

Electroactive Monolithic μ Chip For Electrochemically-Responsive Chromatography

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The EM μ project's focus is ultimately, the development of an electroactive monolith that can be incorporated into a microfluidic system for electroanalytical applications such as sensing and electrochemically-controlled extractions and separations. To date our have made several significant advances to achieving this end goal.

Firstly a facile fabrication method which allows for the production of fully disposable, gasket-free thin-layer cells suitable for EM μ was developed. A polydimethylsiloxane (PDMS)-glass μ chip, configured to house an electrochemical thin-layer flow cell is being used to electrochemically polymerise polyaniline (PANI) monoliths on-chip¹. The feasibility of integrating macro-dimensioned, working electrodes into microfluidic channels being a critical first step of the EM μ project. This platform has been used for amperometric detection of ascorbic acid.

Simultaneously inverse opal monolithic flow-through structures of conducting polymer have been achieved in microfluidic channels via the fabrication of polystyrene (PS) colloidal crystal templates and the subsequent electrochemical or chemical polymerisation of the polymer².

Currently the focus of EM μ is to build on the significant advances to date, to demonstrate electrochemically-responsive chromatography on μ chip which will provide many advantages over solvent gradient-controlled chromatography. To achieve this, high back pressures on chip will be required and thus work to fabricate mechanically robust monoliths from electroactive conducting polymer is necessary. This is currently being examined via compositing with methacrylates which are an existing stationary phase polymer monolith material.

Development of Disposable, Gasket-Free Thin-Layer Cell

Microfluidic chips were fabricated using a glass-PDMS configuration. The bottom piece of the chip comprised of a glass slide that was sputtered with a gold working electrode (5 mm \times 110 μ m) using a TECAN[®] shadow mask. A Cr base layer (~ 50 nm) was used to improve the adhesion of the sputtered gold (~ 100 nm). The upper piece of the chip, comprised of a microfluidic channel (4 cm \times 220 μ m wide) fabricated using SU-8 silicon wafer moulds (produced using photolithography). A number of silicon moulds were produced allowing the preparation of a range of channel depths (35, 60, 110, 180 μ m).

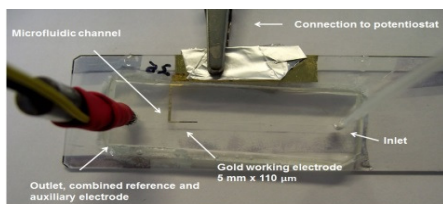


Figure 1: Microfluidic chip integrated with an electrochemical cell.

Fabrication and Characterisation of PANI Monolith On-Chip

Primarily the polymer monolith was electrochemically polymerised *in situ* on chip. This bulk polymer displayed the characteristic PANI electrochemistry and fibrillar morphology, figures 2a & c(i), while the observed uniformity of the polymer thickness along the electrode, figure 2b, implies that there is no significant IR drop along the length of this electrode. Templating of the PANI monolith, figure 2c(ii), was also possible by first constructing a reproducible polystyrene (PS) sphere colloid crystal (CC) via capillary force packing in the channel. This produced a highly ordered 3 dimensional structure. PANI was electrochemically polymerised through this structure prior to the dissolution of the CC. However the mechanical strength of both of these resulting monoliths was not sufficient for the high back pressures required which prompted work to augment the polymers robustness via a compositing approach.

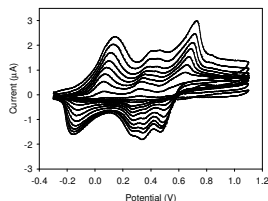


Figure 2a: Electroreduction of PANI in HCl (1 M) on the channel electrode in the microfluidic chip.

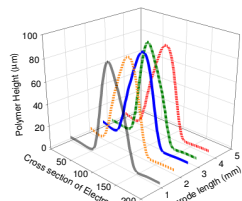


Figure 2b: PANI cross-section along the 5 mm channel electrode (channel depth: 180 μ m) using the 3D microscope.

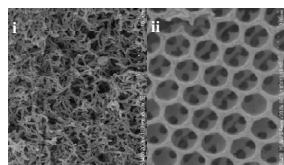


Figure 2c: SEM image of PANI after electrochemical polymerisation in the μ channel. ii) An ordered PANI monolith can be fabricated via polymerisation through a sacrificial PS CC template. Image shows evidence of discreet flow-through pores in the honeycomb structure.

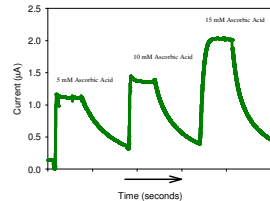


Figure 2d: Amperogram for the detection of ascorbic acid on-chip at the PANI modified channel working electrode.

Enhancing the Rigidity of the PANI Monolith

Achieved via compositing of the PANI with a thermoplastic polymer (poly methyl methacrylate) by a simultaneous polymerisation. The resulting composites possessed greater rigidity, but the CC templating method was not suited to this material. This led to the further development of the compositing technique to include a porogen³ (decanol) which allowed for the synthesis of mechanically robust porous PANI/PMA monolith. The monolith was observed to be not only conductive, figure 4, but also maintained PANI's electrochemistry, figure 5.

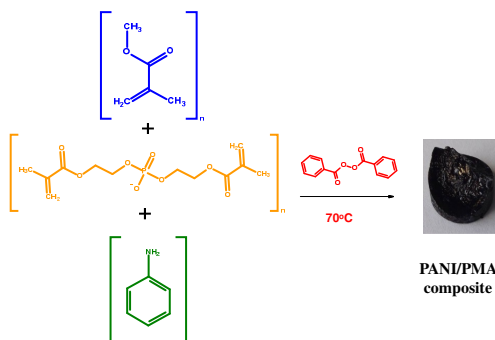


Figure 3: Simultaneous polymerisation method of PANI/PMMA composite. Polymerisation was conducted in presence of proton donor HEMA-phosphate.

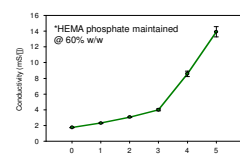


Figure 4: Composite's conductivity dependent on PANI content

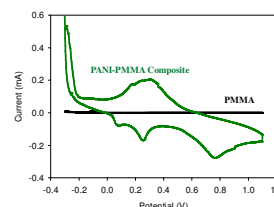


Figure 5: Composite maintained PANI's characteristic electrochemistry, 1 M KCl, scan rate: 10 mVs⁻¹.

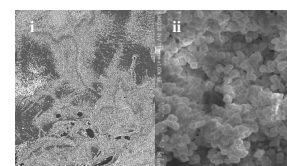


Figure 6: SEM image of PANI composite, composite exhibited increased rigidity however was too dense for final application prompting the incorporation of decanol porogen ii).

Conclusions

An effective thin-layer electrochemical flow cell based on PDMS/glass has been illustrated; where the the PANI-modified channel electrode was demonstrated for an amperometric sensing application via the detection of ascorbic acid. A facile fabrication method for templating these conducting polymer monoliths within the microfluidic channel was also developed.

Augmentation of the conducting polymers mechanical strength was achieved by compositing with a PMMA, while maintaining the conducting polymers electrochemical properties.

Future Work

To incorporate the PANI/PMA monolith on-chip and tether the composite to the surface of the PDMS channel. Characterisation of the flow profile and surface area of the new tethered monolith will be carried out. Ultimately, the platform will be utilised for electrochromatographic applications.

References

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3. D. Connolly, S. Curriaran, B. Paull, *Proteomics*, **2012**, 12, 2904 - 2917