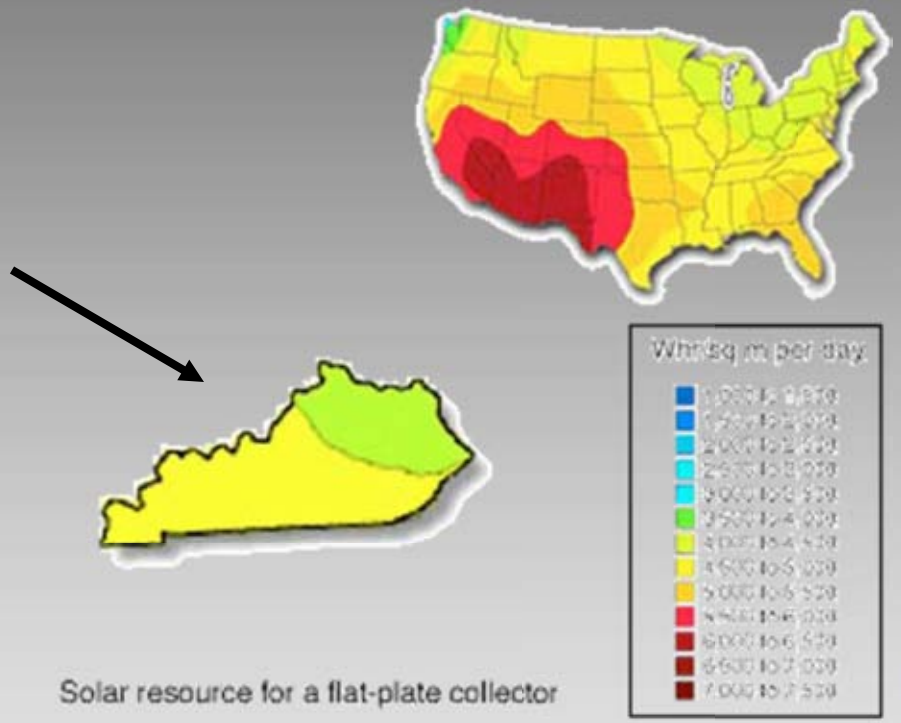
Nanoscale materials & architectures for energy conversion

Eric Grulke, University of Kentucky

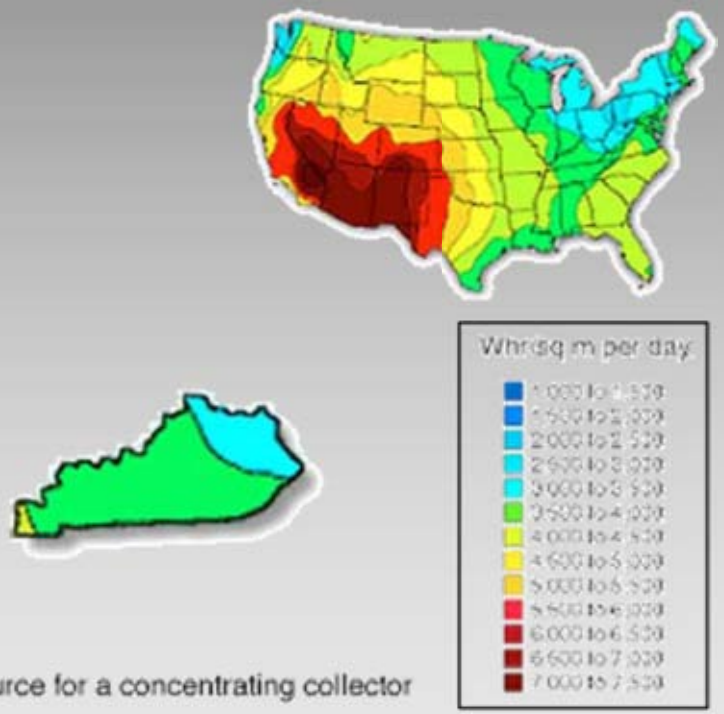
Mahendra Sunkara, technical PI, University of Louisville

Kentucky's alternative energy resources

- Biomass: two demonstration projects. CO2 →algae→biodiesel; cellulose→biodiesel
- Geothermal: low temperature resource for geothermal heat pumps
- Hydropower: INL region 5. 4% of total energy, http://hydropower.inel.gov/prospector/index.shtml
- Solar: suitable for flat plate collectors, http://www.nrel.gov/gis/solar.html
- Wind: low wind speeds in Kentucky, http://www.eere.energy.gov/windandhydro/windpoweringamerica/wind_maps.asp



Solar resource for a flat-plate collector



Solar resource for a concentrating collector

http://www.nrel.gov/gis/solar.html

- Year 1 DOE-EPSCoR implementation project: Nanoscale materials & architectures for energy conversion
- State energy activities
  - 2007 KY energy initiative
  - Energizing Kentucky, 2008
  - 2008 energy strategy, state of Kentucky

Year 1

Project overview

Bullets

Upcoming events

Project overview
- discovery with a focus on control

Design, synthesis, fabrication and characterization of nanostructured materials for:

- photoelectrochemical harvesting of solar energy,
- photoelectrochemical production of hydrogen, and
- thermionic systems for heat recovery

	PEC for Harvesting Solar Electricity	PEC for Hydrogen Production	Thermionic Systems for Heat Recovery
Goal	Utilize nanostructured materials to understand and overcome challenges in developing low cost solar cells with >10% efficiency	Utilize nanostructured materials to tune photoabsorption and catalysis for hydrogen production at high efficiency	Develop portable, scaleable materials that use nanoscale thermoionic emitters to scavenge electricity from waste heat
Synthesis Methods	Chemical vapor deposition, sol-gel processing, self-assembly, nanoparticle synthesis (e.g. emulsion precipitation)		Chemical vapor deposition
Target Structures	Oriented titania and carbon nanotube films, quantum dot sensitized particles and films	3-D architectures of group III-nitride ternary alloys with composition and junction control	Dense arrays of carbon nanopipettes
Fundamental Properties	**Transient absorption spectroscopy to measure reaction kinetics (including hole-electron generation, injection / recombination) and transport dynamics***; UV-vis absorption spectroscopy+; Photoactivity (effiency, fill factor, catalytic activity) and stability; Electrochemistry (AFM); Electronic structure calculations+		Thermionic emission; Electron energy distribution; Field emission
	Kelvin probe, UPS, SEM, TEM, XRD, pore size distribution, particle size distribution		
Issues Anticipated / Addressed	Charge transport and recombination	Band edge energetics	Combining low work function and high conductivity; Effects of nanopipette dimensions, spacing, and distance to collector; Stability / reliability
	Effect of architecture on performance; tuning the absorption spectrum to maximize use of solar spectrum; stability under conditions of use		

* New infrastructure will be developed in the proposed work. + New equipment will be purchased.

A commitment to energy infrastructure…

Kentucky energy infrastructure investments

U of L: Ultrafast spectroscopy system for PEC solar cell characterization via sub-ps measurement of photocurrents; current facilities include a nanotechnology core facility - **Institute for Advanced Materials and Renewable Energy** and **Nanofabrication Lab**

UK: workstations for computational studies (Gaussian 3.0) and UV-Vis spectrometer for rapid screening; current facilities include the **Center for Nanoscale Science and Engineering** and the **Center for Computational Sciences.**

A commitment to energy infrastructure…

links to DOE infrastructure

- **NREL:** for PEC cell device design and durability/efficiency testing (John Turner)
- **ORNL:** for nano-EBIC (Steve Pennycook)

Accomplishments

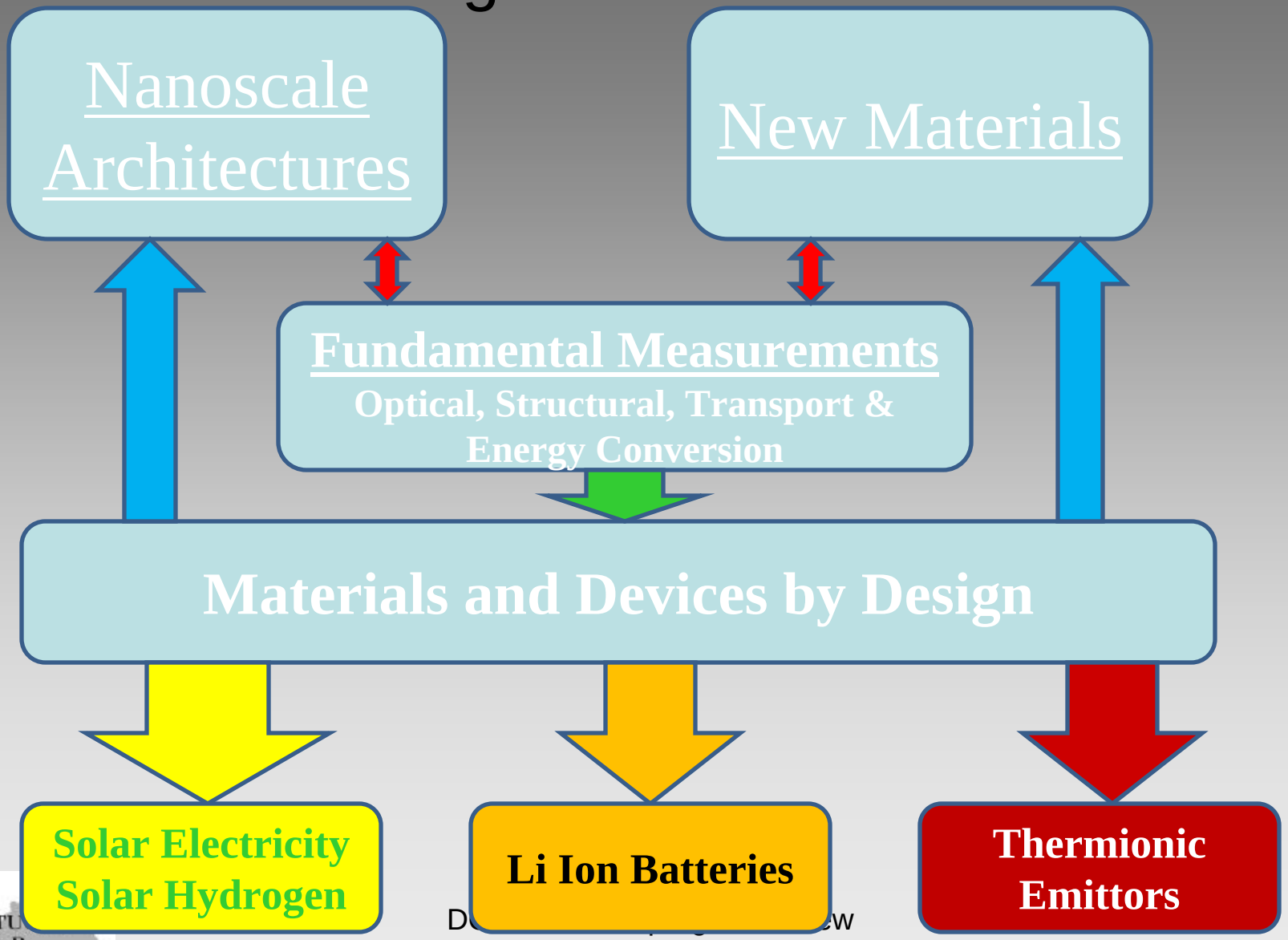
Accomplishment	Significance
Higher efficiency band-edge engineering concept	Higher efficiencies for dye-sensitized solar cells
E-beam irradiation for self-assembly of tailored pores	Creation of pores on semiconductor nanowires for architecture templating
Electrochemical redox couple pins Fermi level via sorbed water	Effects of environment on electrical, optical and photochemical properties
Tunable HCP channels in titania for PEC cells	Scalable, viable alternative to single crystal technology for solar cells
Proof-of-concept for energy storage system in nanotube membranes	Active blocking of CNT pores provides a mechanism for hydrogen storage
Tailored electronic band gap by alloying	Impurities in ZnO modify band gap but do not affect structure

Personnel

Topic	Co-PI	Supervisees	support
Theoretical approach to solar energy for electric power generation	M. Menon	None	
Nanostructures for solar energy conversion	P. Menguc	S. A. Uddin, R.A., Mechanical Engineering	100%
Evaporation-driven synthesis of photoactive semiconducting films	S. Rankin	Fall, 2008	
Aligned carbon nanotubes membranes for photovoltaic energy storage	B. Hinds	Xin Su, R.A., Chemical Engineering	100%
Nanowire-based architectures for dye sensitized solar cells	M. Sunkara	Suresh Gubbala, R.A., Chemical Engineering Dr. Vidhya Chakrapani, Chemical Engineering	100% 50%
New materials for photolysis of water	M. Sunkara	Dr. Vidhya Chakrapani, Chemical Engineering Dr. Jacek Jasinki, TEM research scientist	50% 25%
Photo-electrochemical AFM of PEC cells	G. Willig	Sudhira Pasupuleti, R.A., Chemical Engineering	100%
Transient spectroscopic characterization of PEC cells	H. Rypkema	Amy J. Sanders, R.A., Chemistry	100%
Optical characterization of electrode materials	B. Alphenaar	Hemant M. Shah, R.A., Electrical and Computer Engineering	100%
Thermionic emitter fabrication, modification and array characterization	G. Sumansekera	Santoshrupa Dumpala, R.A., Chemical Engineering David Mudd, B.S in Physics	100% 100%
Thermionic and field emission characterization of individual emittors using in situ SEM	R. Cohn	Abdelilah Safir, R.A., Electrical and Computer Engineering	100%
Administration	E. Grulke	No students	

Project elements, overview, instrumentation.

Nanoscale materials and architectures for energy conversion & storage



Instrumentation.

(KY DOE-EPSCoR)

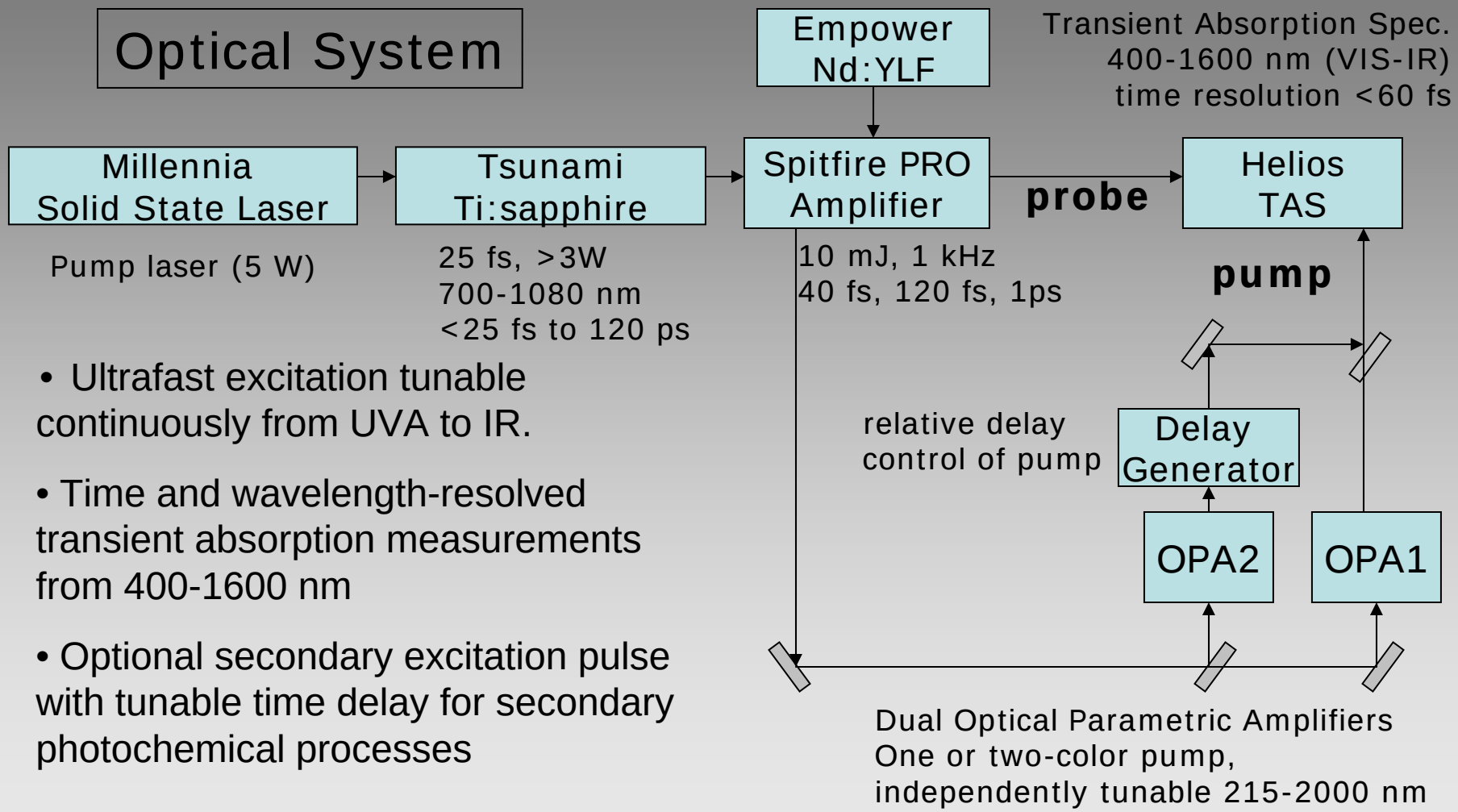
- **Structural, Optical, Photoelectrochemical & electrochemical techniques** (M. Sunkara, S. Rankin, B. Hinds)
  - Essential for materials and process development efforts
- **Theoretical computations & simulations** (M. Menon & M. Sheetz)
- **Ultrafast, transient absorption spectroscopy** (H. Rypkema, UofL)
  - New facility; allows probing of time-resolved processes (>100 fs – ms)
- **Photocurrent Spectroscopy** (B. Alphenaar, UofL)
  - Probe triplet states in organic molecules and dye assemblies
  - Design new assemblies using spin coupling
- **Electrochemical AFM/STM** (G. Willing, UofL)
  - Spatially resoved, nanoscale mapping of photo-electrochemical performance
- **Field emission measurements** (In-situ SEM & bulk)

(G. Sumanasekera, R.W. Cohn & P. Menguc)

Ultrafast Spectroscopy Facility

H. Rypkema, UofL

Optical System



- Ultrafast excitation tunable continuously from UVA to IR.
- Time and wavelength-resolved transient absorption measurements from 400-1600 nm
- Optional secondary excitation pulse with tunable time delay for secondary photochemical processes

Ultrafast Spectroscopy Facility

Materials Applications

- Observe generation and decay of transient species
- Measure electron injection rate
- Distinguish excitation of semiconductor bands from chromophores
- Measure primary and secondary photodegradation processes
- Charge recombination
- Dynamics of hot charge carriers

General Applications

- Photoisomerization dynamics
- Vibrational relaxation
- Photosynthetic electron transfer
- Optical properties of nanostructures
- Time-resolved medical imaging

Point-Source Electrochemical AFM (PSEC-AFM)

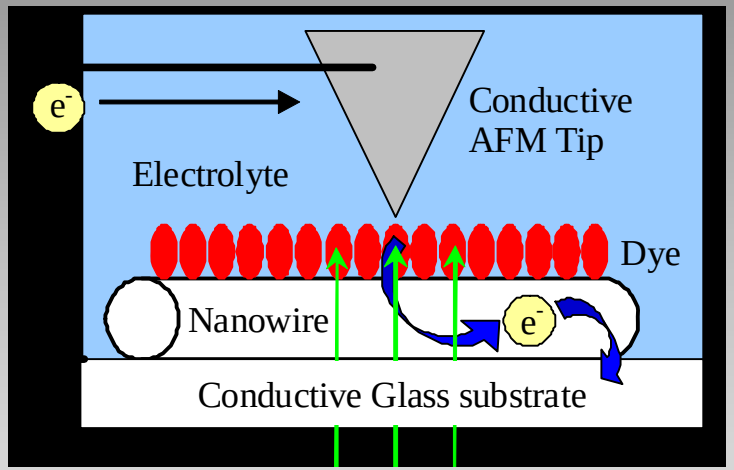
Gerold Willing

Opportunity

- EC-AFM only observes the results of an electrochemical reaction
- Conductive AFM uses current to map conductivity variations across a surface
- PSEC-AFM will combine both techniques for nanoscale EC measurements

Solution

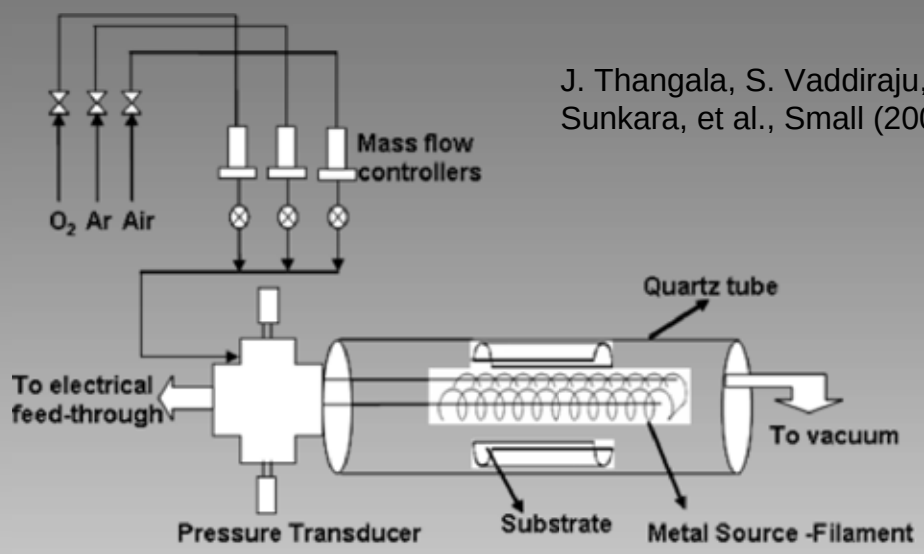
- Unique system w/tip as counter electrode
- Current focused through tip (radius <10 nm)
- I-V measurements with a 10 nm lateral resolution
- PSEC-AFM EIS measurements will help determine electron transfer kinetics



Challenges

- Unique system - very little prior art available for design
- Sample preparation must be compatible with AFM imaging (low nanowire density)
- Electrolyte has to be fairly transparent as AFM deflection measured using a laser

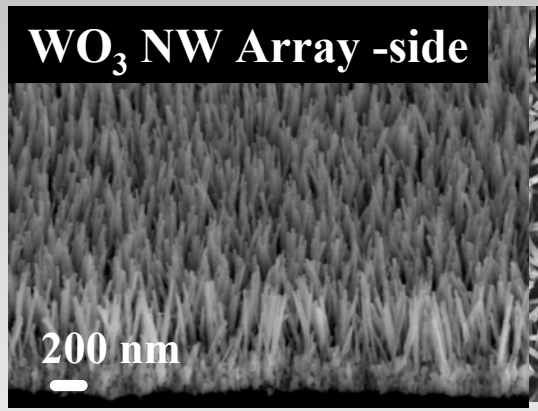
Metal oxide nanowire arrays via hot wire deposition

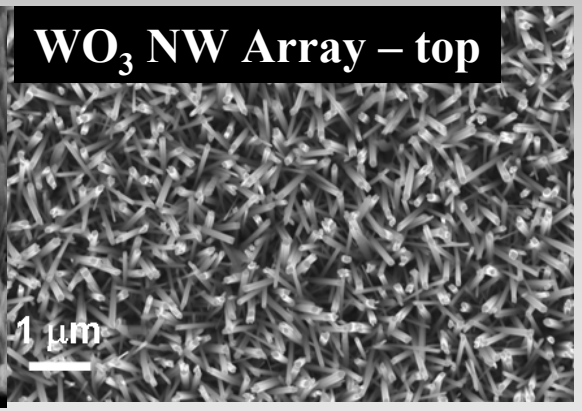


J. Thangala, S. Vaddiraju, M.K. Sunkara, et al., Small (2007)

Fluorinated tin oxide coated glass slide

Quartz slide





Materials Systems

WO_3, NiO, MoO_3, Ta_2O_5
Fe_2O_3 (being tried)

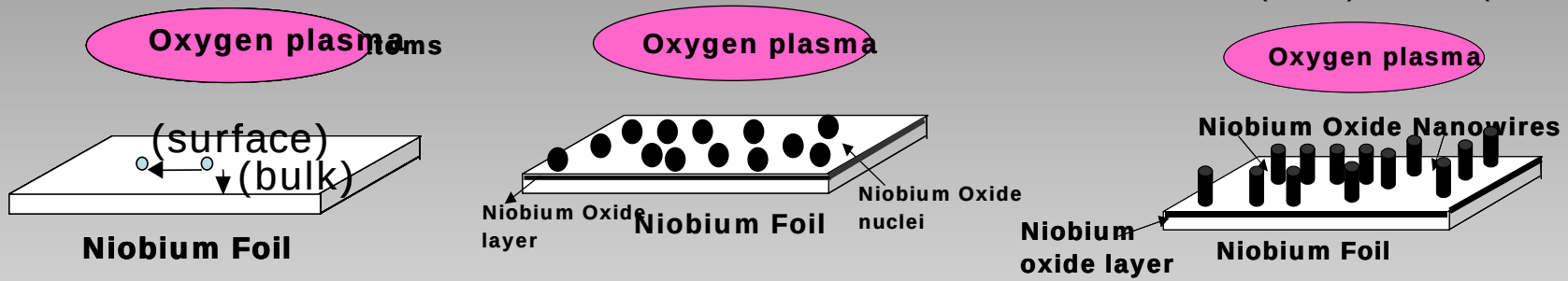
Metal Oxide Nanowire Arrays on Metal Foils

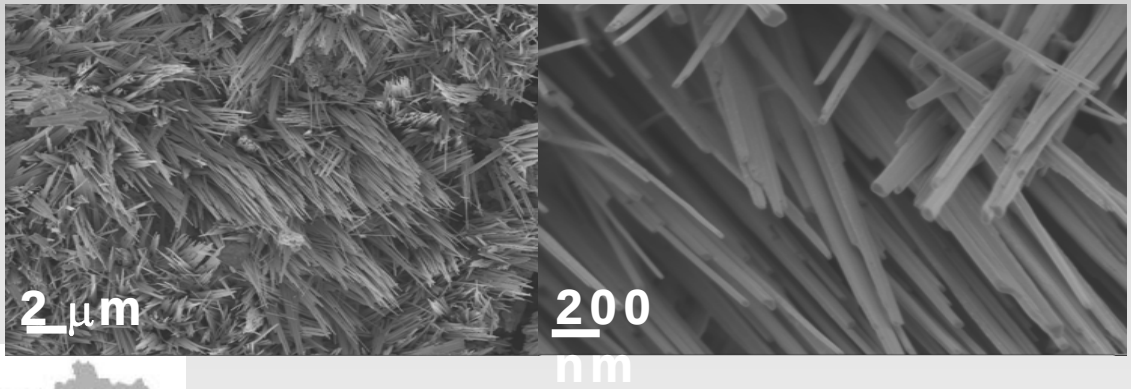
with Dr. Uros Celbar and Dr. Miran Mozetic, IJS, Slovenia

Oxidation Using Highly Disassociated Oxygen Plasmas

- Very high density of oxygen neutrals
- Low temperature oxidation
- Fast oxidation times (seconds)

U. Cvelbar, M.K. Sunkara et al., Advanced Materials (2005); Small (2008)





Materials Systems

V_2O_5, Nb_2O_5, Fe_2O_3

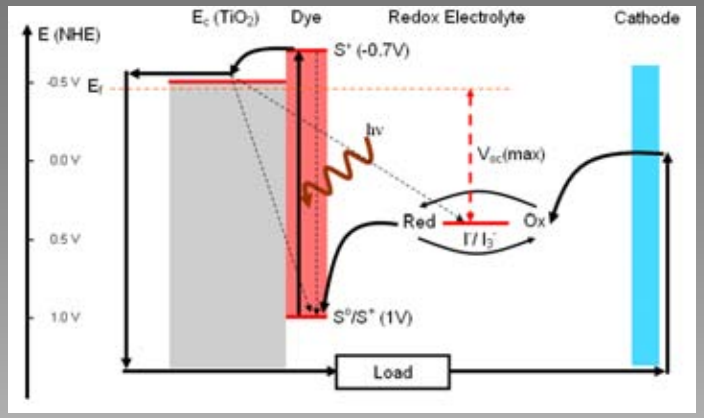
Nanowire-based Materials for Solar Electricity.

Dye Sensitized Solar Cells

Band-edge Engineered Hybrid Structures for Dye-Sensitized Solar Cells

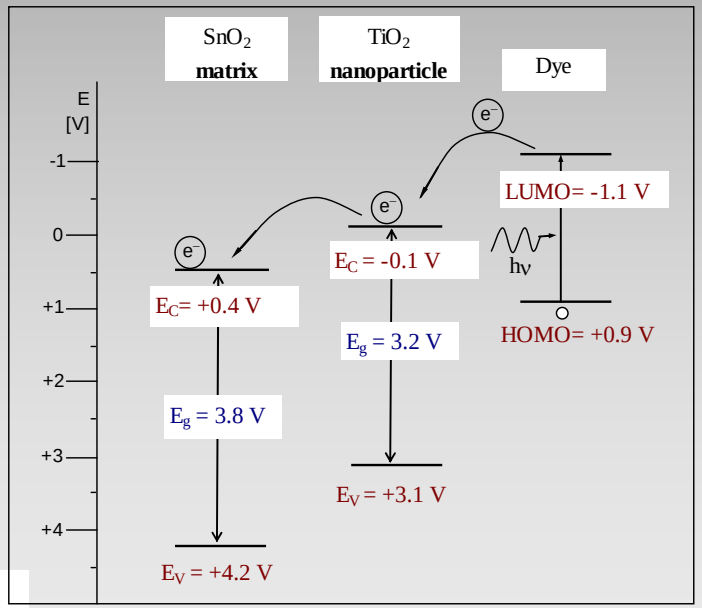
<u>Challenges:</u>

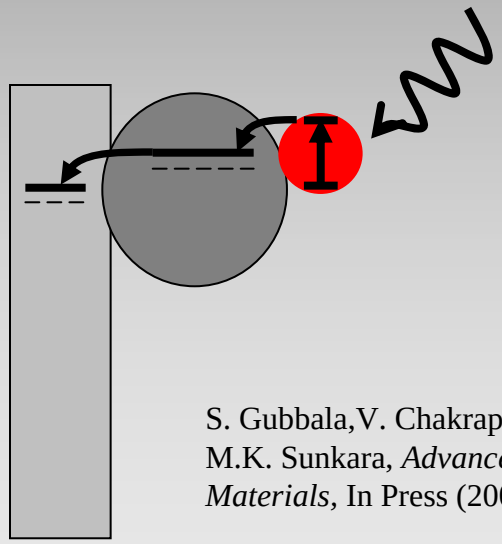
Slow charge transport through the mesoporous semiconductor electrode
High recombination losses
Stability
No IR light absorption



Dye Sensitized Solar Cell

SnO_2 NW / TiO_2 NP / Dye

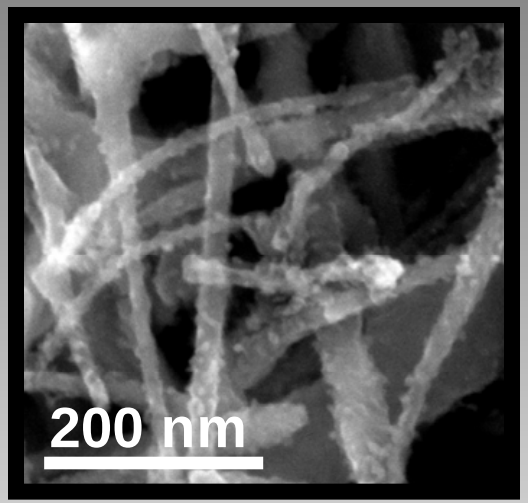


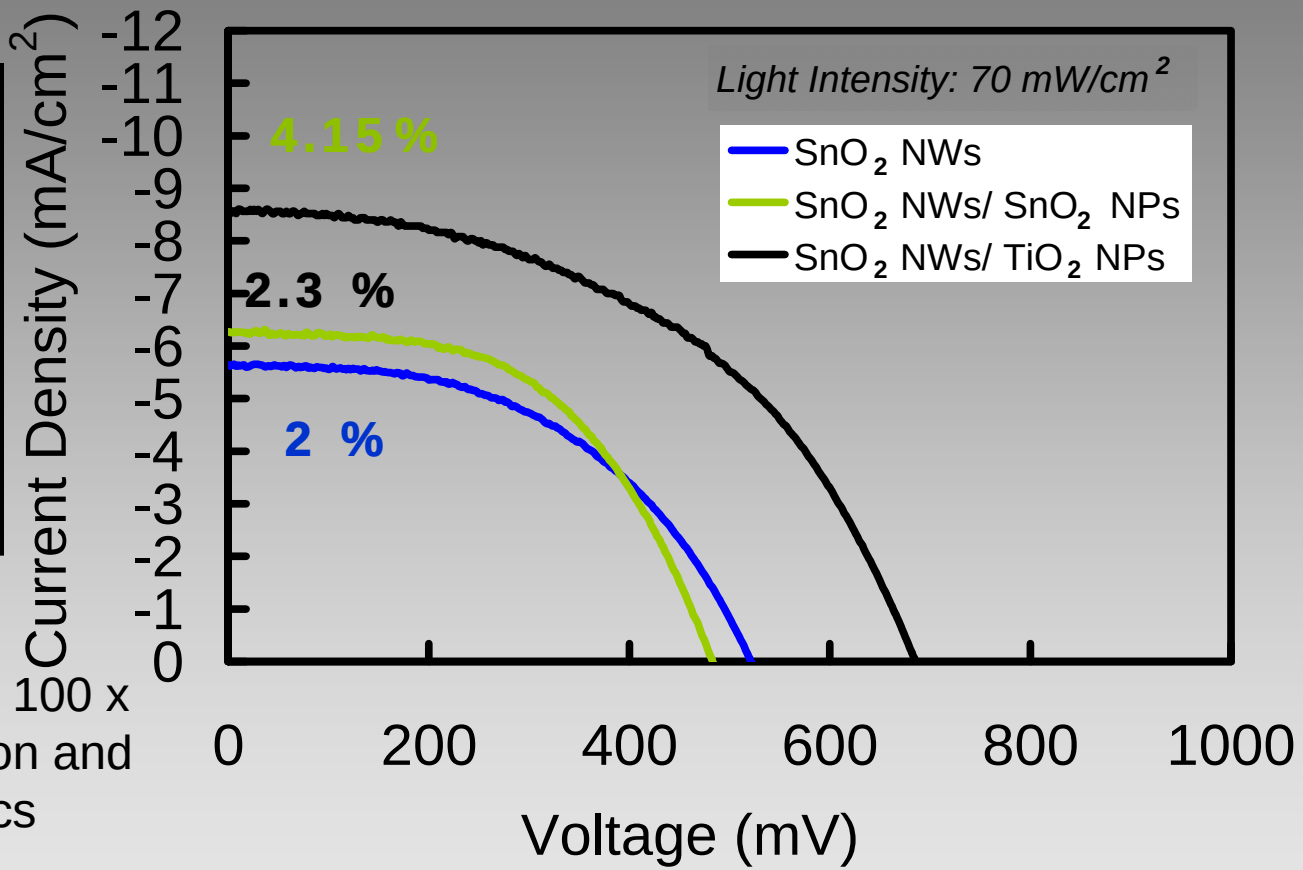


S. Gubbala,V. Chakrapani, V. Kumar and M.K. Sunkara, *Advanced Functional Materials*, In Press (2008)

KENTUCKY EPSCoR PROGRAM

Band-edge engineered hybrid structures for dye-sensitized solar cells – controlled structures



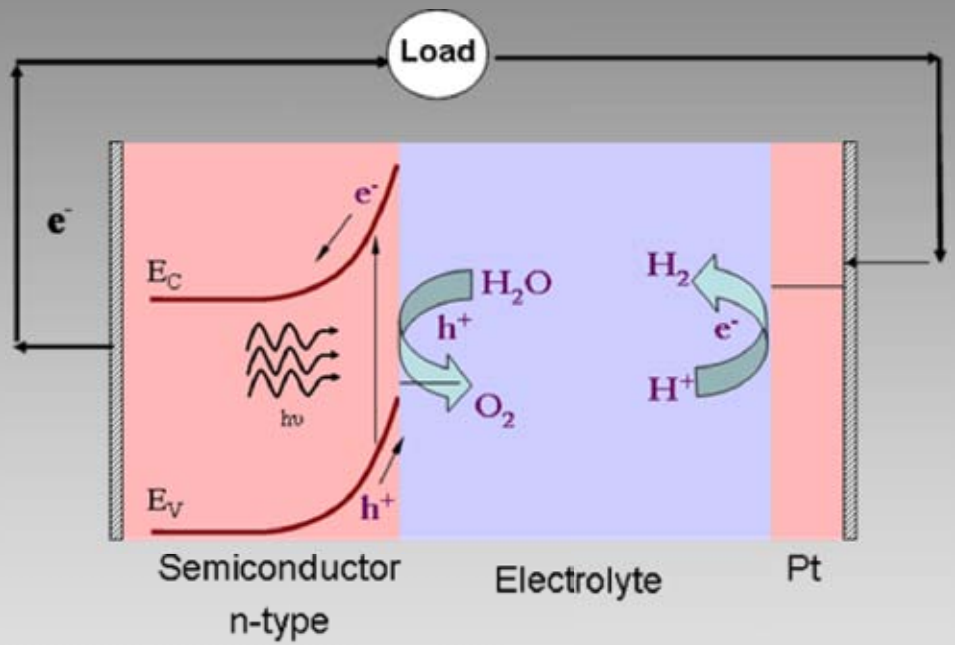


This architecture gave 100 x improved recombination and transport characteristics

S. Gubbala,V. Chakrapani, V. Kumar and M.K. Sunkara, *Advanced Functional Materials*, In Press (2008)

Nanowire-based architectures for solar chemical production

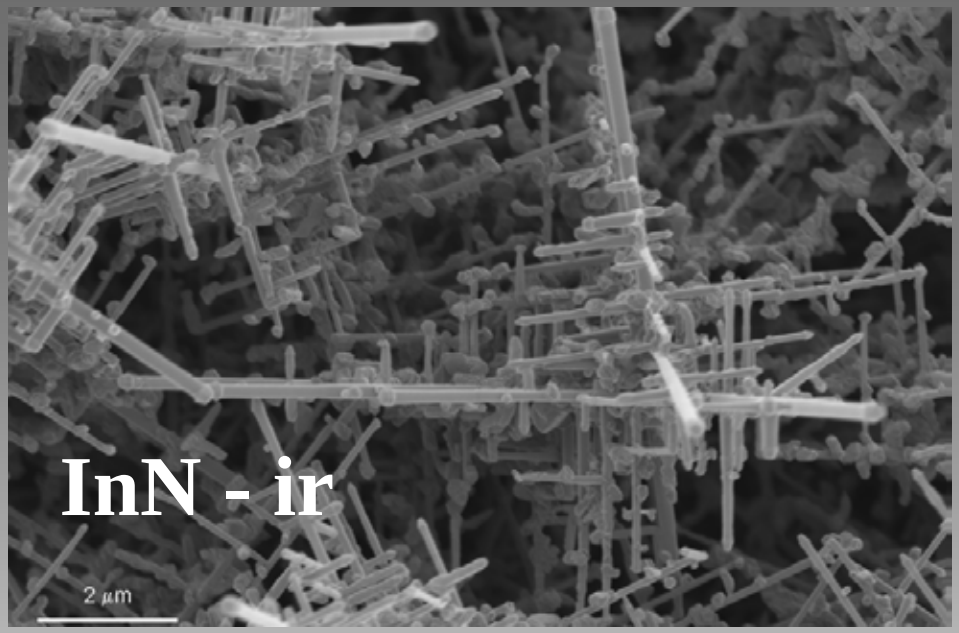
Photolysis of water



Material selection

- Band gap must be between 1.8 – 2.2 eV.
- Band edges must straddle hydrogen and oxygen evolution reactions.
- Need to be stable (no corrosion under photolysis).

3-D "tree-like" nanoscale architectures



Ternary Alloys:

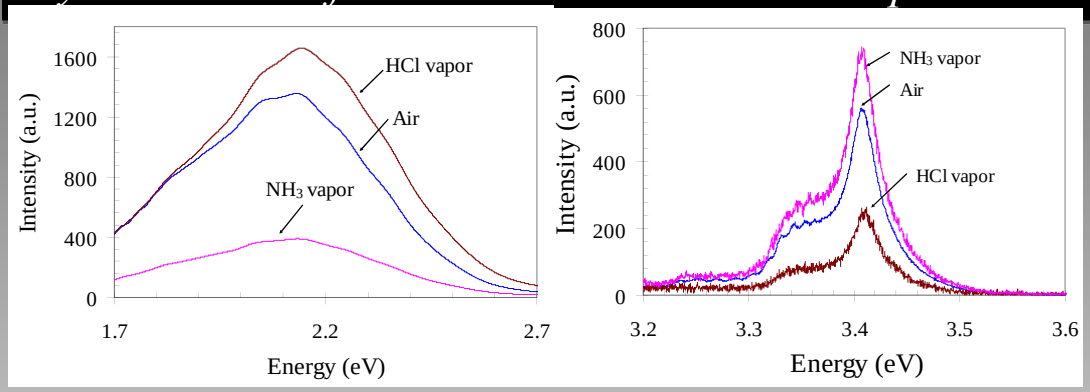
$Ga_{1-x}In_xN$: (0.8 eV (?) –3.4 eV)
$GaSb_{1-x}N_x$: (0.8 eV – 3.4 eV)

Student: C. Pendyala
PI: M.K. Sunkara

Vertical structure, high surface area, many compositions possible

Electrochemical Transfer Doping in GaN and ZnO!

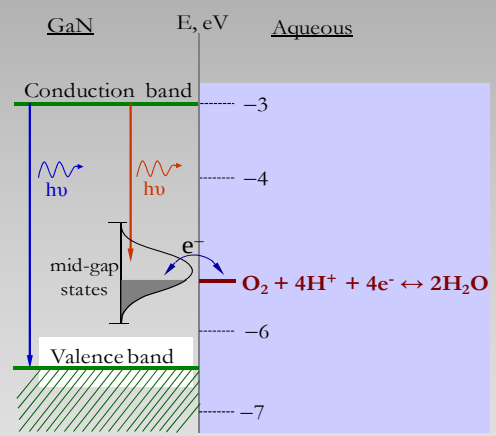
Rationale: *Ambient effects on the electronic and optical properties of semiconductor has been observed before, but not been understood. Sensing is impact by adsorbed water layer. Control of absorbed water could be important.*



Photoluminescence (PL) from both GaN and ZnO changes systematically and reversibly with changes in O_2, humidity and pH of the ambient.

Proposed an electrochemical model to explain this strange and important effect. The PL is modulated due to the electron transfer from defects states in GaN to an electrochemical redox reaction occurring in the adsorbed water layer on the surface, namely:

$$O_2 + 4H^+ + 4e^- = 2H_2O$$



V. Chakrapani, C. Pendyala, K. Kash, M. K. Sunkara, A. B. Anderson, and J. C. Angus, Accepted, J. Am. Chem. Soc., *2008*

Impact: *Fundamental understanding the nature of interactions between defect states and electrochemical reactions is of prime importance to photoelectrochemical systems.*

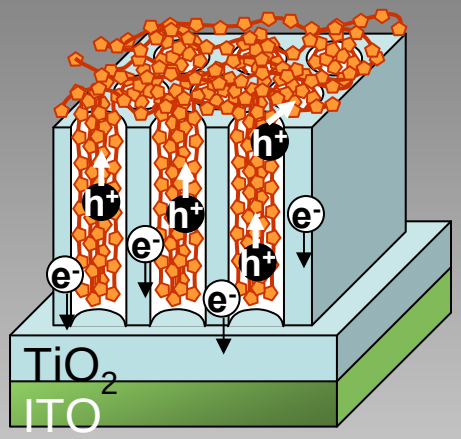
Vertically aligned mesoporous channels for polymeric semiconductors.

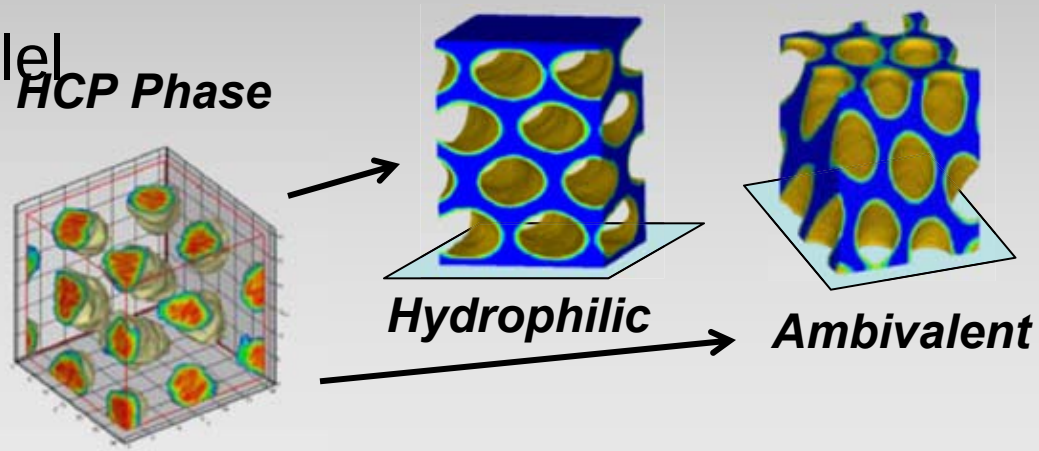
- morphology control for hybrid inorganic/organic solar cells.
- synthesis of structure concepts developed via modeling

Controlling vertically-aligned mesoporous ceramic films

Stephen E. Rankin, University of Kentucky, srankin@engr.uky.edu

- Orthogonally oriented hexagonal close-packed HCP (o-HCP) mesoporous titania films would present array of uniform, cylindrical pores
- Oriented cylindrical pores increase mobility of holes in organic semiconductors* for inorganic/organic hybrid solar cells
- HCP phase grows parallel to hydrophilic walls & perpendicular to ambivalent walls (no interactions)



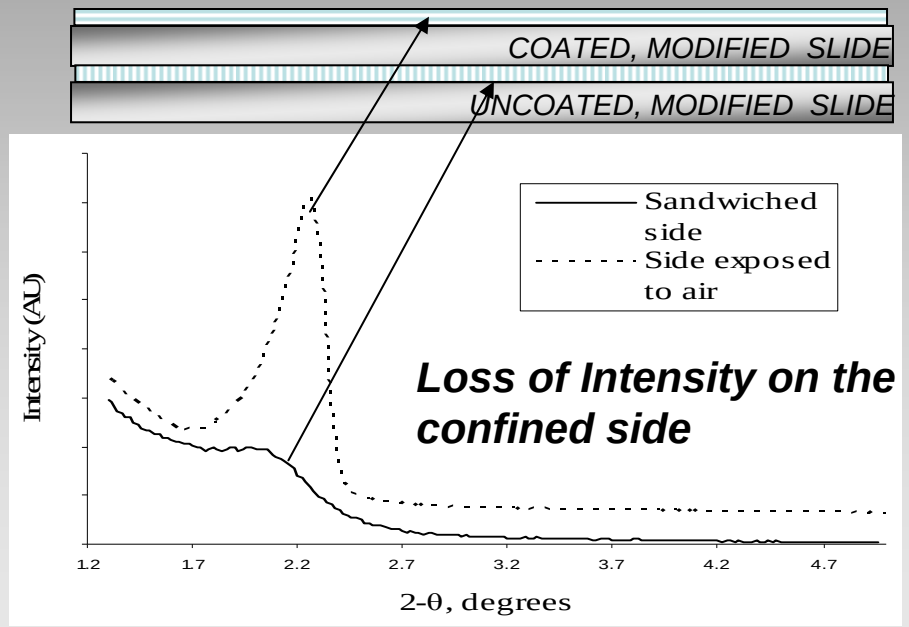


* M. D. McGehee et. al *MRS Bull*. **2005** *30*: 37-40

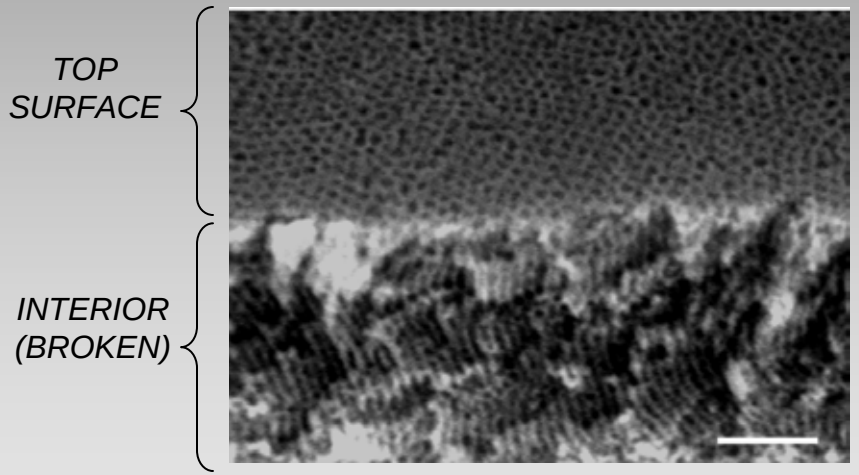
Vertically-aligned mesoporous titania by rapid dip coating

- Titania films prepared by evaporation-induced self assembly (EISA) approach with $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ block copolymer (P123)
- Isocyanate-crosslinked P123 or PEO-r-PPO used to create "ambivalent" surface

XRD → Sandwiching film orients HCP



SEM of oriented titania film



* V.R. Koganti et al. *Nano Letters* **2006** *6*: 2567.

Upcoming events

1st year project review

- 3 October 2008
- co-current with statewide meeting
  - Reps from ORNL, NREL
  - Industry: utility and high tech company
  - Other implementation projects
  - Energy and Environment Cabinet, State of Kentucky
- Objective: developing a successful renewal proposal

A commitment to energy…

Commonwealth of Kentucky activities

- 2007 status report
- “Energizing Kentucky”
- 2008 cabinet appointment
- 2008 comprehensive energy plan
- Energy commercialization grants
- Consortium for carbon sequestration

Kentucky's Energy Opportunities for Our Future

2007 Status Report

August, 2007

(prior administration)

Guiding principles:

- Maintain Kentucky's low-cost energy; responsibly develop Kentucky's energy resources; preserve Kentucky's commitment to environmental quality
- Policy areas: energy efficiency; renewable energy; low-cost electricity, coal, natural gas; Kentucky's energy future
- 54 recommendations

“Energizing Kentucky”

Larry Shinn
Berea College

John Roush
Centre College

Lee Todd
University of Kentucky

James Ramsey
University of Louisville

"Energizing Kentucky," the brainchild of Berea College President Larry D. Shinn, Centre College President John A. Roush, University of Kentucky President Lee T. Todd Jr. and University of Louisville President James Ramsey, **encourages Kentucky to focus on a coherent and integrated energy policy** and will assist this policy formation by bringing together state and national energy experts to discuss the economic, educational, and environmental opportunities and challenges presented by the world's current energy situation.

Outcomes:

- enhanced public policy debate
- engage higher education in solutions
- ensure diverse inputs, including carbon balance, environmental impact, conservation, architecture for energy efficiency, and community planning

State of Kentucky energy initiatives. 2008

New directions,

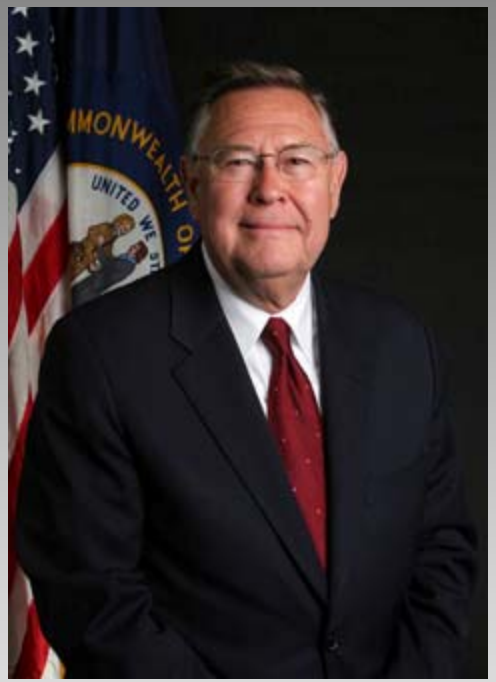
New administration

Summary

- Refocus on energy issues by the state of Kentucky, new directions, new opportunities, integration across state
- Strength in energy-related research at leading research institutions, collaborations, significant current funding

Secretary, Energy and Environment Cabinet

Len Peters, June, 2008.
Dr. Peters is an internationally renowned chemical engineer with demonstrated leadership in research, academia and management. He served for the past five years at the Battelle Memorial Institute in Columbus, a leading nonprofit applied science and technology development company. During his tenure at Battelle, Dr. Peters was senior vice president and director of the Pacific Northwest National Laboratory.



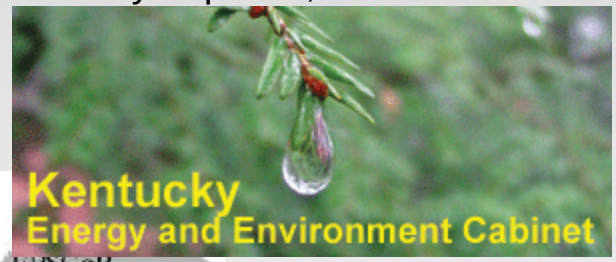
EPSCoR PROGRAM

KY strategy. KRS 152.710 TO 152.725

Technologies for producing alternative transportation fuels and synthetic natural gas from fossil energy resources, biomass resources; process efficiencies, environmental performance, and marketable products, including chemicals, industrial feedstocks, and electricity;

Research, demonstration, and commercial-scale construction and operation of clean coal technology, coal-to-liquid-fuel conversion, synthetic natural gas, alternative transportation fuels, and biomass resources; federal funds for research, development, construction, and operation of alternative fuels or synthetic natural gas plants; establishment of a major federal energy research laboratory in Kentucky; industry participation in research, development, construction, and operation of alternative transportation fuels or synthetic natural gas plants;

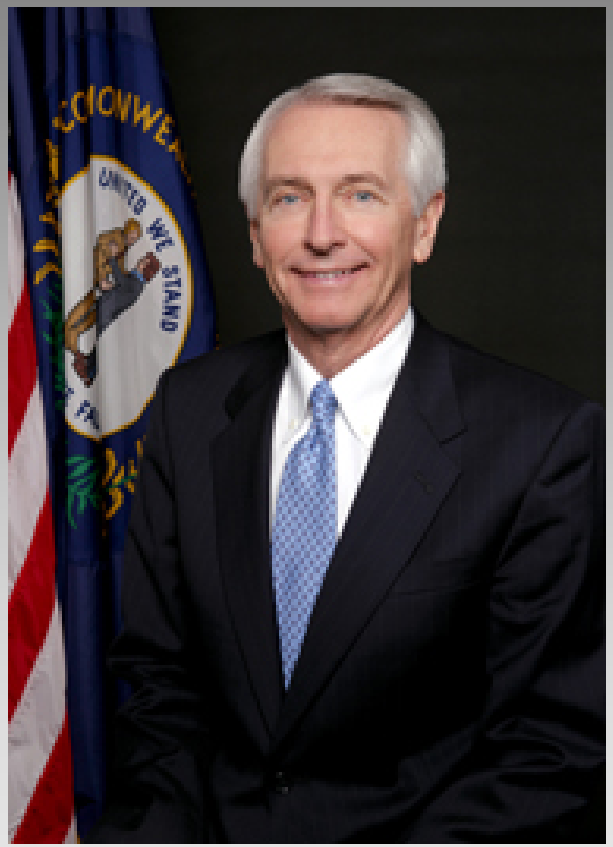
Kentucky state government incentives for development, construction, or operation of alternative transportation fuels and synthetic natural gas production facilities; and development of incentives to encourage energy conservation and renewable fuel and energy use and deployment of renewable energy, including solar power, wind power, hydropower, and others.



Kentucky to Develop Comprehensive Energy plan

- "If ever there was a time for this country to become energy independent, that time is now. Kentucky is sitting on top of all of the resources it will take to aggressively pursue that goal."

Governor Steve Beshear



Governor Steve Beshear
Commonwealth of Kentucky

- Create thousands of additional jobs for Kentuckians in the energy sector
- More fully use wind, solar and other renewable energy resources.
  - Less than 3% of Kentucky's electricity is generated by renewable sources, and most of that is hydro-electric.
- Reduce carbon emissions from electricity generation.
  - Kentucky ranks 7th in the nation in carbon dioxide emissions per capita.

Governor Steve Beshear
Commonwealth of Kentucky

- Maintain and increase the state's coal production levels, thereby protecting the employment of 18,000 Kentucky coal miners.
- Use coal to produce crude petroleum to meet transportation needs.
  - Kentucky currently consumes more than 2 billion gallons of gasoline per year.
- Generate adequate biodiesel from algae production and cellulosic non-food biomass.

Kentucky Consortium for Carbon Sequestration

Oversight and funding from the Kentucky Energy and Environment Cabinet
WKy Deep Test Subproject
EKy Deep Test Subproject
EOR and EGR Subproject
Consortium Members

A research project administered by the Kentucky Geological Survey, University of Kentucky

http://www.uky.edu/KGS/kyccs/

A commitment to energy…

KY EPSCoR research team

University / state collaborations

State of Kentucky

Questions?

Energy efficiency

- 2006: Energy Star Partner, DOE & EPA
- KY's energy efficiency potential study – U of L
- Many local and directed grants

Renewable energy

- Energy grants: biodiesel use, biodiesel plants, research for KY Rural Energy Consortium,…

Low cost electricity

- Electricity infrastructure assessment:
- House Bill 275 (2006): assist aluminum smelters in Western KY
- Future needs: 10 new power plants @ 700 MW each
- Coal:
  - Coal gasification, mining permitting, FutureGen, clean coal technology, Appalachian reforestation, coal slurry reuse
- Gas:
  - Coal bed methane, syngas via co-gasification of coal and coal bed methane
  - Western KY deep gas exploration

KY's energy future

- Executive order on fuel efficiency, energy research, retail rate design, energy education
- R&D:
  - $7.5 million in energy-related research, development and demonstrations, ~ 50 projects

Kentucky Energy Commercialization Grants

- $3.5 M per year
- Research projects: clean coal, new combustion technology,thin-seam coal extraction, safety, tracking and communication devices, coal slurry disposal, syngas from coal, & transportation fuels from coal or biomass resources