Nanomaterial & Nanostructuring Approaches for the Fabrication of Conducting Polymer-Based Biosensors

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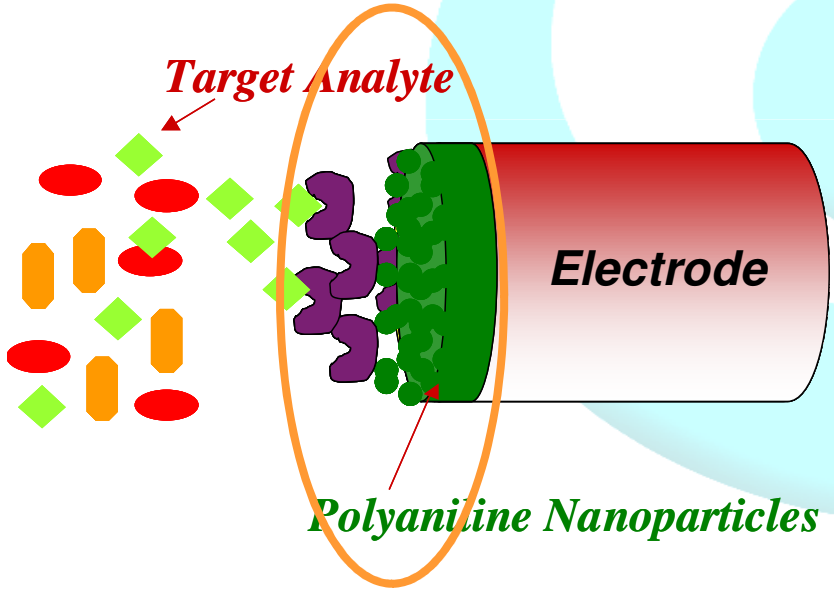
Introduction

- Emergence of nanotechnology opening new horizons for electrochemical bio- and chemo-sensing

- How can nanostructured conducting polymers contribute to this space?

- Explore transduction interface



Overview – Nanostructuring Approaches

- **Nanomaterials**

  Conducting Polymer Nanoparticles

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

  (ii) Casting – *Amenable to Mass Production*

- **Nanostructuring**

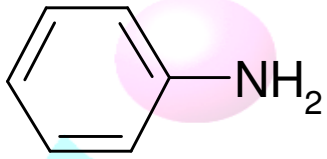
  Template synthesis in bulk polymer films

  (i) Highly sophisticated control of structure at the nano-level

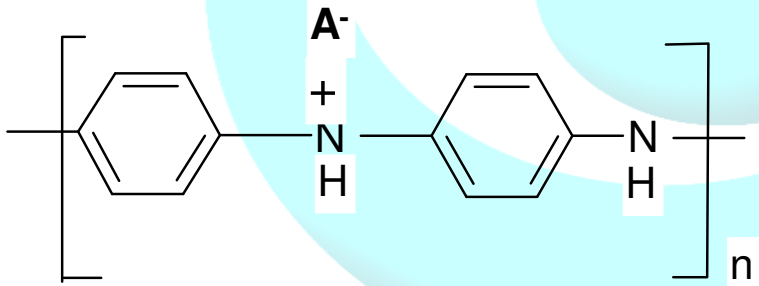
Electrode Modification by Conducting Polymer

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

- Applications:
  - Sensors
    - electrochemical
    - optical
  - Anti-corrosion protection of metals
  - Batteries
  - 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
Amenable to alternate deposition techniques
Higher Conductivity
Nanoscale Sensor Fabrication

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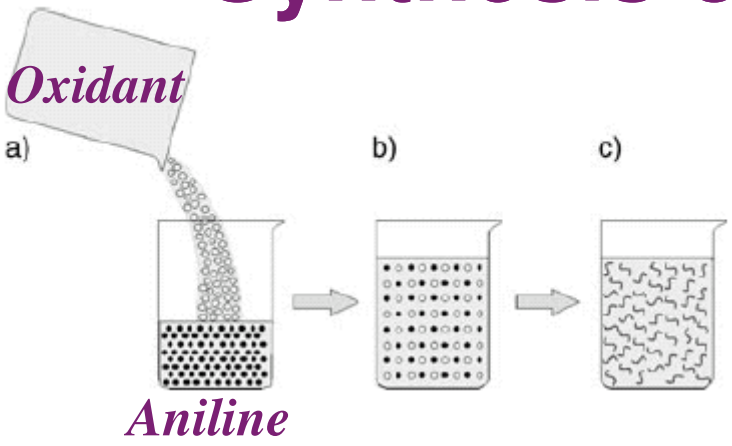
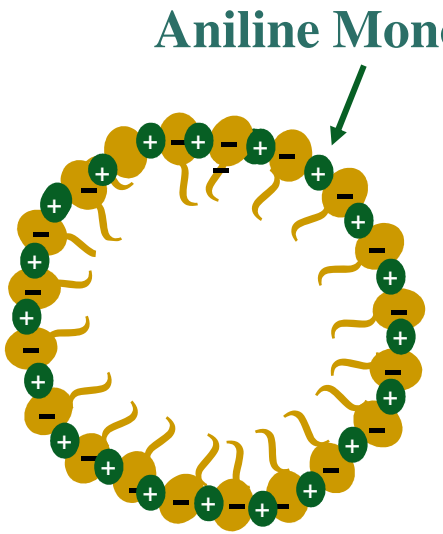
Synthesis of Nanoparticles

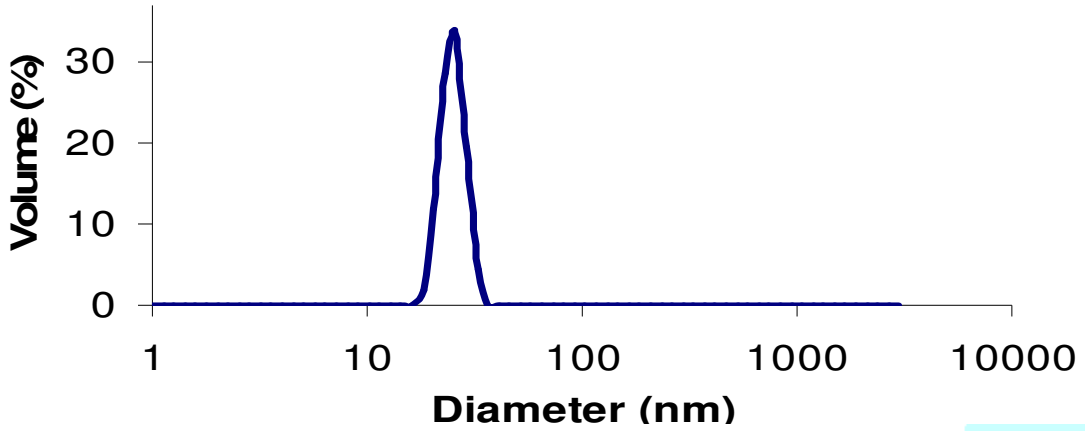




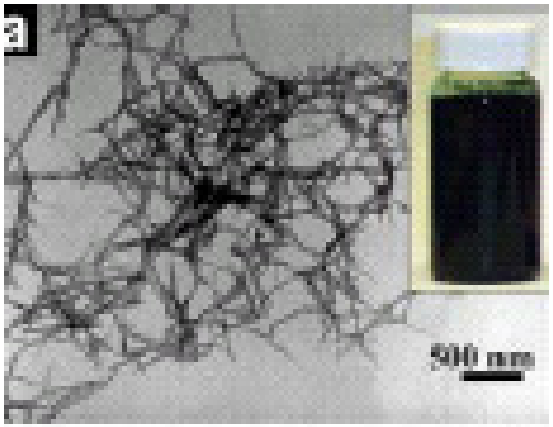
- **Rapid Mixing method***
- **Monomer to Oxidant ratio = 4:1**
- **DBSA added to serve as dopant & surfactant (provide micelle structure to stabilise particles)**
- **SDS present also acts as surfactant for stabilisation**

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

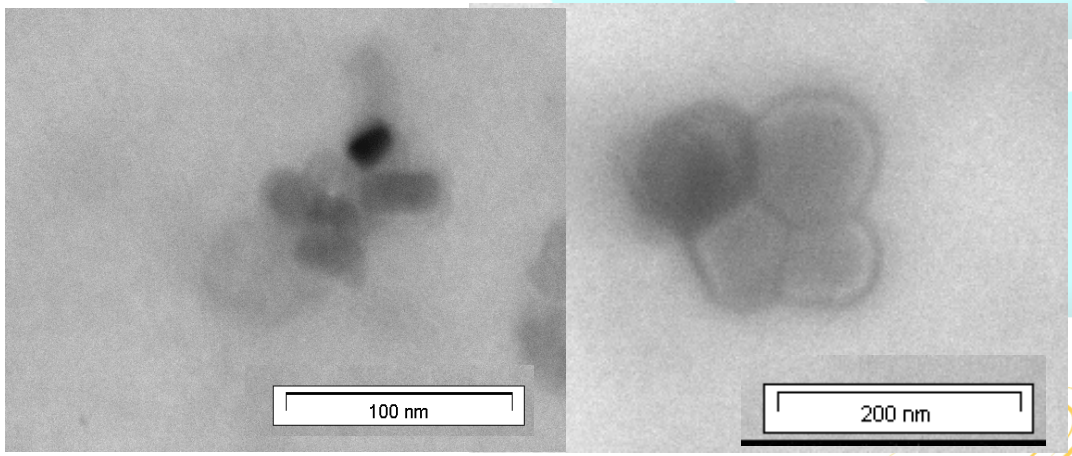
Polyaniline Nanoparticles



No Stabiliser Present



Stabiliser Present



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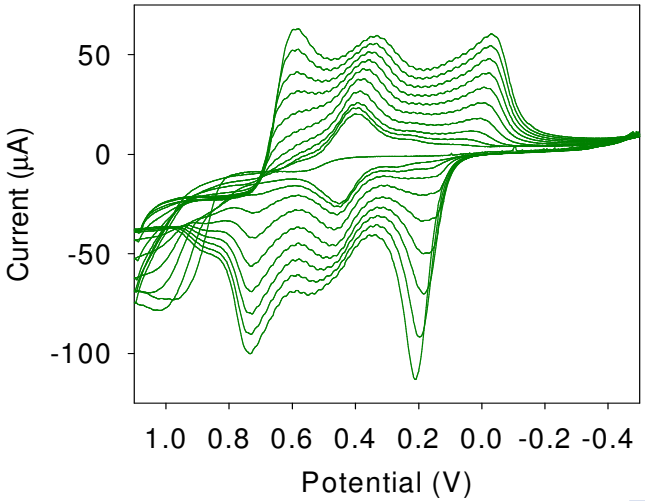
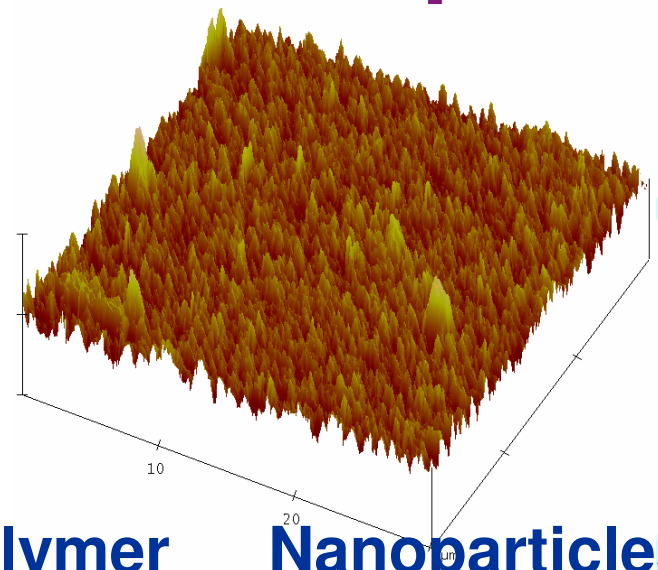
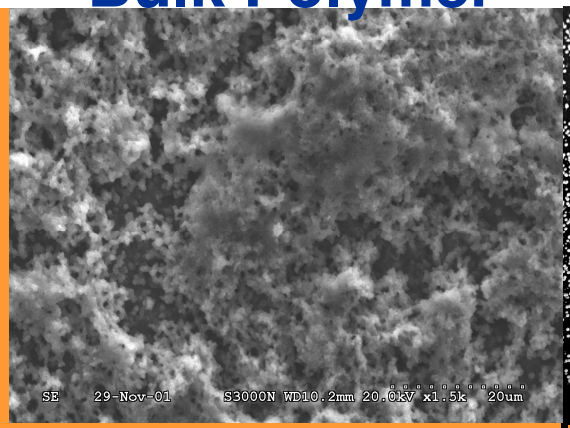
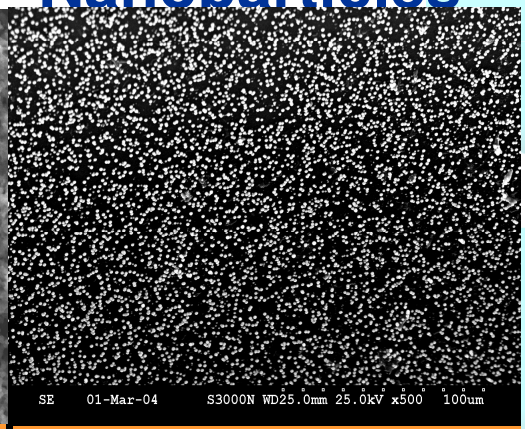
(i) Electrodeposition of Nanoparticles

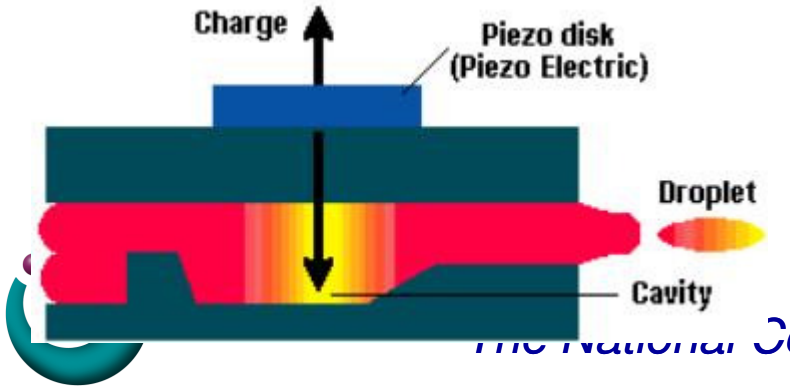


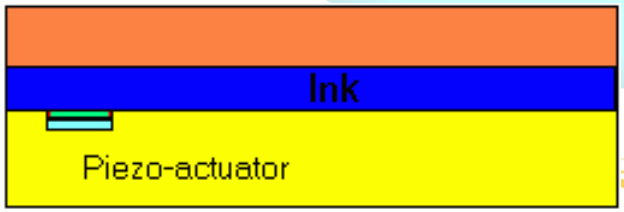


	Bulk Polymer	Nanoparticles
Morphology		
Sensing Characteristics		
Signal to background	17 ± 4	61 ± 13
Response time (sec)	9.5 ± 4.1	0.6 ± 0.1
[Optimal protein]	0.66 mg ml^{-1}	0.1 mg ml^{-1}

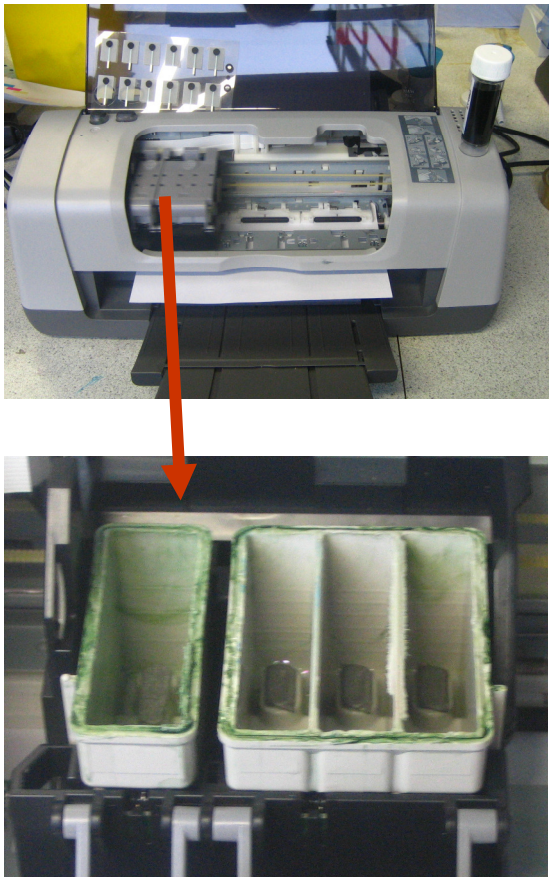
Inkjet Patterning of Nanoparticles

- **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 material**
- **Non-contact Printing (substrate and print head don't touch)**
- **Rapid. Quality of print easily monitored in real time**

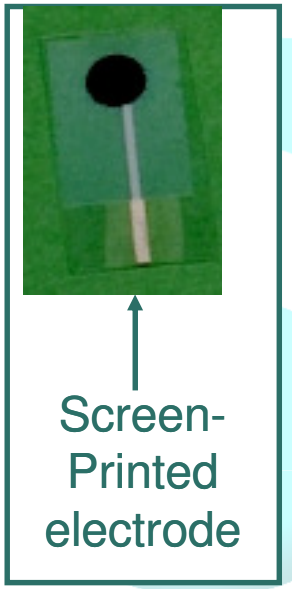




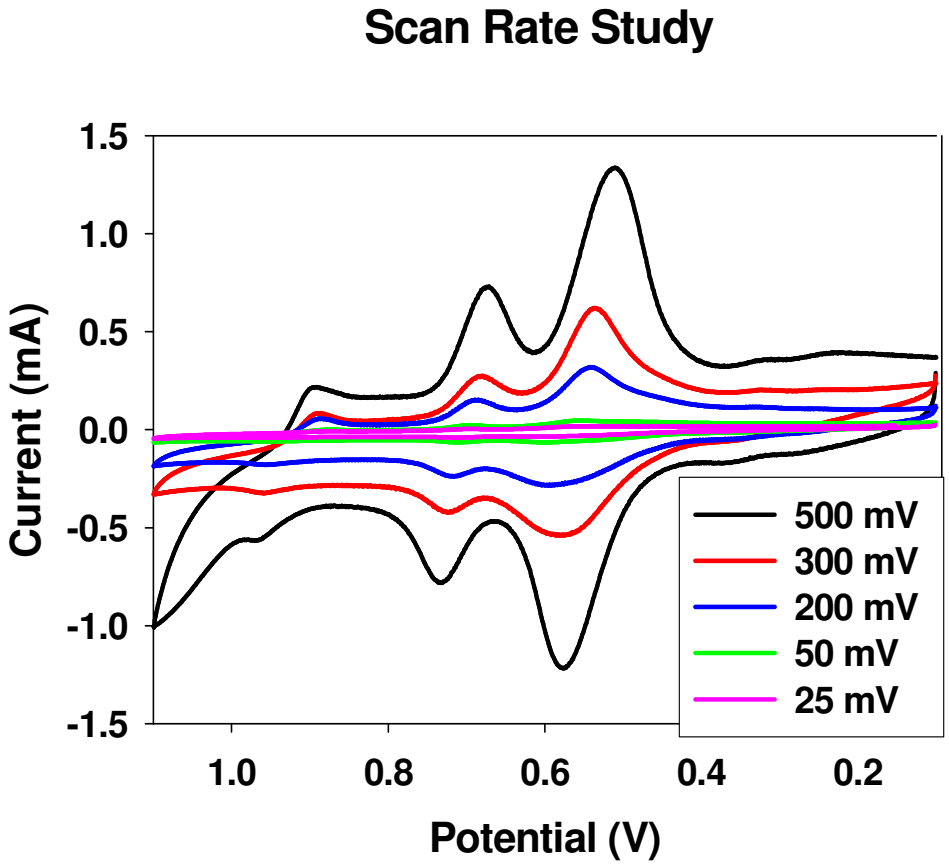
Instrumentation Strategy for Inkjet Printing

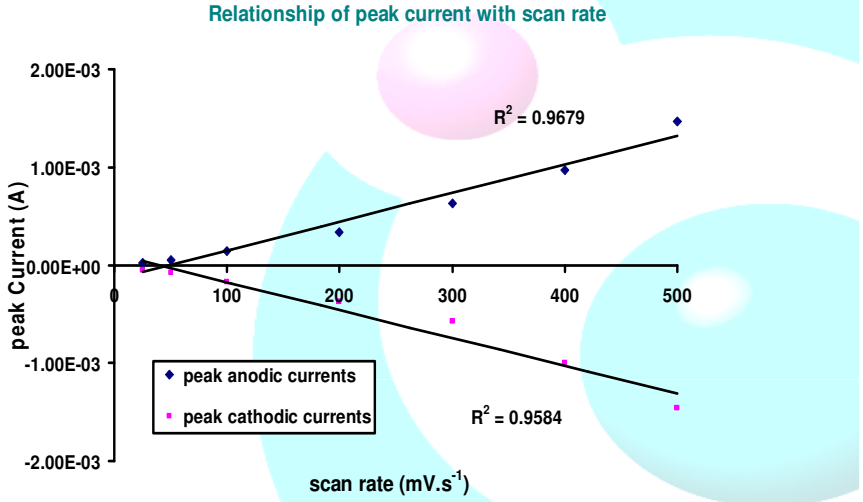


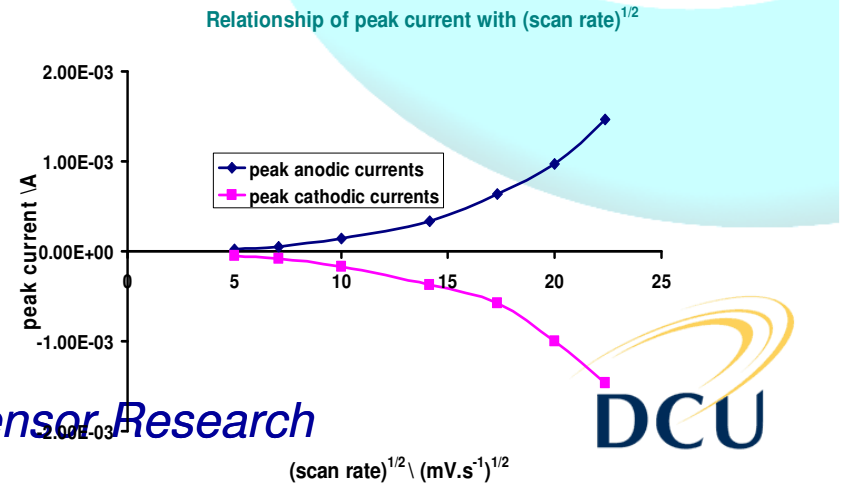
- Epson desktop printer (2880 x 720 drops per inch)
- Uses piezo technology
- Drop on demand
- Favoured over other more expensive single head devices due to the four available reservoirs.



Electrochemistry of Inkjet Printed Polyaniline







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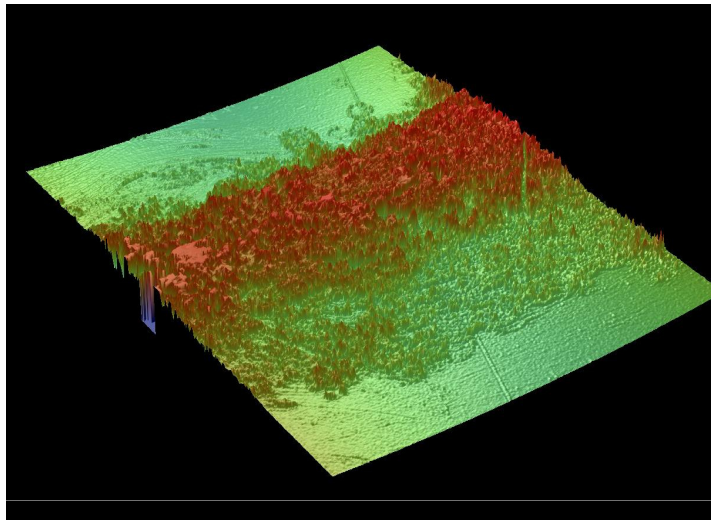
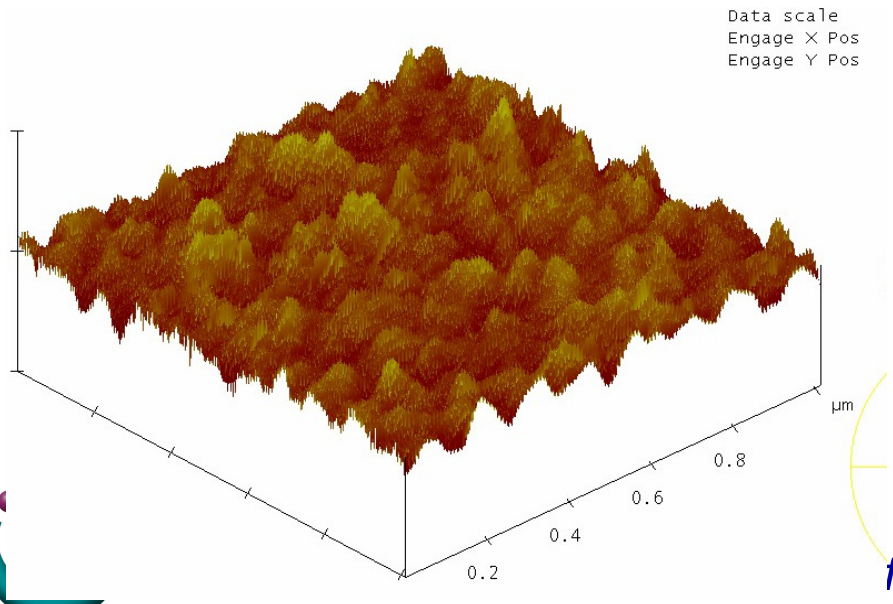
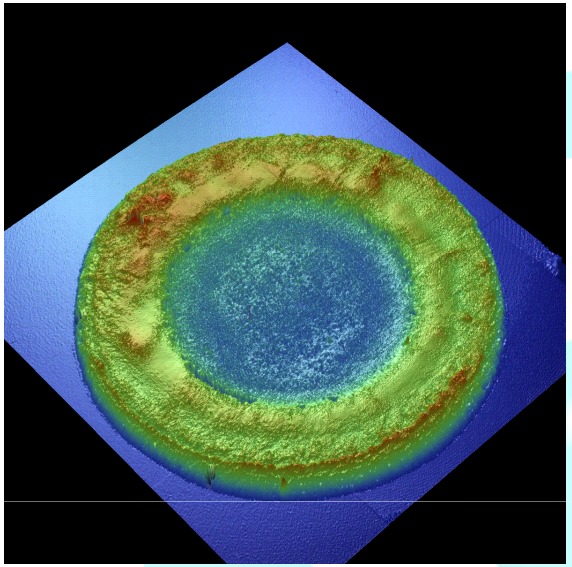
Morphology

Inkjet printed





Drop-coated



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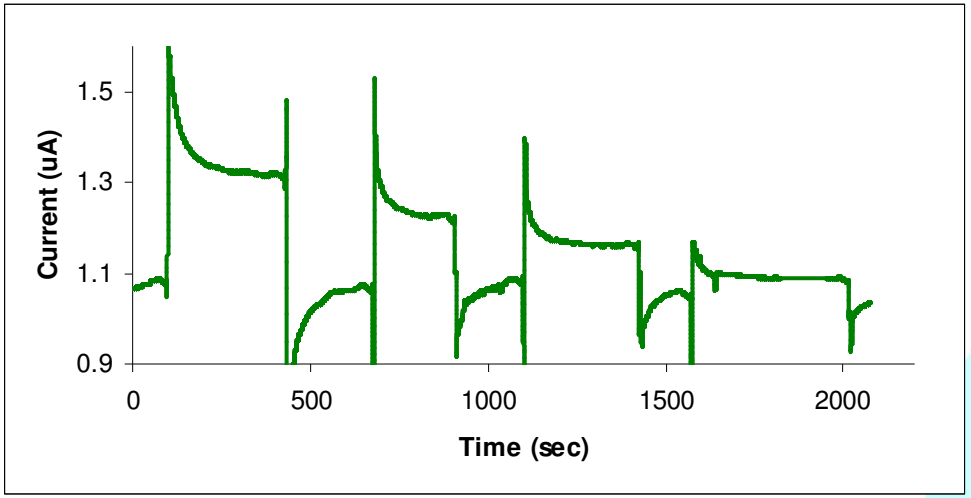
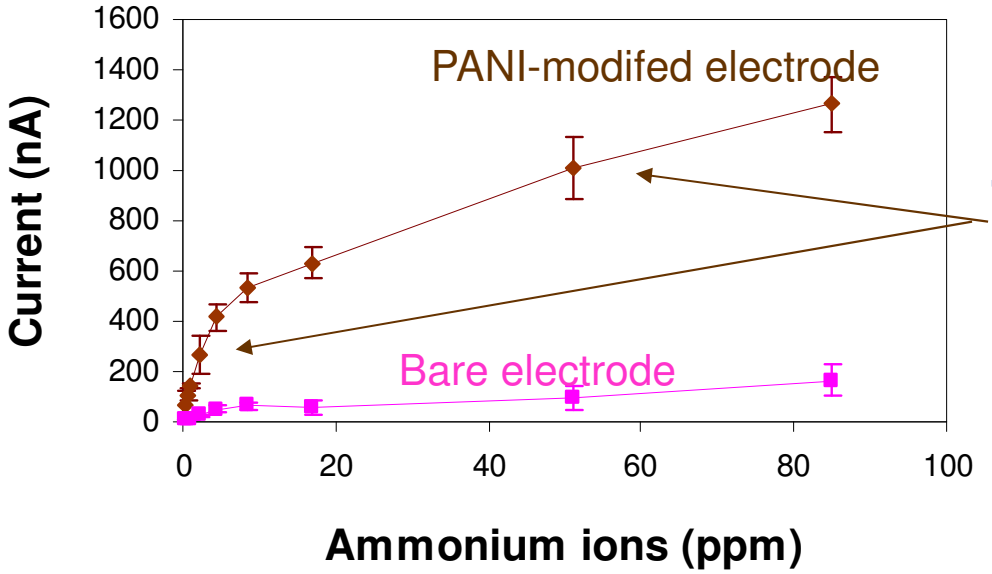
Chemosensing - Ammonia



NH_4^+



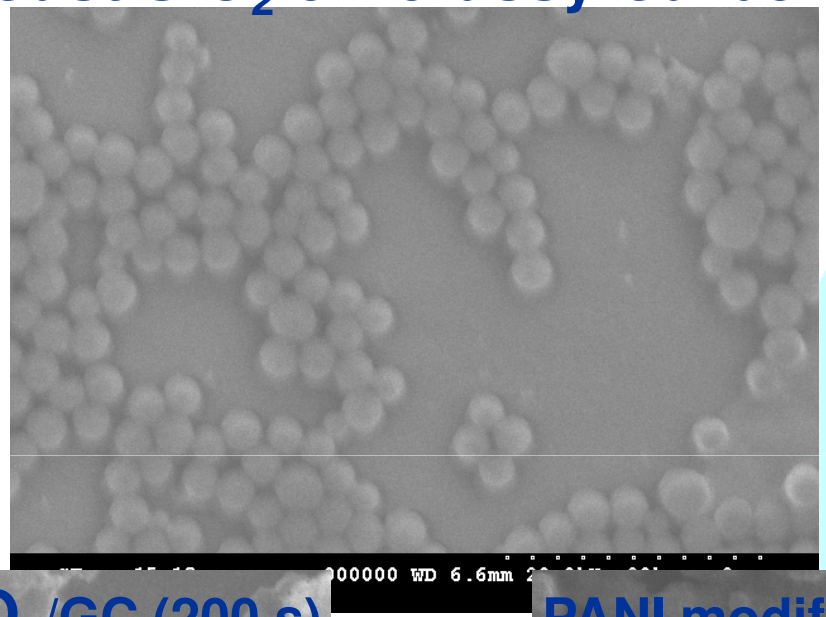
Two available linear ranges – 0 – 5 ppm & 10 – 90 ppm

Nanostructuring of Bulk Polymer

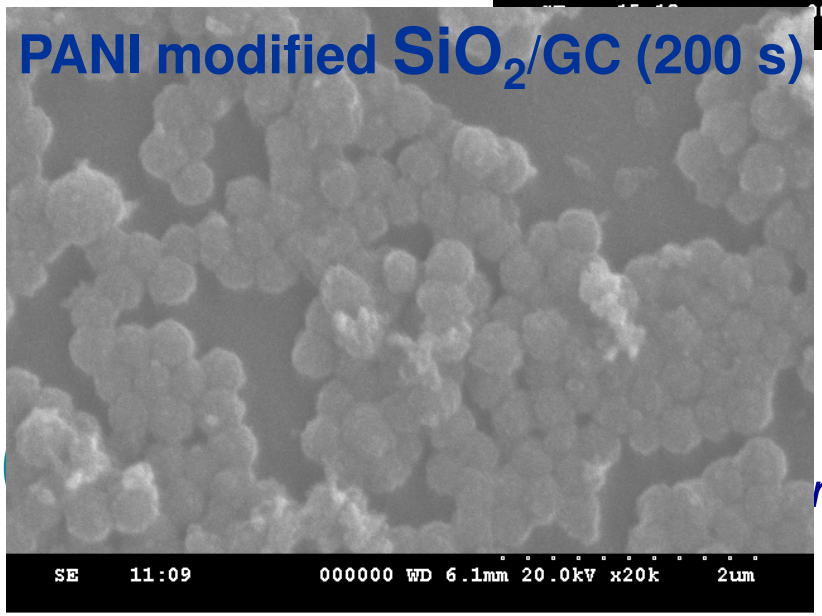
- Micro and nanoparticulate templates
- Silica and latex beads used as scaffold
- Bulk polymer electrochemically grown around scaffold
- Scaffold removed to leave nanostructured bulk polymer films

Silica Scaffold

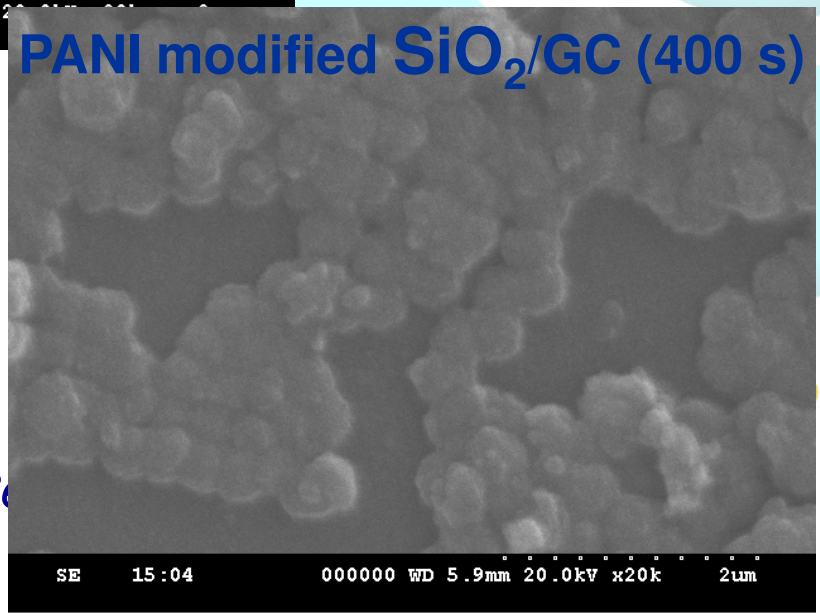
Cast SiO_2 on Glassy Carbon



PANI modified SiO_2/GC (200 s)



PANI modified SiO_2/GC (400 s)



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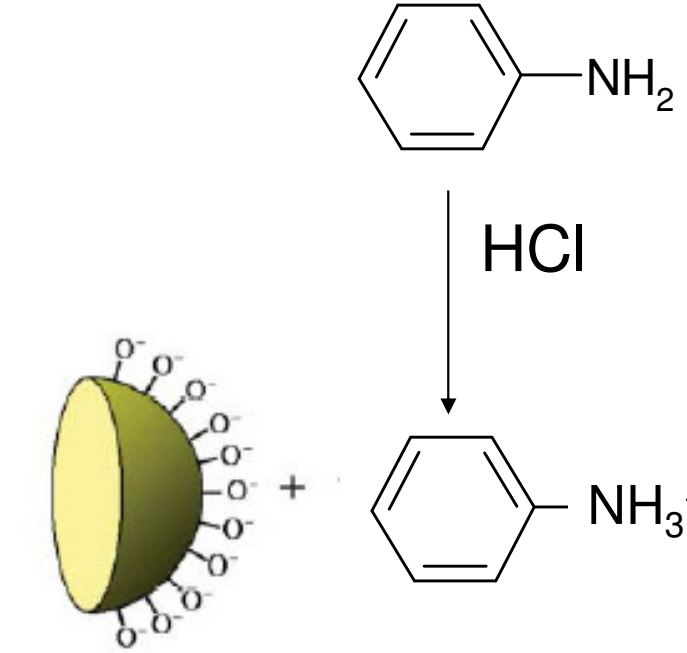
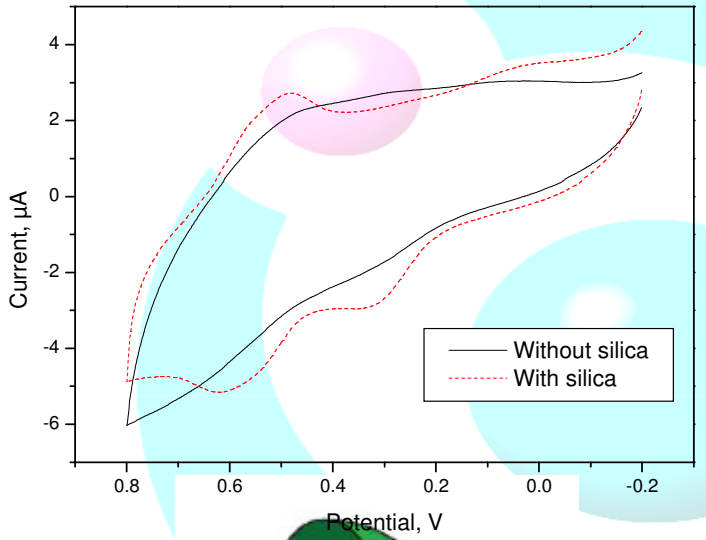
In-Situ Electropolymerised Silica/PANI Core-Shell Nanoparticles

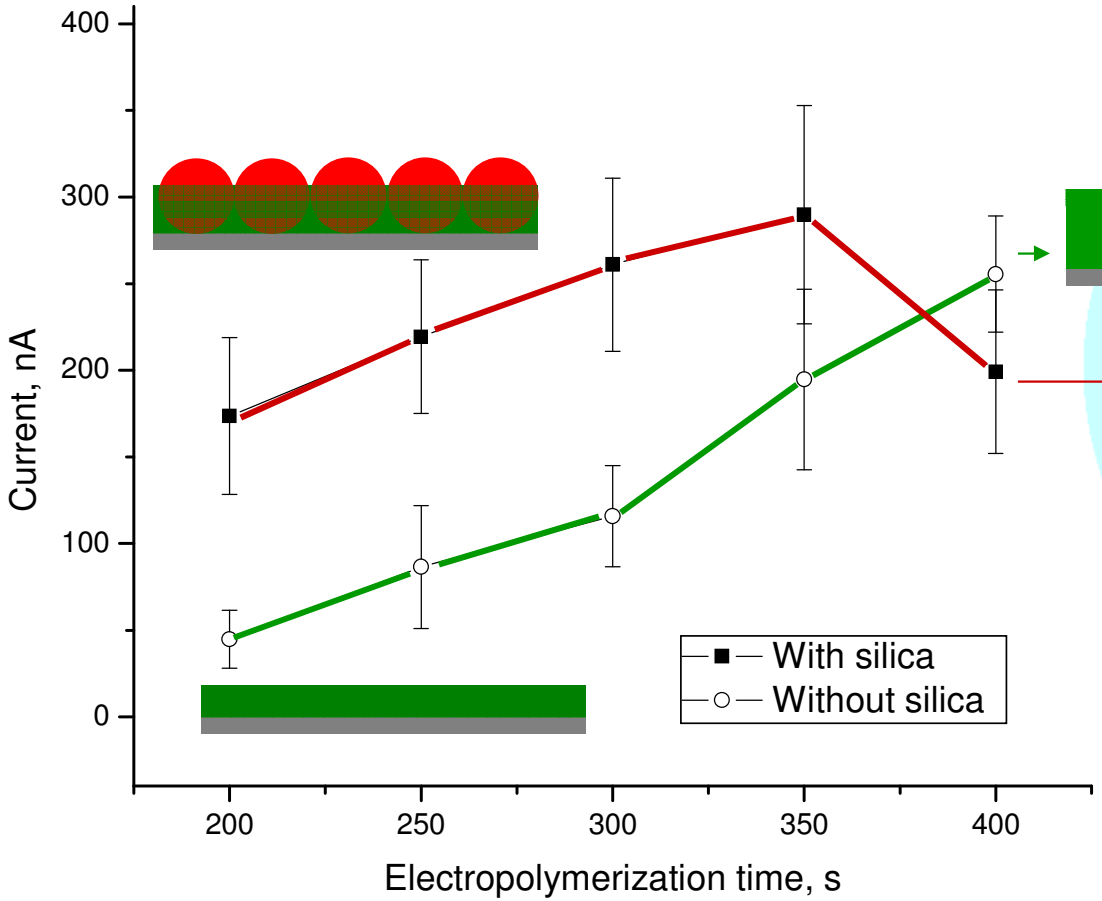


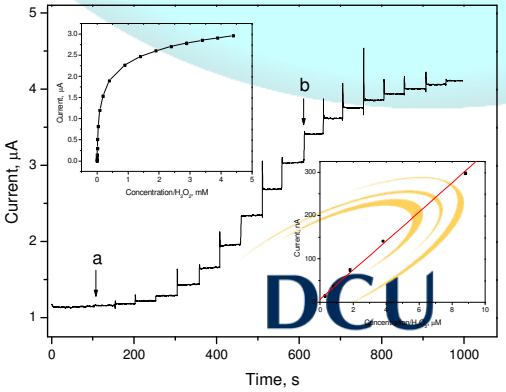
Electrochemical Oxidation



Silica-PANI core-shell nanoparticle

Silica/PANI Core-Shell Nanoparticles - Biosensing





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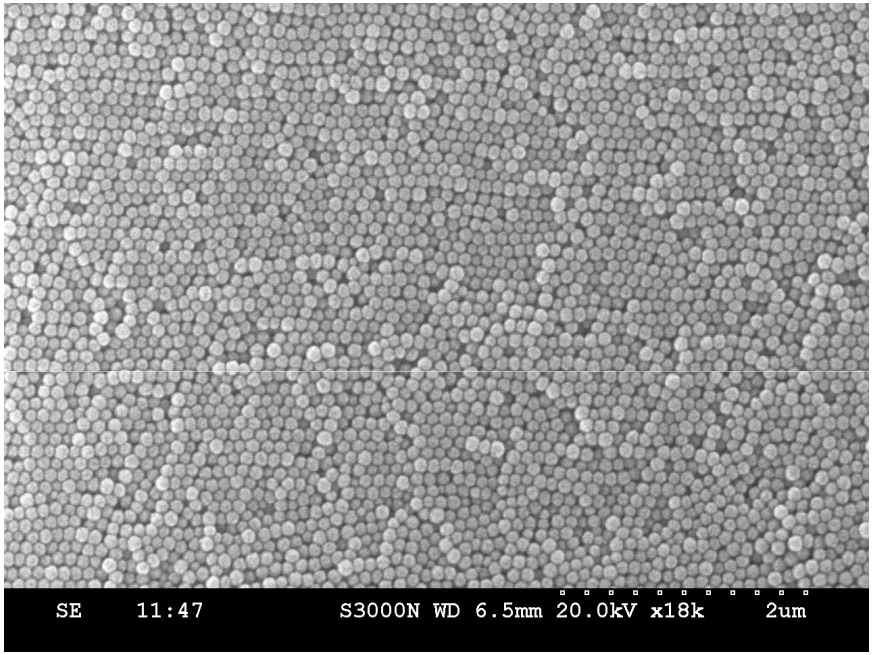
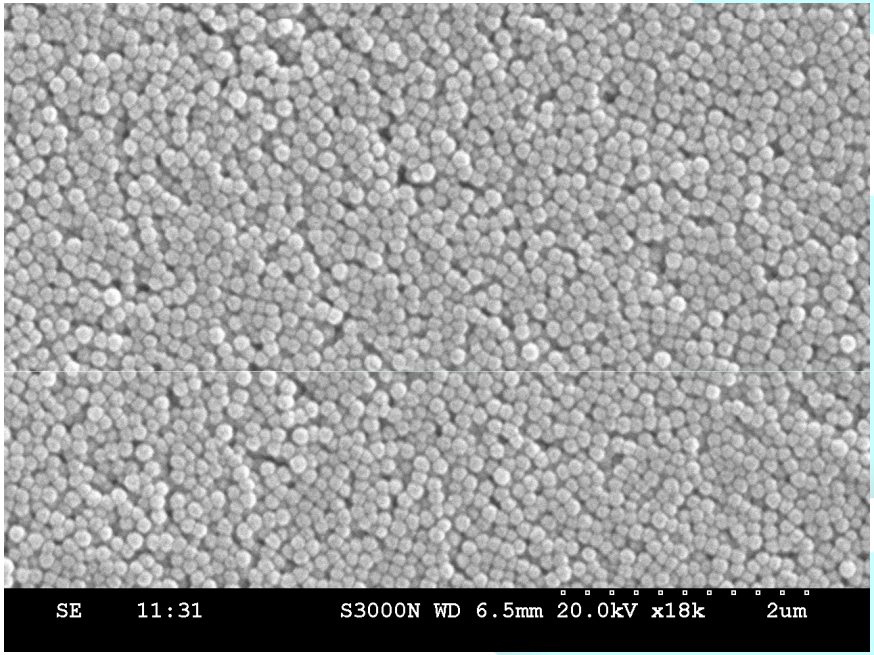
Latex Template

Multi-layered latex on GC



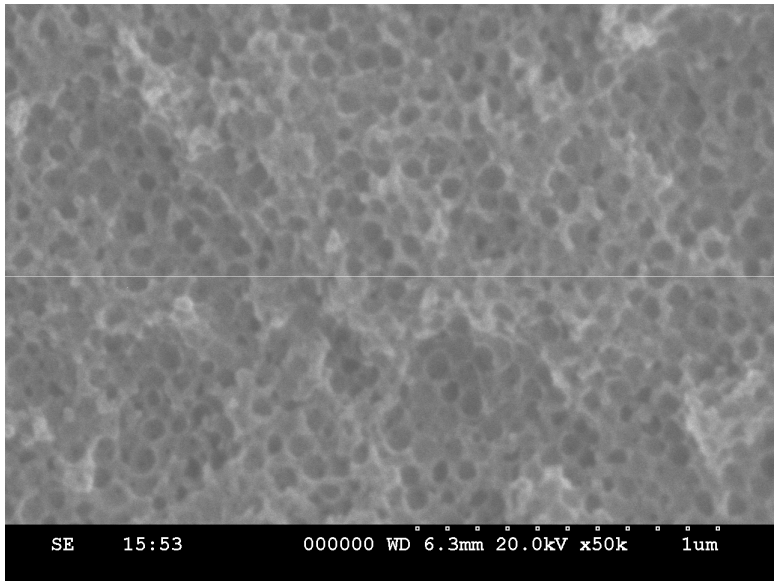
PANI grown on the Latex/GC electrode

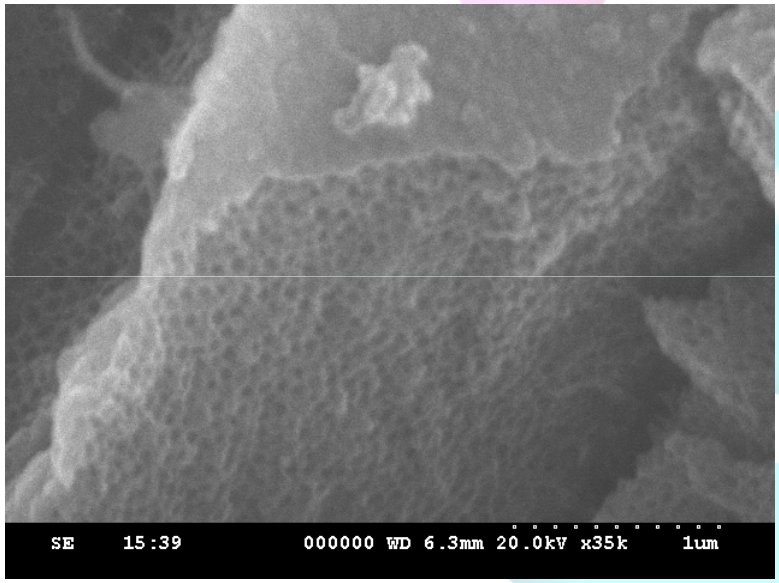


Removal of Latex

Dopant: Polyvinyl Sulphonate (PVS)

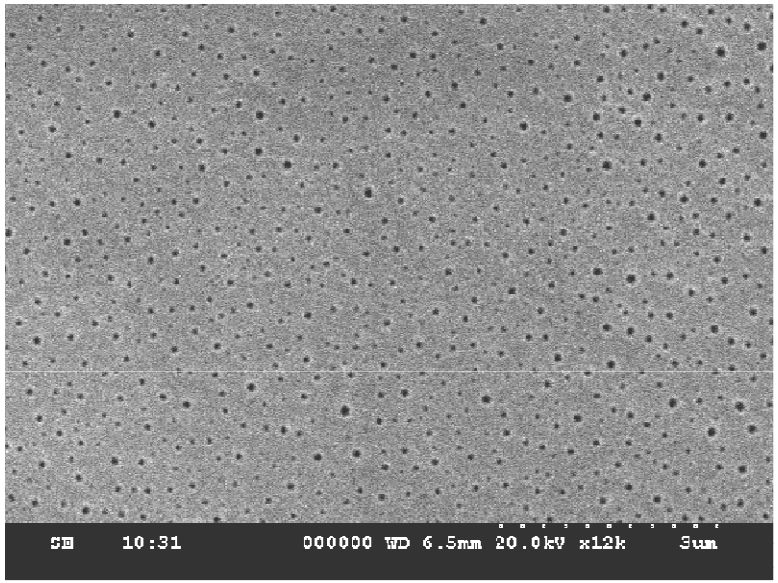
Honeycomb Effect

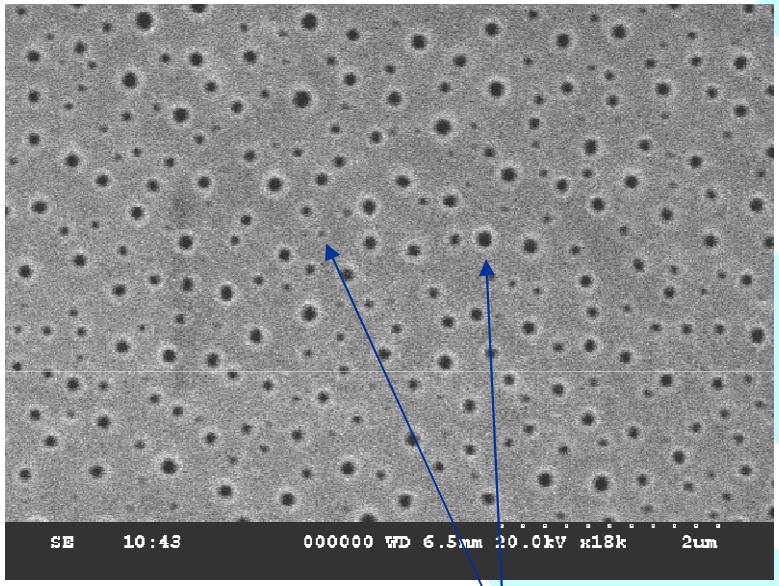




Removal of Latex

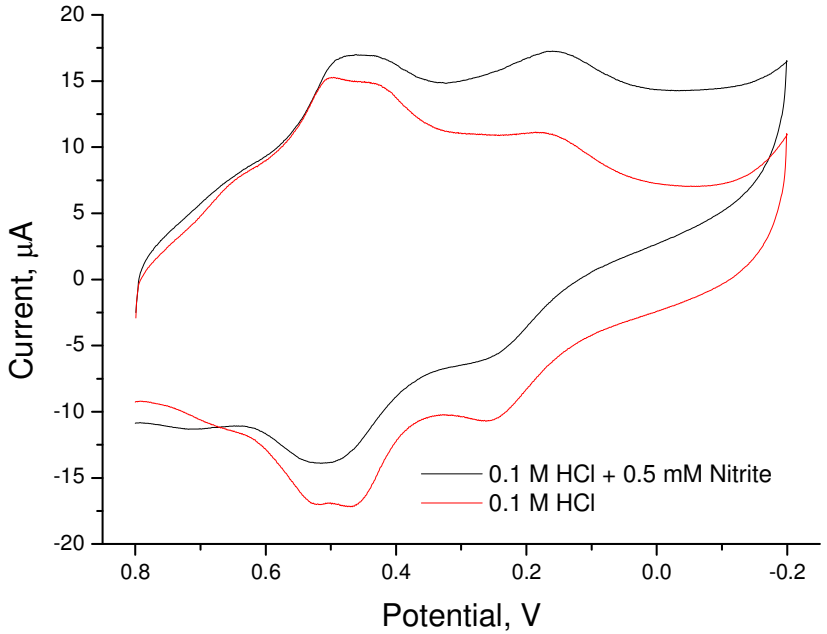
Dopant: Polystyrene Sulphonate (PSS)

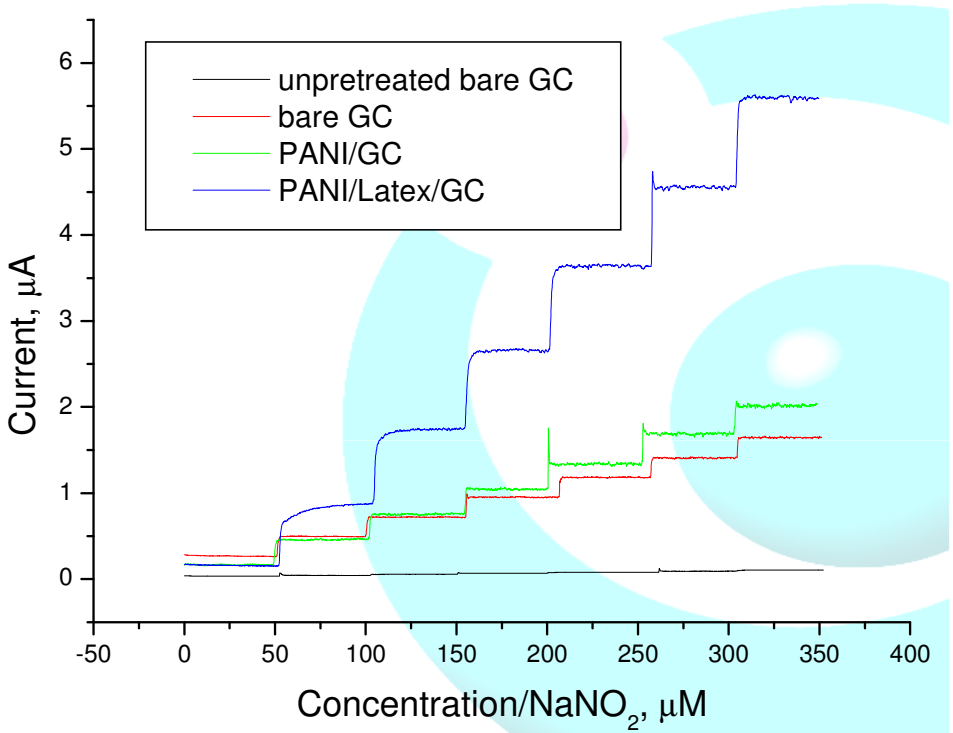




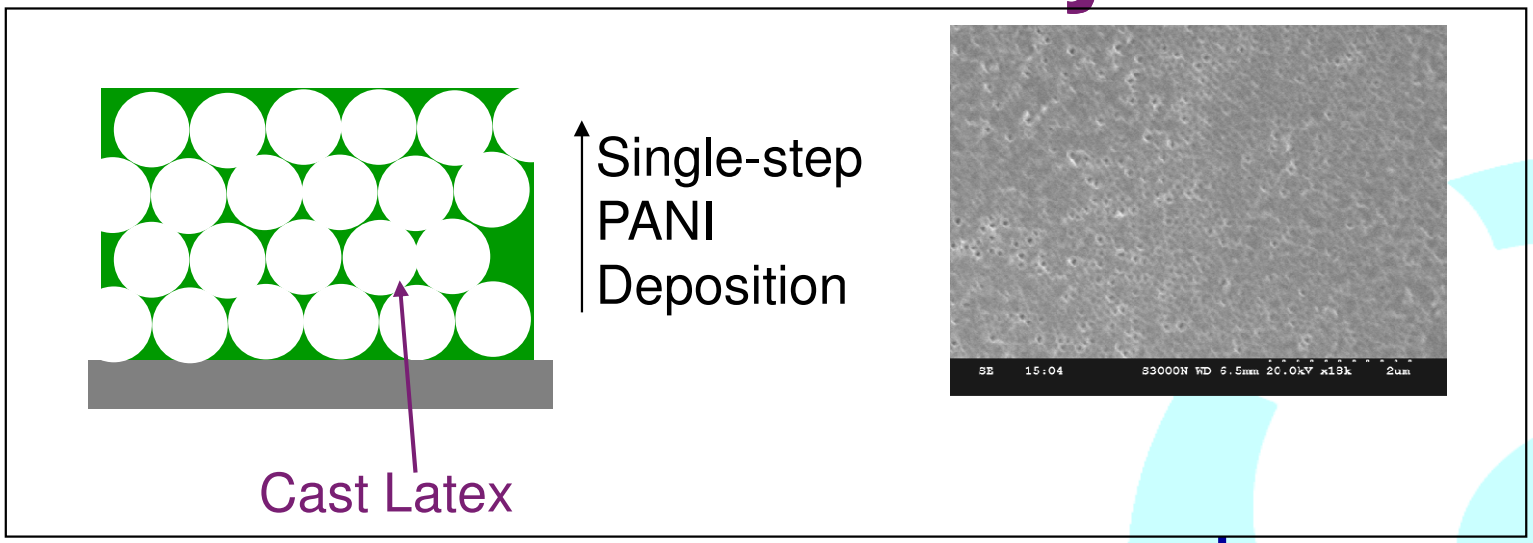
Varying Pore Size Diameters

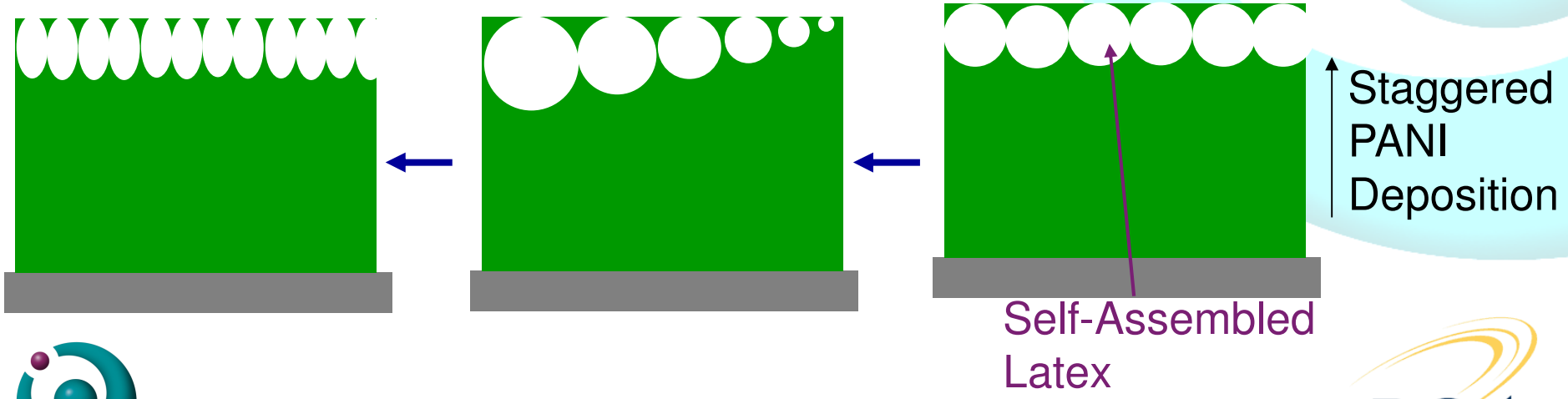
Chemosensing - Nitrite





The Wonderful Windy Road…..





And To Conclude…..

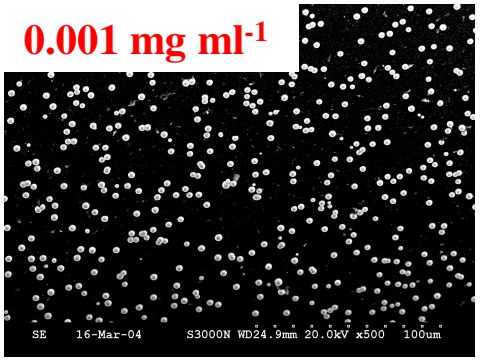
- Two defined approaches to nanostructuring electrode platforms with polyaniline
  - Nanomaterials: Inkjet printing has particular potential in terms of amenability to sensor manufacturing processes
  - Nanostructuring of bulk material: Learning how to nanostructure polyaniline interfaces

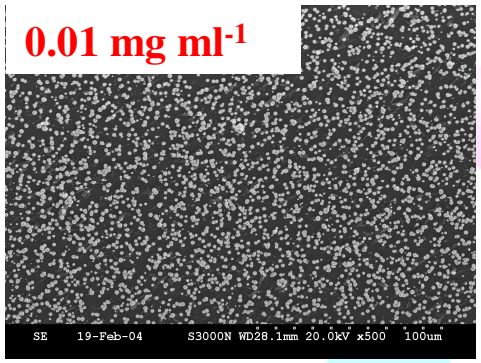
- Exploitations of these approaches will be in the fields of chemical sensing, biosensing and immunosensing

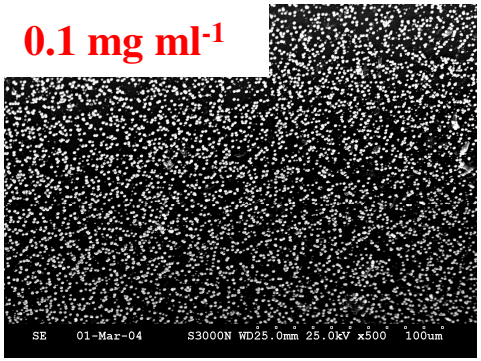
Acknowledgements

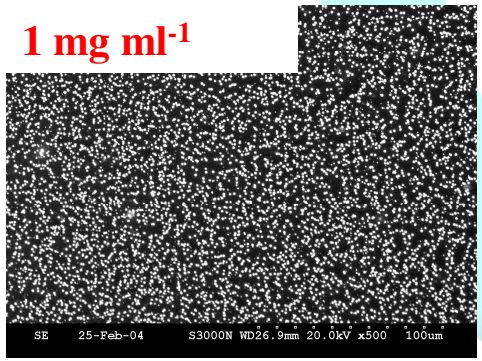
- Prof. Malcolm Smyth
- Dr. Tony Killard
- Dr. Xiliang Luo
- Dr. Máire O'Connor, Eimer O'Malley & all the Sensors & Separations group
- Prof. Gordon Wallace, Dr. Simon Moulton and Dr. Orawan Ngamna (UoW)
- Henry Barry (NCSR)
- € € € € € € € € from Enterprise Ireland under the technological development plan TD/03/107

SEM Imaging of Protein on Nanoparticulate Films

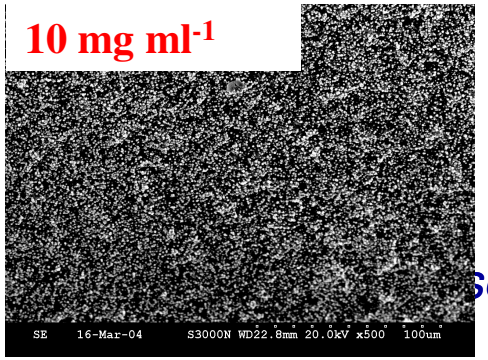








* Imaging done using silver-enhanced gold labelled protein (Mo anti-HCGβ antibody)



20 µm

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

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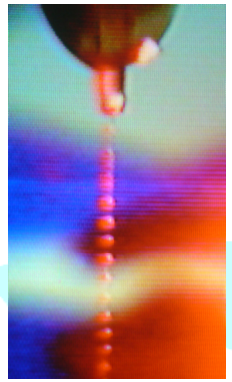
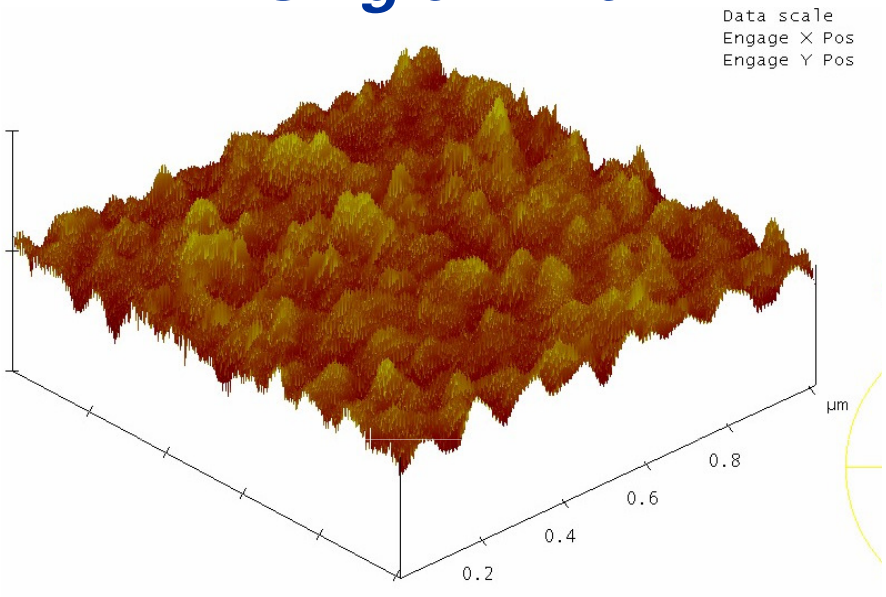
(ii) Inkjet Patterning of Nanoparticles



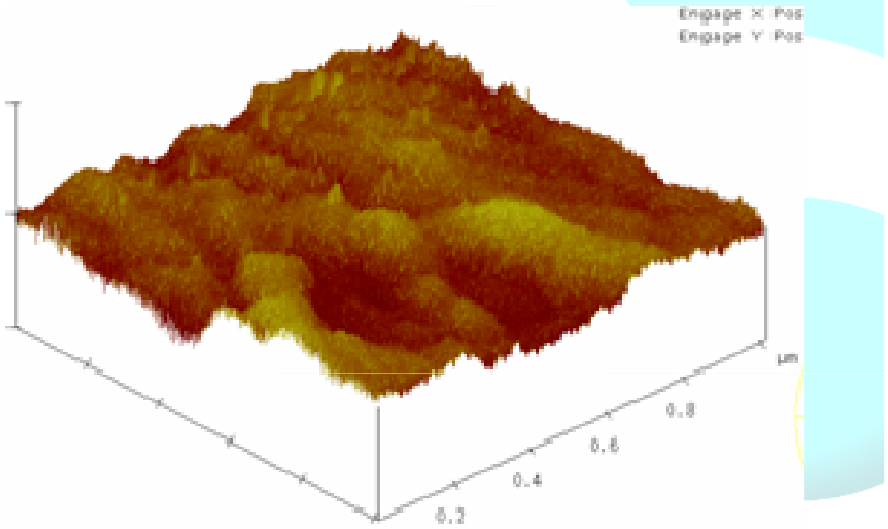
- Method for casting ultra-thin films, (deposits microdroplets of 2-12 pL)
- High precision, resolution of ~ 25 µm
- Amenable to simultaneous deposition of more than one 'ink'
- Non-contact Printing (substrate and print head don't touch)
- Rapid method, quality of print easily monitored in real time

Microscopy

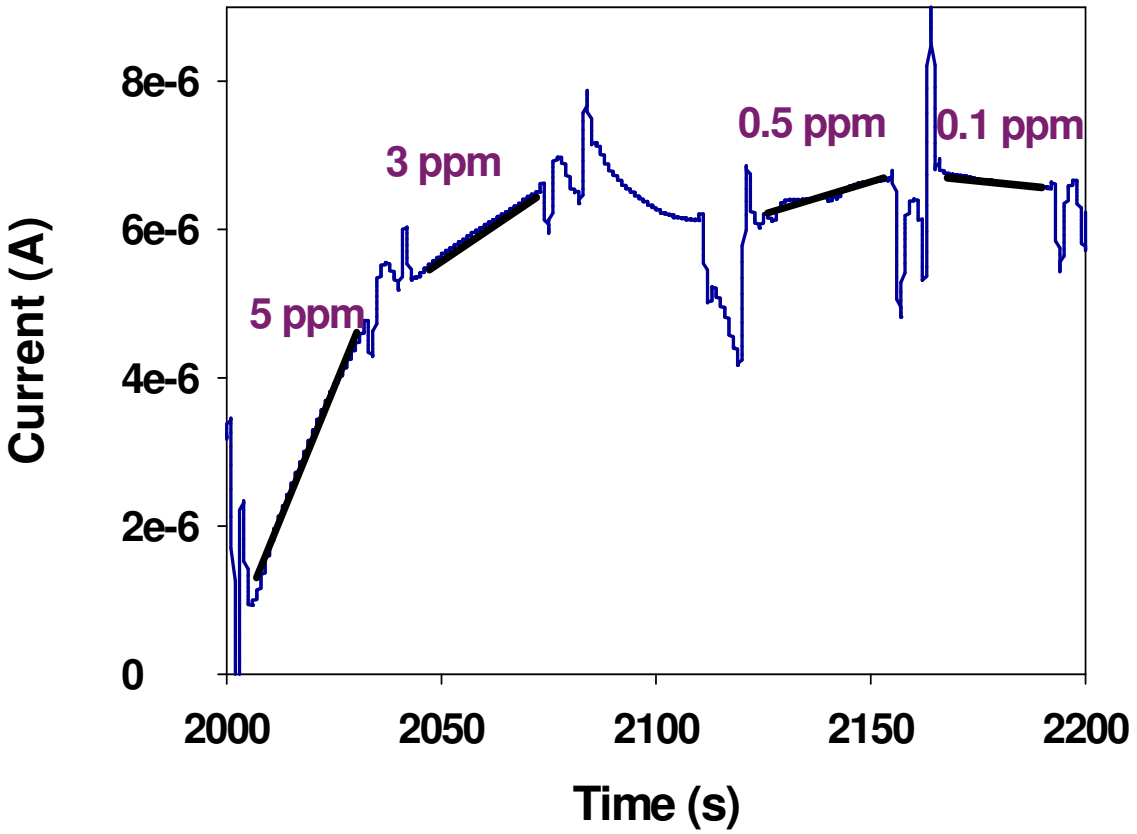
Single Print



Multiple Prints



Biosensor Application



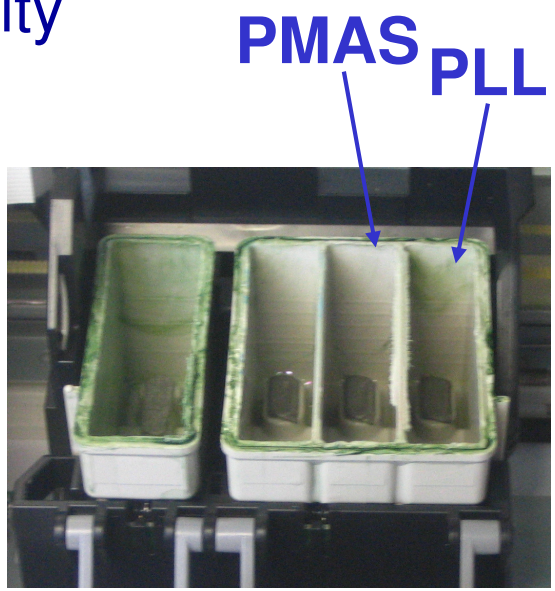
Real-Time Multi-Analysis

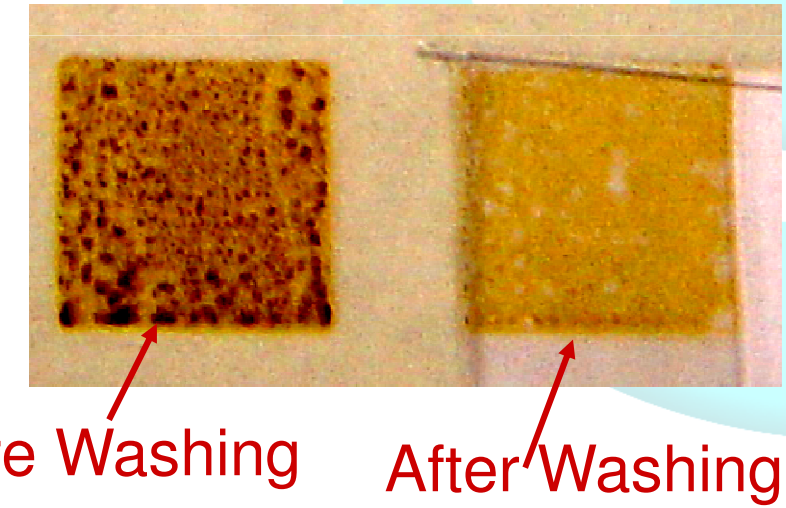
Flow Cell Setup

- 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

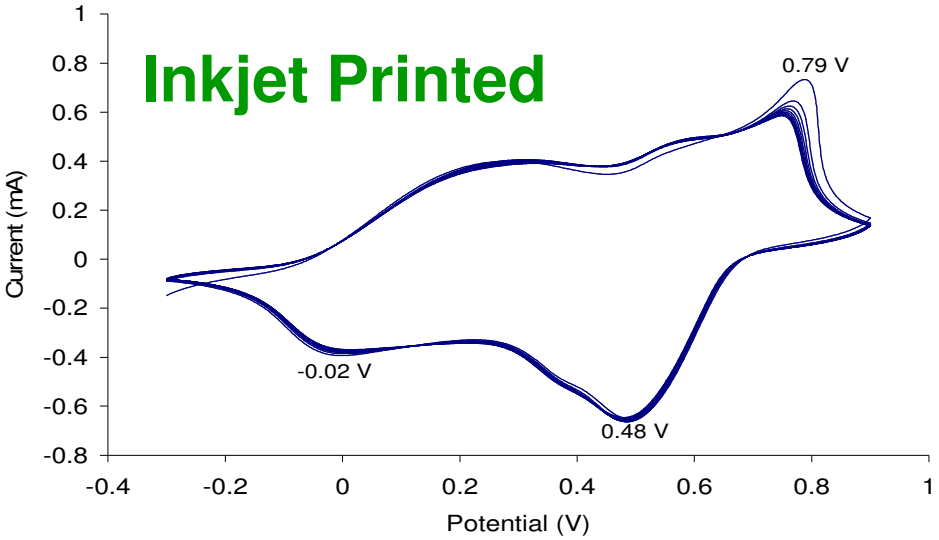
Water-Soluble Polyaniline

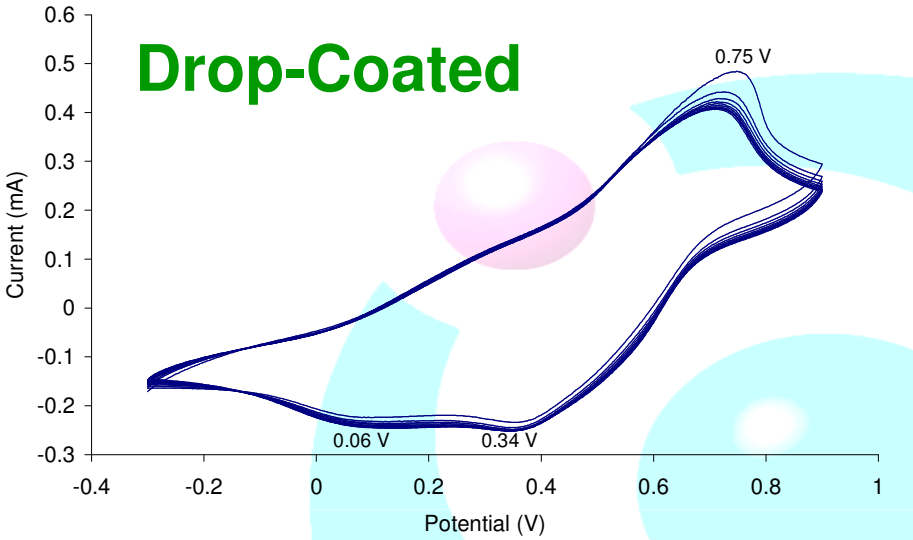
- Poly(2-methoxyaniline-5-sulphonic acid) (*PMAS)* – Sulphonated polyaniline
- PMAS must complex with a polycation (poly-L-lyseine (PLL)) to render it insoluble
- Need to co-deposit, i.e., print simultaneously – Inkjet has that facility





Water-Soluble Polyaniline





- Demonstrates unique advantages of using inkjet printing

- Inkjet printed films show improved electrochemistry compared to the evaporative cast films, indicating more efficient electron transfer process