Conducting Polymer Structures Housed in Thin-Layer Microfluidic Channels for Electroanalysis

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64th Annual Meeting of the ISE
Queretaro, Mexico, 8-13 September 2013
Who we are?

DCU

National Centre for Sensor Research

bdi

MESTECH

Marine & Environmental Sensing Technology Hub
Outline

- Development of a microfluidic-based thin-layer electrochemical cell
  - Electropolymerisation of conducting polymer materials in microfluidic channels
  - Micro-structuring of materials on-chip
- Conducting polymers as coatings on capillary monoliths
- Towards stimuli-responsive chromatography
Integrating an electrochemical cell into microfluidics

Characterisation of thin layer microfluidic format

\[ l \ll (2Dt)^{1/2} \]

\[ 35 \mu m < l < 200 \mu m \]

WE length: 5 mm

Increasing channel depth
Conducting polymer films on-chip

Graph showing current vs. potential.

SEM image of polymer films.

3D cross-section image of electrode with polymer height and electrode length dimensions.
Self-limiting nature of thin-layer cell electropolymerisation

- Peak current - closed channel (µA)
  - Batch cell polymerisation
  - Thin layer flow cell polymerisation
- Peak current - open channel (µA)
- No. of polymerisation cycles

Graph showing the relationship between peak current and number of polymerisation cycles for batch and thin layer flow cell polymerisation.
Self-limiting nature of thin layer cell electropolymerisation

<table>
<thead>
<tr>
<th>Channel depth (µm)</th>
<th>Average PANI thickness (µm) after 50 polymerisation cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>7.53 ± 0.24</td>
</tr>
<tr>
<td>60</td>
<td>27.70 ± 6.58</td>
</tr>
<tr>
<td>110</td>
<td>49.93 ± 1.53</td>
</tr>
<tr>
<td>180</td>
<td>80.53 ± 6.84</td>
</tr>
</tbody>
</table>

![Graph showing the relationship between peak current and number of polymerisation cycles for different channel depths.](image-url)
Can we create order in these materials on chip?

- By creating inverse opal conducting polymer monolithic materials through sacrificial CC templates within channel (open channel format)

- Interesting structure for electrochemically responsive chromatography, drug delivery, flow through sensors on chip

- In terms of chromatography, it could enable high internal surface areas of electroactive materials with periodic flow-through pores
  - Allow for precise electrochemical tuning of stationary phase before & during a separation to influence retention factors without need for gradient elution of mobile phase
  - Gain electrochemical control over hydrophobicity, pore size, ionic capacity
Colloidal crystal formation in the microchannel

1) Capillary flow of PS suspension into channel

2) Pinning of PS suspension to walls of the channel - evaporation flux, \( j_e \)

3) Receding of meniscus line with continuous colloidal crystal growth – particle flux, \( j_p \) and water flux, \( j_w \)
Optimised CC structures in microchannels

Gorey et al. (2013) Fabrication of a 3-dimensionally ordered binary colloidal crystal within a confined channel. Submitted to Chem. Mater.
Conducting polymer monolithic structures

Dry & wetted states of CP monoliths - AFM

Dry State

Wetted State

*Electrochemically grown Ppy doped with DBS
Decreasing current density as it grows away from electrode surface
Overcoming current density gradient using chemical polymerisation

Core-shell flow-through bed comprised electroactive PANI
Fused silica capillary microfluidic channel

- In-situ polymerisation of styrene in the presence of a thermal initiator, a cross-linker, DVB and porogen, dodecanol

- Flush capillary with aniline, acid and oxidant
Characterisation of PANI-coated polymer monoliths

Switchable PANI-coated PS-co-DVB monolith

Dedoped PANI Coating

Doped PANI Coating

Blank Monolith

Current challenge is to integrate an electrochemical cell into this capillary format – control conducting polymer oxidation state by application of a potential.
CPs as separation phases in particulate-based packings

Reduced Oxidised

Caffeine
Theophylline

Retention of Caffeine and Theophylline on PPCI/Si as a Function of the Treatment of the Column with Redox Reagent*

<table>
<thead>
<tr>
<th></th>
<th>k' Caffeine</th>
<th>k' Theophylline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frc</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>red₁</td>
<td>2.7</td>
<td>0.1</td>
</tr>
<tr>
<td>oxd₁</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>red₂</td>
<td>2.4</td>
<td>0.1</td>
</tr>
<tr>
<td>oxd₂</td>
<td>2.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*60% MeOH/H₂O at 1 mL/min. Frc: fresh column; red: after column was treated with 0.1M Na₂SO₃; oxd: after column reoxidation with 0.1M FeCl₃.


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To Conclude…

What do we have?
- Microfluidic thin layer electrochemical cell for conducting polymer bulk films and inverse opal structures
  ▪ Suitable format for exploiting EOF-driven flow?
- Coatings of PANI on polymer monoliths in capillary format
  ▪ V. high surface areas, structurally supported films

Where to next?
- Applications in LoC sensors, drug delivery, electrochemically-responsive chromatography
Thanks!

- Dr. Blánaid White
- Dr. Damian Connolly
- Prof. Gordon Wallace
- Dr. Michael Higgins
- Brian Gorey
- Dr. Aoife Power
- Dr. Patrick Floris

without collaboration

there is no creation

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Characterisation of PANI-coated polymer monoliths

[Graph showing detector response (mV) vs. distance along capillary (mm) with two lines representing PANI-coated monoliths and bare monolith.]

Scanning capacitively coupled contactless conductivity detection (sC⁴D)