Inverse-opal conducting polymer monoliths in microfluidic channels

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Inverse opal monolithic flow-through structures of polyaniline (PANI) were achieved in microfluidic channels for lab-on-a-chip (LOC) applications. In order to achieve the uniformly porous monolith, polystyrene (PS) colloidal crystal (CC) templates were fabricated in channel. An inverse opal PANI structure was achieved on-chip, through a two-step process involving the electrochemical growth of PANI and subsequent removal of the template. The effect of electropolymerisation on these structures is discussed. It was found that growth time is critical in achieving an ordered structure with well-defined flow-through pores. This is significant in order to fabricate optimal porous PANI structures that maximise surface area of the monolith and also provide well-defined flow profiles through the micro-channel.

On-chip PANI monolith fabrication

A polystyrene (PS) sphere colloidal crystal (CC) template was fabricated, 1% w/v 1 µm PS spheres, by capillary force packing within the micro channel of a glass micro-fluidic chip (Fig.1). PANI was subsequently electrochemically grown through the PS CC. A series of monoliths were produced over a range of growth times (90 s – 360 s). The resulting structures were imaged using SEM analysis.

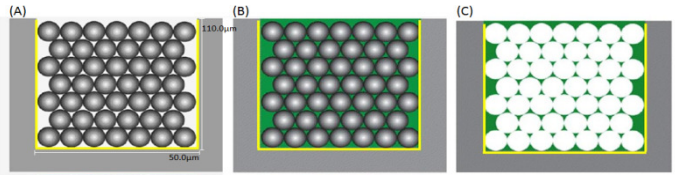

Fig Schematic of templating process in gold-sputtered micro-channel: A) Deposition of PS sphere CC. B) Growth of PANI through 3D CC template. C) Removal of PS CC using toluene. A templated unimodal inverse opal PANI monolith structure remains. Schematic not to scale.

Structure characterisation

The honeycomb morphology of PANI after 90 s polymerisation is shown in Fig.2a. Highly heterogeneous growth is evident with growth along the gold-sputtered base and walls of the chip channel, observed. During template removal the pore size of the structure had low uniformity indicating a collapse in structure and/or inhomogeneous growth. This was also observed at 120 s (Fig.2.d). Some flow-through pores are evident after 120 s polymerisation. But the flow-through nature of these pores is most likely lost due to frailties in the monolith structure and subsequent collapse.

Short PANI growth time

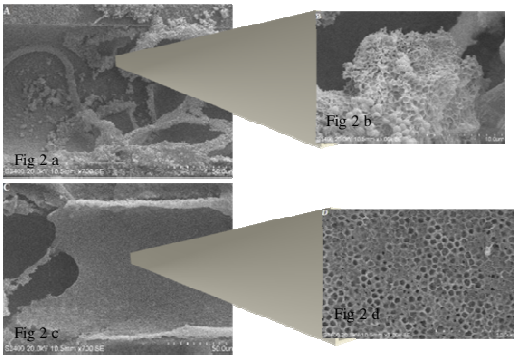

Fig.2. SEM images of PANI after A) & B) 90 s and C & D) 120 s polymerisation time in the micro-channel grown through the sacrificial PS CC template.

Improved stability of the internal PANI structure was observed after 180 s electrochemical growth. The structure was homogeneous and remained intact after removal of the PS template. It was observed that a growth time of between 180 s and 240 s gave the monolith the optimal flow-through structure (Fig. 3a) with improved definition of internal walls was observed, along with the presence of regular flow-through pores (Fig. 3b).

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Intermediate growth time

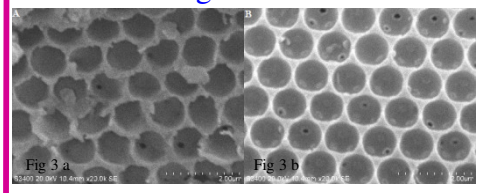

Fig.3 SEM images of PANI growth after 180 s and B) after 240 s polymerisation time. Honeycomb structures are present.

Prolonged growth times resulted in a fibrillar structure Fig.4a (360 s) in contrast to the branched sponge-like morphology that is typical of bulk PANI. These nano-fibres with approx. widths 100 – 200 nm, are thought to be generated as a result of the templating step. The rough morphology of the hollow spheres, observed in Fig. 4b, serves as subsequent nucleation sites for further polymerisation where the beginning of the formation of the small thin shoots of PANI can be observed

Long growth time

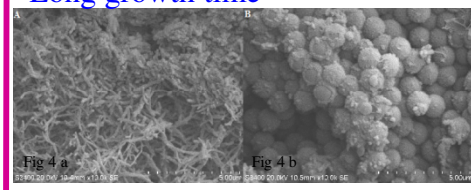

Fig 4 SEM image of A) Excess PANI growth protruding from the channel. B) Hollow spheres formed internal to the channel.

Fig.5 Comparison CV of templated PANI to that of bulk, non-templated PANI grown for 210 s. Both CVs are comparable, showing the electrochemistry of the templated PANI is equivilent to that of a bulk PANI material that has been grown potentiostatically for the same amount of time

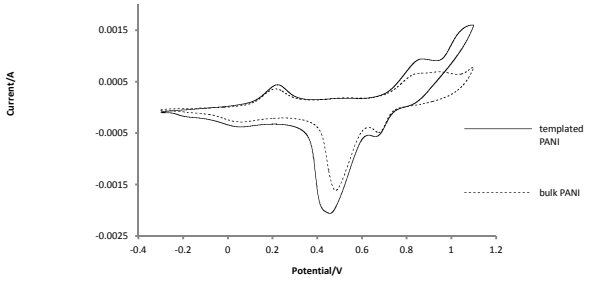

Fig 5 Voltammograms of PS templated and bulk PANI monoliths grown within the microchannek. PS spheres were removed using toluene.

Conclusion:

This work demonstrated that templated conducting polymer structures, such as PANI, can be achieved readily within micro-fluidic channels. It should be noted that the electro-polymerisation time is critical not only to the depth of the PANI, but also to the intrinsic morphology and flow-through nature of the material. This technique shows great potential for the future development of new lab on chip (LOC) applications in particular for sensing applications.

References

B. Gorey, J. Galineau, B. White, M.R. Smyth, A. Morrin. Electroanal. doi: 10.1002/elan.201200083

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