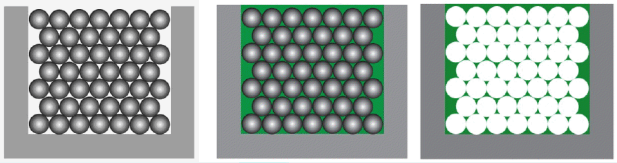
Electroactive Monolithic µChips Based on Nanostructured Polyaniline

Galineau, J., White, B., Smyth, M.R., Morrin, A.*,
Sensors and Separations Group, NCSR, School of Chemical Sciences, Dublin City University, Dublin 9; blanaid.white@dcu.ie

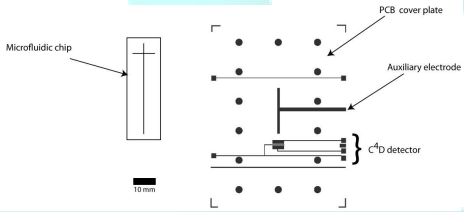
The extensive application of monolithic columns for HPLC is severely hindered by a lack of column-to-column reproducibility. EMµ (Electroactive Monolithic µChip) is a new concept that solves the significant reproducibility problems, as well as allowing miniaturization and improving overall efficiency through electrochemically controlled dynamic separations. This novel µchip has a micro-structured monolith fabricated from intelligent, electroactive polymer. By application of a specific potential, conducting polymers such as polyaniline (PANI) can be reproducibly grown and readily fine-tuned in terms of porosity, hydrophobicity and ionic capacity. This unique chip provides for an Electroactive Monolithic µchip capable of multi-dimensional chromatographic separations.
The monolith microstructuring (provided by templating) will provide reproducibility and improve efficiency by decreasing the A-term of the Van Deemter equation. Furthermore, the use of these intelligent materials will enable gradient control and redox reactions to be exploited during separations of large biomolecules.

Concept



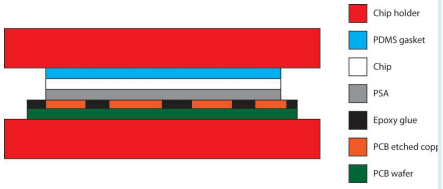
The aim of this project was to create a highly reproducible micro-structured monolithic stationary phase within a commercial glass µchip, using the following steps:
• assemble a reproducible template within the separation channel:
• polymerise the monolith through the template;
• sacrifice the template without damaging the monolith.
Polystyrene (PS) beads were used as the template, with PANI fabricated electrochemically to form the monolithic stationary phase.

Chip Design



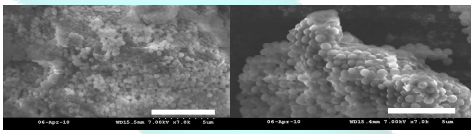
The glass microfluidic chip (Micronit) has cross-shaped channel dimensions 110 µm x 50 µm (width x length). To electrochemically grow the stationary phase, a 20 mm length of the main chip channel was gold-sputtered to serve as the working electrode. PS was packed in an ordered fashion into the main channel via capillary forces, using surface energy directed evaporation-induced self assembly. PANI was electrochemically deposited to the working electrode via a three-electrode cell. The auxiliary electrode and C^{4}D detector were etched into the printed circuit board. The mask used to etch the PCB is shown on the right.

Chip Bonding



Chip bonding was achieved via the pressure sensitive adhesive (PSA) layer. Fluidic connections were made through a polydimethylsiloxane (PDMS) gasket to ensure leakage-free connections. The etched PCB was covered with epoxy glue. The glue was then ground until copper electrodes were revealed in order to obtain a smooth, flat surface. Finally, pressure was maintained by screwing the whole system in a custom made chip holder.

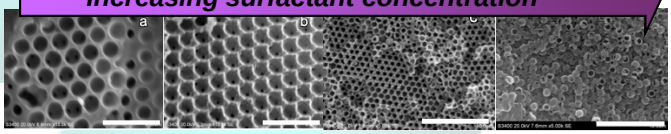
Development of a dissolvable PS bead template



PS beads were synthesised according to Shim *et al.* (J. App. Poly. Sc., 71 (13) 2259). For this synthesis, di-vinyl-benzene (DVB) was used as a cross linking agent during polymer synthesis. Increasing DVB concentration was found to increase the stability and rigidity of the resulting beads, and therefore decrease their solubility (left). By decreasing the DVB concentration to 0.4% during synthesis, PS beads were formed, which were sufficiently rigid, monodispersed and spherical to be used as templating scaffolds, but which readily dissolved in toluene, ensuring that the PS nanostructure could be sacrificed when required (shown on right).

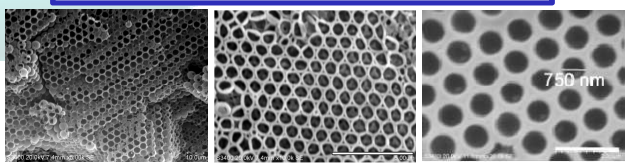
Direction of polymerisation to ensure pore inter-connectivity

Increasing surfactant concentration



Increasing the surfactant concentration in the original PS beads suspensions increased the zeta potential of the PS beads (data not shown). When rewetting the template with the monomer solution, the electrostatic repulsion between the beads disorganised the template (which were PS opals in all cases). Thus by increasing the surfactant concentration, the microstructure of the polymer can be tailored from inverse opals to random hollow spheres. (Scale bars 100 µm)

Microstructured PANI monolithic stationary phase



Inverse opal PANI structures were obtained by electrochemically growing PANI through a sacrificial PS template. PS opals were grown at 40ºC using 1 % (w/v), 1 µm PS beads suspension. PANI was then grown potenstiostatically at +0.9 V vs Ag/AgCl. After removing the PS template using toluene, a typical inverse opal PANI structure was observed. The observed structure is ordered in 3-dimensions, potentially providing a new way for improving chip-to-chip reproducibility of monolithic stationary phases.

Conclusion A micro-structured monolithic stationary phase has been fabricated from intelligent electroactive polymer. The electropolymerisation process allowed good reproducibility of the polymers physico-chemical properties. It has been shown that the surfactant concentration in the the PS beads could be tuned to optimise the final PANI structures. Finally, highly ordered stationary phase structures were formed within the microfluidic channel.