Final Technical Report

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Dr. Marvin Stodolsky
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"Institute for Advanced Materials at University of Louisville"

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Submitted by:

PRINCIPAL INVESTIGATORS

Mahendra K. Sunkara, Ph.D (Lead PI)
Professor of Chemical Engineering

Gamini U. Sumanasekera, Ph.D. (co-lead PI)
Associate Professor of Physics

Thomas L. Starr, Ph.D.
Professor of Chemical Engineering

G.A. Willing, Ph.D.
Assistant Professor of Chemical Engineering

Robert W. Cohn, Ph.D.
Professor of Electrical and Computer Engineering

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PROJECT SUMMARY

In this project, a university-wide, academic center has been established entitled "Institute for Advanced Materials and Renewable Energy". In this institute, a comprehensive materials characterization facility has been established by co-locating several existing characterization equipment and acquiring several state of the art instrumentation such as field emission transmission electron microscope, scanning electron microscope, high resolution X-ray diffractometer, Particle Size Distribution/Zeta Potential measurement system, and Ultra-microtome for TEM specimen. In addition, a renewable energy conversion and storage research facility was also established by acquiring instrumentation such as UV-Vis absorption spectroscopy, Atomic Layer Deposition reactor, Solar light simulator, oxygen-free glove box, potentiostat/galvanostats and other miscellaneous items. The institute is staffed with three full-time staff members (one senior research technologist, a senior PhD level research scientist and a junior research scientist) to enable proper use of the techniques. About thirty faculty, fifty graduate students and several researchers access the facilities on a routine basis. Several industry R&D organizations (SudChemie, Optical Dynamics and Hexion) utilize the facility.

The established "Institute for Advanced Materials" at UofL has three main objectives: (a) enable a focused research effort leading to the rapid discovery of new materials and processes for advancing alternate energy conversion and storage technologies; (b) enable offering of several laboratory courses on advanced materials science and engineering; and (c) develop university-industry partnerships based on the advanced materials research. The Institute's efforts were guided by an advisory board comprising eminent researchers from outside KY. Initial research efforts were focused on the discovery of new materials and processes for solar cells and Li ion battery electrodes. Initial sets of results helped PIs to secure a successful EPSCoR cluster implementation grant by teaming with additional researchers from UK.

In addition to research efforts, the project enabled several other outcomes: (a) helped recruit a junior faculty member (Dr. Moises Carreon) and establish a lab focused on meso-porous materials toward separation and catalysis; (b) enabled offering of three new, graduate level courses (Materials characterization using spectroscopy and microscopy; Electron and x-ray diffraction; and renewable energy systems); and (c) mentoring of a junior faculty members (Dr. Gerold Willing).

HIGHLIGHTS OF ACCOMPLISHMENTS MADE DURING THE PROGRAM

1.0 Infrastructure: acquisition of instrumentation and facilities

- We acquired a high-resolution 200 KV transmission electron microscope (Tecnai G2 F20 X-TWIN) with the following capabilities: STEM hardware and software, EDS (X-ray analysis) hardware and software, HAADF detector, High tilt 3D chemical tomography module, GATAN post-column energy filter (GIF), EFTEM module with EELS, Cyrogenic specimen transfer system and associated specimen holders, and STEM tomography data acquisition software. We renovated space to establish the TEM facility.

- Acquired a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrometer with UV WinLab software with operational wavelength between 175 nm-3300 nm. The optic unit includes: Dual, pre-aligned souces, a reflecting optical system with holographic grating monochomator with 1440 lines/mmUV/Vis blazed at 240 nm and 360 lines/mm NIR blazed at 1100 nm, and Littrow mounting. Also includes peltier cooled PbS detector for NIR. In addition, a 60 mm integrating sphere is included, as well as a Peltier sample holder for heating and cooling.

- Acquired a Brookhaven Instruments model 90Plus particle size analyzer for characterizing nano-colloidal suspensions. This instrument includes complete particle size analysis capability from 0.6 nm to 6000 nm, in a wide variety of polar and non-polar solvents. It also includes complete zeta potential functionality (ZetaPlus) +/-200mv, and a variety of cuvettes and standards.

- Acquired a UHV Kelvin Probe system from McAllister Technical Services that is equipped with a linear translator for work function measurements both in the ambient, and in the existing VG Scientific UHV Surface Science instrument system. This probe system will mount directly to the 2.75" CFF mounting flange on the VG instrument. There are also three different diameter tips for the probe, to maximize sample flexibility.

- Acquired an atomic layer deposition (ALD) system: Savannah 100 from Cambridge Nanotech for uniform conformal deposition of ultrathin films of oxides such as Al_2O_3, TiO_2 and SiO_2. The deposition chamber can be heated up to 300C and contains two heated precursor lines capable of handling various solid, liquid and gaseous precursors. The system can be operated in continuous as well as pulsed exposure modes with high precision enabling great control over the deposition process.

- Acquired a Bruker D8 Advance X-ray Diffraction The D8 DISCOVER is a state-of-the-art, high-quality X-ray diffractometer system that is easy to use, highly accurate, and versatile to meet all needs in X-ray diffraction. It is outfitted with a dynamic scintillation detector, a LynxEye(TM) detector, and a Dome Heating

Stage, DHS 1100 with a gas injection system. During a run samples can be heated to as much as 1100°C. Features:

- Operational Geometry: vertical
- configurations: Theta/2Theta or Theta/Theta
- measuring circle diameter (depending on accessories): predefined positions at 500 or, 600 mm, intermediate setting between 380mm and 760mm possible
- smallest step size (Theta/2Theta): 0.0001°
- reproducibility (Theta/2Theta): +-0.0001°
- maximum slew speed: 1500°/min
- angular positioning: stepper motors with optical encoders
- central opening of Theta ring: diameter 10 cm
- angular range (Theta): unlimited
- angular range (2Theta): -110° to 168°

- Acquired a PowerTome Ultramicrotome is designed to produce ultrathin sections for electron microscopy, as well as semi-thin and thick sections for light microscopy. A microcomputer controls the internal operation of the instrument, but convenient manual controls and easy to operate control buttons give the microtomist complete command of all functions. The controls for automatic sectioning are located on a separate control module which can be conveniently placed on either side of the microtome. All of the mechanical components have been carefully isolated from the cabinet and the bench top to ensure vibration-free sectioning.

- Acquired a Newport Solar Cell simulator which uses a 150 W ozone free xenon lamp producing a collimated beam of 1.3 inches in diameter. It also has the capability to tailor the output spectrum to specific needs. It produces higher than 1 sun power (as high as 1.3) with an AM 1.5G filter.

- Acquired a Oxygen free Glovebox from Vacuum Atmospheres Company which can maintain low oxygen levels (upto 1 ppm) and moisture levels required for the battery assembly. It will filled with an inert atmosphere of argon to prevent the lithium from oxidation. It can be used to test upto 3 cells at a particular time.

2.0 Formal establishment of the Institute

In Year 2007, the Board of Trustees of University of Louisville approved our proposal of an academic institute entitled “Institute for Advanced Materials and Renewable Energy (IAM-RE)” at University of Louisville which included a university-industry service center. PI and co-PI of this project (Dr. M. Sunkara and Dr. G.U. Sumanasekera) assumed founding director and co-director positions of the Institute. In addition, we invited Dr. R.M. Buchanan of the Chemistry department to become another

co-Director of the Institute. We identified several faculty from engineering, science and medicine disciplines as belonging to the core faculty for the institute. We established an external advisory board comprising eminent researchers from KY and outside.

2.1 *Core staff*: The Institute is staffed with a manager and senior research technologist (Mrs. Rodica McCoy), a senior research scientist and a junior research scientist along with a part-time technical person for equipment maintenance. Initially, Dr. Zhiqiang Chen was hired as the senior research scientist and Dr. Biswa Deb as the junior research scientist. In 2008, we recruited Dr. Jacek Jasinksi as the chief scientist for the facility who came to the Institute with 10+ yrs experience in microscopy beyond his Ph.D. in Physics. The facilities within the Institute are open to all faculty, students and researchers from industry. The core staff facilitated access through formal training and direct help on some research projects.

2.2 *External advisory board:* The board met twice during last three years for a day-long meeting both times and provided a strong feedback to University administration.

Dr. John C. Angus: Smith Professor Emeritus of Engineering at CWRU and Member of National Academy of Engineering
Dr. Burton Davis: Associate Director of CAER, UK
Dr. Thomas Mallouk: Professor of Chemistry and Director of MRSEC at Penn. State University.
Dr. Raul Miranda: Program Director in Basic Energy Sciences Div., US DOE.
Dr. Doug Lowndes: Director, Center for Nanophase Materials, ORNL.
Dr. **Mickey R. Wilhelm:** Dean, J.B. Speed School of Engineering, UofL
Dr. Harold Kung: Professor of Chemical Engineering, Northwestern Univ.

2.3 University-Industry service center: We created a service center through which researchers from industry within the region can access the facilities and expertise within the Institute. SudChemie has awarded service contracts in excess of $100K per year over last three years to access the facilities and expertise to understand and improve their catalyst materials. This effort led to a new catalyst that is being adopted by several chemical plants. Other companies such as Optical Dynamics, Inc. and Hexion have also accessed the facilities. Over ten small businesses access these facilities in an on-going basis. The service contracts exceeded $225K in (2007/2008), $120K (2009). This income helped with offsetting partially the maintenance and salary costs.

Graduate students and Post-doctoral associates: Several students were supported directly either fully or partially on the grant:

1. Suresh Gubbala, Graduated with PhD in Chemical Eng. in 2008 and joined Intel.
2. Praveen Meduri, Expected to finish Ph.D. in Chemical Eng. in early 2010.

3. Jyothish Thangala, Expected to finish Ph.D. in Chemical Eng. in early 2010.
4. Dustin Cummins, Finished M.Eng in Chemical Eng. in 2009 and joined Ph.D program under Dr. Sunkara.
5. Eric Benge, Finished requirements for M.Eng in Chemical Eng. in 2009 and joined E-On USA.
6. Vivekanand Kumar, Expected to finish Ph.D. in Chemical Eng. in early 2010.
7. Harry Russell, Finished B.S. degree and is working towards M.Eng degree in Chemical Eng.
8. David Mudd, Finished B.S. degree in Physics and working on M.S./Ph.D. degrees in Physics.
9. Suhail Maholtra, worked as a co-op student. Working towards B.S. degree in Chemical Eng. at Case Western Reserve University in Cleveland.
10. Sri Movva, M.S. student in CECS dept. Finished his M.S. degree.
11. Santoshrupa Dumpala, Female student. Expected to finish Ph.D. in Chemical Engineering in late 2010.
12. Chinmay Deshmane, Ph.D. student working with Dr. M.A. Carreon.
13. Boris Chernomordik, Finished B.S., M.Eng degrees in Chemical Eng. and received a NSF graduate fellowship to attend University of Minnesota for Ph.D. in Chemical Eng.
14. Silpa Kona, Female student. Finished M.S. degree in Electrical and Computer Engineering and is currently working towards Ph.D. degree in ECE (Prof. C.K. Harnett).

Post-doctoral associates

1. Dr. Vidhya Chakrapani, Currently working as a research associate at Notre Dame radiation laboratory.

2. Dr. Biswa Deb, currently in India seeking a faculty position.

Senior research scientists

1. Dr. Jacek Jasinksi, Currently working as Chief Scientist for the Institute.
2. Dr. Zhiqiang Chen, Currently Research Assistant Professor and Manager at Portland State University, Portland, OR.

3. Hiring and establishing new assistant professors:

3.1 Startup lab for a junior faculty member: Recruited a junior faculty member (Dr. Moises Carreon) and helped with acquiring several pieces of instrumentation such as porosimetry for setting up a lab dedicated to micro- and meso-porous materials for catalysis and separations. In addition, his group is given priority access to expertise and facilities within the Institute. This group has been very productive and has published over four publications using the facilities within the Institute.

3.2 Secured additional support for a new lab for the Institute: The senior members (M. Sunkara and T.L. Starr) helped /G. Willing (PI) along with two co-PIs (Sunkara and Starr) received a one year start-up support from the state of KY and DOE funded KY Renewable Energy Consortium (KREC) for setting up a lab and for conducting a set of preliminary and fundamental studies. These studies include scanning tunneling microscopic studies for spatially resolving electron transfer processes during photo-electrochemical energy conversion and designing new dye assemblies using inorganic QDOTs to replace the organic dyes used for visible light absorption.

4. Research accomplishments

4.1 Books and book chapters:

1. **"Inorganic Nanowires:** Applications, Properties and Characterization" by M. Meyyappan and M.K. Sunkara, published by Talor and Francis, CRC Press, FL, USA (2009) ISBN: 978-1-4200-6782-8.
2. Chapter 22: "Carbon Microtubes and Conical Carbon Nanotubes",by S. Dumpala, G. Bhimarasetti, S. Gubbala, P. Meduri, S. Kona and M.K. Sunkara, in the Book entitled "Smart Materials" edited by Mel Schwartz, ISBN: 978-1-4200-4372-3, Published by CRC Press/Taylor & Francis Group, Boca Raton, FL (2008).

4.1 Li-ion battery/Electrochemistry/Nanowire sensors:

1. P. Meduri, J.H. Kim, H.B. Russell, J. Jasinksi, G.U. Sumanasekera and M.K. Sunkara, "Large area synthesis and characterization of carbon microtubes as high capacity and high rate anodes for lithium ion batteries", Submitted, *J. Power Sources,* October (2009).
2. "Hybrid Tin Oxide Nanowires as Stable and High Capacity Anodes for Li-Ion Batteries", Meduri P. Meduri, C. Pendyala, V. Kumar, G. U. Sumanasekera, M. K. Sunkara, *Nano Lett.*, 9 (2), 612 (2009)
3. "Charge transfer equilibria between diamond and an aqueous oxygen electrochemical redox couple", V. Chakrapani , J. C. Angus, A. B. Anderson , S. D. Wolter , B. R. Stoner , G. U. Sumanasekera, *Science*, 318 (5855), 1424 (2007)
4. P. Meduri, G.U. Sumanasekera, Z. Chen and M.K. Sunkara, "Controlled synthesis and Raman analysis of Ge-rich Si_xGe_{1-x} alloy nanowires", *J. Nanosci. and Nanotech.*, 8(6), 3153–3157 (2008).
5. V. Chakrapani, C. Pendyala, K. Kash, A. Anderson, M.K. Sunkara, and J.C. Angus, "Electrochemical pinning of the Fermi level: mediation of photoluminescence from gallium nitride and zinc oxide.", *J. Am. Chem. Soc.,* 130(39), 12944-12952 (2008).
6. B. Deb, S. Desai, G.U. Sumanasekera and M.K. Sunkara, "Gas sensing behaviour of mat-like networked tungsten oxide nanowire thin films", *Nanotechnology,* 18 (28), 285501 (2007).

4.3 Thermionic energy conversion:

7. S. Dumpala, A. Safir, D. Mudd, R.W. Cohn, M.K. Sunkara and G.U. Sumanasekera, "Field Emission Characteristics of Conical Carbon Nanotube Arrays", *Diamond and Related Materials,* 18, 1262-1266 (2009).

4.4 Fundamental studies on growth/defects/phase transformation involving NWs/NTs:

8. Z.Q. Chen, M. Sheetz, U. Cvelbar, M. Menon, M. Mozetic and M.K. Sunkara, "Ultra-Nano Porous Transition Metal Oxide Nanowires", Submitted, *Phys. Rev. Lett.,* September (2009)
9. J. Thangala, Z. Chen, A. Chin, C-Z. Ning and M. K. Sunkara, "Phase Transformation Studies of Metal Oxide Nanowires", *Crystal Growth & Design*, 9, 3177 (2009)
10. J. Thangala, S. Vaddiraju, S. Malhotra, V. Chakrapani and M.K. Sunkara, " A hot-wire chemical vapor deposition (HWCVD) method for metal oxide and their alloy nanowire arrays", *Thin Solid Films*, 517, 3600-3605 (2009).
11. S. Kona, J-H. Kim, C. K. Harnett, and M.K. Sunkara, "Carbon nanotube growth studies using an atmospheric, microplasma reactor", *IEEE Transactions on Nanotechnology,* 8, 286 (2009).
12. U. Cvelbar, K. Ostrikov, I. Levchenko, M. Mozetic, and M. K. Sunkara, "Control of morphology and nucleation density of iron oxide nanostructures by electric conditions on iron surfaces exposed to reactive oxygen plasmas", *Appl. Phys. Lett.*, 94, 211502 (2009).
13. 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).
14. V. Kumar, J-H. Kim, C. Pendyala, B. Chernomordik, and M.K. Sunkara, "Gas-Phase, Bulk Production of Metal Oxide Nanowires and Nanoparticles Using a Microwave Plasma Jet Reactor", *J. Phys. Chem. C*., 112, 46, 17750-17754 (2008).
15. U. Cvelbar, Z. Chen, M.K. Sunkara, M. Mozetic**, "**Spontaneous growth of superstructure α-Fe_2O_3 nanowire and nanobelt arrays in reactive oxygen plasma**",** *Small* **,** 4(10), *1610-1614* (2008).
16. Z. Chen, U. Cvelbar, M. Mozetič, J. He, and M. K. Sunkara, "Long Range Ordering of Oxygen Vacancy Planes in α-Fe_2O_3 Nanowires and Nanobelts", *Chem. of Mater., 20 (9), 3224-3228* (2008).
17. B. Chernomordik, S. Dumpala, Z. Chen and M.K. Sunkara, "Nanodiamond tipped and coated conical carbon structures", *Chemical Vapor Deposition*, 14, 256 (2008)
18. M. Kozan, J. Thangala, R. Bogale, M.P. Menguc and M.K. Sunkara, "In-situ characterization of dispersion stability of WO_3 nanoparticles and nanowires", *J. Nanopart. Res*., 10 (4), 599-612 (2008).
19. J. Thangala, S. Vaddiraju, R. Bogale, R. Thurman, T. Powers, B. Deb and M.K. Sunkara, "Large Scale Synthesis of Tungsten Oxide and Related Transition Metal Oxide Nanowires", *Small*, 3 (5), *890-896* (2007).

20. H.H. Hassan, M.A. Amin, S. Gubbala and M.K. Sunkara, "Participation of the dissolved O-2 in the passive layer formation on Zn surface in neutral media", *Electrochimica Acta*, 52 (24), 6929-6937 (2007).
21. C. A. Deshmane, J. B. Jasinski, M. A. Carreon, "Microwave-Assisted Synthesis of Nanocrystalline Mesoporous Gallium Oxide", *Microporous & Mesoporous Mater.* (2009), accepted.
22. C. A. Deshmane, J. B. Jasinski, M. A. Carreon, "Thermally Stable Nanocrystalline Mesoporous Gallium Oxide Phases" *Eur. J. Inorg. Chem.*, 3275–3281 (2009).
23. 3. S. Roy, C. Tuinenga, F. Fungura, P. Dagtepe, V. Chikan, J. Jasinski, "Progress toward Producing n-Type CdSe Quantum Dots: Tin and Indium Doped CdSe Quantum Dots" *J. Phys. Chem. C*, 113, 13008-13015 (2009).
24. N. Dahal, V. Chikan, J. Jasinski, V. J. Leppert, "Synthesis of Water-Soluble Iron-Gold Alloy Nanoparticles", *Chem. of Mater.*, 20, 6389-6395 (2008).
25. C. Tuinenga, J. Jasinski, T. Iwamoto, V. Chikan, "In situ observation of heterogeneous growth of CdSe quantum dots: Effect of indium doping on the growth kinetics", *ACS Nano*, 2, 1411-1421 (2008).

4.5 Dye sensitized solar cells and electrochromic devices

26. S. Gubbala, H. B. Russell, H. Shah, B. Deb, J. Jasinski, H. Rypkema, M. K. Sunkara, "Surface properties of SnO_2 nanowires for enhanced performance with dye-sensitized solar cells", *Energy Environ. Science*, DOI: 10.1039/b910174h (2009).
27. S. Gubbala, V. Chakrapani, V. Kumar, and M. K. Sunkara, "Band-edge engineered hybrid structures for dye sensitized solar cells based on SnO_2 nanowires", *Adv. Funct. Mater., 18, 2411-2418* (2008).
28. S. Gubbala, J. Thangala and M.K. Sunkara, "Nanowire Based Electrochromic Devices", *Solar Energy Materials and Solar Cells, 91 (9),* 813-820 *(2007)*

5. Patents and presentations

5.1 Patents

1. 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.
2. 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.

4.2 Presentations

- A total of twenty five presentations or more were made by students, post-docs and faculty involved in research at national and international meetings such as AICHE

(American Institute of Chemical Engineers), APS (American Physical Society), ECS (The Electrochemical Society), MRS (Materials Research Society), etc.

- PIs have delivered over twelve invited lectures in USA and abroad.

6. Workshops, short course offerings and new courses

1. **Two day workshop -** KY NanoMAT Workshop focused on the use of nanomaterials for energy and medicine, March 16-18, 2008, The Brown A Camberly Hotel, 335 West Broadway, Louisville, Kentucky 40202.

2. Offered haf-day long, short courses on the use of advanced materials characterization techniques using electron microscopy, surface spectroscopy and scanning probe microscopy. These short courses were attended by about hundred students, postdocs and researchers.

3. **New graduate courses:** PIs introduced and taught new graduate courses due to the availability of infrastructure improvement through this grant. These include
   (a) Materials characterization I – Spectroscopy and Microscopy
   (b) Materials characterization II – Electron microscopy and diffraction
   (c) Renewable energy systems

4. Outreach activities: Mentored over fifteen high school students in research.