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
Overview

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

The National Centre for Sensor Research
Overview

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

The National Centre for Sensor Research
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

The National Centre for Sensor Research
Overview

1. Introduction
2. Inkjet printing of polyaniline
3. High specification, flexible, inkjet printed gas sensor platform
4. Biosensor fabrication & application
Sensor Platforms Based on Polyaniline

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

- 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
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

The National Centre for Sensor Research
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??

The National Centre for Sensor Research
Screen-Printing for Electrode Fabrication

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

The National Centre for Sensor Research
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

The National Centre for Sensor Research
Modification of Electrode: Processable PANI

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

No Stabiliser Present*  DBSA Stabiliser Present

Inkjet Printing of PANI

Multi-Head Desktop Epson Inkjet Printer

Commercial Research Fuji Dimatix Printer

The National Centre for Sensor Research
Inkjet Printed PANI Electrodes

- PANI nanodispersions inkjet printed onto IDAs for gas sensor platform
- Also printed to carbon paste working electrodes
Resulting ‘Smooth’ Morphology

(a) Bare SPE
(b) 10 Prints
(c) 20 Prints
(d) 30 Prints
Morphology

Elimination of classic drop-coated ‘coffee-ring effect’

The National Centre for Sensor Research

No. of Prints of PANi

Film Thickness (nm)
Overview

1. Introduction
2. Inkjet printing of conducting polymer-based sensor
3. High specification, flexible, inkjet printed gas sensor platform
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
  - $V_{\text{app}}$: step or ramp
- Measure change in current on NH$_3$ exposure

The National Centre for Sensor Research
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

\[
y = 60.4 \times -67.2 \\
(200 \times 1500 \text{ IDA}) \\
n = 3 \\
r^2 = 0.9939
\]
Sensor Response Times

- Response times for PANI IDA (n=4)
  - $t_{50} \sim 15$ s
  - $t_{100} < 60$ s
- ~ 60 ppm NH$_3$
- Response times currently within those specified by ISA (Instrument Society of America)
  - $t_{50} < 90$s
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

The National Centre for Sensor Research
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 °C recovery < seconds
Quantitative Analysis

\[ \log(I - I_0) \]

\[ r^2 = 0.9971 \]

The PANI IDA sensor is far superior when compared with a commercial sensor
- Honeywell NH\textsubscript{3} sensor
- Zellweger Impulse XP
- 1 - 100 ppm range

The National Centre for Sensor Research
Extension to Inkjet Printed Gas Sensor Array

- Recently received ‘Proof of Concept’ Funding to build an inkjet printed gas sensor array
- Gases including \( \text{H}_2\text{S} \), \( \text{CO} \), \( \text{Cl}_2 \) and \( \text{NO}_2 \)
- Exploit inkjet printing to fabricate arrays of polymer (polyaniline?) layers modified to be selective towards specific gases
Overview

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

Target Analyte

Induces Physical or Chemical Change

Matrix

Biomolecule

Transducer

Signal Processor

Digital Signal

The National Centre for Sensor Research
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’!!!

<table>
<thead>
<tr>
<th>Field: Publication Year</th>
<th>Record Count</th>
<th>% of 10</th>
<th>Bar Chart</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>1</td>
<td>10.0000 %</td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td>4</td>
<td>40.0000 %</td>
<td></td>
</tr>
<tr>
<td>2005</td>
<td>3</td>
<td>30.0000 %</td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>1</td>
<td>10.0000 %</td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td>1</td>
<td>10.0000 %</td>
<td></td>
</tr>
</tbody>
</table>
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)
Inkjet Printed Cantilever Array Chips

- 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

Characterisation of hydrophilic and hydrophobic inkjet printed SAMs

8 inkjet printed polymers on individual cantilevers

The National Centre for Sensor Research

Bietsch et al. (2004). Nanotechnology (15) 873
Screen-Printed Carbon Paste Electrode

The National Centre for Sensor Research
Electrochemistry of Inkjet Printed Polyaniline

Scan Rate Study

Relationship of peak current with scan rate

Relationship of peak current with (scan rate)$^{1/2}$

The National Centre for Sensor Research

The National Centre for Sensor Research