

Development of Boron Doped Diamond Electrodes for Key Analytes in the Aqueous Environment and Beyond.

Dr Tania Read

Warwick Electrochemistry and Interfaces Group
University of Warwick, UK



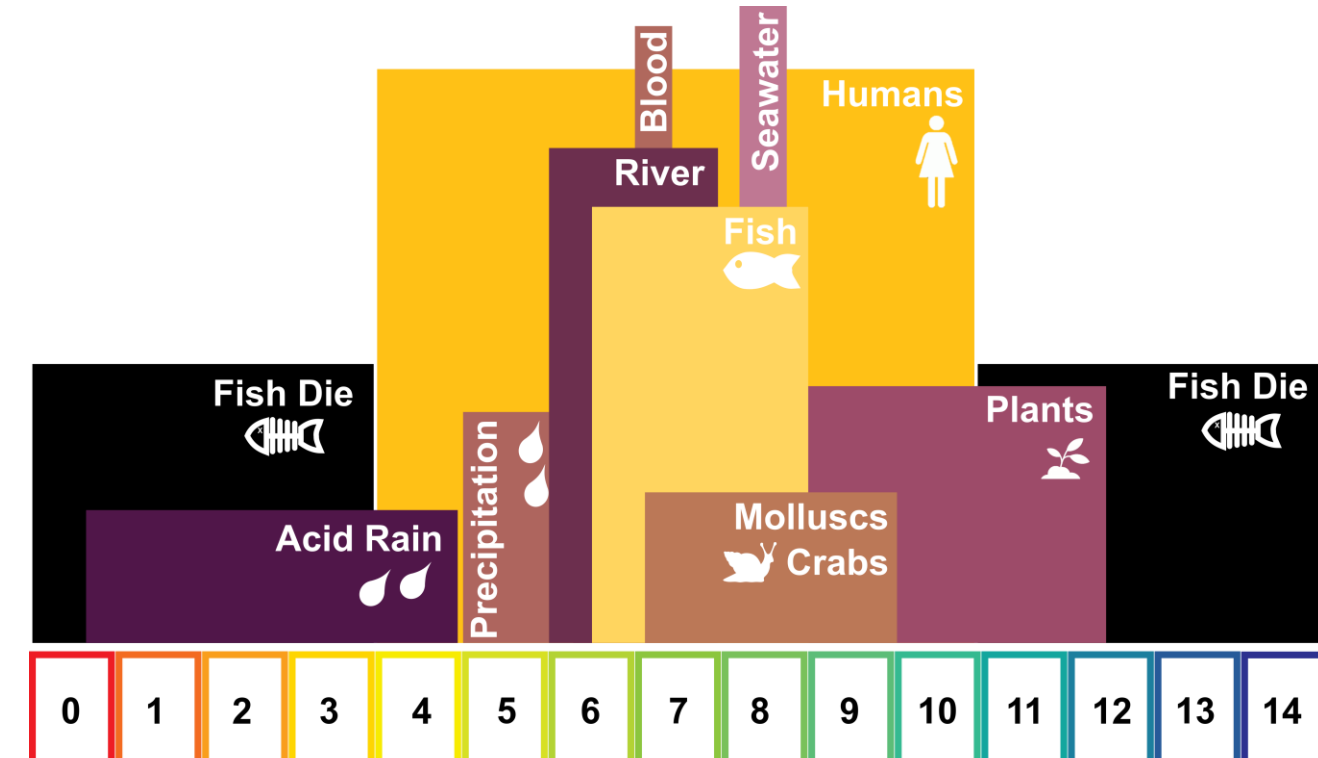
1

Key Analytes in Water Systems

pH, oxygen and carbon dioxide are key to many systems, from the environment to life itself.

Natural variations and those from human intervention can have large effects

In water systems, the availability and therefore toxicity of heavy metals is pH dependent

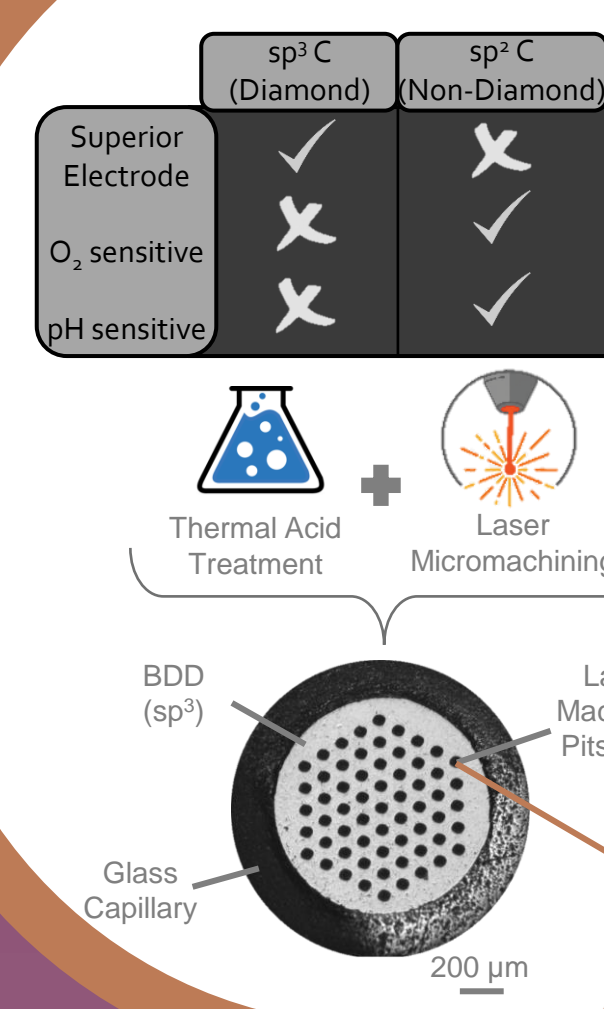


The finely balanced levels of pH, dissolved oxygen and carbon dioxide are indicative of the quality of a water environment, and of human plant and animal health

Measurement is Vital!

Simultaneous Measurement of pH and Oxygen in Aqueous Systems and Beyond

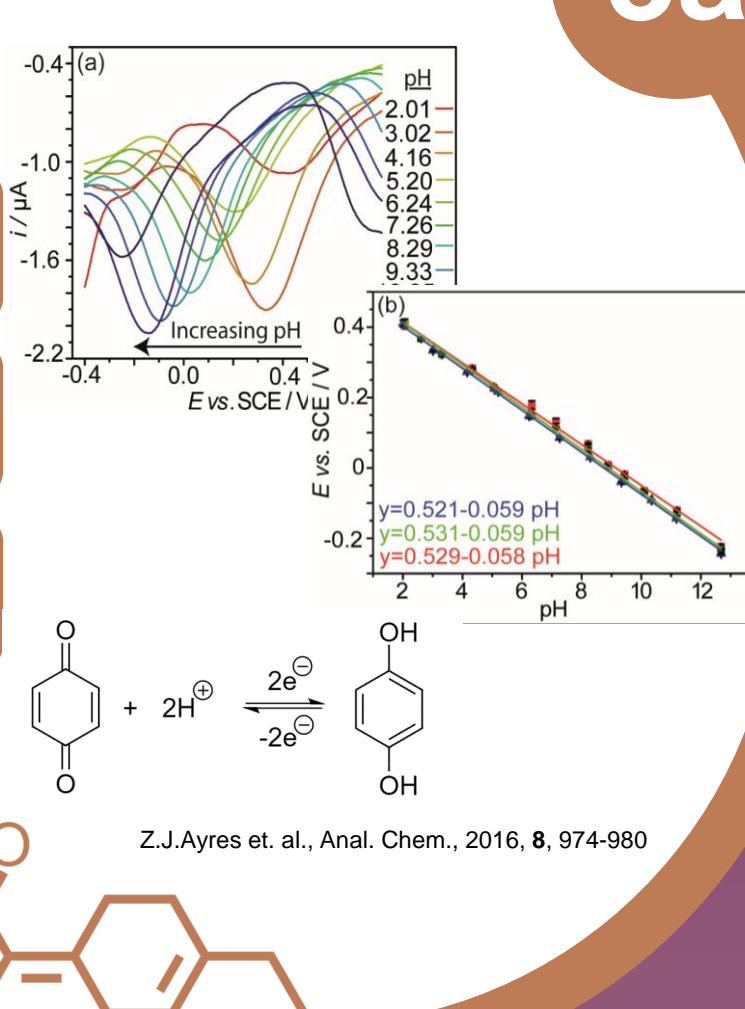
3a



High quality BDD is naturally insensitive to pH and does not catalyse oxygen reduction, unlike sp² (non-diamond) carbon structures.

Previous work demonstrated controlled introduction of robust, sp² carbon regions into a BDD substrate via laser micromachining.

This enables pH sensitivity due to quinone surface terminations on the sp² regions, whilst maintaining the excellent electrode qualities of the BDD.



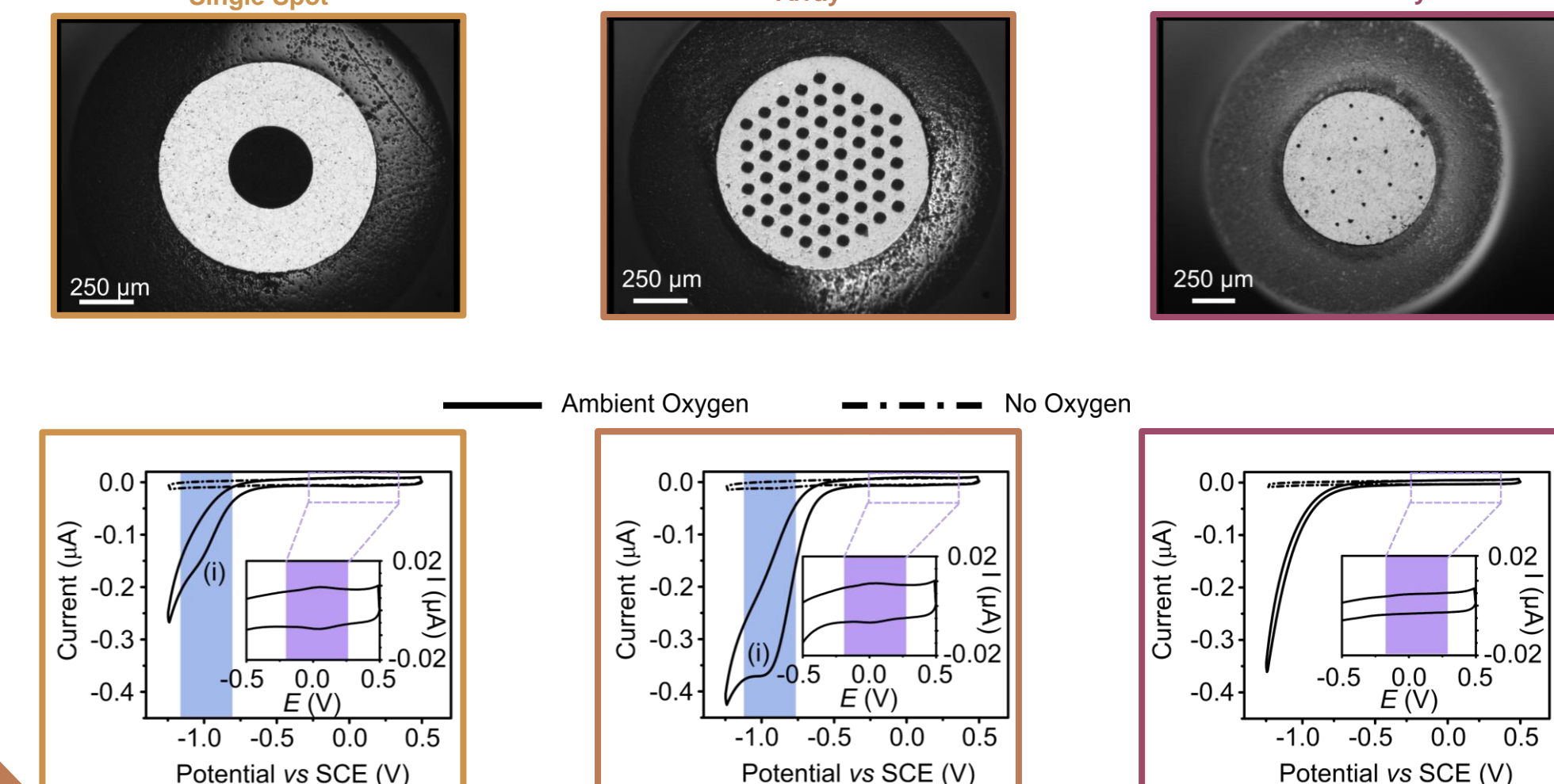
As the sp² carbon which enables this pH measurement is also sensitive to oxygen reduction, it is theoretically possible to use them to measure both pH and Oxygen in a single scan.

3b

Three designs were tested to optimise laser machining area for detection of both analytes.

The pH Signal (purple) was observed using all three; but was significantly smaller on the MicroArray.

The oxygen signal (blue) was only observed on the Single Spot and Array Designs, but was much clearer on the latter.



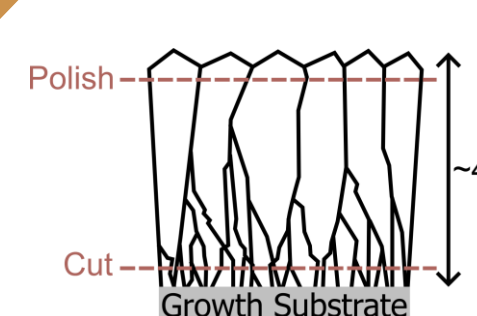
The Array design was used going forwards.

T.L. Read et al., ACS Sens., 2019, 4, 3, 756-763

2

Why is Boron Doped Diamond A Great Sensor Material?

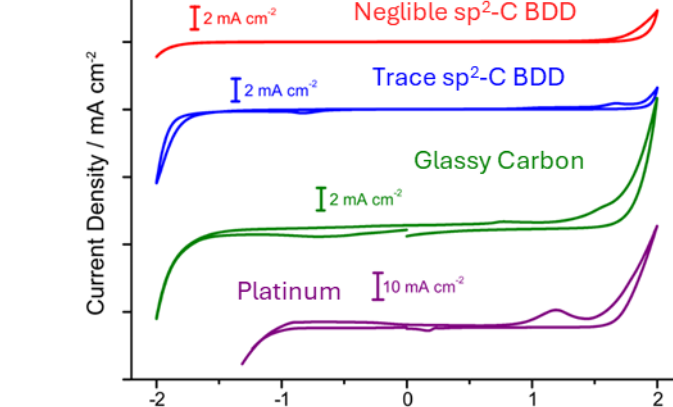
J.V. Macpherson, PCCP, 2015, 17, 2305



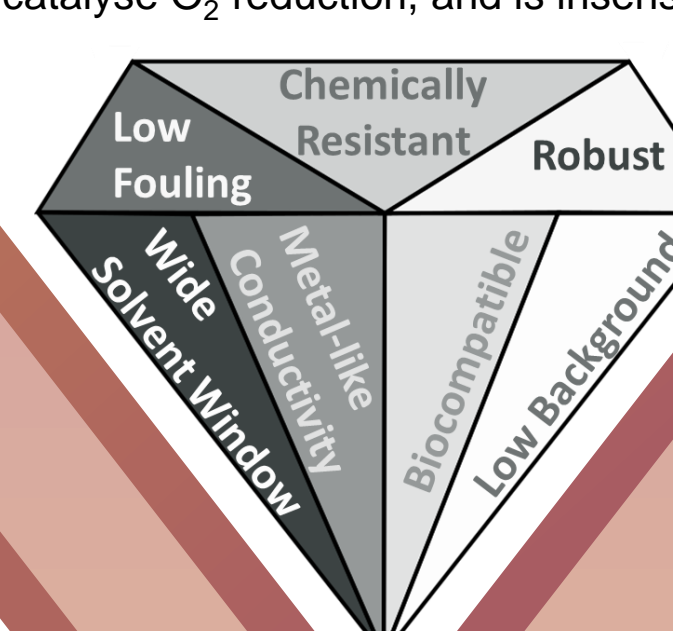
Laboratory grown BDD can be removed from the growth substrate to form high quality freestanding (all BDD) wafers.

Key Electrode Properties:

L.A. Hutton et al., Anal. Chem., 2013, 85, 7230



Wider window of negligible solvent electrolysis compared to other common electrode materials, does not catalyse O₂ reduction, and is insensitive to pH.

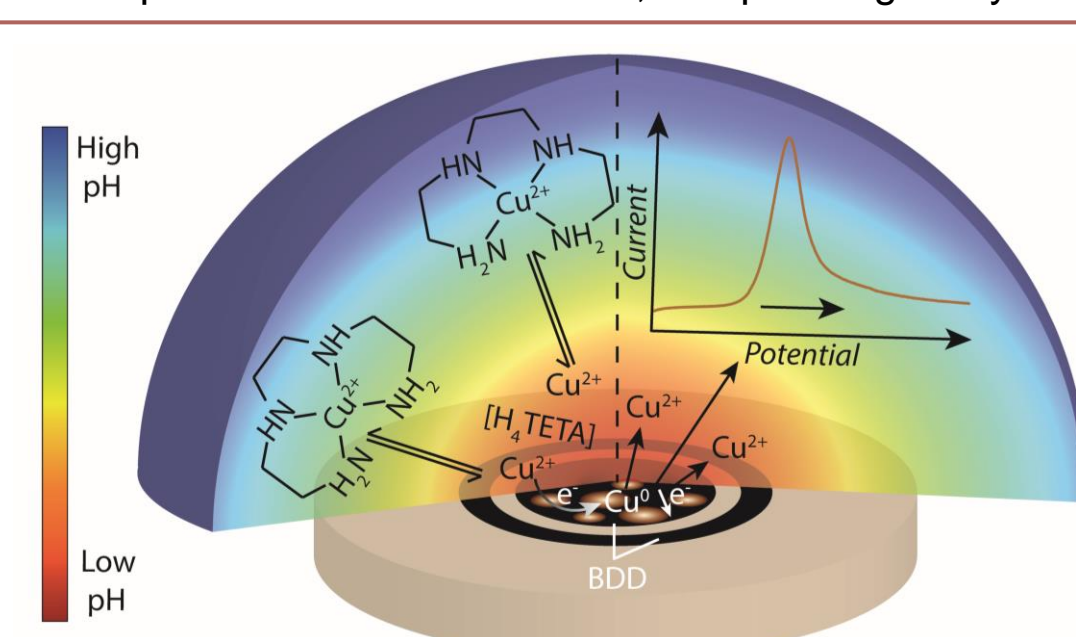


4a

Manipulation of Local pH for Copper Detection and Speciation Control

The binding and complexation of heavy metals such as Cu impacts their toxicity but varies depending on solution pH.

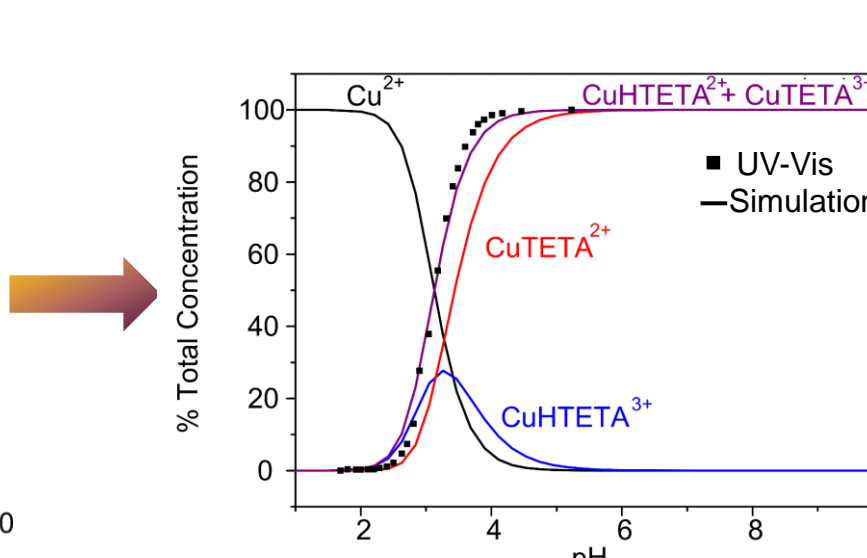
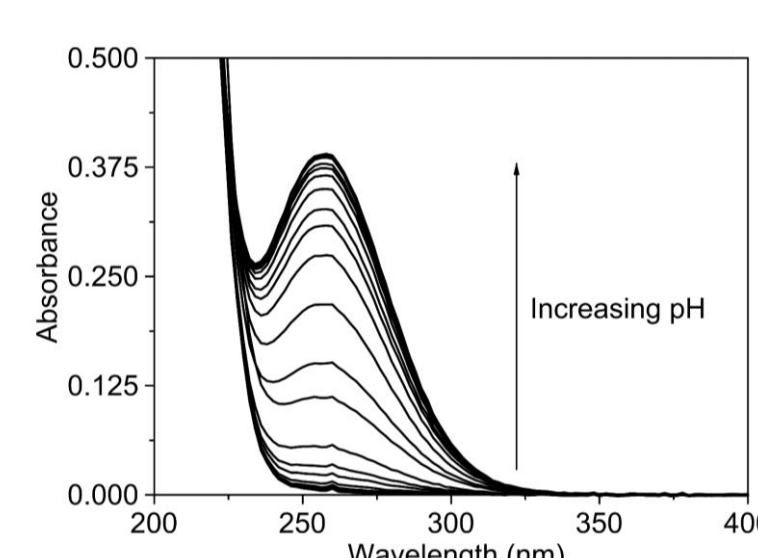
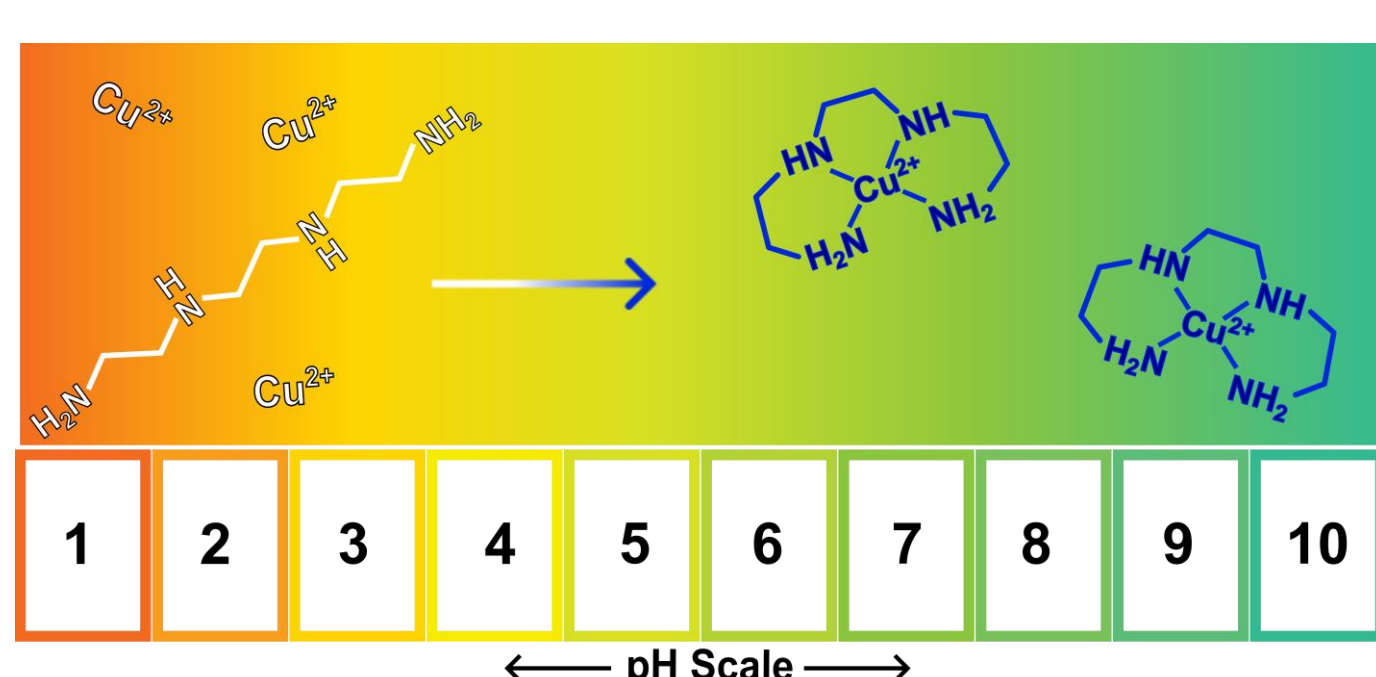
Often their measurement in water environments therefore requires sample removal and treatment, complicating analysis.



In this work we developed a sensor consisting of a BDD disk measurement electrode encompassed by a BDD ring pH control electrode, secured within an epoxy resin-based packaging.

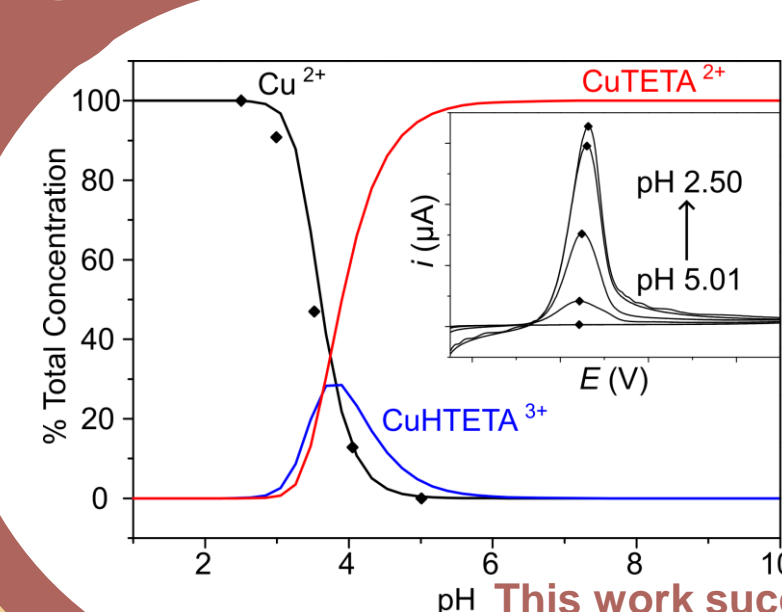
4b

The pH dependent binding of copper with triethylenetetramine (TETA), a copper chelator commonly used in therapeutic treatment to bind excess copper in the body of patients with Wilson's disease, was used as a model system.



UV-Vis absorbance spectroscopy was used to demonstrate the effect of pH on Cu-ligand binding, showing good agreement to speciation simulations.

4c



Electrochemical measurements of Cu in TETA containing solutions at different bulk pH showed good agreement to simulated speciation curves.

By applying different current densities to the ring electrode and measuring the electrochemical Cu signal in a sample of neutral pH a similar response is achieved.

Applied Current Density (mA cm ⁻²)	% Maximum LSV Peak Current	Generated pH from Speciation Curve
0.10	0	5.01 ± 0.02
0.20	34.98	3.76 ± 0.02
0.395	78.92	3.35 ± 0.02
1.98	100	≤ 2.50

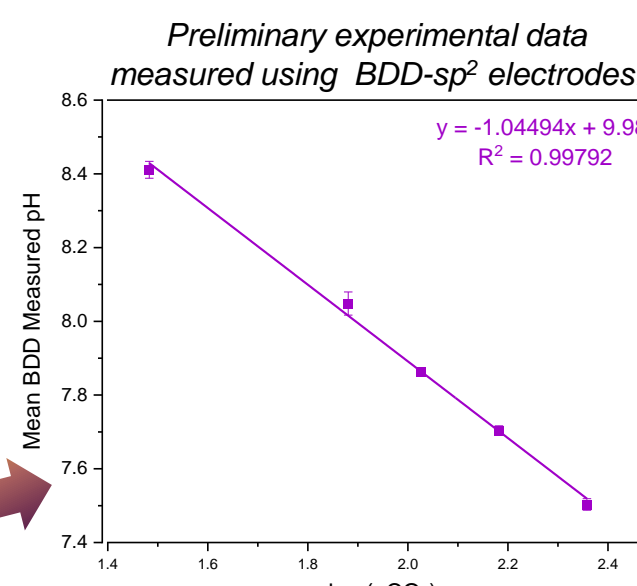
This work successfully demonstrates the applicability of BDD ring-disk systems to control local solution pH, enabling *in situ* monitoring of metal-ligand binding and speciation control.

Moving Forwards

Electrochemical CO₂ measurement is actually a measure of the pH change as a result of the shifting bicarbonate/carbonate equilibrium. In preliminary work (paper in prep) this is demonstrated using BDD-sp² electrodes.

Theoretically described by a modified Henderson-Hasselbalch equation:

$$pH = 6.36 + \log \left(\frac{[HCO_3^-]}{0.0307 \times pCO_2} \right) - \log(pCO_2)$$
$$pH = 6.36 + \log(20 \text{ mM}) - \log(0.0307) - \log(pCO_2)$$
$$pH = -1 \times \log(pCO_2) + 9.17$$
$$y = m \times x + c$$

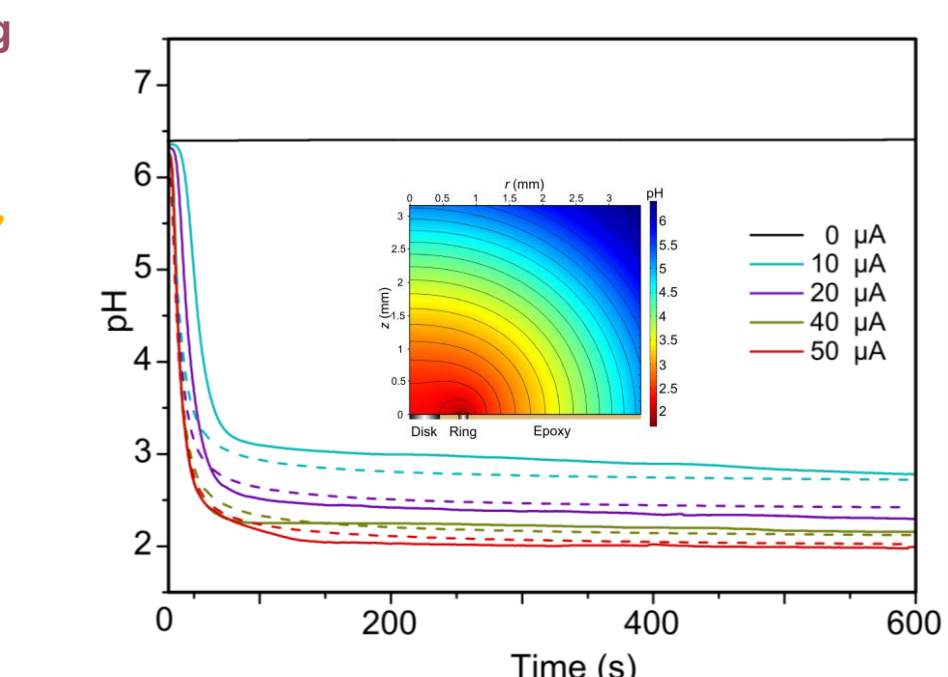
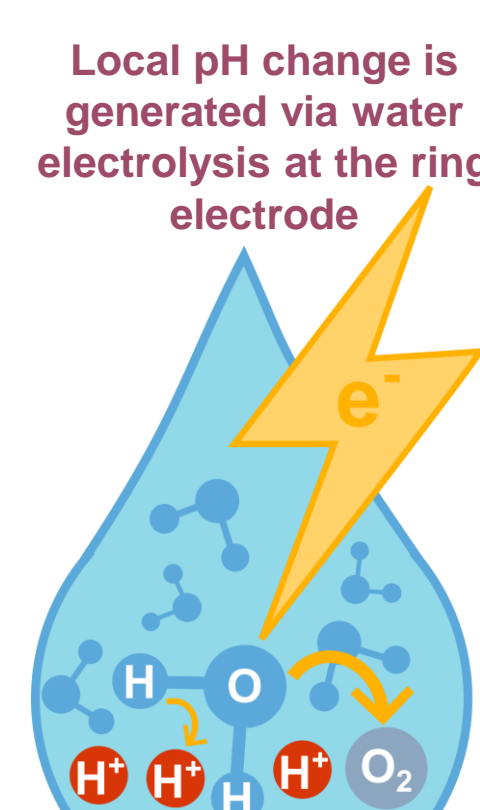
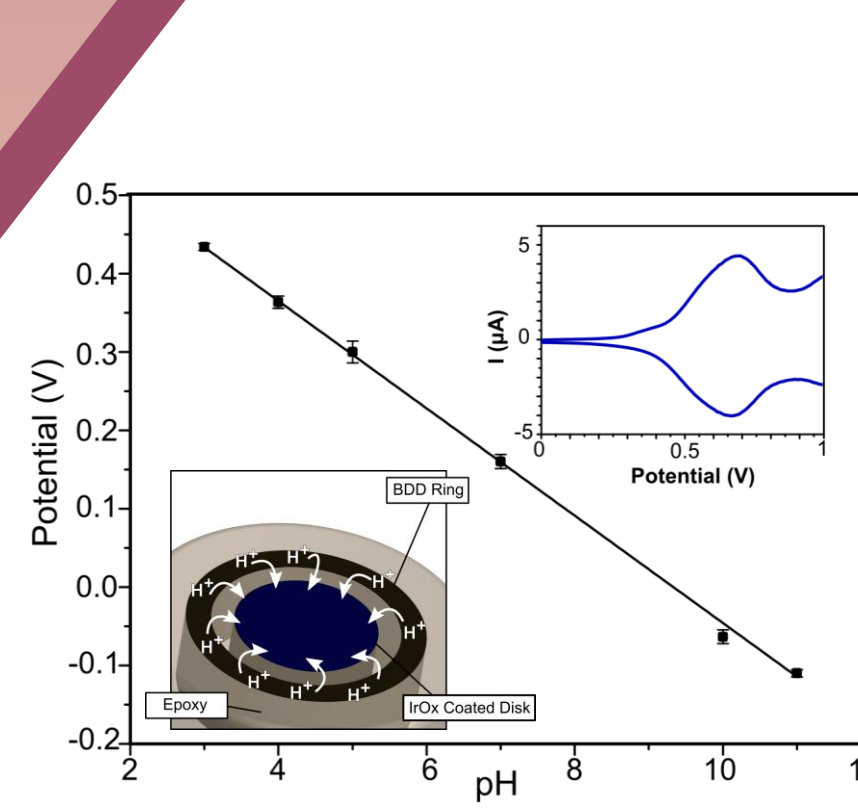


We also note that if two electrochemical peaks in a single measurement were truly independent (e.g. no effect of pH on O₂ signal and vice versa), the relationship between them could be used to inform on reference electrode drift – a major issue for *in situ* sensing

Manipulation of Local pH for Hg Detection

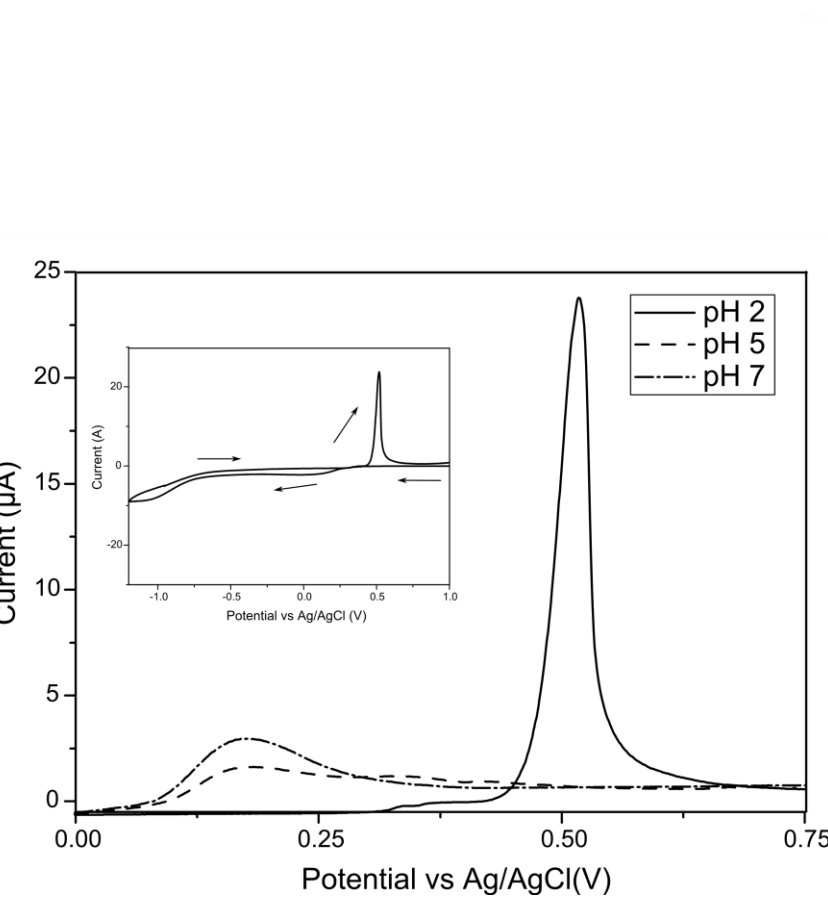
5

Using a BDD ring-disk electrode design we are also able to improve electrochemical mercury detection in less acidic water samples.

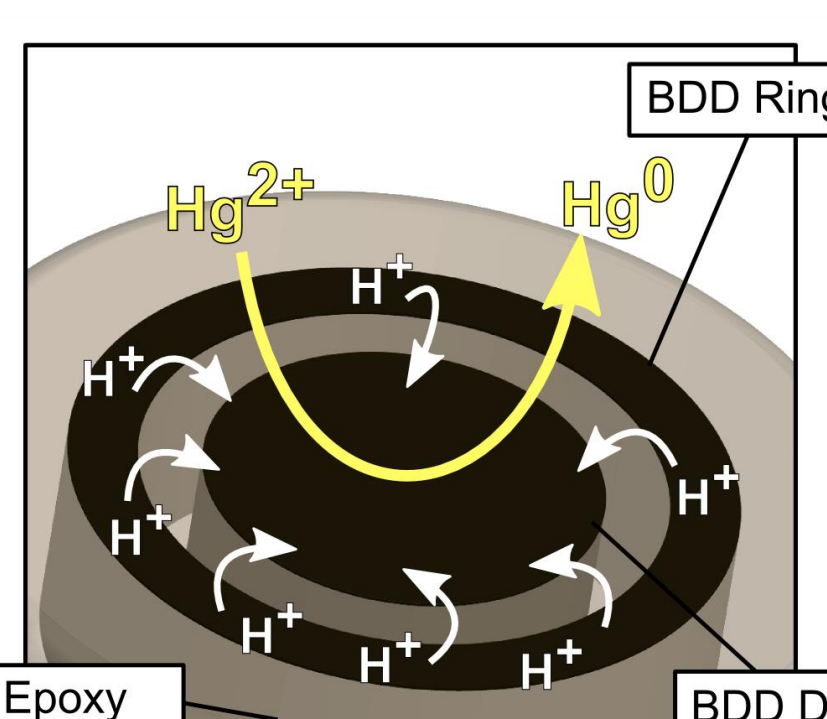


A pH sensitive iridium oxide film was deposited on the sensor electrode and calibrated in solutions of known pH.

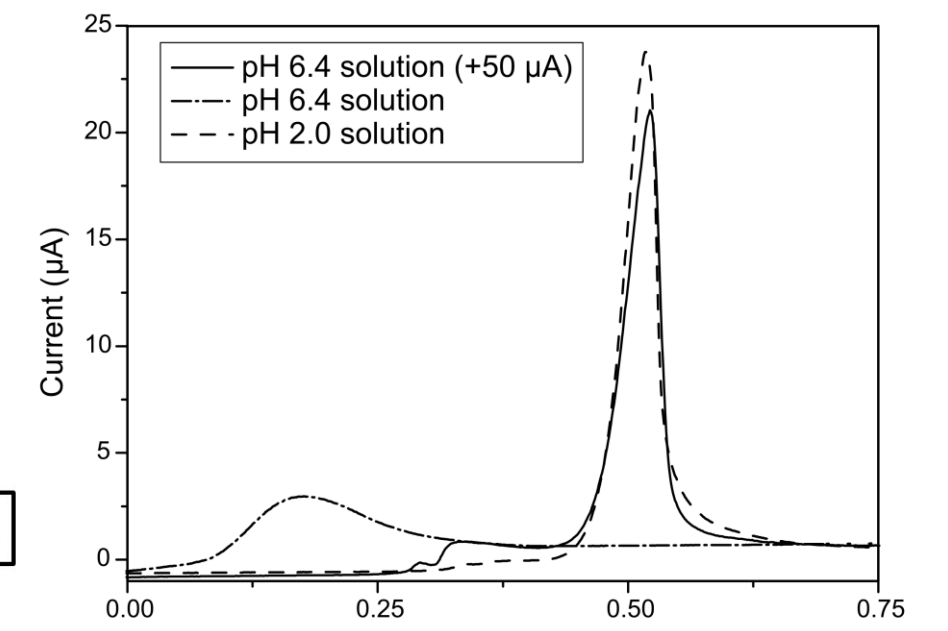
Experimental data (solid lines) comparing pH change over time measured at the disk showed good agreement to simulated data (dashed lines)



In acidic solutions Hg produces a single easy to quantify electrochemical peak. In alkali, this peak shifts and splits making analysis difficult.



Applying 50 μA current, sufficient to generate a local pH 2 environment at the ring should enable facile Hg detection at the disk.



The Hg peak in a pH 6.4 solution under local pH control is shown to be equivalent to that of a bulk pH 2 solution, thus demonstrating *in situ* optimisation of electrochemical Hg detection.

Acknowledgements

Principal Investigator
Professor Julie Macpherson

Funding



Impact Acceleration Fund

Colleagues and Contributors

Dr Eleni Bitziou
Dr Maxim Joseph
Dr Samuel Cobb
Dr Zoe Ayres
Warwick Electrochemistry and Interfaces Group

