

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



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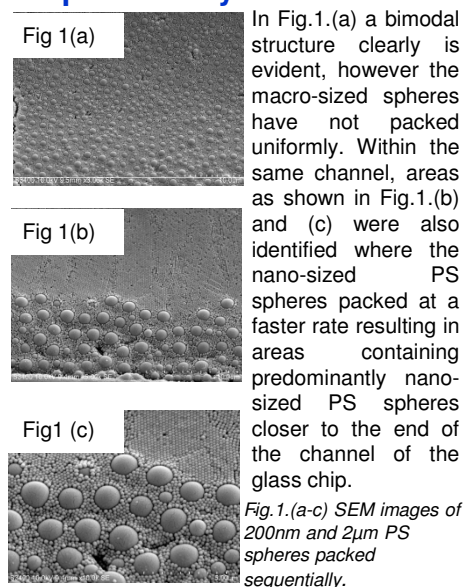
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Current approaches to fabricate hierarchically porous (macroporous-mesoporous) monolithic materials for HPLC include using silica and thermally- or UV-initiated organic polymer. Silica monolith preparation is usually carried out using a sol-gel process 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.

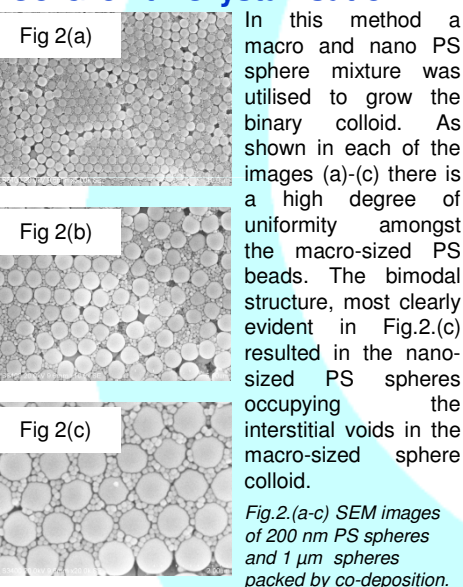
Experimental

Construction of a 3-D binary colloid crystal comprising polystyrene (PS) spheres of various sizes was investigated using different methods to of crystal growth 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.

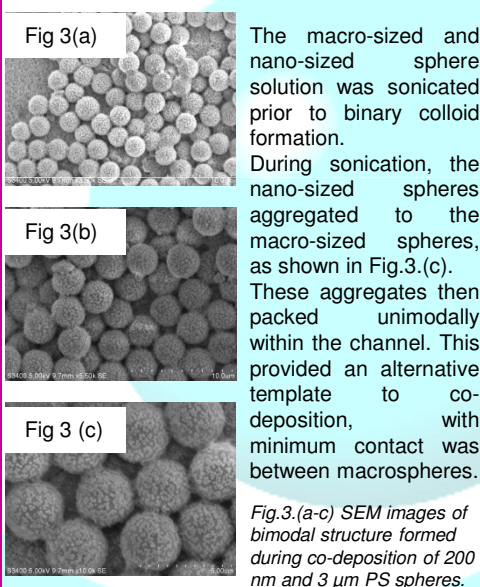
Sequential Crystallisation



Co-Growth Crystallisation



Co-Growth with Pretreatment



Monolith formation through the 3D template

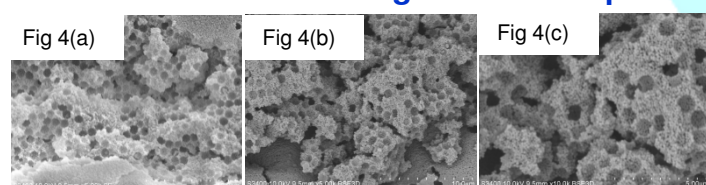


Fig.4.(a-c) SEM images of a bimodal polypyrrole monolith.

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.
- Kitaev, V. and G.A. Ozin, *Self-assembled surface patterns of binary colloidal crystals*. Advanced Materials, 2003. **15**(1): p. 75.

Funding

This work is funded under the SFI / EI Technology Innovation Development Award Programme

