Environment and Natural Resources Trust Fund

2021 Request for Proposal

General Information

Proposal ID: 2021-343

Proposal Title: Small, Cheap, and Fast Nitrobenzene Detector for Water

Project Manager Information

Name: Tianhong Cui

Organization: U of MN - College of Science and Engineering

Office Telephone: (612) 626-1636

Email: cuixx006@umn.edu

Project Basic Information

Project Summary: We propose to develop a small, cheap, and fast photoelectrochemical detector based on a new solar cell to prevent lakes and rivers in Minnesota from the nitrobenzene contamination.

Funds Requested: $200,000

Proposed Project Completion: 2024-06-30

LCCMR Funding Category: Small Projects (H)
Secondary Category: Methods to Protect, Restore, and Enhance Land, Water, and Habitat (F)

Project Location

What is the best scale for describing where your work will take place?
Statewide

What is the best scale to describe the area impacted by your work?
Statewide

When will the work impact occur?
During the Project and In the Future

Narrative

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

Nitrobenzene is an oily yellow liquid with an almond-like odor, which is widely used as a precursor in the petrochemical industry to produce dyes and pesticides. Due to its high toxicity, Minnesota Pollutant Control Agency and Environment Protection Agency have listed nitrobenzene as one of the top priority pollutants in water. Human exposure to nitrobenzene will interfere with bloods ability to carry oxygen, causing respiratory distress, dizziness, and methemoglobin. Long-term and frequent exposure to nitrobenzene damages liver function and even causes death. The current nitrobenzene detection methods usually require expensive instruments and technicians, which greatly limits their applications to field tests. Nitrobenzene sensors for monitoring drinking water and natural water are very important to ensure a safe living environment and high-quality residential health.

Currently, the power consumption of on-line sensors is a bottleneck of distributed sensing networks, and this may hinder the construction of the internet of things. Although in recent years some self-powered physical sensors for monitoring pulse and heart rate have been reported, chemical sensors without an electrical power supply were rarely developed. The integration of sensors with a green energy harvester will pave a way for the establishment of large-area environment monitoring networks with long-term reliability.

What is your proposed solution to the problem or opportunity discussed above? i.e. What are you seeking funding to do? You will be asked to expand on this in Activities and Milestones.

We propose to develop a small, cheap, and fast nitrobenzene detector. This detector is a monolithic device that combines a photoelectrochemical sensor with a light energy harvester. Since the detection process is driven by solar energy, no electrical power supply is needed for this detector. The main structure of this detector includes a solar cell, a light-sensitive $CuSnO3/Cu2O$ layer, and a counter gold electrode. When this detector is soaked in water, the counter electrode, the $CuSnO3/Cu2O$ layer, and the external circuit will form an electric circuit. Upon light illumination, nitrobenzene in the water will be selectively reduced on the $CuSnO3/Cu2O$ layer due to a photochemical reaction. In this process, a photocurrent can be detected in the external circuit. The solar cell can harvest light energy, and facilitate the separation of photon-excited electron-hole pairs in the $CuSnO3/Cu2O$ layer, significantly enhancing the nitrobenzene reduction. Perovskite solar cell is the most promising technique for the next generation solar panels due to its low cost and high energy conversion efficiency. The detector based on a perovskite solar cell will significantly enhance the sensitivity of this detector, realizing a chemical detection using light as its power supply.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

The outcomes of this project aims to investigate a photoelectrochemical detector for monitoring nitrobenzene in water. This work intends to develop a cheap, fast, and portable method for environmental monitoring and pollution prevention. Due to the increasing production volume of nitrobenzene in the US, surface water and underground water are facing pollution threats by nitrobenzene. This detector will help the state protect the natural waters by building up an alarming system for the potential nitrobenzene leakage and sewage. Furthermore, the energy harvesting structure of this detector provides a new method for environmental monitoring and prevention in an energy saving way.

Activities and Milestones

Activity 1: Development of new solar cell structures on fluorine-doped tin oxide (FTO) coated glass and its application as photoelectrode of detectors

Activity Budget: $65,800

Activity Description:
A perovskite solar cell structure will be grown on part of FTO glass as the light-harvesting layer, and the exposed FTO electrode will be tested as the working electrode of the proposed detector. Perovskite is a cheap material for new solar cells. The solar cell structure will be fabricated on FTO glass through a layer-by-layer self-assembly, including a titanium dioxide (TiO2) electron transport layer, a perovskite light-harvesting layer, a Spiro-MeOTAD hole transport layer, and a gold electrode. The TiO2 layer will be synthesized on the FTO glass, using a spin-coating method with a precursor solution and following high temperature sintering. Next, the perovskite material will be grown on the TiO2 layer. Lead halide solution will be spin-coated on the TiO2 layer, and then the device will be placed in a chemical vapor deposition (CVD) furnace, synthesizing perovskite in a gas mixture atmosphere. After the perovskite growth, Spiro-MeOTAD will be deposited on the device by spin-coating. Finally, a gold electrode will be deposited on the device. This entire device will be packaged with a water-proof material, and its energy efficiency and photocurrent response will be recorded to justify the proper function of the solar cell and the FTO electrode.

Activity Milestones:

Description	Completion Date
Design, fabrication, and characterization of perovskite solar cells with exposed FTO electrodes	2022-06-30
Evaluation of perovskite solar cells with exposed FTO electrodes in labs and in fields	2022-06-30

Activity 2: Synthesis, characterization, detection, and performance study of CuSnO3/Cu2O composite as the nitrobenzene sensing layer in labs and in fields

Activity Budget: $66,661

Activity Description:
FTO glass substrates will be used as the substrate material, and Cu2O and CuSnO3 nanomaterials will be synthesized by an electrochemical method and a co-precipitation method. The Cu2O layer will be electrochemically deposited on the FTO substrate to form a compact layer in a solution with Cu2+. As a p-type material, the Cu2O layer will display a cathodic photocurrent. CuSnO3 nanoparticles are synthesized by a co-precipitation method. First, the basic CuSO4 solution is dropwise injected into the Na2SnO3 solution, and the precipitant is collected and washed. Next, the collected powder is sintered at high temperature. Finally, the powder is dispersed in water to prepare a suspension, then drop-coated on the Cu2O film, and dryed to form the composite nanomaterial. The morphology and structure of Cu2O and CuSnO3 will be characterized by scanning electron microscopy (SEM), tunneling electron microscopy (TEM), and X-ray diffraction (XRD). The photocurrent response of the nanocomposite material will be assembled and investigated in details. The sensing performance, including sensitivity, specificity, and low detection limit for water monitoring and prevention will be evaluated and justified. In this activity, the photoelectrochemical test of CuSnO3/Cu2O composite materials will be studied with and without an electrical power supply.

Activity Milestones:

Description	Completion Date
Experiment of a photochemical reaction based on the synthesized material for detection of nitrobenzene	2023-06-30

Synthesis, characterization, and detection of nitrobenzene with $CuSnO_3/Cu_2O$ composites	2023-06-30

Activity 3: Development of monolithic detectors based on a solar cell structure, $CuSnO_3/Cu_2O$ sensing layer, and detection performance optimization

Activity Budget: $67,539

Activity Description:

We will develop a monolithic nitrobenzene detector combining the perovskite solar cell structure and the $CuSnO_3/Cu_2O$ sensing layer. After the solar cell structure fabrication, the Cu_2O film will be formed on the fluorine-doped tin oxide substrate by the deposition of a photoelectrochemical layer. In contrast to the electrochemical method, the photoelectrochemical deposition requires both an external bias potential and light illumination. The $CuSnO_3$ prepared by a co-precipitation method will be modified on the Cu_2O film by drop-coating, and the monolithic device fabrication is completed. The photocurrent response and detection performance of the device will be characterized. The photoelectrochemical test will be conducted without an electrical power supply. The fabrication and testing parameters of the device will be optimized to realize the best detection performance. Since the output power of the solar cell is limited, tuning the area ratio of the solar cell to the sensing part can adjust the applied potential on the detector, resulting in an optimized sensing performance. The size of a nitrobenzene detector will be as small as a penny, at least 1,000 times smaller than the current existing equipment, while the cost is at least 100 times lower than the current machine standard.

Activity Milestones:

Description	Completion Date
Field tests at two nearby chemical factories and in lakes or rivers in Minnesota	2024-06-30
Fabrication and construction of small nitrobenzene detectors, and performance characterization and optimization	2024-06-30

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this be funded?

This detector will be tested with a portable instrument developed by our team for in-lab and on-site nitrobenzene detection. After the completion of this project, we will build up a wireless sensor network based on this detector, and test the performance by distributing the network in factories and natural waters with high contamination risk. We need funds from LCCMR to support this effort. We will plan to file patents on the proposed detectors for commercialization in Minnesota. We will also apply for funding from DOE, NSF, EPA, and private foundations for our future scale-up work.

Project Manager and Organization Qualifications

Project Manager Name: Tianhong Cui

Job Title: Professor

Provide description of the project manager's qualifications to manage the proposed project.

Dr. Tianhong Cui is currently a Distinguished McKnight University Professor at the University of Minnesota. He is a Professor in Mechanical Engineering and an Affiliate Senior Member of the graduate faculty in Department of Electrical Engineering. He joined the faculty of the University of Minnesota in 2003. From 1995 to 2003, he held research or faculty positions at Tsinghua University, University of Minnesota, National Laboratory of Metrology in Japan, and Louisiana Tech University. He is a Distinguished Visiting Fellow at the University of Cambridge, and a Distinguished Visiting Professor at the University of Paris East in France. He is a Fellow of American Society of Mechanical Engineering (ASME).

Dr. Cui is an international leading expert on micro devices and advanced manufacturing. He has more than 320 archived publications in scientific journals and prestigious conferences. He has received awards including the STA & NEDO Fellowships in Japan, the Alexander von Humboldt Fellowship in Germany, the Richard & Barbara Endowed Chair and the Distinguished McKnight University Professorship from the University of Minnesota, the Distinguished Visiting Professorship from University of Paris East, the Distinguished Visiting Fellowship from the Royal Academy of Engineering in UK, the Outstanding Editor Award from Nature Publishing Group, and numerous best paper awards. He is the founding Executive Editor-in-Chief for a Nature journal, Microsystems & Nanoengineering. He is also serving as the founding Editor-in-Chief for the first AAAS/Science Partner Journal titled Research.

Dr. Cui will serve as PI and project manager, responsible for overseeing the project, all reports, and deliverables. He will supervise one Ph.D. student to work on the design, fabrication, and characterization of the nitrobenzene detector for water. He will hold weekly meetings with his advisee to ensure good progress of this proposed work, in addition to some daily technical discussion with his graduate research assistant.

Organization: U of MN - College of Science and Engineering

Organization Description:

This work will be performed at the University of Minnesota in the Technology Integration & Advanced Nano/Microsystems Laboratory (TIAN Lab), located in the Mechanical Engineering Building. Professor Cui is the director of TIAN Lab equipped with the state-of-the-art instrument and facility to conduct the proposed research, with a variety of fabrication and characterization equipment and tools, sufficient for Professor Cui, his postdoc, and Ph.D. student to design, fabricate, characterize and analyze the nitrobenzene detector for water.

Some fabrication work will be done in the Minnesota Nano Center (www.nfc.umn.edu), a state-of-the-art facility for research in nanoscience and applied nanotechnology. It is located at the University of Minnesota in a 7000 square foot facility, including 3000 square feet of class 10 clean room. The Lab contains all of the major pieces of processing equipment. Minnesota Nano Center well maintains these systems, keeps safe operating procedures, and trains students. State support, support from NSF through NNCI, and industry usage allows Minnesota Nano Center to offer academic rates that are normally less than half of the actual cost of operation. In addition to clean room tools available, the center will also operate two new non-cleanroom labs in nanomaterials and nanotechnology.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineli gible	% Bene fits	# FTE	Class ified Staff?	$ Amount
Personnel								
Principle Investigator		To manage the overall project and to conduct the overall research			36.5%	0.06		$24,955
1 Graduate Research Assistant		To design, fabricate, and test detectors in labs and in fields			19.9%	1.5		$156,019
							Sub Total	**$180,974**
Contracts and Services								
							Sub Total	-
Equipment, Tools, and Supplies								
	Tools and Supplies	Materials and supplies, instrument and equipment consumables, lab and filed set-up for sensors testing	To build and test the sensors in labs and in fields					$10,026
	Tools and Supplies	To use the facility and equipment at the Minnesota Nano Center	To fabricate the sensors using the center facility					$9,000
							Sub Total	**$19,026**
Capital Expenditures								
							Sub Total	-
Acquisitions and Stewardship								
							Sub Total	-
Travel In Minnesota								
							Sub Total	-

Travel Outside Minnesota								
							Sub Total	**-**
Printing and Publication								
							Sub Total	**-**
Other Expenses								
							Sub Total	**-**
							Grand Total	**$200,000**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request

Non ENRTF Funds

Category	Specific Source	Use	Status	Amount
State				
In-Kind	In kind: Indirect Cost at the University of Minnesota (55% MTDC)	In-kind support at the University of Minnesota	Secured	$82,896
			State Sub Total	**$82,896**
Non-State				
			Non State Sub Total	**-**
			Funds Total	**$82,896**

Attachments

Required Attachments

Visual Component

File: 97beef58-fef.pdf

Alternate Text for Visual Component

Current technology, proposed technology, sensor scheme, and sensing mechanism.

Optional Attachments

Support Letter or Other

Title	File
University SPA Supporting Letter	432a5b0e-ba6.docx

Administrative Use

Does your project include restoration or acquisition of land rights?

No

Does your project have patent, royalties, or revenue potential?

Yes,

- Patent, Copyright, or Royalty Potential

Does your project include research?

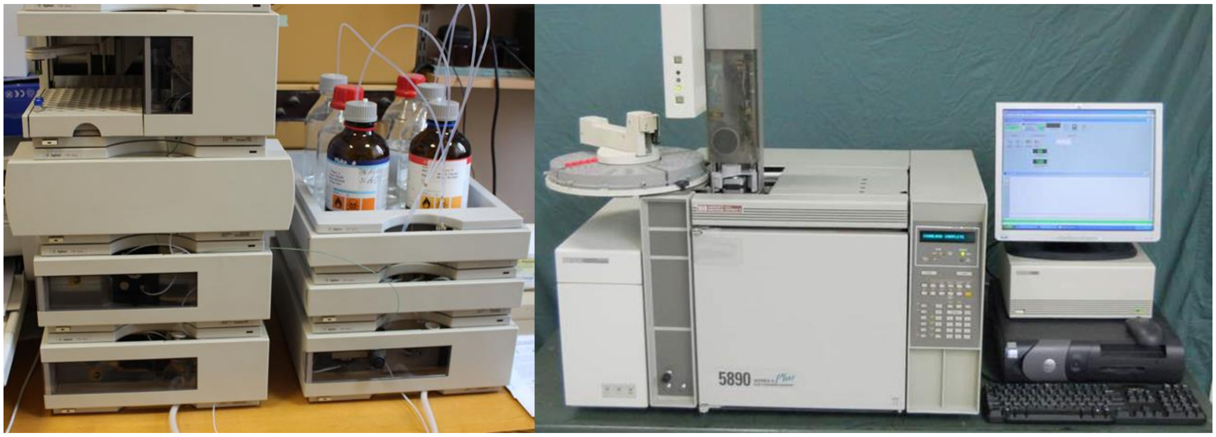
Yes

Does the organization have a fiscal agent for this project?

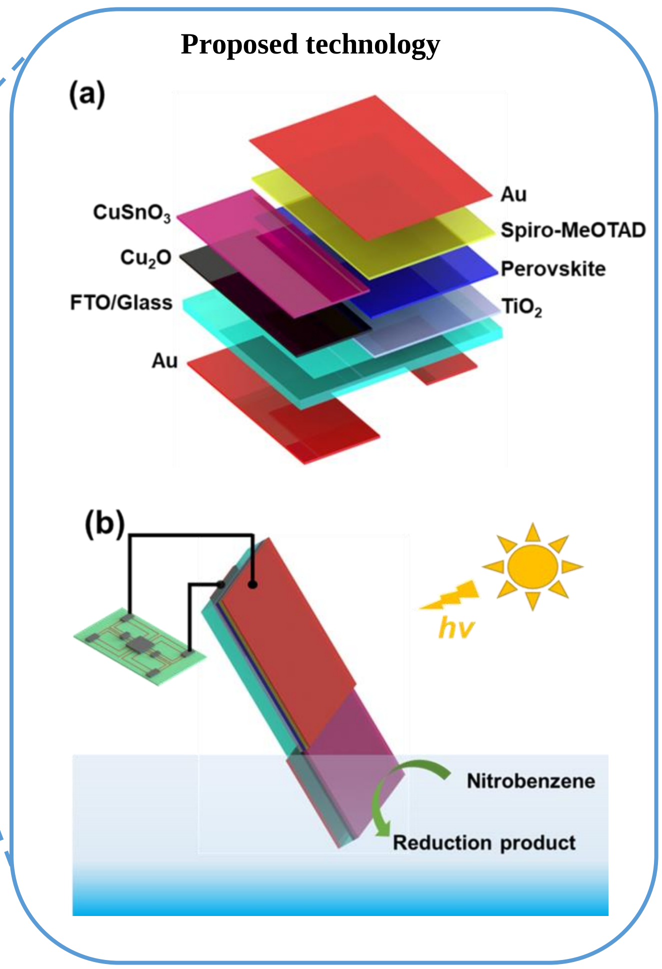
Yes, Sponsored Projects Administration

PI/PD: Tianhong Cui, University of Minnesota

Project Title: Small, cheap, and fast nitrobenzene detector for water



Current technology (large, expensive, slow)



Features of new technology

- **Small, cheap, fast**
- **No power supply**
- **On-line monitoring**
- **Easy to install and use**