

University of South Florida *Hybrid Interfaces for Energy Conversion Devices*

PI: A.M. Hoff, USF Electrical Engineering **Co-PI:** P. Zhang, USF Chemistry; C. Ferekides, USF Electrical Engineering

Project Time Period: 2010-2011, 2011-2012, 1 year no cost extension

Universities: USF

External Collaborators: Mustang Solar, a Division of Mustang Vacuum Systems

Executive Summary

This project focused on the development and characterization of new interfacial materials needed to enhance the performance of charge transport from molecules to electronic materials. Interfaces ultimately control the charge transport through an electronic device and therefore determine its ability to efficiently convert or harvest energy. This project investigated the electrical response of inorganic/organic interfaces and developed novel materials that facilitate the tailoring of charge transport related interfacial properties. The technical approach utilized unique synthesis capabilities developed by Professor Zhang's group in concert with the device fabrication efforts of Professors Hoff and Ferekides.

With resources provided by FESC, this group developed synthetic pathways for new charge exchange molecules. Molecules were tested by conventional chemical diagnostic means and with a material platform of new and emerging dye sensitized solar cells. Porphyrin replacements for dye sensitized solar cell Ru(II) bipyridyl complexes, which demonstrated the highest conversion efficiency of up to 11%, were investigated. Cost and environmental concerns motivated the replacement of the Ru complexes. Porphyrins with high absorption coefficients at Soret (400-450 nm) and Q (550-650 nm) bands were the primary focus. Selecting and synthesizing such compounds that meet these absorption criteria were key. Based on methodology developed at USF for the construction of novel porphyrins via carbon-heteroatom (O, N, S, etc.) formation, USF is now able to synthesize not only nitrogen but also oxygen, sulfur connected porphyrins and derivatives.

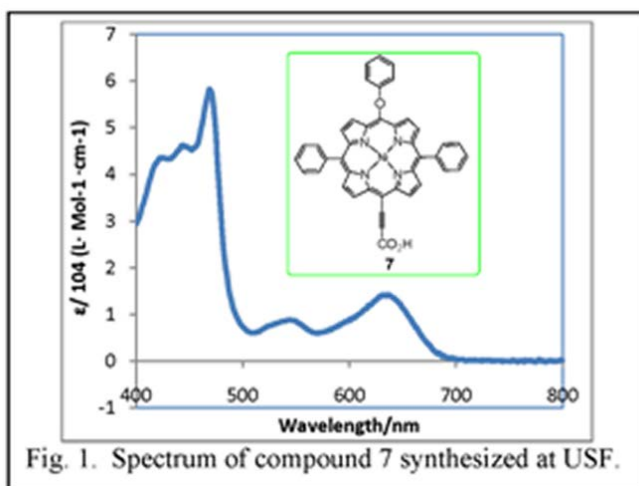


Fig. 1. Spectrum of compound 7 synthesized at USF.

This unique capability of the Hybrid-Interfaces FESC project team has led to the successful synthesis of compound 7 by the chemical group, in which the donor is phenol group and the carboxylic acid group linked on the triple bond directly. Fig. 1 shows the synthesized compound 7 and its spectrum measured at USF. Note the absorption bands as specified above make it a good candidate for solar cell application. In addition, porphyrins with di-carbonic acid also show great promising in DSSCs. A member of this class of molecules, compound 14 (not shown) was also synthesized at USF with good yield. Such materials cannot be obtained reasonably

from commercial sources. The synthesis routes of both compounds are under study for improvement with respect to yield.

Device Development was carried out in the College of Engineering. Considering biocompatibility, the Dye Sensitized Solar Cell (DSSC) based on titanium dioxide should play a major role in the future of solar energy. The photo sensitizer dye is the heart of operation of the DSSC. The most efficient dyes to date are based on ruthenium, noted above, but there is growing evidence regarding issues with their biocompatibility. Ruthenium based dyes have been under extensive research for the last two decades and it is safe to assume that their maximum efficiency has already been reached.

Porphyrins are a group of organic compounds having intense light absorption in the visible spectra. Given their crucial role in photosynthesis, Chlorophyll is member of the porphyrin group, their vast diversity and controllable electrochemical properties, porphyrins are important candidates for DSSC device structures. It is worth mentioning that the best reported dye in terms of solar cell efficiency so far is a Zn-based push-pull porphyrin dye.¹ Design considerations taken for candidate molecules included: (1) Push-pull, wherein strong electron donating groups are positioned at phenyl rings adjacent to the molecular core and so increase the electron density of the pi system in the molecule. Additional acid binding groups “pull” adjacent pi electrons improving injection efficiency to attached structures.² (2) Long chains, where organic alkyloxy groups stabilize the molecule. The chains also retard charge recombination at attachments to semiconducting oxides. (3) Metal such as Zn with excess electronic charge.² (4) Binding group positioning, where symmetric attachment of binding groups about phenyl rings is more important to molecular function to type of bound group.³

Following such principles, a group of push-pull (D- π -A) porphyrins were synthesized, Fig. 2, and their light absorption spectra (UV-Vis) were measured, Fig. 3, in solution at the Department of Chemistry, USF. Methoxy groups were used as electron donor and carboxylic acid group as molecular anchors. A free base without any metal (II-50), a zinc-based (II-92-1), and a nickel-based (II-92-2) porphyrin were each fabricated, Fig. 2.

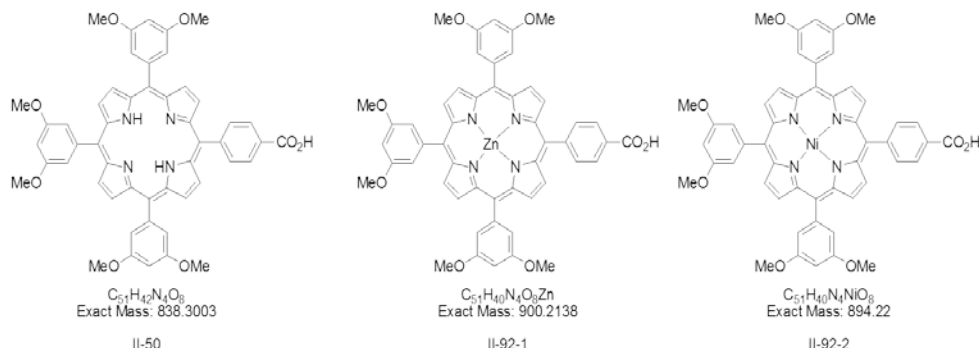


FIG. 2. Chemical Structure Of Usf-Synthesized Porphyrin Dyes.

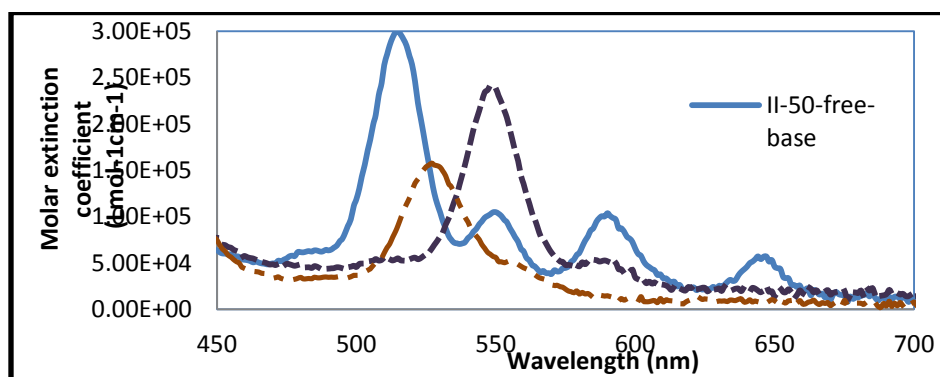


Fig 3. UV-Vis spectra of synthesized Porphyrin Dyes.

The UV-Vis spectra in Fig. 3 may be compared to that of a commercial absorbing dye shown in Fig. 4. Note that the strong molar extinction of all USF dyes were greater in certain spectral locations than the commercial dye.

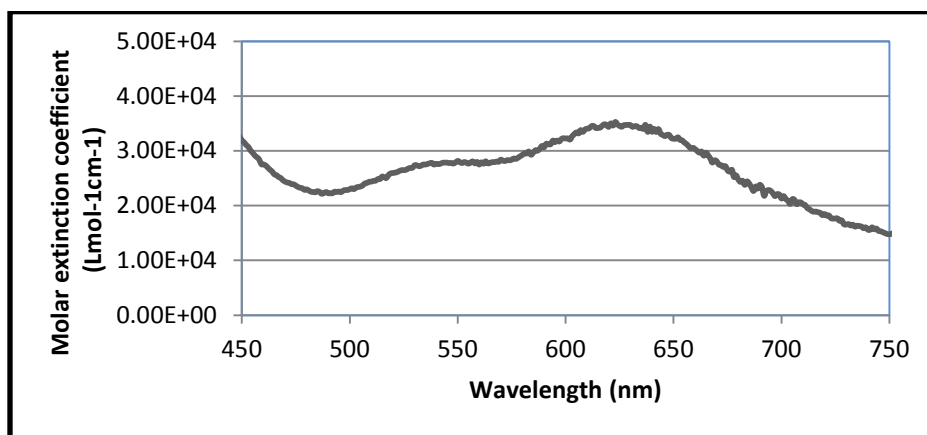


FIG. 4. UV-VIS Spectra of Commercial Black Dye. (4.98×10^{-5} M IN DCM).

Device fabrication was performed in the electrical engineering department at USF utilizing the unique porphyrin dyes synthesized. The solar cells fabricated were characterized using standard current-voltage and spectral response measurements. Table 1 identifies the concentrations of each synthesized dye tested along with current density findings, efficiency of fabricated cells, and other factors typical of solar cell characteristics. Different concentrations of each dye solution were investigated, and also a combination of the synthesized dyes, denoted (I+II+III) was studied. As a control, similar experiments were done with commercially available N749 dye, also known as ‘Black Dye’, for comparison.

Table 1: Dye Sensitized Solar Cells with synthesized porphyrin dyes.

Dye	Dye Conc. (mM)	Voc (V)	FF	Jsc (mA/cm ²)	Efficiency (%)
II-50	0.2	0.37	0.607	0.714	0.16
	0.4	0.4	0.561	1.07	0.24
II-92-1	0.2	0.39	0.625	1.12	0.27
	0.4	0.4	0.613	1.4	0.34
II-92-2	0.2	0.36	0.632	0.218	0.05
	0.4	0.36	0.624	0.23	0.05
I+II+III	0.2	0.39	0.629	0.72	0.18
	0.4	0.31	0.613	0.797	0.19
Black Dye	0.3	0.54	0.435	14.4	3.38

Current-voltage measurement under standard AM1.5 global irradiation showed very low efficiency for each synthesized porphyrin dye compared to the benchmark black dye. Metal may be an unavoidable constituent as the only promising dye among those tested ones was the Zn-based II-92-1. A

small dependence on dye concentration was observed, with a slight increase in performance with concentration of the dye solution applied. However, this difference became more indistinguishable as the sensitization time was increased. A homogeneous mixture of all three synthesized dyes was tested and the resulting cell performance resembled the mathematical average of the three individual cells.

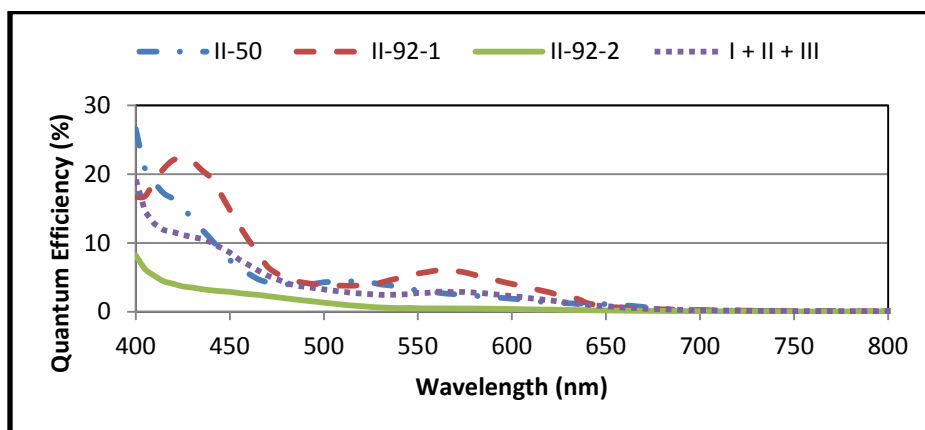


Fig. 5: Quantum Efficiency of DSCs made with porphyrin dyes.

The quantum efficiency plots vs. wavelength are shown in Fig. 5 for the porphyrin sensitized DSSCs. These responses were similar to their corresponding solution spectra. UV-Vis spectra of the dyes, Fig. 3, demonstrated a very high absorbance in UV to low frequency of the visible range for the porphyrin dyes, but decreased in the near infra-red region. Similar analysis for the reference black dye, Fig. 4, showed its absorbance was observed not to be very intense but was relatively uniform over the entire visible spectral region.

In conclusion, the results obtained show that light absorbance was not a problem with the synthesized porphyrin dyes. Given that the cell fabrication was similar for the commercial and designer synthesized dyes alike some other factor limited the performance of the new dyes relative to commercial standards. Electronic band alignment or charge transfer properties may contribute to the observed limited performance. Accordingly, measurements of the band alignment of the dyes with the titanium dioxide semiconductor surface may be needed. Further investigation is required to extend the knowledge of these experiments to synthesize better dyes and subsequently fabricate higher efficiency solar cells.

¹ A. Yella, H. Lee, H. Tsao, C. Yi, A. Chandiran, M. K. Nazeeruddin, E. Diao, C. Yeh, S. Zakeeruddin, M. Grätzel, "Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency," *Science*, 2011, 334, 629.

² Y. Chang, C. Wang, T. Pan, S. Hong, C. Lan, H. Kuo, C. Lo, H. Hsu, C. Lin, and E. Diao, "A strategy to design highly efficient porphyrin sensitizers for dye-sensitized solar cells," *Chem. Comm.*, 2011, 47, 8910-8912.

³ W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. Schmidt-Mende, M. K. Nazeeruddin, Q. Wang, M. Grätzel, and D. L. Officer, "Highly Efficient Porphyrin Sensitizers for Dye-Sensitized Solar Cells," *J. Phys. Chem. C*, 2007, 111(32), 11760–11762.

⁴ W. M. Campbell, A. K. Burrell, D. L. Officer, K. W. Jolley, "Porphyrins as light harvesters in the dye-sensitized TiO₂ solar cell," *Coordination Chemistry Reviews*, 2004, 248, 1363–1379.

Benefits to State:

This project established a new interdisciplinary capability joining important chemical synthesis capabilities to application capabilities in the college of engineering.

A new prototype DSSC capability was established and is in use as a test bed for molecular impact studies on energy harvesting devices.

A postdoctoral scholar and one M.S. student who (was supported for 1 year in the department of chemistry to enhance previously developed synthesis capabilities for unique energy related molecules. The project supported an MS student in the department of Electrical Engineering who wrote and defended the thesis, “A Study on the Optimization of Dye-Sensitized Solar Cells,” on August 24, 2012 and is graduating in the Fall semester of 2012.

This Project has been completed, the final report can be [found here](#).

University of South Florida

Low-Cost Solar Power Through Assembly of High Efficiency Microscale Photovoltaic Cells

PI: Nathan Crane **Co-PI:** P. Zhang

Description:

Project Time Period: 2/1/2010-6/30/2012

Universities: USF

External Collaborators: Greg Nielson, Sandia National Laboratories

Executive Summary

Greg Nielson and other researchers at Sandia National Laboratories have shown that small (<1 mm) photovoltaic (PV) cells manufactured from thin layers (<20 micron) of crystalline semiconductors can achieve favorable scaling when used in concentrating PV systems. The small size of the cells reduces the semiconductor material usage, but more significantly it also reduces the required thickness of the panels which reduces panel costs and the costs of the tracking system. Additional scaling benefits are possible in cooling the cells and conditioning the voltage.

The key to achieving the predicted benefits of these PV cells is to integrate them into modules at very low cost. This is difficult to do using traditional assembly systems—particularly due to the fragile nature of the small cells. This project has investigated the positioning of these cells through fluidic forces as a step toward eventually assembling them. Self-assembly methods can readily create close-packed arrays of repeating components. However, the formation of sparse arrays is more limited. This work has specifically focused on the challenge of creating sparse arrays in which the cells are separated by several cell diameters.

Two different methods were investigated. The first places the part on a droplet that is manipulated on a solid substrate to achieve the final position. The second constrains the parts to a fluid interface and manipulates them by deforming the fluid interface. Each is described briefly below:

1. Part positioning by droplet actuation: Recent work in microfluidics has created numerous methods for manipulating individual droplets. If a part is placed on one of these droplets, these methods can be adapted for the positioning of individual parts. In this project, a method was demonstrated for simple distance actuation of a droplet. This could form the basis of a fluidic conveyor belt.
2. Positioning by surface curvature modulation: Microscale PV cells are very thin and are easily trapped at a liquid interface. We investigated the response of these suspended parts to changes in the curvature of the interface as a possible actuation method. Results show that parts can be moved dynamically using these methods. Over a range of parameters, the parts will not stick to objects that are deforming the interface. This can be used to prevent unwanted bonding between assembly tools and the parts. These results could form the basis of a part positioning and assembly system in which the parts are supported by a liquid interface.

This project has partially supported the training of two masters students, one doctoral student, and several undergraduate students. All but the doctoral student are now employed in Florida—two of them supporting small manufacturing businesses in the state. The accomplishments of this project have been published in two conference papers and three journal papers with additional extensions of the work continuing.

The results of this project have primarily served as proof of principle of novel micro-manipulation approaches. The funds are being leveraged by using the results of this work to support requests for additional funding federal agencies. The droplet actuation positioning system is the basis of a current National Science Foundation Award for \$350k. Another proposal is currently under revision for resubmission based on results obtained in this work. The PI also received \$15k from Sandia National Laboratories to help support this work.

Summary

Microscale part positioning has been demonstrated using two different fluidic actuation methods. The initial results in this work have been used to obtain additional more than seven times more federal funding than the original state investment. The results of this work will provide new means for microscale assembly. These assembly processes will be useful for fabricating photovoltaic modules from millimeter scale photovoltaic cells.

Goals and Objectives

The goal of this project was to address challenges in assembling small components at low cost. Specifically the work focused on methods for positioning fragile components with fluid forces. The objective of this work is to lay a theoretical foundation for cost effective photovoltaic systems based on micro manufacturing methods. The cells have been manufactured and demonstrated at Sandia National Laboratories. However, implementation depends on improving assembly methods.

Project Activities

The two methods that were investigated are positioning by droplet actuation and positioning by surface curvature modification. Preliminary work was done in each of these three areas to better assess the potential of the methods for microscale assembly. The work accomplished in each area is summarized below.

Droplet Positioning

Digital microfluidics manipulates single droplets for applications such as on-chip medical diagnostics (lab-on-a-chip) and novel display technology. Many of these techniques manipulate droplets by changing the surface energy of the surface or the fluid. One common approach is a phenomenon called electrowetting in which an electric field across an interface changes the apparent surface energy of the interface. By applying a field on just one side, a droplet can be induced to move in that direction. One concept that has been examined through this project is the use of moving droplets to position parts. By placing a part on a droplet, the part can be positioned using the same techniques that are applied to the droplets.

Traditionally this is done by arranging a large number of electrodes and sequentially activating each successive electrode to move the droplet. This requires complicated switching and results in stepped droplet motion. Through this work, a new approach was developed that utilized a single electrode pair to obtain long distance motion as illustrated in Figure 1. This enables simplified actuation that can be extended to two dimensions much more easily than schemes requiring the switching of many independent electrodes. This initial demonstration was leveraged to obtain funding from the National Science Foundation to study the potential of these devices for microscale actuation.

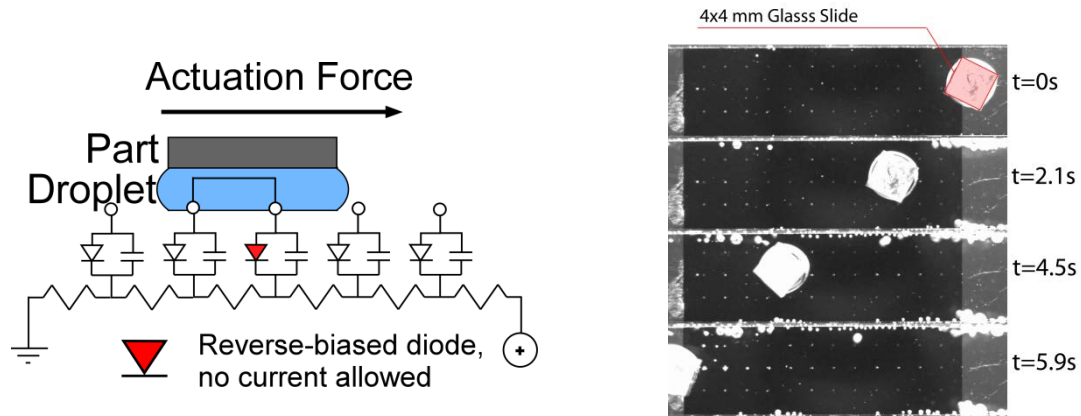


Figure 3 (Left) Schematic of Continuous Electrowetting Actuation System. (Right) Application Of The Continuous Electrowetting Actuation System For Positioning A Glass Plate (4 Mm X 4mm).

Surface Curvature Modification

Small (<1 mm) objects are readily trapped at the interface between two fluids even if they are heavier than the fluid mediums. However, when the interface is curved, gravity will drive the suspended parts up or down the curved surface. This could provide the means to control an assembly process at the microscale with surface curvature adjusted either by inserting and removing objects at the interface or by changing the wetting of the fluids on the interface through electrowetting or other means.

Interface-based assembly is of interest, because it is predominately a two-dimensional process. This reduces the range of errors and motions that need to be controlled for a successful assembly. Additionally, photovoltaic cells and many other devices must eventually be assembled to a two-dimensional substrate.

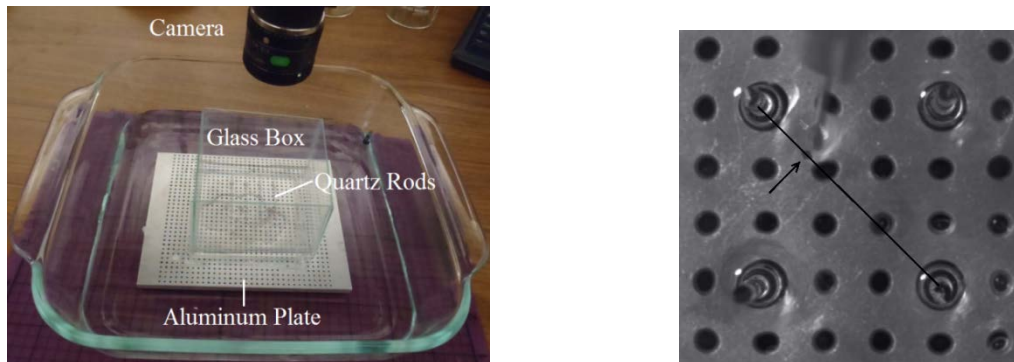


Figure 4 (Left) Experimental set-up. (Right) Deposition of micro part onto interface as viewed by camera. Micro part is indicated with an arrow.

Early experiments conducted with shared support from FESC and Sandia National Laboratories focused on measuring the equilibrium positions of floating parts as illustrated in Figure 2 and Figure 3. Rods were inserted perpendicular to a water/hexadecane interface. The wetting properties and diameters of the rods were selected to create different curvatures of the surface around the rod. These experiments demonstrated that some combinations of rod and part properties resulted in the parts having a minimum energy position a finite distance from the center of the rod as seen in the position vs. time data of Figure 4. This permits the parts to be attracted to the rod without sticking to the rod. Once the parts stick to an object, the capillary forces could make it hard to remove it again.

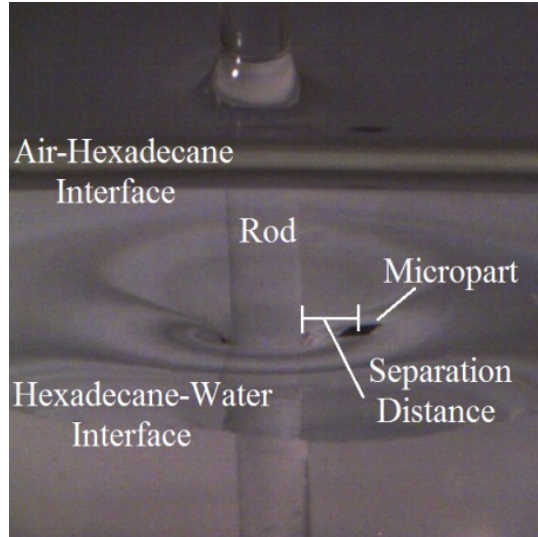


Figure 5: Side View Of Micro Part Having Met An Equilibrium Separation Distance About A Hydrophobic Rod. The Hexadecane-Water Interface Is Convexly Shaped.

Movement of Hydrophobic Micropart, 11.7 mm Rod Spacing

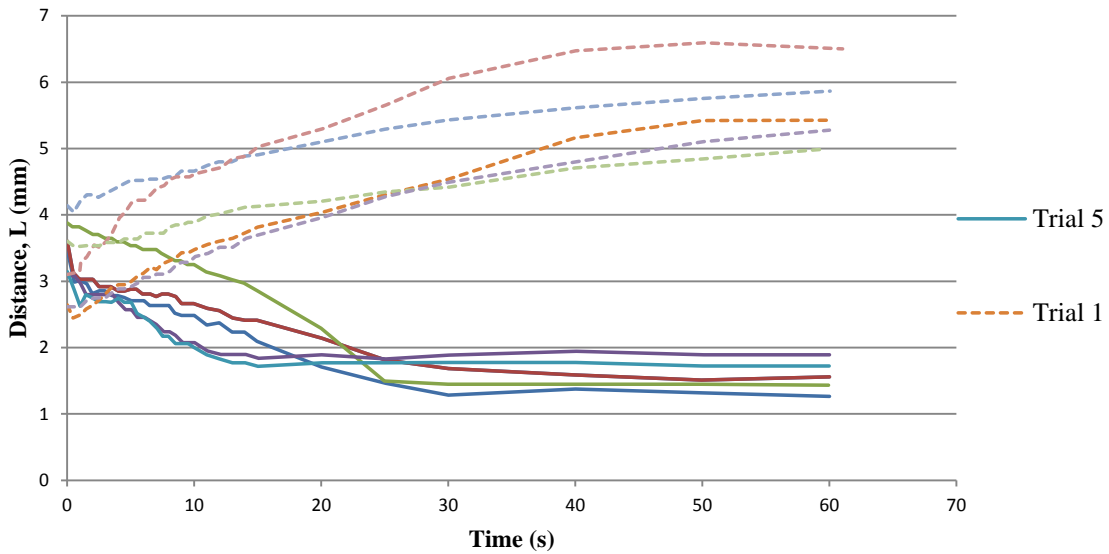


Figure 6 Separation distance of micro part from its closest rod plotted versus time.

This work was later extended by utilizing electrowetting to move objects through a two-dimensional space and assemble them to other floating objects. Currently, additional experimental data is being gathered to support funding applications to develop microscale assembly processes based on this work.

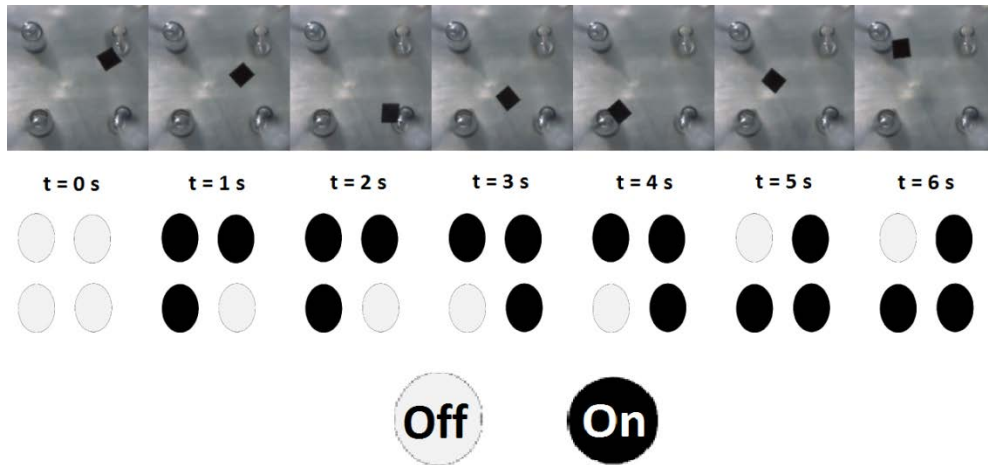


Figure 7 Electrowetting Was Used To Control The Curvature Of The Interface Around The Rods. By Applying Voltages In Different Patterns, Parts On The Interface Could Be Moved To Different Positions.

Accomplishments

The initial state of Florida investment through the FESC in this project has generated more than seven times as much additional funding from federal sources. This funding is being used to continue to advance the aims of this project.

Technical Accomplishments

- Created a novel droplet actuation system that could form the basis of a microfluidic factory
- Created a prototype for a fluid interface assembly system
- Gathered data to test a self assembly rate model
- Identified assembly methods for creating high reliability devices by self assembly

Workforce Development

- Kenza Mouttaki: BS Degree completed, now working for a local manufacturing company
- Caroline Liberti: MS degree completed, now working for a local manufacturing
- Corey Lynch: BS & MS degree completed, performs testing work for a local aerospace company
- Chris Nelson: BS degree completed, pursuing PhD at another institution
- Jose Carballo: Continuing PhD student

Concluding Remarks

This project has shown that fluidic forces have great promise in directed assembly of microscale components. These methods will be further developed to assess key characteristics such as speed, accuracy, and cost through additional funding that has been acquired to leverage the initial state investment. Applications to energy systems will be possible once these research questions are more fully addressed. This project has also resulted in the training of both graduate and undergraduate students that have strengthened the Florida manufacturing and engineering labor force.

Publications

- Crane, N. B., and McKnight, P., “Impact of Self-assembly Process Errors on Thermoelectric Performance,” *Journal of Electronic Packaging*, 2012, Vol 134, pg 031001-1-7.

- Khodayari, M. , Carballo, J., and Crane, N. B., “A reliable low voltage anodic electrowetting material system,” *Materials Letters*, Vol 69, 2012, p 96-99.
- Crane, N. B., Tuckerman, J., and Nielson, G. N., “Self Assembly in Additive Manufacturing: Opportunities and Obstacles,” *Rapid Prototyping Journal*, Vol 17, No 3, 2011, p 211-217.
- Liberti, C., and **Crane, N. B.**, “Investigation of Surface Tension Effects of a Water-Hexadecane Interface on Silicon Microparts,” ASME 2011 International Mechanical Engineering Congress & Exposition November 11-18, 2011, Denver, CO
- Lynch, C. M., Khodayari, M., Volinsky, A. A., and **Crane, N. B.**, “Demonstration of Continuous Electrowetting Actuation,” Proceeding of the ASME 2010 International Mechanical Engineering Congress & Exposition IMECE 2010-40060, November 12-19, 2010, Vancouver, Canada.

This project has been completed, the final report can be [found here](#).

University of South Florida *Sustainable Algal Biofuel Production*

PI: Sarina J. Ergas **Co-PI:** Qiong Zhang, James R. Mihelcic, John Wolan (deceased)

Students: Angela Chapman, PhD Secondary Ed. in progress; Matthew Gaston, MS Environmental Engineering in progress; Benjamin Gillie, BS Chemical Engineering; Trina Halfhide, PhD Engineering Science in progress; Mehregan Jalalizadeh, MS Environmental Engineering; Ruben Jean, BS Environmental Engineering (UF) in progress; Eunyong Lee, PhD Environmental Engineering in progress; Maria Pinilla, MS Environmental Engineering; John Trimmer, MS Environmental Engineering in progress; Innocent Udom, PhD Chemical Engineering in progress; Sarah Watson, MS Environmental Engineering in progress.

Description: Microalgae are productive at utilizing CO₂ and can generate biomass for production of biodiesel, methane, or other fuels as well as valuable co-products (e.g. animal feeds, polymers). Algal biofuel production can be more profitable and sustainable when combined with wastewater treatment and CO₂ utilization from electric power generation facilities. A number of research gaps exist for full scale algal biofuel production including: 1) improvement of algal growth and nutrient uptake rates, 2) integration of systems with waste gas, wastewater, and water reclamation systems, 3) improved gas transfer and mixing, 4) improved algal harvesting and dewatering and 5) life cycle assessment (LCA) and economic analysis. In addition, little attention has been given to the potential use of algal biofuel systems to treat wastewater and produce heating and cooking fuels in developing countries. The overall objective of this project is to develop an interdisciplinary multi-investigator research program that integrates microalgal biofuel production with wastewater treatment and carbon recycling. An algal biofuels lab will be established at the USF Botanical Gardens, which will house several bench-scale algal photo-bioreactors. Initial experiments will focus on optimizing CO₂ uptake from combustion gases, wastewater nutrient removal and production of algal biomass under varying operating conditions. Both oil rich algal species and algae that grow well on wastewater will be investigated. LCA methods will be used to provide insight into the environmental impacts of the process under varying conditions and enable system evaluation based on both technical performance and life cycle impacts. This project is designed to develop PI expertise and collaborations and train graduate students in a new field of research that is critical in establishing Florida as center of algal biofuels production. Future research directions include: 1) integration of algal biofuel production with domestic, agricultural and industrial wastewater, 2) sustainable aquaculture system development, 3) production of jet fuel from algae cake, 4) application of algal biofuels technology in developing countries, 5) development of integrated LCA-economic assessment tools to assist in algal biofuel system decision making.

Budget: \$50,000

Project Time Period: 2/1/2010-6/30/2012

Universities: USF

External Collaborators: Mote Marine Laboratories

Research Summary:

Algae culturing studies were carried out using bag photo-bioreactors (PBRs) in a greenhouse at the USF Botanical Gardens. The reactors were fed anaerobic digester centrate from the Howard F. Curren Advanced Wastewater Treatment Plant in Tampa Florida and synthetic aquaculture wastewater based on Mote Aquaculture Research Park sturgeon program wastewater. The PBRs were operated over a nine month period under natural light conditions. Gas transfer tests were used to determine CO₂ uptake rates

at varying influent CO₂ concentrations (2% and 5%). The results show that wild algae adapted to wastewater nutrients are able to have high productivity, CO₂ and nutrient uptake rates despite high ammonia levels. Life Cycle Assessment (LCA) results showed that the pathway with algae biomass (feedstock), anaerobic digestion and combined heat and power (conversion process), and electricity and heat (energy products) has lower environmental impacts if wastewater and flue gas is used in algae cultivation. Algae harvested from the PBRs were used in algae coagulation tests. Coagulants tested included: alum, ferric chloride, cationic and non-ionic polymers, and natural materials (moringa seeds and cactus mucilage). Results showed that high algae harvesting efficiencies could be obtained with alum (91%), ferric chloride (93%), and cationic polymer (98%). Cationic polymer also resulted in the lowest cost alternative. LCA results; however, showed that the highest energy use and greenhouse gas (GHG) emissions were obtained for the cationic polymer, while ferric chloride resulted in the lowest energy use and GHG emissions. LCA results also showed that the pathway that converts algae biomass through anaerobic digestion and combined heat and power (CHP) process to electricity and heat had a higher overall environmental impact than the pathway that convert algae biomass to liquid biofuels through thermochemical gasification and Fischer-Tropsch Synthesis (FTS) process.

Student research:

PhD: Angela Chapman (Secondary Ed.), Trina Halfhide (Engr. Science), Eunyong Lee (Environ. Engr.), Innocent Udom (Chemical Engr.); Master's (all from Environ. Engr.): Maria Pinilla John Trimmer, Mehregan Jalalizadeh, Matthew Gaston, Sarah Watson; Undergraduates: Benjamin Gillie (Chemical Engr.), Ruben Jean (Environ. Engr. UF).

Outreach:

The project team participated in Earth Day Events at the USF Botanical Gardens in 2011 and 2012. We are currently working with Middleton Magnet School for Science and Technology, an economically challenged high school in East Tampa, on a project that looks at the effect of participation in authentic science research on students understanding of science.

Grant proposals:

Three proposals were funded that tied to this seed funding: PIRE: Context Sensitive Implementation of Synergistic Water-Energy Systems, PI: J. Mihelcic, Faculty Participants: S.J. Ergas and Q. Zhang, NSF, \$3,912,276, 5 years; REU Site: Tampa Environmental Interdisciplinary Research, co-PI: S.J. Ergas, NSF, \$392,000, 3 yrs; Advanced Biological Waste-to-Energy Technologies, co-PI S.J. Ergas, European Commission, student stipends and lab fees, 4 yrs. Two doctoral students obtained fellowships (NASA and Fulbright) based on their research related to this project.

Partnerships:

A. F. Hepp, NASA Glenn Res. Center; J. Bartacek, Asst. Prof., Water Technol. & Environ. Engr., ICT Prague; C. Butler, Asst. Prof., Civil & Environ. Engr. UMass; P. Jenicek Prof. & Head, Water Technol. & Environ. Engr., ICT Prague; P. Lens Prof., Environ. Biotechnol., UNESCO-IHE, Delft; J. Love, Sen. Lec., Plant Mol. Bio., U. Exeter; G. Philippidis Assoc. Prof., Chem. Engr., USF; A.C. Wilkie, Assoc. Prof., Soil & Water Sci. UF-IFAS.

Funded Research Grants and Fellowships:

PIRE: Context Sensitive Implementation of Synergistic Water-Energy Systems, PI: J. Mihelcic, co-PIs: M. Trotz, E.C. Wells, C. McKayle (UVI), **Senior Personnel: S.J. Ergas, Q. Zhang, D. Yeh, L. Whiteford, R. Zarger, F. Muller-Karger, Y. Goswami, D. Durham, A. Feldman, B. Batson, K. Alexandridis, M. Brandt (UVI), National Science Foundation, \$3,912,276, 5 yr.**

REU Site: Tampa Environmental Interdisciplinary Research, PI: M. Trotz, co-PI: S. Ergas, National Science Foundation, \$392,816, 3 yr.

BioWET—Advanced Biological Waste-to-Energy Technologies, European Commission, PI: D. Yeh, co-PI: S. J. Ergas, European PIs: J. Bartacek (ICT –Prague), P. Lens (UNESCO IHE), \$330,000 to EU Partners, Student stipends and laboratory bench fees to USF.

Green Aviation Fuels from Microalgae, NASA-Harriett G. Jenkins Pre-doctoral Fellowship Project (JFPF) award, \$121,500 for support of Innocent Udom, Collaboration with NASA Glenn Research Center.

Examining the Use of Algal Photobioreactor Production Systems for the Dual Purpose of Bioremediation and Biofuel Production under Different Climatic Conditions, Fulbright Fellowship awarded to Trina Halfhide (PhD candidate USF) for 1-year study at the Life Sciences University, Oslo Norway.

Not Funded:

EFRI-PSBR: Sustainable Microalgae Bioenergy Systems, PI: S. Ergas, co-PIs: Q. Zhang, B. Joseph, A.C. Wilkie (UF), G. Phillipidis (USF Polytech), National Science Foundation, \$1,999,361, 4 yr.

Sustainable Microalgal Bioenergy System, PI: Q. Zhang, Co-PIs: S. Ergas, J. Mihelcic, National Science Foundation, \$3299,968, 3 yr.

New Partnerships:

Aloysius F. Hepp, is a Ph.D. Senior Chemist in the Bio Science and Technology Branch Space Processes and Experiments Division of NASA John H. Glenn Research Center in Ohio. Dr. Hepp co-supervises ongoing research being conducted by Innocent Udom as part of the NASA-Harriett G. Jenkins Pre-doctoral Fellowship program. Drs. Ergas and Goswami traveled to NASA Glenn Research Center in December, 2011 to meet with Dr. Hepp and discuss our collaboration.

Middleton Magnet School for Science and Technology is located in East Tampa and has more than 1,300 students (~70% African American, 12% Hispanic, 78% receive free or reduced price lunches). We are currently collaborating with agricultural biotechnology and marine science teachers at Middleton. Students construct simple algal photo-bioreactors using soda bottles and aquarium pumps. The reactors are inoculated with algal consortia from our laboratory and set up in greenhouses at Middleton. Experiments are designed to investigate algal growth rates under varying conditions. Experimental data are used to teach science and engineering principles, statistics, and use of data analysis tools.

Jan Bartacek is an Assistant Professor in the Dept. of Water Technology and Environmental Engineering at the Institute of Chemical Technology (ICT) Prague. Dr. Bartacek is the PI of the BioWET grant and participated in the BioWET summer school at USF.

Caitlyn Butler is an Assistant Professor in the Dept. of Civil and Environmental Engineering at the University of Massachusetts, Amherst. Dr. Butler's research focuses on energy and resource recovery in wastewater treatment, emphasizing the use of bioelectrochemical systems. Dr. Butler participated in the BioWET summer school at USF.

Pavel Jenicek is a Professor and Head of the Department of Water Technology and Environmental Engineering at ICT Prague. He is active in the research of anaerobic wastewater treatment, biogas treatment, anaerobic digestion of sludge, minimisation of sludge production, biological nutrient removal and recovery. Dr. Jenicek is a co-PI of the BioWET grant and participated in the BioWET summer school at USF.

Piet Lens is Professor of Environmental Biotechnology at the Pollution Prevention and Control core of the Department of Environmental Resources of UNESCO-IHE Water Research and Education Institute in Delft, the Netherlands. Dr. Lens is a co-PI on the BioWET grant and participated in the BioWET summer

school at USF. Dr. Ergas spent two weeks at UNESCO-IHE during the summer of 2012 as a visiting scholar.

Dr John Love, Senior Lecturer in Plant Molecular Biology at the University of Exeter. Dr. Love's research group has a productive collaboration with Shell Global Solutions, investigating the molecular and cell biology of hydrocarbon production in algae.

George Philippidis is Associate Professor of Chemical Engineering at USF. He has over 20 years of experience in leading strategic business units in advanced biofuels and renewable energy. Dr. Phillipidis was a participant in the BioWET summer school and a co-PI on the EFRI proposal.

Peter van der Stein is a lecturer in the Pollution Prevention and Control core of the Department of Environmental Resources of UNESCO-IHE Water Research and Education Institute in Delft, the Netherlands. Dr. Van der Stein is a co-PI on the BioWET grant.

Ann C. Wilkie is an Associate Professor of Bioenergy and Sustainable Technology in the Soil and Water Science Department at the University of Florida-Institute of Food and Agricultural Sciences (UF-IFAS). Her specialty is environmental microbiology, with particular emphasis on anaerobic technology and algal biofuels. Dr. Wilkie was a participant in the BioWET summer school at USF and a co-PI on the EFRI proposal. She is currently collaborating with Dr. Ergas on research related to bioprospecting wild algae species.

Annual Progress Report

Algae Culturing Studies:

Algal growth experiments were conducted under natural illumination in a temperature controlled (25-32°C) greenhouse at the University of South Florida Botanical Gardens in Tampa Florida. Three vertical hanging tubular plastic bag photobioreactors (PBRs) were obtained from the Norwegian Life Sciences University in Oslo. Two PBR cells were fed an anaerobic digester centrate feed and the third cell was operated with a 50:50 mixture of centrate and synthetic aquaculture wastewater. Centrate was collected from the Howard F. Curren Advanced Wastewater Treatment Facility (HFCAWTF) in Tampa, FL. The aquaculture-centrate mixture (ACM) was based on research by Watson et al., (2011) showing that incorporation of algae and anaerobic digestion could reduce the nutrient impacts of land based recirculating aquaculture systems. Wild algae harvested from the surface of a secondary clarifier at the HFCAWTF were used to inoculate the reactors. The reactors were maintained at a mean cell residence time of 7-days for approximately nine months. A summary of the biomass production and nutrient removal data from the algal PBR studies is given in Table 1. More detailed results have been presented elsewhere (Dalrymple et al., 2011). The low productivity observed in this study may have been due to the low natural ambient light intensity (2.3-9.4 mol/m²/day) during the wet season in Southwest Florida compared with the light intensity used by other authors. Average algal productivity was higher for the 100% centrate reactor than for the ACM reactor, most likely due to the algae being adapted to centrate during a long acclimatization phase (March-October, 2011), during which the reactor was only fed centrate. Both reactors achieved good overall removal efficiencies for nitrogen and phosphorous.

Table 1: Mean and maximum algae growth and nutrient removal data from the centrate and ACM PBRs. Standard deviations shown in parentheses.

Parameter	Centrate		ACM	
	Mean	Max	Mean	Max
Productivity (g/m ² /day)	2.3 (0.77)	3.6	1.7 (0.89)	4.0
Biomass density (g/L as TSS)	664.4 (222)	1030	478.2 (259)	1,140
TN removal efficiency (%)	65	92	64	91
Effluent TN (mg/L)	76.2 (71.1)	180	60.3 (60.5)	130
NH ₄ ⁺ removal efficiency (%)	95	77	86	100
Effluent NH ₄ ⁺ -N (mg/L)	50 (38.0)	92	5.0 (8.6)	15
TP removal efficiency (%)	72	79	73	93
Effluent TP (mg/L)	12.5 (23.6)	54.6	20.1 (34.2)	71.3

Algal growth kinetics:

Current research is focused on characterizing wild algae in batch photoreactors to provide data for modeling efforts. Algae are cultured in batch systems using anaerobic digester feed under artificial light. Environmental conditions are systematically altered to examine the effects of the following on algal growth rates, lipid production, and nutrient removal: 1) nutrient concentration, 2) CO₂ partial pressure, 3) mixing and 4) light intensity. Kinetic parameters are determined by fitting the experimental data to the Monod-type kinetic equations.

Life Cycle Assessment:

A preliminary LCA was conducted using our algae cultivation and digestion data to evaluate the environmental impacts associated with the energy pathways shown in Figure 1. The results showed that the pathway with algae biomass (feedstock), anaerobic digestion and combined heat and power (conversion process), and electricity and heat (energy products) has lower environmental impacts if wastewater and flue gas is used in algae cultivation, as shown in Figure 2.

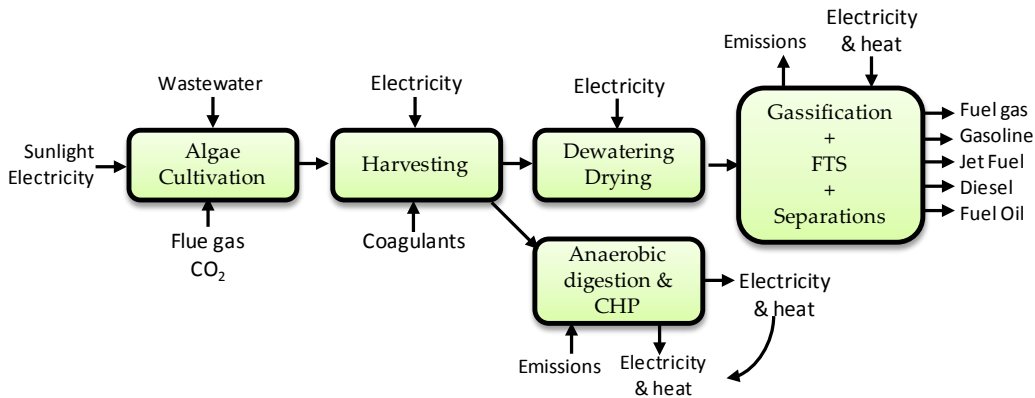


Fig. 1. Schematic of algae bioenergy pathways evaluated.

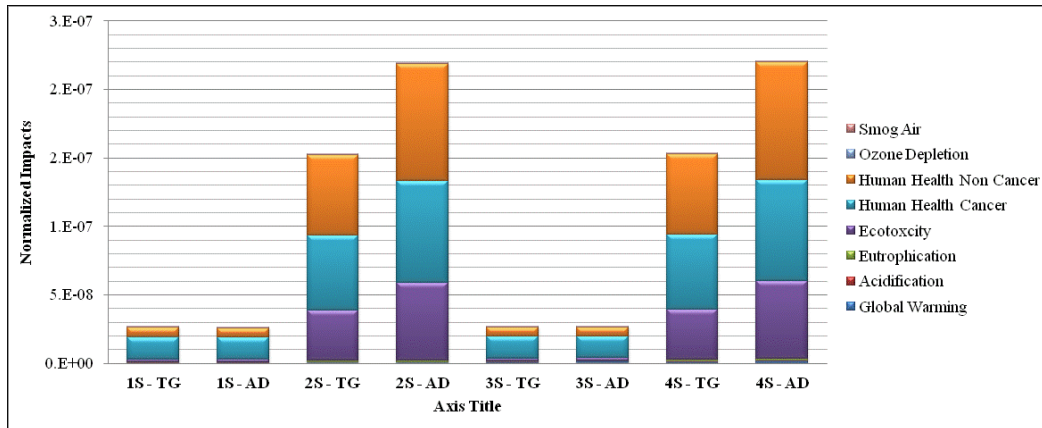


Fig. 2. Overall results from the comparative algae biomass conversion LCA. (TG: thermochemical gasification; AD: anaerobic digestion; 1S: Wastewater is used as a source of nutrients and flue gas is used as a source of CO₂, assuming the process is co-located with a power plant; 2S: Fertilizers are used as a source of nutrients, and Flue Gas is used as a source of CO₂; 3S: Wastewater is used as a source of nutrients, and chemical CO₂ is used as the carbon source; 4S: Fertilizers are used as a source of nutrients, and chemical CO₂ is used as the carbon source.).

Harvesting studies:

Jar tests were conducted using reagent grade (Fisher, Pittsburgh, PA) alum (Al₂(SO₄)₃·12H₂O) and ferric chloride (FeCl₃·6H₂O), Zetag (BASF Chemical Company, Suffolk, VA) 8800 series cationic polymers (8814, 8816, 8818, and 8819), two anionic polymers (Magnafloc E-38 and E-34; BASF Chemical Company, Suffolk, VA) and two natural flocculants (*Moringa Oleifera* and *Opuntia ficus-indica* cactus). Coagulation tests were conducted on suspensions collected from the algal PBRs using a Phipps & Bird Jar Test Apparatus (Richmond, Virginia). An economic and LCA study was conducted to assess the cost and energy and GHG emissions associated with algae harvesting. Costs of coagulants were obtained from bulk vendors of industrial chemicals. The functional unit was production of one metric ton (MT) of dried algae.

Cumulative Energy Demand Analysis (CEDA) in Simapro 7.2 software was used to estimate the life cycle energy (direct energy use as well as the upstream energy consumption) required to produce the amount of alum or ferric chloride needed to harvest one MT of dry algae. The Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI) developed by U.S. Environmental Protection Agency (EPA) was used to estimate the GHG emission resulting from alum or ferric chloride production.

An overall summary of the jar test results for all coagulants tested is shown in Table 2. Among the metal salts tested, FeCl₃ had a lower optimal dose (122 mg/L) and slightly higher recovery (93%) than alum. When using FeCl₃, the color of culture changed from green to brown-yellow. This could have a negative impact on the final product if the algae are to be used for pigments. An initial screening study was conducted with the Zetag 8000 series cationic polymers (8814, 8816, 8819, 8846, 8848) to determine the best cationic polymer for further study (data not shown). Although excellent algae recovery (92-98%) was observed at low polymer concentration (34-41 mg/L) for all of the cationic polymers tested, Zetag 8819 was selected for further study because it provided the highest harvesting efficiency (98%) at the lowest optimal dose (34 mg/L). Zetag 8819 also had the overall best performance, in terms of coagulant dose required and algae recovery, of all of the coagulants tested. Poor performance was observed with the non-ionic and anionic polymers and the natural coagulants.

Table 2: Summary of harvesting experiments, showing optimal dose for each coagulant

Coagulant	Optimal Dose (mg/L)	Supernatant Turbidity (NTU)	Supernatant TSS (mg/L)	Solids Recovered (%)
Ferric Chloride	122	7.65	15	93
Alum	140	5.40	30	91
Zetag 8819	34	6.05	20	98
Magnafloc E-38	NA	760	>500	~0
<i>Moringa oleifera</i>	4,670	20.0	25	85
<i>Opuntia ficus-indica</i> cactus	NA	740	>500	~0

Economic and LCA were carried out to compare costs, energy use and GHG emissions associated with each coagulant (Figure 3). Ferric chloride was the most expensive option (\$130/MT of algae), followed by alum (\$65/MT of algae) and cationic polymer (\$50/MT of algae). However, it can be seen that using cationic polymer (Zetag 8819) for harvesting will result in the highest GHG emissions, with 92 kg CO₂ eq/MT Algae, followed by alum and ferric chloride (51 kg CO₂ eq/MT algae and 13 kg CO₂ eq/MT algae, respectively). The energy consumption results are in line with the GHG emissions, showing that polymer has the highest energy consumption (1983.9 MJ/MT of algae), while ferric chloride has the lowest (204 MJ/MT of algae) among three coagulants evaluated.

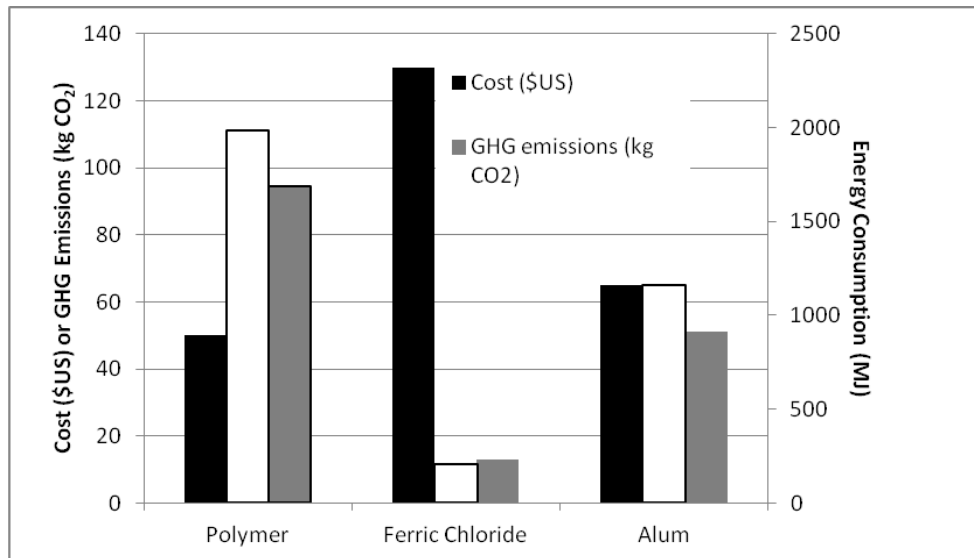


Figure 3: Cost (\$ US), GHG emissions and energy consumption for cationic polymer, ferric chloride and alum.

Gas Transfer Tests:

Initial tests were conducted in one of the bag reactor cells to determine CO₂ gas mass transfer coefficients at varying gas feed flow rates. The concentration of dissolved CO₂ was measured using an Oxyguard CO₂ analyzer (Model # G02C2P, Birkerød, Denmark) and the pH of the reactor was measured using a Teledyne Isco 701 pH/Temperature Module on a 6712 portable Sampler (Lincoln, Nebraska). CO₂ utilization rates in the photo-bioreactors with respect to time are shown in Figure 4. The utilization rates

ranged from 5.56×10^{-3} to 1.5×10^{-2} mol m⁻³ min⁻¹ for the reactor with a 2% CO₂ gas feed. The results were in agreement with the growth rate data.

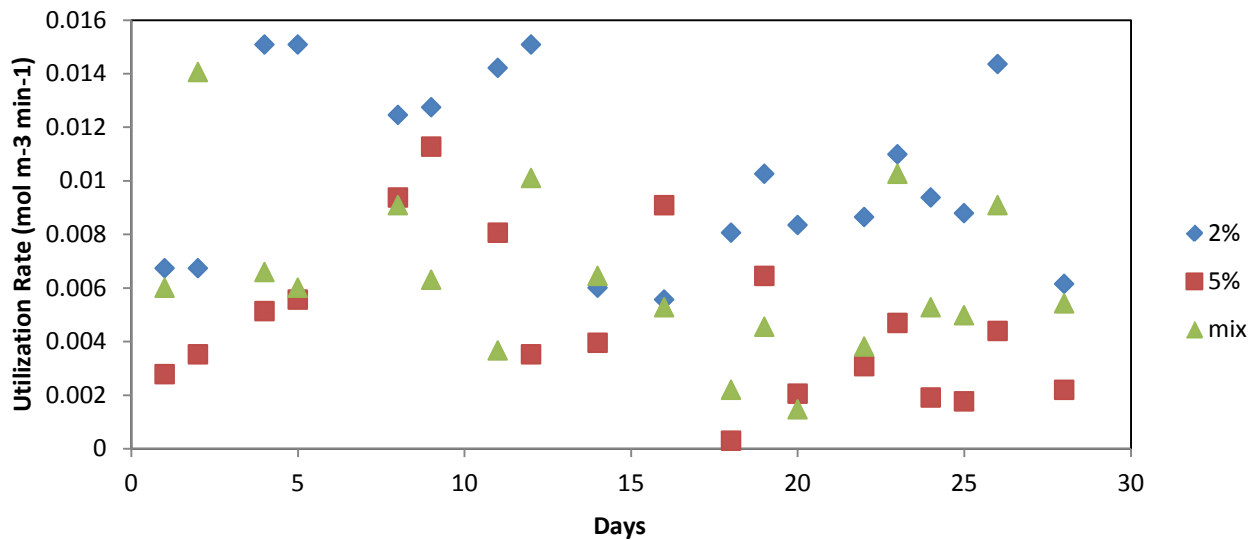


Figure 4: CO₂ Utilization Rates in each reactor vs. time.

Peer Reviewed Journal Publications:

1. Yuan, X., Wang, M., Park, C., Sahu, A.K., Ergas, S.J. (2012) Microalgae Growth Using High Strength Wastewater Followed by Anaerobic Co-digestion, *Water Environ. Research*, 84(5):396-404.
2. Yuan, X., Kumar, A., Sahu, A.K., Ergas, S.J. (2011) Impact of Ammonia Concentration on *Spirulina platensis* Growth in an Airlift Photobioreactor, *Bioresource Technology*, 102(3): 3234-3239.
3. Kumar, A., Yuan, X., Sahu, A.K., Zhang, Q., Ergas, S.J., Malcata, F. X., Van Langenhove, H. (2010) Strategies for CO₂ sequestration using microalgae and cyanobacteria: Recent developments and future directions, *Trends in Biotechnology*, 28(7): 371-380.
4. Dalrymple, O.K., Halfhide, T., Udom, I., Gilles, B., Wolan, J., Zhang, Q., Ergas, S.J. (accepted) A preliminary estimation of the algal feedstock production potential of Tampa Bay utilizing CO₂ emissions and wastewater effluent, *J. Aquatic Biosystems*.

Conference Presentations and Posters:

1. Udom, I., Halfhide, T., Gillie, B., Dalrymple, O., Zaribaf, B. H., Zhang, Q., Ergas, S.J. (2012) Harvesting algae grown on wastewater, *Proc. 85th Annual Meeting of the Water Environment Federation (WEFTEC 12)*, Sept. 29-Oct. 3., New Orleans, LA.
2. Dalrymple, O.K., Halfhide, T., Udom, I., Gilles, B., Wolan, J., Zhang, Q., Ergas, S.J. (2011) A preliminary estimation of the algal feedstock production potential of Tampa Bay utilizing CO₂ emissions and wastewater effluent, *Proc. Florida Energy Systems Consortium (FESC) Summit*, Sept. 26-27, 2011, Gainesville, FL.
3. Halfhide, T., Trimmer, J., Pinilla, M., Bosshart, W., Zhang, Q., Wolan, J., Main, K., Ergas, S. J. (2011) Reducing Carbon and Nutrient Impacts of Aquaculture Using an Algal Photo-bioreactor Production System, *Proc. International Water Association Leading Edge Technologies Conference*, June 6-10, Amsterdam, The Netherlands.
4. Watson, S., Halfhide, T., Trimmer, J., Zhang, Q., Wolan, J., Main, K., Ergas, S.J. (2011) Reducing the Nutrient Impacts of Aquaculture Through the Use of an Algal Photobioreactor Production System, *Proc. 2011 WEF Nutrient Recovery and Management Conference*, Jan. 9-12, 2011, Miami, FL.

5. Udom, I., Halfhide, T., Trimmer, J., Gillie, B. Wolan, J., Ergas, S.J. (2011) Nutrient management using an algal photobioreactor production system, *Proc. Association of Environmental Engineering and Science Professors (AEESP) Research and Education Conference*, Tampa, FL, July 10-12, 2011.
6. Udom, I., Wolan, Ergas, S.J. (2011) Harvesting *Chlorella sp.* for Biofuel Production Using Flocculants, *Proc. 1st International Conference on Algal Biomass, Biofuels and Bioproducts*, July 17-20, St Louis MO.
7. Yuan, X., Wang, M., Park, C., Kumar, A., Sahu, A.K., Ergas, S.J. (2010) High-Strength Wastewater Treatment by Microalgae and Anaerobic Co-Digestion with Residual Solids, *Proc. 79th Annual Meeting of the Water Environment Federation (WEFTEC 10)*, October 3-6, New Orleans, LA.
8. Ergas, S.J., Yuan, X., Sahu, A.K., Halfhide, T. (2010) Growth of Microalgae for Biofuel Production on High Strength Wastewater, *Proc. Florida Energy Systems Consortium (FESC) Summit*, Sept. 28-29, 2010, Orlando FL.

University of South Florida

Development of a Highly Efficient Photocatalyst for CO₂ Reduction with H₂O by Hybrid Construction of Transparent, Conductive Composite (TCC) and nano-Sized MOX/INVO₄/AL₂O₃ Particles

PI: Norma Alcantar, John Wolan (deceased)

Description: Our research focused on three technologies to produce films able to respond to external stimuli. We used conductivity as the intrinsic property that was a prime parameter to consider when performance was measured. We also were interested on the fundamental structure that would make our conducting films and materials to enhance their performance.

Project Time Period: 2/1/2009-6/30/2011

Universities: Department of Chemical and Biomedical Engineering, USF

External Collaborators: Mote Marine Laboratories

Summary

This project's goal was to prepare transparent conductive composites (TCCs) in which organic and inorganic materials were used to produce and characterize a complex material with smart capabilities. Our research had a direct impact in battery production, conducting films and catalysis.

Goals and Objectives

- 1) Determine protocols for synthesis of conductive composites
- 2) Determine performance
- 3) Characterize their structure
- 4) Measure efficiency

Research Description

Our research focused on three technologies to produce films able to respond to external stimuli. We used conductivity as the intrinsic property that was a prime parameter to consider when performance was measured. We also were interested on the fundamental structure that would make our conducting films and materials to enhance their performance. The following is a description of the main accomplishments of this research.

- a) Conductive polymer complexes were prepared by doping optically transparent polymers with bis(ethylenedioxy)-tetrathiafulvalene (BEDO-TTF) and then exposing such films to iodine (anion donator) to form a conducting crystalline surface with the potential for sensing. Our research determine that once polymeric films are doped and exposed to an anion donator, their surface structure is affected by undergoing changes from amorphous to crystalline accommodations as shown in the following Figure.

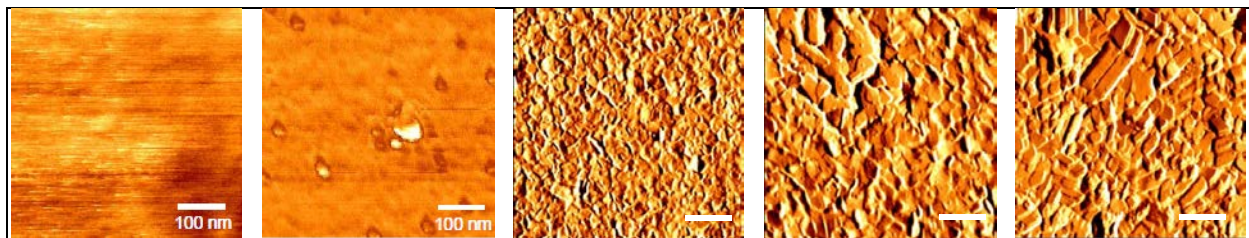
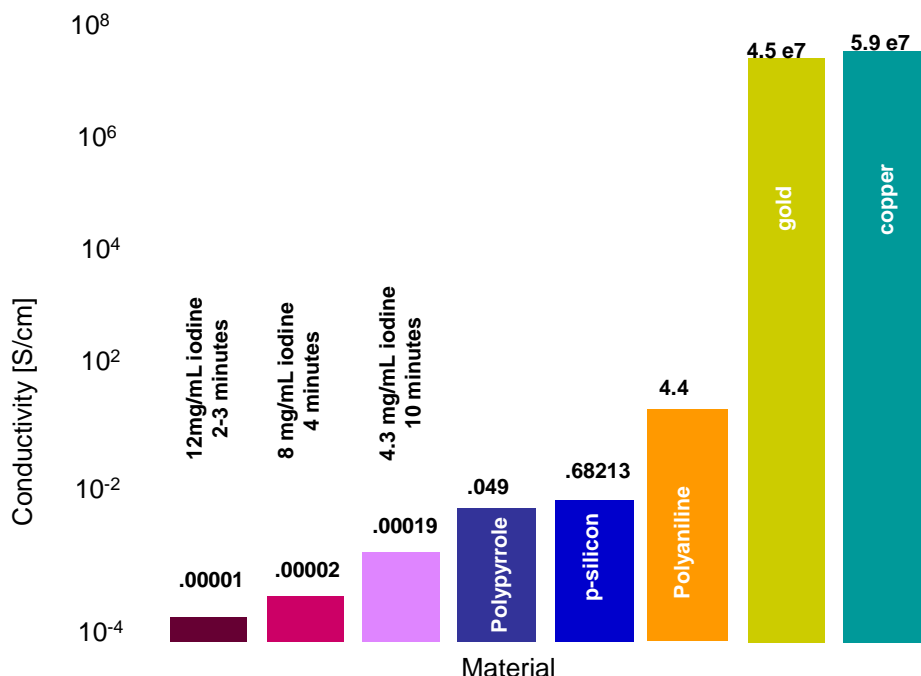


Figure 1. Phase contrast AFM scans: Bare PC (A), BEDO/PC (B), BEDO/PC/1mg/ml-2min exposure to Iodine (C), BEDO/PC/8mg/ml-4min Iodine (D), BEDO/PC/4.3mg/ml-10min Iodine (E). The scan size of A & B is 0.5x0.5 μ m. The scan size of C, D & E is 5x5 μ m, scale bar depicts 1 μ m. High resolution scans for A & B are shown intentionally to discern structure differences due to dye-doping as compare to C, D & E.

Data comparing common conducting materials to BEDO/PC/Iodine films are shown in Figure 2. Our data shows that the film conductivity is high if the coverage is uniform. Consequently, the films need to be exposed to low concentrations of I₂ for longer periods of time. It is also clear that structure and conductivity are related. The film with ordered-crystalline structure reported the highest conductivity (Fig. 1E), while the film with amorphous structure reported poor conductivity (Fig. 1C). The surface of the composite films becomes conductive as a result of complex formation between acceptor (I₂) and donor species from BEDO-TTF. The reverse side of the same film is non-conductive. Hypothesis I in this proposal focuses on controlling surface structure at the nano and micron level. These initial measurements have encouraged further work on optimizing conductivities through correlation to crystal morphologies.

We have submitted a proposal to NSF. Our first attempt was unsuccessful but we will resubmit with comments to the reviews in the next funding cycle.

- b) Our second technology included the production of flexible aluminum and hydrogen peroxide galvanic cells by encapsulating the oxidizer. In this work, we found that the side reactions can be diminished by controlling the cathodic reactant using niosomes (non-ionic surfactant vesicles) and polymeric networks. Results indicate an average energetic output value of 0.57 ± 0.09 KJ vs. 0.54 ± 0.05 KJ without the implementation of the cathodic encapsulation system. In addition, we also found that composition of the aluminum electrode was decreased by 15 %, which could then translate in 79 % in savings according to the market price of aluminum and savings on the secondary reactions.
- c) The third technology included the use of MO_x/InVO₄/Al₂O₃ photocatalysts (both in the UV or visible range) to eliminate off-flavor compounds in recirculating aquaculture systems (RAS). Heterogeneous photocatalysis is a process in which a solid semiconductor catalyst (e.g. titanium dioxide) absorbs light and subsequently initiates the degradation of chemical compounds through direct surface interaction or generation of oxidizing species such as hydroxyl radicals. A major benefit of photocatalysis is that the pollutants are destroyed and not simply transferred to another phase as in the case of activated carbon or membrane processes. In addition, it is much less expensive than using ozone, which requires onsite generation and the setup of expensive equipment.



Concluding Remarks

Our project has made a significant impact in current research areas of national interests. It has branched out into multidisciplinary applications and it has implications in biosensing, environmental science, water purification, and fundamental research involving novel battery systems.

Patents

Patent #: 8,034,302 - Transparent conducting composites (TTCs) for creating chemically active surfaces

Publications

Novel Encapsulation of Oxidizer Applied to Galvanic Cells: Aluminum / H₂O₂ Galvanic Cell as a Case Study by Marlyn Colon to obtain her Masters of Science Degree in Chemical Engineering, University of South Florida (2011). <http://scholarcommons.usf.edu/cgi/viewcontent.cgi?article=5213&context=etd>

Characterization of conductive polycarbonate films by Selma Hokenek to obtain her Masters of Science Degree in Chemical Engineering. University of South Florida, (2009)

Other publications are in the process of being sent out for review. <http://scholarcommons.usf.edu/cgi/viewcontent.cgi?article=3015&context=etd>

Other publications are in the process of being submitted.

University of South Florida

Development of a Smart Window for Green Buildings in Florida

PI: Dr. Sarath Witanachchi
Students: Marak Merlak, Ph.D

Description: This proposal is aimed at developing a smart window concept that has the potential to convert part of the solar radiation falling on windows during daytime to electricity, and to use this harnessed energy to power a phosphor-based, highly efficient white-light LED source to illuminate the building at night. This project pursues two different technologies: (1) use of quantum dot based solar cells to harvest solar energy, and (2) develop an electroluminescent light source based on nanophosphors to provide illumination for buildings. The proposed work brings together two unique nanoparticle growth techniques developed at the Laboratory for Advanced Material Science and Technology (LAMSAT) at USF to fabricate a prototype device that would demonstrate the possibility of significant energy savings. Research accomplishments related to solar device were presented in last annual report. This report focuses on research developments in the solid state lighting device.

Budget: \$38,413
Universities: USF

Progress Summary

The microwave plasma system was used to grow nanophosphors of La₂O₃:Bi and CaS:Eu. The system was modified to accommodate chemical vapor deposition (CVD) of ZnO and ZnS. ZnO coatings were grown by introducing Zinc acetylacetonate (Zn(acac)₂) vapor as precursor near the substrate. Vapor was generated by heating granules of Zn(acac)₂ in a container to 160°C and pushing the vapor with gas that contained a mixture of Ar and oxygen. Dimethylzinc and H₂S were used for the growth of ZnS films. A patent application has been filed for this hybrid process for fabricating nanoparticle embedded coatings.

Microwave plasma process allows control of nanophosphor particle sizes by controlling the precursor concentration. We have demonstrated the ability to deposit La₂O₃:Bi nanophosphors in single crystal form with sizes from 5nm to 100 nm by changing the starting concentration. Transmission Electron Microscopy (TEM) images in Fig 6 (a) & (b) show the hexagonal crystals and clear lattice planes with $d=3.34\text{\AA}$ that corresponds to (100) orientation. BTO layer required for the device structure was sputter deposited at low temperature.

Table 1: Integrated Sphere measurements of luminous flux from a 1cmx1cm area of devices.

Color	Conventional Structure	Proposal Structure
Blue	540 μW	720 μW
Red	580 μW	800 μW

Radiant flux emitted by devices fabricated with the conventional EL structures and devices with the proposed structures were measured by the integrated sphere technique. Measured values in μW for emission area of 1cmx1cm from blue and red devices are presented in Table 1 (rounded to the nearest 10s). These values represent average of 5 similar devices. Even though, the absolute values of emission are low, these measurements show an enhancement in emission resulting from the proposed structure. The observed upward trend confirms the viability of the concept and the

potential of EL devices fabricated under optimum conditions to reach desired outputs of 1300-1500 μW (13-15 W/m^2).

Annual Progress Report

Project Description

Project consists of two main research thrusts: (1) develop a PbSe quantum dot (QD) based polymeric solar cell structure as a window film to convert solar radiation through windows to electricity, (2) Develop a electroluminescence-based (EL) solid state lighting device that can be powered by the harnessed solar energy to provide lighting at night. A novel EL device architecture has been investigated in this project. This report describes the results pertaining to the EL device.

Electroluminescence based light sources:

EL occurs when impurity ions in a crystalline phosphor is excited by high-energy electrons. The electronic states of the dopant ions in the host crystal are split by the crystal field energy, which determines the energy levels available for excited electrons. Bound electrons of impurity ions such as Eu^{2+} , Ce^{2+} , Bi^{2+} , Mn^{2+} etc. are excited to higher energy levels when impacted with high-energy free electrons. Spontaneous de-excitation gives rise to optical emission where the emission wavelength is a characteristic of the type of impurity atom and the host material. Any excess energy will also be released to the lattice as a phonon (Fig. 1), which in general is very small. The band gap of the host material has to be larger than the energy of the emitted photon to prevent reabsorption of the radiation. For this mechanism to work there has to be a source of electrons and an externally applied electric field of the order of 10^6 V/cm to accelerate electrons in the conduction band of the host material.

A simple EL device consists of a phosphor layer such as Mn doped ZnS ($\text{ZnS}:\text{Mn}$) that is sandwiched between two insulating layers (Fig. 1).

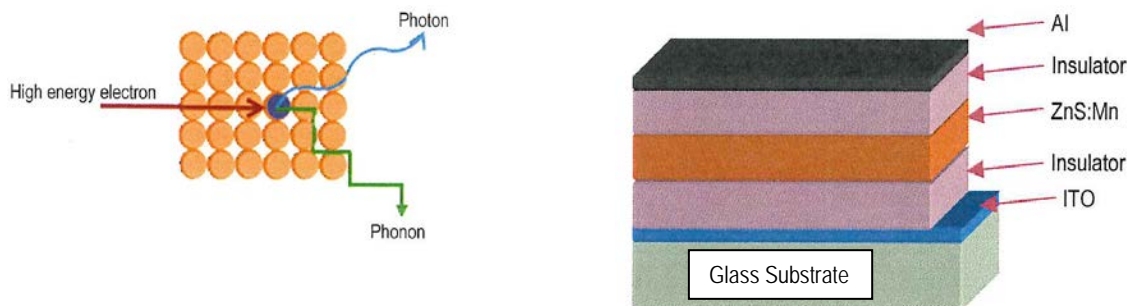


Fig. 1: Mechanism of EL and thin film layered structure of a typical EL device.

One of the electrodes is transparent, such as indium tin oxide (ITO) that allows light to transmit. When a high enough voltage is applied (above a threshold) between the electrodes the localized electrons in the interfacial trap states are injected into the conduction band of ZnS and accelerated by the electric field. These high-energy electrons cause impact excitation of dopants (eg. Mn).

Advantages of EL lights:

Currently available EL lights produce low intensity levels (70-300 $\text{Candela}/\text{m}^2$, EL Inc.) and thus are limited to special applications. If the light output can be increased, EL lights offer significant advantages as grow-lights for agriculture. These advantages include;

- (1) Emission spectrum from phosphors is much broader than that from an LED chip and thus can create light outputs that can be customized to any color temperature. Almost all of the energy from the electrons is converted to optical radiation. Amount of heat generated is much smaller than in an LED. Not having to incorporate heat management components simplifies the light fixture and reduces the device cost.
- (2) Multiple layers of the device can be manufactured by low-cost techniques such as role-to- role fabrication by inkjet printing or screen-printing. Manufacturing cost is much lower than the epitaxial thin film growth techniques used for fabricating LED chips.
- (3) Currently, a 1.5 m² white light panel can produce about 850 lumens, which is equivalent to a 60W incandescent light bulb. EL light is a thin flexible sheet that illuminates a large area uniformly (Fig. 2). The main advantage offered by an EL light source is that it is an extended source where light propagates in almost planar wave fronts. For such an extended source, the decrease in intensity of light (W/m²) with distance from the source is very small. This is a great advantage for a room lighting in contrast to 1/r² variation produced by a point source such as an **LED**.



Figure 2: EL based light sheet.

Function of Phosphors:

Phosphors are oxide, nitride, or sulfide host materials that carry small percentage of (~1%) impurity ions (Ce, Eu, Tb, Mn, Cu, Ag, Pb, Bi) as active ions. The crystal field energy of the host structure causes the splitting of the energy level in the active ions leading to an absorption line in blue and emission lines at longer wavelengths with long lifetimes (phosphorescence). Hundreds of phosphor materials with emission from deep blue to deep red have been synthesized. Some of the well known phosphor materials include, Ce³⁺ and/or Eu²⁺ doped Y₃Al₅O₁₂ (YAG: Ce³⁺, Eu²⁺), Y₂O₃:Eu²⁺, Ba₃MgSi₂O₈:Eu²⁺, Mn²⁺, ZnS:Mn, CaS:Cu, CaS: Pb²⁺, CaS: Eu²⁺.

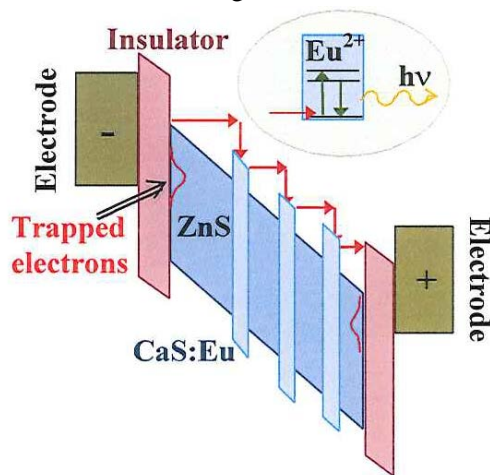


Fig. 3: Band alignment of an EL device structure that is subjected to an external voltage. Inset shows the photon emission from the impurity ion.

Advantages of nanophosphors:

Conventional phosphor materials fabricated by solid state sintering methods are in micrometer scale and thus light scattering at grain boundaries is significant. Light scattering reduces the extraction efficiency of the source. When the phosphor particle size is few tens of nanometers, much smaller than the wavelength of light (400-800 nm), effect of light scattering is significantly reduced. The Mie scattering cross-section of particles below 50nm is very small. In addition, when the phosphor particle size is reduced to the scale of tens of nanometers, the surface area-to-volume ratio of the material is increased, leading to an increase in the luminous efficiency.

The following factors determine (limit) the maximum emission produced by currently available nanophosphor based EL device:

- (1) Electrons required for excitation are derived from trap states at the insulator-host interface. In presence of a high AC voltage (100-200V) they are released from traps (Poole-Frenkel effect) and accelerated in the conduction band of the semiconductor host (Fig. 3). Under the AC field, electrons oscillate between the two sides to generate photons. Higher the voltage higher the emission.
- (2) Emission lifetime of a phosphor (decay time τ) is a characteristic of the host and the impurity. Typical lifetimes are in the range of 1 μ seconds to 100's of milliseconds. The driving frequency should be less than $1/\tau$ to avoid phosphor saturation. Currently devices are operated at about 600 Hz. As the phosphor particle sizes are reduced into the nanometer region, modification of the crystal field of the phosphor host (CaS in CaS:Eu) causes the decay time to be smaller and thus enable high frequency operation.

(3) Higher voltages and frequencies produce higher emission, but at the expense of reduced device lifetime. For low duty cycles, the device may last forever. However, in continuous use at high power outputs, the intensity drops with time and may need replacement in 2-3 years.

Experiments and Results:

The microwave plasma system for nanoparticle growth consist of three main regions; (1) nebulizer to for 1-1.5 μm aerosol droplets of the precursor, (2) plasma reaction zone where microwave energy generates a high temperature reaction zone for evaporation of the solvents and reaction of the chemicals in droplets and plasma gas to form the nanophosphors, (3) substrate placed above the plasma zone for the deposition of the nanophosphors. The system was modified to accommodate chemical vapor deposition (CVD) of ZnO and ZnS . ZnO coatings where grown by introducing Zinc acetylacetonate ($\text{Zn}(\text{acac})_2$) vapor as precursor near the substrate. Vapor was generated by heating granules of $\text{Zn}(\text{acac})_2$ in a container to 160°C and pushing the vapor with gas that contained a mixture of Ar and oxygen. Dimethylzinc and H_2S were used for the growth of ZnS films. For safe handling of the chemicals involved, the entire system was place in a fume hood (Fig. 4). A patent application has been filed for this hybrid process for fabricating nanoparticle embedded coatings.

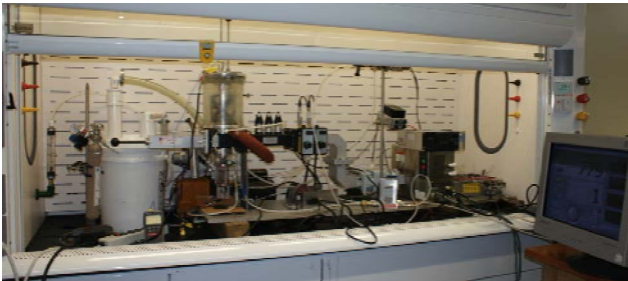


Fig. 4: Picture of the microwave plasma system used in the growth of nanophosphors, ZnO and ZnS layers.

Step 1: The starting point in the fabrication of the layered structure is a commercially available ITO (layer 1) coated glass substrate. The choice of the insulator (layer 2) was BaTiO_3 (BTO) (refractive index (n) = 2.01). BTO and n-ZnO (n = 2.0) films were deposited by sputtering.

Step 2: ZnO films were also grown by the CVD process within the microwave plasma system on sputtered BTO films. Growth by CVD is much simpler and cost effective than sputtering. ZnS films were deposited by CVD process with Dimethylzinc and H_2S gas.

Step 3: The two phosphor materials to be used to generate blue and red radiation are $\text{La}_2\text{O}_3:\text{Bi}$ (blue) and $\text{CaS}:\text{Eu}^{2+}$ (red), respectively. $\text{La}_2\text{O}_3:\text{Bi}$ nanoparticles were grown by the microwave plasma process with starting precursors containing aqueous solutions of the nitrates of La and Bi salts. Depending on the starting concentration, particles of sizes from 5nm to 100 nm were deposited. $\text{CaS}:\text{Eu}$ nanophosphor coatings were grown in two steps. In the first step, $\text{CaS}:\text{Eu}$ nanoparticles of sizes of about 50 nm were grown by solvothermal process. Subsequently, particles were dispersed in ethanol and nebulized in the microwave plasma system to deposit a coating on a substrate. Layers of ZnS and ZnO were grown by the same method used in step 2.

Microwave plasma process allows control of nanophosphor particle sizes by controlling the precursor concentration. We have demonstrated the ability to deposit $\text{La}_2\text{O}_3:\text{Bi}$ nanophosphors in single crystal form with sizes from 5nm to 100 nm by changing the starting concentration. Transmission Electron Microscopy (TEM) images in Fig 5 (a) & (b) show the hexagonal crystals and clear lattice

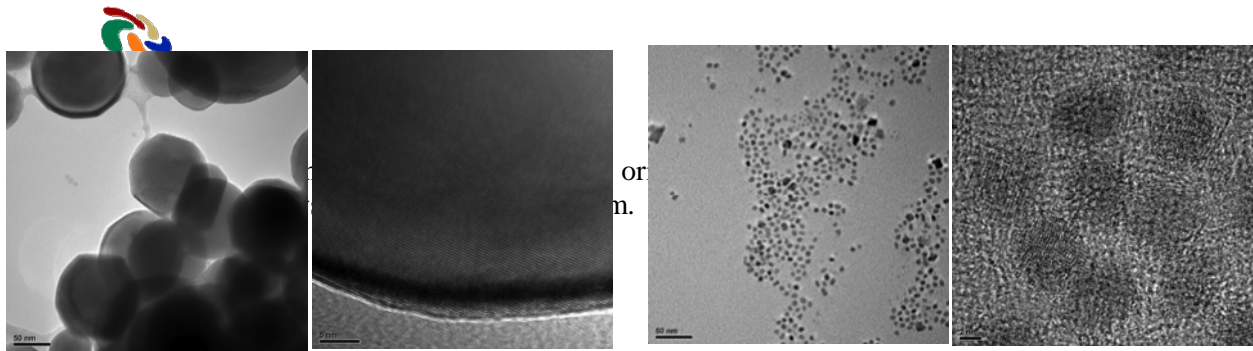


Fig. 5: TEM images of La₂O₃:Bi nanophosphors by microwave plasma process for, (a) 0.1M solution, showing 50-75 nm particles, (b) lattice planes at high resolution indicating single crystal nature, (c) 0.01M solution, particle sizes of 5-6 nm, (d) lattice planes at high resolution.

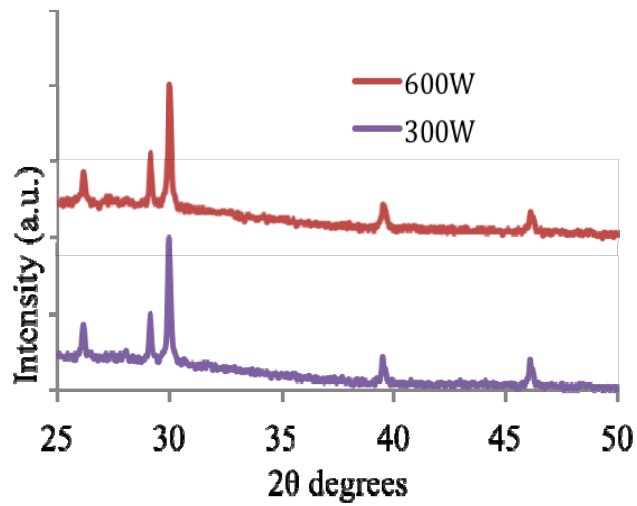


Fig. 6: XRD patterns of as-deposited La₂O₃:Bi³⁺ nanophosphor coatings at two different power levels indicating crystallinity.

Step 4: BTO layer was sputtered at low temperature. Silver ink was used as the back electrode.

Each coating was analyzed by x-ray diffraction for crystallinity and absorption spectroscopy for light transmission. Fig. 6 shows x-ray scans of nanoparticle coatings grown under two different microwave powers. In addition to the n-ZnO/p-ZnS p-n junction structure, n-ZnO-p-NiO junctions were also investigated. Since one of the blue phosphors under consideration is La₂O₃:Bi, possibility of embedding oxide phosphor in a p-type oxide semiconductor rather than ZnS was explored.

Light output measurements: One of the devices fabricated by steps outlined above and the observed blue and red emission from these devices are shown in Fig. 7. Radiant flux emitted by devices fabricated with the conventional EL structures and devices with the proposed structures were measured by the integrated sphere technique. Measured values in μW for emission area of 1cmx1cm from blue and red devices are presented in Table 1 (rounded to the nearest 10s).

Table 1: Integrated Sphere measurements of luminous flux from a 1cmx1cm area of devices.

Color	Conventional Structure	Proposed Structure
Blue	540 μW	720 μW
Red	580 μW	800 μW

These values represent average of 5 similar devices. Even though, the absolute values of emission are low, these measurements show an enhancement in emission resulting from the proposed structure. The observed upward trend confirms the viability of the concept and the potential of EL devices fabricated under optimum conditions to reach desired outputs of 1300-1500 μW (13-15 W/m^2).



Fig. 7: (a) View of a device fabricated with nanoparticle coatings, (b) blue emitting device with La₂O₃:Bi phosphor, (c) red emitting device with CaS:Eu phosphor.

Alternative Energy Potential for Florida From Mechanical and Solar Sources

PI: Robert H. Weisberg

Student: Yong Huang (Post-Doctoral Associate)

Description: The potential for alternative energy generation within the State of Florida and its adjacent waters has its origins with the atmosphere, ocean, sun, and terrestrial sources. Here we are concerned with the mechanical and radiant energy naturally available from atmospheric winds, ocean currents and waves, and incident solar radiation. Our goals are to identify what the potential for alternative energy generation is based on data already available from existing environmental programs and to assess how much of this naturally available energy can be harnessed for electrical energy generation using existing technologies. The wind data are from offshore buoys. These will be scaled up to the hub height of commercially available turbines using atmospheric boundary layer theory checked against model simulations. These same offshore buoys provide data on incident solar radiation. Along with other data sources and models (such as automated coastal ocean circulation and wave models run by the CMS-USF along with other federal agency run models) we also have access to information on ocean currents and waves, both for the west coast of Florida where such energy densities are relatively low and the higher energy east coast counterpart. For all of these potential energy sources we employ specifications from existing commercially available technologies (turbines, solar panels, etc.) to convert what nature has to offer into actual rates of electrical energy production. In other words we propose a reality check on alternative energy generation for the State of Florida by mechanical and solar means.

Budget: \$39,363

Universities: USF

Progress Summary

Progress continued toward meeting the project objectives as follows.

- 1) Weisberg was an invited speaker at the CMS Eminent Scholars Lecture series in April 2011.
- 2) A paper previously submitted to *Jour. Geophys. Res. – Oceans* was judged to be outside the scope of the that journal's mission. The paper was subsequently revived and submitted to the Journal of the Marine Technology Society. The revised paper was peer reviewed and accepted for publication:

Weisberg, R.H., Y. Liu, C.R. Merz, J.I. Virmani, and L. Zheng (2012). A critique of alternative power generation for Florida by mechanical and solar means, *J. Mar. Tech. Soc.*, Sept/Oct 2012, 46, 5, 1-12.

Please note that as of this writing the paper remains in press although the citation was provided as given above.

Funds leveraged/new partnerships created

Our work on this project was in part facilitated by other funded research for observing and modeling the West Florida Continental Shelf ocean circulation and waves. Thus leveraging is from four compatible grants

SC SEAGRANT, federal pass through from NOAA, NA11NOS0120033, Maintaining moored observations for SECOORA, R.H. Weisberg, P.I., 142,500 for the period 6/1/11-5/31/12 (NCE for calendar year 2012).

SC SEAGRANT, federal pass through from NOAA, NA11NOS0120033, Maintaining high-frequency radars for SECOORA, R.H. Weisberg, P.I., 95,000 for the period 6/1/11-5/31/12 (NCE for calendar year 2012).

SURA Federal pass through from NOAA, NA11NOS0120033, USF contribution to US IOOS Super-regional model testbed, R.H. Weisberg, P.I., 30,000 for the period 8/1/11-7/31/12.

FSU, subcontract on Florida Legislature FS1004-647, Catastrophic storm risk management, R.H. Weisberg, P.I., \$153,062 for the period 12/1/9-12/31/11 (NCE for FY12).

Annual Progress Report

Please provide a detailed report of your accomplishments here.

Along with the publication of a paper which provides an analysis on the potential for electrical energy generation for the State of Florida by harnessing the alternative energy sources provided by winds, ocean currents, ocean waves, and insolation, we established a daily automated nowcast/forecast model for ocean waves of use for the general public. This waves model complements a daily, automated nowcast/forecast model for the coastal ocean circulation off the west coast of Florida established under separate funding.

The work on alternative energy generation potential stems from actual field observations of winds, ocean currents, ocean waves and solar insolation made over the course of a decade or more under separate funding. We critically assessed these observations for measure of what nature offers. For wind or solar we then used published information from vendors of windmills and solar panels to convert what nature offers to electrical power generation. For ocean currents and waves, areas where mature industries do not presently exist, we used first principles and reasonable assumptions to convert nature's bounty to alternative energy generation potential. The principal findings are as follows:

- 1) As might be expected, given the fact that commercially available devices may be purchased for wind and solar energy conversion to electrical power, a reasonable potential does exist in Florida for using these alternative energy sources. However, we concluded that such energy conversion may be useful for supplementing the primary generation of electrical power by conventional fuels, versus replacing the primary generation by conventional fuels.
- 2) As might be expected, given the fact that commercial devices are not readily available for extracting kinetic energy from either ocean currents or waves, there does not exist a utility scale potential in Florida for using these alternative energy sources. We recognize that this finding may appear controversial because the Gulf Stream, a swift, relatively steady ocean current flows between the east coast of Florida and the Bahamas. Yet, the potential for extracting energy from the Gulf Stream is both limited and impractical.

Along with the two general findings above, the paper details the reasons for this and provides some crude examples of the economic involved. Factors arguing against watermills, versus windmills are that:

- a) Given that essentially equal area machines are involved for a comparable amount of energy, and that to achieve equal area machines many more smaller machines would have to be deployed at sea versus on land, why would watermills be considered when windmills are so much more practical

- b) Wind energy extracted from the lower portion of the atmosphere boundary layer is readily replenished, whereas water energy extracted from the main portion of the water column itself is not.

Wave energy extraction for Florida is also too limited and impractical.

Whereas our work did not entail new job creation, it may serve to help direct State of Florida alternative energy investment policy in favor of concepts which may prove to be fruitful, versus ones which may not.