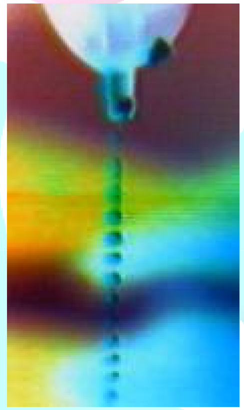
INVESTIGATION OF NANOSTRUCTURED MATERIALS FOR NOVEL BIOSENSOR FABRICATION METHODOLOGIES

Dr. Aoife Morrin



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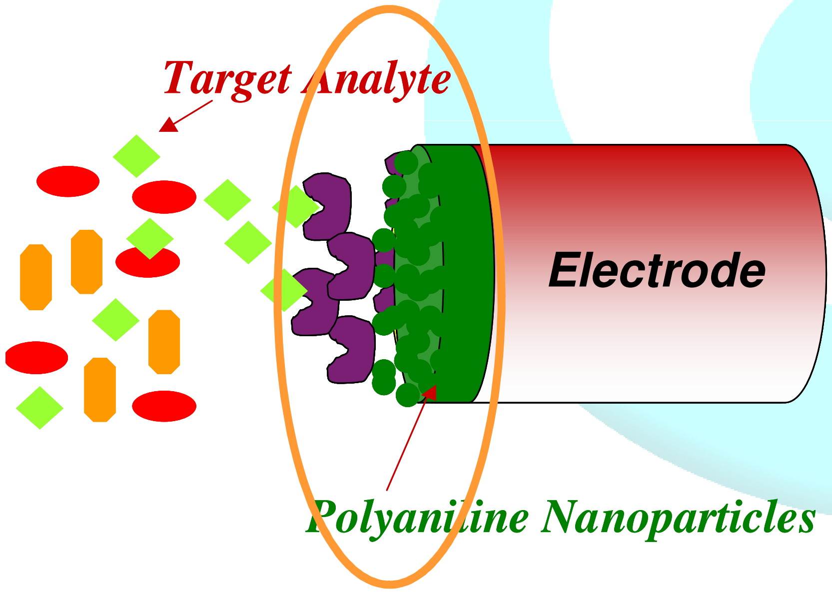
Introduction

• Emergence of nanotechnology opening new horizons for electrochemical biosensing

• How can nanostructured conducting polymers contribute to this space?

• Explore transduction interface



Overview

- **Electrode Interface**

- **Synthetic approaches to fabricating polyaniline nanoparticles**

- **Electrode modification with nanoparticles**

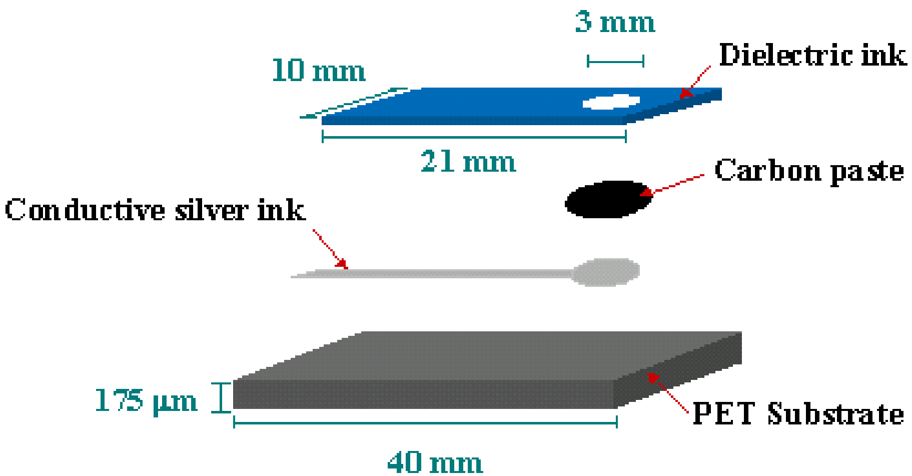
(i) Electrodeposition – ***Excellent control over film thickness***

(ii) Casting – ***Amenable to Mass Production***

- **Sensing Applications**

Sensor Platform

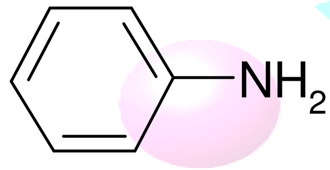
- Screen printing
- Low start up and manufacturing cost
- Mass production
- Disposability
- Flexible design process
- Platform for glucose biosensor industry



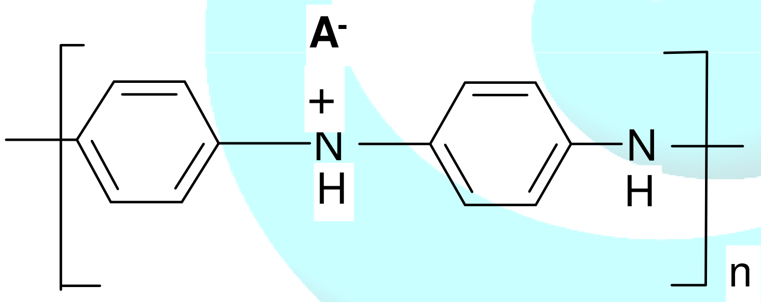
Electrode Modification by Conducting Polymer

- Highly conductive
- Simple doping/dedoping chemistry
- Good environmental stability
- Electrical properties modified by ox. state of main chain

- Applications:
  - Sensors
    - electrochemical
    - optical
  - Anti-corrosion protection of metals
  - Supporting material for catalysts
  - Electrochromic displays



Aniline



Doped Polyaniline (conductive state)

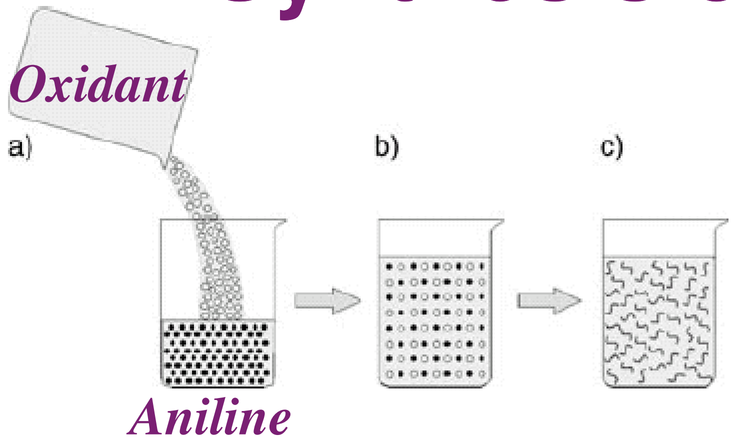
Bulk Polyaniline

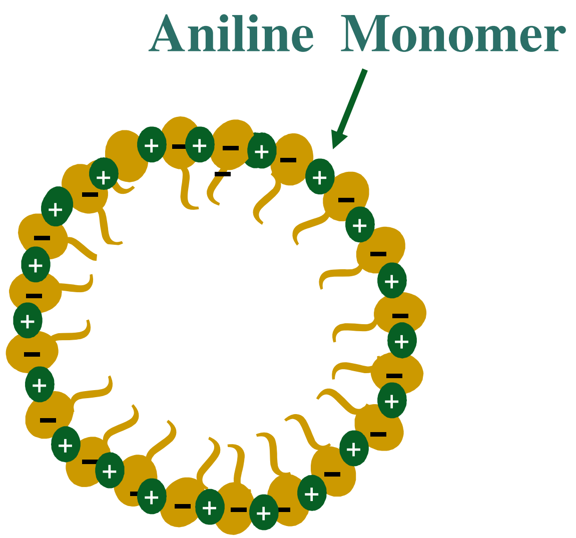
Chemical or electrochemical synthesis
Acidic conditions for deposition
Insoluble in common solvents
Carcinogenic monomer

Nanoparticulate polyaniline

Higher Processibility
Aqueous Dispersions
Higher Conductivity
Amenable to alternate deposition techniques
Nanoscale Sensor Fabrication

Synthesis of Nanoparticles



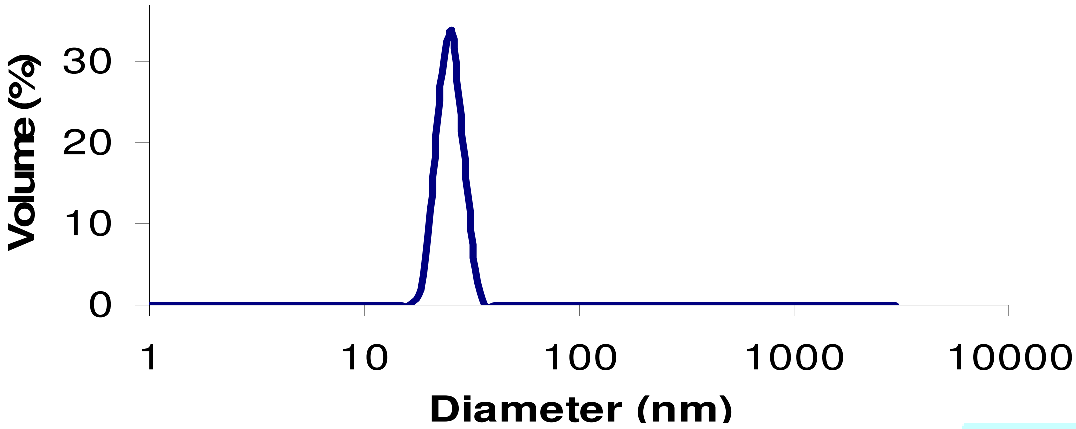


DBSA Micelle

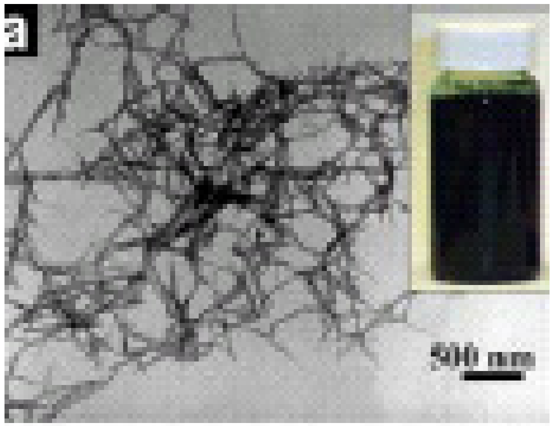
- **Rapid Mixing method***
- **Monomer to Oxidant ratio = 4:1**
- **DBSA added to serve as dopant & surfactant (provide micelle structure to stabilise particles)**
- **SDS present also acts as surfactant for stabilisation**

* Jiaxing Huang, Richard B. Kaner, *Angew. Chem. Int. Ed.* **2004**, 43, 5817-5821

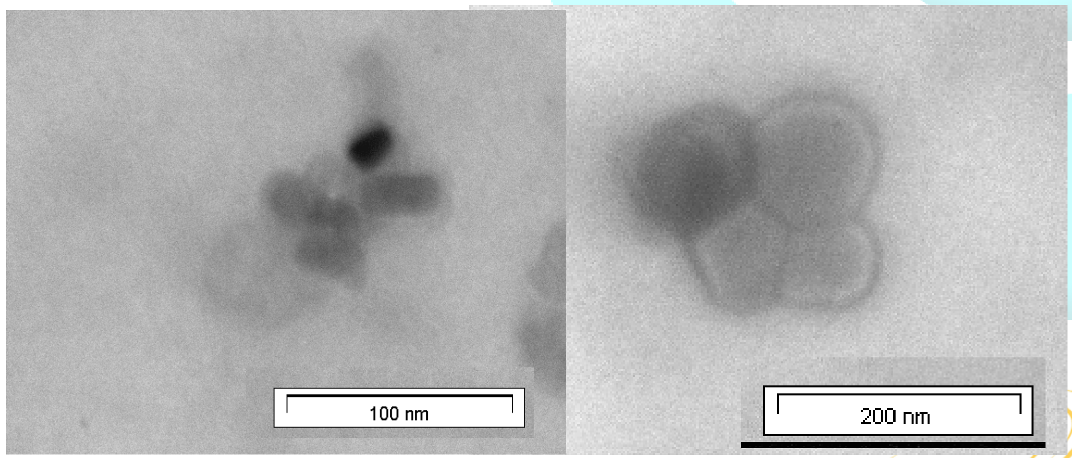
Polyaniline Nanoparticles



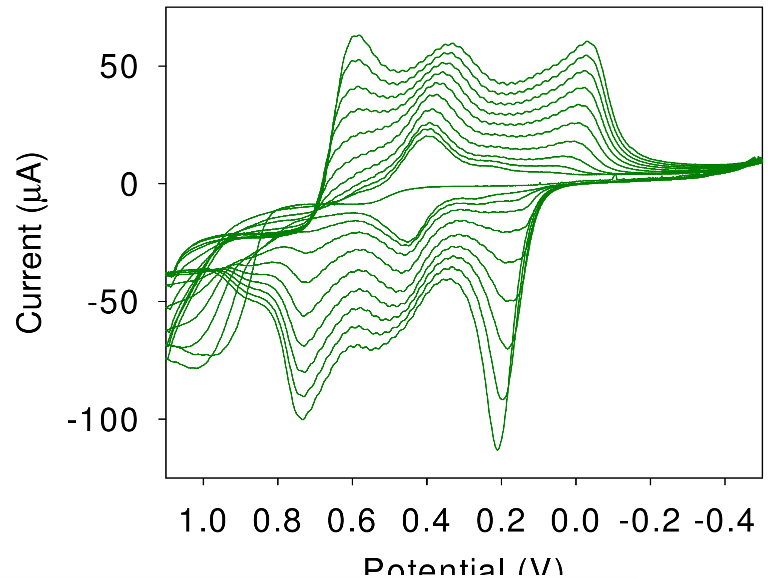
No Stabiliser Present



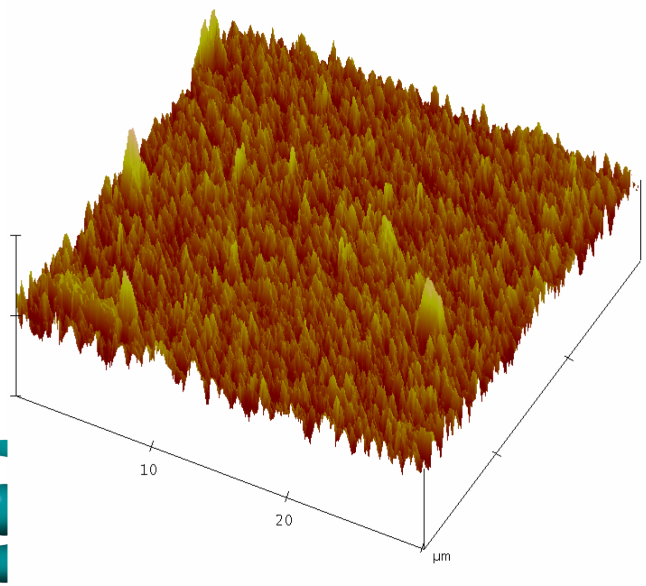
Stabiliser Present

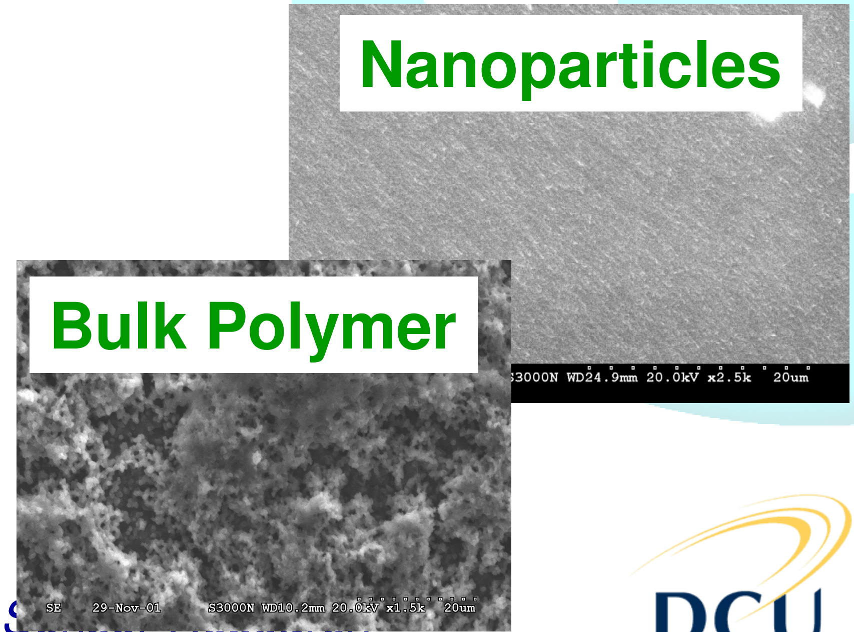


(i) Electrodeposition of Nanoparticles

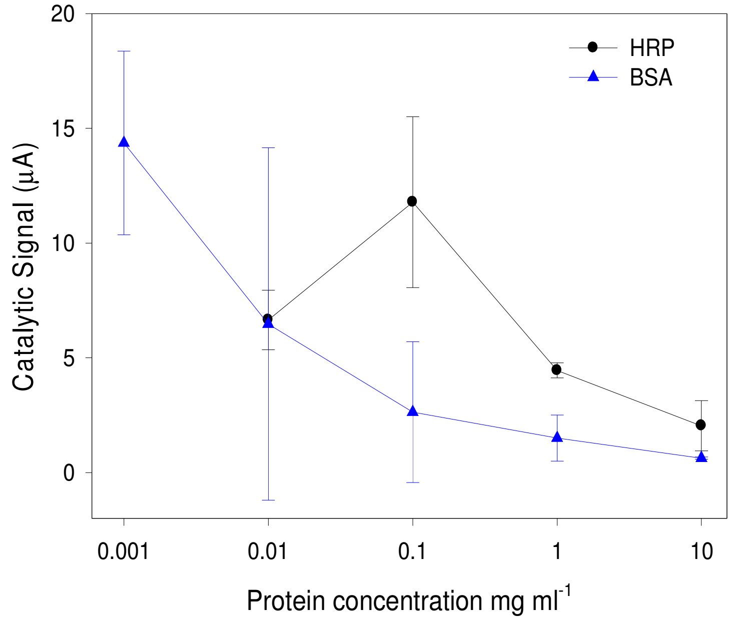


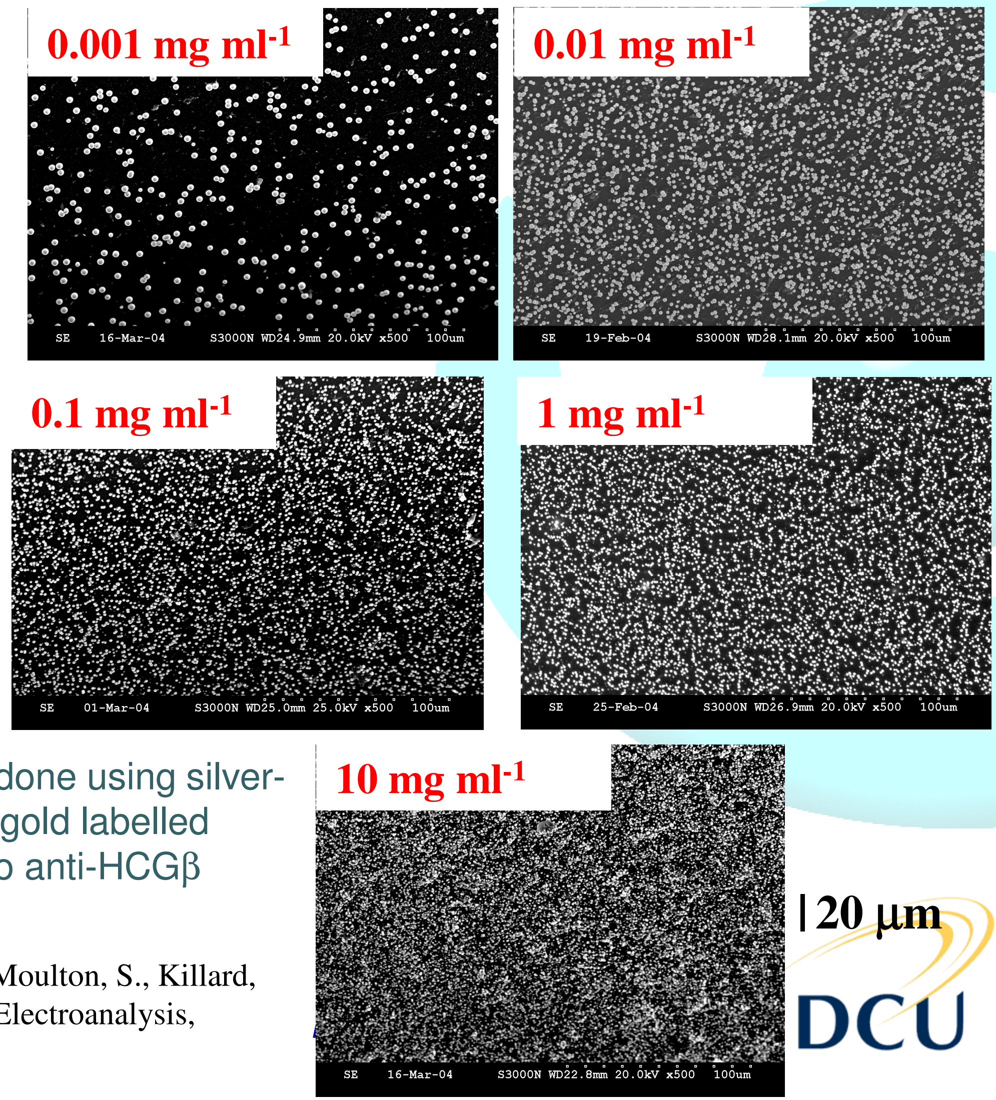
- Potentiodynamic method of deposition
- Doped with DBSA
- Film thickness ~350 nm





SEM Imaging of Protein on Nanoparticulate Films

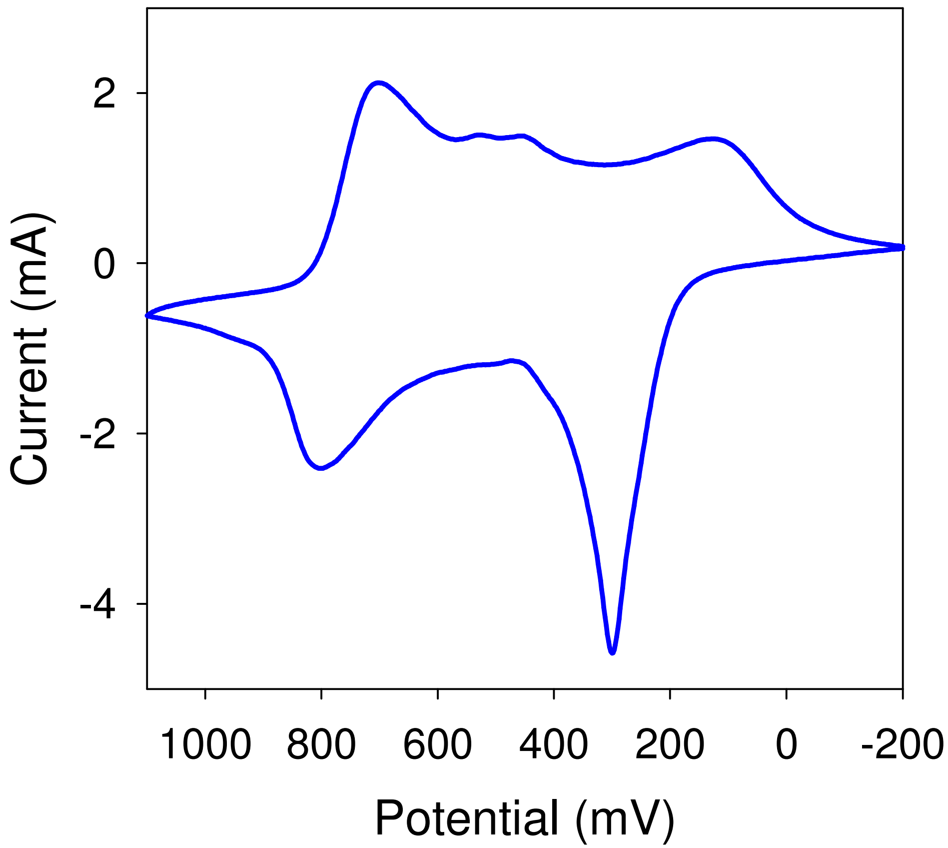


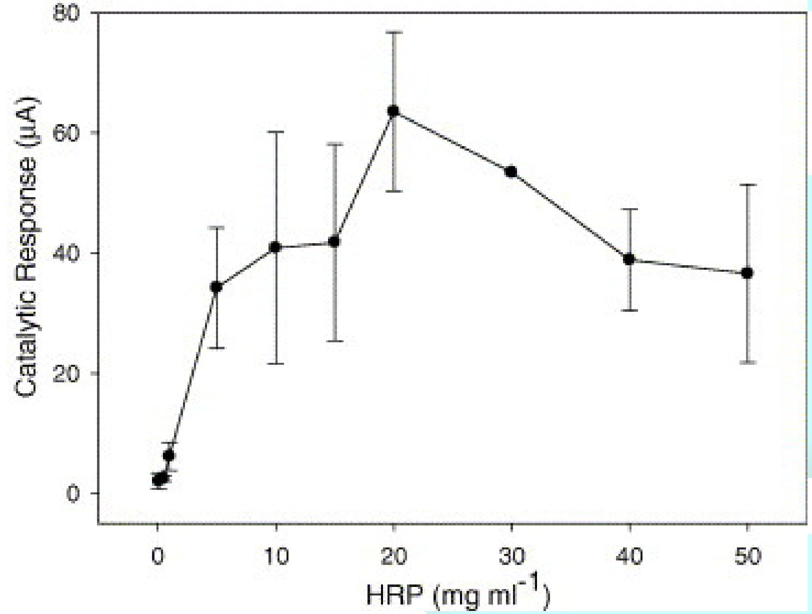


* Imaging done using silver-enhanced gold labelled protein (Mo anti-HCGβ antibody)

*Morrin, A., Ngamna, O., Moulton, S., Killard, A.J., Smyth, M.R. (2004). Electroanalysis, *17:423.*

(ii) Casting

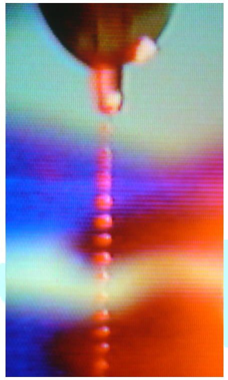




Note: **pH adjusted to 7.0, 5.5 % w/w nanoparticles, 5 μl**

Morrin, A., Wilbeer, F., Ngamna, O., Moulton, S., Killard, A.J., Smyth, M.R. (2004). *Electrochem. Comm., 7:317-322*

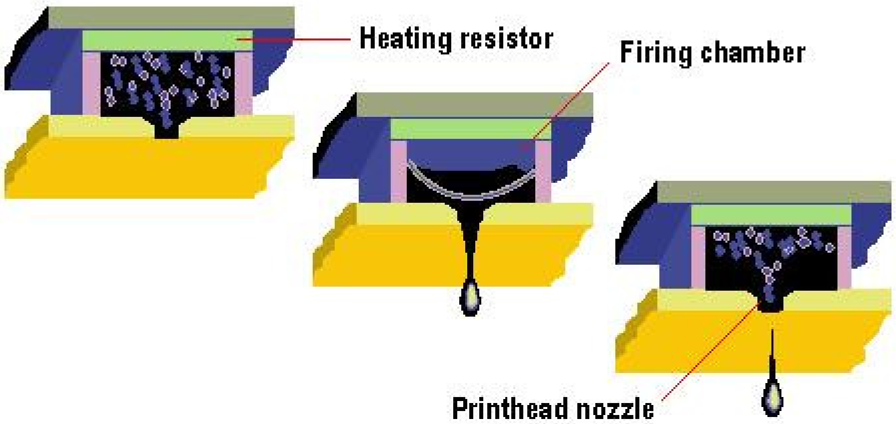
(iii) Inkjet Printing

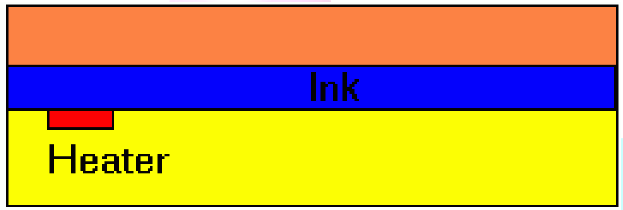


- Method for casting ultra-thin films, (deposits microdroplets of 2-12 pL)
- High precision, resolution of ~ 25 µm.
- Amenable to simultaneous deposition of more than one “ink”.
- Non-contact Printing. (substrate and print head don’t touch)
- Rapid method, quality of print easily monitored in real time.

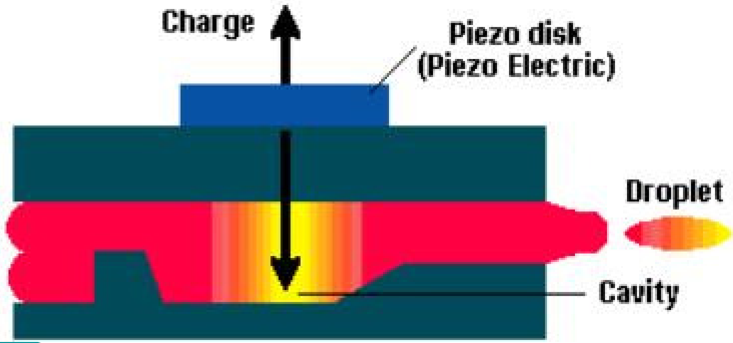
Inkjet Printing Technologies

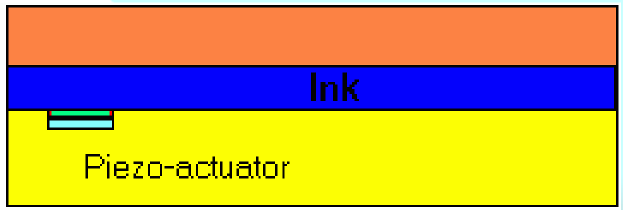
Thermal



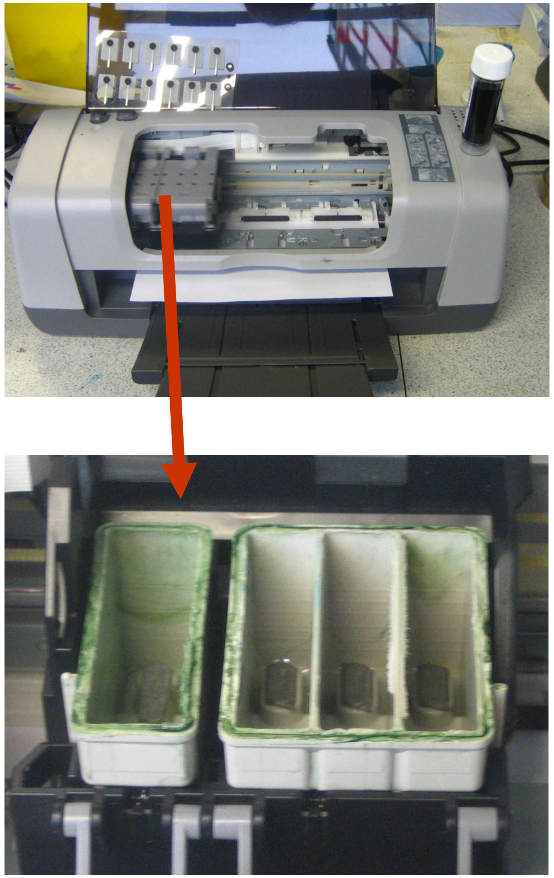


Piezoelectric

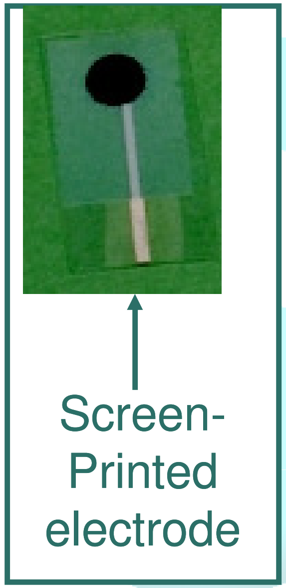




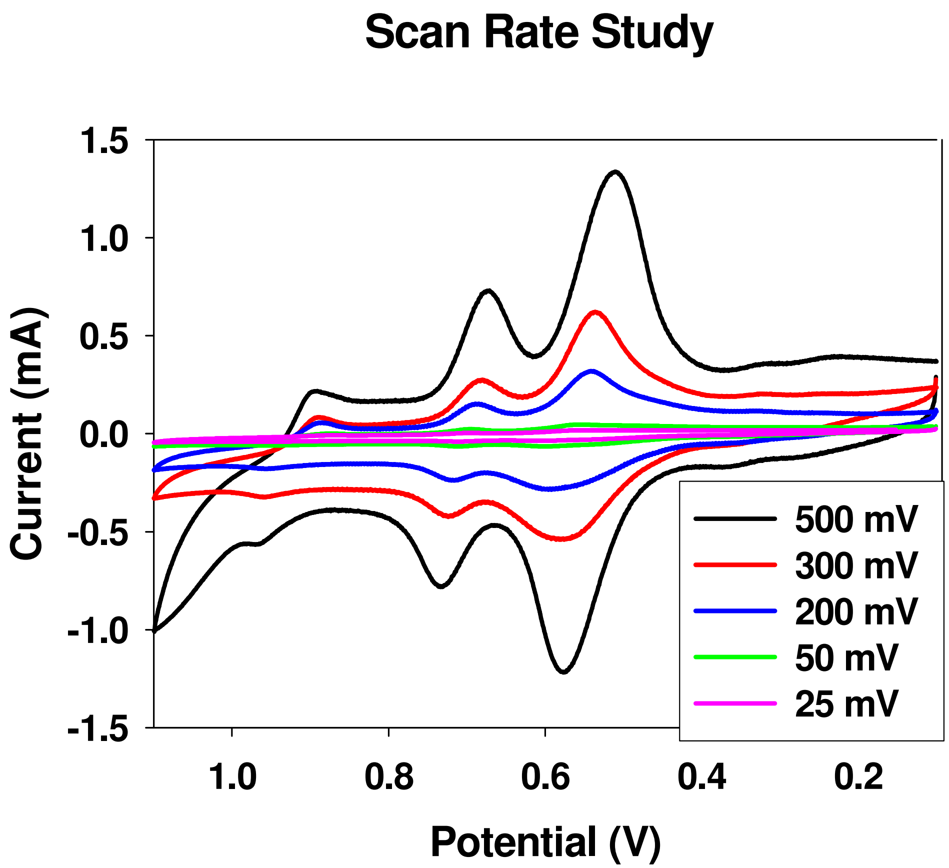
Instrumentation Strategy for Ink-Jet Printing

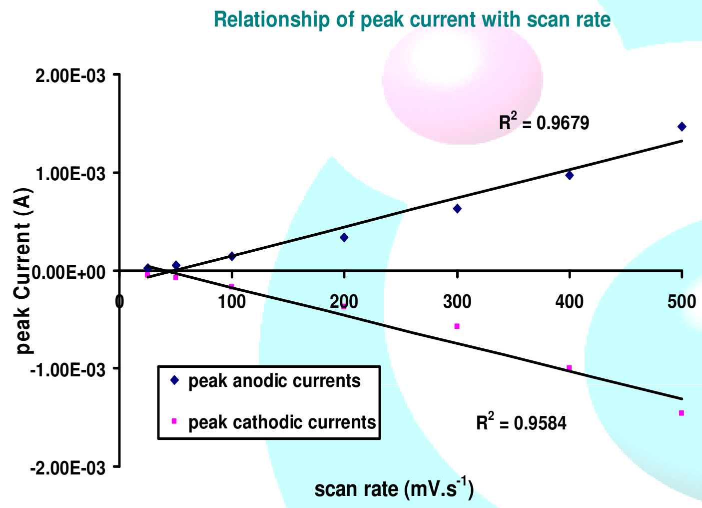


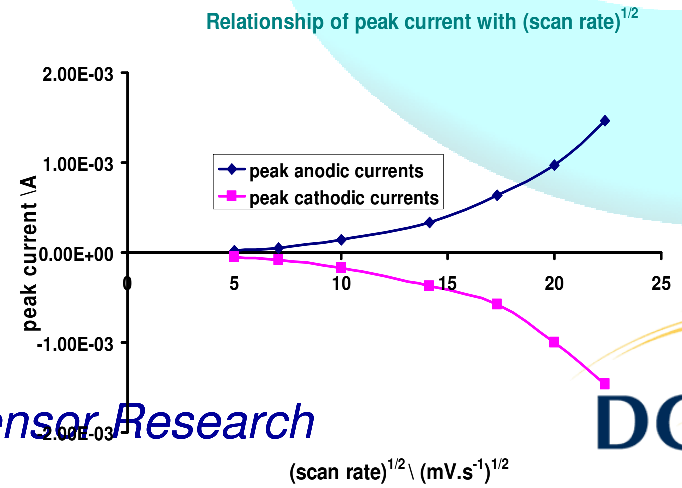
- Epson desktop printer
  (2880 x 720 drops per inch)
- Uses piezo technology
- Drop on demand
- Favoured over other more expensive single head devices due to the four available reservoirs.



Electrochemistry of Inkjet Printed Polyaniline







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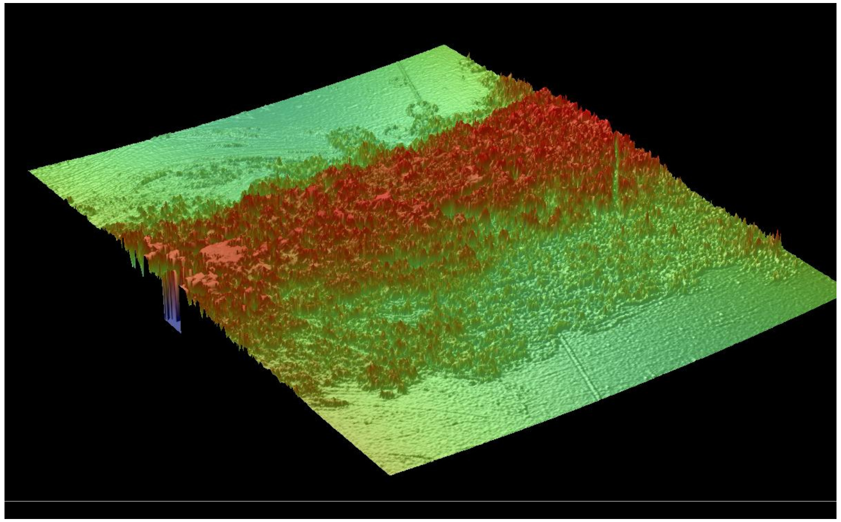
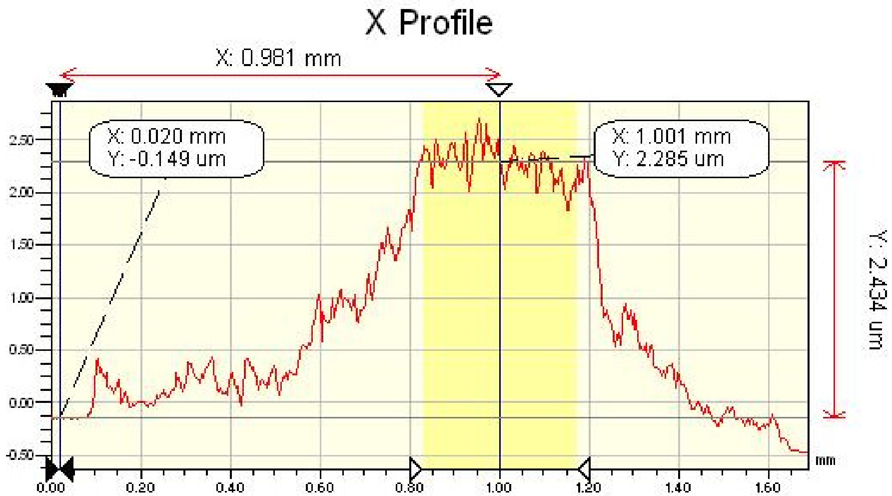
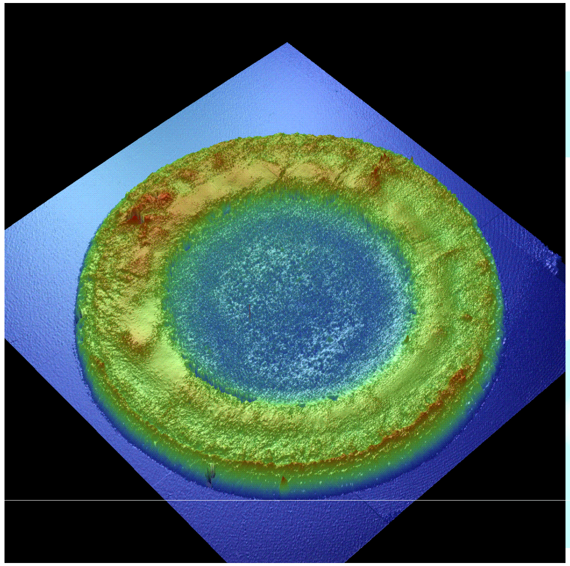
Profilometry

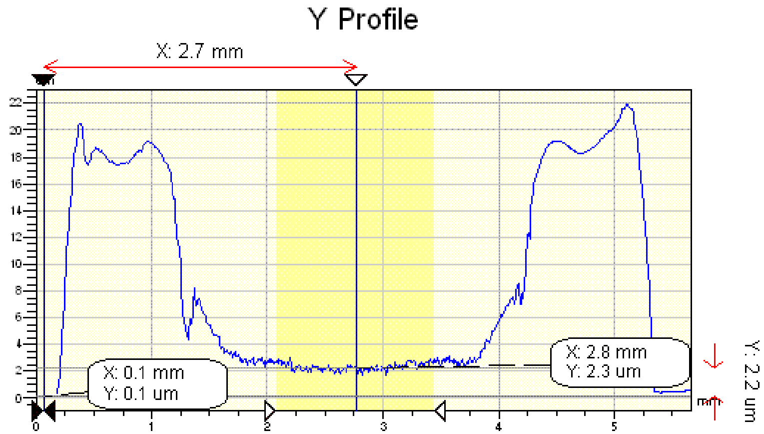
Inkjet printed (50 prints)



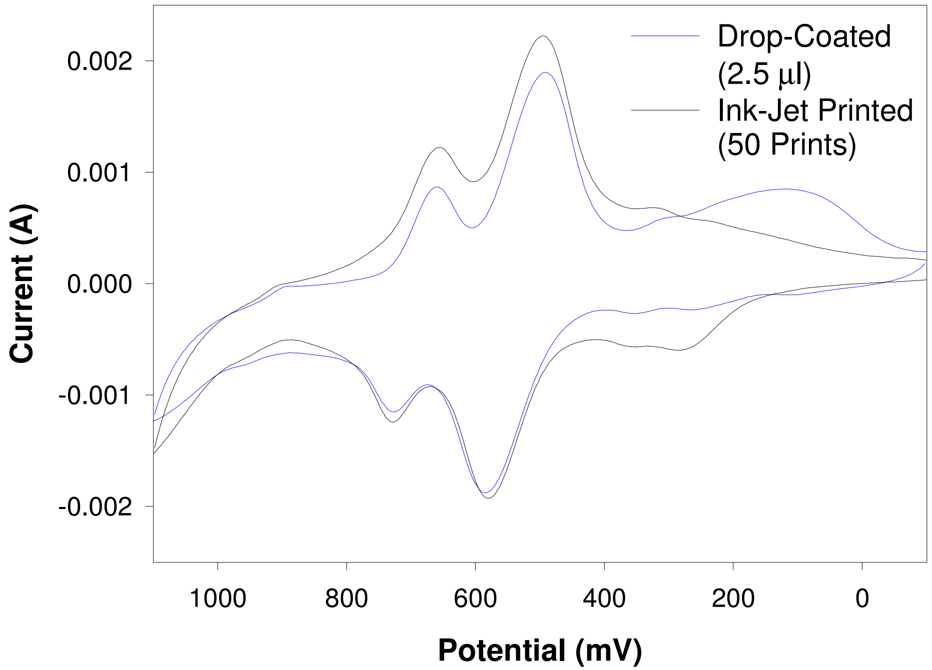


Drop-coated (5 μl)





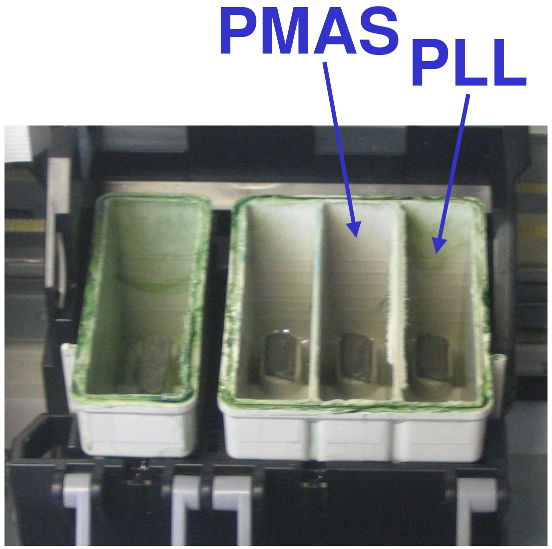
Drop-Coating vs. Inkjet Printing

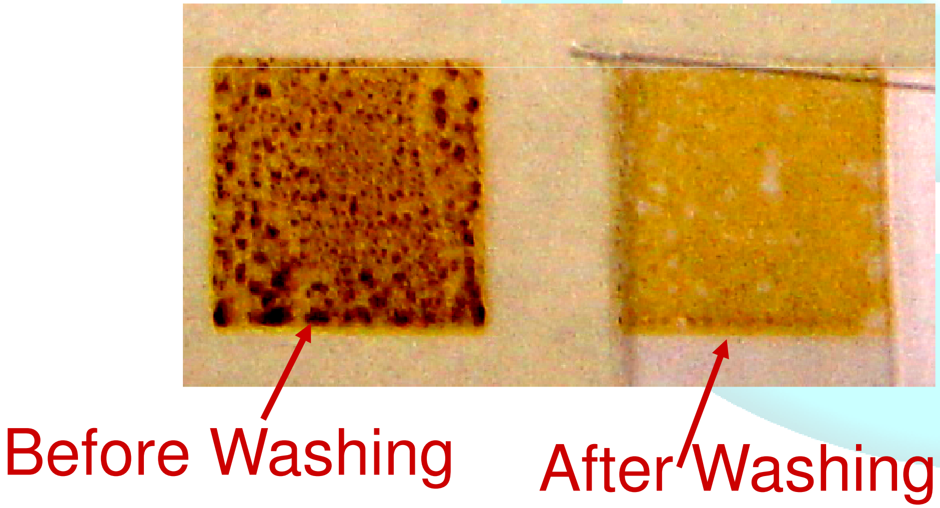


- **50 prints comparable to dropcoating 2.5 µl (Equates to ~ 20 nl / mm^2)**
- **Difference in deposition techniques responsible for comparable CVs.**

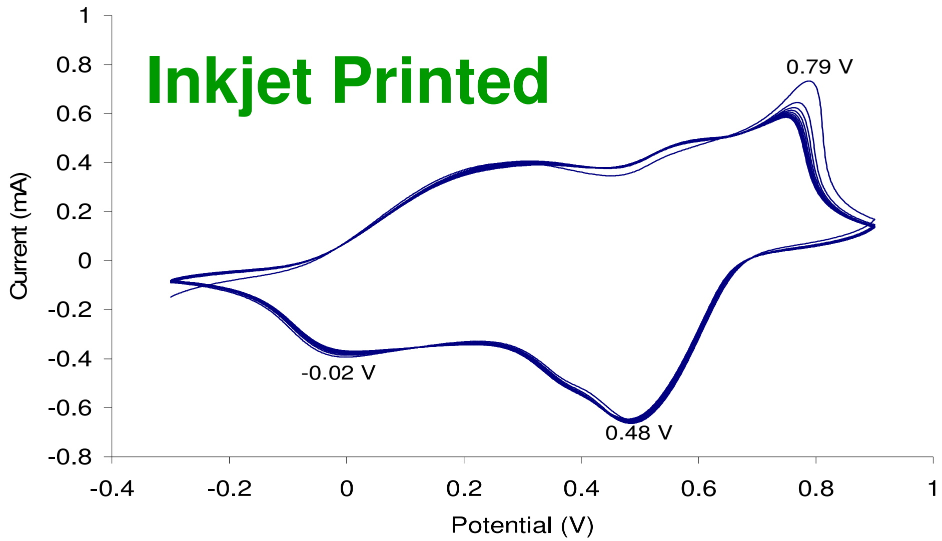
Water-Soluble Polyaniline

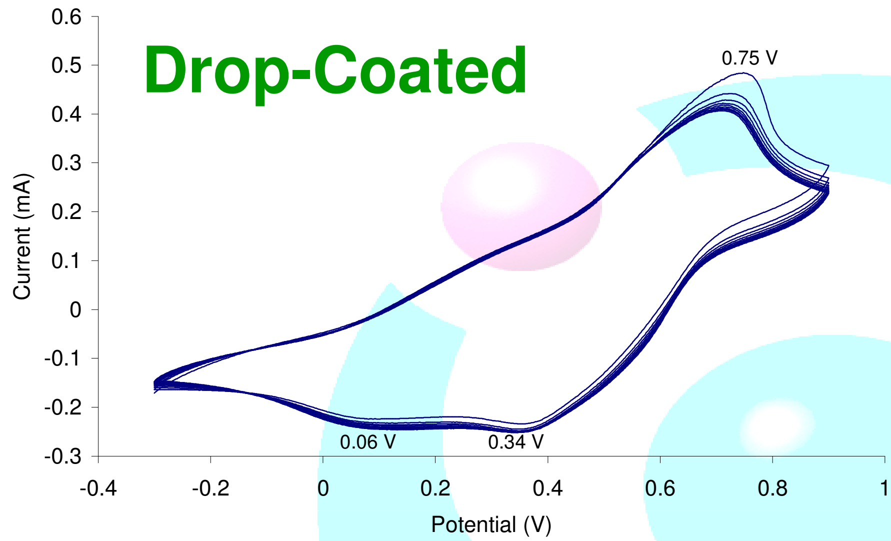
• Poly(2-methoxyaniline-5-sulphonic acid) (*PMAS)* – Sulphonated polyaniline
• PMAS must complex with a polycation (poly-L-lyseine (PLL)) to render it insoluble
• Need to co-deposit, i.e., print simultaneously – Inkjet has that facility





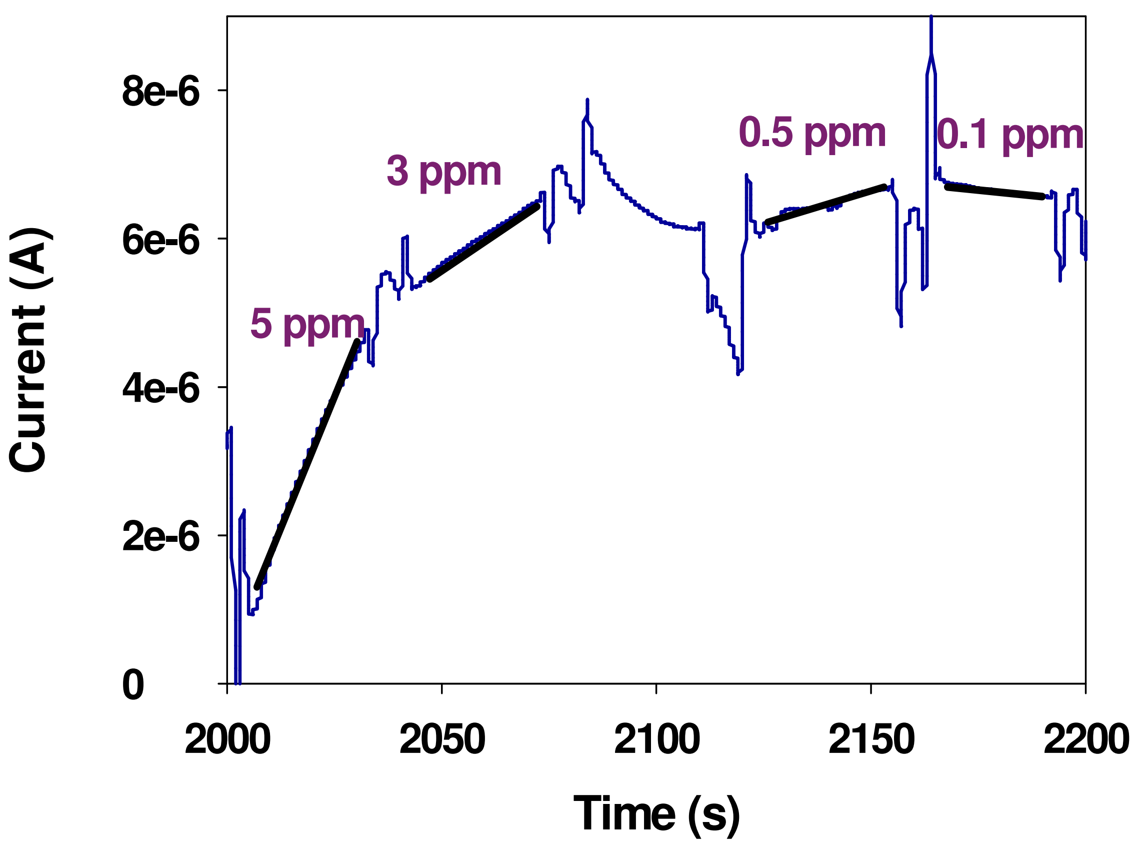
Water-Soluble Polyaniline





- Demonstrates unique advantages of using inkjet printing
- The inkjet printed films show improved electrochemistry compared to the evaporative cast films, indicating more efficient electron transfer process
- This will lead to improvement of biosensor performance

Biosensor Application



Real-Time Multi-Calibration Study

Flow Cell Setup

- HRP & H_2O_2 passed over together for short periods of time.
- Concentrations from 5 ppm to 0.1 ppm HRP with 10 mM H_2O_2 used.
- Decreasing slopes

Ammonia Sensing

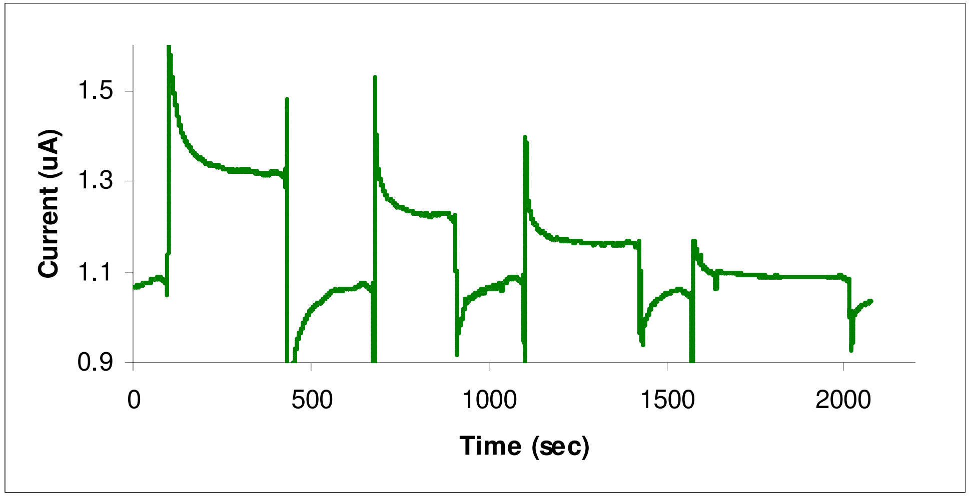
- ***Chemical & Gas Sensing***

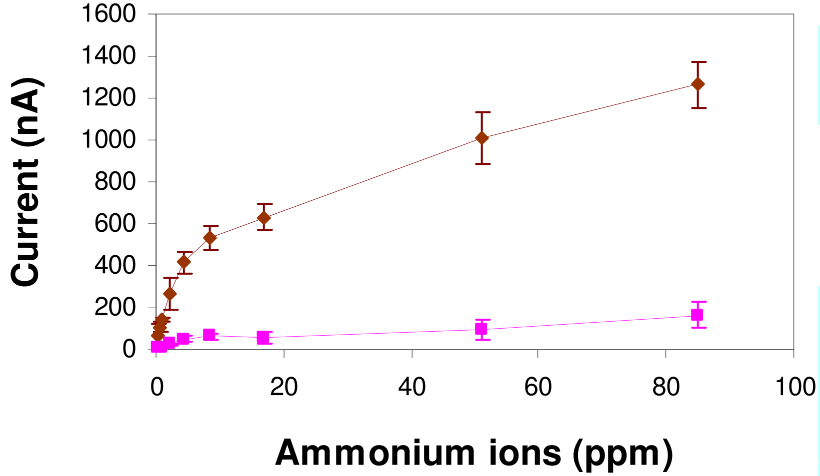
Environmental, Automotive, Chemical, Medical

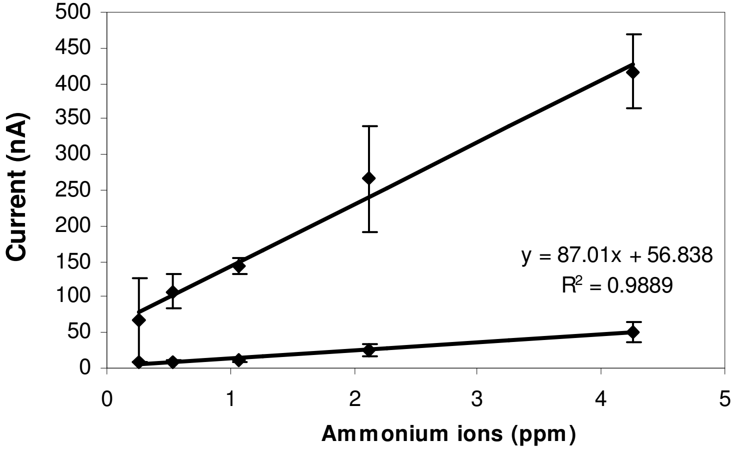
- ***Biosensing***

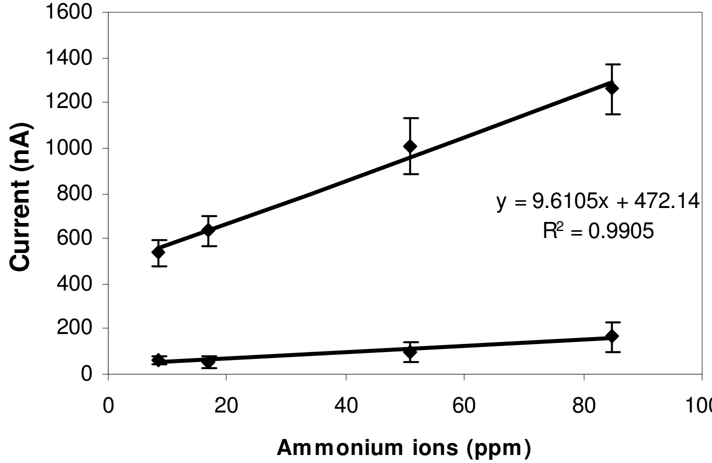
Measurement in biosensors is finding increasing applications as ammonium ions are a metabolic product in many enzymatic reactions.
E.g., Urea and Creatinine can be detected by sensing in this way

Ammonium Ion Sensing









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And To Conclude…..

- Synthesised polyaniline nanoparticles by a ‘rapid-mixing’ method
- Applied nanoparticles for nanostructuring macroscopic electrodes.
- Casting by Inkjet printing: most promising approach: ***high quality & amenable to manufacturing***
- Demonstrated applications for these modified electrodes, e.g., biosensing – catalytic reduction of H_2O_2 and chemical sensing of ammonium ions.

Acknowledgements

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