

A. COVER PAGE

Project Title: Development of a novel continuous-reading sensor for measuring exposures to ammonia in agricultural workplaces and their environs	
Grant Number: 5R21OH011364-02	Project/Grant Period: 09/01/2018 - 08/31/2020
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Change of Contact PD/PI: No	
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Human Subjects: NA	Vertebrate Animals: NA
hESC: No	Inventions/Patents: No

B. ACCOMPLISHMENTS

B.1 WHAT ARE THE MAJOR GOALS OF THE PROJECT?

Aim 1: Fabricate sub-millimeter scale ammonia sensors with sub-ppm sensitivity based on reduced graphene oxide chemiresistors. The sensors will be assessed for sensitivity, selectivity, stability, and accuracy over a range of ammonia concentrations from ~0.1-100 ppm and in the presence of gases that might interfere with the quantification of ammonia (e.g., H₂S, N₂O, NO₂, CO, phenol, acetic acid). Sensor performance will be benchmarked against a laboratory grade ammonia analyzer.

Aim 2: Optimize the reduced graphene oxide (rGO) sensor array for selectivity and sensitivity. This will be achieved through the use of sensor arrays comprised of multiple graphene oxide sensor elements each differentially-responsive to ammonia, and standard chemometric tools to deconvolve the sensor array's response to ammonia from other gases in environmental mixtures.

Aim 3: Incorporate the new ammonia sensor array into an existing portable exposure monitoring device. The ammonia sensor will be incorporated into the Portable UW Particle monitor (PUWP), which includes a low-cost FRM validated PM_{2.5} particle counter and sensing elements for NO_x, VOCs, and N₂O.

Aim 4: Evaluate the performance of the portable monitoring device in the field. We will deploy several of the portable monitoring devices at a research dairy where they will be exposed to complex ammonia-rich mixtures comprised of emissions from animal stalls, waste pits, settling ponds and waste lagoons at the dairy. Ammonia measurements from the portable monitoring device will be compared to data from a co-located reference instrument (e.g. UV laser ammonia analyzer). Together these studies will evaluate the accuracy of the ammonia measurements made using our portable device, in the presence of complex mixtures derived from animal agriculture

B.1.a Have the major goals changed since the initial competing award or previous report?

No

B.2 WHAT WAS ACCOMPLISHED UNDER THESE GOALS?

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B.3 COMPETITIVE REVISIONS/ADMINISTRATIVE SUPPLEMENTS

For this reporting period, is there one or more Revision/Supplement associated with this award for which reporting is required?

No

B.4 WHAT OPPORTUNITIES FOR TRAINING AND PROFESSIONAL DEVELOPMENT HAS THE PROJECT PROVIDED?

File Uploaded : B4 Training opportunities.pdf

B.5 HOW HAVE THE RESULTS BEEN DISSEMINATED TO COMMUNITIES OF INTEREST?

NOTHING TO REPORT

B.6 WHAT DO YOU PLAN TO DO DURING THE NEXT REPORTING PERIOD TO ACCOMPLISH THE GOALS?

Not Applicable

Project Accomplishments

1. Laboratory grade ammonia analyzer (Picarro G2103 Cavity ring-down spectrometer) was been purchased and study staff became proficient in using this instrument, and wrote an SOP to train new users to operate the instrument.
2. We upgraded our exposure/calibration chamber by replacing rotameters with mass flow controllers to provide more reliable control over the chamber atmospheres. We also built a smaller testing chamber to reduce the dead volume of the chamber and increase the speed with which the chamber responded to changes in ammonia concentrations. A faster response time for the exposure chamber was needed so that we could accurately measure the response time of our ammonia sensors.
3. An initial three batches of sensors were fabricated using microfabrication facilities at the University of Washington. The sensors were fabricated using a nano ink bridge-induced capillary pen printing process. The sensors were then doped with different polymers using the drop cast method. These polymers were used to enhance the effects of the sensor's sensitivity to the target gas (ammonia). The first batch of sensors was separately doped with Nafion and PEI, the second batch was doped with Nafion, and the third batch was also doped with Nafion. The input and output data streams to and from the sensor are multiplexed using the Arduino Nano microcontroller.
4. Ammonia was injected into the testing chamber at concentrations ranging from 0.07 to 100 ppm. The ammonia sensor shows sensitivity throughout the range. However, these tests indicated that (i) the response time for the sensor needed to be improved, and (ii) the resolution of the sensor needed to be improved.
5. Additional changes were made to the electronics controlling the sensor as follows:
 - i. The testing circuit was modified to add a 16-bit analog-to-digital convertor, increasing the data precision by a factor of 64.
 - ii. The firmware was modified to allow for up to four sensors to be tested at the same time, increasing testing efficiency.
 - iii. The testing circuit was modified to include a low-dropout regulator to limit the voltage through the sensor to less than 1V to increase the lifespan of the sensors.
6. Software was developed to improve testing efficiency as follows:
 - i. Real-time data visualization software was created to increase testing efficiency.
 - ii. Software is currently in development to enable quick and customizable data analysis.
7. A new batch of sensors was fabricated using a thinner sensor surface, in an effort to shorten the response time for the sensor.
8. The sensors were tested against ammonia mixed with zero-air and ammonia mixed with medical grade air. There was no noticeable difference, which allows for the use of the more cost-effective medical air in future experiments.

Section B.4 Training Opportunities

The following undergraduate students developed technical skills as described below while working on this project:

Nathan Hose

- Critical thinking and analysis of experimental results
- Managing a team of undergrad students and overseeing the progress of multiple concurrent tasks
- Implementation of electrical components into a circuit
- Report writing

Cheng Zhu (student)

- Circuit and Hardware testing
- Circuit design

Yui Suzuki (student)

- Arduino coding and circuit design utilizing microcontroller-based hardware
- Reading research papers efficiently

Colin Holzman-Klima

- Technical writing
- Python programming – specifically with the Matplotlib library

Andrew Hall

- Sensor design
- Arduino coding and circuit design utilizing microcontroller-based hardware
- Managing a team of undergrad students
- Reading research papers efficiently
- Communicating with others to get the required material for experimentation
- Data analysis, sensor calibration, circuit troubleshooting, report writing

Fan Deng

- Circuit Troubleshooting
- Soldering, wiring, report writing, communication
- Employing the scientific method for data collection, computer scripting, and computer literacy

Tyler Darby

- Soldering, wiring, 3D printing, Laser cutting (for specific 3D-printed parts)
- Arduino coding and circuit design
- Data analysis with Python

C. PRODUCTS

C.1 PUBLICATIONS

Are there publications or manuscripts accepted for publication in a journal or other publication (e.g., book, one-time publication, monograph) during the reporting period resulting directly from this award?

No

C.2 WEBSITE(S) OR OTHER INTERNET SITE(S)

NOTHING TO REPORT

C.3 TECHNOLOGIES OR TECHNIQUES

NOTHING TO REPORT

C.4 INVENTIONS, PATENT APPLICATIONS, AND/OR LICENSES

Have inventions, patent applications and/or licenses resulted from the award during the reporting period? No

If yes, has this information been previously provided to the PHS or to the official responsible for patent matters at the grantee organization?

C.5 OTHER PRODUCTS AND RESOURCE SHARING

Category	Explanation
Protocols	Standard operating procedures and QA protocols were developed for calibrating the ammonia sensors, and for evaluating their sensitivity, specificity and stability

D. PARTICIPANTS

D.1 WHAT INDIVIDUALS HAVE WORKED ON THE PROJECT?

Commons ID	S/K	Name	Degree(s)	Role	Cal	Aca	Sum	Foreign Org	Country	SS
CDSIMPSON	Y	SIMPSON, CHRISTOPHER D	BS,MS,PHD	PD/PI	0.3	0.0	0.0			NA
MAMISHEV	Y	MAMISHEV, ALEXANDER V	BS,MS,PHD	PD/PI	1.0	0.0	0.0			NA
EDSETO	Y	Seto, Edmund	PHD	Co- Investigator	0.3	0.0	0.0			NA
	Y	Zielinski, Aaron		Research Consultant	1.0	0.0	0.0			NA

Glossary of acronyms:

S/K - Senior/Key

DOB - Date of Birth

Cal - Person Months (Calendar)

Aca - Person Months (Academic)

Sum - Person Months (Summer)

Foreign Org - Foreign Organization Affiliation

SS - Supplement Support

RE - Reentry Supplement

DI - Diversity Supplement

OT - Other

NA - Not Applicable

D.2 PERSONNEL UPDATES

D.2.a Level of Effort

Not Applicable

D.2.b New Senior/Key Personnel

Not Applicable

D.2.c Changes in Other Support

Not Applicable

D.2.d New Other Significant Contributors

Not Applicable

D.2.e Multi-PI (MPI) Leadership Plan

Not Applicable

E. IMPACT**E.1 WHAT IS THE IMPACT ON THE DEVELOPMENT OF HUMAN RESOURCES?**

Not Applicable

E.2 WHAT IS THE IMPACT ON PHYSICAL, INSTITUTIONAL, OR INFORMATION RESOURCES THAT FORM INFRASTRUCTURE?

NOTHING TO REPORT

E.3 WHAT IS THE IMPACT ON TECHNOLOGY TRANSFER?

Not Applicable

E.4 WHAT DOLLAR AMOUNT OF THE AWARD'S BUDGET IS BEING SPENT IN FOREIGN COUNTRY(IES)?

NOTHING TO REPORT

G. SPECIAL REPORTING REQUIREMENTS SPECIAL REPORTING REQUIREMENTS

G.1 SPECIAL NOTICE OF AWARD TERMS AND FUNDING OPPORTUNITIES ANNOUNCEMENT REPORTING REQUIREMENTS

NOTHING TO REPORT

G.2 RESPONSIBLE CONDUCT OF RESEARCH

Not Applicable

G.3 MENTOR'S REPORT OR SPONSOR COMMENTS

Not Applicable

G.4 HUMAN SUBJECTS

G.4.a Does the project involve human subjects?

Not Applicable

G.4.b Inclusion Enrollment Data

NOTHING TO REPORT

G.4.c ClinicalTrials.gov

Does this project include one or more applicable clinical trials that must be registered in ClinicalTrials.gov under FDAAA?

G.5 HUMAN SUBJECTS EDUCATION REQUIREMENT

NOT APPLICABLE

G.6 HUMAN EMBRYONIC STEM CELLS (HESCS)

Does this project involve human embryonic stem cells (only hESC lines listed as approved in the NIH Registry may be used in NIH funded research)?

No

G.7 VERTEBRATE ANIMALS

Not Applicable

G.8 PROJECT/PERFORMANCE SITES

Not Applicable

G.9 FOREIGN COMPONENT

No foreign component

G.10 ESTIMATED UNOBLIGATED BALANCE

Not Applicable

G.11 PROGRAM INCOME

Not Applicable

G.12 F&A COSTS

Not Applicable

I. OUTCOMES

I.1 What were the outcomes of the award?

Ammonia is an irritant gas that has been associated with diseases of the respiratory tract at concentrations below the current occupational exposure limit. Unfortunately, the monitoring equipment currently available that has adequate sensitivity to detect ambient concentrations of ammonia is expensive, is often not portable, and requires regular attention from trained technicians to ensure quality data. These instruments, therefore, are poorly suited for monitoring personal exposures to ammonia amongst exposed populations. To address these limitations we fabricated and tested a low cost ammonia sensor for use in exposure assessments of ammonia concentrations in impacted communities such as those living near animal feeding operations and in urban centers.

These are some of the key outcomes from this project:

1. We fabricated a variety of sensors based on single walled carbon nano tubes (SWCNT), doped with either Nafion or polyethyleneimine (PEI).
2. The input and output data streams to and from the sensor are multiplexed using the Arduino Nano microcontroller. A 16-bit analog-to-digital convertor was incorporated into the testing circuit to enhance the resolution of the sensor response.
3. The initial iteration of the Nafion doped SWCNT sensors responded to ammonia at concentration between 0.07 to 100 ppm, however the performance of these sensors was limited by slow response and recovery times.
4. In order to improve sensor response times, an additional batch of sensors with a thinner sensor surface was fabricated and tested.