Comments on NASA's Draft Nanotechnology Roadmap
Technology Area 10

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Gary Rubloff - Background

- **Current – University of Maryland (1996-present)**
  - *Founding Director, Maryland NanoCenter*
  - *Director/PI, DOE EFRC Nanostructures for Electrical Energy Storage*
  - *Research in nanostructure synthesis for energy storage and generation; atomic layer deposition; biofabrication and bioMEMS*

- **Past**
  - *IBM Research & management (1973-93)*
  - *NCSU (1993-96)*
  - *Director, Institute for Systems Research (NSF-ERC), U. Maryland (1996-2001)*
  - *Research in ultraclean integrated processing, in-situ sensing & process control, semiconductor technology & manufacturing*

Maryland NanoCenter (2004)

Bringing world-class <u>scientists and engineers</u> as well as <u>fabrication and characterization infrastructure</u> together to drive technology and fundamental understanding in nano

Institute for Research in Electronics & Applied Physics

Engineering
A. James Clark School of Engineering

Sciences
College of Computer, Mathematical and Natural Sciences

MARYLAND NANOCENTER

Research
- Faculty research groups
- Partnerships
- Collaborative research laboratories

Education
- Nano educational programs
- Outreach

Industry & govt
- One-stop shopping
- Partners' Program

Infrastructure
- Initiatives
- Shared user facilities
- Operations – web, facilities, information

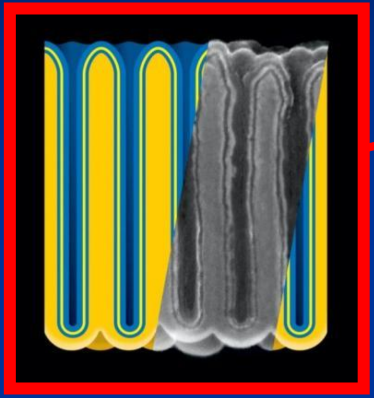
Nanofabrication (FabLab)

Nanocharacterization (NispLab)

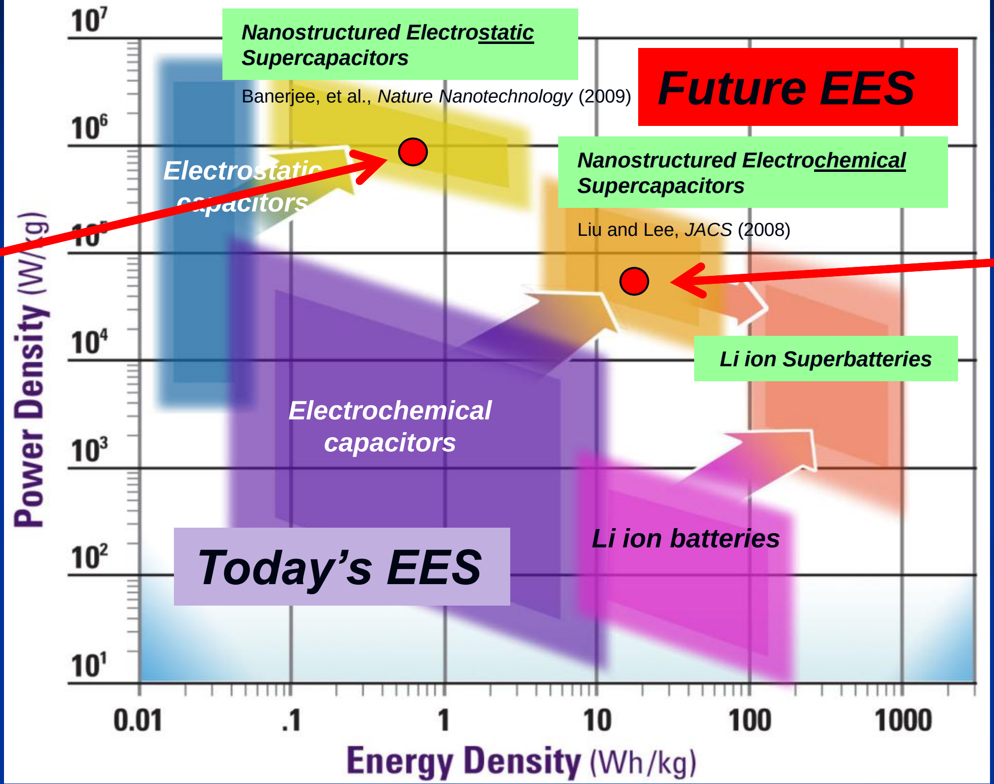
Shared experimental facilities

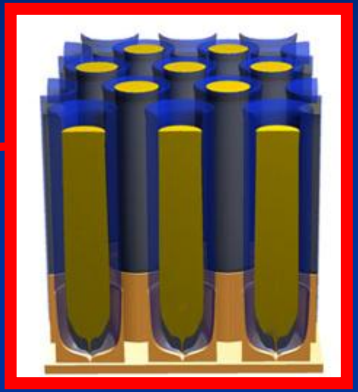
80+ faculty groups
Top 10 rankings (Small Times)
www.nanocenter.umd.edu

Advances from Nanotechnology



AAO-ALD embedded metal-insulator-metal device





Free-standing MnO_2/PEDOT coaxial nanowires

Nanostructures for next-generation electrical energy storage

- Massively parallel nanoengineered devices formed within nanopores
- Much higher power and higher energy density

Nanostructures for Electrical Energy Storage (NEES)

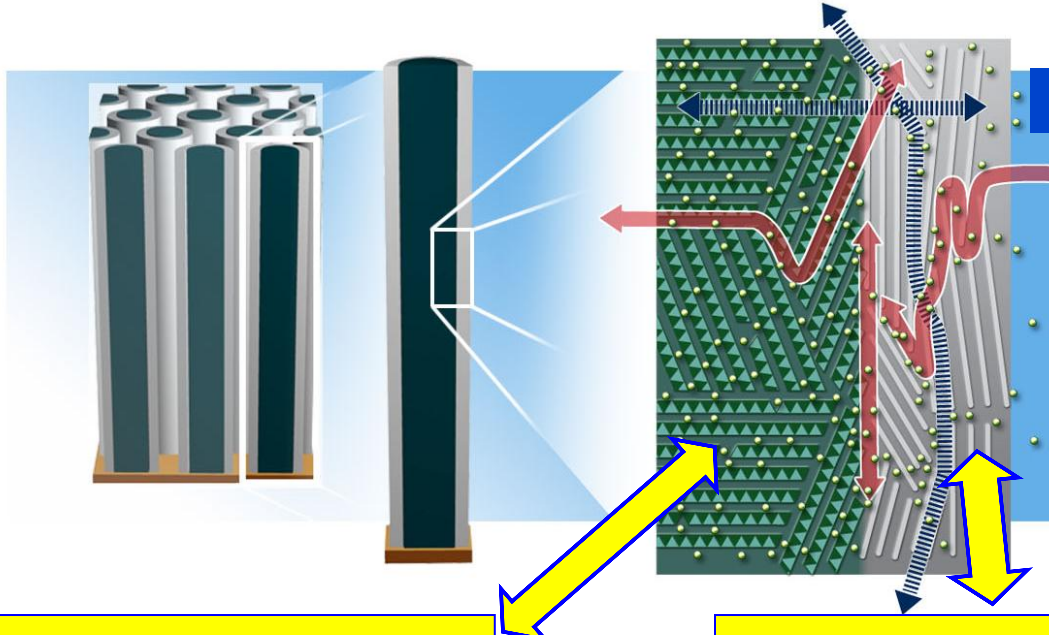
A Department of Energy Energy Frontier Research Center

Initial $14M over 5 years

The EFRC will pursue multifunctional nanostructures as the basis for a next generation of high performance electrical energy storage to:

- **power electric vehicles over long distances and recharge quickly, and**
- **capture, hold, and deliver energy from renewable sources.**

Heterogeneous Multifunctional Nanostructures



EFRC's – science
Opportunity for synergies

Charge storage material

- High energy density
- Low electrical, ionic conductivity
- Low mechanical stability

Cathode: $LiMnO_2$, $LiFePO_4$, $LiCoO_2$

Anode: Si

Transport & support material

- High electrical conductivity
- High mechanical stability
- High ionic conductivity

Low-D carbon, conducting polymer

Executive Summary → Energy Generation and Storage

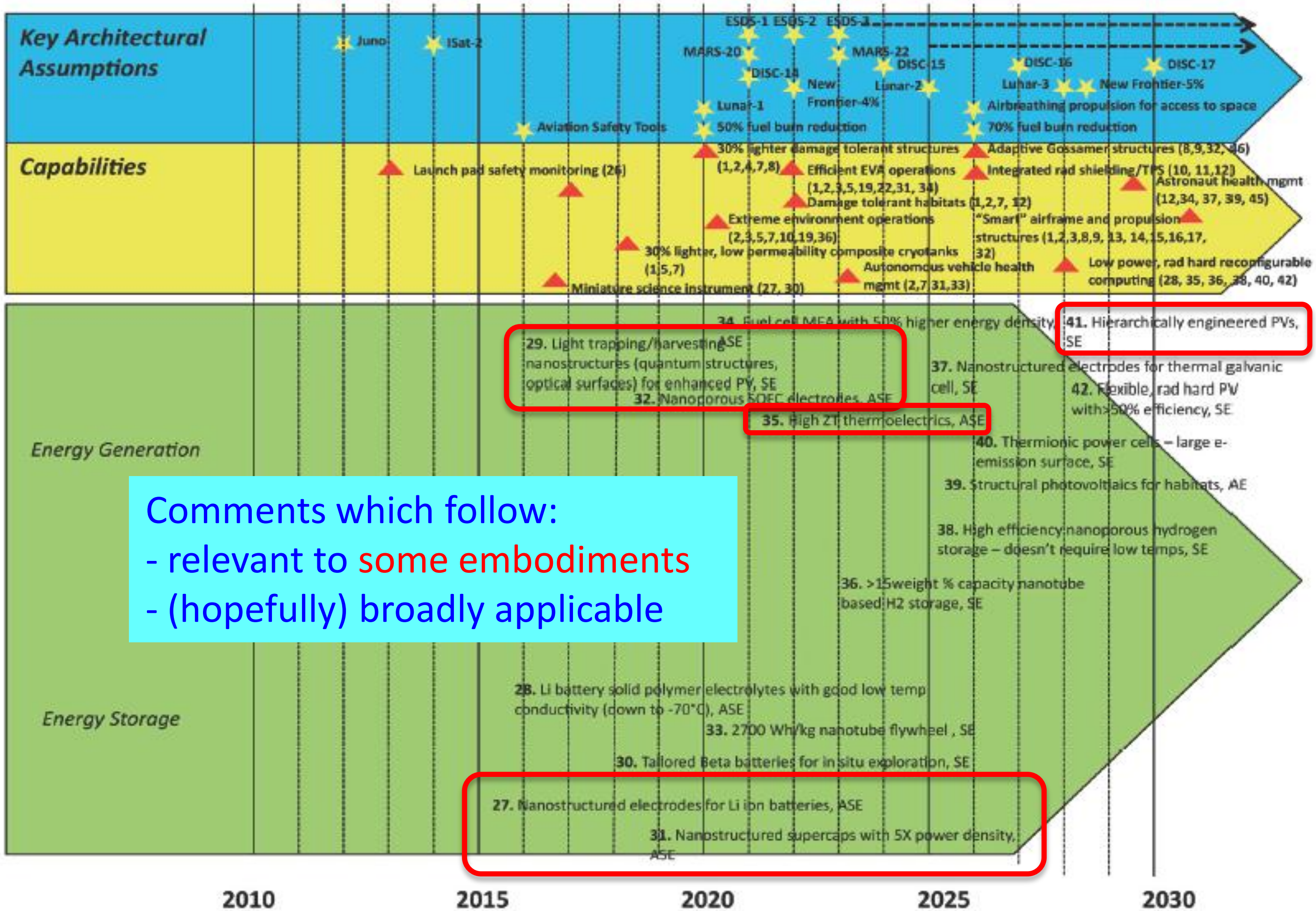
1. Reduced vehicle mass
2. Improved functionality and durability
3. **Enhanced power generation and storage** and propulsion
4. Improved astronaut health management
5. Development of scalable methods for the controlled synthesis (shape and morphology) and stabilization of nanopropellants
6. **Development of hierarchical systems integration tools across length scales (nano to micro)**
7. **Development of integrated energy generation, scavenging and harvesting technologies**
8. Development of nanostructures materials 50% lighter than conventional materials with equivalent or superior properties
9. Development of graphene based nanoelectronics

1. Power generation & storage

3. Hierarchical systems

2. Integration of components

Energy Generation, Storage and Distribution



Comments which follow:
- relevant to some embodiments
- (hopefully) broadly applicable

Sandia National Laboratories
UNIVERSITY OF FLORIDA
YALE
Los Alamos NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY Office of Basic Energy Sciences

1. Power Generation and Storage

Enhanced Power Generation and Storage and Propulsion

Nanotechnology affords the possibility of creating high surface area materials with inherently higher surface activities and reactivity that could significantly enhance the performance of batteries and fuel cells and improve the handling characteristics of propellants. Use of nanostructured metal catalysts in PEM fuel cells could increase their energy density by 50%. Use of nanoporous materials and nanocomposites could enable the development of new batteries that could operate over a wide temperature range, from -100 to 100°C, to provide surface power for rovers and EVA suits. Nanoscale metal based propellants could replace cryogenic propellants and hypergolics leading to simplified storage, transfer and handling and reduced launch pad and in-space operational requirements.

- **Nanostructures with high surface area, enhanced reactivity**
- **Nanomaterials engineered to further enhance surface reactivity**

- *Design guidelines based on physics & chemistry at the nanoscale*
- *Processes, equipment, and process integration*
- *Mechanisms controlling defects and reliability*

2. Integration of Nanocomponents

Development of integrated energy generation, scavenging and harvesting technologies.

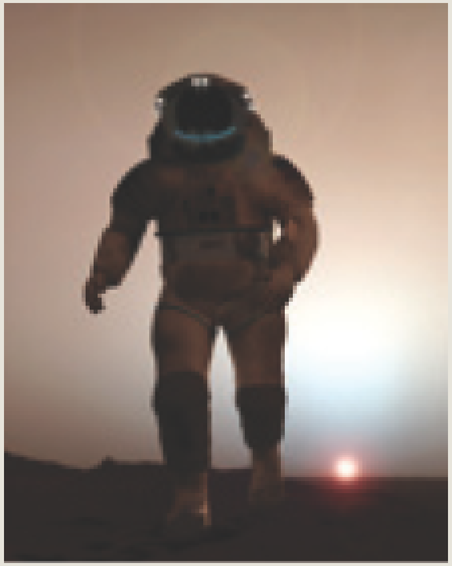
The use of quantum structures (dots and rods) to enhance absorption of solar energy and carbon nanotubes to improve charge transport and develop transparent electrodes will enable the development of flexible, radiation hard solar cells with greater than 50% efficiencies. Nanostructured electrode materials, self-assembled polymer electrolytes and nanocomposites will enable the development of new ultracapacitors with 5 times the energy density of today's devices and new, lighter and safer lithium batteries. Incorporation of flexible, conformal photovoltaics and improved efficiency, lightweight, flexible batteries into EVA suits and habitats would lead to enhanced power and reduced mass and enable longer duration EVA sorties and missions. Developments needed in this area include functionalization chemistries to allow incorporation of carbon nanotubes into devices, reliable, repeatable large scale manufacturing methods, as well as approaches to enhance radiation tolerance and nanoengineered coatings to prevent dust accumulation. An increased NASA investment in this area can be leveraged against ongoing efforts at Energy Frontier Research Centers as well as the upcoming NNI Solar Energy Signature Initiative.

- **Integration of nanoscale components into nanodevices**
  - *Solar absorption & transport*
  - *Electrodes & electrolytes*
- **Flexible substrates, platforms**
- **Large scale manufacturing**
- **Defects & reliability**

- *Integration of multiple energy functions at nanoscale (and above)*
- *Manufacturing processes & equipment*
- *Defect & reliability management strategies*

Integration of Nanocomponents

Grand Challenge - Structures with Integrated Energy Generation and Energy Storage (2017-2022)



Significant progress is currently being made in the areas of energy generation and energy storage using nanotechnology. The extremely high surface area and high reactivity of nanomaterials allows for power and energy densities far above that of conventional materials. One step forward in the field of energy related nanotechnology is to integrate multiple systems together allowing for an overall mass savings greater than each individual component could achieve on its own. The development of high efficiency organic/polymer photovoltaics would enable the production of conformal solar cells that could be incorporated into the exterior of a habitat or rover to provide auxilliary power. Developments needed in this area include functionalization chemsitries to allow incorporation of carbon nanotubes into these devices to enhance energy transfer and their use in the development of flexible, transparent nanotube or graphene electrode materials. Incorporation of quantum dots or structures will lead to a broader use of the available solar spectrum. Methods to enhance the radiation tolerance of these devices and nanoengineered coatings to prevent dust accumulation are also needed. Flexible, safe lithium ion batteries could also be incorporated into EVA suit garments or habitats leading to signficant weight savings. The development of new, flexible solid polymer elecrolytes with the capability of operating at temperatures as low as -60°C could be enabled through the use of self-assembly processes, nanoporous polymers and nanoscale additives. Improvements in the electrochemical efficiencies of these batteries could be achieved through the development of high surface area electrode materials. The integration of both energy generation and subsequent energy storage allows for greatly reduced overall mass, helping to enable new long-duration missions that need additional power.

3. Hierarchical Systems

Development of hierarchical systems integration tools across length scales (nano to micro).

High sensitivity and low power sensors (ppb to ppm level at μW - nW), high-speed (hundreds of GHz) electronics, and measurement enabling nanocomponents for miniature instruments are bound to interface with larger (micro, meso, and higher) systems to accomplish desired operation. System integration issues at that level can pose significant challenges and require the design of devices and processes that are suitable for both nano and microstructure fabrication schemes (chemical, thermal, and mechanical issues), structural integration techniques that are mechanically and thermally robust, and the development of efficient interconnects. In addition, a better understanding of factors that can degrade system performance, such as the effect of nano-micro-meso interfaces, packaging, and signal interference at component level, is needed along with effective mitigation strategies. NASA investments in meeting these challenges can be leveraged with those of other federal agencies to accelerate developments in this area and address NASA specific needs.

- **Nano-to-macro component integration**
- **Device & process integration coupling micro- and nano-fabrication**
- **Packaging and system-level performance**

- *Hierarchical modeling and simulation to inform system design*
- *Concurrent development at single process and system architecture levels*
- *Adaptive modeling architectures that exploit growing knowledge at the nanoscale*

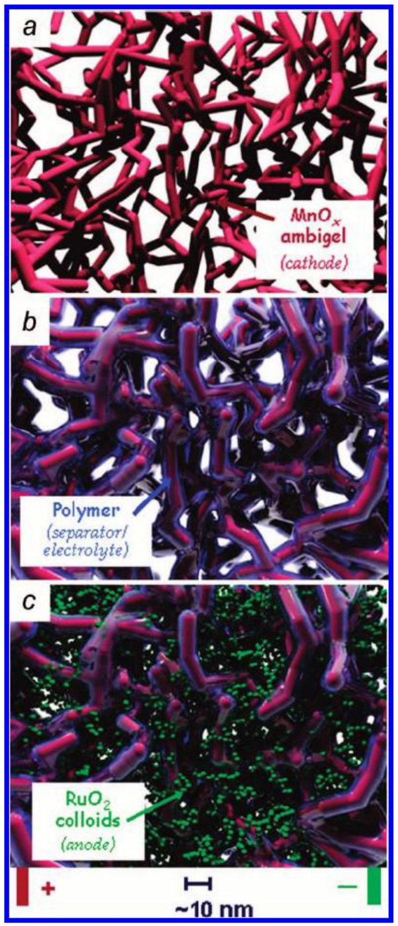
Hierarchical Systems

Grand Challenge - Hierarchical System Integration Issues (Nano to Micro to Meso) (2023-2028)

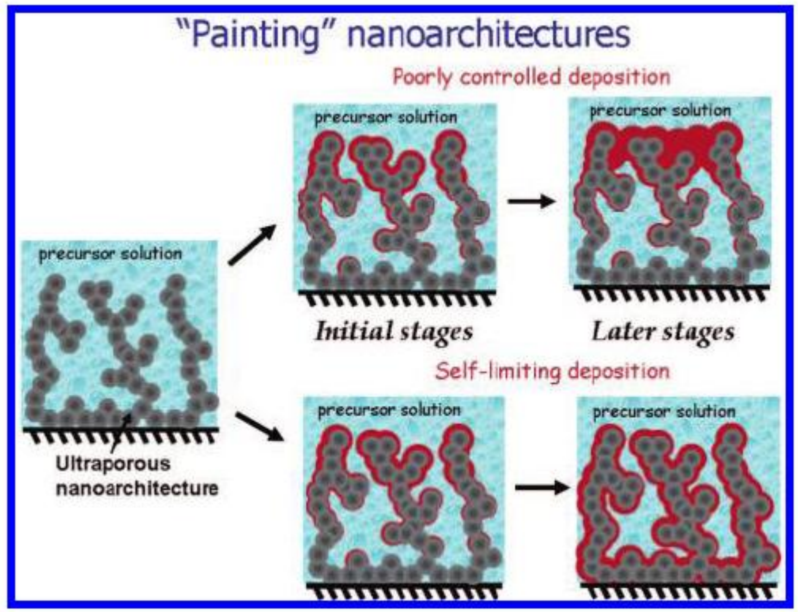
For any given Observatory-development, system-integration can be one of the most challenging aspects of the development. Facilitation of intra-instrument, intra-spacecraft, and instrument to spacecraft communication, power, data & telemetry collection, transfer, & storage, are both essential and highly complicated functions which must be enabled for any mission to perform effectively. The effective integration of nanotechnology products with applications requires resolving hierarchical system integration issues. It is expected that nanocomponents function as part of microsystems, or mesosystems that are in effect can be either stand-alone systems or sub-systems. High sensitivity sensors (ppb to ppm level), high-speed (hundreds of GHz) electronics, and measurement enabling nanocomponents for miniature instruments are bound to interface with larger (micro, meso, and higher) systems to accomplish desired operation. System integration issues at that level can pose significant challenges including: the design of devices and processes that are conducive for both nano and microstructure fabrication schemes (chemical, thermal, and mechanical issues), structural integration techniques that are mechanically and thermally robust, development of efficient interconnects, effect of nano-micro-meso interfaces, packaging, and signal interference at component level that can potentially degrade system performance. Overcoming these challenges systematically is critical, and it enables introduction of nanotechnology-based systems as identified in this roadmap into future NASA missions.

"Random" Heterogeneous 3-D Nanostructures

Scheme 2. Schematic Showing the Three Steps Needed to Assemble a Fully Interpenetrating Nanoscale Battery in Which All Three Functional Components (cathode–ion-conducting separator–anode) Are Sized on the Order of 10 nm and Are Separated by <50 nm



Scheme 1. Cross-Sectional Illustration of Poorly Controlled versus Self-Limiting Deposition onto Aperiodic Nanoarchitectures from Solution-Phase Precursors



J. W. Long, D. R. Rolison, *Acc Chem Res* 40 (9), 854-862 (2007)

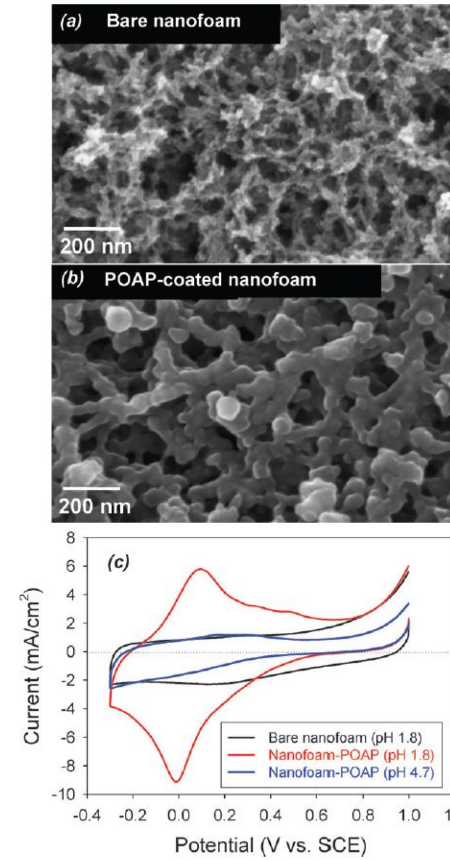
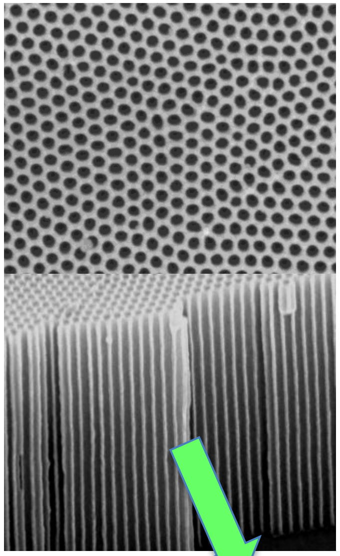


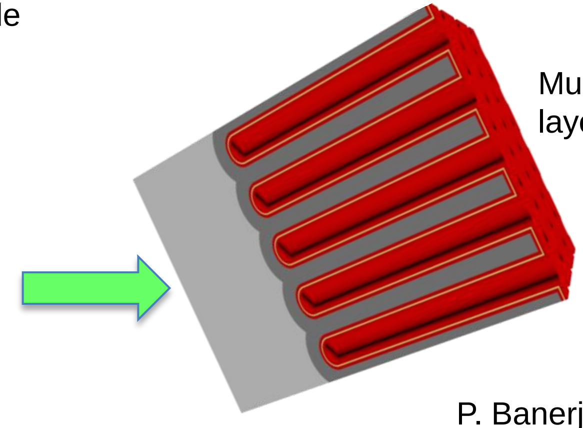
Fig. 7 Scanning electron micrographs for (a) bare and (b) carbon nanofoam paper coated with poly(*o*-aminophenol), POAP; and (c) cyclic voltammetry at 2 mV s^{-1} for the bare and POAP-coated carbon nanofoams in aqueous electrolytes of different pH.

D.R. Rolison et al, *Chem Soc Revs* 38 (1), 226-252 (2009)

“Regular” Heterogeneous 3-D Nanostructures

Nanoporous anodic Al oxide
10^{10} nanopores/cm^2

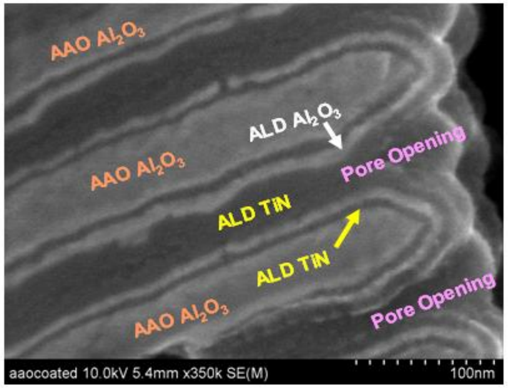


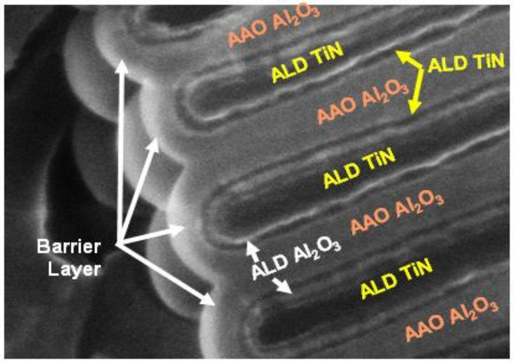


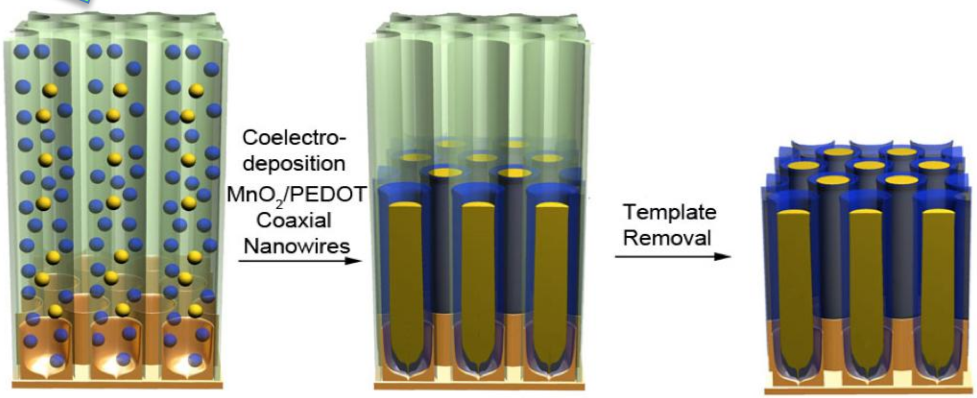
Multilayer atomic layer deposition

P. Banerjee et al, *Nature Nanotechnology* (2009)

SEM images







Liu & Lee, *J. Am. Chem. Soc.* (2008)

Nanostructures: Regular or Random?

Regular (periodic)

- Rapidly growing research activity
- More amenable to characterization and understanding
- Tighter distributions for manufacturing

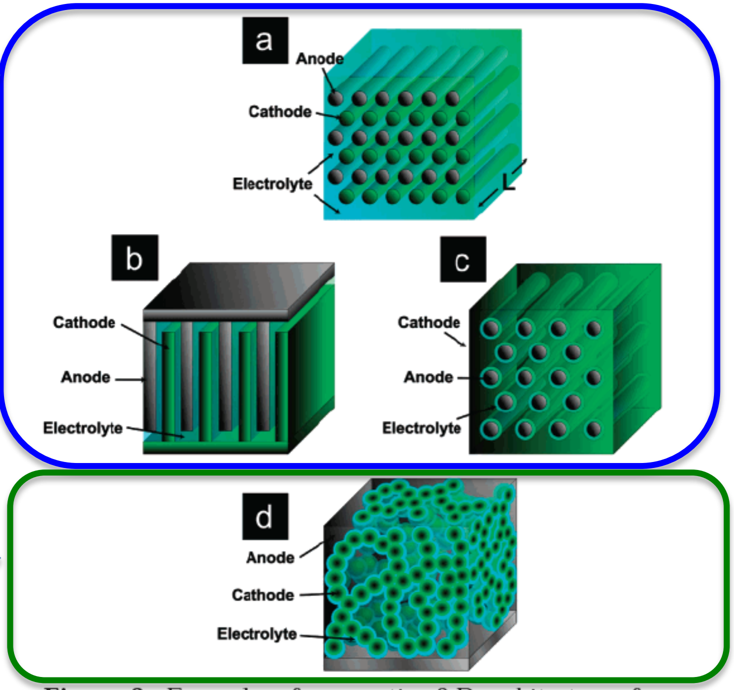


Figure 2. Examples of prospective 3-D architectures for charge-insertion batteries: (a) array of interdigitated cylindrical cathodes and anodes; (b) interdigitated plate array of cathodes and anodes; (c) rod array of cylindrical anodes coated with a thin layer of ion-conducting dielectric (electrolyte) with the remaining free volume filled with the cathode material; (d) aperiodic "sponge" architectures in which the solid network of the sponge serves as the charge-insertion cathode, which is coated with an ultrathin layer of ion-conducting dielectric (electrolyte), and the remaining free volume is filled with an interpenetrating, continuous anode.

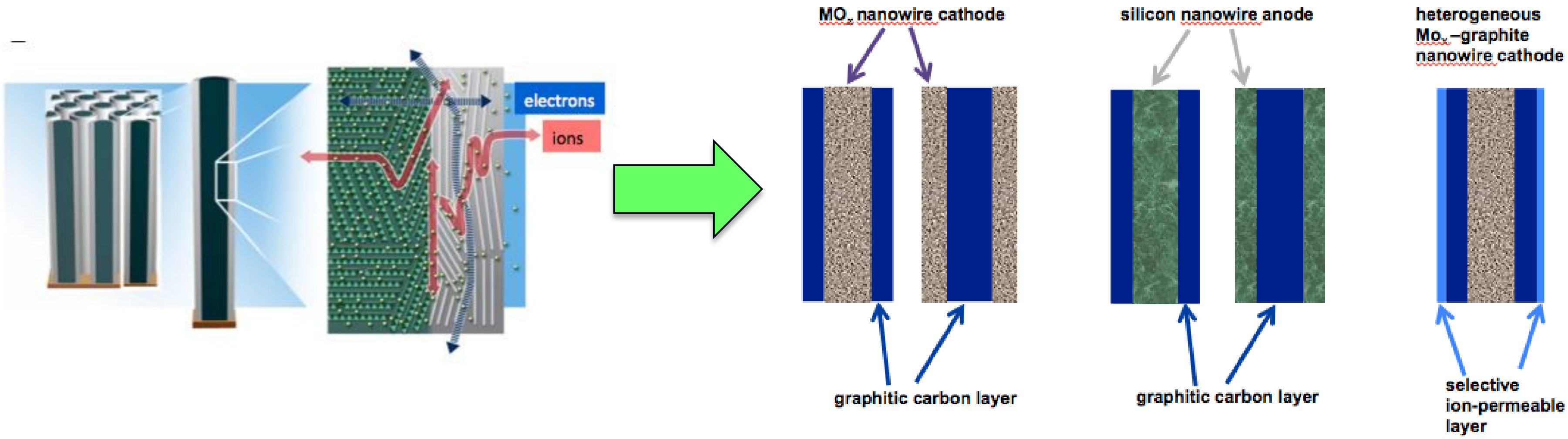
J.W. Long, B. Dunn, D. R. Rolison and H. S. White, *Chem Rev* 104, 4463–4492 (2004)

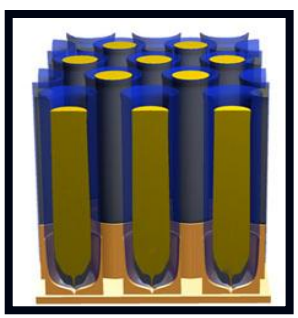
Random (aperiodic)

- Larger experience base
- Easier, cheaper manufacturing processes
- Potentially higher surface area

Upon scaleup to unprecedented, massive integration levels, what factors will dominate?

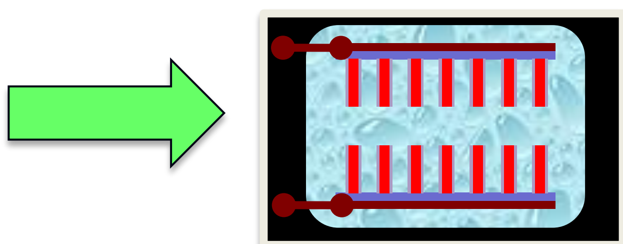
Exposed Nanostructures





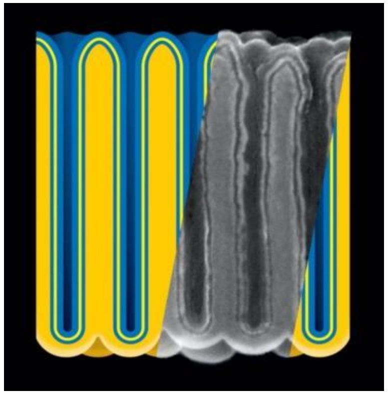
Nanowire electrochemical supercap
Liu & Lee, *J Am Chem Soc* 130, 2942 (2008)

Nanowire electrode supercap



Active interfaces are exposed to fluids
- ***batteries***
- ***supercapacitors***
- ***fuel cells***
- ***thermoelectrics***

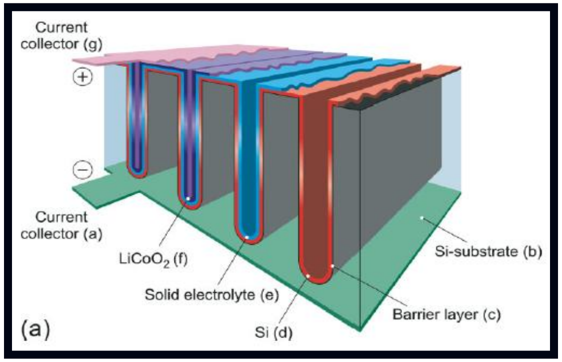
Embedded Nanostructures



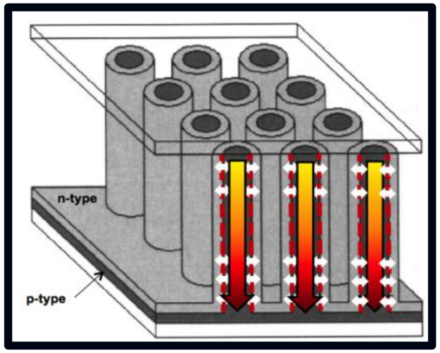
Nanotube electrostatic supercap
Banerjee et al, *Nature Nanotechnology* 4, 292 (2009)

Active interfaces are buried within solids

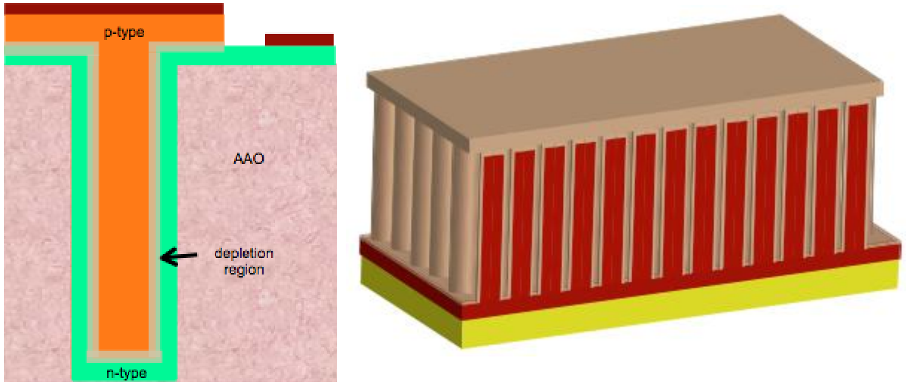
- ***solar cells***
- ***solid batteries and supercapacitors***



3-D solid state nanobattery
Roozeboom et al, *Adv Materials* 19 (24), 4564 (2007)



Nanorod solar cell concept, modeling
Kayes, Atwater, Lewis,
J Appl Phys 97, 114302 (2005)



Embedded nanowire solar cell
Banerjee et al, in progress

Nanostructures: Exposed or Embedded?

Exposed

- Primarily relevant to batteries, supercapacitors, and fuel cells
- Liquid electrolytes for storage devices have degradation and vapor pressure concerns

Embedded

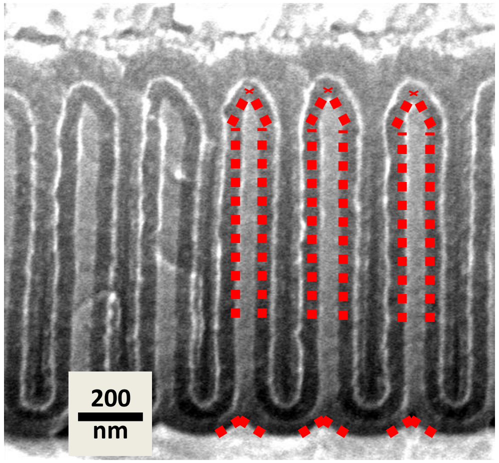
- Well suited to solar PV
- Growing opportunity for batteries and supercapacitors

Significant issues for device design and process integration

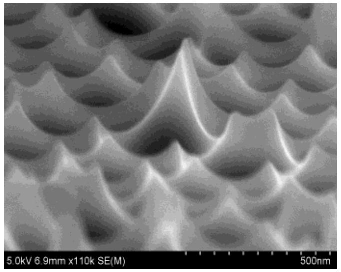
Novel processes and combinations have impact on both

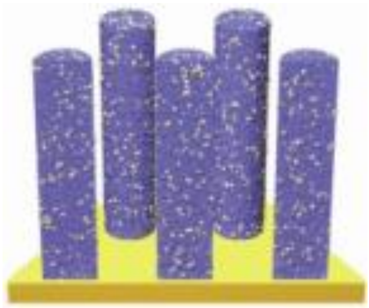
Engineering 3-D Structures at the Nanoscale

- **Specific processes and process sequences to form**
  - *heterogeneous multifunctional nanostructures*
  - *specific 3-D shapes*
- **3-D geometry, material properties, and interfaces determine performance**

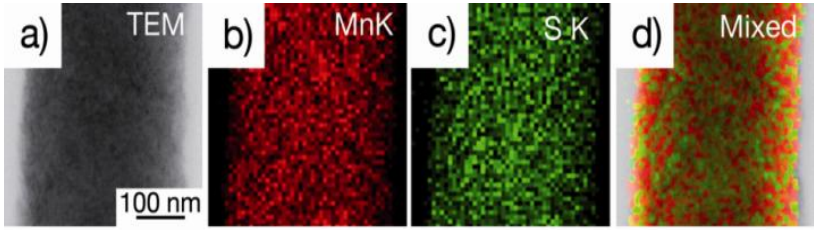


embedded nanostructures





exposed nanostructures



"3 self's": Processes Enabling Synthesis of Heterogeneous Nanostructures

Self-assembly ➔ *massive arrays of nominally identical, regularly arranged nanostructures*

let nature do the work

Self-alignment ➔ *devices built upon/within the self-assembled templates*

know where to go

Self-limiting (controllable) ***reaction*** ➔ *atomic scale control for thickness and conformality*

stop when done

add minimal lithography, top-down processes where needed

Process & Device Integration at the Nanoscale

- Integration is complex: process & equipment, sequencing, patterning, device design, massive interconnects, …
- Massive levels of integration ➔ 10^{10} nanodevices/cm^2 , 100 billion/in^2
- **Emphasize integration at nano level ➔ major benefit** in reducing mass, volume, footprint

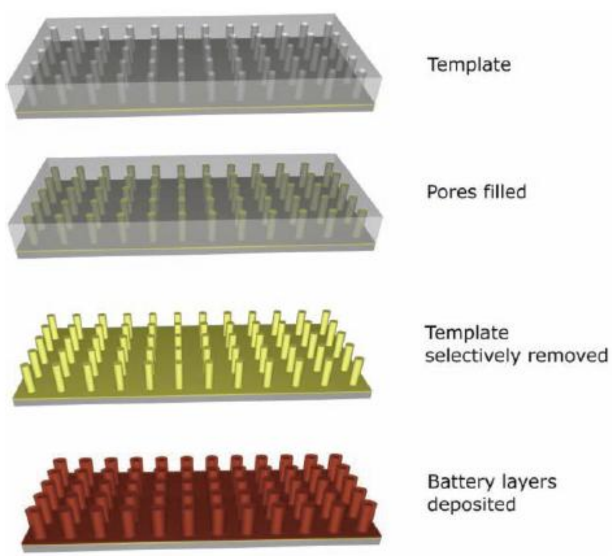


Figure 3. 3D battery manufacturing based on template deposition of nanorods.

J.F.M. Oudenhoven, L. Baggetto, and P.H.L. Notten, *Adv Energy Mats* 1, 10-33 (2011)

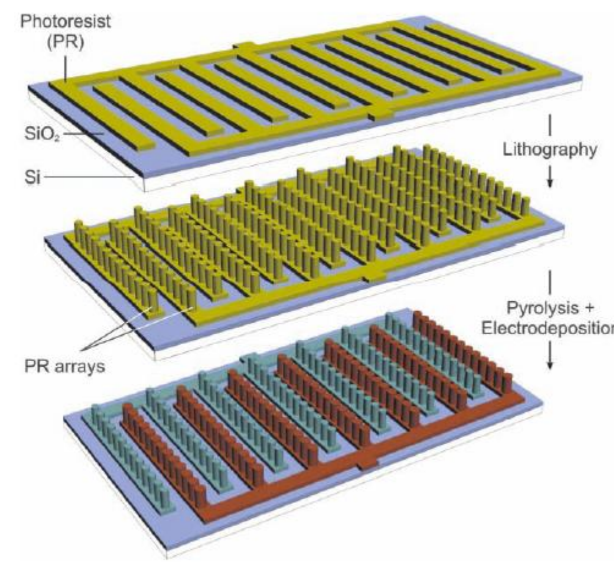
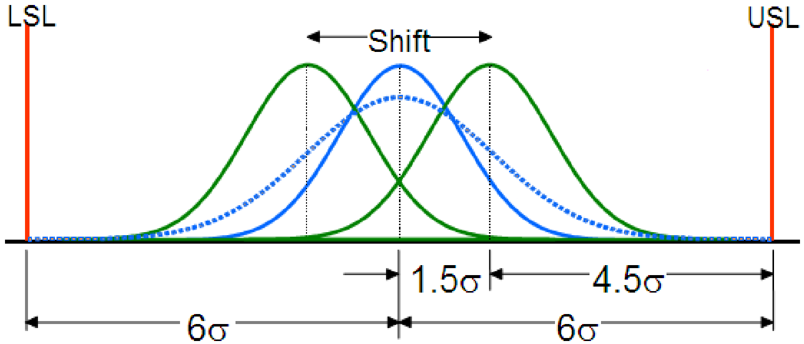


Figure 4. Manufacturing of a 3D microrod structure of pyrolized photoresist. (Figure based on ref. [167].

H.S. Min, B.Y. Park, L. Taherabadi, C.L. Wang, Y. Yeh, R. Zaouk, M.J. Madou, B. Dunn, *J Power Sources* 178, 795 (2008)

Creating Viable Technology

- **Nanostructure-based energy devices require massive integration levels**
  - *At levels of semiconductor chips or beyond*
- **Acceptable manufacturing yield demands "identical" structures with tight distributions**
  - *Well known for regular nanostructures, mostly true for random nanostructures as well*
- **Multistep nanostructure fabrication requires "centering" of tight distributions to achieve acceptable yield**



1.5 σ drift ➔ 3.4 ppm defects

http://mvpprograms.com

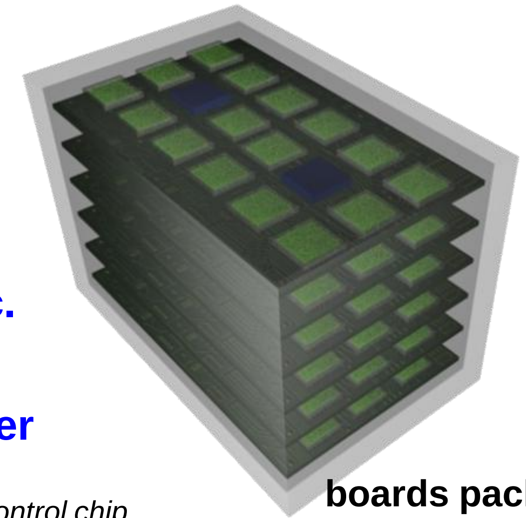
- **Reliability requirements compound the challenge**

Massive Integration above the Nano Level

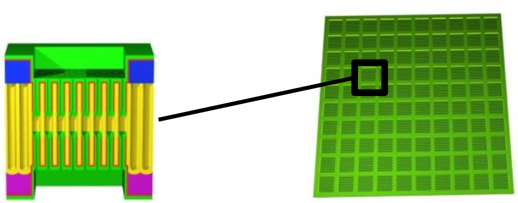
- Packaging is critical (as always)
- Requires defect and reliability management

- System-level on-board sensors
- Control chips to dynamically manage power, heat, etc.

- Underscores value of integration at nanoscale ➔ lower weight & volume



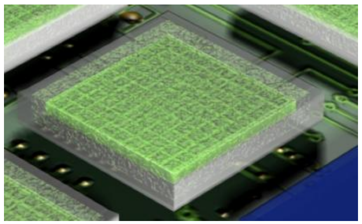
boards packaged in system



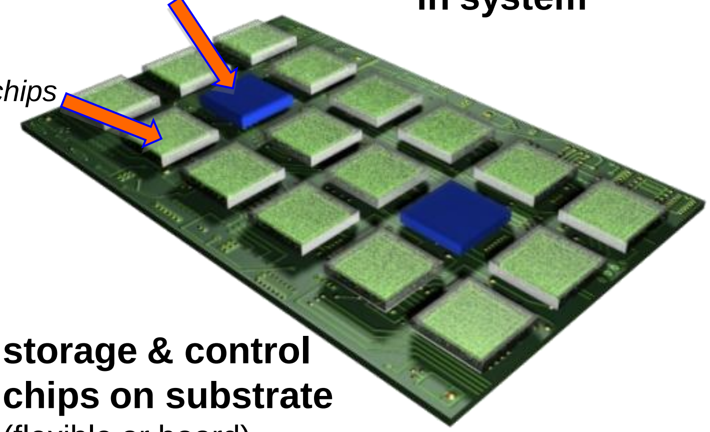
storage cell

electrical energy storage chip

exposed



packaged

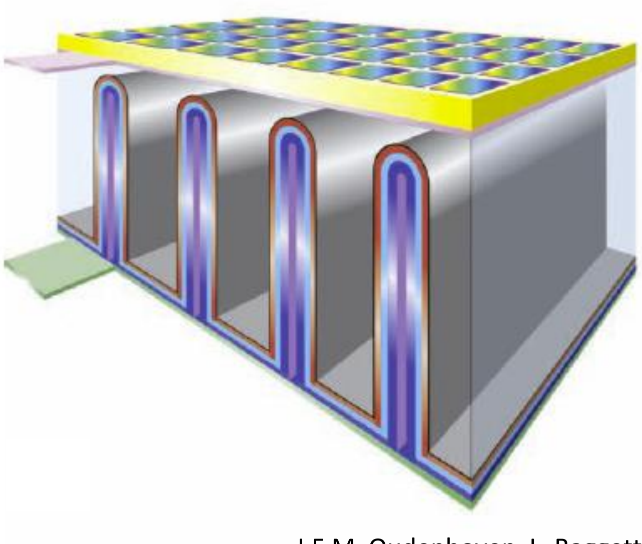


storage & control chips on substrate
(flexible or board)

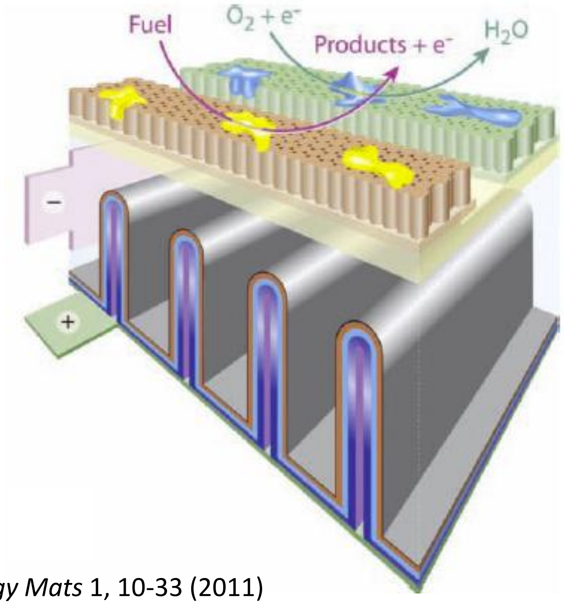
Multifunctional Nanosystems

- **Functional integration at the nanoscale**
  - *Can lower mass, volume*
  - *Can improve dynamic system management*
  - *Processes and equipment common to different device functions*

solar (PV) and electrical energy storage



biofuel cell and electrical energy storage



J.F.M. Oudenhoven, L. Baggetto, and P.H.L. Notten, *Adv Energy Mats* 1, 10-33 (2011)

Hierarchical, Adaptive Modeling & Simulation

- **Energy systems – vertically heterogeneous**
  - *Nano components, micro fabrication, macro packages*
  - *Design is difficult, optimization even harder*
  - *Dependent on sometimes rudimentary nanoscience*
- **Hierarchical systems modeling & simulation**
  - *Represent vertical layers and interconnects between them*
  - *Reflect state-of-art physical knowledge*
  - *Adaptive: (sub)models can be updated with new knowledge*
- **Drive & optimize design by systems level metrics**
  - *Performance metrics, utility functions*
  - *Optimization and tradeoff analysis*
  - *Optimization under uncertainty*
  - *Prioritize research needed*

The Institute for Systems Research

Responses and Recommendations

- Top technical challenges in the area of your presentation topic?
  - *Materials, processes, and sequences to achieve predictable, heterogeneous high performance nanostructures*
  - *Understanding of tradeoffs betweeen regular and random nanostructure architectures*
  - *Identification of credible application domains for exposed and embedded nanostructure devices*
  - *Fundamental mechanisms for defects and reliability in massive nanostructure arrays*

- What are technology gaps that the roadmap did not cover?
  - *Caveat: relevant roadmap section is quite brief, rendering question dubious*
  - *Modeling and simulation platforms to guide systems design and prioritize research*
  - *System-level strategies for managing defects, reliability and dynamic power and heat*

Responses and Recommendations

- What are some of the high priority technology areas that NASA should take?
  - *Defect and reliability mechanisms that emerge with massive integration of nanostructures*
  - *Integrated systems aimed at demonstrating multifunctionality at the nanoscale*
  - *Model-based system level design architecture, including adaptability to new nanoscience*

- Do the high priority areas align well with the NASA's expertise, capabilities, facilities and the nature of the NASA's role in developing the specified technology?
  - *DOE-BES and NSF investments are very significant, with different goals ➔ opportunity for synergy*
  - *NASA roadmap aligned to missions ➔ emphasize integration and nanoscience issues critical to serious applications*

Responses and Recommendations

- What specific technology we can call it as a “Game Changing Technology”?
  - *Nanostructures as basis for next-generation energy devices and systems*
  - *Multicomponent, multifunctional nanostructures where components are optimized for nanosystem performance*
  - *Manufacturing processes at acceptable cost (shared with DOE, …)*

- Is there a technology component near the tipping point? (tipping point: technology insertion with small additional investment)?
  - *Possible: nanodevices for solar PV, batteries/supercaps, SOFC*

- In your opinion what is the time horizon for technology to be ready for insertion (5-30 year)?
  - *5-8 yrs*

Responses and Recommendations

- Provide a sense of value in terms of payoffs, risk, technical barriers and chance of success.
  - *High value, payoff and success likely within 10-15 yrs IF investment portfolio includes focus on:*
  - *Integration issues AND methodology to manage and optimize (use modeling, include integration at nano level)*
  - *Defect and reliability mechanisms at nanoscale that impact massive integration levels*
  - *Manufacturing equipment and processes, and their integration*