Bridging Technologies

Paul V. Braun

pbraun@illinois.edu
http://braungroup.beckman.illinois.edu

Department of Materials Science and Engineering,
Frederick Seitz Materials Research Laboratory, and Beckman Institute

University of Illinois at Urbana-Champaign, Urbana, IL

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“new form factors of matter lead to new functions”
Google: “Nanotechnology” images (June 7, 2012 – June 7, 2013)

Products: 3
(all thin films)

Tiny things: 10+

How to reverse the ratio?
Going Beyond 2D

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 the value added component.

“It’s hard to get excited about 2-D”
Macroscopic Nanotechnology

Examples of Macroscopic Nanotechnology

• 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

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.
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


### Heat Transfer
Ultralow thermal conductivity in self-assembled 3D structures


### Rechargable Batteries
Ultrahigh power density through electrode nanostructuring

Multibeam Holography: Macroscopic Nanostructuring

2 beams (1D)  3 beams (2D)  4 beams (3D)

\[ I = \sum_j E_j^2 + \sum_{i<j} 2E_i E_j \cos \theta_{ij} \cos[(K_i - K_j)r + \varphi_{0i} - \varphi_{0j}] \]

- power
- polarization
- wavevector
- phase

Reflectance vs. wavelength

- beam geometry
- wavelength
- refractive index

SEM cross-section

2µm

(111)
Multibeam Interference Patterning of Materials

Low cost, large area periodic structures

Interference pattern → Resulting Structure

Remove unexposed material

4 Laser beams

Sample

Polymer Photoresist (SU-8)

Chen, Braun, et al. APL 2007
First example of:
* Electrically pumped emission from a 3D PC LED
* Epitaxial growth of porous 3D semiconductors

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

Limits to Thermal Conductivity (in solids)

How does nanotechnology relate to thermal conductivity?

- Thermal conductivity $\Lambda$ is a property of the continuum

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

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

$$\mathcal{J} = G \Delta T$$

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

Potential Impact
- Thermoelectrics
- Insulation
- Thermal switch
- Thermal isolation
- Thermal solar

Layered WSe$_2$
(vacuum deposited)

Cahill Science 2007
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

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
Pathways to Increase Power & Energy Density

1. New Materials

2. Structure Design
   - 3D electrode architecture
   - Large surface area
   - Thin film of active materials

REDUCE TRANSPORT LENGTHS

- Nanowires
  - Efficient 1D electron transport
  - Facile strain relaxation
  - Good contact with current collector

- Nano-pillar current collectors
  - Cu nanorods
  - Cu cathode

3D Bicontinuous Electrodes

Chemical Society Rev. 2009, 38, 226

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

Opal Template → Electrodeposit Nickel → Remove Template → Electropolish Nickel → Electrodeposit Active Materials

Zhang, Braun Nature Nanotechnology, 2011
3-D Metal Foams – The Electrode Support

95% Air Metal Foams Possible

Green | Red | Yellow

- FF = 26%
- FF = 20%
- FF = 13%
- FF = 5%

Formed via self-assembly followed by electroplating

FF = 13%

FF = 10%

FF = 10%

Bicontinuous Battery Electrode (Cathode)

<table>
<thead>
<tr>
<th>NiMH (NiOOH)</th>
<th>Li-ion (LiMnO$_2$)</th>
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<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
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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


Lithium-ion Cathode

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

NiOOH cathode

Nanostructured Lithiated MnO₂/Graphite Cell

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

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

Zhang, Braun Nature Nanotechnology, 2011
New Materials: Bicontinuous Silicon Anodes

\[ \text{Li}_x\text{Si} \rightleftharpoons \text{Si} + x\text{Li}^+ + xe^- \]


- Lithiated: ~30 nm Si layer
- De-lithiated: SEI?
- Ni scaffold

(a) Lithiated
(b) De-lithiated

Scale: 500 nm and 200 nm

Bicontinuous Silicon Anodes

(a) Graph showing potential (V vs Li/Li⁺) vs capacity (mAh g⁻¹) for different cycles (1st, 15th, 30th).

(b) Graph showing capacity (mAh g⁻¹) vs cycle number for Si in scaffold (-) and Si on foil (○).

(c) Graph showing dQ/dV (10⁻⁴ mAh g⁻¹ V⁻¹) vs potential (V vs Li/Li⁺).

(d) Graph showing capacity (mAh g⁻¹) vs cycle number with a decrease in efficiency (Coulombic Efficiency).
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
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