



Fabrication of a 3-dimensional nanostructured binary colloidal crystal within a confined channel



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ABSTRACT

The reproducible fabrication of nanostructured 3Dimensional (3D) binary colloidal crystal (bCC) in a defined geometric space through a simple one step process is detailed. This method allows for the potential fabrication of a bCC in a sealed μ chip within a defined area or channel by capillary forces, unlike other bCC formation methods such as dip-drawing, where the substrate must be submerged in a suspension to form a bCC, or bCC monolayers, which are fabricated at the water air interface. Through simple variation in volume fraction ratio ($VF_{S/L}$) of nano-(denoted small, S) and macro-sized (denoted large, L) polystyrene (PS) spheres and diameter size ratio ($D_{S/L}$), the manipulation of bCC structures was also achieved. Variation of nano-sized PS sphere number within the interstitial voids formed between neighbouring macro-sized spheres enabled the reproducible fabrication of LS_2 and LS_6 structures, which contain 1 and 3 nano-spheres respectively in each interstitial void. It must be noted that while $VF_{S/L}$ allows for control of the final LS_n structure, thickness of bCC formation in this manner is independent of $VF_{S/L}$.

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1. Introduction

Unimodal and bimodal colloidal crystals have been the subject of extensive research in recent times, for a variety of reasons, due at least in part to their potential application in photonics, biosensors and 3Dimensionally ordered material (3-DOM) fabrication.[1–4] Literature details numerous fabrication methods for both unimodal [5–8] and bimodal [9,10] PS templates, as discussed below.

Unimodal crystals can be formed reproducibly through well understood methods such as dip-drawing [7] and capillary force packing [6,8]. Other methods such as drop-casting have low reproducibility [11] due to the coffee ring phenomena with areas of reduced reproducibility in the centre of the colloidal crystal thus limiting their use in templating. Recent examples of bimodal colloidal crystal fabrication have used macro-spheres in conjunction with nano-spheres of either PS or silica. Formation of bCCs through self-assembly [12–16] and solvent evaporation [17] have been shown with nano-spheres present in the interstitial voids of the

macro-spheres. Uniformity in the resulting structures depend heavily on volume fraction ($VF_{S/L}$) of the macro (denoted large, L) and the nano (denoted small, S) sized spheres and size ratio, denoted by $D_{S/L}$, in solution during bCC formation [18]. Boundary conditions for $VF_{S/L}$ and $D_{S/L}$ have been detailed extensively by Ozin et al. during fabrication of bCC monolayers by evaporation induced self-assembly [19]. To date much of the work fabricating ordered PS and silica bCCs has been achieved in monolayers through convective self-assembly at the water air interface [12,19], or in multilayers through drop-cast convective self-assembly [16,20] and dip-drawing methods [21]. While each method has shown fabrication of ordered bCC structures, to date these structures within defined geometric channels have not been achieved.

Colloidal crystals with specific microstructures and patterns are expected to play a key role in the structural and performance design of colloidal crystals in the future, and can be fabricated by guided assembly, as recently reviewed by Cong et al. [22]. However, most research has not specifically quoted film thickness beyond reporting that a 3D structure is obtained. Visual examination of 3D structures can be utilised to estimate thickness, e.g. 3D CCs fabricated Kubrin et al. via evaporation induced self-assembly indicates that structures are typically less than 5 μ m in depth [23]. By the incorporation of tetraethyl orthosilicate (TEOS) in the PS self-assembly process, Cai and co-workers reported crack free bCCs with film thicknesses of up to 16 layers [13].

Abbreviations: 3D, 3Dimensional; bCC, binary colloidal crystal; $VF_{S/L}$, volume fraction ratio; $D_{S/L}$, diameter size ratio; PS, polystyrene; 3-DOM, 3Dimensionally ordered material; TEOS, tetraethyl orthosilicate; LOC, lab-on-chip; PDMS, Polydimethylsiloxane; EICSA, evaporation induced co-operative hierarchical self-assembly.

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In this work the investigation of strategies for the fabrication of 3D PS bCC templates in defined channel dimensions initiated by capillary force packing is presented. Attempts to fabricate 3D bCC have typically been limited by $VF_{S/L}$. However, by directing the convective self-assembly process so that it propagates from the side walls of a microfluidic channel instead of upwards from a flat substrate these typical limitations have been overcome, so that the bCC can be fabricated to the depth of the microfluidic channel. This work details a single step approach to achieve 3D nanostructured bCC formation in channel using capillary force packing. The method allows for colloid formation in the absence of an air–water interface over the entire dimensions of the colloid, enabling lab on chip (LOC) designs for analytical applications. Additionally, as the thickness is independent of $VF_{S/L}$, significantly thicker films than previously reported have been achieved. 3D bCC fabrication in channel creates this potential due to the resulting bCC flow-through (or resulting inverse) structure that can be used as a stationary phase for separations and extractions, and can also be modified with target molecules (e.g. antibodies) for the development of highly sensitive LOC bioassays.

Variation of $D_{S/L}$ and $VF_{S/L}$ during fabrication allowed distinct structures to be controllably formed for potential analytical applications. 3D bCC structures were fabricated exclusively within the channels within 12 h which were ordered along the length, width and depth of the cuboid channel it was formed within (albeit with some defects). 3D bCCs with both 1 (LS_2) and 3 (LS_6) nano-sized PS spheres within the tetrahedral/octahedral interstitial void of the close packed macro-spheres were successfully fabricated.

2. Materials and methods

2.1. Materials

200 nm ($\pm 2.3\%$) and 1 μm ($\pm 3\%$) PS spheres were purchased from Duke Scientific (Palo Alto, California, USA). All PS sphere suspensions as received contained 0.1–0.5% surfactant to inhibit agglomeration and promote stability. Deionized water was purified using a MilliQ system to a specific resistance of greater than 18.2 M Ω -cm. Polydimethylsiloxane (PDMS) (101697) (Dow Corning 184 silicone elastomer), was purchased from Farnell (Ireland). Tetraethyl orthosilicate reagent plus >99% purchased from Sigma–Aldrich (Dublin, Ireland). Hydrochloric acid ~37% was purchased from Fisher Scientific UK Bishops Meadows Road, Loughborough. All other chemicals were purchased from Sigma–Aldrich (Dublin, Ireland) and were of analytical grade.

2.2. Instrumentation

SEM micrographs were obtained using a Hitachi S3400N scanning electron microscope (Hitachi, UK) at an acceleration voltage of 20 kV, probe current of 35 μA and working distance of 10 mm. All samples were gold-sputtered using a 750T sputter coater, Quorum Technologies (UK). Harrick plasma cleaner (PDC-002) was used for all oxygen plasma performed on PDMS chips. A Malvern nanosizer ZS was used for all zeta potential measurements.

2.3. PS sphere preparation

Immediately prior to use (to prevent aggregation [24]), anionic surfactant was removed from PS sphere stock suspensions. 1 μm PS sphere suspensions were centrifuged and re-dispersed in deionized water three times at 5000 rpm for 7 min. 200 nm PS sphere suspensions were centrifuged and re-dispersed in deionized water three times at 12,000 rpm for 45 min. Zeta potential measurements for 200 nm and 1 μm PS spheres were low to neutral with

zeta potentials of 0.0997 mV for 200 nm and -2.84 mV for 1 μm PS spheres. 50 zeta runs were performed in triplicate in an aqueous medium at 25 °C after removal of surfactant.

2.4. PDMS chip fabrication

Silicone elastomer and curing agent were mixed in a 1:10 w/v ratio, degassed for 45–60 min under vacuum, and poured onto a silicone mould prepared using photolithography. The resulting PDMS chip with cross channel of dimensions of 0.035 mm \times 0.110 mm \times 40 mm or 0.110 mm \times 0.110 mm \times 40 mm, was cured at 100 °C on a hotplate for 45 min. PDMS chips were then cut to correct size, 45 mm \times 20 mm, after curing.

2.5. 3D binary colloidal crystal fabrication

During 3D bCC fabrication macro-sized PS spheres were seen to pack into a closed packed fcc (111) structure. The resulting closed packed structure can be affected by temperature during CC formation [25]. For example Cong et al. determined that lower temperatures can aid the formation of a square array [26]. Therefore a temperature of 45 °C was employed throughout this work. Equal volumes of μm and nm PS sphere suspensions were premixed and homogenized through vigorous manual shaking. Oxygen plasma was performed on all microfluidic chips to activate the surface of the PDMS before capillary force packing for 5 min. This resulted in a reduction in hydrophobicity from $124 \pm 6^\circ$ prior to oxygen plasma treatment to $24 \pm 6^\circ$ post treatment (results from triplicate analysis of 3 samples). Oxygen plasma was performed under an atmosphere of air using a Harrick plasma cleaner (PDC-002) before the chips were placed into the PS suspension ensuring the channel base was immersed in the suspension. This was then heated at 45 °C for 12 h to allow PS spheres to form the bCC in the micro-channel. To anneal the structure to allow for SEM imaging, the micro-chip containing the fabricated bCC was heated at 90 °C for 30 min.

2.6. Preparation of tetraethyl orthosilicate (TEOS) sol–gel inverse opal

After 3D bCC fabrication in channel a TEOS sol–gel inverse opal was fabricated as follows [27]: 3 mL ethanol, 6 mL TEOS, 3 mL D.I. water and 1 mL concentrated HCl were mixed with constant stirring for 5 min. 1 mL was poured over the microfluidic chip containing the bCC in channel and cured at 65 °C for 2 h. After curing the PS sphere bCC was removed by immersion of the chip in toluene at room temperature for 20 min. and the TEOS sol–gel imaged using SEM analysis.

2.7. UV–visible spectroscopic analysis of 3D CC in PDMS micro-channels

UV–visible results were obtained using an Ocean Optics UV–visible spectrophotometer with spectra suite software. A 400 μm fibre beam width was used to measure each sample in triplicate. The PDMS micro-chip with micro-channel of dimensions 220 μm width \times 60 μm depth containing no CC, uCC or bCC crystals were each 4 mm thick, 12 mm wide and 40 mm in length.

3. Results and discussion

3.1. 3D PS colloidal crystal fabrication

3D PS bCC templates were formed through capillary force packing of surfactant free PS sphere suspensions into a straight channel in a microfluidic chip. Fig. 1 shows a schematic representation of

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