Nanoscale materials and architectures for energy conversion and scavenging

KY EPSCOR

Implementation award

UofL

UK UNIVERSITY OF KENTUCKY College of Engineering Research

Rationale

- Nanostructured materials to improve technology for converting solar radiation and heat to electricity and hydrogen
- Synthesis + fundamental studies of energy absorption and transport + design and fabrication of novel energy device architectures
- Challenges include: photoelectrochemical production of hydrogen from water, photoelectrochemical cells for electricity and thermionic emission for thermal to electrical energy conversion

Unique approaches

- Versatile route to 3-D “tree” architectures of high-purity III-nitride materials
- Scalable process of oxidation of Nb foils for high density vertical arrays of nanowires
- High density GaN nanowires decorated with < 5 nm InN quantum dots
- Super-aligned nanoscale pores within titania films
- High density CNT membranes for ion separation and storage
- Usable arrays of tapered, robust carbon nanostructure-based architectures for TE applications.

Link to Commonwealth's focus areas for research excellence

Kentucky's technologies for economic development (HR1, 2000)

- Human health and development
- Biosciences
- Information technology
- Environmental and energy technologies
- Materials science and advanced manufacturing

EPSCOR project technologies and infrastructure development

- New advanced materials in electronic and photonic applications
- Fuel cell power
- Synthetic fuels
- U of L: Institute of Advanced Materials and Renewable Energy
- UK: Center for Nanoscale Science and Engineering
- Ultrafast spectroscopy (U of L): femtosecond laser, ultrafast absorption spectrometer, optical parameter amplifier
- UV-vis spectrophotometer, workstations for computational studies, UK

Research Team

- 10 university PIs with prior collaborations
- Focus on material elements that are not now well understood and are barriers to commercial systems
- Supported by and improving two nanoscience technology centers
- NREL - John Turner, joint students/post-docs.; ORNL – Steve Pennycook, Z-STEM w/EBIC to map energy conversion efficiency to local structure, CNMS – Functional Nanomaterials, Macromolecular Complex Systems, Functional Nanomaterials (laser-based nanoscience labs)

PEC cells for hydrogen production via solar

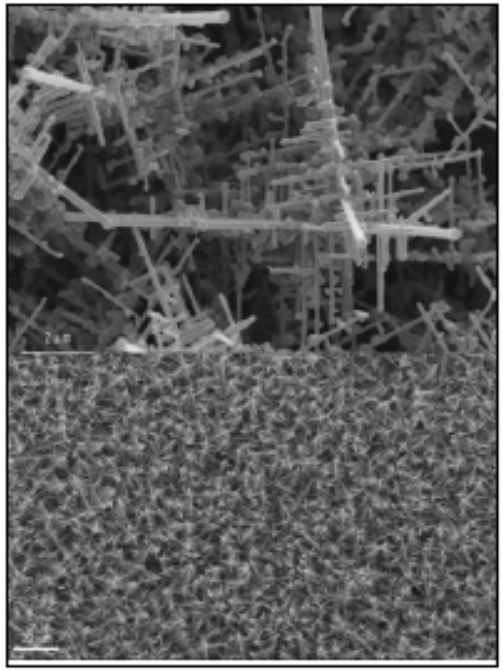


Fig. 5: Vertical arrays of Indium Nitride "tree" structures: (a) Higher magnification SEM image showing 3-D, six-level branched InN; (b) Low magnification SEM image showing uniform deposition over large areas.[15]

3-D nanoscale architectures of multijunctions for light harvesting

Ternary & quaternary nitrides of III-V compounds should be stable under photolysis for hydrogen.

Beach, Collins, and Turner, J. Electrochem. Soc., 150, A899 (2003).

Approach

1. Change composition during branch formation leading to multi-junction cells
2. Crystalline pathways between branches and substrate
3. Extend to III-V compounds
4. Alloy InN + Ga to achieve $IN_xGa_{1-x}N$ tree structures w/doping
5. Create < 10 nm diameter branches

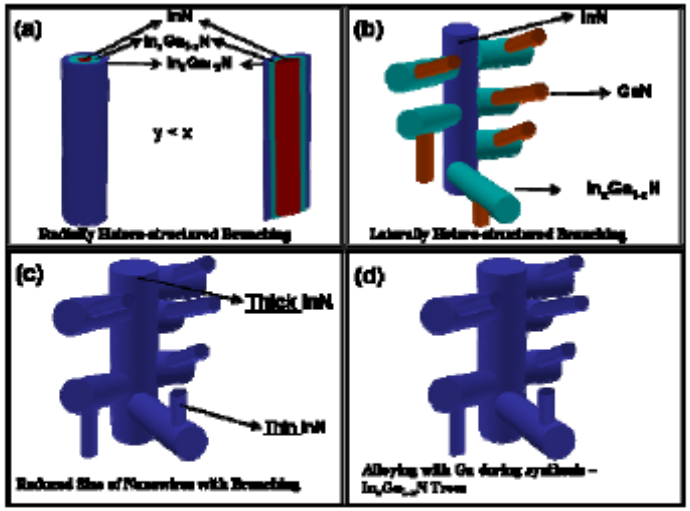


Fig. 6: Schematics illustrating several possibilities with the proposed synthesis method and the 3-D nanoscale architecture: (a) radial heterostructured trees; (b) Hetero-structured branches; (c) gradual reduction in InN nanowire sizes; and (d) monolithic, alloy tree-structures.

3-D nanoscale architectures of multijunctions for light harvesting

Synthesis: IAM-RE

1. IN + NH3 in plasma deposited T < 475C.
2. Tree-like growth occurs due to continuous formation of In droplets initiating branches
3. Characterize nucleation and growth mechanisms
4. Perform p-type doping

Nano-EBIC (ORNL) correlates local structure to energy conversion efficiency

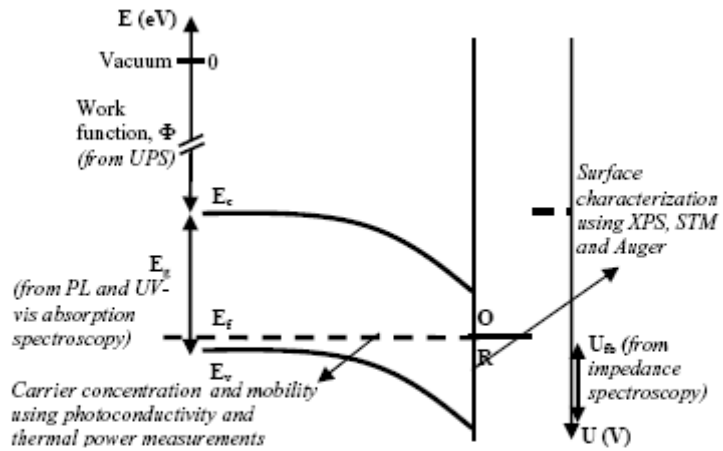


Figure 7 : The band energy diagram of the equilibrated photolytic interface with a redox couple and the corresponding characterization techniques.

Durability/efficiency tests. Joint post-doc (J. Turner, NREL) to investigate several design configurations: multi-junction, tandem, sandwich, monolithic

Computational studies of PEC electronic structures

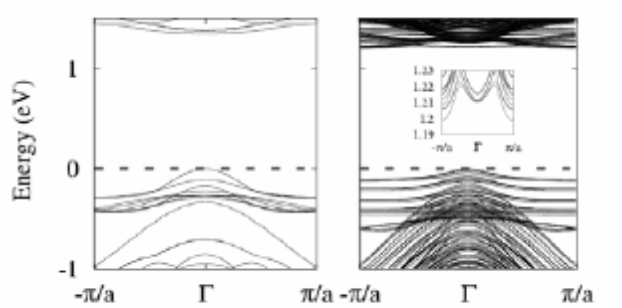


Fig. 8. Band structure for Si-nanowires of diameter 1.4 nm (left) and 5.3 nm (right). The small diameter wire has a direct band gap with a value larger than in bulk Si. The inset shows magnified low lying conduction bands.

Menon and Richter, Phys. Rev. Lett., 83: 792 (1999).

Computations to screen materials, identify compositions/geometries for enhancing bandgaps in the visible region; co-doping of donors and acceptors to be investigated

Tight binding molecular dynamics (TBMD) + density functional theory (DFT)

Nanoscale architectures for direct PEC electricity generation

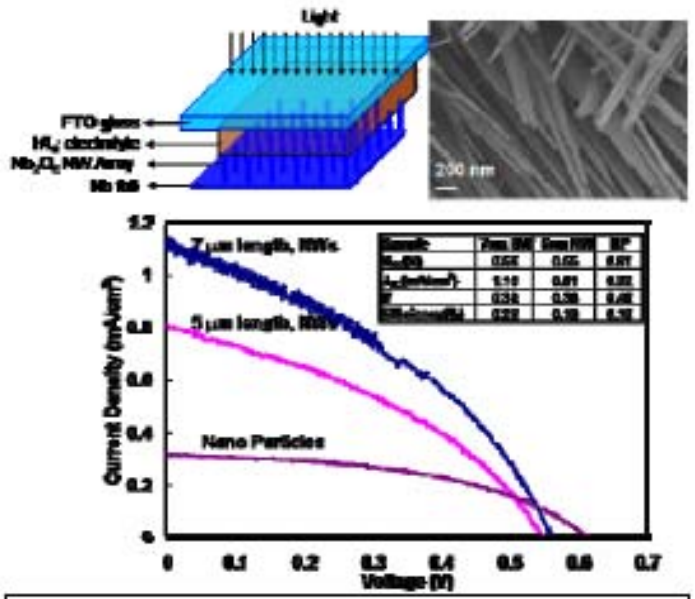
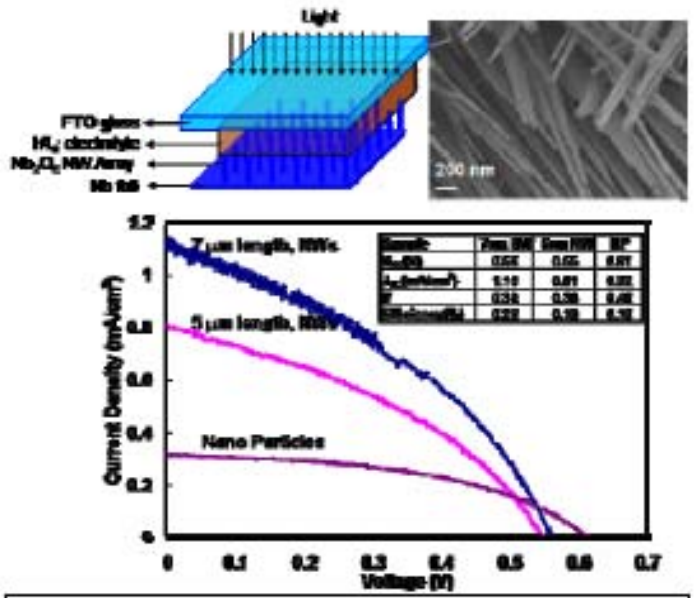


Figure 9: Solar cells using Nb_2O_5 nanowire arrays on Nb foils at UofL: (a) schematic of the solar cell using oxidized Nb foils; (b)SEM image of Nb_2O_5 NW arrays and (c) photo-electro-chemical data.

Nanowire architectures for dye-sensitized solar cells



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- Move from 1-D morphologies to nanorod/nanowire arrays
- Recent work on ZnO nanorods arrays showed better electron transport, faster charge transfer kinetics at the dye-semiconductor interface, high current density with nanowires coated with nanoparticles
- The synthesis of Nb2O5 nanowires on Nb foil can be scaled for high density arrays and show improvements over nanoparticles
- Proposed architectures are: a) 3-D III-nitrides (InN, GaN), b) homo-epitaxially grown InGaN on InN “trees”, c) hetero-epitaxially grown InN, GaSb clusters on GaN nanowires
- Material compositions guided by computational studies

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Evaporation-driven synthesis of photoactive films with oriented nanopores

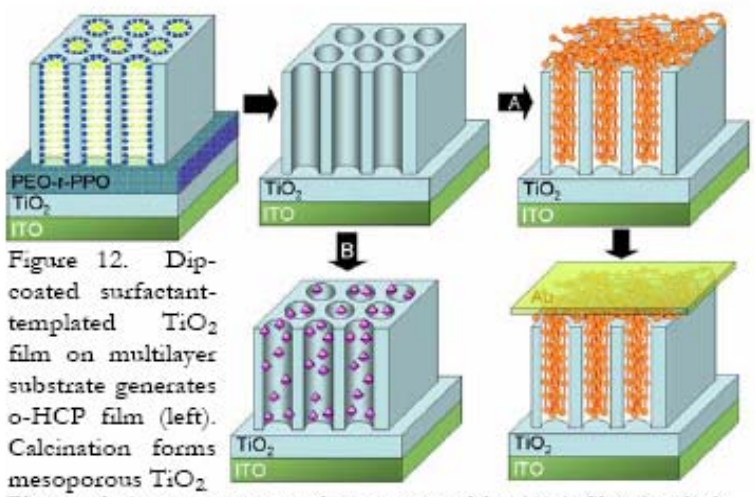

Figure 12. Dip-coated surfactant-templated TiO_2 film on multilayer substrate generates o-HCP film (left). Calcination forms mesoporous TiO_2. Photovoltaic structures are then generated by (A) infiltrating hole-conducting polymer and coating with gold electrode, or (B) adsorbing Ru dye for iodide-based cell.

- Ceramic films of orthogonally aligned hexagonal close packed cylindrical pores (based on work by Brinker, SNL)
- Chemically neutral substrates to synthesize o-HCP mesoporous SiO2 films by evaporation-driven assembly
- Extend to titania as components for organic-inorganic PEC cells – continuous pathway for electron transport and high surface areas, easily loaded with sensitizer dyes, QDOTS, metallic or semiconducting particles, nanowires
- o-HCP titania has been synthesized without confinement between two substrates, which could lead to dip or spray manufacturing
- P3HT and other hole conductors will be studied for h+/e- formation, transport and recombination

Integrated energy storage with oriented CNT membranes

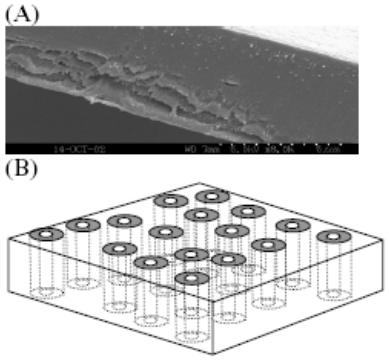

Figure 13. (A) Cleaved film (upper bright area is top surface) of aligned MWCNT membrane embedded in polystyrene and (B) Schematic of membrane structure. The rigid inner tube diameter of the CNT forms the accessible pores in these membranes.

- MWCNT array in polystyrene films
- Electrochemically oxidize the MWCNTs below the membrane surface, add counterelectrode, generate wet cell with precise electrode distances
- Use the fast fluid flow through nm-scale electrode pores to reverse triiodide flow away from the counter electrode for localized chemical storage of energy

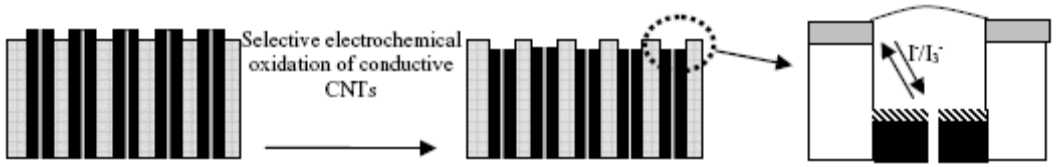

Figure 14. Schematic of electrochemical modification of CNT membrane to produce robust electrochemical well with enhance diffusion transport. Conductive CNTs are selectively oxidized in insulating polystryrene matrix to reduce length in membrane. After subsequent processing steps iodide can quickly diffuse to counter electrode on the top surface (grey) from dye-sensitized TiO_2 bound to CNT tip.

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Links with NREL, ORNL

- ORNL: Nano-EBIC, neutron diffraction, advanced nanofabrication and nanoelectronic measurements at CNMS
- NREL: final PEC cell device design, durability & efficiency testing
- Notre Dame: femtosecond photoabsorption spectroscopy

	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.

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