Environment and Natural Resources Trust Fund (ENRTF) M.L. 2014 Work Plan

Date of Report: 23 December 2013

Date of Next Status Update Report: 1 January 2015

Date of Work Plan Approval:

Project Completion Date: 30 June 2017

Does this submission include an amendment request? no

PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals

Project Manager: Lee Penn and Eray Aydil

Organization: Univerisity of MN – Twin Cities ; Department of Chemistry

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Location: Hennepin County (Univerisity of MN – Twin Cities ; Department of Chemistry and Department of Chemical Engineering and Materials Science); anticipated impact is expected to be at the statewide level.

Total ENRTF Project Budget:		
	ENRTF Appropriation:	**$494,000**
	Amount Spent:	**$0**
	Balance:	**$494,000**

Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 08a

Appropriation Language:
$494,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop solar cell materials using nontoxic and common metals combined with sulfur. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2017, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals

II. PROJECT STATEMENT:

Safe and clean energy production is a grand challenge facing our society. The development of sustainable electrical energy sources is an urgent need in the state of Minnesota and in the United States. Solar energy is renewable and is a viable and attractive option. To become commonplace, solar cells must be inexpensive and robust, and they must be comprised of abundant, cheap, nontoxic materials. We propose to develop innovative methodology for producing thin films of metal sulfides for use in solar cells. Instead of using toxic elements like cadmium, we propose to use iron, copper, and other far less toxic metals combined with sulfide. By targeting sulfides for use in solar cells, sulfur waste from mining and other industrial operations could become a viable resource in the production of robust and inexpensive solar cells. Finally, we propose to exploit microwave energy so as to reduce the energy required to produce photovoltaic quality materials.

We aim to develop a method for producing CZTS, for example, with the high efficiencies required for realistic implementation of the affordable photovoltaic devices but without the hazards associated with using rare and/or toxic elements and other source materials.

The biggest outcome expected is a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS.

Major Results Expected:

1. Generalized, green synthetic methods for the controlled production of kesterite nanoparticles.
2. Successful methods for preparation of high quality, microcrystalline thin films directly onto conductive substrates using the microwave synthesis method.
3. Prototype solar cell fabricated using promising candidate materials.

Deliverables: Open scientific presentations and papers addressing the above objectives; patents for methods to produce photovoltaic quality thin films of CZTS using our new method.

III. PROJECT STATUS UPDATES:

Project Status as of January 1, 2015:

Project Status as of July 1, 2015:

Project Status as of January 1, 2016:

Project Status as of July 1, 2016:

Project Status as of January 1, 2017:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: *Develop synthetic process using sulfur, common metals, and a microwave-based method for producing mixed metal sulfides*

Description: Using Nature as a guide and applying eight of the twelve principles of Green Chemistry, we will develop a rational approach to the green synthesis of CZTS thin films with properties ideal for incorporation into advanced technologies. Critical control parameters include the degree to which the material is nonstoiciometric (e.g., some degree of Cu deficiency is good from the perspective of electrical and optical properties), crystal size (i.e., hundreds of nanometers for the best photovoltaic properties), and defects (concentration, type, and distribution).

Using less toxic metals in combination with sulfur, we will develop methods for producing nanoparticles composed of common and less toxic elements. Systematic experiments will use metal salts in combination with sulfur sources in order to determine the best synthetic conditions for phase pure product. These experiments will enable development of a general synthetic procedure for producing pure materials that will have excellent performance in solar cells. Using microwaves will enable both faster production and dramatically reduced energy requirements.

The products of the above syntheses will be characterized using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy. XRD will enable quick determination if the material synthesized has a structure that is consistent with the kesterite structure and whether impurities of quite different structures (e.g., oxides or other sulfide structures) are present. In kesterites, it has been found that the S sublattice determines the unit cell dimensions. Consequently, it is difficult to identify and distinguish different kesterites based on XRD alone. Raman spectra are sensitive to the metal cations, making Raman spectroscopy a sensitive characterization method for kesterites. Thus, Raman spectroscopy will be the second technique employed. For materials that look promising by XRD and Raman spectroscopic characterization, UV-Vis spectroscopy will be used to determine the band gap of the material using methods well established in our laboratories. Finally, STEM with EELS and/or EDS will be employed to determine whether the elements are distributed homogeneously or heterogeneously.

Materials will be tested using established methods in order to predict performance in solar cell applications.

Summary Budget Information for Activity 1:

ENRTF Budget: $ **240,000**
Amount Spent: **$ 0**
Balance: **$ 240,000**

Completion Date: *Spring 2016*

Outcome	**Completion Date**	**Budget**
1. . Develop effective synthetic methods for pure transition metal sulfides	Summer 2015	$140,000
2. Preparation of photovoltaic quality materials and extensive testing	Spring 2016	$ 100,000

ACTIVITY 2: *Preparation of Thin films*
In order to prepare solar cells, the material must be made into a high quality thin film. The above methods will be adapted to enable production of thin films of metal sulfides on both rigid and flexible materials. Using the synthetic conditions determined from the above work, thin films will be synthesized directly onto conductive substrates. Important properties include an ideal thickness of on the order of 2 microns, a grain size in the range of hundreds of nanometers, and phase purity. Synthetic conditions may have to be modified in order to achieve these goals with a thin film. A major goal is to retain the low energy requirements and directly synthesize thin films that are pure, have excellent particle size, and optimal properties for use in solar cells.

Microwave heating of a conductive material submerged in a solution results in preferential heating of the conductive material while leaving the surrounding solution comparatively cool. We will exploit this effect in order to directly coat substrates with CZTS. Results from the work described above, in which CZTS is synthesized by precipitation from the solution phase, will inform the experimental design for the controlled synthesis of

CZTS onto conductive substrates. In fact, we have successfully prepared CZTS thin films by submerging substrates coated with conductive material into metal precursor solutions. When the microwave energy is absorbed strongly by the thin conductive coating, its temperature increases enough to deposit films exclusively onto the conductive layer, leaving the uncoated portions of the substrate CZTS-free and the surrounding solution free of precipitates. To date, resulting films are approximately 1-3 microns thick, which is a suitable thickness for use as a photovoltaic material. However, the crystal size is ca. ten nanometers in diameter, which is not large enough.

In addition, the ideal crystal size is hundreds of nanometers for the best photovoltaic properties. Post-deposition microwave annealing in neat solvent increased crystallite volume by eightfold, but this has only resulted in increasing the average crystal size to a few tens of nanometers. When nanocrystalline CZTS films are annealed in sulfur gas at high temperature (ca. 500 °C), substantial grain growth is achieved (results in the Aydil lab). At typical annealing temperatures, the S exists as vapor, and we have developed strategies to avoid S condensation on the films. Sintering and Ostwald ripening occur simultaneously, which results in substantial grain growth to sizes in the 0.5-2 µm size range. Here, we propose to tuning solution conditions during the microwave anneal step (see below) in order to achieve the larger size needed for the best photovoltaic properties. Experimental variables include the solvent properties and the solubility of S-bearing species in that solvent. Employing microwaves will enable drastic reduction in the energy required to anneal the films and may enable the use of flexible substrates.

The CZTS films will be annealed using the microwave approach, in which the sample is placed in a solution prepared using the target solvent and elemental sulfur or sulfur-containing molecules and exposed to microwaves so as to preferentially heat the underlying conductive layer and the CZTS film. In addition, CZTS films will be annealed using the more conventional high temperature approach, in which the sample is sealed into an ampule containing elemental sulfur or H2S gas and heated to high temperature, for comparison. Films will be characterized using the techniques described below. We hypothesize that employing a solvent in which CZTS is sparingly soluble but sulfur is moderately soluble will enable improved annealing so as to achieve the necessary crystal size (i.e., hundreds of nanometers).

The thin films produced will be characterized using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy.

Summary Budget Information for Activity 1: **ENRTF Budget:** $ **254,000**
Amount Spent: **$ 0**
Balance: **$ 254,000**

Completion Date: *Summer 2017*

Outcome	**Completion Date**	**Budget**
1. Photovolatic quality thin films combined with extensive testing	Summer 2017	$ 154,000
2. Data synthesis, reporting, and recommendations	Summer 2017	$ 100,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017:

Final Report Summary:

V. DISSEMINATION:

Description: Open scientific presentations and papers addressing the above objectives; patents for methods to produce photovoltaic quality thin films of CZTS using our new method; incorporation of solar cell in outreach activities.

Status as of January 1, 2015:

Status as of July 1, 2015:

Status as of January 1, 2016:

Status as of July 1, 2016:

Status as of January 1, 2017:

Final Report Summary:

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Explanation
Personnel:	$104,250	Support for graduate student (3 years funding plus fringe); co-advised and working in close collaboration with the post-doctoral researcher; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Prepare the prototype solar cell(s) in direct collaboration with the post-doctoral researcher.
Personnel:	$166,635	Support for Post-doctoral researcher (; 3 years funding plus fringe); co-advised; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Provide some supervision and mentoring towards the graduate student. Prepare the prototype solar cell(s) in direct collaboration with the graduate student.
Personnel:	$60,841	Support for R. Lee Penn, project manager. 1.5 months summer salary per year (plus fringe). Supervise post-doc and graduate student; perform electron micrscopy on samples; evaluate data and design experiments.
Personnel:	$55,366	Support for Eray Aydil (co-project manager; 1

		months summer salary per year + fringe); supervise post-doc and graduate student; design characterization experiments; evaluate data and design experiments.
Equipment/Tools/Supplies:	$36,000	User fees for instrumentation (electron microscopes, X-ray scattering equipment, spectroscopic methods) at the University of Minnestoa - College of Science and Engineering's Characterization Facility ($12k/yr)
Equipment/Tools/Supplies:	$35,908	Chemicals (metal precursors, elemental sulfur and other sulfur containing precursors, solvents), standards, conductive glasses as well as polymers for thin film support, lab supplies including reactors for microwave system, and supplies for materials testing
Equipment/Tools/Supplies:	$10,000	Repairs and maintenance
Capital Expenditures over $5,000:	$25,000	Research-grade microwave system.
TOTAL ENRTF BUDGET:	**$494,000**	

Details are provided in the accompanying excel file.

Explanation of Use of Classified Staff:

Explanation of Capital Expenditures Greater Than $5,000: Research-grade microwave system optimized for thin film production (based on quote from one of the major equipment producers). This equipment is substantially more specialized than a conventional microwave oven. The system enables use of flow-through cells (fresh reagents can flow into the cell and concentrations of ingredients varied as a function of time) as well as enable monitoring of temperature and pressure during synthesis. Finally, the microwave enables very fine tuning of power output. This equipment will be used for its full useful life and made available to other researchers at no charge.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 6.62

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
	$232,722	$	**In-kind Services During Project Period:** *During Project Period: Dr. Penn and Dr. Aydil will also devote 1% time per year in kind ($2900). Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (52% of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind ($229,822)*
State			

	$	$	
TOTAL OTHER FUNDS:	**$232,722**	**$**	

Add or remove rows as needed

VII. PROJECT STRATEGY:

A. Project Partners: Project Managers Lee Penn and Eray Aydil are the supervising partners on this project. The graduate student and post-doc will be recruited and hired once funding is in place. We do not have additional partners involved.

B. Project Impact and Long-term Strategy: Safe and clean energy production is a grand challenge facing our society. The development of sustainable electrical energy sources is an urgent need in the state of Minnesota and in the United States. Solar energy is renewable and is a viable and attractive option. To become commonplace, solar cells must be inexpensive and robust, and they must be comprised of abundant, cheap, nontoxic materials. Innovative methodology for producing thin films of metal sulfides for use in solar cells resulting from the proposed work will move us closer to commonplace installation of solar cells. Solar cells produced in the proposed work will be composed of less toxic elements like iron, copper, and other far less toxic metals, combined with sulfide. By targeting sulfides for use in solar cells, sulfur waste from mining and other industrial operations could become a viable resource in the production of robust and inexpensive solar cells. Finally, we propose to exploit microwave energy so as to reduce the energy required to produce photovoltaic quality materials.

C. Spending History: *Related to this project*

Funding Source	**M.L. 2008 or FY09**	**M.L. 2009 or FY10**	**M.L. 2010 or FY11**	**M.L. 2011 or FY12-13**	**M.L. 2013 or FY14**
NSF grant for previous data analysis and testing					$42,000

VIII. ACQUISITION/RESTORATION LIST:

IX. VISUAL ELEMENT or MAP(S):

X. ACQUISITION/RESTORATION REQUIREMENTS WORKSHEET:

XI. RESEARCH ADDENDUM: We have prepared a research addendum, which has been submitted to the LCCMR office separately. It is being kept confidential to protect against potential unintended release of information that could compromise patents that might result from the research.

XII. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted not later than January 1, 2015; July 1, 2015; January 1, 2016; July 1, 2016, and January 1, 2017. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund
M.L. 2014 Project Budget

Project Title: Solar Cell Materials from Sulfur and Common Metals
Legal Citation: *M.L. 2014, Chp. 226, Sec. 2, Subd. 08a*
Project Manager: *R Lee Penn*
Organization: University of Minnesota
M.L. 2014 ENRTF Appropriation: $*494,000*
Project Length and Completion Date: *3 Years, June 30, 2017*
Date of Report: *20 Janaury 2014*

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	***Develop synthetic process***			***Preparation of Thin films***				
Personnel (Wages and Benefits): overall	$171,613	$0	$0	$215,479	$0	$0	$387,092	$387,092
Support for graduate student (3 years funding plus fringe); co-advised and working in close collaboration with the post-doctoral researcher; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Prepare the prototype solar cell(s) in direct collaboration with the post-doctoral researcher. [Estimated total $104,250]								
Support for Post-doctoral researcher (; 3 years funding plus fringe); co-advised; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Provide some supervision and mentoring towards the graduate student. Prepare the prototype solar cell(s) in direct collaboration with the graduate student. [Estimate $166,635]								
Support for R. Lee Penn, project manager. 1.5 months summer salary per year (plus fringe). Supervise post-doc and graduate student; perform electron micrscopy on samples; evaluate data and design experiments. [Estimated $60841]								

Support for Eray Aydil (co-project manager; 1 months summer salary per year + fringe); supervise post-doc and graduate student; design characterization experiments; evaluate data and design experiments. [Estimated $55,366]								
Equipment/Tools/Supplies							$0	$0
User fees for instrumentation	$18,000	$0	$18,000	$18,000	$0	$18,000	$36,000	$36,000
These are the instruments, and their hourly rates, we intend to use. The budget is based on rough estimates of time required for materials characterization. We will report on the actual hours used for each piece of equipment. TEM $44.00, SEM $44.00, SAXS $25.00, Raman $25.00, XRD $20.00, XPS $40.00, Elliposmetry $20.00, Maskmaking $360.00, Metal Evap $60.00, Sputtering $40.25							$0	$0
Equipment/Tools/Supplies	$20,387	$0	$20,387	$15,521	$0	$15,521	$35,908	$35,908
Chemicals (metal salts, sulfur sources, nitrogen gas, solvents) [Estimated $9,303]								$0
Vials and caps for microwave systems [Estimated $4,500]								$0
Lab equipment (pH probe, balance, XRD sample holders, stir plate, UV-Vis flow cell) [Estimated $3,900]								$0
Grids and stubs for electron microscopy [Estimated $1,600]								$0
Lab supplies (safety supplies like gloves, pipets and pipet tips, vials, weigh boats, lab tape, centrifuge tubes, quartz cuvettes) [Estimated $7,800]								$0
Glove box (for preparation of precursors in controlled atmosphere) [Estimated $2,500]								$0
Substrates and materials for thin film preparation (e.g., conductive film (indium tin oxide) coated glass, flexible substrates, glass for use with molybdenum conductive films, silicon substrates) [Estimated $6,305]								$0
Equipment/Tools/Supplies: Repairs and maintenance	$5,000	0	$5,000	$5,000	$0	$5,000	$10,000	$10,000
Capital Expenditures Over $5,000 ***Research-grade microwave system.***	$25,000	$0	$25,000	$0	$0	$0	$25,000	$25,000
COLUMN TOTAL	**$240,000**	**$0**	**$68,387**	**$254,000**	**$0**	**$38,521**	$494,000	$494,000

Title: Solar cell materials from sulfur and common metals

We will develop solar cell materials using nontoxic and common metals combined with sulfur, a mining waste product. Success will help progress towards the 2002 MN solar energy policy standard.

Figure 1: This photovoltaic system consists of 9 dual tracking arrays and is located at the Audubon Center of the Northwoods in Sandstone, MN.

We propose to make solar cell materials using less toxic and common metals like copper and iron rather than the more toxic and rare elements like cadmium. Furthermore, the use of the more common metals means that less material must be mined, which reduces environmental impact.

Solar cells are an important component of achieving clean and safe energy by reducing emissions of green house cases and toxic pollutants like mercury.

Fabricating solar cells using less toxic elements also addresses the full life cycle of the solar cell by reducing hazardous waste at the end of the cell's useful life.

Figure 2: This photograph shows what acid mine drainage looks like.

When sulfur rich ore is mined, the exposure of the sulfur-rich rock to weathering produces waters that are heavily loaded with toxic pollutants and so acidic that they can cause serious skin burns.

A major focus of our proposal is using waste sulfur, which could reduce acid mine drainage by reducing the amount of sulfur waste resulting from mining.

Photograph courtesy of ElyMinnesota (http://elyminnesota.com/blog/?p=3).

LCCMR: Penn and Aydil from the University of Minnesota – twin cities campus