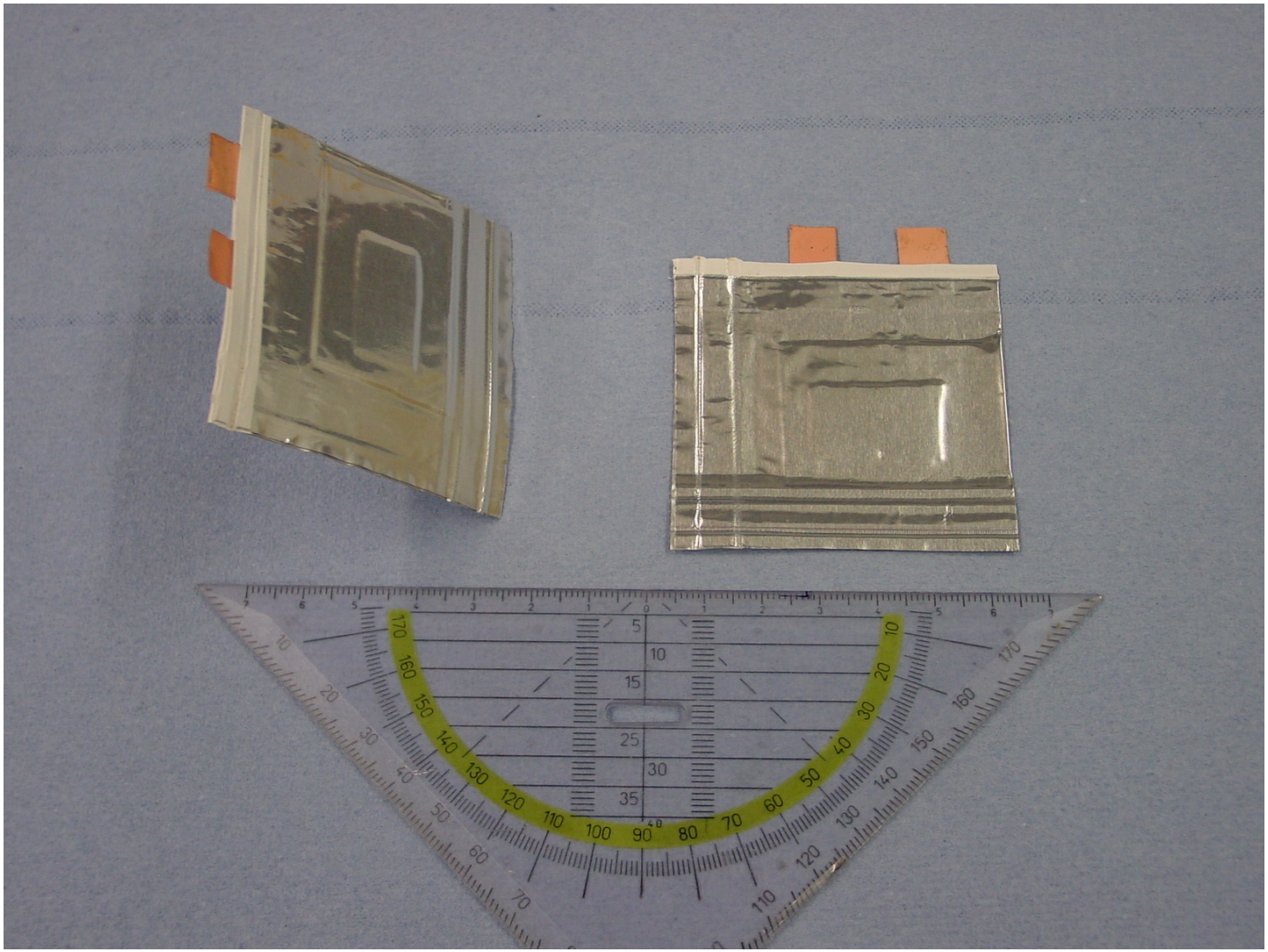


Si Nanowires
Scanning Electron Micrograph



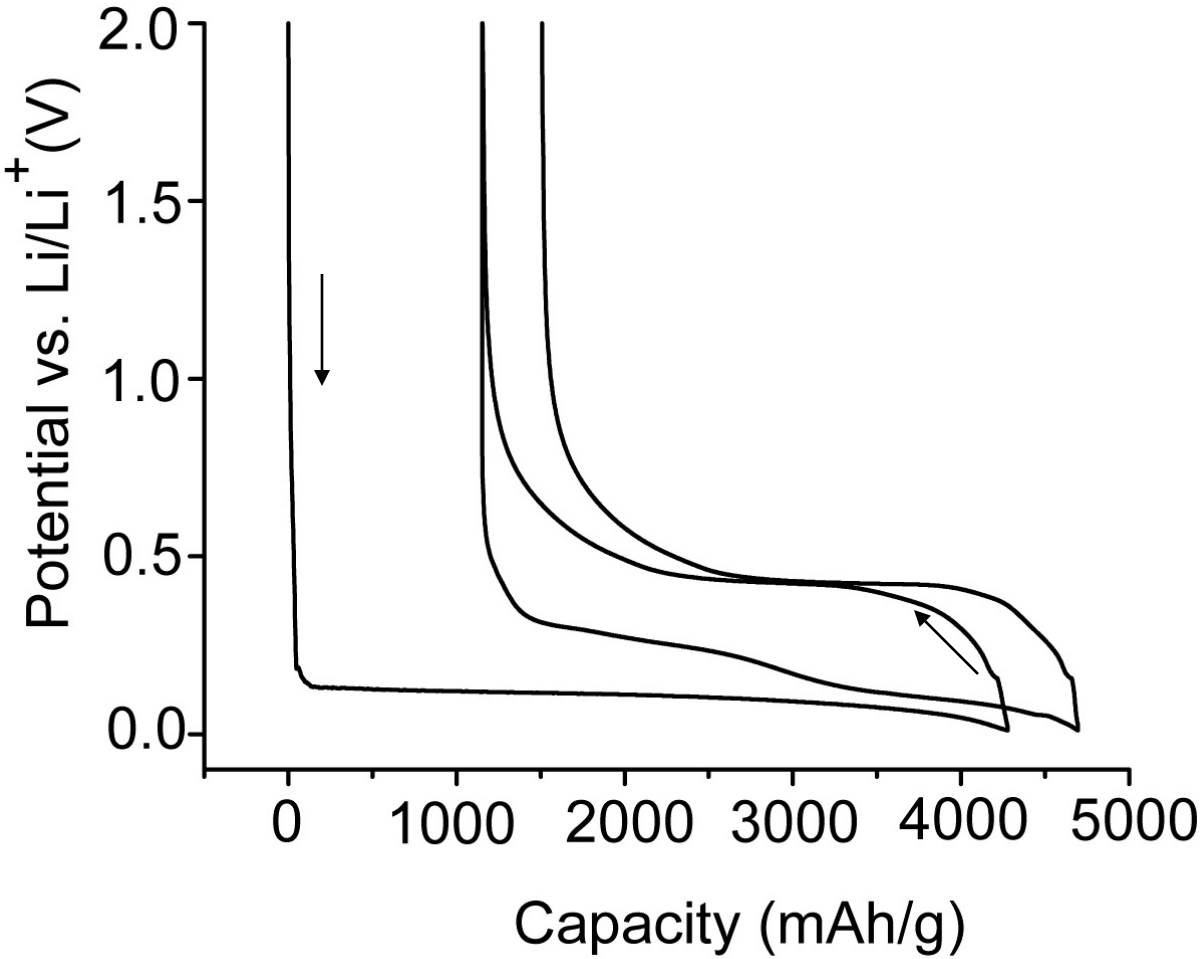
Nanowire Battery Testing

Pouch Cell

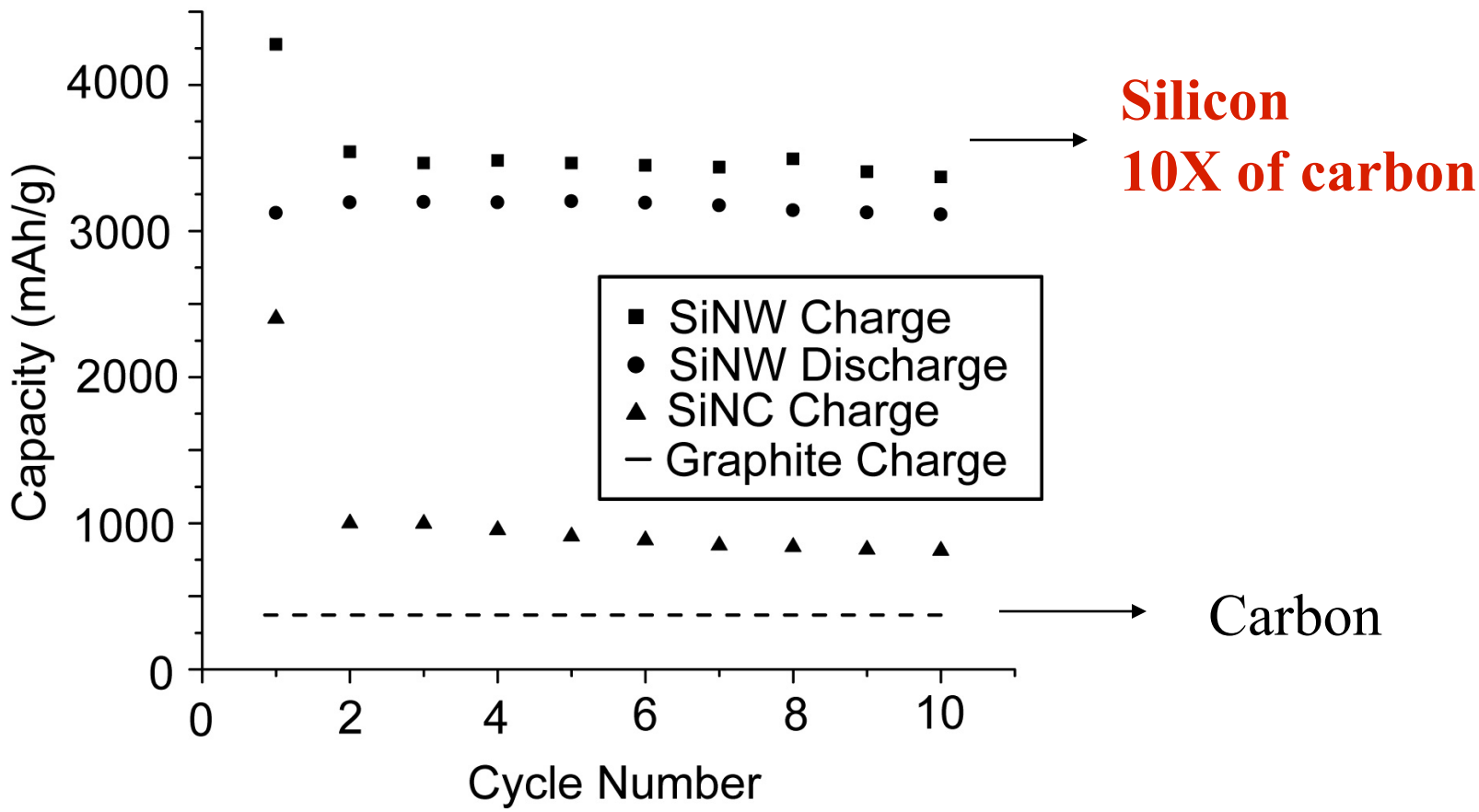


Ultrahigh Capacity Si Nanowire Anodes

At C/20 rate



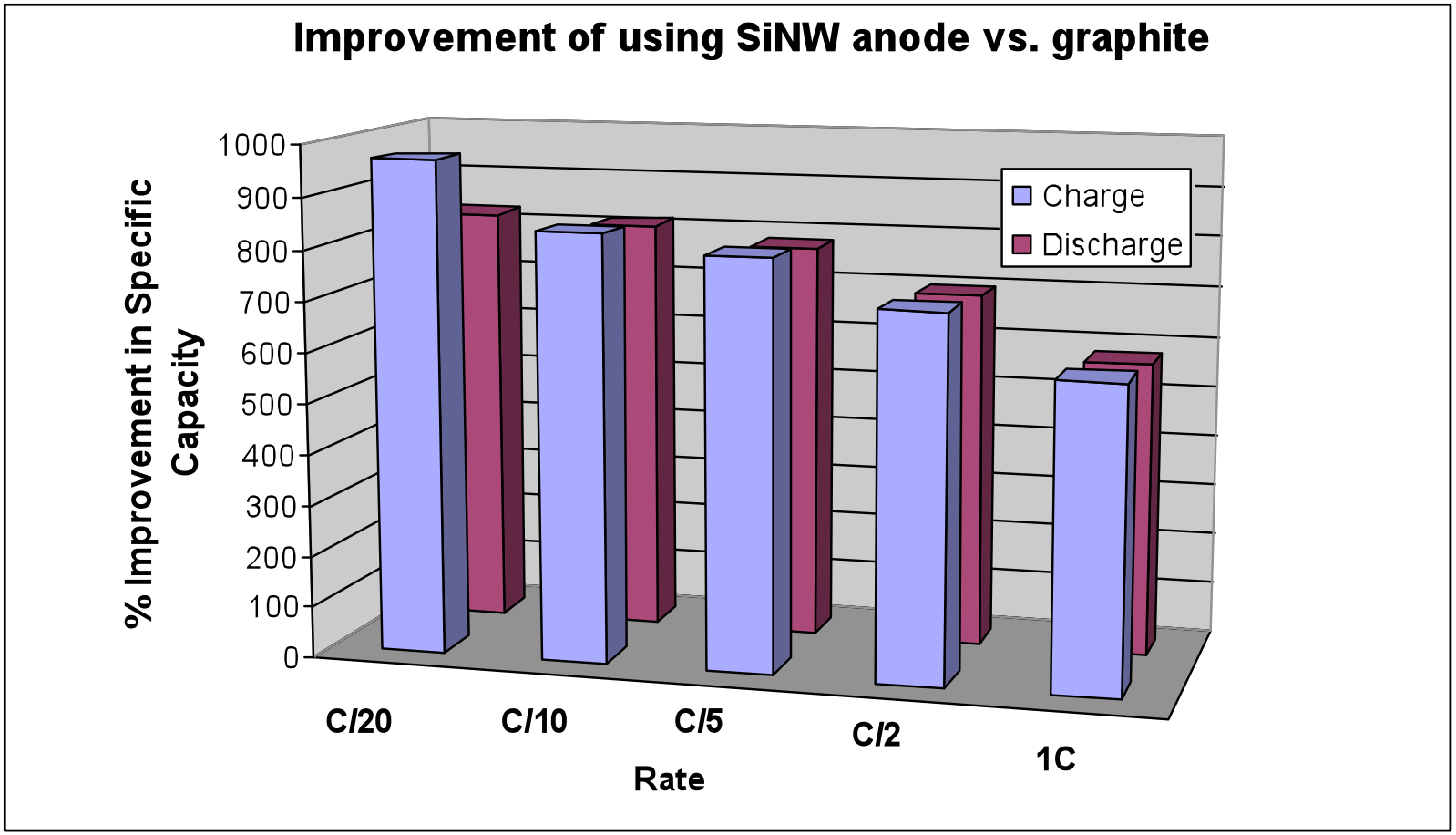
Ultrahigh Capacity Si Nanowire Anodes



- Si nanowires show 10 times higher capacity than the existing carbon anodes.
- Si nanowires show much better cycle life than the bulk, particle and thin film.

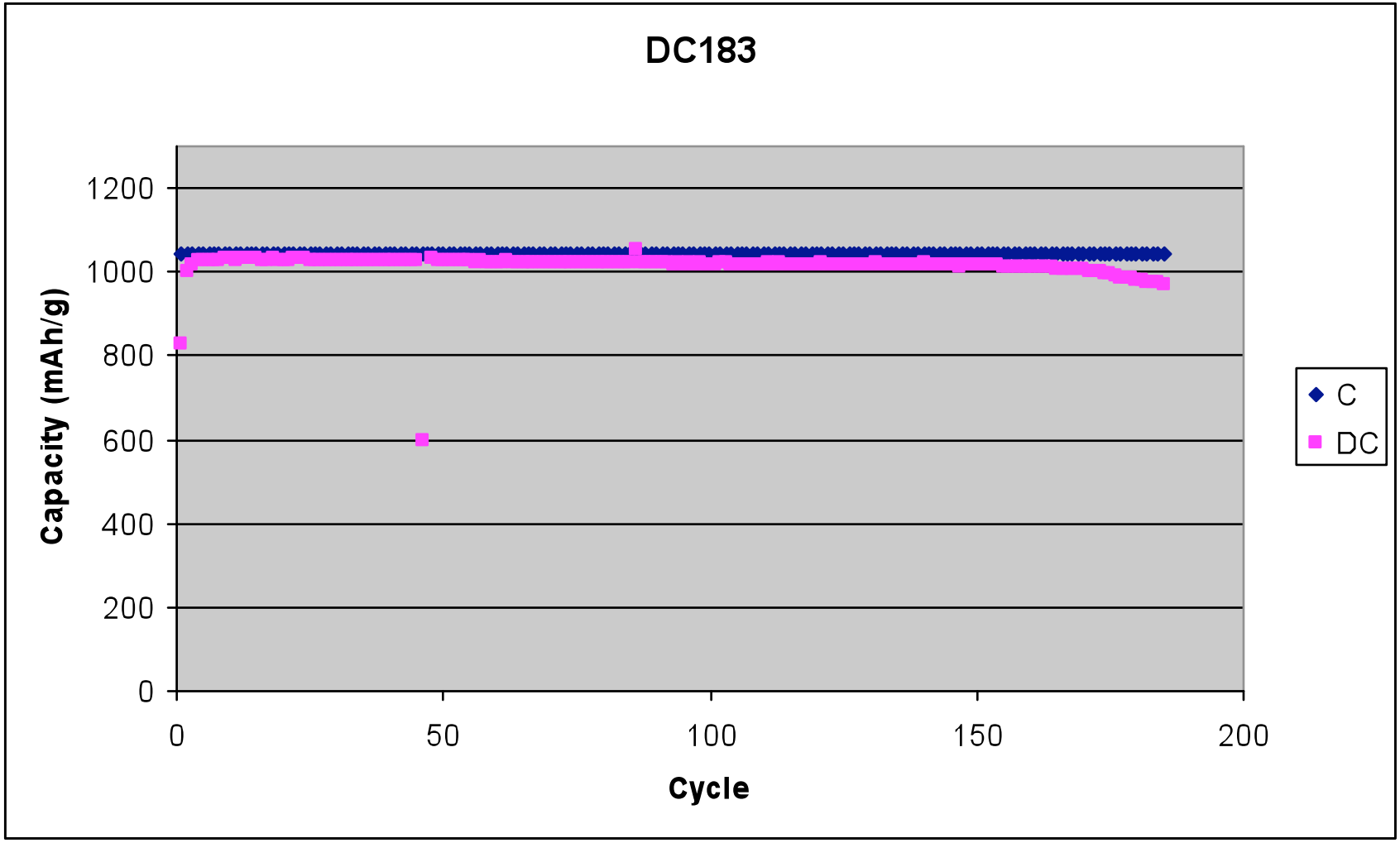
C. K. Chan, R. Huggins, Y. Cui and co-workers *Nature Nanotechnology* 3, 31 (2008)

Good Power Performance



C. K. Chan, R. Huggins, Y. Cui and co-workers *Nature Nanotechnology* 3, 31 (2008)

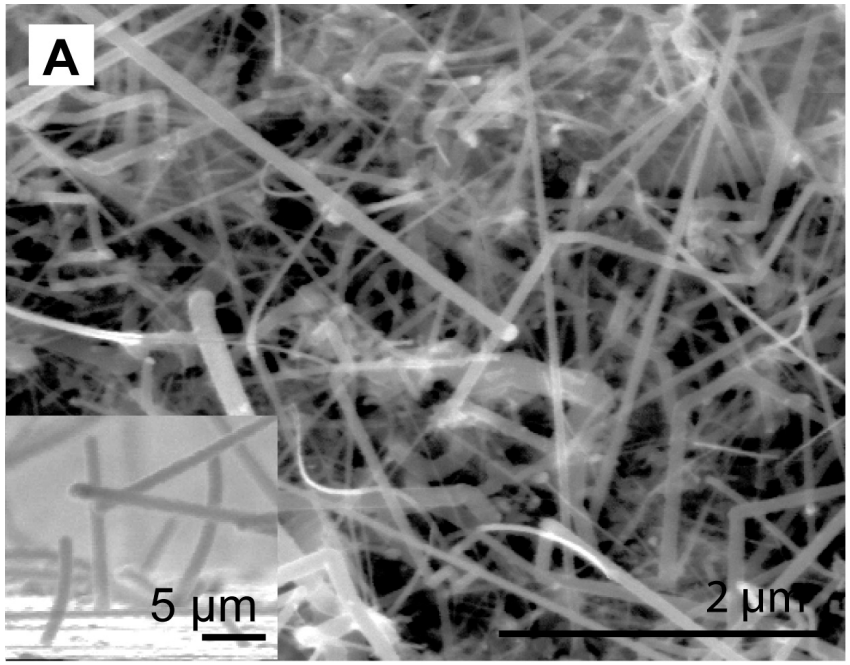
Cyclic Test Data @ C/5 rate



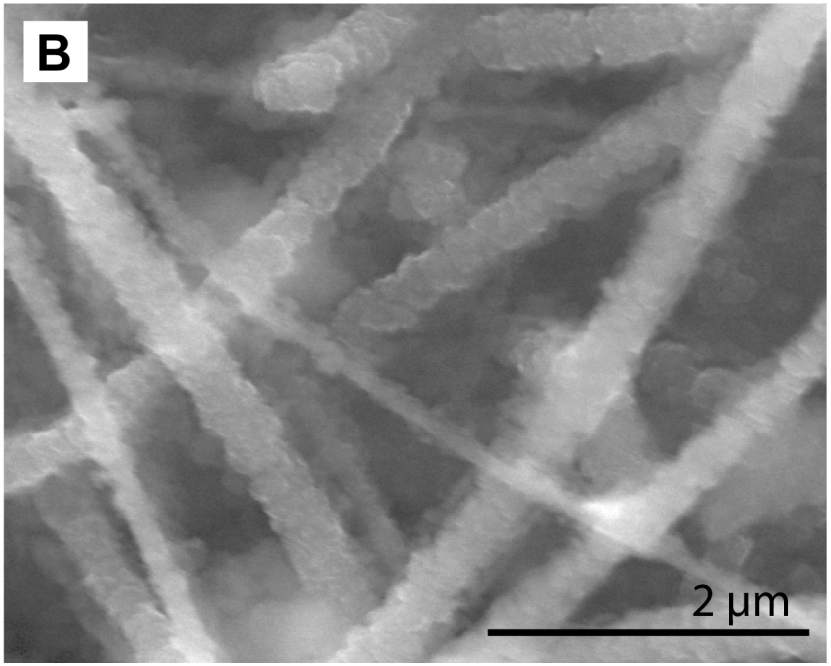
95% of capacity is retained after 185 cycles.

Diameter Change of Si Nanowire Anodes

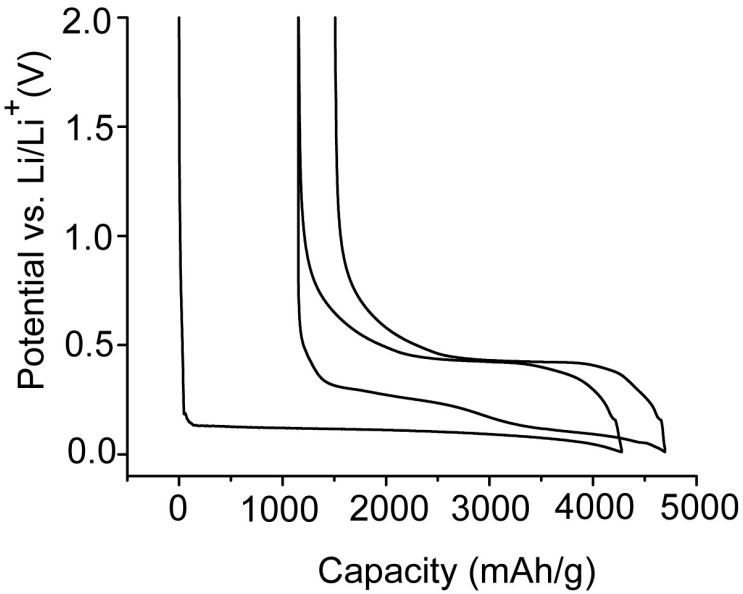
Before



After

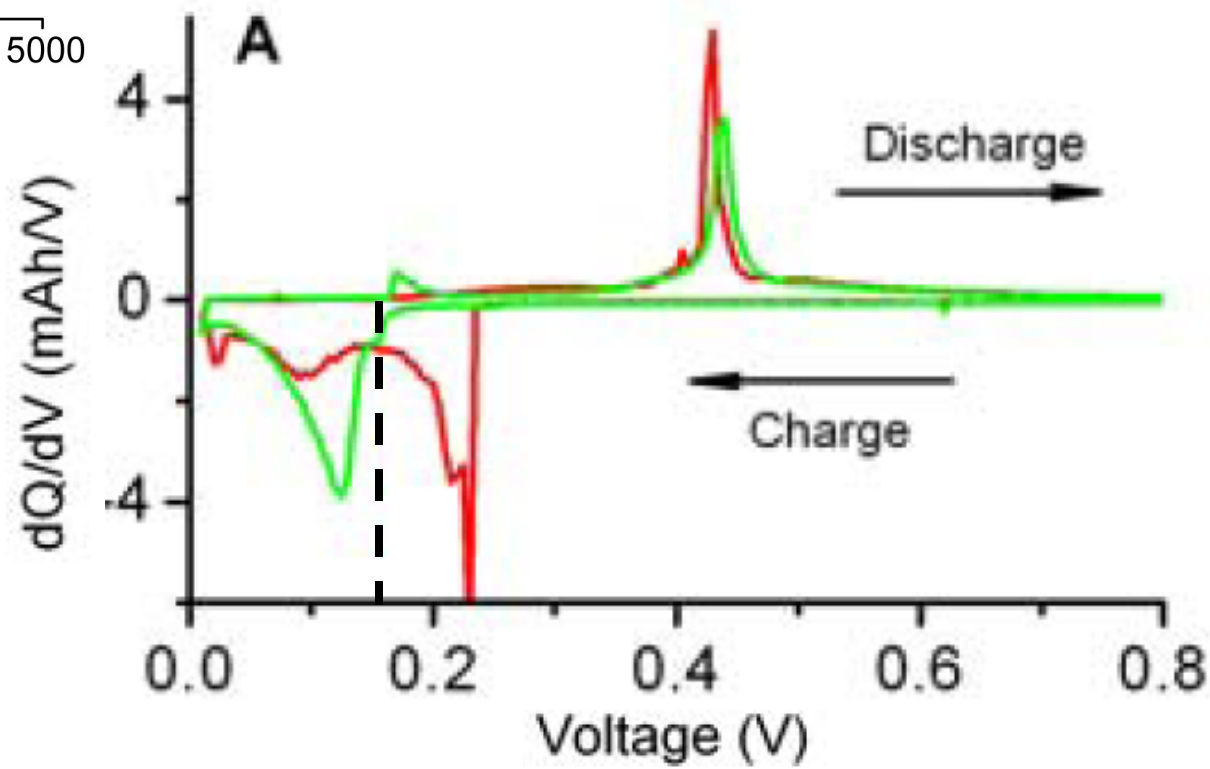


Electrochemical Potential Spectroscopy

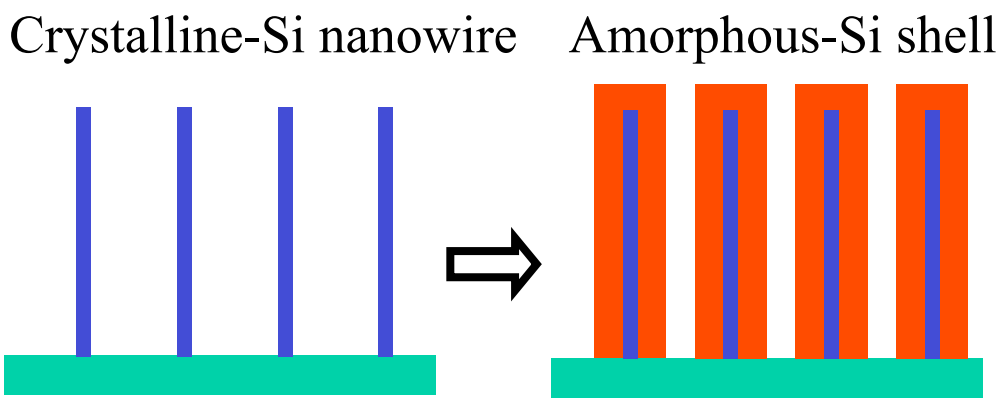


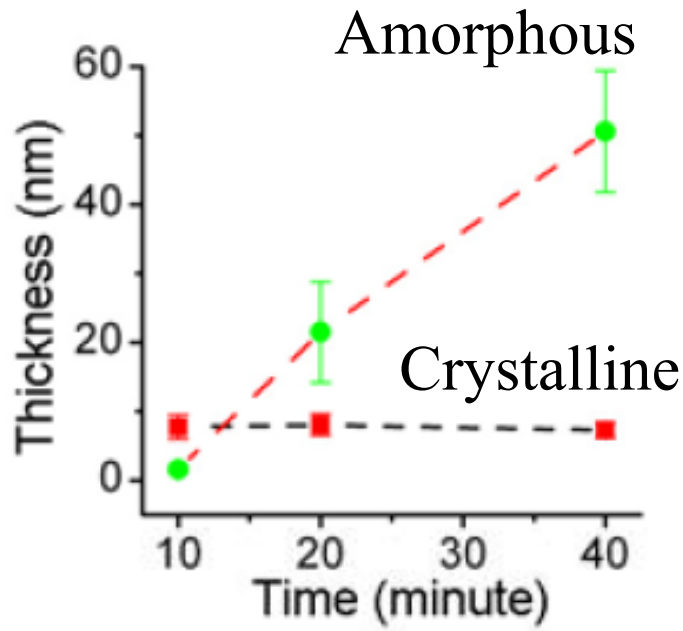
Crystalline

Crystalline-amorphous



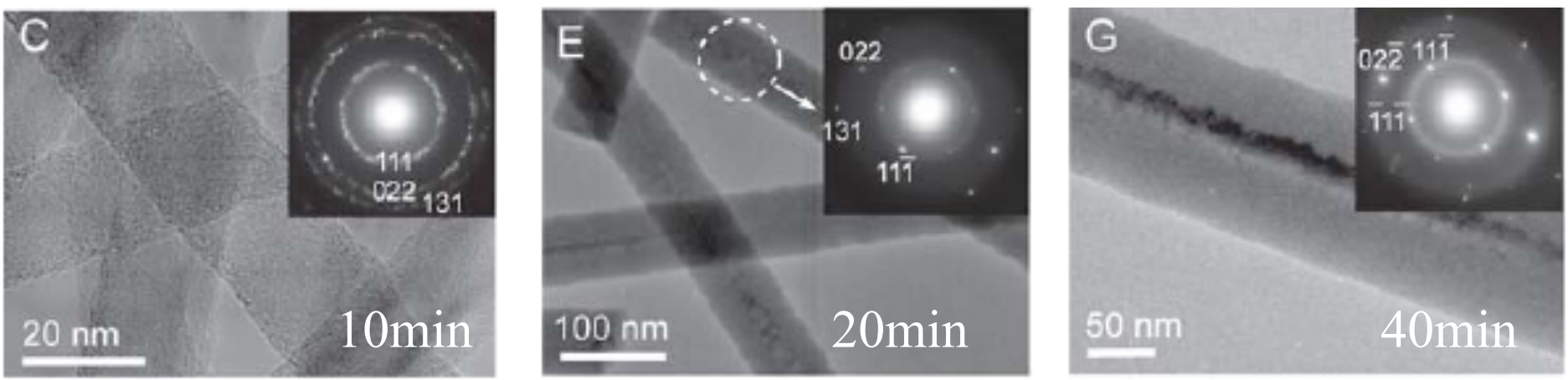
Crystalline-Amorphous Core-Shell Si Nanowire





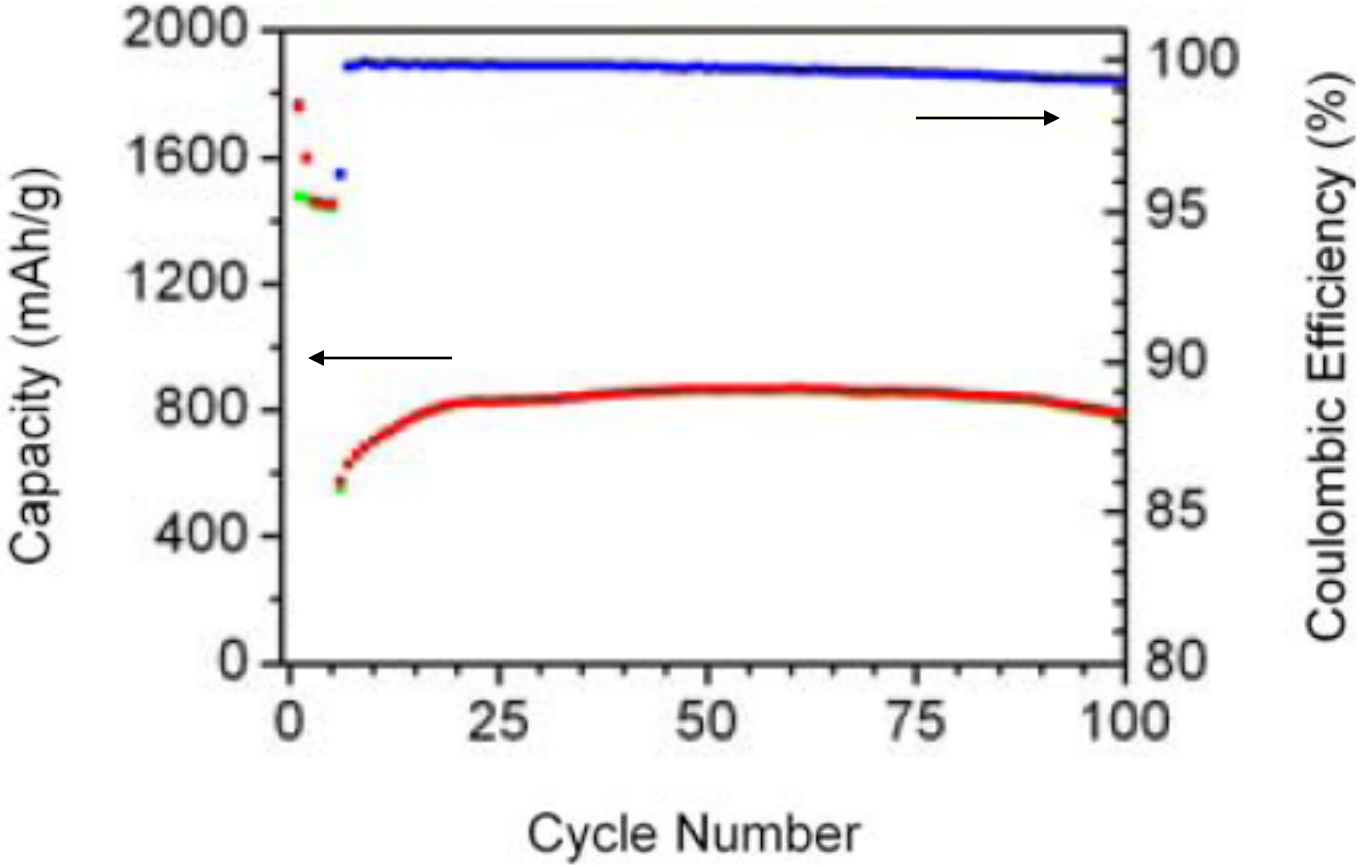
Crystalline-Si

Crystalline-amorphous core-shell Si



L. Cui and Y. Cui, *Nano Letters* (2009).

Core-Shell Si Nanowire: 7 min Charge/Discharge



Summary of Si Nanowire Anodes

- **Mechanical breaking problem is solved using Si nanowires.**

- **Only metallurgical grade Si (not solar grade) is needed. There is plenty of Si available.**

- **Mature semiconductor processing can be used for manufacturing.**

- **Safety: Si is safer.**

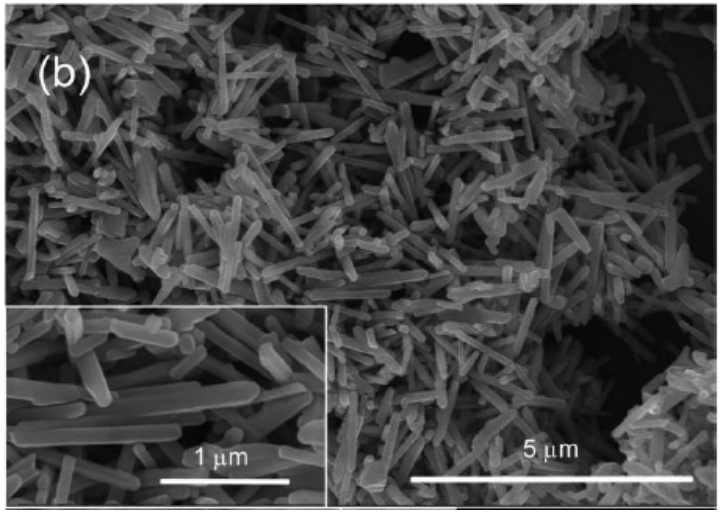
- Si has a little bit higher charging potential (0.1-.0.2V) than C (~0V). This prevents lithium dendrite formation.

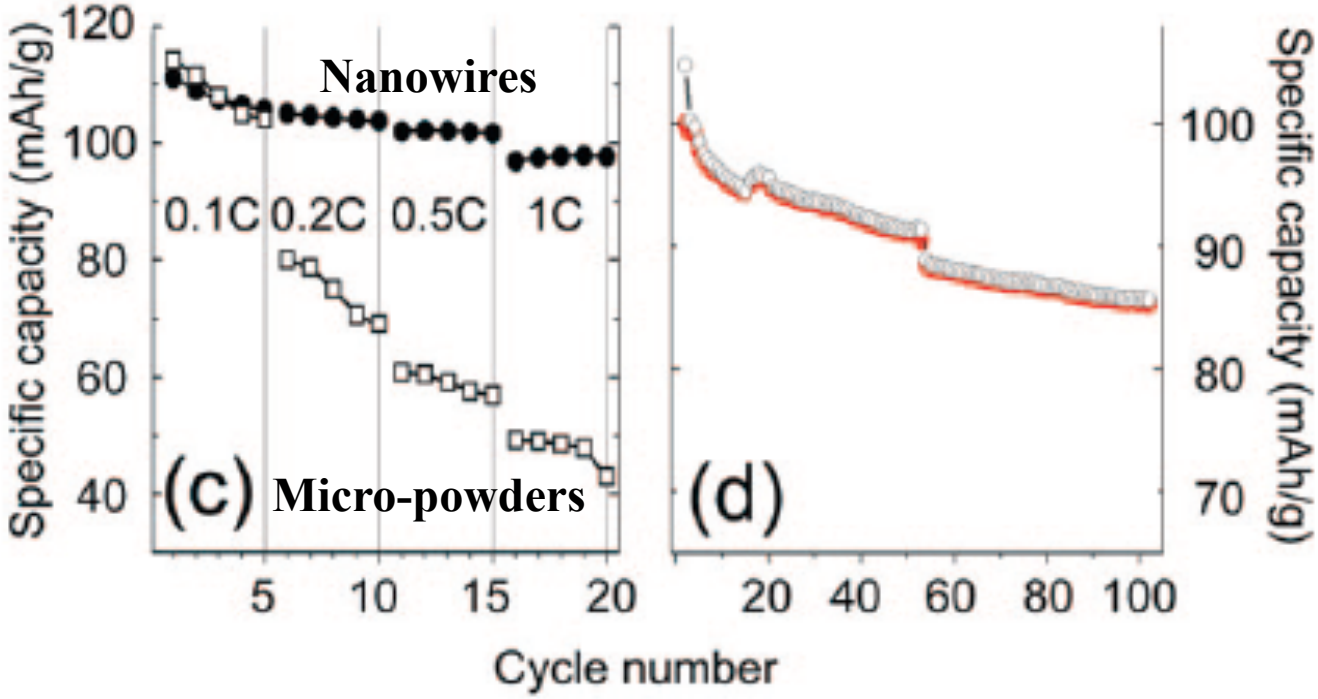
-When Si burns, it produces sand. When C burns, it produces CO_2 gas.

New Cathode Nanowire Materials

LiMn2O4 nanowires perform better.

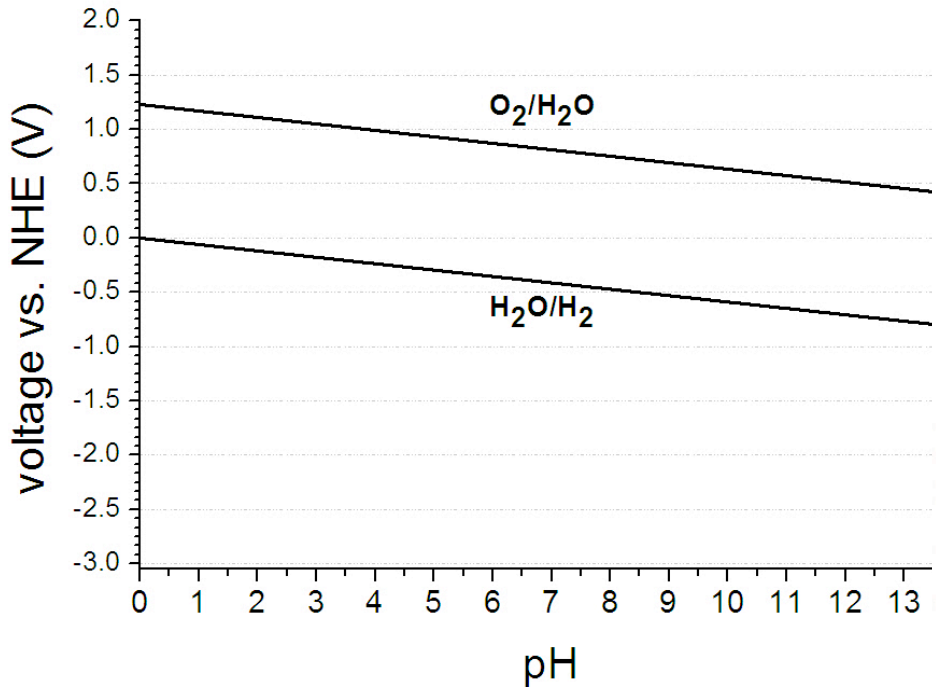
D. Kim, Y. Yang, Y. Cui, Nano Letter (2008)

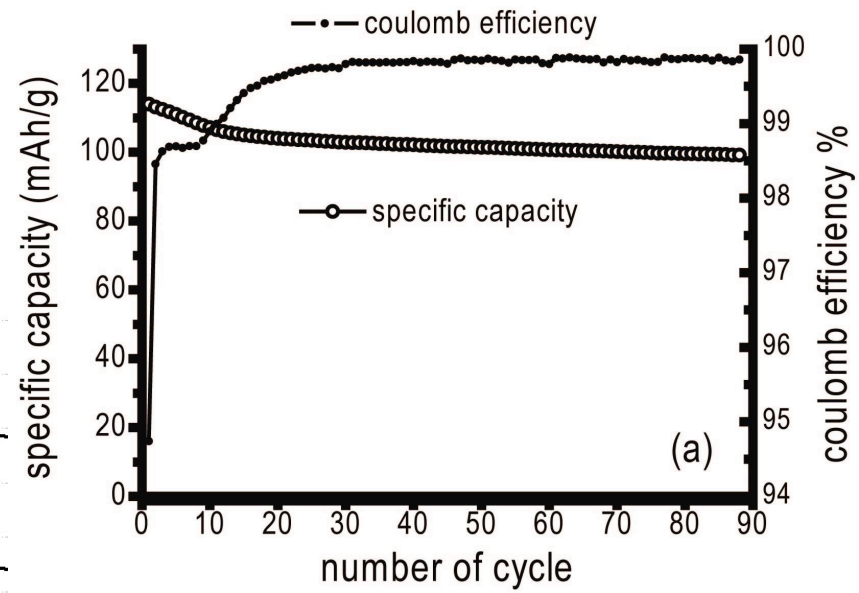


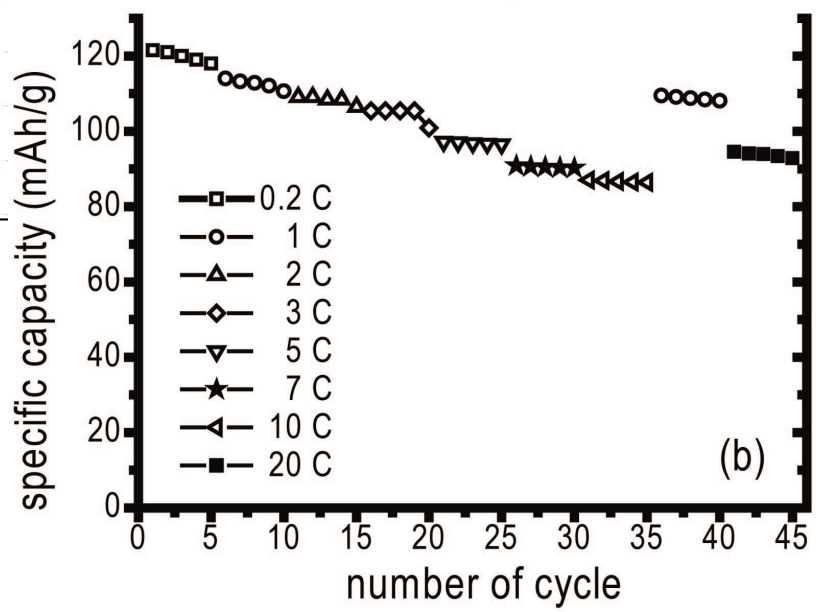


Aqueous Lithium Ion Batteries

- Superhigh power
- Safe batteries



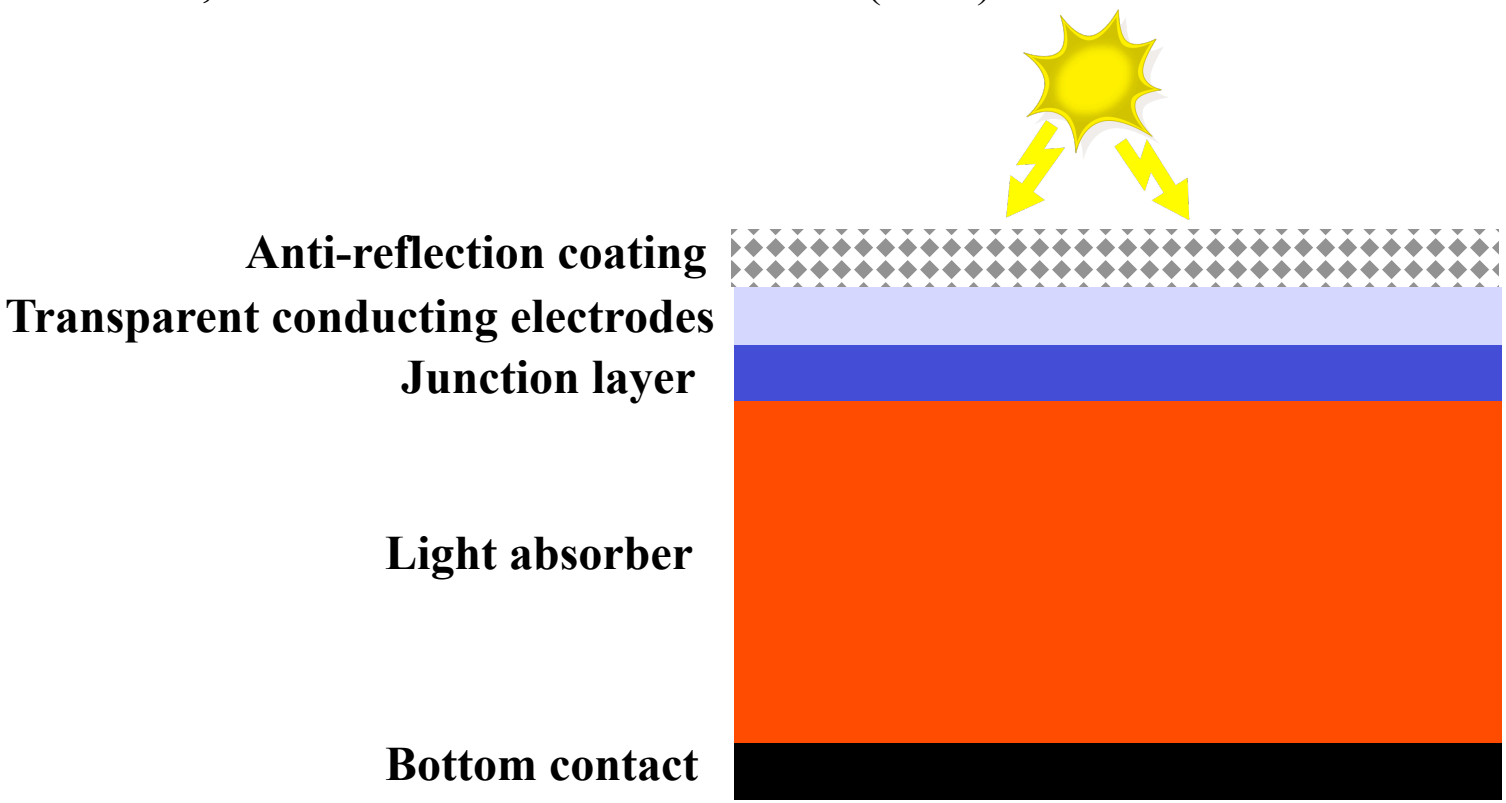




R. Ruffo, Y. Cui *Electrochem. Com.* (2008)

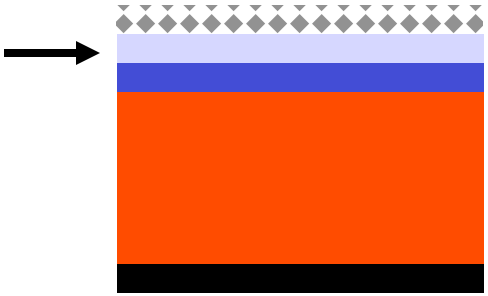
2. Nanowire, Nanopillars and Nanocones as Solar Cell Components

- J.-Y. Lee, S. T. Connor, Y. Cui, P. Peumans *Nano Lett. 8,* 689-692 (2008).
- C.-M. Hsu, S. T. Connor, M. Tang, Y. Cui *Appl. Phy. Lett. 93*, 133109 (2008).
- J. Zhu, Y. Cui and coworkers *Nano Lett.* (2009).



Metal Nanowire Mesh Transparent Electrodes

Transparent conducting electrodes

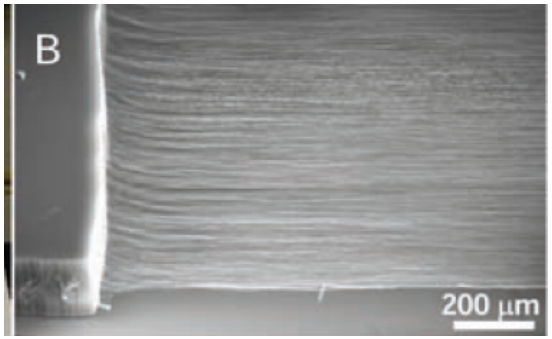


Current Technology

- Sputtering: high cost for large area
- Brittleness when bent.
- Damage to absorber layer (if it is organics)

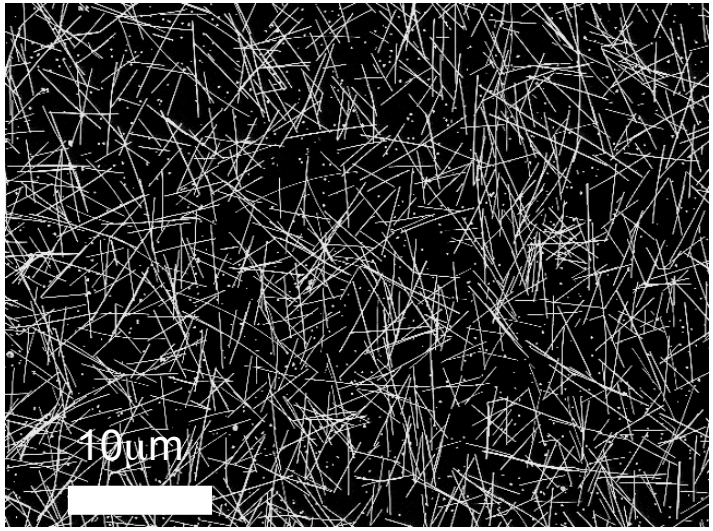
Carbon nanotube transparent electrodes

(Rinzler,Baughman, Gruner, McGehee)

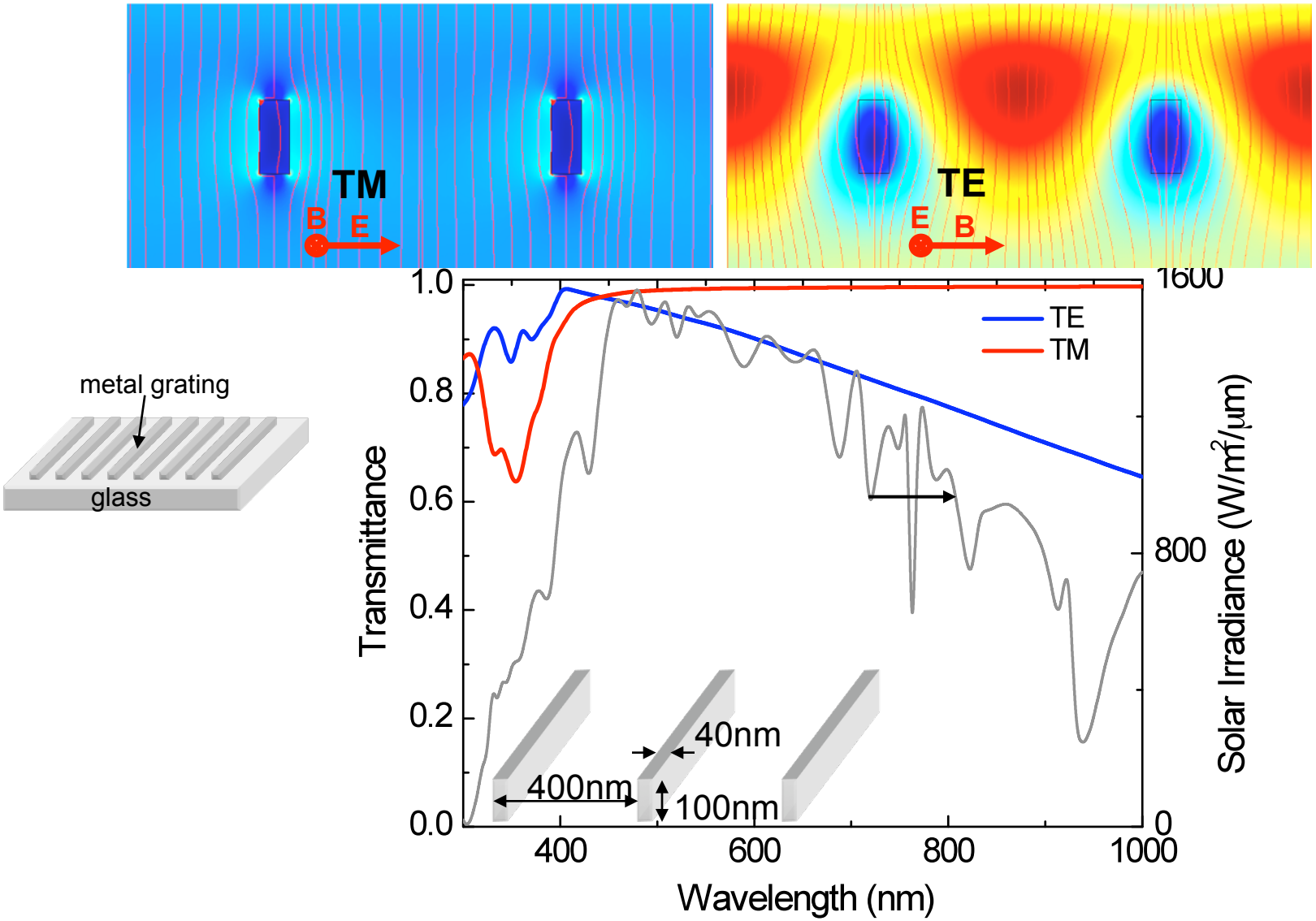


- Coexistence of metallic and semiconducting tubes

Metal nanowire transparent electrodes

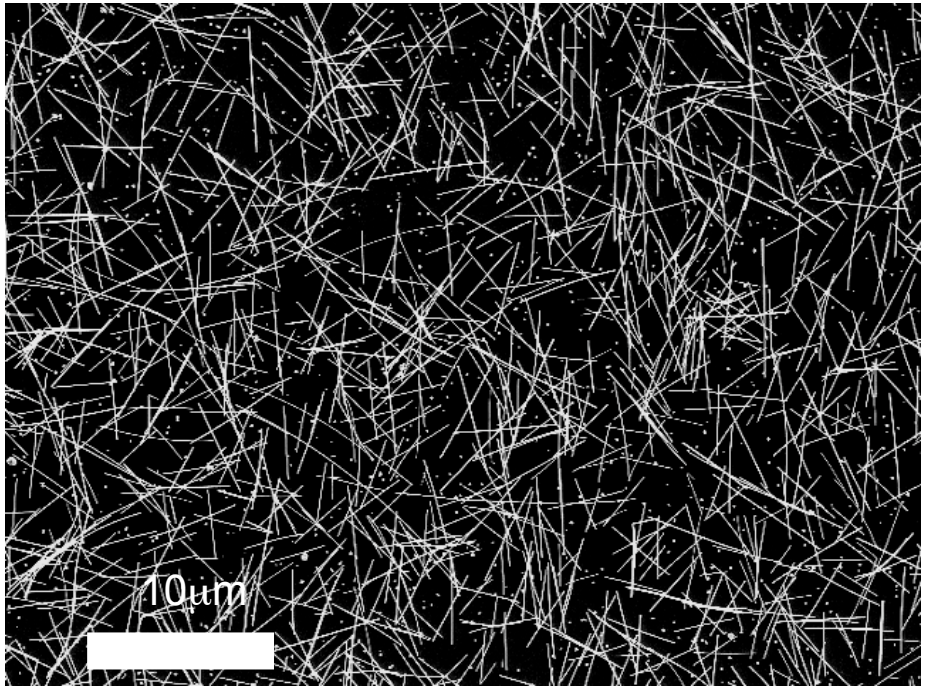


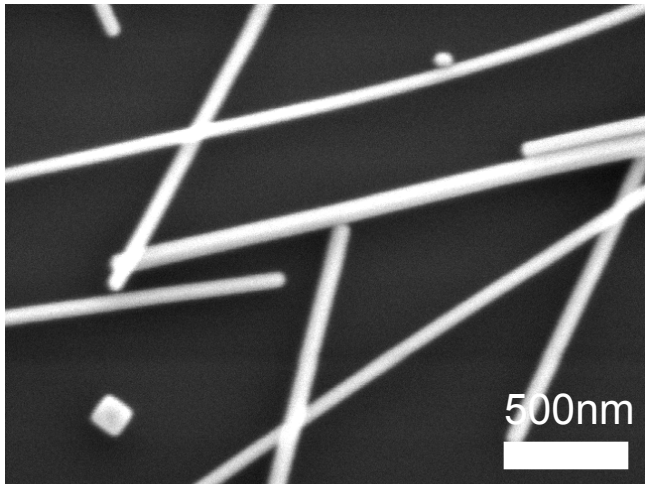
Simulation of Metal Nanowire Grating



J.-Y. Lee, S. T. Connor, Y. Cui, P. Peumans *Nano Lett. 8,* 689-692 (2008).

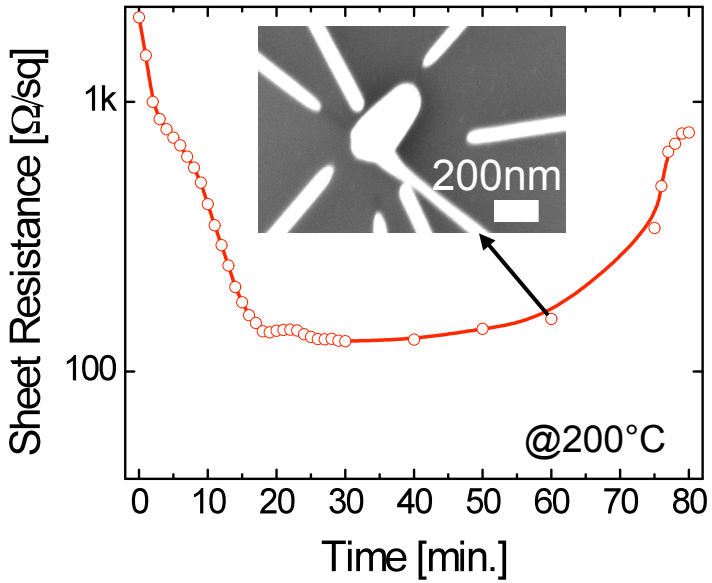
Ag Nanowire Networks



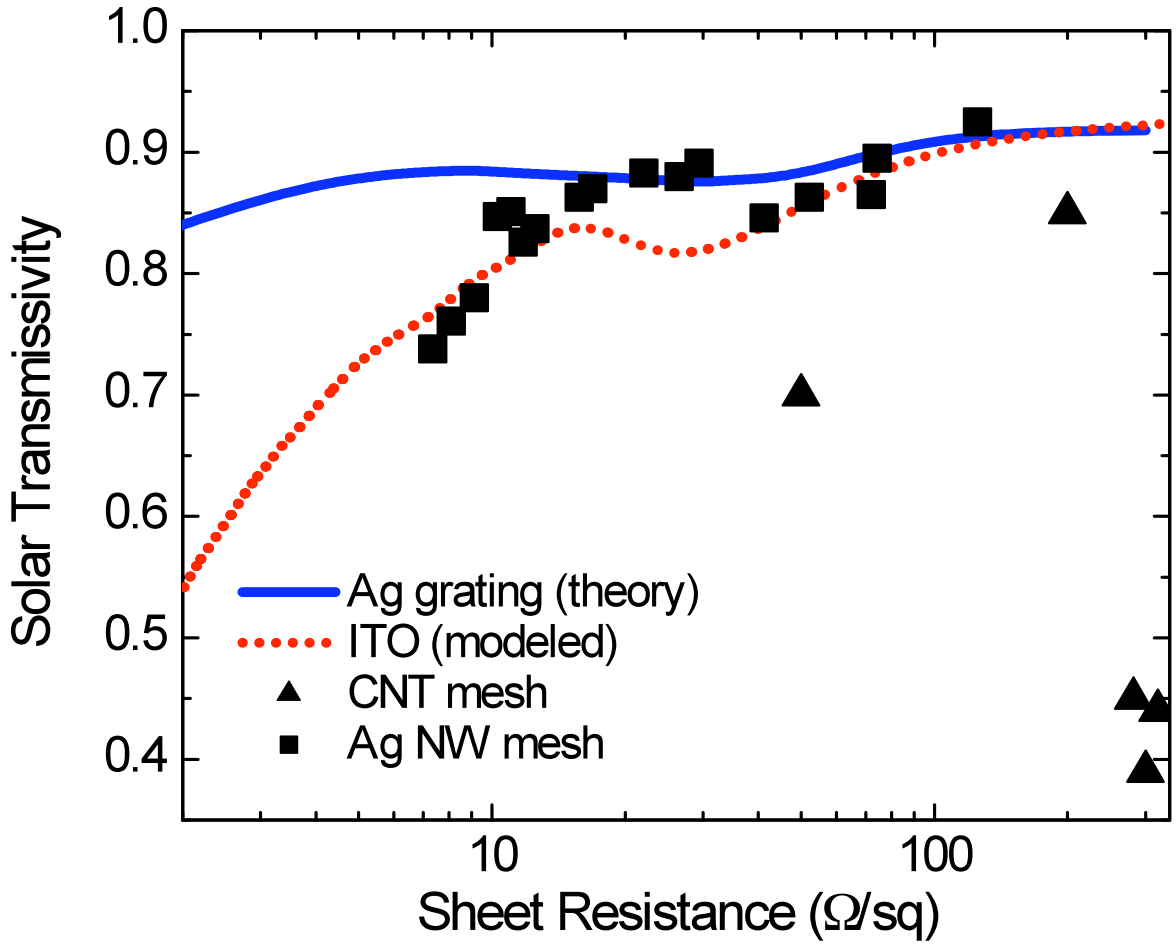


(Synthesis procedure: Y. Xia, P. Yang)

Length: 5-20 μm
Diameter: 40-150 nm



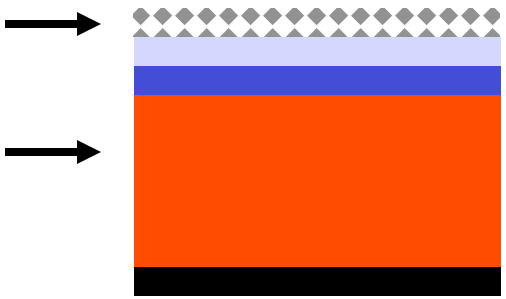
Ag Nanowire Networks

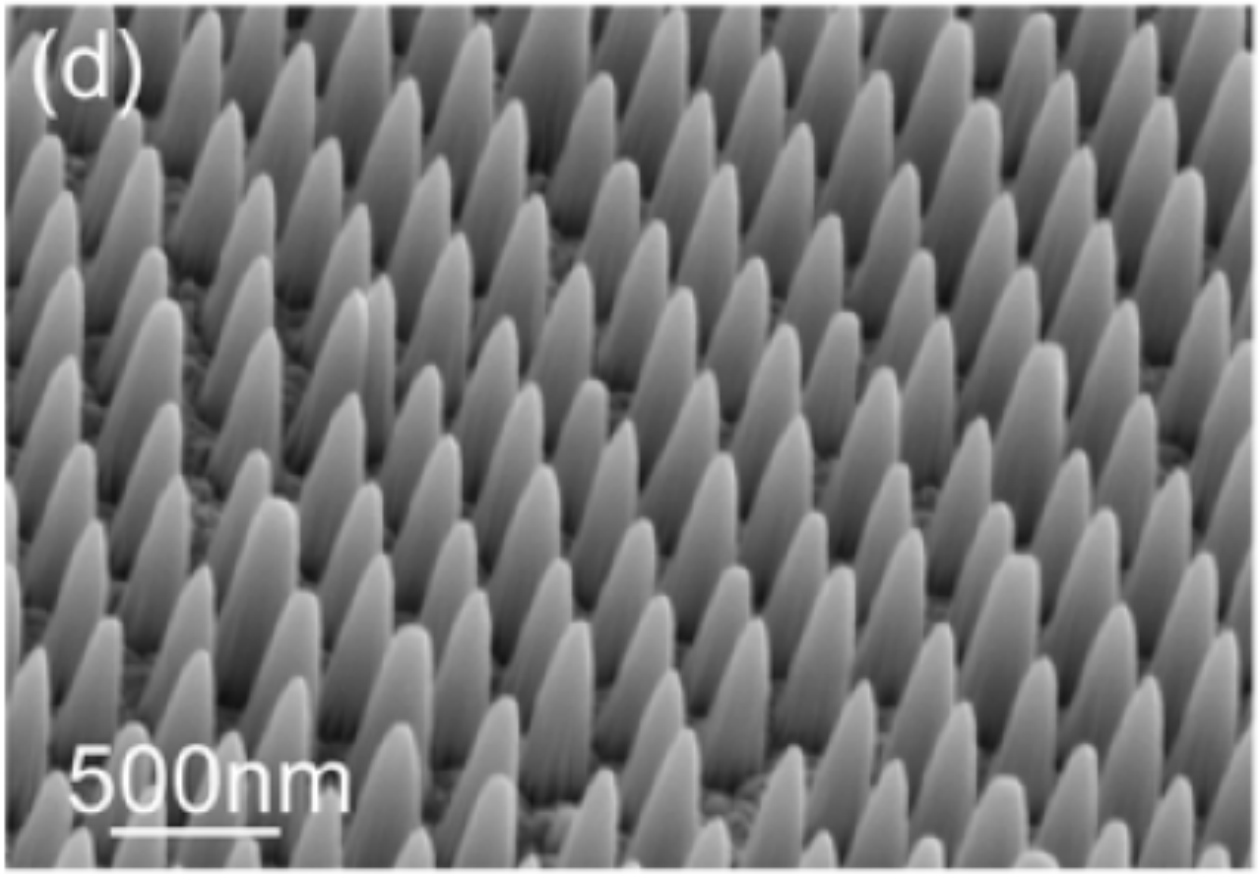


Nanowire networks perform as well as or better than ITO.

Nanocones for Enhanced Light Absorption

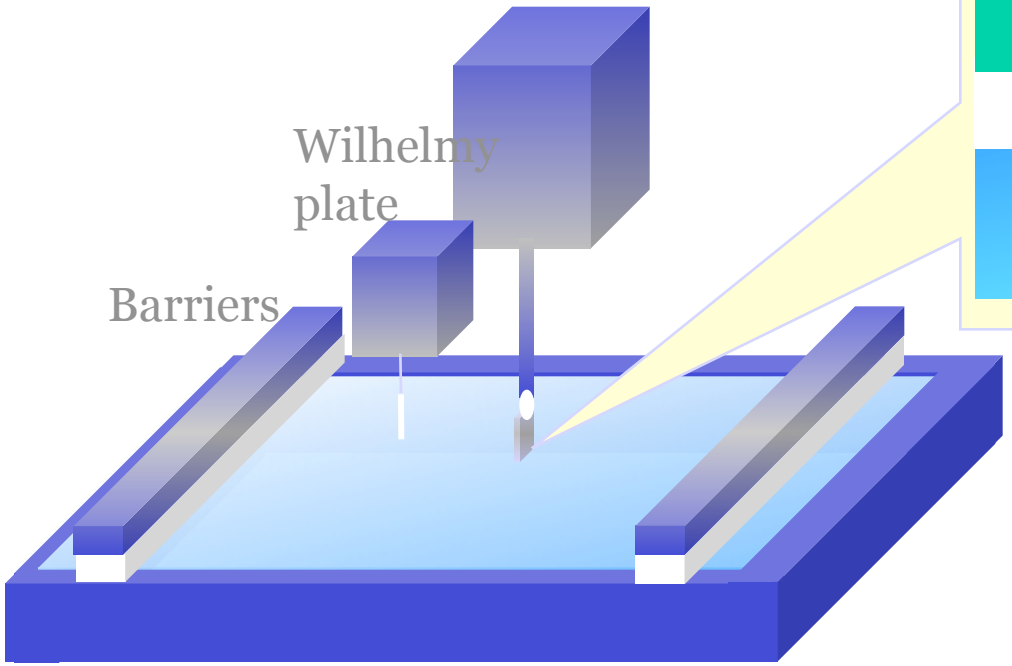
Absorber layer and anti-reflection

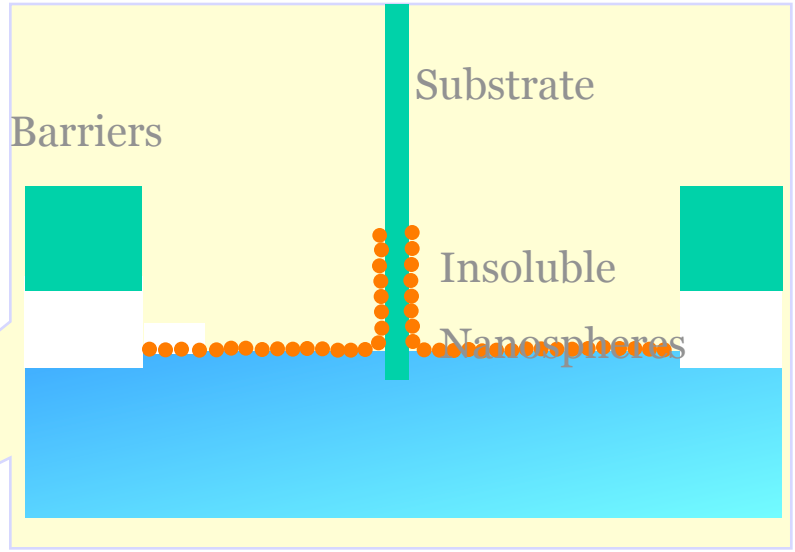




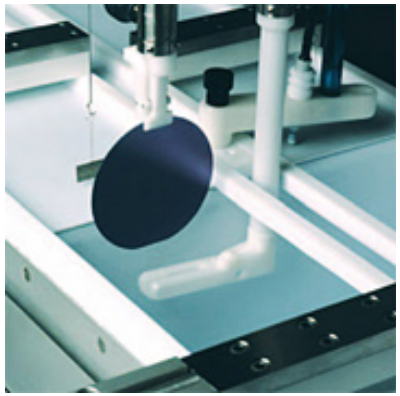
Combine absorber and anti-reflection layers together.

Langmuir-Blodgett Deposition of Silica Nanospheres

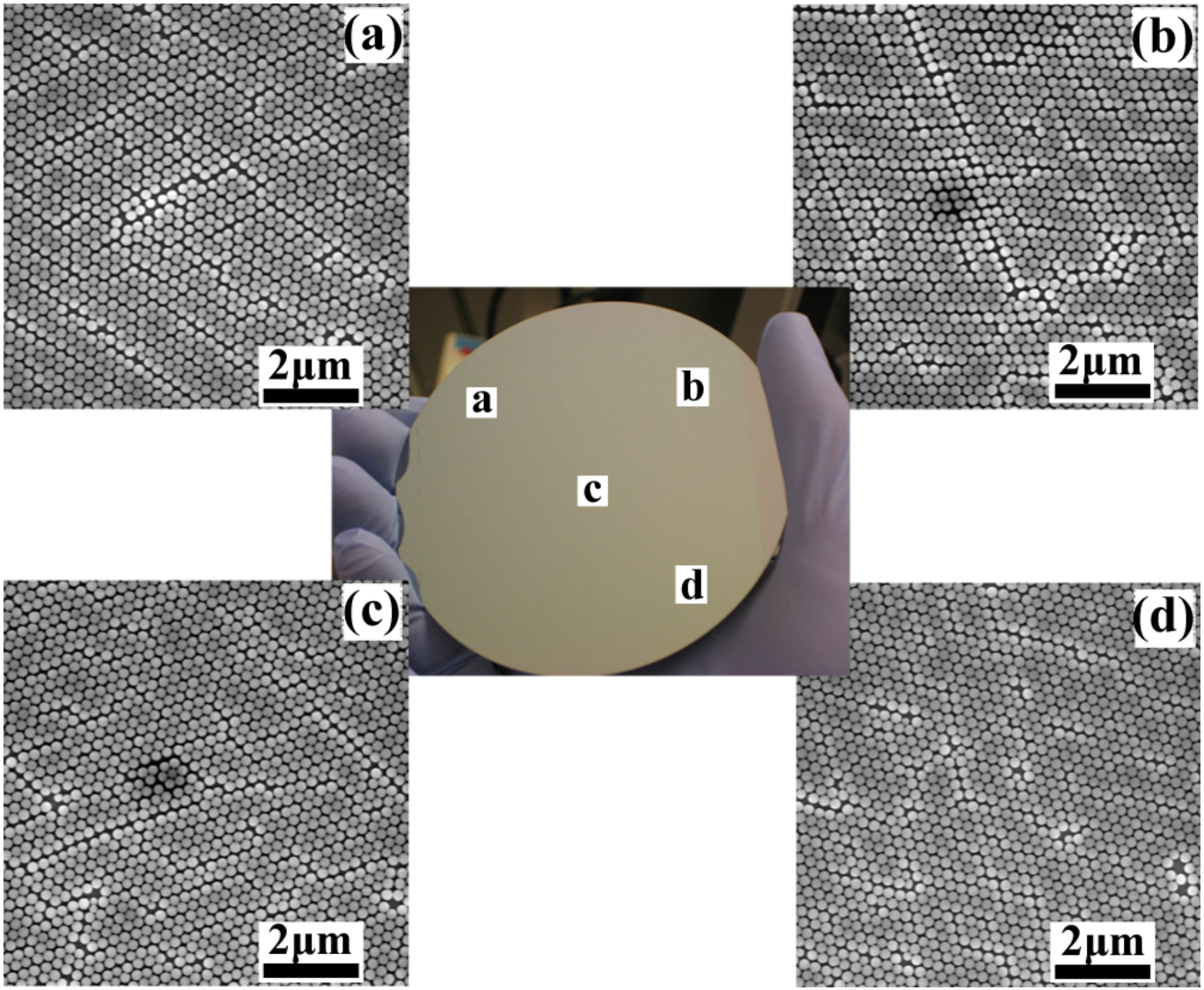




Schematic drawing of LB trough



Wafer-Scale Coverage of Monolayer Closepacked Particles



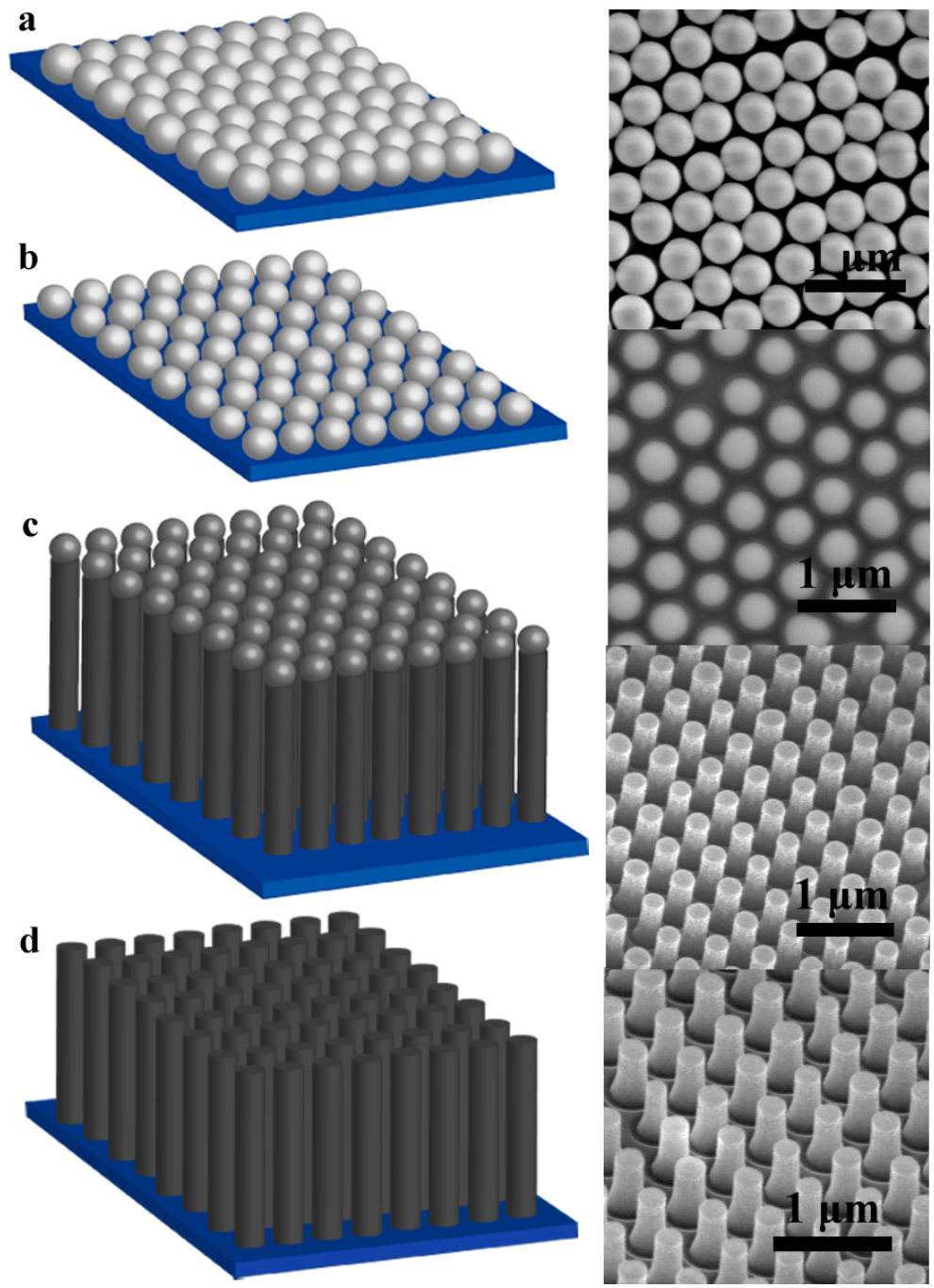
C.-M. Hsu, S. T. Connor, M. Tang, Y. Cui *Appl. Phy. Lett. 93*, 133109 (2008).

LB deposition

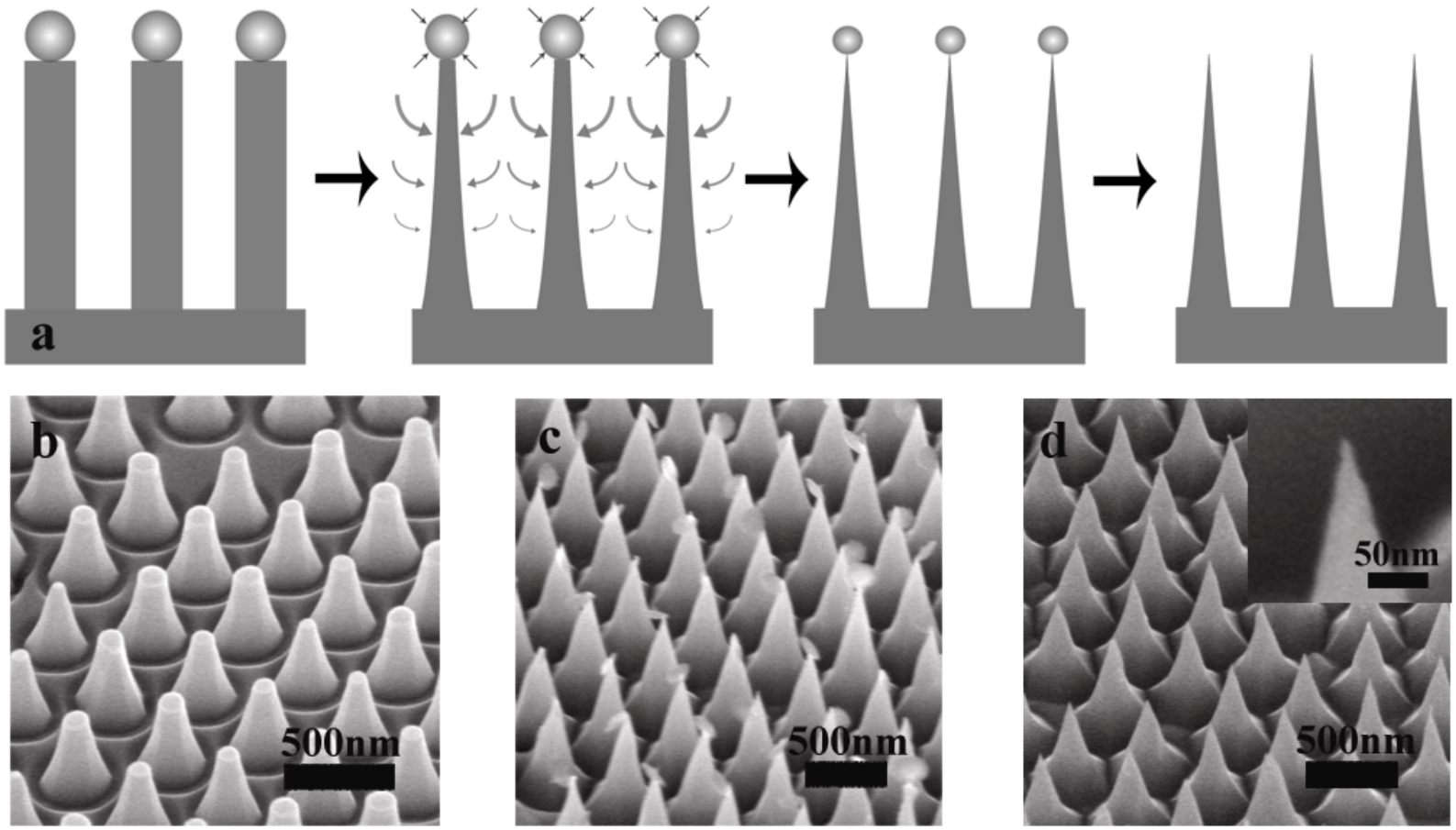
Shrinking particles

Reactive ion etching

Remove particles

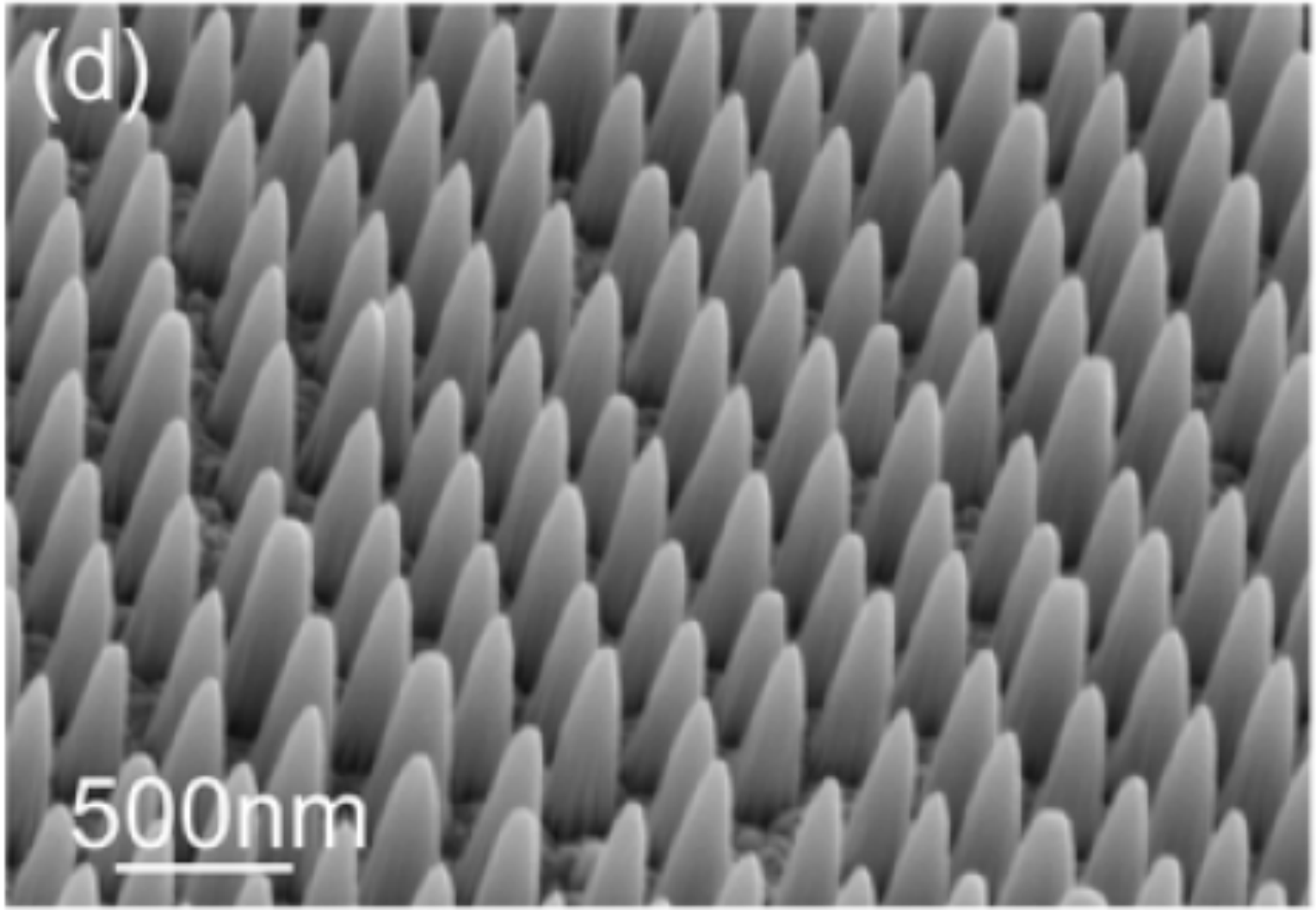


Si Nanocones



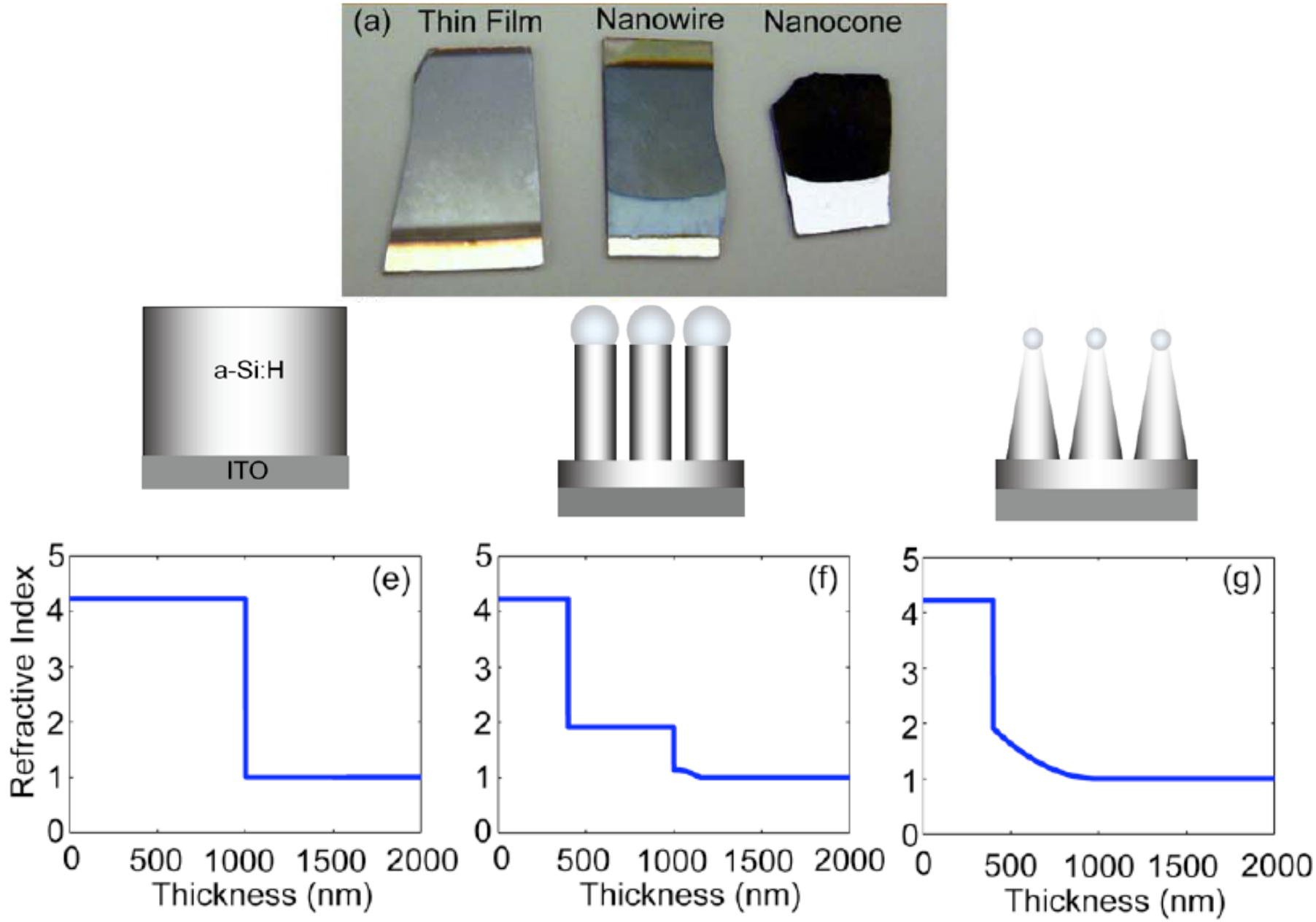
C.-M. Hsu, S. T. Connor, M. Tang, Y. Cui *Appl. Phy. Lett. 93*, 133109 (2008).

Amorphous Si Nanocones



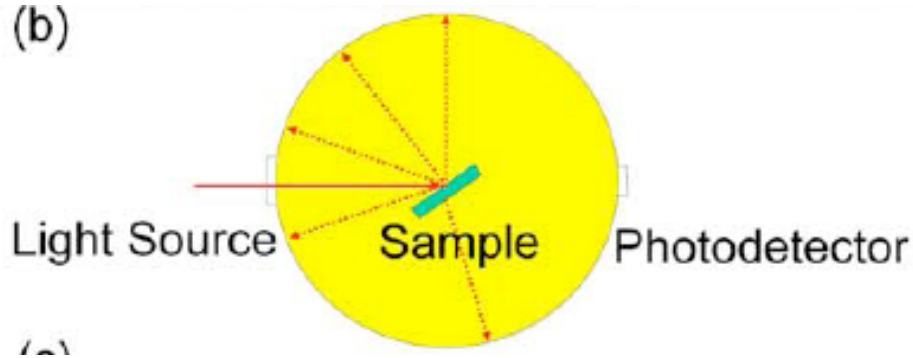
J. Zhu, Y. Cui and coworkers *Nano Lett.* (submitted, 2008).

“Black”Amorphous Si Nanocones

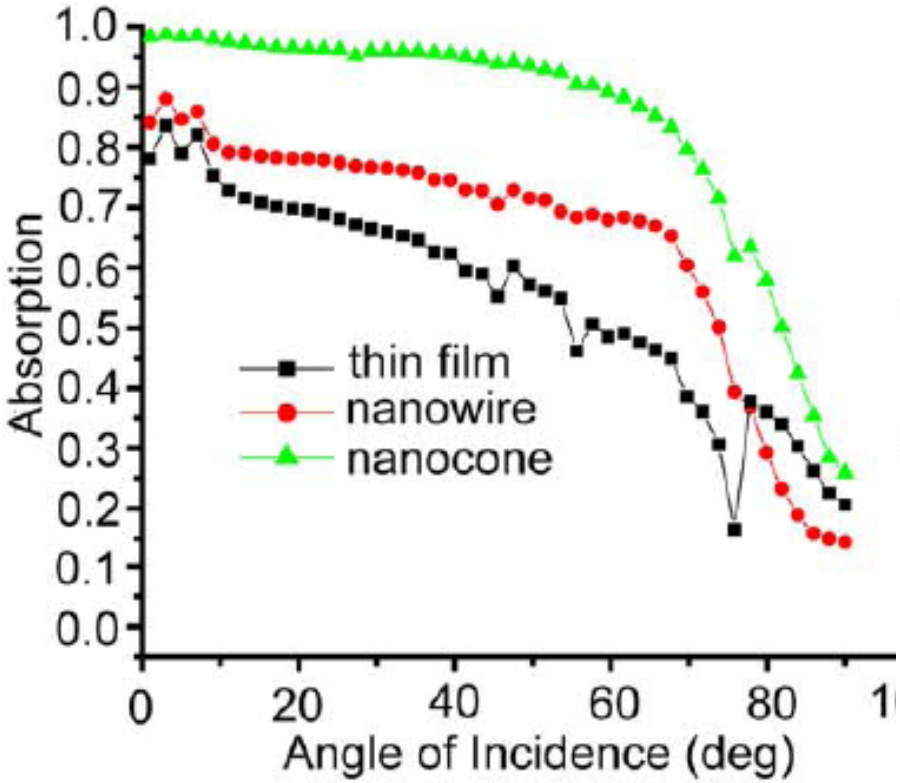


Absorption Measurements of Amorphous Si Nanocones

Integrating sphere measurement



Experiment



Simulation