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

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Who we are?

DCU

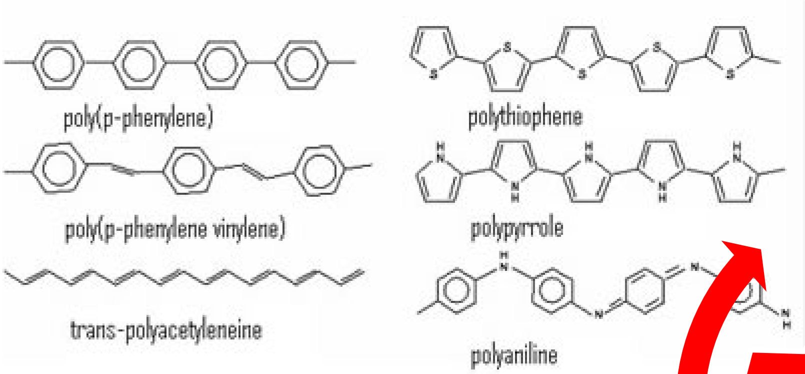
QS World University Rankings
Top 50
Under 50
DCU

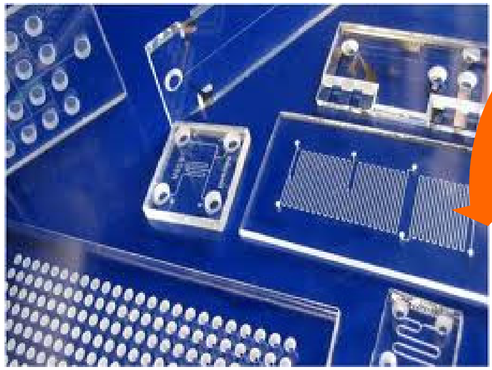
NCSR
National Centre for Sensor Research

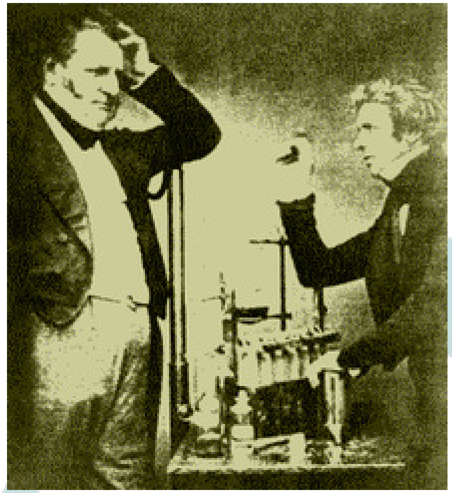
bdi
bio medical diagnostics institute

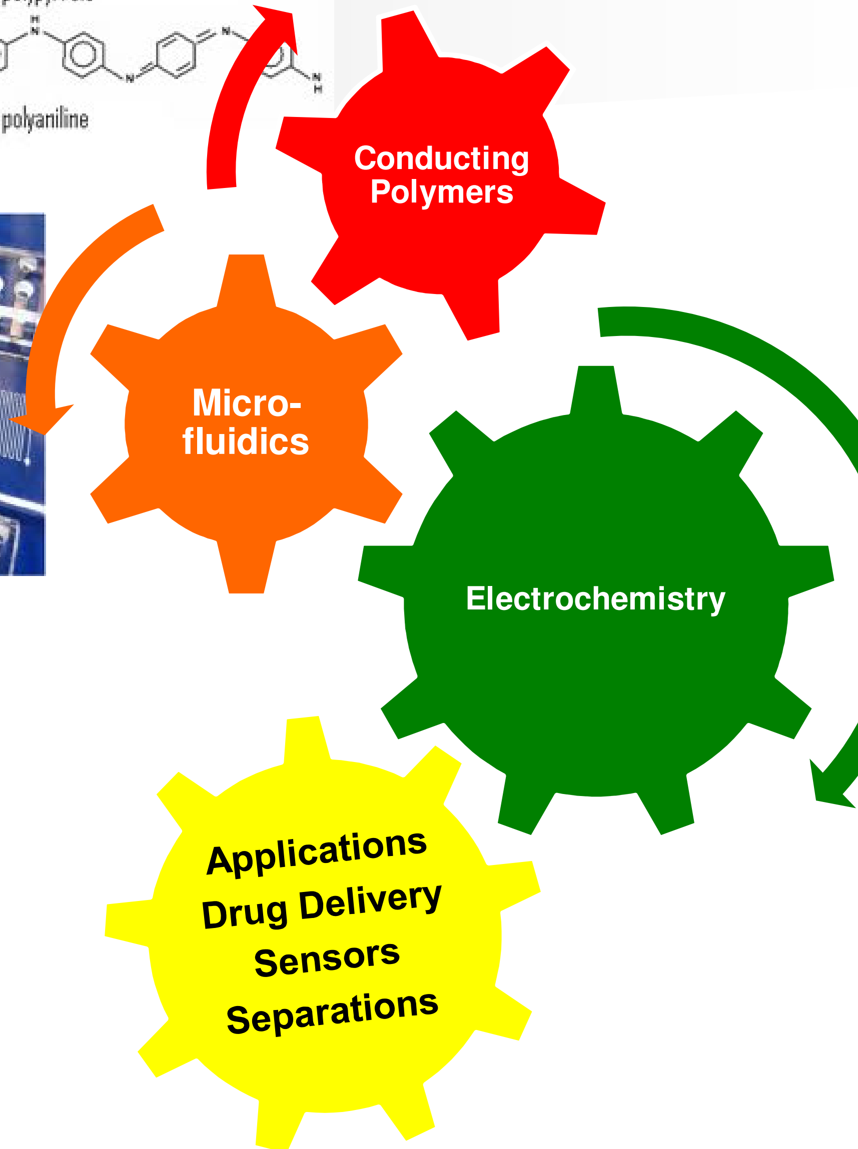
MESTECH
Marine & Environmental
Sensing Technology Hub

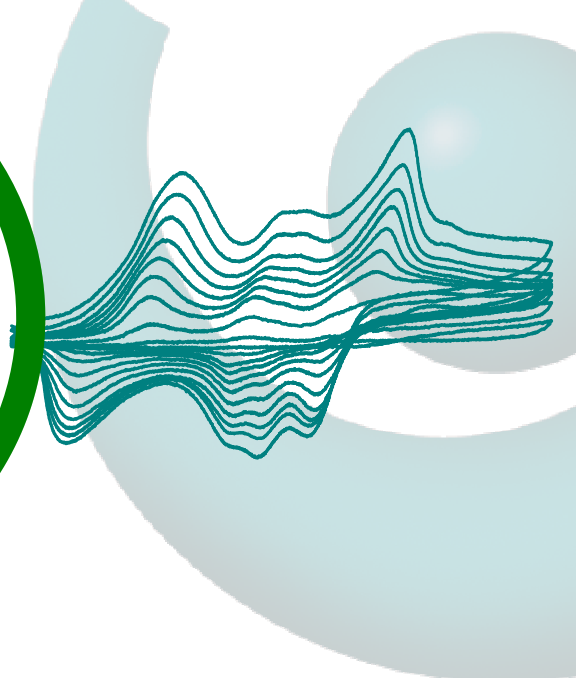
DCU


poly(p-phenylene)
polythiophene
poly(p-phenylene vinylene)
polypyrrole
trans-polyacetyleneine
polyaniline





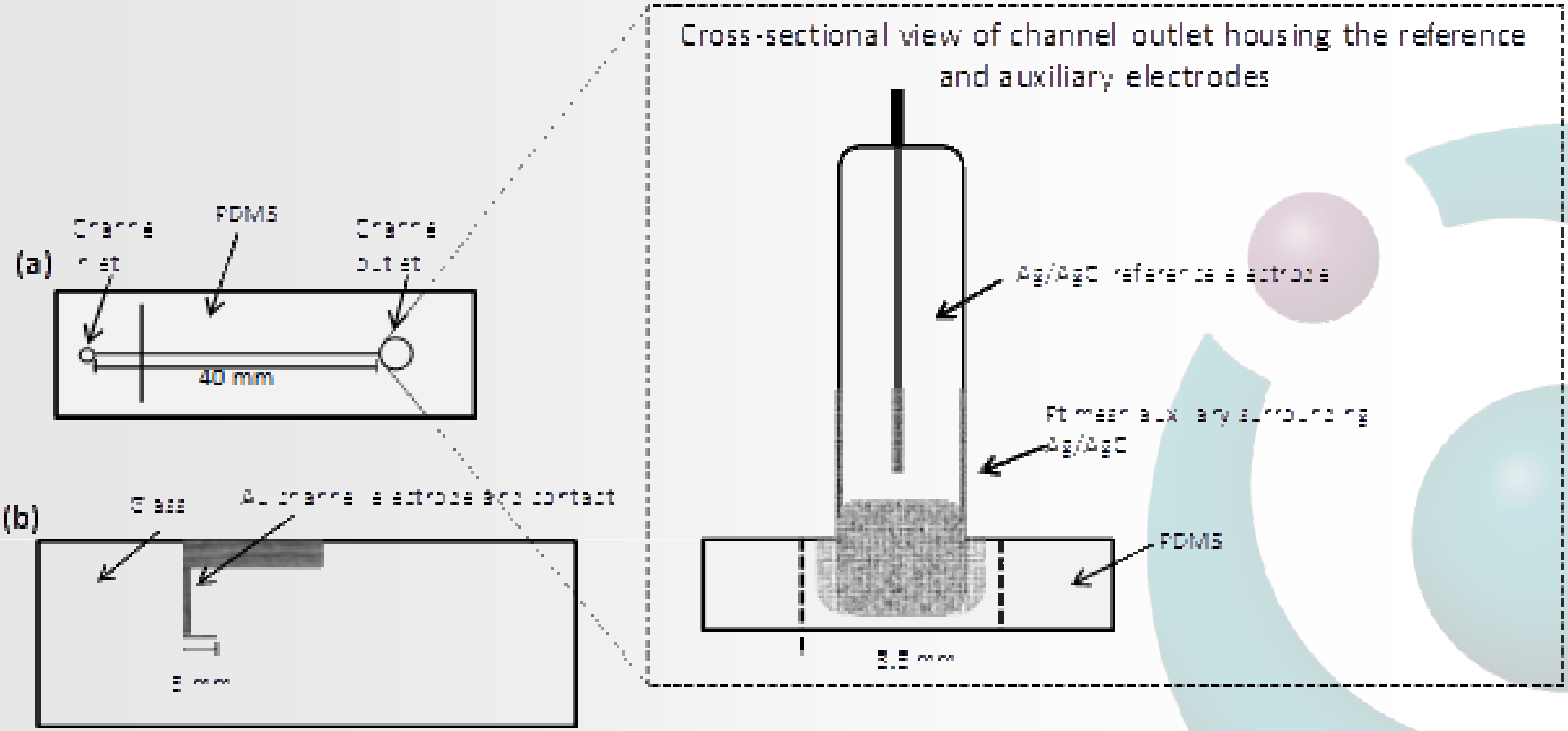

Conducting Polymers
Micro-fluidics
Electrochemistry
Applications
Drug Delivery
Sensors
Separations

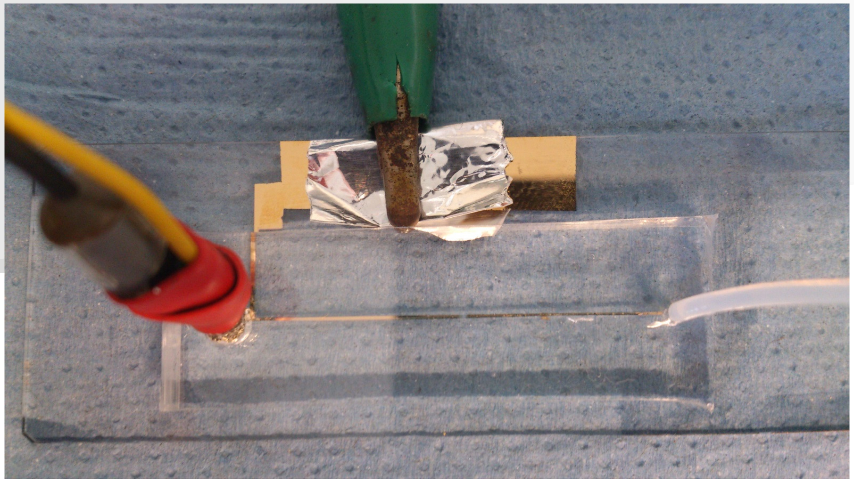


Outline

- 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



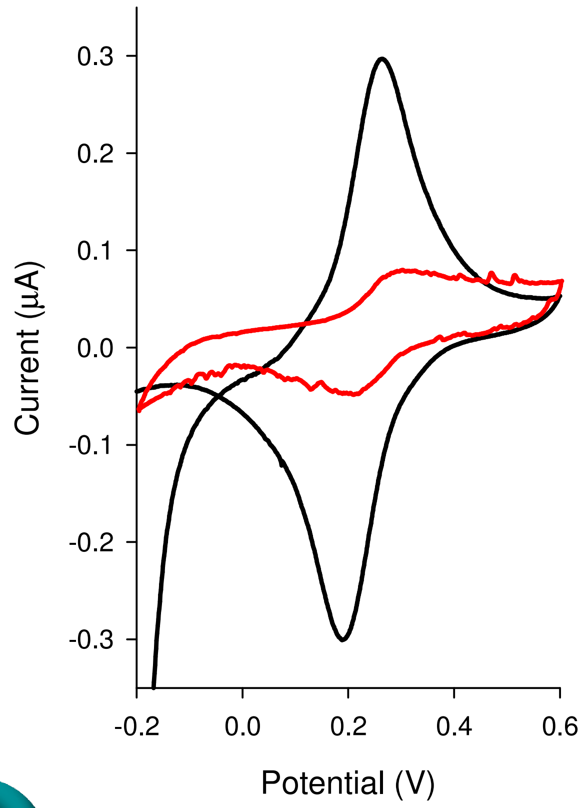


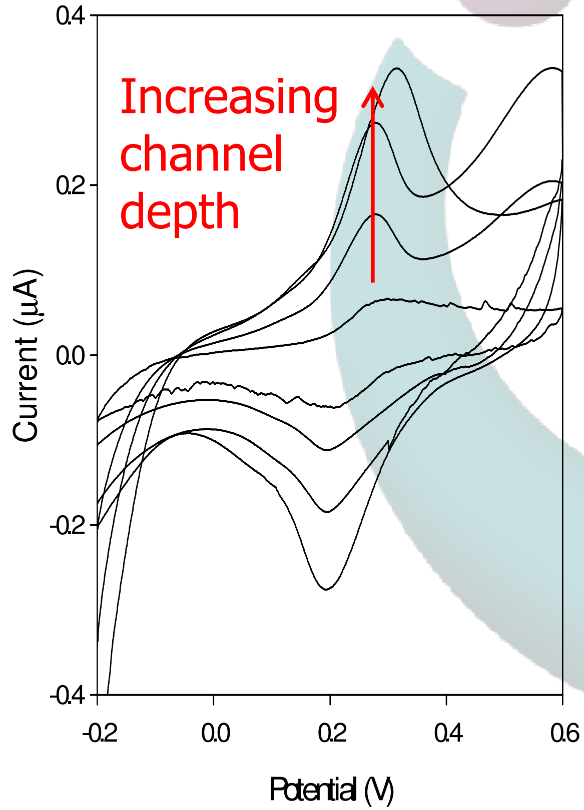
A.C. Power, B. White, A .Morrin, *Electrochimica Acta* , 2013, DOI:10.1016/j.electacta.2013.04.091

Characterisation of thin layer microfluidic format

$$l << (2Dt)^{1/2}$$

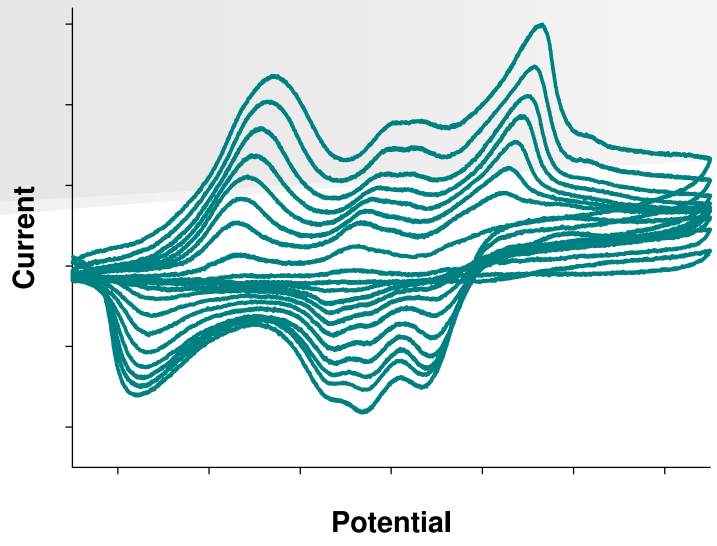
$$35\mu m < l < 200\mu m$$

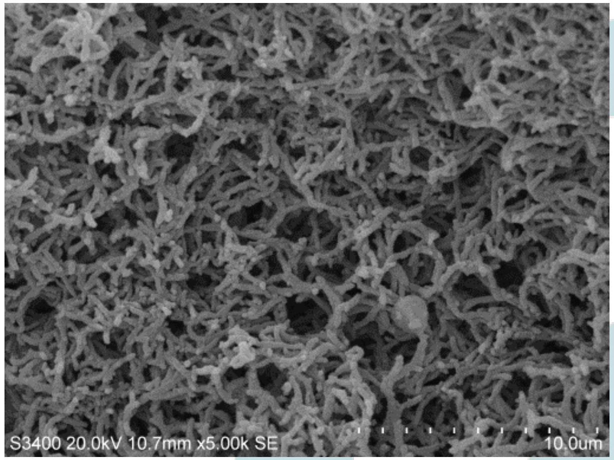


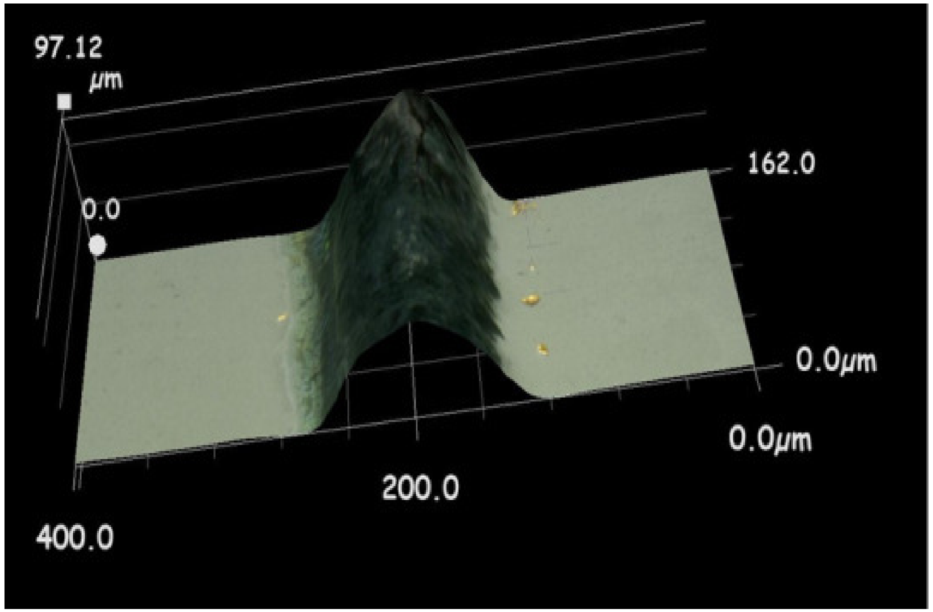


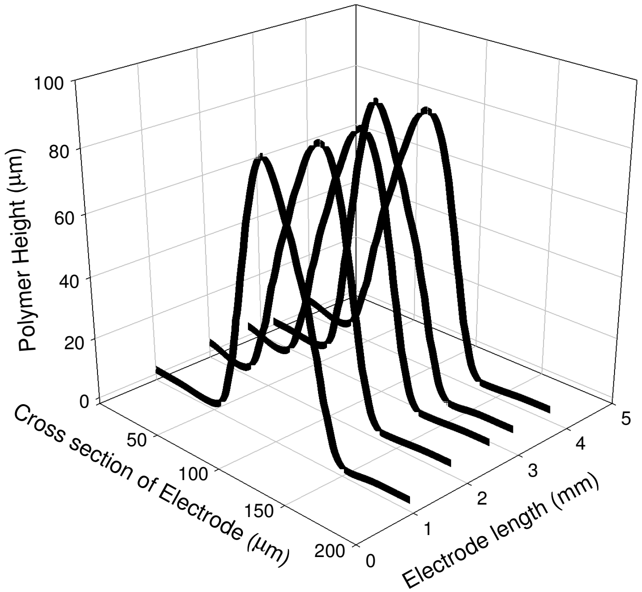
WE length: 5 mm

Conducting polymer films on-chip

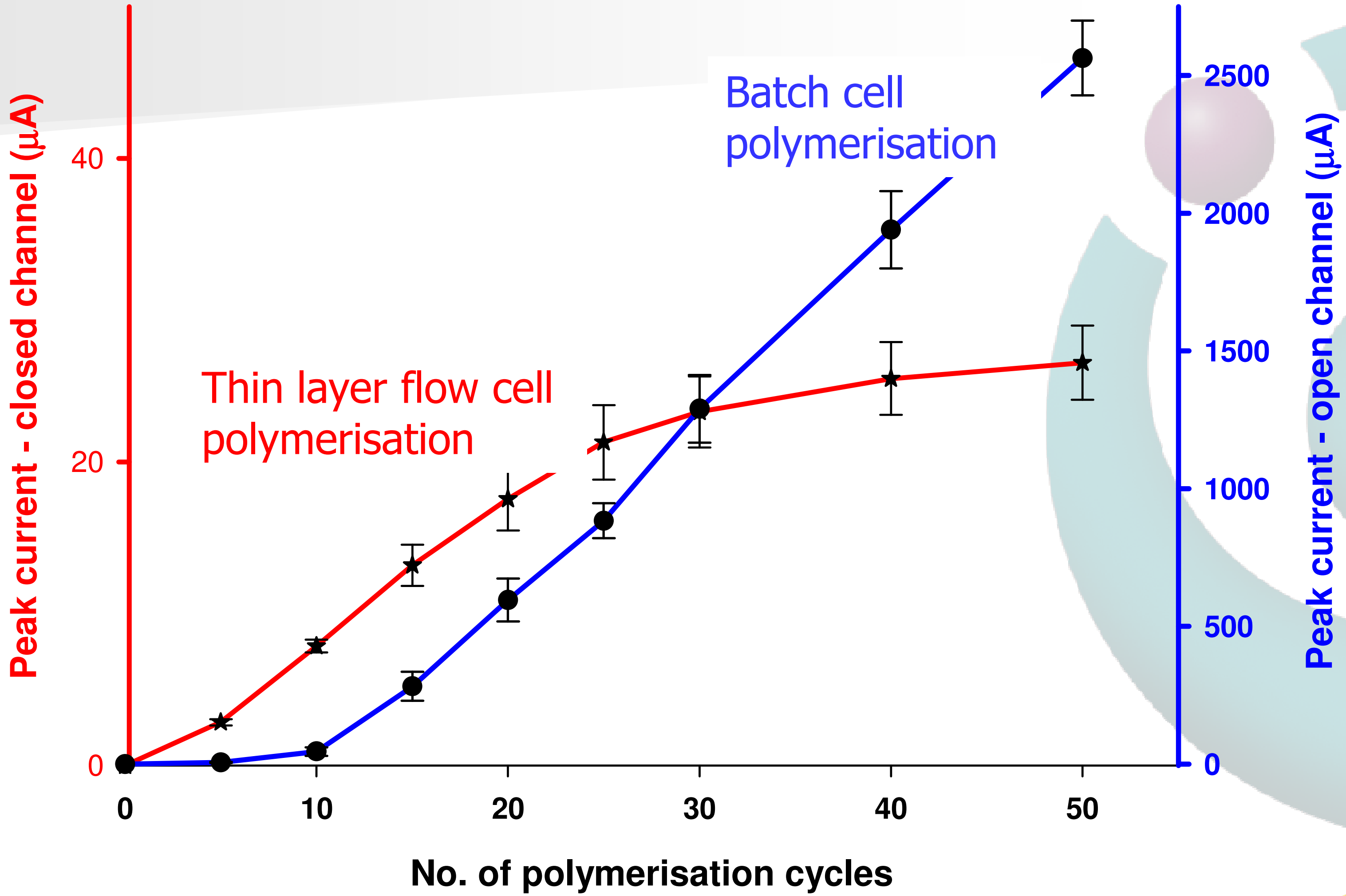






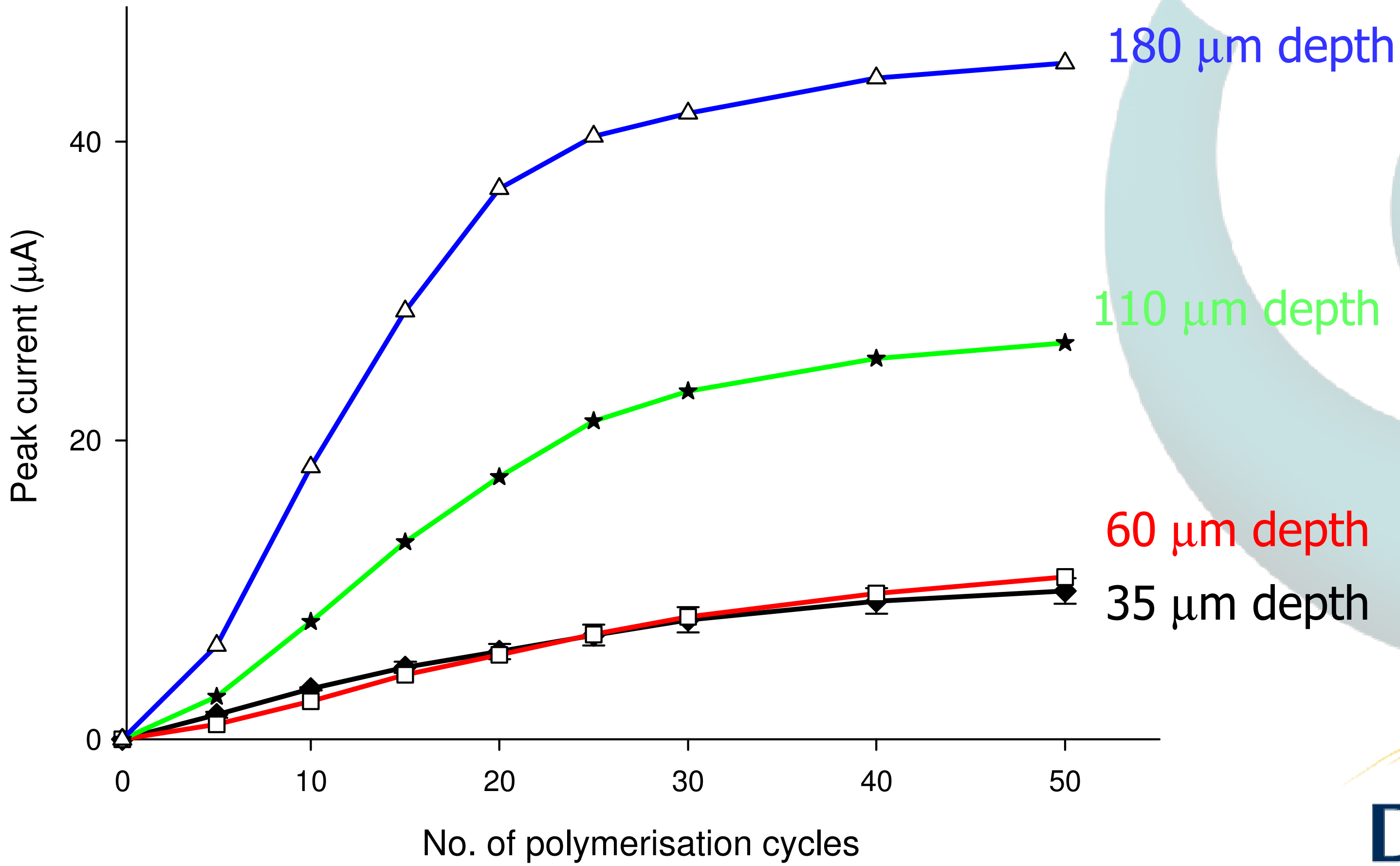


Self-limiting nature of thin-layer cell electropolymerisation



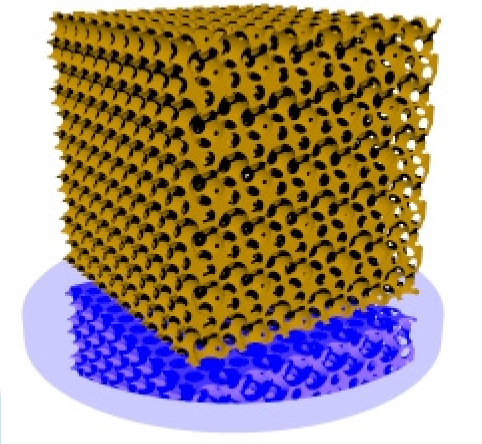
Self-limiting nature of thin layer cell electropolymerisation

Channel depth (µm)	Average PANI thickness (µm) after 50 polymerisation cycles
35	7.53 ± 0.24
60	27.70 ± 6.58
110	49.93 ± 1.53
180	80.53 ± 6.84

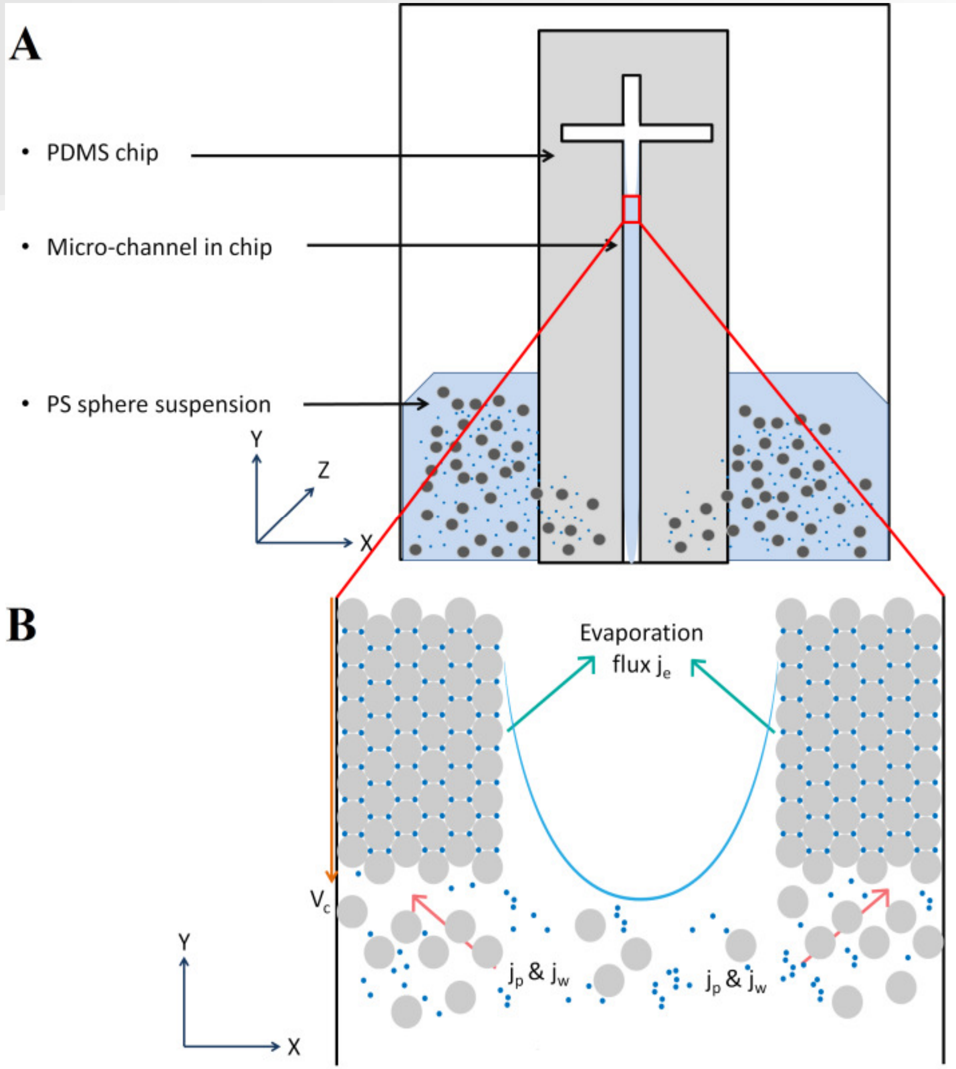


Can we create order in these materials on chip?

- 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



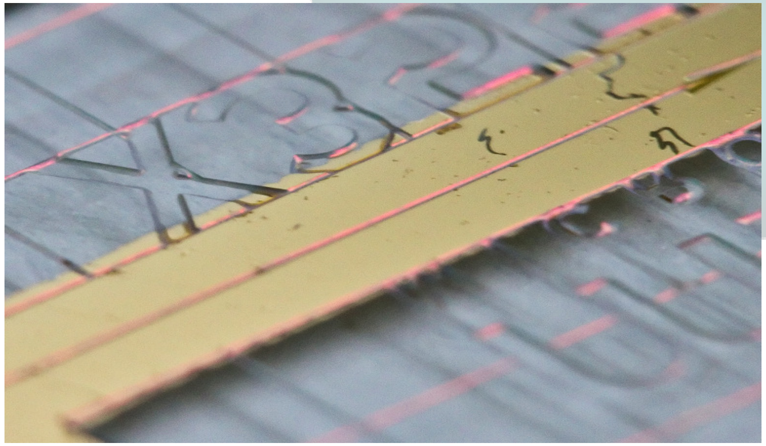
Colloidal crystal formation in the microchannel



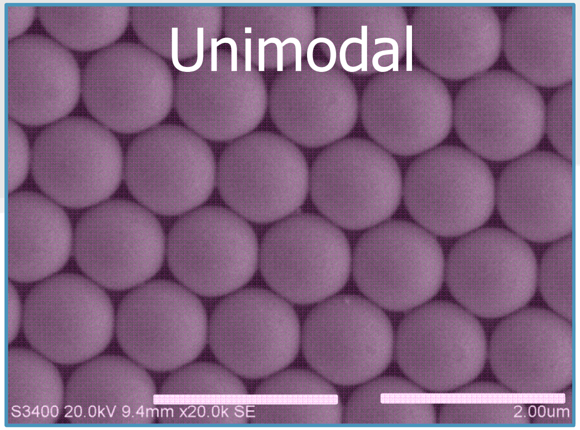
1) Capillary flow of PS suspension into channel

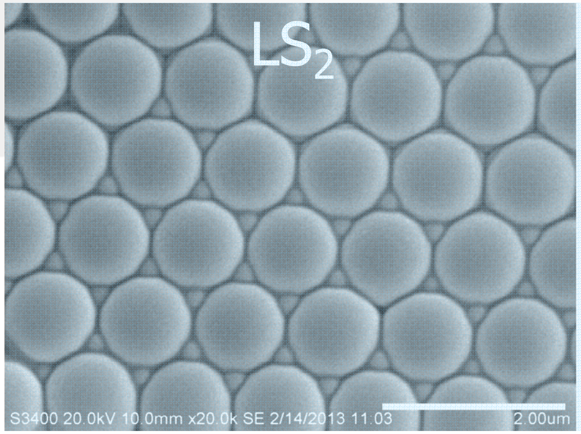
2) Pinning of PS suspension to walls of the channel - evaporation flux, j_e

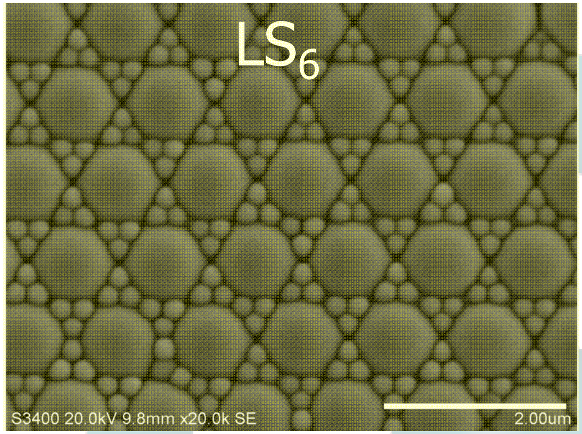
3) Receding of meniscus line with continuous colloidal crystal growth – particle flux, j_p and water flux, j_w

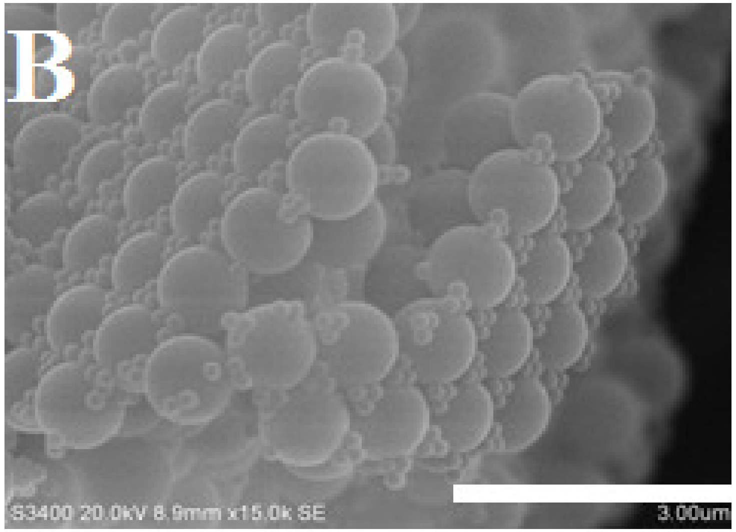


Optimised CC structures in microchannels



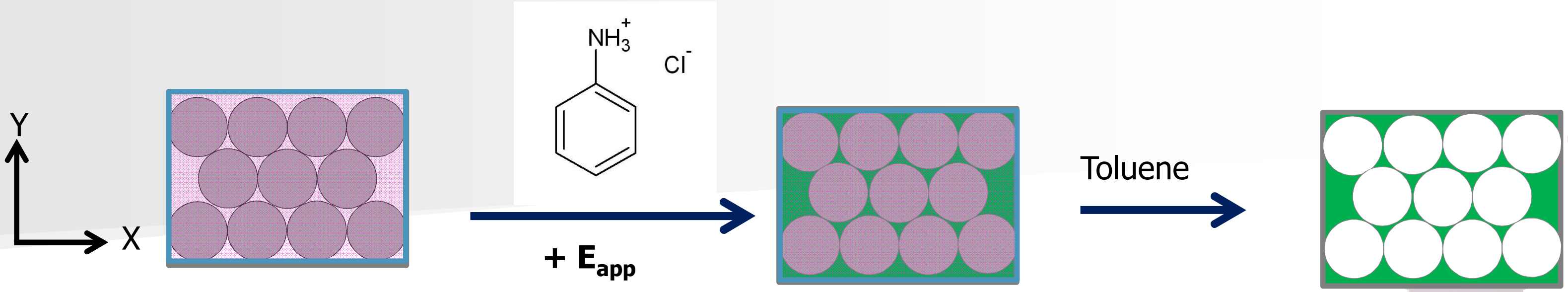


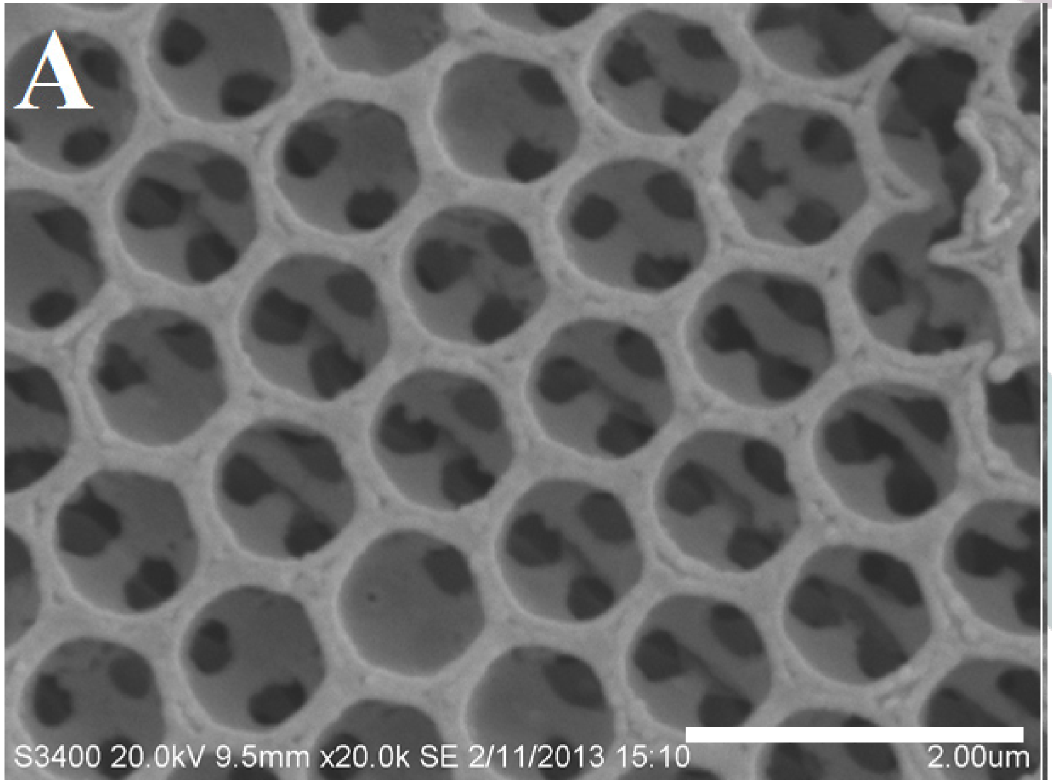




Gorey et al. (2013) Fabrication of a 3-dimensionally ordered binary colloidal crystal within a confined channel. Submitted to Chem. Mater.

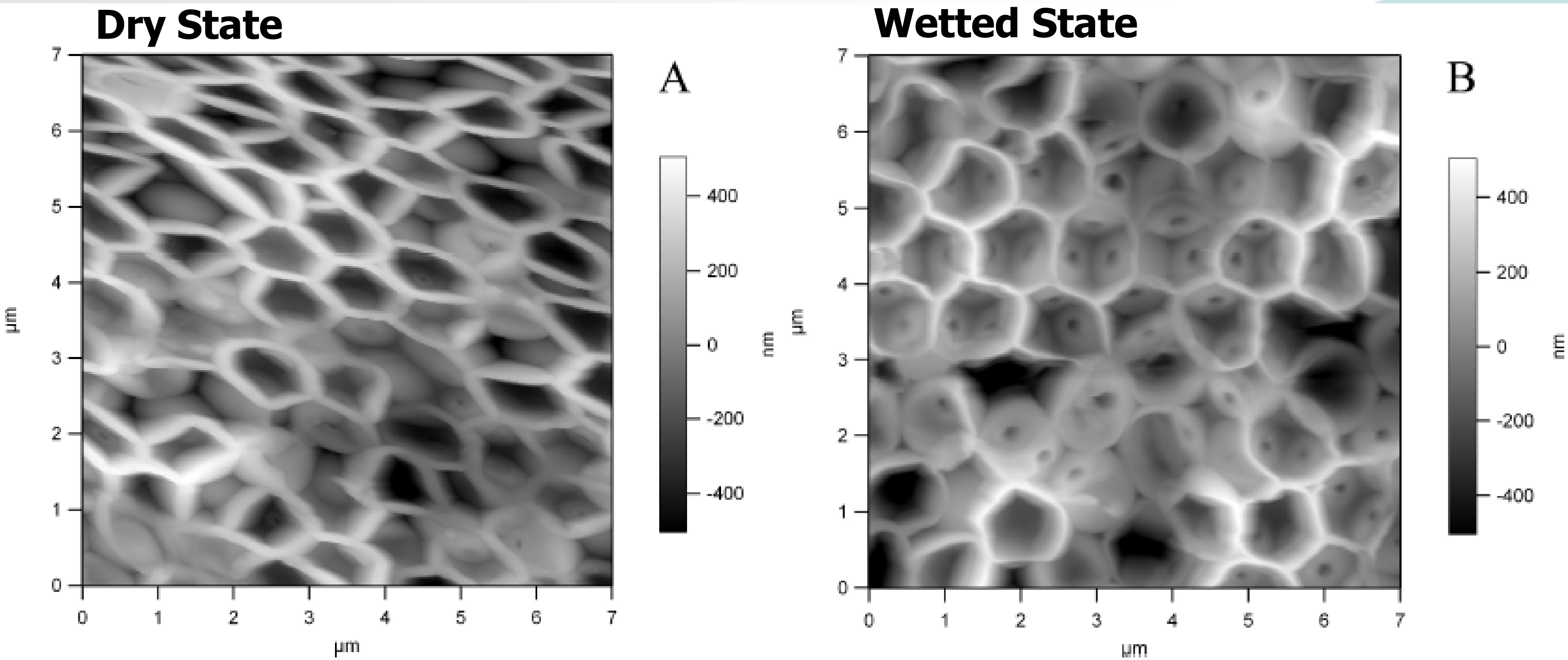
Conducting polymer monolithic structures



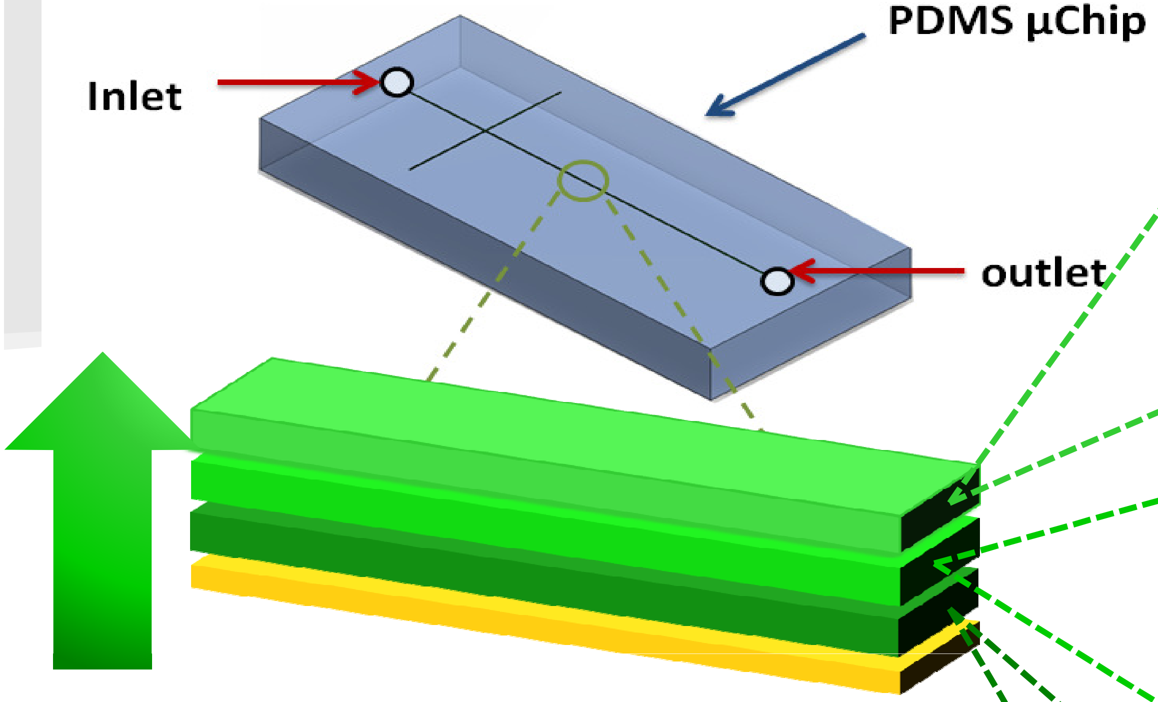


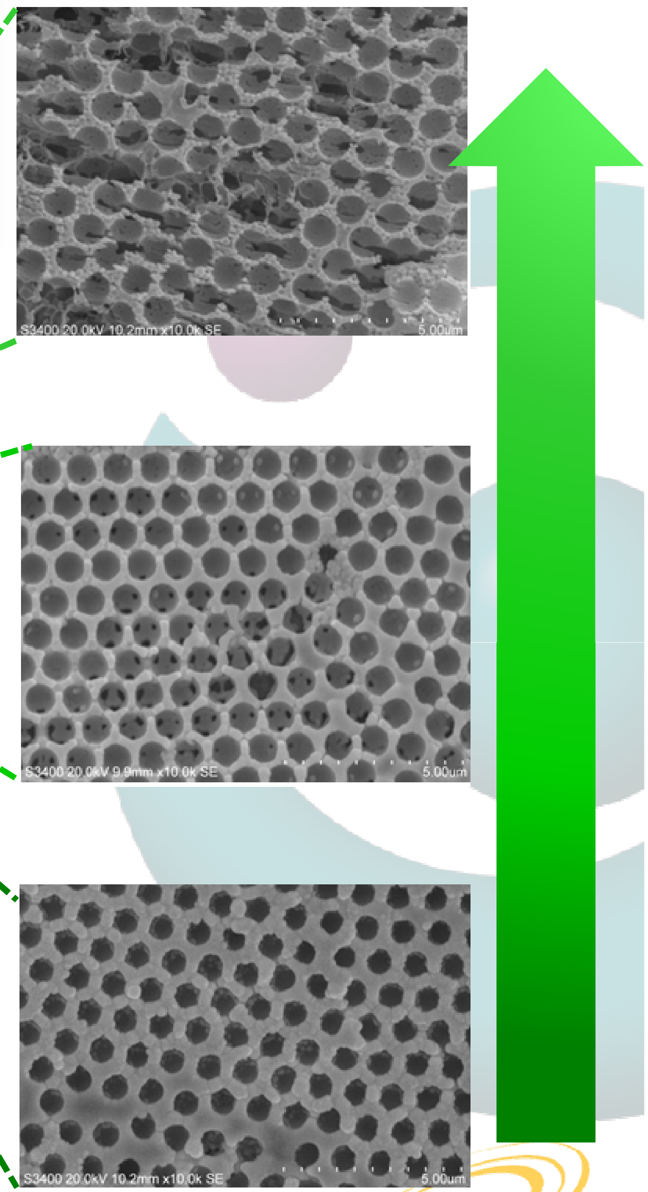
B. Gorey, J. Galineau, B. White, M.R. Smyth, A. Morrin, *Electroanalysis* **2012,** 24, 1318 - 1323

Dry & wetted states of CP monoliths - AFM



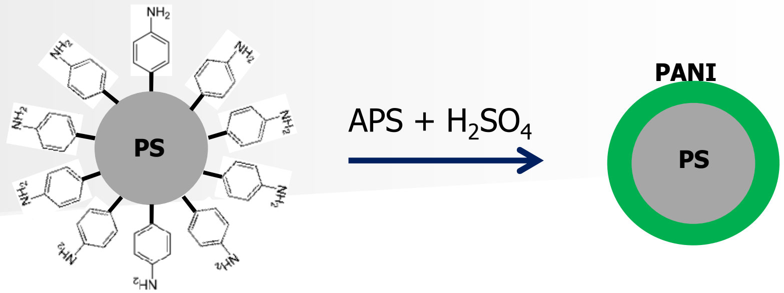
*Electrochemically grown Ppy doped with DBS

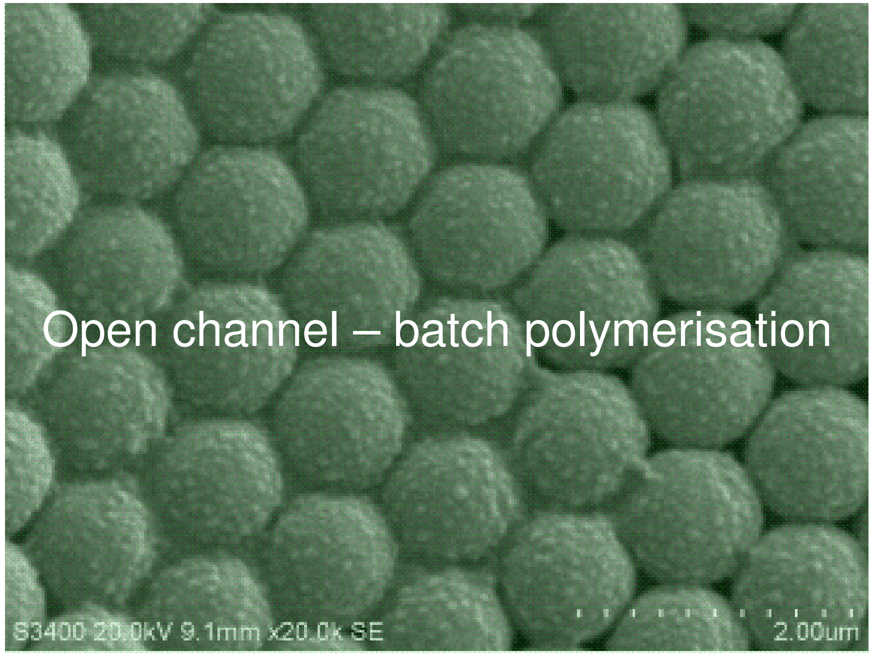


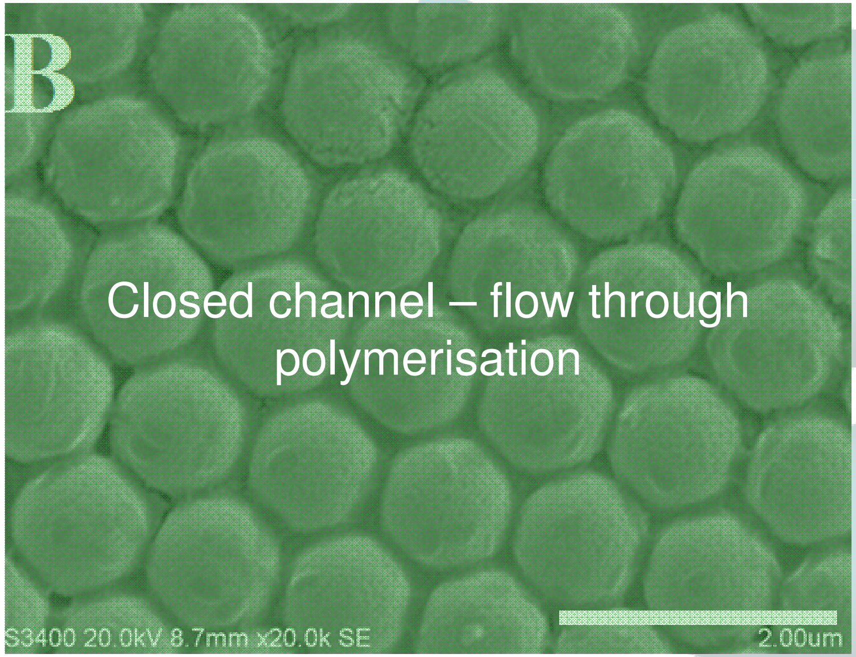


Decreasing current density as it grows away from electrode surface

Overcoming current density gradient using chemical polymerisation



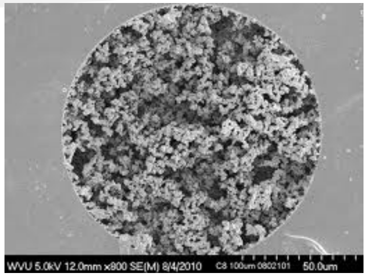




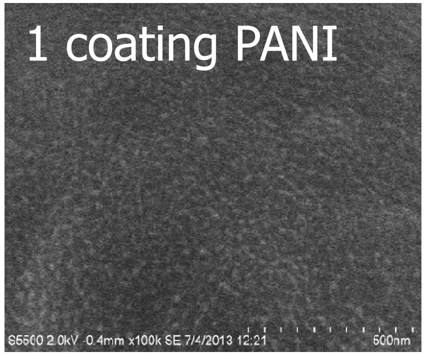
Core-shell flow-through bed comprised electroactive PANI

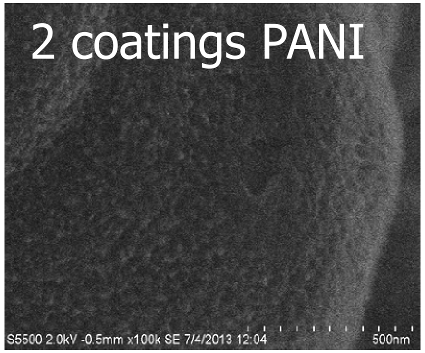
Fused silica capillary microfluidic channel

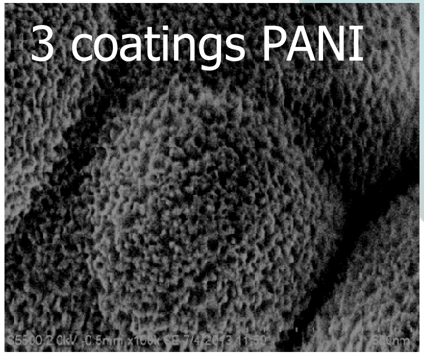
- In-situ polymerisation of styrene in the presence of a thermal initiator, a cross-linker, DVB and porogen, dodecanol



- Flush capillary with aniline, acid and oxidant



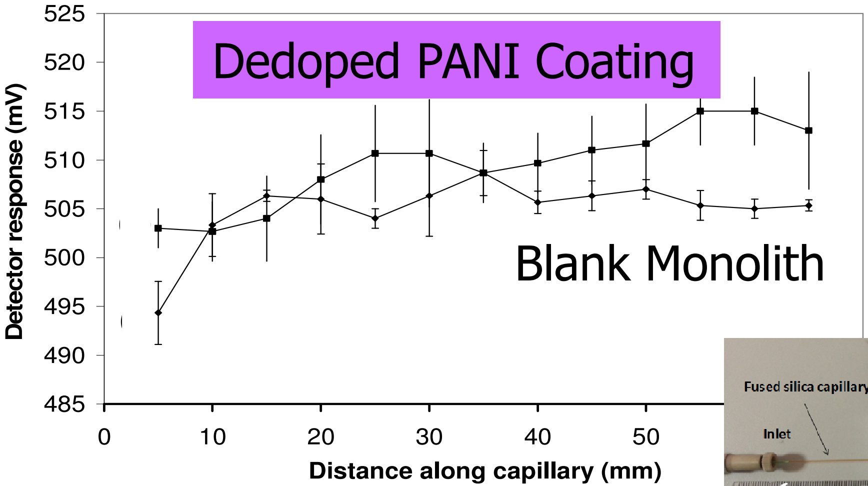


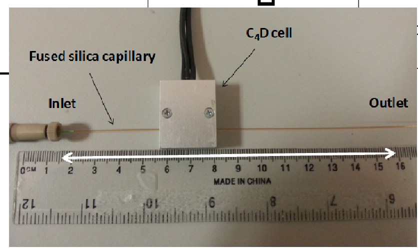


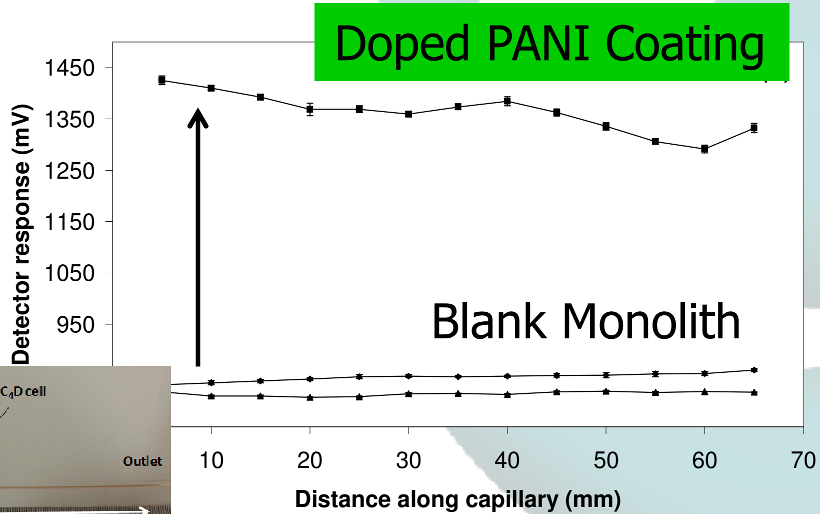
Characterisation of PANI-coated polymer monoliths

Switchable PANI-coated PS-co-DVB monolith

Decrease pH





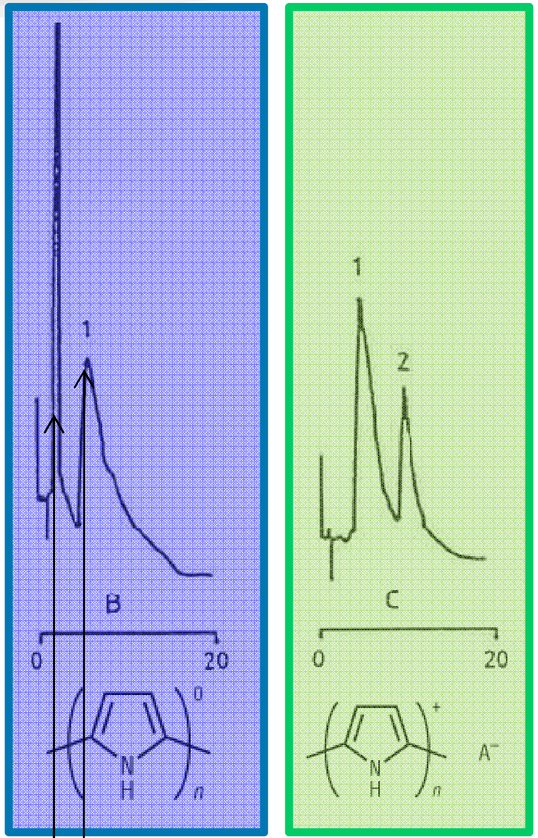


Current challenge is to integrate an electrochemical cell into this capillary format – control conducting polymer oxidation state by application of a potential

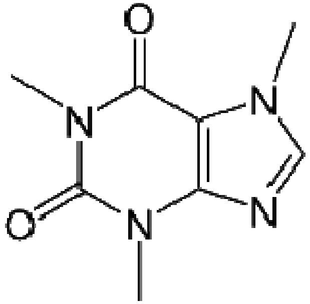
DCU

CPs as separation phases in particulate-based packings

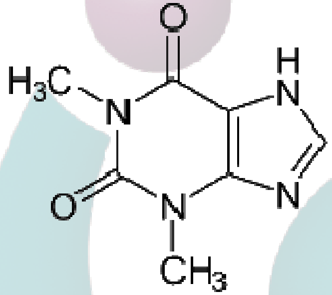
Reduced Oxidised



Caffeine
Theophiline



Caffeine



Theophylline

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

	k′ Caffeine	k′ Theophylline
Frc	2.6	2.2
red_1	2.7	0.1
oxd_1	2.3	2.0
red_2	2.4	0.1
oxd_2	2.1	1.8

*60% $MeOH/H_2O$ at 1 mL/min. Frc: fresh column; red: after column was treated with 0.1M Na_2SO_3; oxd: after column reoxidation with 0.1M $FeCl_3$.

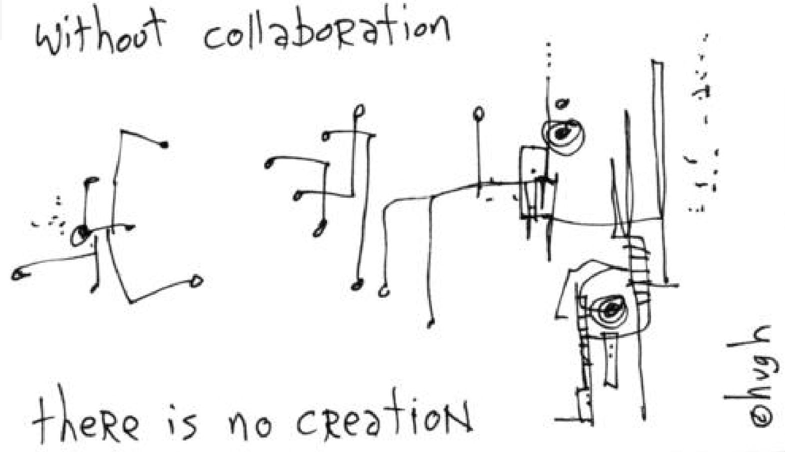
Chriswanto & Wallace, J. Liq. Chrom. & Rel Technol., 19:2457 (1996)

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



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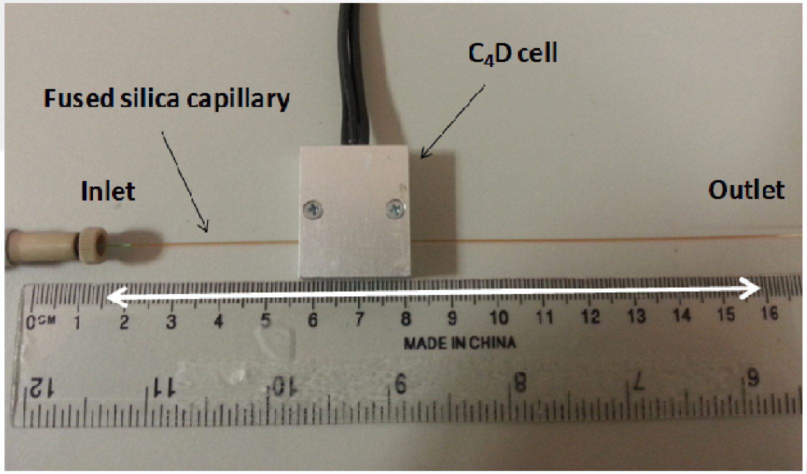
Characterisation of PANI-coated polymer monoliths



Scanning capacitively coupled contactless conductivity detection (sC[4]D)