DOE CDP Final Report

Cover Sheet

Project Title:	University of Louisville Research and Energy Independence Program	
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Cost-Sharing Partners:	University of Louisville, University of Louisville School of Interdisciplinary and Graduate Studies, Kentucky Energy & Environment Cabinet	
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Project Objective:

Initiate a center focused on renewable energy research at UofL with the following research themes.

1. Materials manufacturing
2. Solar energy conversion
3. Renewable energy storage
4. Biofuels
5. Energy efficient buildings

Background:

The development of domestic, environmentally friendly and sustainable sources of energy and liquid fuel is a critical need for the United States (US). Kentucky (KY) is rich in natural energy and agricultural resources that could provide sustainable energy for the state and for the nation. New technology is needed to capture, store, and distribute this sustainable energy in KY. Development of KY's sustainable energy resources will create economic benefit for the citizens of KY and can serve as a model for other states in the US. Existing technologies for solar energy collection and storage are practical for regions with high and consistent solar intensity, such as the southwest US. Solar energy is plentiful in KY, but is less intense and less regular. As such, novel innovative technology is needed to capture, store, and distribute this energy. KY also has plentiful biomass resources that can be converted to renewable fuels. In addition, the state offers low energy rates, which are conducive for any type of manufacturing industry. A manufacturing R&D center at the University of Louisville (UofL) can help attract high-tech manufacturing industries to the city of Louisville and the state of KY.

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1.0 Executive Summary

This overall objective for this Congressionally Directed Project (CDP) was to initiate and expand research and development on various renewable energy and energy efficiency technologies at UofL toward strengthening an emerging center for renewable energy research. Specific objectives included: (a) set up unique research facilities for facilitating research by students and faculty from various disciplines; (b) expand research efforts at UofL by initiating theme-specific research projects involving faculty and students; (c) develop and offer a multi-disciplinary course; and (d) initiate a number of outreach efforts toward inspiring undergraduate and high school students. In order to accomplish the above objectives, the funding from the US Department of Energy was supplemented with support from the KY Department of Energy Development and Independence (DEDI) and UofL through two Clinical and Translational Science Awards (CTSAs).

The following are the highlights of our accomplishments from 2010-2012.

- Established unique core research facilities in the following areas:
    - bulk production facility for nanomaterials (an atmospheric plasma reactor for continuous manufacturing of nanowire powders)
    - lithium ion batteries (fabrication of coin/pouch cells; test facilities)
    - low cost solar cell manufacturing including roll to roll facility (a facility for fabricating dye-sensitized solar cells on large glass plates; and custom-designed R2R with several deposition and low-temperature sintering facilities).
    - waste to energy research facilities (batch and continuous upflow anaerobic digestion reactors and analysis equipment)
    - Inkjet printing research facility (

- Recruited: Dr. Thad Druffel as low cost solar manufacturing R&D theme leader; Dr. Jagannadh Satyavolu as biofuels theme leader; and Dr. Arjun Thapa as senior post-doctoral associate for battery R&D for the center.

- Involved 13 faculty, 10 senior research staff, 27 graduate students, and 27 undergraduates in various research projects initiated as part of this project. See the participant list in the following pages.

- Developed and offered a new multi-disciplinary course on “Renewable Energy Challenges”. The enrolled students developed hands-on educational renewable energy exhibits to inspire 4-6 grade students. These exhibits are part of a new Capital Education Center in Frankfort KY promoted by the Office of the First Lady of Kentucky (Jane Beshear). Approximately 5000 students are expected to visit every year as part of educational visits to the State Capital.

- Developed an annual solar flight competition that involves over twenty undergraduate students and six faculty mentors.

- Developed a solar decathlon team and a successful proposal for competing in 2013 competition held by US Department of Energy in Irvine, CA.

- Accomplished a number of research projects with following highlights:

- 20 journal publications; 4 patent filings
- Demonstrated and optimized continuous manufacturing of ZnO nanowire powders. A startup, Advanced Energy Materials, LLC, was created to license and further develop the technology.
- Several different types of nanoscale materials were developed and tested in lithium ion batteries. Some of them showed promise as anodes with high capacity retention and durability.
- Demonstrated and optimized 6" x 4" glass plate panels involving dye sensitized solar cells. Optimized the sealing process to achieve durability beyond two months.
- Developed a new process for making water based pastes that yield efficiencies >9% for dye sensitized solar cells.
- Demonstrated a new low temperature sintering process for dye sensitized solar cells that exhibited efficiencies >2% at this time. Further development is underway.
- Using anaerobic digestion R&D facilities, the Conn Center has developed processes for treating industrial waste into biogas suitable for generating power.
- A new process was developed for converting waste cooking oils to jet fuels using low amounts of hydrogen. This has been patented and licensed to a startup, AliphaJet, LLC.
- A number of research findings have resulted through initiated research projects: (a) smaller gold/silver particles showed interesting properties for oxygen reduction reaction – useful for zinc-air batteries; (b) new formulations involving phase change materials and concrete were tested for concretes to be used for energy efficient buildings; (c) thermally activated luminescent behavior was observed and explained for Indium Nitride; (d) a new scalable process was developed for producing copper and copper oxide nanowire arrays on copper foils and other metal foils; (e) a new process was developed for producing silicon coatings onto copper and MoO_3 nanowire arrays; (f) a new process was developed for low-temperature growth of silicon nanowires on various metallic substrates – a potentially useful technique for high capacity anodes in lithium ion batteries; etc.

1.1 List of Researchers Involved in this Effort (2010-2012).

Between the DOE CDP, CTSA, and DEDI funding, the following faculty, staff, postdocs, grad students, and undergraduate students were included in the research/outreach efforts.

Faculty

1. Dr. Bruce Alphenaar, Professor of Electrical Engineering
2. Dr. Delaina Amos, Assistant Professor of Chemical Engineering
3. Dr. Lihui Bai, Assistant Professor of Mechanical Engineering
4. Dr. Eric Berson, Associate Professor of Chemical Engineering
5. Dr. Matt Bohm, Assistant Professor of Mechanical Engineering
6. Dr. Moises Carreon, Associate Professor of Chemical Engineering
7. Dr. Yongsheng Lian, Assistant Professor of Mechanical Engineering
8. Dr. Jinjun Liu, Assistant Professor of Chemistry
9. Dr. Mark McGinley, Professor of Civil Engineering
10. Dr. Sam Park, Assistant Professor of Mechanical Engineering
11. Dr. Gamini Sumanasekera, Associate Professor of Physics
12. Dr. Mahendra K. Sunkara, Professor of Chemical Engineering
13. Dr. Frank Zamborini, Professor of Chemistry

Staff

1. Dr. Julia Aebersold, Manager, Micro/Nano Technology Center
2. Dr. Thad Druffel, Theme Leader, Solar Manufacturing R&D, Conn Center
3. Dr. Jacek Jasinski, Theme Leader, Materials Characterization, Conn Center
4. Mr. Jeong Hoon Kim, Research Technologist, Advanced Energy Materials, Conn Center
5. Ms. Eugenia Macias, Research Technologist, Biofuels, Conn Center
6. Mr. Andrew Marsh, Assistant Director, Conn Center
7. Ms. Rodica McCoy, Program Manager, Materials Characterization, Conn Center
8. Ms. Kelly Jackson, Research Grants Coordinator, Conn Center
9. Dr. Paul Ratnasamy, Theme Leader Emeritus, Biofuels, Conn Center
10. Dr. Jagannadh Satyavolu, Theme Leader, Biofuels/Biomass Conversion/ Biogas, Conn Center

Postdocs

1. Dr. Timothy Gutu, Materials Characterization
2. Dr. Robert Lupitskyy, Biogas
3. Dr. Matthew Turner, SmartGrid Roadmap Initiative
4. Dr. Arjun Thapa, Energy Storage R&D

Graduate Students

1. Mr. Meysem Akhtar, Physics
2. Mr. Dustin Cummins, Chemical Engineering
3. Mr. Chinmay Deshmane, Chemical Engineering
4. Ms. Rupa Dumpala, Physics
5. Mr. Kasun Fernando, Physics
6. Mr. Alejandro Martinez Garcia, Chemical Engineering
7. Ms. Maria Carreon Garciduenas, Chemical Engineering
8. Mr. Mahyar Ghorbanian, Chemical Engineering
9. Mr. Jeffrey Kiesel, Civil and Environmental Engineering
10. Ms. Sowmya Kolli, Electrical Engineering
11. Mr. Vivekanand Kumar, Chemical Engineering
12. Mr. Tulashi Luitel, Chemistry
13. Mr. Rafael Masitas, Chemistry
14. Mr. Tu Nguyen, Chemical Engineering
15. Mr. Chandrashekar Pendyala, Chemical Engineering
16. Mr. Franz Petzold, Chemical Engineering
17. Mr. Harry Russell, Chemical Engineering
18. Mr. David Russ, Chemical Engineering
19. Mr. Hemant Shah, Physics
20. Mr. Andriy Sherehiy, Physics
21. Ms. Swathi Sunkara, Chemical Engineering
22. Mr. Venkat Vendra, Chemical Engineering
23. Mr. Zhuoliang Ye, Chemical Engineering
24. Mr. Christopher Woodbury, Chemical Engineering
25. Mr. Stephen Zwanzig, Mechanical Engineering
26. Ms. Dominika Ziolkowska, University of Warsaw
27. Ms. Minqui Zhu, Chemical Engineering

Undergraduate Students

1. Mr. Jason Absher, Chemical Engineering
2. Mr. Joseph Albrecht, Engineering Fundamentals
3. Mr. Gailen Bridges, Chemical Engineering
4. Mr. Joseph Bohrman, Chemical Engineering
5. Ms. Yan Chen, Chemical Engineering
6. Mr. Ezra Clark, Chemical Engineering
7. Mr. Connor Click, Mechanical Engineering
8. Ms. Christine Dolin, Chemical Engineering
9. Mr. Tyler Dorsey, Chemical Engineering
10. Ms. Marianne Eaves, Chemical Engineering
11. Mr. Samuel Ellis, Mechanical Engineering
12. Mr. Michael Ench, Mechanical Engineering
13. Ms. Samantha Farmer, Chemical Engineering
14. Ms. Amelia Gandara, Chemical Engineering
15. Mr. Lukus Guhy, Engineering Fundamentals
16. Ms. Xue Han, Physics
17. Mr. Alan Jimenez, Chemical Engineering
18. Ms. Kelsey King, Mechanical Engineering
19. Mr. Robert Knear-Bell, Chemical Engineering
20. Mr. Quintin Kuntz, Mechanical

Engineering

21. Mr. Christopher Latino, Chemical Engineering
22. Mr. William Menkhaus, Engineering Fundamentals
23. Mr. Michael McCreary, Chemical Engineering
24. Ms. Stephanie Miles, Electrical and Computer Engineering
25. Mr. Kane Miller, Mechanical Engineering
26. Mr. Cory Milligan, Chemical Engineering
27. Mr. Stephen Miranda, Mechanical Engineering
28. Ms. Jacqueline Orth, Engineering Fundamentals
29. Mr. Russell Prater, Mechanical Engineering
30. Mr. Caleb Sheehan, Engineering Fundamentals
31. Mr. Bryon Staebler, Chemical Engineering
32. Ms. Natalie Tapolsky, Engineering Fundamentals
33. Mr. Eli Wilborn, Chemical Engineering
34. Ms. Zhenzhen Xie, Chemical Engineering
35. Ms. Caitlyn Young, Chemical Engineering

2.0 Detailed Report

2.1 Task 1 - Materials Development and Manufacturing Initiative

This task is primarily funded through translational research funding from UofL's clinical and translational science and application (CTSA) program. The support from CTSA program funded the following two projects: (1) "A platform technology and reactor for bulk production of nanowires (NanowireX)"; and (2) "High capacity and durable electrode materials for next generation Li ion batteries".

2.1.1 Bulk Production of Nanowire Powders and Reactor Facility Development

Nanowire Production Reactor Facility: The scale up of nanowire (NW) production to grams per day is necessary to use them in dye sensitized solar cells and lithium ion battery technologies. We proposed to conduct continuous production experiments involving tin oxide NWs for obtaining grams of materials. As a part of this task, we proposed to optimize the process for continuous manufacturing of zinc oxide NWs first and then develop the process for other materials. The Sunkara group at UofL discovered that NW nucleation and growth can occur directly out of micron scale metals with direct gas phase reaction for their respective compound NWs. This scheme is implemented in an atmospheric plasma flame reactor in which micron scale metal powders are fed at the top, as shown in schematic in Figure 1. The metal powder melts and oxidizes to form high densities of metal oxide NWs during their residence in flight. The resulting NW powders are collected at the bottom using a filter bag. Earlier, we implemented the above scheme using a highly dense plasma jet confined within quartz tube and shaped by flowing sheath gases near the wall inside the tube, as shown in Figure 1. The commonly known methods of NW formation use catalyst droplets that lead 1-D growth through a mechanism called V-L-S scheme. Several other researchers exploited such a scheme using catalyst coated substrates in a number of approaches such as thermal evaporation, laser ablation, hydrothermal synthesis, deposition inside templates.

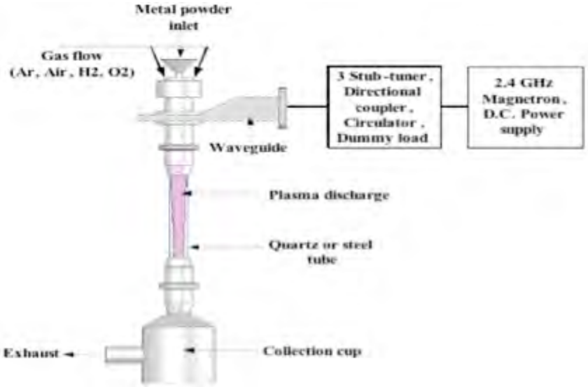


Figure 1. Schematic of AdEM's atmospheric plasma oxidation reactor for rapid oxidation of metal powders.

Figure 2. Nanowire bulk production reactor with all safety measures: Equipped with a microwave plasma flame for fast bulk production of nanowires; powder feeder and exhaust treatment.

In order to optimize the above type of process, we needed to design and build a reactor that would operate continuously and then house it in a safe enclosure. In this task, we designed a reactor facility with the following modifications: (a) House the reactor in a Plexiglas chamber; (b) Provide exhaust for gaseous flow through activated carbon filter; (c) Acquire and optimize a continuous powder feeder for supply of powder to the reactor at the top; and (d) Re-design a filter for effective collection of resulting NW powders. The reactor facility is designed as shown in Figure 2. This facility allows students to perform bulk production experiments with downstream bulk production reactor housed in a Plexiglas enclosure with a separate, leak-tight enclosure for powder feeder region. We also acquired a commercial plasma powder for continuous nanowire powder production experiments.

- Acquired and installed a new powder feeder (Plasma Powders, Inc. PF700).

Large-scale Production of ZnO and SnO_2 NW Powders: In 2010, a startup, Advanced Energy Materials, LLC. (AdEM), was created to license our technology and develop the scaled-up process for pre-commercial and commercial scale production of NW powders for batteries and catalysts. Sunkara's group, in collaboration with the startup AdEM, have demonstrated and optimized bulk production (hundred gram scale) of ZnO NW powders using the above reactor through continuous processing of metal powders. The results with zinc oxide were encouraging, i.e., continuous production at 0.2 gm per minute or 100 grams per day. The results also indicate that the powder collection needs to be improved for running the process over several hours and days continuously. Particularly, NW powders collected in the new filter bag had ultra-fine dimensions (10-15 nm diameter and several tens of microns long). We prepared over couple of hundred grams of zinc oxide NW powders. See Figure 3 for SEM images and pictures of ZnO NW powders. We used some of these powders toward use as hydro-desulfurization catalyst. Based on the results, we were awarded a grant from the Kentucky Commercialization Fund to develop the catalyst technology based on ZnO NW powders.

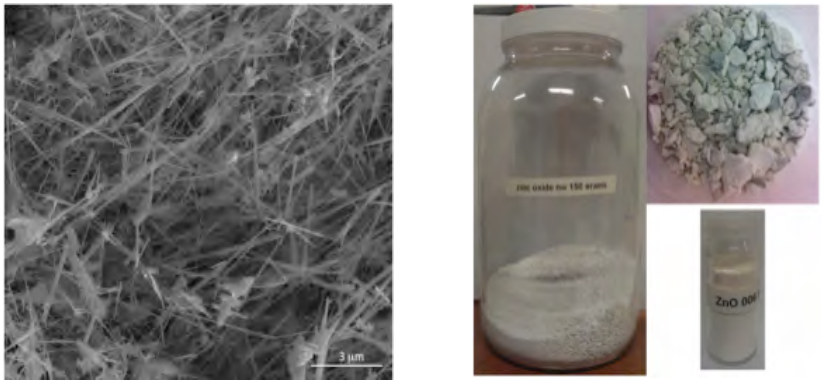


Figure 3. (a) SEM image of ZnO NW powders produced using the reactor shown in Figure 2. (b) The photographs of bottles containing ~250 grams of ZnO NW powder and 6 gms of ultrafine NW powder (~5-20 nm diameter; >20 microns length).

Preliminary sets of experiments were conducted to produce aluminum doped zinc oxide NW powders. The experiments produced Al alloyed ZnO nanoparticles and ZnO NWs. We also conducted several preliminary studies to study the feasibility of producing aluminum alloyed zinc oxide NW powders. These experiments were conducted by pouring aluminum and zinc powders through our reactor and the resulting oxide powders were collected. The resulting powders contained aluminum alloyed zinc oxide nanoparticles (spherical or faceted) and zinc oxide NW powders. The experiments are partially successful but need to be optimized to produce aluminum alloyed zinc oxide NWs. These materials will find tremendous uses as replacement materials for those currently used for transparent conducting oxide coatings.

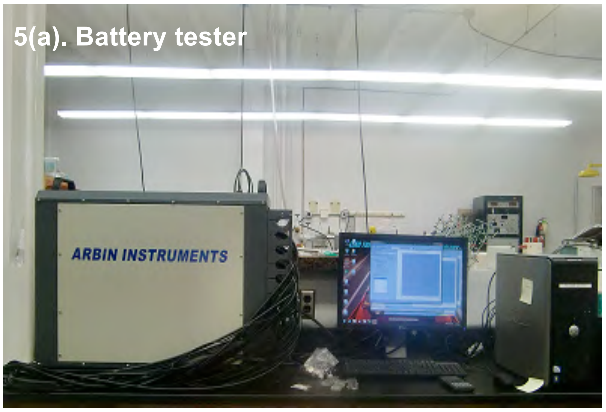
Following our success with a technique termed here as “solvo-plasma” oxidation, the experiments using tin metal powder mixed with KOH were performed. The results indicate that this concept could be converted in to a bulk production strategy. The experiments using Zn metal powders were also successful. Several experiments were conducted using powder feeder for metal oxide powders mixed with KOH. There is more work to be done to optimize this scheme for continuous production, i.e., smooth powder flow and good mixing between KOH and metal oxide powders.

2.1.2 Development and Testing of Nanoscale Materials for Li-ion Batteries

In this task, our objective was to set up research facilities necessary for lithium ion (Li-ion) battery research and develop new materials for improving durability of Li-ion batteries.

Development of Li-ion Battery Research Facilities: We acquired several pieces of equipment to set up coin cell and pouch cell fabrication and testing facilities for Li-ion batteries. We hired Dr. Arjun Thapa, who finished his PhD dissertation in Li-ion battery materials development working with Dr. M. Yoshio of Japan and acquired over three years of research experience beyond PhD. He joined Conn Center in August, 2011. After establishing the facilities, we standardized procedures for fabrication and testing of coin cells.

Fabrication of coin and pouch cells: The electrochemical measurements were performed using CR2032 coin-type cells assembled in a dry argon-filled glove box in which both moisture and oxygen contents were below 5 ppm. The test cell consisted of a working cathode electrode $LiNiMnCoO_2$ NWs and an anode electrode (SnO_2 NW), which were separated by a Celgard 2400 membrane. The electrolyte solution used was 1 M $LiPF_6$-EC:DMC (1:2 by volume). The working electrodes were prepared by casting slurry containing 85% of active material, 8% of acetylene black and 7% of PVDF onto aluminum foil using doctor blade. The counter electrode was SnO_2, which is prepared by casting slurry containing 80% of active material, 10% of acetylene black and 10 % of PVDF onto copper foil. The active mass of both cathode and anode electrode were 2.0 cm^2. The cathode and anode electrodes were dried under vacuum at 160°C for 5 h using vacuum pump to remove the moisture content in the electrode and transferred to glove box for assembling the coin cell. An exploded view of a CR2032 coin-type cell is shown in Figure 5. The galvanostatic charge-discharge cycling test measurements were performed using an Arbin instrument.


5(a). Battery tester


5(b). Li-ion cell connected to battery

We have also successfully tested pouch type full cells for Li-ion battery prototypes using commercially available cathode $LiNiCoMnO_2$ and SnO_2 NW as an anode with 4 × 4 cm^2 of capacity 50.0 mAh. This preliminary result for Lithium-ion battery prototype shows similar results like commercially available Li-ion batteries currently on the market. The Li-ion battery prototype full cell is prepared in our laboratory as shown in Figure 6. We will further develop 8×8 cm^2 with capacity of 200 mAh full cell battery prototypes in the near future.

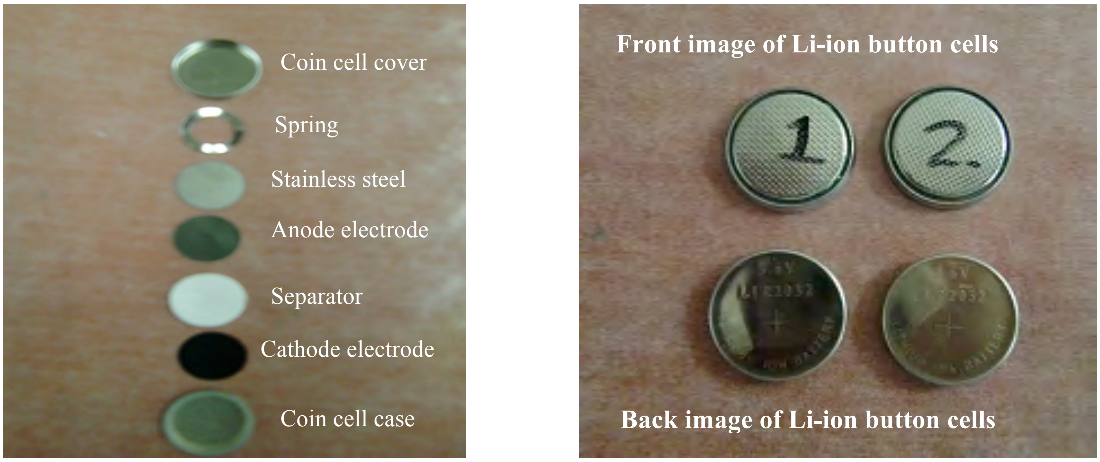


Figure 5. Schematic image of a CR2032 coin-type cell before and after assembling.

Development and Testing of Nanoscale Materials for Li-ion Batteries: Dr. Arjun Thapa worked with various PhD students to develop and test various NW powders and arrays for Li-ion battery applications. Example studies are highlighted below.

A new process was developed to produce silicon coatings on MoO_3 NW arrays and copper NW arrays. The silicon coated MoO_3 NW arrays showed promise in terms of improved capacity and durability. However, a detailed study is necessary to optimize the process of silicon film deposition and film thickness necessary to achieve a capacity at 1500 mAh/g with enhanced durability. The samples involving silicon coating on copper exhibited Cu_9Si phase, which did not show much Li-ion intercalation behavior. Some other samples involving silicon coating on copper NW arrays exhibited a clathrate structure with much lower Li-ion capacity.

A detailed study was conducted to understand the role of modifications of tin oxide NW arrays and powders on the capacity retention and durability. The modifications included coverage of tin nanoclusters and thin layers of titania using atomic layer deposition. The results showed that tin oxide NW powders and arrays retained capacity as high as 800 mAh/g with modifications using thin layers of titania. Figure 7(a) shows the charge discharge capacities vs. voltage of thin ALD of TiO_2 @ SnO_2 electrode at 3.0-1.0 V, which are used to confirm whether the TiO_2 layer is contributing some capacities on SnO_2 NW. Here, we observed that TiO_2 contributes an initial discharge capacity of 20 mAh g^{-1} during the first cycle. Further charge/discharge measurement at 3.0-1.0 V from the 2nd up to 10th cycles shows that thin layer ALD of TiO_2 contribute 6 mAh g^{-1} only. This indicates all the capacities that we observed were mainly from SnO_2 NW. Figure 7(b) shows the charge/discharge capacities with time vs. voltage profile of thick layer ALD of TiO_2 @ SnO_2 electrode at 3.0-1.0 V. In the case of thick layer ALD of TiO_2@SnO_2, we observed that TiO_2 contributes an initial discharge capacity of 6 mAh g^{-1} during the first cycle. Further charge/discharge measurement at 3.0-1.0 V from the 2nd up to 10th cycles shows that thick layer ALD of TiO_2

Figure 6. Photograph of a pouch cell fabricated and tested.

contributes 3 mAh g^{-1} only up to the 10th cycles. This was the opposite result, as we expected that the thick layer coating TiO2 would have more capacities at 3.0-1.0 V than the thin layer TiO_2.

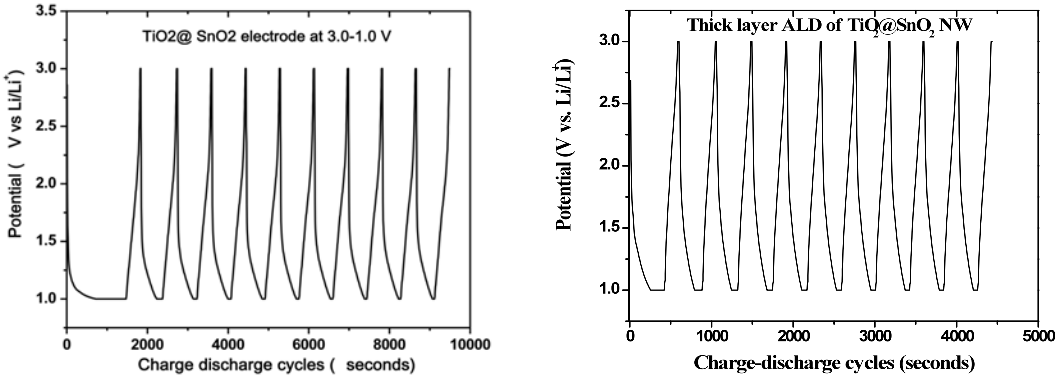


Figure 7. (a) The charge/discharge capacities with times vs. voltage profiles of thin layer ALD of $TiO_2@SnO_2$ electrode at 3.0-1.0 V. (b). The charge/discharge capacities with times vs. voltage profiles of thick layer ALD of $TiO_2@SnO_2$ electrode at 3.0-1.0 V.

A number of titania and hydrogen titanate NW based materials developed by the startup AdEM were also tested as part of the NSF SBIR Phase I support. Figure 8(a) shows the charge/discharge curves of $H_2Ti_3O_7$ electrode in the voltage range of 1.0 – 3.0 V with current of 10 mA/g. It shows an initial discharge capacity of 110 mAh/g during the first cycle. However, further charge/discharge measurement shows the decrease in discharge capacity of 80 mAh/g during the second cycle. The discharge plateau was flat at 1.6-1.5 V, which was comparable to other reports of TiO_2. Figure 8(b) shows the comparison of capacity vs. cycle number of of $H_2Ti_3O_7$ electrode in the voltage 1.0 – 3.0 V with current of 10 mA/g. It has an initial discharge capacity of 110 mAh/g during the first cycle. However, charge/discharge measurement shows the decrease in discharge capacity. After 50 cycles, it still retains the capacity of 60 mAh/g.

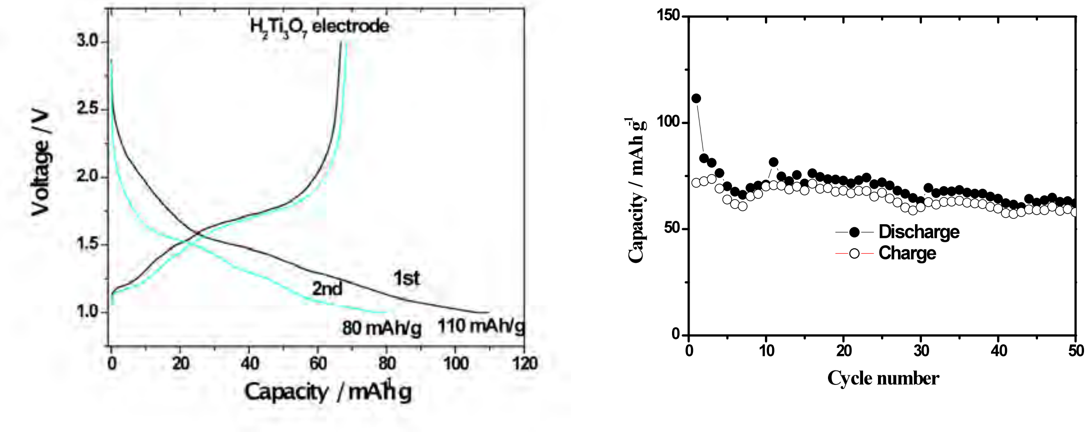


Figure 8. (a) Charge/discharge curves of $H_2Ti_3O_7$ electrode in the voltage range of 1.0 – 3.0 V with current of 10 mA/g. (b) Capacity vs. cycle numbers of $H_2Ti_3O_7$ electrode in the voltage 1.0 – 3.0 V with current of 10 mA/g.

2.2 Task 2 – Roll-to-roll (R2R) manufacturing R&D initiative for low cost solar cells

The R2R manufacturing technique involves depositing several layers and patterning of materials on long sheets of plastics or metal foils using ink or powder dispersions or chemicals. Active layers comprised of inorganic materials, organic molecules, or their mixtures will be deposited using various deposition equipment in a continuous fashion. In addition to continuous processing, batch processing equipment will also be made available for researchers to optimize or screen materials quickly.

One of the challenges in R2R processing for low cost solar cells occurs with the use of vacuum-deposited Indium Tin Oxide (ITO) or Fluorine-doped Tin Oxide (FTO) for transparent, conductive oxide coatings. There is an urgent need to develop alternative materials to ITO as well as alternate processing schemes for integration into a R2R facility. This is one of our objectives for this project.

2.2.1 Inkjet Facility (D. Amos)

We acquired Inkjet printing research equipment as the startup research lab facilities for newly recruited chemical engineering professor, Dr. Delaina Amos. Dr. Amos worked for thirteen years at Kodak research after her PhD in chemical engineering at University of California, Berkeley. She is planning to develop a research program on inkjet printing, production of QDOT dispersions, organic-inorganic assemblies, and polymer electrolytes toward low cost solar cells and light emitting diode technologies. Much of her work will be integrated into R2R manufacturing R&D on various renewable energy and energy efficiency technologies.

2.2.2 R2R (T. Druffel)

Significant Accomplishments:

- Hired a senior research engineer, Thad Druffel, PhD, PE to lead the R2R manufacturing initiative for low cost solar cells. Dr. Druffel is a talented engineer with 15+ years experience in industry as mechanical engineer and five years as research engineer after obtaining a PhD in chemical engineering with patents in optical thin film technologies using nanoparticle assemblies.

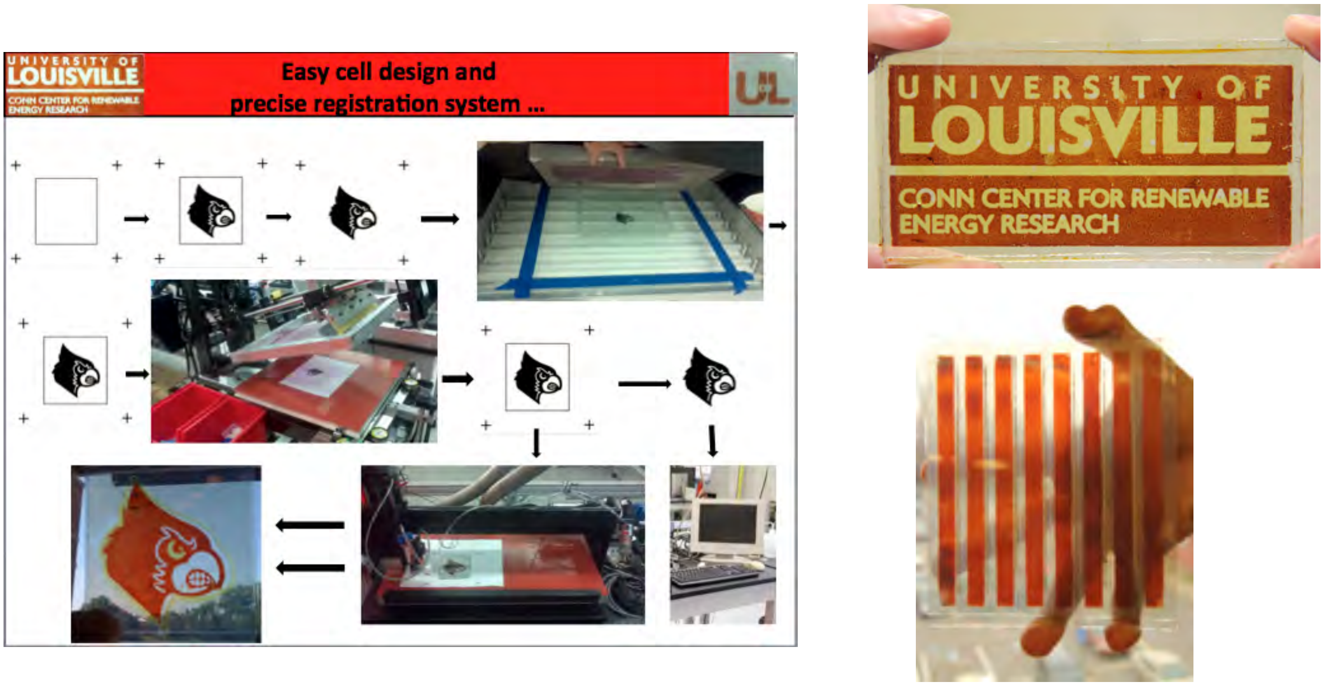
- An existing lab space (1000 sq ft) was renovated and includes two fume hoods, overhead power (single phase 120, 240 and three phase 208), overhead air, water and gas ports and exhaust connections.
- Three thin film manufacturing lines have been implemented into the lab 1) static, 2) intermediate and 3) roll-to-roll. These lines will allow the deposition of thin films over a wide range of areas using scalable near-atmospheric techniques. The lab is also capable of a number of converting processes to manufacture thin film devices such as photovoltaics, electrochromics and batteries. The roll-to-roll equipment was designed by the senior research engineer and built using a local original equipment manufacturer.
- The above equipment has been used to manufacture Dye Sensitized Solar Cells (DSCs) with a maximum efficiency of 9.2%. This equipment has been used to study:
    - area dependence of DSCs
    - formulations for inkjet DSCs
    - near-atmospheric processing of DSCs
    - increased durability using a silane blocking layer
    - durability of scalable seals for DSCs
    - nanocomposite DSC anodes
    - alternative redox shuttles for DSCs
    - NWs as a scattering layer
    - aqueous DSC anode formulations
- Support of ½ effort from a post-doctoral assistant
- Support of 1 co-op student toward solar cell manufacturing for three semesters.

In this initiative, we established manufacturing R&D facilities that can be used initially for low cost solar cells and extended for various other technologies (e.g., electrochromic windows). Toward the initial objective, we have acquired three separate manufacturing lines 1) static, 2) intermediate and 3) roll-to-roll. The facility is capable of numerous near-atmospheric thin film deposition and processing techniques as well converting processes for manufacturing complete devices.

1- Static Manufacturing Facility

The static manufacturing line enables researchers with limited materials or experience with PV manufacturing to create cells at their own pace using small amounts of materials. This line has been designed for DSC manufacturing and is installed and completely documented. Examples of cells and the workflow are shown in Figure 9.

Figure 9. Demonstration of DSC devices built on the static line (A&B) and work flow (C).



Easy cell design and precise registration system ...

2- Intermediate Manufacturing

The intermediate manufacturing line is designed to bridge the gap between the static line and the roll-to-roll line. This line maintains the discrete processing of the static line, but is accomplished using the in-line processing available in the roll-to-roll. The line utilizes conveyors and linear platforms fitted with vacuum tables to move coupons discretely through a process. This is shown schematically in Figure 10, below.

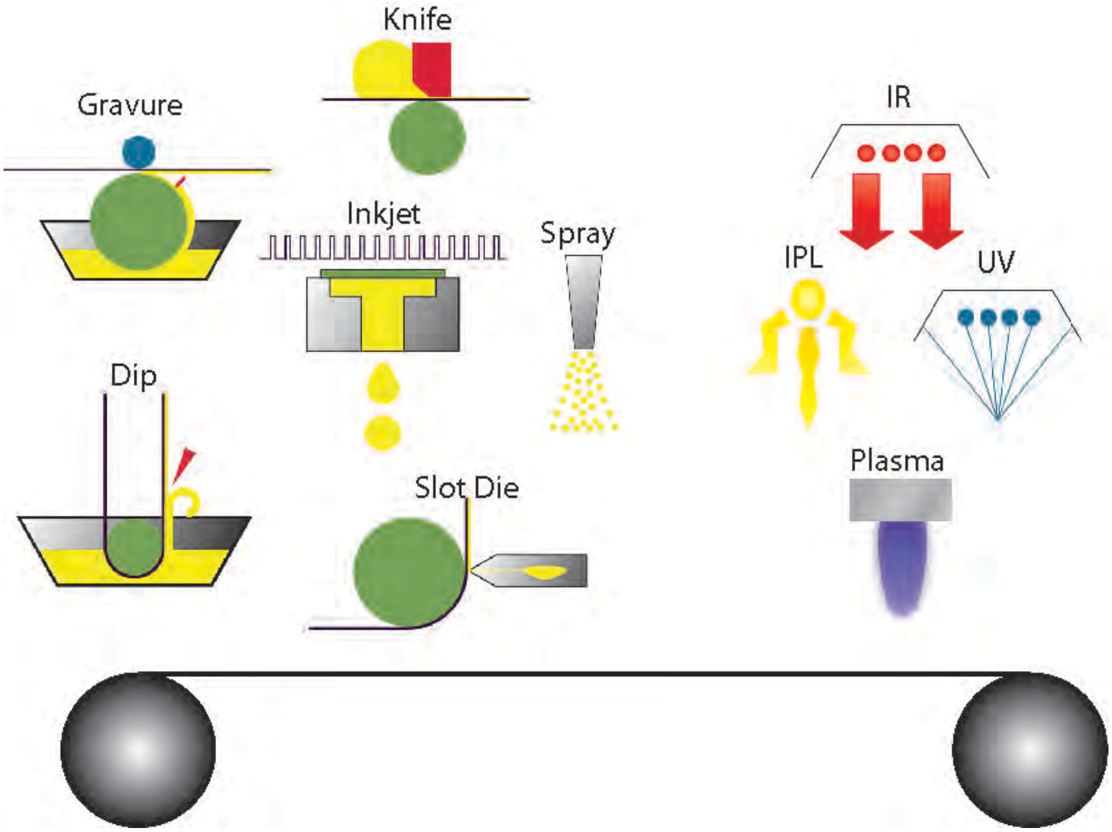


Figure 10. Processes in place for the intermediate line, which also can be fitted onto the roll-to-roll line.

Module	**Supplier**
Enclosure	Craig Machinery (CM)
Unwind/Rewind	CM, Industrial Belting and Technology (IBT) (Mitsubishi HF-KP23)
Idler rollers	CM (Bluegrass Rollers)
Controls	IBT (Mitsubishi FX)
Ink Jet	Dimatix Spectra
Spray	EFD/Nordson 787MS-SS
UV	Fusion UV F3002
Slot Die	Premier Dies (CM) VersaDie
Gravure	CM, Southern Graphics Systems
Ultrasonic Spray	SonoTek Widetrack
Dip	CM
Electrodeposition	CM
IR	DRI RA089-165A-24
Atm Plasma	Plamax 150S
Intense Pulsed Light	Xenon Corporation Sinteron 2000

Table 1. Available R2R capabilities, including suppliers.

3- Roll-to-roll Manufacturing

The roll-to-roll manufacturing line was established to study continuous manufacturing of PV utilizing several in-line processes (Figure 11). The design concept of this particular piece of equipment is modularity and includes a framework of rails that are completely enclosed in a HEPA environment. Each process is a distinct package that can be fitted anywhere on the rails. See Appendix B for the “Thin Film Roll-to-Roll Deposition Equipment at the Conn Center Solar Manufacturing R&D Laboratory” booklet.

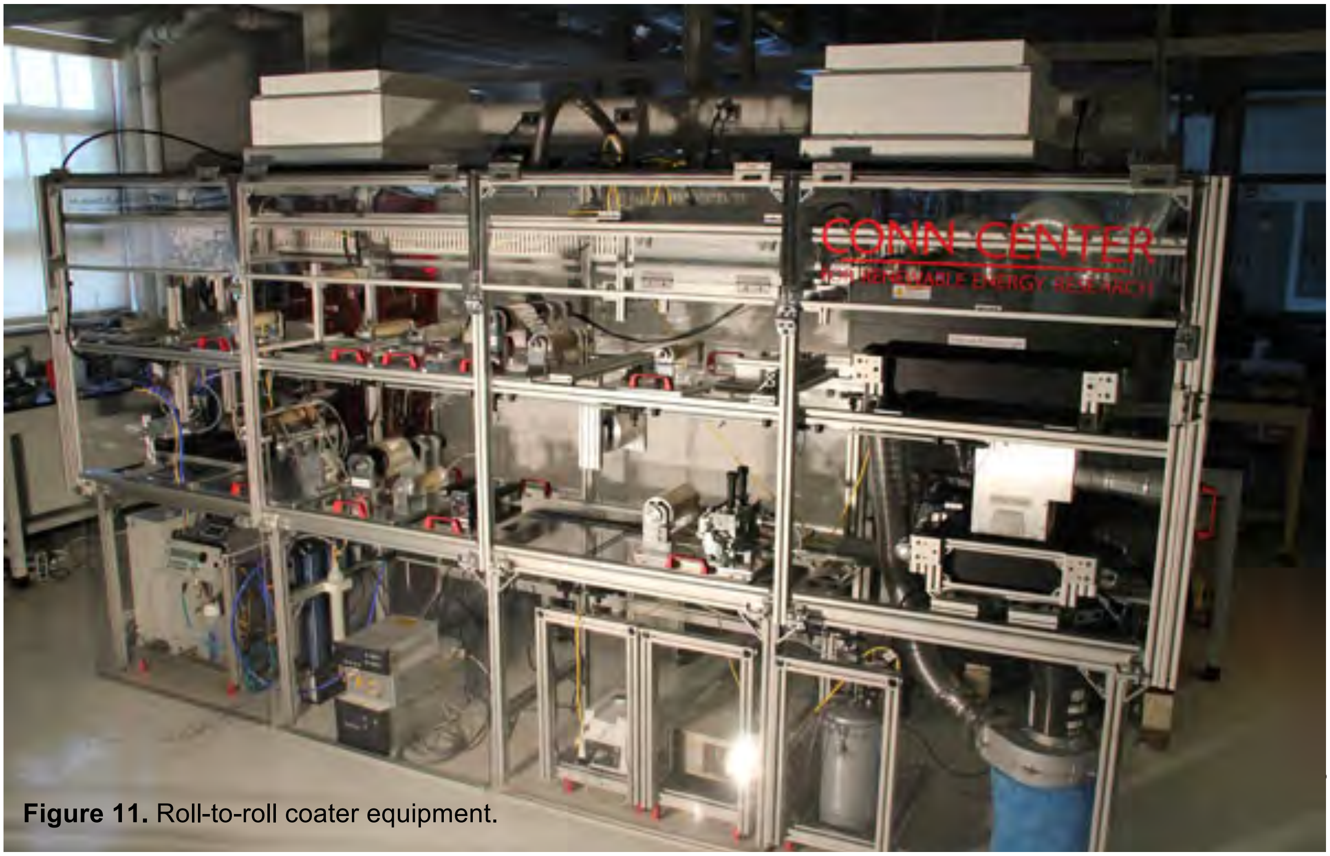


Figure 11. Roll-to-roll coater equipment.

A major issue with the DSC technology is the durability of the device that is closely tied to a polymer seal that must contain a liquid electrolyte. The most commonly used sealant is surlyn made by Dupont, which is a thermoplastic and requires a thermal treatment to complete the seal. We have been interested in replacing the thermal seal with a UV curable or epoxy type. These sealing methods are simpler to scale and are applied as a liquid. The initial testing shows that the UV and epoxy cured seals are stable for over two months, and compares well with the surlyn seal and outperforms a commercially available UV curable sealant (Figure 12).

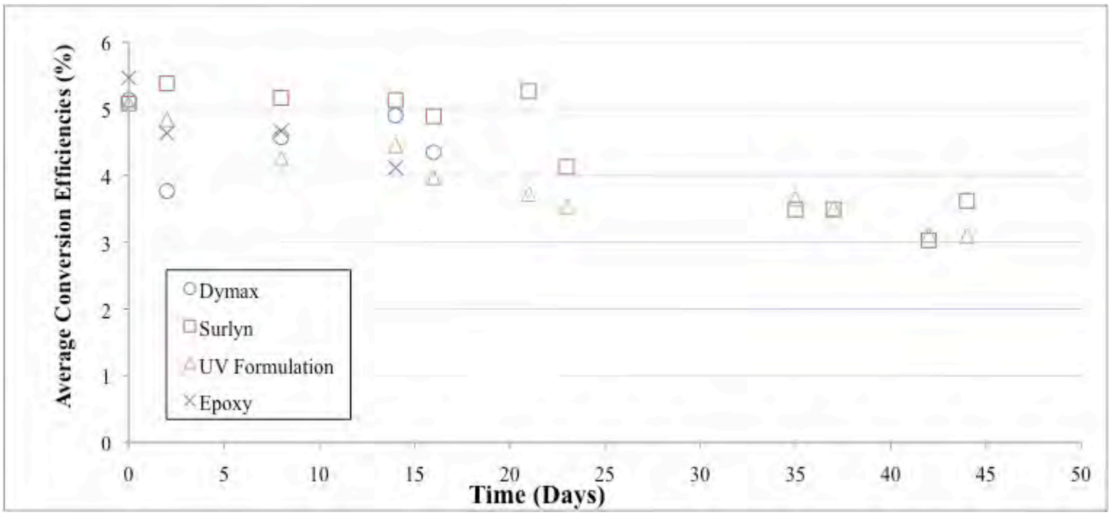


Figure 12. Performance of seals for DSC

An objective of the manufacturing laboratory is to determine the area-dependant performance of a DSC. It was noted that as the area of a DSC was reduced to below 0.1 cm^2, the efficiency rose drastically (Figure 13). Venkat Vendra along with Drs. Druffel and Sunkara studied this phenomenon using standard tools as well as time resolved photo-spectrophotometry. The study also included the use of NWs. The results have been published by *The Journal of the Electrochemical Society*.

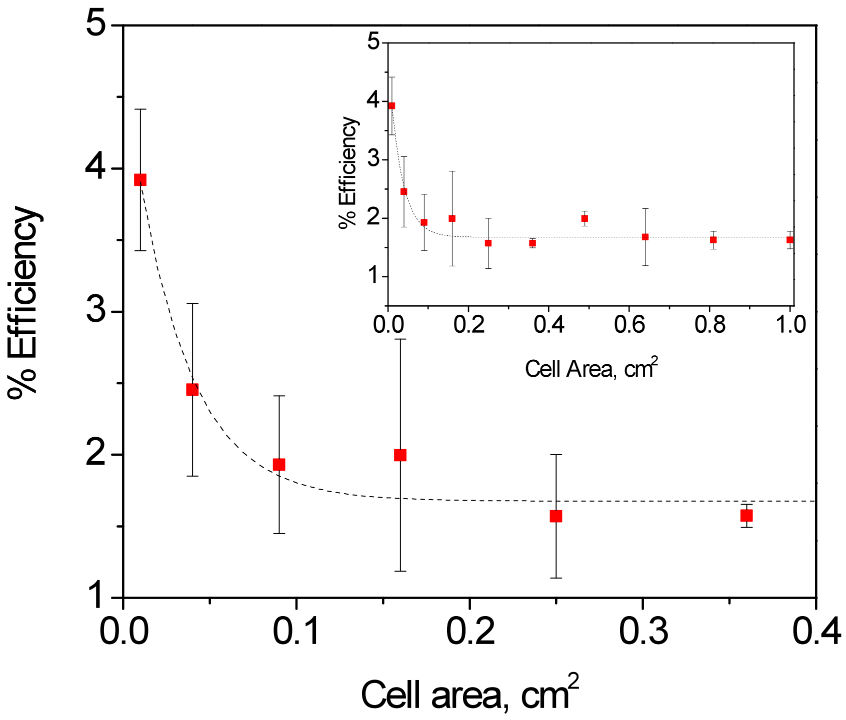


Figure 13. Efficiency of a DSC as a function of active area.

Work has been initiated into developing a low temperature sintering system for the DSCs utilizing UV radiation and intense pulsed light (IPL). In the first experiment, a solution of TiO_2 NPs (Degusa P25), titanium bis (ammonium lactacto) dihydroxide (TALH) (Sigma Aldrich), a small amount of surfactant to improve wetting Triton-X (Sigma Aldrich) and water was applied to a glass slide using a knife coating method. This coating, at approximately 10 mm thick, was then subjected to a single UV-vis light pulse using a Xenon Corp Sinteron 2000 set at 3800 Volts, 830 Joules. The SEM image of the coating after the processing indicates that there is some sintering of the TiO_2 NPs and a mesoporous film is observed (Figure 14a). These experiments were performed at Xenon Corp, and no attempt was made to optimize the process.

In the second experiment, the coating was subjected to UV using a mercury vapor source built by the CCRER for varying lengths of time. The Fourier transform (FT)IR spectra of each of the durations was recorded to determine the efficacy of the UV and TiO_2 in breaking down of the organics (Figure 14b), in which the peaks at 1114 and 1051 cm^{-1} (methyl group skeletal vibration) are decreasing in intensity with prolonged UV exposure. The film, subjected to a 10 min exposure, was then prepared into a working DSSC and resulted in a V_{oc} of 0.55 V, J_{sc} of 3.8 mA/cm^2, and an h of 1.3% (Figure 14c). This work was then extended to include $Sn0_2$ NWs, which should reduce the recombination losses, and was subjected to thermal sintering, UV radiation and oxygen plasma. Initial results show that this concept is feasible; however, work needs to be done to establish the correct formulation and process parameters.

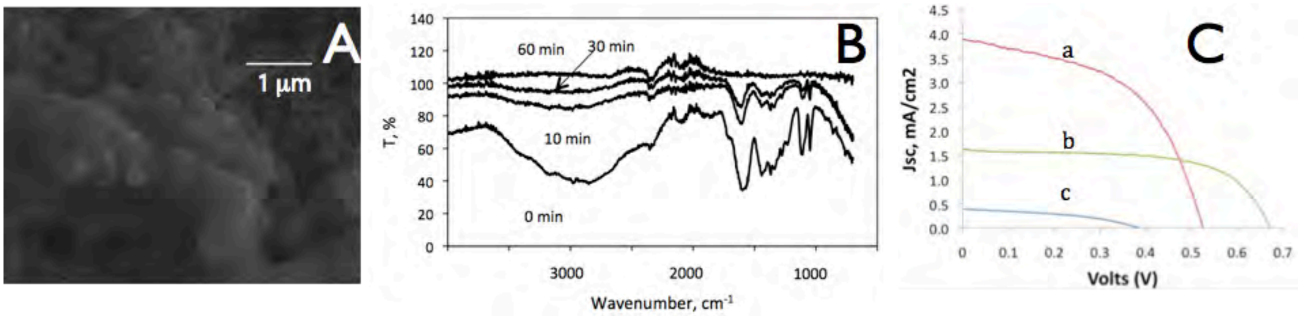


Figure 14. A) SEM of an IPL sintered nanocomposite, B) FTIR of a UV treated TiO_2 film and C) performance curves of a thermally sintered DSC (a), an IPL sintered DSC (C) and a hybrid SnO_2/TiO_2 DSC (c).

Work continues on the Intense Light Pulse (IPL) sintering of a TiO_2 nanocomposite thin film for a DSC. Initial work has shown that a DSC can be fabricated using the IPL process; however, the performance of the cell remains low (~1%). During this period, we have concentrated on working with different number of pulses and the formulation of the paste. These results are shown in Figure 15. These cells have also been treated in an atmospheric plasma, which improves the functioning of the cell. There remains some confusion over the roll of the IPL and the atmospheric plasma.

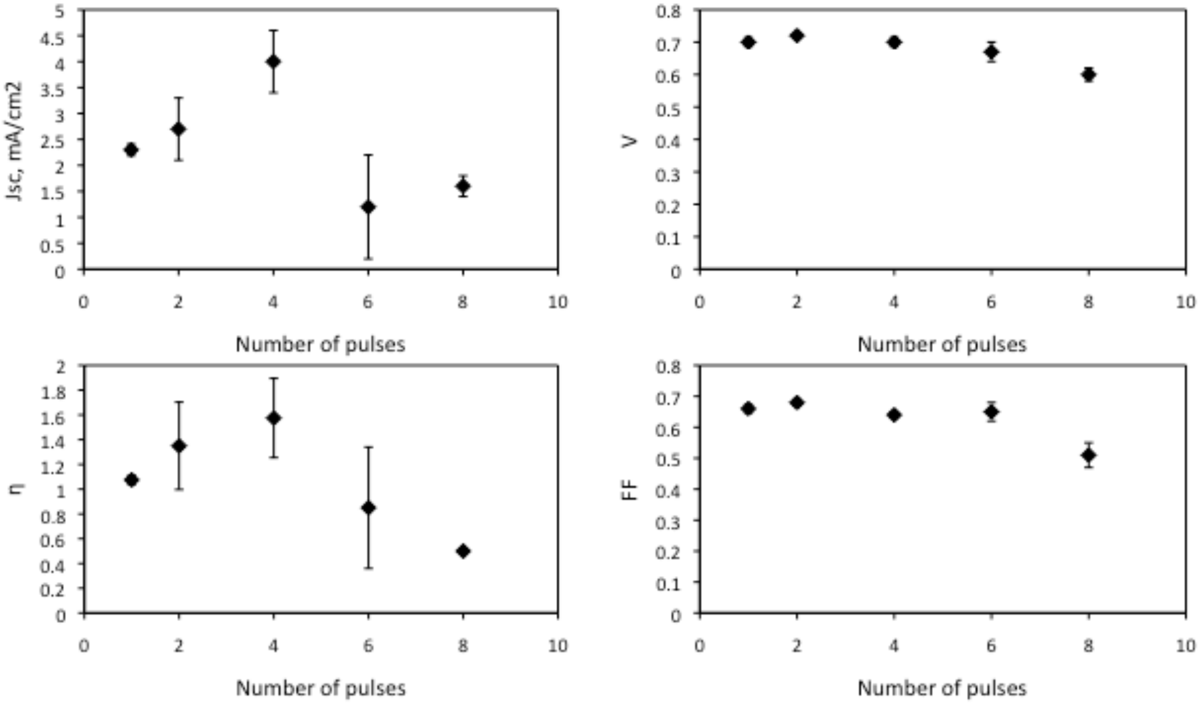


Figure 15. Performance of DSC photoanodes processed with IPL.

A series of DSCs were prepared using paste with molar ratio of titania powder (P25) to Titanium(IV) bis(ammonium lactato)dihydroxideTALH ranging from 0 to 10:1. The Current-voltage characteristics of single layer DSCs fabricated from TiO2 formulations with varying TALH concentrations are shown in Figure 16 and summarized in Table 2. The DSCs assembled without TALH exhibit a short-circuit current density (Jsc) of 10.8 mA/cm2, an open circuit voltage (Voc) of 0.71V, a fill factor (FF) of 0.63, and an overall conversion efficiency (η) of 4.8%. These results are consistent with the previously reported performance of a DSC made with a binder-free H2O/t-butanol formulation. As the TALH concentration in the aqueous P25 formulation was increased, the Jsc, Voc and η increased until a maximum was reached at 0.33 molar (M). At this optimum concentration, a Jsc of 16.64 mA/cm2, Voc of 0.74 V, FF of 0.66 and η of 8.1% were observed. Further increase in TALH concentrations resulted in lower performance reducing both the Voc and Jsc. A complete DSC prepared with blocking and scattering layers sandwiching the active layer prepared using the optimized formulation resulted in a high efficiency of 9.2%. This is similar to efficiency obtained by Ito et al. who prepared P25 nanoparticle films by a long processing method using organic solvents and a polymeric binder.

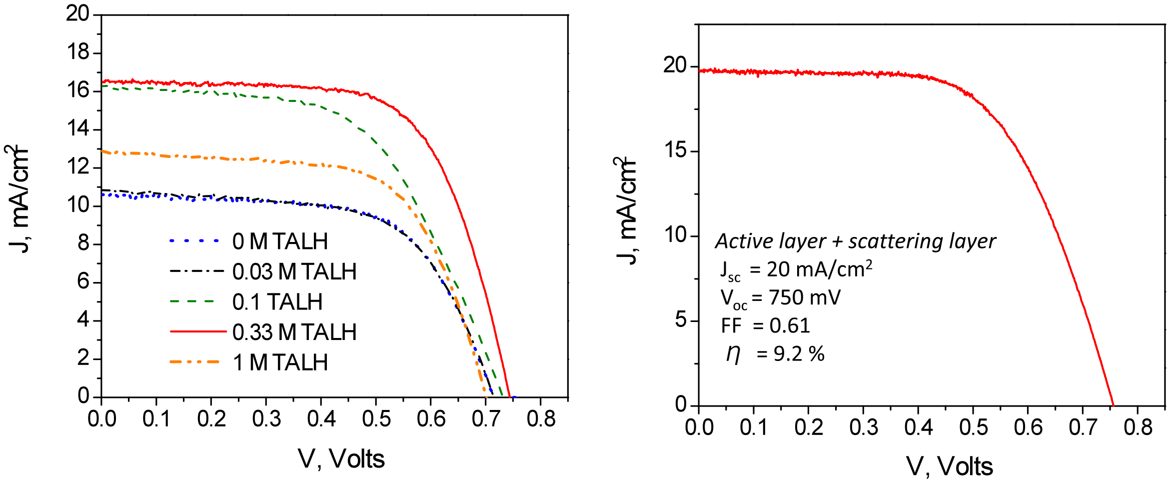


Figure 16.

Table 2.

Concentration of TALH, M	J_{sc}, mA/cm^2	V_{oc}, V	FF	η, %	Average thickness, µm
0	10.8	0.71	0.63	4.8	12.0±4.1
0.033 (10:0.1)	10.9	0.71	0.61	4.8	11.7±3.3
0.1 (10:0.33)	16.4	0.73	0.56	6.7	13.1±2.5
0.33 (10:1)	16.64	0.74	0.66	8.1	11.9±1.8
1.0 (10:3)	13	0.7	0.64	5.8	10.2±1.6

2.3 Task 3 – Process R&D for conversion of KY biomass to transportation fuels.

We proposed to establish process R&D aligned with the Commonwealth of KY's future goals in technology development for biomass conversion. In this project period, senior personnel assisted in identifying the target biomass, defining the corresponding technology routes, and working towards enabling a consortium for technology development and commercialization in collaboration with industry and other academic partners in the region.

Several pieces of equipment were acquired to support fuel characterization efforts, which include freezing point, calorimetric value, density, and viscosity, etc.

2.3.1 Biogas & AD Lab

Further research infrastructure and industrial partnerships were established for processing C5-rich liquors for biofuels/biochemicals as well as waste-to-biogas anaerobic digestion capabilities. We procured and set up batch (Fig. 17) and continuous (Fig. 18) anaerobic digestion systems to be able to generate the needed rate, performance, and biogas generation data. This equipment is housed in a dedicated biomass and biofuels pilot plant located on UofL campus. The pilot area has 700 square feet floor space with 25' ceiling height. The pilot plant provides us the ability to set up and evaluate different pre and post treatment technologies to AD. The pilot plant has a dedicated lab for any of the related liquid and gas analysis and has access to a state of the art Surface Characterization Facility.

Figure 17. 1 Liter Batch Anaerobic Respirometry Reactor

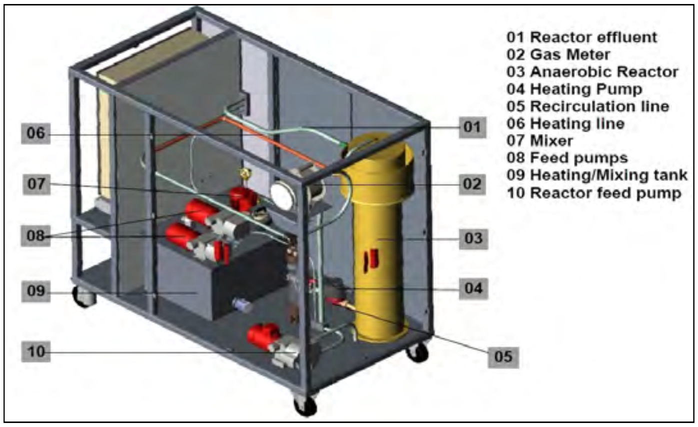


Figure 18. 60 Liter Continuous Up-flow AD Reactor

The equipment has helped us conduct process development work as well as undergraduate and graduate research work. We tested with industrial wastewaters from four industry partners. These industry partners represent an industrial soy protein company, a distillery, an oat bran processor, and a toll ethanol processor – all based in Louisville. The tests generated batch and continuous data. We conducted batch AD testing using a RSA unit and continuous AD testing in a pilot upflow AD reactor (60 L volume). The batch and continuous testing allowed us to determine the activity variation in the biomass for various industrial streams; any toxicity resulting from the composition in the waste water to biomass; as well as the amount and quality of generated biogas. Such data will help us design robust systems for AD and biogas cleanup. Based on the promise of the preliminary data, we secured a gift of $200K from one of our industry partners in support and continuation of our biomass research work.

2.3.2 Biofuels/KY DEDI

In addition to the DOE funding, the effort in this task was primarily funded by a grant from the Commonwealth of Kentucky Energy and Environment Cabinet Department for Energy Development and Independence (DEDI) through its energy commercialization grant program. The Conn Center specifically proposed four projects to develop technologies that will enable commercialization of KY's abundant but untapped resources such as non-food biomass, natural gas, and carbon dioxide. All of these resources have the potential to be developed for creating positive economic impact and, most importantly, in reducing carbon dioxide and other emissions. Commercialization of any of these resources depends critically upon the availability of cost-effective and scalable technologies and their demonstration at a scale that is attractive for commercial entities. Specifically, a novel, continuous technology for converting any type of lipid-based biomass resource into hydrocarbons or jet fuel was identified and licensed to AliphaJet, LLC.

The final report for this program, “Technologies for commercialization of biofuels, natural gas, and carbon dioxide (4 projects)” is included in Appendix C.

2.4 Task 4 – Applied R&D studies in various renewable energy and energy efficiency themes.

One of the most important goals of this project (besides improving the infrastructure through personnel and facilities development within Conn Center at UofL) is to engage faculty and their students to work along with Conn Center personnel to advance manufacturing R&D in renewables and energy efficiency. Toward this objective, various projects were undertaken in which graduate students and their mentors along with Center personnel worked together in the following areas: biomass conversion; hydrokinetics; solar conversion of fuels; new materials design and development for Li-ion batteries; and energy efficient building research themes.

We initiated several projects with topics ranging from windmill design, phase change materials, solar fuels, Li-ion battery materials, lithium-air battery catalysts, and solar cells. PhD and M.Eng students were recruited for working on these projects. The students were encouraged to produce manuscripts based on results obtained and their funding has been transitioned to other sources of support to continue with their dissertation research.

2.4.1 Table 3. Applied R&D studies of Task 4.

Student Name(s)	Faculty Mentor(s)	Title
Absher, Jason	Sunkara	Mass Production of Nanowires
Garciduenas, Maria de Lourdes Carreon	Sunkara	Nanowires with Si/Ge Interfaces
Ellis, Sam	Druffel	Dye Sensitized Solar Cells
Ench, Michael	Park	A Novel Approach Using Honeycomb Structures Solid Oxide Fuel Cells Fueled by Biomass
Fernando, Kasun; Stallard, Robert	Sumana-sekera, Druffel, Sunkara	Use of Graphene as conducting transparent electrodes in Dye sensitized solar cells.
Gandara, Amelia	Amos	Ink Analysis for Renewable Energy Applications
Kiesel, Jeffrey; DeRoche, Roy	McGinley	Phase Change Materials in Concrete Masonry Units for Improved Energy Efficiency
King, Kelsey	McGinley, Druffel	Solar Decathlon Initiative
Kolli, Sowmya	Sunkara, Alphenaar	Fundamental studies of light absorption in vertical nanowire arrays
Masitas, Raphael	Zamborini	Ag nanoparticles attached to ITO as an electrocatalyst for oxygen reduction reaction
Miranda, Stephen; Dorsey, Tyler; & Kurtz, Kevin	McGinley, Druffel	UofL Solar Decathlon Initiative
Shah, Hemant	Alphenaar	Organic Bulk Heterojunction Solar Cells
Sherehiy, Andriy	Sumanasekera; Cohn; Sunkara	Thermionic Energy Conversion using doped-diamond tipped conical carbon nanotubes
Sunkara, Swathi	Sunkara	Conversion of Carbon Dioxide into fuels using renewable energy sources
Vendra, Venkat	Sunkara, Amos, Druffel	Photoanode area dependent efficiency and recombination in dye-sensitized solar cells
Chen, Yan	Lian	Numerical Simulation of an H-rotor
Young, Caitlin	Amos	Inkjet Printing for Quantum Dot Hybrid Light Emitting Diodes

2.4.2 Follow on progress (highlight)

The results of these research projects were multi-fold. Students were able to prepare and submit manuscripts for publication, which are detailed in Section 3.1, and were invited to present their research in a number of locally supported forums. These included poster sessions at the 2011 Kentucky RE3 Workshop (Section 2.5.1.) and 2010 and 2011 Conn Center Technical Advisory Board meetings, as well as oral presentations in a special session seminar course in Fall of 2011 and at the 2012 Conn Center Technical Advisory Board meeting. These opportunities were designed to push these students to hone their written, verbal, and poster presentations of research methods and contributions, which is not practiced in the academic curriculum.

2.5 Task 5 – Educational and workshop initiatives

In this task, we orchestrated a number of educational and outreach activities to enable students, engage the community, and increase the visibility of the Conn Center.

Significant Accomplishments

- Developed and delivered the 2011 Kentucky Workshop on Renewable Energy and Energy Efficiency and made all presentations available online at http://conncenter.org/energy-education/workshops/.
- Developed and held the Mickey R. Wilhelm Solar Flight Competition in 2011 and 2012.
- Supported the development of a successful Solar Decathlon 2013 Competition proposal.
- Delivered two courses on Renewable Energy Challenges.
- Formed “Renewable Energy & Energy Efficiency (RE3) Club”, a registered student organization, at UofL.

2.5.1. 2011 Kentucky Workshop on Renewable Energy and Energy Efficiency

The Kentucky Statewide Workshop on Renewable Energy & Energy Efficiency, held March 13-15 in downtown Louisville, KY, brought together top minds currently focused on research and policy for solar energy, biofuels, advanced energy materials, energy efficiency, and energy storage. About 200-250 people from throughout the state participated in the two-day event, consisting of engaging lecture presentations, industry exhibit booths, a student research poster competition, and a panel discussion on commercialization challenges for KY. The student poster competition attracted about 60 posters. Of these, a total of six winners were chosen by a multi-institutional faculty jury.

Dr. James Ramsey, UofL President, Dr. Len Peters, Kentucky Cabinet Secretary for Energy, and Mr. Gil Sperling, Senior Advisor for the US DOE Office of Energy Efficiency and Renewable Energy, opened the conference by highlighting the university, state, and federal commitments to support renewable energy and energy efficiency research. Their remarks reinforced the need for diversification and innovation in energy resources, and set a positive tone for the work in progress at institutions and businesses across the state. An international cadre of 23 speakers presented the latest in research findings, policy developments, and technology successes from numerous national and university labs, federal programs, and industries.

This workshop was organized by the Conn Center of Renewable Energy Research at the UofL in partnership with the Center for Applied Energy Research at the University of Kentucky; the Center for Renewable and Alternative Fuel Technologies at Eastern Kentucky University; the Commonwealth of Kentucky Department of Energy Development and Independence; faculty members from Kentucky State, Murray State, Western Kentucky, and Northern Kentucky

Universities; and representatives from Sud-Chemie Inc., LG&E, Owensboro Grain, and Svaya Nanotechnologies. Over $40K was raised from sponsorships for conducting the workshop. The workshop presentations and support materials are now available online at **http://conncenter.org/energy-education/workshops/.**

Figure 19. Dr. Ed Etzkorn from the Solar Energy Technologies Program of the Dept. of Energy's Office of Energy Efficiency & Renewable Energy (EERE) gives a talk during the 2011 Kentucky Workshop on Renewable Energy and Energy Efficiency in Louisville, KY.

2.5.2. Mickey R. Wilhelm Solar Flight Competition

We developed and initiated a solar flight competition for students and faculty mentors in Speed School of Engineering at UofL in 2011 and held the competition in 2011 and 2012. Teams were challenged to design and build variations on solar powered aircraft, either from scratch or through modifications to off the shelf radio-controlled units, and to display their solutions and posters as part of the Speed School's Engineering Expo held in March. In both 2011 and 2012, the final flight competitions were held in April in the UofL Papa John Cardinal Stadium. Through this competition, our objective has been to encourage involvement of undergraduate students in

Figure 20. Students fly a scratch-built, solar powered zeppelin during the 2011 MRW Solar Flight Competition.

renewable energy-related projects and the Conn Center-related activities, create a hands-on experience that is inclusive of all engineering students, and host a fun, highly visible activity associated with the Conn Center as a publicity vehicle.

We enabled four teams/year with $400 seed money each toward the expense of aircraft, solar panels, and specialty materials. Prizes were $300 for first place, $200 for second place, and $100 for third place. All four teams submitted scientific posters to the Conn Center that explained their aircraft and design concepts, which are currently on display in the Speed School of Engineering's Duthie Center. Preparations have already begun for the 2013 competition.

Figure 21. Top three finishing teams from the 2012 MRW Solar Flight Competition.

2.5.3. Solar Decathlon 2013 Competition proposal

The Conn Center enabled the final push for the Kentuckiana Solar Decathlon Team to create a proposal for the 2013 Solar Decathlon Competition, which was submitted for consideration in October and <u>selected</u> for competition! The faculty mentor, students, and collaborators have begun the design process and execution of early stage deliverables. Conn Center research scientist and Solar Manufacturing R&D theme leader Thad Druffel has participated as a collaborator to advise on the solar energy conversion aspects of the house. Conn Center Assistant Director Andrew Marsh has also enabled the team's communication deliverables by facilitating the selection press release announcement nationwide, and advising and hosting a branding competition and team web site development.

EXHIBITS FOR
CAPITAL EDUCATION CENTER

- Conn Center delivered four exhibits on behalf of our school.
- Involved students as part of the course on "renewable energy challenges" over summer. Special thanks to Ms. Jael Harrington of Louisville Science Center.
- About 5000 4-6 grade students visit the center per year.

Figure 22. Exhibits for Capital Education Center.

The Conn Center has begun to raise financial support through large industrial partners that are interested in various renewable energy and energy efficiency technologies. These industries include, but are not limited to: General Electric, Louisville Gas & Electric, Sud Chemie (now Clarient), Yum! Brands, the Ford Motor Company, UPS, and many other medium and smaller scale companies. See Appendix C. for the 2-page brochure for "Team Kentuckiana: Solar Decathlon 2013, Low-cost Permanent Housing Solution for Disaster Relief."

2.5.4. Renewable Energy Challenges courses

PI (Sunkara) along with several faculty colleagues taught a graduate level course on the science and engineering aspects of various renewable energy and energy efficiency technologies to address grand energy challenges. The courses were offered during Summer 2011 and Summer 2012 semesters. As part of the 2011 course, the students were asked to participate in a solar car competition. The 2012 students were mentored to develop a series of scientific exhibits that are housed in the capital education center next to the state capital building in Frankfort, KY. This center is an initiative of Kentucky First Lady Jane Bershear and is expected to host approximately 5000 4th-6th grade students per year. (Fig. 22)

2.5.5. Renewable Energy & Energy Efficiency (RE3) Club

We formed a registered student organization at UofL to promote and educate on renewable energy & energy efficiency themes, coordinate lecture series on renewables & sustainability, build relationships across campus, and serve as a conduit for demonstration & outreach activities related to renewable energy & energy efficiency on campus and in the community. This club holds monthly meetings and conducted workshop sessions for solar cell fabrication. The RE3 Club undertook and completed a campus project to fabricate and install a solar cell for powering a circulation fan on the campus greenhouse.

Figure 23. Students and faculty gather for the RE3 Club Solar Cookout.

3.0 Outcomes

3.1 Publications

1. M. Zhu, S.R. Venna, S. Li, M.A. Carreon, Knudsen Diffusion through ZIF-8 Membranes Synthesized by Secondary Seeded Growth, *J. Mater Science* Under review January **2013**.
2. M. Duke, B. Zhu, C. Doherty, M. Hill, A. Hill, M. A. Carreon, Structural effects on SAPO-34 membranes exposed to seawater solutions, to be submitted, *J. Mater. Chem. (2013)*
3. S. Kolli, C.S. Pendyala, M.K. Sunkara, J. Jasinski and B. Alphenaar, "Thermally Activated Luminescence in InN Nanowires", Submitted to *J. of Luminescence, (2013).*
4. B.K. Abeyweera and B.W. Alphenaar , "Thickness dependent red shift of the photocurrent spectrum in bulk heterojunction solar cells", *Appl. Phys. Lett*., in press.
5. T. Bansal, A.D. Mohite, H.M. Shah, C. Galande, A. Srivastava, J.B. Jasinski, P.M. Ajayan, and B. Alphenaar, "New insights into the density of states of graphene oxide using capacitive photocurrent spectroscopy", *Carbon*, 50 808-812 (2012).
6. H.M. Shah, A.D. Mohite, T. Bansal, and B.W. Alphenaar, 'Photovoltage bleaching in bulk heterojunction solar cells through population of the singlet exciton,' *Appl. Phys. Lett.* 97, 263301 (2010).
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8. Z. Ye and R.E. Berson, "Kinetic Modelling of Cellulose Hydrolysis with First Order Inactivation of Adsorbed Cellulase", *Bioresource Tehcnology*, 102(24),11194-11199 (2011)
9. S. Sunkara, V. K. Vendra, J-H. Kim, T. Druffel, and M. K. Sunkara "Scalable synthesis and photoelectrochemical properties of copper oxide nanowire arrays and films", Catalysis Today, 199, 27-35 (2013).
10. R. Lupitskyy, V.K. Vendra, J. Jasinski, D.A. Amos, M.K. Sunkara, and T. Druffel, "Towards High Efficiency Dye Sensitized Solar Cells with a Photoanode Fabricated Via a Simple Water Based Formulation" has been submitted to Progress in Photovoltaics (2013).
11. V. Kumar, J-H. Kim, J.B. Jasinski, E.L. Clark, and M.K. Sunkara, "Alkali assisted, atmospheric plasma production titania nanowire powders and arrays", Crystal Growth and Design, 11 (7), 2913 (2011).
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13. P. Meduri, E.L. Clark, J-H. Kim, E. Dayalan, G.U. Sumanasekera, and M.K. Sunkara,"MoO_{3-x} nanowire arrays as stable and high capacity anodes for Lithium-Ion Batteries", Nano Lett., 12(4), 1784-1788 (2012).
14. A. K. Thapa, T. H. Shi, S. Ida, G. U. Sumanasekera, M. K. Sunkara, T. Ishihara "Gold-Palladium nanoparticles supported by mesoporous b-MnO2 air electrode for rechargeable Li-Air battery", , J. of Power Sources, 220, 211 (2012)
15. K. W. Adu, M. D. Williams, M. Reber, R. Jayasingha, H. R. Gutierrez, and G. U. Sumanasekera, "Probing Phonons in Nonpolar Semiconducting Nanowires with Raman Spectroscopy", Journal of Nanotechnology, 264198, 18 doi: 10.1155/2012 (Review Article) (2012).
16. A. N. Sidorov, G. W. Sławin´ski, A.H. Jayatissa, F. P. Zamborini, G. U. Sumanasekera, A surface-enhanced Raman spectroscopy study of thin graphene sheets functionalized with gold and silver nanostructures by seed-mediated growth", Carbon, 50, 699 (2012)
17. J. B. Jasinski, S. Dumpala, G. U. Sumanasekera, M. K. Sunkara, and P. J. Ouseph "Observation and interpretation of adjacent Moire patterns of different shapes in bilayer

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19. P. Meduri, H. J.Kim, H. B. Russell, J. Jasinski, G. U. Sumanasekera, M. K. Sunkara, "Thin-Walled Carbon Microtubes as High-Capacity and High-Rate Anodes in Lithium-Ion Batteries, J. of Phys. Chem. C., 114 (23), 10621 (2010)

3.2 Patents & Invention Disclosures

1. P. Ratnasamy and M.A. Carreon, "Catalytic isomerisation of fatty acid esters" US Patent application publication 0295027 A1 (**2011)**. (DEDI)
2. T. Druffel, V.Vendra, R. Lupitskyy, M.Sunkara, "Low Temperature Sintering of Nanocomposites Using Light", Invention disclosure submitted to ULRF Case #10265 (2012). (DOE CDP)
3. M.K. Sunkara and F. Petzold, "Catalyst Compositions and Methods for Desulfurization", US Provisional Patent Application 61671384, 7/13/2012. (CTSA)
4. M.K. Sunkara, V. Kumar, J-H. Kim and E.L. Clark, "Methods for Synthesizing Metal Oxide Nanowires", US Patent Application 13/183,191, Filed 7/14/2011. (CTSA)

Appendix A. “Thin Film Roll-to-Roll Deposition Equipment at the Conn Center Solar Manufacturing R&D Laboratory” booklet.

UNIVERSITY OF LOUISVILLE®

CONN CENTER FOR RENEWABLE ENERGY RESEARCH

Thin Film Roll-to-Roll Deposition Equipment at the Conn Center Solar Manufacturing R&D Laboratory

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7/17/2012

Introduction

The thin film roll-to-roll deposition equipment at the Conn Center Solar Manufacturing R&D Laboratory is intended to aid researchers and companies in developing scalable techniques for the production of renewable energy devices. A variety of thin films up to 15 cm wide can be continuously deposited on flexible substrates via roll-to-roll modular processes. These printing and finishing modules can be configured within the custom designed enclosure to fine tune production schemes.

The Conn Center Solar Manufacturing R&D Laboratory is led by a full time Senior Research Engineer with extensive industry and R&D experience.

This equipment can be useful in numerous ways including:
- Scaling new material depositions
- Advancing lab innovations to pilot scale
- Testing new manufacturing processes at production speed
- Optimizing in-line feedback and quality control
- Manufacturing scaled devices for durability
- Prototyping supporting new venture fund raising

Controls

The Roll-to-Roll equipment is controlled through two Mitsubishi FX3 Programmable Logic Controllers (PLC) using LabView as the human-machine interface (HMI) running on a Windows PC. The PLCs and the PC communicate through an ethernet connection. This enables a simple, familiar, programmable HMI for students and professionals to configure operation. All machine controls are wired through three emergency stops.

FIGURE 2.1 External Control Cabinets

OVERVIEW

1. Unwind/Rewind Programmable Logic Controller (PLC)
2. Process PLC

The two supervisory PLCs communicate over an ethernet connection. The first PLC is fully programmed to control the Mitsubishi servo motors driving the unwind/rewind modules. The second PLC controls the remaining processes and is designed to be programmed by the user for specific functions including timing, fluid delivery and other process and supervisory tasks. The programming can be done through the supervisory PC using Mitsubishi GX Works software. Generic code for this PLC is available for each process.

All outputs from the PLC are tied to the emergency stop.

FIGURE 2.2 Table of control modules in Process PLC

COMPONENT	DESCRIPTION
FX3U-48MT/DSS	24 VDC PLC with 48 digital I/O
FX3U-4AD-ADP	4 Analog Input Module
FX3U-4DA-ADP	4 Analog Output Module
FX3U-20SSC-H	2 Axis Positioning Module
FX3U-Enet	Ethernet Communication
MR-J3W-22B	2 Axis Servo Motor Control

Mitsubishi Process PLC

PLC Cabinet

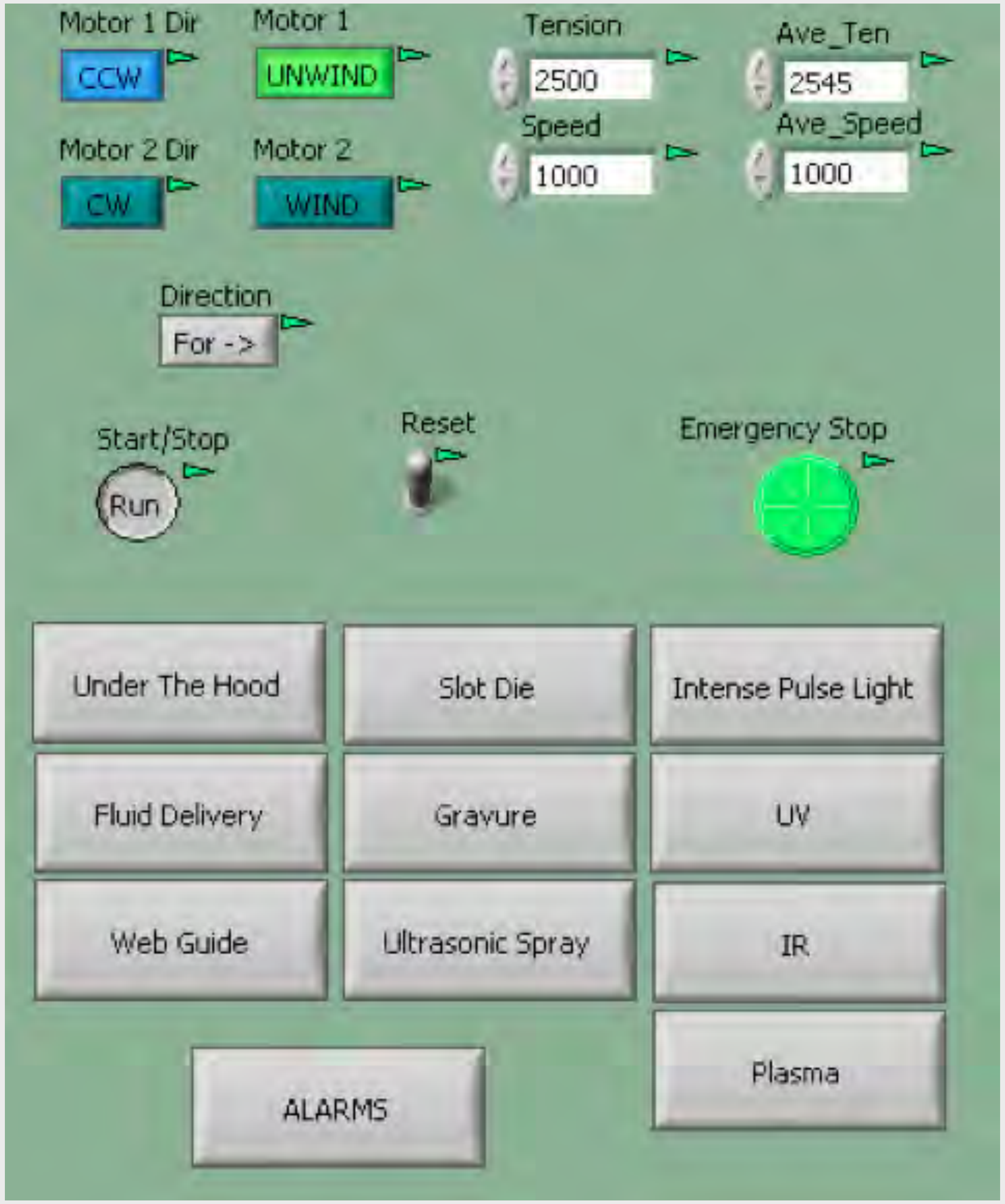
- Input power 240 VAC
- Output 120VAC and 24VDC
- 12-5 pole panel connectors for external modules
- 5 pole 5 meter cord set per connector
- Fused outputs
- Emergency control relay

HUMAN-MACHINE INTERFACE (HMI)

OVERVIEW

The two PLCs communicate to a Windows PC via two ethernet connections. The PC is equipped with National Instruments Labview software and includes an open process control (OPC) server for real time data sharing between the HMI and PLCs. Labview is a widely used tool for data acquisition and control and allows a simple programming environment for researchers. The Mitsubishi PLCs offer numerous communication protocols that could be adapted to other HMI systems provided by an end user.

FIGURE 2.3 Main HMI Screen

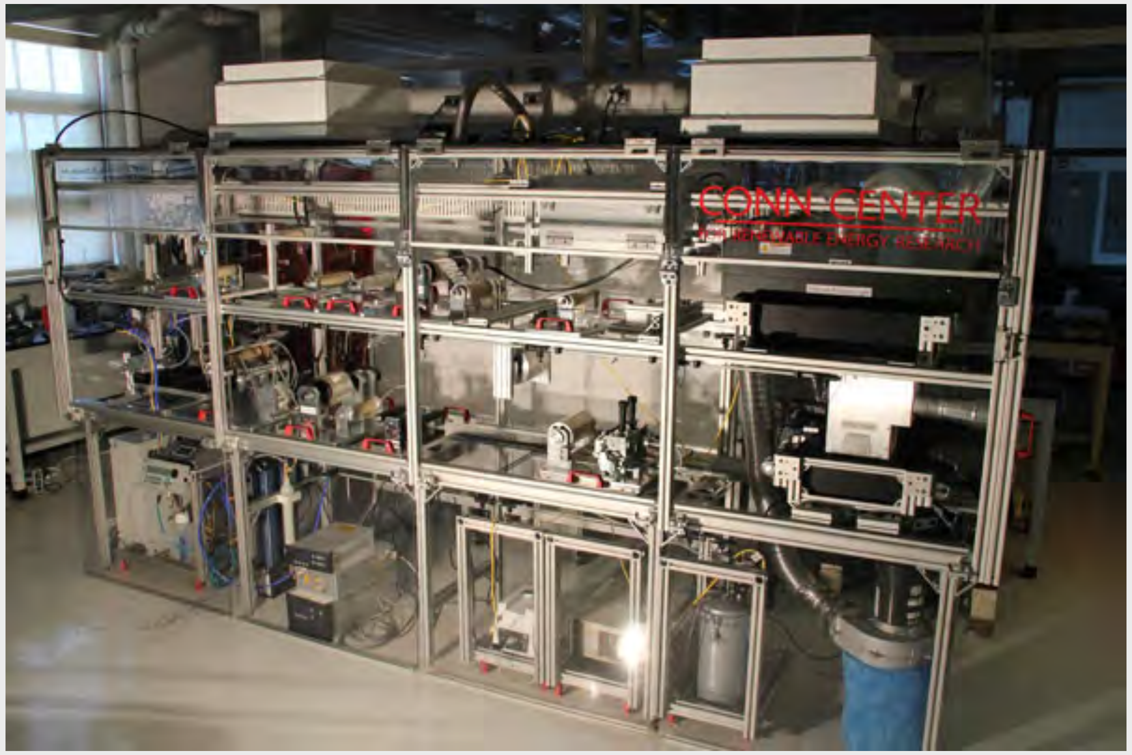


Motor 1 Dir: CCW
Motor 1: UNWIND
Motor 2 Dir: CW
Motor 2: WIND
Tension: 2500
Ave_Ten: 2545
Speed: 1000
Ave_Speed: 1000
Direction: For ->

- Main page control
- Buttons access remaining process control pages
- Completely user configurable
- Allows for simple addition of new control pages

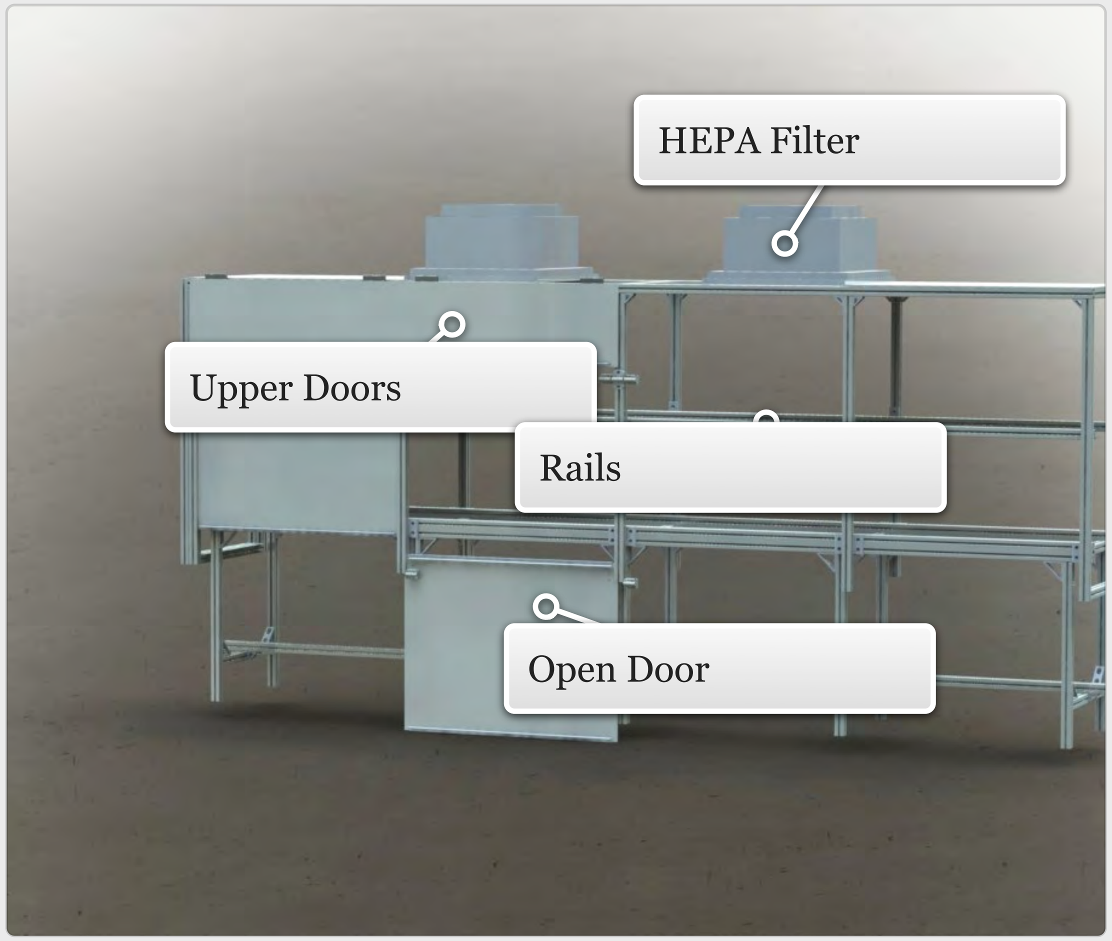
Enclosure

FIGURE 3.1 Enclosure



The equipment enclosure is a sealed HEPA filtered environment with three mounting level rails for flexible module placement. When opened, the side doors allow complete access to the process modules inside. When closed, operators are safely separated from the equipment.

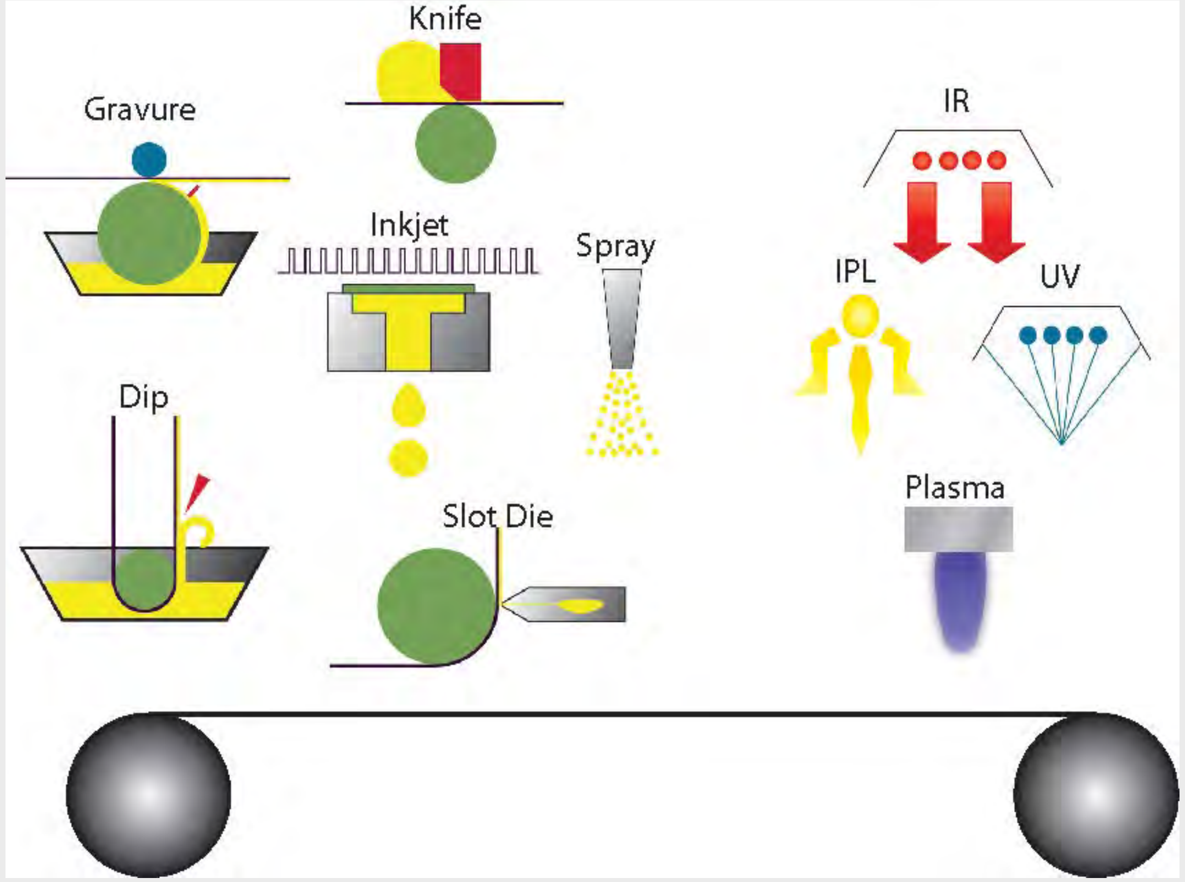
INTERACTIVE 3.1 Features of Enclosure



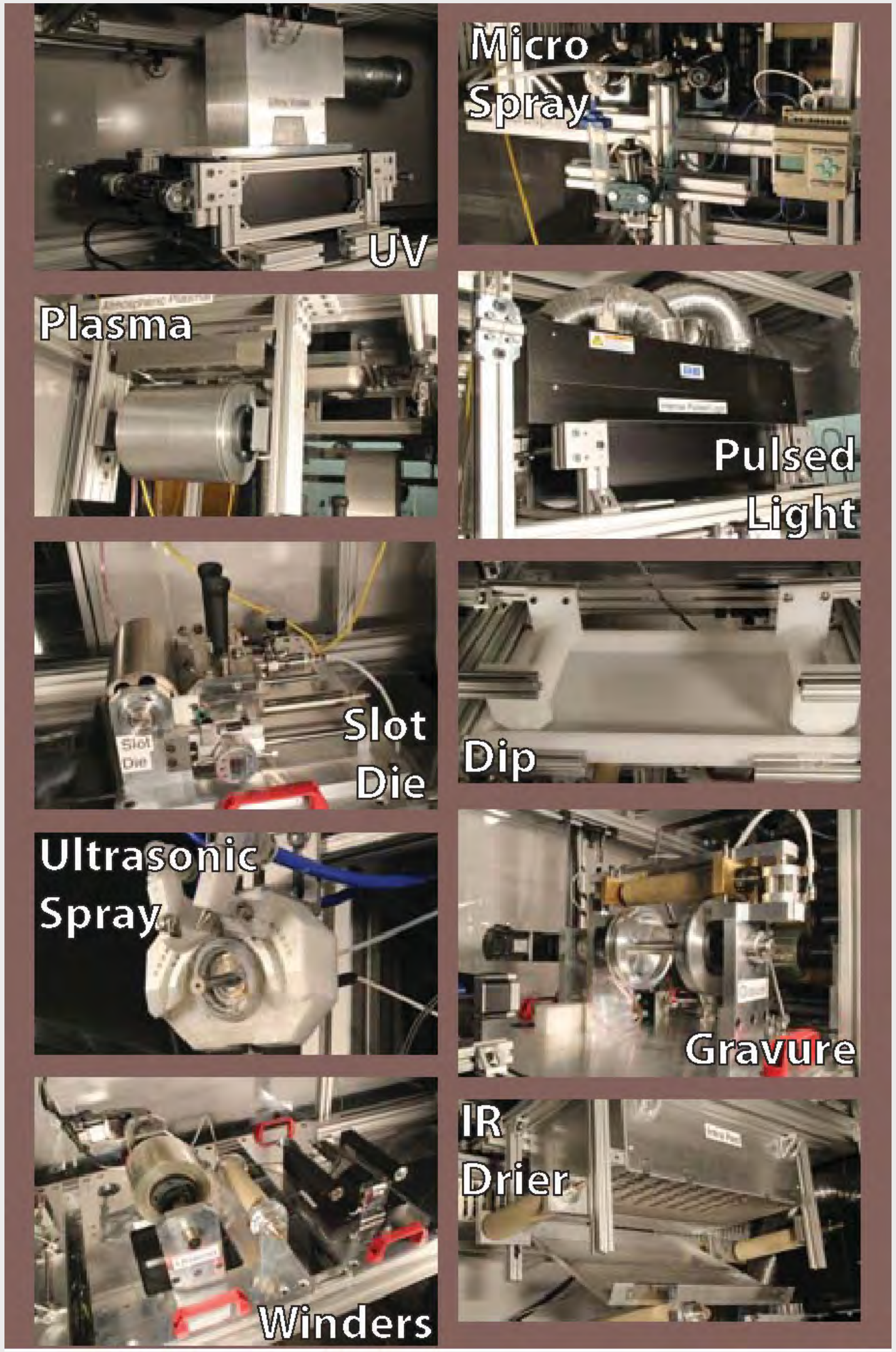
- Built by Craig Machinery and Design
- 3 safety switches
- Sturdy 8020 Aluminum Frame Construction
- 3 levels for module placement
- Over 2.5 cubic meters of HEPA enclosed space for modules
- Main doors slide down providing easy access
- Numatics air drier
- 16 air and 8 vacuum taps inside enclosure
- Ample space under HEPA enclosure for fluid delivery systems
- Data and cables connect modules to external PLCs

Modules

Modular Roll-to-roll setup

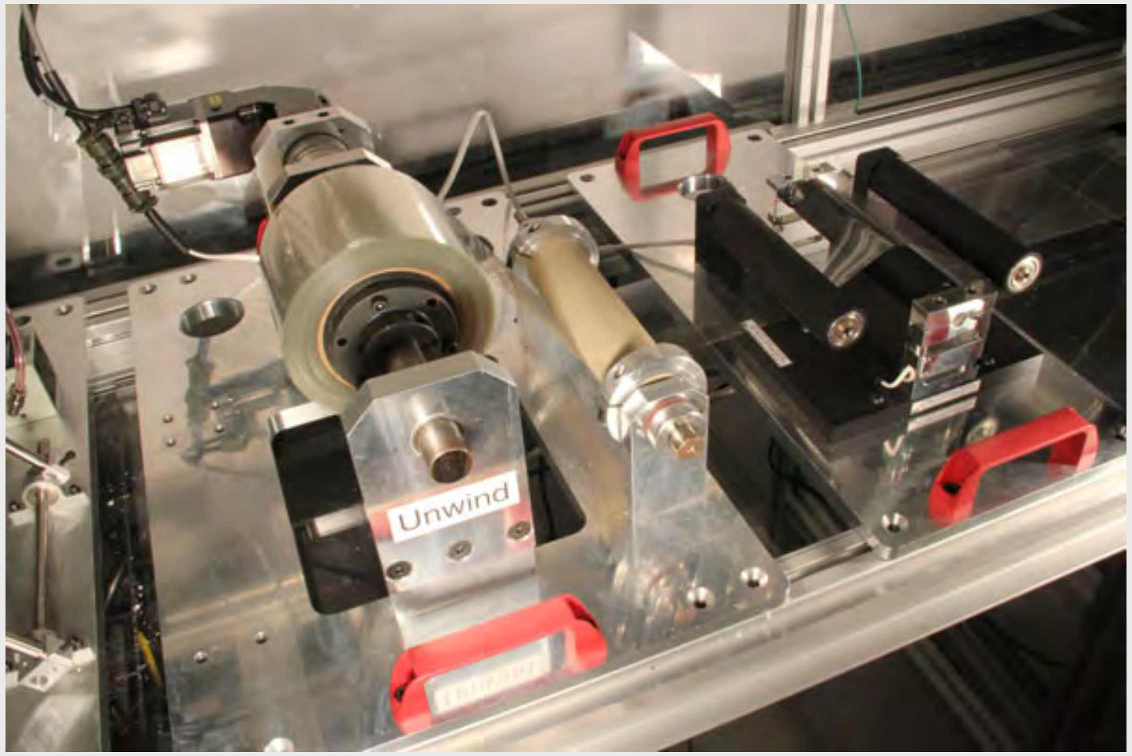


Over ten thin film processing modules are available for discrete operation. These modules can be placed on one of three rails throughout the enclosure for custom work flow configurations. New modules can be added as needed.



UNWIND & REWIND

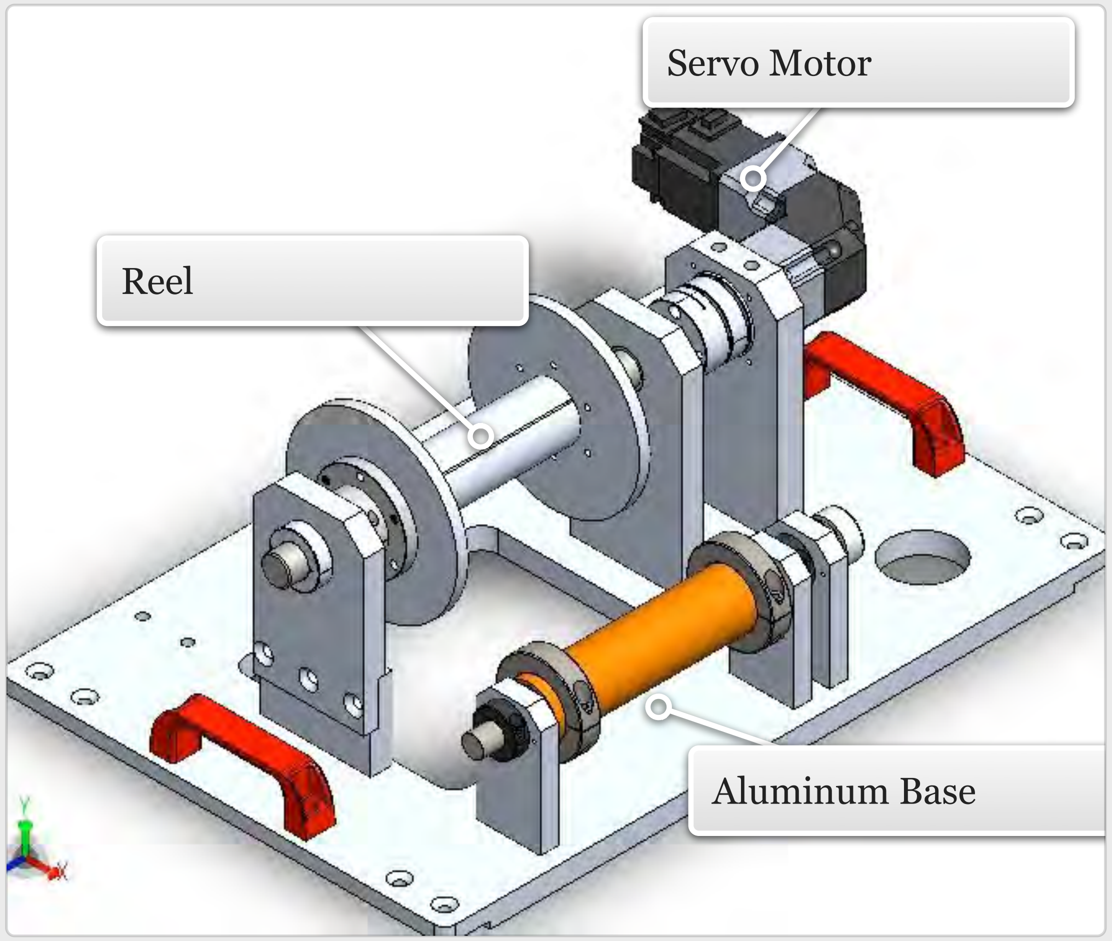
FIGURE 4.1 Unwind and Rewind Modules



SUMMARY

The primary components for the roll-to-roll equipment are the unwind & rewind modules. Each is powered by a 1/4 hP Mitsubishi motor with tension and speed feedback through a Mitsubishi servo motor controller. The equipment can handle a large range of modulus materials (plastics and metals) at speeds from 1 mm/min to 25 m/min at a maximum tension of 10 kg. This equipment is bi-directional with accurate start/stop capabilities.

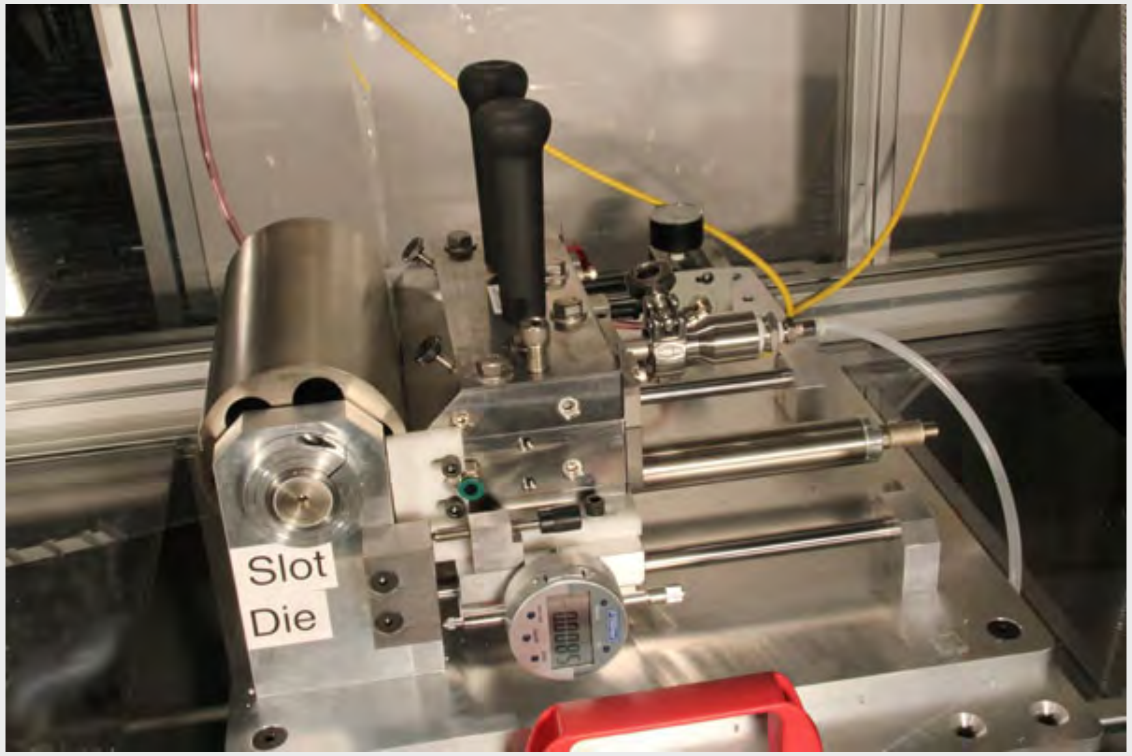
INTERACTIVE 4.1 Unwind/Rewind Assembly



- Two high quality modules (unwind/rewind)
- Each configured with 1/4 hP Mitsubishi Servo Motor
- Speed feedback (1 mm/min - 25 m/min)
- Tension feedback (0 - 10 kg force)
- Smooth bi-directional operation
- Quick start/stop capability
- Mounted onto 1” cast aluminum plate
- Can be mounted to web guide for more accurate positioning
- Configured for 3” and 6” cores

SLOT DIE

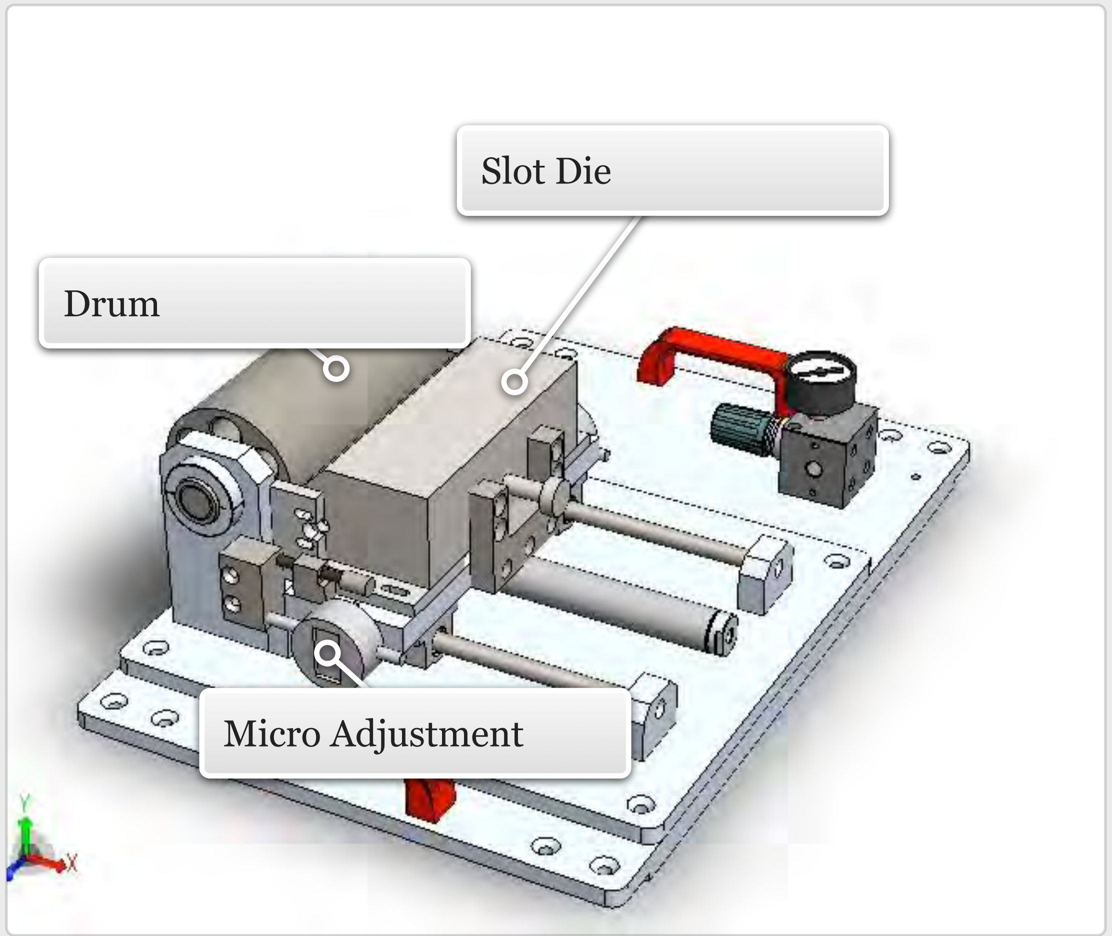
FIGURE 4.2 Slot Die Module



SUMMARY

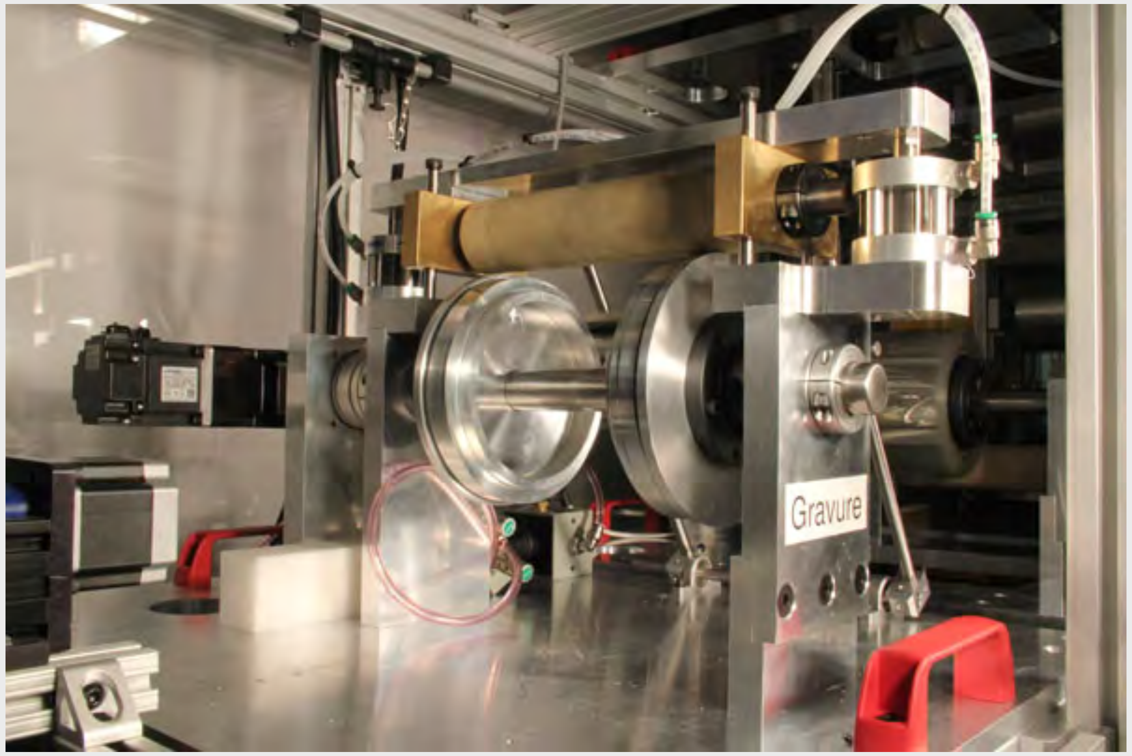
The slot die coating is an efficient and versatile tool for thin film coatings utilized in a wide range of industries including solar and battery production. A wide range of material can be deposited at thicknesses ranging from sub micron to 3 mm at viscosities from 1 to 100,000 cP. The material is supplied using a positive displacement pump. This allows application of high solids films and directly reduces processing time and waste.

INTERACTIVE 4.2 Slot Die Assembly



- Premier Dies Versa Die
- Micro adjustment for accurate positioning
- Can be mounted vertically or horizontally
- 5” diameter nickel plated web drum
- Simple control of slot width and pattern

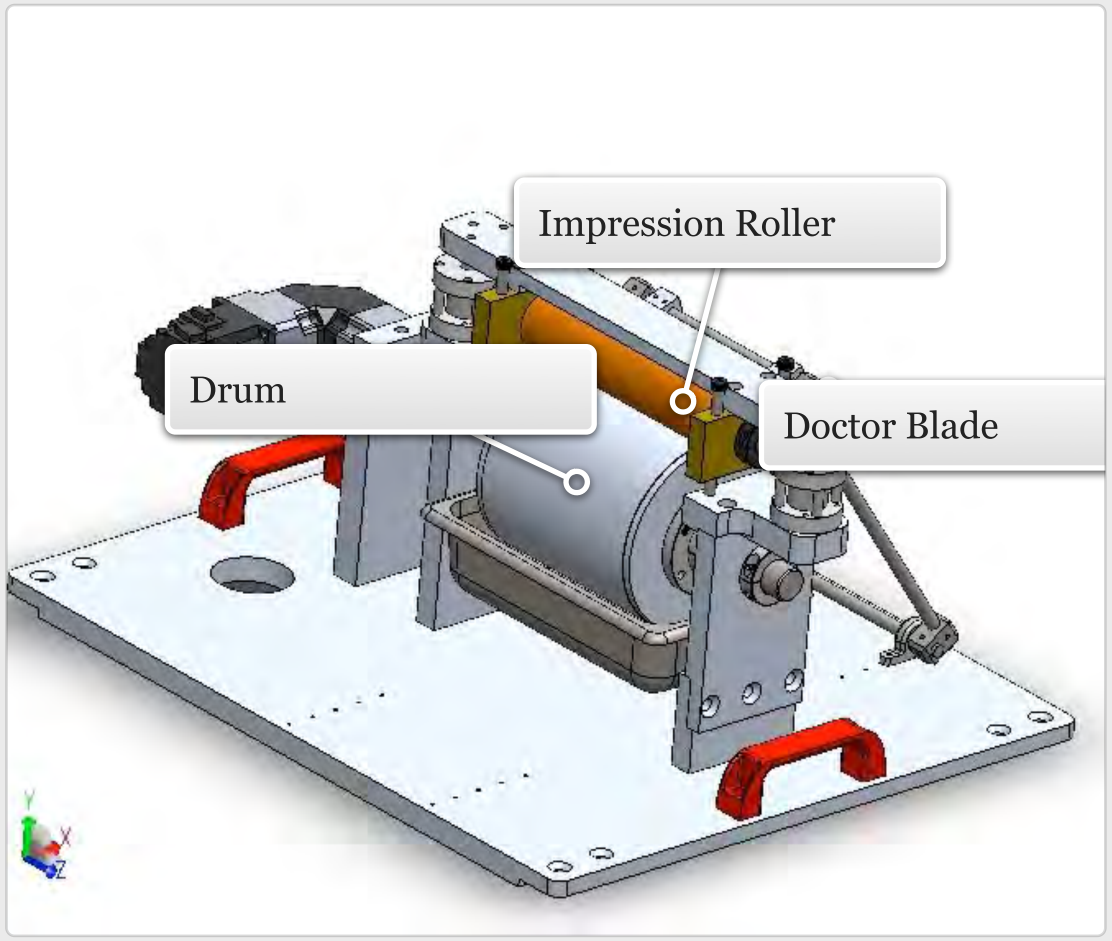
FIGURE 4.3 Gravure Module



SUMMARY

Gravure coating is a simple and versatile technology utilized throughout graphic and electronics printing. Microcells engraved on the printing cylinder deposit high quality patterned thin films repeatedly along a substrate. Printing cylinders can be made to specification. Both solvent and water based coating formulations can be used and the direct application reduces waste.

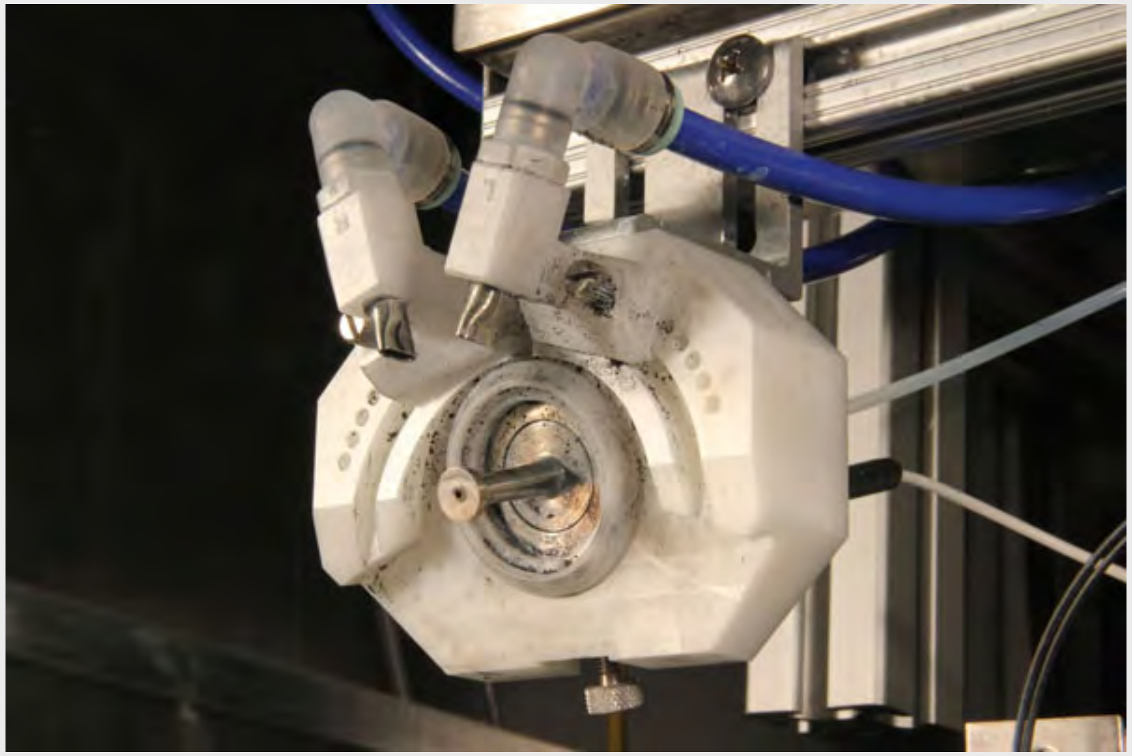
INTERACTIVE 4.3 Gravure Assembly



- Southern Graphics Systems Screens
- Controlled impression roller force up to 150 lb.
- Screen driven by servo motor from 1 mm/min to 25 m/min
- Universal doctor blade holder
- Controlled doctor blade angle
- Simple fluid recirculating reservoir

ULTRASONIC SPRAY

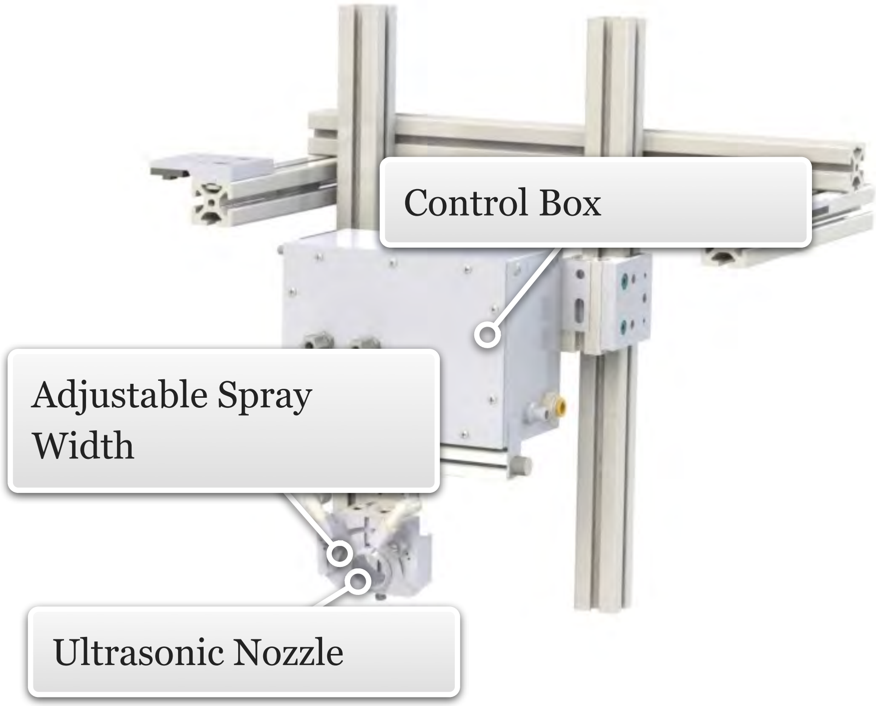
FIGURE 4.4 Ultrasonic Module



SUMMARY

Ultrasonic spray nozzles are quickly replacing existing spray technologies. They produce an extremely fine mist that results in defect-free thin film coatings with applications in electronics, photovoltaics and batteries. These nozzles reduce overspray and the patterning jets allow for fine control of spray width.

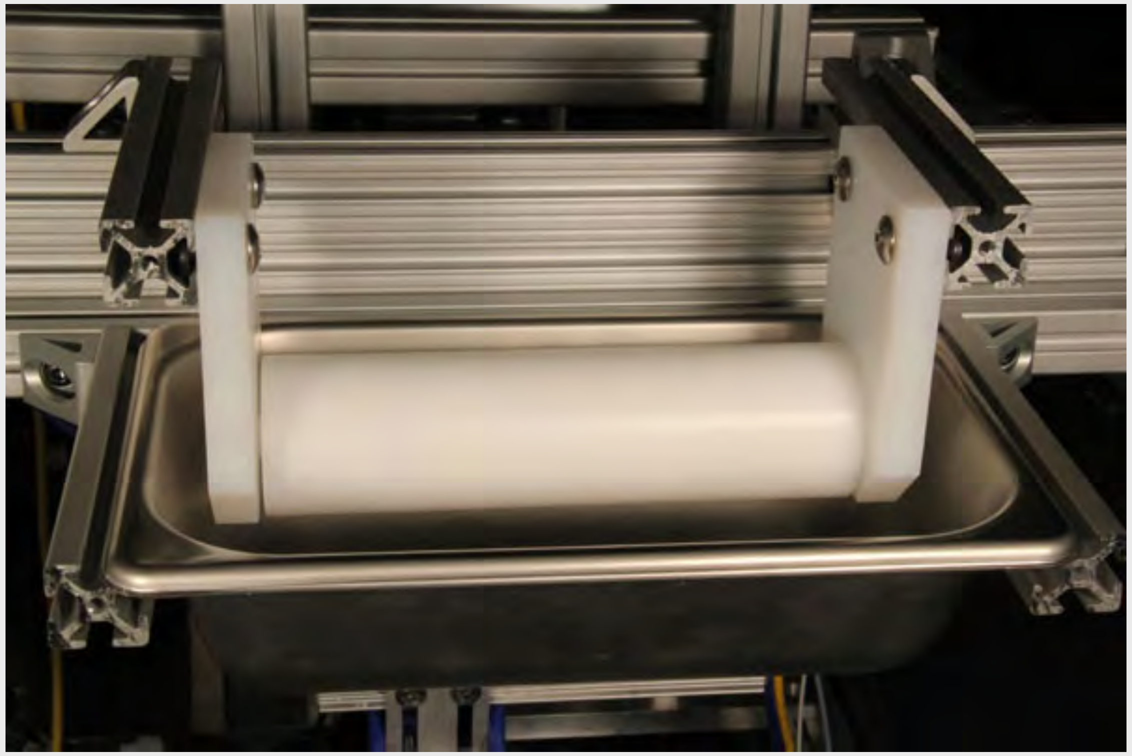
INTERACTIVE 4.4 Ultrasonic Spray Assembly



- SonoTek Widetrack Ultrasonic System
- Two ultrasonic nozzles - 48 and 120 kHz
- Controlled spray width up to 24 inches
- Adjustable spray height
- Positive displacement syringe pump
- Adjustable power and flow rate

DIP

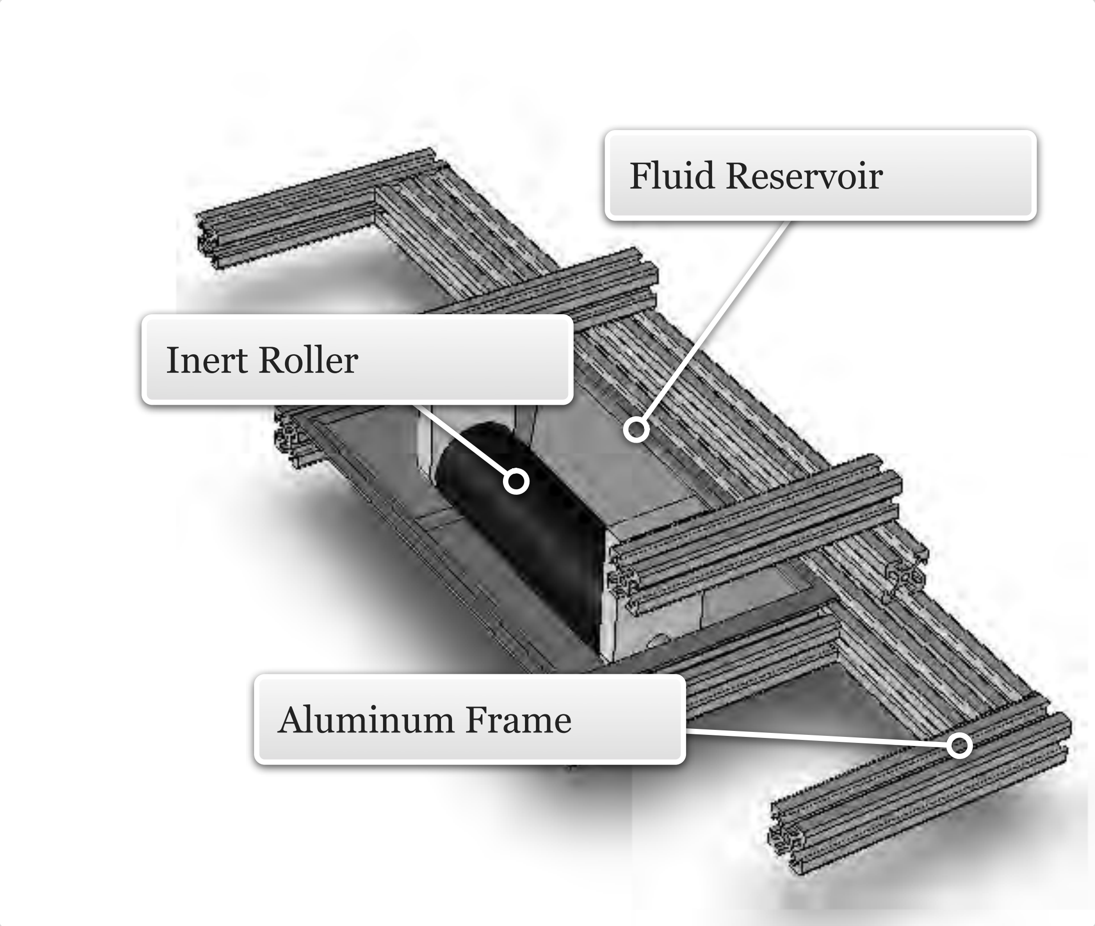
FIGURE 4.5 Dip Module



SUMMARY

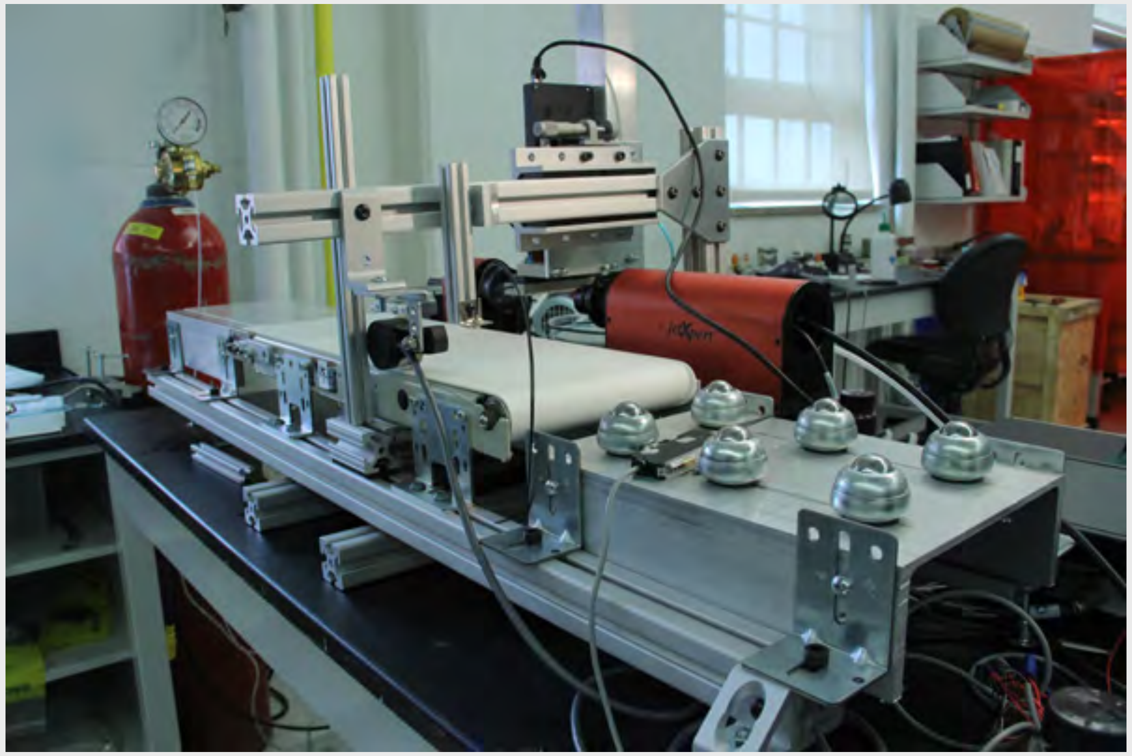
Dip coating is a simple method to clean substrates and apply thin films using evaporation. The process is highly economical and easy to implement for a variety of advanced energy materials. There are four individual dip modules that can be configured linearly for multiple chemistries. These can also be incorporated into an electrodeposition process.

INTERACTIVE 4.5 Dip Coater Assembly



- Chemically inert rollers
- Configurable frame for numerous fluid reservoirs.

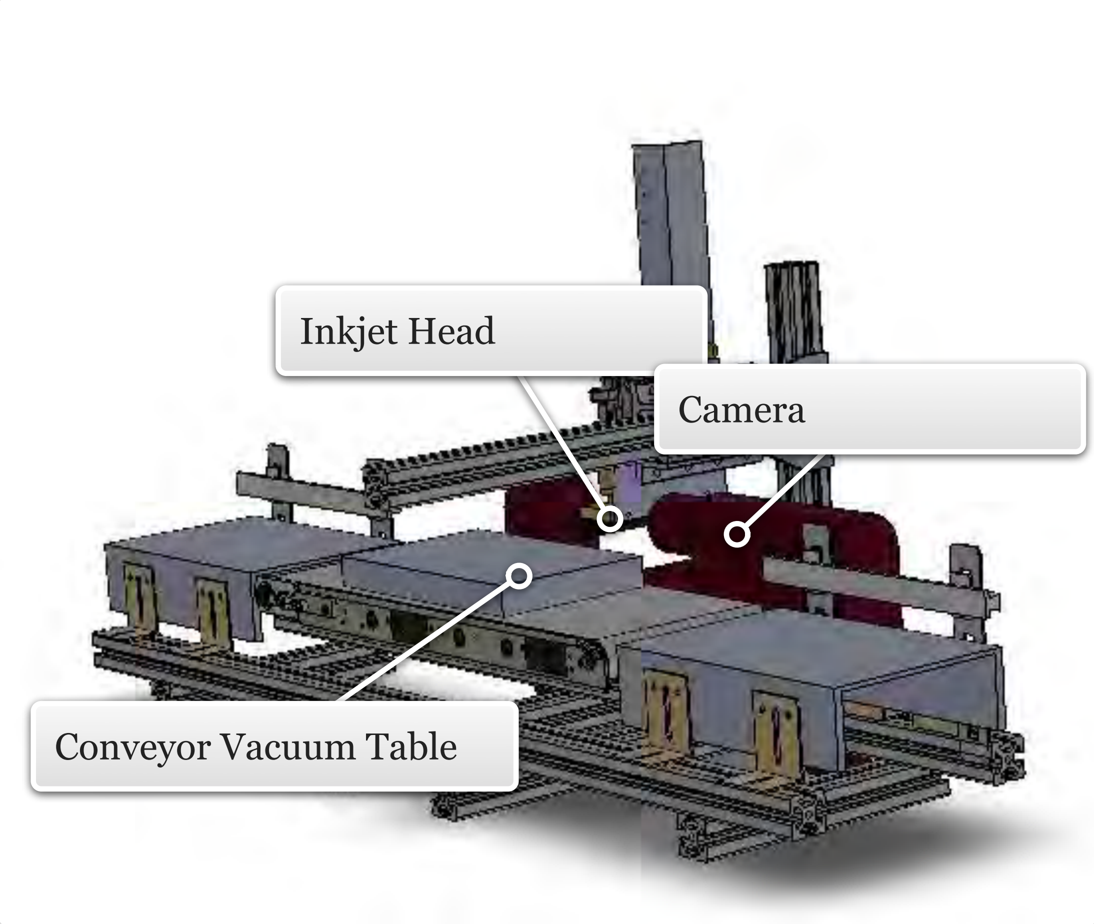
FIGURE 4.6 Inkjet Module



SUMMARY

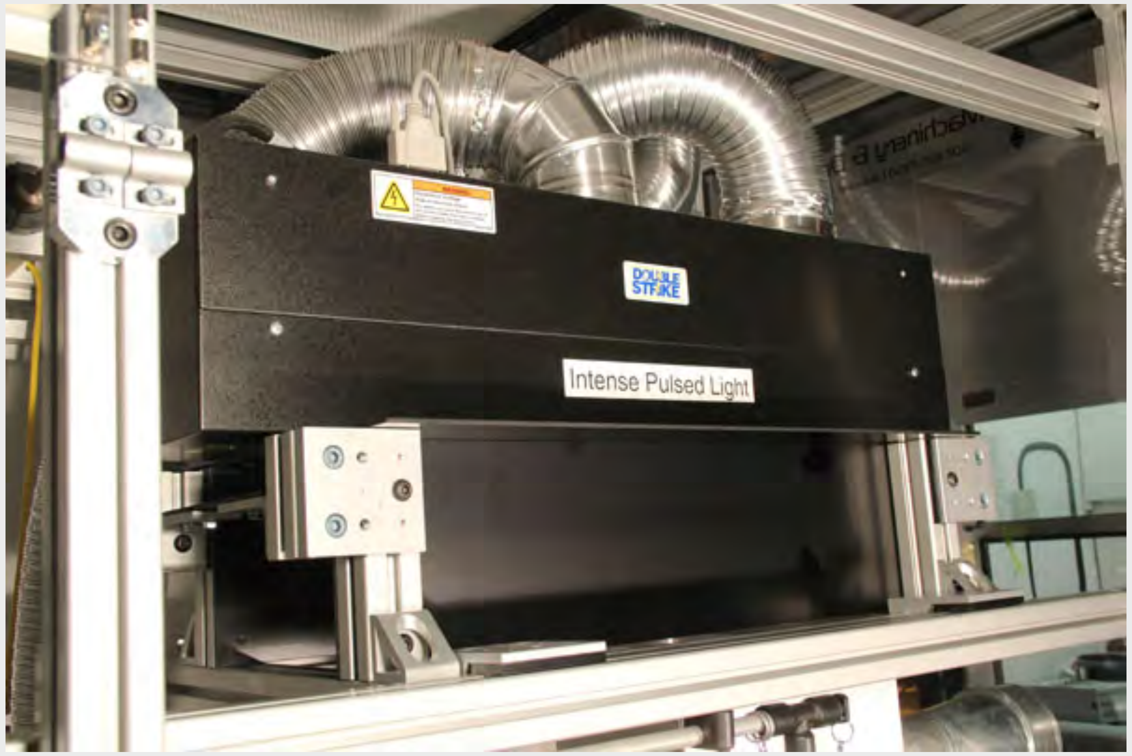
Inkjet printing is a valuable processing technology in roll-to-roll applications with the capability to digitally adjust images. Inks are precisely deposited with superb control of droplet size and position, which reduces waste and improves thin film accuracy. This process is widely used in the development of PVs, LEDs, flexible electronics and other devices where precise thin films are desired.

INTERACTIVE 4.6 Inkjet Assembly



- Dimatix Spectra Galaxy printhead
- ImageExpert imaging tool
- ImageExpert driver for linear printing
- Flatbed conveyor with vacuum table
- Micro adjustment of head position
- Controlled frequency
- Multiple head configurations available
- Upstream pressure control of ink
- Faculty expertise in ink formulation

FIGURE 4.7 Intense Pulsed Light Module



SUMMARY

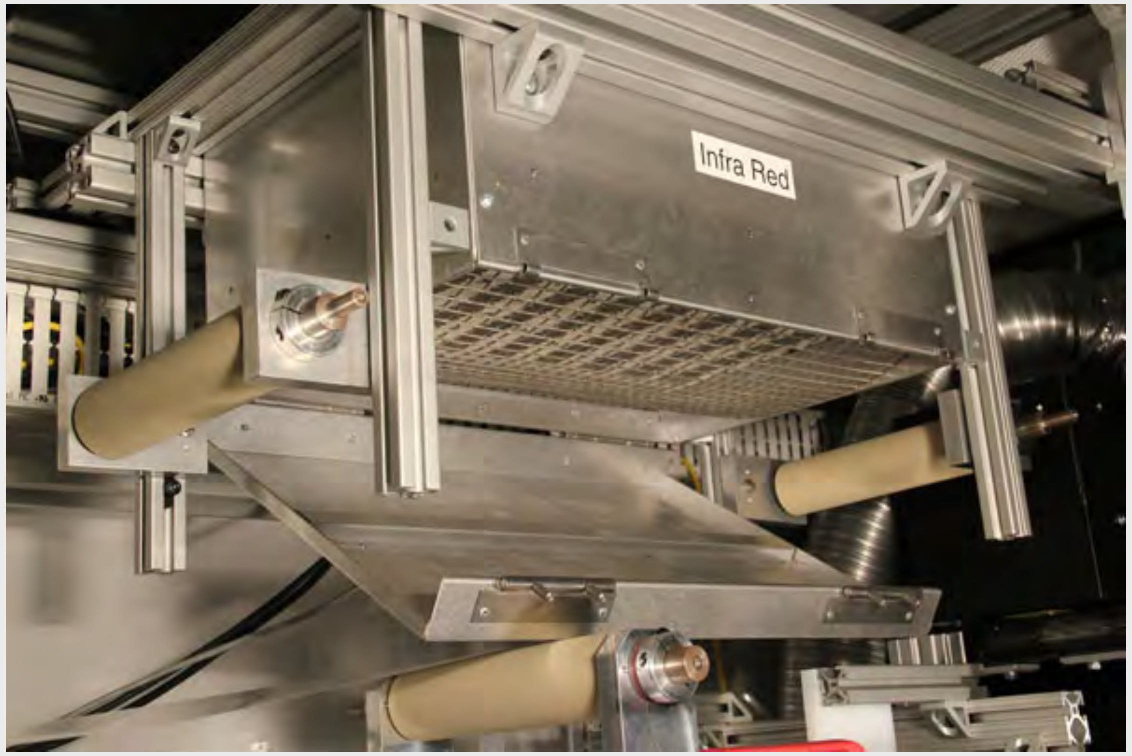
Sintering nanoparticles using Intense Pulsed Light (IPL) Radiation is a novel technique to fuse high temperature materials using very localized heating. This method has been very successful in thin film electronics in which silver nanoparticles are printed and sintered resulting in conductive patterns on plastic substrates. The low temperature and fast processing makes IPL an important technology for roll-to-roll photovoltaics.

INTERACTIVE 4.7 Intense Pulsed Light Assembly

- Xenon Corporation Sinteron 2000
- Selectable pulse duration 580 to 2000 micro seconds
- Adjustable pulse energy 150 - 2000 Joules
- Sintering area 58 cm^2
- Lamp cutoff 370 and 200 nm

IR HEATER

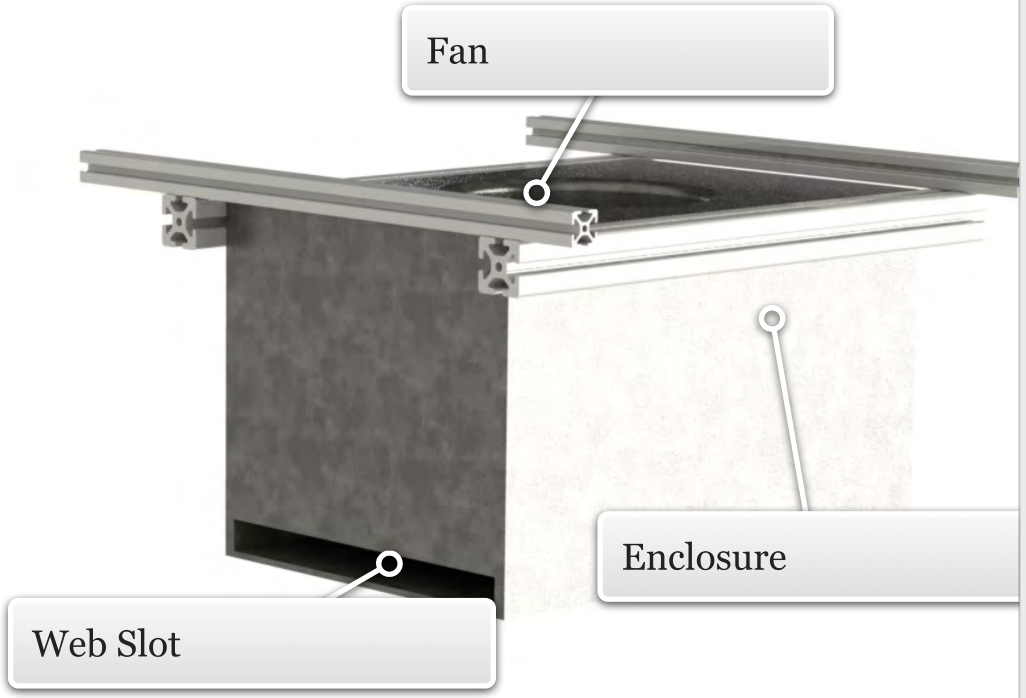
FIGURE 4.8 IR Heater Module



SUMMARY

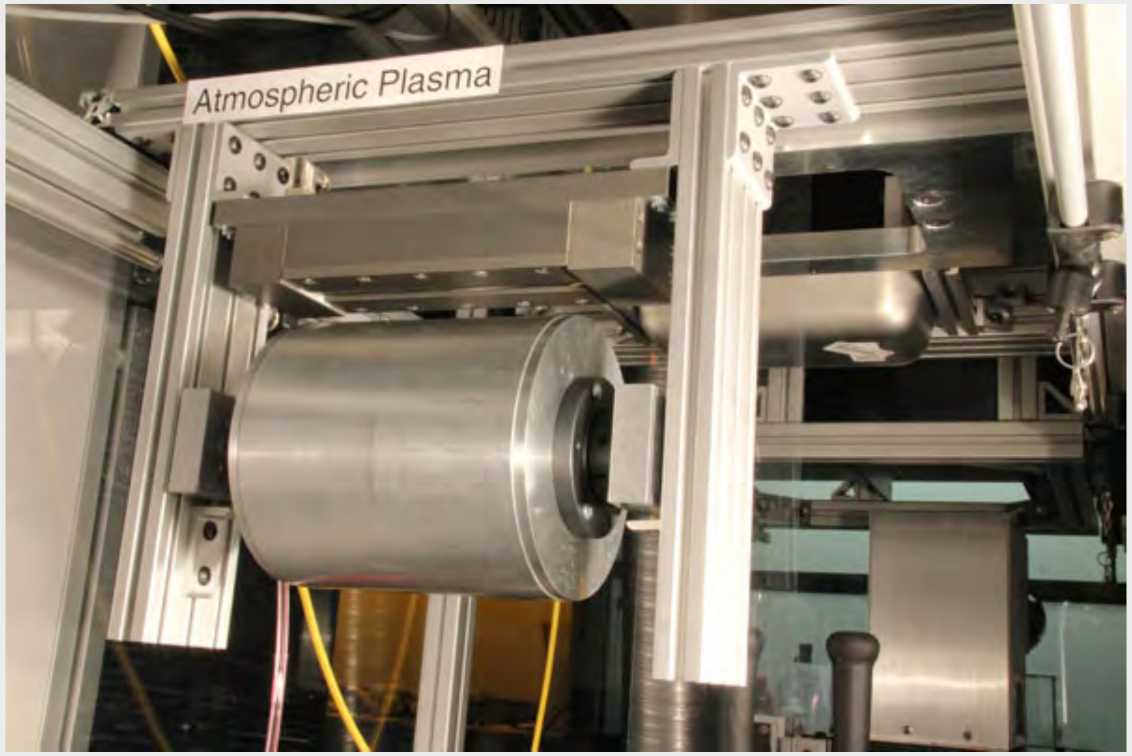
Infrared (IR) Driers are used extensively in the printing industry to remove water and solvents from a printed ink. The absorption of IR by the thin film through radiative processes makes this a faster option than typical air driers.

INTERACTIVE 4.8 IR Assembly



- Driir Infrared drying and heating equipment
- Solid state triac power controller
- Variable speed fan
- Ample air flow for exhausting solvents

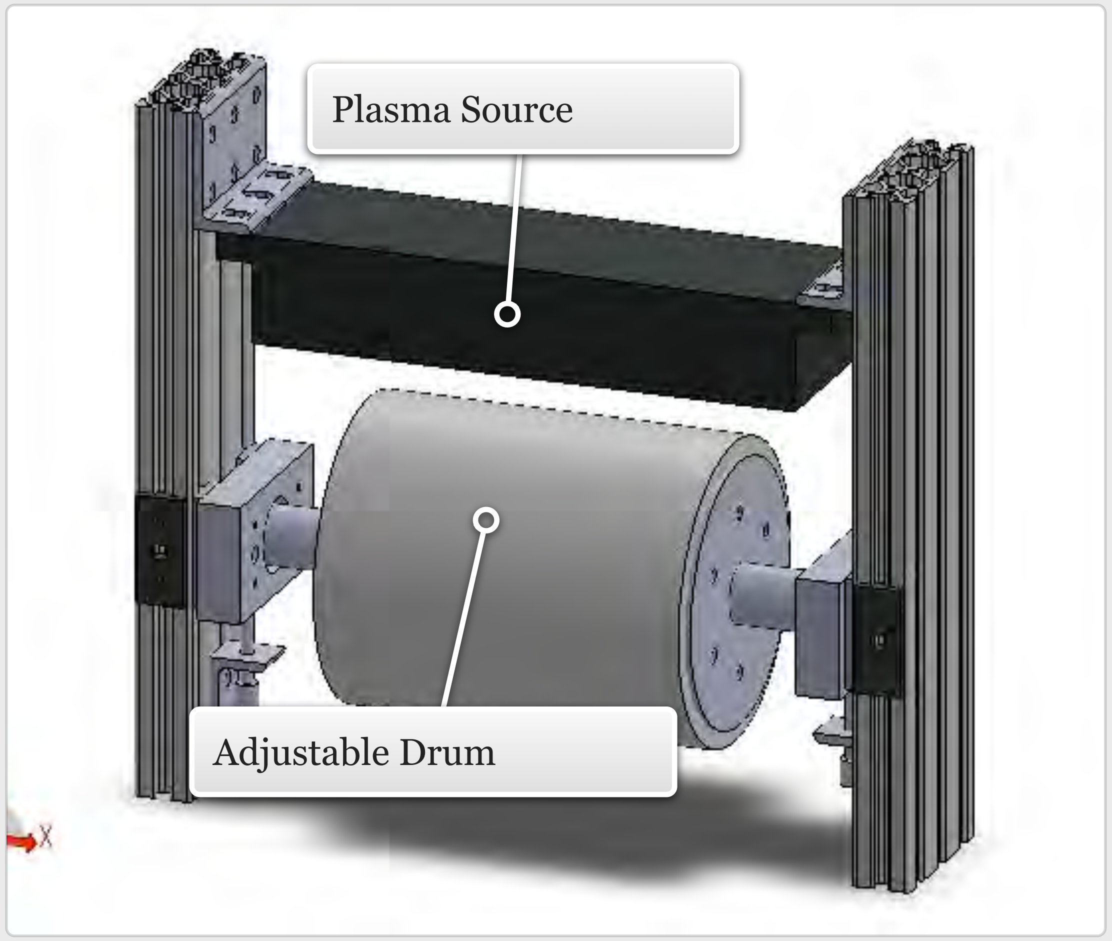
FIGURE 4.9 Atmospheric Plasma Module



SUMMARY

Atmospheric plasmas are typically used for rapid surface treatment of polymer substrates to improve adhesion to coatings. They can also drastically change the surface wetability, improving coating cosmetics. The energetics of the plasma can also be used to produce nanoscaled structures at low processing temperatures.

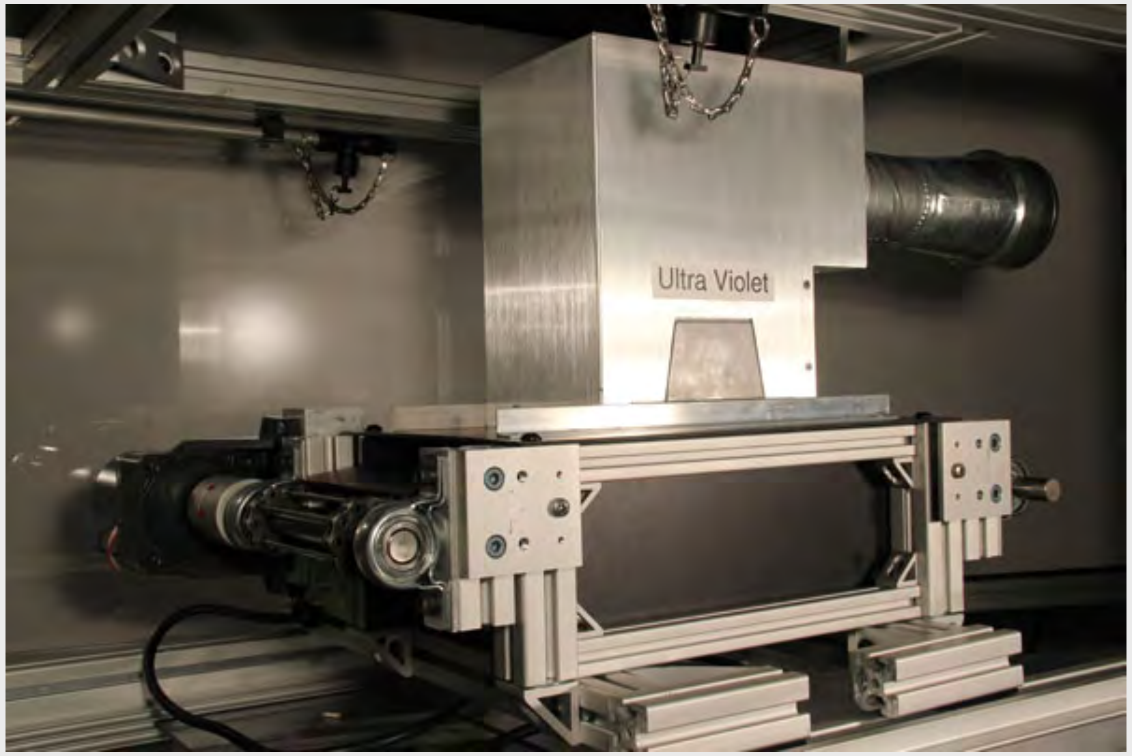
INTERACTIVE 4.9 Atmospheric Plasma Assembly



- Plamax 150S Head
- 600 Watt RF Power Supply
- Ar and O_2 gas mass flow controlled inputs
- Adjustable drum height

UV CURING

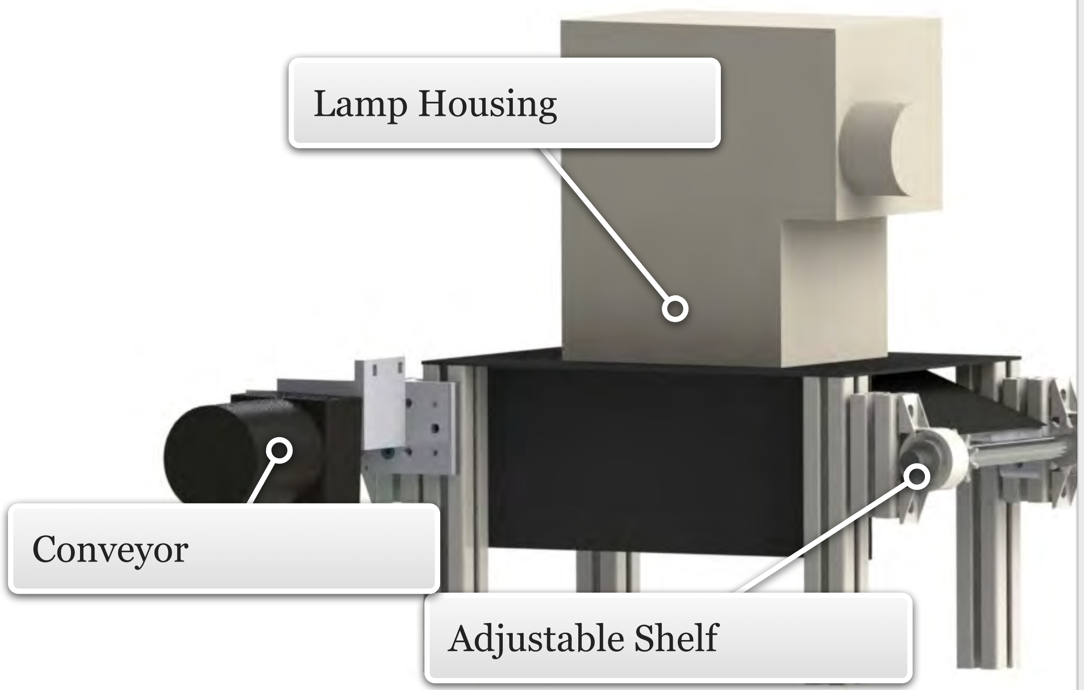
FIGURE 4.10 Ultraviolet Module



SUMMARY

Ultraviolet (UV) radiation curing is a very popular technique for the printing and coatings industry. The technology replaces costly (energy input and time) thermal curing techniques and is well suited for high throughput roll-to-roll processing. A number of UV curable water borne solutions are now available commercially, making this a more environmentally friendly process.

INTERACTIVE 4.10 UV Curing Assembly



- Fusion Corporation F300S
- 300 W/in UV bulb
- Several available spectrums
- Web speed control
- Adjustable height between lamp and substrate

FIGURE 4.11 Fluid Delivery Modules

SUMMARY

Many of the atmospheric deposition processes utilized in the roll-to-roll equipment are solution based. In some cases, these will be pumped from a reservoir using discrete metering processes. A number of positive displacement pumps are available to precisely meter solutions with a wide range of viscosities.

PUMP	DESCRIPTION	MAKE/MODEL
Air Tank	2.5 Stainless Steel	
Syringe Pump	Programmable stepper motor syringe pump	
Motor	Remote control 0-600 rpm motor	Masterflex 7528-10
Peristaltic Pump	Easy load Peristaltic Pump	Masterflex 77200-50
Gear Pump	0.56 mL/rev inert gear pump	Masterflex 73004-02
Diaphragm Pump	10-100 mL/min PTFE diaphragm pumo	Masterflex 7090-62
Piston Pump	Stainless steel 100 psi piston pump	Masterflex 7104-62
Micropump	Seal less low flow gear pump	Micropump L3468

- Manual/automatic pressure control
- Manual/automatic motor control
- Inert valving
- Fully integratable with PLC and HMI
- Mounted on roller carts for storage under HEPA enclosure

Appendix B. The final report for Commonwealth of Kentucky Energy and Environment Cabinet Department for Energy Development and Independence's energy commercialization grant program, "Technologies for commercialization of biofuels, natural gas, and carbon dioxide (4 projects)."

Technologies for commercialization of biofuels, natural gas, and carbon dioxide. (4 projects)

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EXECUTIVE SUMMARY

In this project, the Conn Center proposed four one year-long projects to develop technologies that will enable commercialization of Kentucky's abundant but untapped resources such as non-food biomass, natural gas, and carbon dioxide. All of these resources have the potential to be developed for creating an economic impact and, most importantly, in reducing carbon dioxide and other emissions. Commercialization of any of the above resources depends critically upon the availability of cost-effective and scalable technologies and their demonstration at a scale that is attractive for commercial entities. Specifically, we initiated development of the following four technologies:

(a) a cost-effective, continuous, and scalable method for refining large amounts of natural gas from undesirable inerts;
(b) a low-power, high-solids, enzymatic hydrolysis process for a large-scale ethanol demonstration plant;
(c) a novel, continuous technology for converting any type of lipid-based biomass resource into hydrocarbons or jet fuel; and
(d) a set of new materials that can be potentially used for converting carbon dioxide into hydrocarbons or other fuels using renewable sources of energy.

In last one year, the Conn Center initiated the above four technological development efforts and the following are highlights.

- All four projects developed interesting preliminary results that suggest that all four technologies can be commercialized with further development.
- One of the projects, i.e., lipids to jet fuel, resulted in a patent which has been licensed to a company that is promising to set up a ten million gallons per year.
- Three Ph.D. level graduate students are trained.

Project 1: A high-solids saccharification process for a cellulosic ethanol demo plant. E. Berson (PI).

Key findings in regards to commercialization potential:

1. High-solids enzymatic hydrolysis may not be mass-transfer limited as previously thought. Although the results do not define the actual rate-limiting step, this may indicate the ability to operate a commercial-scale processing system at higher than previously thought solids loadings, provided the rate-limiting step can be identified and a strategy developed to overcome it.

2. Kinetic modeling indicated the maximum reaction rate velocity decreased over time. This is the first time it has been suggested that the maximum reaction velocity was not constant. We propose it is a function of loss of total available enzyme as adsorbed cellulases become inactivated. Commercial-scale reactor design is intrinsically linked to reaction kinetics.

SUMMARY of RESULTS:

Task1. Study the effects of mass transfer limitations on high-solids saccharification.

Understanding solids loading limits is necessary for designing commercial scale processing systems. Maximizing solids will reduce: reactor size and capital costs, water usage, and energy usage spent on heating the water. Preliminary results, prior to this project, showed that glucose yields from cellulose were maintained when solids content of pretreated corn stover increased from 20 to 30 % in the absence of mass transfer limitations. Since rates and yields remained steady even as solids content and viscosity increased significantly, this provided evidence that the reaction was mass transfer limited. Verifying this for other substrates would allow for commercial-scale processing strategies since power consumption, which is directly proportional to power draw, can become prohibitive at this scale.

Three different substrates were tested here under the same conditions: i)corn stover pretreated under basic conditions rather than acidic conditions used in the preliminary results, ii)miscanthus, and iii)switchgrass. *All three substrates are widely grown throughout Kentucky.*

Tests were perfomed using a resonating acoustic mixer, designed for overcoming mass transfer limitations in viscous slurries. Dispersion coefficients measured in the mixer were on the order of those measured for water flowing through a cylinder (~<10 cm^2/sec).

Figure 1. *Labram Resonating Acoustic Mixer*

New results contradicted previous results. The table in the page below shows a comparison between previous results on dilute acid pretreated corn stover and new results on dilute base pretreated corn stover. Similar results were found for miscanthus and wheat, although conversions were much lower for these substrates, even at 20%, indicating the base pretreatment method may be ineffective for these substrates.

The significance of these findings are that the reaction may not be mass-transfer limited. Although the results do not define the actual limitation, this may indicate the ability to operate the commercial-scale processing system at higher than previously thought solids loadings, provided the rate-limiting step can be identified and a strategy developed to overcome it.

	Dilute-base Pretreated Corn Stover (new)	**Dilute-acid Pretreated Corn Stover (previous)**
20% solids	62.6%	73.5%
30% solids	36.8%	68.5%
Difference	**70%**	**7%**

Task 2. Investigate the occurrence of enzyme isomerization after binding.

This task consisted of two steps:

i)Kinetic modeling associated with enzyme binding characteristics (with experimental validation)

ii)AFM studies in order to detect morphological changes of the enzyme.

Key findings for (i):

Reactor design for production is intrinsically linked to reaction kinetics. A kinetic model to describe the hydrolysis reaction was refined that incorporates a first order inactivation of adsorbed cellulases to account for experimental hydrolysis data. First, Langmuir adsorption, which has been broadly used and well accepted by researchers to model cellulase adsorption was employed to derive the hydrolysis rate equation. Second, model parameter values were determined by fitting the equations to experimental hydrolysis data using two different substrates: Solka Floc, a regenerated cellulose containing minor xylan contamination, and Sigmacell Type 20, a microcrystalline cellulose, to examine whether the derived parameters were valid for substrates with different properties.

The kinetic model predicts hydrolysis kinetics within 10% of experimental results for both substrates. Modeling and experiments suggest V_{max} *decreases with a first order exponential decay* due to inactivation of adsorbed enzyme (see figure to right). This is the first time it has been suggested that the maximum reaction velocity is not constant. We propose it is a function of loss of total available enzyme as adsorbed cellulases become inactivated. The apparent hydrolysis rate (k_2=33 min^{-1}) and inactivation rate (k_f=0.38 h^{-1}) were within 5% for the two substrates and comparable to values reported elsewhere, further strengthening the value of the model. This combined with an unexpectedly low order of magnitude for k_2/K_m implies a common but yet undefined rate-limiting step associated with loss of enzyme activity during hydrolysis, which we hypothesize may be isomerization of the bound enzyme.

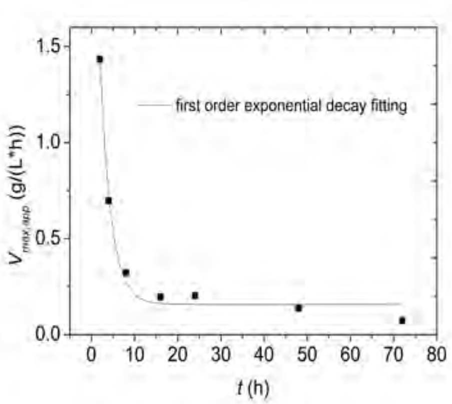


Figure 2. V_{max} *is not constant.*

Key findings for (ii):
AFM work continued in order to detect morphological changes of the enzyme. An AFM tip with its surface coated with a CH_3 group was used to increase the imaging resolution. Surface modification of the tip increased resolution to detect fine structures less than 10 nm. Unidirectional fibers were then prepared on a mica surface by dragging the mica (on a steel disk) out of the fiber solution, so that imaging in a certain direction can be easily performed, and imaging from different directions can be compared. The imaging has been performed with the fast moving direction of the tip perpendicular to the orientation of the fiber and the slow moving direction along the orientation of the fiber (Figure 3).

The enzyme, with dimensions of 4×18 nm, could not be observed on the fiber surface, even though the imaging was performed at a very small scale (100 nm × 100 nm). One reason might be that CBH1 moves along fiber processively with a rate of 3.5 nm/s, which is faster than the movement of the tip (~0.3 nm/s) along the slow moving direction. Therefore, the tip would only have a single encounter with the enzyme during the imaging, and it would be difficult to differentiate the signal from an error signal.

The next attempt was to image with the fast moving direction (at a rate of 100 nm/s) along the orientation of the fiber and the slow moving direction perpendicular to the fiber orientation. Two methods were attempted. In the first method, the sample was removed, the orientation of the sample was shifted 90^0 from the initial position, then the sample was returned to the AFM, and then re-image the replaced sample. In the second method, the scanning angle of tip was shifted with the AFM operating software (XE Data Acquisition program). However, the software could only shift the new scanning angle $\pm 45^0$ from the default scanning angle.

Neither method provided the desired imaging. One possible reason the first method did not work is that the radius of the current tip was too big (10 nm) to pick up the small fiber, and the resolution was not sufficient when the fast moving direction was nearly along the orientation of the fiber. In future work, tips with a sharper radius (1 nm) will be tested to determine if the fast moving direction parallel to fiber orientation can be imaged.

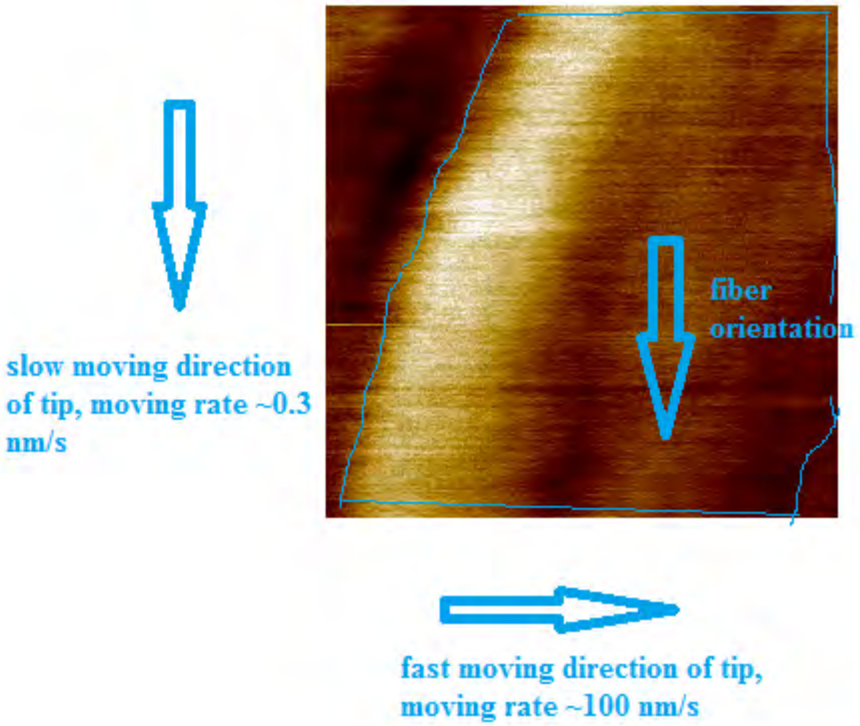


Figure 3. *Phase image (100× 100 nm) of cellulose fiber. Image was taken at a scanning rate of 1Hz. The area of the fiber is boxed with blue lines. A phase image is expected to differentiate materials with different stiffness (such as enzyme and cellulose).*

Personnel: The funds from this project (1) enabled one PhD student finish an important part of his dissertation and (2) train a new PhD student in enzymatic hydrolysis and modeling.

Travel: The PI and two students attended the annual *Symposium on Biotechnology for Fuels and Chemicals* in Seattle, Wa.

Publications: One manuscript has been submitted to Bioresource Technology (*Kinetic Modeling of Cellulose Hydrolysis with First Order Inactivation of Adsorbed Cellulase*) and another will be submitted in August (*Deactivation Extents of Individual Cellulase Components*).

Presentations: Student received an honorable mention award for a poster presentation at the statewide Renewable Energy and Energy Efficiency Workshop.

Project 2: Nanocrystalline zeolite membranes for the separation of carbon dioxide and nitrogen from natural gas. M. Carreon (PI)

Objective 1. Development of selective and highly permeable zeolite membranes that can effectively separate CO_2 from CH_4 at typical industrial conditions required in natural gas wells.

Task 1a. Synthesis of SAPO-34 seeds.

- SAPO-34 seeds were prepared by hydrothermal treatment of saturated gels containing a molecular structure-directing agent (SDA). In a typical synthesis, 5.1 g of aluminum isopropoxide, 2.9 g of phosphoric acid, and 13.12 g of deionized H_2O were stirred for 2 hrs to form a homogeneous solution. Then, 0.56 g of Ludox AS-40 colloidal silica was added, and the resulting solution was stirred for 3 hrs. To this solution, 5.27 grams of tetraethylammonium hydroxide were added, and the resultant solution was stirred for another 0.5 hr. Finally, 2.05 g of dipropylamine were added, and the solution was aged for 3 days at 323 K under vigorous stirring.
- The seed molar ratio was: $1Al_2O_3:1.33P_2O_5:0.16SiO_2:1TEAOH:1.6DPA:77H_2O$. The solution was placed in a sealed Teflon-lined autoclave under autogenous pressure and treated hydrothermally at 493 K for 24 hrs in a conventional oven. After the solution was cooled to room temperature, the seeds were centrifuged at 4000 rpm for 20 min to separate the seeds and the seeds were washed with deionized water. Centrifugation-washing process was repeated 3 times. The resultant precipitate was dried overnight at 343 K. The template was removed from the SAPO-34 framework by calcination using flowing air in a computer-controlled muffle furnace, using a ramp procedure at heating and cooling rates of 1 K/min and 10 K/min respectively. The resultant crystals were employed as seeds in the preparation of continuous membranes.

Task 1b. Synthesis of SAPO-34 membranes

- SAPO-34 membranes were prepared by secondary seeded growth inside tubular porous stainless steel supports (0.1 grade, 0.27-μm pores, Mott Corporation). The synthesis gel preparation and molar ratios were the same we employed for SAPO-34 seeds synthesis.
- The membranes were prepared by rubbing the inside surface of porous supports with dry, calcined SAPO-34 seeds using cotton swabs. The rubbed porous supports, with their outside wrapped with Teflon tape, were then placed vertically in an autoclave and filled with synthesis gel. The hydrothermal treatment was carried out at 493 K for 24 hrs. The resulting membranes were washed with deionized water and dried overnight at 343 K. The membranes were calcined using a computer-controlled muffle furnace at 673 K for 8 hrs in atmospheric air to remove the organic templates from the SAPO-34 framework.
- The resultant SAPO-34 membranes have been evaluated for the separation of CO_2/CH_4 gas mixtures. CO_2/CH_4 selectivities as high as 190 with CO_2 permeances of $\sim 4 \times 10^{-7}$ mol/m^2 s Pa at 295 K and 138 KPa.

Task 1c. Functionalized SAPO-34 membranes

- SAPO-34 membranes have been functionalized with several organic amino cations such as ethylenediamine, hexylamine and octylamine.

- The resultant SAPO-34 membranes have been evaluated for the separation of CO_2/CH_4 gas mixtures. CO_2/CH_4 selectivities as high as 245 with CO_2 permeances of ~ 5 x10^{-7} mol/m^2 s Pa at 295 K and 138 KPa, were observed for an optimum ethylenediamine functionalized membrane, which corresponded to a ~ 40% increase in separation index as compared to the nonfunctionalized SAPO-34 membrane.
- The separation performance of our best functionalized membranes compares with the so far best SAPO-34 membrane reported in the open literature.

Objective 2. Demonstration of the potential of scaling-up these membranes for pilot plant consideration.

Task 2a. Scale-up of SAPO-34 Membranes

- We have employed the best SAPO-34 compositions (formulations) and have prepared 1 SAPO-34 membrane on tubular 25 cm stainless steel support.
- We have prepared high flux SAPO-34 membranes on porous tubular 25 cm stainless steel supports displaying CO_2/CH_4 selectivities as high as 250 with CO_2 permeances of ~ 4 x10^{-7} mol/m^2 s Pa at 295 K and 138 KPa.The membrane was tested at Gas Technology Institute.

Figure 1 shows the separation system employed to test our membranes. Figure 2 shows the alumina and stainless steel supports employed to grow the membranes.

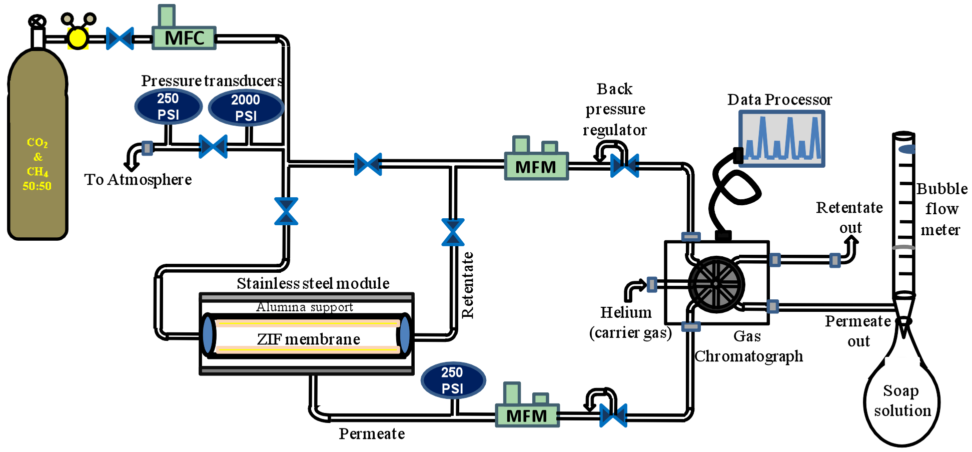


Figure 1. Separation system used for CO_2/CH_4 gas separation experiments.

Figure 2. 6 cm and 25 cm long porous stainless steel supports (silver-gray colored) used to grow the membranes.

Project 3: A novel process for the production of jet fuels from sustainable biomass raw material. P. Ratnasamy (PI).

Project Objectives. The major objective of the project is the development of a technically and economically viable process for the conversion of lipids to hydrocarbons boiling in the range of aviation turbine fuels using solid catalysts.

Project Strategy. Lipids consist essentially of triglyceride esters and acids derived from vegetable or animal fats and oils. The conversion of the triglyceride esters into fatty acids is a well-known technology already in industrial use in the soap industry. Hence, if the fatty acids can be converted into hydrocarbons boiling in the aviation turbine fuel (ATF) range (150-300^{o}C), one will have a viable technology to convert the lipids into ATF-range hydrocarbons.

Our strategy to achieve this consisted of a two-stage process: In the first stage, the fatty acids derived from the lipids (by technologies similar to those used in the soap industry, like soap splitting) were deoxygenated over a solid catalyst yielding long chain paraffinic hydrocarbons as the products from the first stage of the process; in the second stage, these long chain paraffins were molecularly rearranged into branched isomers with functional properties appropriate for ATF, like low freezing points (<-40^{o} C and smoke points higher than 25 mm).

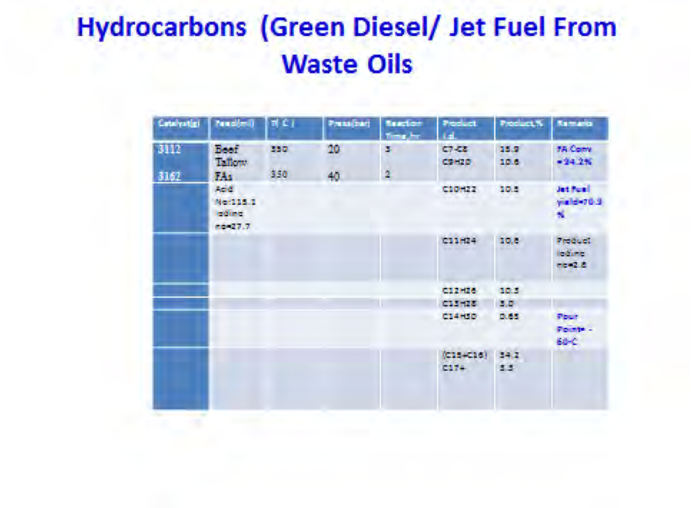
An alternate strategy would have been to rearrange the fatty acids into branched chain analogs and then in a second stage, deoxygenate the branched chain fatty acids into hydrocarbons boiling in the range of ATFs and with appropriate functional properties. This alternate strategy, however, was not finally adopted since initial experiments indicated that the strategy indicated earlier (deoxygenation of the lipid fatty acids followed by the molecular rearrangement of the resulting hydrocarbons) was more promising.

Schedule Of Tasks. To achieve the objectives of the project with the strategy outlined above, the following schedule of tasks was drawn up and implemented:

- Task 1 (months 1-3). Exploration of the feasibility of development of a catalyst and process for the skeletal isomerization of linear unsaturated fatty acids to their branched analogs. As mentioned earlier, our studies indicated that this route, though feasible in principle, would not be economical in practice: the product yields were not high and there were also problems in catalyst stability during long-term trials.
- Task 2 (months 4-6). Exploration of the feasibility of development of a catalyst and process for the deoxygenation of the linear fatty acids in the lipids raw material into linear paraffinic hydrocarbons.
- Task 3 (months 7-9). Exploration of the feasibility of development of a catalyst and process for the rearrangement of the linear paraffinic hydrocarbons resulting from Task 2 into branched chain hydrocarbons boiling in the ATF range.
- Task 4 (months 10-12). Standardization and optimization of the two-stage process and validation of the quality of the ATF produced in the project by an external agency. A final report containing all the results will then be made.

Summary of Project Activity. The major objectives of the project have been achieved. Two examples of the experimental results on deoxygenation of the lipid fatty acids and rearrangement/reforming of the resulting linear paraffins to hydrocarbons boiling in the 150-300 C range are shown in **Tables 1 and 2.**

Table 1. Conversion of Beef Tallow into hydrocarbons boiling in the Green Diesel/Jet fuel boiling range (150-300 C).



Hydrocarbons (Green Diesel/ Jet Fuel From Waste Oils

Catalyst(g)	Feed(ml)	T(C)	Press(bar)	Reaction Time, hr	Product i.d.	Product,%	Remarks
3112 3162	Beef Tallow FAs	350 350	20 40	3 2	C7-C8 C9H20	15.9 10.6	FA Conv =94.2%
	Acid No:115.1 Iodine no=27.7				C10H22	10.5	Jet Fuel yield=70.9 %
					C11H24	10.6	Product Iodine no=2.8
					C12H26	10.5	
					C13H28	5.0	
					C14H30	0.65	Pour Point= -60-C
					(C15+C16) C17+	34.2 5.5	

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a. **Catalysts for Stage 1.** The following catalysts were prepared, characterized, and evaluated for their activity in the deoxygenation of lipid fatty acids (Stage 1 of our process):
   - Palladium on amorphous carbon
   - Palladium on graphitic carbon
   - Palladium on alumina
   - Platinum on alumina; various grades of alumina with differing acidity and porosity were prepared.
   - Palladium on basic supports like MgO, lanthanum oxide and hydrotalcite
   - NiO-MoO_3-alumina
   - CoO-MoO_3-alumina

b. **Catalysts for Stage 2.** The following catalysts were prepared, characterized, and evaluated for their activity in the molecular rearrangement of the linear hydrocarbons resulting from Stage 1:
   - Platinum on zeolites like mordenite, HZSM-5, beta zeolite, and Y zeolite
   - Platinum on silicoaluminophosphates like SAPO-11
   - Platinum on mesoporous mixed oxides of Ga-Nb.

c. **Reaction Conditions.** Fixed bed, continuous flow, and batch autoclave reactors were used. A photo of the fixed bed continuous flow reactor is shown below. As feedstocks, various fatty acids (stearic, palmitic, lauric, etc.) from various lipid oils were used. In addition, a sample of beef tallow fatty acids was also used as representative of a real-life industrial feedstock.

d. Product Analysis. The products from the first deoxygenation stage were analyzed for acid number (to indicate the degree of conversion of the fatty acid), iodine number (to indicate the degree of unsaturation), the freezing point and gas chromatography (Hewlett Packard Model 4965) to indicate the carbon number distribution in the sample. The same analytical methods were also adopted to analyze the products from Stage 2. In addition to such in-house analysis, the second stage products were also sent to South West Research Institute for independent analysis and validation. The following Table 2 compares the properties of our sample of bio ATF with industry specifications. Our product satisfies all the specifications of bio ATF.

Figure 1. Fixed bed continuous flow reactor.

e. **External Validation of the Quality of our sample of ATF.** Selected samples from the outlet of Stage 2 were sent to the Southwest Research Institute to confirm the quality of our samples. The results are given in Table 2 below.

Table 2. Properties of a Laboratory Sample of Jet Fuel From Conn Center, University of Louisville –Comparison with D-1655 Specifications.

Property	*D-1655 Specifications*	*UofL sample's value (as reported by SWRI)*	*Test method*
Net Heat of Combustion MJ/Kg	Min 42.8	43.8	ASTM D-4809

Freezing point, °C	< -47	-75	
Smoke Point, mm	Min 25	26.7	ASTM D-1322
Total sulfur, ppm	Max,3000	4	ASTM D-1266
Elemental comp: %, C H O		 85.0 15.0 0	
Boiling range, °C, < 254 254-300		 ~10 ~90	

4. Project Outputs during the period 9-1-2010 to 6-30-2011 (10 months).

- **Journal publications:** One manuscript titled " Catalytic properties of mixed Ga-Nb oxides " has been sent to the Journal of Material Science for publication.
- **Patent Filed:** Process for the Production of paraffinic hydrocarbons; U.S. 61,439,112 on February 3, 2011.
- **Research Disclosure:** 25 January, 2011: ULRF- 11060: Process for the production of branched chain olefinic hydrocarbons.
- **The patent has been licensed to Alipha Jet, a startup from California.**

Project 4: Conversion of carbon dioxide into fuels using renewable energy sources. M. Sunkara (PI).

In this project, the main objective is to develop a photoelectrocatalyst/electrocatalyst materials system toward reduction of carbon dioxide to fuels. In one year of the revised work plan, we completed work on producing and testing p-type copper oxide (Cu_2O) films for their photoelectrochemical properties and producing and initiated testing copper nanowire arrays as electrocatalysts.

Task 1. Electrocatalyst development using boron-doped diamond electrode.

In the first objective, we propose to develop heavily doped, semi-metallic, diamond thin films onto high surface area platforms for supporting high current densities and allow for optimizing selectivity using different metal nanoparticles. Herein, we propose a special architecture consisting of diamond nanocrystals grown on conical carbon nanotubes. Intermediate deliverables include boron-doped diamond electrodes and their data with carbon dioxide reduction when sensitized with copper nanowire arrays and as a function of pH.

- Boron-doped diamond films were grown on heavily doped silicon and metallic electrodes using a microwave chemical vapor deposition reactor.
- Cyclic voltammetry of boron-doped diamond samples were performed to establish baseline data with water electrolysis potential window. The results show 2.5 V potential window and small baseline currents similar to the published results.
- Plasma exposure studies were performed using copper foils to create copper nanowire arrays.
- Copper nanowires are synthesized in two steps. First, copper oxide nanowires are synthesized us using exposure to atmospheric plasma discharges; and in the second step, the copper oxide nanowires are reduced using hydrogen plasma as shown in Figure 1.

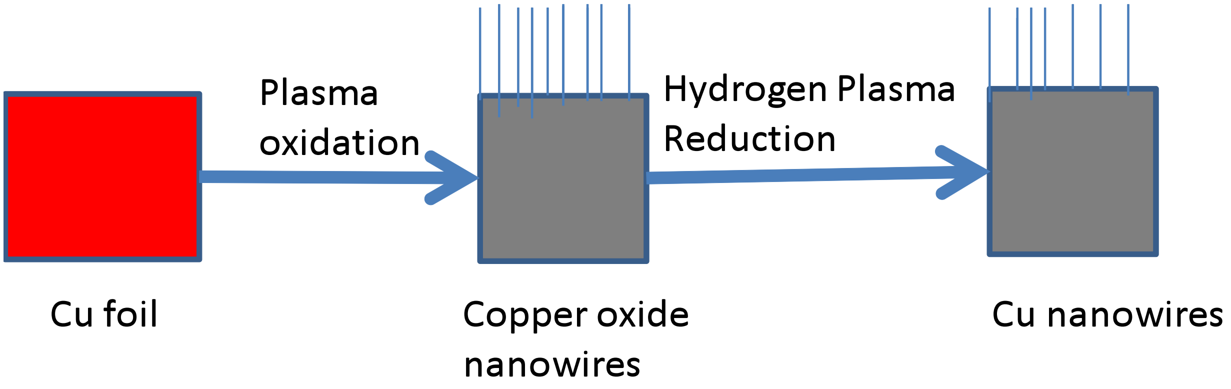


Figure 1. Proposed scheme of producing copper nanowire arrays.

It has been observed that temperature has major control on the growth of nanowires. To control the temperature of the substrate during exposure, heat sink is attached to the substrates exposed to plasma. Future work is to get high density copper oxide nanowires and reduce to copper nanowires using hydrogen plasma.

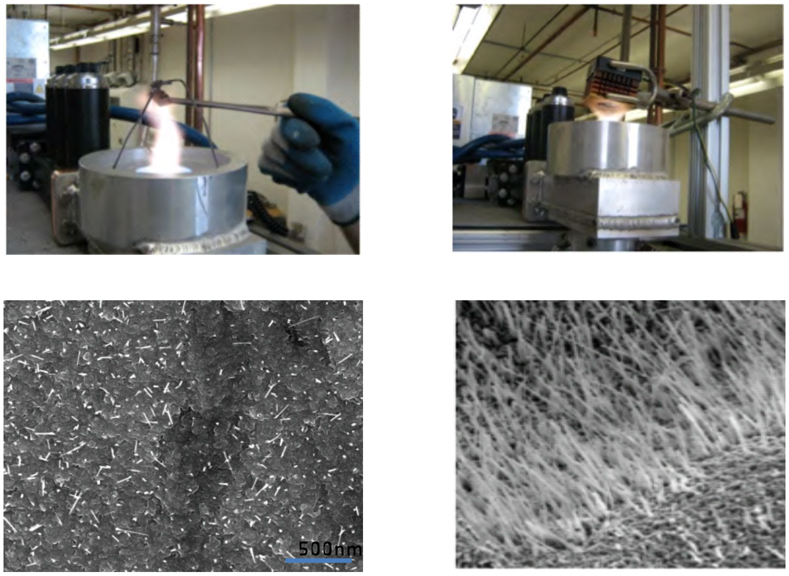


Figure 2. Photographs showing direct plasma oxidation methods used: (a) Photograph shows direct exposure of metal foil to plasma and the scanning electron microscope image shows low density nanowire array on metal foil; (b) Photograph shows exposure of metal foil mounted on a heat sink (for lower temperature) and the scanning electron microscope image shows high density nanowire array over copper foil.

Task 2. Preliminary experiments involving Synthesis and Photoelectrochemical Characterization of a semiconductor material.

Cuprous oxide (Cu_2O) thin films are widely being researched as cathode materials for water splitting and solar cells due to their high absorption coefficient in the visible region, long carrier diffusion lengths. Cu_2O is a wide band gap semiconductor with a bandgap of 2.1 ev. It is a p-type semiconductor which is inexpensive and non-toxic. The Cu_2O thin films can be prepared directly on Cu foils and expensive precursors are not required for synthesis. We were able to produce cuprous oxide films using a scalable plasma oxidation process. The process took only a few minutes (approx. 3 minutes) for producing 2 micron thick oxide film. This synthesis technique is is very fast when compared to other reported techniques for producing Cu_2O films (Table 1).

Technique	Synthesis time	Reference
Thermal evaporation	4 hours	X.C.Jiang et al., “Preparation of large scale cupric oxide nanowires by thermal evaporation method,”J.Crystal Growth 260, 130(2004)

Thermal oxidation	48 hours	M.L Zhong et al., “Synthesis, growth mechanism and gas sensing properties of large scale CuO nanowires

Fig.3. shows a SEM image of the cuprous oxide film

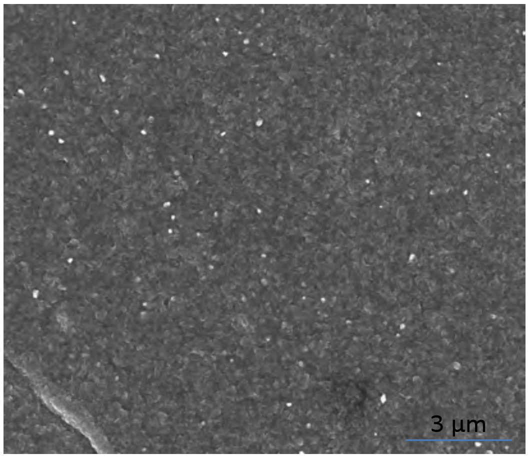


Fig.3. Scanning Electron microscope image of Cu_2O thin film at 420W and 3 minutes

Cu_2O is unstable in aqeous solutions. In order to test these films in to photoelectrochemical applications for both water splitting and solar cells. p-type Cu_2O films are coated with n-type titania (TiO_2). Titania is coated on the Cu_2O films through atomic layer deposition (~20 nm) which enhances the chemical stability and protects the Cu_2O film from corroding.

Electrochemical testing for water splitting was performed using a 3-electode configuration with Cu_2O/TiO_2 as working electrode, Ag/AgCl as reference and Pt mesh as the counter electrode using a potentiostat. Electrolyte used here is 1M sodium sulfate with pH buffered to 5.1 using 0.1M potassium phosphate. Fig. 5 shows the photoresponse of Cu_2O/TiO_2 electrode. From fig.5 p-type behavior can be observed as current going positive while increasing.

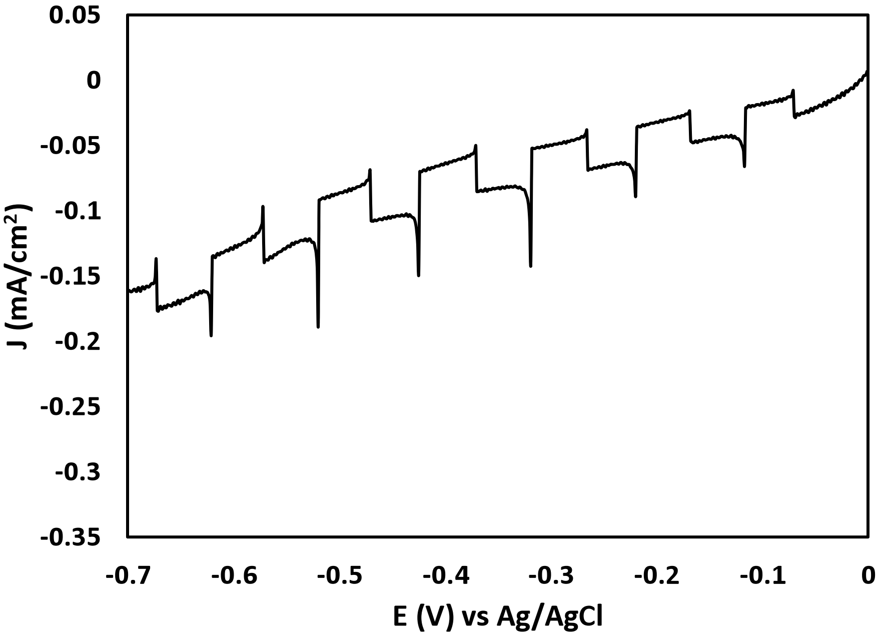
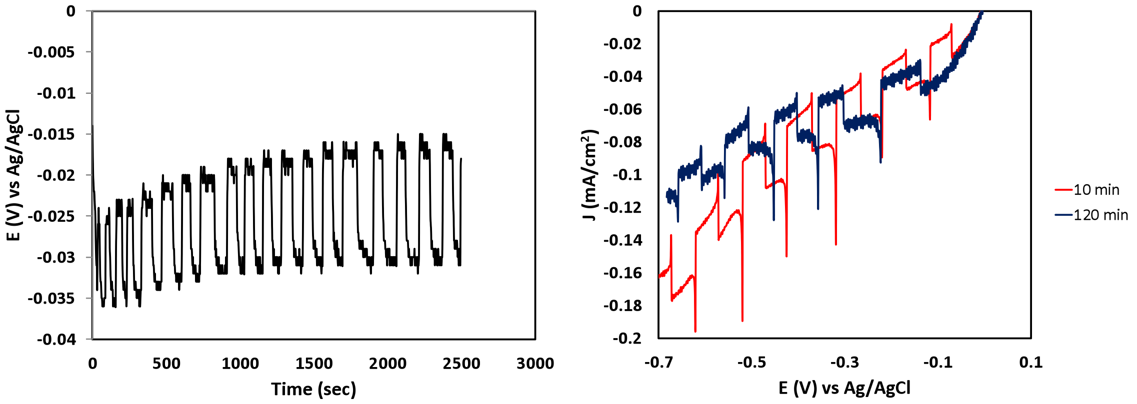


Fig.5. The Cu_2O/TiO_2 electrode photocurrent in 1 M sodium sulfate solution, under a chopped light illumination of 100 W/m^2

The electrode used for this study is highly stable for 100 minutes and Fig.6. shows the stability of the electrode and the photoresponse of the electrode after 100 minutes.



(a) (b)

Fig.6.(a). The Cu2O/TiO2 electrode open circuit voltage in 1 M sodium sulfate solution, under a chopped illumination of 100 W/m2. (b). Cu20/TiO2 electrode photoresponses at 10 mins and after 100 minutes.

Platinum is deposited on the surface through electrodeposition in 5 mM chloro platinic acid solution for 15 minutes with platinum counter electrode to increase the photoresponse of the electrode. Applied voltage used is -0.1V vs Ag/Agcl. Pt is deposited after the electrode is tested for 150 minutes and it has been observed that current is high when compared to the photoresponse of the electrode after 100 minutes and it regained its catalytic activity as fresh electrode. Fig.7. shows the photoresponse of the electrode after platinum is coated.

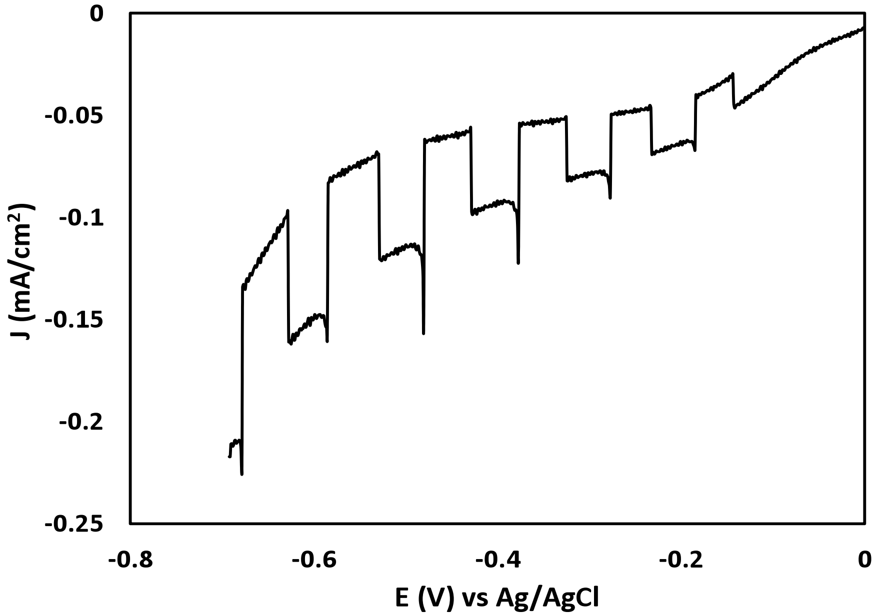


Fig.7. The Cu_2O/TiO_2 electrode photoresponse after electrodeposition of platinum.

Testing of solar cells using cu_2o thin films:

In this work cuprous oxide photoelectrodes prepared by plasma oxidation method exhibited open circuit voltage of 450mV in contact with iodide redox couples. Previously it has been reported that it is difficult to get a high quality n-type Cu_2O and interfacial copper formation degrades the performance of p-Cu_2O heterojunctions so the titania is coated on the cuprous oxide films to get a high quality n-type Cu2O. Voltage exhibited from semiconductor/liquid junctions used here is high compared to the voltage resulting from schottky junctions.

The preparation of Cu_2O electrode working on Cu foil was similar to that followed for PEC testing. A platinized FTO (Flourinated Tin Oxide) electrode was prepared by brush deposition of chloroplatinic acid followed by the annealing the electrode at 450° C for 15 mins. The platinized electrode served as the counter electrode and was assembled on to working electrode using an epoxy (Hysol 9462 and E 120HP). Holes were drilled into the counter electrode and iodide/tri-iodide electrolyte was injected. The holes were sealed using epoxy.

The current-voltage characterization was performed at different light intensities (Figure 8). The solar cell exhibited an open-circuit voltage of 450 mV. A current density of 0.3 mA/cm^2 was observed at 1 sun illumination.

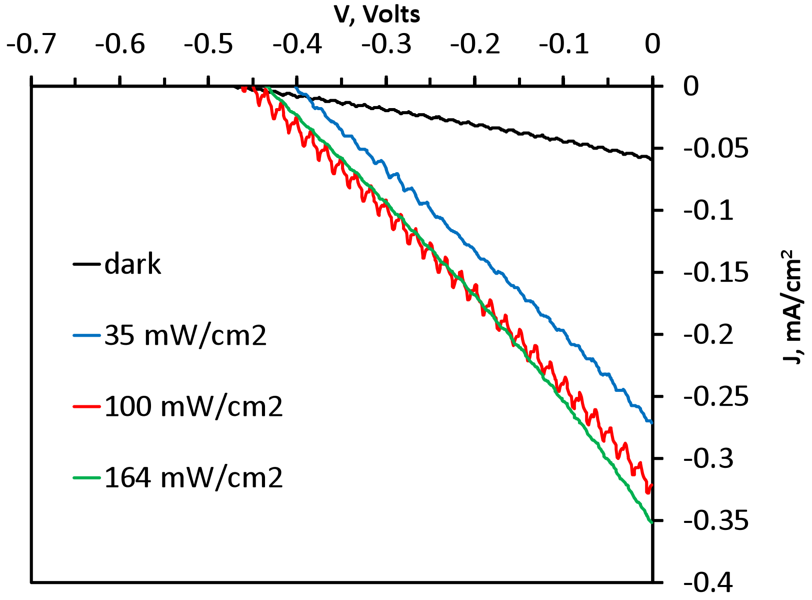


Fig.8. The photoresponse of Cu_2O/TiO_2 solar cell at different light intensitiies

Task 3: Cost and technological assessment and analysis toward commercialization

The plasma oxidation of copper foils represent as a cost effective technique for producing large area copper oxide films, copper nanowire arrays toward both photoelectrochemical and electrochemical reduction of carbon dioxide and water splitting applications.

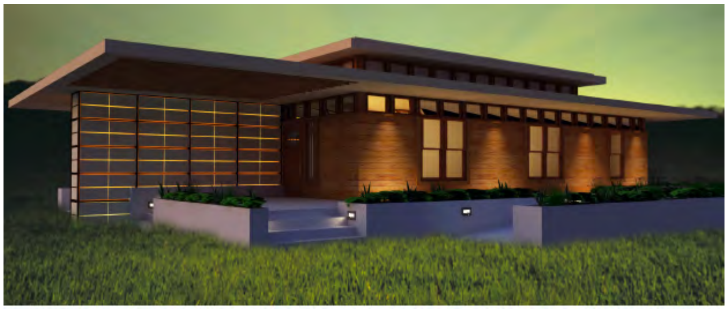
Personnel and publications: A Ph.D. level graduate student in chemical engineering was hired and trained. A manuscript is currently being prepared for publication.

Appendix C. 2-page brochure for “Team Kentuckiana: Solar Decathlon 2013, Low-cost Permanent Housing Solution for Disaster Relief.”

Team Kentuckiana: Solar Decathlon 2013

"Low-Cost Permanent Housing Solution for Disaster Relief"

Over 70,000 disaster events affect people worldwide each year, with nearly 100 FEMA-declared disasters occurring in the US annually. Such events include severe storms and flooding, tornadoes, earthquakes, and wildfires that destroy property, uproot lives, and devastate communities and cause economic havoc. Housing for persons displaced by these unavoidable events is of primary concern and critical for swift and effective recovery efforts, both immediately following the disaster and during the longer-term clean up and rebuilding. In the past, FEMA has provided one-bedroom manufactured homes as intermediate term shelters and as a replacement for tents.

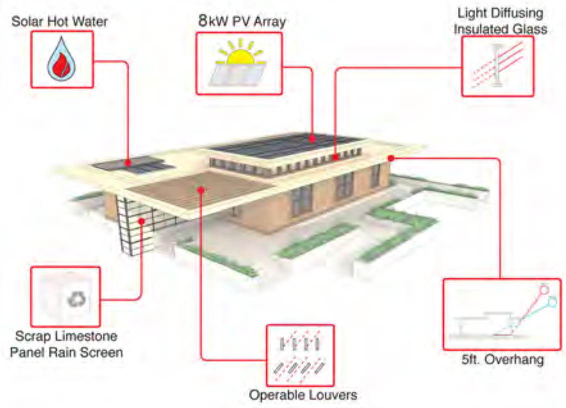


This niche of disaster relief housing caught the attention of Team Kentuckiana, a group of students and faculty from the University of Louisville, Ball State University, and the University of Kentucky, who were selected to compete in the 2013 Solar Decathlon (SD) Competition sponsored by the Department of Energy (www.solardecathlon.gov). This biennial competition challenges 20 collegiate teams from across the US to design, market, and build a cost-effective, energy-efficient, and attractive house that runs on solar energy. Houses will be showcased in Fall 2013 at the national competition site at Orange County Great Park in Irvine CA.

During the design phase of the competition, Team Kentuckiana identified the need for low-cost, solar-powered habitats for disaster relief that could be permanent housing solutions. The team is working toward a quickly and easily deployed structure powered independently of the electric power grid. Unlike a typical FEMA trailer, the house is intended to serve as the foundation for an expandable and permanent dwelling. The home features a grid-compatible power system for net metering and can be linked with other homes to form local microgrids.

Team Kentuckiana home features

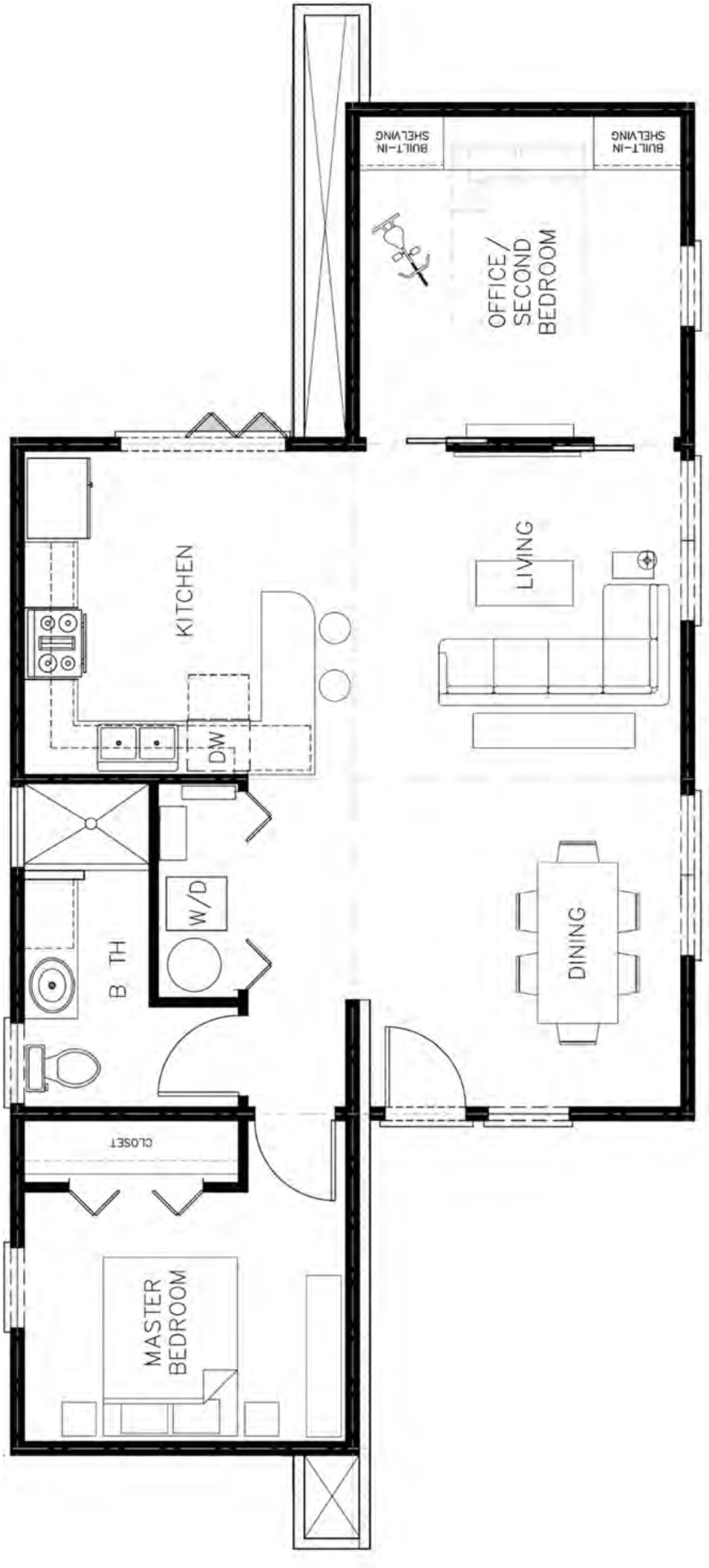
- 1000 square feet modular space
- Portability
- Entirely solar powered
- Grid-compatible 8kW PV array
- Light diffusing insulated glass windows
- Expandable into permanent housing



Team Kentuckiana's house will balance low-cost utilitarianism, ease of construction, and transportability with tasteful aesthetics and lighting, an adaptable interior environment, and obvious curb appeal. The two-bedroom structure will unify the kitchen, bathroom, and mechanical spaces into a core that forms the functional heart of the home. This core opens outward into the living areas and can be expanded further using additional house modules or conventional construction. Although not a part of the Solar Decathlon competition, the home will be configured to purify potable water as well, an absolute necessity in disaster relief. Flexibility of the core modules to support a variety of façade appearances is also an SD design criterion.

After the SD competition, the Speed School of Engineering will utilize the Team Kentuckiana home on the UofL campus as a student outreach center and for further technology studies and testing. Additionally, the house can also help address the pressing need for low-cost, energy efficient housing in rural areas where power access can be prohibitive. Typical manufactured homes used in these areas are very inefficient and key contributors to elevated energy costs. The team's housing system, which will be designed to be comparable in cost to conventional manufactured housing and utilities, can be used in rural areas with greater efficiency and long-term equity.

Team Kentuckiana: Solar Decathlon 2013



The Team Kentuckiana Solar Decathlon House example floor plan groups together the kitchen, bathroom, and HVAC closet, which are mechanically intense areas. The living spaces radiate outward from this core in an open plan that maximizes the space and facilitates future expansion through additional house modules and/or conventional construction.

Centralized mechanical areas equate to production cost savings via shorter pumbing and electrical runs as well as efficient distribution of heating and air conditioning.

The 8kW PV array provides enough power for the lighting, stove, refridgerator, dish washer, hot water heater, HVAC, and personal electronic amenities.

Light diffusing insulated glass windows, operable shade louvers, and deep roof overhangs integrate energy efficiency into the structure and spec components.

Built-in shelving, closets, and kitchen cabinet space allow for compact storage of essentials while de-cluttering the 1000 square foot dwelling.

Top to bottom, inside and out, the entire home design utilizes readily available, conventional systems and off the shelf componets to keep costs low and maintanence simple.

For more information, contact Dr. Mark McGinley, Professor of Civil Engineering at UofL, at 502/852-4068 and m.mcginley@louisville.edu.