Conducting Polymers In μChannels For Electroanalytical Applications

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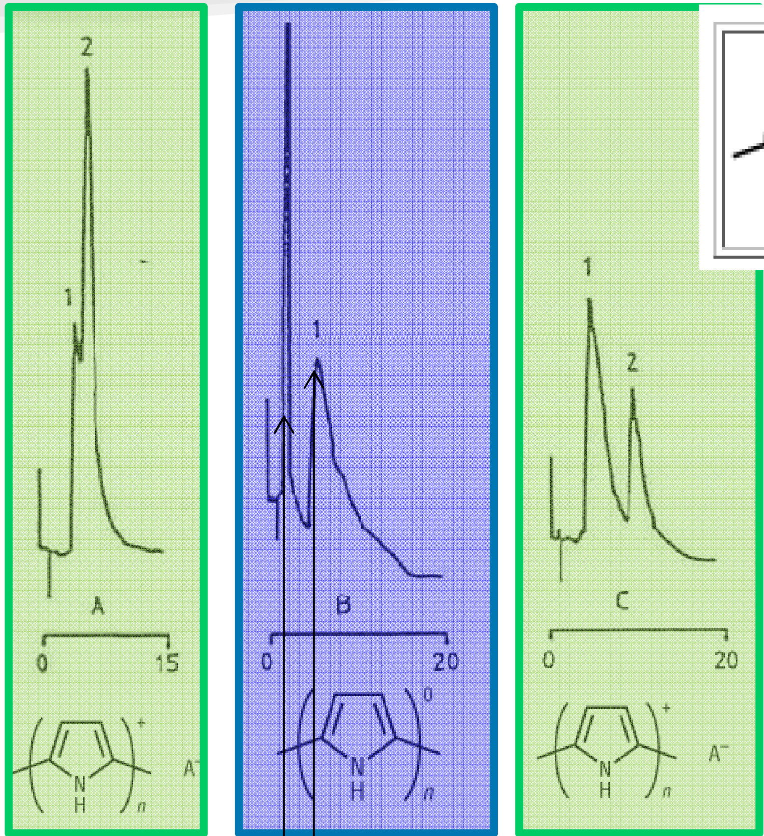
Outline

- Conducting polymers in electroanalytical applications
- Conducting polymers applied in separation science
- EMμ concept
- Development of a microfluidic-based thin-layer electrochemical cell
- Microstructure 3D monoliths of conducting polymers on-chip
- Look towards applications

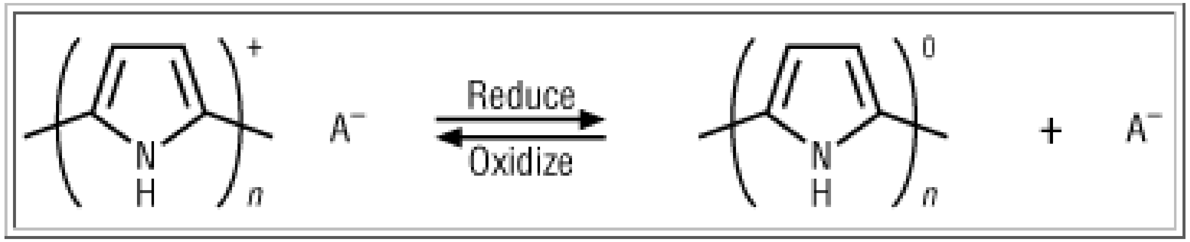
CPs as separation phases in particulate-based packings

Fresh Reduced Oxidised



Caffeine

Theophiline



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 $FeCl_3$.

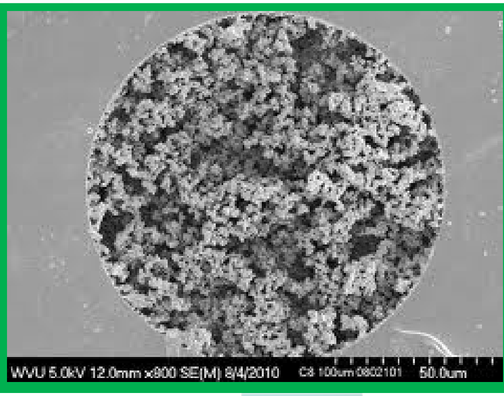
Chriswanto & Wallace, J. Liq. Chrom. & Rel Technol., 19:2457 (1996)

DCU

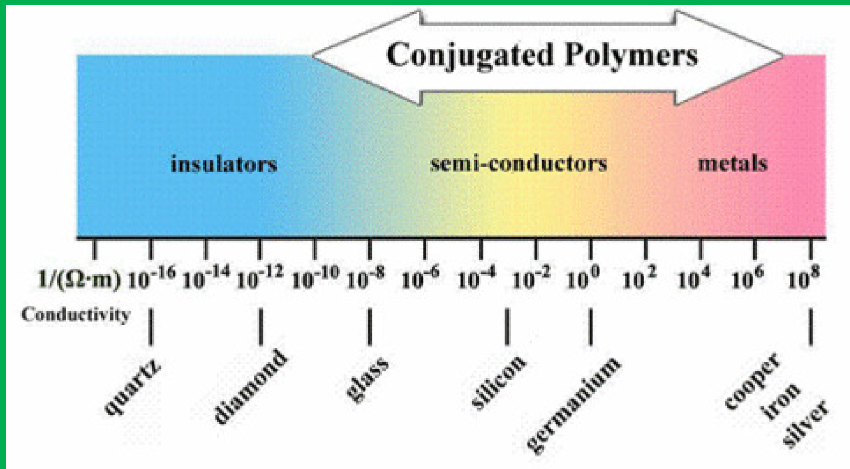
From particulates to monoliths in chromatography

Passive, inert structures comprised of rigid polymer rods

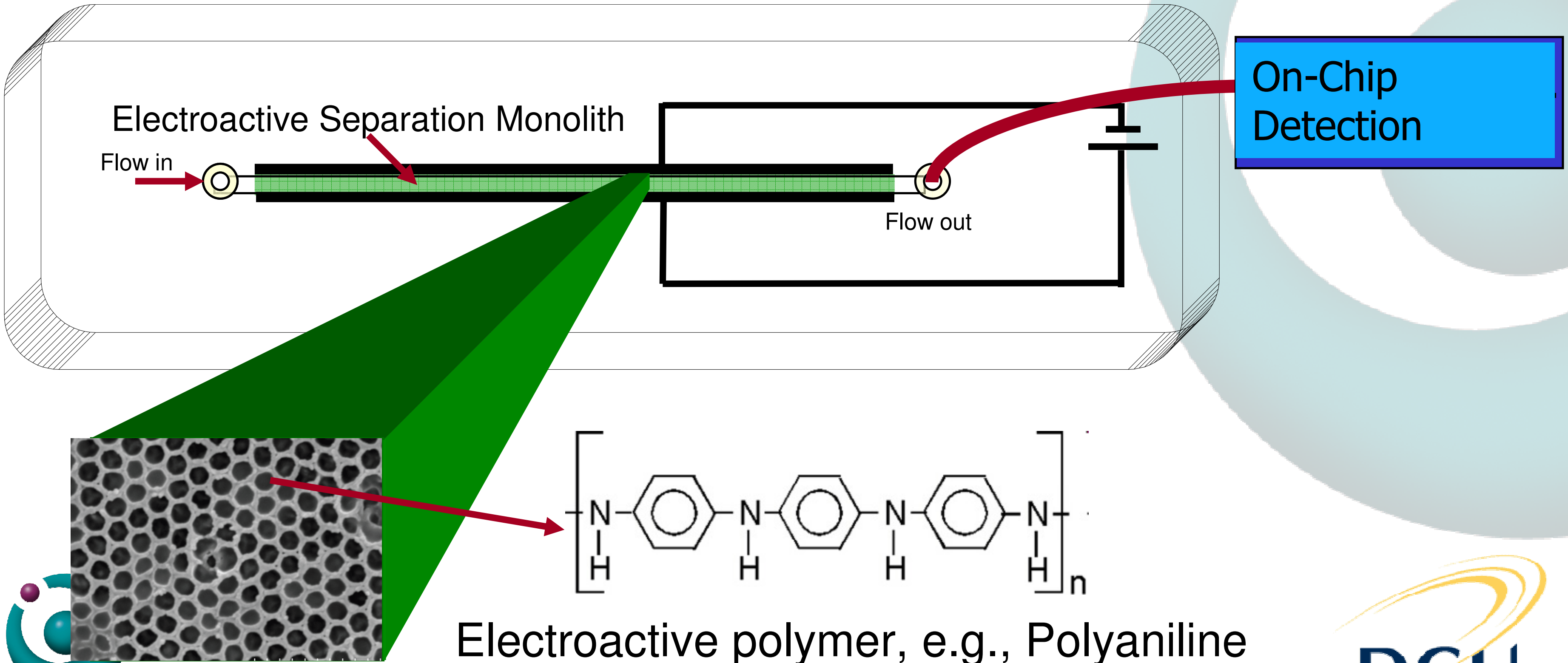
UV or thermally curable monomers, e.g., methacrylates, styrenes etc.



Do functional materials offer a viable alternative???



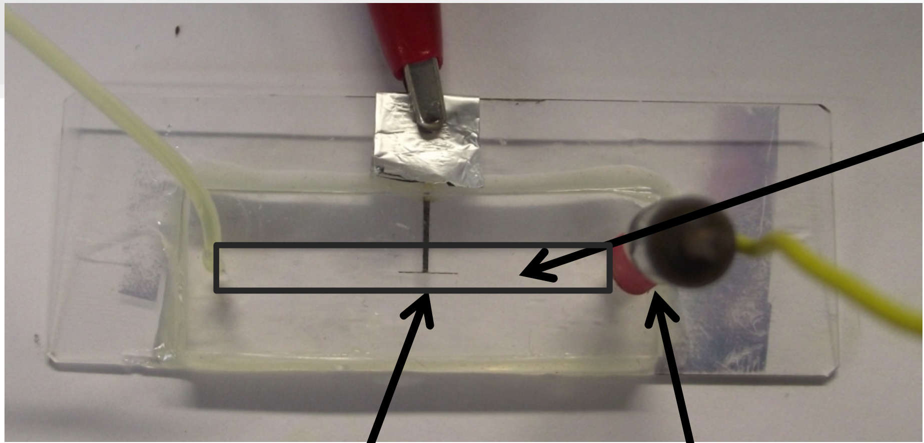
Electro-responsive Monolith µChip (EMµ)



EMμ for separations

- Electrochemical growth of uniformly templated polyaniline monolithic materials on-chip
- Precise control over monolithic stationary phase fabrication enabling high levels of reproducibility
- Micro-structuring of the monolithic stationary phase enabling:
  - Further decrease of the A-term in Van Deemter
  - Large flow through pores
  - Small skeleton size
- Precise electrochemical tuning of stationary phase before & during separation to influence retention factors without need for gradient mobile mobile phases
  - Hydrophobicity
  - Pore size
  - Ionic capacity

Electrochemical thin-layer cell on-chip



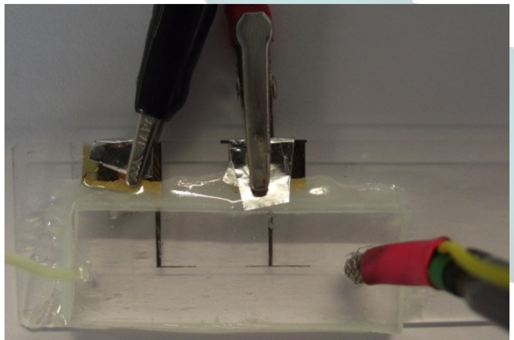
μChannel: 110 x 35 micron

WE: 5 mm x 110 micron

External ref & aux electrodes

Cell Volume: 154 nL

Fully integrated system

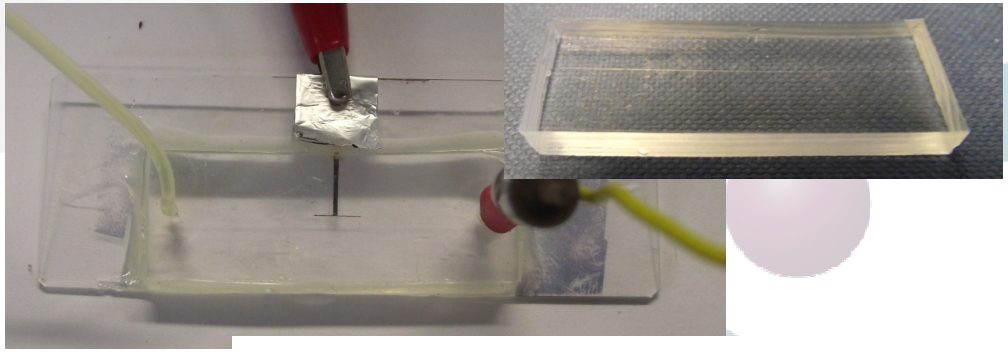


Compensate for non-uniform potential distribution

Characterisation using Fe^{2+}/Fe^{3+}

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

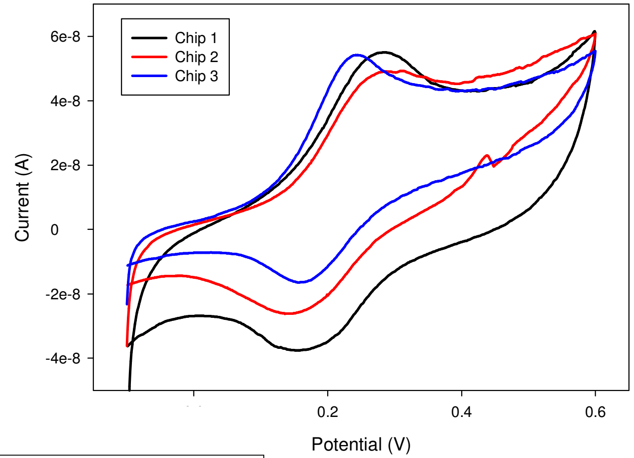
$$35\mu m < l < 200\mu m$$



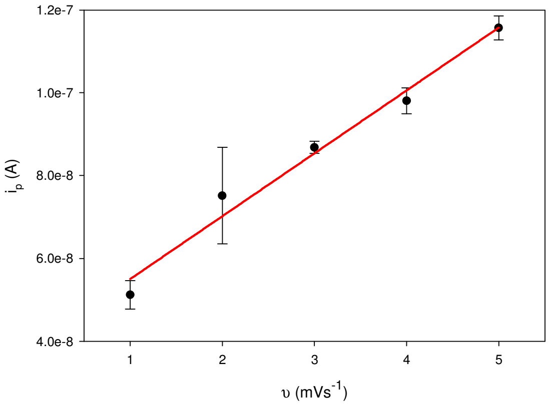
Theoretically $\Delta Ep = 0$

Typically $\Delta Ep \approx 115\,\text{mV}$

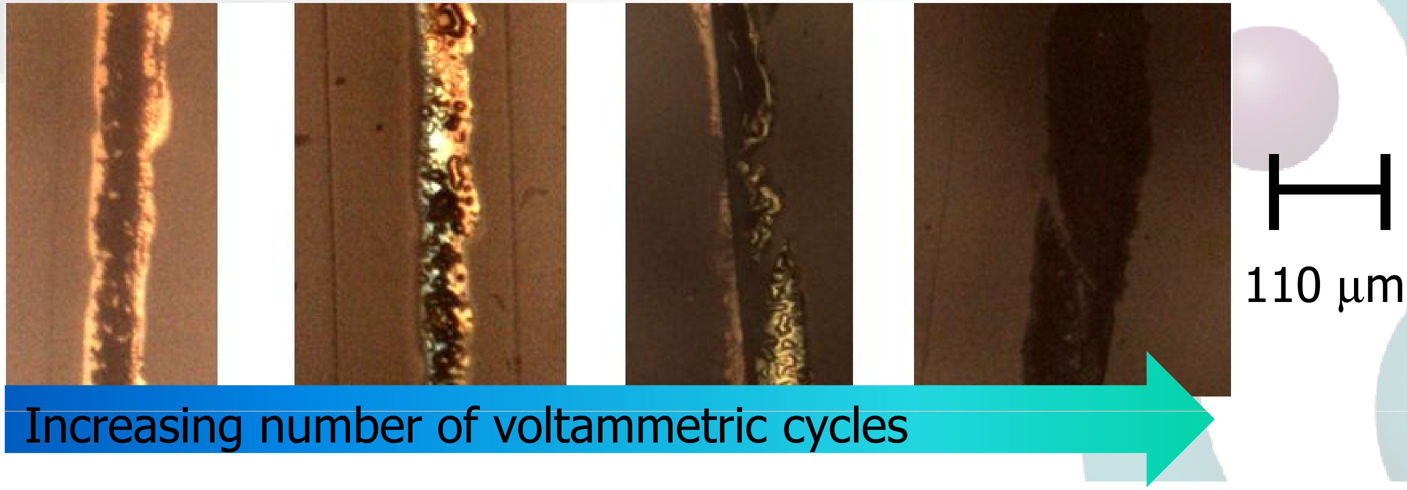
$\nu = 1\,\text{mVs}^{-1}$

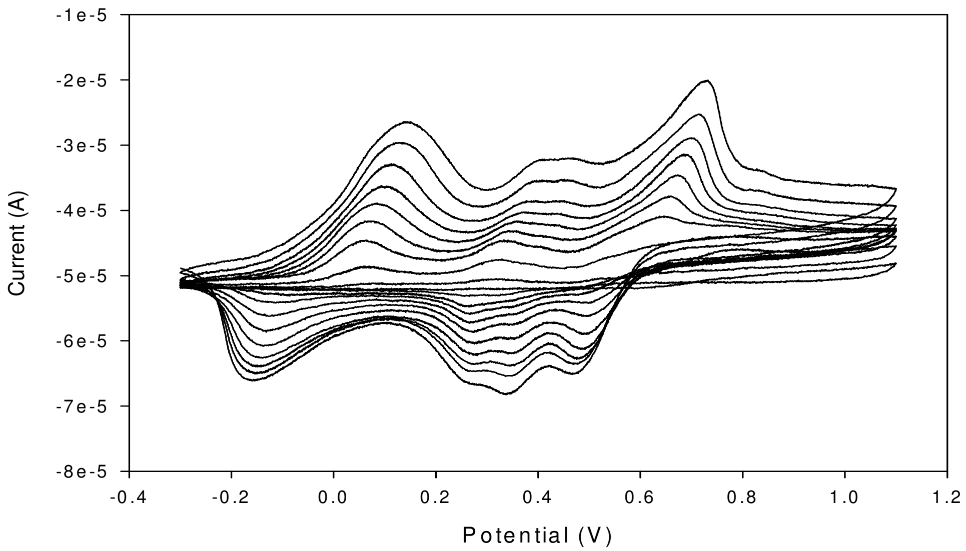


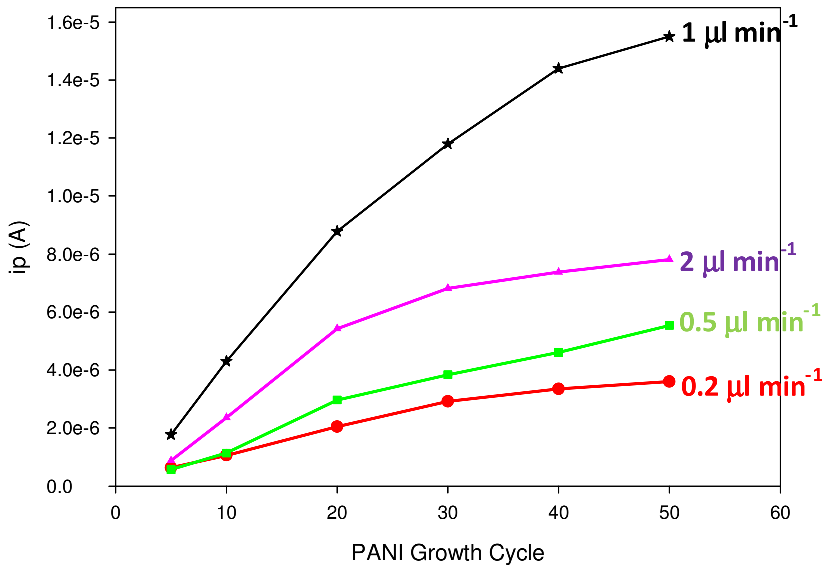
$$i_p = \frac{n^2 F^2 \nu V C_0^*}{RT}$$



Characterisation of PANI growth in μchannel







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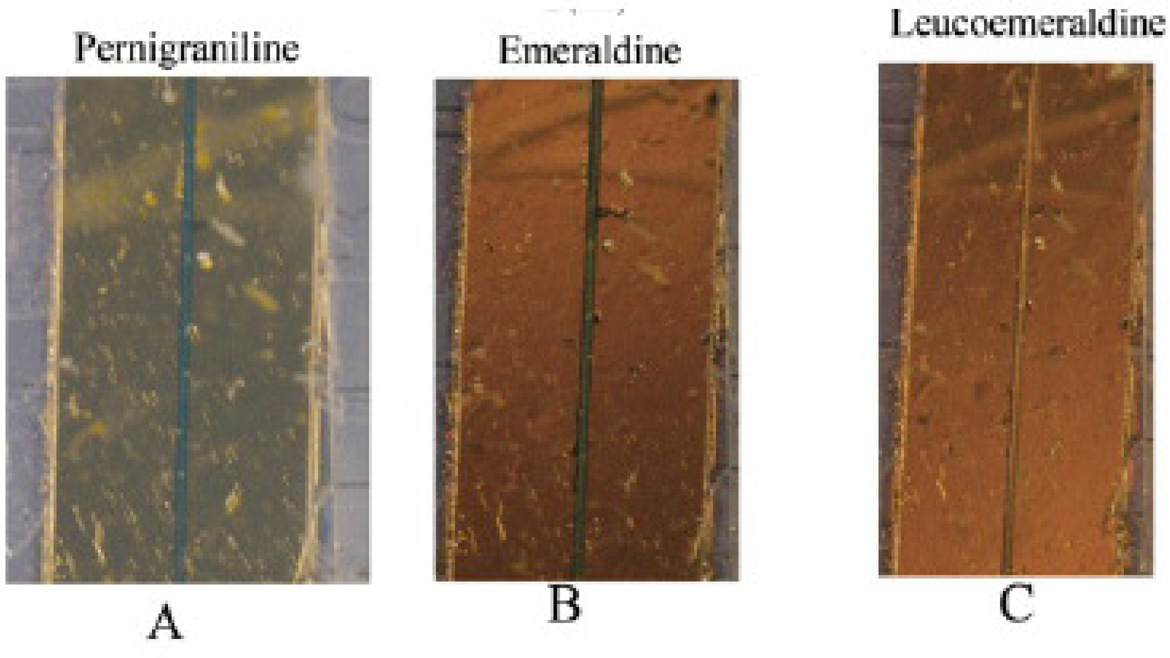
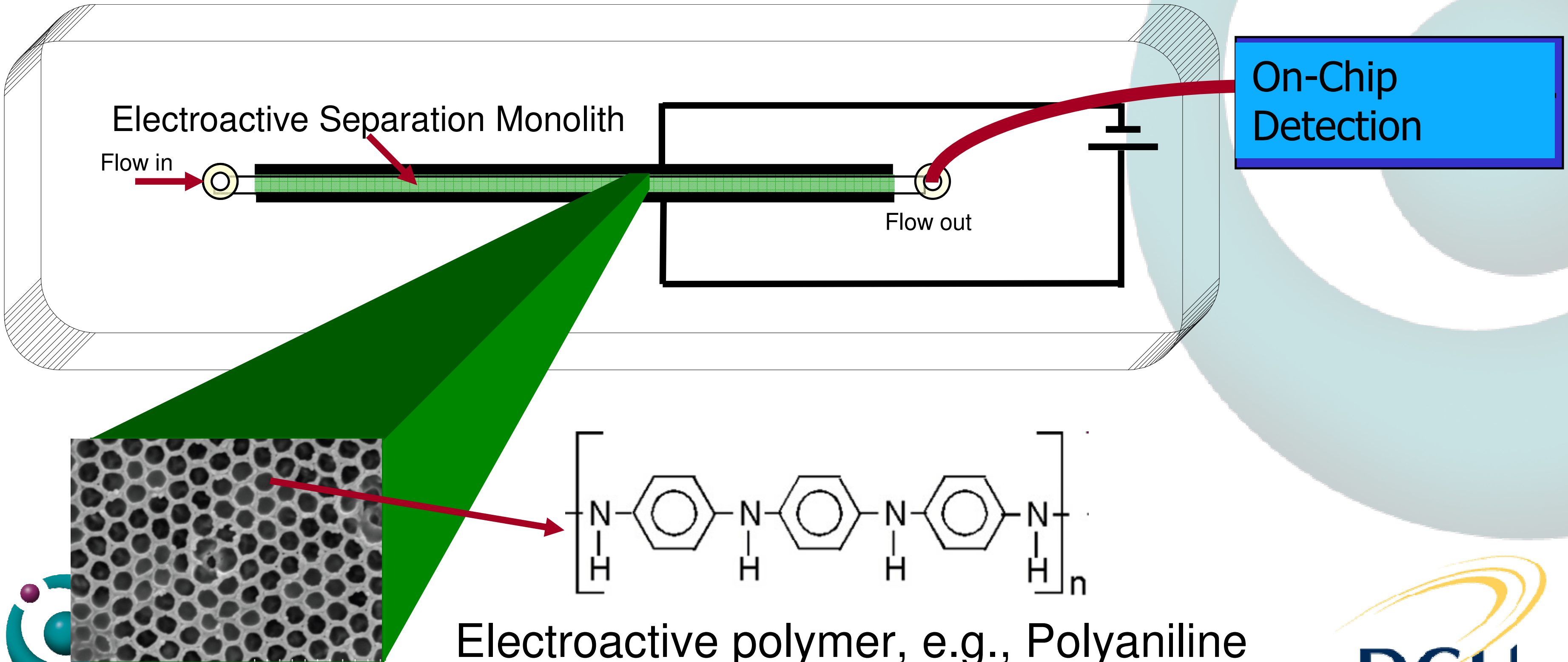


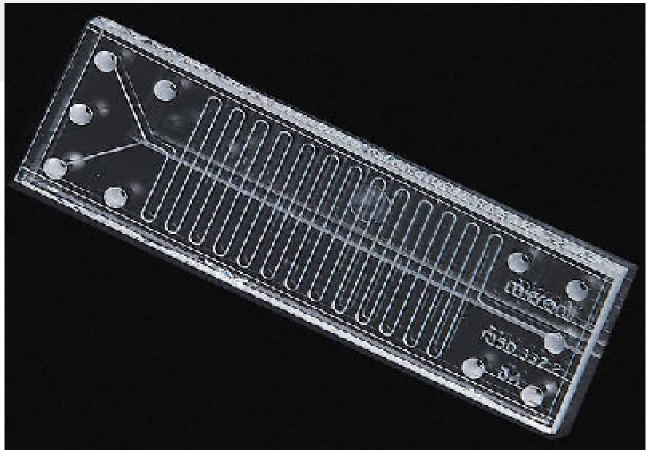
Channel Width: 110 μm

Electro-responsive Monolith µChip (EMµ)

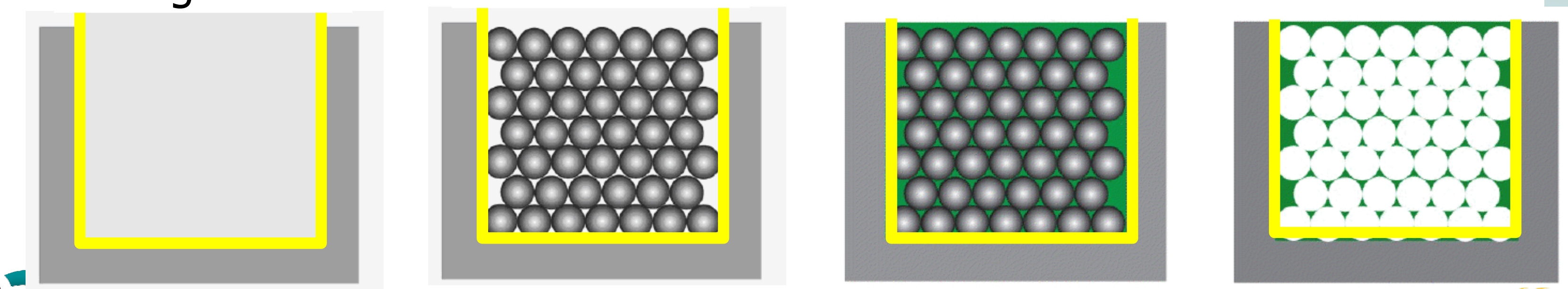


Electroactive polymer, e.g., Polyaniline

EMμ



Working Electrode Integration → Template Deposition → Electrochemical Polymer Growth → Dissolution of Template



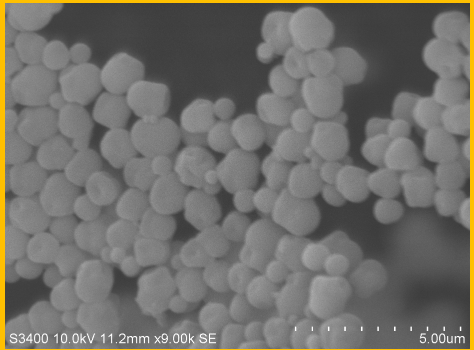
Channel Dimensions: 110 micron x 20 micron x 40 mm

PS template

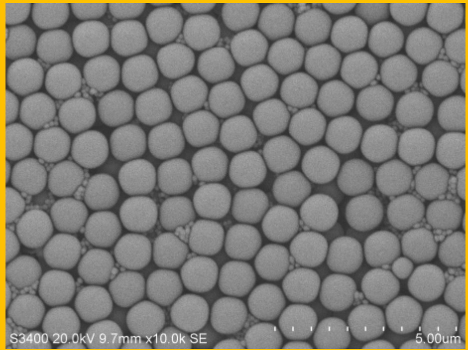
PS bead synthesis

2 critical factors:

Appropriate [cross-linker] to give uniformity and permit dissolution

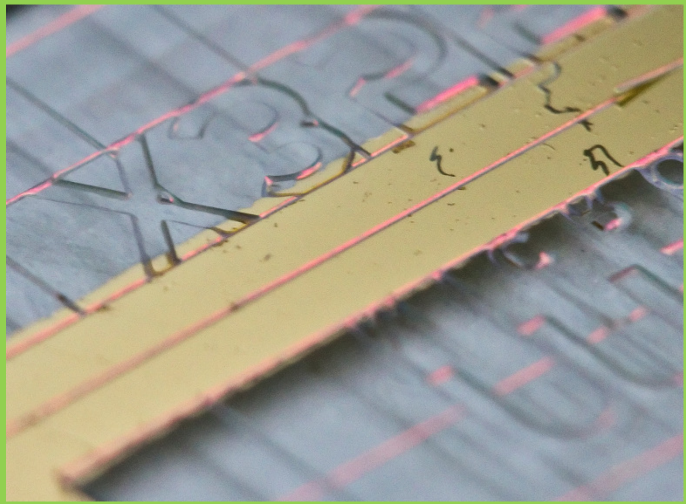


vs.



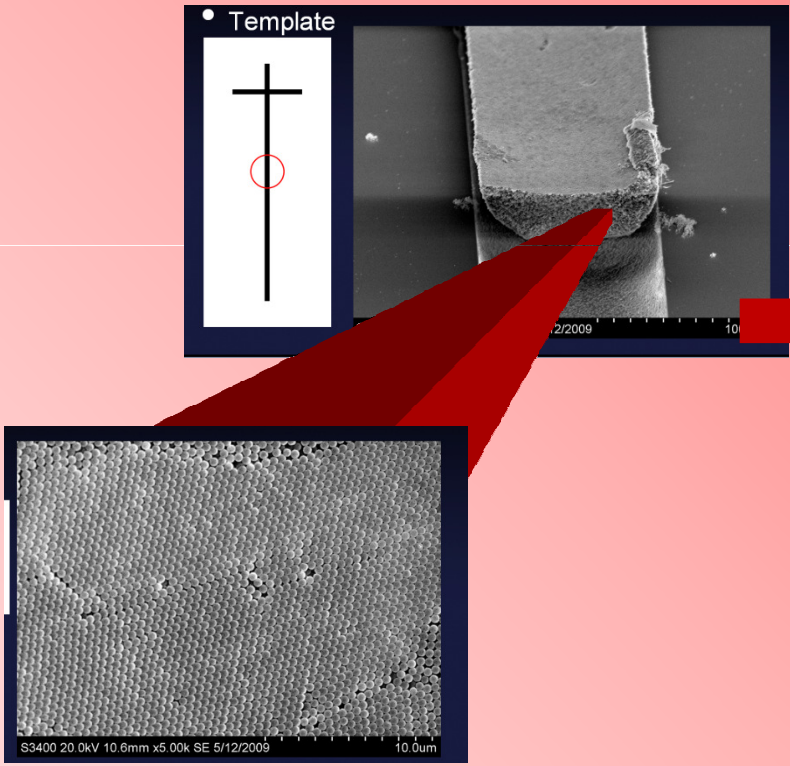
Surfactant content of dispersions

PS crystal in μchannel

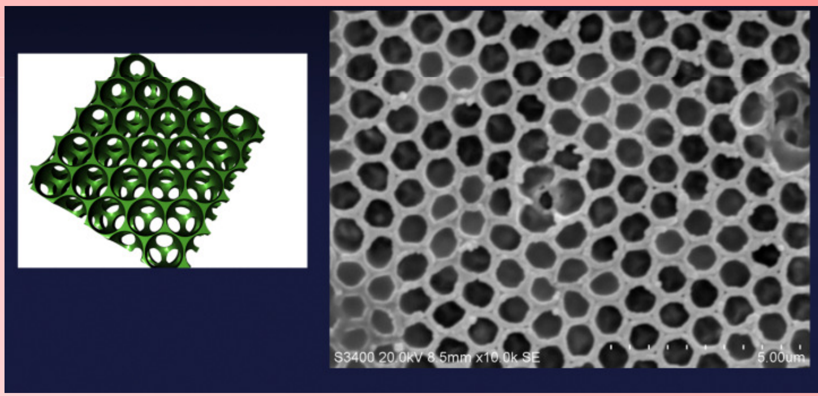


Templated conducting polymer monolith

PS template

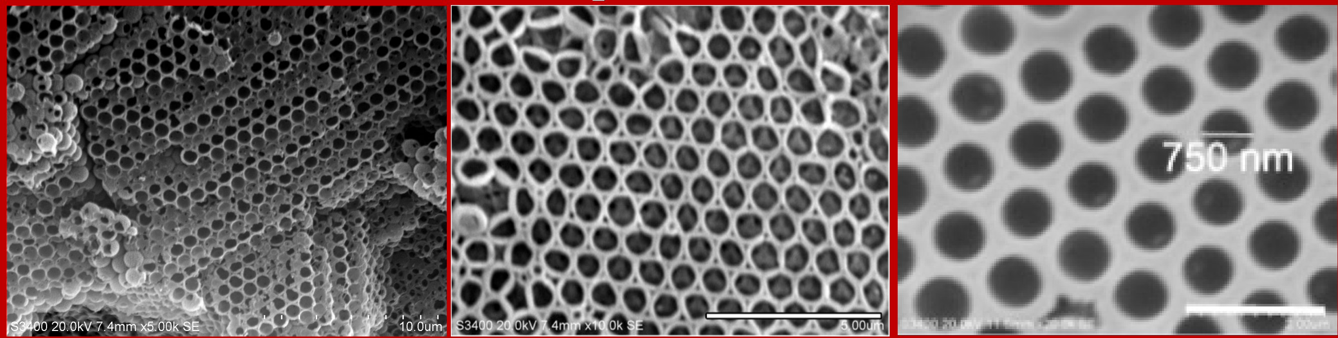


PANI inverse opal

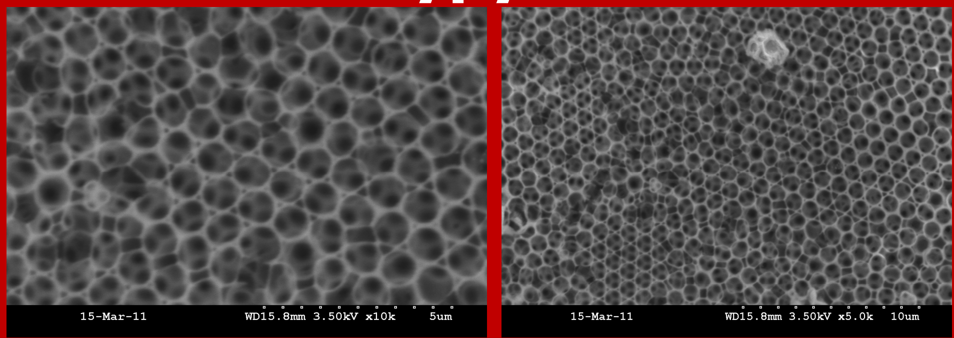


Templated CPs - unimodal

Polyaniline



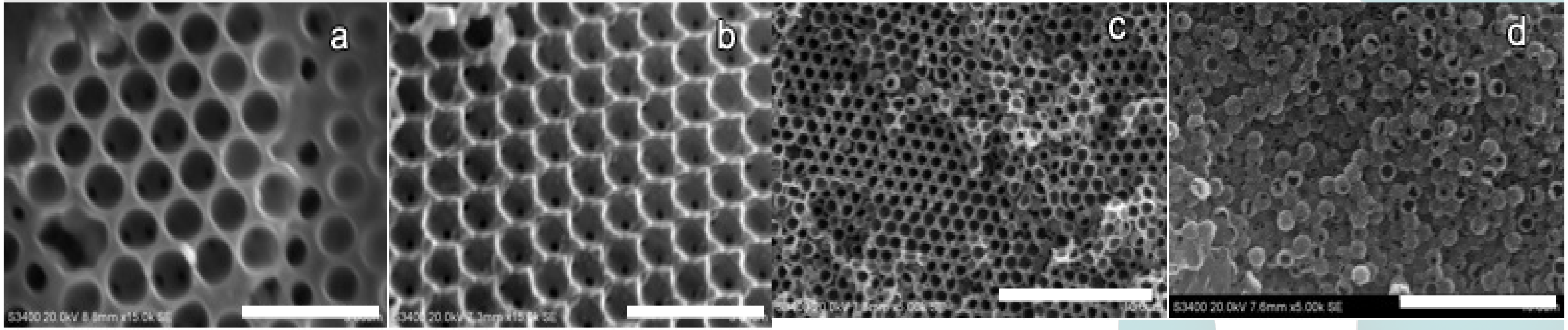
Polypyrrole



Order in 3-D

A new way for producing monolithic phases on-chip

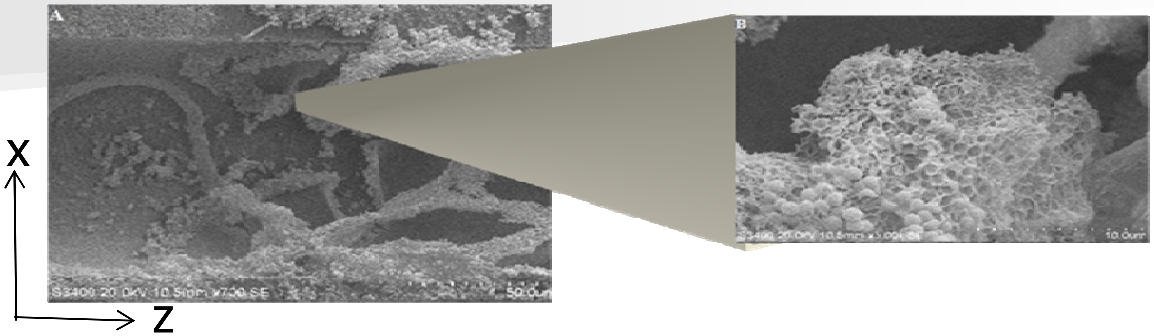
Surfactant levels in PS dispersions – resulting PANI structures



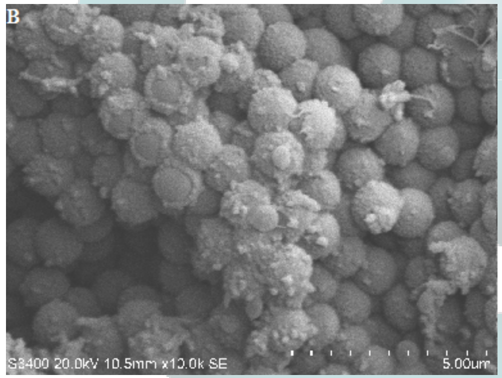
Deionised Water | 0.01 % w/v SDS | 0.1 % w/v SDS | 1 % w/v SDS

Increasing %w/v surfactant in dispersions - Order in resulting structures changes

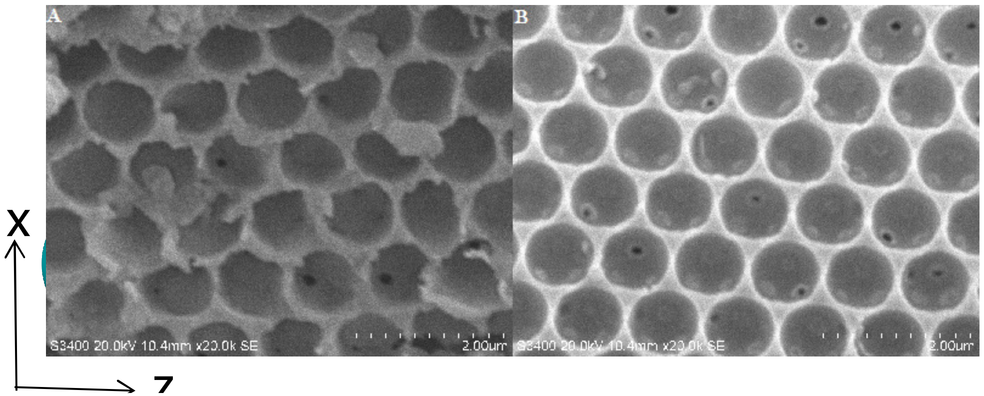
Growth times for templated PANI on-chip



Polymerisation time too short: fragile film collapses



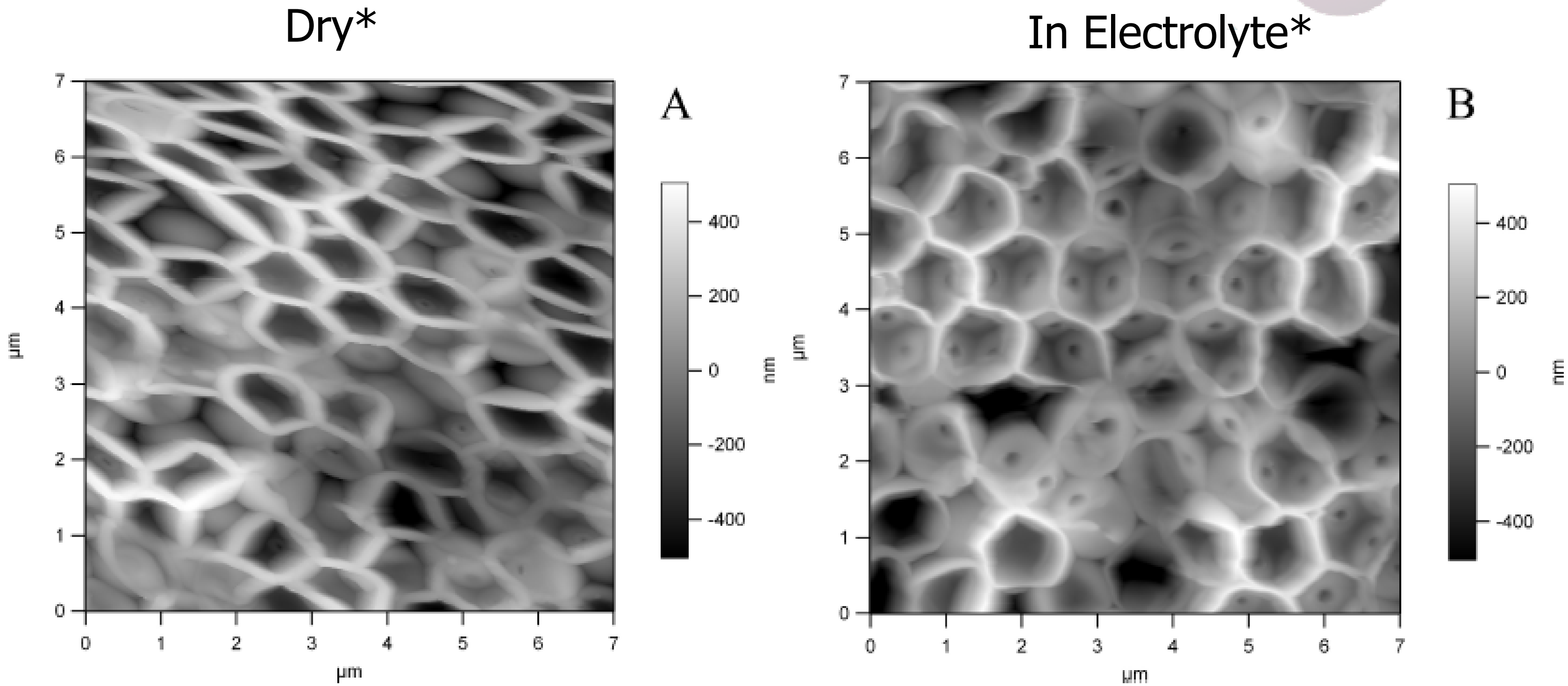
Excessive polymerisation times: Loss of order and pore interconnectivity



Optimised polymerisation time
Reproducible structured film with interconnecting pores

DCU

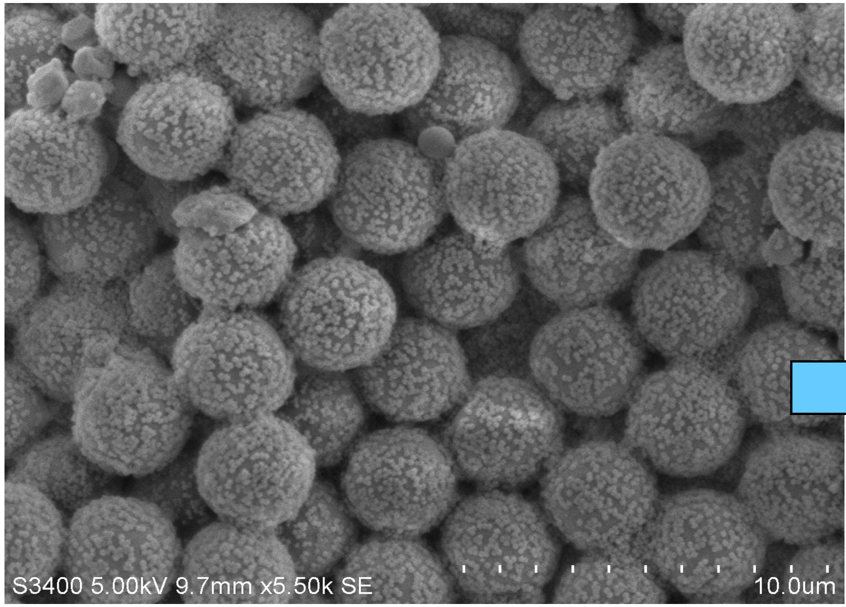
Dry & wetted states of templated CPs - AFM



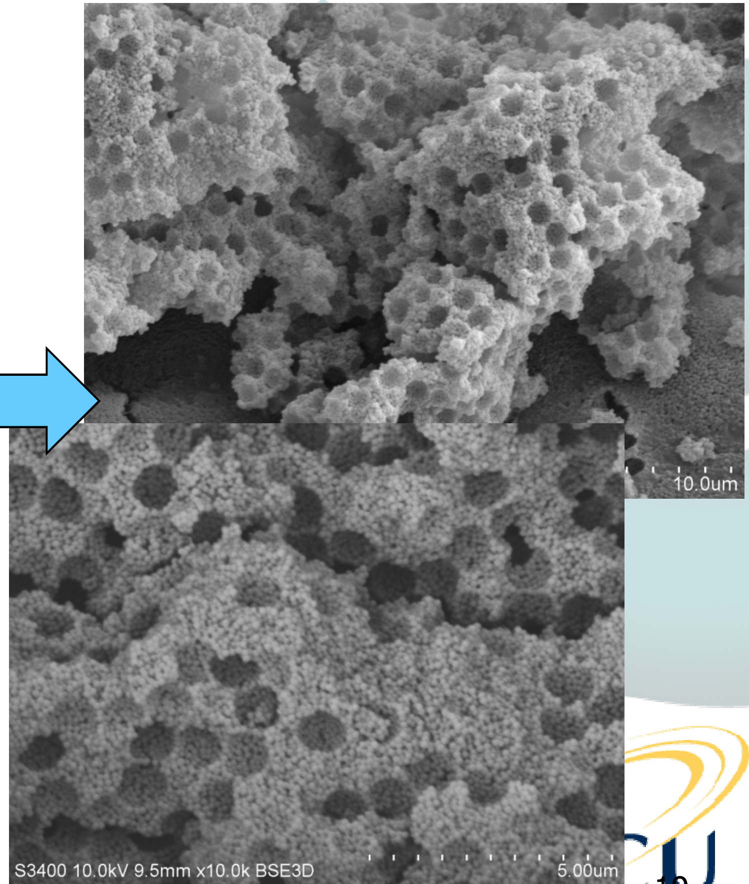
*Electrochemically grown Ppy doped with DBS

Templated CPs - bimodal

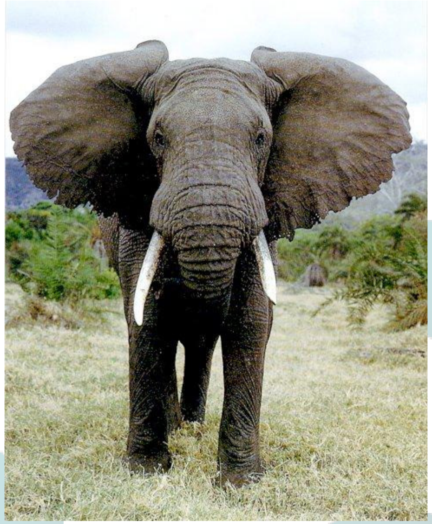
Bimodal PS template



Ppy bimodal monolith



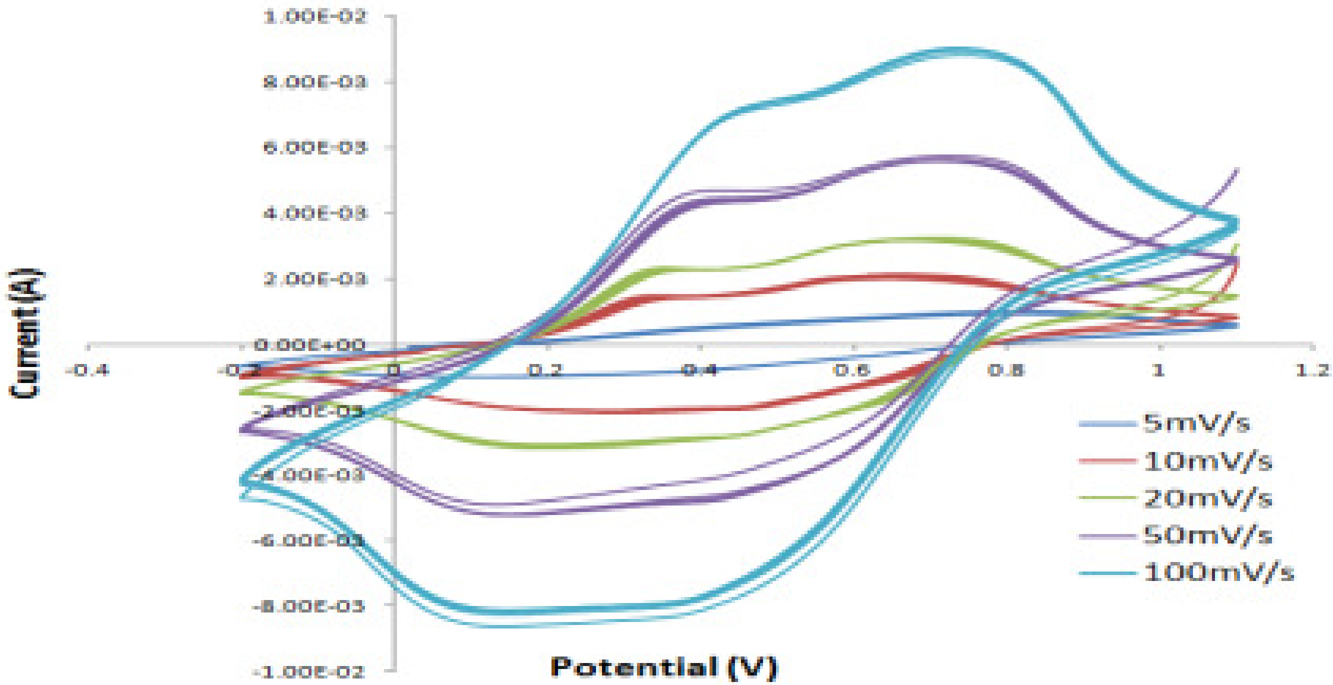
Elephant in the room…..



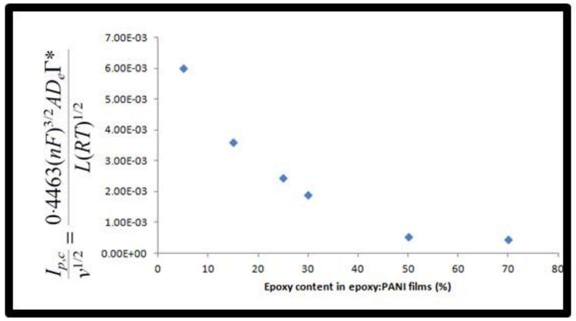
- Conducting polymers will not withstand high pressures for chromatographic and other sensing applications that require a pressure-driven flow
- …..Need to look at improving the mechanical properties

Compositing CPs with other polymers

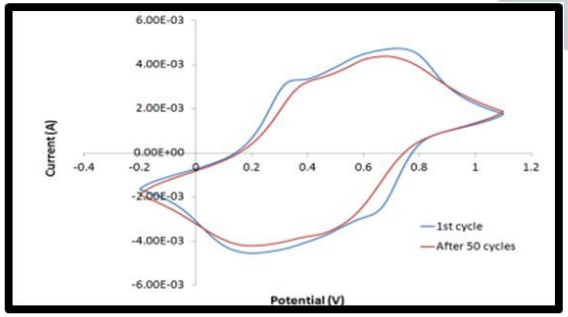
Epoxy-PANI composite: blending Araldite Rapid®, with emeraldine base powder



Diffusion Coefficient Trend



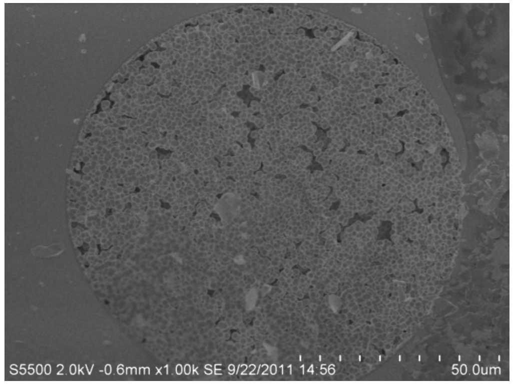
Cycling Stability

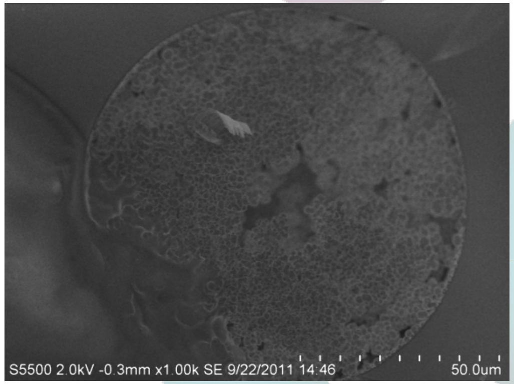


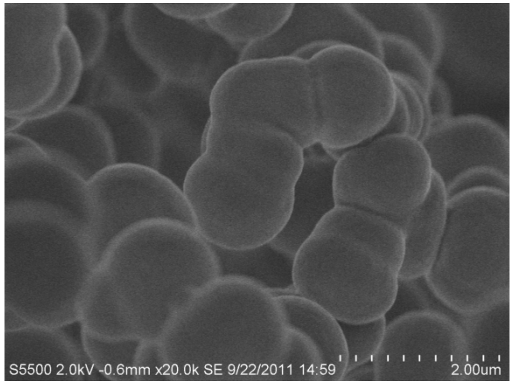
Coating CPs onto existing polymer monoliths

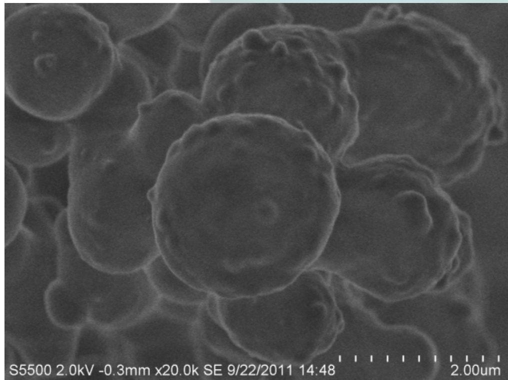
Bare lauryl methacrylate monolith

Ppy-coated monolith









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To Conclude

- What do we have?
  - Microfluidic thin layer electrochemical cell
  - Well-behaved, templated, high surface area conducting polymer materials
  - Good spatial control over polymerisation
  - Nano/micro structuring on-chip
  - Suitable format for exploiting EOF-driven flow
  - Early investigations into improved rigidity/mechanical stability of CP materials for pressure-driven flows
- Where to next?
  - Applications in LOC sensors, drug delivery, electrochromatography, electrocatalysis

Thanks!

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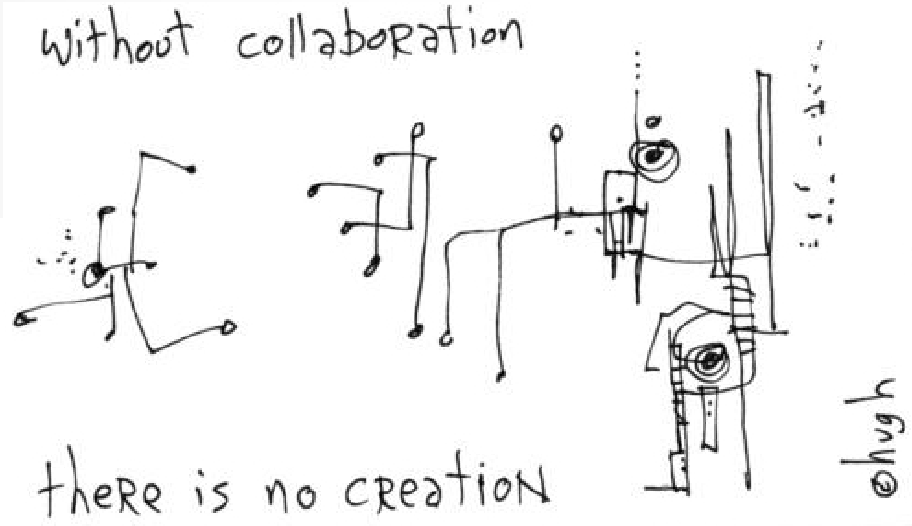
- Dr. Fuqiang Nie
- Dr. Aoife Power
- Nicky McKenna



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