Bridging Technologies

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"new form factors of matter lead to new functions"

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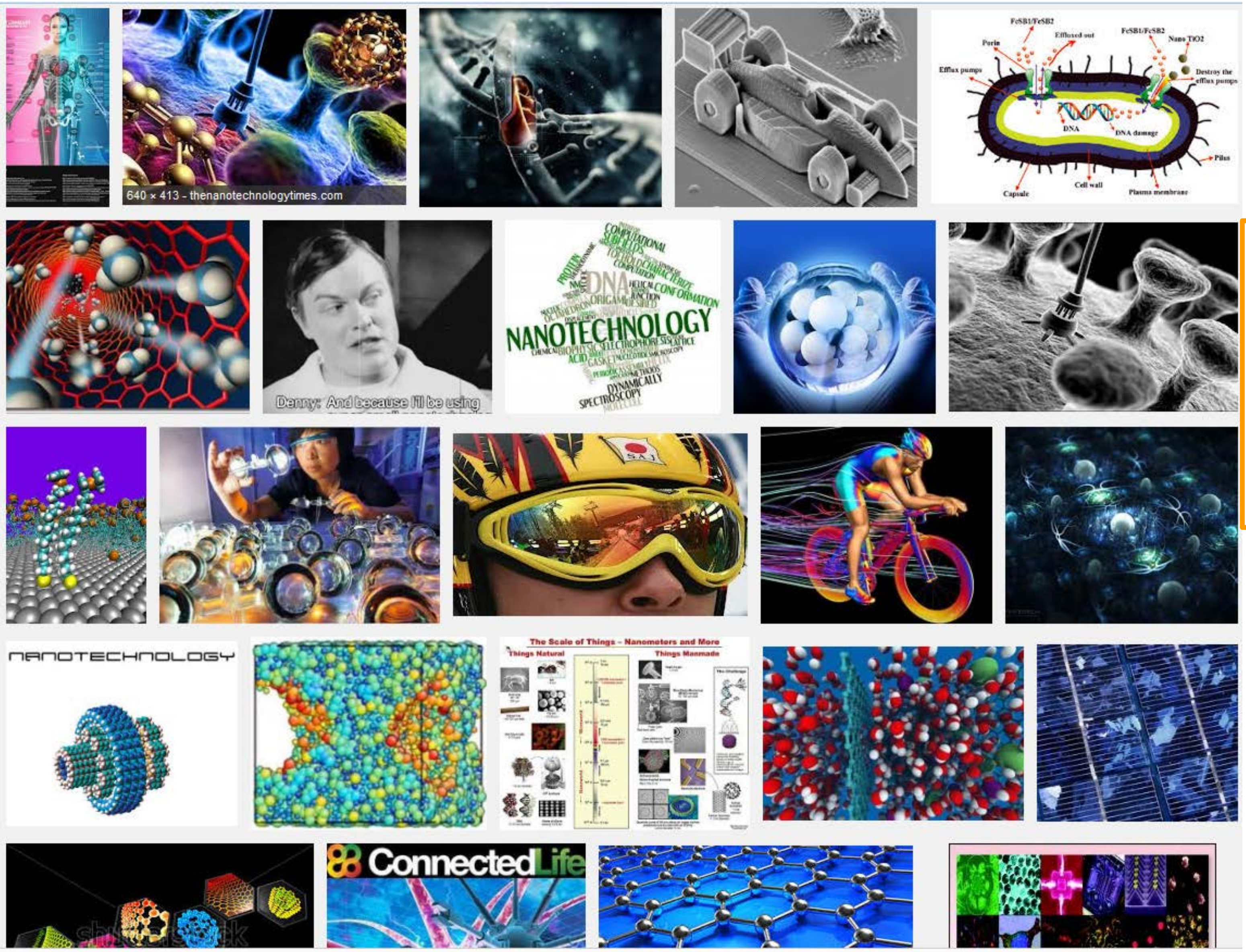
Google: “Nanotechnology” images (June 7, 2012 – June 7, 2013)

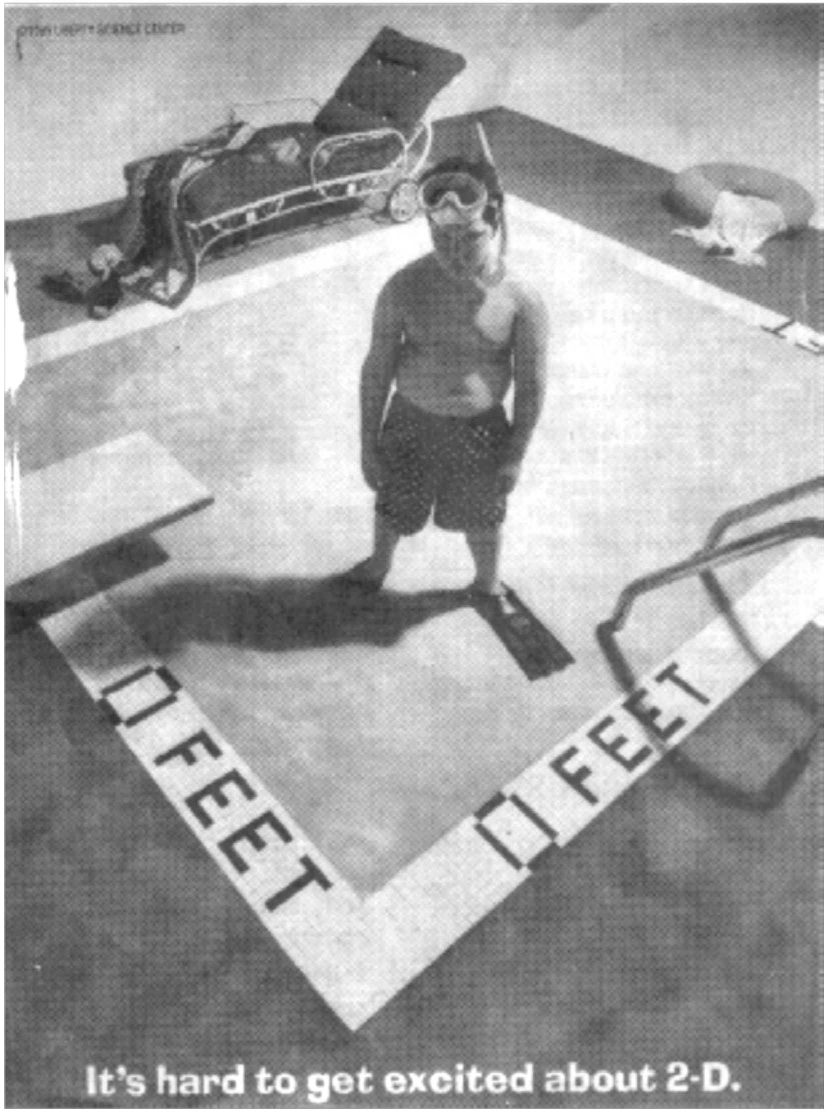


<u>Products</u>: 3
(all thin films)

<u>Tiny things</u>: 10+

How to reverse the ratio?

Going Beyond 2D



“It’s hard to get excited about 2-D”

2D nanotechnology is virtually everywhere, and of critical importance. But high-value nanotechnology needs to expand its impact beyond microelectronics, thin films, and medicine.

Necessary to Bridge Technologies from nano to macro to make nanotechnology <u>the</u> value added component.

Macroscopic Nanotechnology

Most are commodities. Price only slightly greater than raw materials cost + energy input cost.

Existed long before "nanotechnology". Term "nano-technology" first used in 1974 by Taniguchi.

<u>Examples of Macroscopic Nanotechnology</u>

- Carbon Black
  - world production ~10,000,000 tons
  - Tires are ~50 wt% carbon black
  - Volume production since ~1900
- Fumed Silica and Silica Fume
  - used in cement and as polymer reinforcement
  - Volume production since ~1950
- Clay
  - used for 15,000 years
- Alloys
  - many metal alloys are nanostructured
- Polishing media
  - from low tech to high tech
- Pigments
  - e.g. for paints and coatings
  - many variations, often nanostructured
- Energy Storage

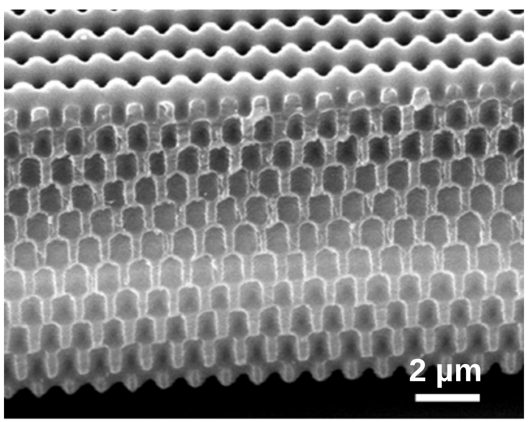
Translating Nanotechnology into Macroscopic Systems

May require some level of "bottom-up" (but not necessary exclusively so)

- **Needs to be much more than just building blocks**
  - add value through functionality
  - add value through substantive and broad IP (hard for building blocks)
- **Must provide a paradigm change. Otherwise the steady rate of progress of established products will surpass the functions of the "nanotechnology"**

Structural Complexity

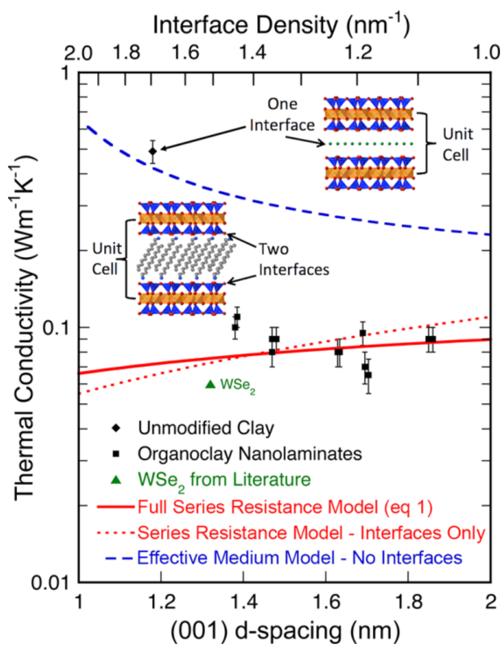
Interference lithography provides 3D structures in a single step



Campbell, et al. *Nature* **2000**
Yang, Wiltzius, et al. *Chem. Mater.* **2002**

Heat Transfer

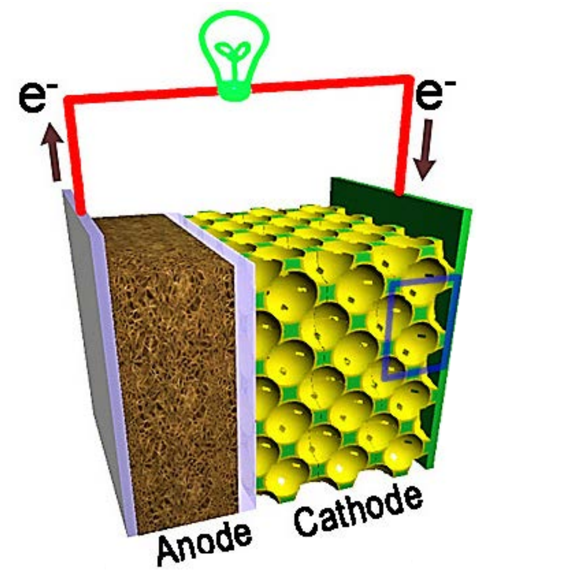
Ultralow thermal conductivity in self-assembled 3D structures



Losego, Braun, et al. *Nano Letters* **2013**

Rechargable Batteries

Ultrahigh power density through electrode nanostructuring



Zhang, Yu, Braun *Nature Nanotech.* **2011**

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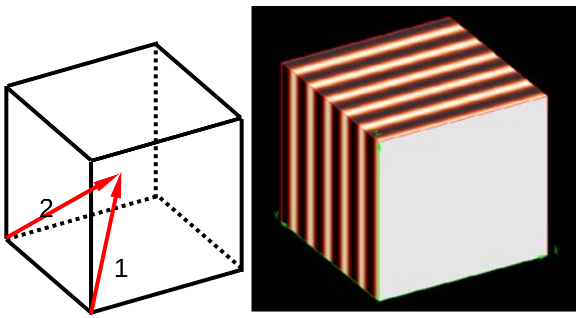
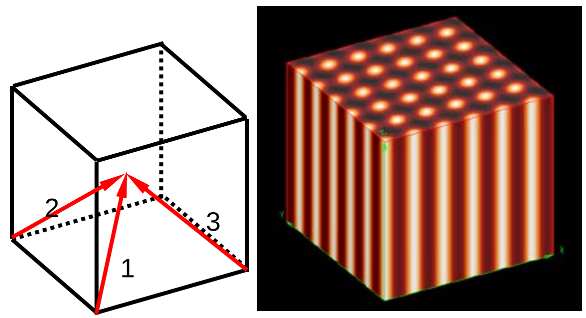
Multibeam Holography: Macroscopic Nanostructuring

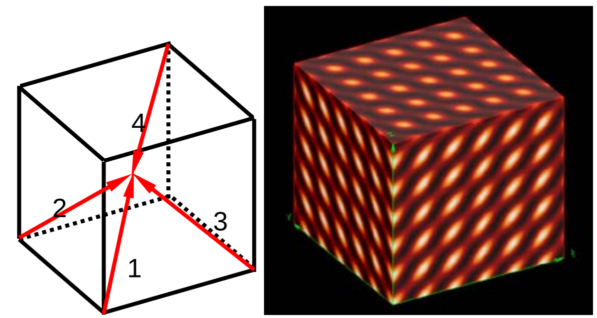
2 beams (1D)



3 beams (2D)



4 beams (3D)

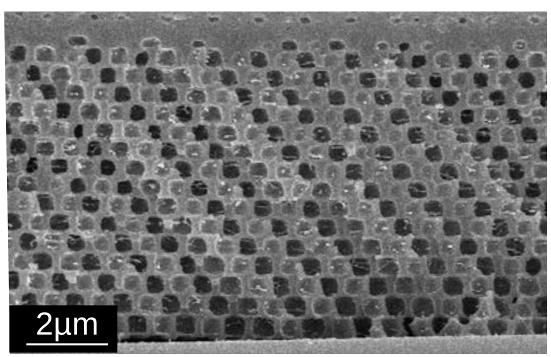


$$I = \sum_j {E_j}^2 + \sum_{i<j} 2E_iE_j \cos\theta_{ij} \cos[(\mathbf{K}_i - \mathbf{K}_j)\mathbf{r} + \varphi_{0i} - \varphi_{0j}]$$

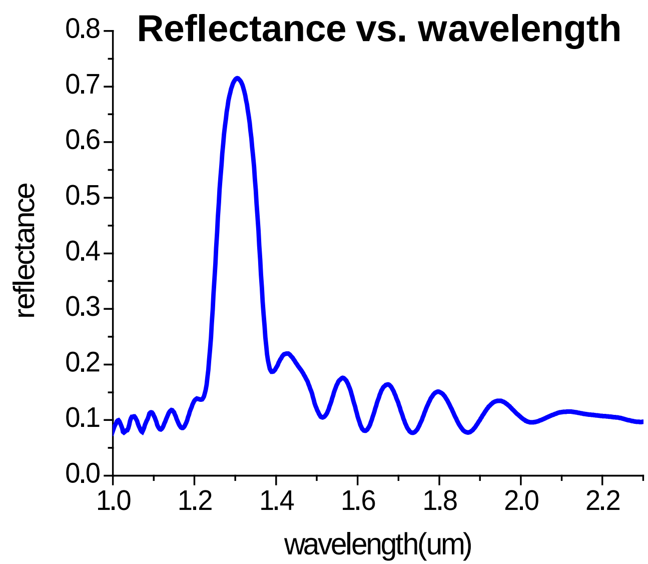
power — polarization — wavevector — phase

wavevector
- beam geometry
- wavelength
- refractive index

(111)

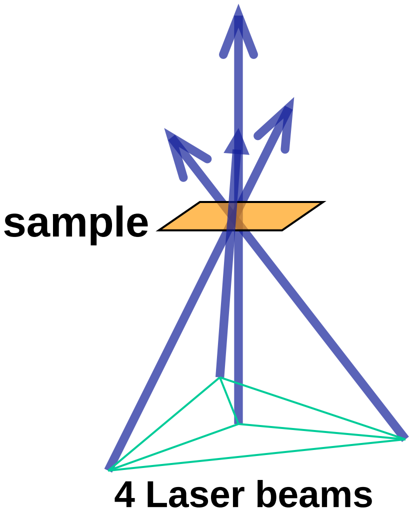


SEM cross-section

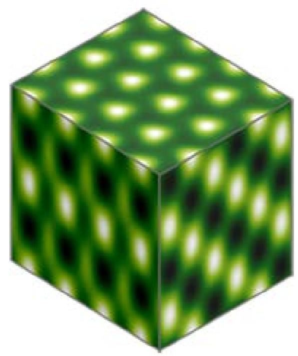


Multibeam Interference Patterning of Materials

Low cost, large area periodic structures

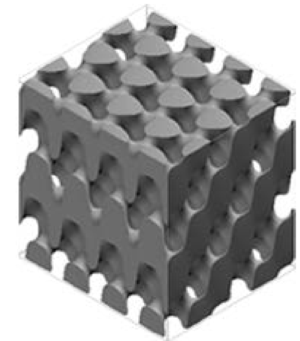


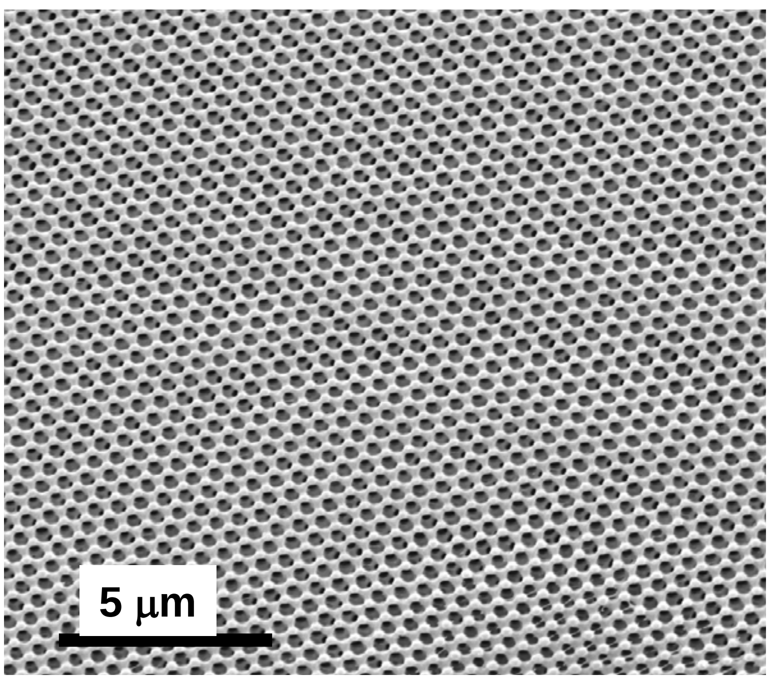
Interference pattern

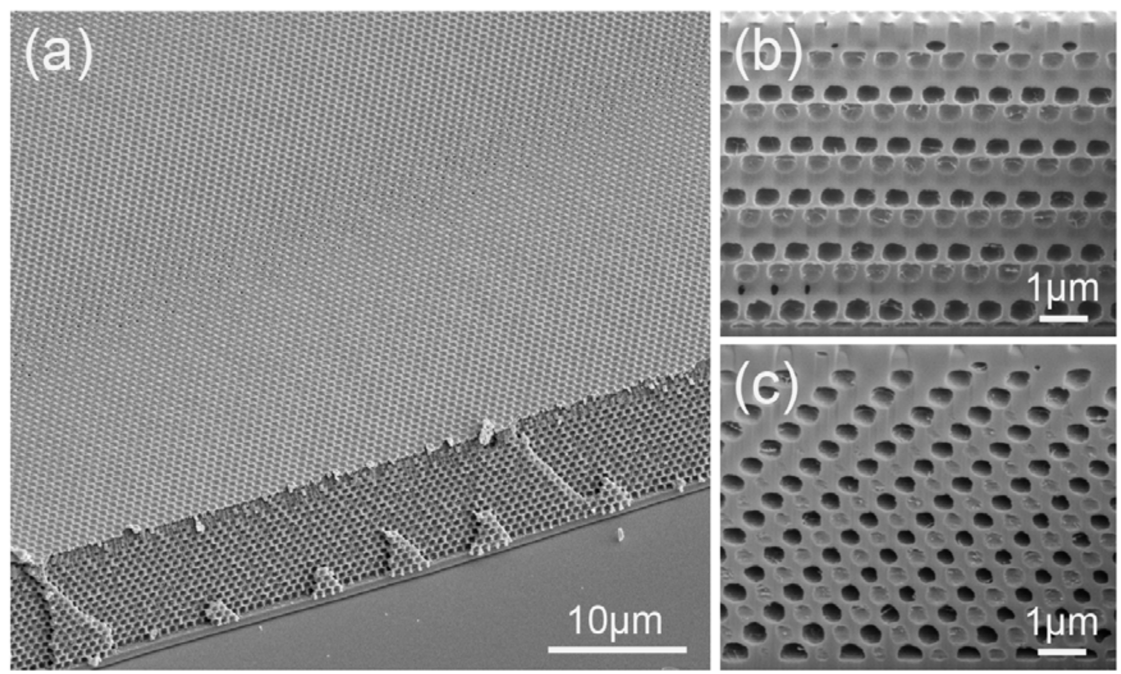


Remove unexposed material

Resulting Structure







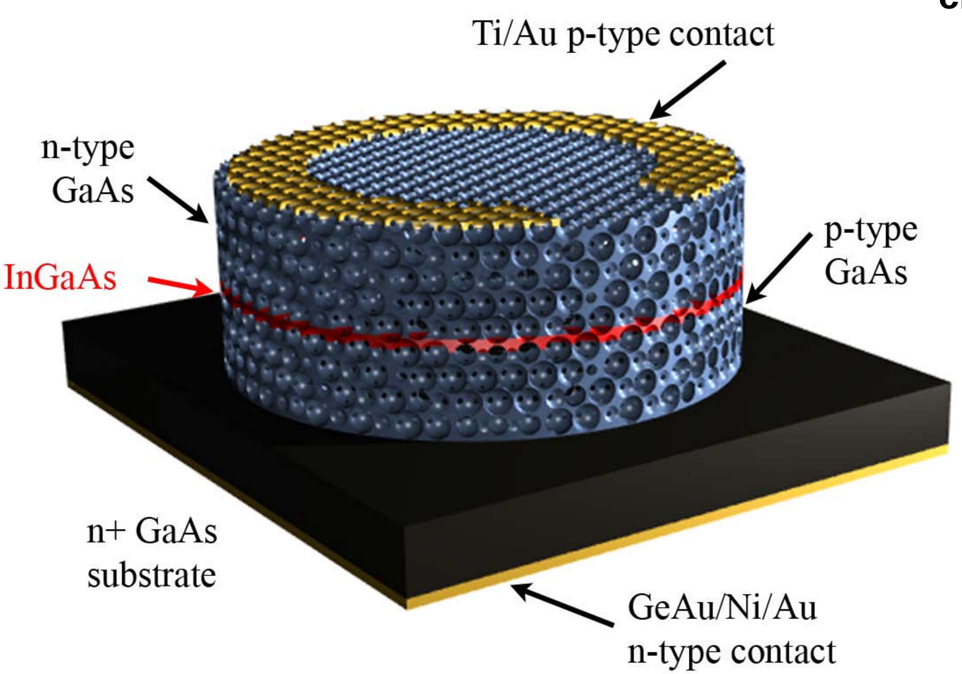
Polymer Photoresist (SU-8)

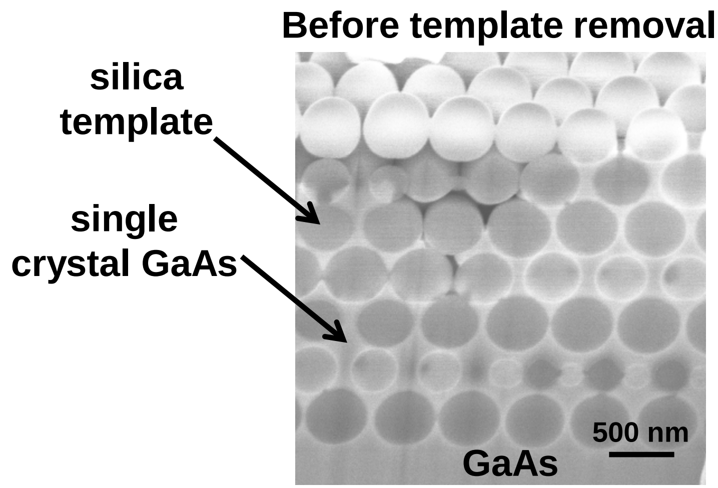
Chen, Braun, et al. *APL* **2007**

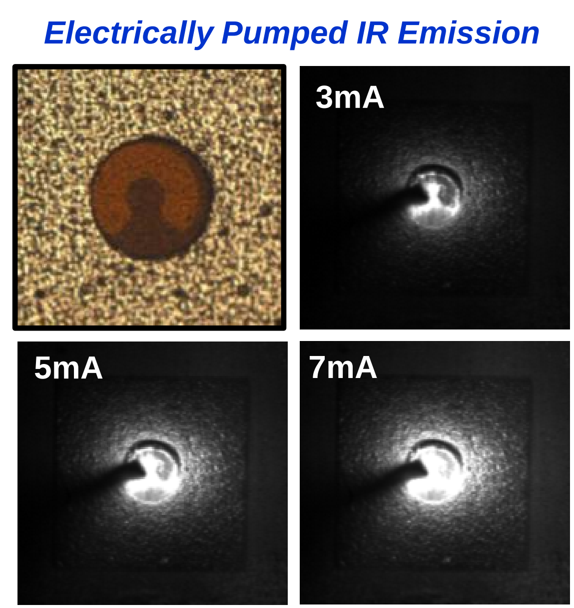
3D Photonic Crystal-Based LED

First example of:

- * Electrically pumped emission from a 3D PC LED
- * Epitaxal growth of porous 3D semiconductors







Required merging a common 2D semiconductor growth with a 3D self-assembled template

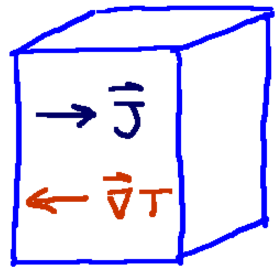
Nelson, Braun, et al. *Nature Materials* **2011**

Limits to Thermal Conductivity (in solids)

How does nanotechnology relate to thermal conductivity?

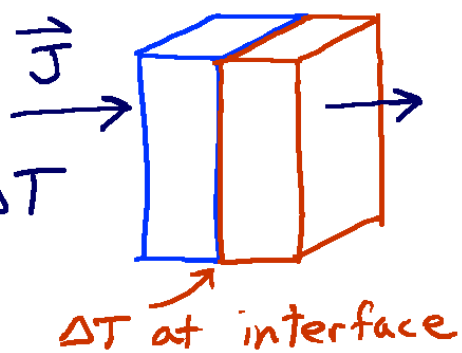
- **Thermal conductivity Λ is a property of the continuum**

$\vec{J} = -\Lambda \vec{\nabla} T$

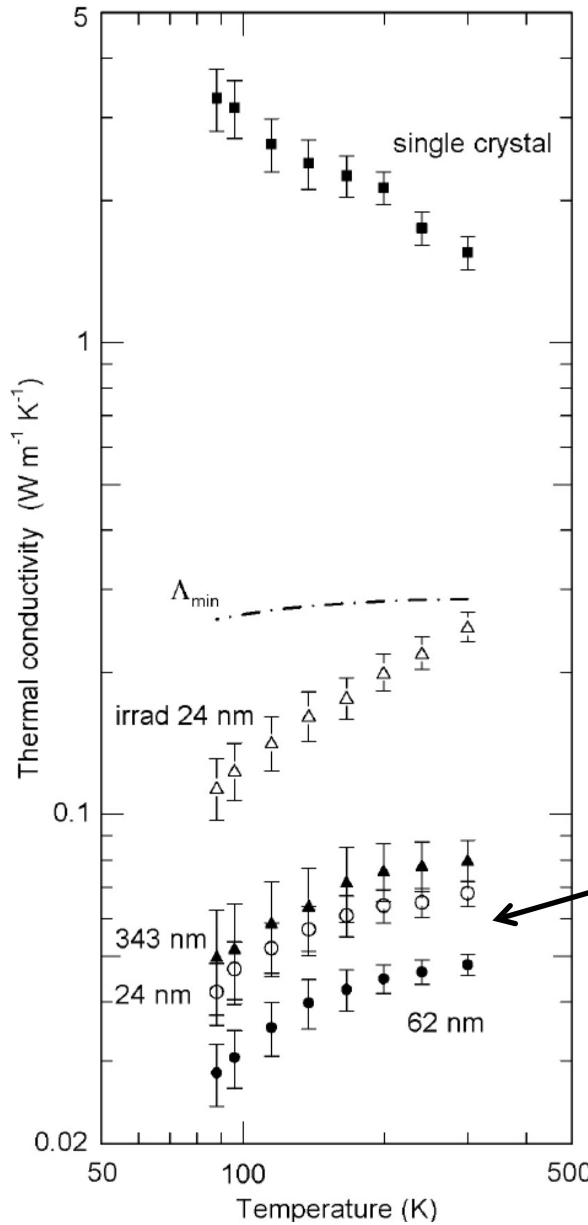


- **Thermal conductance (per unit area) *G* is a property of an interface**

$J = G \Delta T$



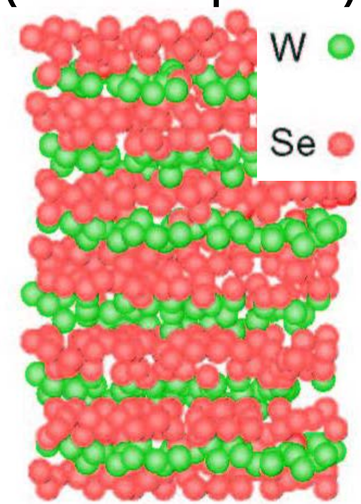
So, as the density of interfaces increases, thermal conductivity decreases. Interfaces important only for very high interface densities (~1 nm^{-1})



<u>Potential Impact</u>

- **Thermoelectrics**
- **Insulation**
- **Thermal switch**
- **Thermal isolation**
- **Thermal solar**

Layered WSe_2 (vacuum deposited)



Cahill *Science* **2007**

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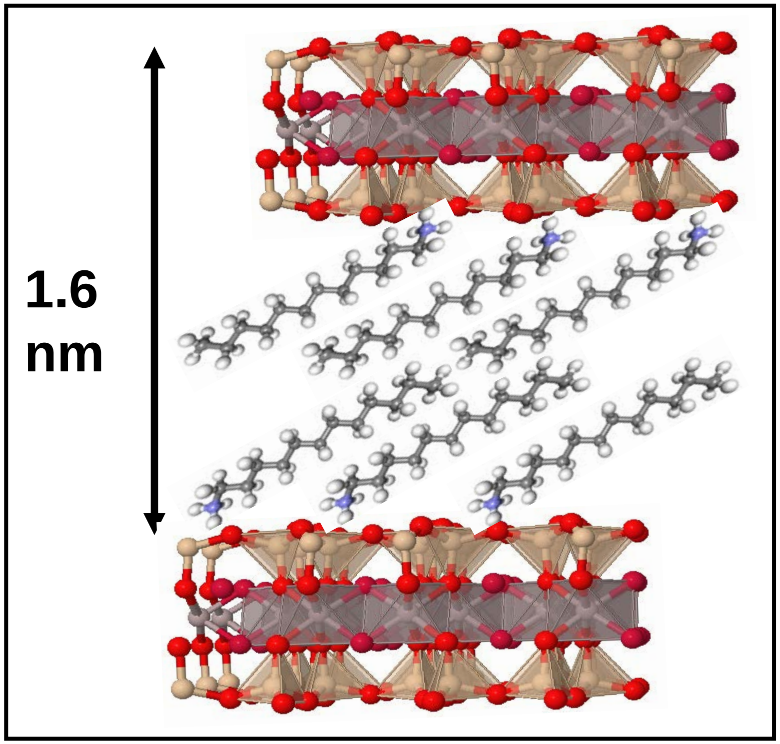
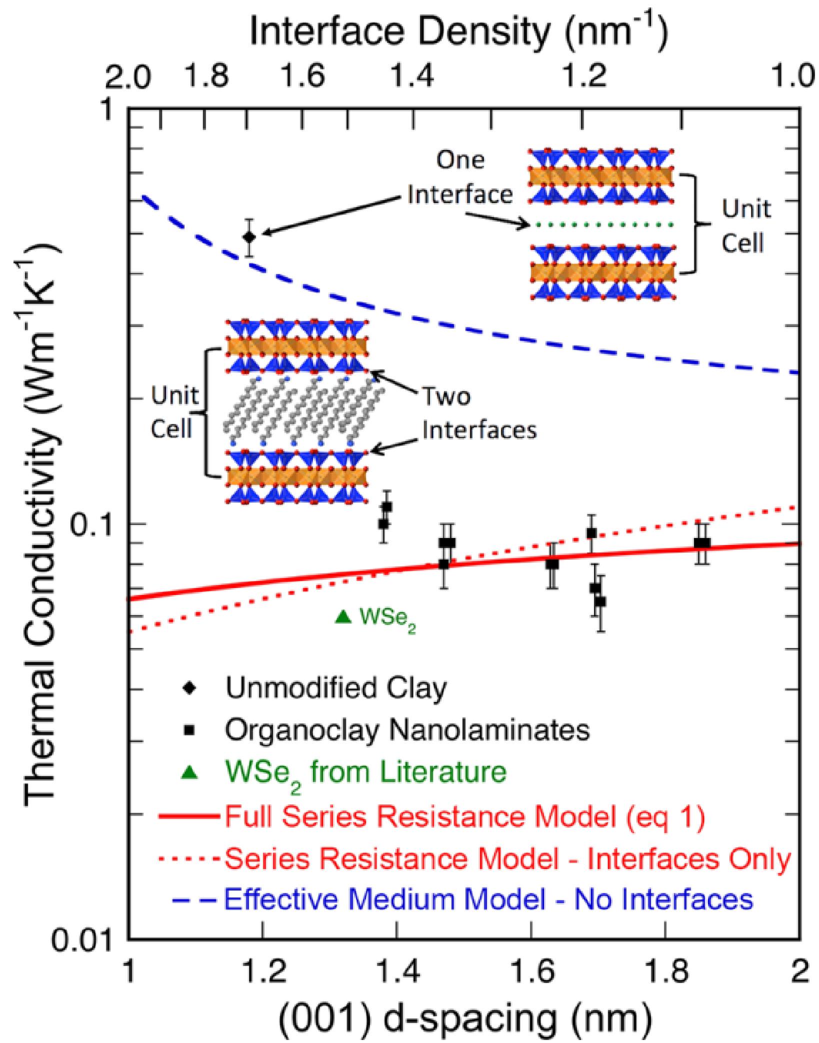
Ultra-low Thermal Conductivity: Towards Macroscopic Systems

Layered Clays

- **~1 interface/nm**
- **Self-assemble into layered structures**
- **Produced worldwide in high volume**

Organically Modified Layered Clay





Nanostructuring results in a thermal conductivity which is 50% of a typical plastic and 10% of glass

Losego, Braun, et al. *Nano Letters* **2013**

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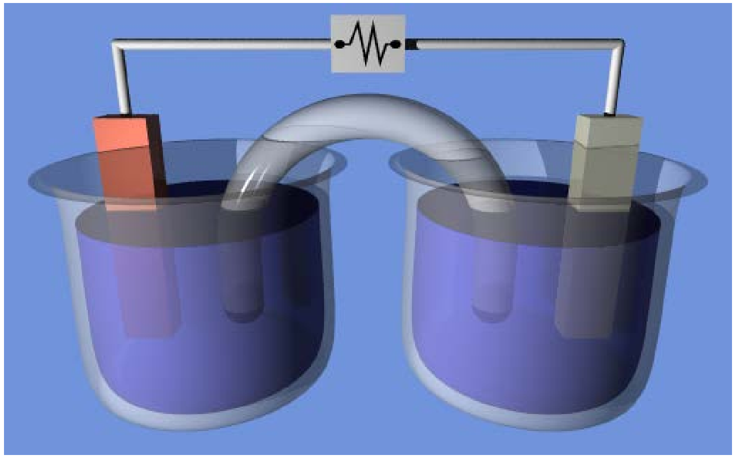
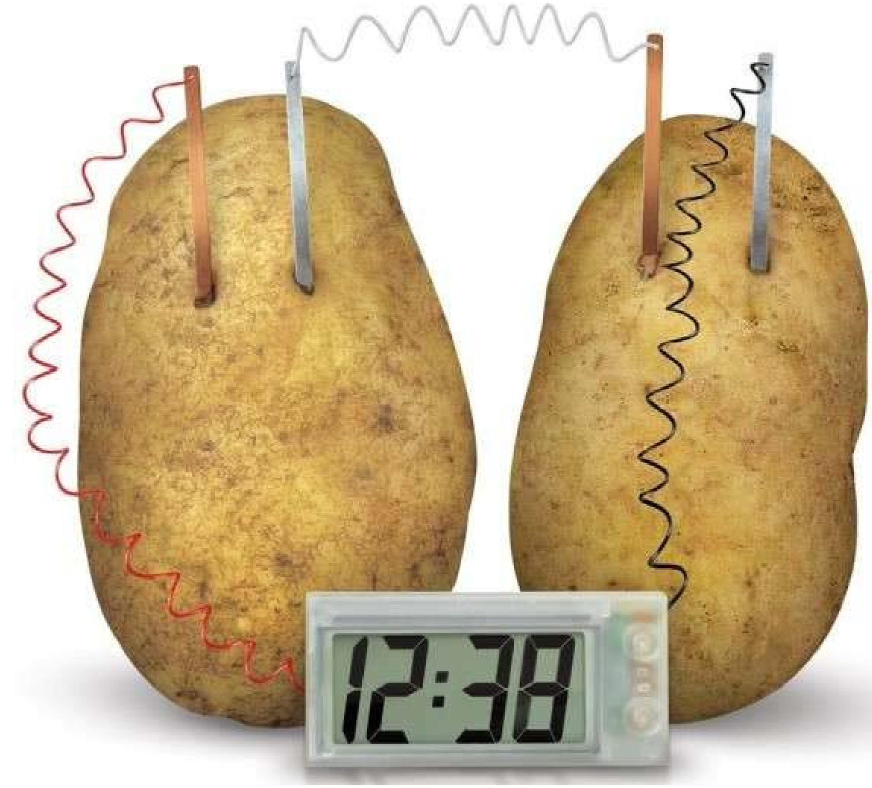
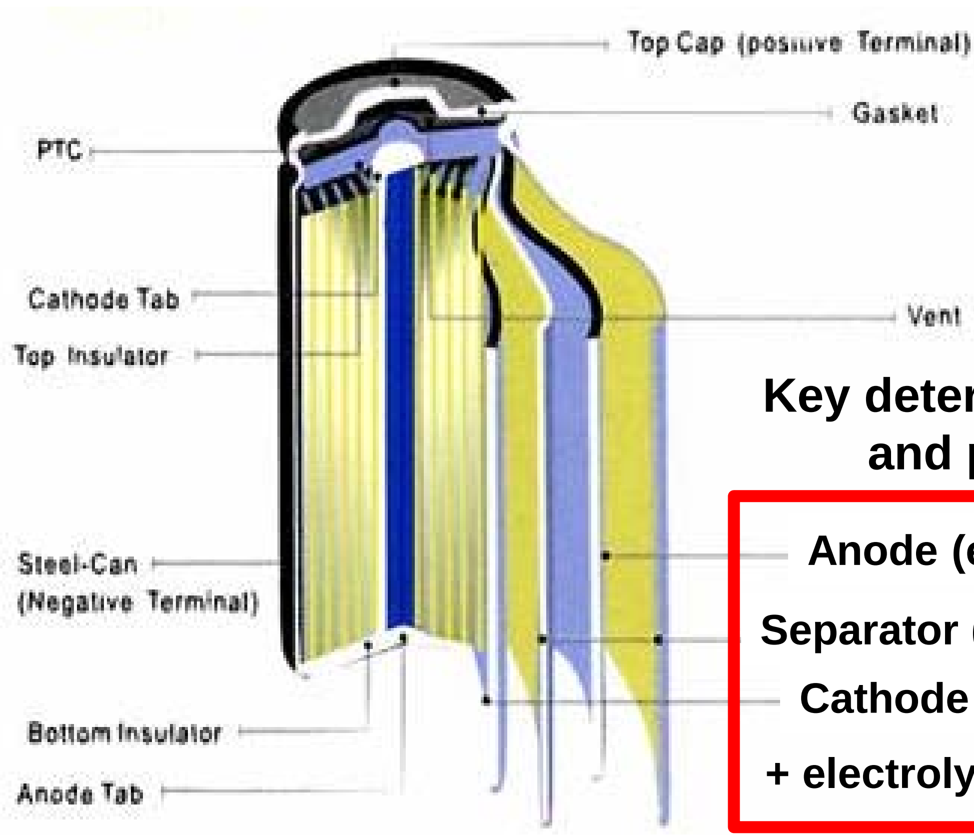
Batteries (always "Bulk" materials)



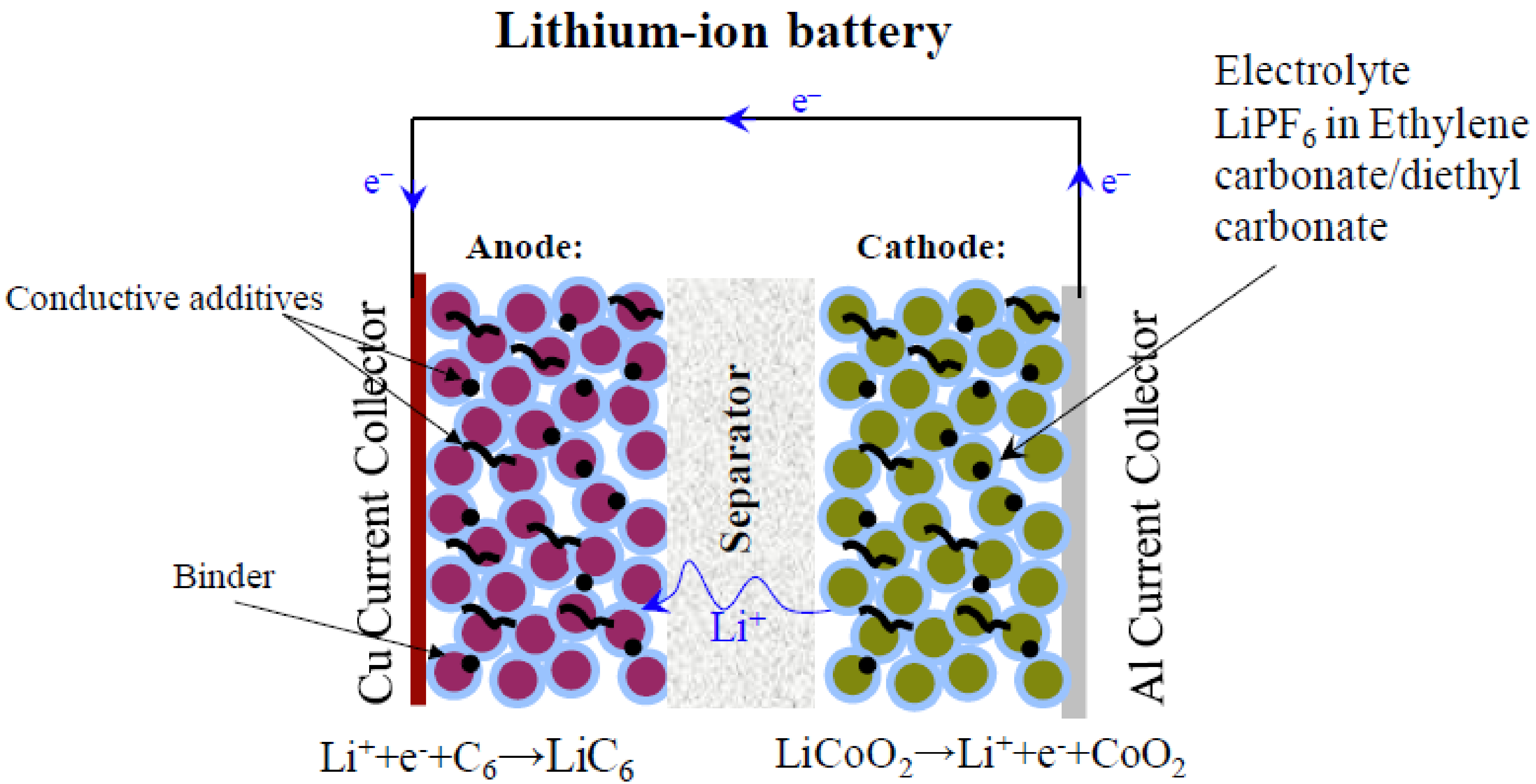




Key determinants of energy and power density

- Anode (e.g. carbon)
- Separator (porous polymer film)
- Cathode (e.g. $LiMnO_2$)
- + electrolyte (solid or liquid)

Inside a Li-ion Battery



Continuous ion and electron transport pathways in electrodes critical
Provided by pore network and conductive additives

Venkat Srinivasan, LLNL
http://berc.lbl.gov/venkat/files/batteries-for-vehicles.pdf

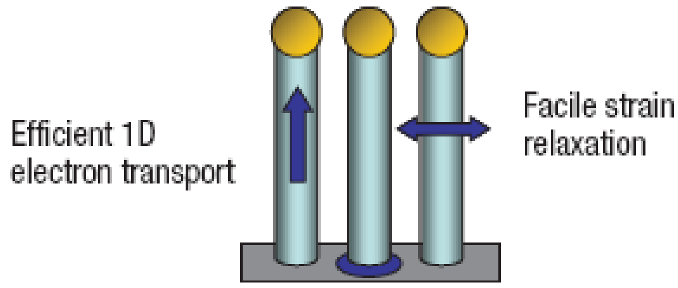
Pathways to Increase Power & Energy Density

1. New Materials

2. Structure Design → REDUCE TRANSPORT LENGTHS

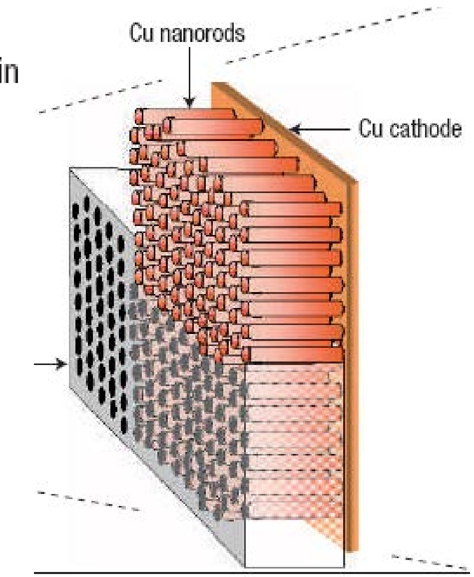
- 3D electrode architecture
- Large surface area
- Thin film of active materials

Nanowires

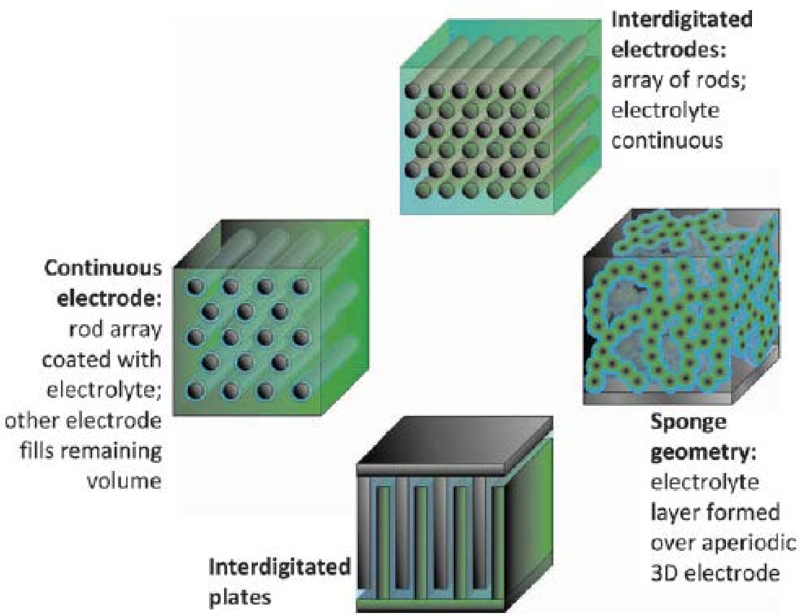


Nature Nanotechnology **2008**, 3, 31

Nano-pillar current collectors

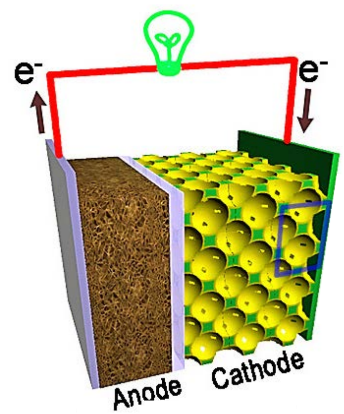


Nature Materials **2006**, 5, 567



Chemical Society Rev. **2009**, 38, 226

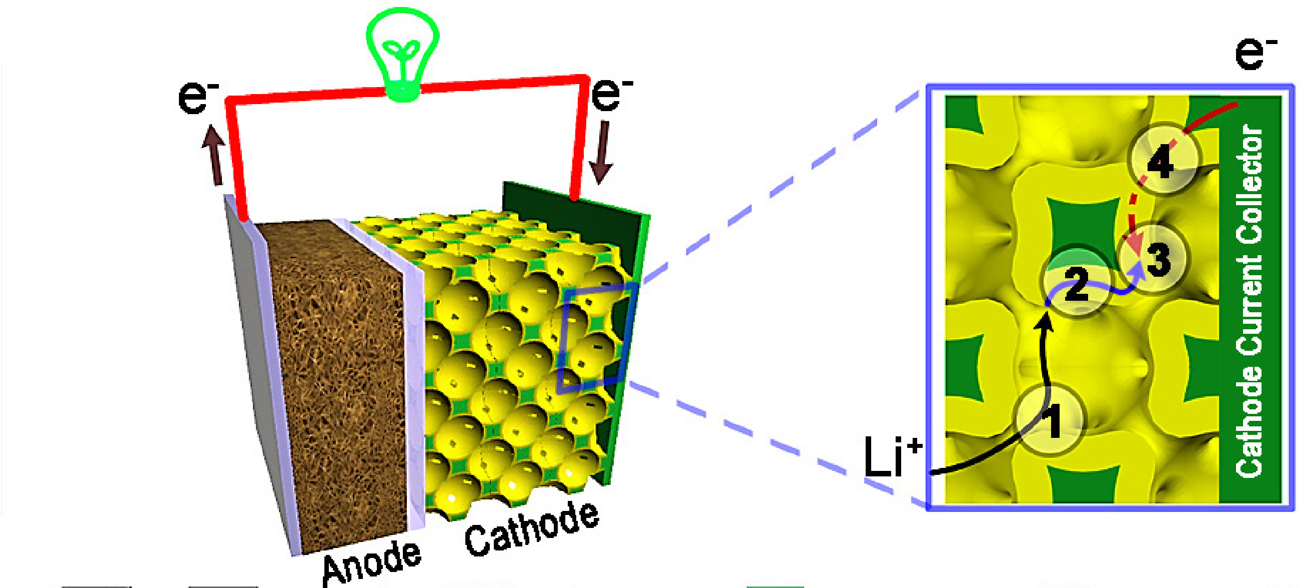
3D Bicontinuous Electrodes



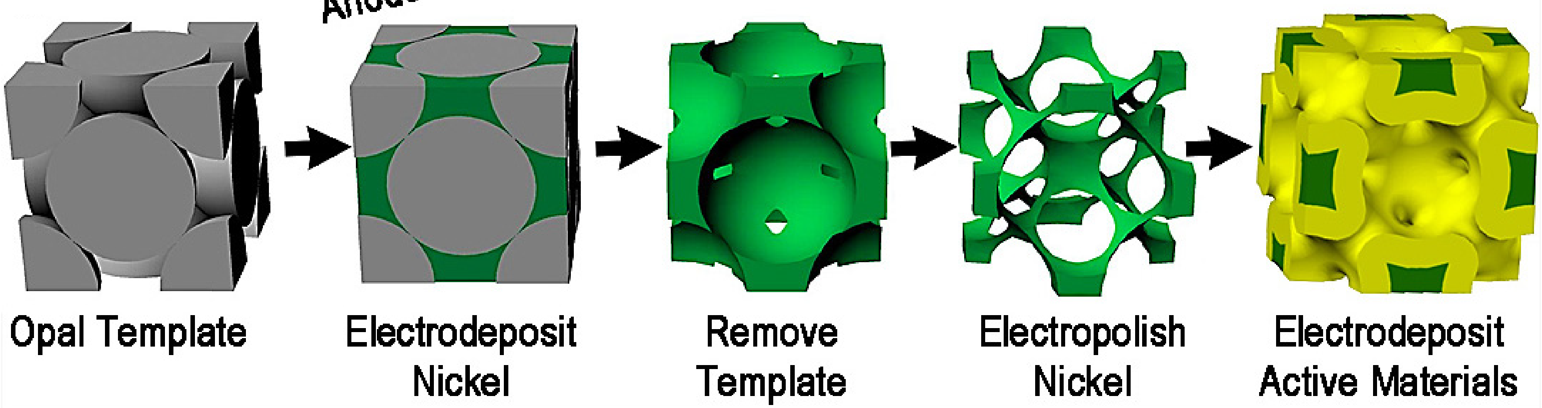
Zhang, Yu, Braun *Nature Nanotech.* **2011**

Bicontinuous Battery Electrode (Cathode)

Wrap a surface into a 3D structure maximizing kinetics and capacity



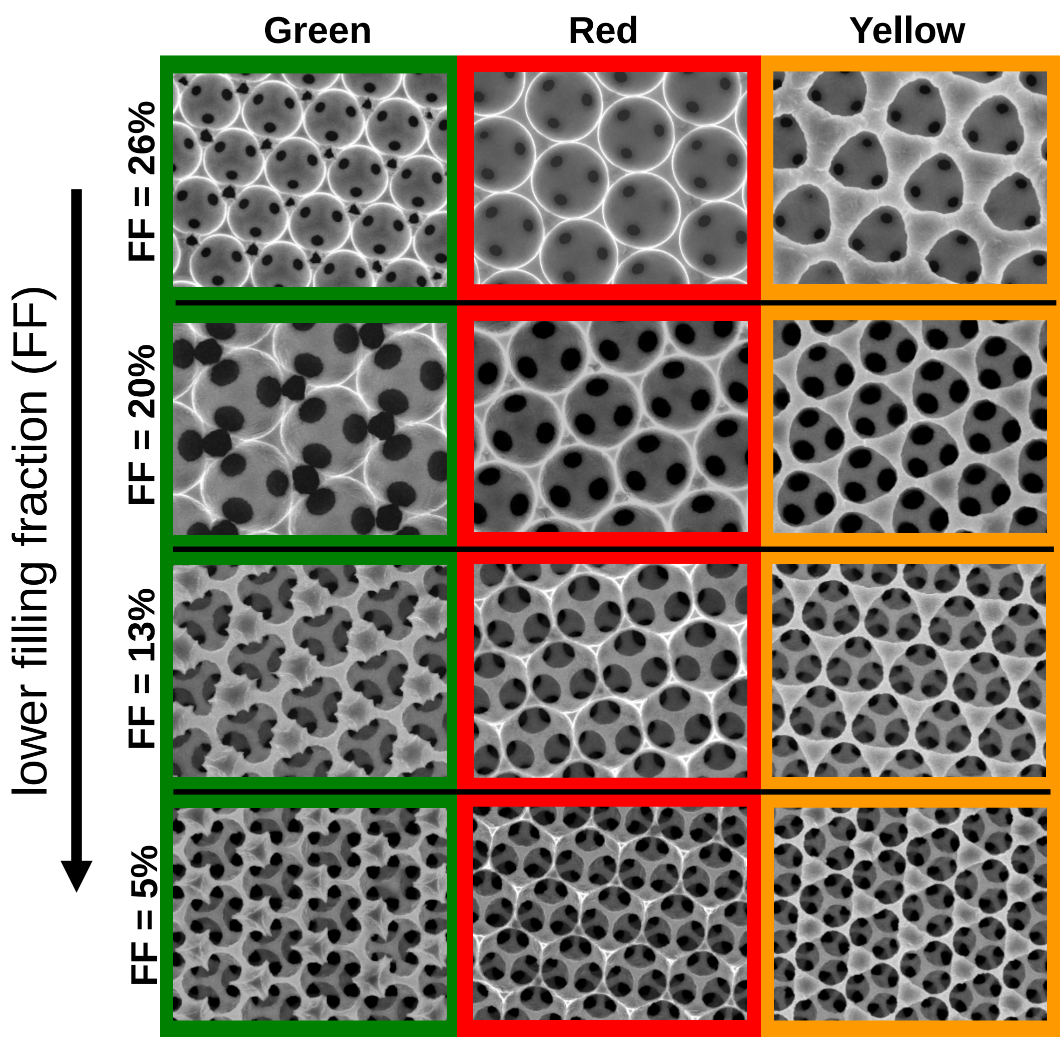
1) **Facile ion transport through connected pore network**
2) **Short solid-state ion diffusion length**
3) **Rapid electrochemical processes (large surface area)**
4) **Low resistance electrical network**



Zhang, Braun *Nature Nanotechnology*, **2011**

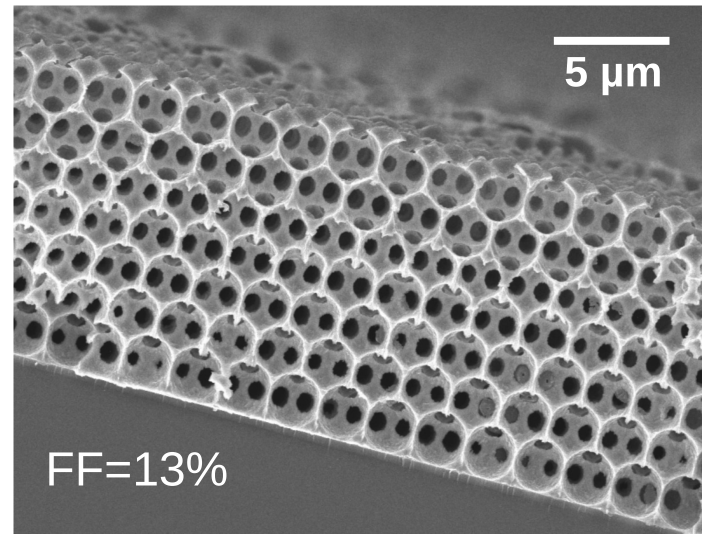
3-D Metal Foams – The Electrode Support

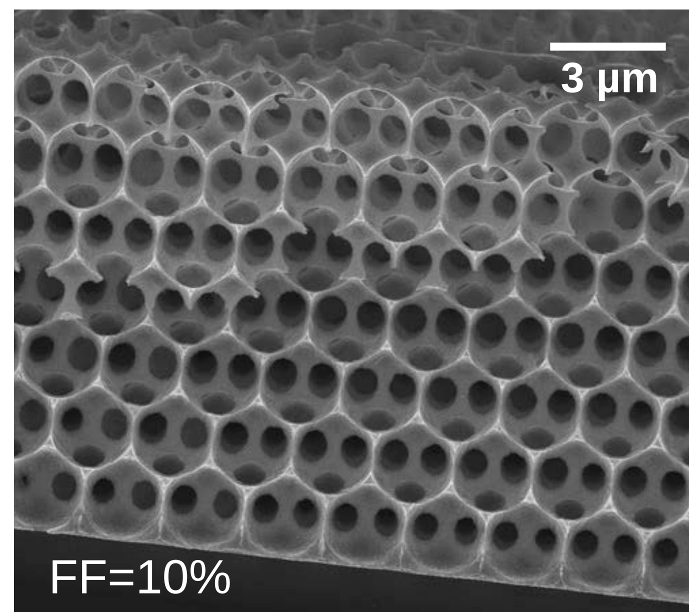
95% Air Metal Foams Possible



Formed via self-assembly followed by electroplating

Side Views

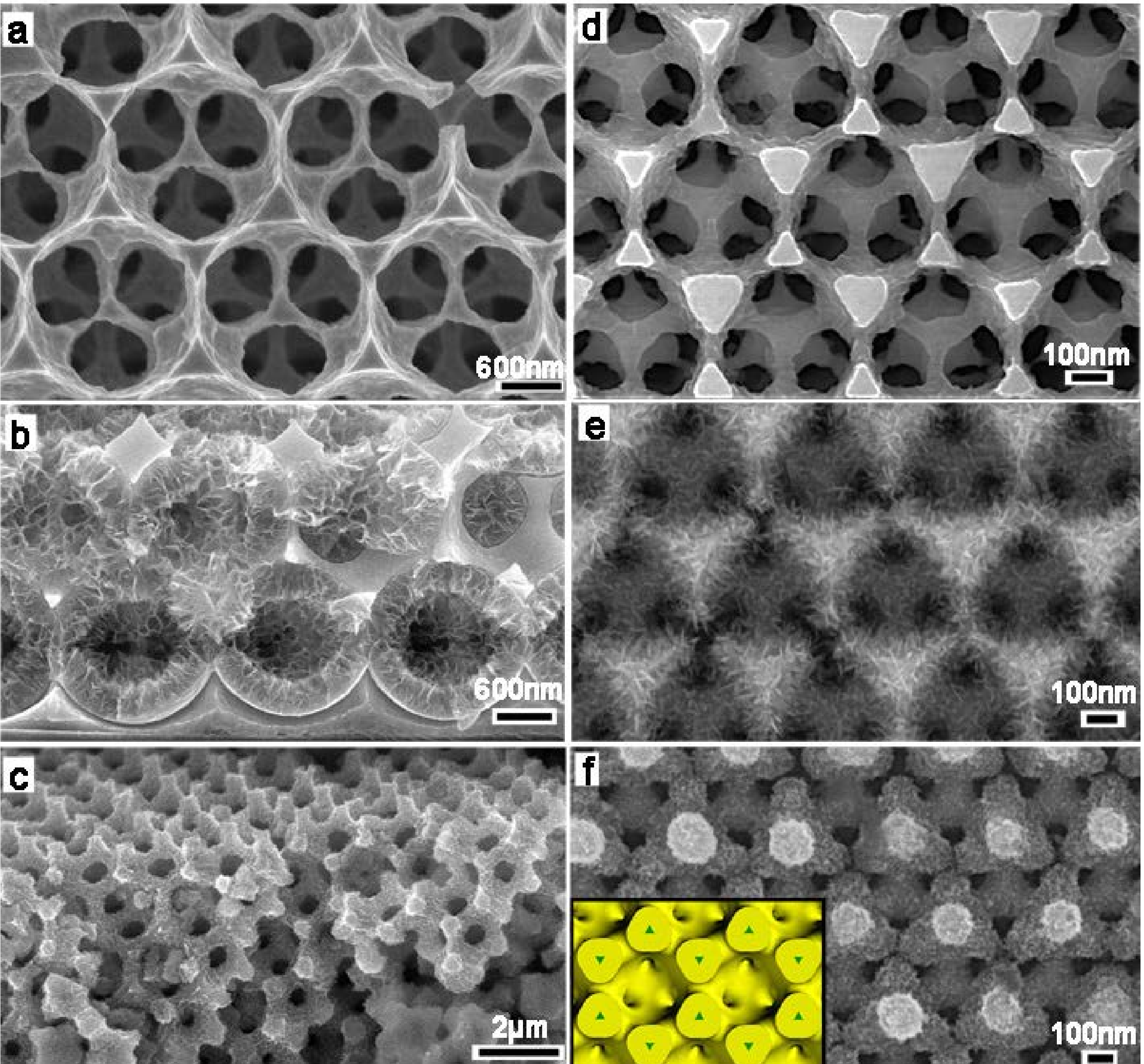


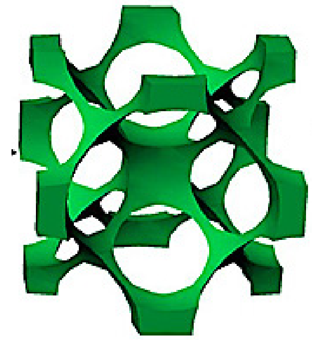


X. Yu, Braun, et al. *Advanced Materials* (2007)

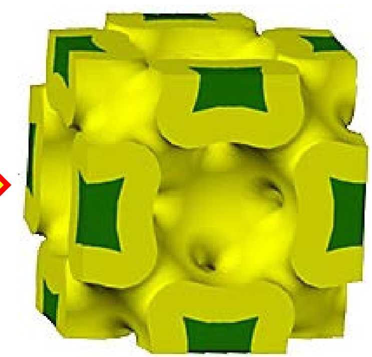
Bicontinuous Battery Electrode (Cathode)

NiMH (NiOOH) | **Li-ion ($LiMnO_2$)**





Metal Framework



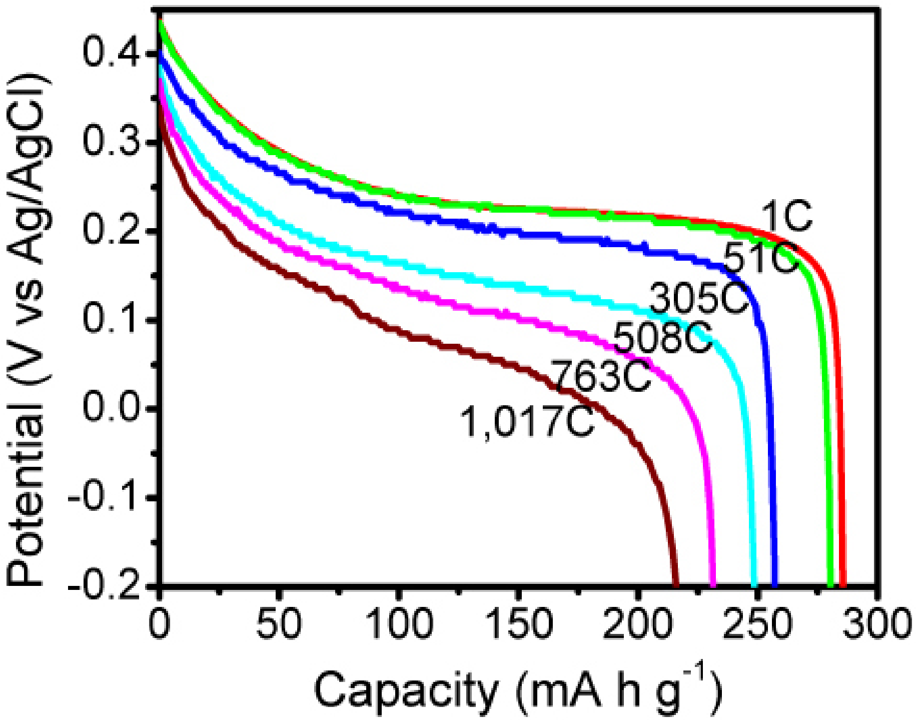
Coated Framework

Ultrafast Discharge Characteristics (high power)

Nickel Metal-Hydride Cathode

75% capacity retention at 1000C discharge!

(1C is the current required to fully discharge the battery in 1 hour, 1000C is the current required for a full discharge in ~3.6 sec.)

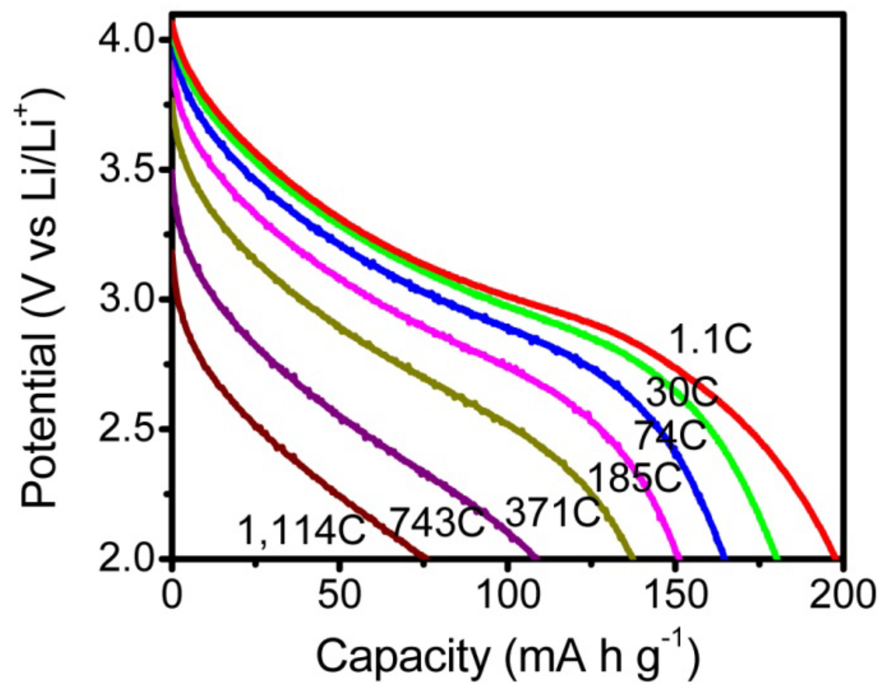


In a typical NiMH cathode, capacity drops dramatically above ~25C

Electrochem. Solid-State Lett. 2007, 10, A56-A59

Lithium-ion Cathode

Significant capacity retention at 371C (complete discharge in ~10 sec.)



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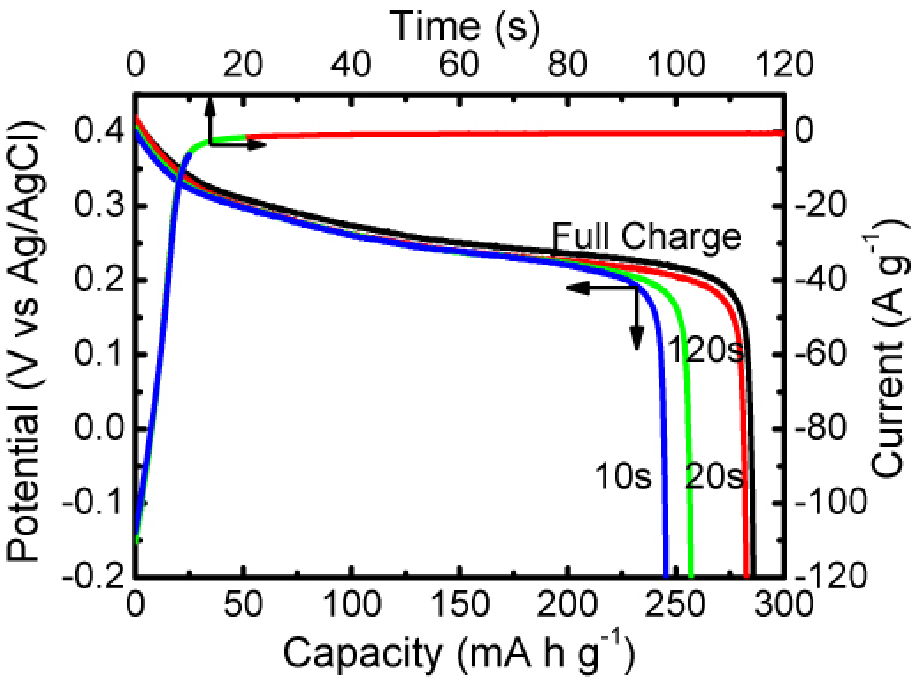
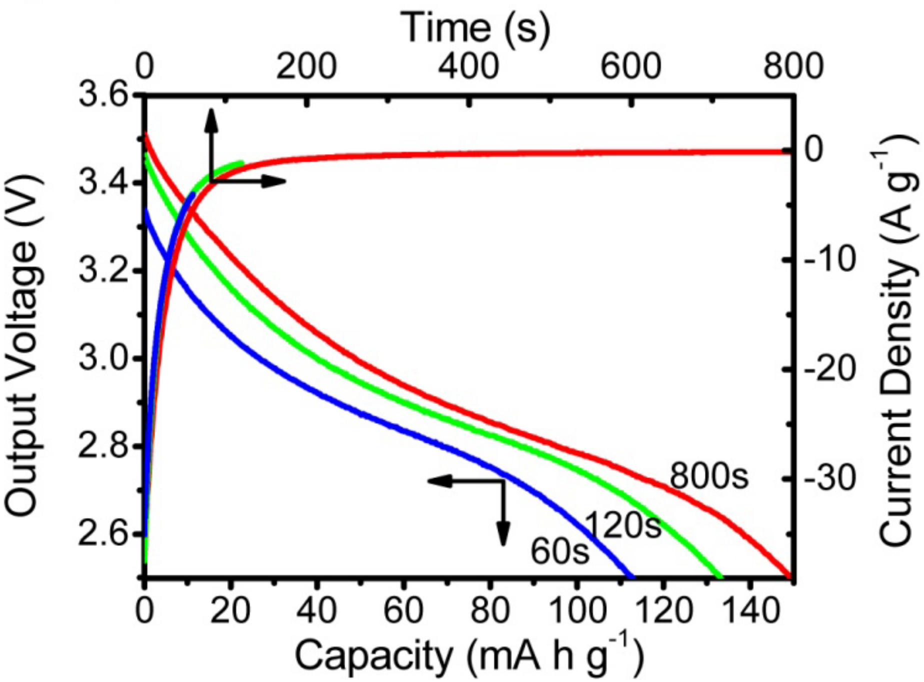
Ultrafast Charging

NiOOH cathode



Potentiostatic charging (0.4V vs Ag/AgCl)
3C discharge
Nearly complete charge after 120 sec.

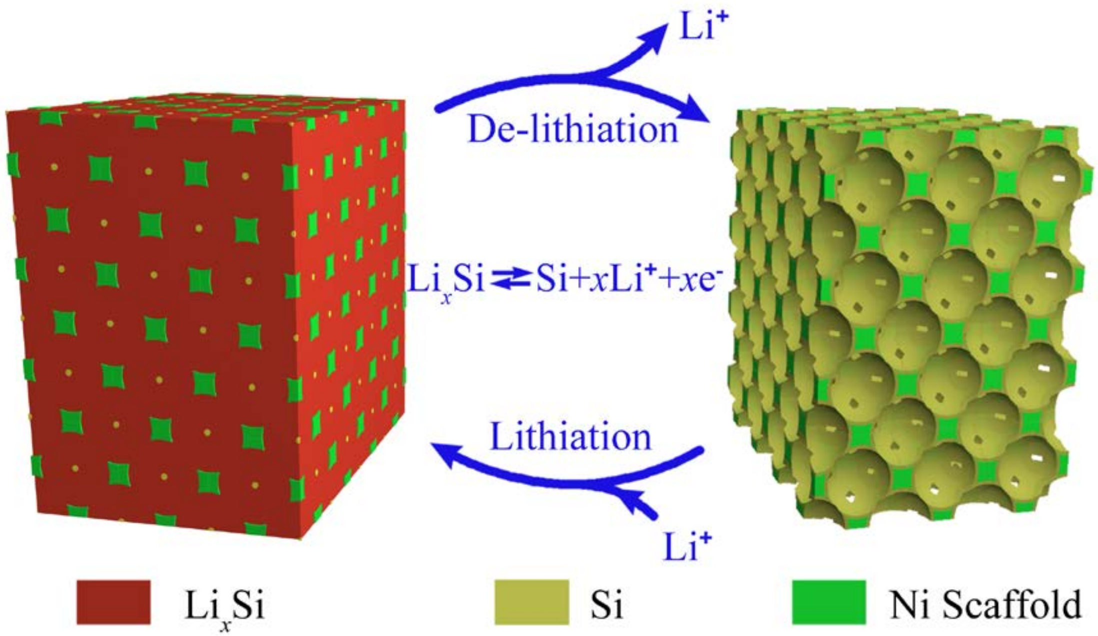
Nanostructured Lithiated MnO_2/Graphite Cell

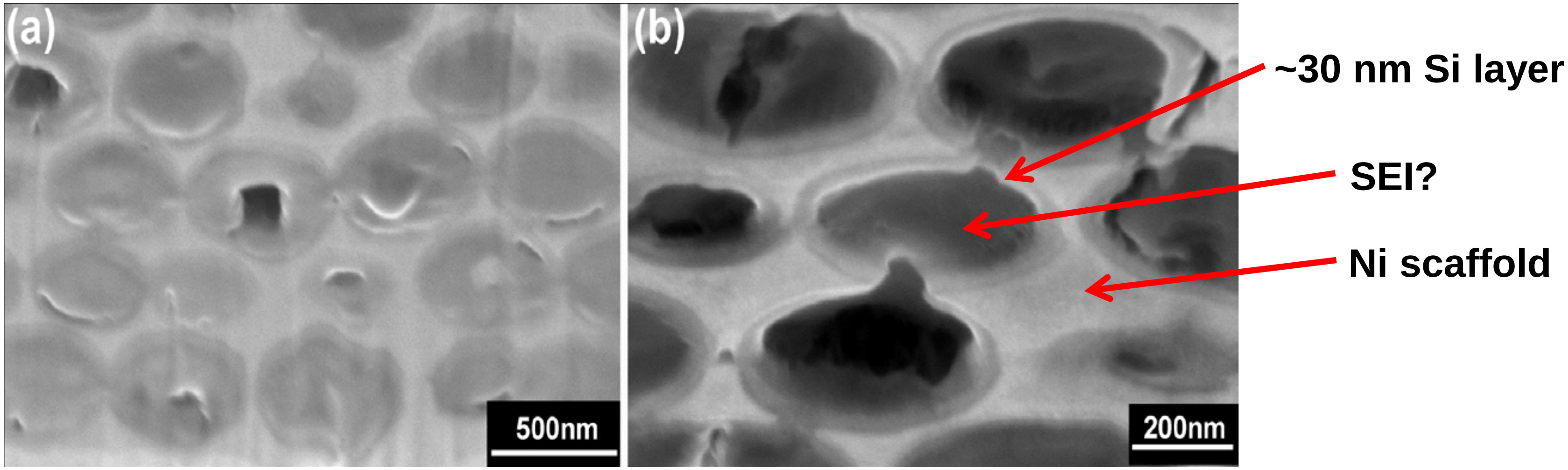


Potentiostatic charging (3.5V)
3C discharge
Nearly complete charge after 120 sec.

Zhang, Braun *Nature Nanotechnology*, **2011**

New Materials: Bicontinuous Silicon Anodes

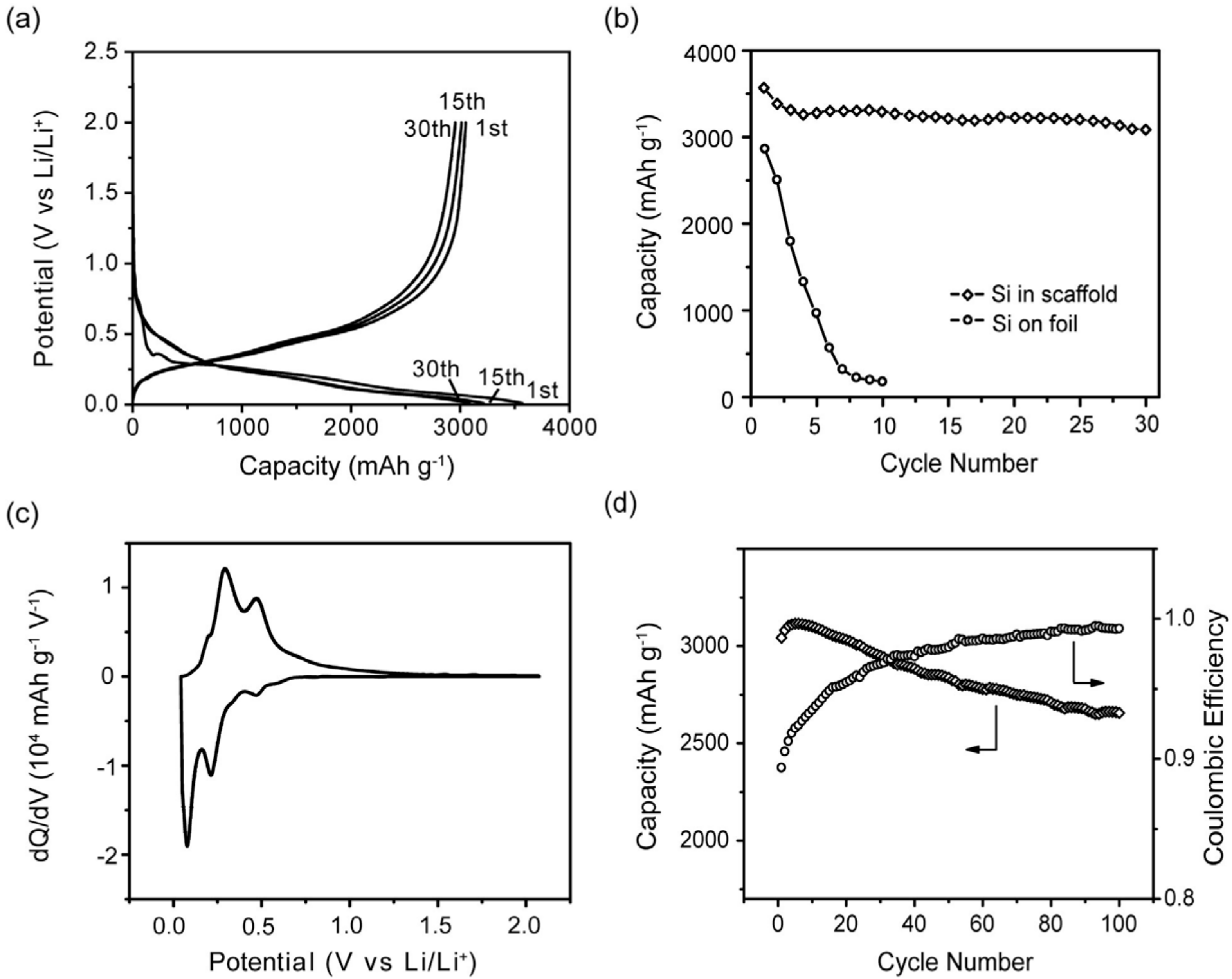




lithiated **de-lithiated**

Zhang, Braun, et al. *Nano Letters*, **2012**

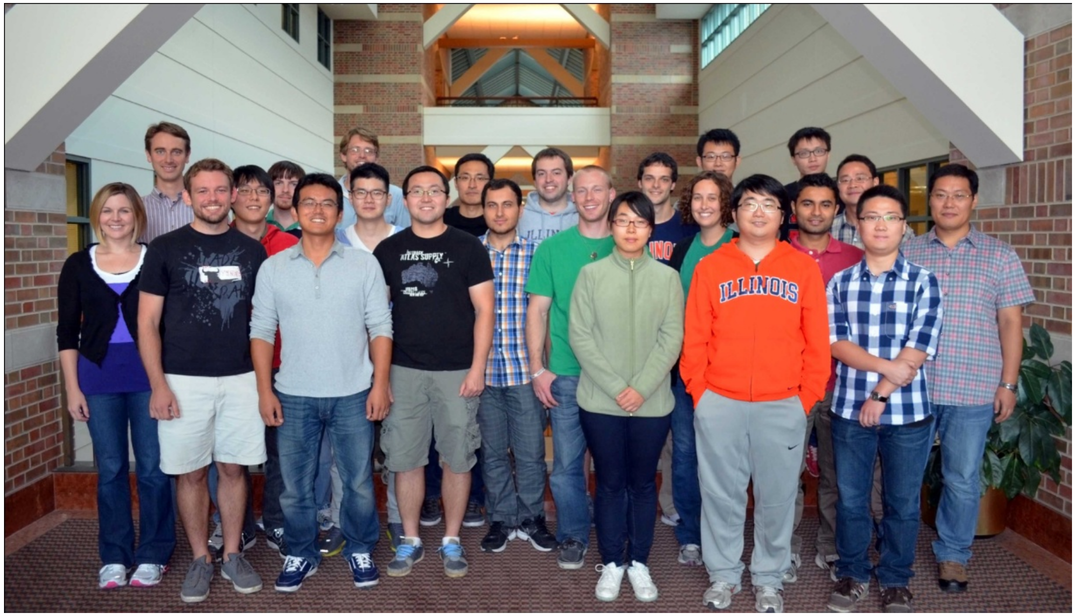
Bicontinuous Silicon Anodes



Concluding Thoughts

- Nanotechnology can have “macroscopic” impact
  - Providing new properties important
  - Important to consider what will provide high value added
  - Minimize necessity of top-down processing ($$)
- Ask, what are the critical needs of industry?
  - Mechanical
  - Thermal
  - Energy storage/harvesting
  - Optical
- Long-term goal: make nanotechnology “invisible”
  - Boring
  - Commonplace
  - Normal
- Think beyond electronic materials and medicine

Acknowledgements



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