EAST TENNESSEE STATE UNIVERSITY

Nitrogen-doped Chemical Vapor Deposition Carbon Ultramicroelectrodes for Hydrogen Peroxide Detection

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Outline

- Background
  - H_2O_2
  - UMEs
  - Nitrogen-doping (N-doping)
- Research approach
  - Chemical vapor deposition (CVD) and N-doping methods
- Results and Discussion
  - Characterization via voltammetry and amperometry
- Conclusions and Future work

Background – H_2O_2

- Why is hydrogen peroxide (H_2O_2) important?
  - H_2O_2 is produced in every cell in the body
  - Key roles in cellular processes such as gene expression and cellular differentiation [1]
- Why measure H_2O_2?
  - Reactive oxygen species (ROS)
  - Fenton reaction [2]
  - H_2O_2 buildup has been linked to diseases [1]

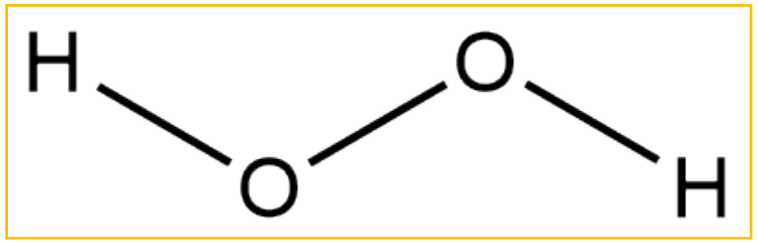


Figure 1. Molecular structure for hydrogen peroxide.

Eq (1). $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet$

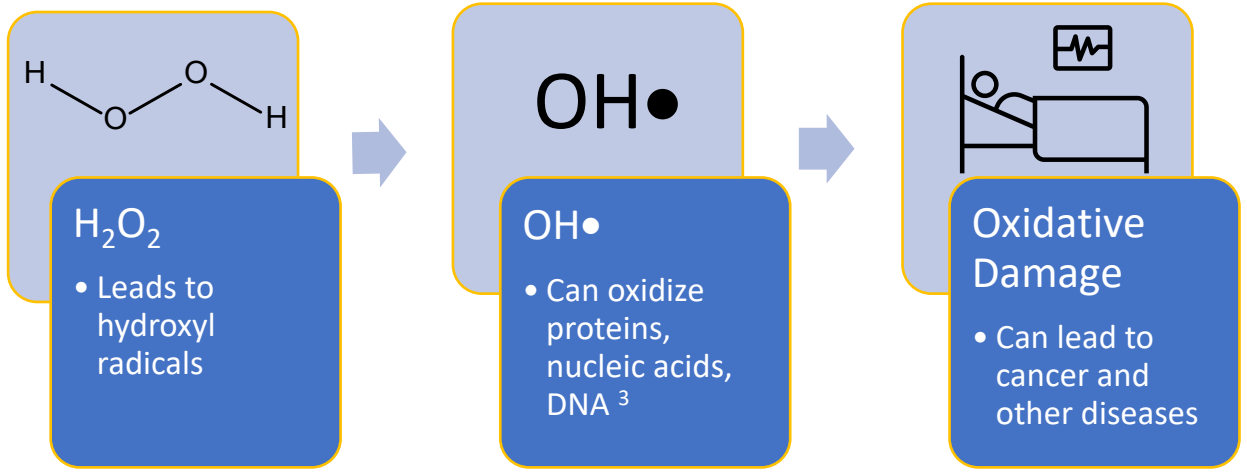


Figure 2. Timeline of what H_2O_2 can lead to.

Background - UMEs

- Ultra-micro electrodes (UMEs)
  - Characteristic dimension ≤ 25 μm
  - Ideal for in vivo measurements
    - Neurotransmitters [3]
  - Measures the transfer of e^- between electrode surface and species
- UMEs composition
  - Noble metals as catalytic surfaces
    - Excellent sensitivity
    - Expensive [3]
  - Carbon allotropes
    - Okay sensitivity, inexpensive
    - Modifiable [3]

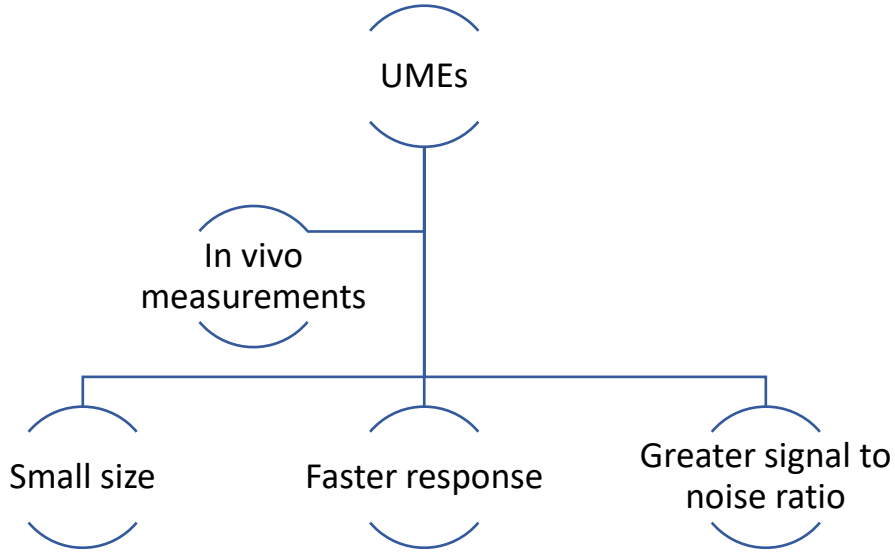


Figure 3. Summary of ultramicroelectrodes advantages.

Eq (2) Oxidation. $H_2O_2 \rightleftharpoons O_2\ (g) + 2\ H^+ + 2\ e^-$

Eq (3) Reduction. $H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$

Background – Nitrogen-doping

- H_2O_2 reduction comprises two key steps
  - Adsorption on electrode surface
  - Breakage of the O-O bond [4]
- Impact of nitrogen groups
  - Introduced via substitutional doping
  - Charge density of the adjacent carbons becomes more positive (i.e., more electrocatalytic) [4]
  - More attractive for the oxygen, facilitates breakage of O-O bond

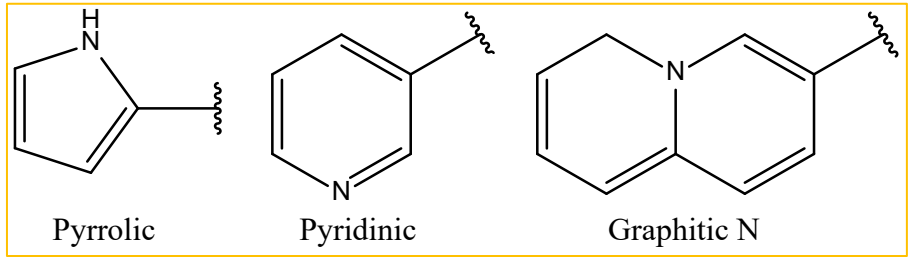


Figure 4. Examples of nitrogen groups that can be introduced into carbon materials. [4]

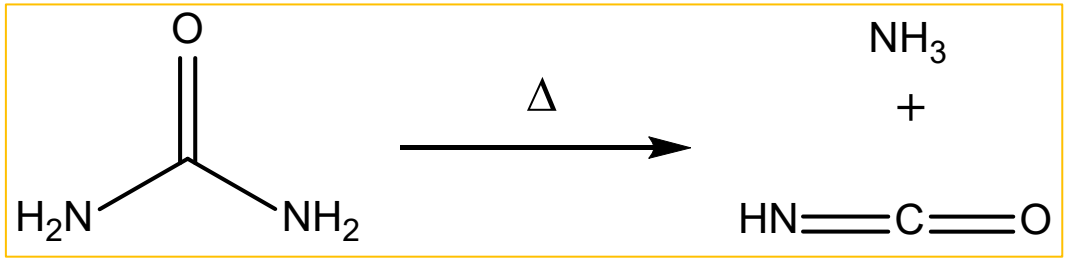


Figure 5. Chemical equation for the thermal decomposition of urea. [5]

Background – Previous Work by Bishop Group

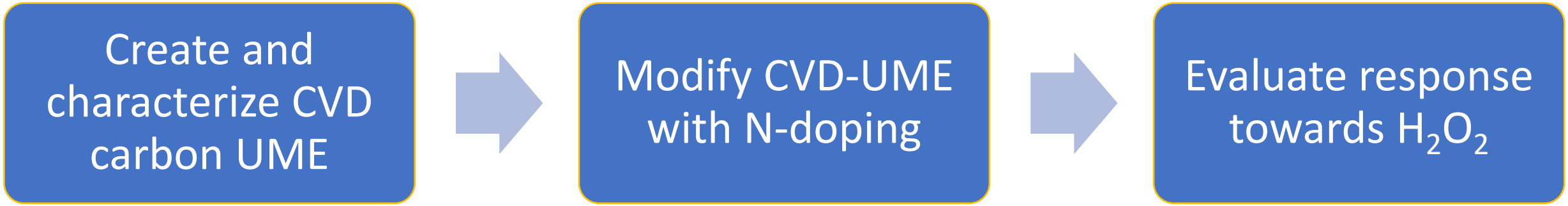
Table 1. Previous examples from the Bishop group of detecting H_2O_2 using various carbon ultramicroelectrodes.

Electrode	Linear Range (µM)	Sensitivity (µA mM^{-1} cm^{-2})	Detection Limit (µM)	Notes
N-CF-UME [3]	100 - 5600	5.5	137	Modify fiber and then seal in glass. Laser likely damages the fiber, leading to lower sensitivity
CF-UME (epoxy-sealed) [6]	60 - 720	91	27	Unanticipated benefits from epoxy for unmodified carbon fiber, likely due to nitrogen content
N-CF-UME (epoxy-sealed) [6]	60 - 720	120	27	Good sensitivity but does not necessarily show that N-doping is providing the benefits
N-SPCE [7]	0.02 – 5.3	264	2.5	Non-ultramicroelectrode example

Hypothesis and Approach

- Hypothesis
  - Applying N-doping to CVD carbon electrodes during or after the fabrication process will allow for greater evaluation of how N-doping affects the response towards H_2O_2 compared to previous methods

- Approach



Research Approach – CVD Carbon UMEs

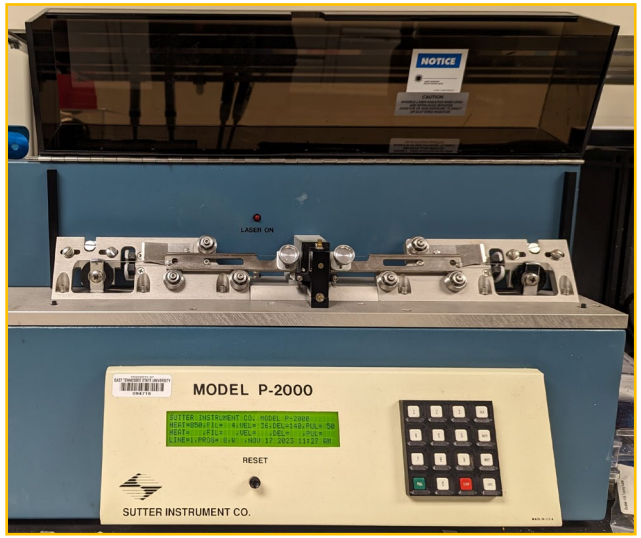


Figure 6. Laser pipette puller used for electrode fabrication.

Figure 7. Setup for chemical vapor deposition micro-torch method for making carbon electrodes. Utilizes a 70:30 butane/propane mixture as precursor gas. Opposing argon flow provides inert atmosphere for pyrolysis.

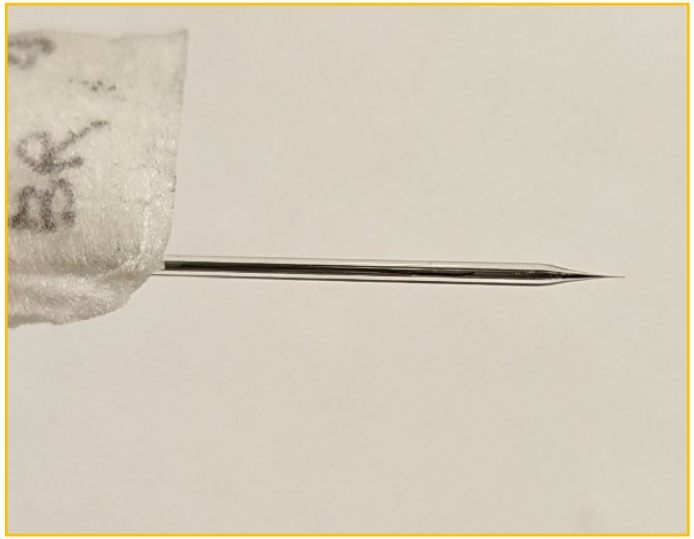


Figure 8. Graphitic carbon electrode with metal wire inserted.

Research Approach – Nitrogen doping

- Ammonium hydroxide method [9]
  - An electrode was suspended in a 2% (w/w) solution of ammonium hydroxide (NH_4OH) [6]
  - The solution was then heated to 80 °C and allowed to react for 15 minutes
  - Afterwards the electrode was left to dry before evaluation towards H_2O_2 reduction

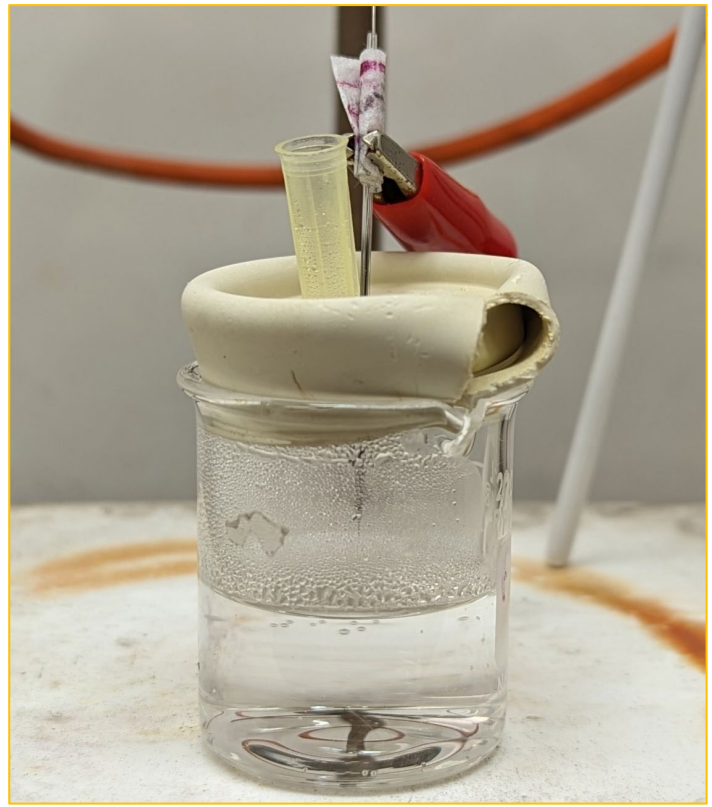


Figure 9. Ammonium hydroxide method of N-doping.

Research Approach – Characterization

- Cyclic voltammetry
  - Ferrocene methanol (FcMeOH)
    - Used to evaluate electrode size
    - 0.1 mM FcMeOH and 0.1 M KCl
    - Reversible, highly stable
  - Phosphate buffer solution (PBS) (7.4 pH)
    - Used to evaluate response towards H_2O_2
    - De-aerate PBS by bubbling nitrogen through, then blanket solution during analysis
    - Spike in known concentrations of hydrogen peroxide
- Amperometry
  - Same as above method for H_2O_2 response, but at a constant potential
  - Allows for evaluation of electrode sensitivity and detection limit

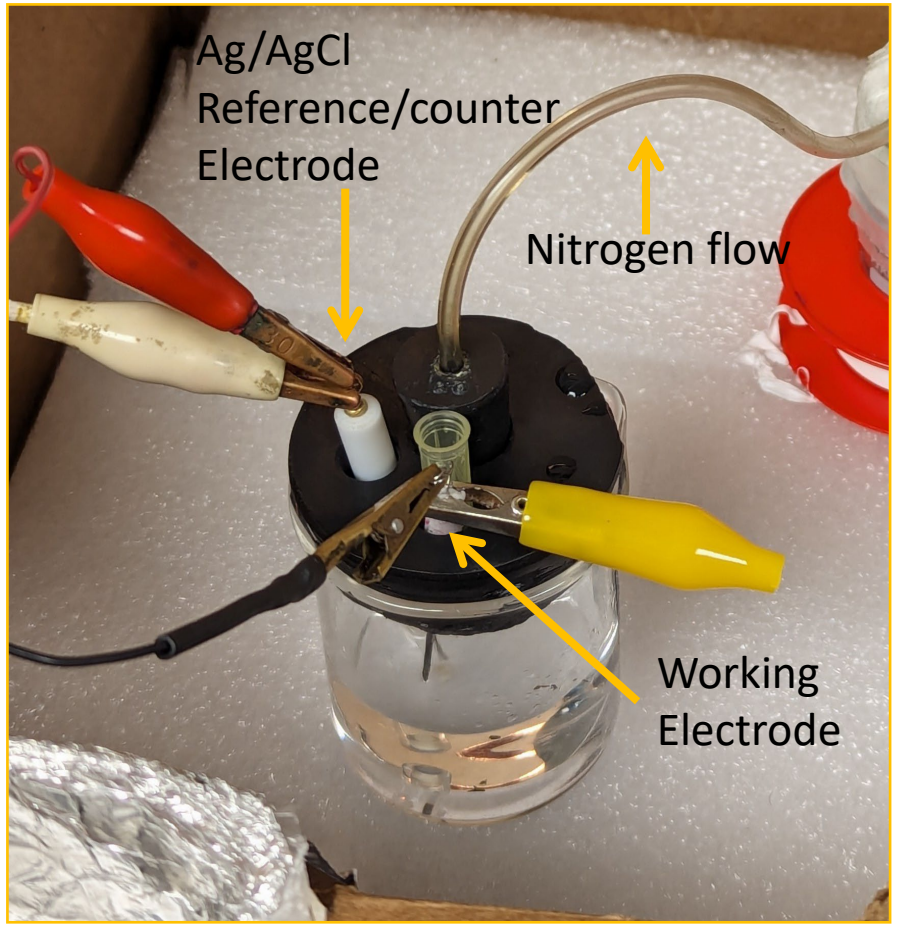


Figure 10. Setup for the electrochemical cell used for all experiments.

Results and Discussion - Voltammetry

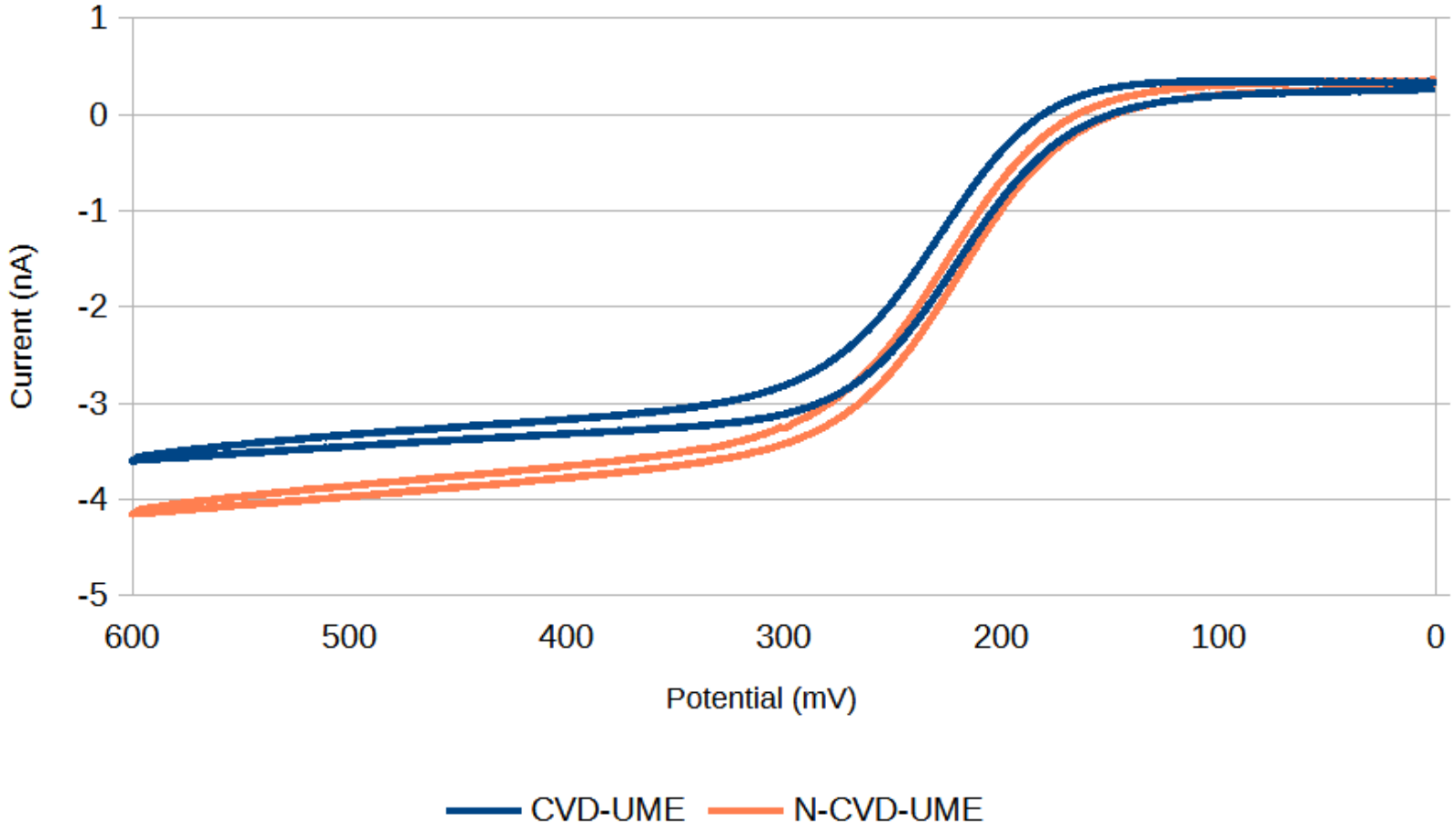


Figure 11. Cyclic voltammogram in 0.1 mM FcMeOH with 0.1 M KCl showing response of an electrode (22 μm) before and after N-doping with ammonium hydroxide. Potential was scanned from 0 to 600 and back to 0 mV at a rate of 50 mV/s.

Eq (3). $I_{SS} = 4nFDRC$

I_{SS} = steady state current
n = # of e^- transferred in redox reaction per mole of reactant
F = Faraday's constant
D = diffusion coefficient (7.80E-06 $cm^2\ s^{-1}$
R = radius of electrode
C = bulk concentration of redox molecule

Results and Discussion - Voltammetry

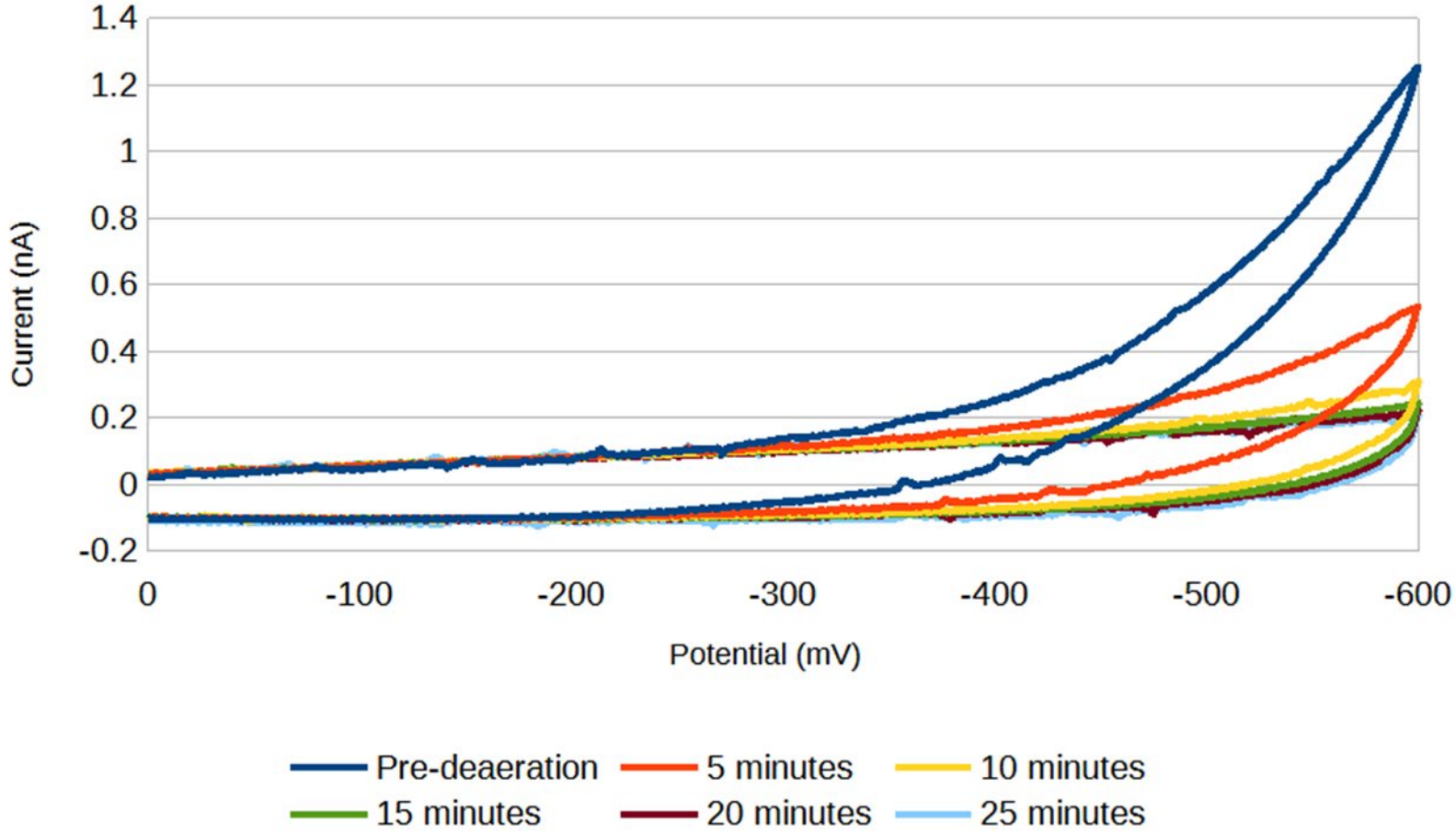


Figure 12. Cyclic voltammogram showing a graphitic carbon electrode in 25 mL of de-aerated 7.4 pH phosphate buffer solution (PBS) over the 25 minutes. Potential was Scanned from 100 mV to -600 and back to +100 mV at a rate of 50 mV/s.

Results and Discussion - Voltammetry

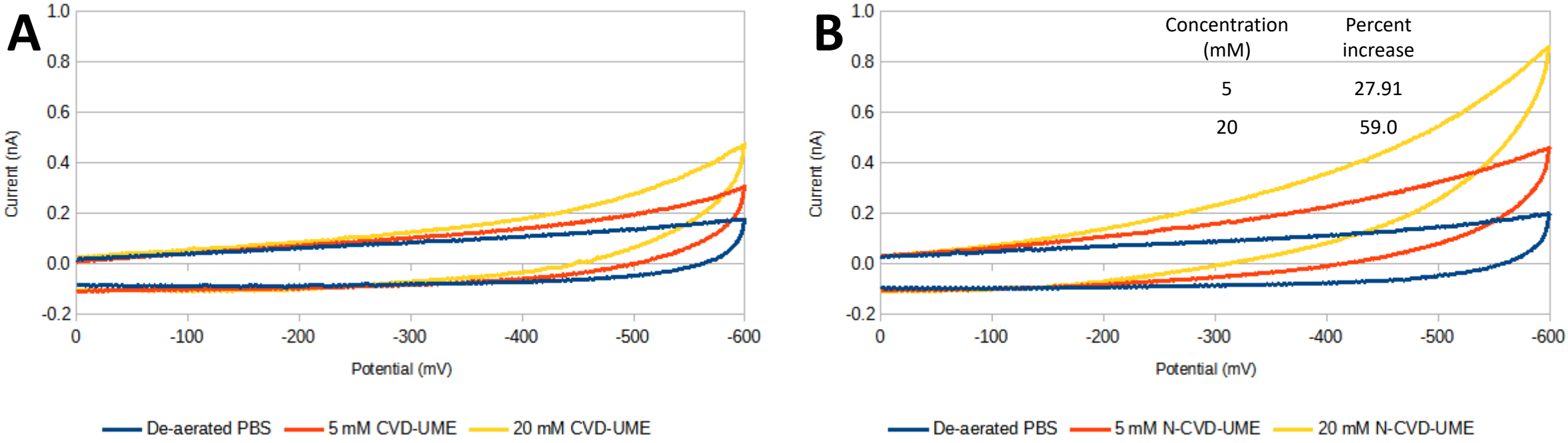


Figure 13. Cyclic voltammograms showing responses of unmodified CVD-UME (A) and nitrogen-doped CVD UME (B) towards H_2O_2 reduction at 5 and 20 mM injected H_2O_2 concentrations. The potential was scanned from 100 to -600 and back to +100 mV at a rate of 50 mV/s for both experiments.

Results and Discussion - Amperometry

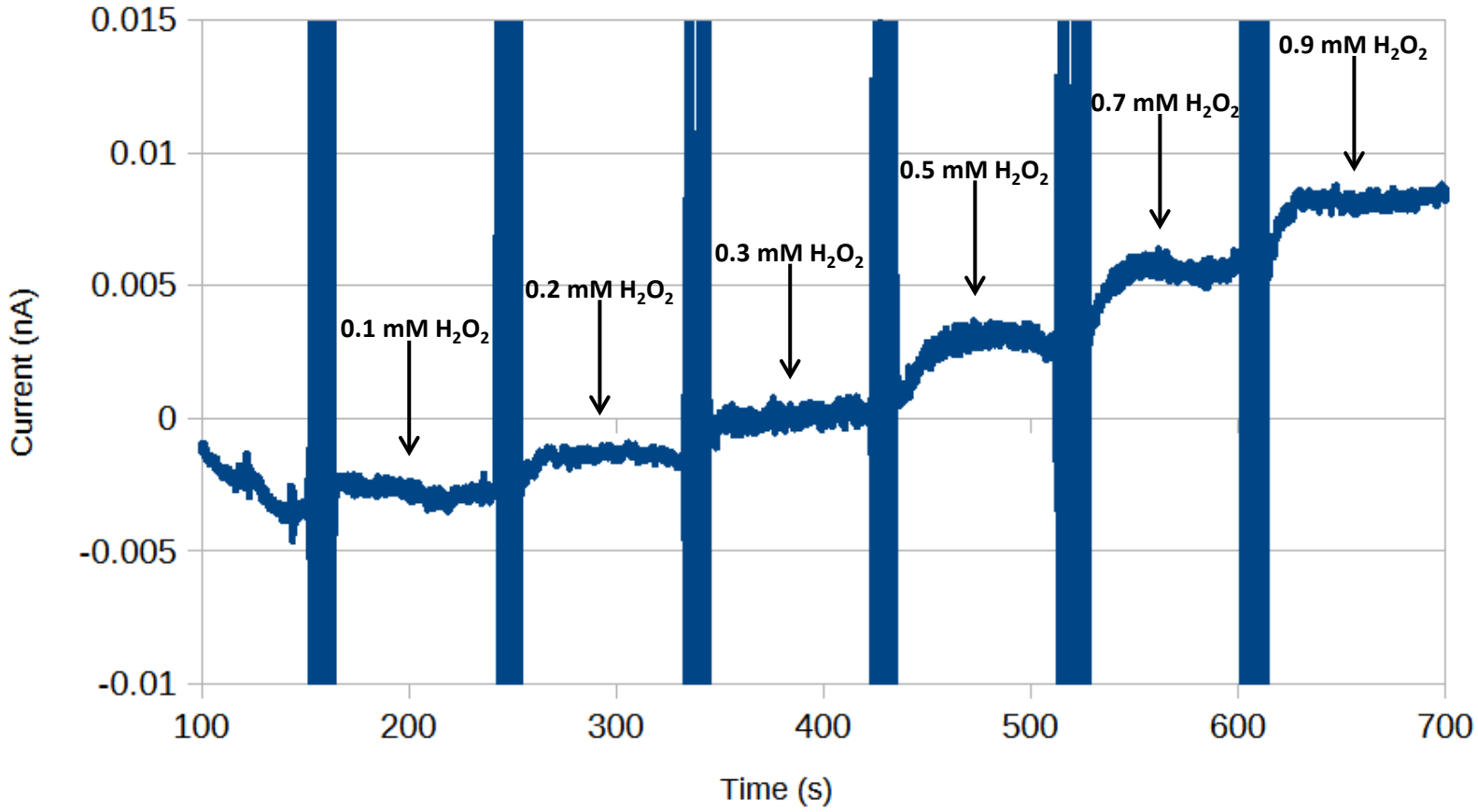
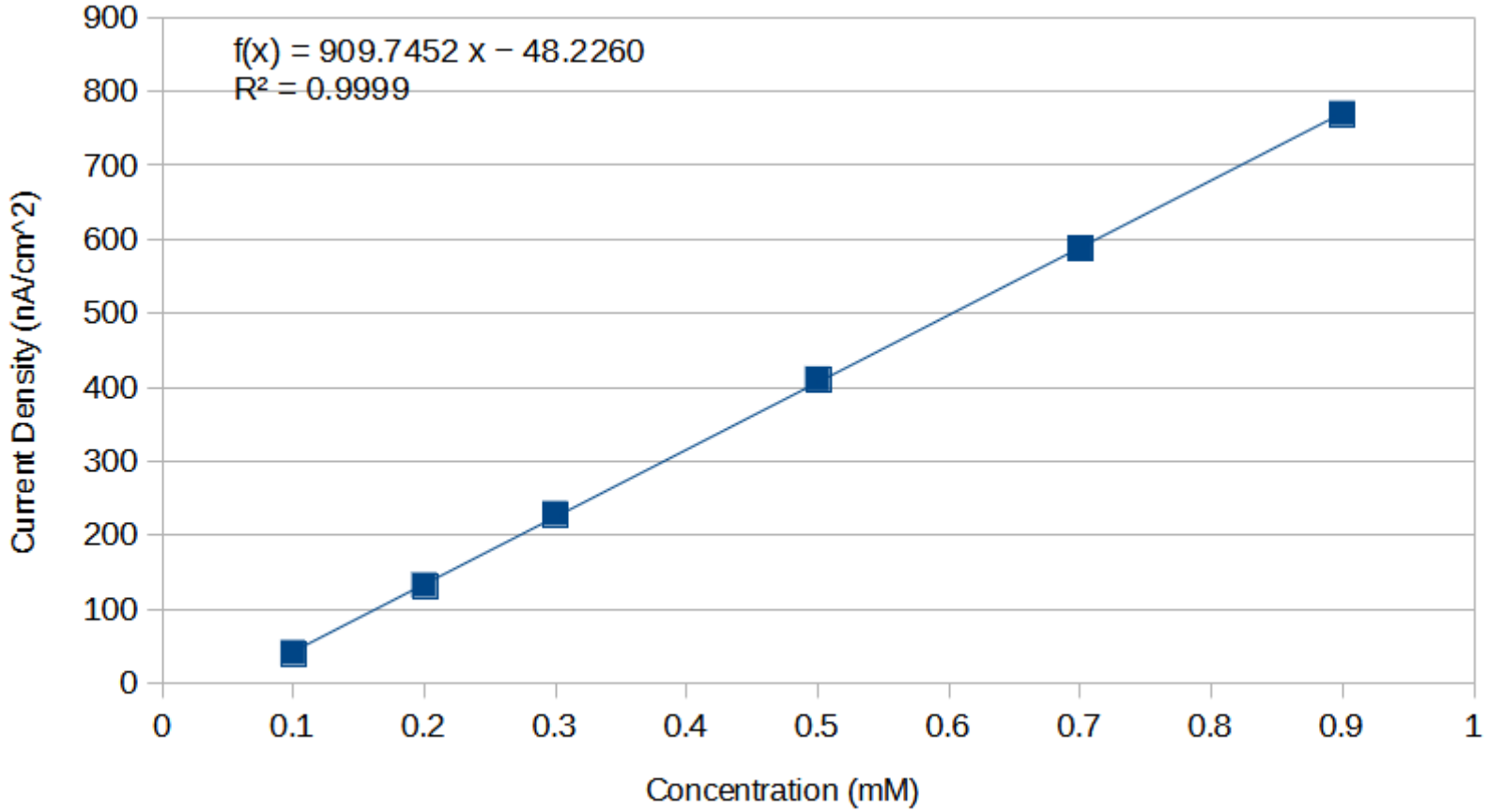


Figure 14. Direct current potential amperometry (DCPA) showing linear response of N-UME towards H_2O_2 injections made every 90 seconds over 0.1 to 0.9 mM concentration range. Large vertical lines are noise from opening the faraday cage. Potential was set to -400 mV.

Results and Discussion - Amperometry



Electrode characteristics	Value
Sensitivity (µA/mM)	0.9097
Detection limit (µM)	63.0

Figure 15. Calibration plot of concentration vs. current density for DCPA data showcasing excellent linear relationship.

Results and Discussion – Comparison

Table 2. Sensitivity and detection limit comparison of N-CVD-UME to other electrodes from the Bishop research group.

Electrode	Sensitivity ($\mu A\ mM^{-1}\ cm^{-2}$)	Detection Limit (µM)
N-CF-UME [3]	5.5	137
CF-UME (epoxy-sealed) [6]	91	27
N-CF-UME (epoxy-sealed) [6]	120	27
N-SPCE [7]	264	2.5
N-CVD-UME from this work	**0.91**	**63**

Conclusions and Future Work

- Voltammetry
  - Created and characterized a sigmoidal CVD-UME
- Amperometry
  - Excellent linear relationship between H_2O_2 concentration and current
  - Much worse sensitivity and generally higher detection limit
- Future work
  - Try alternative N-doping methods to improve sensitivity
    - Aqueous urea solution [9]
    - Pyrolysis of nitrogen containing precursor such as urea or melamine [10]

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