Final Report to

Dr. Timothy Fitzsimmons
Program Manager, DOE EPSCoR Program
C% Cheryl L. Howard, SC-22.2
Office of Basic Energy Sciences
U.S. Department of Energy
Germantown Building
1000 Independence Avenue, SW
Washington, DC 20585-1290
301.903.3428 - Office
301.903.9515 - Fax
Cheryl.Howard@science.doe.gov

"Nanoscale Materials and Architectures for Energy Conversion"

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Program Director: Dr. Eric A. Grulke
University of Kentucky, Lexington, UK

Technical Principal Investigator: Dr. Mahendra K. Sunkara,
University of Louisville, Louisville, KY 40292

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1. ACCOMPLISHMENTS DURING OVER THE COURSE OF PROJECT (July 1, 2007 – March 14, 2011)

Major accomplishment: On January 26, 2009, Governor Steve Beshear announced that the Commonwealth of KY is giving a mandate to the University of Louisville to develop a center for renewable energy and environmental stewardship for the commonwealth of KY. A UofL alumnus (Hank Conn) and his wife (Becky Conn) pledged $20M + support to the center. The existing center, the Institute for Advanced Materials and Renewable Energy (IAM-RE) will be named as the Conn Center for Renewable Energy Research and will be expanded to house a number of manufacturing R&D facilities for solar, biofuels, energy storage and materials. The center will also be focusing to develop strategies for increasing energy efficiency of homes and buildings. Governor constituted a board with thirteen members from various constituencies and the energy cabinet secretary (Dr. Len Peters) as the chair. In addition, the Conn Center organized a technical advisory board comprising Mr. Hank Conn, Dr. Len Peters, Dr. Burt Davis, Dr. John C. Angus, Dr. Mickey R. Wilhelm (Dean), and Mr. Kris Kimel. All PIs involved in this cluster will play key role in building this center of excellence. Particularly, M. Sunkara is appointed as the Interim Director for the center.

The research progress in this research project entitled "*Nanoscale Materials and Architectures for Energy Conversion"* is accomplished through the following three main cluster projects:

Cluster Project 1: Photoelectrochemical Solar Cells for Electricity
Investigators: M. K. Sunkara, S.R. Rankin, B. Alphenaar, G. Willing, H.A. Rypkema, B.J. Hinds

Cluster Project 2: Photoelectrochemical (PEC) Solar Cells for Hydrogen
Investigators: M.K. Sunkara, M. Menon, B.J. Hinds and S.R. Rankin

Cluster Project 3: Thermionic Energy Conversion
Investigators: G.U. Sumanasekera, R.W. Cohn, M.K. Sunkara, P. Menguc

The accomplishments made during first year period from Jan 2009 – July 2011 are described below for each of the above three cluster projects.

Cluster Project 1: Photoelectrochemical Solar Cells for Electricity

Long term goals are to understand various basic energy conversion processes (light absorption, charge separation and charge transport) in photoelectrochemical solar cells and organic solar cells and develop new materials that can provide efficient energy conversion and stable operation.

I. Nanoscale materials and architectures:

a. *Nanowire and nano-tree based architectures for dye sensitized solar cells:* Nanowire based architectures offer highly ordered surfaces which potentially exhibit fast charge transport and slow recombination properties. These properties are not understood for a number of nanowire based materials.

b. *Nanoporous titania based architectures for organic solar cells:* TiO_2 (and other semiconducting metal oxide) films with o-HCP channels are ideal components for organic-inorganic PEC and PV cells. They feature a continuous pathway for electron transport through the TiO_2 and tremendous surface areas (> 250 cm^2 of pore surface / cm^2 of substrate for a 240 nm thick film) for photo-generation of electron/hole pairs or reactions.

c. *Oriented carbon nanotube membranes for chemical energy storage:* The remarkable properties and unique geometry of aligned carbon nanotube membranes allows us to address two important issues in chemical solar cells: 1) increasing efficiency by accelerating transport to the counter electrode (thus avoiding recombination) and 2) utilizing extremely fast fluid flow through nm-scale electrode pores to reverse the normal diffusional flow of photogenerated triiodide to the counter electrode for localized chemical storage of solar energy.

II. **Probing and Design of Dye/Semiconductor Interface and Nanoscale Semiconductors:** The timescales of pertinent processes that occur within both PEC and PV cells range from femtosecond (i.e. electron transfer) to millisecond (charge transport). So, a number of interrelated methods must be used to fully characterize the system. Perhaps most critical among these methods is ultrafast transient absorption spectroscopy (UTAS), which provides rate information on the order of 100 femtoseconds or longer and can identify short-lived transient species such as excited states and semi-oxidation/reduction products. The timescales accessible by UTAS enable measurement of charge injection from the photosensitizer into the carrier band of the semiconductor, back electron transfer, and charge recombination, all of which are key elements in the overall energy conversion efficiency

III. **Probing and Design of Dye or Organic Molecular Assemblies:** Probe the triplet states within organic semiconductors and dyes used in excitonic solar cells. Introduce spin filtering materials within the organic semiconductor or dyes (creating new dye assemblies) to allow optical coupling to the triplet exciton state. Also of interest is to probe the organic semiconductor-contact interface to understand the dissociation of excitons across the interface and find ways to modify the exciton binding energy at the interface.

IV. **Probing and Design of Nanoscale Dye Assemblies/Semiconductor Interface:** Develop new dye systems based on a combination of organometallic complexes, metallic nanoparticles and quantum dot materials to enhance the generation and transport of charge in a dye sensitized solar cell (DSC)

During the project, we made a significant progress in all of our above goals for this project as detailed below.

Nanowire based architectures: SnO_2 nanowires exhibited fast transport and slow recombination kinetics compared to their nanoparticle counterparts. These results were obtained with SnO_2 nanowire powders and not as vertical arrays. Most importantly, the open circuit potentials were 250 mV higher than those exhibited by nanoparticle counterparts. These results are not obvious and require a number of spectroscopic techniques to understand the reasons for such behavior. SnO_2 nanowires due to the relative location of its conduction band edge (about 0.4V below that of titania) can have an universal appeal as nanoscale matrix for band-edge engineering with a number of nanoparticles of semiconductor materials. Using a number of surface science and spectroscopy techniques, the high photovoltages observed with tin oxide nanowires compared to nanoparticles are attributed to differences in work function values and charge transport and recombination properties.

Mesoporous Titania: The plan for the thin mesostructured films work was to develop methods to increase pore size, wall thickness, and degree of anatase crystallinity in titania films with oriented cylindrical nanopores prepared by nanocasting. The first two goals met with some success through the addition of swelling agents (butanol and polypropylene glycol) to the micelle pore templates, and by decreasing the micelle concentration, respectively. The third goal was approached by starting the development of heating techniques to optimize the rate of crystallization while avoiding mesopore collapse. Improved crystallization was found in some films, and experiments at DOE user facilities (the Advanced Photon Source specifically) are planned in the time interval between the end of the first round of funding and the projected renewal to quantify the rate of crystallization vs. pore collapse. This will set the stage for future studies of hole conductor (such as P3HT) incorporation into the pores and photovoltaic efficiency.

CNT membrane for electrochemical storage: The key step in using CNT membranes as the active element in a chemical battery is blockage of pore entrances by electrochemically generated nm-scale bubbles. This prevents the diffusion of high energy chemicals back to the working electrode to discharge stored energy. Recently blocking efficiencies as high as 95% were seen using a 100 Hz sine potential. Another key aspect for making the system successful was to electrochemically burn the CNTs into the polymer matrix leaving a 50 nm diameter 'well' above the CNT to stabilize the nm-scale bubble. The blockage was reversible by applying small pressures to induce fluid flow. Also the generation of nanobubbles under small pressures served to 'pump' chemicals across that can be used to increase the current density of the device. A complete working fuel cell based on the concept was demonstrated in the 3rd year. Fe^{2+} pumped across the CNT membrane and oxidized to Fe^{3+}.and stored via blocking of the membrane with nanobubbles. The high concentrations of undiluted reactants gave a cell voltage of 1.18V that decayed only 3% over 3000 minutes of storage using nanobubble valves.

Probing and Design of Dye or Organic Molecular Assemblies: We have characterized organic solar cells using capacitive photocurrent spectroscopy, (CPS) a novel spectroscopy technique developed in our laboratory that is particularly sensitive to the exciton dissociation process. Using CPS we are able to identify a photo-absorption state lying at an energy below the main exciton peak in an MDMO-PPV/PCBM solar cell. This peak has low absorbance, but very high dissociation efficiency, and its energy correlates well with previous observations of the charge

transfer state. Illumination at the peak energy results in a decrease in the photo voltage signal by more than 70 %, while no decrease is observed under lower or higher energy illumination. This strongly suggests that this state has a significant role in the charge dissociation process. The experimental results counter intuitively demonstrate that increasing the amount of light on a BHJ solar cell can actually cause the output to go down. This implies that the solar cell efficiency could be improved by filtering out the light over a narrow band of wavelengths corresponding to the interfacial state energies.

In an effort to better understand these results we have recently applied the CPS technique to the PCBM/ITO contact interface. These measurements reveal the presence of a low energy absorption state at 1800 nm with high dissociation efficiency. Published calculations suggest that such this state is formed due to the interaction between the PCBM and the highly conducting ITO substrate. Further experiments confirm this conclusion. When the CPS measurement is performed on a PCBM layer with the ITO replaced by a remote metal contact, the 1800 nm feature disappears. Because the interfacial absorption lies in the near infrared regime, it has the potential to expand the usable optical spectrum PCBM based solar cells. We are now investigating methods to enhance the 1800 nm absorption by combining the PCBM with high surface area ITO nanowires synthesized in the Sunkara laboratory.

We have also developed a theoretical fitting procedure to extract the electronic density of states from the CPS results. We have applied this procedure to graphene oxide samples, where we observe three mid-gap states along with the graphene π /π^* states. Transitions between these states are able to account for the absorption and photoluminescence spectra for graphene oxide and reported in the literature. This procedure can now be applied to solar cell materials synthesized in the Sunkara laboratory including individual FeS_2 and Cu_2S nanowires.

Probing of nanoscale semiconductor-dye interface: We have been able to visualize the variation in photocurrent along the length of an individual, partially dye-coated nanowire. To do this, we developed a tip manufacturing procedure that limited the area exposed for electron exchange in the redox reaction in the electrolyte. Additionally, we have found that the procedure requires a dilution of the electrolyte by at least a factor of 8 to obtain an appropriate level of lateral resolution in the images. Both of these suggest that our imaging mechanism is dependant upon ionic diffusion of the electrolyte between the nanowire surface and the ECSTM tip that functions as a counter electrode as opposed to a tunneling current induced by the presence of incident photons. This is further supported by measurements of the current vs. the tip-sample distance which shows that the photocurrent can be measured out to distances of almost 10 microns. We have observed a leakage/dark current in our measurements on the order of 100 pA, but we suspect that this does not interfere with out lateral resolution as our photocurrent is typically 1 to 2 orders of magnitude larger.

Effect of Linking Chemistry and Gold Nanoparticles on Dye-Sensitized Solar Cells:

- Prepared dye-sensitized solar cells (DSSCs) with the dye molecules attached by physisorption to (1) bare TiO_2 films and (2) TiO_2 films functionalized with aminopropyltriethoxysilane (APTES) and by covalent bonding to 3) TiO_2 films functionalized with APTES.
- All three films displayed similar photovoltages and photocurrent when measured in air in a beaker cell.

- DSSCs prepared with dye molecules covalently bound to TiO_2 displayed similar voltages and photocurrents for several months, while those attached by physisorption lost the photoactivity within a few days.
- Presented a poster presentation on this work at the 2011 Kentucky Statewide Workshop: Renewable Energy and Energy Efficiency in Louisville, KY in March 2011; A manuscript on this work is in preparation and will be submitted sometime in the summer.
- Prepared DSSC photoanodes with dye and Au nanoparticles assemblies attached electrostatically to TiO_2 films. Interestingly, there have been certain combinations of dye and Au nanoparticles that have led to significant improvements in photovoltage over the standard DSSC.
- Improved stability, photovoltage, and photocurrent would greatly benefit DSSC technology.
- Future studies will involve large-scale processing, fundamental electron transport and femtosecond spectroscopy measurements to better understand the photochemistry, and fundamental microscopic and electron transport measurements and individual TiO_2 nanomaterials.

Probing semiconductor-dye interface: Capital equipment for the Ultrafast Transient Absorption Spectroscopy (UTAS) facility has been purchased from Clark MXR. Elements of this system include a model CPA-2110 amplified pump laser, emitting 775 nm pulses with energy >1mJ at 1 kHz, with a pulse duration of <150 fs. A portion of the beam from this amplifier drives a Non-collinear Optical Parametric Amplifier (NOPA), which converts the light to a beam that is continuously tunable between 240-1600 nm, with a pulse duration of <50 fs. Pulse duration between 500-700 nm (the range most relevant to energy conversion studies in DSSCs and PECs) is <30 fs. This fast output from the NOPA is used as a pump pulse to initiate photoprocesses in the sample. A second portion of the amplified beam is used to generate a whitelight continuum beam with a duration of <200 fs within the integrated TAPPS spectrometer. This beam serves as a probe for monitoring visible absorption features of liquid, solid, or liquid-solid interface samples. Within the TAPPS system, a computer-controlled delay stage controls the time duration between when the NOPA pump hits the sample, and when it is sampled by the white light probe. Transmitted light is detected by a CMOS based linear array spectrograph with a detection range of 450-900 nm. Data are automatically imported into customized visualization software on the controlling PC.

Cluster Project 2: "Photoelectrochemical (PEC) Solar Cells for Hydrogen"

Light absorption by a direct bandgap semiconductor results in the creation of hole (h^+) and electron(e^-) pairs. At a semiconductor-electrolyte interface, the charges can either be separated to directly generate current or can cause chemical reactions, depending on the system. The minimum energy required at nominal current densities of 10-20 mA/cm^2 for water splitting is 1.5-1.7 eV, via the following redox reactions:

At a p-type electrode:	At an n-type electrode:
$2H_2O + 2\ e^- = 2\ OH^- + H_2$	$H_2O + 2h^+ = 2\ H^+ + 1/2O_2$

In order to maximize the solar radiation absorption at visible wavelengths, the bandgap of the semiconductor material should be ~2 eV and it should not decompose or degrade as a result of photolysis. Titania and III-Nitrides do not degrade under photolysis conditions, but they both have bandgaps > 3.0 eV (in the UV portion of the solar spectrum). Improved photo-electrode materials must exhibit (a) better visible light absorption (b) appropriate band-edge energetics with respect to water splitting; (c) fast electrochemical reactions to reduce surface charge build-up; (d) low bulk and surface recombination from trap and defect states; and (e) fast charge transport. Currently, there is no suitable material identified that satisfies the above requirements and stable. Our long term goal is to develop new alloy materials and new nanoscale materials that can potentially be suitable for photoelectrochemical water splitting. We will address the challenges using novel nanoscale synthesis and modification approaches guided by computational and fundamental spectroscopic studies. The computational approaches will involve the use of various ab initio codes including ESPRESSO, GAUSSIAN-03, VASP and CASTEP and TURBOMOLE to understand the electronic band gap, mobility and surface defect states in the new alloy materials. The spectroscopic studies will use Kelvin Probe and UV Photoelectron Spectroscopy, Photoluminiscence and UV-Vis absorption spectroscopy of the alloy materials synthesized.

A new direction developed from the theory work by M. Huda, Y. Yan and J. Turner regarding bulk iron oxide. Bulk iron oxide exhibits a bandgap appropriate for water splitting and would be expected to have excellent stability in an aqueous environment. However, the bulk iron oxide has been shown to behave as a Mott insulator. These results do not necessarily apply to nanoscale iron oxide. In addition, we hypothesize that it is possible to use iron oxide nanostructures if they can be synthesized at dimensions less than the diffusion lengths of carriers (~2-4 nm). But, at nanoscale, the surface states can prove to be detrimental to the photoactivity of the iron oxide. So, theoretical computations of nano-iron oxide are of universal interest and can guide our experimental synthesis work. We synthesized and characterized iron oxide nanowire arrays and iron oxide nanoparticles supported on mesoporous substrates.

Accomplishments during this project:

- *MOCVD of ternary nitride alloys:* A metal organic chemical vapor deposition setup is established and was used to study epitaxial growth of ternary nitride on GaN nanowires. The results showed that the Indium content of ternary nitride (InGaN) layers could be controlled from 0 to 100% and thick layers can be grown using thin (<30 nm size) nanowires as substrates. Several techniques such as electron diffraction, X-ray diffraction, elemental composition mapping and UV-Vis absorption measurements confirmed composition control, epitaxial growth and single crystal growth over the entire length of nanowires. UV-Vis diffuse reflectance data confirm the band gap to vary from 3.45 eV from GaN to 0.8 eV for InN for the epi-layers grown. No phase segregation effects were observed for thicknesses of several hundred microns. A manuscript is currently submitted. The work is underway to understand p-type doping using Mg as dopant in the epi-grown layers.

  Theoretical predictions: A major, surprising discovery resulted from theoretical computational work involving GaN alloying with Sb. The results suggested that the band gap of GaN alloy containing Sb can quickly reduce from 2 eV from 3.4 eV with very low

composition of Sb (<1.5 at %). This is completely unexpected and is a new result. There are no prior theoretical and experimental studies on nitrogen rich GaSbN alloys. This is the very first time a simple ternary alloy has been shown to have this remarkable property. The work has been accepted for publication in Phys. Rev. B and is also under appeal for publication in Phys. Rev. Lett. [1]. The theoretical work has also made other headways during the last year of this grant. A well known shortcoming of the widely used density functional theory (DFT) is the underestimation of the electronic band gap. The standard approach currently used is to add a Hubbard U term by □fitting to the experimental band gap. This approach makes the band gap determination empirical and lacking in predictive power. This becomes a major problem when dealing with the optical properties of new multi-component alloys where experimental information of their band gaps are unavailable. We have proposes a new approach in which the U value for obtaining the exact band gap is calculated based entirely on first principles [2,3]. This allows us to make accurate prediction for the band gaps of multi-component alloys and, therefore, most reliable predictions for optical transitions to date.

[1] R. M. Sheetz, E. Richter, A. N. Andriotis, C. Pendyala, M. K. Sunkara and M. Menon, "Visible light absorption and large band gap bowing in dilute alloys of gallium nitride with antimony", Provisional acceptance in to Phys. Rev. B., Petition pending for acceptance to Phys. Rev. Lett. (2011).
[2] A. N. Andriotis, R. M. Sheetz and M. Menon, "LSDA+U approximation: An effi-cient calculation of the U-values", Phys. Rev. B, Vol. 81, p 245103 (2010).
[3] A. N. Andriotis, G. Mpourmpakis, R. M. Sheetz and M. Menon, "Complimentary use of the LSDA+U and B3LYP functionals for obtaining U-values", submitted to Phys. Rev. (2011).

- *Nanotube/titania Composites:* The Hinds and Rankin groups initiated an opportunity project addressing the photochemical properties of carbon nanotubes coated with titania films and nanoparticles. As a probe reaction of the properties, photochemical oxidation of dyes has been studied. The composites show improved photocatalytic activity under UV irradiation but (in contrast to prior studies) no visible-light activity. The role of adsorption in the measurements of apparent photocatalytic activity was found to be quite important. The composites were also found to be active for photocatalytic water splitting, with the best composites showing photon conversion efficiencies over 7%.

- *Engineered Metal Oxide Catalysts*: A new route to well-defined catalytic sites in an otherwise inert matrix was developed. This route involves using mixed surfactants where one complexes with a transition metal to bind it at the material interface, and the other assembles with silica to form a well-ordered support. The materials were shown to have turnover frequencies twice that of the commercially used titanosilicate zeolite TS-1 for aqueous epoxidation of styrene. A comprehensive study of acidity by DRIFTS was undertaken and the role of the type and density of acid sites was illuminated.

- *CNT mattes as catalysis support:* CNT mattes with high surface areas (50 m^2/gr) can be easily formed by filtration methods (Bucky paper). The high conductivity and chemical intertness of the CNTs make them a strong electrode candidate for corrosive

electrochemical storage environments. Unfortunately the inertness (high surface energy) makes it difficult to have uniform coatings of expensive catalysis materials such as Pt. The Hinds' group has recently used diazonium electrochemical grafting to result in uniform sub 2nm thick films of Pt on CNTs. The Pt has the highest reported mass activity for MeOH oxidation due to the large percentage of surface atoms. Also a new voltage pulse sequence was discovered to eliminate CO poisoning on Pt surface. Another method was developed to reduce Pt to a single monolayer on CNTs. This was achieved by first plating a monolayer of Cu, which has a very different reduction potential than bulk Cu. In a second step, this monolayer is then exchanged with Pt^{2+}, which has a much lower reduction potential. This technique established the new catalytic mass activity record on CNTs of the expensive Pt resource.

- *CNT mattes for H_2O splitting:* The approach of CNT chemical modification can be used for thin films of Fe_2O_3 with band energies close to that of H_2. The nm-thin layer can allow a for effient electron/hole transfer to the CNT electrode. Collaborations with theory groups would allow an understanding of the orbital overlaps of graphitic CNTs with Fe_2O_3 and the location of band levels at the surface relative to nm-scale Fe_2O_3. Ir catalyst grafted to CNTs was also found to be highly stable for the oxidation reaction.
- Synthesis of mesoporous indium tin oxide thin films was initiated in the Rankin group. These films are to serve as conductive supports for iron oxide nanoparticles and nanowires. They are being developed by surfactant templating and crystallization of the ITO framework; conditions were found for stable, crystalline mesoporous frameworks.

CLUSTER PROJECT 3: THERMIONIC ENERGY CONVERSION

Direct thermal to electrical energy conversion using thermionic emission from nanoscale materials structures represents another emerging technology with a huge potential for efficient energy conversion (close to 75% of Carnot limit). The goal of this project is to design, fabricate and characterize direct energy conversion systems that meet the above requirements. Conical carbon nanopipettes, which naturally grow as arrays with high densities (no patterning required) and mechanical robustness will be processed and modified to be used as efficient thermionic energy converters. More specifically, diamond nanocrystals will be selectively grown on graphene carbon nanopippettes (CNP). The diamond will be subsequently doped (both n- and p-type) appropriately. First the field emission and thermionic emission properties of these composite structures will be studied extensively. The hemispherical analyzer within the UHV surface science facility (IAM) will be used for determining the electron energy distribution of the emitted electrons. Finally thermal to energy conversion will be tested. Emission properties of individual structures by *in situ* SEM measurements accompanied my theoretical modeling will be carried out throughout the project. In addition, the near-field radiative transfer effects will be analyzed.

Accomplishments made during the project:

- Conical carbon nanotubes (CCNTs) grown on platinum wires showed improved emission properties with (a) field enhancement factor (β) as high as ~8000 and thermionic work function (ϕ) ~4.2 eV (compared to ~ 5 eV for mutiwalled carbon nanotubes).

- CCNTS were successfully grown on planar graphite substrates and diamond crystals (hydrogen terminated) were grown at the tips as well as over the entire surfaces of the CCNTs. Diamond crystal decorated CCNT hybrid structures showed improved thermionic emission properties showing onset of emission at temperatures as low as 800 ^{0}C with a reduced work function of ~ 2.7 eV. Phosphorous doping was successfully achieved into the diamond crystals of the hybrid structure and the thermionic work function was found to further reduce to ~ 1.5 eV. Ultraviolet photo emission spectroscopy (UPS) results are in agreement with the observed thermionic emission results. A manuscript is currently under preparation.
- Exfoliated CCNTs were studied to compare the emission properties of edge plane vs. basal planes of graphitic nanostructure.
- A heater assembly was installed and tested in the existing UHV surface-science-equipment that is equipped with a hemispherical electron energy analyzer for performing thermionic electron energy distribution measurements.

- In-situ SEM measurements were made to determine the field emission properties of conical carbon nanostructures. A manuscript is currently under preparation.

2. RESEARCH OUTPUT

PUBLICATIONS:

Project 1: Solar electricity

1. V. Kumar, J-H. Kim, J.B. Jasinski, E.L. Clark, and M.K. Sunkara, "Alkali assisted, atmospheric plasma production titania nanowire powders and arrays", In Press, *J. Crystal Growth and Design*, (2011).
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6. B. Hu, B. J. Hinds,'Photocurrent Enhancement of Copper (II) Phthalocyanine film on Nano-gap electrode generated by the exposed edge of Au/Al2O3/Au structure', *IEEE Transactions Nanotechnology* revision submitted May (2011)
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14. X. Li and S.E. Rankin, "Ring Size Effects in a Multiscale Model of Sol-Gel Silica Film Formation: Tetrasiloxane Rings," submitted to *Macromolecules* (2011).
15. X. Li and S.E. Rankin, "Influence of Unlimited 3-Membered Ring Cyclization on a Multiscale Dynamic Monte Carlo / Continuum Model of Drying and Curing in Sol-gel Silica Films," *Chem. Eng. Sci*., 66, 1015 (2011).
16. X. Li and S.E. Rankin, "Multiscale Dynamic Monte Carlo / Continuum Model of Drying and Curing Nonideal Polycondensation in Sol-gel Silica Films," *AIChE J.*, 56, 2946 (2010).
17. J-H. Kim, V. Kumar, B. Chernomordik, and M.K. Sunkara, "Design of an efficient microwave plasma reactor for bulk production of inorganic nanowires", *Informacije MIDEM-J. of Microelectronics Electronic Components and Materials*, 38 (4),237 (2008).
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<u>Project 2: Solar hydrogen</u>

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Project 3: Thermionic Energy Conversion

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2. G. U. Sumanasekera, G. Chen, K. Takai, J. Joly, N. Kobayashi, T. Enoki, P. C. Eklund, "Charge transfer and weak chemisorption of oxygen molecules in nanoporous carbon consisting of a disordered network of nanographene sheets", *J. of Phys.-Cond. Matt*., 22 (33), 34208 (2010)
3. M. Francoeur, M.P. Menguc, and R. Vaillon, " Local density of electromagnetic states within a nanometric gap formed between two thin films supporting surface phonon polaritons", *J. Appl. Phys.*, 107, 034313 (2010).
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Publications from related efforts that acknowledged DOE support

1. Z. Chen, D. Cummins, E.L. Clark, B. Reinecke, M.K. Sunkara, and T.F. Jaramillo, "Ultra-thin MoS_2 Coatings on MoO_3 Nanowires as Efficient, Stable, and Non-Precious Catalysts for the Hydrogen Evolution Reaction (HER) in an Acidic Environment, Received reviews from Nature Materials and submitted to *Nano Letters*, May (2011).
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3. P. Meduri, V. Kumar, C. Pendyala, G.U. Sumanasekera and M.K. Sunkara, "Hybrid Tin Oxide Nanowires as Stable and High Capacity Anodes for Lithium-Ion Batteries", *Nano Lett.*, 9(2), 612 (2009).
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5. J. Ambati and S.E. Rankin, "Determination of ^{29}Si-^{1}H Spin-Spin Coupling Constants in Organoalkoxysilanes with Nontrivial Scalar Coupling Patterns," *J. Phys. Chem. A* 114, 12613 (2010).
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8. M. M. Yazdanpanah, M. Hosseini, S. Pabba, S. M. Berry, V. V. Dobrokhotov, A. Safir, R. S. Keynton and R. W. Cohn, "Micro-Wilhelmy and related liquid property measurements using constant-diameter nanoneedle-tipped atomic force microscope probes," *Langmuir* **24**(23),13753–13764 (6 November 2008)
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11. B.J. Hinds, "Dramatic Transport Properties of Carbon Nanotube Membranes for a robust protein channel mimetic platform", *Curr. Opin. in Solid. State & Mater. Sci.,* Revision submitted May 2011

PRESENTATIONS

1. A. Sherehiy, G. Sumanasekera, S. Dumpala, M. Sunkara, R. Cohn, "Thermionic Emission Properties of Surface modified conical carbon nano tubes (CCNT)", American Physics Society March Meeting, March 21–25, 2011; Dallas, Texas
2. J. Jasinski, C. Pendyala, and M. Sunkara, "Hetero-epitaxial Growth of Ternary InxGa1-xN Alloys on GaN Nanowires", Symposium H : Novel materials for alternative energy sources: Hydrogen technology, fuel cells and Lithium batteries, E-MRS 2010 Fall Meeting, Warsaw, Poland, September 13- 17, 2010.
3. R. Jayasinghe, A. Sherehiy, T. M. Paronyan, J. Jasinski, G. Sumanasekera, "Evidence for Electrochemically-Assisted Charge Transfer Between Oxygen and Large Area Graphene", Symposium D : Multidimensional electrical and chemical characterization at the nanometer-scale of organic and inorganic semiconductors, E-MRS 2010 Fall Meeting, Warsaw, Poland, September 13- 17, 2010.
4. J. Jasinski, T. M. Paronyan; and G. Sumanasekera, "Growth and Characterization of Large Area Monolayer Graphene for Photovoltaic Applications", Symposium C : Materials, devices and economics issues for tomorrow's photovoltaics, E-MRS 2010 Fall Meeting, Warsaw, Poland, September 13- 17, 2010.
5. Resolving the charge transfer complex (CTC) state in organic heterojunction solar cell using capacitive photocurrent technique Shah, Hemant; Mohite, Aditya; Bansal, Tanesh; Alphenaar, Bruce American Physical Society, APS March Meeting 2010, March 15-19,2010, abstract #D16.003.
6. "Spin filtering of Photo-excited charge from Organic Nanostructures," Mohite, Aditya; Alphenaar, Bruce, Santos, Tiffany; Moodera, Jagadeesh, American Physical Society, 2009 APS March Meeting, March 16-20, 2009, abstract #P32.006
7. S. Pasupuleti and **G. A Willing**, "Electrochemical Scanning Tunneling Microscopy of Dye Sensitized Solar Cells", 2009 AICHE Annual Meeting, Nashville, TN, November 8–13, 2009
8. S. Gubbala, H. Russell, H. Shah, B. Deb, J. Jasinski, H. Rypkema, and **M.K. Sunkara**"Surface Properties of SnO2 Nanowires forEnhanced Performance with Dye-sensitized Solar Cells", 216th Electrochemical Society Meeting, Vienna, Austria, October 4-9, 2009.
9. **P. Meduri**, C. Pendyala, V. Kumar, G.U. Sumanasekera and M.K. Sunkara, "Hybrid nanostructured tin anodes for Li ion batteries", 216th Electrochemical Society Meeting, Vienna, Austria, October 4-9, 2009.
10. **S.E. Rankin**, "Design Principles for Surfactant-Templated Nanoporous Metal Oxides," Ohio State University, Columbus, OH, November 2008.
11. **S.E. Rankin**, Q. Wu and V.R. Koganti, "Tuning the properties of orthogonally oriented hexagonal mesoporous titania for photovoltaics," 235th American Chemical Society National Meeting, New Orleans, LA, April 6-10, 2008.
12. **S.E. Rankin**, M.S. Rahman, R. Xing, S.M. Vyas, H.J. Lehmler and B.L. Knutson, "Synthesis of Mesoporous Silica using Mixed Surfactant Templates: Predictions from

Ternary Liquid Crystal Phase Diagrams", 6th European Congress of Chemical Engineering, Copenhagen, Denmark, September 20, 2007.

13. **S.E. Rankin** and X. Li, "Cyclization effects in continuum / dynamic Monte Carlo model of drying and curing in sol-gel silica films", 6th European Congress of Chemical Engineering, Copenhagen, Denmark, September 18, 2007.
14. **J. Ambati** and S.E. Rankin, "^{29}Si NMR of bridged organoalkoxysilanes: Challenges and solutions," American Chemical Society Meeting, San Francisco, CA, March 25, 2010.
15. **J. Ambati** and S.E. Rankin, "Dynamic Monte Carlo Simulation of Sol-Gel Polymerization of Bridged Alkoxysilanes," American Institute of Chemical Engineers Annual Meeting, Nashville, TN, November 10, 2009.
16. **J. Ambati** and S.E. Rankin, "Study of the reaction kinetics of bis(triethoxysilyl)ethane and methyltriethoxysilane," 238th American Chemical Society National Meeting, Washington, DC, August 16-20, 2009.
17. **J. Ambati** and S.E. Rankin, "^{29}Si NMR Study of Bis(triethoxysilyl)ethane Polymerization Kinetics," 50th Experimental NMR Conference, Ansilomar, CA, March 29 – April 3, 2009.
18. **J. Ambati** and S.E. Rankin, "Investigation of NMR Signal Loss during Hydrolytic Polycondensation of Organoalkoxysilanes," American Institute of Chemical Engineers Annual Meeting, Philadelphia, PA, November 16-21, 2008.
19. **J. Ambati** and S.E. Rankin, "DFT Calculation of ^{29}Si-^{1}H Indirect Spin-Spin Coupling Constants in Organoalkoxysilanes," American Institute of Chemical Engineers Annual Meeting, Philadelphia, PA, November 16-21, 2008.
20. **S. Joshi**, S. Navaladian, G. Osei-Prempeh, B.L. Knutson, H.-J. Lehmler and S.E. Rankin, "Synthesis and Characterization of Sugar-Imprinted Titanosilicate Materials Prepared by Surfactant Co-Templating," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, UT, November 2010.
21. **X. Li** and S.E. Rankin, "Multiscale Modeling of Cyclization Effects in Drying Sol-Gel Silica Films," 07 AIChE Annual Meeting, Salt Lake City, UT, November 4-9, 2007.
22. **M.S. Rahman** and S.E. Rankin, "Silica-Titania Mixed Oxide Mesoporous Thin Films: Incorporation of Ti by Surfactant Complexation," 07 AIChE Annual Meeting, Salt Lake City, UT, November 4-9, 2007.
23. **S.E. Rankin**, "Design of Surfactant-Templated Nanoporous Metal Oxides for Alternative Energy" Missouri University of Science & Technology, Rolla, MO, April 2011.
24. J. Ambati, H. Saiyed and **S.E. Rankin**, "Quantum Mechanical Investigation of Ammonia Adsorption On Mixed Hydroxylated Copper Sulfate-Silica System," American Institute of Chemical Engineers Annual Meeting, Salt Lake City, UT, November 2010.
25. **S.E. Rankin** and X. Li, "Multiscale Simulation of Sol-Gel Silica Polycondensation in Drying Films," 26th Annual Meeting of the Polymer Processing Society, Banff, Canada, July 2010.
26. **S.E. Rankin**, R. Xing and M.S. Rahman, "Sugar / Cationic Surfactant Templating of Functional Mesoporous Metal Oxides," 8th World Congress of Chemical Engineering, Montreal, Quebec, Canada, August, 2009.
27. **S.E. Rankin**, M.S. Rahman and S.T. Kahn, "Sweetening Kentucky's Energy Future with Functional Nanoporous Materials Prepared by Sugar-based Surfactant Templating," Kentucky Innovation and Enterpreneurship Conference, Louisville, KY, April 7, 2009.

28. **P. Meduri,** G.U. Sumanasekera, and M.K. Sunkara, "Hybrid Tin Oxide Nanowires as Stable and High Capacity Anodes for Lithium-Ion Batteries", Advanced Automotive Battery Conference, June 8-12, 2009, Long Beach, CA.
29. **S.E. Rankin**, "Predictive Synthesis of Mesoporous Metal Oxide Adsorbents, Catalysts, and Membranes," University of Strathclyde, Glasgow, UK, June 2009.
30. **S.E. Rankin**, "From Interface Science to Advanced Materials for Energy," Kentucky Innovation and Entrepreneurship Conference, Louisville, KY, April 2009.
31. **S.E. Rankin**, Q. Wu and V.R. Koganti, "Evaporation-Driven Assembly and Tuning of Titania Thin Films with Orthogonally Aligned Hexagonal Channels," Kentucky Innovation and Enterpreneurship Conference, Louisville, KY, April, 2009.
32. **Q. Wu** and S.E. Rankin, "Preparation of ITO Mesoporous Thin Films by a Surfactant-Templated Sol-Gel Route," American Institute of Chemical Engineers Annual Meeting, Nashville, TN, November 13, 2009.
33. **B. Alphenaar,** "Spin filtering of photoexcited charge from organic nanostructures," (invited), Spins in Organic Systems, Salt Lake City, Utah, February 2009.
34. A. Mohite, **B. Alphenaar**, T. Santos, J. Moodera, "Spin filtering of photoexcited charge from organic nanostructures – carbon nanotube," APS March Meeting, Pittsburgh, PA, March, 2009.
35. **B. Alphenaar,** A. Mohite, J. Moodera, T. Santos, "Photoexcitation of the triplet exciton in single wall carbon nanotubes," (invited), SPIE conference, San Diego, CA, August 2009.
36. M.K. Sunkara, "Alkali Metal Assisted Plasma Oxidation for Metal Oxide Nanowires", Keynote Speaker, Plasma Nanoscience II, Murramarang Resort, NSW, Australia, December 12-15, 2010.
37. M.K. Sunkara, C. Pendyala, J.B. Jasinksi, J-H. Kim, D.R. Cummins, H.B. Russell, *"New materials search using nanowires for solar hydrogen"*, Invited Paper, Solar Nanotechnology Symposium, SPIE Photonics West, San Diego, CA, August 3-6, 2010.
38. M.K. Sunkara, *"Nanowire Based Materials for Solar Electricity, Solar Hydrogen and Li Ion batteries*, Colloqium Speaker, Physics Department, IIT Bombay, July 9 (2010).
39. M.K. Sunkara, C. Pendyala, D. Cummins, B. Chernomordik, V. Kumar, H. Russell, V. Chakrapani and J. Thangala, "Materials Search for Solar Hydrogen Using Nanowires", Invited Presentation, ECS Spring Meeting, April 25-30, Vancouver, Canada (2010).
40. M.K. Sunkara, *"Nanowire Based Materials for Solar Electricity, Solar Hydrogen and Li Ion batteries*, Colloqium Speaker, Department of Chemical and Biomolecular Engineering, Rice University, February 4 (2010), Houston, TX.
41. M.K. Sunkara, *"Nanowire Based Materials for Solar Electricity, Solar Hydrogen and Li Ion batteries"*, CHEMCON Distinguished speaker, December 27-30, 2009, IICHE annual meeting, Visakhapatnam, A.P., India.
42. M.K. Sunkara, "*Nanowire based materials for solar cells and Li Ion batteries*", Symposium on Chemical Applications of Nanomaterials, FACSS (Federation of Analytical Chemistry and Spectroscopy Societies) Conference, October 18-22, Louisville, KY. 2009. (Invited)
43. M.K. Sunkara, *"Nitride based materials and nanowire based assemblies for photolysis of water"*, Solar Nanotechnology Symposium, SPIE Conference, San Diego, CA, August 17, 2009. (Invited)

44. M.K. Sunkara, *"Nanowire based materials for solar energy conversion and energy storage applications"*, Department of Chemical Engineering, Colorado School of Mines, Golden, CO., April 2009. (Invited)
45. **C. Pendyala**, J. Jasinksi, and M.K. Sunkara, "Growth mechanism and properties of ternary InxGa1-xN alloys on GaN nanowires", 2010 Fall Annual Meeting of AICHE, Salt Lake City, UT, November 11-17 (2010).
46. **L. Brockway**, C. Pendyala, M.K. Sunkara, and S. Vaddiraju, "A post-synthesis decomposition strategy for Group-III nitride quantum wires", 2010 Fall Annual Meeting of AICHE, Salt Lake City, UT, November 11-17 (2010).
47. **V. Kumar**, J-H. Kim, J.B. Jasinksi, and M.K. Sunkara, "Bulk production of titania nanowires in a plasma reactor", 2010 Fall Annual Meeting of AICHE, Salt Lake City, UT, November 11-17 (2010).
48. **D.R. Cummins**, J.B. Jasinksi, and M.K. Sunkara, " Phase transformation of Iron oxide nanowires to Iron sulfide", 2010 Fall Annual Meeting of AICHE, Salt Lake City, UT, November 11-17 (2010).
49. V. Kumar, J. Kim, and **M.K. Sunkara**, "Bulk production of metal oxide nanowires using an atmospheric plasma reactor", ECS Spring Meeting, April 25-30, Vancouver, Canada (2010).
50. **C. Pendyala**, S. Vaddiraju, J. H. Kim, J. B. Jasinski, Z. Chen and M. K. Sunkara, "Controlling the Nucleation and Growth of III-V Semiconductor Nanowires", AIChE Annual Meeting, November 8-13, 2009, Nashville, TN.
51. **S. Dumpala**, A. Safir, D. Mudd, R.W. Cohn, G. U. Sumanasekera and M. K. Sunkara, "Conical Carbon Nanotube Arrays: Large Area Synthesis, Field Emission Characteristics", AIChE Annual Meeting, November 8-13, Nashville, TN.
52. **V. Kumar**, J. H. Kim, M. K. Sunkara, "Bulk Production of Metal Oxide Nanowires Using a Novel Microwave Plasma Reactor", AIChE Annual Meeting, November 8-13, 2009, Nashville, TN.
53. S. Gubbala, H. Russell, H. Shah,B. Deb, J. Jasinski, H. Rypkema, and **M.K. Sunkara,** "Surface Properties of SnO2 Nanowires forEnhanced Performance with Dye-sensitized Solar Cells", 216th Electrochemical Society Meeting, Vienna, Austria, October 4-9, 2009.
54. **P. Meduri**, C. Pendyala, V. Kumar, G.U. Sumanasekera and M.K. Sunkara, "Hybrid nanostructured tin anodes for Li ion batteries", 216th Electrochemical Society Meeting, Vienna, Austria, October 4-9, 2009.
55. **M.K. Sunkara**, B. Chernomordik, V. Chakrapani, C. Pendyala, D. Cummins, J. Kim, P. Meduri and J. Thangala, "Nitride based materials and nanowire based assemblies for photolysis of water", Gordon Conference on Solar Fuels, February 2-6, 2009, Ventura, CA.
56. **P. Meduri,** G.U. Sumanasekera, and M.K. Sunkara, "Hybrid Tin Oxide Nanowires as Stable and High Capacity Anodes for Lithium-Ion Batteries", Advanced Automotive Battery Conference, June 8-12, 2009, Long Beach, CA.
57. **M. Menon** and A. N. Andriotis, ``Dopants and Impurities in Semiconducting Nanowires", Centre Europeen de calcul Atomique et Moleculaire (CECAM), July 4-9, 2009, Lousanne, Switzerland.
58. B.J. Hinds 'Aligned Carbon nanotubes: flow enhancement and gatekeeper activity' European Membrane Society Meeting, Mount Pellier Fr. Sept. 1-10, 2009 (keynote talk, emerging membrane materials workshop, young investigator workshop)

59. B.J. Hinds 'Workshop: Emerging Membrane Materials and Manufacturing methods' North American Membrane Society, June 22 2009 (highest paid attendance of offered workshops)
60. B.J. Hinds 'Carbon Nanotube Membranes for Pressure Retarded Osmotic Power Generation' Statkraft Corporation, Oslo Norway June 5 2009
61. B.J. Hinds 'Aligned Carbon nanotubes: flow enhancement and gatekeeper activity' IGERT Seminar, Univ. Massachusetts Amherst, May 7 2009
62. B.J. Hinds 'Aligned Carbon nanotubes: flow enhancement and gatekeeper activity' Lawrence Berkeley Laboratory March 5 2009
63. S. Dumpala, A. Safir, D. Mudd, R.W. Cohn, G. U. Sumanasekera, M. K. Sunkara, "Conical Carbon Nanotube Arrays: Large Area Synthesis, Field Emission Characteristics", Annual meeting of the American Institute for Chemical Engineers (AICHE), Nashville, TN, Nov. 8-13 (2009) (oral).

3. LIST OF STUDENTS/POST-DOCTORAL ASSOCIATES

1. Qingliu Wu – August 2007 onwards: Mr. Wu is a PhD student (mentor – S. Rankin) whose dissertation is based on the mesoporous thin film fabrication work described in our DOE-EPSCoR project. He has developed methods to control pore size, pore orientation, wall thickness, and crystallinity in titania thin films.
2. H. Shah – June 2008 onwards: Hemanth Shah is a PhD student (mentor – B. Alphenaar) working on probing excitons and triplet states.
3. S. Pasupuleti – October 2007 onwards: Sudhira is a M.S. student (mentor – G. Willing) working on scanning probe photoelectrochemical technique. She finished her M.S. thesis in December 2009.
4. Tulashi Liutel – A new Ph.D student in chemistry (mentor - H. Rypkema) started working on scanning probe photoelectrochemical technique.
5. Amy Sanders – January 2008 onwards: Amy is a Ph.D. student (mentor – H. Rypkema) working on GaAs semiconductors for DSSCs
6. Xin Su – Ph.D. student (mentor – B. Hinds) is working on CNT array membranes and electrodes.
7. A. Safir, a Ph.D. student in ECE department (mentor – R.W. Cohn) is working on thermionic and field emission studies from single nanostructures.
8. D. Mudd, a part-time student in Physics department (mentor – G.U. Sumanasekera) is working on bulk thermionic emission studies.
9. C. Pendyala (Mentor- M.K. Sunkara) – August 2008 onwards (He was supported on a University Fellowship and later on DOE-EPSCoR): Mr. Pendyala worked on MOCVD reactor and ternary alloy nanowire growth studies.
10. S. Uddin (a PhD student at UK Mechanical Engineering)
11. A. Sherehy (a PhD student at UL Physics working on thermionics; mentors: Sumanasekera/Cohn)

Postdoctoral Scholars

1. Dr. Michael Sheetz, a senior research scientist working with M. Menon, has been working on computations of structure-property relationships for ternary alloys and iron oxide nanostructures.
2. Dr. Navaladian Subramanian – November 2009 onwards: Dr. Navaladian (mentors – S. Rankin and B. Hinds) is investigating photovoltaic and photoelectrochemical systems based on combining the strong light absorbing / highly conductive properties of carbon nanotubes with the photocatalytic activity of titania and other transition metal oxides.
3. Dr. Vidhya Chakrapani (Received her PhD from CWRU in May 2007 and joined our group in June 1, 2007): She was recruited to work on our PEC hydrogen project and is supported through DOE-EPSCoR till Jan 2009. She joined Dr. Prashanth Kamath's group at Univ. of Notre Dame.
4. Dr. Jacek Jasinksi (25-50% support from DOE-EPSCoR from August 2008): Dr. Jasinksi has about twelve years of experience with electron microscopy of materials. He was recruited to help with IAM-RE's service center in June 2008 and will spend about 25% of his time with electronic microscopic studies for PEC hydrogen materials.
5. Mr. Jeong H. Kim, a research technologist working with M. Sunkara, is supported partially (40% time) to work on helping with the MOCVD reactor and bulk production of nanowires.

Students who received either partial support or from other sources

1. Boris Chernomordik – Supported on fellowship from Kentucky Space Grant Consortium (KSGC); 2008-2009. Boris worked on iron oxide nanowire array electrodes for PEC hydrogen. Boris graduated with M.Eng degree and is currently pursuing Ph.D in Chemical Engineering with Prof. E.A. Aydil at U. of Minnesota.
2. Jyothish Thangala – He has been receiving support from August 2007 from another DOE infrastructure grant. He is working on the development of materials that are of interest to PEC hydrogen project.
3. Dustin Cummins – Supported by Grosscurth Fellowship. Working on the development of various materials in collaboration with Stanford group.
4. Harry Russell – Supported by KSGC fellowship. He is continuing Boris' work on iron oxide nanowire arrays and their performance with water splitting.
5. Santoshrupa Dumpala (a PhD student in Chemical Engineering department): She is being supported on a Pullin fellowship.
6. Praveen Meduri and V. Kumar, Ph.D students received partial support for help with construction of MOCVD setup and bulk production of nanowires.
7. Suvid Joshi – October 2008 onwards: Mr. Joshi (mentor – S. Rankin) is also supported by the same USDA grant as Mr. Pennington, and will begin his dissertation work by investigating lyotropic phase behavior of surfactants that can be used as pore templates for metal oxide bulk materials and films.
8. Suresh Gubbala – Finished Ph.D. thesis (mentor – M. Sunkara) on Dec 1st 2008 on nanowire based solar cells and electrochromic devices. He was supported on another DOE's infrastructure grant.
9. P. Meduri – Finished Ph.D thesis (mentor – M. Sunkara) on Dec. 2010 on the hybrid nanowire structures for lithium ion batteries. He was primarily supported on another

DOE infrastructure grant but helped with synthesis and characterization of nanowire based materials toward this DOE-EPSCoR project.

10. V. Kumar received partial support from DOE-EPSCoR project working on nanowire synthesis and production for use in energy conversion and storage applications.
11. M. Shahidur Rahman – Finished Ph.D. thesis (mentor – S. Rankin) in May 2009 on preparation of catalytic materials with isolated titanium sites by surfactant templating and complexation. He was supported by Rankin's NSF CAREER award and Kentucky Science and Engineering Foundation funds.
12. X. Li – Finished Ph.D. thesis (mentor – S. Rankin) in December 2008 on modeling sol-gel polycondensation of silica in drying thin films. She was supported by a DOE EPSCoR National Laboratory Partnership grant.
13. S. Greenwell (a M.Eng student working with G. Willing) worked on dye sensitized solar cells.

4. PLANNED ACTIVITIES FOR RENEWAL PHASE

CLUSTER PROJECT 1: "PEC SOLAR CELLS FOR ELECTRICITY"

I. Nanoscale Materials and Architectures:

a) Mesoporous oxide films for photovoltaics:

- Will complete studies of crystallization to develop methods to achieve all three structural goals. Within two or three months, we project having oriented titania films with ~10 nm pores and ~7 nm walls with a degree of crystallinity suitable for testing with loading of P3HT and other n-type organic and inorganic species.
- In conversation with the Louisville group and others, will develop methods for infiltration of hole-conducting polymers, and will begin assessing photovoltaic performance of titania / P3HT interdigitated films.
- Will expand characterization of transport properties of film components, including electron transport in titania walls, and hole conduction in polymers within oriented cylindrical channels. This work began recently.
- Will expand synthetic procedures to include mixed metal oxides (to be determined via discussions with collaborators on this project).
- Detailed studies of crystallization and mesostructure development / loss in surfactant-templated oriented titania films will be performed with a grant of beam time at the Advanced Photon Souce, Argonne National Labs (obtained by a proposal developed by Q. Wu).

b) *Nanowire architectures for DSSCs:* Study the band-edge engineering concept using SnO_2 nanowires for band-edge engineering using nanoparticles of a variety of semiconductors (for rainbow absorption using semiconductors of different bandgaps such as GaSb for IR, dye for visible light, etc.). Optimize surface modification and nanowire/nanoparticle composite films to reach efficiencies greater than 10%. Tin oxide nanowires will be coated thicker and with nanocrystals of semiconductors such as GaSb (0.8 eV). In this concept, due to low recombination kinetics with tin oxide

nanowire backbone, it is also possible to change the redox couples for increasing the open circuit voltage.

c) *Carbon Nanotube Membranes:* The chemical energy storage aspect of the project will be concluded in the coming year with the demonstration of Fe^{2+}/Fe^{3+} battery. Use of the developed CNT surface chemistry on bucky paper mattes (or other high area nano-structures) and the highly efficient catalytic metal plating will be continued in collaboration with Sunkara and Rankin groups.

- ***Nanoscale Characterization of Semiconductor-Dye Interface:*** Our next steps are to verify the distance over which the photocurrent can be measured and utilize this to model the diffusional processes responsible for the imaging mechanism to provide an upper limit for the lateral resolution of the technique. We are also attempting to determine the lateral distance between the light source and the measurement of photocurrent in an effort to further define our imaging mechanism. Identify new linker molecules to enhance electron transport across the dye-metal oxide interface and develop the processes for their incorporation. Utilize nanoparticles as a means of enhancing charge production and transfer in a DSC and determine the enhancement both on the nanoscale and bulk scale.

II. ***Probing and Designing of Dye Assemblies and Organic Solar Cells:***

- Inclusion of the triplet excitonic state expands the absorption spectrum into the infra-red regime. In addition, a 3:1 ratio of triplet to singlet excitonic states means that a larger than normal charge carrier distribution is made available through triplet (versus singlet) state absorption. A few nanometers of a spin-orbit coupling layer at the polymer–contact interface is sufficient to allow absorption into the triplet state. Eu compounds have often been used as spin orbit couplers in OLEDs, so are likely to function in a similar way for organic solar cells. Initial proof-of-concept measurements will thus be done by depositing Yttrium coated EuS films on top of MEH-PPV, and measuring the photocurrent as a function of magnetic field (the Yttrium is necessary to protect the EuS from degradation).
- The exciton binding energy is determined in part by the local electrostatic environment. For piezoelectric materials, strain can be used to create a built-in electric field, and thereby alter the excitonic spectrum. This can be used to shift absorption into the infra-red, or to increase the capture efficiency of the photoexcited carriers. Initial experiments will be done by testing the influence of strain on the photocurrent spectrum of ITO contacted MEH-PPV samples deposited on a quartz substrate. It is likely that the polymer / contact interface will need to be within an exciton recombination length of the quartz substrate for the effect of strain to be observed, so experiments will be performed on 10-20 nm thick polymer films. Composite materials that incorporate piezoelectric polymers (such as PVDF) will also be tested.
- Our experiments show that the photocurrent signal decreases when the sample is exposed to near-infrared radiation corresponding to the CTC state. Evidently,

efficient photocurrent generation requires that the CTC level be unoccupied, in order for charge separation to occur. We will experiment with the use of optical filters to block the radiation corresponding to the CTC to see if this results in an increase in the photocurrent signal. If true, this would provide a straightforward method to improve efficiency of organic photovoltaic devices. To help in these experiments, we will assemble a high power tunable white light spectrometry system so that the pulsed laser is not required. Our proposed research does include an exploration of different OPV material systems to determine the prevalence of the polaron limiting transport phenomenon. It is also possible that the limitation is not generally observed, and that by replacing one or more of the OPV constituents, we can resolve the problem. For example, the efficiency of C70 based OPVs is higher than that of the C61 based OPVs, and the polaronic effect might also be reduced. Another area of research will be on the influence of the contact geometry and the location of the bleaching beam with respect to the contact on the magnitude of the bleaching effect. The region closest to the electron accepting contact is likely to be most influenced by the bleaching beam. By blocking the long wavelength light in the contact region (with a high pass filter), the efficiency could be improved without requiring a narrow band filter at a precise wavelength.

- The pyrite (FeS_2) and chalcocite (Cu_2S) have indirect band gap energies of 0.95 and 1.21 eV respectively, which puts them both near the apex of the solar efficiency curve. Pyrite also has an unusually high absorption (~105 cm^{-1}) and requires significantly less material to absorb solar energy. Interest in Cu2S and FeS2 dwindled at the end of the last century, as CdTe and CIGS became the de facto materials for thin film photovoltaics. Many of the limitations of the FeS2 and Cu2S devices were attributed to phase impurities within the thin films and interdiffusion of components across the heterojunction during fabrication. In nanowire form, however, the materials should have few if any grain boundaries. It is not clear, however, if there is an increase in defects, impurities or surface states during nanowire formation. To answer these questions, we will use the CPS technique to characterize individual FeS_2 and Cu_2S nanowires grown in the Sunkara laboratory. The CPS technique will also be used to determine the homogeneity of bulk heterojunction solar cells and correlate the material properties with the solar cell efficiency.

III. ***Probing semiconductors and semiconductor-dye interfaces:*** Establish the transient spectroscopy facilities and obtain preliminary data on charge injection and charge transport in nanowire and mesoporous titania based architecture solar cells.

CLUSTER PROJECT 2: "PEC SOLAR HYDROGEN"

In the renewal phase of the project:

<u>Materials theory:</u>

1. Investigate ternary alloy system Ga-In-N
2. Investigate alloying of Ga-N using Sb using GaN nanowire substrates.
3. Investigate the electronic properties of a-Fe_2O_3 nanowires and nanoparticles for electronic mobility and surface states (in collaboration with NREL's theory group headed by Y. Yan and M. Huda).

Materials development:

1. Creation of hetero-epitaxy of ternary alloys of $Ga_{1-x}In_xN$, $GaSb_xN_{1-x}$, $GaP_{1-x}N_x$, and $GaP_{1-x}Sb_x$ with desired composition onto GaN nanowires on stainless steel substrates;
2. PEC testing of the above sets of materials with appropriate compositions and p-type doping;
3. Development of one-dimensional structures with compositionally graded layers for enhanced solar light absorption and PEC performance
4. Create doped, a-Fe2O3 nanowire arrays
5. Create a-Fe_2O_3 nanoparticles supported on mesoporous matrices with varying compositions and pore structures prepared by evaporation-driven assembly with surfactant templating of the pores
6. Use of Molybdenum disuflide nanowire arrays as eletrocatalysts for hydrogen evolution with low over potential

Behavioral studies:

7. Perform a thorough photoelectrochemical characterization of the samples (at UofL by the research associate) and send some selected samples to Dr. J. Turner's lab for further characterization (absolute efficiency and stability against corrosion).
8. Structural and electronic property studies using transmission electron microscopy (Dr. Jacek Jasinksi)

CLUSTER PROJECT 3: "THERMIONIC ENERGY CONVERSION"

- Optimize the synthesis method for producing conical carbon nanotube arrays on large area, flat substrates.
- Perform field emission measurements on CCNT arrays modified with various materials – (a) Deposit uniform layers of SiO_2 or Al_2O_3 using atomic layer deposition (ALD) and expose just the tip area. The measurements from such structures will allow us to isolate the emission from tips with that from side walls; (b) Deposit diamond crystals on the tips of CCNT arrays.
- Optimize the heater assembly for the existing UHV surface-science-equipment that is equipped with a hemispherical electron energy analyzer for performing thermionic electron energy distribution measurements.
- Study doping and surface modification of diamond nanocrystals and their work function properties through UPS and thermionic emission measurements.

9. UPDATED LIST OF OTHER RELEVANT SUPPORT

1. "A reactor and method for production of titania and related metal oxide nanowires", subcontract to Advanced Energy Materials, LLC (SBIR Phase I), J.H. Kim (PI), M.K. Sunkara (subcontract PI), $38K, 01/01/2011-06/30/2011.

(A startup has been created to commercialize the bulk production research – the produced materials could be used for samples in some dye sensitized solar cell studies).

2. "University of Louisville Research and Energy Independence", DOE CDP, $2M, 08/01/2010-07/30/2012, M.K Sunkara (PI).

   (This is used for developing infrastructure within Conn Center for Renewable Energy research for setting up roll to roll and glass plate manufacturing R&D facilities for dye and organic solar cells; hiring a new senior research scientist; startup junior faculty and expand energy research capacity by seeding research projects for Univ. of Louisville faculty). Some of the personnel (students) are supported in the bridging periods for funding. The facilities could be used for the proposed studies with organic and dye sensitized solar cell development (the facilities allow for standardized processes for improved reliability and durability).

3. "Technologies for commercializing biofuels, natural gas and carbon dioxide", M.K. Sunkara (PI) along with M. Carreon, E. Berson and P. Ratnasamy, KY DEDI, $250K, 08/01/2010-07/30/2012. (One project out of four projects dealing with electrochemical reduction of carbon dioxide using copper nanowire array electrodes) – Minimal overlap to proposed studies.

4. "High capacity and durable electrode materials for next generation Li ion batteries", M.K. Sunkara (PI) along with G.U. Sumanasekera (co-PI), $225K, Clinical & Translational Science Pilot Grant Program, 07/01/2010-06/30/2012. (Synthesis and fundamental electrochemical characterization of nanowire/nanoparticle architectured materials for anodes) (Minimal overlap).

5. "A platform technology and reactor for bulk production of nanowires (NanowireX)", M.K. Sunkara (PI), $225K, University of Louisville Clinical & Translational Science Pilot Grant Program, 07/01/2010-06/30/2012. (Bulk production effort – reactor and process chemistry development; the process developed here could be used to prepare nanowire samples necessary to do proposed studies).

6. M.K. Sunkara and G.U. Sumanasekera, "Li Ion Batteries for Electric Vehicles", $200K, 10/01/2009-4/15/2011, KY Renewable Energy Consortium (KREC). (This grant supported mainly tin/tin oxide anode development work). (minimal overlap).

7. M.K. Sunkara, “A reactor for commercial production of metal oxide nanowires”, KY Commercialization Fund program, Kentucky Science and Technology Corporation (KSTC), $75K, 01/01/2010 – 12/31/2010.

This support is mainly for optimizing our reactor for producing bulk quantities of nanowires (at ten to hundred grams scale).

8. “Nanostructured Interfaces for Fusion Energy Systems”, DOE SBIR Phase I program, a subcontract from Technova Corp., $8K, 07/01/2008-03/31/2009. (Tungsten nanowire array samples are grown on tungsten plates and are supplied to Technova corp.). (no overalp).

9. M. K. Sunkara, (DE-FG02-05ER64071)“Institute for Advanced Materials at University of Louisville”, $3.34M, Department of Energy, **P.I.** (along with G. Sumanasekera, T.L. Starr, R.W. Cohn and G. Willing), 07/01/05-06/31/09.

This support is mainly used for improving the equipment and personnel infrastructure that includes acquisition of instrumentation such as FE-SEM, FE-TEM, XRD and other related characterization techniques for Li Ion batteries and solar cells, etc. The DOE-EPSCoR project uses the above facilities and personnel support. In addition, the above grant also supports partially the research projects within the DOE-EPSCoR through student support.

10. R. W. Cohn, B. W. Alphenaar, S. Y. Wu, G. U. Sumanasekera, M. K. Sunkara and C. K. Jayanthi, “Nanowire technology for missile defense,” U. S. Army Space Missile Defense Command, W9113M-04-C-0024, $7,293,330. (15 January 2004 to 30 June 2009)

(This support was used for improving facility and personnel infrastructure which helps tremendously with the conduct of this project. Some of the nanowire synthesis and production methods developed under this contract are being utilized for preparing materials for energy applications).

6. “Single walled nanotubes and Graphene based multiplexed sensors for hypergolic fuel detection” (NSF) (PI: Sumanasekera) $160,677(07/01/09 - 06/30/12).

7. “Plasmonic Enhancenment of Optical Fiber Interfaces for Graphene Interrogation”, (KSEF) (Co-PI: Sumanasekera) $100K (07/01/09 to 06/30/11)

8. M. M. Yazdanpanah (NaugaNeedles) and Robert W. Cohn (subcontract PI), “SBIR Phase I: Batch fabrication of high aspect ratio metallic AFM probes,” National Science Foundation IIP0944435, $150,000. (1 January 2010 to 30 June 2010)

9. M.K. Sunkara, “A closed loop regenerative energy and fuel system for space exploration”, Fellowship support to Boris Chernomordik, $18K, NASA EPSCoR, 07/1/2008-6/30/2009. (Fellowship support for a student working on a related project on solar fuels).

10. M. Menon, DOE Award (DE-FG02-00ER45817), ``Magnetism in Low-Dimensional Carbon Materials", 6/1/2006 - 5/30/2009 Amount of Award: $300,000.

11. G.U. Sumanasekera, “Selective Growth, Characterization, and Understanding of Fundamental Properties of SWNTs”, (Honda Research Institute), $485,000 08/01/05 - 03/31/09. (No overlap).

12. S.Rankin, CAREER: Kinetics and Engineering of Functional Nanoscale Organic-Inorganic Hybrids. $405,500. National Science Foundation. 3 years. April 2004 - March 2009. 100%. PI = Rankin. [no overlap]

13. R. W. Cohn, J. F. Kielkopf, J. F. Naber (UofL), L. G. Hassebrook (U. Kentucky), J. Trenkle (Michigan Aerospace), “Optical intrusion alarm for defense of critical infrastructure under conditions of fog, smoke or fire,” National Institute for Hometown Security, $1,610,350. (2 February 2009 to 1 February 2012) (no overlap)

14. A. S. Gobin, C. Harnett, M-J. Lee, S. McNamara, S. Mendes, P. Sethu, B. W. Alphenaar, R. S. Keynton, R. W. Cohn, K. M. Walsh (UofL) and M. Saunders, A. Patwardhan and D. Puleo (U. Kentucky), “Engineering platforms for exploring cellular and molecular signaling processes,” Kentucky NSF EPSCoR thru NSF cooperative agreement 0814194, $5,451,351. (19 September 2008 to 18 September 2013) (no overlap).

15. R. W. Cohn, “Market development and manufacturability scale up of nanoneedle probes,” Kentucky Commercialization Fund, Kentucky Science and Technology Corporation, Commfund-1045-RFP-007, $75,000. (1 April 2008 to 31 March 2009) (no overlap)

16. C. K. Harnett and R. W. Cohn, “Thin-film bimorphic components for shock-mounting and actuation of lunar micro-rovers,” Kentucky NASA EPSCoR, $41,000. (1 August 2007 to 30 April 2009) (no overalp)

17. R. W. Cohn, R. S. Keynton, G. H. McKinley (MIT) and G. N. Tew (U. Mass Amherst), “NIRT: Directed self-assembly of suspended polymer fibers in the fabrication of three-dimensional nanodevices,” National Science Foundation, ECCS-0506941, $1,307,001. (1 September 2005 to 31 August 2009) (no overalp)

18. J. F. Kielkopf, R. W. Cohn and J. F. Naber, “Space technology center for national security research on signature exploitation,” U.S. Air Force, FA8718-05-C-0055, $3,296,300. (7 June 2005 to 30 September 2009) (no overlap)

19. B.J. Hinds, “R01: Gated Carbon Nanotube Membrane Transdermal Drug Delivery” NIH (co-I Stinchomb) 7/1/06-6/31/10 $1,445,613. (55% IDC) {use voltage applied to CNT membrane is skin patch to modulate doses. Minimal overlap with DOE but current DOE grant benefits from membrane fabrication advances.

20. B.J. Hinds, “CAREER: Aligned Carbon Nanotube Composite Array as Permeable Membrane”, NSF, 4/1/04-3/31/09 $485,000. (sole PI, 100%) {study mass transfer through CNT membranes and modify chemistry at the pore entrances. Minimal overlap with DOE but current DOE grant benefits from functional chemistry at CNT pore entrances}

21. B.J. Hinds, “Aligned Carbon Nanotube Membranes for Forward Osmosis Power Generation” Statkraft Corp., Norway 7/1/08-6/31/12 $312,465 (sole PI, 100%) {Developing ion rejection at CNT tips to develop forward osmosis pressure to drive turines to produce electricity. Minimal overlap with DOE but progress in clean energy generation is of interest to DOE mission.}

22. B.J. Hinds, “Ordered Molecular Transporters” DARPA, 1/1/09-12/31/09 $398,871 (68% IDC) Administrative approval in process. {Inducing electric field at CNT tip to induce dipole orientation of water flowing through CNT core. Minimal overlap

23. B.J. Hinds, “Advanced Materials Relating to Applications in Epitaxial Thin Films and Device Structures” NSF EPSCoR subcontract of ‘EPSCoR RII: Transforming Kentucky's New Economy’ (P.I. G. Cao, 5 co-I) 9/1/08-8/31/13 $4.044M (UK portion) (17% #PIs) (Infrastructure to develop magnetic material fabrication and characterization. Hinds’ group working on molecular electronics with well defined spin states to induce long range ferromagnetic ordering and magneto-resistance changes. Minimal overlap)

24. B.J. Hinds, “NIRT: Novel One-Dimensional Horizontally Aligned Array of Nanopores: Nanoscale Fabrication for Molecular and Electronic Devices” NSF (3 co-PI. PI Zhi Chen) 7/1/06-6/31/09 $1,200,000. (20% IDC) (Molecular conductors are placed in horizontal pore geometry resulting in nm-scale electrodes. Minimal overlap)

25. B.J. Hinds, “Advanced Carbon Nanotechnology Consortium” ARO (P.I. J. Davidson, Vanderbuilt $22M (4 universities, co-PI Janet Lump (7 UK investigators) $5M for UK) 1/1/03-4/31/09 subcontract to B. J. Hinds $227,158. (50% subcontract) {making sensors from CNT membranes, minimal overlap}

26. G. Willing, Center for Nanobiotechnology Research at Alabama State University, NSF CREST, S.R. Singh@Alabama State, PI, $4,900,000, 9/01/07-08/31/11 (No overlap)

22. G. Willing, “Nanofluids for Advanced Military Mobility Systems - Coolants, Fuels and Lubricants”, US Army Tank-Automotive Command, T.L. Starr PI., $124,000, 10/01/07-09/30/08 (No overlap).

27. S.E. Rankin, “Interfacially Controlled Incorporation of Transition Metal Oxides within Ordered Mesoporous Ceramics,” January 2007 – December 2009, $100,000, Kentucky Science and Engineering Foundation.

28. B.L. Knutson (PI), **S.E. Rankin**, S.E. Nokes (UK Dept. of Biosystems & Agricultural Engineering) and H.J. Lehmler (U. Iowa Dept. of Occupational and Environmental Health), “Separation and recovery of high value pentose derivatives from cellulosic biomass using

molecular imprinting," $1,366,214, July 2008 – July 2011, USDA (with Kentucky Energy & Environment Cabinet matching), $1,366,214.

29. M. Menon, DOE Award (DE-FG02-00ER45817), ``Magnetism in Non-Traditional Materials", 6/1/2009-5/30/2012, Amount of Award: $360,000 (partial support for a senior scientist working on a related project on solar fuels).

6. COST STATUS

A separate report is provided on the cost details.

7. OUTREACH & TECHNOLOGY TRANSFER ACTIVITIES

- Three PIs (Sunkara, Sumanasekera, and Willing) collaborated with other UofL faculty members (X. Fu, M.A. Carreon and E. Berson) collaborated and offered an elective, graduate course on "Renewable Energy Systems" during summer semesters of 2009, 2010 and 2011.
- Sumanasekera and Sunkara offered a graduate elective course on materials characterization using surface science, diffraction and optical techniques.
- Sunkara mentored about twelve (12) high school students from Dupont Manual High School, Ballard High School with various projects involving photoelectrochemical energy conversion. Megan Mercer (from Ballard) won regional science fair and won awards at Intel and other national/international competitions.
- Delivered Saturday workshop to 12 Seneca High School students and their science teacher. Students each selectively grew and mechanically manipulated metallic nanowires inside a scanning electron microscope.
- Willing mentored Tim Scott (DuPont Manual High School) on a science fair project developing a methodology of creating a more organized nanoparticle oxide film for use in dye sensitized solar cells.
- Two PIs (Sunkara and Willing) and their graduate students helped 400 freshmen engineering students make their own DSSCs in the Intro to Engineering course
- Several PIs delivered lectures to visiting student groups.
- Cohn, Sunkara, and Sumanasekera participated in National Nanodays event. They provided talks and demonstrations at the Louisville Science Center in collaboration with the event held that week across the country (Spring 2009).
- Sunkara participated in DOE PEC focus group in which he helped with authoring a review article on standardization of procedures used for PEC water splitting research.
- Sunkara organized various sessions on renewable energy topics both at the annual meetings of the Electrochemical Society (ECS) and American Institute of Chemical Engineers (AICHE).
- Continued collaborative activities with Dr. T. Deutsch and Dr. J. Turner and initiated new collaborative activities with Dr. Nicolas Gailard of Univ. of Hawai and Dr. T.F. Jaramillo of Stanford University on materials search for photoelectrochemical water splitting.
- An invited talk was given featuring the mesoporous metal oxide film synthesis approach advocated here at the Kentucky Innovation and Entrepreneurship Conference, Louisville,

KY, April 2009 by S. Rankin. Dr. Rankin emphasized the role of interface science in developing new materials for energy applications.

- Several undergraduate students were mentored by Dr. Rankin on research projects related to the goals of the current project, including computational simulation of adsorbent / adsorbate interactions for catalysis and materials synthesis.
- Sunkara founded a startup, Advanced Energy Materials, LLC which received NSF SBIR support to further develop and commercialize bulk production technology for nanowires. The company is in the process of obtaining exclusive license for eight US Patents issued and applied based on Sunkara's research.
- Patents issued: (1.) Sumanasekera and Cohn, "Method for electrostatic deposition of graphene on a substrate" (U.S. Patent #7790242)
  (2.) Sumanasekera, "Methods and systems for fabrication of graphene nanoribbons", (U. S. Patent #7887888)
- Sumanasekera, Cohn and Sunkara filed several patents: (a) Patent pending: "Conical Carbon Nanopipettes: Methods of Making and Applications"; (b) Patent Pending (U. S. Patent), (c) Patent Pending (U. S. Patent), R. W. Cohn, M. M. Yazdanpanah, S. A. Harfenist, F. P. Zamborini, M. Hosseini, S. Pabba, V. V. Dobrokhotov, A. Safir and B. H. Fasciotto, "Metallic nanostructures self-assembly and testing methods." (Filed 2 June 2008).
- M.K. Sunkara, V. Kumar and J-H. Kim, "Methods for synthesizing metal oxide nanowires", US Patent Application filed (2011).
- M.K. Sunkara, H. Chandrasekaran, and H. Li, "Growth of textured gallium nitride thin films and nanowires on polycrystalline substrates", **US Patent** 7, 819, 974, October 26, 2010.
- M.K. Sunkara, H. Chandrasekaran, and H. Li, "Bulk synthesis of metal and metal based dielectric nanowires", **US Patent** 7,771,689, August 10, 2010.
- M.K. Sunkara, S. Sharma, H. Chandrasekaran, H. Li, and S. Vaddiraju, "Synthesis of fibers of inorganic materials using low-melting metals", **US Patent** 7, 713, 352, May 11, 2010.
- M.K. Sunkara, P. Meduri and G.U. Sumanasekera, "High capacity anode materials for Li Ion batteries", US Provisional Patent Application 61/141,502, December 2008.
- M.K. Sunkara, J-H. Kim and V. Kumar, "A new process and a new reactor for bulk production of metal oxide nanowires", US Patent Application 12248731, October 2008 (Provisional Patent Application 60/978,673 on October 2007).
- M.K. Sunkara, M. Mozetic, U. Celbar, and S. Vaddiraju, "A method for rapid synthesis of metal oxide nanowires at low temperatures", US Patent 7,591,897, September 22, 2009.
- M.K. Sunkara, S. Vaddiraju, B. Deb and J. Thangala, "Vapor phase synthesis of metal and metal oxide nanowires", US Patent Application 20070087470, April 19, 2007
- M.K. Sunkara and G. Bhimarasetti, "Tubular Carbon Nano/Micro Structures and Method of Making the Same", US Utility Patent 7,597,941, September 9, 2009.
- M.K. Sunkara, S. Dumpala, R.C. Mani, R.D. Lowe, G.U. Sumanasekera, and R.P. Baldwin, "Conical Carbon Nanopipettes: Methods of Making and Applications", US Patent Application 12176632, 21 July 2008.

Final Report to

Dr. Timothy Fitzsimmons
Program Manager, DOE EPSCoR Program
C% Cheryl L. Howard, SC-22.2
Office of Basic Energy Sciences
U.S. Department of Energy
Germantown Building
1000 Independence Avenue, SW
Washington, DC 20585-1290
301.903.3428 - Office
301.903.9515 - Fax
Cheryl.Howard@science.doe.gov

"Nanoscale Materials and Architectures for Energy Conversion"

(Grant Number: DE-FG02-07ER46375)

Program Director: Dr. Eric A. Grulke
University of Kentucky, Lexington, UK

Technical Principal Investigator: Dr. Mahendra K. Sunkara
Conn Center for Renewable Energy Research
University of Louisville, Louisville, KY 40292

Date of the Report: February 6, 2015
Period covering: July 15, 2011 – December 31, 2014

Brief Description of the Project

The Kentucky EPSCoR Program continued an inter-university, multidisciplinary energy-related research cluster in nanomaterials for converting solar radiation and residual thermal energy to electrical energy and hydrogen. It created a collaborative center of excellence based on research expertise in nanomaterials, architectures, and their synthesis. Fundamental processes of light absorption, charge separation/transport, and electron emission within nanostructured materials are examined to improve solar and thermal energy conversion processes.

The research strengthened and renewed collaboration between the University of Louisville, University of Kentucky, and NREL. A new faculty member is hired for fundamental research studies using ultra-fast transient spectroscopy. The cluster enabled mentoring of one research scientist, two postdoctoral scholars, and ten graduate students. The program enhanced the annual Kentucky renewable energy and energy efficiency workshop and makes a positive impact on several new energy research and development infrastructure initiatives. The research is accomplished through the following three main focused cluster projects: (i) Organic and Photoelectrochemical Solar Cells; (ii) Solar Fuels; and (iii) Thermionic Energy Conversion.

FINAL REPORT

CLUSTER 1: ORGANIC AND PHOTOELECTROCHEMICAL SOLAR CELLS *(M. Sunkara, B. Alphenaar, F. Zamborini, S. Rankin, J. Liu)*

Research in this cluster is focused on creating new nanoscale absorbers, materials and architectures for manipulating light absorption, charge separation and charge collection processes towards improving efficiencies and durability of dye sensitized solar cells and organic/inorganic hybrid system.

***a*. Alternate Redox Couples and alternate absorbers in DSSCs (Sunkara):** We focused on developing novel electrode architectures for using alternate redox couples and alternate absorber materials that result in improved stability and performance of the solar cells. Alternate redox couples have significant advantages over the commonly used iodide electrolyte, such as low light absorption, low toxicity, low corrosivity and more positive redox potential which reduces the barrier for dye regeneration. However, many of these alternate redox electrolytes cannot be used in titania nanoparticle based DSCs due to fast recombination kinetics of the electrons in semiconductor with the oxidized form the electrolyte. We previously showed that tin oxide nanowires exhibit fast transport and slow recombination characteristics. Thus, tin oxide nanowire based architectures have been studied using alternate redox couples such Fc/Fc^+ and $TEMPO/TEMPO^+$. The tin oxide nanowires generate order of magnitude higher short-circuit current densities (~ 2 mA/cm^2) when compared to the conventionally used titania nanoparticles (< 0.4 mA/cm^2). The open circuit voltage with tin oxide nanowire based architectures) was limited by the poor dye absorption and the lower conduction band edge position of the tin oxide. See Figure 1. Fundamental investigations of electron lifetimes and electron transport times in the alumina coated hybrid architectures were performed. See Figure 2. It was found that the electron transport time in the hybrid architectures was much faster (τ_c = 2 ms) than the alumina coated titania nanoparticles (τ_c = 5 ms). Further studies involving, tin oxide nanoparticle/nanowires, titania nanoparticles/wires showed unexpected trends in the electron lifetimes, which are quite opposite to what one would expect without the alumina coating. *We investigated several new absorbers including iron sulfides (FeS) that showed potential to replace dyes in solar cells. In addition we also developed an electrode architecture to prepare moisture resistant metal-organic perovskites which have gained a lot of attention as a promising absorbers in solar cells.*

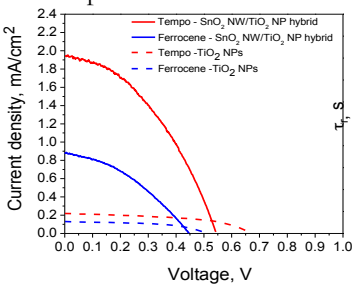

Figure 1. Comparison of the current voltage curves of tin oxide NWs-titania dioxide NP hybrids with the titania NPs after surface passivation with a submonolayer of alumina.

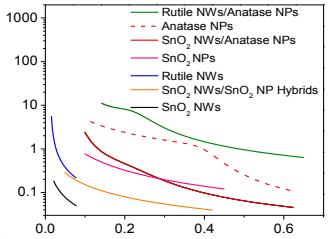

Figure 2. Comparison of electron lifetimes in different architectures- nanowires, nanoparticles, and hybrids of both tin oxide and titania after surface passivation with *alumina*

b. Rare-Earth Oxides in DSSCs (Alphenaar): Over the course of the grant we have been exploring the use of rare earth oxides to either supplement or replace the transition metal oxides (e.g., TiO2) normally used in hybrid solar cells. Rare earth (RE) oxides are stable, wide band gap semiconductors or insulators, with a range of band gaps, similar to the transition metal (TM) oxides. Energetically, the RE oxides have lower electron affinities than TM oxides, meaning that photo excited electron conduction would be preferentially blocked compared to hole conduction. RE oxides also contain an unusual band structure combining itinerant s and d states, and localized f states. Optical transitions among the f-states are similar to the localized excitonic transitions in organic materials; however, high dielectric constants mean that exciton binding energies are relatively low. We first combined oxidized neodymium (Nd_2O_3) particles with [6,6]-phenyl C61 butyric acid methyl ester (PCBM) to form the solar cell active layer. The short circuit current and open circuit voltage are both enhanced compared to pure PCBM. In addition, the photoinduced absorption decay rate increases, and photobleaching is observed. This provides evidence for charge transfer between the organic and rare earth inorganic components. We next incorporated microscale neodymium oxide Nd_2O_3 particles (5% by weight) into the TiO_2 film used as the collector in the photoanode of a dye sensitized solar cell. We observed that incorporation of the RE oxide using this simple technique greatly improved the photocurrent and efficiency higher than previously reported.

c. Mesoporous Titania Based Materials for Hybrid Inorganic-Organic Solar Cells (Rankin): In addition to the publications listed, the Rankin group at UK was able to prove using the GISAXS capabilities at Argonne National Lab that vertically aligned mesostructured TiO_2 thin films form directly by a disorder-order transition during aging at 4 °C and high relative humidity with templating by Pluronic surfactant P123. It was shown that modifying the substrate surface with crosslinked P123 induces vertical orientation of the micelles, but also that aging at 4 °C is essential to generate this structure (Fig. 3a/b). Aging at 23 °C (Fig. 1c/d) generates TiO_2 films with randomly oriented mesostructure including a significant fraction of parallel pores as in Fig. 3c. GISAXS also revealed that the vertically oriented samples have significantly greater thermal stability than horizontal or randomly oriented mesostructures – specifically that they can be calcined at up to 600 °C without loss of mesostructure while randomly oriented mesostructures rapidly lose stability at 450 °C. One GISAXS manuscript has been published [Das *J. Phys. Chem. C* 2014].

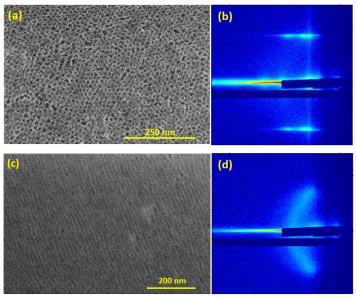

Figure 3. (a) Top-view SEM and (b) GISAXS pattern of P123-templated film with vertical cylindrical micelles (rods above and below the beam stop) aged at 4 °C, and (c) SEM and (d) GISAXS of the same sol aged at 23 °C with randomly oriented micelles.

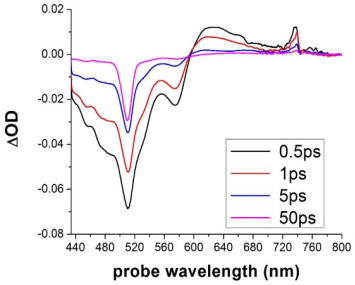

Figure 4. Transient absorption spectra obtained for P3HT/TiO_2 film.

The pore channels of these films were subsequently used for two energy applications. First, photovoltaics were generated by incorporating p-type materials into the vertically oriented pores of thin TiO_2 films. Poly(3-hexylthiophene) (P3HT) was shown by neutron reflectometry and UV-vis spectroscopy to infiltrate 15 nm into the films upon vacuum annealing of P3HT for 60 min at 200 °C. Ultrafast pump-probe spectroscopy with the Liu group at UofL (Fig. 4) shows a positive peak at 740 nm due to intraconduction band transitions after electron transfer from P3HT to TiO_2, suggesting a photovoltaically active interface. Unfortunately, photovoltaic performance of solar cells has been poor (<0.1% efficiency) and efforts are ongoing to improve light absorption and contact quality. Continued detailed pump-probe spectroscopy studies are continuing with the Liu group and two publications are anticipated based on this new collaboration. Incorporating CdTe with Vijay Singh (UK Electrical Engineering) showed decidedly more impressive results – an unoptimized record efficiency of 5.5% due to the high contact area between CdTe and TiO_2 and follow-on work is underway. The second application is a new collaboration was initiated with Doo-Young Kim (UK Chemistry) to introduce nitrogen by N_2/Ar plasma doping and to reduce Ti using H_2 plasma treatment. Both approaches produced visible color changes indicating visible light absorption. Enhanced visible light photocatalytic activity was observed with both types of doping. Three manuscripts are expected in short order, and an NSF proposal for follow-on support has already been submitted.

***e*. Dye-Sensitized Solar Cells with Chemically-Linked Dye and Gold Nanoparticles (Zamborini):**

In this project, we explored the efficiency and stability of dye-sensitized solar cells with N719 dye covalently-linked to a TiO_2 semiconductor film through a siloxane bond to TiO_2 and amide bond between the silane linker and N719 dye. The timescale of electron injection from dye to TiO_2 slowed down with the linker when compared to dye directly attached to TiO_2, but the injection time was still on the picosecond time scale and faster than recombination processes. The use of an aromatic linker increased the electron injection rate relative to a similar sized alkane linker. The stability increased dramatically, especially the air stability of the dye-coated TiO_2 film. Stability against heat, acid, base, and water also improved. Figure 5 shows the air stability of the photoanode with covalently-linked dye by showing the efficiency as a function of time exposed to air. The covalently-linked

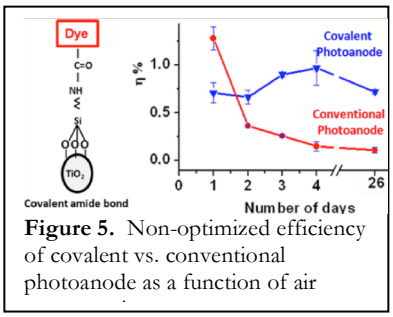

Figure 5. Non-optimized efficiency of covalent vs. conventional photoanode as a function of air

photoanode could be stored in air at least 90 days with no noticeable degradation, whereas traditional directly-attached TiO_2/dye photoanodes degraded significantly within a week. We also performed preliminary work with the Graetzel lab on the covalent attachment of porphyrin dyes on TiO_2 using our strategy, but the coverage was low.

Gold nanoparticles have been used for several years to improve the photovoltaic efficiency of dye-sensitized solar cells by improving light collection because of the gold plasmonic properties and favorable shifting of the TiO_2 Fermi level. In the majority of these studies, the gold nanoparticles are simply mixed in with the TiO_2 particles prior to sintering. In our work, we attached 4 nm diameter gold nanoparticles electrostatically to the outside of the TiO_2 film through a silane linker prior dye sensitization on top of the TiO_2/linker/gold. We observed an increase in both the photovoltage and photocurrent for an impressive power conversion efficiency greater than 11%. Figure 6 shows scanning electron microscopy images of a traditional and gold nanoparticle modified electrodes and the corresponding best efficiencies measured. The gold nanoparticles improve the device performance by increasing dye coverage and facilitating electron injection between multilayer dye molecules and TiO_2 that would usually be inactive on traditional cells. Also, the silane linker reduces electron recombination, increasing the photovoltage. This results in near best efficiencies that are 25-30% higher than traditional photoanodes.

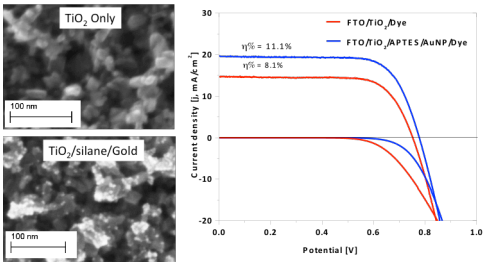

Figure 6. Comparison between SEM images and i-V curves of traditional FTO/TiO_2/Dye and FTO/TiO_2/silane/gold/Dye photoanodes in DSSCs. Bright gold spots are observed in SEM images and efficiency increased ~30%.

***g* Ultrafast Transient Absorption (TA) Spectroscopy Investigation of Solar Cell Materials (J. Liu):** Ultrafast laser spectroscopy provides a powerful tool to quantitatively measure and elucidate charge and energy transfer processes. Supported by DOE-EPSCoR, an ultrafast transient absorption (TA) spectroscopy system has been built to investigate photoinduced processes with sub-picosecond time resolution and is dedicated to research of novel solar cell materials. Over the funding period, several systems have been investigated: Dyes attached to photoanodes; semiconductor nanocluster-ligand conjugates; inorganic-organic hybrid solar cell materials, new absorbers and rare-earth oxides in titania. Two examples are detailed below.

a) ***Covalently attached DSSC photoanodes:*** TA spectroscopy has been used to study the electron injection process from N719 dye molecules to TiO_2 nanoparticles in DSSC photoanodes with and without the presence of two covalently attached silane-based linker molecules: 3-aminopropyltriethoxysilane (APTES) and p-aminophenyltrimethoxysilane (APhS) (Fig. 7). Analysis of the ultrafast kinetics shows that injection from both singlet and triplet excited states of the N719 dye to the TiO_2 conduction band are hindered by the molecular linkers. Several important conclusions are made on the hindering effect of the linkers: The hindering effect is less significant with the aromatic APhS linker than the APTES linker and is more significant for the singlet-state channel than the triplet-state one. Electron injection from the vibrationally excited states is less affected by the linkers. The spectroscopic results unravel the photoinduced processes in the photoanodes with and without molecular linkers and can be used to guide selection of molecular linkers for DSCs with better device performance.

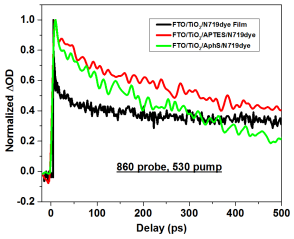

Figure 7. The electron injection dynamics observed with 530 nm pump and 860 nm probe wavelengths for conventional FTO/TiO_2/N719 photoanode, and covalently attached FTO/TiO_2/APTES/N719 and FTO/TIO_2/AphS/N719 photoanodes. OD=optical density.

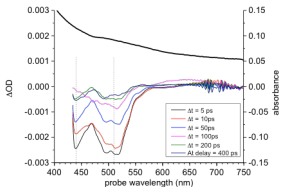

Figure 8. Steady-state absorption spectrum and TA spectra at different pump-probe delay times of FeS:TiO_2 nanowires with 388 nm pump.

b) ***FeS:TiO$_2$ nanowire hybrid structure.*** Iron monosulfide (FeS) is a promising candidate as an absorber layer and photocathode for solar cells. For the first time, FeS nanotubes was made using sulfurization of hematite nanowire by Cummins et al.[4] As the first step toward FeS-based solar cells, ultrafast photoinduced processes in FeS:TiO_2 nanowire hybrid structure have been investigated by TA spectroscopy. Different ultrafast kinetics have been found with different pump wavelengths. The measurements providex insight into charge transfer mechanism from FeS to TiO_2 nanowires.

CLUSTER PROJECT 2: SOLAR FUELS *(M. Sunkara, M. Menon and J. Jasinski):* In this cluster, the group used both theory and experiment to discover and develop new semiconductor alloys and their nanostructures for photoelectrochemical water splitting.

a. Synthesis of ternary nitride alloys*:* In this project, the group used metalorganic chemical vapor deposition and we demonstrated that InGaN alloys can be synthesized using hetero-epitaxy onto thin GaN nanowire substrates with complete control over compositions ($In_xGa_{1-x}N$ with x varying from 0 to 100). The thickness of layers can be as large as 200 nm making them useful for photoelectrochemical applications. Photoelectrochemical measurements show significant photoactivity and appropriate photocurrent onset potential that is expected for the indium composition within InGaN alloy. Later, following theoretical predictions, the synthesis of $GaSb_xN_{1-x}$ alloys (x from 0 to 0.08) was carried out using metal organic chemical vapor deposition (MOCVD) on different planar substrates and gallium nitride (GaN) nanowire substrates. The synthesis was performed at much lower temperatures (~ 590 -700 ºC) than that of the GaN to allow for incorporation of Sb. The MOCVD of $GaSb_xN_{1-x}$ alloys on GaN nanowire substrates allowed for epitaxial growth even at low temperatures. Optical measurements showed that band gap reduced from 3.45 to 1.7 with an increase in antimony from 0 to 8%. Band gap reduction and lattice expansion observed in experiment are in excellent quantitative agreement with theoretical predictions using first principles density functional theory (Figure 9) thus confirming this alloy's potential for use as a photocatalyst for direct water splitting under visible light. The optical band gap results suggest direct nature of band gap for antimony incorporation at levels below 6 at%. Moreover, theoretical computations predict that the band gap of GaSbN alloys change from direct to indirect at antimony concentrations above 7 at%. GaSbN layers were grown epitaxially on GaN nanowire substrates which were shown to be single crystalline containing some stacking faults.

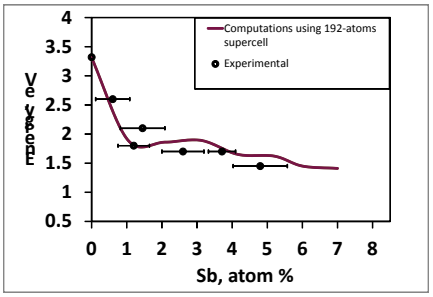

Figure 9. Experimental and theoretical energy band gap of $Ga(Sb_x)N_{1-x}$ as a function of Sb concentration.

b. **Materials Theory:** We have investigated Ga-In-N ternary alloy system using a new formalism within the the density functional theory (DFT) in the generalized gradient approximation (GGA) in conjunction with the Hubbard-U approximation [1]. The resulting GGA+ U approach goes well beyond the current empirical way of determining the U-components and has strong ab initio footing. The Ga-In-N coaxial nanowire was simulated using a 192 atom supercell. Full symmetry unrestricted optimization was performed for this structure using the DFT method. The structural relaxation resulted in the strain release through a rearrangement of the atoms throughout the nanowire. Two significant results were obtained: (1) There is a seamless integration of GaN and InGaN structures across the coaxial interface confirming the suitability of GaN nanowire for growing InGaN crystals. (2) Periodic dislocations are predicted if planar GaN surfaces are used to grow InGaN crystals. We have also investigated the optical and electronic properties of GaN alloyed with Sb for various concentrations of Sb. By considering very large supercells we are now able to consider a large variation of Sb concentration that has not been possible previously. Our results show an initial precipitous drop in band gap from 3.4 eV for pristine GaN to 1.8 eV for very low composition of Sb (<1.5%). The decrease in the gap values is then more gradual till the Sb concentration reaches 6% after which the band gap

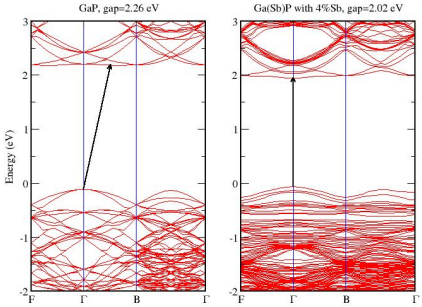

Fig. 10 (caption): Band Structures for GaP (left) and GaP alloyed with 4% Sb (right). The indirect to direct band gap transition is seen with Sb alloying.

becomes indirect. The optical properties show significant absorption in the visible for Sb concentration in the range 3%-6%. Finally, we have investigated GaP alloys with various concentrations of Sb using relatively large 216 atom supercells. $Ga(Sb_x)P_{1-x}$ structures are obtained by substituting P atoms with Sb. In each case considered, both the cell volume and the individual atomic positions have been fully optimized without any symmetry constraints. The doping of GaP by Sb introduces impurity (*spd*-hybridized Sb-related) states at the gap edges. Those at the VBM are more pronounced. The Sb-related states lead to significant modifications in the energy bands. Specifically, there is a strong coupling between the localized Sb states and the conduction band of the host GaP that results in a significant anticrossing interaction leading to the lowering of the bands at the Γ-point which results in turning the indirect gap into a direct one (see Fig. 10). On the other hand, new Sb bands are introduced at the VBM. These lead to a band repulsion that lifts the degeneracy of the GaP-bands at the Γ-point which, in turn, leads to a (small) reduction in the energy gap.

CLUSTER PROJECT 3: THERMIONIC ENERGY CONVERSION *(G. Sumanasekera, M. Sunkara, and J. Jasinski)*: During the scope of this work primarily we studied novel hybrid structures of conical carbon nanotubes (CCNTs) coated with phosphorous (P) doped diamond nanocrystals. Such hybrid architecture is essential and unique due to (a) true performance of nanocrystals is possible without interference from grain boundaries (as in diamond films) and (b) the incorporation of dopants in to nanoscale crystals can be enhanced due to high surface to volume ratio. We also studied W/WO_x nanowires as an alternative material in place of CCNT. Considering its specific properties. As a part of the study of the thermionic emission properties of the hybrid structures, first we concentrated on the pristine CCNT, as they play an important role as the conducting backbone for the P doped diamond. Beyond CCNT structures, we studied the emission properties of the CCNT/diamond hybrid structure and the ultraviolet emission from P doped diamond films..

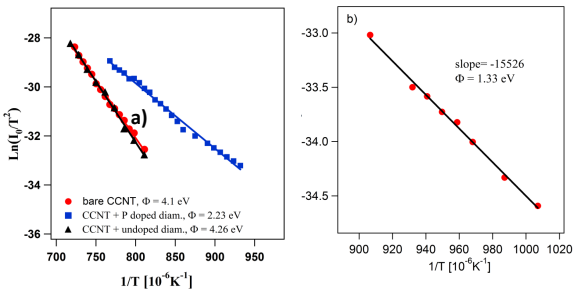

Figure 11 (a) Thermionic emission data plotted as $Ln\left(\frac{J_0}{T^2}\right)$ vs $\frac{1}{T}$ and best fit (line) to Richardson-Dushman equation from thermionic emitters based on bare CCNTs (red), CCNT coated with undoped diamond (black) and CCNT coated with phosphorus doped diamond (blue) (b) Thermionic emission from P doped diamond film grown on W foil.

In addition, the work function reduction of phosphorus doped diamond nanocrystals grown on conical carbon nanotubes (CCNTs) was compared with that of diamond films grown on silicon substrates. Thermionic emission measurements from phosphorus doped diamond crystals on CCNTs resulted in work function value of 2.23 eV as shown in Fig. 11. The presence of hybrid structure with combination of diamond, CCNTs and graphite, prevented the determination of accurate work function of diamond by UPS. Instead, the Ultraviolet Photoelectron spectroscopy studies on phosphorus doped diamond films yielded a work function value of 1.8 eV with observed NEA value of 1.2 eV. We proposed three possible scenarios which could explain the observed work function values for P doped diamond grown on CCNTs: (i) pinning of the bulk Fermi level to the surface Fermi level and resulting band bending (ii) combination of the pinning and the presence of a midband-gap (MBG) state originating from defects (due to doping and morphology of the individual diamond crystals) (iii) the presence of the defects and impurities could cause lowering of the bulk Fermi level. As an additional effect surface states could be compensated by the donors and defects. Thermionic emission results from the P doped diamond films grown on W foil revealed that these structures have lower value of work function in the range 1.0 – 1.33 eV in agreement with the value reported by Nemanich et al. For P doped diamond films, the further decrease of work function value is attributed to negative electron affinity. In order to realize the idea of an alternative hybrid structure, vertically grown Tungsten oxide ($W_{18}O_{49}$) nanowires on W foil were studied. The reduction of $W_{18}O_{49}$ nanowires by hydrogen plasma resulted in porous W/WO_x nanowire structures. Thermionic emission measurements from the alternative hybrid structure of W/WO_x nanowires coated with P doped diamond showed a high work function value exceeding 4.0 eV.

List of Patents from DOE EPSCoR Implementation Award (2011-2014)

1. M Menon, M Sheetz, MK Sunkara, C Pendyala, S Sunkara, JB Jasinski, "PHOTOELECTROCHEMICAL CELL INCLUDING Ga(Sbx)N1-x SEMICONDUCTOR ELECTRODE", US Patent 20,130,081,940 (2013).

List of Publications from DOE-EPSCoR Implementation Award (2011 – 2014)

Cluster 1. Solar Cells

1. B. Pandit, T. Luitel, D. Cummins, A. K. Thapa, T. Druffel, F. P. Zamborini, and J. Liu, "Spectroscopic investigation of photoinduced charge transfer Processes in FTO/TiO_2/N719 photoanodes with and without covalent attachment through silane-based linkers", *J. Phys. Chem. A.* **117**, 13513-13523 (2013).
2. T. Luitel, B. Pandit, J. Liu, and F. P. Zamborini "Improved photovoltaic performance of dye-sensitized solar cells by using chemically-linked gold nanoparticles", (in preparation).
3. K. Fernando, B. Pandit, J. Liu, and B. W. Alphenaar, "Charge transfer in rare earth oxide hybrid solar cells", *Chem. Phys. Lett.* **592**, 155-159 (2014).
4. Y. Xie, M. B. Teunis, B. Pandit, R. Sardar, and J. Liu, "Molecule-like CdSe nanoclusters passivated with strongly interacting ligands: energy level alignment and photoinduced ultrafast charge transfer processes", Acceptred, *J. Phys. Chem. C.* (2015).
5. B. Pandit, R. Dharmadasa, I. M. Dharmadasa, T. Druffel, and J. Liu, "Ultrafast charge carrier relaxation and charge transfer processes in CdS/CdTe thin films" (in preparation).
6. T. Luitel, K. Fernando, B. S. Tatum, B.W. Alphenaar, F.P. Zamborini, "Record high-efficiency dye- sensitized solar cell using a rare earth oxide/titania composite acceptor." J. Phys. Chem. Lett 2014, Submitted.
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9. T. Luitel, K. Fernando, B.S. Tatum, B.W. Alphenaar, F.P. Zamborini, "Record High Efficiency Dye-Sensitized Solar Cell Using a Rare Earth Oxide/Titania Composite Acceptor Electrode" *J. Phys. Chem. Lett* **2014**, submitted for publication.
10. T. Luitel, F.P. Zamborini, "Covalent Modification of Photoanodes for Stable Dye-Sensitized Solar Cells" *Langmuir 29*, 13582-13594 (2013).
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13. N. Rajamanickam, V.K. Vendra, S. Kumari, B.W. Lavery, K. Ramachandran, T. Druffel and M.K. Sunkara, "Moisture Resistant Methyl Ammonium Lead Iodide Perovskite Solar Cells", *Nature Communications*, Under Review (2014)

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19. S. Das, S. Nagpure, R.K. Garlapalli, Q. Wu, S.Z. Islam, J. Strzalka and S.E. Rankin, "Pore Orientation Effects on the Kinetics of Mesostructure Loss in Surfactant Templated Titania Thin Films," submitted to *Phys. Chem. Chem. Phys*. 2014.
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Cluster 2. Solar Fuels

1. N. Andriotis and M. Menon, "Band gap engineering via doping: A predictive approach", submitted to *Phys. Stat. Solidi. B* (2014).
2. A. N. Andriotis, G. Mpourmpakis, S. Broderick, K. Rajan, S. Datta, M. Sunkara and M. Menon, ``Informatics Guided Discovery of Surface Structure-Chemistry Relationships in Catalytic Nanoparticles", *J. Chem. Phys*. **140**, 094705 (2014).
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4. H. Shah, A. Carver, K. Fernando, S. Kolli, B. Abeyweera, S. Lisenkov, M. Menon and B. Alphenaar, ``Optical Generation and Detection of Polaronic States in PCBM", *J. Phys. Chem C*, **117**, 26538 (2013).
5. A. N. Andriotis, R. M. Sheetz, E. Richter and M. Menon, ``Band alignment and optical absorption in Ga(Sb)N alloys", *J. Phys.: Condens. Matte*r **26**, 055013 (2014).
6. S. Sunkara, V. KalyanVendra, J. Jasinski, T. Deutsch, A. N. Andriotis, M. Menon and M. Sunkara, ``New Visible Light Absorbing Materials for Solar Fuels, $Ga(Sb_x)N_{1-x}$ Alloy, *Advanced Materials*, 2014, (DOI: 10.1002/adma.201305083).
7. D. R. Cummins, H. B. Russell, J. B. Jasinski, M. Menon, and M. K. Sunkara, ``Iron Sulfide (FeS) Nanotubes Using Sulfurization of Hematite Nanowires", *Nano Lett.* **13**, 2423 (2013).
8. A. N. Andriotis, G. Mpourmpakis, S. Lisenkov, R. M. Sheetz and M. Menon, ``U-calculation of the LSDA+U functional using the hybrid B3LYP and HSE functionals", *Phys. Status Solidi B* **250**, 356 (2013).
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12. S. Sunkara, V. K. Vendra, J-H. Kim, T. Druffel, and M. K. Sunkara "Scalable synthesis and photoelectrochemical properties of copper oxide nanowire arrays and films", *Catalysis Today*, 199, 27-35 (2013).
13. C. Pendyala, J. B. Jasinski, J. H. Kim, V. K. Vendra, S. Lisenkov, M. Menon and M. K. Sunkara, "Nanowires as semi-rigid substrates for growth of thick, $In_xGa_{1-x}N$ (x>0.4) epi-layers without phase segregation for photoelectrochemical water splitting", *Nanoscale*, 4, 6269-6275 (2012).
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Cluster 3. Thermionic Emission

1. A. Sherehiy, S. Dumpala, M. K. Sunkara, J. B. Jasinski, R. W. Cohn, G. U. Sumanasekera, "Thermionic emission from phosphorus (P) doped diamond nanocrystals supported by conical carbon nanotubes and Ultraviolet Photoelectron Spectroscopy study of P-doped diamond films", *Diamond & Related Materials*, 50, 66-76 (2014)
2. A. Sherehiy, S. Dumpala, A. Safir, D. Mudd, I. Arnold, R. W. Cohn, M. K. Sunkara, and G. U. Sumanasekera, "Thermionic emission properties and the work function determination of arrays of conical carbon nanotubes", *Diamond & Related Materials*, 34, 1–8 (2013)
3. S. Dumpala, J. B. Jasinski, G. U. Sumanasekera, M. K. Sunkara, "Large area synthesis of conical carbon nanotube arrays on graphite and tungsten foil substrates", *Carbon*, 49, 2725 (2011)

Other Related Publications that Acknowledged DOE Support:

1. N. Andriotis, E. Richter, S. Lisenkov, R. M. Sheetz and M. Menon, ``Electronic structure, optical properties and electronic conductivity of SiC nanowires", Journal of Computational and Theoretical Nanoscience (JCTN) **9**, 2008 (2012).
2. S. Lisenkov, A. N. Andriotis and M. Menon, ``Magnetic anisotropy and engineering of magnetic behavior of the edges in Co embedded graphene nanoribbons", Phys. Rev. Lett., **108**, 187208 (2012).
3. A. N. Andriotis and M. Menon, ``The synergistic character of the defect-induced magnetism in diluted magnetic semiconductors and related magnetic materials", J. Phys: Condens. Matter **24**, 455801 (2012).
4. A. N. Andriotis and M. Menon, ``The synergistic character of the defect-induced magnetism in diluted magnetic semiconductors and related magnetic materials", J. Phys: Condens. Matter **24**, 455801 (2012).
5. A. N. Andriotis and M. Menon, ``Defect-induced magnetism: Codoping and a prescription for enhanced magnetism", Phys. Rev. B **87**, 155309 (2013).
6. A. N. Andriotis and M. Menon, ``Tunable Magnetic Properties of Transition-Metal Doped MoS$_2$", Phys. Rev. B**90**, 125304 (2014).
7. M. Carreon, J. Jasinski and M.K. Sunkara, "Low Temperature Synthesis of Silicon Nanowire Arrays", *Materials Research Express,* 1, 045006 (2014).
8. L. Brockway, V. R. Vasiraju, M.K. Sunkara, and S. Vaddiraju, "Engineering Efficient Thermoelectrics from Large-scale Assemblies of doped ZnO Nanowires: Nanoscale Effects and Resonant-Level Scattering", *ACS Applied Materials & Interfaces*, 6 (17), 14923-14930 (2014).

9. A. K. Thapa, B. Pandit, R. Thapa, T. Luitel, H. S. Paudel, G. Sumanasekera, M. K. Sunkara, N. Gunawardhana, T. Ishihara, M. Yoshio, Synthesis of mesoporous birnessite-MnO_2 composite as a cathode electrode for lithium battery, *Electrochimica Acta*, 116, 188-193 (2014).
10. T.Q. Nguyen, A.K. Thapa, V.K. Vendra, J.B. Jasinski, G.U. Sumanasekera and M.K. Sunkara, " High rate capacity retention of binder free, tin oxide nanowire arrays using thin titania and alumina coatings", *RSC Adv.*, 4(7), 3312-3317 (2014).
11. S. Kolli, C. S. Pendyala, M.K. Sunkara, J.B. Jasinski and B.A. Alphenaar "Thermally activated luminescence in InN nanowires", *J. Luminiscence*, 141, 162-165 (2013).
12. A. K. Thapa, T.-H. Shin, S. Ida, G. U. Sumanasekera, M. K. Sunkara, T. Ishihara, "Gold-Palladium nanoparticles supported by mesoporous β-MnO_2 air electrode for rechargeable Li-Air battery", *J. Power Sources* 220, 211-216 (2012).
13. U. Cvelbar and M.K. Sunkara, "Chapter 5: Large Scale Plasma Assisted Growth of Nanowires", pp109-146, Book on Plasma Processing of Nanomaterials edited by R.M. Sankaran, CRC Press, Boca Raton, FL (2012).
14. U. Cvelbar, Z. Chen, I. Levchenko, R. M. Sheetz, J.B. Jasinski, M. Menon, M. K. Sunkara, K. Ostrikov, "Sub-oxide-to-metallic, uniformly-nanoporous crystalline nanowires by plasma oxidation and electron reduction". Chem. Comm. 48, 11070-11072 (2012).
15. P. Meduri, E.L. Clark, J-H. Kim, E. Dayalan, G.U. Sumanasekera, and M.K. Sunkara,"MoO_{3-x} nanowire arrays as stable and high capacity anodes for Lithium-Ion Batteries", Nano Lett., 12(4), 1784-1788 (2012).
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17. L. Brockway, C. Pendyala, M.K. Sunkara, and S. Vaddiraju, " A post-synthesis decomposition strategy for Group III nitride quantum wires", Crystal Growth and Design, 11 (10), 4559-4564 (2011).
18. V. Kumar, J-H. Kim, J.B. Jasinski, E.L. Clark, and M.K. Sunkara, "Alkali assisted, atmospheric plasma production titania nanowire powders and arrays", Crystal Growth and Design, 11 (7), 2913 (2011).
19. P. Meduri, E.L. Clark, E. Dayalan, G.U. Sumanasekera, and M.K. Sunkara, "Kinetically limited de-lithiation behavior of nanoscale tin covered tin oxide nanowires", Energy and Environ. Science, 4, 1695 (2011).
20. M K Sunkara, C Pendyala, D Cummins, P Meduri, J. Jasinski, V Kumar, H B Russell, E L Clark, and J H Kim, "Inorganic nanowires: a perspective about their role in energy conversion and storage applications", J. Phys. D: Appl. Phys., 44 (17), 174032 (2011).
21. J.B. Jasinksi, S. Dumpala, G.U. Sumanasekera, M.K. Sunkara, and P.J. Ouseph, "Transmission Electron Microscopy Study of Moire Patterns of Few Layer Graphene", Appl. Phys. Lett., 99, 073104 (2011).
22. R. Jayasinghe, A. K. Thapa, R. R. Dharmasena, T. Q. Nguyen, B. K. Pradhan, H. S. Paudel, J. B. Jasinski, A. Sherehiy, M. Yoshio, G. U. Sumanasekera, "Optimization of MWNT based CFx electrodes for improved primary and secondary battery performances", Journal of Power Sources, 253, 404-411 (2014).
23. R. Przeniosło, I. Sosnowska, M. Stękiel, D. Wardecki, A. Fitch, J.B. Jasiński, "Monoclinic deformation of the crystal lattice of hematite α-Fe_2O_3" Physica B: Condensed Matter, 449, 72–76 (2014).
24. J. Jasinski, D. Ziolkowska, M. Michalska, L. Lipinska, K. Korona, M. Kaminska, "Novel Graphene-Oxide/Manganese Oxide Nanocomposites" RSC Adv., 2013, 3, 22857-22862.
25. M. Krajewski, M. Michalska, B. Hamankiewicz, D. Ziolkowska, K.P. Korona, J. B. Jasinski, M. Kaminska, L. Lipinska, A. Czerwinski, "$Li_4Ti_5O_{12}$ modified with Ag nanoparticles as an advanced anode material in lithium-ion batteries", Journal of Power Sources 245, 764-771 (2014).
26. D. Ziolkowska, K.P. Korona, B. Hamankiewicz, S.-H. Wu, M.-S. Chen, J.B. Jasinski, M. Kaminska, A. Czerwinski, "The role of SnO_2 surface coating on the electrochemical performance of $LiFePO_4$ cathode materials" Electrochimica Acta 108 (2013) 532– 539.

27. W. Slawinski, R. Przenioslo, I. Sosnowska, D. Wardecki, A. N. Fitch, M. Bieringer, J. B. Jasinski, "Particle and crystallite size effects on the modulated structure of multiferroic $CaMn_7O_{12}$", J. of Solid State Chemistry 198 (2013) 392–398.
28. B. W. Alphenaar, T. Bansal, A. D. Mohite, H. M. Shah, C. Galande, A. Srivastava, J. B. Jasinski, and P. M. Ajayan "(Invited) Experimental Determination of the Electronic Density of States for Graphene Oxide", *ECS Trans.* 2012 45(3): 31-39
29. T. Bansal, A. D. Mohite, H. M. Shah, C. Galande, A. Srivastava, J. B. Jasinski, P. M. Ajayan, B. W. Alphenaar, "New insights into the density of states of graphene oxide using capacitive photocurrent spectroscopy" Carbon 50(3), 808-814 (2012).

Personnel for DOE EPSCoR Implementation Award (August 2011 – July 2014)

S.No	Personnel	Role	Advisor	% effort on DOE	% Support from DOE	Technical role
1	M.K. Sunkara	PI	N/A	10	10	Technical PI for the effort; led three clusters on solar cells; solar fuels and thermionic emission
2	G.U. Sumanasekera	Co-PI	N/A	10	10	Thermionic emission
3	B. Alphenaar	Co-PI	N/A	10	10	Organic/inorganic solar cells
4	F. Zamborini	Co-PI	N/A	10	10	Solar cells; spatial mapping studies
5	S. Rankin	Co-PI	N/A	10	10	Organic/Inorganic solar cels
6	B.J. Hinds	Co-PI	N/A	10	10	Solar fuels
7	M. Menon	Co-PI	N/A	10	10	Computational materials science & modeling studies
8	J. Liu	Co-PI	N/A	10	0	Led the effort on ultrafast spectrosocpy
8	J. Jasinski	Co-I	N/A	30%	30%	Materials characterization using advanced electron microscopy & spectroscopy techniques
9	N. Subramanian	Postdoc	S. Rankin/B. Hinds	50%	50%	Solar Fuel Materials
10	J.C. Mohandas	Postdoc	S. Rankin	50%	50%	Solar Fuels Materials
11	T. Guhu	Postdoc	J. Jasinski	5%	5%	Materials Characterization
12	B. Pandit	Postdoc	J. Liu	100%	0%	Helped with Ultrafast Spectroscopy Studies

13	A.Q. Jamhawi	PhD Student	J. Liu	100%	0%	Ultrafast spectroscopy studies
14	Y. Xie	PhD Student	J. Liu	100%	0%	Ultrafast spectroscopy studies
15	S. Sunkara	PhD Student	M. Sunkara	70	70	Materials synthesis: Cu2O NW and MOCVD of GaSbN films
16	D. Cummins	PhD Student	M. Sunkara	70	50	Phase transformation studies; ultrafast spectroscopy setup; solar fuels materials
17	V. Vendra	PhD Student	M.Sunkara/D. Amos	100	80	Fundamental studies on solar cell materials
18	A. Garcia	PhD Student	M. Sunkara	30	0	Phase purification of Cu2O thin films and nanowires
19	S. Dumpala	PhD Student	M. Sunkara/G. Sumanasekera	25	25	n-type doping of diamond crystals for thermionic emission
20	A. Sheriy	PhD Student	G. Sumanasekera	100	85	Thermionic emission properties characterization
21	K. Fernando	PhD Student	B. Alphenaar	100	100	Organic/inorganic solar cells
22	S. Islam	PhD Student	S. Rankin	100	100	Solar cell materials
23	N. Linck	PhD Student	B. Hinds	100	100	Solar fuels
24	S. Nagpure	PhD Student	S. Rankin	100	100	Highly oriented porous materials
25	H. Shah	PhD Student	B. Alphenaar	10	10	Solar cells
26	C. Pendyala	PhD Student	M. Sunkara	10	10	Solar fuels
27	X. Sun	PhD Student	M. Sunkara	20	20	Solar cell materials
28	Q. Wu	PhD	S. Rankin	20	20	Solar cell materials

		Student				
29	H. Russell	PhD Student	M. Sunkara	30	0	Solar fuels materials
30	S. Das	Ph.D Student	S. Rankin	30	30	Solar cell materials

OTHER SUPPORT (2011-2014)

Awarded Support

1. J. Jasinski (PI) and M.K. Sunkara "STTR Phase I: An Innovative Spray Pyrolysis Process for Producing Pyrochlore Catalysts", Harrison (PI), National Science Foundation STTR Program, $36,000 (ULRF subaward), 07/01/14-06/30/15, The objective of this project is to develop spray pyrolysis process to fabricate pyrochlore catalysts. Jasinski provides structural characterization of the produced materials to support the synthesis effort. There is no overlap between this grant and the DOE EPSCoR project.

2. G. Prater, S. Park and M.K. Sunkara, I/UCRC on Electrical Vehicles and Sustainable Transportation Systems (EV-STS), National Science Foundation, 08/01/2014-07/31/2015, $14,999. No overlap.

3. M.K. Sunkara, G.U. Sumanasekera, J. Jasinski, S. Rankin, B.J. Hinds, M.Menon are part of 45 PIs, NSF EPSCoR Track I, Powering the Kentucky Bioeconomy for a Sustainable Future, $4.2M, 08/01/2014-07/31/2019. UofL sub-portion from $24M package. No overlap with DOE EPSCoR Implementation Award. In this multi-institutional project, in collaboration with several other researchers, Jasinski works on the development of efficient storage devices. In particular, he is working on the development of high surface area electrodes for supercapacitors or lithium batteries. The electrodes are based on highly porous materials such as porous 1D nanostructures or 3D carbon structures.There is no overlap between this grant and the DOE EPSCoR project.

4. M.K. Sunkara, "Transition Metal Chalcogenide Nanostructures for Solar Energy Conversion", PI, KY NASA EPSCoR, Graduate Fellowship for Dustin Cummins, 01/01/2014-12/31/2014, $30,000. This helped in supporting graduate student working on DOE-EPSCoR related studies.

5. T. Druffel, G. Willing and M.K. Sunkara, "Energy Efficient Improvements for Household Appliances via Sorption Technologies, Phase II", GE Appliances, $170K, Phase I & II, 07/01/2013 – 12/31/2014. No overlap.

6. M.K. Sunkara (PI), K. Rajan, S. Datta, J. Jasinski and M.Menon, "SOLAR: New Materials Search for Solar Energy Conversion to Fuels National Science Foundation, $1.1M, 09/15/2011-09/14/2015 The objective of this project was the development of materials informatics-based methods to explore new chemistries and identify new promising materials for solar energy conversion. The samples created using DOE EPSCoR support were used to create some of the data used in these studies.

7. M.K. Sunkara (PI), "Novel Hydro Desulfurization Catalysts", KY Commercialization Fund, $75K, 01/01/2012-4/30/2013. No overlap.

8. M.K. Sunkara (PI), "Hematite nanowire array electrodes for photoelectrochemical water splitting", KSGC fellowship support to Harry Russell, $30,000, 01/01/2012-12/31/2012. Supported a student who provided samples for DOE-EPSCoR related studies.

9. M.K. Sunkara (PI), "A reactor and method for production of titania and related metal oxide nanowires", subcontract to Advanced Energy Materials, LLC (NSF SBIR Phase I), $38K, 01/01/2011-06/30/2011. No overlap.

10. M.K Sunkara (PI). "University of Louisville Research and Energy Independence", DOE CDP, $2M, 08/01/2010-07/30/2012. This support was used for building equipment and personnel infrastructure for Conn Center and expanding research efforts at UofL. This grant supported few students for partial periods and after which these students worked on DOE EPSCoR supported studies. Also, this support led to development of facilities such as roll to roll coating and dye sensitized solar cell fabrication and testing which were used for DOE EPSCoR studies.

11. M.K. Sunkara (PI) along with M. Carreon, E. Berson and P. Ratnasamy, KY DEDI, "Technologies for commercializing biofuels, natural gas and carbon dioxide", $250K, 08/01/2010-07/30/2012. Some of the studies provided partial support to one student who continued her studies with support from DOE EPSCoR. Other studies did not have overlap.

12. M.K. Sunkara (PI) along with G.U. Sumanasekera (co-PI), "High capacity and durable electrode materials for next generation Li ion batteries", $225K, Clinical & Translational Science Pilot Grant Program, Office of Vice President for Research, University of Louisville, 07/01/2010-06/30/2012. No overlap.

13. M.K. Sunkara (PI), "A platform technology and reactor for bulk production of nanowires (NanowireX$225K, University of Louisville Clinical & Translational Science Pilot Grant Program, Office of Vice President for Research, University of Louisville, 07/01/2010-06/30/2012. No overlap.

14. B. Alphenaar (PI) and S. Mendes. "MRI:Development of an Electron State Depletion Microscop at the University of Louisville", NSF-DMR, $629,992, 10/01/11-9/30/15 No overlap with DOE project.

15. B. Knutson (PI), S. Rankin and B. Webb, "Enveloped porous nanoparticles for RNA delivery to insects, subcontract from NSF IU/CRC Center for Arthropod Management Technologies (CAMTech)", January 2015-December 2016, $65,000, No overlap with DOE EPSCoR Implementation Award.

16. J. Littleton (PI) and S. Rankin, "Harvesting specific plant metabolites from hairy root cultures using magnetized nanoparticles", subcontract to NIH STTR grant from Naprogenix, Inc., August 2014 – July 2015, $75,000. No overlap with DOE EPSCoR Implementation Award.

17. B.L. Knutson (PI), S. Rankin and J Littleton, "Engineered Porous Thin Films for Screening and Production of Therapeutics Derived from Plant Biotech", Kentucky Science and Engineering Foundation, July 2013 – June 2015, $30,000. No overlap with DOE EPSCoR Implementation Award.

18. J. Littleton (PI) and S. Rankin, "Accelerated Implementation of Commercialization Plan for Novel Pharmacotherapies for Alcoholism", subcontract to KSTC SBIR matching grant from Naprogenix, Inc., July 2013 – June 2015, $160,000. No overlap with DOE EPSCoR Implementation Award.

19. S.E. Nokes (PI), S. Rankin- part of 20 PIs, "On-Farm Biomass Processing: Towards an Integrated High Solids Transporting / Storing / Processing System", U.S. Department of Agriculture (Biomass Research & Development Initiative), July 2011 – June 2015, $6,932,786 No overlap with DOE EPSCoR Implementation Award.

20. K.W. Anderson (PI), S. Rankin along with 14 PIs, "REU Site: A Multidisciplinary Research Experience in Engineered Bioactive Interfaces and Devices", NSF, June 2012 – May 2015, $319,909, one of 14 co-PIs. No overlap with DOE EPSCoR Implementation Award.

21. S. Rankin (PI) and B.L. Knutson (co-PI), "Collaborative Research: Design of Templated Ceramic Materials for Separation and Purification of Complex Carbohydrates", National Science Foundation, April 2010 – April 2014, $301,130. No overlap with DOE EPSCoR Implementation Award.

22. B.L. Knutson (PI), S.E. Nokes, S. Rankin and H.J. Lemhler (Iowa Dept), "Separation and recovery of high value pentose derivatives from cellulosic biomass using molecular imprinting, USDA" (with Kentucky Office of Energy Policy matching), July 2008 – July 2012, $1,366,214. No overlap with DOE EPSCoR Implementation Award.

23. S.E. Rankin (PI), B.L. Knutson and S.E. Nokes "Interfacial Engineering of Biomass Saccharification by T. reesei Enzymes," Kentucky Science and Engineering Foundation, July 2010 – June 2013, $90,000. No overlap with DOE EPSCoR Implementation Award.

24. K.W. Anderson (PI), S.E. Rankin as part of 20 co-PIs, "IGERT: Building Leadership Through a Program on Engineered Bioactive Interfaces and Devices", NSF, September 2007 – August 2013, $3,000,000. No overlap with DOE EPSCoR Implementation Award.

25. K.W. Anderson (PI), S.E. Rankin as part of 14 PIs, "REU Site: A Multidisciplinary Research Experience in Engineered Bioactive Interfaces and Devices", NSF, June 2009 – May 2012, $321,000. No overlap with DOE EPSCoR Implementation Award.

26. G.U. Sumanasekera, "Single walled nanotubes and Graphene based multiplexed sensors for hypergolic fuel detection" (NSF), $160,677(07/01/09 - 06/30/12). No overlap.

27. B.J. Hinds, "Aligned Carbon Nanotube Membranes for Forward Osmosis Power Generation" Statkraft Corp., Norway 7/1/08-6/31/12 $312,465 (sole PI, 100%) {Developing ion rejection at CNT tips to develop forward osmosis pressure to drive turbines to produce electricity. Minimal overlap with DOE but progress in clean energy generation is of interest to DOE mission.

28. B.J. Hinds, "Advanced Materials Relating to Applications in Epitaxial Thin Films and Device Structures" NSF EPSCoR subcontract of 'EPSCoR RII: Transforming Kentucky's New Economy' (P.I. G. Cao, 5 co-I) 9/1/08-8/31/13 $4.044M (UK portion) (17% #PIs) (Infrastructure to develop magnetic material fabrication and characterization. Hinds' group working on molecular electronics with well defined spin states to induce long range ferromagnetic ordering and magneto-resistance changes. Minimal overlap)

29. J. Liu, PI, "Spectroscopic Investigation of Vibronic Interactions in Molecules with Low Symmetry", PI, American Chemical Society Petroleum Research Fund - Doctoral New Investigator Program (53476-DNI6) - 09/01/2013-08/31/2015

Pending Support

1. M.K. Sunkara, J. Jasinski and T.L. Druffel, "A scalable method for production of pyrochlore materials", $40K, Subcontract from KSTC Matching Grant to NSF STTR to PCC, 01/01/2015-06/31/2015. No overlap.

2. New Semiconductor Alloy Materials for Un-assisted Solar Hydrogen Production, M. Sunkara, J. Spurgeon, M.Menon, NSF, $306, 595, 7/1/2015-6/31/2018. This project is based on the data & concepts generated from DOE EPSCoR studies.

3. B. Alphenaar, K. Walsh, and S. McNamara, Exploration of Damage Mechanisms in MEMs based Memory and Logic Devices, DTRA, $1,050,000, pending. No overlap with DOE project.

4. B. Alphenaar and F. Zamborini.Rare Earth Oxides for Hybrid Photovoltaics, NSF, $421,053, pending, Extension of work performed in DOE contract.

5. S. Rankin and D-Y.Kim, "H_2 and N_2/Argon Plasma Induced Electronic Heterojunctions in Nanoporous TiO_2 Films for Photocatalysis, NSF, $359,240, Follow on based on materials and techniques developed as part of this DOE EPSCoR Implementation Award.

6. S. Rankin (PI) and C. Harnett, "Collaborative Research: Electroosmotic Flow in Conductive Nanoporous Membranes," NSF, $195,344, University of Louisville Electrical Engineering (separate budget). No relation to the DOE EPSCoR Implementation Award.

7. S. Rankin (co-PI along with 6 other PIs) REU Site: A Multidisciplinary Research Experience in Engineered Bioactive Interfaces and Devices, NSF, $434,019 No relation to the DOE EPSCoR Implementation Award.

8. S. Rankin, co-PI (along with 18 other PIs) NRT: SEE (Science, Engineering, and Entrepreneurship) Convergence for the Translation of Bioactive Interfaces into Devices, NSF, $2,999,521. No relation to the DOE EPSCoR Implementation Award.

9. J. Jasinski (PI) along with collaborators from University of Warsaw (Poland), "Collaborative Research: Cost-Effective, Scalable and Earth-Abundant Transition Metal-Based Nanocomposites for High Performance Electrodes", NSF-DMR/Solid State and Materials Chemistry, $357,639, 07/01/15-06/30/18. The objective of this project is to use the concept of recently demonstrated nonocomposite systems for the fundamental study of structure-property relationships in several promising electrode materials, including several lithium transition metal oxides ($LiMn_2O_4$, $LiFePO_4$, $Li_4Ti_5O_{12}$) and Li-rich layered oxides, of the $xLi_2MnO_3(1-x)LiMO_2$-type. There is no overlap between this grant and the DOE EPSCoR project.

10. G.U. Sumanasekera, NSF: Engineering of graphene and h-BN surfaces via in-situ transport characterization: experimental and theoretical, $364569. 07/01/15-06/31/18. No overlap.

11. G.U. Sumanasekera (PI), "KSEF: Utilization of the solar spectrum for optimum energy generation using a hybrid solar-thermionic converter", 05/01/15-04/31/17. This project is based on the data generated using DOE-EPSCOR project. IR portion of the concentrated solar spectrum is used to heat P-doped diamond to generate thermionically emitted electrons to replenish electrons in a Schottky-barrier solar cell.

12. J. Liu, "CAREER: Laser Spectroscopic Investigation of Vibronic Interactions in Free Radicals and Molecular Complexes" - National Science Foundation, $435,542.00, 7/1/2015-6/30/2020

13. J. Liu, "Looking for Molecular Funnels: Spectroscopy and Dynamics Beyond the Born-Oppenheimer Approximation" – Kentucky Science and Engineering Foundation, $30,000, 07/01/2015 - 06/30/2016