Design and Fabrication of Flexible, Paper-based Electrochemical Sensors to Detect Heavy Metals in Groundwater

Justin Platero[1], Michael Nelwood[2], Katelyn Wilson[1], Jasmine Charley[1], Makeiyla Begay[1], Samantha Francis[1]
Khaled Abdelazim[2], and Thiagarajan Soundappan[1*]
[1]Navajo Technical University, Crownpoint, NM [2]Harvard University, Department of Chemistry and Chemical Biology, Cambridge, MA
PREM VENTURES: NSF DMR-2122195 and Harvard MRSEC: NSF DMR-2011754

Introduction

The history of mining and mineral extraction across the Navajo Nation has resulted in considerable contamination of the land and the groundwater resources Water is essential for human and livestock consumption as well as agriculture production. Many people rely on access to the sparse water resources to provide for themselves and their families across the Navajo Nation. Our main concern is that the groundwater has been contaminated with heavy metals such as Arsenic (As), Cadmium (Cd), Lead (Pb), Copper (Cu), and Uranium (U) which have dangerous long-term health effects. Chronic arsenic exposure can lead to painful skin lesions, cardiovascular diseases, and diabetes mellitus Through a partnership between Navajo Technical University and Harvard University, we have designed and fabricated flexible, paper-based sensors in tandem with electrochemical techniques to determine heavy metal concentrations in test samples Paper-based electrodes are low-cost, easy to make, environmentally friendly, and can be deployed for field testing across the Navajo Nation.

Clean up efforts at an abandoned Uranium mine on the reservation

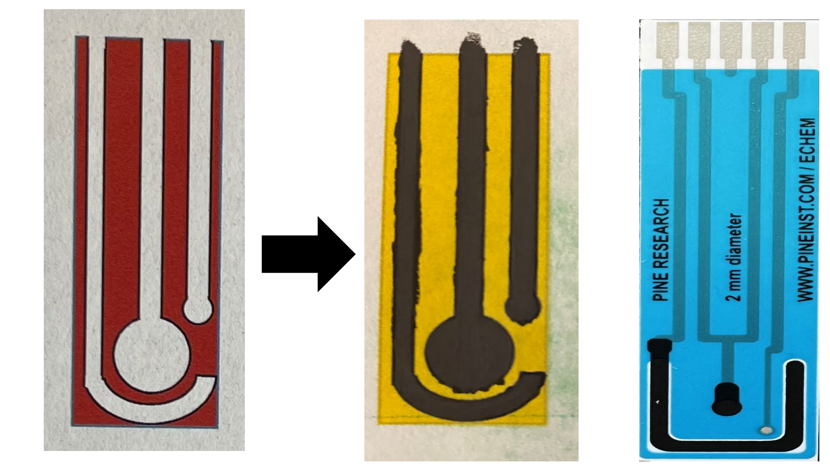
Students and faculty members at Navajo Technical University (NEST LAB)

Methods: Paper Sensor Fabrication

Materials

The materials required to fabricate the paper-based sensors include chromatography paper, electrochemically active carbon paste, a wax printer, and paint brushes We use chromatography paper because it is slightly thicker than printer paper The wax coating ensures that the electrodes will retain their shape as they are submerged in solution We manually coat the carbon paste onto the electrodes using paint brushes We have determined the optimum electrochemically active ink through a series of test experiments The chosen ink (carbon paste) gives good stability as well as the ability to oxidize the target analytes

Student performing electrochemical test.



Printed paper-based electrodes: (left) without electrochemically active ink, (middle) with electrochemically active ink hand-painted, (right) commercially available screen-printed electrode.

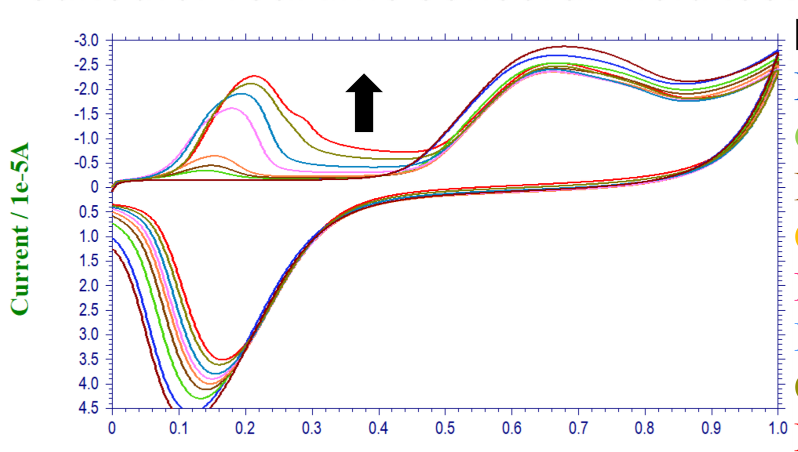
Printing

We begin by designing and printing an outline of the three-electrode system created using Microsoft Word. We designed our paper electrodes to mimic the commercially available screen-printed electrodes. We create a barrier on paper by printing the electrode design using a commercial wax printer (as shown *top right*). We leave the channels blank, so that we can coat the carbon paste onto it. The backside of the electrode has a solid wax coating to ensure stability in aqueous solution After the electrode is printed, we manually apply a uniform coating of conductive carbon paste to serve as the working, counter, and pseudo reference electrodes We use a hotplate to dry the carbon paste While the electrode is drying, we apply gold nanoparticles to increase sensitivity to heavy metals Once dry, the electrode is ready to use

Paper-based Electrochemical Sensor connected to potentiostat

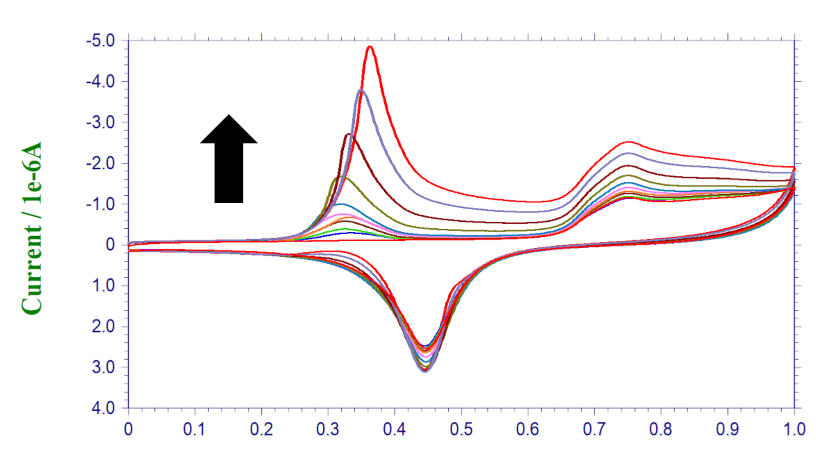
Results: Electrochemical Detection of Arsenic (As)

We used our optimized fabricated paper electrodes to test for the presence of arsenic Chronic arsenic exposure can lead to painful skin lesions, cardiovascular diseases, and diabetes mellitus We used a potentiostat to measure the current of our analyte as the potential is varied using an electrochemical method called Voltammetry Voltammetry relies on the movement of electrons to either reduce or oxidize the target analyte Arsenic was oxidized, which is shown as a change in current, or "peak" at 0.2 V for cyclic voltammetry and 0.5 V for linear sweep voltammetry The current obtained after oxidation is directly correlated to the concentration of arsenic Furthermore, the linear electrochemical response and sensitivity of our electrodes, for detecting heavy metals, makes them well suited for real-time sensors in field-testing applications



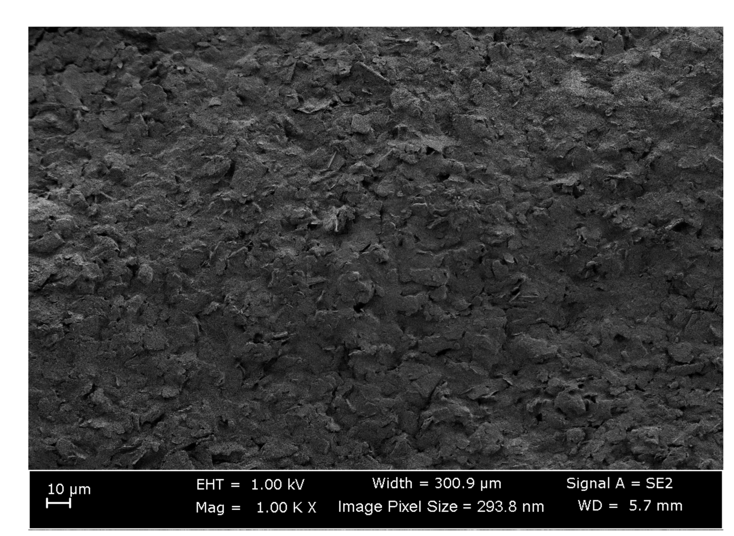
Legend:
Blue: 0.1 mM
Green: 0.4 mM
Brown: 0.7 mM
Orange: 1.0 mM
Pink: 2.0 mM
Light Blue: 3.0 mM
Olive: 4.0 mM
Red: 5.0 mM

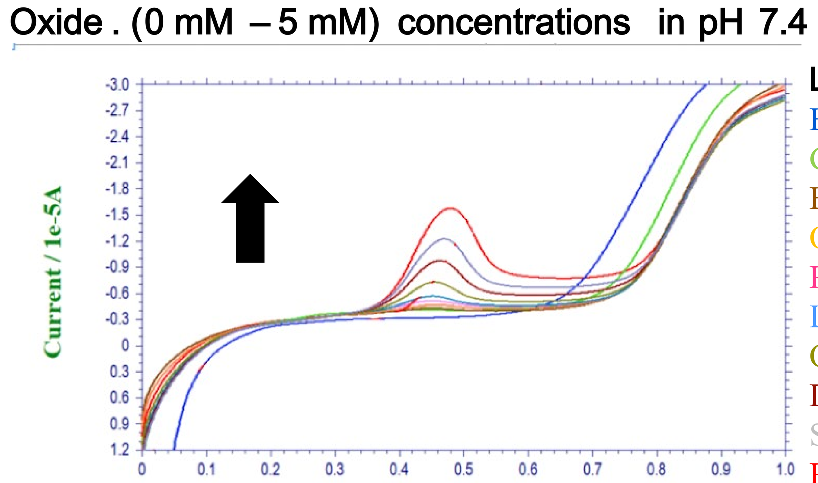
Electrochemical oxidation peaks (Cyclic Voltammetry) of Arsenic Oxide. (0 mM – 5 mM) concentrations in pH 7.4 PBS using paper.



Legend:
Blue: 0.1 mM
Green: 0.2 mM
Brown: 0.3 mM
Orange: 0.4 mM
Pink: 0.7 mM
Light Blue: 1.0 mM
Olive: 2.0 mM
Dark Brown: 3.0 mM
Silver: 4.0 mM
Red: 5.0 mM

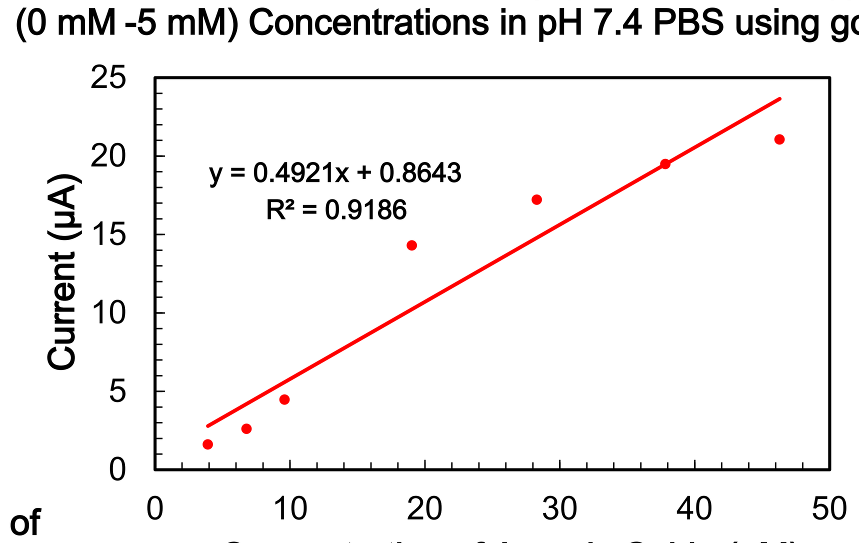
Electrochemical oxidation peaks (Cyclic Voltammetry) of Arsenic Oxide. (0 mM -5 mM) Concentrations in pH 7.4 PBS using gold electrode.

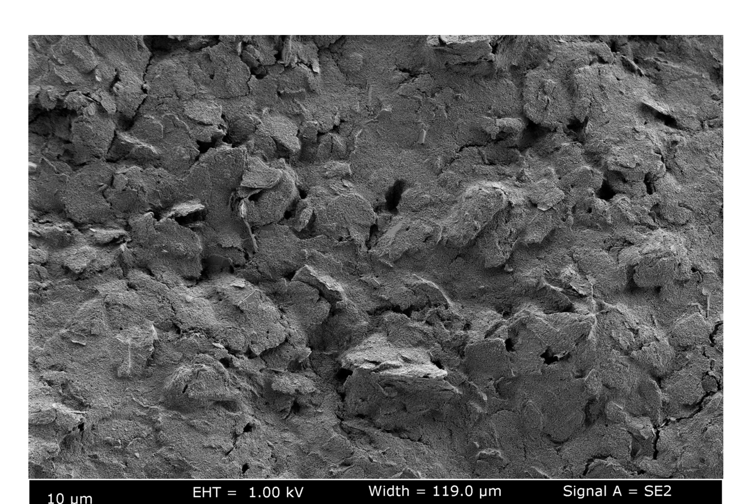




Legend:
Blue: 0.1 mM
Green: 0.2 mM
Brown: 0.3 mM
Orange: 0.4 mM
Pink: 0.7 mM
Light Blue: 1.0 mM
Olive: 2.0 mM
Dark Brown: 3.0 mM
Silver: 4.0 mM
Red: 5.0 mM

Electrochemical oxidation peaks (Linear Sweep Voltammetry) of Arsenic Oxide. (0 mM – 5 mM) concentrations in pH 7.4 PBS using paper.





Conclusion & Future Work

The low-cost paper electrodes we have fabricated can successfully detect several concentrations of Arsenic Using these inexpensive techniques opens the possibility to test for several other toxic metals We would also like to further optimize our fabrication method by including screen printing technology Once we have fully optimized our electrodes, we plan on distributing them to local Navajo chapter houses to test their groundwater resources

Acknowledgments

We gratefully acknowledge the support of the National Science Foundation (**NSF PREM DMR-1828012, 2122195, MRSEC DMR-2011754**) for the collaborative work on heavy metal detection and for the support from the USDA-NIFA (**2018-38424-28521**) for the work on endocrine disruptor sensing We thank members of the Harvard University MRSEC for their assistance in transferring the paper-based electrode technology to Navajo Technical University

References:

- Lan, Maxwell, "Paper-based electroanalytical devices with an integrated, stable reference electrode" (2013)
- Jarup. (2003). "Hazards of heavy metal contamination". British Medical Bulletin
- Lin, Hoover, J. "Environmental risk mapping of potential abandoned uranium mine contamination on the Navajo Nation, USA, using a GIS-based multi-criteria decision analysis approach" (2020)

Contact:

*Dr. Thiagarajan Soundappan
tsoundappan@navajotech.edu

Justin Platero
justin.platero@student.navajotech.edu