Applying Anodic Stripping Voltammetry to Complex Wastewater Streams for Rapid Metal Detection

FE0030456

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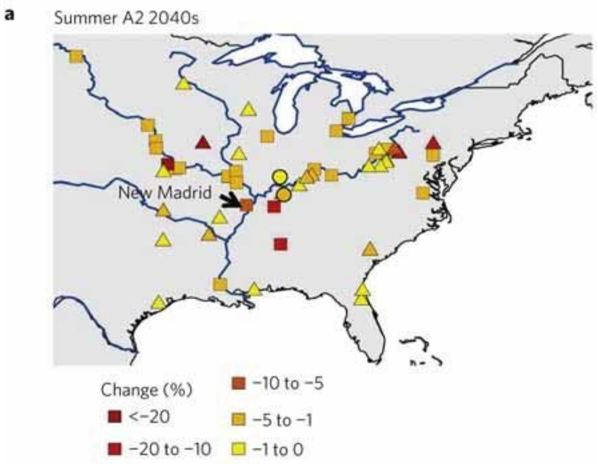
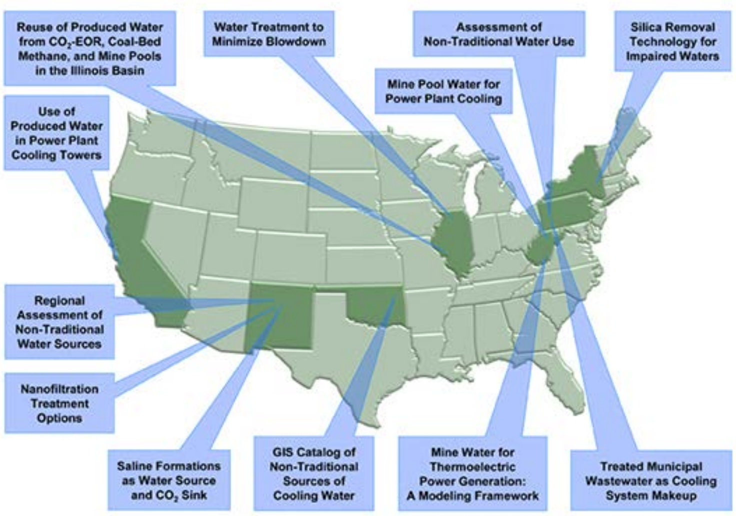
Project Objectives

- **Motivation:** Water is a critical component of thermoelectric power generation
  - Changes in water availability and quality can impact electricity production
    - Increasing water temperatures
    - Decreasing flows
    - Recent drought in SE forced a drop in power production
  - Alternative water resources will be needed to meet cooling and other demands of thermoelectric power plants



Project Objectives

- Wastewater is an attractive alternative water source
  - Reliable flows
  - Uniform water quality
  - Co-located with population centers
- Wastewater (mining, municipal, O&G) already used in several locations
- Heavy metals often detected in wastewater
  - **Discharge of water containing heavy metals is highly regulated**
    - Pb (2.5 μg/l)
    - Cd (0.72 μg/l)
    - As (150 μg/l)

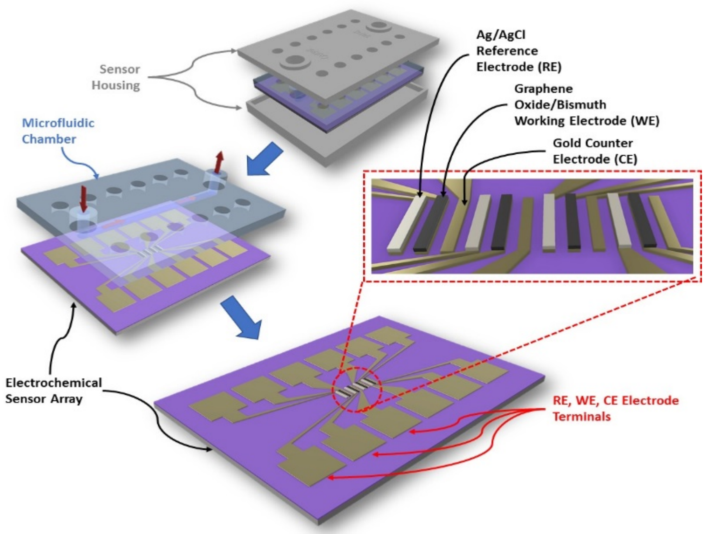


Project Objectives

- In raw wastewater, some heavy metals are in particulate form (>0.45 µm)
  - Removed by coagulation/sedimentation
- Dissolved metals sail through the wastewater treatment process
- **Critical to monitor incoming and discharged water quality from thermal power plants**
- **There is a need for sensing methods that enable highly sensitive, rapid, and autonomous detection of metal contaminants in complex waste streams**
  - Method must detect ALL forms of heavy metals

Project Objectives

- **Overall Objective:** Development of a lab-on-a-chip (LOC) electrochemical sensor capable of measuring heavy metal (Pb, Cd, and As) concentrations in complex aqueous streams, such as wastewater
- **Technology:** Miniaturized anodic stripping voltammetry (ASV) sensor using highly sensitive reduced graphene oxide (rGO)/metal complexes combined with appropriate sample pre-treatment steps, for the autonomous and rapid detection of metals
- **Challenges with current practice:** Grab samples analyzed with expensive analytical equipment (e.g., ICP-MS)
  - Measurements not in "real time"
    - If contamination is present, hours/days can pass before detection, resulting in fines
  - Expensive (highly skilled labor and equipment)

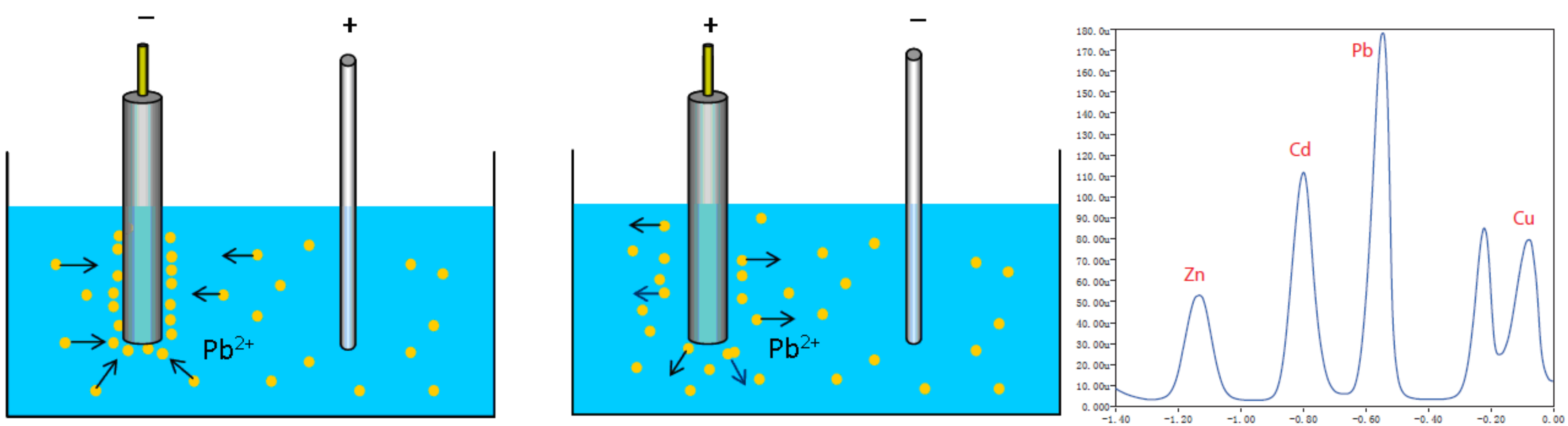


Progress to Date on Key Technical Gaps/Challenges

The electrochemical detection of heavy metals using Anodic stripping voltammetry

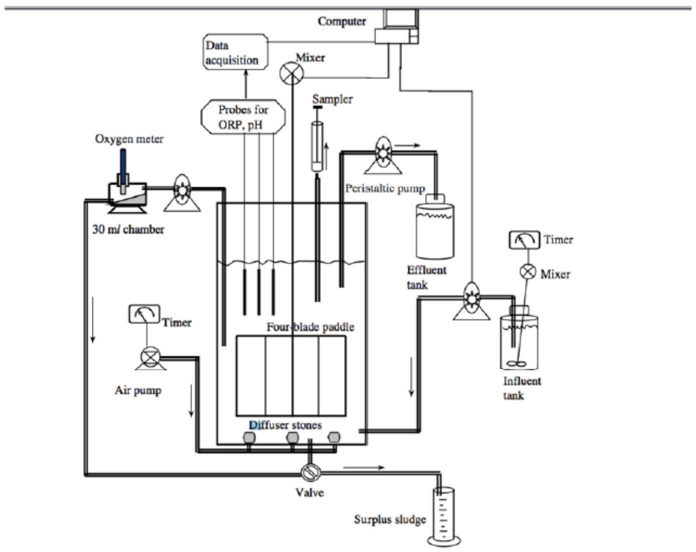
Principle

Anodic stripping voltammetry：Electro-deposition of metal ions onto the electrode surface, after a potential scanning, get multiple stripping currents of heavy metals, the current is proportional to the concentration of heavy metals.



Progress to Date on Key Technical Gaps/Challenges

- A lab-scale activated sludge reactor has been built to simulate different steps of wastewater treatment
  - Primary (coagulation/flocculation/sedimentation)
  - Secondary (biological)
  - Tertiary (sand filter)
- Heavy metals will be spiked into feed stream and speciation, extraction efficiency, and removal will be evaluated at each step
- Real wastewater (from Hyperion wwtp) will be used as well



Progress to Date on Key Technical Gaps/Challenges

- Heavy metals in wastewater come in multiple forms
  - Dissolved (ionic)
  - Carbonates
  - Sorbed/chelated by organic matter
  - Bound to iron and/or manganese
- Some heavy metals are bound in large (>0.45 μm) particulate matter
- **Sensing method must capture all forms of heavy metals**
  - ASV only capable of detecting/measuring ionic metal species
- An understanding of heavy metal speciation from different wastewater treatment steps is needed
- Appropriate pre-treatment steps must be integrated into sensing device
  - Transform all metal species to ionic form

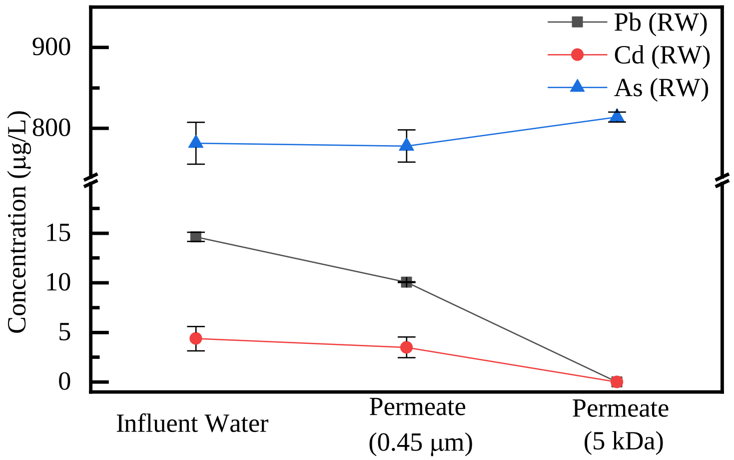
Progress to Date on Key Technical Gaps/Challenges

- Fractionation of heavy metals in raw wastewater (measured using ICP-MS)

Pb: ~30% as large particulate (> 0.45 μm)
~67% as small particulate (> 5 kDa)
~3% as "dissolved"

Cd: ~15% as large particulate (> 0.45 μm)
~80% as small particulate (> 5 kDa)
~5% as "dissolved"

As: Almost all as "dissolved"



Progress to Date on Key Technical Gaps/Challenges

- It is assumed that large (>0.45 μm) particles will be effectively removed by primary wastewater treatment step
  - coagulation/flocculation/sedimentation
- Important to understand speciation of heavy metals in fraction <0.45 μm
  - Likely present in influent to power plant
  - Need to identify appropriate pre-treatment steps for ASV detection
    - Will depend on metal speciation

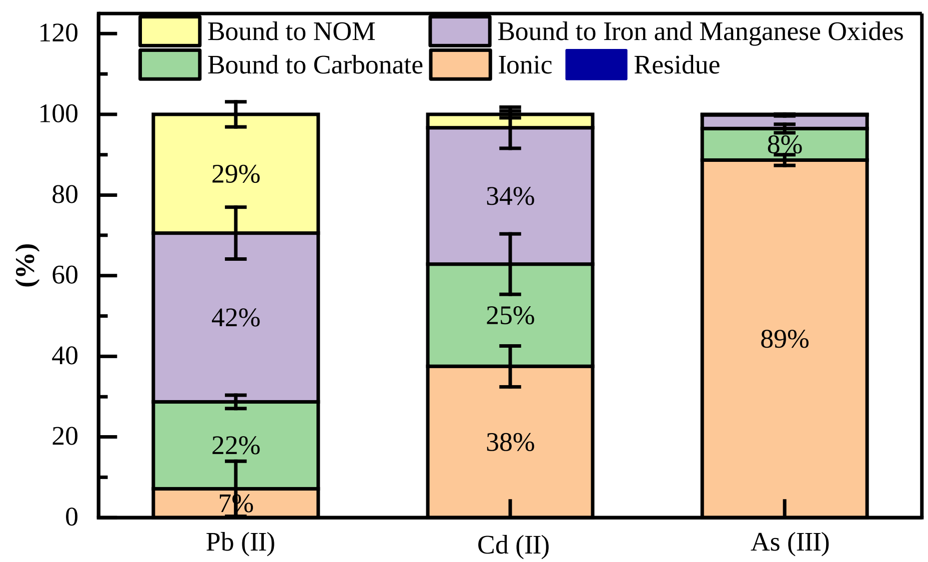
Progress to Date on Key Technical Gaps/Challenges

- Sequential extraction of heavy metals in raw wastewater (<0.45 μm)

  Pb: 29% bound to organics
  42% bound to Fe/Mn,
  22% bound to carbonate
  7% ionic

  Cd: 3% bound to organics
  34% bound to Fe/Mn
  25% bound to carbonate
  38% ionic

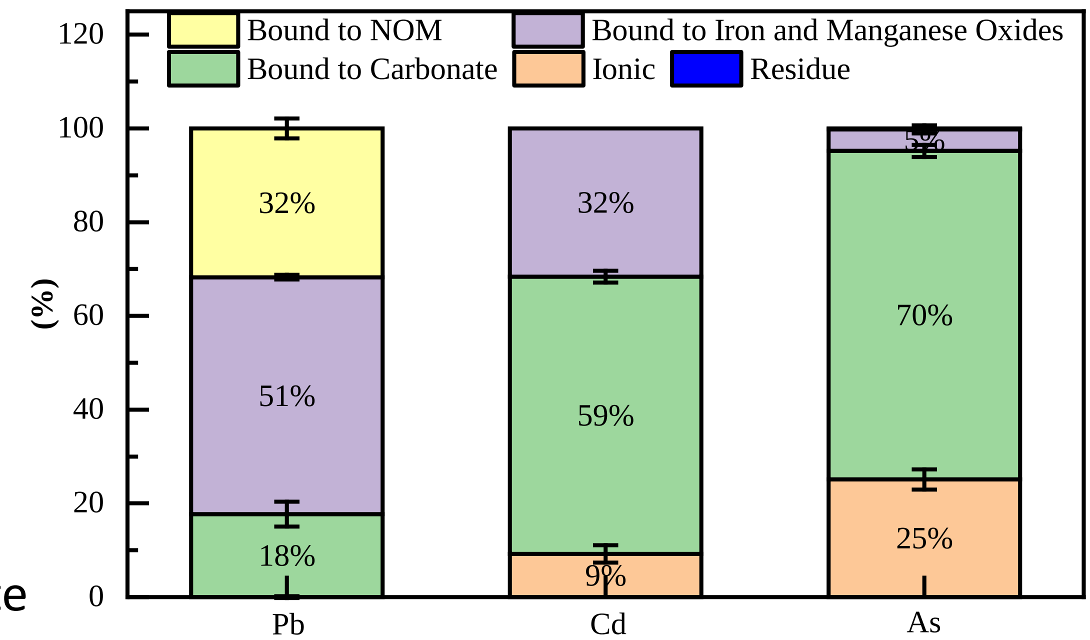
  As: 3% bound to Fe/Mn
  8% bound to carbonate
  89% ionic



- **Likely that Pb and Cd detection by ASV will require more extensive pre-treatment**

Progress to Date on Key Technical Gaps/Challenges

- Sequential extraction of heavy metals in secondary effluent (<0.45 μm)
  - **Pb:** No ionic species detected
    - Primarily bound to iron and NOM
  - **Cd:** Less ionic Cd detected
    - Primarily bound to carbonate and NOM
  - **As:** Significantly less ionic As
    - Mostly bound to carbonate



- **Likely that all metals will require pre-treatment for ASV detection**
- **These are extreme conditions – drying drives complexation**

Progress to Date on Key Technical Gaps/Challenges

- Fabrication and Application of Electrodes for ASV detection of Cd(II) and Pb(II)
  - Synthesis and physico-chemical characterization of Bi nanoparticles (BiNP)-functionalized reduced graphene oxide (rGO-Bi) electrode material
  - Fabrication and electrochemical characterization of rGO-BiNP modified electrode for ASV
  - Evaluation of rGO-BiNP modified electrode to detect Cd and Pb
  - Testing and validation of ASV detection in synthetic water

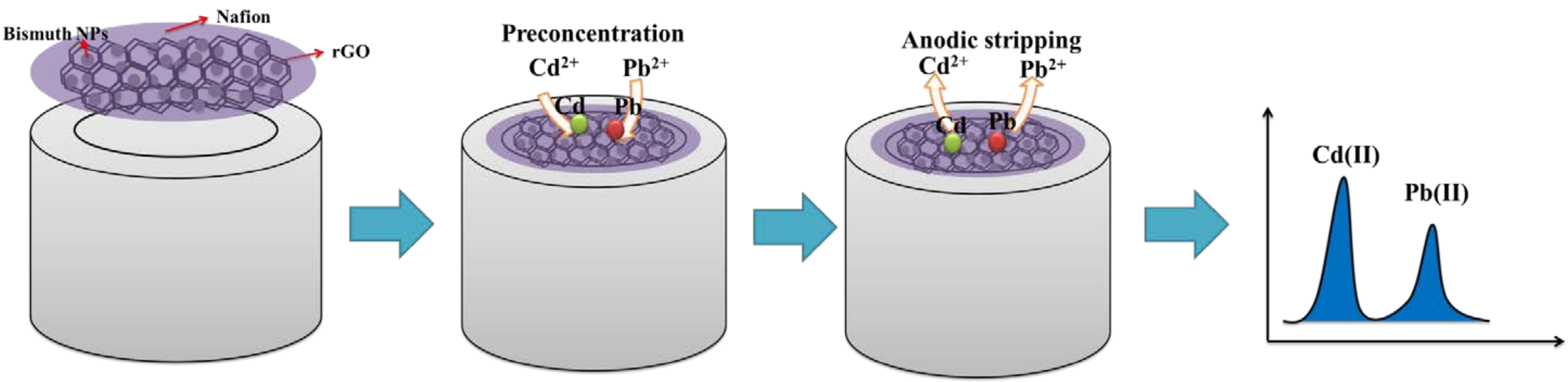
Progress to Date on Key Technical Gaps/Challenges

- Synthesis of Bi nanoparticles (BiNP)-functionalized reduced graphene oxide (rGO-Bi)

1. Disperse 20 mg graphene oxide in 40 mL ethylene glycol
2. Add 340 mg $Bi(NO_3)_3.5H_2O$ GO/Bi^{3+} solution
3. Add 0.456 g $NaBH_4$ and react at 90 °C for 2 h with stirring
4. Centrifuge, wash and dry rGO-BiNP nanocomposite

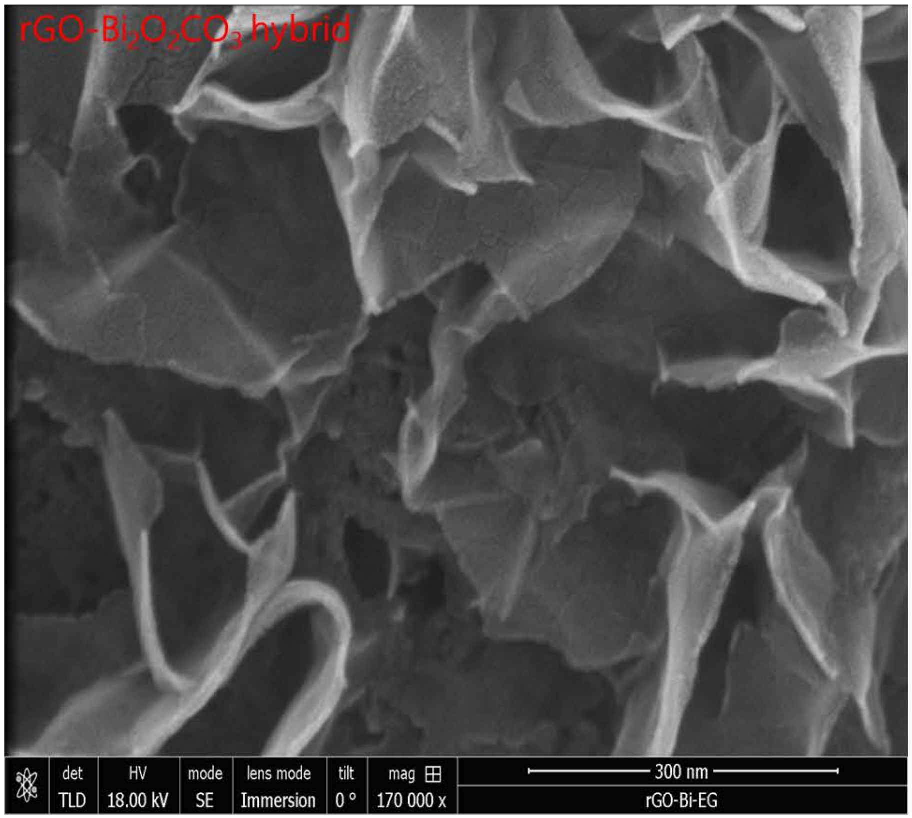
Progress to Date on Key Technical Gaps/Challenges

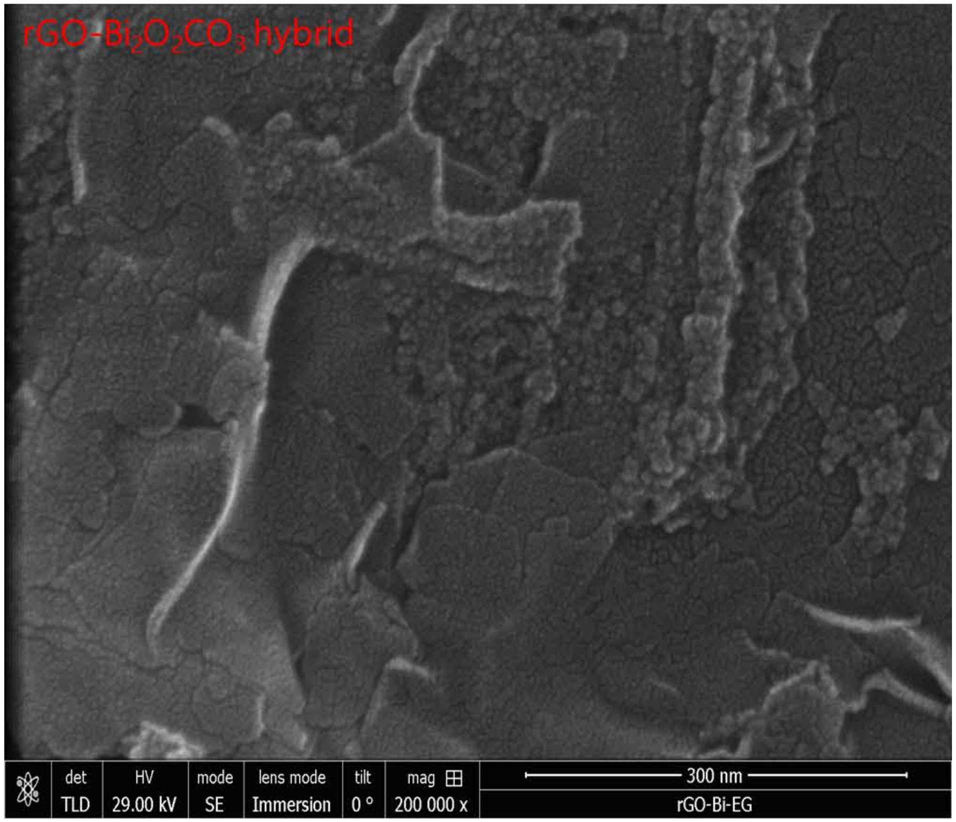
- Fabrication of rGO-BiNP-modified electrode and ASV protocol



Progress to Date on Key Technical Gaps/Challenges

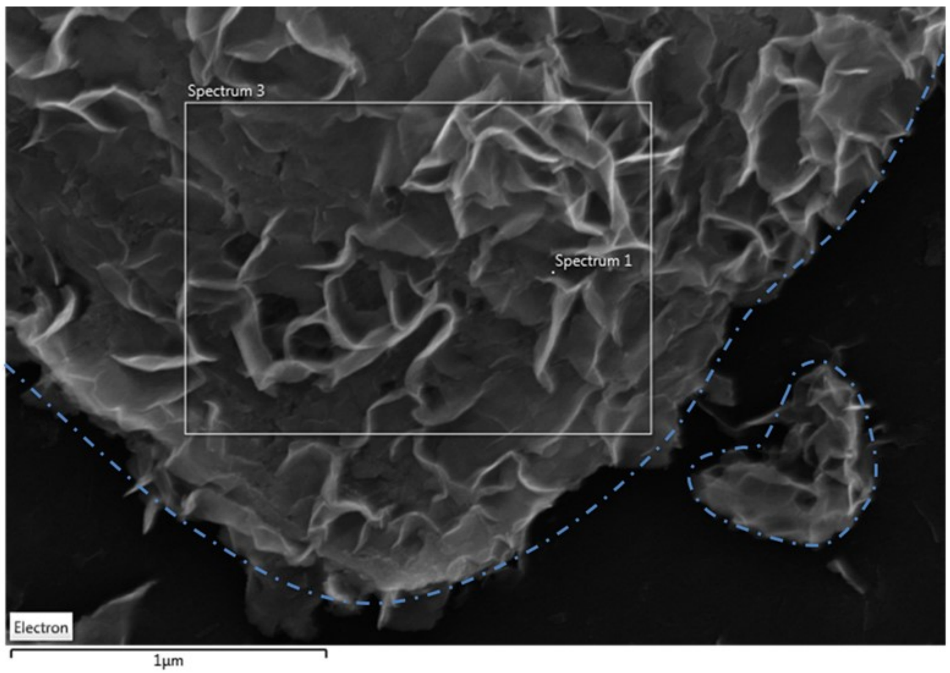
- Material Characterization - SEM



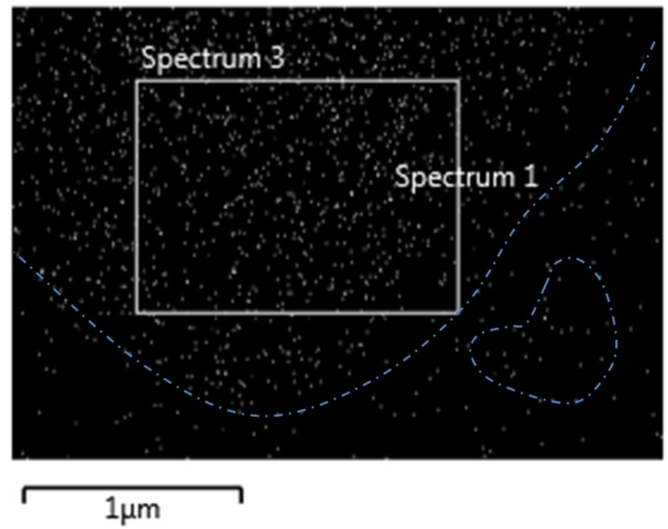


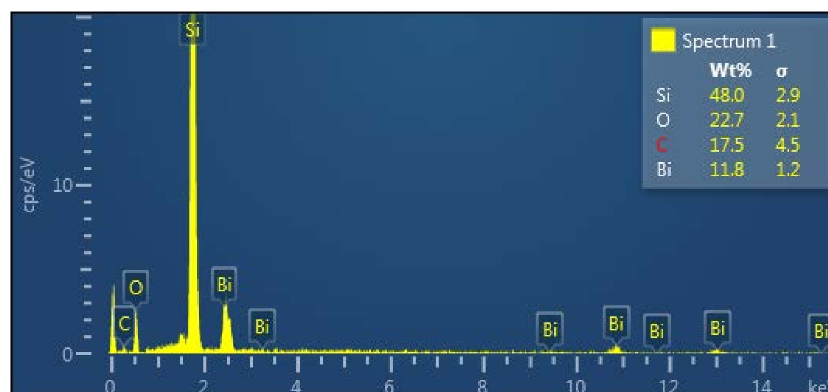
Progress to Date on Key Technical Gaps/Challenges

Material Characterization - EDAX



Bi Lα1

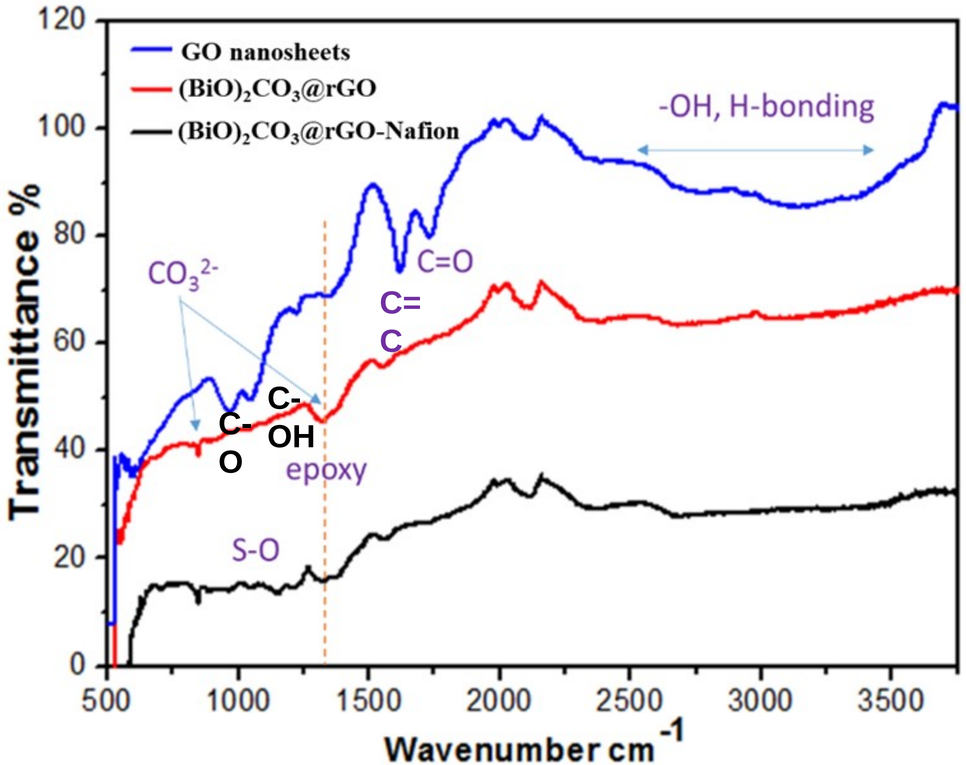




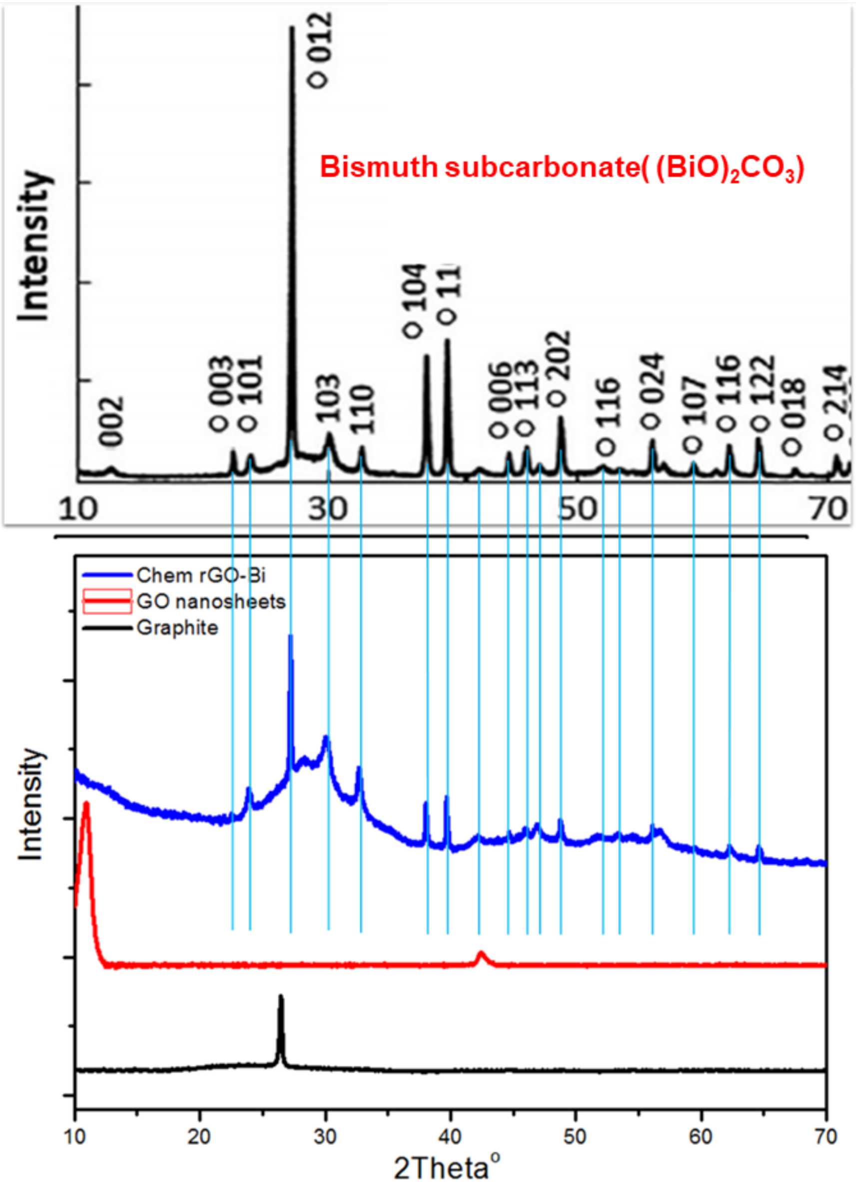
Progress to Date on Key Technical Gaps/Challenges

Material Characterization – FTIR

- Absorption peaks of OH, C=O, C-O and C-OH of graphene oxide (blue), disappear post reduction (red)



Progress to Date on Key Technical Gaps/Challenges

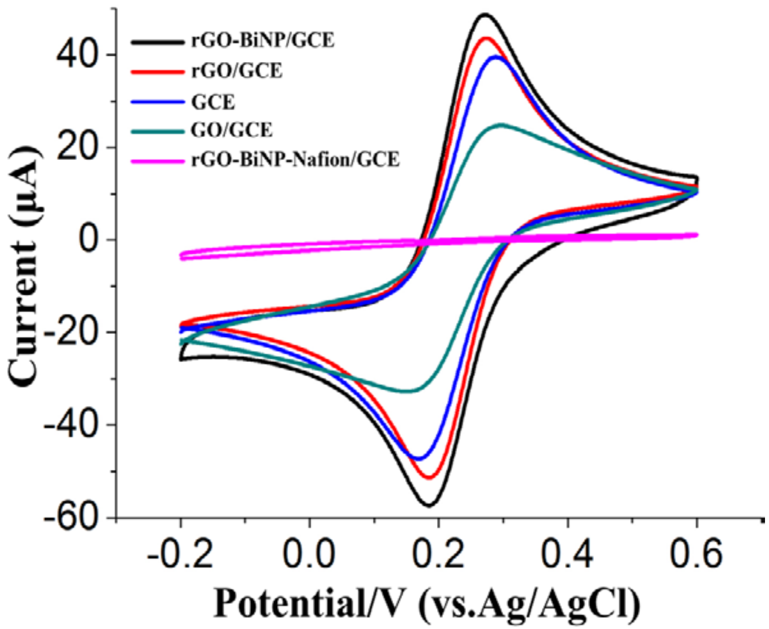


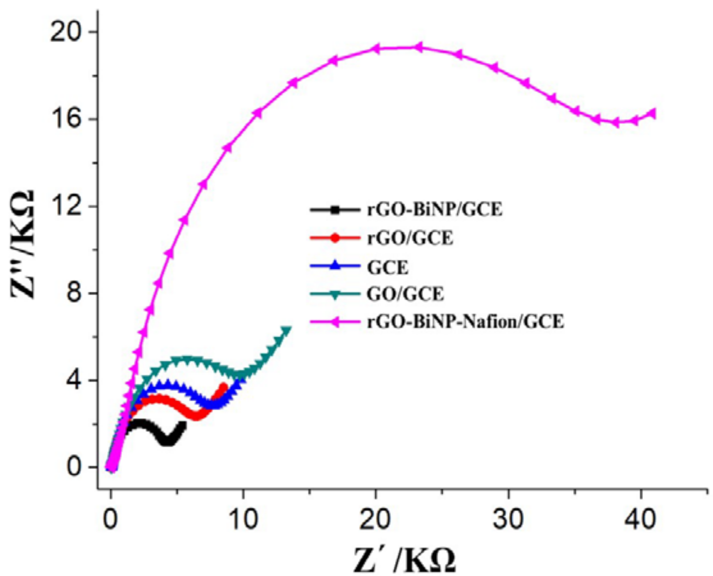
- Material Characterization – XRD

Results show the BiNP to be Bismuth subcarbonate ($(BiO)_2CO_3$)

Progress to Date on Key Technical Gaps/Challenges

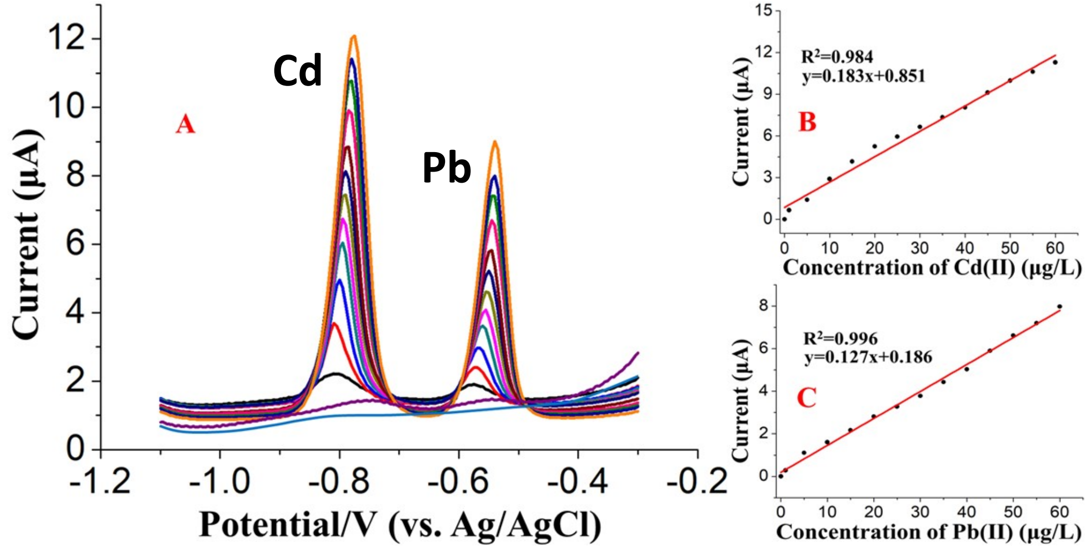
- Electrochemical characterization of rGO-BiNP-modified electrode ($Fe(CN)_6^{-3}$)
  - Nafion coating reduces interference from negative ions
  - Nafion increases impedence

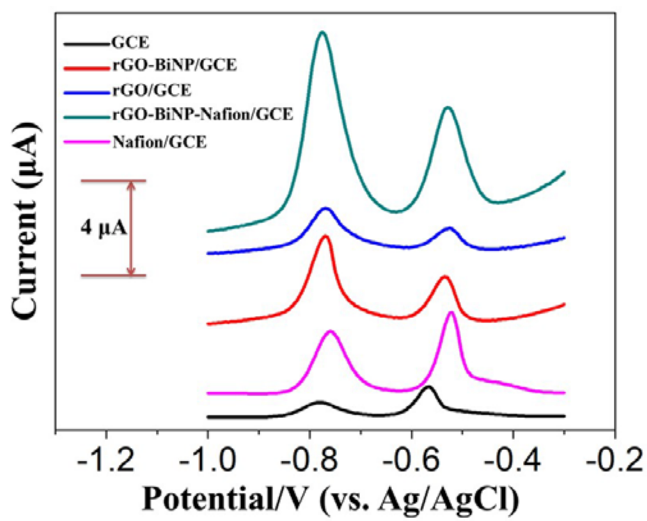




Progress to Date on Key Technical Gaps/Challenges

- Effective detection of Pb, Cd, and As
  - Ionic solutions
- Low ppb detection
  - Very sensitive
  - Can detect below MCL
  - Good linear response
- Measurement takes <10 minutes
  - Cleaning, stabilizing, reducing, and oxidizing
- Without NPs, sensing is not great…



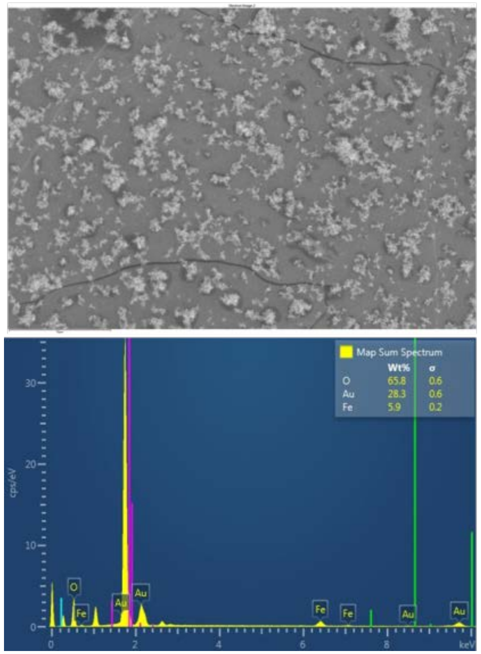


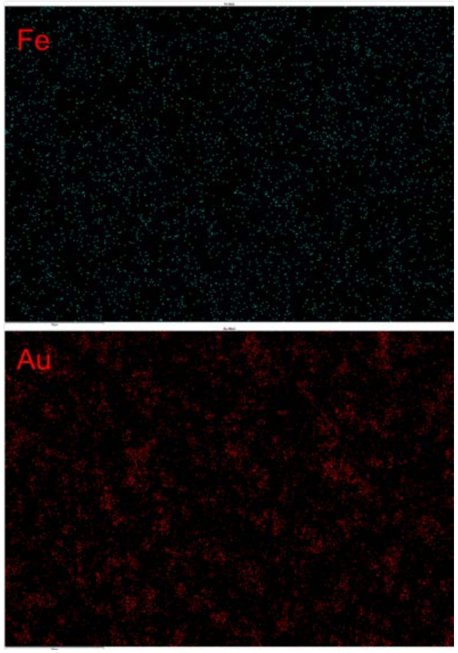
Progress to Date on Key Technical Gaps/Challenges

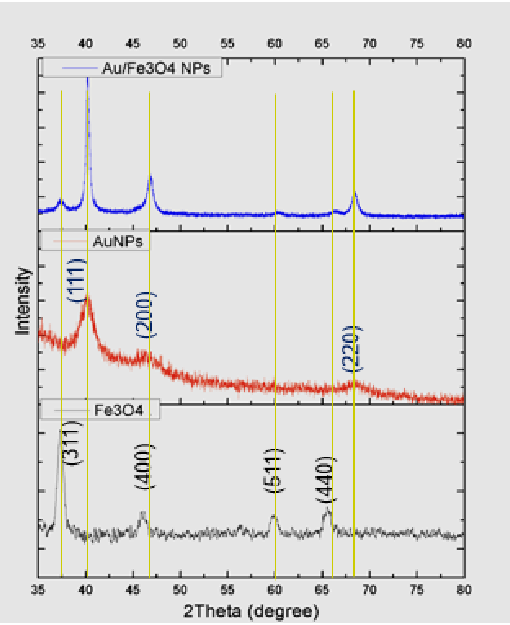
- Fabrication and Application of Electrodes for ASV detection of As(III)
  - Synthesis and physico-chemical characterization of Fe_2O_3/Au nanoparticles-functionalized rGO electrode material
  - Fabrication and electrochemical characterization of rGO-Fe_2O_3/Au modified electrode for ASV
  - Evaluation of rGO-Fe_2O_3/Au modified electrode to detect As
  - Testing and validation of ASV detection in synthetic water

Progress to Date on Key Technical Gaps/Challenges

- Low temperature fabrication of Fe_2O_3 (80° C, pH 9)
- Au NPs decorated on Fe_2O_3 by in-situ reduction of $AuCl_4^-$
- SEM, EDAX, and XRD confirm presence of AuNP@Fe3O4 NPs
- NPs were drop-cast on GCE electrode

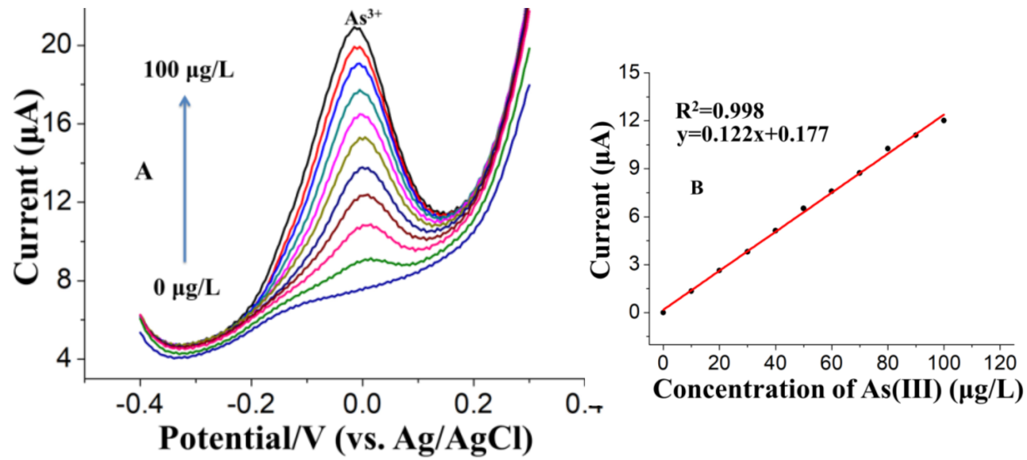


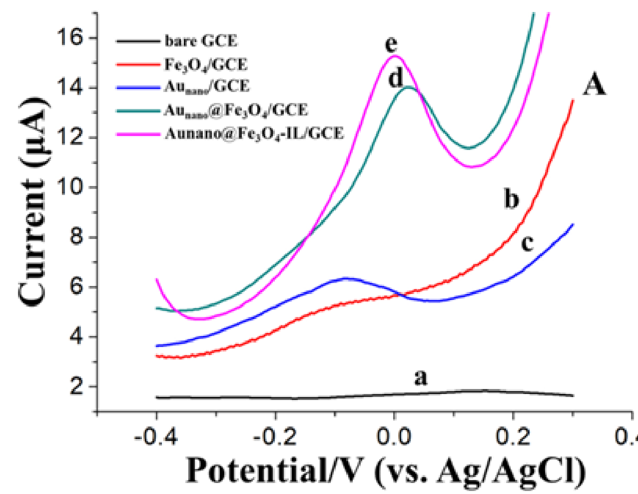




Progress to Date on Key Technical Gaps/Challenges

- Highly sensitive detection of As(III)
  - Very low ppb levels
  - Good linear response
- Significantly higher detection with AuNP@Fe3O4 modified GCE

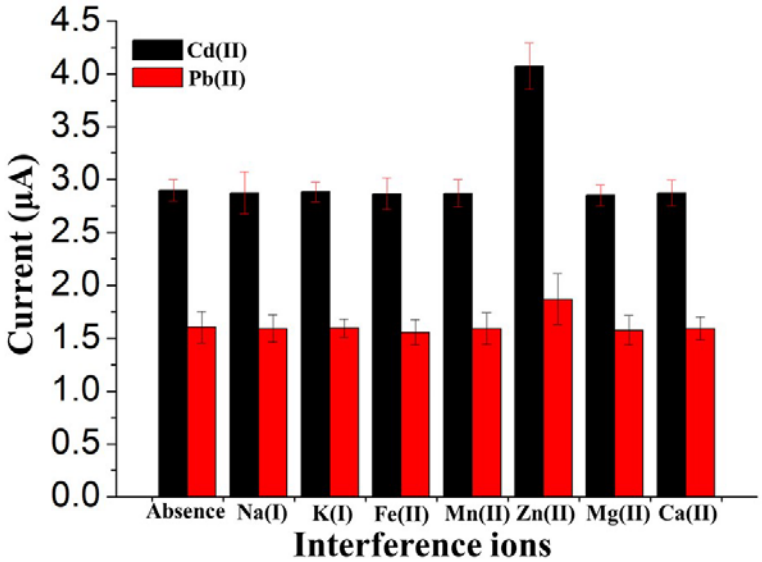




Progress to Date on Key Technical Gaps/Challenges

- Complicating factors
  - Other aqueous constituents
    - NOM-complexed metals
    - Overlapping redox peaks
  - Other metal ions
    - Overlapping oxidizing potentials (Zn)
- Pre-treatment is critical for effective detection
  - Transform all metals to ionic form
  - Mineralize organics (?)
  - In progress…

Synthetic wastewater sample	Detected By SWASV (μg/L)	
	Cd(II)	Pb(II)
With humic acid	0	6.43±0.69
Without humic acid	13.45±0.59	2.16±0.73



Plans for Remaining Technical Gaps/Challenges

- **Explore ability of ASV to detect heavy metals that are ionic and/or complexed with organics, carbonates, and Fe/Mn**
  - Real wastewater matrices
  - Design appropriate pre-treatment steps (pH modification, chemical oxidation)
- **Fabricate a microfluidic electrochemical cell with sensor arrays for ASV and evaluate its electrochemical performance**
  - Open source hardware and software
- **Construct and test an LOC ASV device**
  - Real wastewater

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