Development of 3-dimensional nanostructured unimodal and bimodal polystyrene templates



Brian Gorey^I, Aaron Newman Blánaid White^I, Aoife Morrin^I, Malcolm R. Smyt.

National Centre for Sensor Research

(NCSR), School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

brian.gorey2@mail.dcu.ie

The aim of this project is to construct a reproducible nanostructured polystyrene (PS) sphere colloid. The polystyrene colloidal crystal must incorporate both macro-sized (µm) and nano-sized (nm) spheres to further advance the potential applications of such templates. However the preparation of bimodal structures with a repeatable macropore-mesopore structure is not a straight forward process. Multiple methods were explored in the construction of unimodal and bimodal colloid crystal templates. Areas of interested such as variation in sphere size, up to two orders of magnitude between macro and nano-sized were investigated, along with determination of the rate at which each PS sphere size packed by capillary forces. Two methods have been singled out sequential deposition and co-deposition. Sequential deposition utilised two separate solutions one containing nano-sized PS spheres, the second macro-sized. During packing the glass chip is transferred between the macro and nano solutions before predetermined times. It was found that while packing sequentially formation of a nano-sized unimodal colloid was preferable. This was due to a faster rate of capillary force packing for the nano-sized PS spheres was homogenised and packed for a period of twelve hours. To date co-deposition has shown the most promise as a reliable method to produce bimodal colloidal crystals.

Experimental

Construction of a reproducible nanostructured polystyrene (PS) sphere colloid was investigated using different methods to pack a glass chip with PS spheres. Two contrasting methods were utilised sequential and co-deposition. During sequential deposition two solutions one containing macro-sized PS spheres, the second containing nano-sized spheres were packed. A glass Micronit chip was transferred for predetermined intervals between the two solutions giving equal time for each solution to pack. The second method utilised was co-deposition. In this method a homogenised solution of macro-sized and nano-sized PS spheres were allowed to pack for 12 hours at 45°C within the glass chip.

Results & Discussion



Fig.1.(a-c) SEM images of 200nm and $2\mu m$ PS spheres packed sequentially. The resulting structure has many areas of interest. 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.2.(a-c) SEM images of 200 nm PS spheres and 1 µm spheres packed by co-deposition. In this method the two solutions were mixed but no homogenisation of the solution was undertaken. As shown in each of the images (a)-(c) there is a high degree of uniformity amongst the macro-sized PS beads. From this the bimodal structure, most clearly evident in Fig.2.(c) resulted in the nano-sized PS spheres occupying the spaces between the macro-sized spheres.

Funding

Sensor Foundation of Ireland SFI.



Fig.3.(a-c) SEM images of bimodal structure formed during co-deposition of 200 nm and 3 μ m PS spheres. During this experiment sonication was used to homogenise the solution. The solution became more homogenised the nanosized spheres aggregated to the macro-sized spheres Fig.3.(c). However it was found that the 3 μ m PS spheres settled out of solution very quickly and as a result without constant agitation it would not be possible to pack them successfully.



Fig.4.(a-c) SEM images of a bimodal polypyrrole monolith. A bimodal template was constructed using 200 nm and 2 μ m PS spheres within the channel of a glass chip. The solution of PS spheres was homogenised using sonication prior to packing. Pyrrole was then polymerised through the template. The PS template was subsequently dissolved out 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, the construction of a 3-dimensional bimodal template was successfully completed.

Conclusion:

The construction of a bimodal PS sphere template has been successfully achieved using both sequential and co-deposition. PS spheres ranging in size from 100 nm to 3 μ m have been used with some sizes showing more suitability than others due to the rate of capillary force packing. It was found in the initial stages of co-deposition that the homogeneity of the solutions was of great importance. The resulting structure formed showed the highest enhancement in surface area through aggregation of the nano sized beads around each of the macro-sized. With this knowledge future experiments will focus on ensuring homogeneity of the solutions of PS spheres during co-deposition with variations in concentrations of PS spheres then being investigated further.

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-+.



