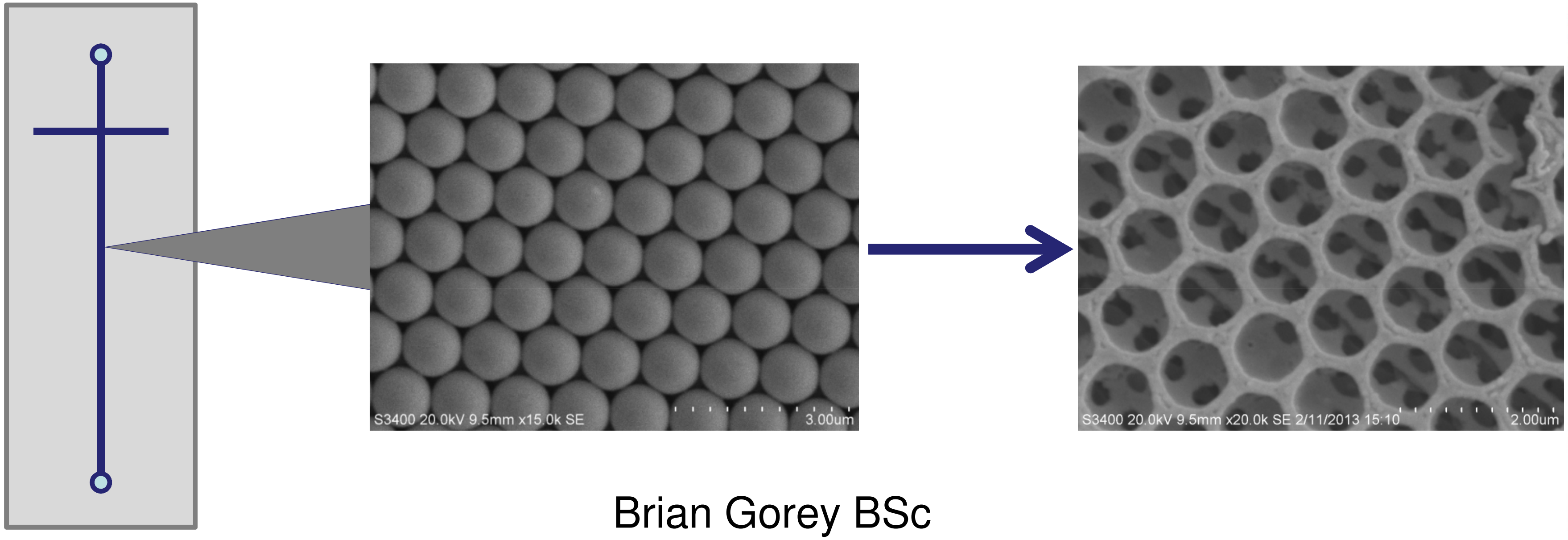
Controlled Surface Morphologies for Conducting Polymer Monoliths On-Chip



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ARF 2013

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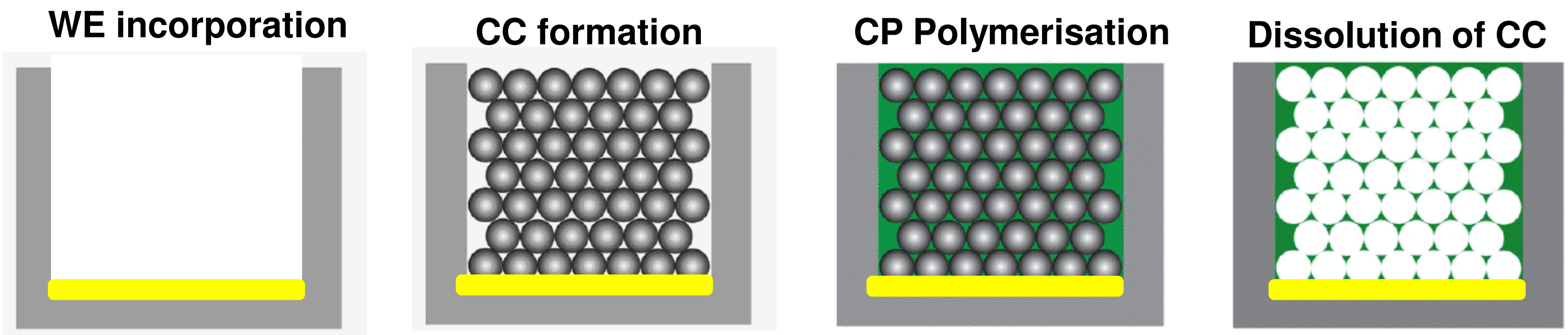
Overview

- Introduction:

- Microfluidics - advantages

- Conducting polymers (CP) - potential stationary phases

- Overview



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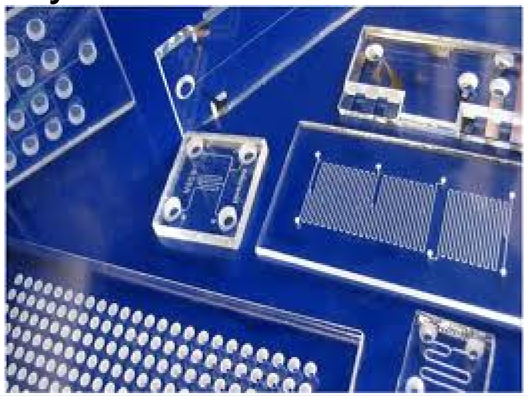
Benefits of Microfluidic Analysis

- Low sample consumption – *nano-litre volumes*
- Multiple processes in a single chip – *no sample transfer*
- Shortened analysis time
- Potential automation of process - increased reproducibility



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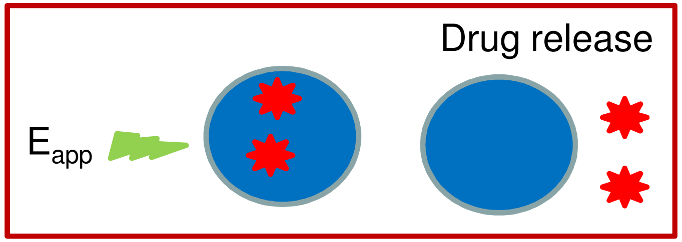
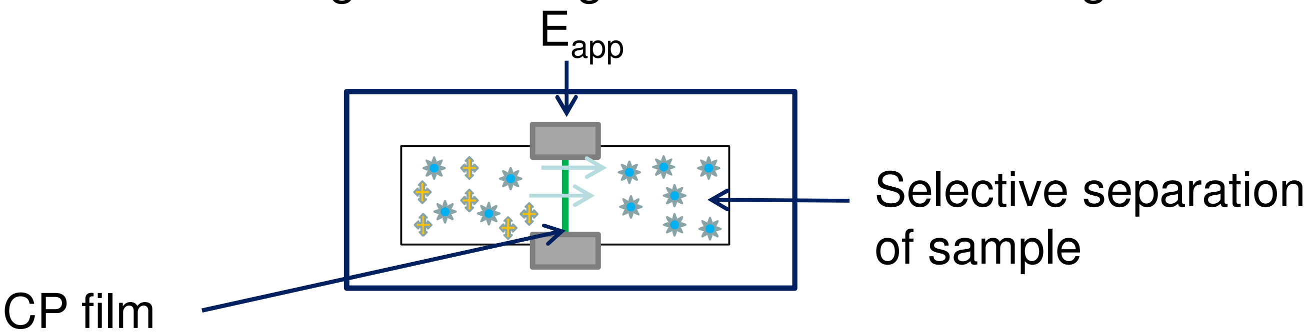
Potential Benefits of CPs On-Chip

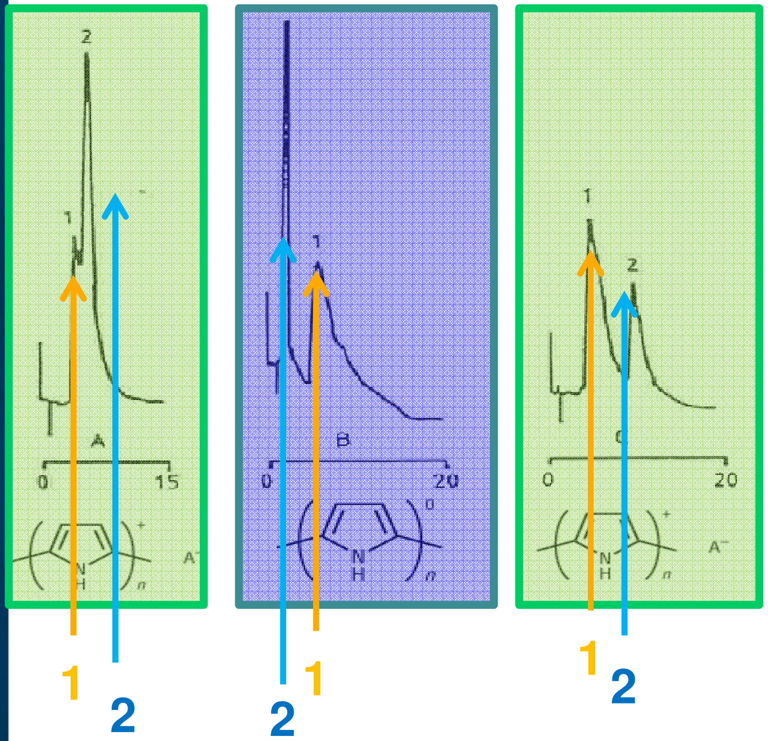
- Miniaturised electrochemical and optical sensors
- Drug delivery formats
- Actuation e.g. for controlling liquid flow

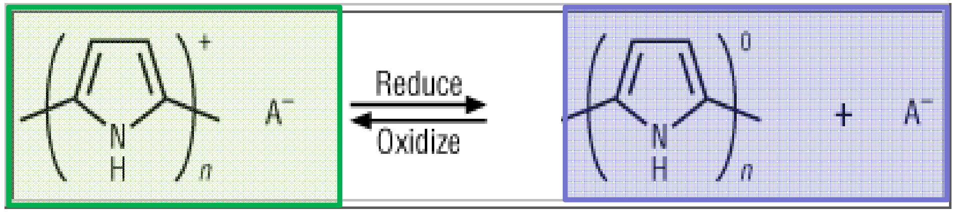


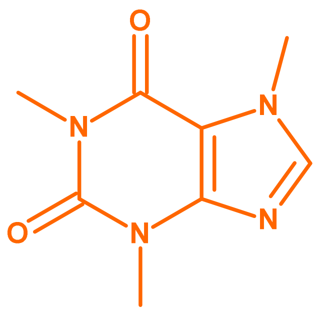
- Electrochemically-responsive material – useful for separations???
  - Alter retention characteristics based on applied potential
  - Increasing/decreasing the number of exchange sites based on redox state



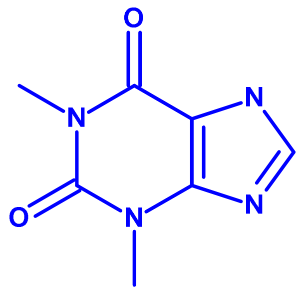
CPs as Potential Electrochemically-Responsive Stationary Phases







1. Caffeine



2. Theophyline

H. Chriswanto, G.G. Wallace, *Journal of Liquid Chromatography & Related Technologies*, 1996, 19, 2457-2476

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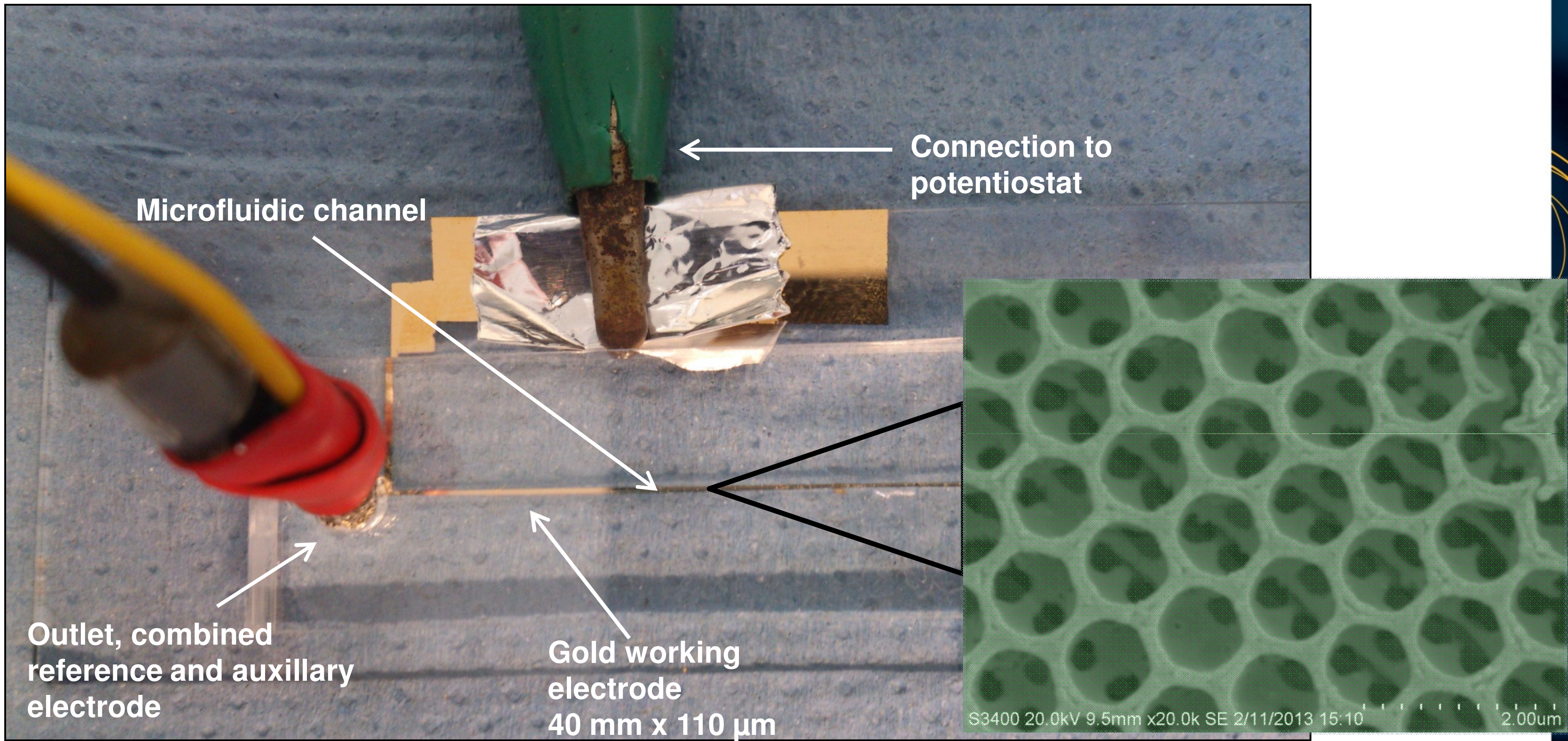
µChip Design



A.C. Power, B. White, A .Morrin, *Electrochimica Acta* , **2013,** 104, 236 – 241

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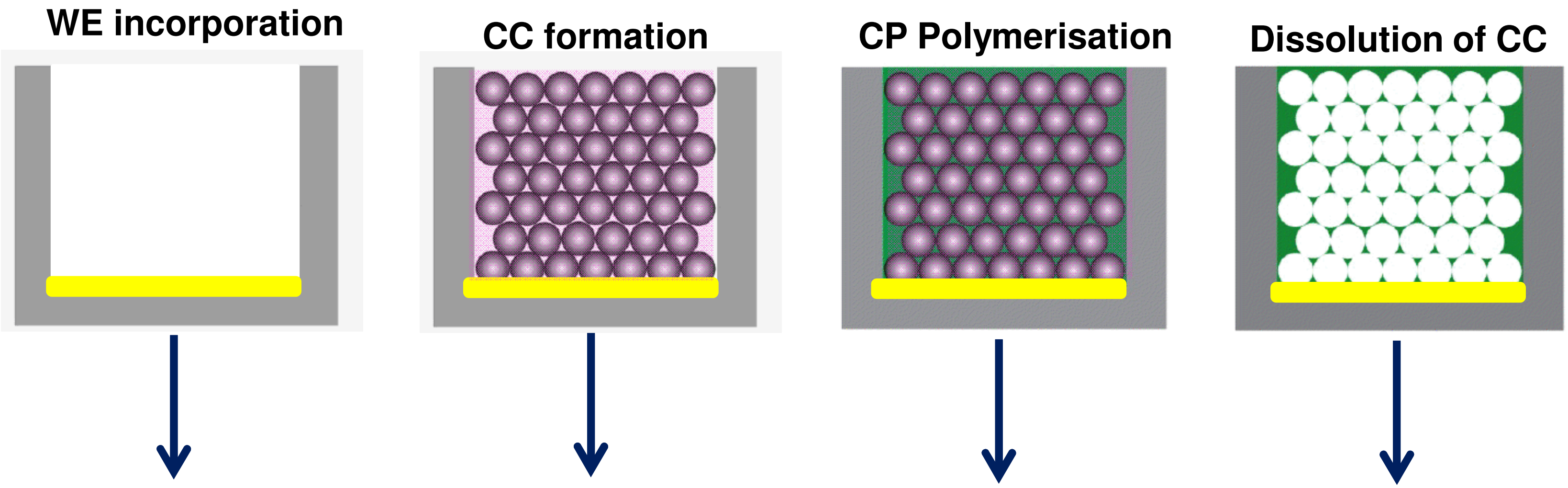
Fabrication of CP Monolith in Confined µChannel - overview



Step 1. Incorporation of working electrode in channel	Step 2. Fabrication of sacrificial CC template	Step 3. CP template directed polymerisation	Step 4. Dissolution of PS spheres and investigate electrochemical potential

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

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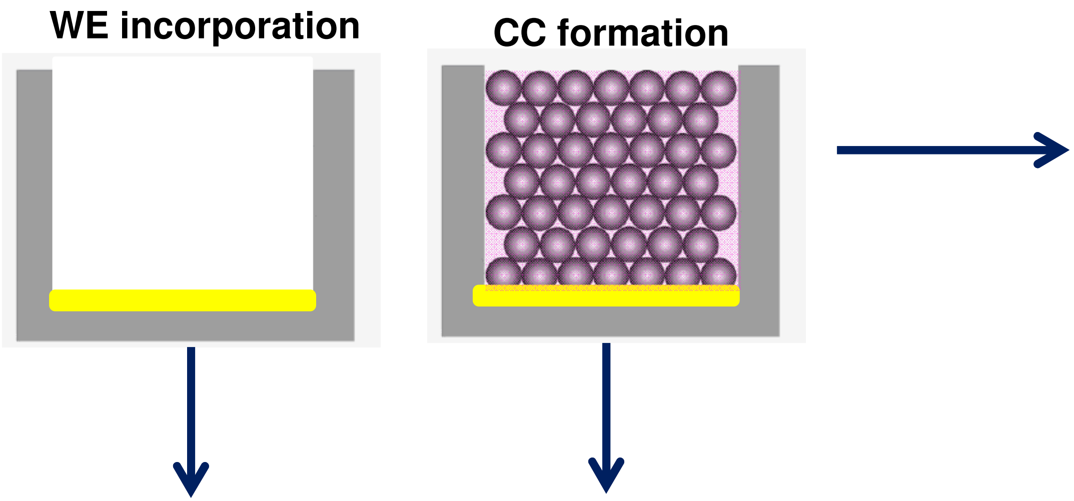
Colloidal Crystal Fabrication



Step 1.
Incorporation of working electrode in channel

Step 2.
Fabrication of sacrificial CC template

Aim: CC fabrication

1) Fabricated within a micro-channel

2) High surface area

- unimodal vs. bimodal

3) 3D structure

Current Methods to Form CC - Limitations:

- ***CC monolayer – fabrication at air water interface***
  - Monolayer
  - Cannot be fabricated in channel

- ***Dropcast multilayer CC – convection self-assembly***
  - Multi-layer
  - Little control over area templated
  - Cannot be fabricated reproducibly in channel

- ***Dip-drawing – convection self-assembly***
  - Multi-layered and reproducible
  - Time consuming CC fabrication methods
  - Extensive multistep process to surface manipulation the channel to form CC in channel

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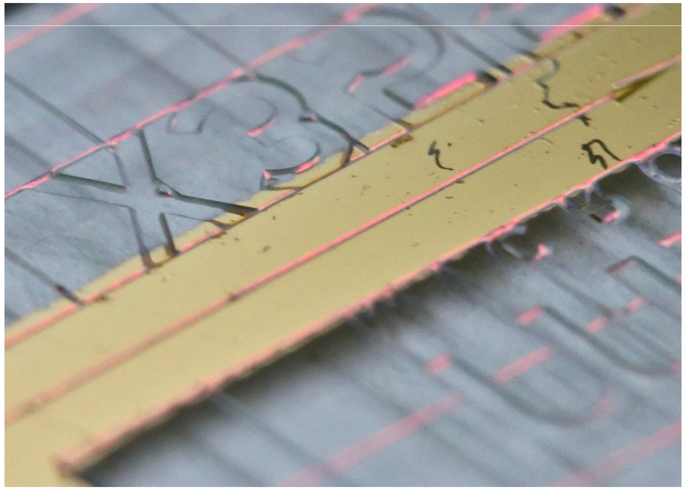
Our Approach

- One step convective self-assembly ✓
- CC confined within a defined geometric area (μchannel) ✓
- Unimodal and biomdal CC achievable ✓
- Sealing of channel post CC fabrication ✓
- Flow through CC structure in channel ✓



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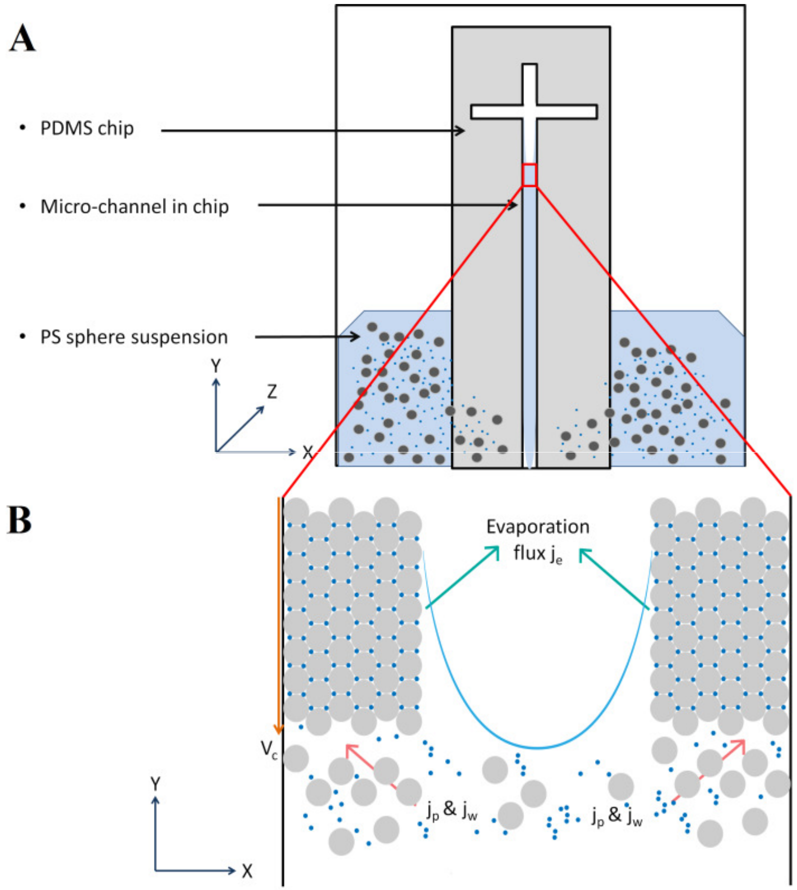
CC Formation in the Microfluidic Channel



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

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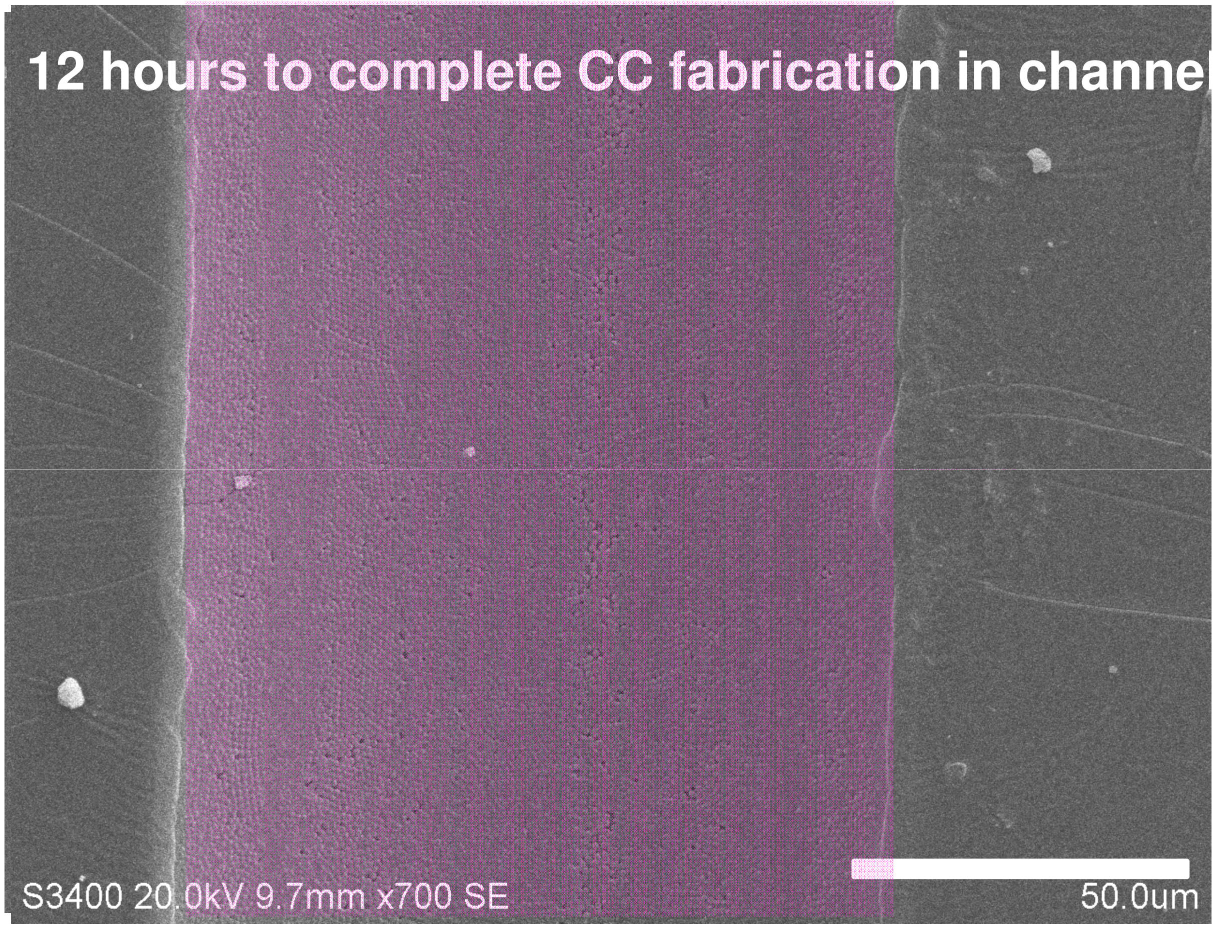
Real-Time Packing Mechanism



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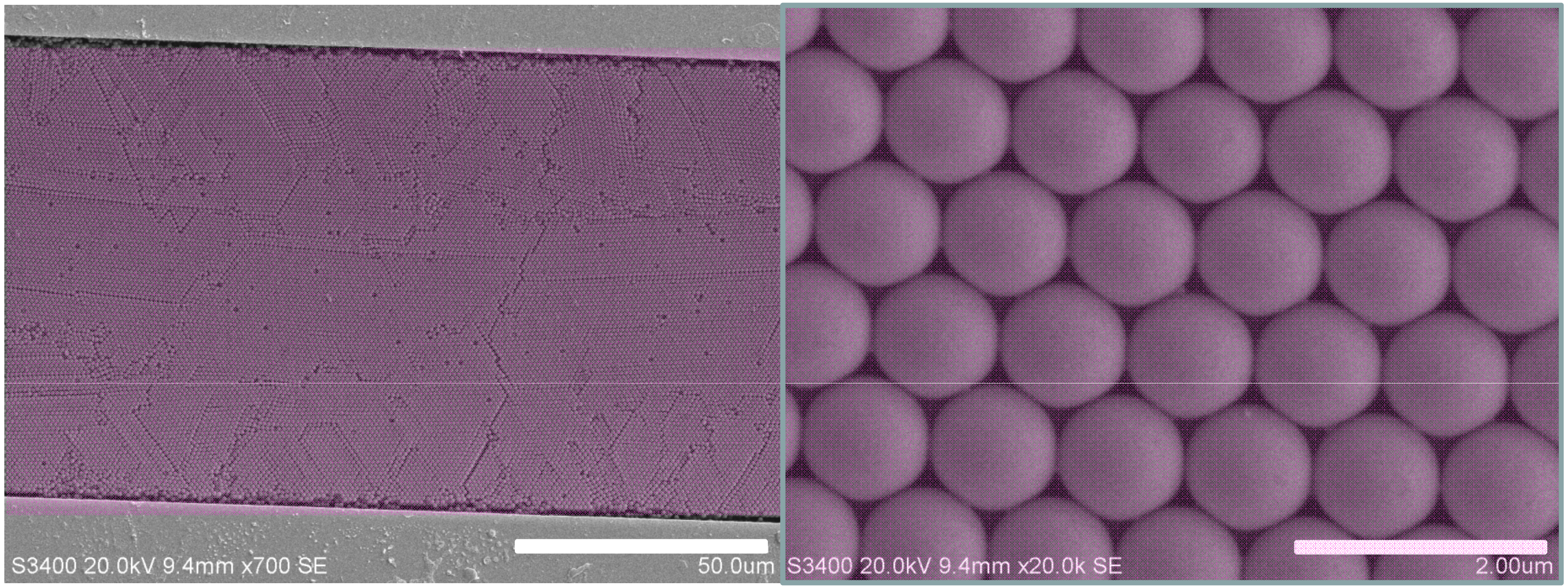
Optimised CC Structure in the µChannel Unimodal



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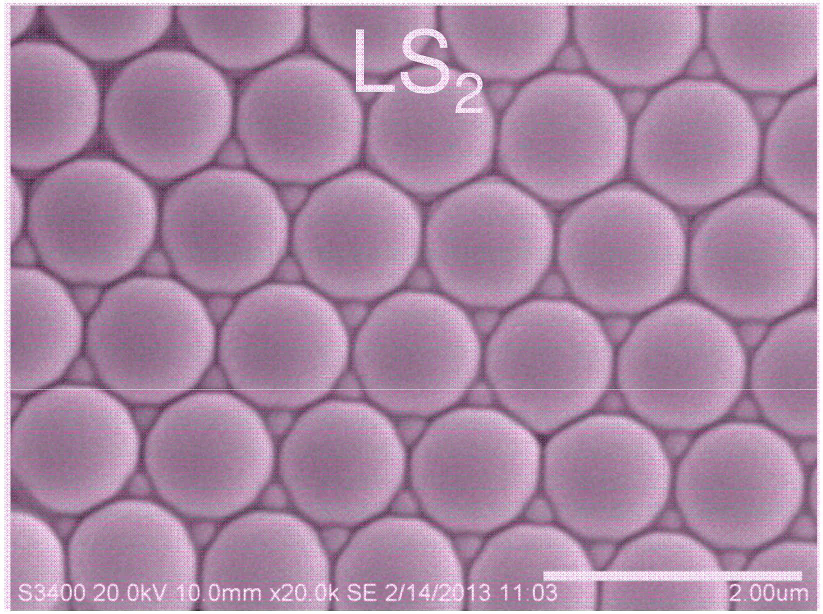
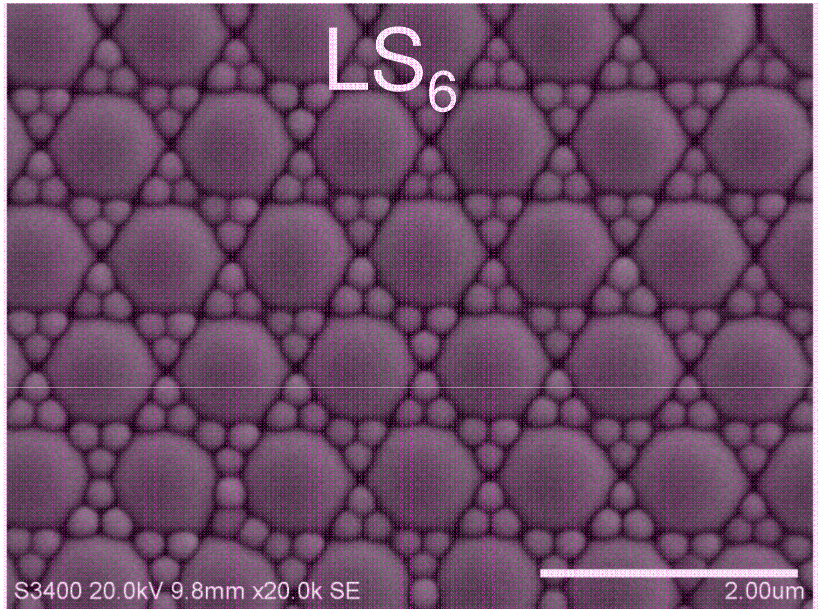
Optimised CC Structure in the µChannel Bimodal





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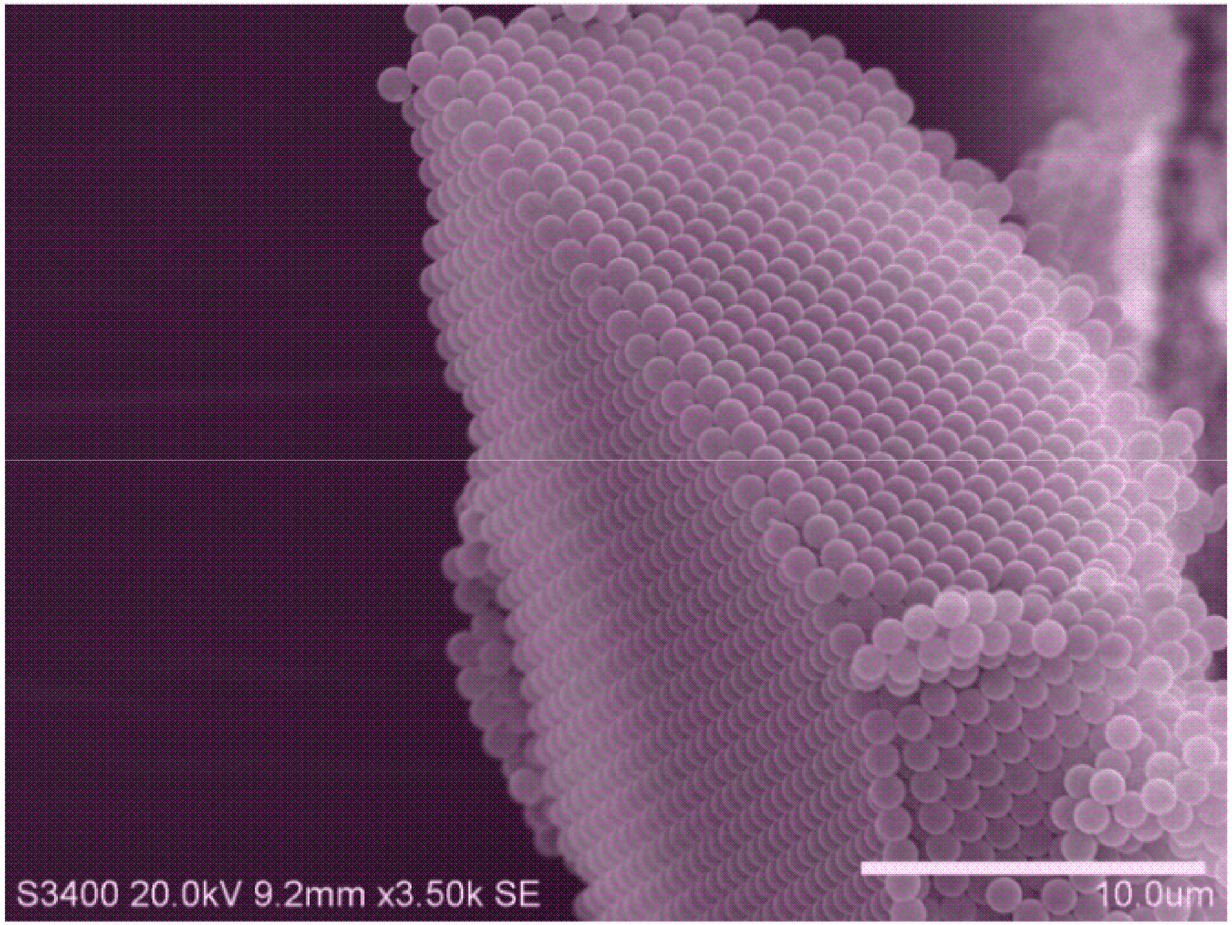
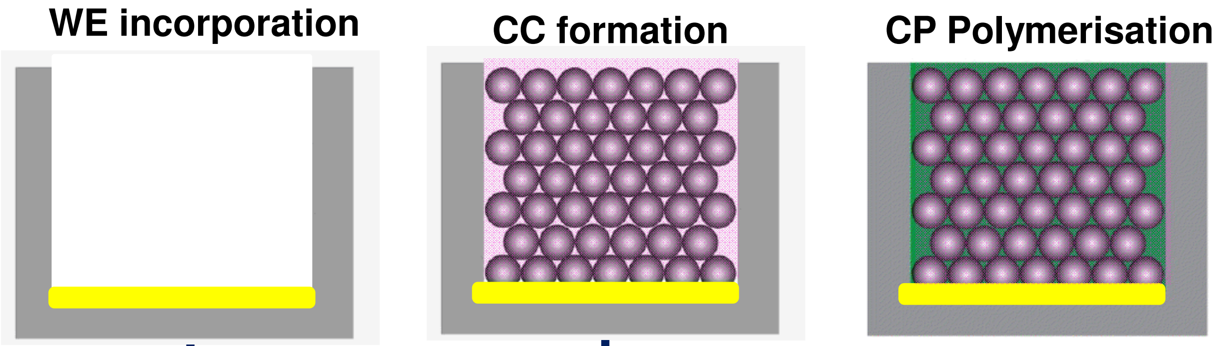
3D PS Colloidal Crystal Structure



Template directed CP polymerisation



Step 1. Incorporation of working electrode in channel

Step 2. Fabrication of sacrificial CC template

Step 3. CP template directed polymerisation

Aim: CP polymerisation

→

1) Reproducible & homogeneous structure
2) Flow through macro-pores
3) Meso-porosity surface area increase

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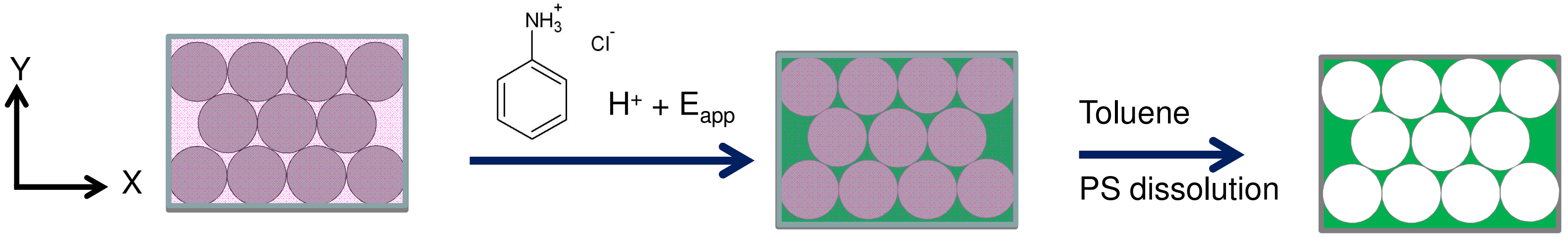
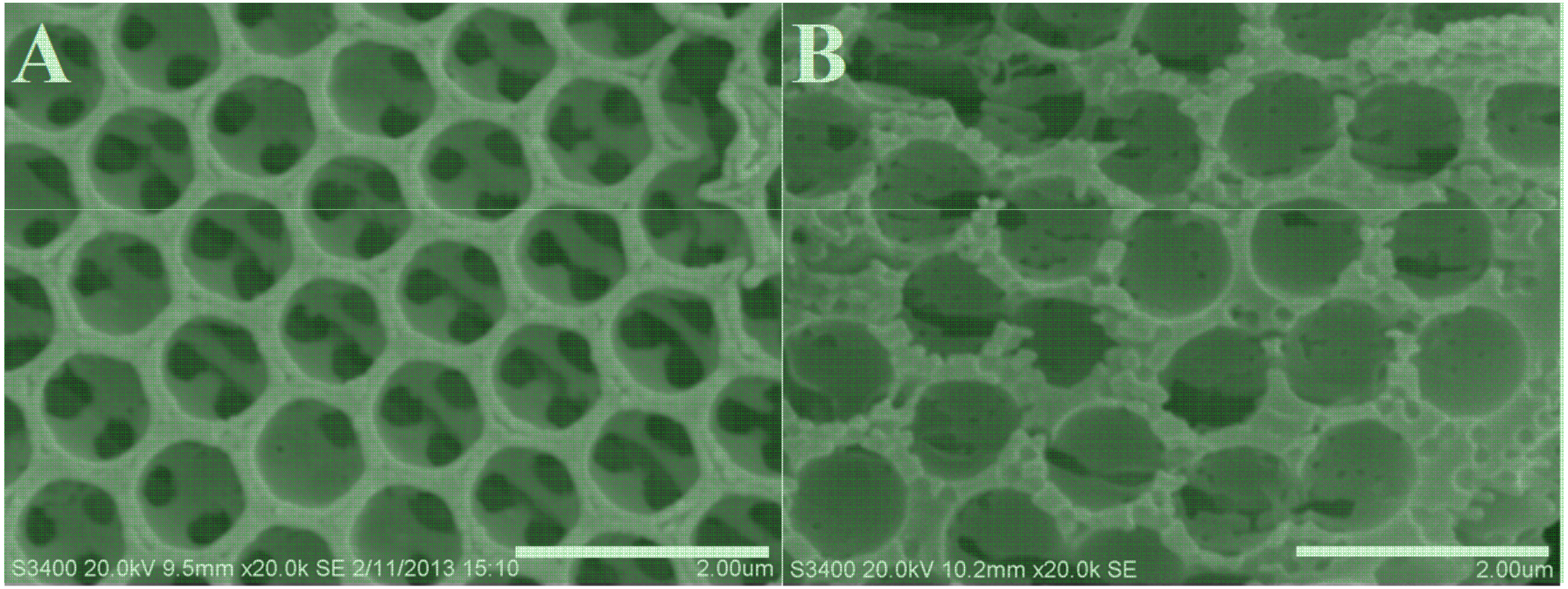
1. E_{chem} CP growth through CC templates





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

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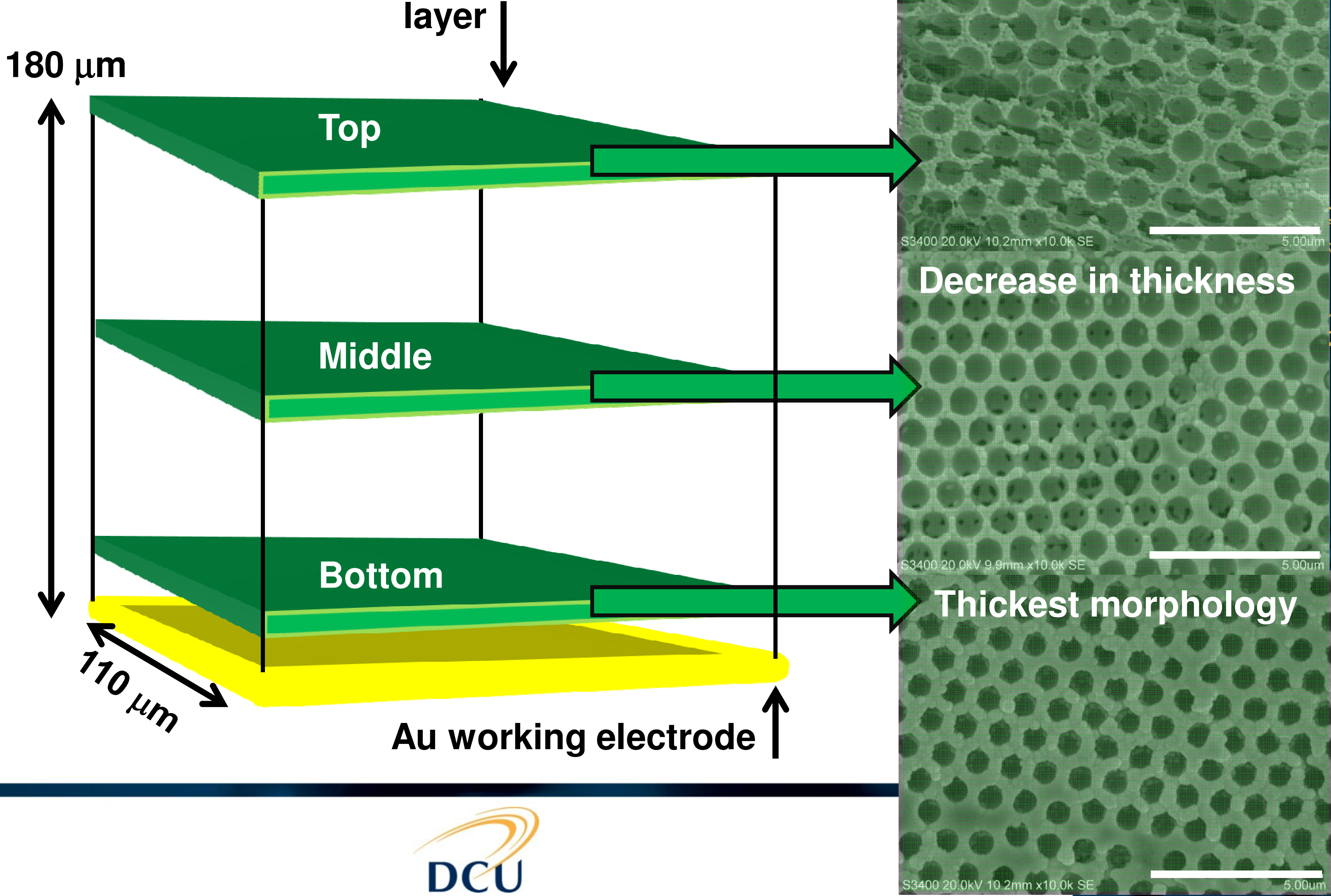
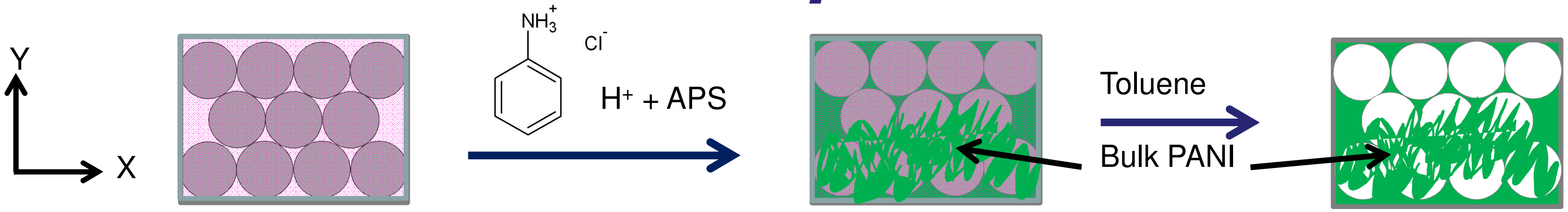
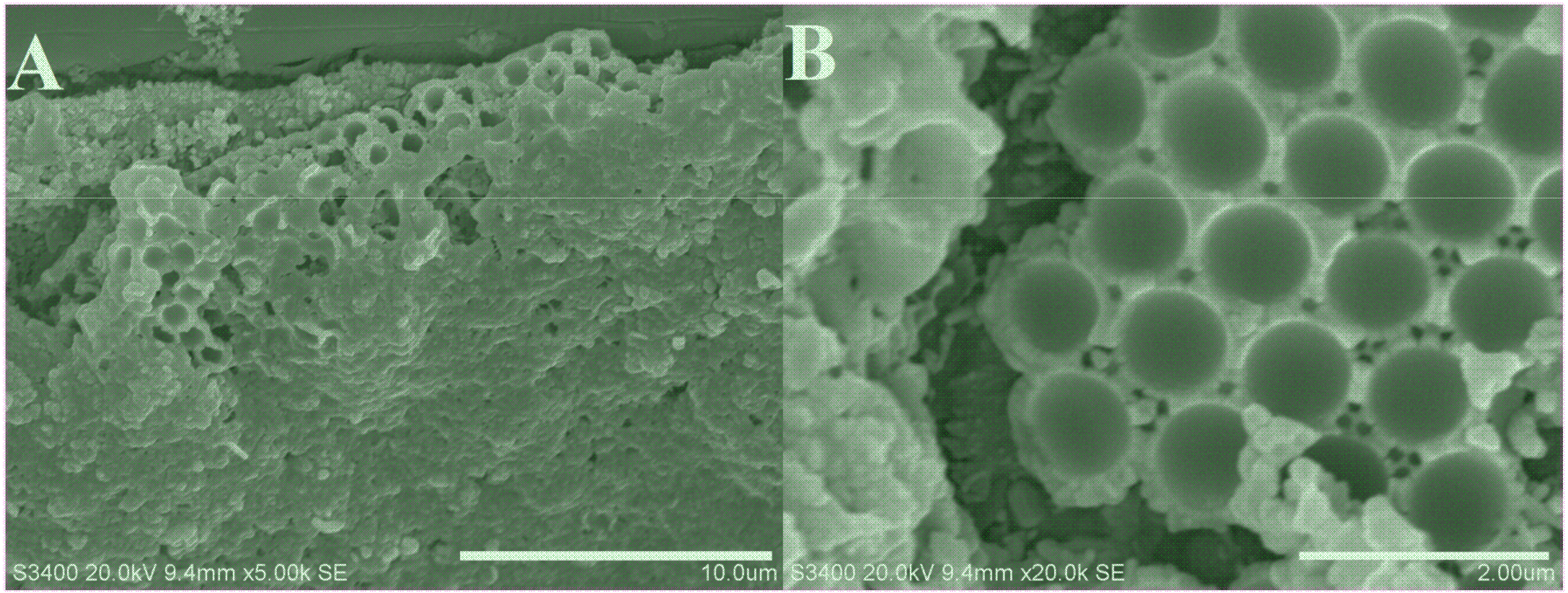
PANI monolith in channel morphologies layer by layer



2. Bulk Chemical CP Growth through CC Templates





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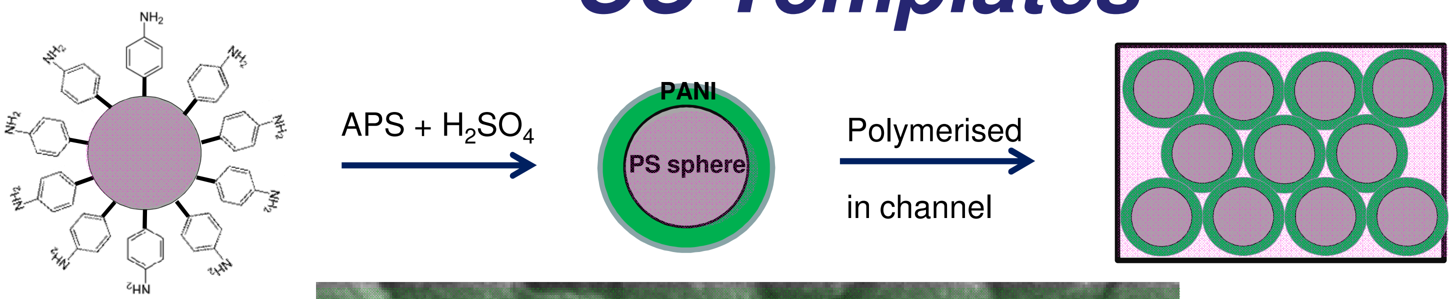
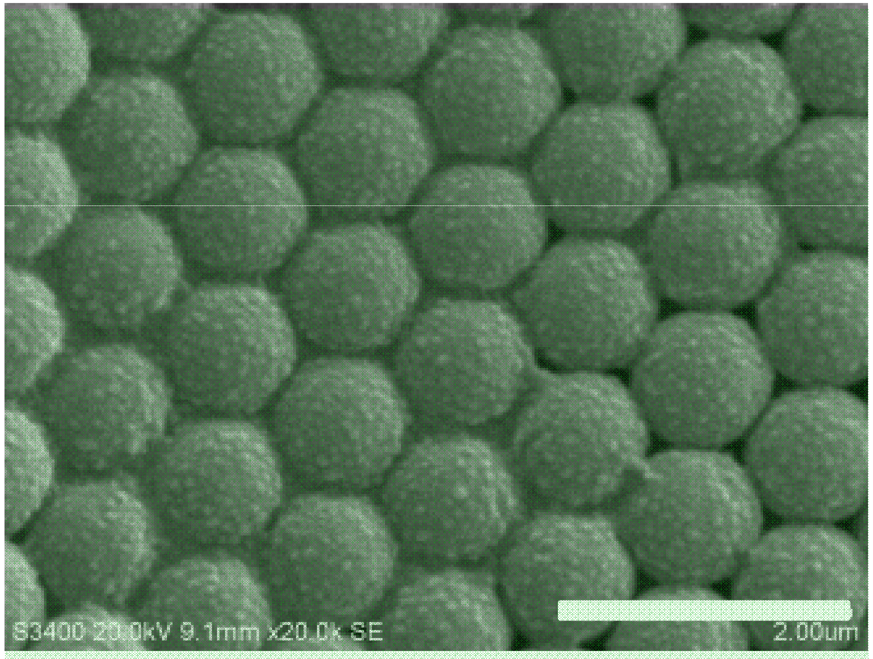
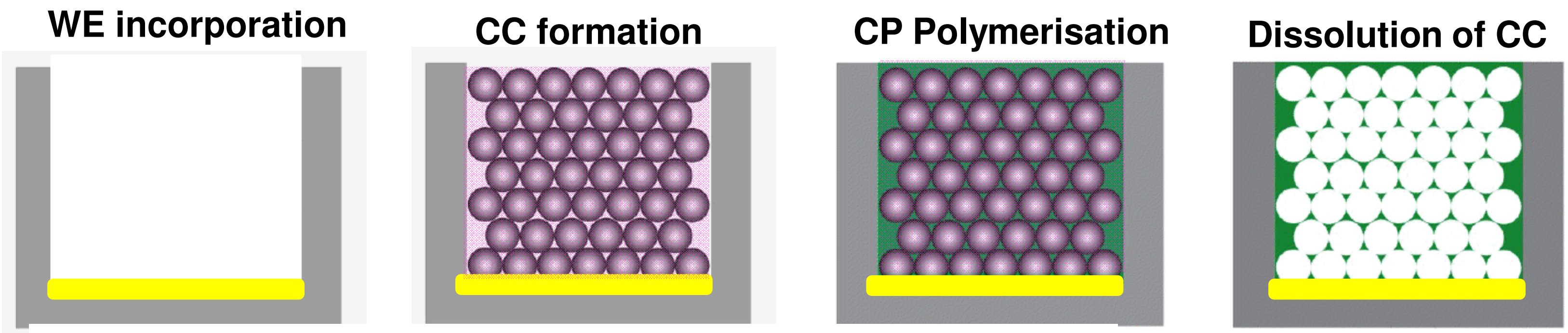
3. Surface Confined CP Growth through CC Templates





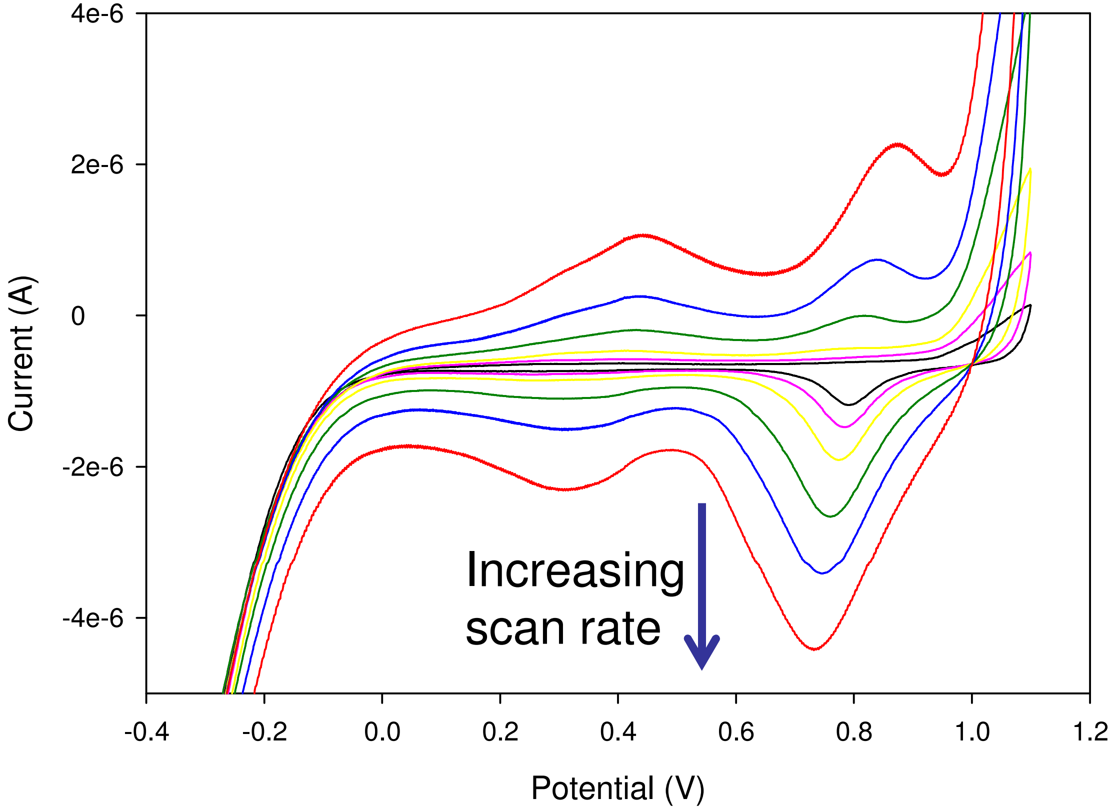
Electrochemical control

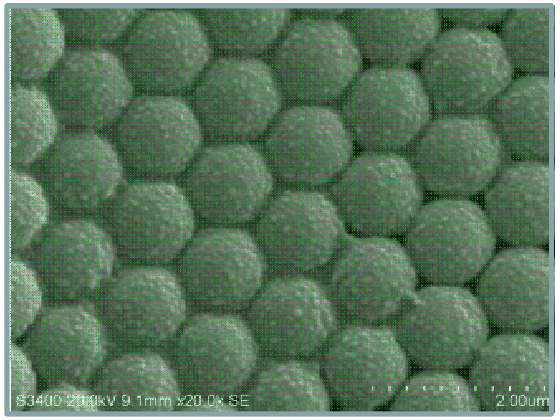


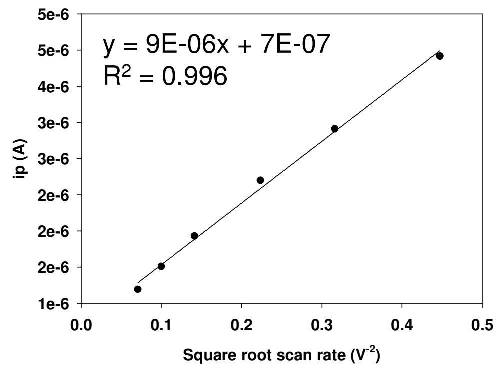
Aim: Monolith

1) Electrochemically responsive material

Surface-Confined PANI Electrochemistry in Sealed µChannel







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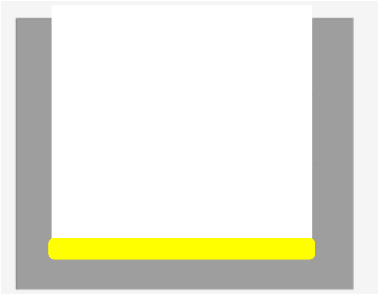
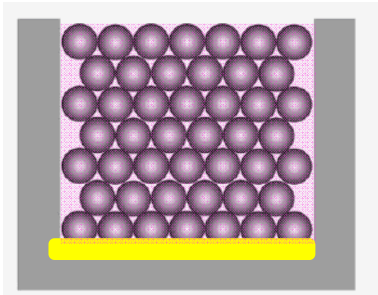
Conclusion

WE incorporation



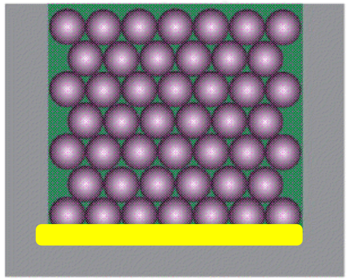
- *Incorporate in channel*

CC formation



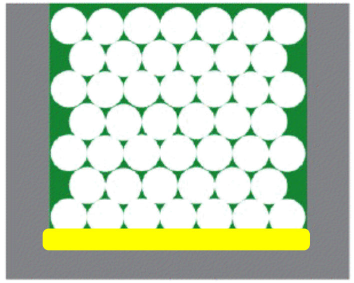
- *3D unimodal*
- *3D bimodal*

CP Polymerisation



- *Template directed*
- *Electrochemical*
- *Bulk chemical*
- *Surface confined chemical*

Dissolution of CC



- *Electrochemically active PANI coating*

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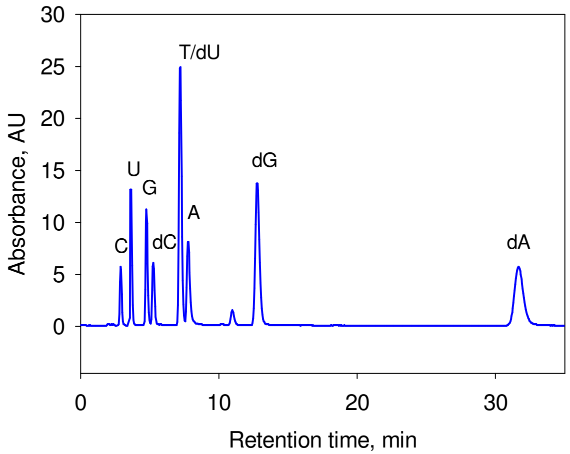
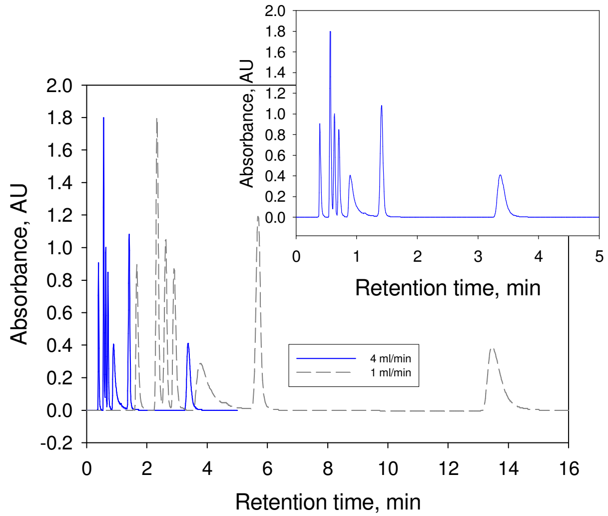
Future Work

- Apply this new microfluidic platform to develop a new stimuli-responsive chromatographic material based on polyaniline monoliths

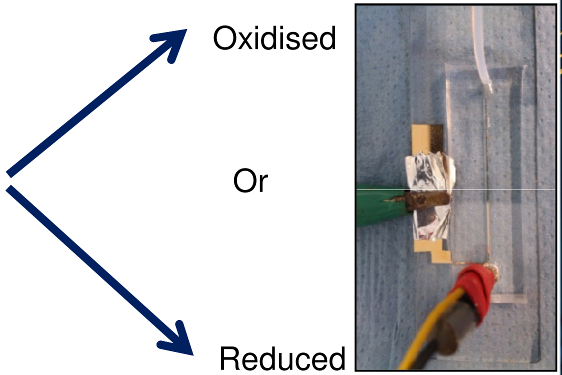
A) Packed HPLC column



B) Monolith HPLC column



C) Microfluidic monolith stationary phase – electrochemically responsive???



M.C. Kelly, B. White, M.R. Smyth, *Journal of Chromatography B*, 2008, 863, 181–186

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Many thanks to

Enterprise Ireland & SFI (TIDA) for funding, Dr. Aoife Morrin, Dr. Blanaid White and Prof. Malcolm Smyth for all their support and guidance during the course of the project and finally everybody in the School of Chemical Sciences, DCU, particularly the members of the Separations and Sensors Group for their assistance during the experimental work.

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