Inkjet Printing as a Tool for the Fabrication of Conducting Polymer-Based Sensors & Biosensors

Dr. Aoife Morrin

National Centre for Sensor Research
School of Chemical Sciences
Dublin City University
Ireland

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Overview

1. Introduction
2. Inkjet printing of conducting polymer
3. High specification, flexible, inkjet printed gas sensor platform
4. Biosensor fabrication & application

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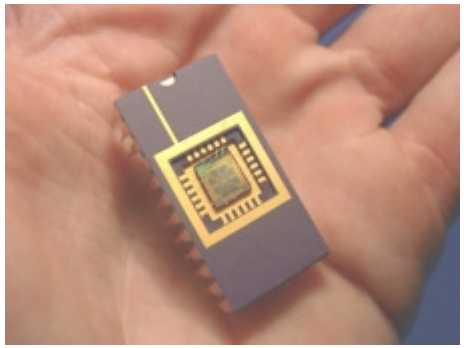
Introduction

- **Advances in materials and engineering are paving the way for new and more capable sensors**

- **Most recent advances are not originating from new transduction materials, but more from materials and innovations that *reduce overall cost* and *improve quality***

- ***'Enabling technologies'* are principle drivers in sensor fabrication development**



Printed Sensors

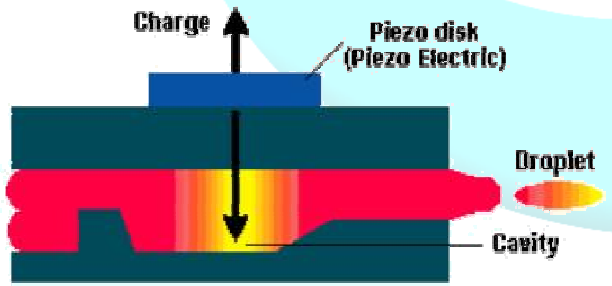
- Mass market application areas

- High demand for low-cost, mass-producible sensor products in specific key markets such as point-of-care medical diagnostics and smart packaging, remote environmental sensing, etc….

- Early 1980s saw the enormous commercial success of the screen-printed glucose biosensor

- 9 billion glucose tests performed annually

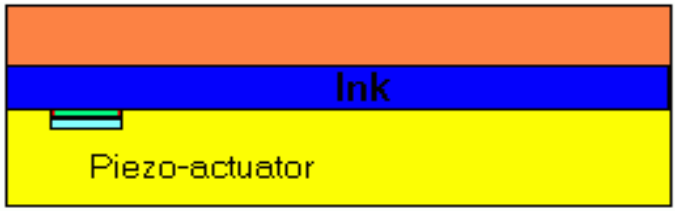
- Inkjet printing – set to surpass screen-printing???



- Today we have more sophisticated materials available…

Enabling Technology: Inkjet Printing….

- Rapid, reproducible, cheap way to manufacture sensors
- Easily scaled up, suited to large and small production volumes
- Quality control in real time
- High precision, claiming a resolution of ~ 25 µm
- Thin film deposition (nm). Thinner films can yield faster response times
- Amenable to simultaneous deposition of more than one material – multi-component layers, microarrays
- Sensor optimisation through combinatorial printing
- Non-contact printing (substrate and print head don't touch), suitable for fragile substrate e.g., membranes
- Aqueous solution are printable – important for biological species
- Low wastage, important for precious materials
- Flexible design process
- ……



…..Combined With Processable, High Quality Sensing Materials….

Interesting Functional Materials for Sensing Include:

Electroactive/Optically active materials
Conducting Polymers
Metallic Inks
Biomolecules for Biosensing
Membranes

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Overview

1. Introduction
2. **Inkjet printing of polyaniline**
3. High specification, flexible, inkjet printed gas sensor platform
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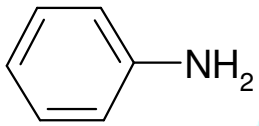
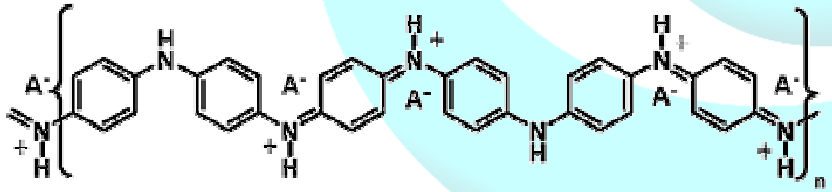
Sensor Platforms Based on Polyaniline

- Suitable for ***chemical sensing*** of acids and bases through its excellent doping/dedoping capabilites

- Desirable material for ***biosensing*** because of its good redox properties and hence can act as a diffusionless mediator for electron transfer between enzyme centres and the electrode transducer



Aniline Monomer



Doped Polyaniline (conductive state)

PANI-based Sensor Research

- Developing various electrochemical sensor/biosensor platforms using polyaniline-based polymers

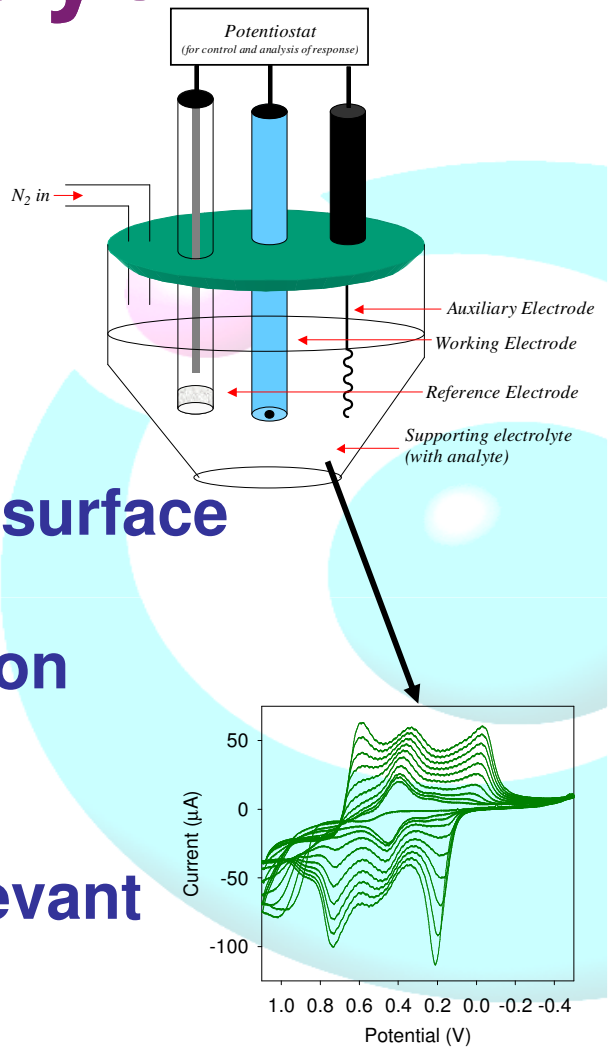
- Examining various sensor fabrication approaches such as
  - electrochemical deposition
  - nano-templating
  - **printing approaches**

- Printing methods permit processability, low cost and disposability

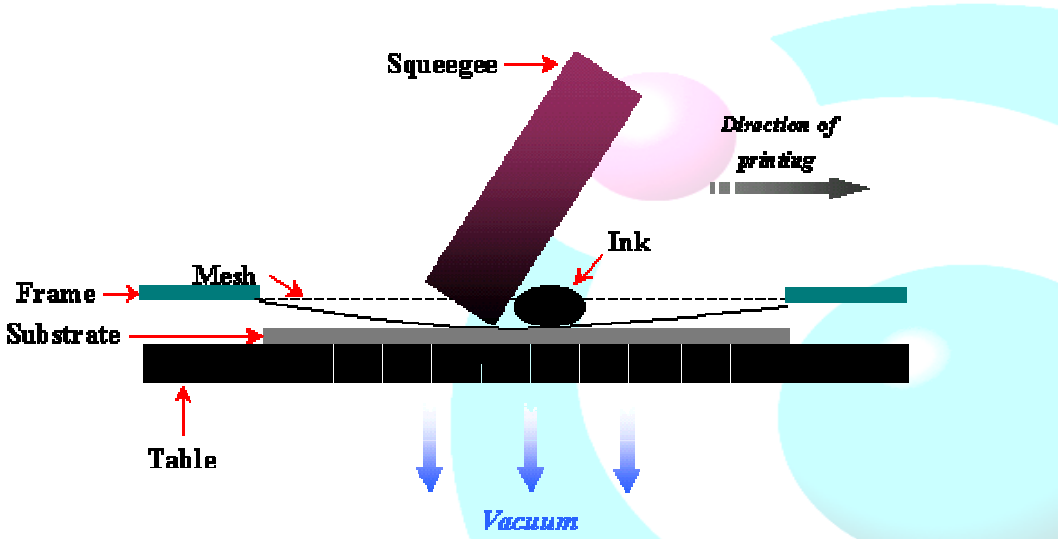
- Aiming to demonstrate that inkjet printing, combined with the right materials is a feasible, valid approach to sensor fabrication

Back In The Old Days....

- Glassy Carbon Electrode Platform
- Traditional 3-electrode cell setup to electropolymerise PANI films to electrode surface
- Works really well, but laborious fabrication procedure
- How to translate into a commercially relevant product??



Screen-Printing for Electrode Fabrication



- Low start up and manufacturing cost
- Mass production
- Disposability
- Platform for glucose biosensor industry

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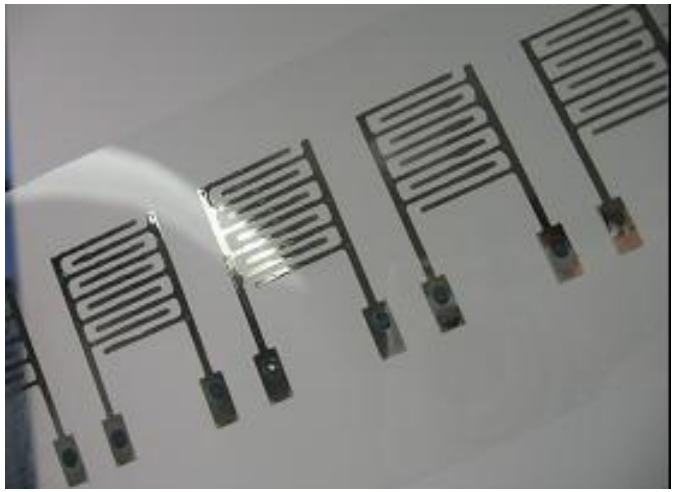
Inkjet Printing of Silver for Electrode Fabrication

Silver Inter-Digitated Array (IDA)



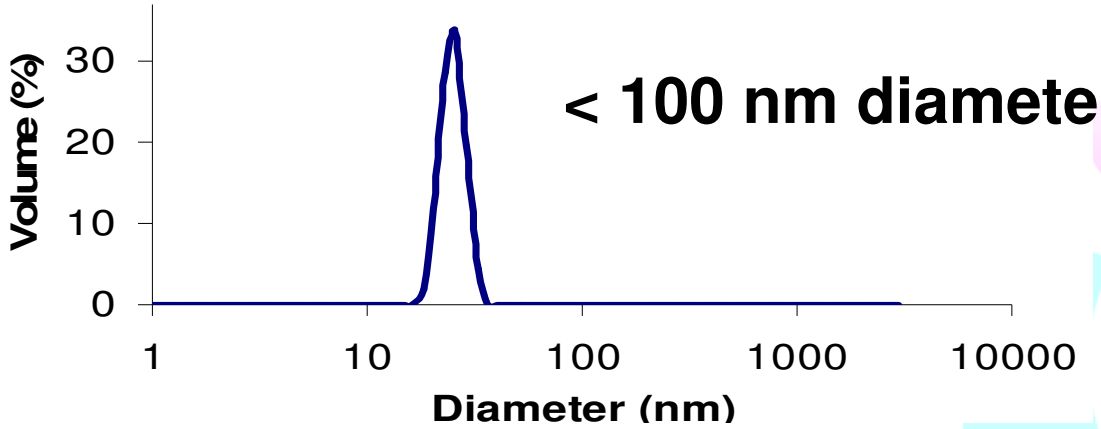
Single Electrode

- Commercial Ag product
- ~ 1 Ω cm^{-1} (1 layer)
- Challenge will be to print inert carbon electrode layers comparable to screen-printed carbon
- Can print gold or platinum as alternatives

Modifcation of Electrode:
Processable PANI

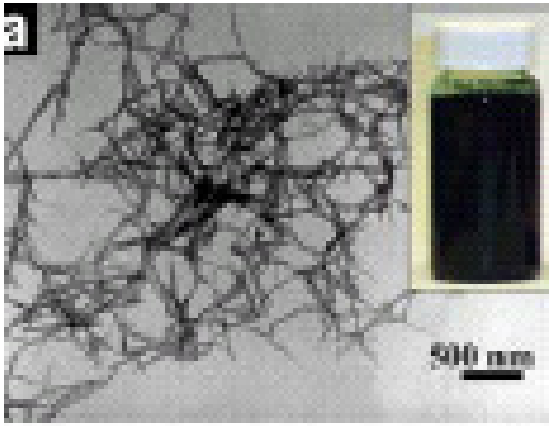
- New, processible materials
- Water-soluble, or stable nanodispersions
- High processibility
- Aqueous-based
- Good redox activity and conductivity

PANI Nanodispersion Characterisation

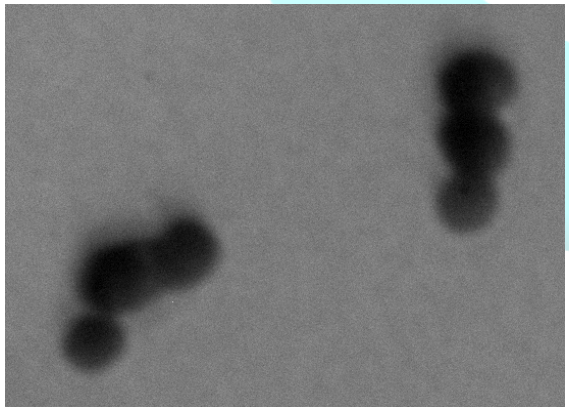


< 100 nm diameter

No Stabiliser Present*



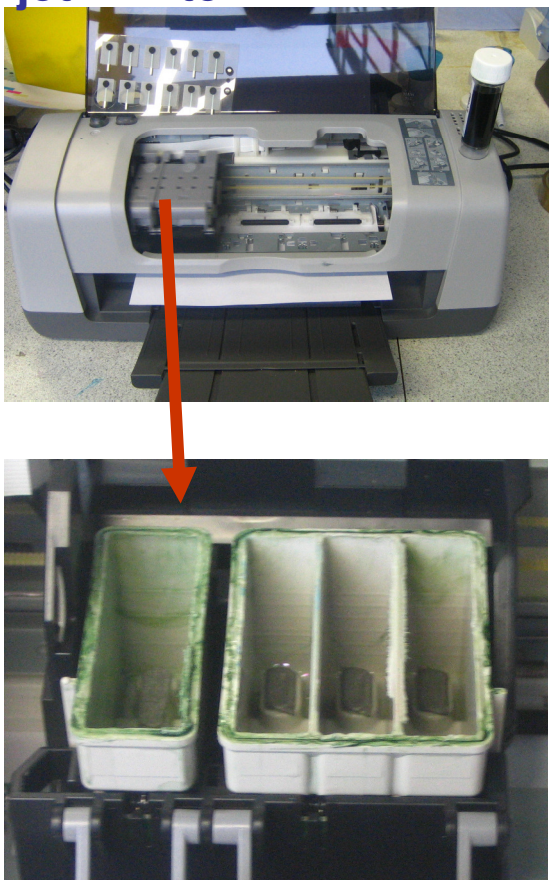
DBSA Stabiliser Present



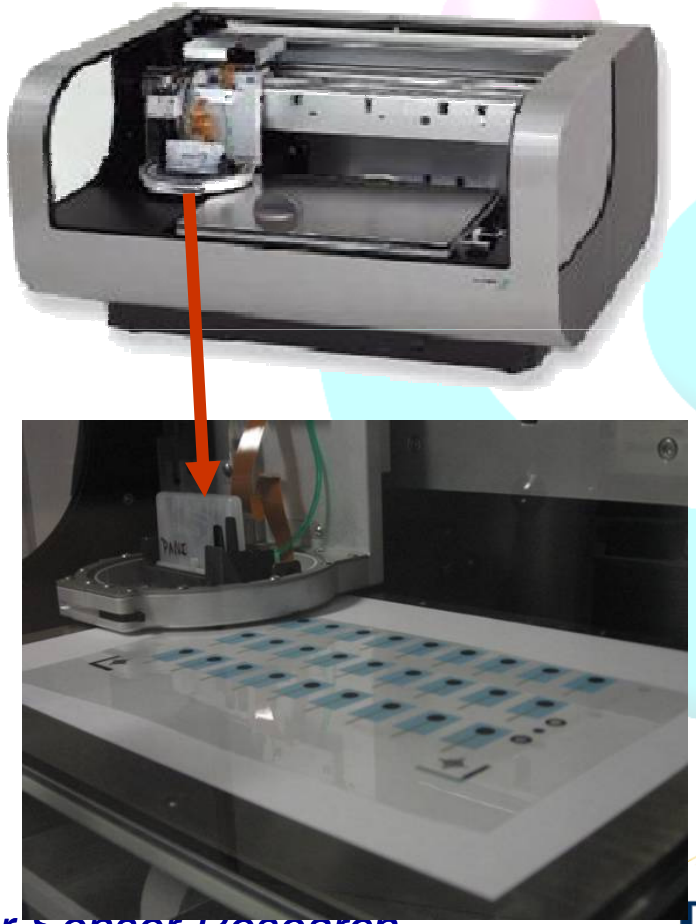
*Jiaxing Huang, Richard B. Kaner, *Angew. Chem. Int. Ed.* **2004**, 43, 5817-5821

Inkjet Printing of PANI

Multi-Head Desktop Epson Inkjet Printer

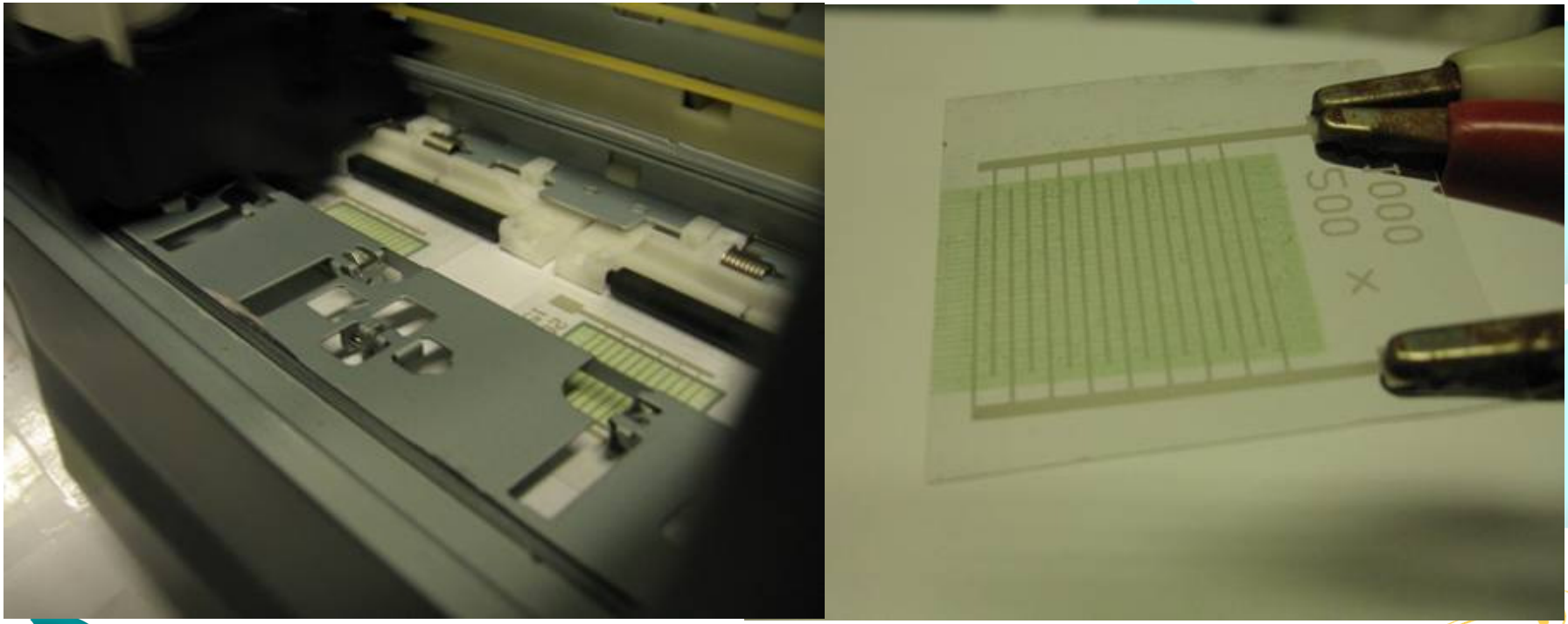


Commercial Research Fuji Dimatix Printer

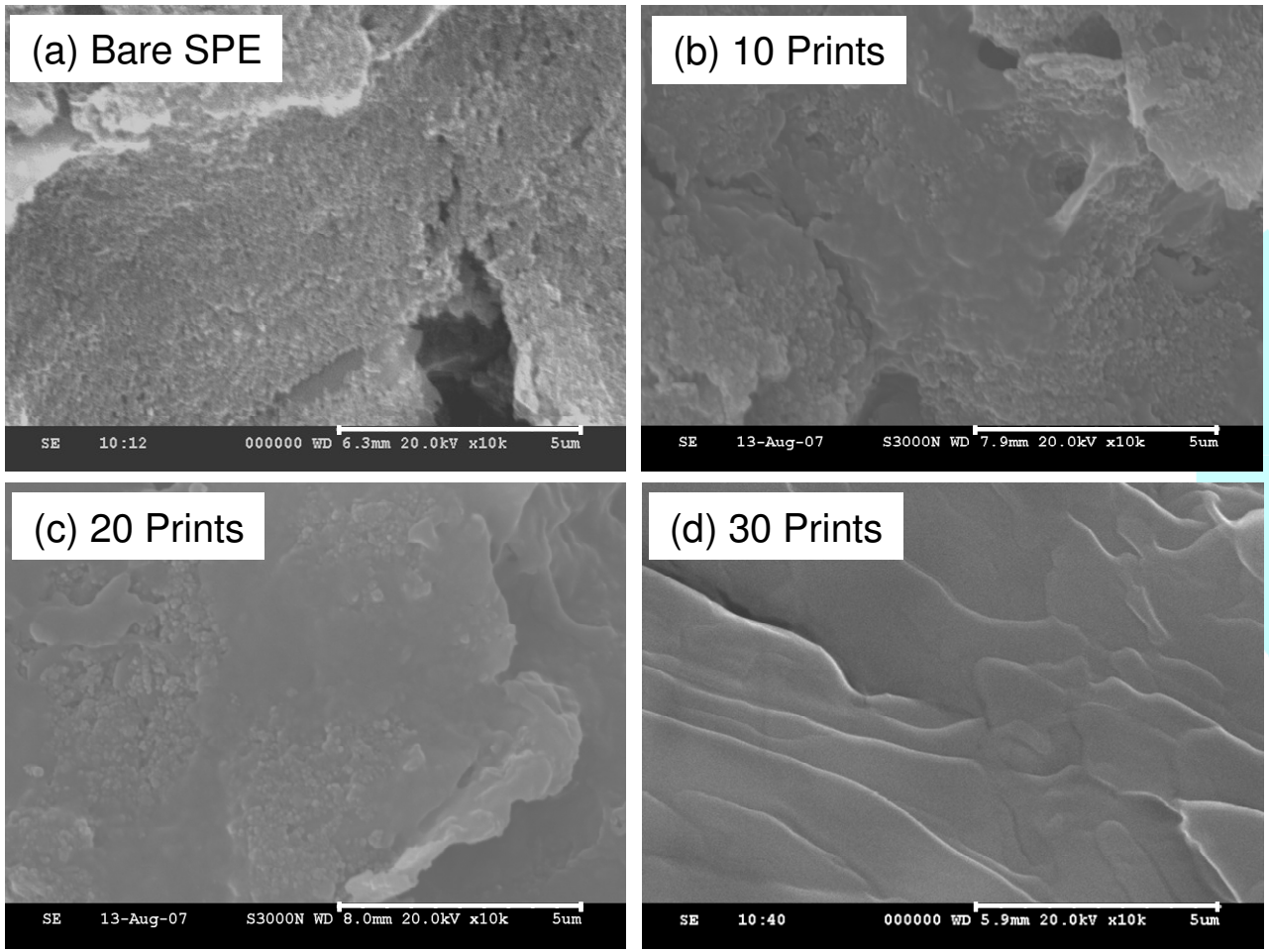


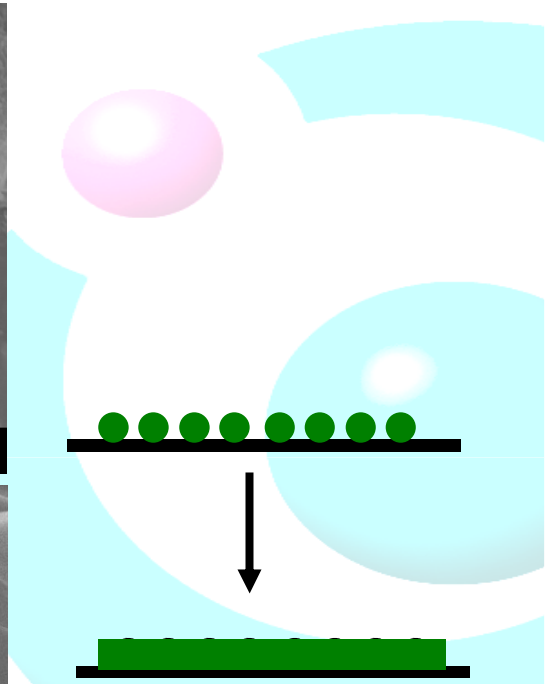
Inkjet Printed PANI Electrodes

- PANI nanodispersions inkjet printed onto IDAs for gas sensor platform
- Also printed to carbon paste working electrodes

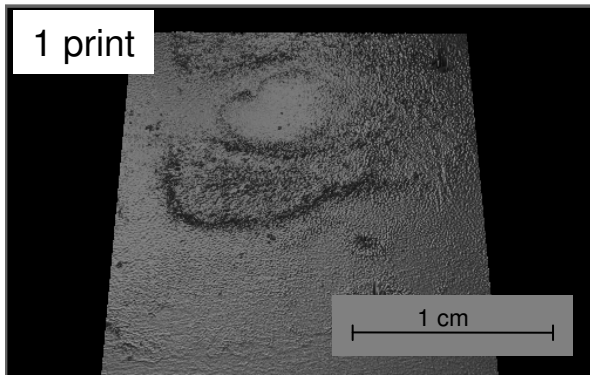


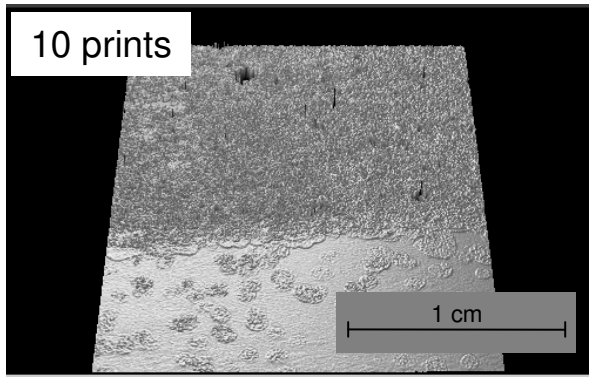
Resulting ‘Smooth’ Morphology

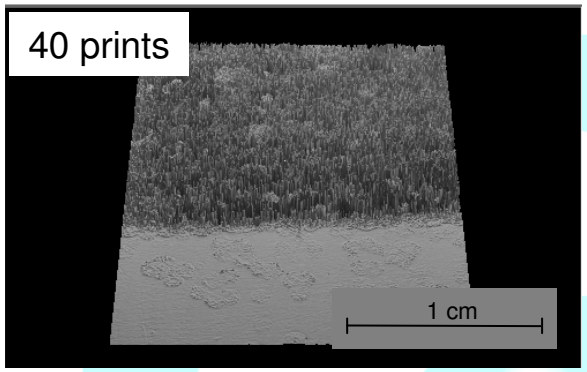




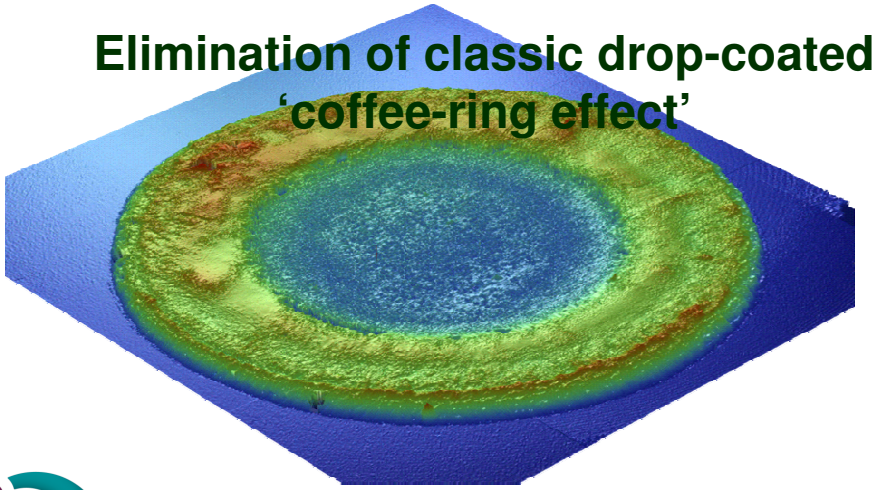
Morphology

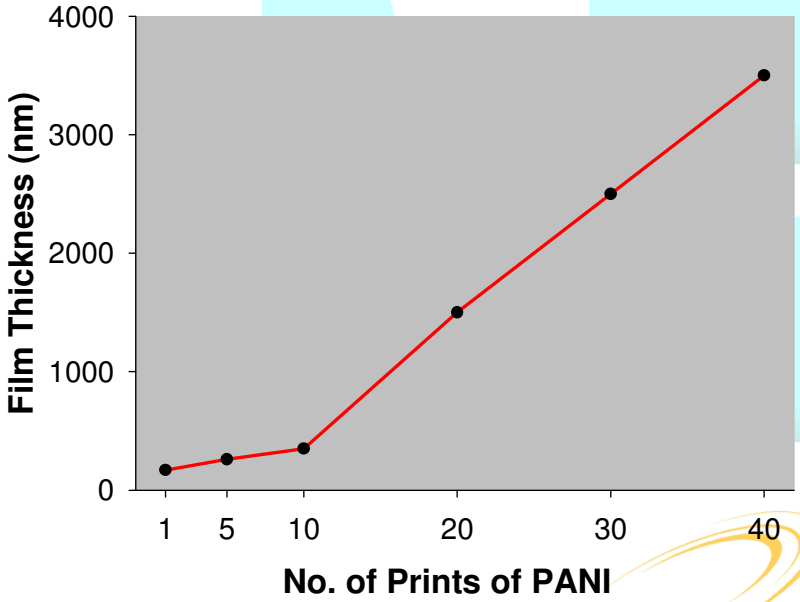






Elimination of classic drop-coated 'coffee-ring effect'





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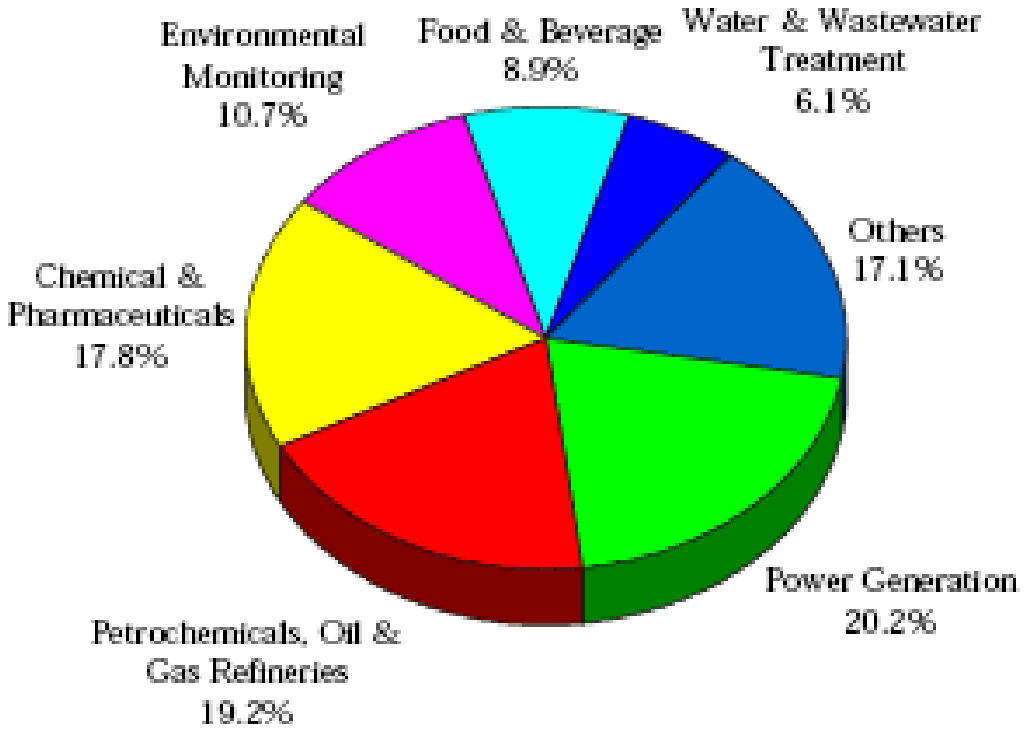
4. Biosensor Fabrication & application

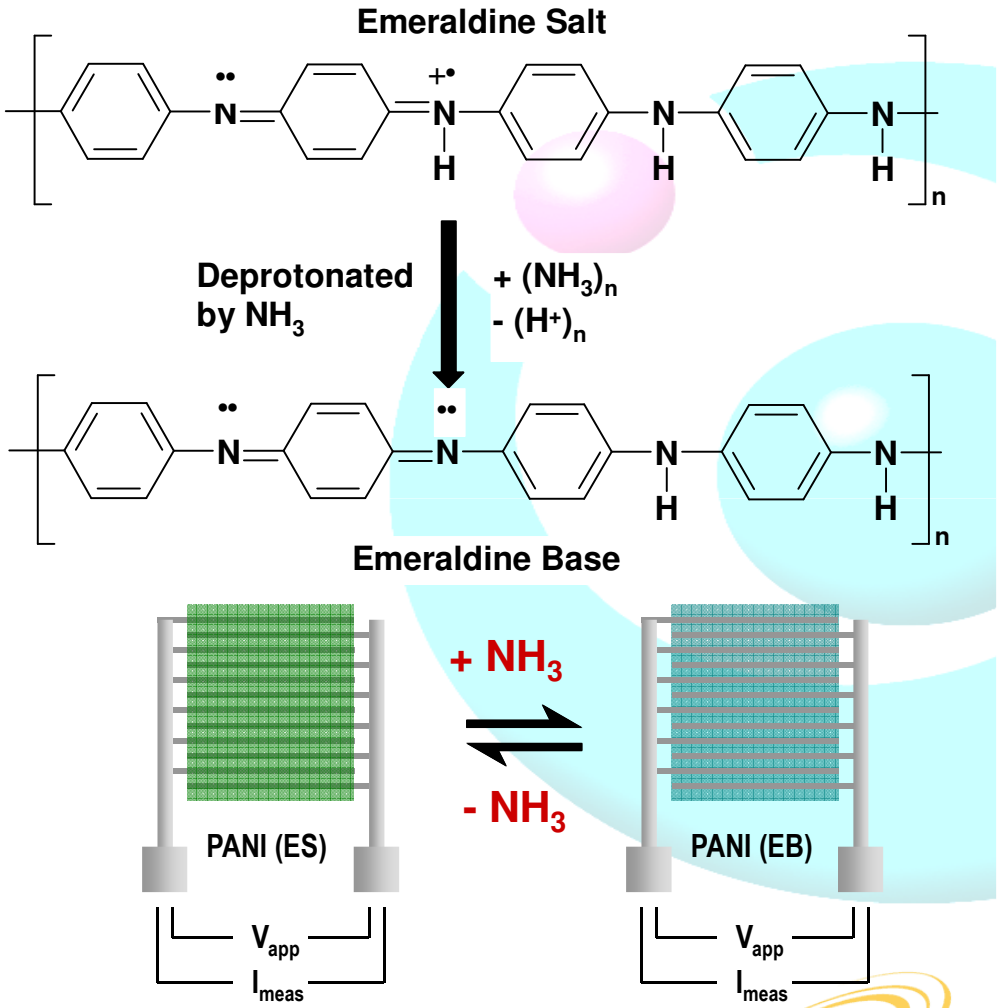
Ammonia Sensing

- Ammonia is a highly toxic chemical species
- Classified as a major pollutant
- The ammonia sensing industry spans a wide range of markets
- Mature market, lacking in innovation
- Niche for low-cost portable sensors e.g., for health & safety

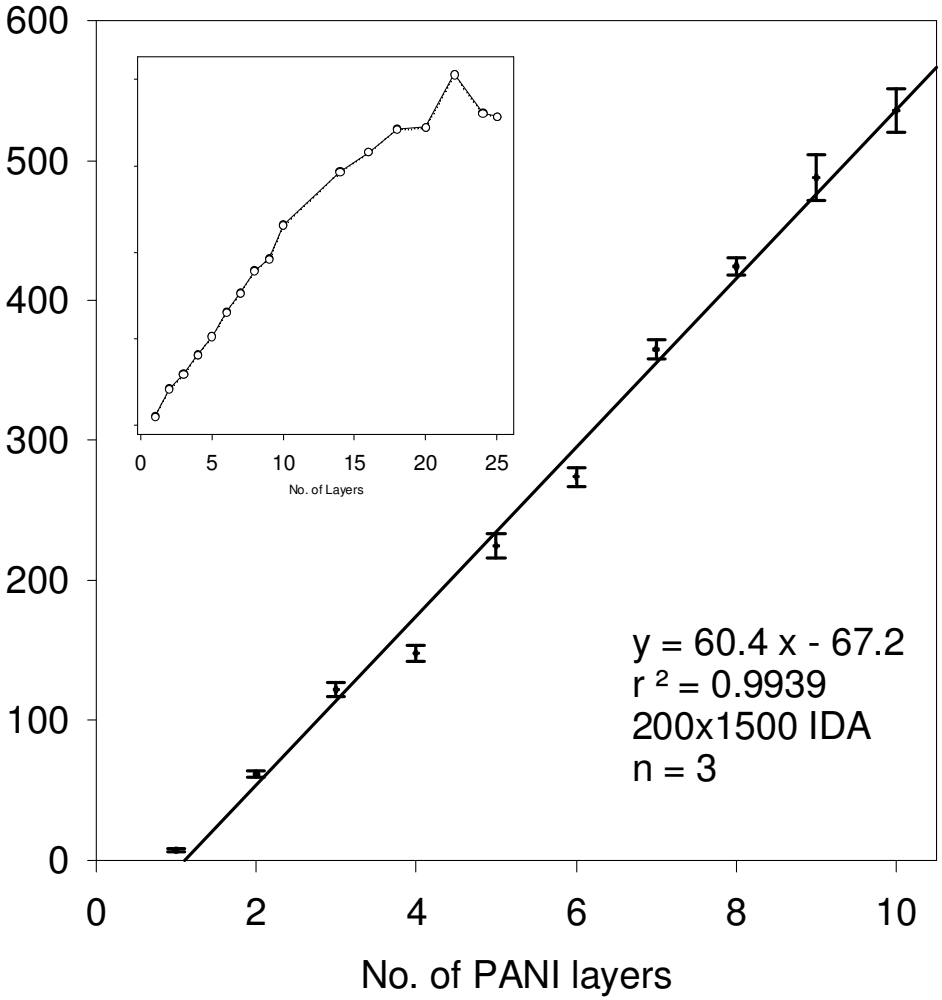


Detection Mechanism – Gas Sensing

- Conductimetric mode
  - 2 electrode cell
- Ammonia deprotonates PANI backbone
  - Emeraldine salt (ES) to emeraldine base (EB) form
  - Decrease in conductivity
- Apply potential to IDA
  - current flows through PANI film
  - V_{app} : step or ramp
- Measure change in current on NH_3 exposure

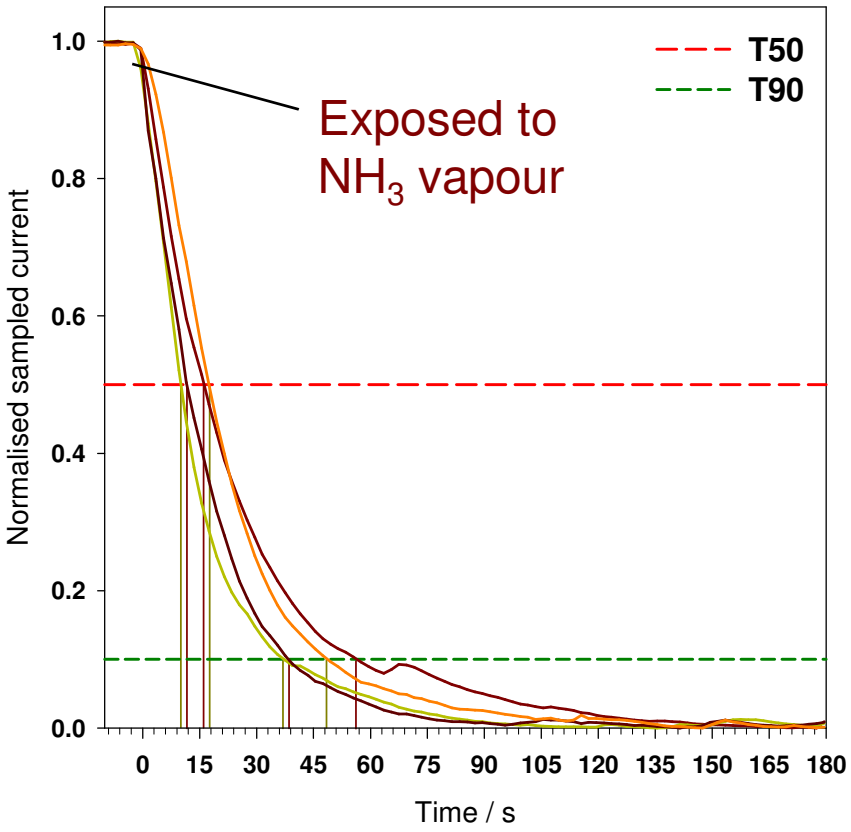


Increasing Print Layers – Increasing Current



- Sequential inkjet printed layers
  - Quasi-linear increase from 1 – 10 layers
  - Begins to plateau above 10 layers (inset)
  - Thicker layers do not seriously effect response/recovery times – porous film

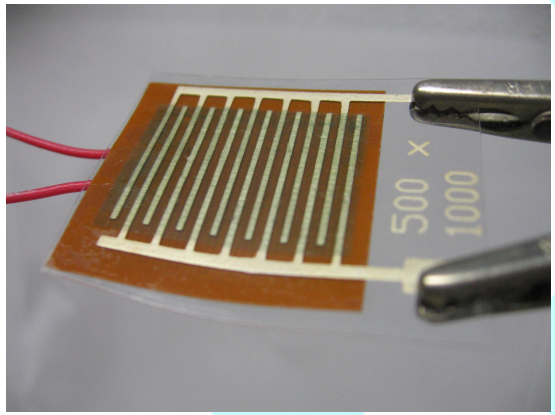
Sensor Response Times

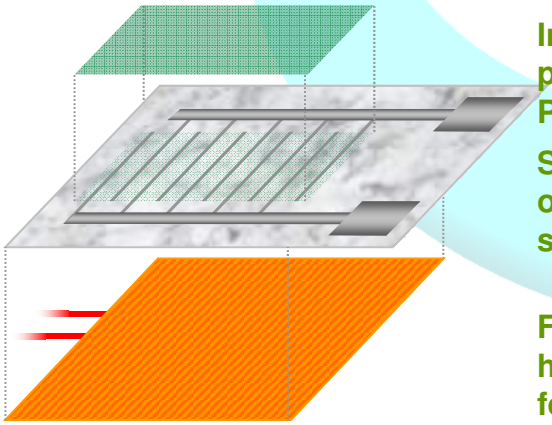


- Response times for PANI IDA (n=4)
  - t_{50} ~ 15 s
  - t_{100} < 60 s
- ~ 60 ppm NH_3
- Response times currently within those specified by ISA (Instrument Society of America)
  - t_{50} < 90s

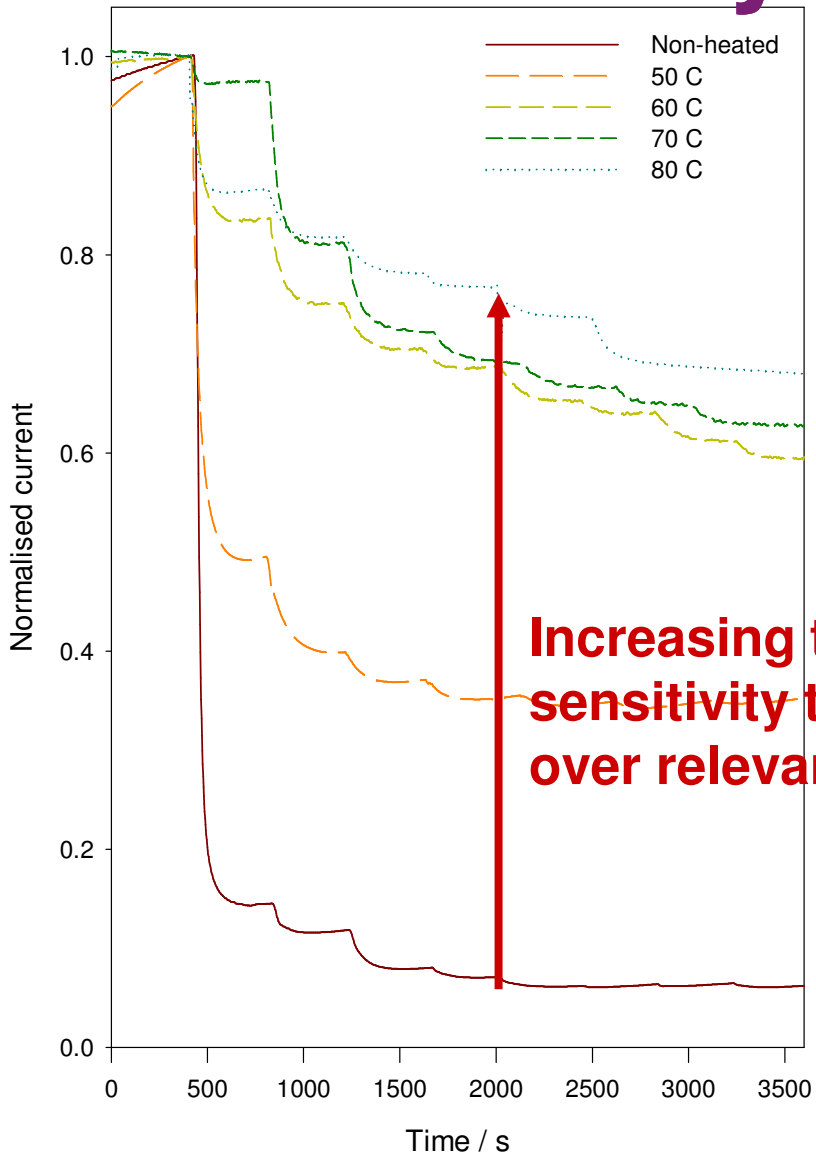
Flexible Heater Substrate

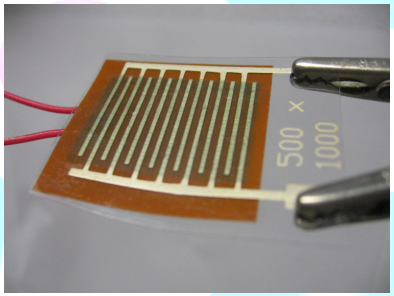
- Minco™ thermofoil heaters
- Thin and flexible
  - fast temperature equilibration
- up to 200°C
  - sub 100°C used for PANI sensors
- Compatible with inkjet printing
- Possibility of printing directly to heater substrate





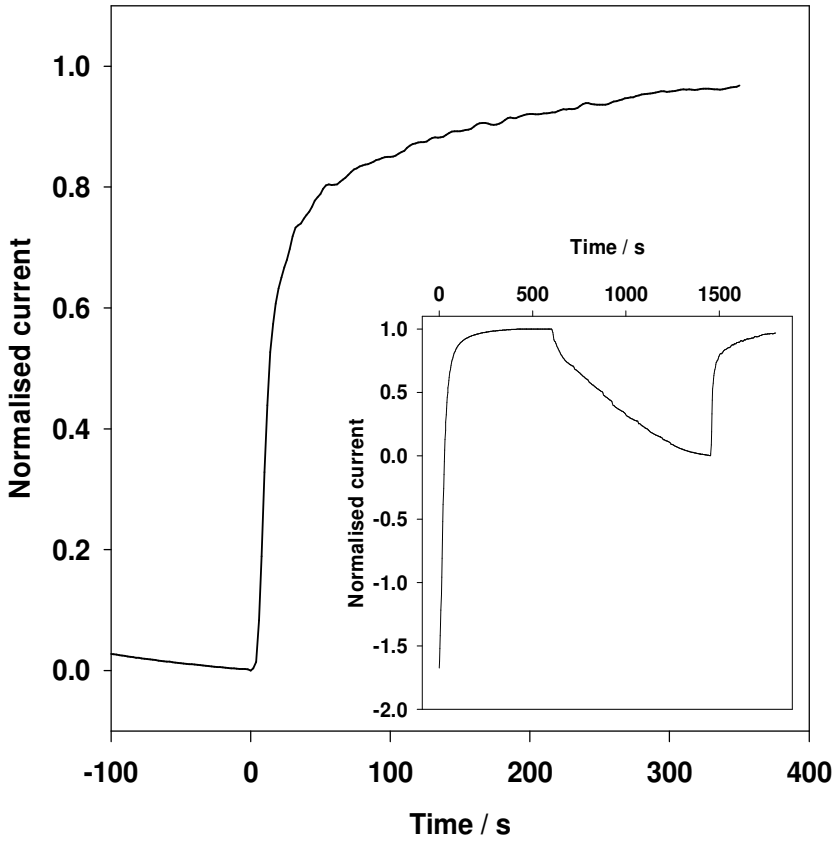
Response Behaviour Using Flexible Heater System



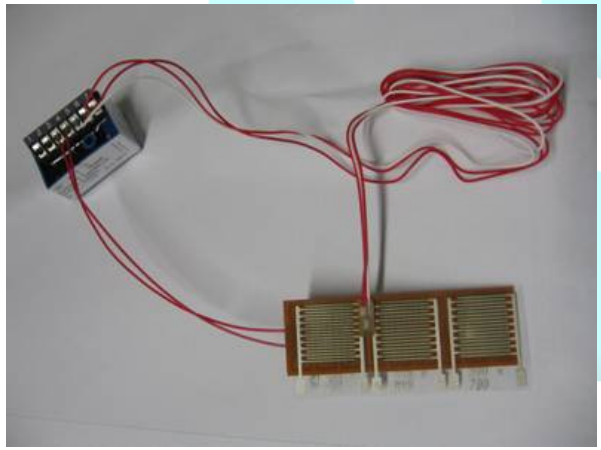


Increasing temperature reduces sensitivity to increase linearity over relevant range

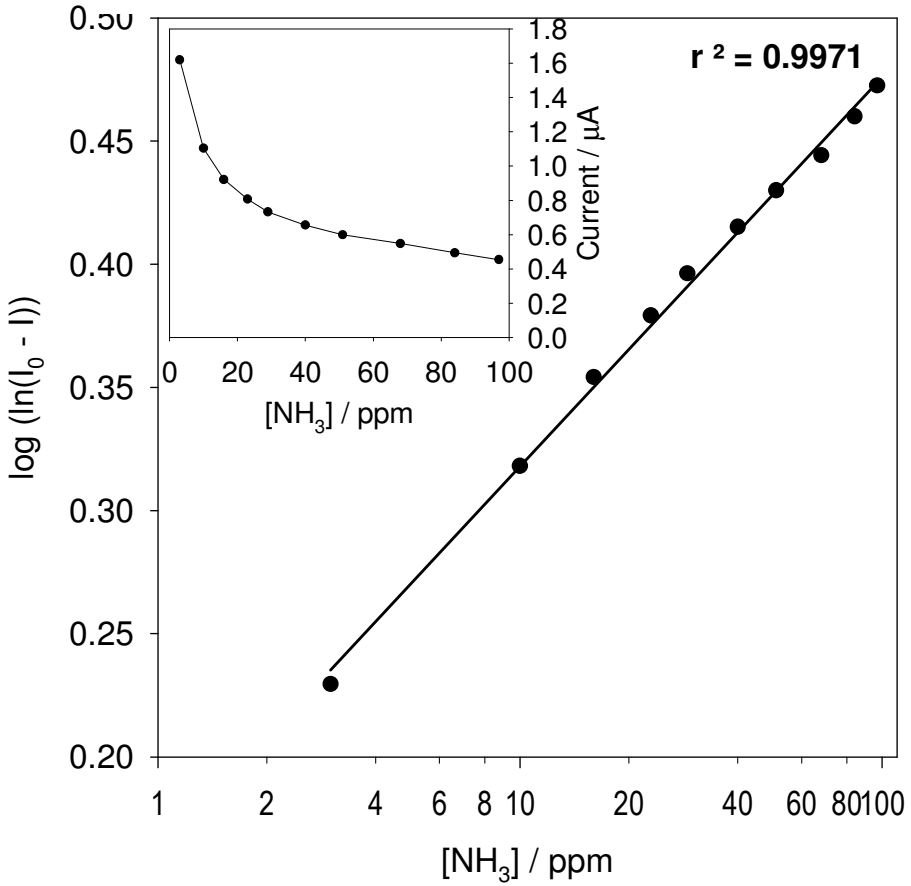
Sensor Recovery Using Flexible Heater System



- Room Temp recovery > hours
- 80℃ recovery < seconds



Quantitative Analysis



PANI IDA sensor is far superior when compared with a commercial sensor

- Honeywell NH_3 sensor
- Zellweger Impulse XP
- 1 - 100 ppm range

Extension to Inkjet Printed Gas Sensor Array

- Recently received 'Proof of Concept' Funding to build an inkjet printed gas sensor array
- Gases including H_2S, CO, Cl_2 and NO_2
- Exploit inkjet printing to fabricate arrays of polymer (polyaniline?) layers modified to be selective towards specific gases

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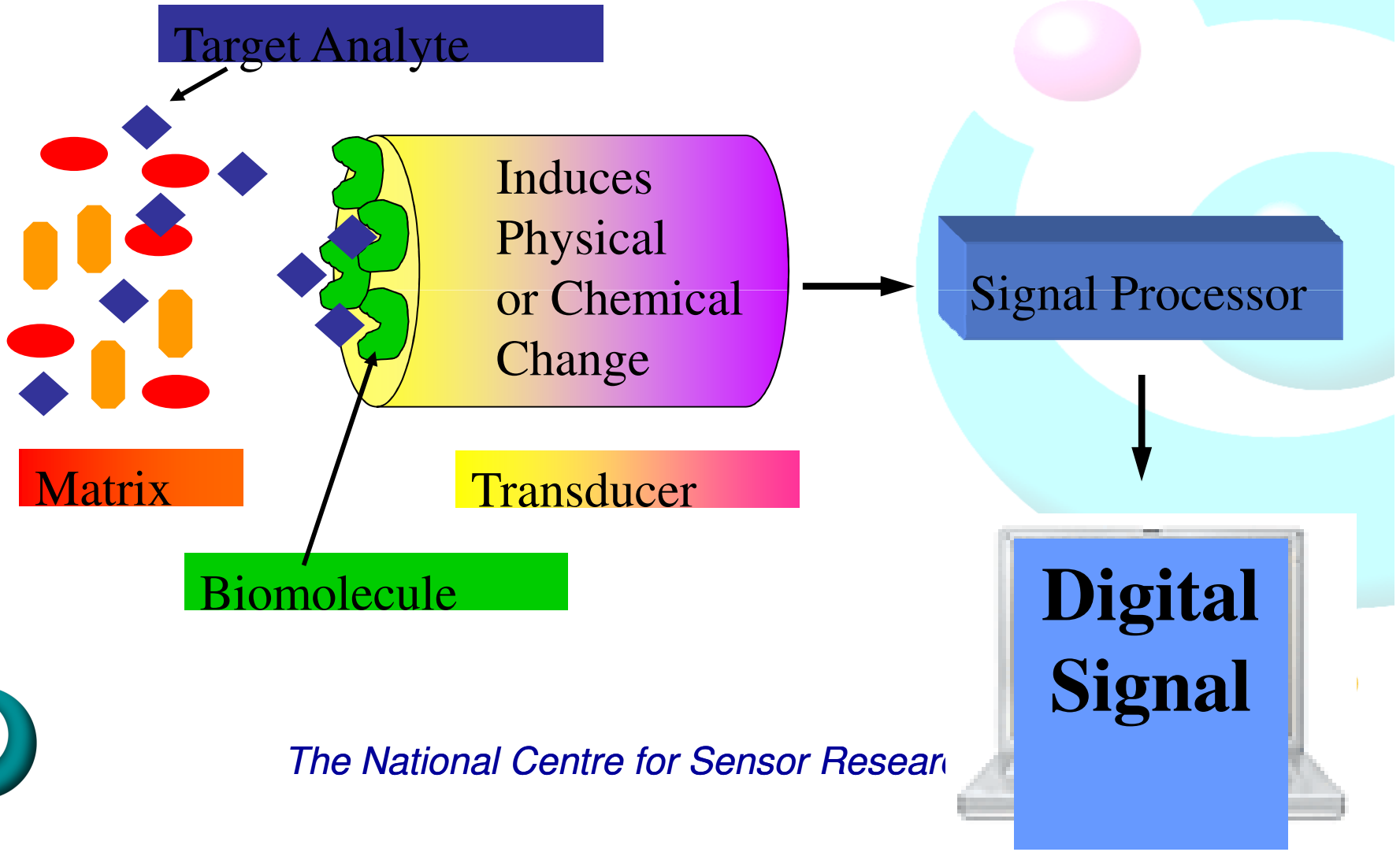
Biosensor


Target Analyte
Induces
Physical
or Chemical
Change
Signal Processor
Matrix
Transducer
Biomolecule
Digital
Signal

Inkjet Printed Biosensor Publications

> **13,000** hits for '**biosensor**' on Web of Science

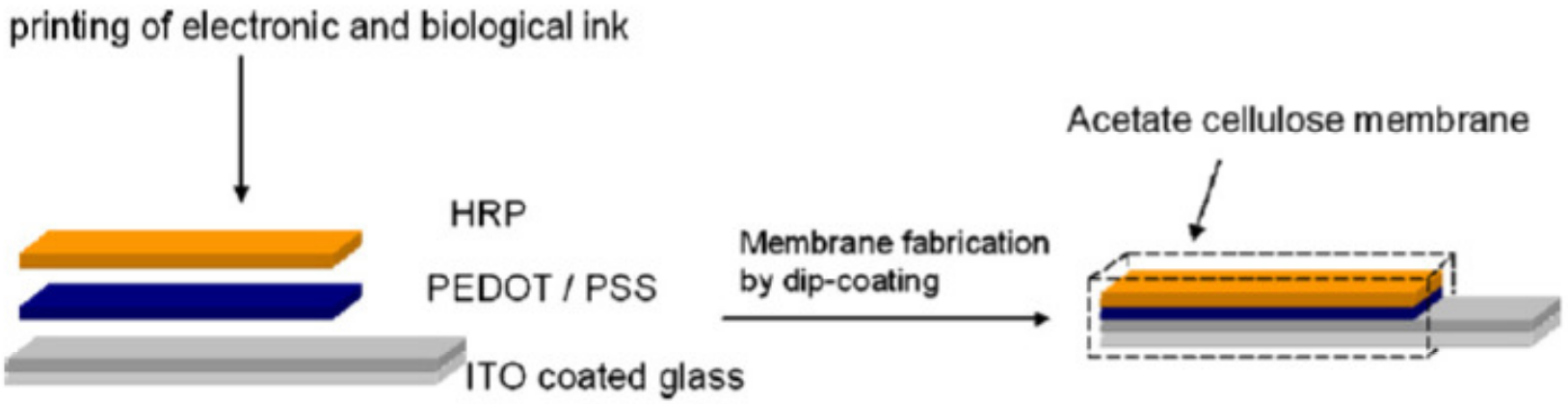
> **500** Peer-Reviewed Publications on '**screen-printed and biosensor**'

Just **10** Peer-Reviewed Publications on '**inkjet and biosensor**'!!!

Field: Publication Year	Record Count	% of 10	Bar Chart
2002	1	10.0000 %	
2004	4	40.0000 %	
2005	3	30.0000 %	
2006	1	10.0000 %	
2006	1	10.0000 %	

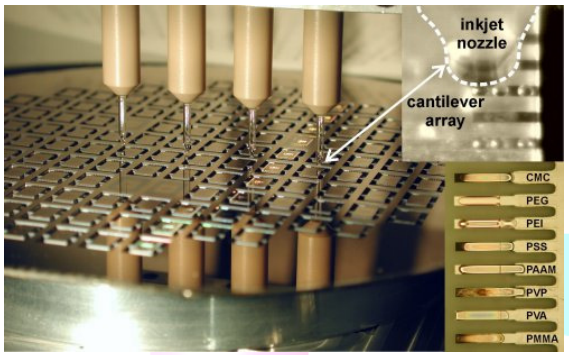
Thermally Printed Biosensor

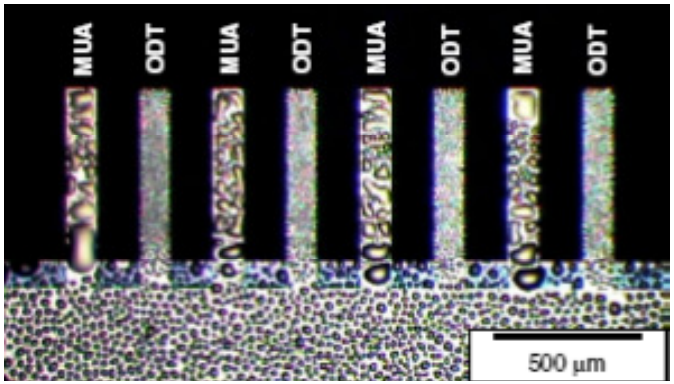
- **Horseradish Peroxidase (HRP) and Glucose Oxidase (GOD)-based biosensors**
- **Thermal printing does *not* affect the activity of the enzymes**
- **PEDOT/PSS electronic communication with enzyme *(but employed a soluble mediator to enhance this)***



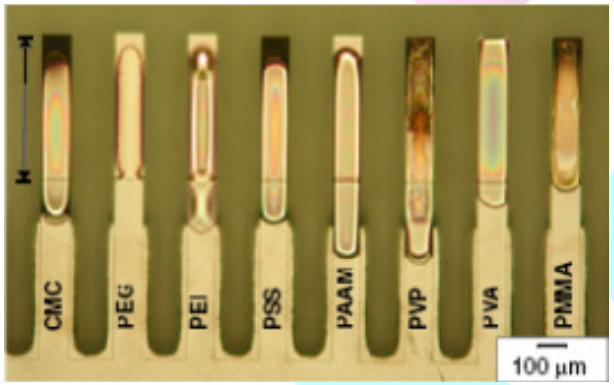
Setti et al. (2007). Sens. Actuat. (126) 252

Inkjet Printed Cantilever Array Chips





Characterisation of hydrophilic and hydrophobic inkjet printed SAMs



8 inkjet printed polymers on individual cantilevers

- Highly controlled deposition of inkjet printed functional layers
- Demonstrated prototype as a DNA biosensor and a gas sensor array
- Inkjet printing can, uniquely functionalise cantilevers individually very easily
- Fast, easy to assemble, scalable

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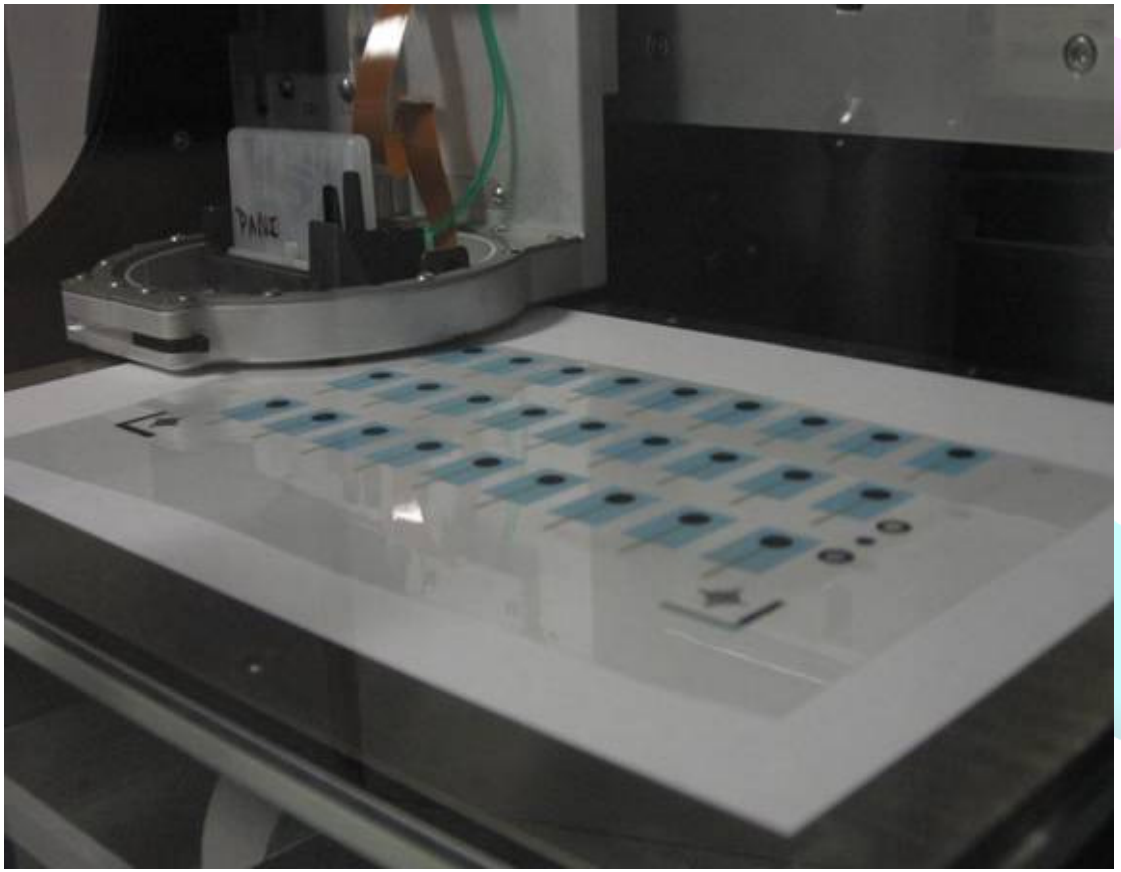
Bietsch et al. (2004). Nanotechnology (15) 873

Screen-Printed Carbon Paste Electrode



Electrochemistry of Inkjet Printed Polyaniline