Environment and Natural Resources Trust Fund
2014 Request for Proposals (RFP)

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Project Title:

Solar Cell Materials from Sulfur and Common Metals

Category: E. Air Quality, Climate Change, and Renewable Energy

Total Project Budget: $ 494,092

Proposed Project Time Period for the Funding Requested: 3 Years, July 2014 - July 2017

Other Non-State Funds: $ 0

Summary:

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.

Name: Lee Penn

Sponsoring Organization: U of MN

Address: Department of Chemistry, 207 Pleasant St SE
Minneapolis MN 55455

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Web Address

Location

Region: Statewide

County Name: Statewide

City / Township:

MP: 0613-2-140-proposa

Budget: 0613-2-140-bud

Qual: 0613-2-140-qualifi

Map: 0613-2-140-map-2

Resolution:

List:

_____ Funding Priorities _____ Multiple Benefits _____ Outcomes _____ Knowledge Base

_____ Extent of Impact _____ Innovation _____ Scientific/Tech Basis _____ Urgency

Capacity Readiness Leverage Employment TOTAL

PROJECT TITLE: Solar cell materials from sulfur and common metals

I. 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. However, there are major obstacles to widespread use of solar cell technology. Current technology is expensive, making it difficult for businesses and homeowners to implement. In addition, solar cells are commonly made using toxic and rare elements like cadmium and arsenic and/or using processes that require large amounts of energy, which results in the production of substantial green house gas and toxic emissions. To become commonplace, solar cells must be inexpensive and robust, and they must made of abundant, cheap, nontoxic materials.

Why solar energy? Solar energy is a renewable source of energy that can reduce our dependence on fossil fuels and reduce emissions of mercury, which is a toxic pollutant threatening Minnesota water quality, and carbon dioxide, a major green house gas. Furthermore, in May of 2013, Minnesota Gov. Mark Dayton signed into law an energy bill requiring solar energy to comprise 1.5% of total energy production by utilities by 2020. Progress in the area of producing cheaper but also high performing materials for solar cells will help us meet this new policy standard.

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. Our target material is a sulfide, which also means that we can address a pressing need regarding sulfur waste produced by mining in Minnesota. By targeting sulfides for use in solar cells, we have the opportunity to solve two problems simultaneously. That is, the sulfur recovered during mining could become a resource in the production of robust and inexpensive solar cells. Such a result would drastically reduce threats to our water quality by acid mine drainage, which produces a wide range of toxic pollutants.

Specifically, we will:

- **Use common elements rather than rare elements**, thus reducing the amounts of ore required to produce solar cell materials and demand for rare and precious metals. Every technology developed without rare elements preserves those elements for use in the broad diversity of applications for which we use them– including the transparent conductive films used in touch screens as well as life-saving applications.
- **Use less toxic elements** like iron, copper, tin, and zinc rather than the more toxic cadmium and arsenic, thus reducing environmental impact throughout the life cycle of the solar cell (from production to the end of the solar cell's usable life).
- **Use SULFUR as a main ingredient**, thus turning a common and problematic mining waste material to a resource for the production of green energy. Furthermore, using sulfur in the production of these materials will decrease damage to water quality as a result of acid mine drainage (sulfur will be removed from the mining sites).
- **Drastically reduce the energy and time** required to make thin films of the solar cell materials by taking advantage of microwave technology. Reducing energy requirements will lead to reductions in green house gas emissions and costs associated with the production of solar cell materials.

Finally, a major goal is to develop material synthesis methods that can be used to make flexible solar cells so that they can be implemented in applications such as panels in back packs or in roofing shingles that can double as robust solar cells.

Grand challenges in the area of sustainable energy is the green design high performing materials ideal for particular applications (e.g., the focus of this proposal, solar cells). We aim to develop materials, 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.

II. DESCRIPTION OF PROJECT RESULTS –

Result 1: *Develop synthetic process using sulfur, common metals, and a microwave-based method for producing mixed metal sulfides* **Budget:** $ 240,000

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

Deliverables	Completion Date
1. Develop effective synthetic methods for pure transition metal sulfides	Summer 2015
2. Preparation of photovoltaic quality materials and extensive testing	Spring 2016

Result 2: *Preparation of Thin films* **Budget:** $ 254,000

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. 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.

Deliverables	Completion Date
1. Photovolatic quality thin films combined with extensive testing	Winter 2017
2. Data synthesis, reporting, and recommendations	Summer 2017

III. PROJECT STRATEGY

A. Project Team/Partners

Dr. Lee Penn (University of Minnesota, Department of Chemistry) will lead the project and work closely with ***Dr. Eray Aydil*** (University of Minnesota, Department of Chemical Engineering and Materials Science) in coordinating experiments geared towards efficient production of thin films of photovoltaic materials on flexible substrates. Drs. Penn and Aydil will co-advise one graduate student and one post-doctoral researcher. All will be responsible for reporting results to LCCMR. Our combined groups have extensive expertise in synthesizing nanocrystals in organic solvents. In addition, we have extensive expertise in preparing pilot devices in order to test state-of-the-art materials as potential solar cell materials. Our collaboration combines state of the art knowledge and experience in materials synthesis and device development to develop an effective, cheap, and flexible solar cell.

B. Timeline Requirements

The project will require three years to complete.

C. Long-Term Strategy

Transition metal sulfides (for example, iron, zinc, and copper) are ideal materials for use in solar cells. We will develop an energy efficient method for producing films made using less toxic metals and elemental sulfur. We will begin by synthesizing materials using sulfur, a common and problematic byproduct of mining, and microwaves, which reduces energy required to make the materials. Then, we will develop the method to produce thin films on a variety of substrates that could be directly incorporated into solar cells. Our results will lead to substantial progress towards producing affordable solar cell technology as well as meeting the 2020 MN solar energy policy standard.

2014 Detailed Project Budget

Project Title: Solar cell materials from sulfur and common metals

IV. TOTAL ENRTF REQUEST BUDGET 3 years

BUDGET ITEM	AMOUNT
Personnel: *R. Lee Penn (project manager ; 1.5 months summer salary per year + fringe); supervise post-doc and graduate student; perform electron micrscopy on samples; evaluate data and d esign*	60,841
Personnel: Eray Aydil *(co-principal investigatorr ; 1 months summer salary per year + fringe); supervise post-doc and graduate student; design characterization experiments; evaluate data and d esign experiments.*	55,366
Personnel: Post-doctoral research (to be determined; 3 years funding plus fringe); co-advised; Design and execute synthetic methods for preparation of thin films using green methods. Characterize films for suitability as photovoltaics.	166,635
Personnel: Graduate student (to be determined; 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 films for suitability as photovoltaics.	104,250
Equipment/Tools/Supplies: 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)	36,000
Equipment/Tools/Supplies: 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.	25,000
Equipment/Tools/Supplies: chemicals (metal salts, sulfur, solvents), standards, conductive glasses as well as polymers for thin film support, lab supplies including reactors for microwave system, and supplies for materials testing ($12k/yr)	36,000
Equipment/Tools/Supplies: repairs and maintenance	10,000
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	494,092

V. OTHER FUNDS

SOURCE OF FUNDS	AMOUNT	Status
Other Non-State $ Being Applied to Project During Project Period: *National Science Foundation proposal pending: DMREF: Synergistic Computation, Experiment, and Characterization for Building a Materials Genome Database of Earth Abundant Materials for Advanced Applications. Overlap with this proposal - limited materials overlap. A major focus of this NSF proposal is materials exploration by combining computational research with experimental research. The synthetic methodology proposed here is substantially different than that proposed in the NSF proposal. The source of sulfur is a key element of the work proposed here.*	$1,590,379.00	*PENDING*
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)*	$ 232,722	*Indicate: Secured*
Funding History: *Through a collaboration with IRG (Interdisciplinary Research Group) 4 through the U of MN's MRSEC (Materials Research Science and Engineering Center), we have successfully obtained preliminary data demonstrated the feasibility of our approach. We can make these sulfide materials using elemental sulfur and the substantially lower energy microwave method. This project long term goal is the successful development of methods for producing high performance thin films of these materials directly on conductive substrates. Finally this project's funding expires in 2014*	$87,245.00	Current

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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).

Project Management and Qualifications (including selected publications): Dr. Lee Penn (University of Minnesota, Department of Chemistry) will lead the project and work closely with Dr. Eray Aydil (University of Minnesota, Department of Chemical Engineering and Materials Science) in coordinating experiments geared towards efficient production of thin films of photovoltaic materials on flexible materials. Drs. Penn and Aydil will co-advise one graduate student and one post-doctoral researcher.

Prof. Lee Penn is the project manager and has extensive experience developing synthetic methods for the production of nanoparticles of specific compositions and narrow size and shape distributions. In addition, her research group uses electron microscopy and other advanced methods to extensively characterize materials in order to elucidate links between size, composition, and shape and materials' properties (including electrical, optical, and magnetic).

Undergraduate: Beloit College, Chemistry Major, 1988 - 1992
Graduate: University of WI, M.S. and Ph.D. in Materials Science, 1992 – 1998
Postgraduate: Johns Hopkins University, Sept. 15, 1998 – April 30, 2001

1. Aggregation of ferrihydrite nanoparticles in aqueous systems, Virany M. Yuwono, Nathan D. Burrows, Jennifer A. Soltis, Tram Anh Do, and R. Lee Penn (2012) Faraday Discussions, in press.
2. Effect of Ionic Strength on the Kinetics of Crystal Growth by Oriented Aggregation, Nathan D. Burrows, Christopher R. H. Hale, and R. Lee Penn (2012) Crystal Growth and Design, DOI: 10.1021/cg3004849 Article ASAP.
3. Size-Dependent Anatase to Rutile Phase Transformation and Particle Growth, Kairat Sabyrov, Nathan D. Burrows, and R. Lee Penn (2012) Chemistry of Materials, DOI: 10.1021/cm302129a Article ASAP.
4. On the nucleation and crystallization of silicalite-1 from a dilute clear sol, Kumar, S.; Penn, R. L.; Tsapatsis, M. (2011) Microporous and Mesoporous Materials, 144 (1-3), 74-81.
5. Sub-40 nm Zeolite Suspensions via Disassembly of Three-Dimensionally Ordered Mesoporous-Imprinted Silicalite-1, P.S. Lee, X.Y. Zhang, J.A. Stoeger, A. Malek, W. Fan, S. Kumar, W.C. Yoo, S. Al Hashimi, R.L. Penn, A. Stein, M.Tsapatsis (2011) Journal of the American Chemical Society, 133, 493-502.

Prof. Eray Aydil is co-PI and has extensive experience developing methods for the synthesis and characterization of semiconductor nanocrystals including CZTS. He has recently begun using colloidal CZTS nanocrystal dispersions (inks) to make thin (~1-5 μm) polycrystalline films by first coating various substrates with nanocrystals and then annealing them in S or Se vapor. Moreover, Aydil has extensive experience in electrical characterization of thin films and assembling and characterizing solar cells.

Undergraduate**:** University of California, Berkeley CA, B.S. in Chemical Engineering and in Materials Science; 1986
Graduate: University of Houston, Houston TX, Ph.D. in Chemical Engineering, 1991
Postgraduate: AT&T Bell Labs, Murray Hill, NJ, 1991-1993

1. A. Khare, B. Himmetoglu, M. Cococcioni and E. S. Aydil, "First principles calculation of the electronic properties and lattice dynamics of $Cu_2ZnSn(S_{1-x}Se_x)_4$," *J. Appl. Phys.* **111**, 123704 (2012).
2. A. Khare, B. Himmetoglu, M. Johnson, D. J. Norris, M. Cococcioni and E. S. Aydil, "Calculation of the Lattice Dynamics and Raman Spectra of Copper Zinc Tin Chalcogenides and Comparison to Experiments," *J. Appl. Phys.* **111**, 083707 (2012).
3. A. Khare, A. W. Wills, L. M. Ammerman, D. J. Norris and E. S. Aydil, "Size Control and Quantum Confinement in Cu_2ZnSnS_4 Nanocrystals," *Chem. Commun.* **47**, 11721-11723 (2011).
4. C. A. Wolden, J. Kurtin, J. B. Baxter, I. Repins, S. E. Shaheen, J. T. Torvik, A. A. Rockett, V. M. Fthenakis and E. S. Aydil, "Photovoltaic Manufacturing: Present Status, Future Prospects and Research Needs," *J. Vac. Sci. Technol. A* **29**, 030801 (2011).
5. A.-J Cheng, M. Manno, A. Khare, C. Leighton, S. Campbell and E. S. Aydil, "Imaging and Phase Identification of Cu_2ZnSnS_4 Thin Films Using Confocal Raman spectroscopy," *J. Vac. Sci. Technol. A* **29**, 051203 (2011).