



# **Nanostructures for Electrical Energy Storage (NEES)**

a DOE Energy Frontier Research Center

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Director, DOE-EFRC Nanostructures for Electrical Energy Storage (NEES)  
Dept of Materials Science & Engineering and Institute for Systems Research

# Creating the EFRC

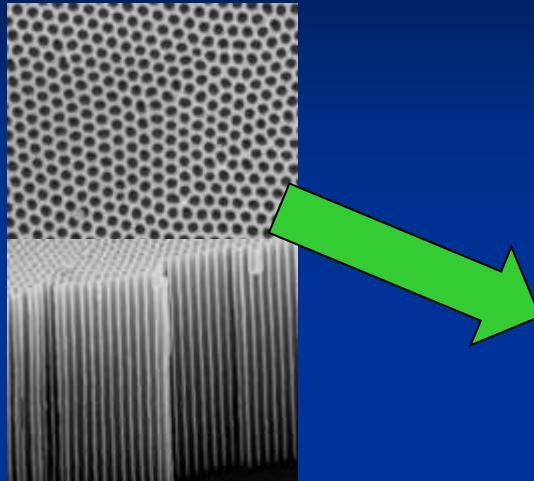


Rubloff: NRC CMMRC 5-2-2011

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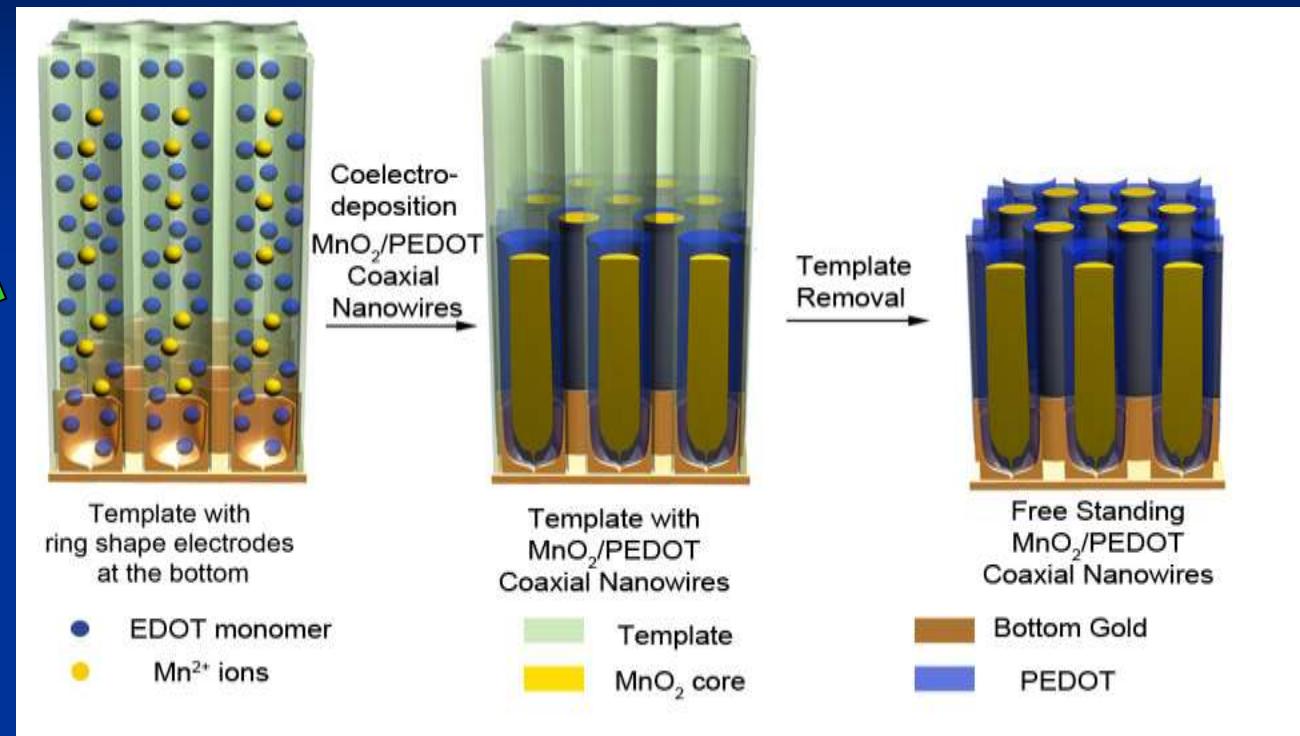
Office of  
Basic Energy Sciences

# Electrodeposition into Nanopores → Coaxial Nanowires



**AAO nanopores**

60nm dia, 1-30 $\mu$ m deep

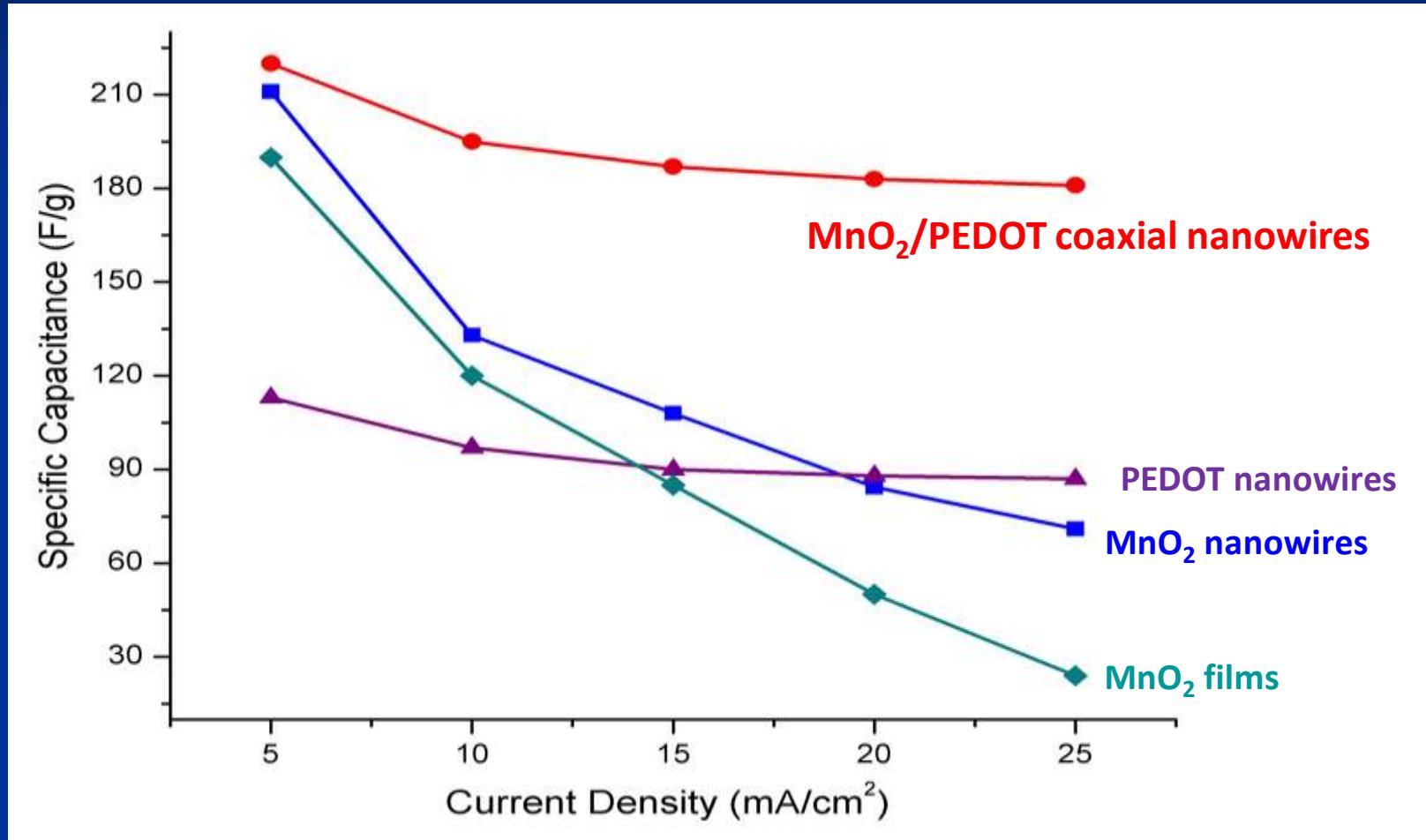


Simultaneously electrodeposit:  
 $\text{MnO}_2$  charge storage material  
Conducting polymer charge transport material

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

**100 billion coaxial electrochemical nanowires per square inch**

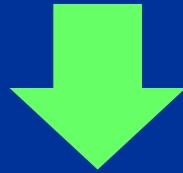
# $\text{MnO}_2/\text{PEDOT}$ Coaxial Nanowires for High Power & Energy



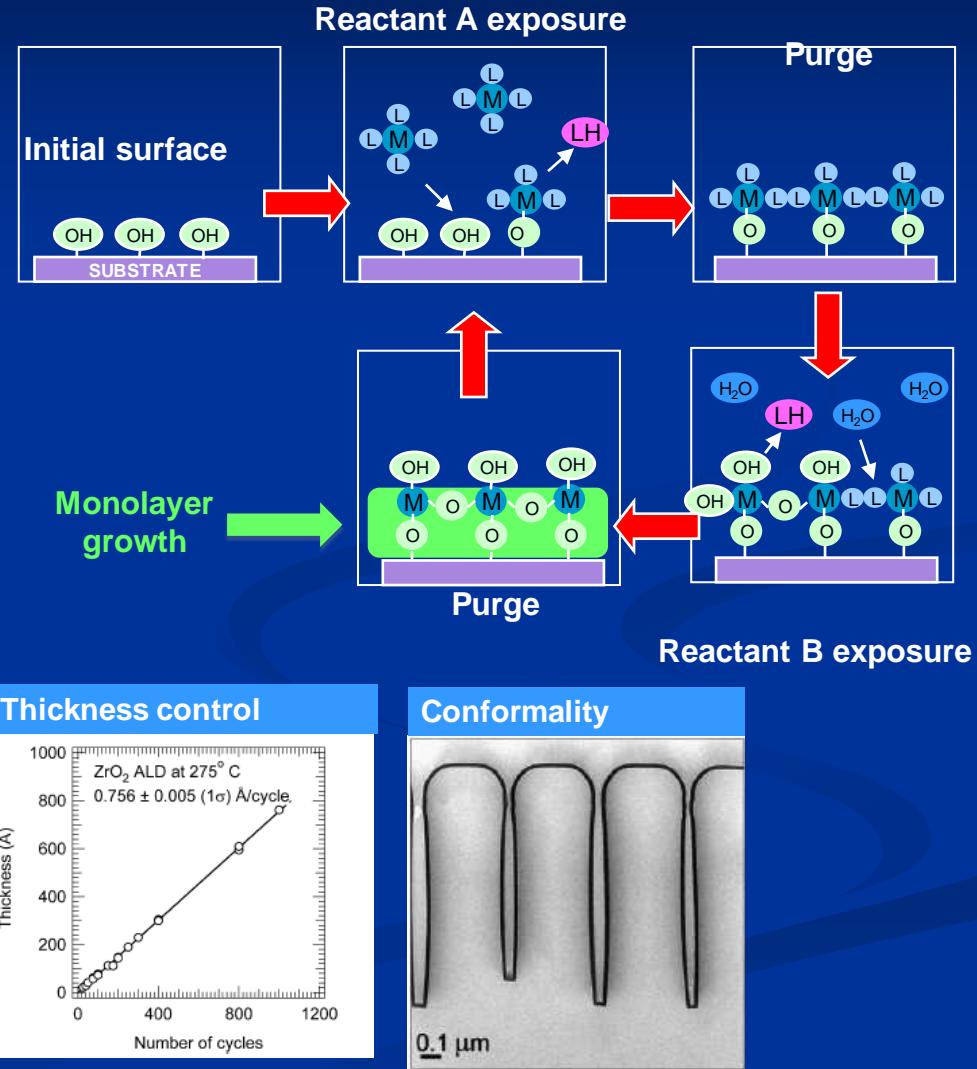
Liu & Lee, *J. Am. Chem. Soc.* (2008)

# Atomic Layer Deposition (ALD)

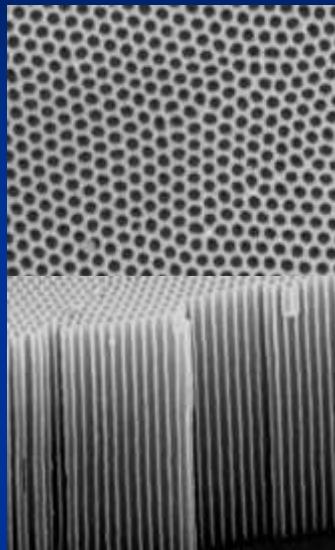
- Reactive CVD precursors alternately and separately exposed to surface
- Self-limiting adsorption/reaction



- Monolayer thickness control
- Superb conformality and uniformity

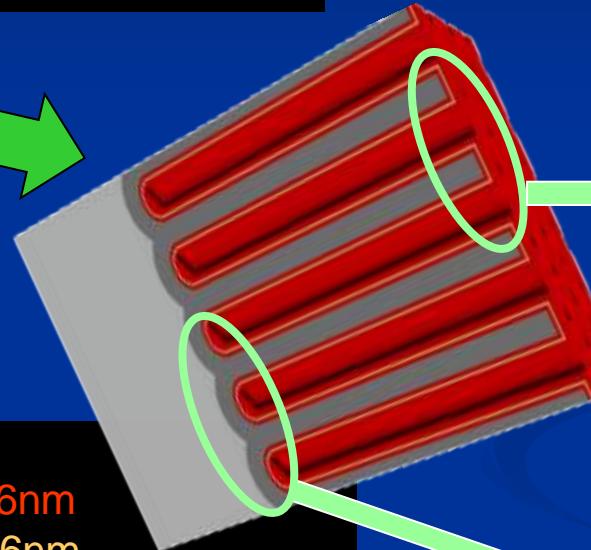


# AAO-ALD for MIM Electrostatic Supercapacitor



AAO nanopores

60nm dia, 1-10 $\mu$ m deep



ALD MIM layers:

Top electrode: TiN 12.6nm

Dielectric:  $\text{Al}_2\text{O}_3$  6.6nm

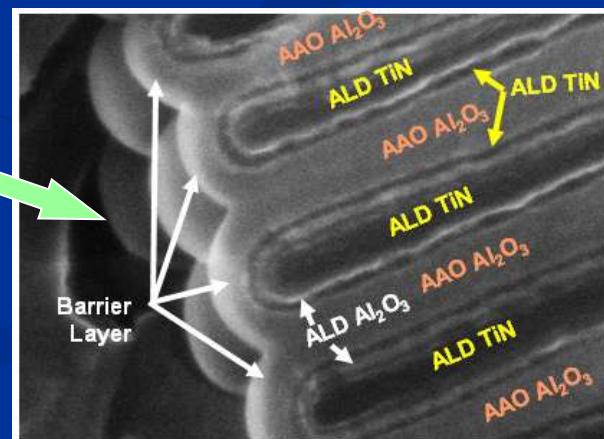
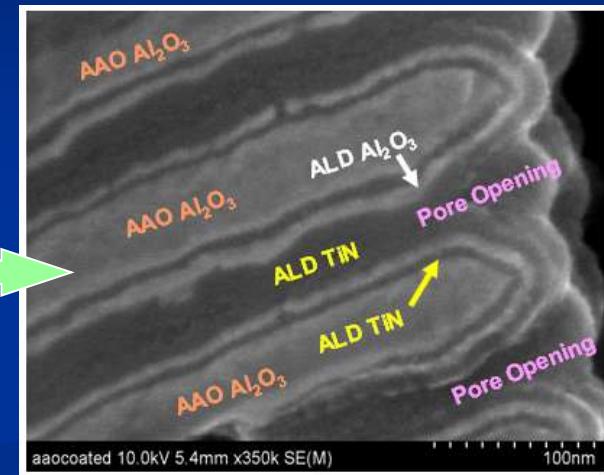
Bottom electrode: TiN 5.6nm

Aspect ratios 200-1000 (depth/width)

ALD conformality >93% in all layers

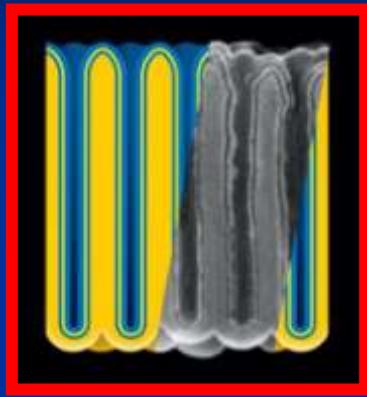
100 billion nanocapacitors per square inch

SEM images

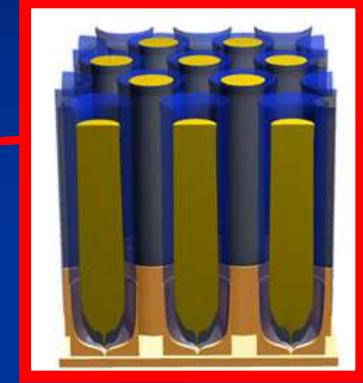
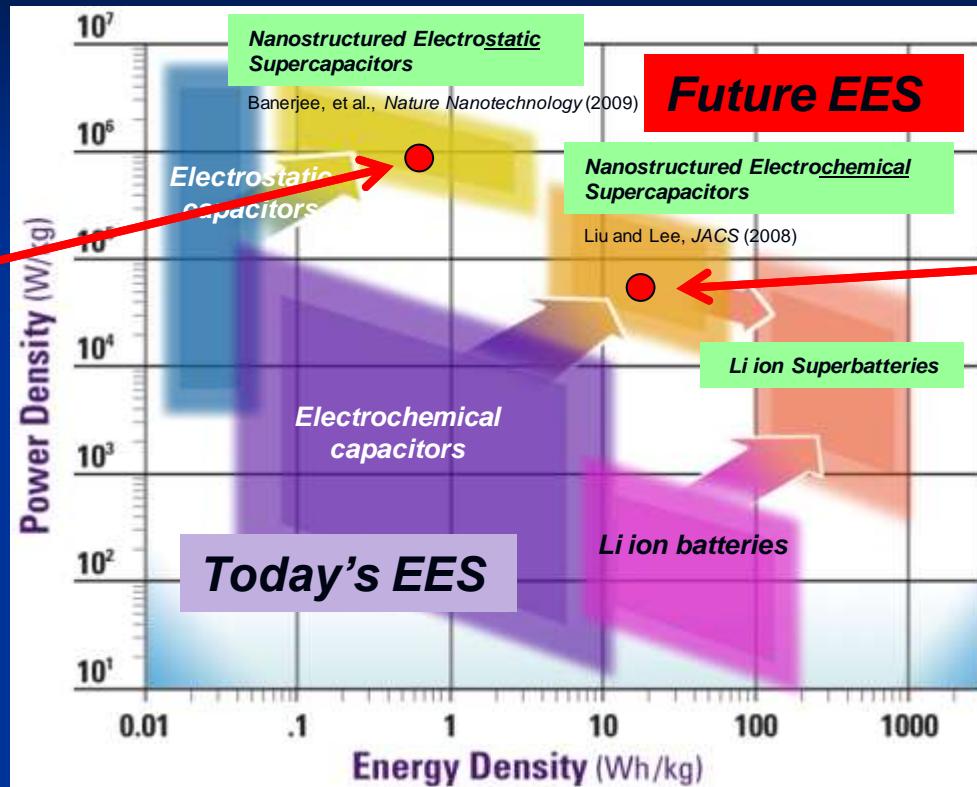


P. Banerjee et al, *Nature Nanotechnology* (2009)

# Advances from Nanotechnology



AAO-ALD embedded metal-insulator-metal device



Free-standing  $\text{MnO}_2/\text{PEDOT}$  coaxial nanowires

## 1. Nanostructures for next-generation electrical energy storage

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

# Nano-Enabled Energy Devices

One material to do the basic job

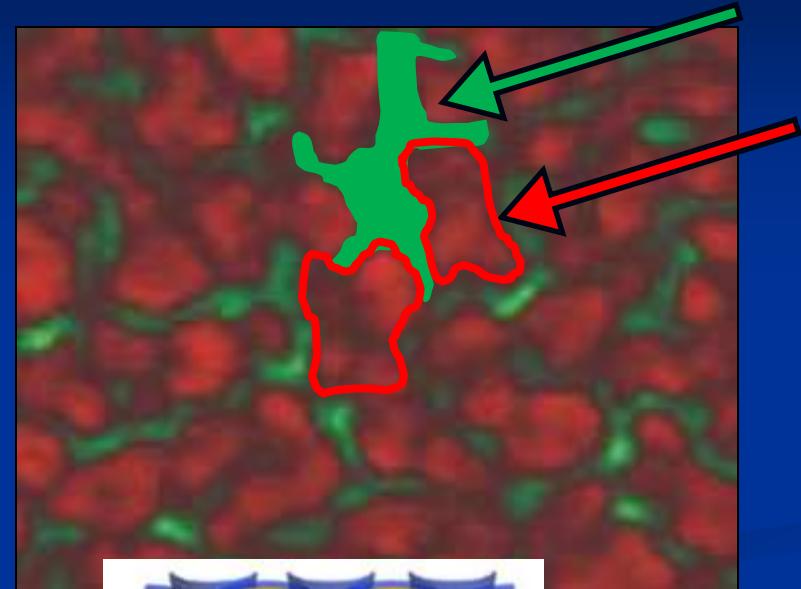
- Store electricity
- Capture sunlight

At least a second material and/or interface to add other essential functions

- Move energy where it's needed
- Assist in energy conversion

## 2. Multiple, heterogeneous materials for multifunctional performance

“Designer nanomaterials & nanostructure systems” for efficient energy devices



# Nanostructures – Regular or Random?

## Regular (periodic)

Rapidly growing research activity

**More amenable to characterization  
and understanding**

**Tighter distributions for  
manufacturing**

## Random (aperiodic)

Larger experience base

Easier, cheaper manufacturing  
processes

Potentially higher surface area

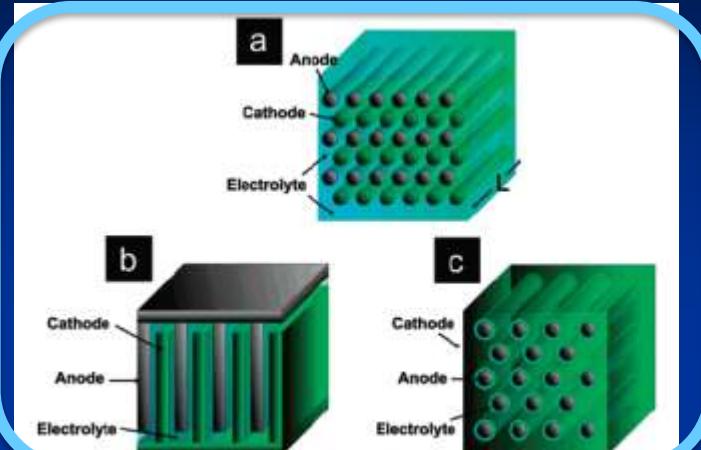


Figure 2. Examples of prospective 3-D architectures for charge-insertion batteries: (a) array of interdigitated cylindrical cathodes and anodes; (b) interdigitated plate array of cathodes and anodes; (c) rod array of cylindrical anodes coated with a thin layer of ion-conducting dielectric (electrolyte) 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.

## 3. Focus on regular nanostructures

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

# Processes for Nanostructure Integration

## 4. Use the “3 self’s”

- **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 reaction** → atomic scale control for thickness and conformality  
*stop when done*

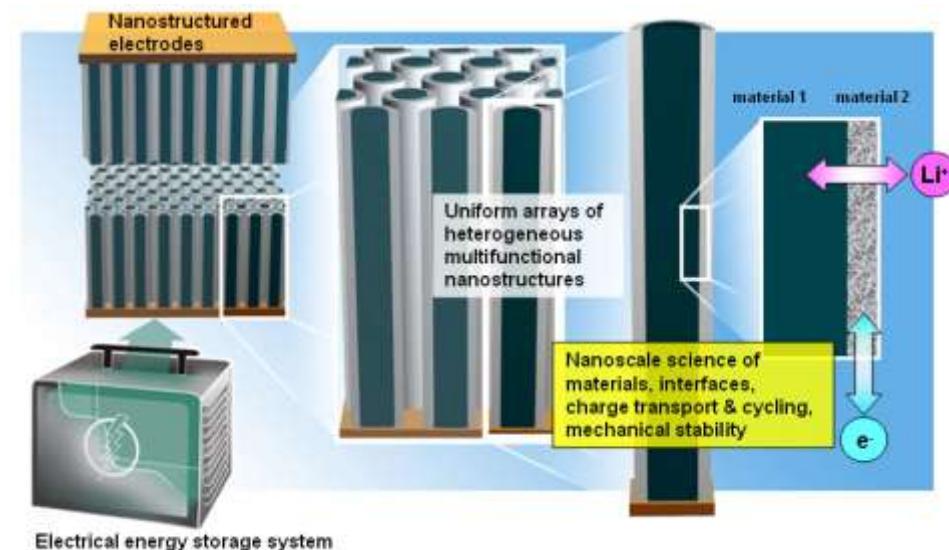
stated as mantras  
by P. Banerjee

# Nucleating the EFRC

- **Initiate from small, familiar group**
- **Expand gradually as vision and strategy emerge**
- **Iterate themes, highlights, and expertise**
- **Exploit available resources (technical and administrative)**
- **Seek:**
  - *Highly interwoven, synergistic program working through flexible thrust area organization*
  - *Coherent team and program through effective intellectual stimulation and communication*
  - *Program enrichment through outreach to broader technical community*
  - *Proactive management of program evolution*
  - *Strong support for important management and operations functions*

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

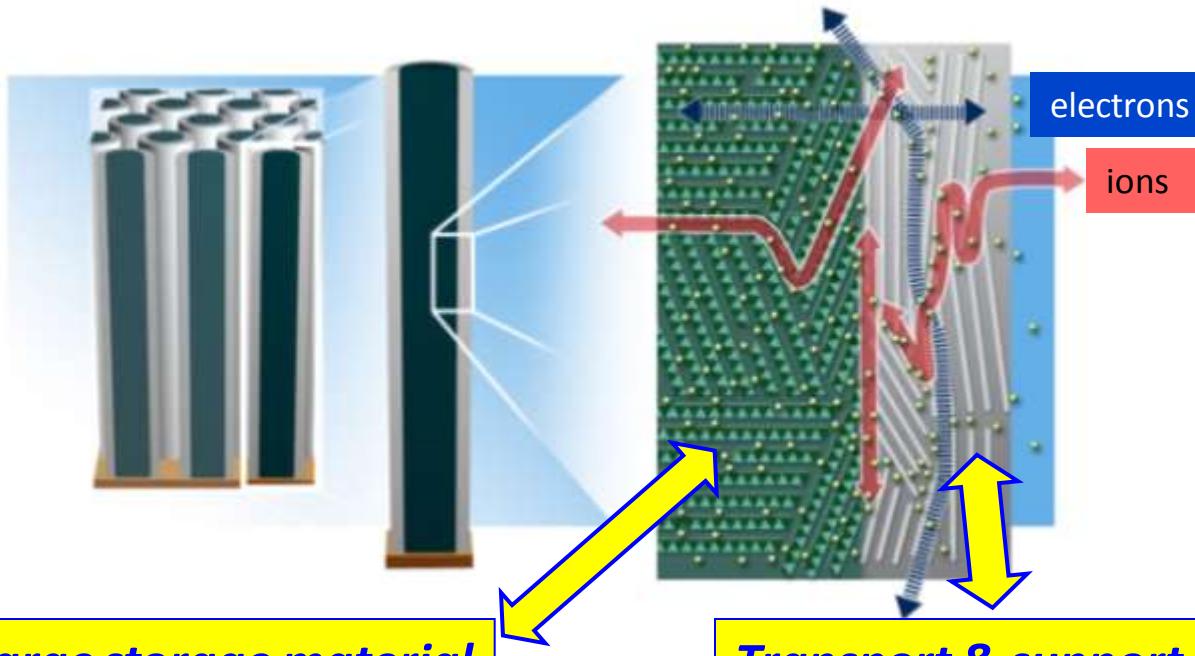
- power **electric vehicles** over long distances and recharge quickly, and
- capture, hold, and deliver energy from **renewable sources**.



#### EFRC features:

- **Metal oxide and silicon nanowires** to hold and cycle charge
- **Carbon-nanowire composite nanostructures** for faster charge transport and structural stability during charge cycling
- **Fundamental understanding** of nanostructure synthesis, properties, and electrochemical behavior, supported by novel instruments and theory
- **Uniform, predictable structures** for scientific analysis and as prototypes of massive arrays in future technology

# Heterogeneous Multifunctional Nanostructures



## 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*

# Center for Science of Precision Multifunctional Nanostructures for Electrical Energy Storage



## 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**.

UNIVERSITY OF MARYLAND

DEPARTMENT OF ENERGY  
**NES**  
 NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

Sunday, November 8, 2009

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University of Maryland Energy Frontier Research Center

**The Challenge**  
 The severity of the world energy shortage demands far more efficient ways to store energy, particularly from renewable sources like solar and wind. With capability for storing much more energy, delivering higher power, and recharging faster, next-generation electrical energy storage (EES) systems will enable new, green solutions to energy storage in smaller, lighter packages.

**Our Vision**  
 We believe that nanostructures are the key to next-generation EES. By creating structures at the nanoscale, we can design and exploit the energy storage capacity of optimized nanomaterials while also combining different materials in geometries that speed up movement of charge (electrons and ions) to and from the storage nanomaterials.

**Science is Needed**  
 Understanding how to fabricate such nanostructures and make them perform well poses profound new challenges, from the design and construction of nanomaterials as multicomponent structures for rapid charge transfer to the stability of the structures as charge is cycled in and out.

**Our Goal**  
 The Energy Frontier Research Center for Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NES) will develop the fundamental science required for creating predictable, regular arrays of nanostructures, optimizing their materials and understanding their charge transfer behavior at the nanoscale, and optimizing the design of multifunctional EES nanostructures. The Center's advances will underpin a nano-enabled next-generation EES technology.

A schematic diagram of the proposed nanostructure energy storage device.

[www.efrc.umd.edu](http://www.efrc.umd.edu)

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University of Maryland  
 13.2 M\$ total

University of Maryland

Sandia National Laboratories

University of Florida

Los Alamos National Laboratory

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# Research Strategy

... an  
integrated  
approach

## Science thrust A → *Faster charge transport*

## Science thrust B → *Stability under charge cycling*

## Enabling thrust C → *Nanoscale dynamics*

### *Thrust C. Nanoscience of electrochemical interfaces*

Electrochemical dynamics by scanning probe microscopy  
Nanoprobe imaging and chemical spectroscopy of surface  
models for electrochemical systems  
Density functional theory for Li transport in nanoscale  
heterostructures

UMD: Reutt-Robey (lead)  
SNL: Zavadil (co-lead), Leung

### *Thrust A. Multifunctional nanostructures for fast ion transport*

Oxide nanostructures for high-energy cathodes  
Graphitic carbon for accelerated transport  
Synthesis of nanoscale oxide-carbon heterostructures  
Electrochemistry at nanowires surfaces and defects  
Permselective membranes

UMD: Lee (co-lead), Fuhrer (co-lead)  
U Florida: Martin  
UC Irvine: Penner, Collins, Siwy

### *Thrust B. Self-healing nanostructures for electrodes*

Silicon nanostructures for high-energy anodes  
Graphitic carbon for mechanical stabilization  
Synthesis of nanoscale silicon-carbon heterostructures  
Nanostructure mechanics

UMD: Cumings (co-lead), CWang, YHWang  
LANL: Picraux (co-lead)  
Yale: Reed

## Enabling thrust D → *Nanostructure stability*

### *Thrust D. Atomic scale mechanics and kinetics in heterogeneous nanostructures*

Stimulus-response of heterogeneous nanostructures by  
electrochemical transmission electron microscopy  
Mechanical and optical MEMS sensing of nanostructure response to  
actuation and cycling  
Multilayer hetero-nano-structures for all-solid-state storage

UMD: Ghodssi (co-lead), Rubloff  
SNL: Sullivan (co-lead), Huang, Hwang

# Research Team Profile

**4 universities**

	Nanotech	Mixed	Electrochemistry
U Maryland (lead)	Gary Ruboff, Michael Fuhrer, Reza Ghodssi, Janice Reutt-Robey, YuHuang Wang, John Cumings	Sang Bok Lee	Chunsheng Wang
UC Irvine		Phil Collins	Reg Penner, Zuzanna Siwy (new)
U Florida			Charles Martin
Yale U	Mark Reed		

**2 nat'l labs**

Sandia Nat'l Lab	Jianyu Huang, Bob Hwang	John Sullivan	Kevin Zavadil, Kevin Leung
Los Alamos Nat'l Lab	Tom Picraux		

**Intellectual and institutional mixes**  
→ challenge and opportunity



# External Advisory Board (EAB)

**2 academia**

Name	Institution	Position
Henry S. White	U. Utah	Distinguished Professor President, Soc. Electroanalytical Chemistry
Wade Adams	Rice U.	Director, Richard E. Smalley Institute Chairman of Board, Nanotechnology Initiative

**2 nat'l labs**

Debra Rolison	Naval Res Lab	Head, Advanced Electrochemical Materials Section
Martin Green	NIST	Electronic and Optoelectronic Group Leader

**3 industry**

Mike Wixom	A123	CTO and Vice-President for R&D
Glen Merfeld	General Electric Global Research	Manager, Chemical Energy Systems Laboratory
Tushar Shah (formerly Ned Allen)	Lockheed Martin	Energy Storage technology leader

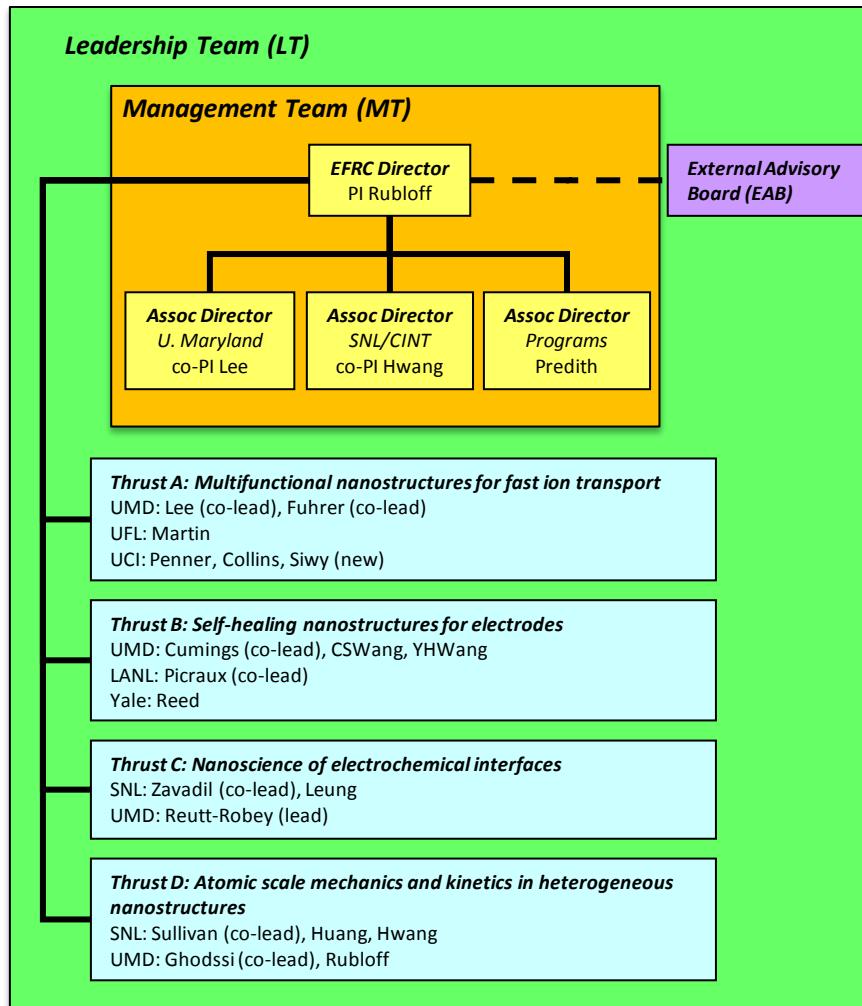
**Diverse technical and management experience**



# Operation of the EFRC



# Organization to Achieve Strategy & Goals



## Director

*EFRC overall performance and management  
 Foster & express vision  
 Resource and people management to achieve vision  
 Direct interface to DOE, BES  
 Convey EFRC accomplishments to multiple audiences*

## Management Team (MT)

*Confidant, sounding board to Director  
 Assist in identifying and resolving issues*

## Leadership Team (LT) – thrust leaders & MT

*Coordinating respective thrust areas  
 Assisting overall EFRC goals, strategy, tactics*

## External Advisory Board (EAB)

*Review and feedback on EFRC program, balance, consistency with goals  
 Suggest new opportunities and directions  
 Facilitate new collaborations, funding opportunities, and partnerships, particularly with their home institutions*

# Key Management Strategies

- **Stimulate scientific excitement**

- *Integrating focus topics at NEES strategy meetings and teleconferences*
- *Spring 2010 strategy: design of multifunctional nanostructured electrodes; electrochemistry at the nanoscale; frontiers of characterization*

- **Foster cross-EFRC collaborations**

- *Support summer visits between sites*

- **Exploit existing resources**

- *Maryland NanoCenter, SNL-LANL CINT*

- **Evolve the portfolio**

- *Collaboration Initiation Grants*

- **Focus on highlights**

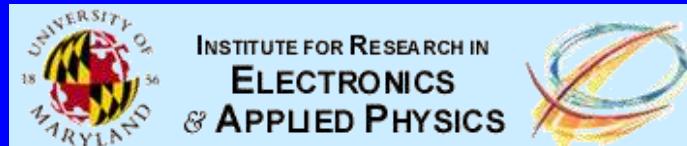
- *Careful construction, iteration, and management review*

- **NEES self-assessment & management review**

- *Science roadmap to focus and integrate projects*

# A Shared Vision (2004)

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



## Engineering

A. James Clark School of Engineering

## Physical Sciences

College of Computer, Mathematical and Physical Sciences

## Life Sciences

College of Chemical and Life Sciences



Nanofabrication  
(FabLab)

Nanocharacterization  
(NispLab)

Shared experimental facilities

## 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

80+ faculty groups  
Top 10 rankings (Small Times)  
[www.nanocenter.umd.edu](http://www.nanocenter.umd.edu)

# Staffing

- **NEES staff**

- **Dr. Ashley Predith**

Associate Director for Programs

Supported by UMD matching funds

PhD 2006, MIT, Materials Science, Computational  
Studies YSZ for fuel cells (advisor Gerbrand Ceder)

Science policy and communications (NSF, MRS Bulletin,  
Natl Bureau Econ Res, ACS)



Ashley Predith

- **Maryland NanoCenter**

- **Ernie Cleveland**, IT coordinator

- **Alice Mobaидin**, web update, events, etc.



Ernie Cleveland



Alice Mobaيدin



Jason Strahan

- **Institute for Systems Research**

- **Jason Strahan**, Director of Finance

# NEES Website

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**NEES News**

Congratulations, Chao-Ming Hu will receive the 2010 Award in Distinguished from the American Chemical Society. Details: [http://www.acs.org/acswebconf/acsmedals/acsmedals.html](#)

**The Challenge**

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**Our Vision**

We believe that nanostructures are the key to enabling EES. By creating structures at the nanoscale, we can design and expand the energy storage capacity of optimized nanostructures while also combining different materials in geometries that speed up movement of charge electrons and limit its flow from the storage nanostructures.

**Science is Needed**

Understanding how to fabricate such nanostructures and make them battery, will pose a series of new challenges. From the design and construction of nano materials to its measurement, structures for rapid charge transfer to the storage of the structures as storage is critical to set out.

**Our Goal**

The Energy Frontier Research Center for Science of Precision Multifunctional Nanostructures for Electrical Energy Storage (NEES) will develop the fundamental science required for creating predictable, regular arrays of nanostructures, tailoring their materials and understanding their charge transfer behavior at the nanoscale, and optimizing the design of multifunctional EES nanostructures. The Center's advances will underpin a nano-enabled next-generation EES technology.

2002 University of Maryland

Sandia National Laboratories, University of Florida, YALE, Los Alamos National Laboratory

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**NEES Intranet**

The NEES Intranet contains information and functionality to facilitate the collaborative work of the NEES members and community. If there is some additional information that you want to share or some function that would be helpful please send a note to [Email Cleveland](#) ([cleveland@umich.edu](mailto:cleveland@umich.edu), 301-405-0028).

**Calendars**  
 View upcoming NEES events and conferences.

**NEES Files**  
 Here you can access shared files as well as share your files with the NEES EFRC community.

**Listserv Information**  
 View list members, quick instructions to manage how you receive emails from the lists to which you belong, as well as joining and leaving lists.

**GoTo Meeting Online Conference (Powerpoint and Desktop Sharing)**  
 GoToMeeting is an online meeting hosting company. The EFRC has an account with them for use by our members to facilitate meetings with people anywhere around the world.

**UMD Tele-Conferencing Information**  
 Important information for utilizing the UMD tele-conferencing system to help facilitate meetings of collaborators across the country.

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# Center for Integrated Nanotechnologies

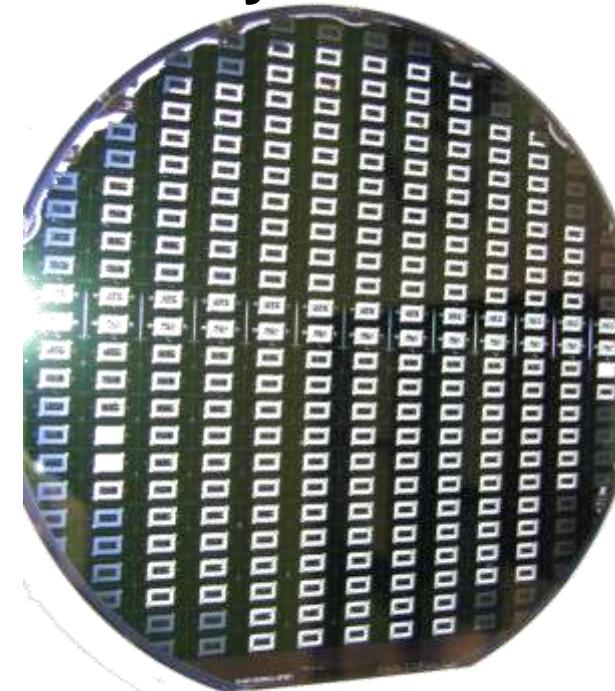


Core Facility in Albuquerque  
96,000 sq. ft.

Gateway to Los Alamos  
36,500 sq. ft.

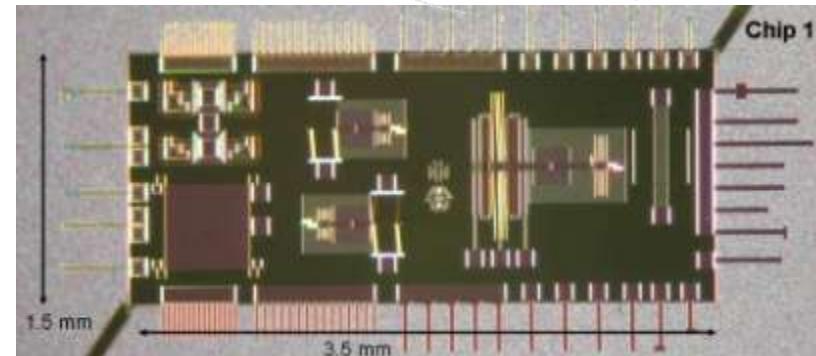


# Sandia MESA Facility – CINT Discovery Platforms



Microsystems and Engineering Sciences  
Applications (MESA) Complex  
274 people, 131,000 GSF  
16,600 ft<sup>2</sup> Class 10 and 100 cleanroom

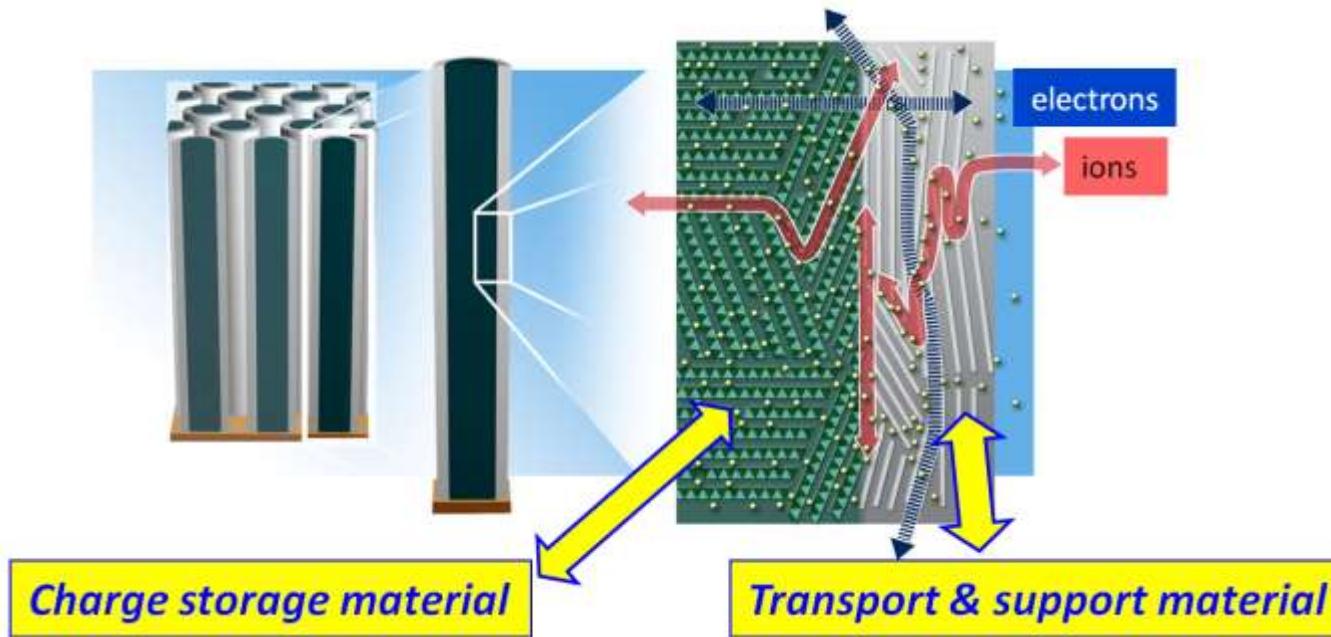
**Discovery Platforms – User Facilities**  
Cantilever – nanomechanics  
In-situ TEM - nanoelectrochemistry



# Vision, Mission, Expected Outcomes



# Vision



*Inspire and guide a scientifically diverse group of research leaders to major advances in understanding and designing next-generation nanostructures for electrical energy storage*

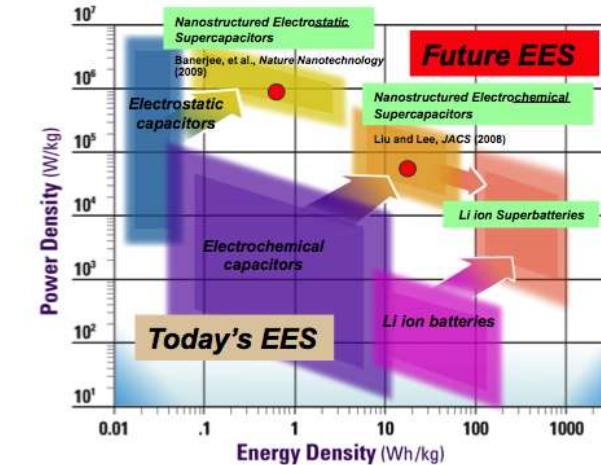
# Nanostructures for Electrical Energy Storage

- Mission:

- *provide scientific underpinnings for dramatically enhanced generation of EES devices*
  - ✓ 10-100X in power density
  - ✓ 10X in energy density

- Goals:

- *Understanding electrochemistry at the nanoscale*
- *Creating innovative nanostructure designs*
  - ✓ Large volume fraction for charge storage
  - ✓ Efficient charge transport to/from storage regions
  - ✓ Stability under charge cycling (volume change, stress/strain)

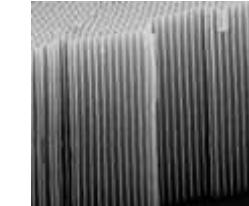
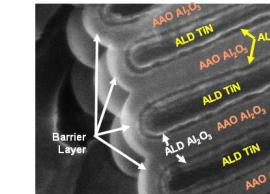
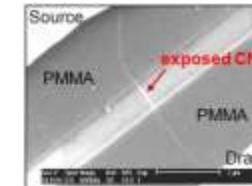


interdependent

# Research Approaches Which Distinguish NEES

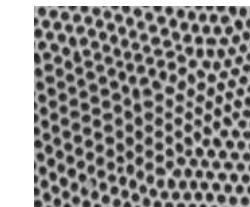
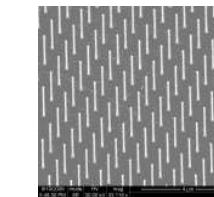
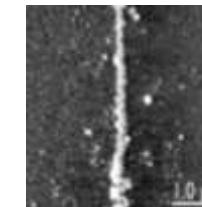
- **Multicomponent nanostructures**

- *Heterogeneous, multifunctional*
- *Well-defined, highly controlled*



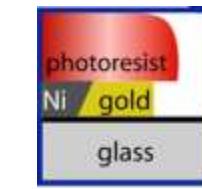
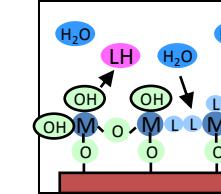
- **Multiscale scope**

- *Single defects and individual nanostructures to massive arrays*



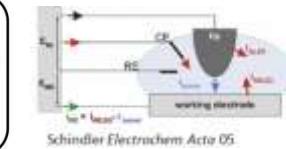
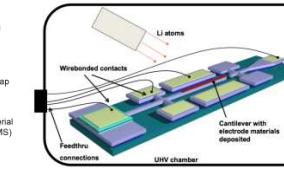
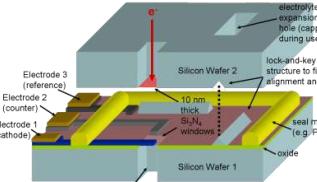
- **New processes & combinations**

- *Self-assembly, self-limiting, self-aligned*

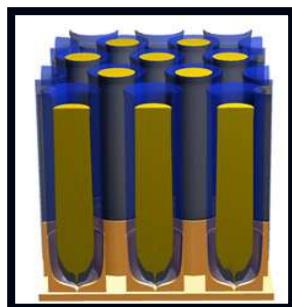


- **Innovative experimental platforms**

- *Imaging: in-situ TEM/MEMS, electrochemical SPM/Raman*



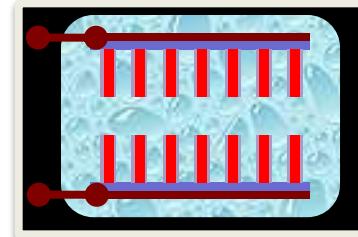
# Multicomponent Nanostructures



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

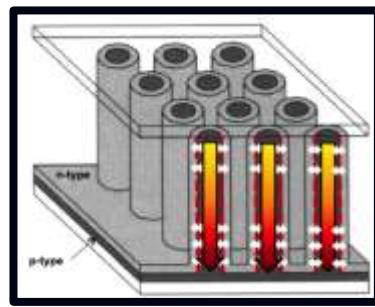
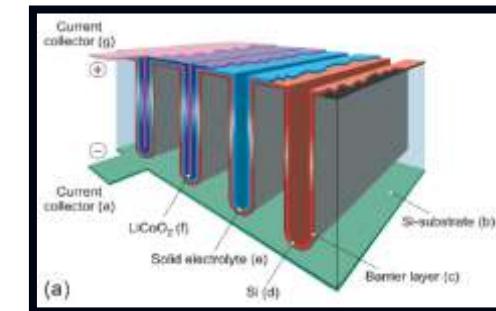


Nanowire electrode supercap



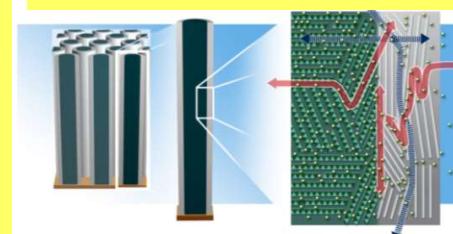
*exposed  
nanostructures*

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

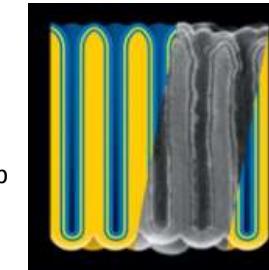


Nanorod solar cell modeling  
Kayes, Atwater, Lewis  
J Appl Phys 97, 114302 (2005)

*surfaces, interfaces, and thin  
films at the nanoscale*



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



*embedded  
nanostructures*

# Scientific Accomplishments



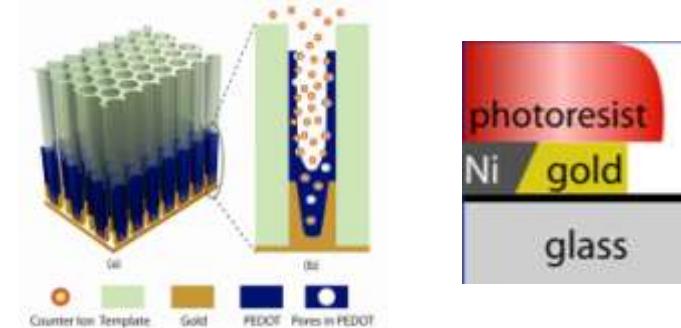
Rubloff: NRC CMMRC 5-2-2011

31

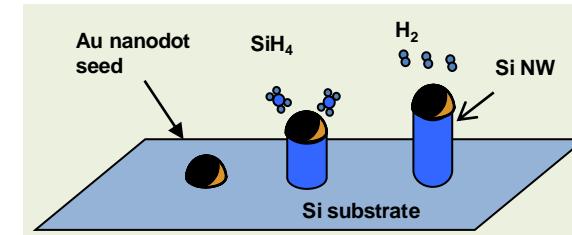


# Nanomaterials Synthesis

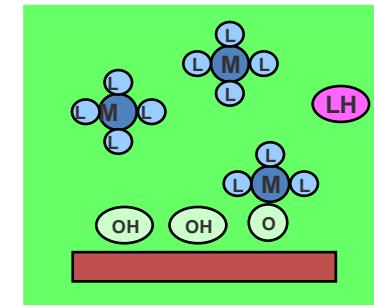
- Electrochemical anodization and deposition



- Catalytic chemical vapor deposition

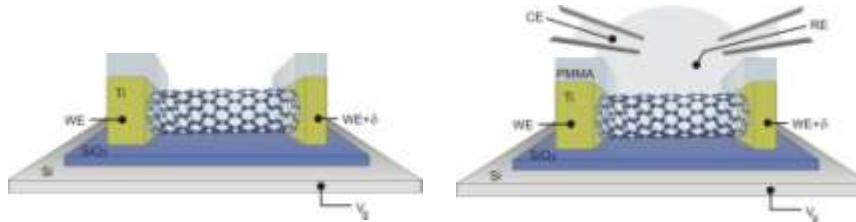
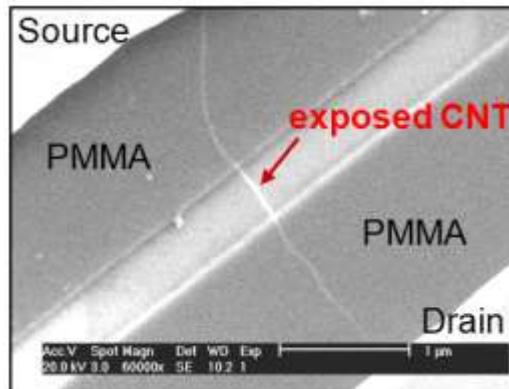


- Chemical vapor deposition
- Atomic layer deposition



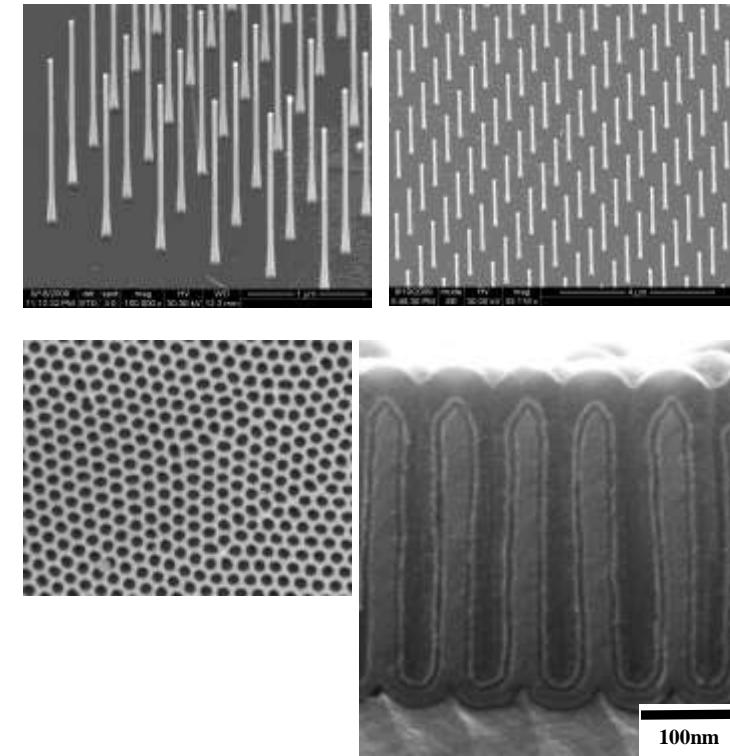
# Bridging Knowledge across Length and Aggregation Scales

Single nanostructures and individual defects



Goldsmith et al, Nano Lett 8 (1) 189-194 (2008)

Massively parallel nanostructures



# Carbon-MnO<sub>2</sub> Nanocomposites for High Power Cathodes

## Accomplishment

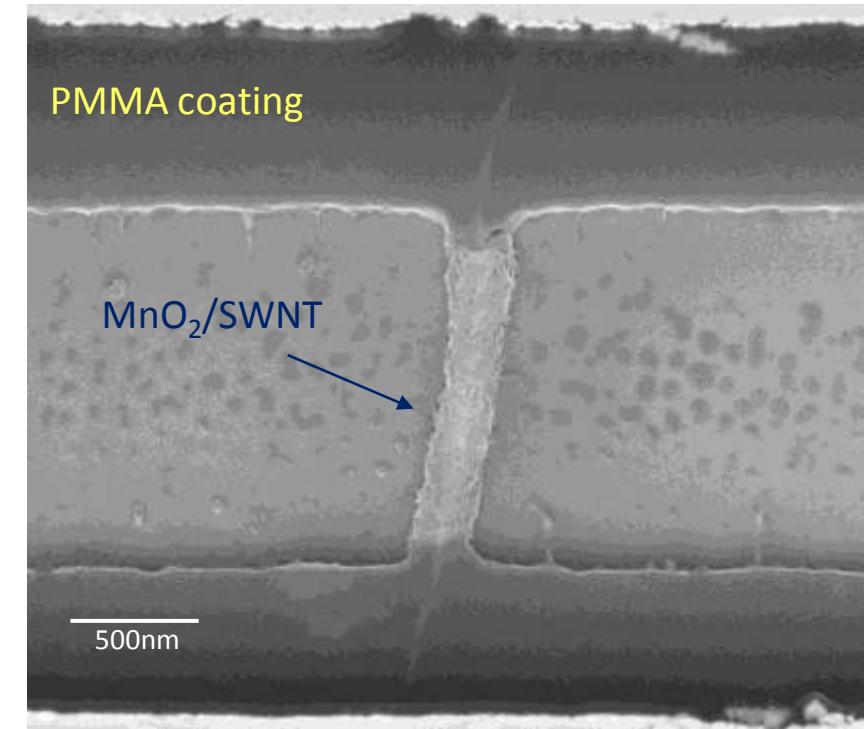
Thin MnO<sub>2</sub>-coated carbon nanotubes.

MnO<sub>2</sub> thickness of 4nm and higher are controlled with 1nm precision.

The Nanotubes (individual, single-walled conductors) are wired into 3-terminal transistors to exploit their sensitive electronic properties during charge-discharge cycles of the MnO<sub>2</sub>.

## Significance

This unique test structure allows us to study both electrochemical kinetics and degradation of the C-MnO<sub>2</sub> system in the absence of pre-existing graphitic edges or defects.



(source and drain connections not shown)

I. Perez, B. Corso, V. Khalap, P. Collins\*, "Conformal MnO<sub>2</sub> electrodeposition onto defect-free graphitic carbons", *Electrochemistry Communications* (accepted).

Collaborators: Israel Perez, Vaikunth Khalap, Brad Corso, Tatyana Sheps, and Profs. PG Collins and R. Penner

# Simultaneous Conductivity and Solubility in Double-Wall CNTs

## Accomplishment

Selective oxidation of the outer wall of double-wall carbon nanotubes (DWCNTs) by oleum and nitric acid made the CNTs water soluble.

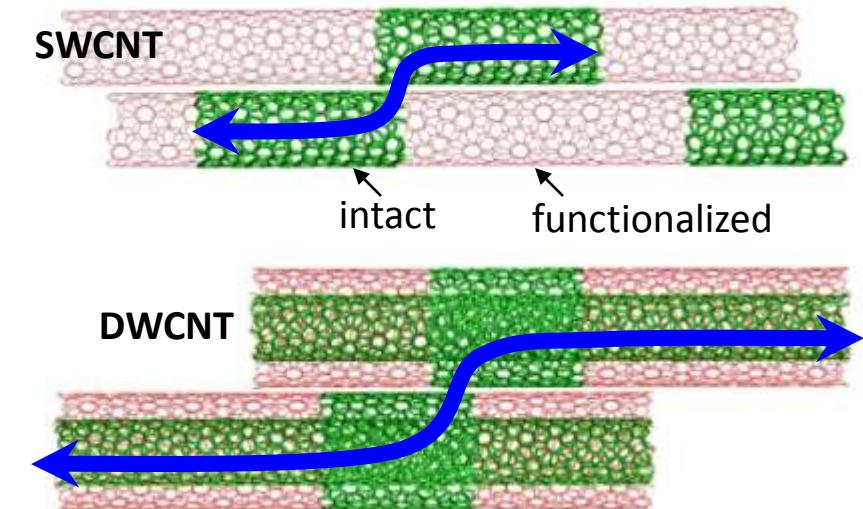
Inner wall remains intact, preserving CNT electrical conductivity properties. Outer wall is mostly functionalized, but intact regions enable contacts to inner walls.

Thin film conductivity of functionalized DWCNTs is up to 65% better than for SWCNTs

## Significance

CNT benefits in conductivity are normally compromised by the functionalization often needed for nanoassembly and use of the CNTs

Two walls of DW-CNTs allow outer wall to be functionalized, providing for flexible design, assembly and use of CNT's in nanostructures, while retaining unique conductivity properties of CNTs in the inner wall



## Collaborators

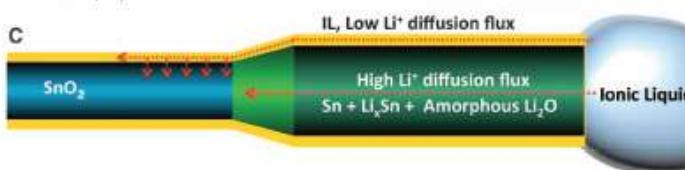
A.H. Brozena, J. Moskowitz, B. Shao, S.-L. Deng, H.W. Liao, K.J. Gaskell, Y.H. Wang  
UMD Chemistry

## Supporting material

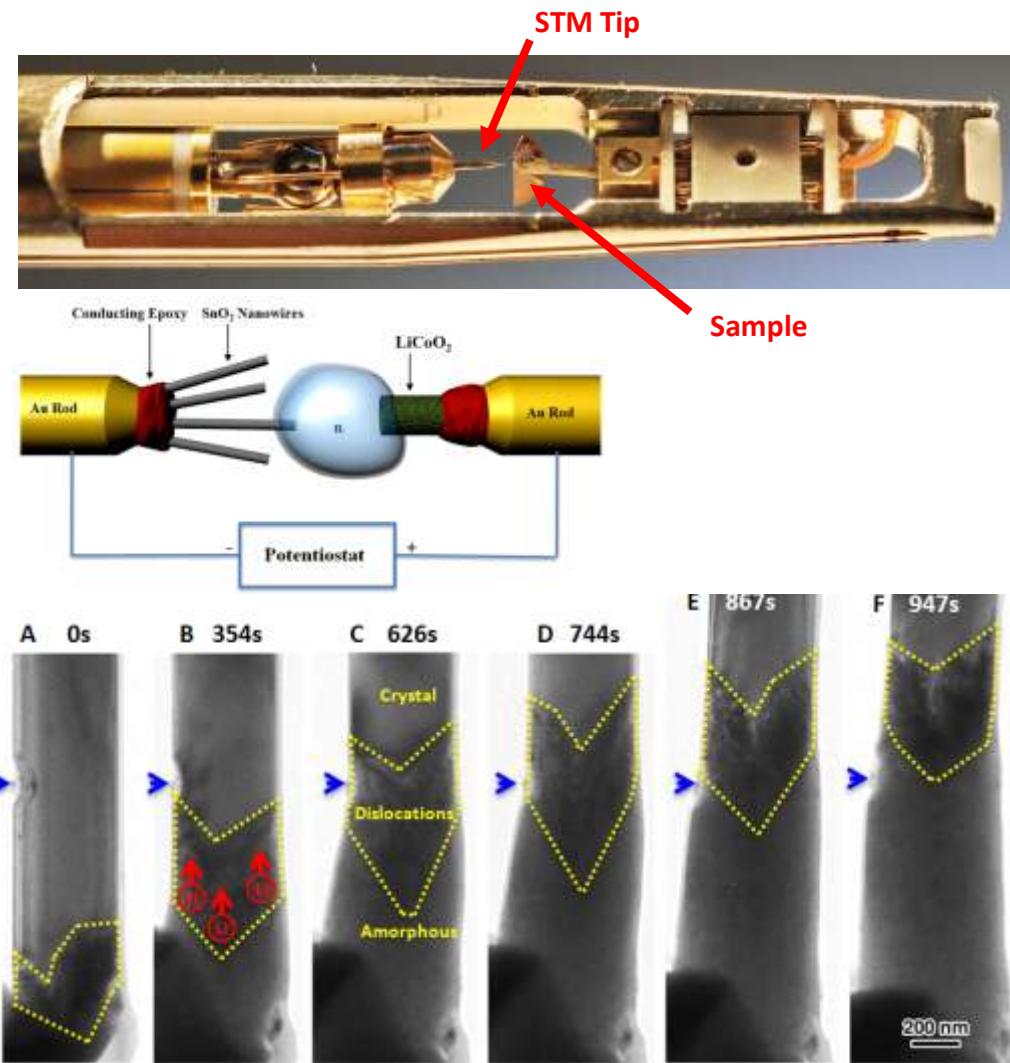
A.H. Brozena *et al*, *J. Am. Chem. Soc.* **2010**, 132, pp 3932–3938.

# Lithiation of $\text{SnO}_2$ Nanowire in TEM

- In-situ TEM imaging of nanowire transformation during lithiation
  - Nanowire  $\text{SnO}_2$  anode
  - Bulk  $\text{LiCoO}_2$  cathode
  - Ionic liquid (IL) electrolyte to enable open electrochemical nanocell within TEM vacuum
- Precursor to Sandia MEMS/TEM platform
- $\text{SnO}_2$  crystal  $\rightarrow$   $\text{Li}_2\text{O}$  glass with  $\text{Li}_x\text{Sn}$  ( $0 \leq x \leq 4.4$ ) nanocrystalline precipitates
- Moving dislocation cloud accompanies major volume change and structural distortion



Jianyu Huang et al (SNL)  
 Science 330, 1515-20 (10 Dec 2010)  
 with Perspective by Yet-Ming Chiang



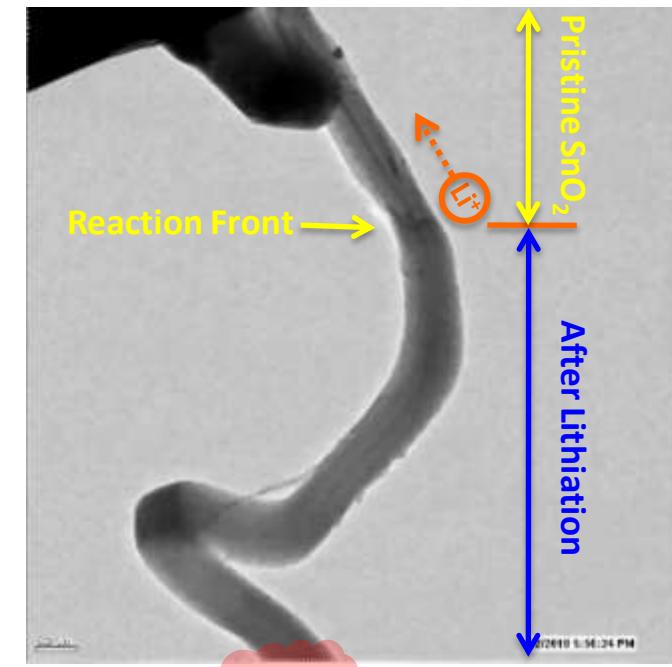
# Real-time observation of the charging process of a single $\text{SnO}_2$ nanowire anode

## Accomplishment

- Direct real-time structural evolution and phase transformation of a  $\text{SnO}_2$  nanowire anode during electrochemical lithiation by transmission electron microscope
- $\text{SnO}_2$  nanowire was placed in contact with an ionic liquid electrolyte loaded with Li salt that was in contact with a  $\text{LiCoO}_2$  cathode.
- Li moves primarily through bulk diffusion into  $\text{SnO}_2$ , reacting to form  $\text{Li}_2\text{O}$  and initiating mechanical changes observed as nanowire bending and distortion.

## Significance

- First definitive experiments of monitoring an electrochemically-induced reaction in Li-ion battery materials with atomic-scale resolution inside a TEM.
- The approach is general and may be applied to most any Li-ion battery material of suitable thin cross-section or even to other electrochemical phenomena, such as electrodeposition.
- Major advance in methodology to identify fundamental mechanisms of Li-ion battery reactions.



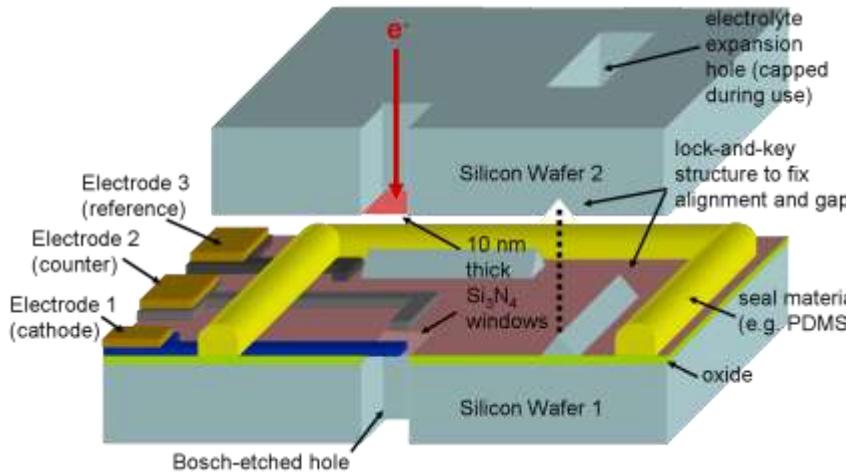
Jianyu Huang et al (SNL)  
*Science* 330, 1515-20 (10 Dec 2010)  
 with Perspective by Yet-Ming Chiang

### Collaborators

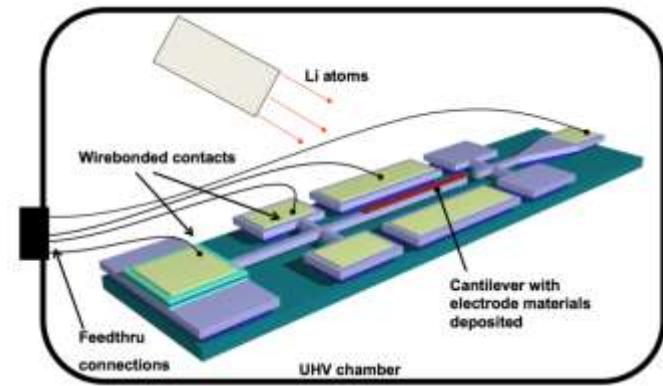
Jianyu Huang, John P. Sullivan (Sandia)  
 Chongmin Wang (Pacific Northwest Lab)  
 Scott Mao (Univ. Pittsburg)  
 Ju Li (Univ. Pennsylvania)

# Microsystems for Characterization

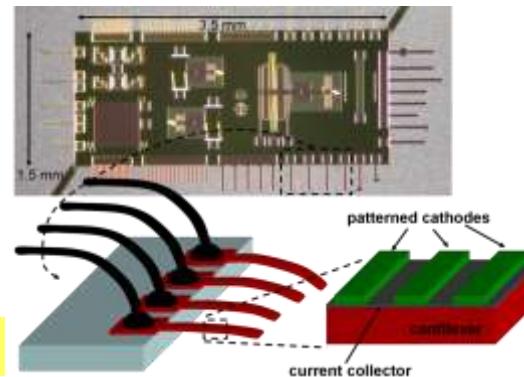
## In-situ TEM Discovery Platform



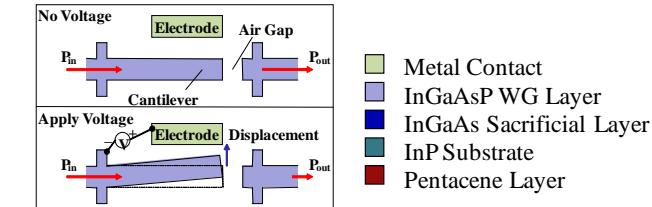
## Optical waveguide cantilever



## Cantilever Array Discovery Platform



SNL/CINT group



Nathan Siwak, et al. *Journal of Microelectromechanical Systems*, Vol. 18, No. 1, pp. 103-110, February 2009.

Ghodssi group (UMD)

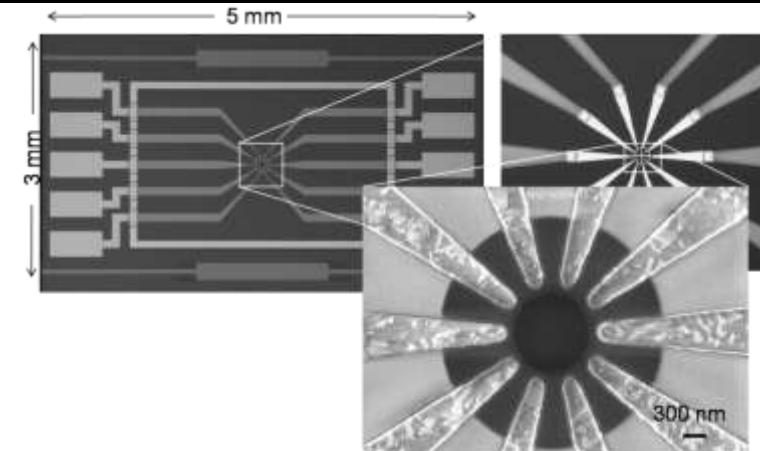
# Development of platforms for understanding Li-ion battery processes at the atomic to nano-scale

## Accomplishment

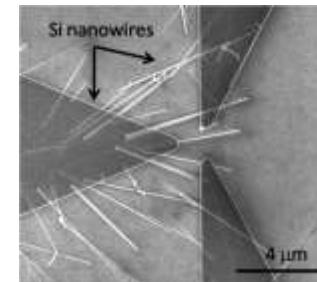
- The development of a suite of platforms and techniques for the in situ characterization of Li-ion battery materials.
- MEMS-based platform for in situ TEM characterization of Li-ion battery materials
- Initial experiments in isolating nanowires and measuring the electrochemical behavior of  $\text{MnO}_2$  nanowires.

## Significance

- Probes with atomic to nano-scale spatial resolution and the capability to follow changes in real-time.
- Understanding the structural changes that occur with the lithiation and delithiation of Li-ion battery materials
- Electrochemical investigations inside a TEM using liquid electrolytes.



Optical microscope image (upper left) and scanning electron microscope (SEM) images of the bottom chip showing one of the twenty electrode configurations.



SEM image showing the assembly of silicon nanowires onto one of the electrode configurations of the platform.

## Collaborators

*J. P. Sullivan, J. Huang, M. J. Shaw, A. Subramanian, N. Hudak (Sandia) & J. Lou, Y. Zhan (Rice U.)*

## Supporting material

*J. P. Sullivan, J. Huang, M. J. Shaw, A. Subramanian, N. Hudak, Y. Zhan, and J. Lou, Proc. SPIE 7683, 76830B-1 (2010).*

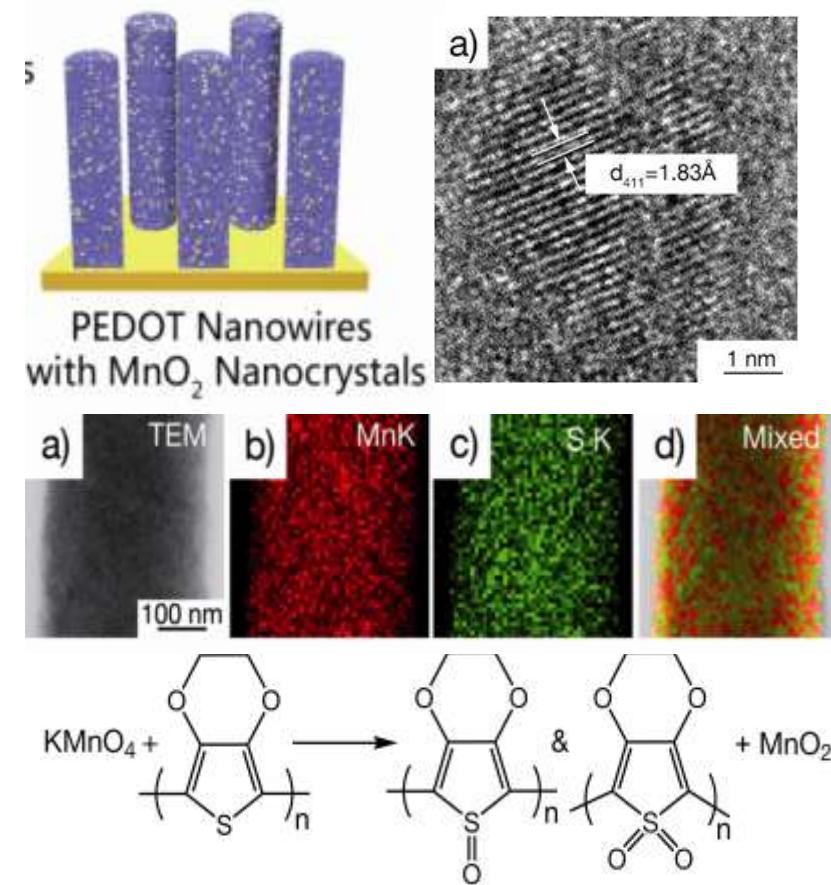
# Redox Exchange Induced $\text{MnO}_2$ -Nanoparticle Enrichment in PEDOT Nanowires

## Accomplishment

- Synthesis of  $\text{MnO}_2$  nanoparticles (likely alpha) in PEDOT conductive polymer matrix, with control over nanoparticle size and ability to achieve uniform distribution in the PEDOT
- High electrochemical performance: very high specific capacitance (410 F/g) as the supercapacitor electrode materials as well as high Li ion storage capacity (300 mAh/g) as cathode materials of Li ion battery with good cyclability.
- Revealed the mechanism of  $\text{MnO}_2$  nanoparticle formation in the PEDOT: triggered by the reduction of  $\text{KMnO}_4$  via the redox exchange of permanganate ions with the functional group 'S' on PEDOT.

## Significance

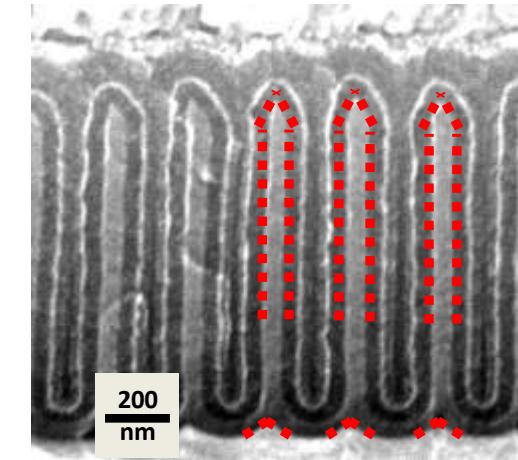
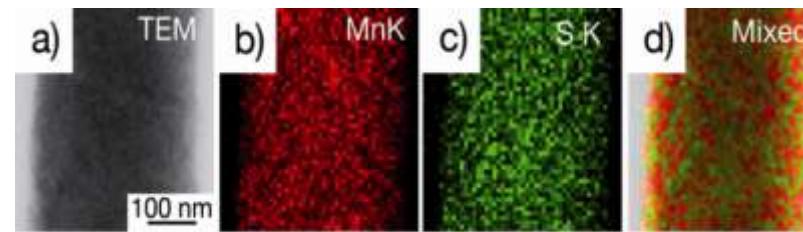
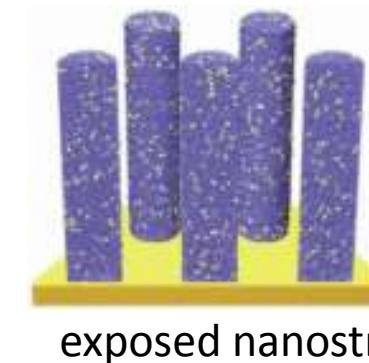
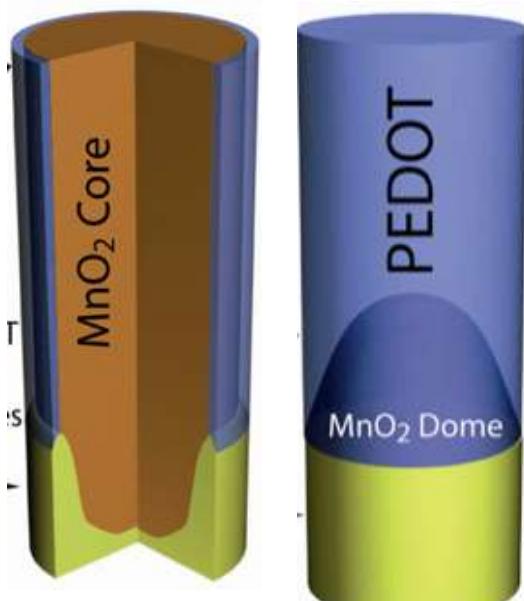
- Identified a new reaction pathway model to synthesize metal oxide nanoparticles in conductive polymer and graphitic carbon matrices.
- Determined that the reaction primarily involves the S group on PEDOT, rather than the oxidized polymer backbone as previously believed
- This synthesis route offers design flexibility to control and optimize  $\text{MnO}_2$  nanoparticle size for Li storage (insertion/desertion)



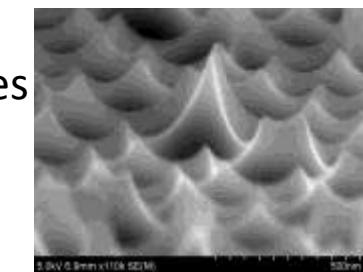
R. Liu, J. Duay, S.B. Lee. *ACS Nano*, **2010**, 4 (7), pp 4299-4307 DOI: 10.1021/nn1010182

# 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



# Virus-Templated Silicon Anode for Li Ion Batteries

## Accomplishment

- Assembly of a novel Si nanowire anode from *Tobacco Mosaic Virus* (TMV1cys) template
  - TMV's are identical nanotubes 300nm long, 4 nm ID, 18 nm OD
  - Self-assemble TMV on stainless steel through TMV 3' thiol group
  - Electroless deposition Ni current collector, then Si sputter deposition, onto TMV
- High capacities (3300mAh/g), nearly 10x capacity of graphite
- Excellent charge-discharge cycling stability (0.20% loss per cycle at 1C), and consistent rate capabilities (46.4% at 4C) between 0 and 1.5 V.

## Significance

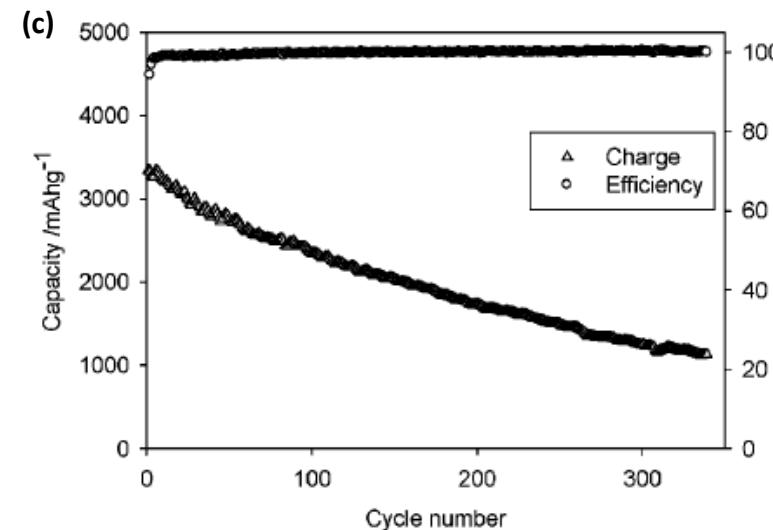
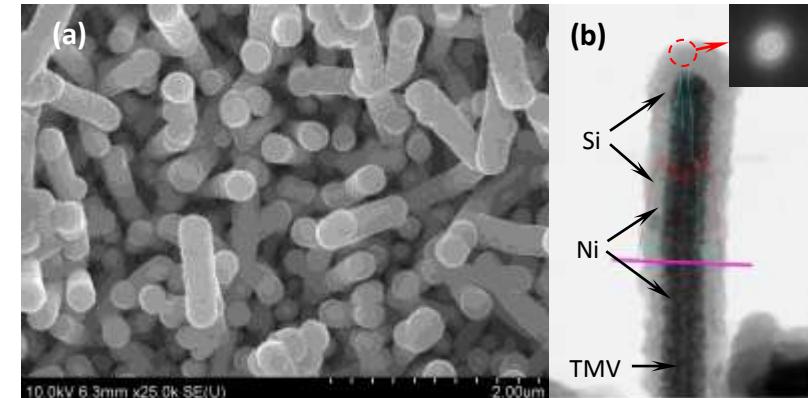
- TMV provides precisely reproducible template for a nanostructured electrode, ideal for assessing the benefits of highly regular nanostructures
- High capacity, comparable to other silicon nanostructured electrodes, demonstrates viability for TMV, biologically based nanoassembly strategy
- TMV offers technology advantages: very low cost, easily self-assembled on surfaces, highly reproducible nanostructures, in room temperature, neutral pH processes

## Collaborators

Xilin Chen, Konstantinos Gerasopoulos, Juchen Guo, Adam Brown, Chunsheng Wang, Reza Ghodssi, James N. Culver, *UMD*

## Supporting material

Xilin Chen et al, "Virus-Enabled Silicon Anode for Lithium-Ion Batteries", *ACS Nano*, Article ASAP (Aug. 13, 2010); DOI:10.1021/nn100963.



Si/Ni/TMV1cys nano wire (insert: Fast Fourier Transform image of silicon) (c) Cyclic performance of the 3-D TMV1cys/Ni/Si anode at 1C (2000mA/g)

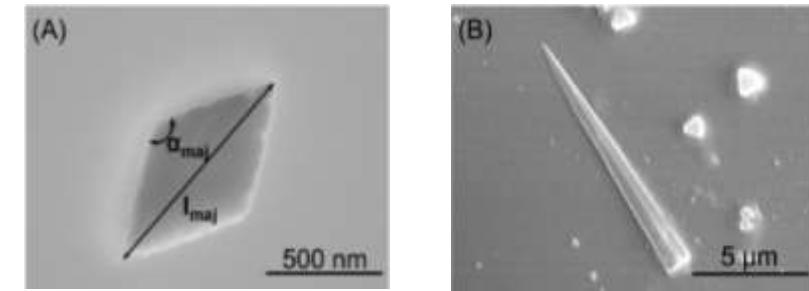
# Electro-osmotic Flow Rectification in Pyramidal-Pore Mica Membranes

## Accomplishment

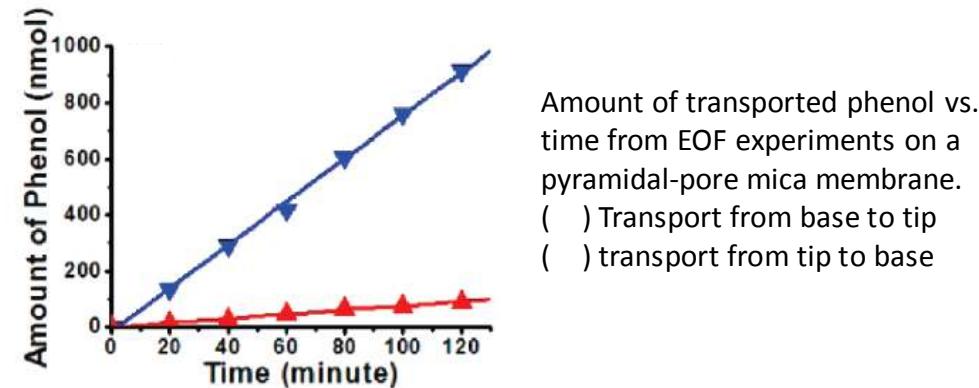
- Electro-osmotic flow (EOF) rectification has been demonstrated in membranes containing pyramidal nanopores, using phenol transport to decorate the flow rectification.
- EOF velocities are larger when phenol is transported from base-to-tip than from tip-to-base.
- EOF rectification in tapered pores complements our prior findings on ion transport rectification.

## Significance

- Nano-engineering of pore design offers opportunity to control electro-osmotic flow phenomena.
- Understanding of these ion and fluid transport processes at the nanoscale may prove important for electrochemical performance in high density nanowire forests, the focus of next-generation nanostructure-based electrodes.



Electron micrographs of (A) the base opening of a pore in a mica membrane and (B) a carbon replica of a pyramidal mica pore.



Amount of transported phenol vs. time from EOF experiments on a pyramidal-pore mica membrane.  
 (—) Transport from base to tip  
 (—) transport from tip to base

## Collaborators

Jin, P.; Mukaibo, H.; Horne, L. P.; Bishop, G. W.; Martin, C. R.,

## Supporting material

*J. Am. Chem. Soc.* 2010, 132 (7), 2118-2119.