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# The self-assembly of monodisperse nanospheres within microtubes

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### Abstract

Self-assembled monodisperse nanospheres within microtubes have been fabricated and characterized. In comparison with colloidal crystals formed on planar substrates, colloidal nanocrystals self-assembled in microtubes demonstrate high spatial symmetry in their optical transmission and reflection properties. The dynamic self-assembly process inside microtubes is investigated by combining temporal- and spatial-spectrophotometric measurements. The understanding of this process is achieved through both experimentally recorded reflection spectra and finite difference time domain (FDTD)-based simulation results.

(Some figures in this article are in colour only in the electronic version)

# 1. Introduction

Colloidal crystals self-assembled from monodisperse nanospheres have recently attracted intense interest due to their applications in photonic crystals, the photonic analogue of semiconductors [1, 2]. The most common self-assembly methods for colloidal crystals are based on the slow sedimentation of nanospheres in aqueous suspensions [3]. Unfortunately, the sedimented colloidal crystals contain numerous defects, such as grain boundaries, dislocations and vacancies. These defects deteriorate the colloidal crystals' functionality. Intense research on the controlled self-assembly of nanospheres has yielded production of colloidal crystals with fewer defects [4-7]. However, better-controlled colloidal crystals and other crystal structures are not possible without a fundamental understanding of the self-assembly mechanisms. There have been comprehensive studies on the two-dimensional (2D) self-assembly of colloidal spheres [8, 9]. Understanding of the three-dimensional (3D) self-assembly mechanism though presents a greater challenge due to more complicated crystal formation processes and difficulties in process visualization.

Asher *et al* have used the dynamic Bragg diffraction method to investigate crystalline colloidal arrays [10]. With laser scanning confocal microscopy, Gasser *et al* have conducted a real-space study of the crystallization of concentrated colloidal suspensions and clarified the nucleation process [11]. Norris *et al* have investigated the

convective assembly of colloidal crystals [12]. A recent real-time microscopic visualization study by the same group has revealed that the thickness of the transition regions played an important role in the crystallization process [13]. Despite these advancements toward understanding 3D self-assembly [10–14], a comprehensive study on the dynamic self-assembly process for 3D configurations (i.e. how the randomly distributed aqueous suspensions develop into colloidal crystals spatially and temporally) has not yet been reported in the literature.

In this paper, the dynamic self-assembly process of monodisperse nanospheres inside microtubes is investigated. The use of microtubes slows down the self-assembly process and facilitates real-time spectrophotometric characterization. Because the spectrophotometric signals are highly sensitive to the 3D regularity of the nanospheres, they provide significant information about the 3D self-assembly process. Analyses of the temporal and spatial spectra reveal that multiple mechanisms occur during the self-assembly process. These mechanisms include layer-by-layer deposition, shrinkage of spherical lattice spacing, spatial reorganization and continued evaporation of aqueous medium within colloidal crystals. Understanding of the self-assembly process of monodisperse nanospheres inside microtubes is achieved through experimental reflection spectra and finite difference time domain (FDTD)-based simulation results.



Figure 1. (a) Schematic illustration of the experimental set-up. (b) Scanning electron microscopy (SEM) image taken of the colloidal crystals assembled on the microtube sidewall. The image reveals a close-packed hexagonally arranged (111) plane.



**Figure 2.** (a) A set of reflection spectra recorded from colloidal crystals inside a microtube at different incident angles. (b) A set of transmission spectra recorded from colloidal crystals on a planar glass substrate at different incident angles. Insets are schematics of the experimental configuration.

# 2. Experimental details

Figure 1(a) shows a schematic of the experimental set-up. Cylindrical glass microtubes with an internal diameter of  $\sim$ 865  $\mu$ m were prepared and cleaned according to a procedure described previously [15]. Polystyrene (PS) nanospheres with a diameter of 320 nm were purchased from Bangs Laboratories, Inc. The as-purchased 10 wt% aqueous suspension was diluted into 2 wt% with deionized water. The diluted suspension was pulled into a pre-cleaned microtube by capillary action, forming a cylindrical column that resided The suspension-filled microtube was held at one end. horizontally by an adjustable stage. An ultraviolet-visibleinfrared spectrophotometer from Ocean Optics Inc. was operated in reflection mode. A spectrophotometer probe consisting of both source and detector optical fibres was mounted on an adjustable stage and aligned vertically with respect to the microtube wall. The distance between the probe and microtube was optimized to obtain a maximal reflected optical signal. The well-aligned probe was able to move along the microtube horizontally to conduct spatial measurements. The scanning electron microscopy (SEM) image (figure 1(b)) of the colloidal crystals on the microtube sidewall reveals a closely packed, hexagonally arranged (111) plane.

# 3. Results and discussion

Figure 2(a) shows reflection spectra recorded from a fixed cross section of the microtube at various incident angles. The reflection spectra were recorded by rotating the angle of the incident light from the spectrophotometer about the centre of the microtube (inset of figure 2(a)). There is no obvious distinction among the spectra recorded at different incident angles, likely because the colloidal crystals are axisymmetric. In contrast, the optical properties of colloidal crystals formed on a planar glass substrate exhibit strong angular dependence (figure 2(b)). Here, the transmission spectra were obtained by rotating the angle of incidence from the normal to an angle of  $80^{\circ}$  (the inset of figure 2(b)). The valley of the transmission spectra blueshifts as the incident angle first increases, but redshifts at higher angles. The angle-dependent transmission spectra for the planar colloidal crystals arise from Bragg diffraction within different crystalline planes.

Figure 3(a) shows reflection spectra recorded temporally, with the spectrophotometer probe directed through the middle of the suspension column. Data was not recorded until a Bragg diffraction peak appeared in the spectra. Figure 3(b) shows the variation of peak position and intensity as a function of time. The self-assembly process can be divided into three periods (denoted by I, II and III in figure 3(b)). As



**Figure 3.** (a) A set of reflection spectra recorded temporally while directing the spectrophotometer probe towards the middle of the suspension column. (b) The variation of peak position and intensity as a function of time.



**Figure 4.** (a) Calculated bandgap (in normalized frequency) of a FCC structure with a dielectric contrast of 2.4336. The ordinate is normalized frequency in units of c/d, where c is the speed of light and d is the diameter of the nanospheres. Attenuation in a 2D square lattice is calculated as a function of (b) the number of layers in the crystal, (c) lattice spacing and (d) dielectric contrast.

self-assembly advanced, the peak position of the reflection spectrum blueshifted and finally became stable. The peak intensity first increased (I), then decreased (II) and again increased (III) before a stable spectrum was obtained.

To understand the temporal spectrophotometric measurement results shown in figure 3, a numerical simulation of the colloidal crystals' optical properties was conducted. Figure 4(a) shows the simulated bandgap of colloidal crystals with a face-centred-cubic (FCC) structure. The results were obtained by using the MIT photonic bandgap software, based on the plane wave expansion (PWE) method [16]. The PWE method can be used to calculate the eigenstates and eigenvalues of Maxwell's equations for periodic dielectric boundaries. In simulating the colloidal crystals, the refractive indices of PS nanospheres and air were taken as 1.56 and 1, respectively. A FCC structure with a dielectric contrast of 2.4336 was modelled. The simulation results show a partial bandgap in the L- $\Gamma$  direction (the [111] direction in FCC) where light gets completely reflected; the corresponding non-complete photonic bandgap of this configuration occurs at a wavelength range of 714–758 nm. The calculated bandgap matches well with the final crystal reflection spectrum



**Figure 5.** (a) A set of reflection spectra recorded at uniformly spaced positions along the microtube's suspension column (the recording positions are indicated by the numbers in the schematic inset). (b) Reflection peak position and intensity as a function of spatial position (N).

measured along the [111] direction, the plane parallel to the sidewall of the microtube, as shown by the SEM image in figure 1(b).

Multiple processes could occur during the self-assembly of nanospheres inside a microtube, including layer-bylayer deposition, shrinkage of sphere lattice spacing, spatial reorganization and continued evaporation of aqueous medium within colloidal crystals. All of these processes could contribute to the observed temporal trends of peak intensity and position (figure 3). To understand the contribution from each process of self-assembly, the FDTD method [17] was used to calculate the transmission spectra on a regular 2D lattice. FDTD uses second-order difference equations to compute the propagation of electromagnetic energy in a discrete computational grid. Perfectly matching layers (PML) are used as absorbing boundary conditions to avoid numerical reflections in the simulation domain. The use of a 2D lattice, as opposed to a 3D one, allows qualitative understanding of the self-assembly process within a reasonable computation time. Figure 4(b) shows the calculated attenuation in the crystal structure due to formation of successive layers (n). The attenuation increases as the lattice layers accumulate, resultantly causing an increase in the reflection intensity. Figure 4(c) shows the shift towards lower wavelengths as the lattice constant (a) decreases from 300 to 250 nm, and Figure 4(d) depicts increased the attenuation increases. transmission attenuation as well as a shift to lower wavelengths due to changes in the crystals' dielectric contrast. This effect would occur when water in the crystals evaporates and is replaced by air.

Based on experimental (figure 3) and numerical (figure 4) results, a mechanism is proposed as follows for the self-assembly process of monodisperse nanospheres within microtubes: during period I in figure 3(b) the randomly distributed nanospheres arrange into a regular lattice structure. This is caused by an increased suspension concentration arising from water evaporation. The increased suspension concentration also decreases the lattice spacing. In addition, the nanospheres in the high-concentration suspension self-assemble onto the sidewall of the microtube, layer by layer. Both the formation of the regular structure and the layer-by-layer deposition of nanospheres result in an increased Bragg diffraction signal. The enhanced peak intensity in the spectra confirms this notion. The decrease in the lattice spacing causes

a blueshift in the peak position. During period II, the shrinking of lattice spacing and the layer-by-layer deposition from water evaporation cause a further blueshift of the peak position. However, further increases of suspension concentration lead to stronger interactions among nanospheres. The enhanced interactions among local nanospheres cause non-uniformity of the lattice structure, decreasing the Bragg diffraction peak intensity. The nanospheres then self-assemble into closely packed colloidal crystals (period III). Initially, the interstices of the crystals are filled with water, but further evaporation yields a colloidal crystal surrounded by air. This replacement drives the crystals into a regular packed arrangement and increases the peak intensity. It also increases the dielectric contrast of the interstices causing an additional blueshift in the peak position.

To further study the spatial behaviour of the self-assembly process, reflection spectra were recorded at uniform positions along the suspension column in figure 5(a). A schematic drawing of the suspension column is shown in the inset of figure 5(a), and the numbers (from 1 to 15) represent the recorded positions on the column. The total length from position 1 to 15 is about 40 mm, and the recording positions (from position 1 to 15) are evenly located along the column. A spectrum with no Bragg diffraction peak was recorded starting from position 7. The absence of a peak suggests a randomly distributed colloidal suspension. To the left or right of position 7, the reflection peak position blueshifted continuously. The peak intensity increased first (I), and then decreased (II) towards the left. Towards the right, the peak intensity increased (I), then decreased (II) and increased again (III). The data in figure 5 are not symmetric. This is because the right side of the suspension column is closer to the tube opening and thus has a faster evaporation speed than the left side. Figure 5(b) shows reflection peak position and intensity as a function of spatial position. The self-assembly process starts at the ends of the suspension column, where concave menisci form due to the hydrophilic surface of the pre-cleaned microtube. The assembly progresses towards the middle of the column. The continual blueshifts of peak position and changes in peak intensity from the left or right are caused by different water evaporation rates at each position. Toward the ends of the column (positions 1 and 15), the water evaporated faster. The trends in peak position and intensity (towards the left or right from position 7) match well with the temporal response

shown in figure 3(b), indicating that water evaporation speed varies as a function of position.

### 4. Conclusion

In summary, the self-assembly of monodisperse nanospheres inside microtubes was studied. Combinational spatialand temporal-spectrophotometric characterizations enabled identification of the mechanisms involved in the self-assembly process. FDTD numerical calculations were carried out to support these identifications.

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