# Utilising 3D binary colloidal crystals to customise macropore and mesopore morphology and porosity

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Current approaches to fabricate hierarchically porous (macroporous-mesoporous) monolithic materials for HPLC include using silica and thermally- or UV-initiated organic polymer. Silica monolith preparation is usually carried out using a sol–gel process to induce a hierarchical pore structure. Polymer monoliths, which contain primarily macropores have emerged as complimentary stationary phases to silica monoliths. It has proven difficult to date to prepare polymer monoliths in a single-step that possess a hierarchical pore structure, *i.e.* large through-pores, to enable flow at low back pressure, and a multiplicity of mesopores to increase surface area. 3D binary colloidal crystals may be formed by packing uniform spheres, followed by filling the interstitial space with a fluid that is subsequently converted into a solid skeleton. Upon removal of the spheres, a solid skeleton is created in the former interstitial spaces and interconnected voids where the spheres were originally located. By virtue of creating the solid skeleton, smaller pores (small macropores, mesopores, or micropores) can naturally be formed, *e.g.* as occurs during silica monolith fabrication. Further control of the skeleton architecture can be obtained when a secondary template is employed, *e.g.* ionic and nonionic surfactants, block copolymers, small colloids, *etc*. Micro- and nano-structuring using sacrificial templating approaches can induce both macropores and mesopores into polymer monoliths that can increase surface area by several orders of magnitude in a highly controlled fashion.

## Experimental

Construction of a 3-D binary colloid crystal comprising polystyrene (PS) spheres of various sizes was investigated using different methods to of crystal grwoth within the separation channel of a glass chip. Controlled assembly of 3D binary colloidal crystals was successfully achieved in the separation channels using evaporation-driven convective self-assembly with PS spheres ranging in size from 100 nm to 3 µm. Pyrrole was then polymerised through the template.The template was subsequently dissolved using toluene, leaving behind a hierarchically porous polypyrrole structure containing both larger macropores and surface area enhancing mesopores.

## Sequential Crystallisation

Fig 1(a)

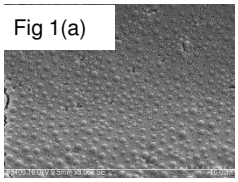


Fig 1(b)

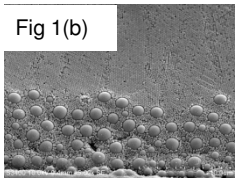
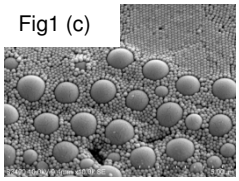


Fig1 (c)



In Fig.1.(a) a bimodal structure clearly is evident, however the macro-sized spheres have not packed uniformly. Within the same channel, areas as shown in Fig.1.(b) and (c) were also identified where the nano-sized PS spheres packed at a faster rate resulting in areas containing predominantly nano-sized PS spheres closer to the end of the channel of the glass chip.

*Fig.1.(a-c) SEM images of 200nm and 2µm PS spheres packed sequentially.*

## Co-Growth Crystallisation

Fig 2(a)

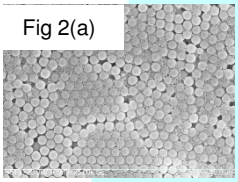


Fig 2(b)

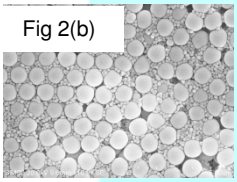
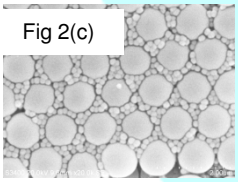


Fig 2(c)



In this method a macro and nano PS sphere mixture was utilised to grow the binary colloid. As shown in each of the images (a)-(c) there is a high degree of uniformity amongst the macro-sized PS beads. The bimodal structure, most clearly evident in Fig.2.(c) resulted in the nano-sized PS spheres occupying the interstitial voids in the macro-sized sphere colloid.

*Fig.2.(a-c) SEM images of 200 nm PS spheres and 1 µm spheres packed by co-deposition.*

## Co-Growth with Pretreatment

Fig 3(a)

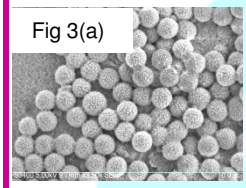


Fig 3(b)

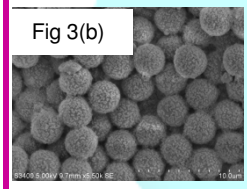
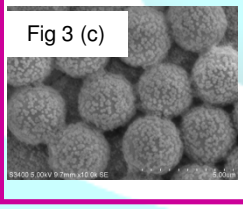


Fig 3 (c)



The macro-sized and nano-sized sphere solution was sonicated prior to binary colloid formation.

During sonication, the nano-sized spheres aggregated to the macro-sized spheres, as shown in Fig.3.(c).

These aggregates then packed unimodally within the channel. This provided an alternative template to co-deposition, with minimum contact was between macrospheres.

*Fig.3.(a-c) SEM images of bimodal structure formed during co-deposition of 200 nm and 3 µm PS spheres.*

## Monolith formation through the 3D template

Fig 4(a)

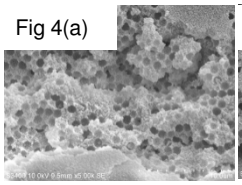


Fig 4(b)

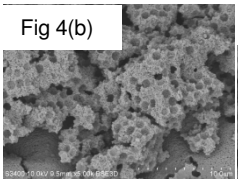


Fig 4(c)

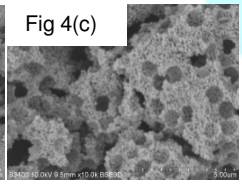


*Fig.4.(a-c) SEM images of a bimodal polypyrrole monolith.*

A 3D bimodal colloid crystal was constructed using 200 nm and 2 µm PS spheres within the microchip separation channel, using PS aggregates formed by binary crystal co-growth with pretreatment. Pyrrole was then polymerised through the template. The PS template was subsequently dissolved using toluene. The SEM images above Fig.4.(a-c) show the resulting mesoporous-macroporous structure. Although the uniformity of the structure has not been optimised, a hierarchically porous polypyrrole structure containing both larger macropores and surface area enhancing mesopores was obtained.

## Conclusions

The construction of a 3-D binary colloid crystal has been successfully achieved using a number of crystallisation techniques. Sequential growth using macro and nano PS spheres lead to the least homogeneous template, which was expected due to differences in self assembly rates arising from size and concentration ratios. These ratios were exploited during cogrowth strategies to create a binary colloid containing a primary macrosphere colloid with nanospheres crystallising within the interstitial voids. An alternative cogrowth strategy pretreated the macro and nano PS spheres to create aggregates with nano beads coating the macrobeads, which crystallised unimodally. Future experiments will focus on increasing the homogeneity of the colloid throughout the crystal.

## References

Wang, L.K., Y. Wan, Y.Q. Li, Z.Y. Cai, H.L. Li, X.S. Zhao, and Q. Li, *Binary Colloidal Crystals Fabricated with a Horizontal Deposition Method.* Langmuir, 2009. **25**(12): p. 6753-6759.

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NCSR National Centre for Sensor Research

NDP NATIONAL DEVELOPMENT PLAN

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