Smart Polymers in Microfluidics for Lab-On-A-Chip Applications

Aoife Morrin

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QS World University Rankings
Top 50
Under 50
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NCSR
National Centre for Sensor Research

bdi
bio medical diagnostics institute

MESTECH
Marine & Environmental Sensing Technology Hub

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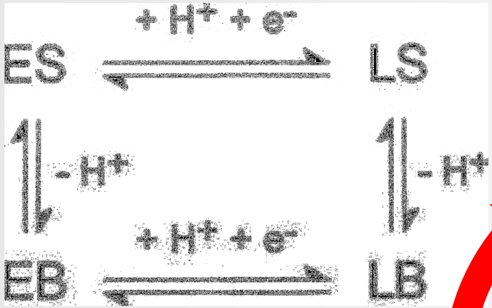

ES
+ H+ + e-
LS
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- H+
EB
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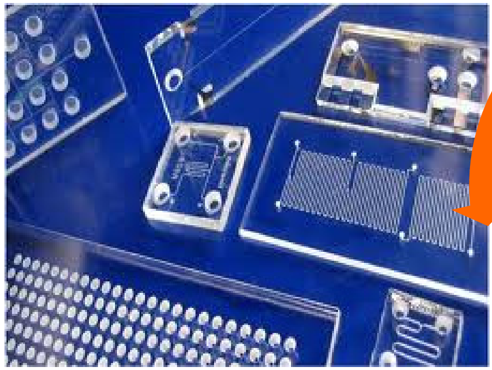
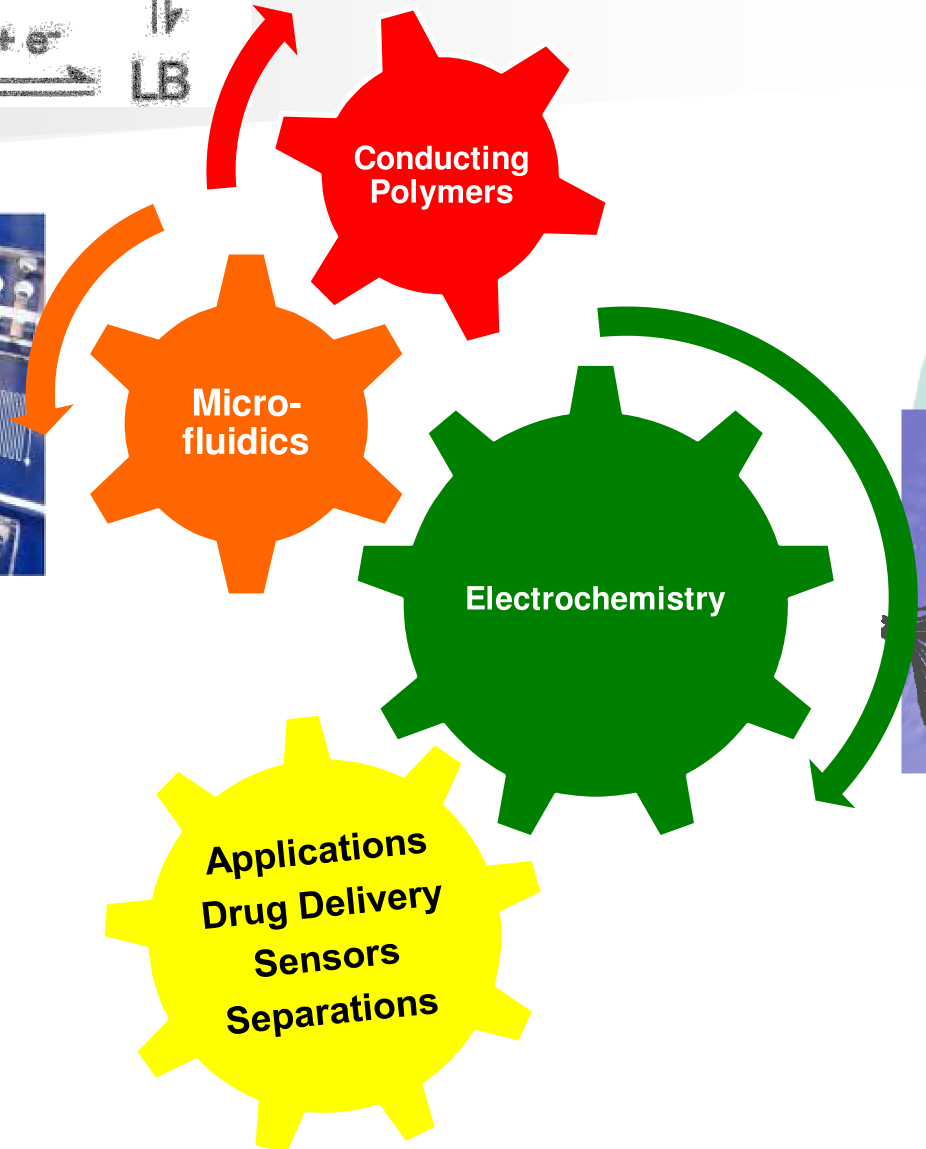
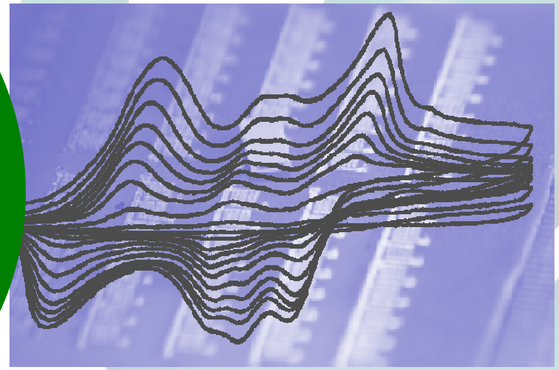
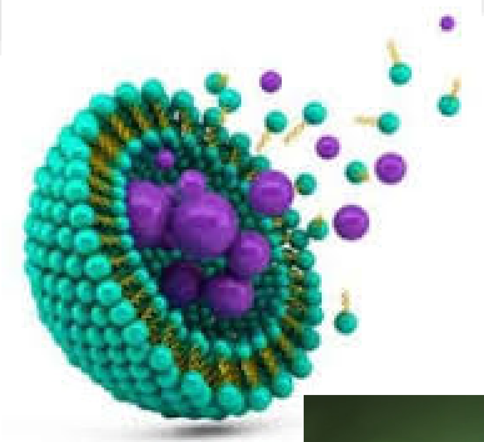


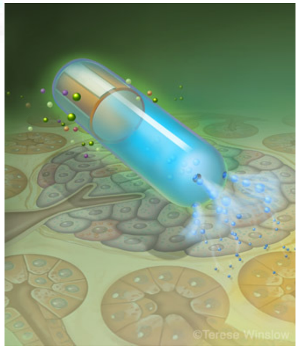


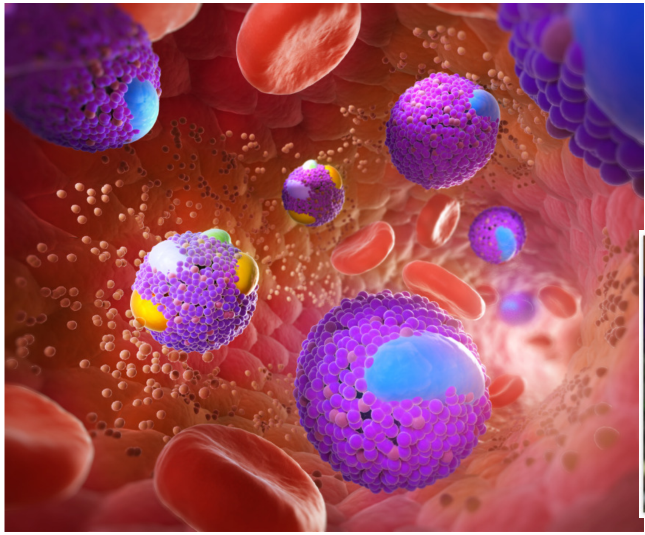
Conducting Polymers
Micro-fluidics
Electrochemistry
Applications
Drug Delivery
Sensors
Separations



.....To Solve Healthcare Challenges

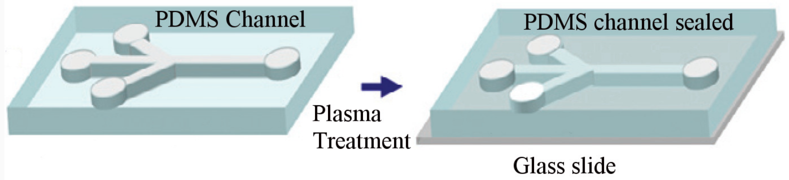




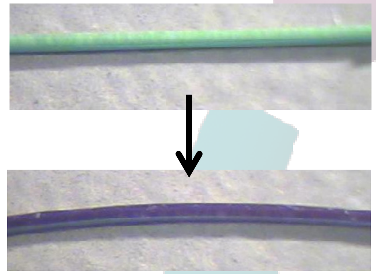


So….How Do We Build 'Em?

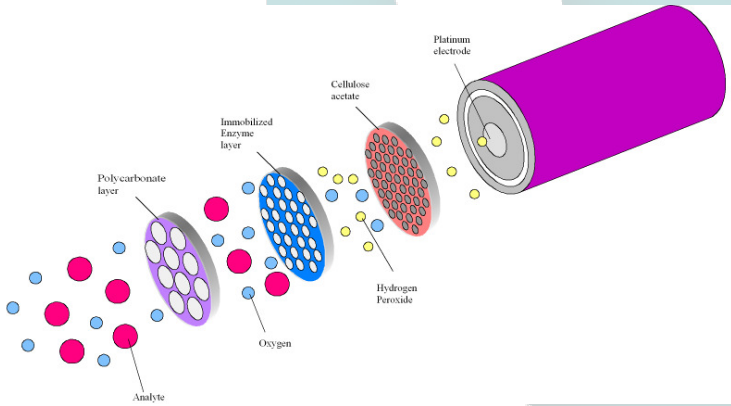
- Enabling Microfluidic Platforms



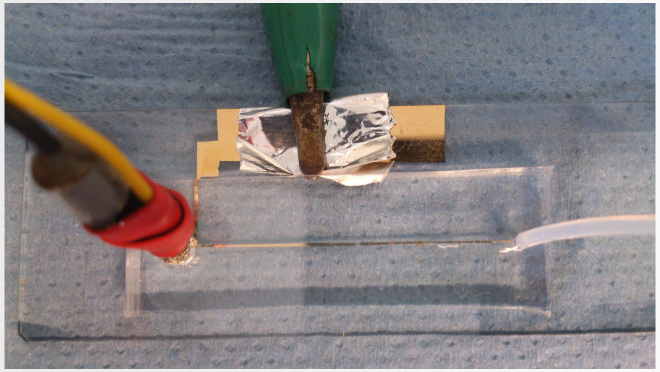
- Smart Materials Integration
  - And detection mechanism

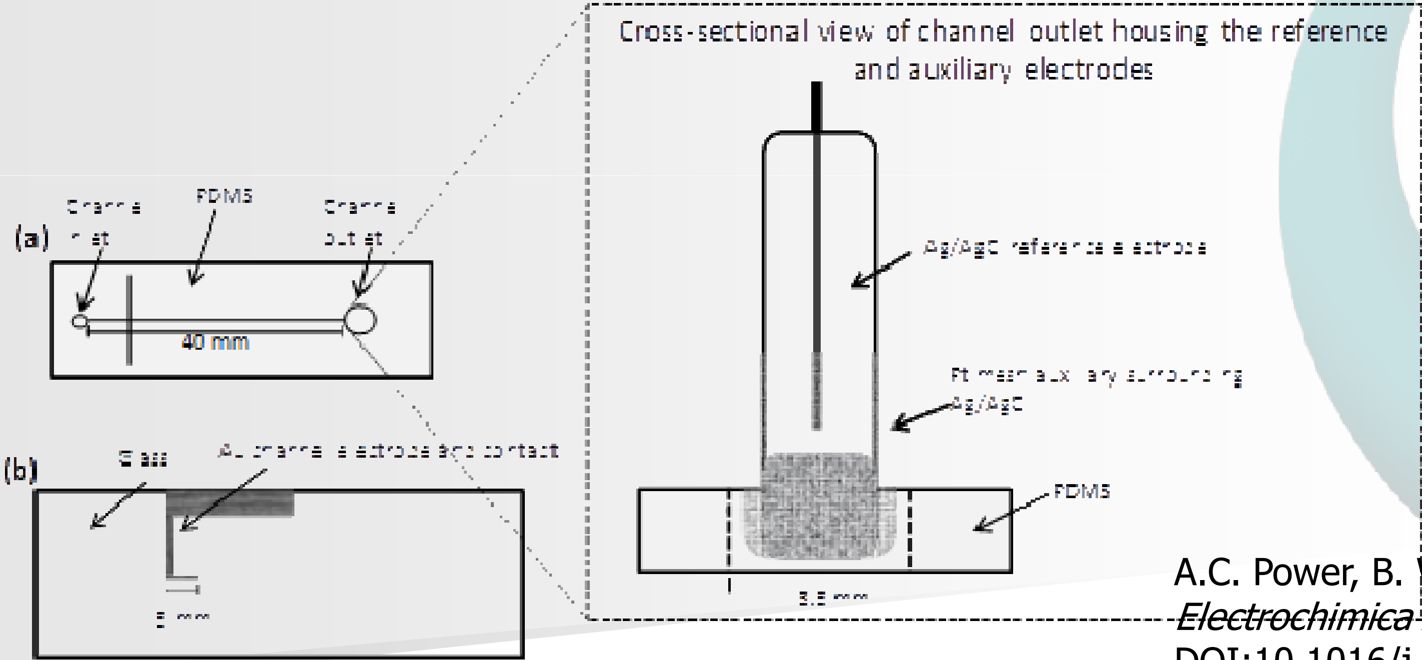


- Tailor for Application
  - Urea detection in serum
  - Ammonia detection in breath
  - Glucose detection in saliva
  - Cholesterol detection in whole blood



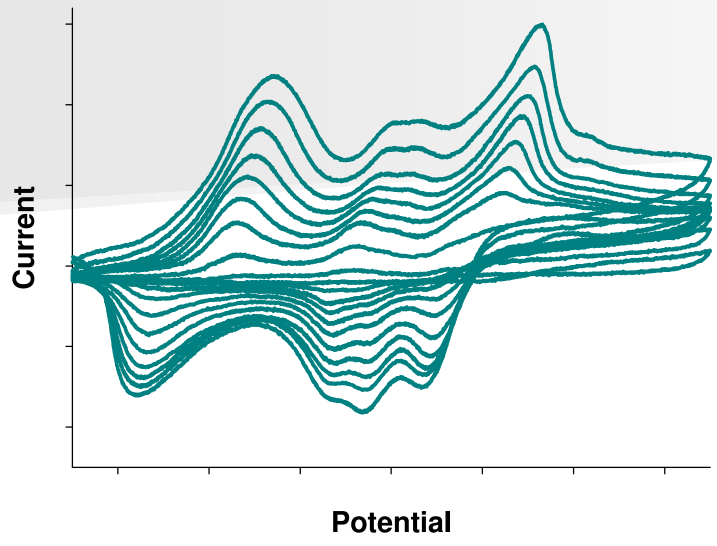
Direct Incorporation of Electrochemistry into Microfluidics

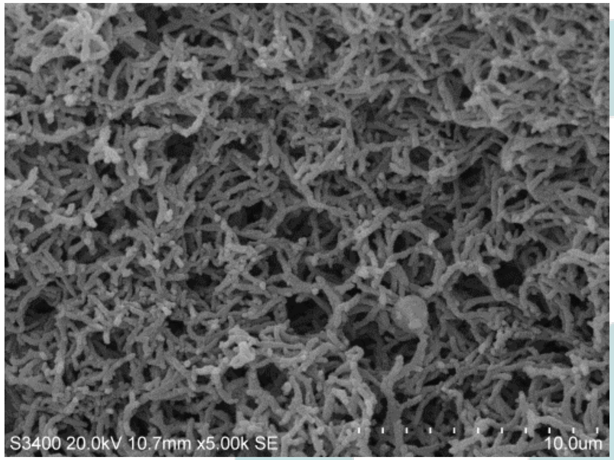


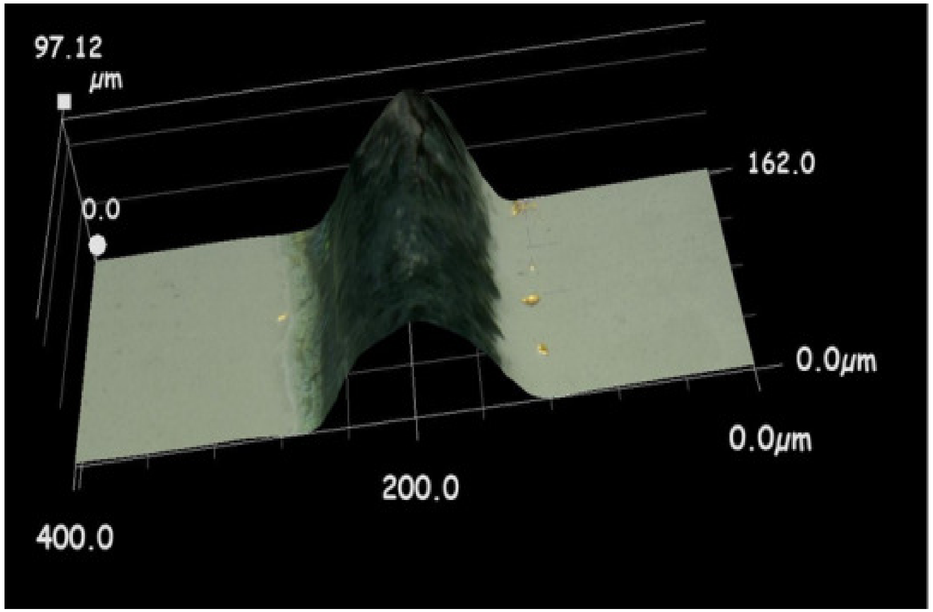


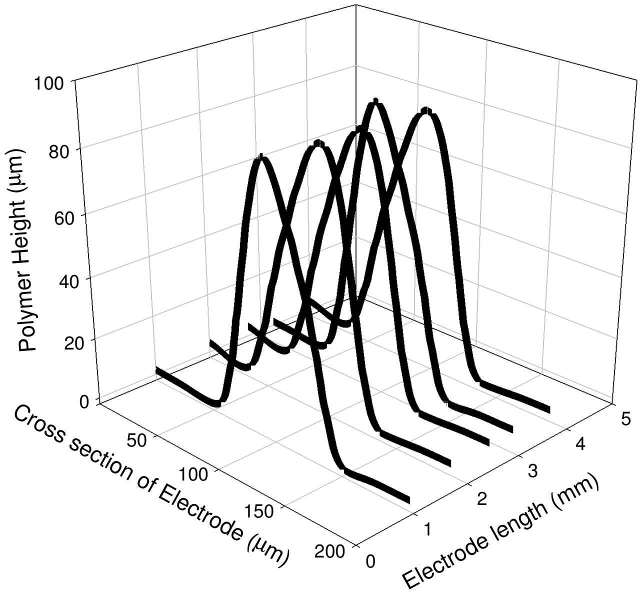
A.C. Power, B. White, A .Morrin, *Electrochimica Acta* , 2013, DOI:10.1016/j.electacta.2013.04.091

Conducting polymers on-chip

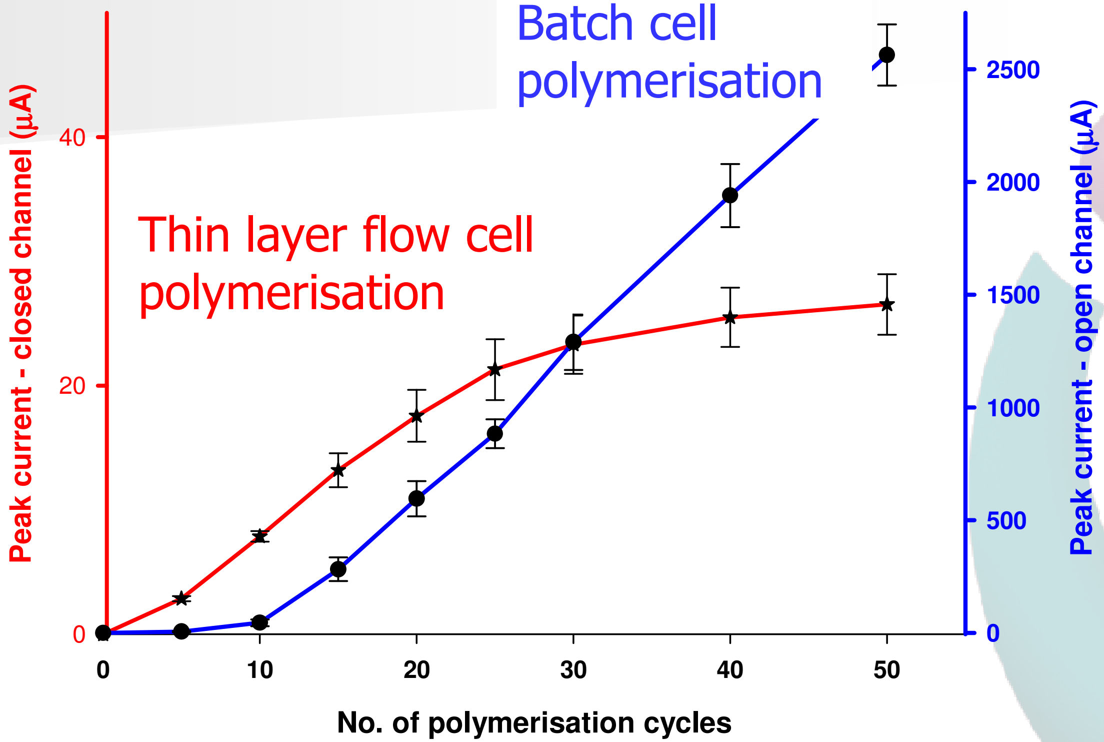








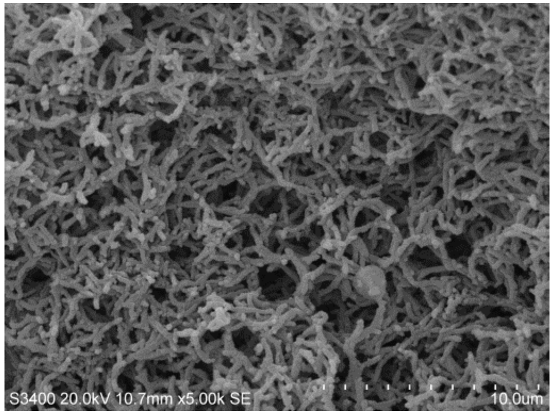
PANI electrochemical growth behaviour in channels

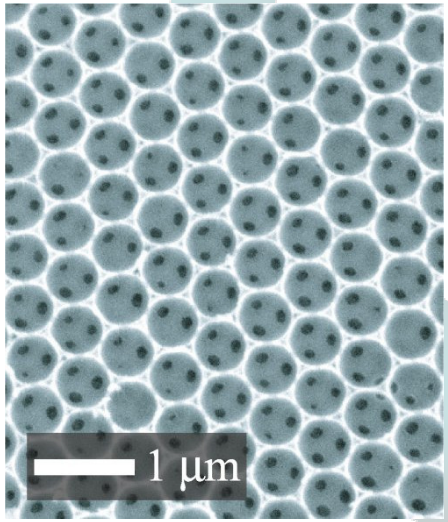


Channel depth (µm)	Average PANI thickness (µm) after 50 polymerisation cycles
35	7.53 ± 0.24
60	27.70 ± 6.58
110	49.93 ± 1.53
180	80.53 ± 6.84

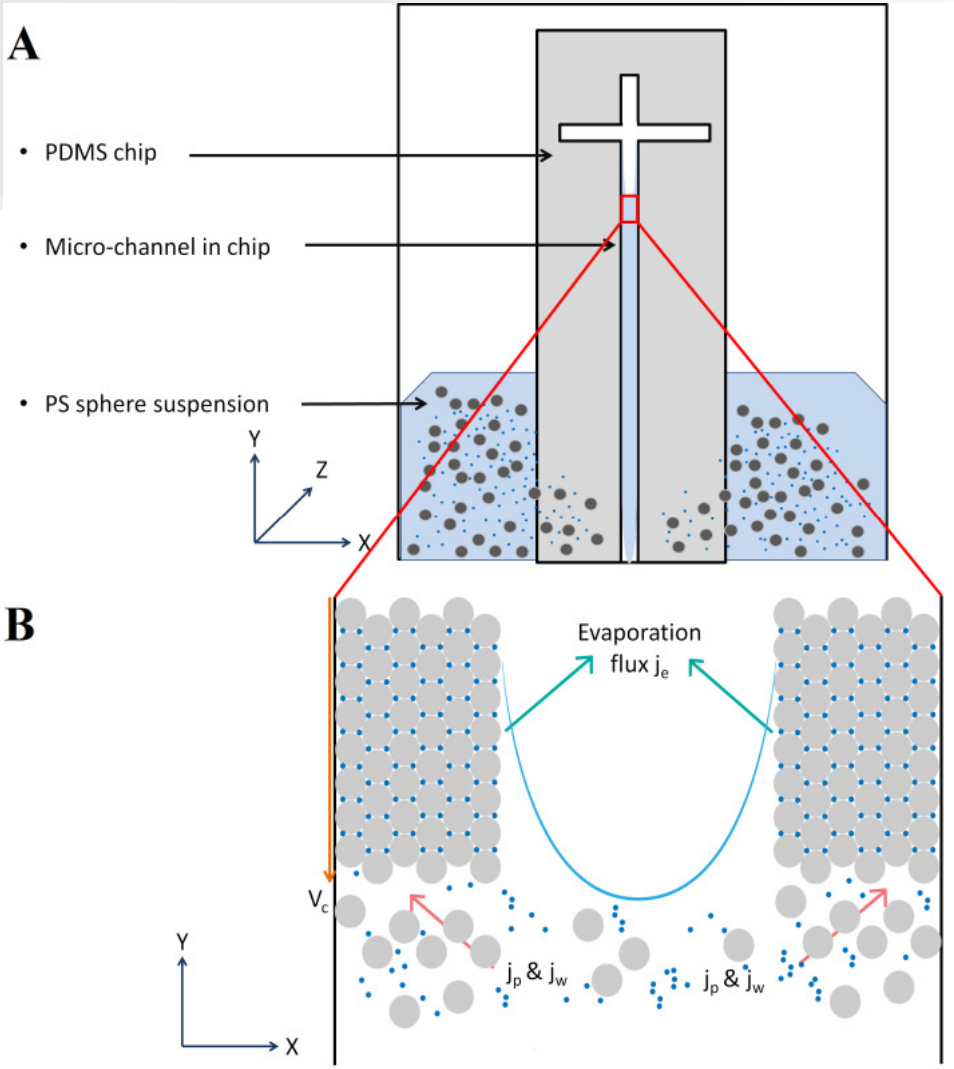
Can We Template These Materials On-Chip?

- By creating inverse opal conducting polymer monolithic materials through sacrificial CC templates within channel
- High surface area monolithic structures for predictable flow profiles, electrochemically responsive chromatography, drug delivery, flow through sensors on chip, etc

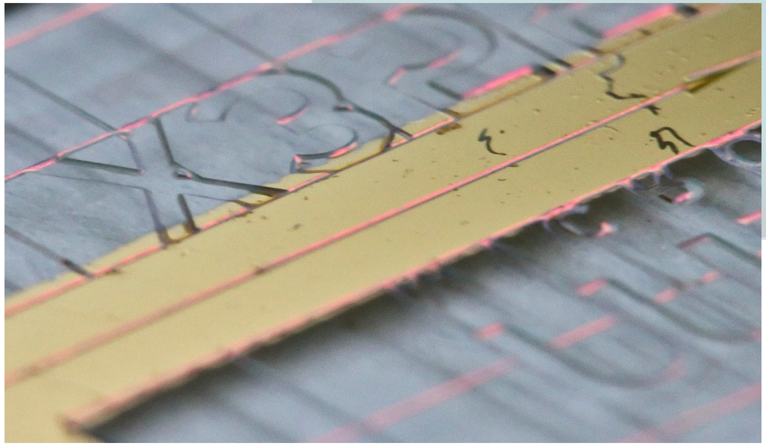




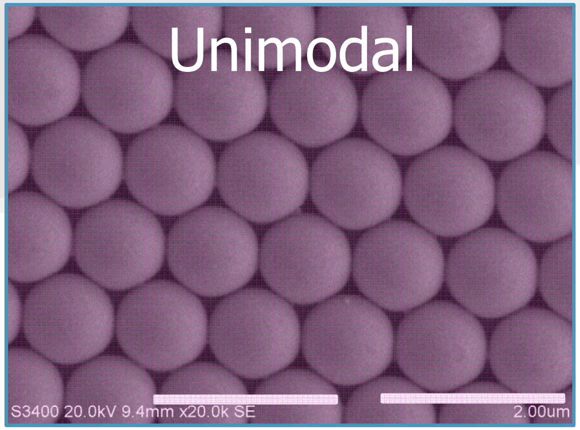
Colloidal Crystal Formation On-Chip

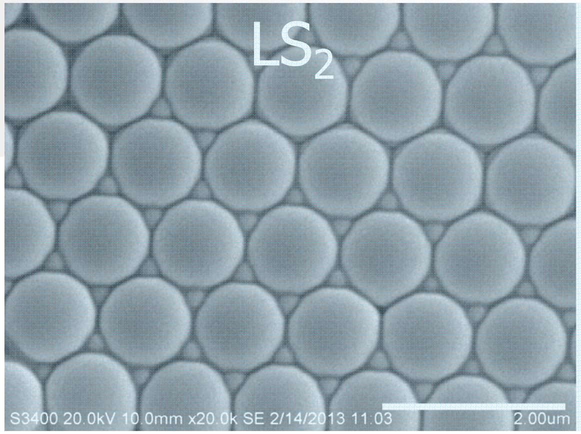


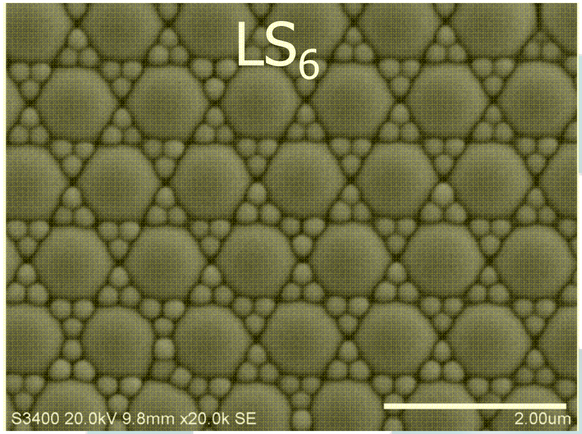
1) Capillary flow of PS suspension into channel
2) Pinning of PS suspension to walls of the channel - evaporation flux, j_e
3) Receding of meniscus line with continuous colloidal crystal growth – particle flux, j_p and water flux, j_w

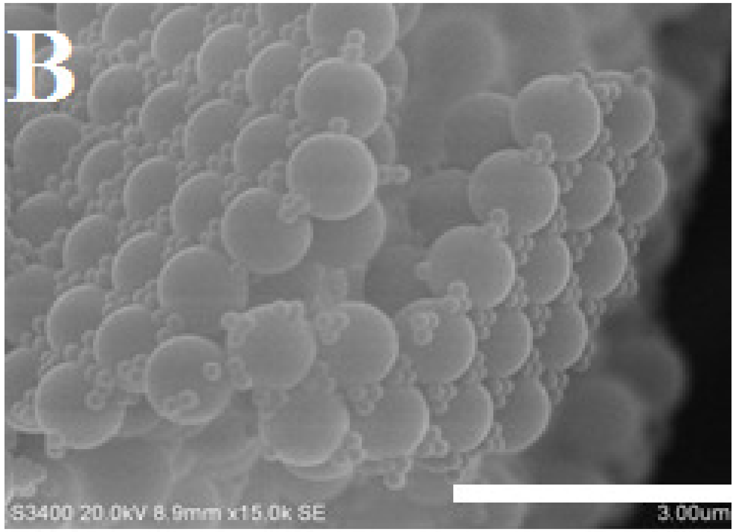


Optimised CC Structures In Microchannels









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

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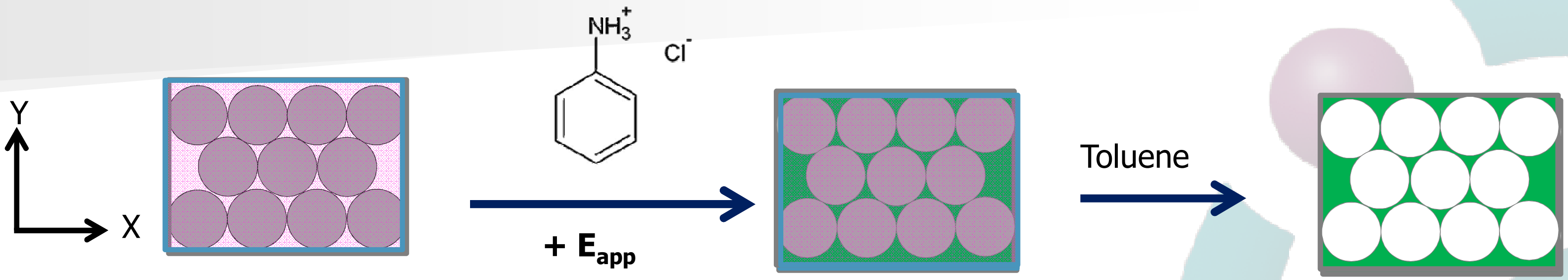
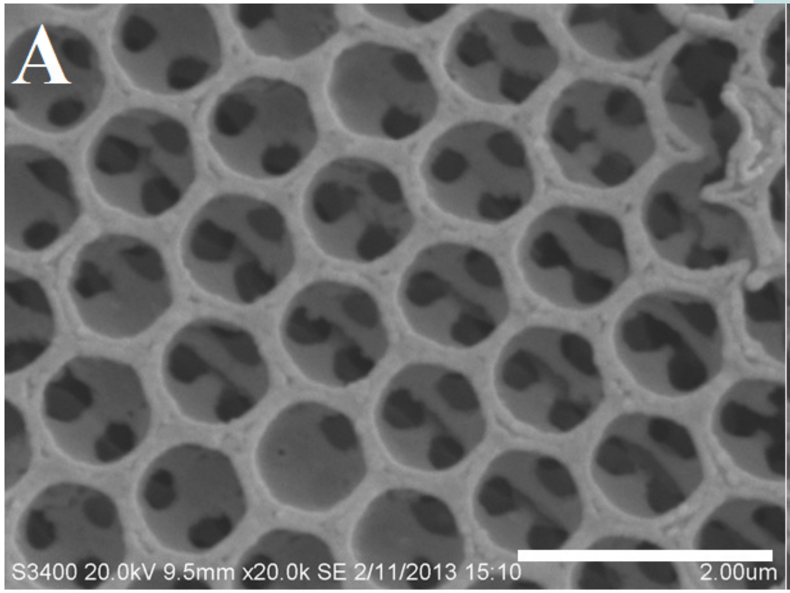
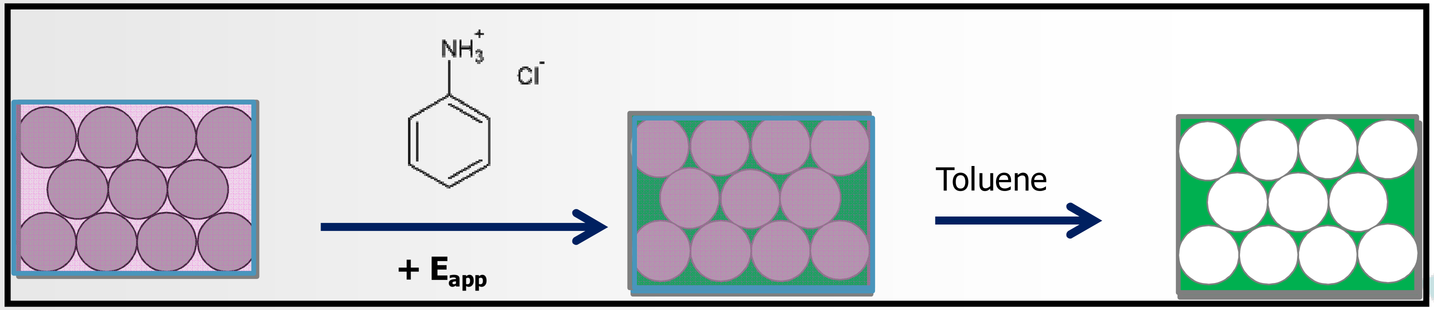
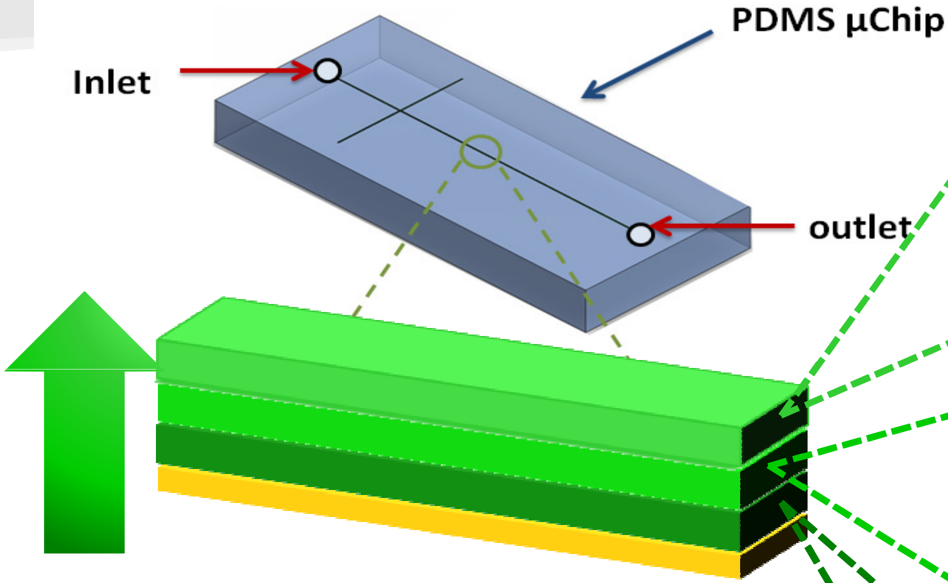
PANI Inverse Opal Monoliths On-Chip – Electrochemical Synthesis

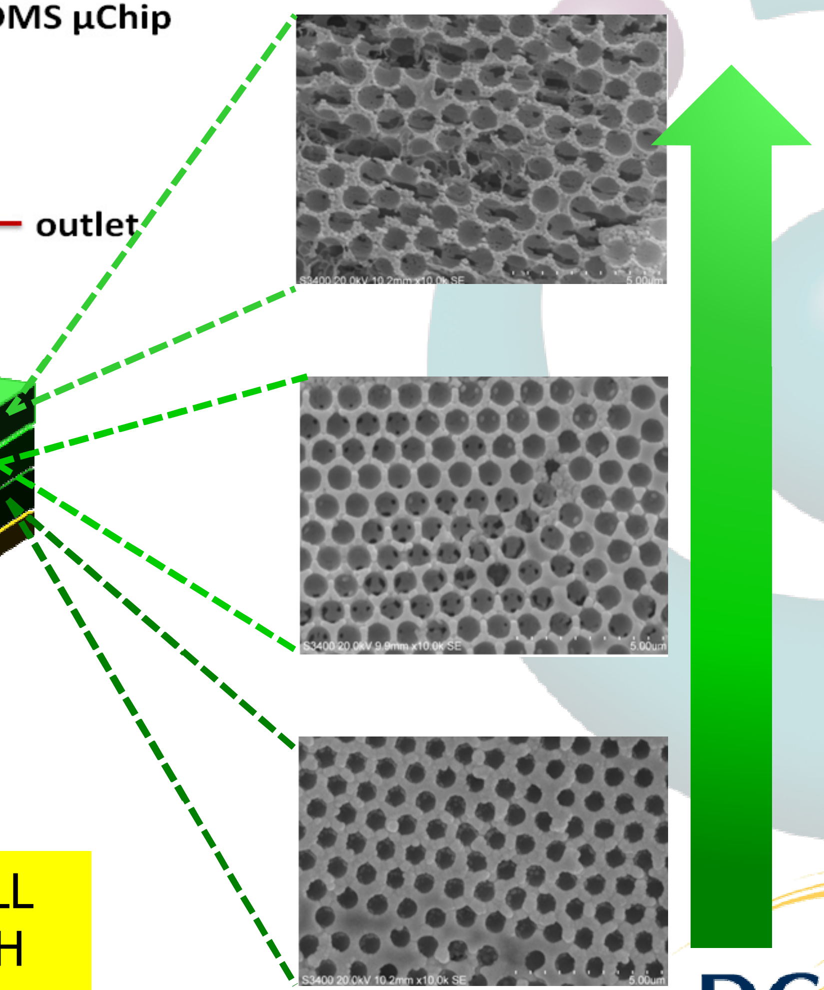




B. Gorey, J. Galineau, B. White, M.R. Smyth, A. Morrin, *Electroanalysis* **2012,** 24, 1318 - 1323



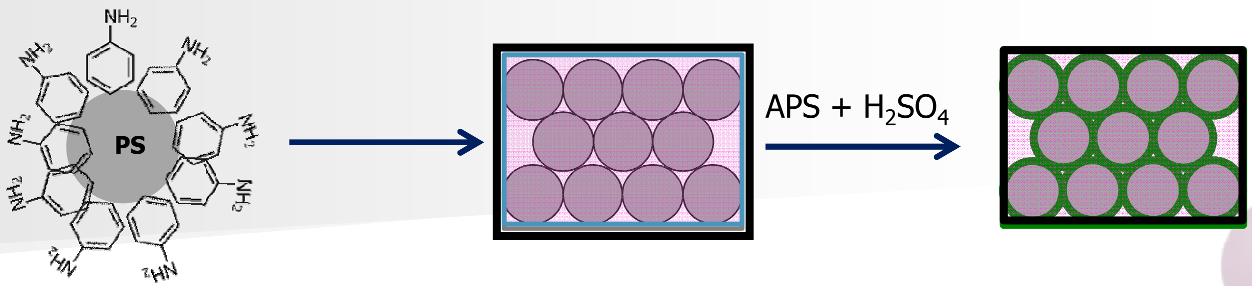


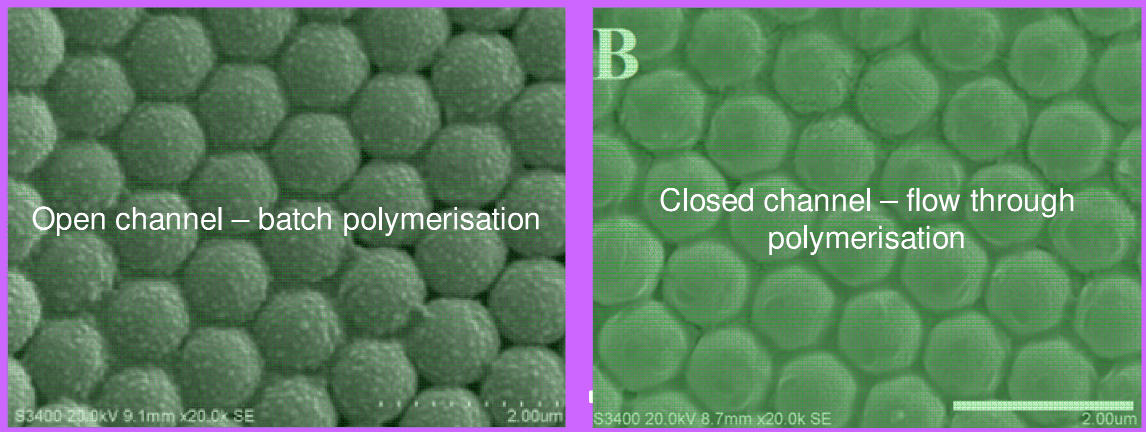


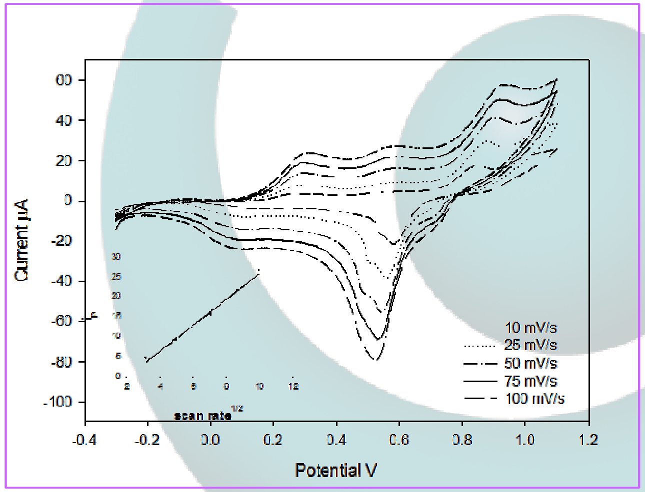
Decreasing current density as it grows away from electrode surface

SOFT MATERIAL – WILL NOT WITHSTAND HIGH PRESSURES

PANI Monoliths On-Chip - Chemical Polymerisation





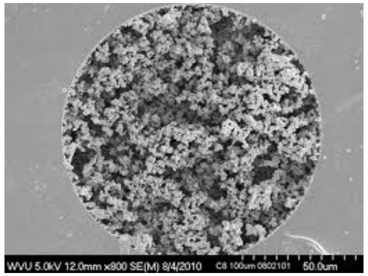


Core-shell flow-through bed comprised electroactive PANI

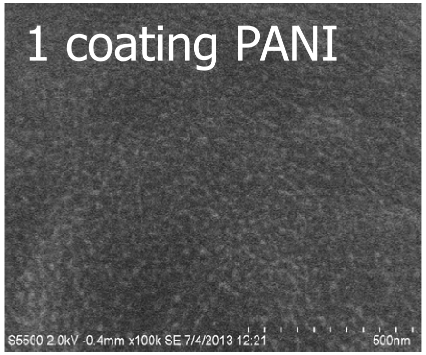
Overcomes self-limiting nature of electrochemical polymerisation
Overcomes gradient issues of electrochemical polymerisation
Overcomes structural integrity issues….to a point…..

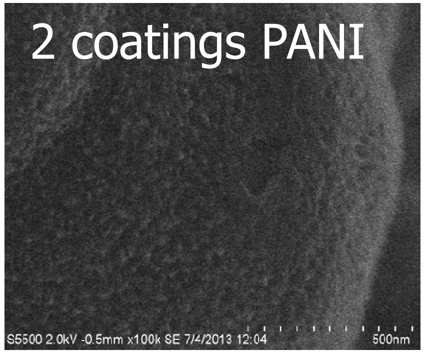
From Beads…to Monolithic PS supports

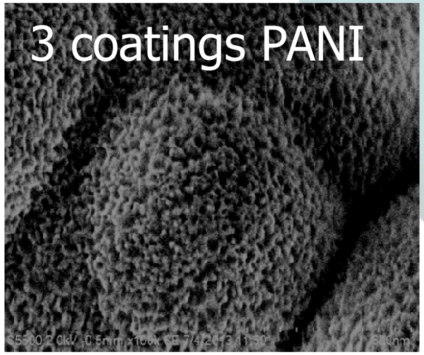
- In-situ polymerisation of styrene in the presence of a thermal initiator, a cross-linker, DVB and porogen, dodecanol



- Flush capillary with aniline, acid and oxidant

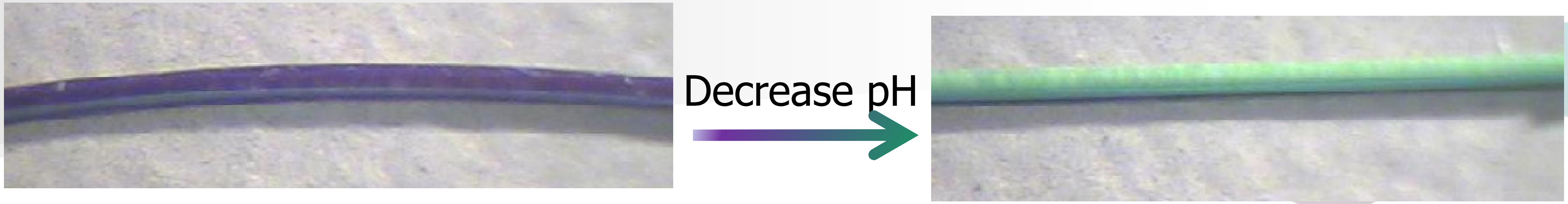


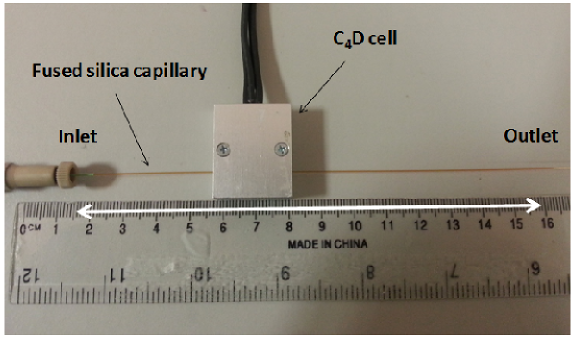


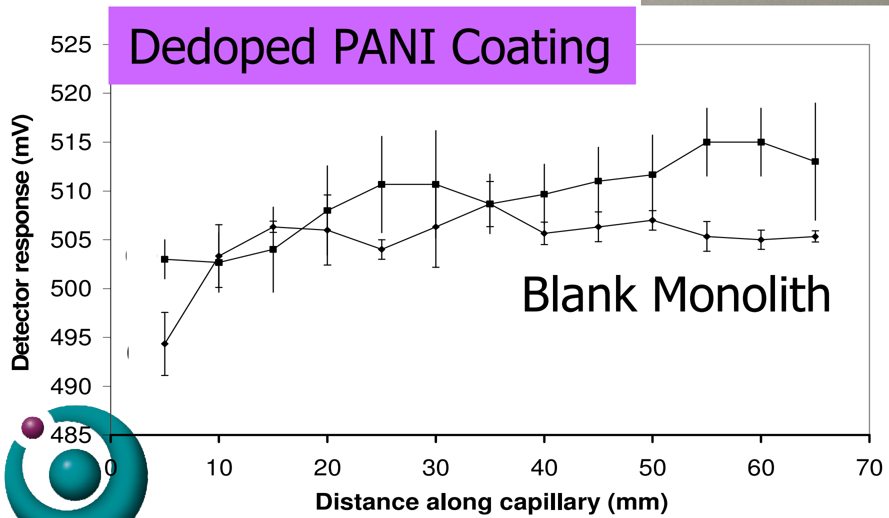


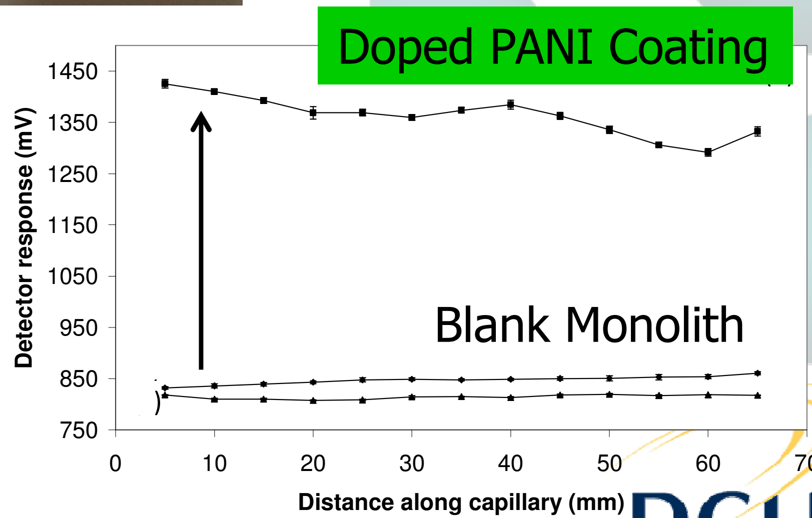
Characterisation of PANI-coated polymer monoliths

Switchable PANI-coated PS-co-DVB monolith

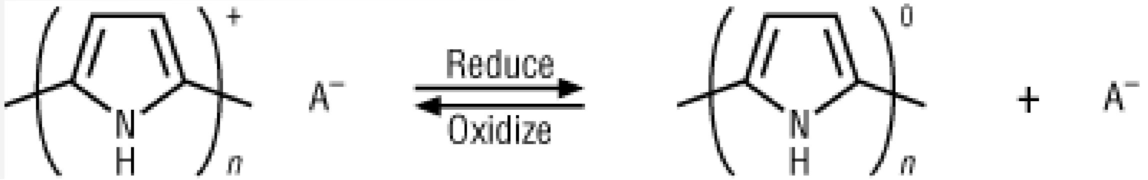




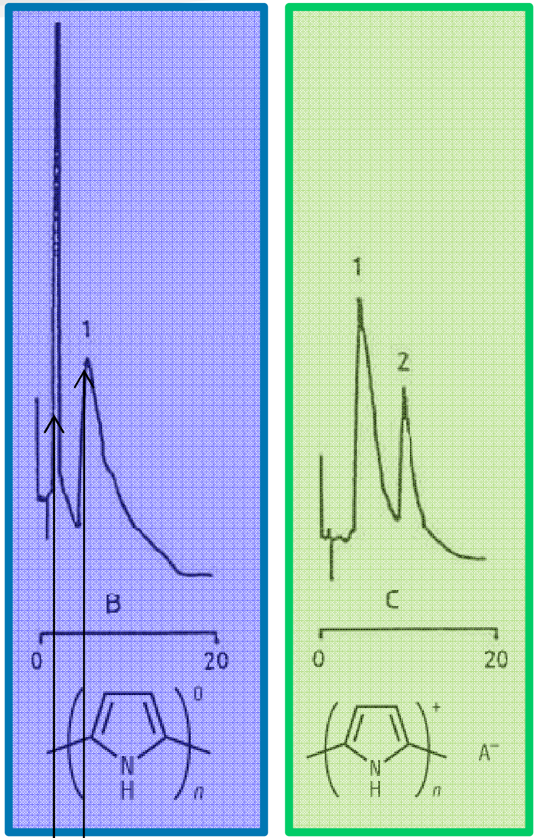




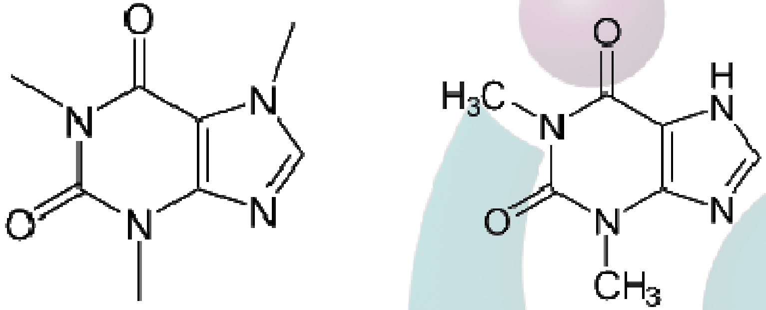
Conducting Polymers as Stationary Phases – particulate packings



Reduced Oxidised



Caffeine
Theophiline



Caffeine Theophylline

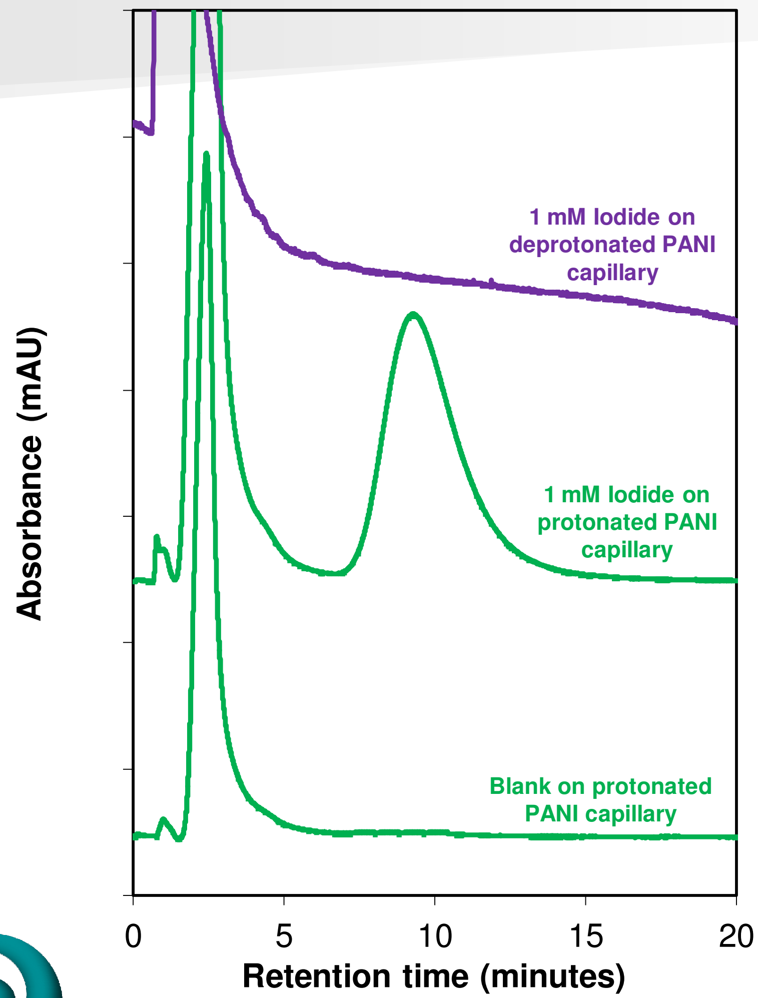
Retention of Caffeine and Theophylline on PPCl/Si as a Function of the Treatment of the Column with Redox Reagent*

	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)

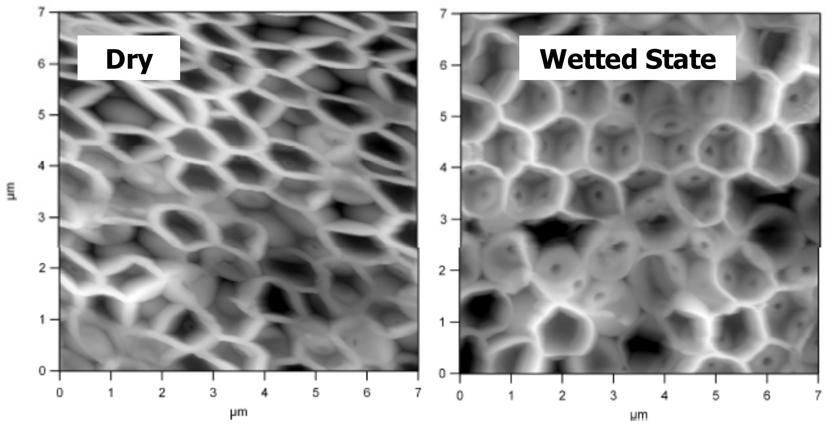
Conducting Polymers as Stationary Phases - Monoliths

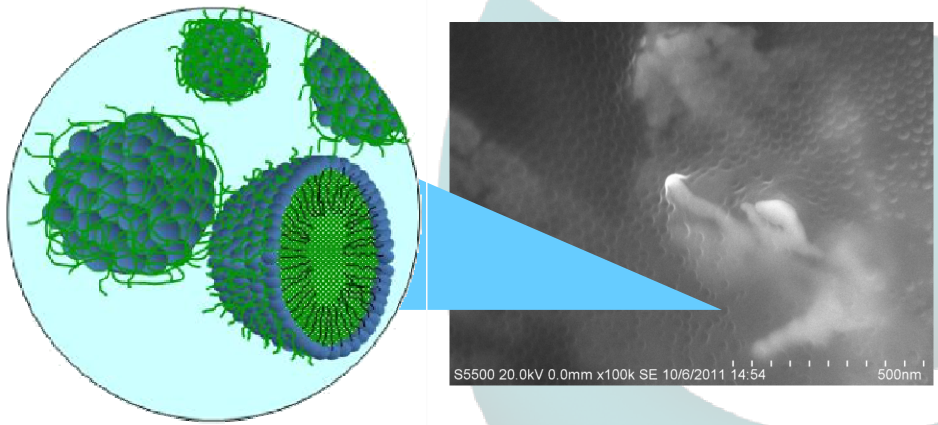


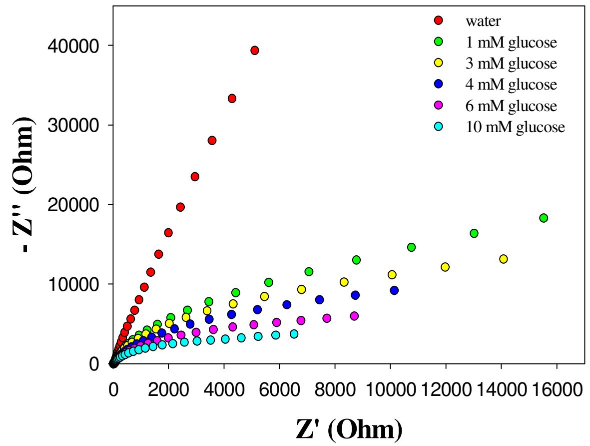
Current challenge is to use electrochemistry to switch polymer state
-Drug delivery
- Stimuli-responsive chromatography

Processable "Smart" polymers

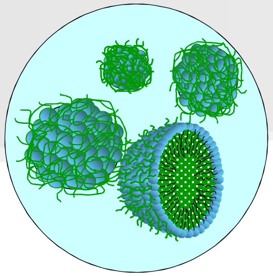
Decrease pH

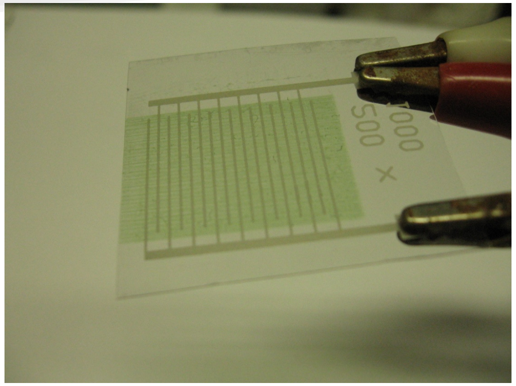


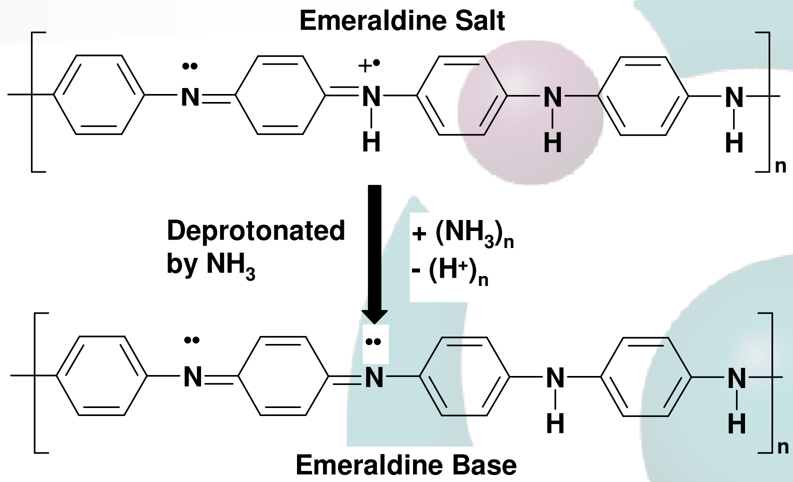




Inkjet printed PANI nanoparticles for ammonia gas and ammonium ions

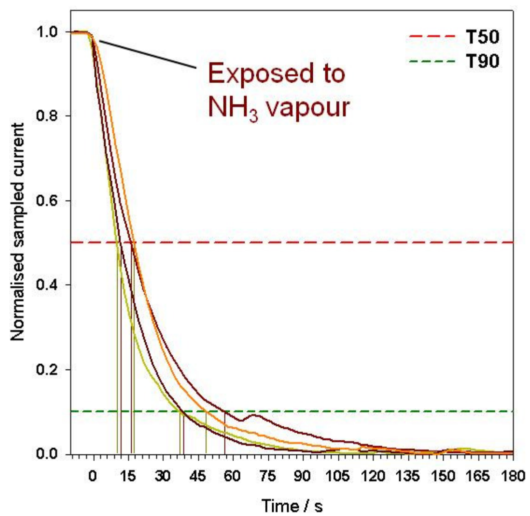






IDEs fabricated by screen printing

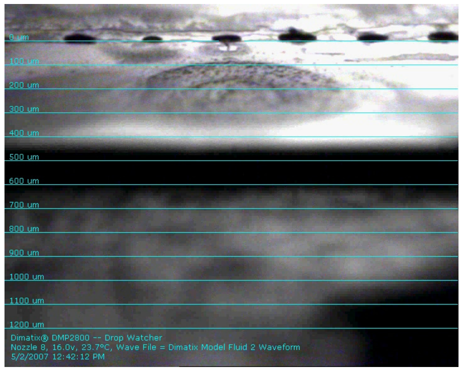
PANI nanoparticles inkjet printed onto silver interdigitated (IDE) design

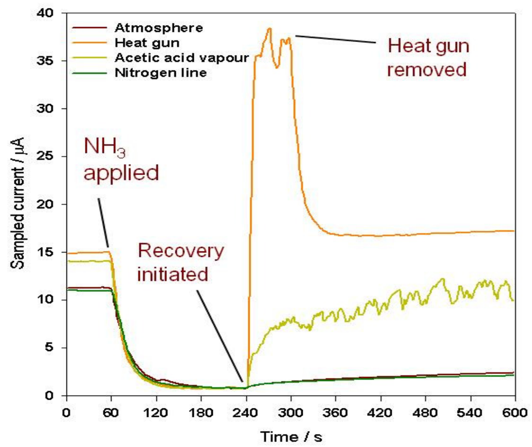


Early days...(circa early 2007)

- Sensors inkjet printed using commercial printers Epson C42/C46
- Cartridges emptied and refilled with nanoPANI formulation
- Unreliable, contact method

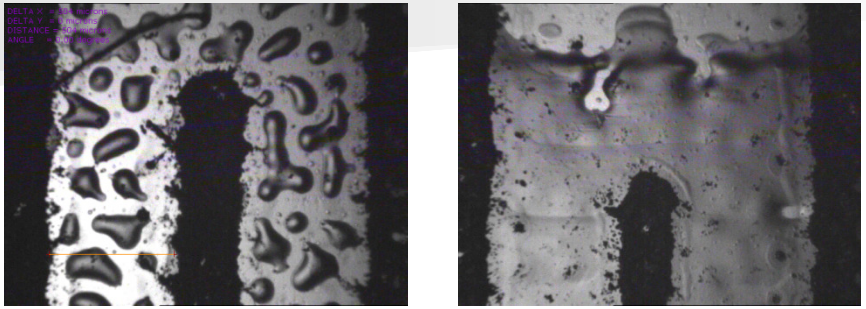
And now….Dimatix Materials Printer 2831



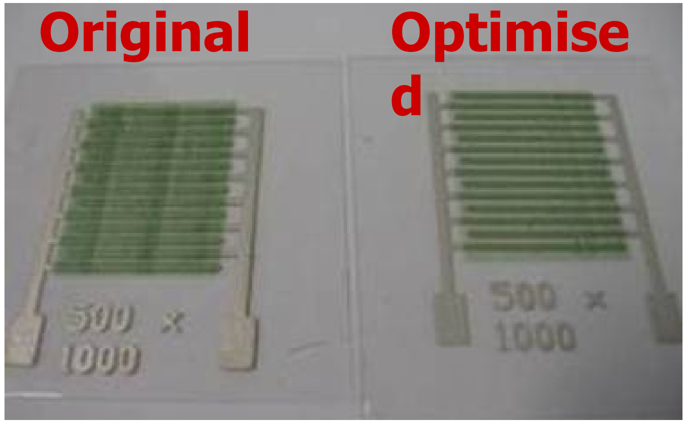


Inkjet Printing Overview

A) Film optimisation



Example of substrate/ink mismatch. Hydrophilic ink (PANI-PMAS) on hydrophobic surface (PET) leads to discontinuous



Many parameters affect quality:

- Piezo potential (16 V default)
- Pitch (dot spacing)
  - typically 10 – 50 μm
  - Too low – discontinuous films
  - Too high – beading.
- Nozzle temp (ambient to 70℃)
  - reduce viscosity
- Stage temp (ambient to 60℃)
  - faster drying times
- Many others…
  - Applied waveform
  - Fluid rheology, substrate surface energy....

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