

2019 Project Abstract

For the Period Ending June 30, 2019

PROJECT TITLE: Development of Innovative Sensor Technologies for Water Monitoring

PROJECT MANAGER: Tianhong Cui

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FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2016, Chp. 186, Sec. 2, Subd. 04j

APPROPRIATION AMOUNT: \$509,000

AMOUNT SPENT: \$509,000

AMOUNT REMAINING: \$0

Sound bite of Project Outcomes and Results

This project developed very tiny, cheap, fast, accurate sensors and sensor networks to monitor pollutants including phosphate, nitrate, mercury, and chlorine in Minnesota's waters. The team successfully conducted field tests at Mississippi River, Minnesota River, Minnehaha Creek and Calhoun Lake in Minnesota.

Overall Project Outcome and Results

The University of Minnesota team completed the project successfully by June 30, 2019. Professors Cui, Ruan, and Chen worked with one full-time research assistant, one full-time visiting student, and one post-doc conducting the research. The team finished the proposed research in the proposed Activity 1 and Activity 2. The team developed graphene sensors for testing and continuous monitoring of water quality indicators including phosphate, nitrate, mercury, and chloride. They very successfully got initial testing results using tiny sensors in response to pollutants in lab. They developed software coding for signal process and data display for the small sensing system. They tested the graphene sensors in comparison with the conventional lab tests, and did a compressive assessment of the sensing results. They developed a prototype of sensing network with tiny graphene sensors. The detection limits of the developed graphene sensors for phosphate, nitrate, mercury, and chloride are 0.1 ppm, 0.1 ppm, 1 ppb, and 0.1 ppm, respectively. The response time of the graphene sensors are 10 seconds. The team developed sensing systems and networks for field tests at Mississippi River, Minnesota River, Minnehaha Creek and Bde Maka Ska in Minnesota. The testing results demonstrate the capability of using the graphene sensors and sensing network for real-time monitoring of water pollutants including phosphate, nitrate, mercury, and chloride.

Project Results Use and Dissemination

On-site demonstration and sensing tests as described in the activities at Mississippi River, Minnesota River, Minnehaha Creek and Bde Maka Ska in Minnesota from May to June, 2019. Communications with interested entrepreneurs have been ongoing with interested parties including local companies and individuals. Collaboration on using the graphene sensors and sensor networks with MPCA and Metro have been conducted in the last year. We use the testing station from MPCA for field tests of pollutants at their Fort Snelling stations in Minnesota River.

Multiple papers were published in archived journals and prestigious conferences. Professor Tianhong Cui presented five invited public seminars and talks on water sensors at: École Normale Supérieure (ENS), Paris, France; Imperial College London, London, UK; Plenary talk, Design, Test, Integration & Packaging of MEMS and MOEMS (DTIP 219), Paris, France; Invited Talk, Microsystems & Nanoengineering Summit, Shanghai, China; Plenary talk, IEEE Nano Conference, Macau.



Environment and Natural Resources Trust Fund (ENRTF) M.L. 2016 051-B Project Report, Final Report

Date of Report: April 7, 2020

Final Report

Date of Work Plan Approval: June 7, 2016

Project Completion Date: June 30, 2019

Does this submission include an amendment request? No

PROJECT TITLE: Development of Innovative Sensor Technologies for Water Monitoring

Project Manager: Tianhong Cui

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Location: Minneapolis, MN

Total ENRTF Project Budget:

ENRTF Appropriation: \$509,000

Amount Spent: \$509,000

Balance: \$0

Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 04j

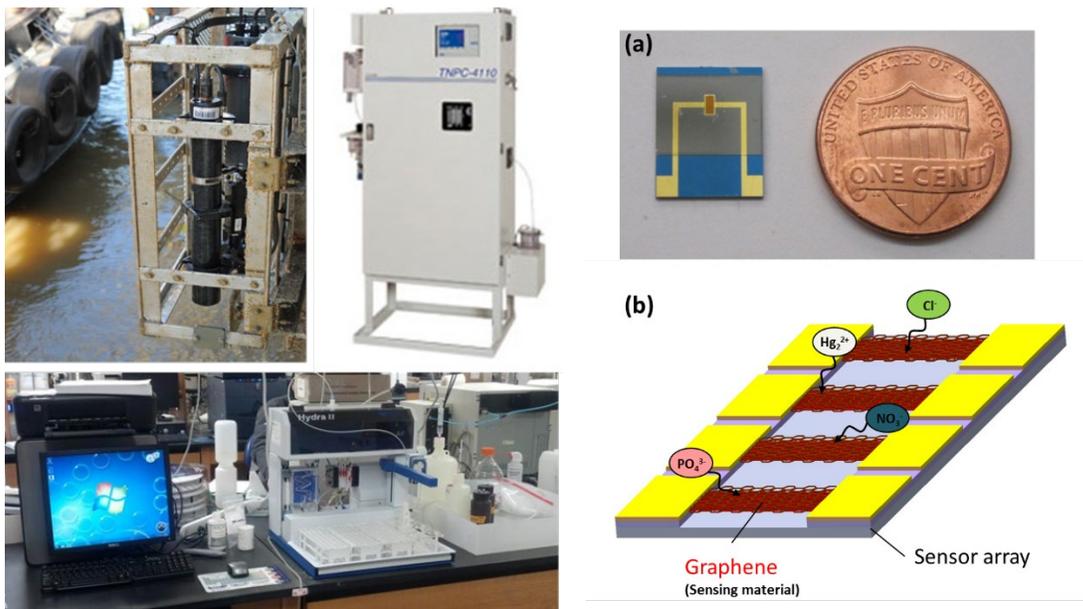
Appropriation Language:

\$509,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop inexpensive and efficient sensitive sensors and wireless sensor networks for continuous monitoring of contaminants in lakes and rivers in Minnesota. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2019, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Development of Innovative Sensor Technologies for Water Monitoring

II. PROJECT STATEMENT:

The objective of this project is to develop very tiny, cheap, fast, accurate sensors to continuously monitor pollutants including phosphate, nitrate, mercury, and chlorine in Minnesota’s waters (Figure 1). This is a new testing and monitoring technique, which can provide remote sensing capability to accurately assess the conditions of Minnesota’s waters at very low cost. The proposed new technology is to manufacture graphene micro sensors using the micro-manufacturing capability available in Minnesota, and to build wireless sensing networks based on the sensors. Graphene is a monolayer of carbon atoms with outstanding material properties, a newly developed material very sensitive to molecules in liquids. This will enable the tiny sensors to detect pollutants in lakes and rivers with very high sensitivity and super short response time to pollutants in waters. In contrast, currently environmental control agencies have to rely on bulky and expensive equipment to conduct off-line detections and analyses. The advanced manufacturing techniques at the University of Minnesota allow us to develop the sensors in a very high quantity at a super low cost, while surmounting the performance of pollutants detection using large equipment or devices. In addition, the sensors can be further developed into sensing networks so that we can form wireless detection for continuous monitoring of water quality in Minnesota. This will help the end-users including clear water agencies, researchers, and advocacy groups for continuous detection and analyses of Minnesota waters and prevent from ecological contaminations. This project is intended to develop the tiny cheap sensors, to prove its feasibility, and to provide foundational knowledge of the technique. In the next phase of the research, we will closely collaborate with state agencies, water researchers, and industry to develop an implementation plan for pollutants monitoring in broader water regions in Minnesota.



Current Technology

New Technology Proposed

Figure 1. A comparison of pollutants monitoring in waters between the current and proposed new technologies.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of December 31, 2016:

The University of Minnesota team started this project on July 1, 2016. Professors Cui, Ruan, and Chen recruited one full-time research assistant, one part-time research assistant, and one post-doc conducting the work. Significant progress has been made. In this report are summaries of progress including design of single sensor structure and fabrication flowchart, fabrication of sensors, initial testing of sensors, design of software and hardware for testing systems, determination of pollutant levels in Minnesota waters, and testing set-up for technology assessment. We designed two structures of graphene sensors, single strip and multiple strips. Based on the designed structures, photo masks were designed and fabricated for micro manufacturing. Chemical vapor deposition and layer-by-layer self-assembly were adopted to form the graphene film for the sensors. Preliminary experiments were conducted for Nitrate testing in different concentrations, which verified the sensing principles. Software and hardware were design to form the testing systems. Based on literature search and information collection, pollutant levels in Minnesota waters were identified for further design of graphene sensors. To assess our graphene sensor technology, a lab testing set-up using traditional technology was conducted. In summary, the initial 6-month work was successful.

Project Status as of June 30, 2017:

The University of Minnesota team made great progress from January 1, 2017 to June 30, 2017. Professors Cui, Ruan, and Chen worked with one full-time research assistant, one full-time visiting student, and one post-doc conducting the research. In this report are summaries of progress including fabrication and characterization of phosphate sensors with chemical vapor deposition (CVD) graphene as a sensing material, and nitrate and mercury sensors with layer-by-layer self-assembled graphene as a sensing component. In addition, we investigated different water testing methods approved by EPA and MPCA, and collected information on the pollutants level in various water bodies, including lakes, rivers and wastewater resources. We also investigated the methods and instruments used by MPCA. Resources and labs have been lined up for testing needs. In summary, the second 6-month work was productive and successful.

Project Status as of December 31, 2017:

The University of Minnesota team made great progress from July 1, 2017 to December 31, 2017. Professors Cui, Ruan, and Chen worked with one full-time research assistant, one full-time visiting student, and one post-doc conducting the research. In this report are summaries of progress including a new way to design and fabricate a nitrate sensor based on graphene ion sensitive field effect transistor (ISFET) and polymer selective membrane, a gold nanoparticles decorated sensor for mercury detection, a self-assembled graphene and nanoparticles composite sensor for nitrate detection, an electric testing system, and a comparison between the graphene sensors and other traditional testing methods. In summary, the third 6-month work was also productive and successful. We set up on a water site and data transmission through relay for the field tests using the graphene sensing system.

Project Status as of June 30, 2018:

The University of Minnesota team made great progress from January 1, 2018 to June 30, 2018. Professors Cui, Ruan, and Chen worked with one full-time research assistant, one full-time visiting student, and one post-doc conducting the research. In this report are summaries of progress including development of selective membranes for sensors' selectivity, solution-gated ion sensitive field effect transistor (IS-FET) sensors with selective membranes for nitrate and phosphate detection, anodic stripping voltammetry sensors for mercury detection, initial field tests at Minnesota River using micro sensors, and laboratory tests using traditional approaches. In summary, the fourth 6-month work was very productive and successful.

Amendment Request (09/04/2018):

This is a request for a re-budget of this LCCMR project. In Professor Roger Ruan's part of work, the researcher spends more time on the characterization experiments. Professor Ruan's researcher use some existing chemicals for the testing. We selected a closer rivers and lakes for testing. Therefore, we request to move \$2,000 from travel to personnel, and to move \$785 from supplied to personnel. In addition, Professor request his part of travel to cover domestic travels to present research papers at conferences.

Amendment Approved by LCCMR 10/23/2018.

Project Status as of December 31, 2018:

The University of Minnesota team made good progress from July 1, 2018 to December 31, 2018. Professors Cui, Ruan, and Chen worked with one full-time research assistant, one full-time visiting student, and one post-doc conducting the research. In this report are summaries of progress including graphene based chloride sensitive field-effect transistor (IS-FET) sensors with a chloride selective membrane, hardware and software modification on the portable sensing system, portable sensing system calibration and its application to field tests, and lab mercury tests compared with the results using the newly developed sensors. In summary, the fourth 6-month work was very productive and successful. They also developed a data networking protocol and hardware for the small sensing system.

Overall Project Outcomes and Results as of June 30, 2019

The University of Minnesota team completed the project successfully by June 30, 2019. Professors Cui, Ruan, and Chen worked with one full-time research assistant, one full-time visiting student, and one post-doc conducting the research. The team finished the proposed research in the proposed Activity 1 and Activity 2. The team developed graphene sensors for testing and continuous monitoring of water quality indicators including phosphate, nitrate, mercury, and chloride. They very successfully got initial testing results using tiny sensors in response to pollutants in lab. They developed software coding for signal process and data display for the small sensing system. They tested the graphene sensors in comparison with the conventional lab tests, and did a compressive assessment of the sensing results. They developed a prototype of sensing network with tiny graphene sensors. The detection limits of

the developed graphene sensors for phosphate, nitrate, mercury, and chloride are 0.1 ppm, 0.1 ppm, 1 ppb, and 0.1 ppm, respectively. The response time of the graphene sensors are 10 seconds. The team developed sensing systems and networks for field tests at Mississippi River, Minnesota River, Minnehaha Creek and Calhoun Lake in Minnesota. The testing results demonstrate the capability of using the graphene sensors and sensing network for real-time monitoring of water pollutants including phosphate, nitrate, mercury, and chloride.

Amendment Request (10/15/2019):

We are requesting an exception to our original budget as our research spending needs ended up being different than anticipated in the amendment requested 06/30/2018):

- Equipment/tools/supplies budget would be reduced by \$9,948. Project tasks involving sensor design, fabrication, testing and optimization for activity 1 involved fewer supplies and equipment than originally anticipated.
- Travel budget would be reduced by \$6,800. Travel costs were minimized by the selection of local bodies of water for pollution monitoring field tests, creating savings for both activity 1 and 2. Planned travel to conferences requested in the 06/30/2018 amendment was deferred.
- Other expense budget would be reduced by \$9,304. We had originally anticipated needing to contract for outside professional services to complete certain tasks, but were able instead to employ staff capable of doing the work. These savings primarily affect activity 1.
- Personnel budget would be increased by \$26,052 in total, with savings of \$4,370 in activity 1 and added costs of \$30,422 in activity 2. Using local bodies of water reduced labor costs in activity 1. Added effort by Professor Cui was required for activity 2 in the final period of the award to optimize the sensor networks.

Amendment Approved by LCCMR 4/7/2020.

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Development of tiny cheap sensors and sensor arrays

Description: The objective of this activity is to develop tiny sensors using graphene, which is very tiny, cheap, fast, accurate, sensitive, and durable for pollutants monitoring in lakes and rivers in Minnesota. Multiple sensors as a sensor array will be designed and fabricated for continuous monitoring of phosphate, nitrate, mercury, and chlorine in waters. The size of a single sensor or a sensor array will be as small as a rice grain. The sensor network system together with the sensors will be at least 10,000 times smaller than the current existing equipment, while the cost is at least 1,000 times lower than the bulky machine currently used for water quality detection, overrunning performance of the bulky equipment being used.

We propose a new sensor that promises to be an alternative to conventional sensors. Graphene, known as a one-atom-thickness carbon material, is used as a sensing material in our sensors. Graphene exhibits following excellent characteristics: (1) ease of being used in current microfabrication technology, (2) high sensitivity due to exposure of species to every single carbon atom, (3) low inherent

electrical noise, (4) capability of being integrated in tiny sensors, and (4) high carrier mobility. Due to its simplicity, low cost, and high performance, graphene sensors solve major problems with the current sensors, and empower the water monitoring system for environmental protection.

Specific tasks will be:

1. Single and multi-array sensors hardware will be developed for testing and continuous monitoring of water quality indicators including phosphate, nitrate, mercury, and chlorine. Initial testing results of tiny sensors in response to pollutants in lab.
 - a. Design, simulation, and optimization of single sensor and sensor array structures.
 - b. Design of fabrication flow chart of single sensor and sensor array.
 - c. Fabrication of sensor and sensor array using the micro- and nano-fabrication technology.
 - d. Lab test of single sensor and sensor array in phosphate, nitrate, mercury, and chlorine.
2. Software for signal process and data display will be developed
 - a. Develop and optimize program codes for signal process from the sensor and sensor array.
 - b. Develop and optimize program codes for data display for the sensor and sensor array.
3. Tiny sensors will be tested in comparison with conventional results in lab; Improved sensors with optimized design, fabrication, and testing; Sensors testing of pollutants monitoring of waters sampled from lakes and rivers in Minnesota.
 - a. Lab test single sensor and sensor array together with experiments based on conventional tests of pollutants.
 - b. Analyze and compare the results from the sensors developed and the conventional approaches.
 - c. Improve and optimize the design, fabrication, and testing of single sensor and sensor array.
 - d. Field test single sensor and sensor array from selected lakes and rivers in Minnesota.
4. Comprehensive assessment of the techniques will be completed.
 - a. Assess the design of the structures of single sensor and sensor array.
 - b. Assess the fabrication techniques of single sensor and sensor array.
 - c. Assess the sensor performance including selectivity, sensitivity, detection limit, and response time of single sensors and sensor array in lab.
 - d. Assess the sensor performance including selectivity, sensitivity, detection limit, response time, and life time of single sensors and sensor array in field tests of lakes and rivers.

Summary Budget Information for Activity 1:

ENRTF Budget: \$ 309,791

Amount Spent: \$ 309,791

Balance: \$ 0

Outcomes	Completion Date	Budget
<i>1. Single and multi-array sensors hardware will be developed for testing and continuous monitoring of water quality indicators including phosphate, nitrate, mercury, and chlorine; Initial testing results of tiny sensors in response to pollutants in lab</i>	6/30/2017	\$110,000
<i>2. Software for signal process and data display will be developed</i>	6/30/2017	\$80,000
<i>3. Tiny sensors will be tested in comparison with conventional results in lab; Improved sensors with optimized design, fabrication, and testing; Sensors testing of pollutants monitoring of waters sampled from lakes and rivers in Minnesota</i>	6/30/2018	\$99,791

4. Comprehensive assessment of the techniques will be completed	6/30/2018	\$20,000
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Project Status as of December 31, 2016:

Design and fabrication of sensors (Cui, Kim, and Wang)

Professor Cui and his research assistants designed graphene sensors with two structures, a single strip and multiple strips. Based on the two designs, the team designed the fabrication flow charts for micro manufacturing of graphene sensors. The photo masks for lithography was designed using L-Edit software, and two photo masks were fabricated by laser printing at Minnesota Nano Center at the University of Minnesota.

Graphene was synthesized by CVD system. The methane gas was used as the source material for the carbon and a Cu foil was used for a substrate. The as-synthesized graphene sheet was transferred to the Si/SiO₂ substrate for the fabrication of graphene sensors. The synthesized and transferred graphene sheets are characterized by Raman spectroscopy. In the spectrum, the intensity of 2D band is almost 2 times higher than G band. This means the synthesized graphene is single layer.

We also formed graphene composites thin film using layer-by-layer (LbL) self-assembly approach. LbL self-assembly technique is known as one of the most reliable “bottom-up” methods in micro-/nano-scale fabrication. In this study, the self-assembly process required three types of charged suspensions to form graphene sheets from graphene nano-platelets.

44 sensors were fabricated on a Si wafer using CVD approach and LbL self-assembly. For sensing the nitrate ion, the nitrate ionophore solution was coated to synthesis membrane on the graphene before applying NaNO₃ solution. This membrane allows only nitrate ions and blocks other ions. By using this selective membrane, we can detect nitrate ions in the solution. The testing shows that the sensor responds with NaNO₃ solutions in different concentrations. The response time and T_{90%} were 50s and 15s, respectively. The sensor with a nitrate selective membrane shows a response from 10 mg/L of nitrate concentration with decrease of resistance.

Design of software and hardware for testing systems is conducted. This system can provide a simple, fast, safe and steady testing method through wireless communication with the smartphone apps while achieving high resolution and small volume at the same time. The testing system is equipped with embedded processor, micro-current detection module, display screen, keyboard, battery, multi-voltage supply and charging module. It can be adapted with the micro sensor through detection port and communicate with smartphone app through wireless transmission module.

Determination of Pollutant Levels in Minnesota Waters (Ruan, Chen, and Addy)

The understanding of the levels of targeted pollutants in Minnesota waters is necessary to guide the development of the proposed sensors with desirable detection sensitivity and lower and upper limits. Based on the pollutants level in natural water body, the suggested specification for the sensor development is listed in Table 1. However, the specifications will be refined according to the progress of the sensor developed.

Table 1. The suggested specification for sensor development (tentative).

<i>Pollutant</i>	<i>Range</i>	<i>temp</i>	<i>pH</i>
Phosphate-P	0.1 – 50 mg/L	0-40	6-9
Nitrate-N	0.1-100 mg/L	0-40	6-9
Mercury	0.1-50 ng/L	0-40	6-9
Chlorine (free)	0.02-10.0 mg/L	0-40	6.5-7.5

Set up reference Testing Methods (Ruan and Chen)

We have identified and set up reference testing methods used for comparison between the proposed methods and conventional methods based on literature review and our experience. This is an important effort to provide objective assessment of the proposed methods.

Project Status as of June 30, 2017:

Fabrication and Characterization of Sensors for Phosphate, Nitrate, and Mercury (Cui, Kim, and Wang)

The phosphate sensor has three electrodes including source, drain, and reference electrodes. KMPR was coated on the surface of the device to cover gold electrodes. The KMPR layer can prevent from current leakage. The patterned KMPR has windows allowing graphene to expose to solutions. The selective membrane was coated on the graphene. Only phosphate ions can penetrate the selective membrane. In other words, other ions cannot go through the membrane. Therefore, the sensor selectivity can be ensured with coating the selective membrane on the sensor. The phosphate sensors were characterized by a semiconductor analyzer. The detection limit was about 50 µg/L and the response time was about 1 minute. Four different concentrations (0.05, 0.1, 1 and 10 mg/L) of the phosphate, chloride, nitrate and sulfate ion solutions, were tested using the phosphate sensors to verify the selectivity function of the membrane. It turns out that the selectivity is excellent.

Nitrate and mercury sensors with layer-by-layer self-assembled graphene as a sensing component were fabricated and tested. The sensors were integrated with three electrodes including a working electrode, a counter electrode, and a reference electrode. On the working electrode surface, nanoparticles were decorated to offer the target ions more area to enhance the sensor sensitivity. Layer-by-layer graphene is used in some cases to combine nanoparticles to improve the sensing performance. The reference electrode provides a stable potential so that the target can be detected and identified precisely. Layer-by-layer graphene and copper nanoparticles decorated sensors were designed, fabricated and applied to nitrate detection. A limit of detection of 0.49 mg/L was obtained with linear range from 0.62~5.58 mg/L. Gold nanoparticles decorated sensors were utilized to detect trace mercury. A limit of detection of 1 mg/L was obtained. Lower detection limits and higher sensitivity may be achieved by improving design and decoration parameters of the sensors.

Investigation of Different Water Testing Methods (Ruan, Chen, and Addy)

In the past six months, we investigated different water testing methods that are approved by EPA and MPCA and collected information on the pollutants level in various water bodies, including lakes, rivers and wastewater resources. We also investigated the methods and instruments used by MPCA. Resources and labs have been lined up for testing needs. In this project, four pollutants, phosphate (PO_4^{3-}), nitrate (NO_3^-), mercury (Hg), and chloride (Cl^-) were selected for sensor development and water quality testing. Currently, the test methods use primarily colorimetric methods which are tedious, time-consuming, and costly. The proposed sensing techniques should be able to test the pollutant level in just a second which would save time and reduce costs. During the sensor development stage, the traditional methods will be served as the reference check for the results measured by the sensors. The current lab testing methods could meet MPCA water testing requirement and provide reference check for the sensors being developed.

Project Status as of December 31, 2017:

Fabrication and Characterization of ISFET Sensors for Phosphate, Nitrate, and Mercury (Cui, Kim, and Kim)

We investigated a new way to design and fabricate a nitrate sensor based on ion sensitive field effect transistor (ISFET) and polymer selective membrane. Graphene is used as the sensing material in the ISFET and polyvinyl chloride (PVC) based membrane is applied to the graphene for a selectivity. For a proof of a concept, the sensing area of ISFET is coated with the PVC-based membrane including a plasticizer and an ionophore to detect nitrate in water. The sensor response is measured as a shift in Dirac point, reference voltage, using a semiconductor analyzer. The sensor was characterized with four different solutions including chloride, sulfate, phosphate, and nitrate. The sensor performance was confirmed by measuring the shift of Dirac point of graphene with the different ion solutions. The sensor does not show the response with chloride, sulfate and phosphate, Dirac point obviously changes from -0.27 V to -0.18 depending on the concentration of the nitrate

solutions. We successfully demonstrated that the ISFET has a high sensitivity, a short response time, and a great selectivity. The nitrate detection limit of the device is 0.1 mg/L.

Fabrication and Characterization of Electrochemical Sensors for Mercury and Nitrate (Cui, Ruan, Chen, Raddy, Kim, and Wang)

Gold nanoparticles decorated sensor was successfully investigated for mercury detection. Gold is one of the least reactive chemical elements with excellent conductivity. The ability of forming amalgam with mercury makes gold an ideal material for mercury detection. In order to enlarge the surface area of the working electrode, gold was deposited on the working electrode in the form of nanoparticles. A low detection limit of 0.001 mg/L was obtained. Layer-by-layer (LbL) self-assembled graphene and nanoparticles composite sensors were developed to detect nitrate in waste water, and the results were in good agreement with those from standard methods. Reusability of the LBL graphene and copper nanoparticles composite sensor was investigated by detecting 50 μ M nitrate solutions consecutively for ten times. Pre-treatment was conducted between two adjacent detections to form a fresh copper layer. The change and variation of peak current values was analyzed to evaluate the suitability for reusing the proposed sensor. Real water detection was investigated by analyzing standard nitrate solutions and lake water samples with the proposed sensor. As comparison, a standard spectroscopic method was also adopted to analyze the above samples. Fresh lake water samples were taken from Lake Como in Minnesota. Filtration was operated to remove big particles in lake water before experiments. Standard spectroscopic method was operated with Hach DR1900 Spectrophotometer.

Development of Software and Hardware for a Sensing System (Cui and Wang)

An electric testing system was developed for the detection of ions. This system can accomplish the analysis of signals both from the three-terminal system and the two-terminal system. It also provides friendly user interface to make the operation process easier and more comfortable for customers. The testing system is equipped with embedded processor, micro-current detection module, display screen, keyboard, battery, multi-voltage supply and charging module. It can be adapted with the micro sensor through detection port and communicate with smartphone app through wireless transmission module.

Project Status as of June 30, 2018:

Development of selective membranes for sensors' selectivity, solution-gated ion sensitive field effect transistor (IS-FET) sensors with selective membranes for nitrate and phosphate detection (Cui and Kim)

Nitrate and phosphate selective membranes were synthesized and coated on the sensing areas on the IS-FET sensors using a spin-coater. The IS-FET sensors were tested by a semiconductor analyzer. The sensor responses were characterized with different ionic solutions, and the concentration was logarithmically changed. We also successfully fabricated a sensor probe for field tests using PDMS. The selectivity of each membrane was successfully demonstrated by analyzing the sensor response data. New batch of micro sensors was fabricated to optimize the sensors for improved performance and field tests.

Development of anodic stripping voltammetry (ASV) sensors for mercury detection (Cui, Liu, and Kim)

Design, fabrication, and characterization of anodic voltammetry sensors were conducted for mercury detection. The sensors consist of a working electrode, a counter electrode, and a reference electrode. Based on the ASV method, -0.4V (to the Ag/AgCl reference electrode) was firstly applied to the working electrode for the accumulation process, when mercury ions were reduced to mercury and attached on the electrode. Next, a sweeping potential from -0.4 V to 0.8 V was applied to the electrode to oxidize the reduced mercury. The experiments show that the sensors performed well as an approach for mercury detection.

Lab tests of mercury and nitrate for comparison with results from micro sensors (Ruan, Chen, Raddy, Liu)

In the past six months, several lab and field water tests of nitrate and mercury were conducted to compare with the results obtained using the newly developed sensors. The Minnesota Pollution Control Agency (MPCA)

follows the EPA procedures for water testing, and uses service at the Minnesota Health Department (MHD) for the water test. Based on the MPCA approach, the results of lab tests were tested and recorded to compared with results from micro sensors.

Project Status (Integration Work with Activity 2) as of December 31, 2018:

N/A

Final Report Summary (Integration Work with Activity 2) as of June 30, 2019:

The team developed graphene sensors for testing and continuous monitoring of water quality indicators including phosphate, nitrate, mercury, and chloride. They very successfully got initial testing results using tiny sensors in response to pollutants in lab. They developed software coding for signal process and data display for the small sensing system. They tested the graphene sensors in comparison with the conventional lab tests, and did a compressive assessment of the sensing results. They developed a prototype of sensing network with tiny graphene sensors. The detection limits of the developed graphene sensors for phosphate, nitrate, mercury, and chloride are 0.1 ppm, 0.1 ppm, 1 ppb, and 0.1 ppm, respectively. The response time of the graphene sensors are 10 seconds.

ACTIVITY 2: Development of wireless sensing networks and field testing

Description: A prototype unit will be designed and constructed to demonstrate the feasibility. Data networking protocol and hardware will be developed and tested. Field testing will include setting up a test site and three data relay stations. Upon completion of the project, we will demonstrate the integrated system to the stakeholders and LCCMR committee members and officials.

We will develop data networking protocol and hardware in order to send and receive signals from the graphene sensors wirelessly. This enables us to visualize pollutant levels at a monitoring station (Figure 2). The new technology will make great impacts on easy and low-cost monitoring of waters, promising that it advances monitoring a large number of lakes and rivers in Minnesota for environmental protection and human health safety.

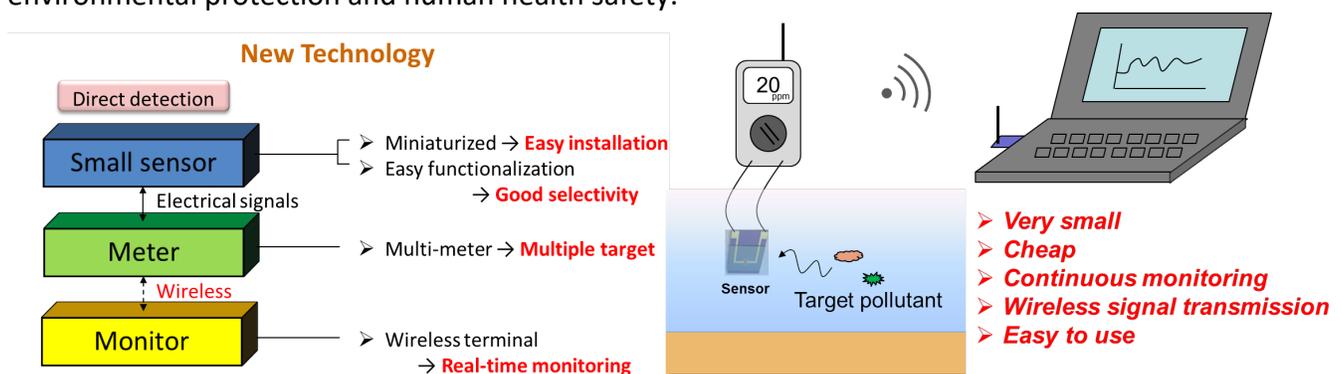


Figure 2. Sensor network proposed in this project for monitoring pollutants in waters

Specific tasks will be:

1. A prototype of sensing network with tiny sensors unit will be developed.
 - a. Design, simulate, and optimize sensing network with tiny sensors.
 - b. Assemble and test electrical signal process of sensing network.

- c. Lab test sensing network in solutions of phosphate, nitrate, mercury, and chlorine.
2. Data networking protocol and hardware will be developed.
 - a. Develop and optimize data networking protocols.
 - b. Develop and optimize sensing network hardware.
 3. The prototype unit will be set up on a water site and data transmission through relay will be tested.
 - a. Lab test sensing networks with experiments based on conventional tests of pollutants.
 - b. Analyze and compare the results from the sensing networks and the conventional approaches.
 - c. Improve and optimize the design, assembly, and testing of sensing networks.
 - d. Field test sensing networks from lakes and rivers in Minnesota.

Summary Budget Information for Activity 2:

ENRTF Budget: \$ 199,209
Amount Spent: \$ 199,209
Balance: \$ 0

Outcomes	Completion Date	Budget
<i>1. A prototype of sensing network with tiny sensors unit will be developed</i>	<i>6/30/2019</i>	<i>\$60,000</i>
<i>2. Data networking protocol and hardware will be developed</i>	<i>6/30/2019</i>	<i>\$60,000</i>
<i>3. The prototype unit will be set up on a water site and data transmission through relay will be tested</i>	<i>6/30/2019</i>	<i>\$79,209</i>

Project Status as of December 31, 2016:

N/A

Project Status as of June 30, 2017:

N/A

Project Status as of December 31, 2017:

N/A

Project Status as of June 30, 2018:

Initial Field Tests (Cui, Ruan, Chen, Kim, Liu, and Raddy)

The Fort Snelling site at Minnesota River is equipped with a small shed with multiple sensors located both inside and outside. The river water was pumped into a small water pot inside the shed, and the pH probe, conductivity sensor, nitrate/nitrite sensor and temperature were located inside the pot for real time testing. Since our developed sensor is very small, the device can collocate with the sensors in the same pot. Using our self-designed portable instrument, the mercury sensor was firstly calibrated and then tested in the field. The results from the electrochemical workstation showed better performance than that from the micro sensors. Therefore, there is still room for us to improve the performance of the micro sensors.

Project Status as of December 31, 2018:

Chloride field-effect transistor (IS-FET) sensors with a chloride selective membrane (Cui, Liu, and Kim)

The synthesized chloride selective membrane was applied to IS-FET for the chloride detection. The selective membrane solution coated on the sensing area using spin-coater. We also prepared several solutions (nitrate, phosphate, sulfate and chloride) that have different ions and concentrations to demonstrate the sensitivity and selectivity of the sensors. For the selectivity test, Dirac point was linearly shifted depending on the concentration that is logarithmically changed. The selectivity of the sensors is also characterized by the different ionic solutions. The sensor shows an only small response (about 2~5%) with nitrate, phosphate and sulfate. However, the amount of change of Dirac point is about 25% when 100 mg/L chloride solution was applied to the sensor.

Modification, calibration and field tests of portable sensing systems (Liu, Kim, and Cui)

Previous field test results showed that the electrical noise of the portable ASV instrument was the main factor limiting the detection performance in Hg(II) measurement. Therefore, after analyzing the source of electrical noise of the portable instrument, the data acquisition module is modified to reduce the noise. After adjustment, the smoothness of stripping curves recorded by the portable system is comparable to the one recorded by electrochemical workstation. Apart from hardware modification, the software of the portable instrument is also improved to get a better repeatability of the test results. After above system adjustment, higher consistency between the calibration curve and the field test curve is observed. The field tests were implemented at Mississippi River.

Lab and field tests comparison (Ruan, Chen, Cui, Raddy, Liu, and Kim)

In the past six months, we have been focused on lab and field mercury test and compare with the results obtained using the newly developed sensors. It was found that the water matrix had a significant effect on the present form of mercury in water. Using a portable mercury sensor for a natural water test is still facing a lot of challenge. In natural water body, the mercury level is around 10 ppt or less. However the low limit of detection (LoD) of the developed mercury sensor is about 2 ppb, therefore, adding mercury standard to spike the mercury concentrations to ppb level was used for the sensor testing. From the past experiments that the sensor produced good predictability and repeatability in DI water based samples and it was expected that the sensor would work equally well in the natural water matrix (e.g. river water or lake water). However it was found that the added mercury would go through various chemical, biological or physical reaction affecting the existing form of mercury in water. The current developed mercury sensor was designed to detect Hg(II), while the added Hg(II) would experience methylation/demethylation transformations and adsorption/desorption process that resulted in deviation for the sensor readings.

Final Report Summary as of June 30, 2019:

Prototype of sensing network with sensors and data networking protocol and hardware (Liu, Kim, and Cui)

Two types of wireless communication systems based on different protocols are established. The wireless system is divided into two parts, the internal network of distributed server/client sensing units and the remote host computer. The internal sensing networks in both systems are based on wireless 433 MHz communication, and are composed of distributed clients and servers. The theoretical effective communication distance between the server and clients is 2 kilometers. Clients are responsible for the monitoring of the environment, while servers act as relays to manage the communication between the host computer and the distributed sensing network. For topological structure, the communication between servers and host computer is realized by wired UART (Universal Asynchronous Receiver/Transmitter), GPRS (General Packet Radio Services) communication is adopted to establish the communication between servers and host computer, which allows global data transmission from the server to the host computer but needs the service of communication carriers. Commercialized 433 MHz module, UART module, and GPRS module are adopted in the hardware development.

We choose STM32ZET6 as the central control chip. The server and client are developed based on this chip and are embedded with our self-developed system. For the host computer part, LabView is used to develop the user interface (UI) software, where operators can monitor and manipulate the functioning of every single distributed client. Multiple parameters, including working hour, battery capacity, ion concentration, and temperature, can be shown on the UI software.

Field tests at water sites (Kim, Liu, Randy, Chen, Ruan, and Cui)

The team developed sensing systems and networks for field tests at Mississippi River, Minnesota River, Minnehaha Creek and Calhoun Lake in Minnesota. The testing results demonstrate the capability of using the graphene sensors and sensing network for real-time monitoring of water pollutants including phosphate, nitrate, mercury, and chloride. Field tests at different sites are conducted to test the wireless communication function of the systems. As an example, the UART system was tested. Before the field tests, the sensing system and sensors have been calibrated in the lab with mercury solutions of controlled mercury concentration (20, 50, 100, 150 ppb). Water samples are collected from the sources, and controlled amount of mercury is injected into them. Due to the low concentration of mercury in natural waters, the injection induced concentration is assumed to be the true concentration, and three different concentrations (40, 80, 120 ppb) are tested. It can be concluded from the test results that all field test results are basically consistent with the calibrated curves. In our tests, no pretreatment, such as filtration, is conducted, and through naked eye observation, sample water from Mississippi River is the dirtiest one. Water samples from River Mississippi with injected mercury are sent to the Minnesota Department of health for lab tests. The test method is cold vapor atomic absorption spectrometry and the results are consistent with our testing results.

Lab tests for a comparison with that from the sensor networks (Randy, Chen, Ruan, Kim, Liu, and Cui)

In this project, the group from BBE mainly focused on determination of pollutant levels in Minnesota waters, set up reference testing methods in comparing with the developed sensors, coordinated with field test regarding the four targeted pollutants including phosphorus, nitrate, chloride and mercury, and also provided guidelines for sensor development specifications. The main findings were as follow. According to field test and literature review, the pollutant level in Minnesota waters varied by locations. Higher phosphorus, nitrate, chloride level were observed near the agricultural heavy locations where total phosphorus can be as high as 0.25 mg/L, nitrate 4 mg/L, and chloride 30 mg/L. The soluble total mercury levels were usually low in few ppt (ug/L) level that can be hard for the sensor to detect. According to the water quality standard, the total Hg should be less than 6.9 ng/L., nitrate less than 10 mg/L, chloride 230 mg/L and total phosphorus ranges from 50 to 150 µg/L which provided a guideline for the detection range for the sensor we are trying to develop. In addition, other metal such as calcium and sodium can be interference element for the sensor test since it was tested that in Como Lake the Ca was 18 mg/L and Na was 72 mg/L. For the nitrate sensor test, two reference test methods were used to compare the accuracy. They were (1) Nitrate TNT835 Vial Test with Hach DR5000 spectrometer, and (2) Lachat Quickchem 8500 conducted by the Soil Testing Lab at the University of Minnesota, St. Paul campus. Both methods provided test accuracy of around 2-5%. The total phosphorus test was Hach kit TNT 845 that the test accuracy was 5%. The mercury test was sent to MHD and tested with the method of EPA 245.2 for total mercury with reported accuracy around 10%. And the chloride was used the EPA 300.1 with 10% of accuracy. During the field test, the Fort Snelling site which is in the Watershed Pollutant Load Monitoring Network and under the management of MPCA were selected for the mercury test. Due to the natural mercury test was low in Minnesota River, the sample was tested with spike of mercury standards. The reference test result usually showed 20% less compared with the accrual mercury level even with sample filtration and HCl preserve addition. In summary, the reference test is accurate enough to provide reference test for the sensors developed.

V. DISSEMINATION:

Description:

The findings will be disseminated through:

- (1) On site demonstration as described in the activities
- (2) Public seminars
- (3) Progress update on biorefining.cfans.umn.edu and www.me.umn.edu
- (4) Presentations at national and international technical conferences
- (5) Communications with interested entrepreneurs
- (6) Peer reviewed papers
- (7) Collaboration with MPCA

The technologies, if demonstrated successfully, may be implemented to many lakes and rivers in the State of Minnesota and beyond. Any intellectual properties and related revenues as a result of the program will be shared between UMN and LCCMR.

Project Status as of December 31, 2016:

N/A

Project Status as of June 30, 2017:

N/A

Project Status as of December 31, 2017:

N/A

Project Status as of June 30, 2018:

One conference paper was accepted in the following:

“Solution-Gated Ion-Sensitive Field Effect Transistor with Polymer Selective Membrane for Nitrate Detection”, Jungyoon Kim, Li Wang, and Tianhong, ASME International Mechanical Engineering Congress & Exposition, Pittsburg, PA, November 9-15, 2019.

Project Status as of December 31, 2018:

One conference paper was published in the following:

“Solution-Gated Ion-Sensitive Field Effect Transistor with Polymer Selective Membrane for Nitrate Detection”, Jungyoon Kim, Li Wang, and Tianhong, ASME International Mechanical Engineering Congress & Exposition, Pittsburg, PA, November 9-15, 2019.

Final Report Summary as of June 30, 2019

The technologies, if demonstrated successfully, may be implemented to many lakes and rivers in the State of Minnesota and beyond. Any intellectual properties and related revenues as a result of the program will be shared between UMN and LCCMR.

The findings will be disseminated through:

- (1) On site demonstration as described in the activities

On-site demonstration and sensing tests as described in the activities at Minnesota River on June 6, 2018.

On-site demonstration and sensing tests as described in the activities at Mississippi River, Minnesota River, Minnehaha Creek and Calhoun Lake in Minnesota from May to June, 2019.
On-site demonstration and sensing tests as described in the activities at Mississippi River, Minnesota River, Minnehaha Creek and Calhoun Lake in Minnesota from May to June, 2019.

(2) Public seminars

Professor Tianhong Cui presented five invited public seminars and talks on water sensors:

- 1) École Normale Supérieure (ENS), Paris, France, January 25, 2019
- 2) Imperial College London, London, UK, March 21, 2019
- 3) Plenary talk, Design, Test, Integration & Packaging of MEMS and MOEMS (DTIP 219), Paris, France, May 12-15, 2019
- 4) Invited Talk, Microsystems & Nanoengineering Summit, Shanghai, China, July 7-10, 2019
- 5) Plenary talk, IEEE Nano Conference, Macau, July 23-26, 2019

(3) Progress update on biorefining.cfans.umn.edu and www.me.umn.edu

Progress update on biorefining.cfans.umn.edu and www.me.umn.edu will be posted on 11/15/2019.

(4) Presentations at national and international technical conferences

1. Jungyoon Kim, Li Wang, and Tianhong , “Solution-Gated Ion-Sensitive Field Effect Transistor with Polymer Selective Membrane for Nitrate Detection”, ASME International Mechanical Engineering Congress & Exposition, Pittsburg, PA, November 9-15, 2019.
2. Li Wang, Jungyoon Kim and Tianhong Cui, “A Low-Cost Ion Selective Nitrate Sensor Based on Self-Assembled Graphene Microelectrode Arrays”, the 20th International Conference on Solid-State Sensors, Actuators and Microsystems (Transducers 2019 - EUROSENSORS XXXIII), Berlin, Germany, June 23-27, 2019.
3. Jungyoon Kim, Li Wang, and Tianhong Cui, “Graphene Based Ultra Sensitive Ion Sensor for Phosphate Detection”, the 21st International Conference on Miniaturized Systems for Chemistry and Life Sciences (MicroTAS 2017), Savannah, Georgia, USA, October 22-26, 2017.
4. Li Wang, Jungyoon Kim, and Tianhong Cui, “Highly Sensitive Sensor Based on Decorated Copper Nanoparticles and Self-Assembled Graphene for Nitrate Detection”, the 21st International Conference on Miniaturized Systems for Chemistry and Life Sciences (MicroTAS 2017), Savannah, Georgia, USA, October 22-26, 2017.

(5) Communications with interested entrepreneurs

Communications with interested entrepreneurs have been ongoing with interested parties including local companies and individuals.

(6) Peer reviewed papers

1. Jungyoon Kim, Li Wang, Tarik Bourouina, and Tianhong Cui, "Ion Sensitive Field Effect Transistor Based on Graphene and Ionophore Hybrid Membrane for Phosphate Detection", *Microsystem Technologies*, Vol. 25, No. 9, 2019: 3357-3364.
2. "Solution-Gated Ion-Sensitive Field Effect Transistor with Polymer Selective Membrane for Nitrate Detection", Jungyoon Kim, Li Wang, and Tianhong, ASME International Mechanical Engineering Congress & Exposition, Pittsburg, PA, November 9-15, 2019.
3. Li Wang, Jungyoon Kim and Tianhong Cui, "A Low-Cost Ion Selective Nitrate Sensor Based on Self-Assembled Graphene Microelectrode Arrays", the 20th International Conference on Solid-State Sensors, Actuators and Microsystems (Transducers 2019 - EUROSENSORS XXXIII), Berlin, Germany, June 23-27, 2019.
4. Li Wang, Jungyoon Kim, and Tianhong Cui, "Self-Assembled Graphene and Copper Nanoparticles Composite Sensor for Nitrate Determination", *Microsystem Technologies*, Vol. 24, No. 9, 2018: 3623-3630.
5. Jungyoon Kim, Li Wang, and Tianhong Cui, "Graphene Based Ultra Sensitive Ion Sensor for Phosphate Detection", the 21st International Conference on Miniaturized Systems for Chemistry and Life Sciences (MicroTAS 2017), Savannah, Georgia, USA, October 22-26, 2017.
Li Wang, Jungyoon Kim, and Tianhong Cui, "Highly Sensitive Sensor Based on Decorated Copper Nanoparticles and Self-Assembled Graphene for Nitrate Detection", the 21st International Conference on Miniaturized Systems for Chemistry and Life Sciences (MicroTAS 2017), Savannah, Georgia, USA, October 22-26, 2017.

(7) Collaboration with MPCA

Collaboration on using the graphene sensors and sensor networks with MPCA and Metro have been conducted in the last year. We use the testing station from MPCA for field tests of pollutants at their Fort Snelling stations in Minnesota River.

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	\$ Amount	Overview Explanation
Personnel:	\$ 451,969	<ul style="list-style-type: none"> • Dr. Tianhong Cui PI (4.3 weeks (.11FTE) + fringe 33.7% fringe) for 3 years. 9 months appointment • Dr. Roger Ruan (3.12 weeks (.08FTE) + fringe 33.7% fringe) for 3 years. 9 months appointment • Dr. Paul Chen (14.5 weeks (.28FTE) + fringe 33.7% fringe) for 3 years. 12 months appointment • Post-Doc (Ruan and Chen) (6 months + 22.4% fringe) for 3 years

		<ul style="list-style-type: none"> Graduate Research Assistant 50% FTE (fall & spring include 17.6% fringe plus \$18.29/hour tuition, summer 17.6% fringe only) for 3 years
Professional/Technical/Service Contracts:	\$28,196	Scientific Services (Cui): User fees at Minnesota Nano Center and Characterization Facility at the University of Minnesota. The cost is about \$541 per month for the Post-Doc, and \$500 per month for the graduate research assistant for 3 years.
Equipment/Tools/Supplies:	\$28,635	Lab Supplies (Cui): fabrication materials & supplies including silicon wafers (\$3,413), polymer substrates (\$4,000), chemicals (\$6,000), graphene substrate and solutions (\$5,000), carbon based gases (\$3,000), bottles, gloves, other electronics for testing, etc. (\$2,500) Lab Materials & Supplies (Ruan & Chen): Purchase of chemical reagents (\$3,000), analytical kits (\$2,500), compressed gases (\$500), glassware (\$855), consumable supplies (standards and columns) for analytical instruments (\$5,000), instrument maintenance and repair (\$3,600)
Travel Expenses in MN:	\$200	Ruan & Chen domestic travel (year 2 &3): Mileage, lodging, and meals for travel between the sensor testing sites and the university; Cui, Ruan, and Chen need work together on the testing. This cost is based on the university compensation policy.
TOTAL ENRTF BUDGET:	\$509,000	

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than \$5,000: N/A

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 4.41 FTE

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0

B. Other Funds:

Source of Funds	\$ Amount Proposed	\$ Amount Spent	Use of Other Funds
Non-State			
Mocon Inc.	\$173,199	\$50,000	Developing graphene gas sensors
State			
The university overhead unpaid	\$237,500	\$0	Developing tiny sensors for pollutants monitoring in waters
TOTAL OTHER FUNDS:	\$410,699	\$50,000	

VII. PROJECT STRATEGY:

A. Project Partners:

Tianhong Cui, professor in Mechanical Engineering, will serve as PI and project manager. He will be responsible for overseeing the project, all reports, and deliverables. He will also develop the tiny sensors, portable sensor network units, and data transfer protocols. Roger Ruan, professor in

Bioproducts and Biosystems, will be a collaborator responsible for setting up field testing of the proposed techniques. Paul Chen, associate professor in Bioproducts and Biosystems, will be another collaborator responsible for lab analysis of water quality using conventional and the proposed techniques.

B. Project Impact and Long-term Strategy:

Minnesota Pollution Control Agency (MPCA) works together with other agencies and advocacy groups in developing strategy to prevent, control, and abate discharges that cause water pollution and violate water quality standards. The first task in the strategy is testing and assessment to provide information on the conditions of the waters. Currently, many of our water bodies are unmonitored despite the requirement of the federal 1972 Clean Water Act. The proposed tiny sensors will provide low-cost, but high-performance techniques and infrastructure, i.e. unique sensors and sensing networks, for assessment of Minnesota’s waters in much greater geographic area. Upon completion this project will realize economical and high-performance tiny sensing technique for continuous monitoring of water conditions. The knowledge learned throughout the project will provide a solid foundation for further research and development efforts that would lead to eventual implementation of the novel technique practically enabling broader monitoring of Minnesota’s waters with remote sensing and data transmission via wireless capability. This will provide a solution to current resources strapped monitoring programs in Minnesota, ultimately help implement the MPCA’s clear water strategy, and thus enhance the ecological benefits of Minnesota waters.

In addition, we will plan to file patents on the proposed sensors and sensor networks for commercialization in the future. We can also use the sensors or sensor networks for monitoring and detection of drinking water, juice, liquid food, etc. As a result, the innovative technology can also benefit the local industry by developing new products in Minnesota including new graphene tiny sensors and sensor networks for broader applications.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	\$ Amount
Mocon Inc., Graphene gas sensors	Nov. 2014 - July 2016	\$173,199
Alexandria Extrusion Inc., Microstructures for Heat Transfer	Nov. 2011 - Dec. 2015	\$165,516
DARPA, MEMS-Based Active Heat Sink Technology	Jan. 2009 - Sept. 2013	\$2,579,025
MN Partnership, Nano-Sensors	Jan. 2010 – Dec. 2012	\$637,500

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:

IX. VISUAL COMPONENT or MAP(S):

X. RESEARCH ADDENDUM:

Enclosed

XI. REPORTING REQUIREMENTS:

Periodic work plan status update reports will be submitted no later than September 2016, March 2017, September 2017, March 2018, September 2018, and March 2019. A final report and associated products will be submitted on June 30, 2019.

Environment and Natural Resources Trust Fund
Final M.L. 2016 Project Budget
Project Title: Development of Innovative Sensor Technologies for Water Monitoring
Legal Citation: M.L. 2016, Sec. 116P.10., Subd. 04k
Project Manager: Tianhong Cui
Organization: Univeristy of Minnesota
M.L. 2016 ENRTF Appropriation: \$509,000
Project Length and Completion Date: 3 Years, June 30, 2019
Date of Report: April 7, 2020



ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Revised Activity 1 Budget 4/7/2020	Amount Spent	Activity 1 Balance	Revised Activity 2 Budget 4/7/2020	Amount Spent	Activity 2 Balance	Revised Total Budget 4/7/2020	Amount Spent	TOTAL BALANCE
BUDGET ITEM									
Personnel (Wages and Benefits)	\$276,779	\$276,779	\$0	\$175,190.00	\$175,190.00	\$0	\$451,969	\$451,969	\$0
Tianhong Cui, PI: \$21,909 (75% salary, 25% benefits); 11% FTE each year for 3 years, 3% increase years 2-3. \$67,720 for 3 years in total.		\$57,678			\$ 46,968.00				
Ruan, Co-PI: \$10,252 (75% salary, 25% benefits): 8% FTE each year for 3 years, 3% increase years 2-3. \$31,688 for 3 years in total.		\$16,794			\$ 14,644.00				
Chen, Co-PI: \$32,183 (75% salary, 25% benefits): 28% FTE each year for 3 years, 3% increase years 2-3. \$99,474 for 3 years in total.		\$76,072			\$ 27,639.00				
PostDoc or other appropriate research categories \$27,315 (82% salary, 18% benefits): 50% FTE each year for 3 years, 3% increase years 2-3. \$84,428 for 3 years in total.		\$45,433			\$ 18,354.00				
1 RA's at 50%: \$45,736 (58% salary, 24% benefits); 50% FTE each year for 3 years, 3% increase years 2-3. \$139,822 in total.		\$80,802			\$ 67,585.00				
Equipment/Tools/Supplies	\$15,161	\$15,161	\$0	\$13,474	\$13,474.00	\$0	\$28,635	\$28,635	\$0
Lab Supplies (Cui): fabrication materials & supplies including silicon wafers (\$3,413), polymer substrates (\$4,000), chemicals (\$6,000), graphene substrate and solutions (\$5,000), carbon based gases (\$3,000), bottles, gloves, other electronics for testing, etc. (\$2,500)		\$13,721			\$ 8,257.00				
Lab Materials & Supplies (Ruan & Chen): Purchase of chemical reagents (\$3,000), analytical kits (\$2,500), compressed gases (\$500), glassware (\$855), consumable supplies (standards and columns) for analytical instruments (\$5,000), instrument maintenance and repair (\$3,600)		\$1,440			\$ 5,217.00				
Travel expenses in Minnesota	\$48	\$48	\$0	\$152	\$152	\$0	\$200	\$200	\$0
Ruan & Chen domestic travel (year 2 &3): Mileage, lodging, and meals for travel between the sensor testing sites and the university; Cui, Ruan, and Chen need work together on the testing. This cost is based on the university compensation policy. Cui or his student need present research papers at a domestic conference in Year 2 or 3.		\$48			\$152				
Other	\$17,803	\$17,803	\$0	\$10,393	\$10,393	\$0	\$28,196	\$28,196	\$0
Scientific Services (Cui): User fees at Minnesota Nano Center and Characterization Facility at the University of Minnesota. The cost is about \$541 per month for the Post-Doc, and \$500 per month for the graduate research assistant for 3 years.		\$17,803			\$10,393				
COLUMN TOTAL	\$309,791	\$309,791	\$0	\$199,209	\$199,209	\$0	\$509,000	\$509,000	\$0