

Constructing 3D crystal templates for photonic band gap materials using holographic optical tweezers

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Abstract: A simple and robust method is presented for the construction of 3-dimensional crystals from silica and polystyrene microspheres. The crystals are suitable for use as templates in the production of three-dimensional photonic band gap (PBG) materials. Manipulation of the microspheres was achieved using a dynamic holographic assembler (DHA) consisting of computer controlled holographic optical tweezers. Attachment of the microspheres was achieved by adjusting their colloidal interactions during assembly. The method is demonstrated by constructing a variety of 3-dimensional crystals using spheres ranging in size from $3\ \mu\text{m}$ down to 800 nm. A major advantage of the technique is that it may be used to build structures that cannot be made using self-assembly. This is illustrated through the construction of crystals in which line defects have been deliberately included, and by building simple cubic structures.

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1. Introduction

Photonic band gap (PBG) materials were first conceived in 1987 [1] and have many potential applications including low threshold lasing [2], quantum computing [3], all-optical computation [4] and data transferral [5]. Three dimensional photonic crystals are required to realise many of these applications and these have been made by several methods including lithography [6], two photon polymerisation [7] and self-assembly [8].

The existing methods have a number of drawbacks which limit the utility of the resulting structures. For example, while lithography is a flexible technique for generating different optical structures, the technique is essentially 2-dimensional, meaning that many steps must be repeated to create a 3-dimensional structure. Self-assembly, on the other hand, allows the creation of extensive regions of 3-dimensional order, through the stacking of close-packed layers of silica spheres. These may then be used as templates for a silicon PBG material, by infilling using chemical vapour deposition or electrodeposition to produce an inverted opal. The close-packed structures are formed from a microsphere suspension either by evaporation or by allowing it to settle under gravity. Such techniques produce relatively large crystal templates but fail to give the control over crystal defects that is required to achieve the applications listed above. Also, it is difficult to control the stacking sequence of the layers to produce a perfect

face-centred cubic (FCC) structure (–ABCABC–), as there is a tendency for plane stacking faults and regions of hexagonal close-packed (HCP) structure (–ABAB–) to occur. A reliable method to produce crystals with tunable defects is clearly needed.

In situ two photon polymerization is a useful technique for the production of bespoke structures. A computer controlled laser can create a solid shape to a high degree of accuracy by moving the focused laser light through a liquid monomer solution. The light induces localised polymerization. A wide variety of photo-resists have been used, including organic polymers and a range of inorganic/organic hybrid materials, enabling the production of templates for inverse opals, as well as the direct fabrication of 3-dimensional PBG structures. Structural defects are readily incorporated although, as far as these authors are aware, it is not currently possible to include defects made from a second type of material. Recent work has combined the two photon approach with self-assembly to produce waveguide structures in inverse opals [9].

Techniques exploiting directed assembly may be more useful to create a PBG device, especially if large amounts of PBG material are not needed. This idea was first demonstrated by Garcia-Santamaria *et al.* who used a micromanipulator within a SEM to construct 3-dimensional arrays of spheres [10]. A similar approach that showed assembly of 2-dimensional structures using optical tweezers was recently published [11]. In that work, the electrostatic double-layer repulsion between the silica beads was reduced by adding salt to the solution until the particles adhered. An alternative approach involves holding arrays of particles in position using holographic tweezers [12, 13, 14], and then gelling the surrounding medium to fix them in place [15, 16]. Directed assembly of non-optical structures including nanowires has also been demonstrated [17].

The approach to directed assembly used in the present paper is to force microspheres together using holographic optical tweezers and cause them to adhere by controlling the colloidal interactions in the system. Holographic optical tweezers use a computer controlled hologram to produce multiple focused beams which can be translated in realtime in three dimensions [18, 19]. By using multiple traps, it is possible to use holographic tweezers as a micro- or nanoassembler. In this paper, we demonstrate the application of such a dynamic holographic assembler (DHA) to the assembly of templates for PBG devices containing a variety of tailor-made defects.

2. Equipment and methods

2.1. DHA apparatus

As described above the DHA consists of computer controlled holographic optical tweezers. The DHA is built around an inverted microscope (Zeiss Axiovert 200) with a 1.3NA, 100× objective (Plan-Neofluor Zeiss) and a motorised 3-axis translation stage (ASI MS-2000). The trapping beam is provided by a Ti-sapphire laser (Coherent 899), pumped by a solid state laser (Coherent Verdi-V18), emitting up to 4W at 800 nm. The beam is expanded to fill an optically addressed spatial light modulator (SLM) (Hamamatsu X8267-14DB) and imaged onto the back aperture of the objective lens. The beam enters the microscope through the bottom port. A half-waveplate and polarizing beamsplitter pass the Ti-sapphire laser while reflecting the illumination light onto a conventional CMOS camera (Prosilica EC1280) or onto a high-speed camera capable of measuring the positions of the microspheres at rates up to 500 Hz (microCam-128, Durham Smart Imaging, U.K.). When fluorescence imaging is required the beam also passes through a dichroic prism. The fluorescence excitation wavelength is provided by a halogen lamp (X-Cite-120), which passes through a notch filter (470 ± 20 nm), and reflects off the dichroic mirror onto the sample. Wavelengths other than the emitted wavelength may then be filtered out immediately prior to the camera. See [19] for further equipment details.

2.2. Materials

In this study we employed commercially available spheres of silica with diameters of 800 nm, 2 and 3 μm , as well as polystyrene with a diameter of 3 μm . Where possible the microspheres were labelled with a fluorescent green dye to assist with visualization. The fluorescent dye was not found to have any other observable effect on the experiment as non-fluorescent microspheres were equally effective at building crystals. The microspheres are supplied suspended in a surfactant and this was cleaned off in the early experiments; later studies showed the surfactant had no observable effect on the construction of the crystals.

As supplied, the microspheres show little tendency to aggregate. This is due to electrostatic repulsion resulting from the formation of ionic double layers at the surfaces of the spheres, which is sufficient to overcome any van der Waals attraction. As is well known, the strength of the double layer repulsion may be reduced by the addition of salt to the solution [20], as exploited by Erenso *et al.* [11] in creating 2-dimensional structures. However, as the size of structure being constructed increases, it becomes important to gain greater control over the interactions. The main requirements are (1) to increase the overall attraction, thus reducing the danger of inadvertently breaking the structure and (2) to avoid attraction at other times, thus preventing the spheres attaching to each other before they are located correctly within the structure. Here we achieve both aims by exploiting depletion interactions in the system.

Depletion interactions are caused by the addition of polymer molecules, or other small particles, to a colloid, and generally result in attraction [20]. The effect is osmotic in origin, and arises from a depletion in the concentration of polymer in the region between each pair of spheres which leads to a migration of solvent out of that region. The strength of the attraction may be controlled by adjusting the concentration of polymer. A number of theories now exist to quantify the strength of depletion interactions, and these cover the entire concentration range of the polymer, from dilute to concentrated solutions (see Ref. [21] and references therein).

In the present application, poly(sodium 4-styrenesulfonate) (PSS) with a molecular weight of 7×10^4 (Aldrich Limited) was used. Interestingly, PSS is a polyelectrolyte, which means that, as well as creating a depletion force, it will screen out the electrostatic double-layer repulsion. This system has been studied in detail by Cosgrove *et al.* [22], who have confirmed the existence of a depletion zone around the silica particles using NMR measurements. It has also been studied by Tavacoli *et al.* [23], who have demonstrated that the interactions may be modelled effectively using a combination of dispersion interactions, screened electrostatic interactions and depletion theory. In the present work, an empirical approach was taken to establish the optimal concentration of PSS i.e. the concentration was gradually increased until reliable adhesion was obtained. At this point the particles will adhere reversibly to one another. The final concentrations used are summarised in Table 1.

Table 1. The minimum concentration of PSS required for reproducible adhesion of each size of sphere. The concentrations appear to be independent of the type of sphere used.

Sphere diameter (μm)	PSS concentration (% w/w)
0.8	7
2	5
3	23

The use of polymer-induced depletion interactions has a useful side-effect. The diffusion time for a high molecular weight polymer is long compared with experimental times, which

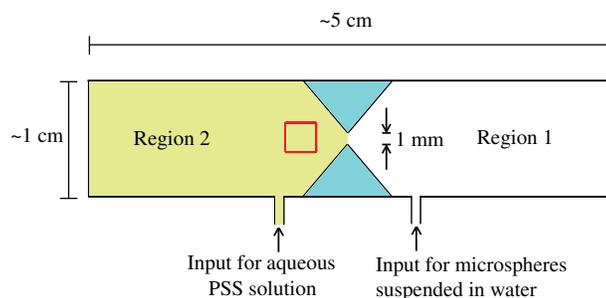


Fig. 1. The sample cell used for the production of crystals made from silica and polystyrene spheres. The production area is shown by the red square. The wedges, shown in blue, are used to limit the diffusion and circulation of the PSS solution and microspheres.

means that it is possible to confine the polymer to a small region of an experimental cell. A stock of microspheres may be kept in a polymer-free area, and then moved into a polymer-rich area when adhesion is required, thus avoiding the microspheres adhering prematurely.

Following the attachment of the silica microspheres, chemical bonding occurs increasing the inter-microsphere attraction and creating a more stable structure [24]. The process occurs through the creation of siloxane bridges between the particles, followed by a reorganisation of the silica to form a neck. The process takes place over a period of hours in neutral water, but may be catalysed by the addition of hydroxyl ions. The resulting structure is effectively permanent. No comparable bonding occurs in the case of the polystyrene spheres, which rely on van der Waals and depletion attractions for adhesion.

2.3. The assembly process

As indicated above, the approach used to make the crystals relies on there being two regions in the sample cell (see Figure 1). The first region contains a 0.5% by volume suspension of microspheres in water, in which aggregation does not occur. The second region contains a solution of PSS in water (see Table 1). The choice of microsphere material does not appear to affect the concentration of PSS required. The diffusion of microspheres and polymer between the two regions, is reduced by use of wedges. The large molecular weight of the polymer also slows diffusion; it was found that a sample cell created by this method could still be used after eight hours with little degradation in the adhesion.

Particles are initially trapped in region 1 and then translated into region 2. The translation speed is directly related to the power of the optical trap and the viscosity of the PSS solution. For example, a typical translation speed for a $3\ \mu\text{m}$ diameter sphere in 23% w/w PSS held with a beam power of 2.0 W is about $250\ \mu\text{m/s}$. Once moved into the production area, indicated by the red box in Fig. 1, the microspheres are translated vertically to bring them into contact either with the glass slide (for the first layer) or with the growing crystal. As the DHA system uses an inverted microscope arrangement for the trapping beam, the first layer of crystal is formed on the top of the sample cell (see Fig. 2(a)), and subsequent layers built downwards, so that we avoid the trapping beam passing through previous layers. The flexibility of the technique is illustrated by Fig. 2(b), which shows the letters “DHA” spelled out using $2\ \mu\text{m}$ diameter silica spheres. As indicated above, the bonds formed between the microspheres, when first brought into contact, are reversible. This allows for the possibility of repositioning the spheres. In the case of the silica spheres however, a more permanent bond forms after a few minutes, at which point it becomes impossible to relocate them.

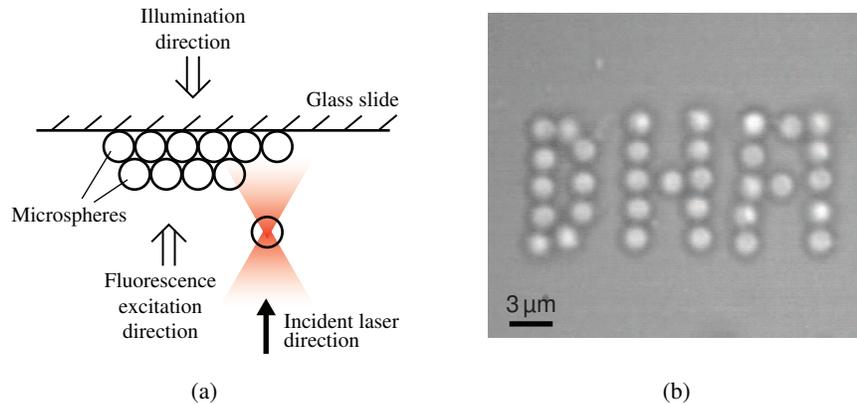


Fig. 2. (a) The sample geometry used to build crystals. The trapping beam is incident from below. The sample is illuminated from above for conventional imaging or from below for fluorescence imaging. The camera is located below the sample. (b) The letters “DHA” constructed from $2\ \mu\text{m}$ diameter silica spheres.

3. Results

In this section we show a range of different crystalline structures, illustrating the flexibility of directed assembly in the DHA compared with other techniques. In all figures the structures are viewed from below, i.e. from the incident laser side as shown in Fig. 2.

Figure 3 shows stages in the construction of an FCC crystal. The first layer of the crystal is formed by placing $3\ \mu\text{m}$ diameter silica microspheres in a close-packed arrangement on the top slide of the sample cell (Fig. 3(a)). The second layer (Fig. 3(b)), contains a line defect which could form a waveguide in a photonic device. Each sphere was translated to the appropriate point below the first layer and then pushed upwards into the interstitial sites. The third complete layer (Fig. 3(c)) was created in a similar manner. A video showing a through-focus sequence of images is available in the online supporting materials.

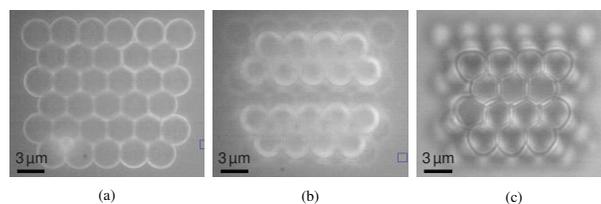


Fig. 3. (a) The first layer, (111) plane, of an FCC crystal template made from $3\ \mu\text{m}$ diameter, fluorescent silica spheres. A single, out of focus, particle is visible in the second layer. (b) The first and second layers of the same crystal, showing a line defect along one of the in-plane [110] directions. (c) The final structure showing all three layers but focussing on the third. (a) and (b) are fluorescence images while (c) is a conventional image. A video showing a through-focus sequence is available online ([Media 1](#)).

In Fig. 3 modification of the colloidal interactions was used to attach silica to silica. However, the approach is not limited to this material. By way of an example, Fig. 4 shows a similar three-layer crystal constructed using $3\ \mu\text{m}$ diameter polystyrene spheres. As previously, the crystal was built on a glass substrate. From these results it is clear that the same depletion interactions

may be used to attach either silica or polystyrene to polystyrene. In Fig. 4, the second layer contains a line-defect incorporating a 60° bend which, again, could be envisaged as a waveguide in a photonic device.

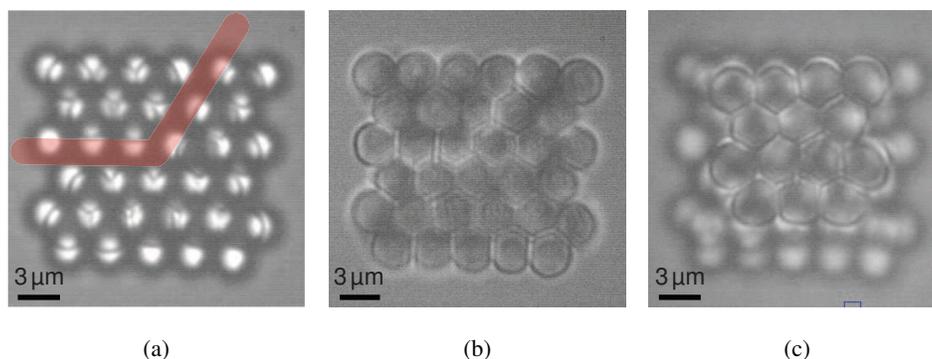


Fig. 4. (a) The first and second layers of an FCC crystal template made from $3\ \mu\text{m}$ diameter polystyrene spheres. A line-defect containing a 60° bend is present, highlighted in red. (b) The same structure slightly defocused to show the line-defect more clearly. (c) The final crystal, focussing on the third layer.

A big advantage of directed-assembly compared with self-assembly is that directed-assembly can be used to create structures which are not found naturally, and where normal rules of self-organisation do not apply. The simple cubic structure is one case in point. When spherical objects pack together, their lowest energy state is always one of the close-packed arrangements i.e. FCC or HCP. The simple cubic structure is therefore difficult to realise by conventional self-assembly, but straightforward using the DHA. Figure 5 shows a simple cubic crystal structure consisting of a $3 \times 3 \times 3$ array of $3\ \mu\text{m}$ diameter silica spheres.

While it is unlikely that a simple cubic structure would have any advantage over a close-packed structure in terms of its photonic band gap, Lin *et al.* [25] have noted that the symmetry of the simple cubic structure may be better suited to certain types of waveguide than the FCC arrangement. Alternatively, the square array shown in Fig. 5(a) could form the first layer of an FCC structure built on a (100) face rather than a close-packed (111) face. Whether or not the simple cubic arrangement turns out to be technologically significant, nevertheless the example provides a clear illustration of the flexibility of the use of the DHA for building structures that would not be available by other methods, and whose optical properties may be tailored to suit particular applications.

All of the structures shown above were constructed from comparatively large spheres, with $3\ \mu\text{m}$ diameters. To construct a PBG that will operate at communications wavelengths (i.e. $1.55\ \mu\text{m}$), it will be necessary to construct templates from spheres which are about $870\ \text{nm}$ in diameter [26]. These templates will ultimately be infilled with silicon to produce inverse opals. As a first step towards this size range, we constructed a waveguide structure using $2\ \mu\text{m}$ diameter silica spheres (see Fig. 6). The method described above was repeated exactly except that the polymer concentration was reduced to 5% (see Table 1). The resulting structure consists of three close-packed (111) planes with a linear cavity running in an out-of-plane [110] direction. There is in principal no difficulty in working with spheres of this size, although a little more care is needed when adding each sphere to avoid damaging the existing structure.

Extending the technique to even smaller spheres is more challenging. The relatively high r.m.s. displacements of spheres of this size due to Brownian motion means that the trend shown

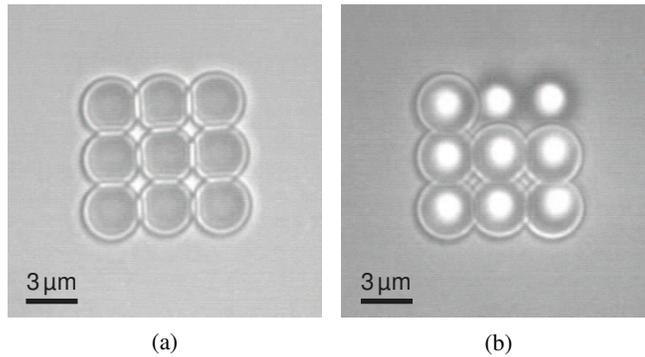


Fig. 5. Images of a simple cubic structure constructed from 3 μm diameter fluorescent silica spheres: (a) the first layer and (b) the partially constructed second layer. A video of the completed $3 \times 3 \times 3$ crystal is available online ([Media 2](#)).

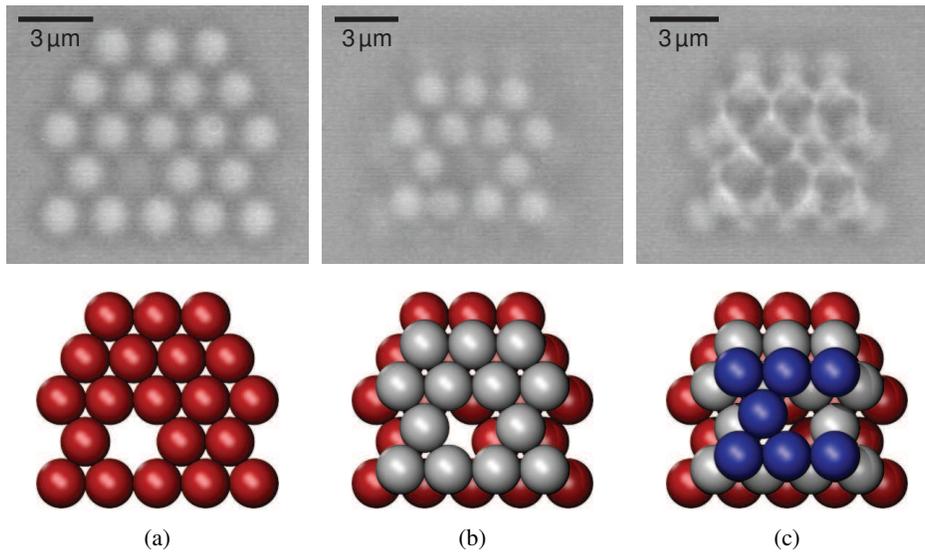


Fig. 6. An FCC crystal constructed from 2 μm diameter non-fluorescent silica microspheres. In this case, the crystal contains a channel running in an out-of-plane [110] direction. The top images are taken from the microscope, focussing on (a) the first layer, (b) the second layer and (c) the third layer. The illustrations beneath are to aid the reader.

in the polymer concentrations for use with 3 and 2 μm diameter spheres does not continue. A polymer concentration of 7%, which is more than that used with the 2 μm diameter spheres, was needed to produce the simple cubic crystal shown in Fig. 7. Also, spheres of 800 nm diameter are much more difficult to organise into a crystal, largely because the beam waist of the trapping laser is comparable with the particle diameter. As a result the attempted addition of a sphere to the crystal, before permanent attachment of the previous sphere has occurred, often results in destruction of the crystal. To avoid this, an additional five minutes was allowed after the attachment of each sphere in order to give time for stronger bonds to develop between the spheres in the crystal. A further consequence of this fragility was that it was not possible to form a close packed array of 800 nm spheres, because those spheres already deposited were disturbed too easily with the trap. It appears that the more open arrangement of the simple cubic structure was just sufficient to allow construction to proceed. Figure 7 shows two snapshots of the partially complete $3 \times 3 \times 2$ simple cubic structure.

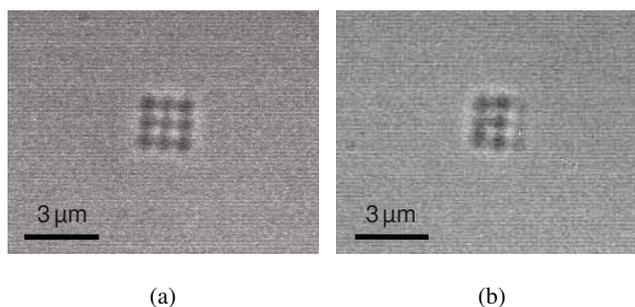


Fig. 7. A $3 \times 3 \times 2$ simple cubic structure assembled out of 800 nm diameter silica spheres. (a) The first layer of the crystal. (b) The crystal during construction of the second layer; the right hand column is incomplete.

4. Discussion

There are many advantages to the use of directed assembly in the construction of PBG materials. The bulk techniques, such as self-assembly, two-photon polymerization or lithography, can make a large volume of PBG in a short amount of time but they are limited in the type of structures they can produce. Self assembly, for example, is usually restricted to the construction of close-packed structures, and the resulting crystals are usually highly defective. The bulk methods are also limited to one type of material, i.e. it is difficult to introduce defects of a different material in a controlled manner. On the other hand, by direct [19] or indirect [18] manipulation of individual components using the DHA, material with special optical properties such as non-linearity or birefringence could be controllably positioned within the crystal. The method could also be used to create lattices with different optical properties. For example, it could be used to construct a diamond lattice, building the structure out of silica and polystyrene spheres, and then selectively dissolving the polystyrene spacers once the silica spheres were adequately bonded to each other, in a manner similar to that described by Garcia-Santamaria *et al.* [10].

As each of the spheres in the figures were positioned manually mistakes occasionally occurred in the structures. However, it was found that the trapped spheres were able to roll over the deposited spheres and could be removed from the structure provided they had not been left attached for more than a few seconds. This initial non-permanent attraction enables mistakes

to be corrected during the building phase. In the case of silica, after about 10 minutes most microspheres become irreversibly attached to the crystal. These structures were stable unless the microscope stage was knocked. However, after two days the silica microspheres were firmly bonded together and the sample could be moved without destruction of the crystal. As noted above, the bonding process may be accelerated by increasing the pH. There is no equivalent bonding in the case of the polystyrene structures.

A similar approach to directed assembly was demonstrated recently by Erenso *et al.* [11] who used NaCl and glycol to adjust the colloidal interactions between the spheres. In that work, the concentrations of NaCl and glycol were the same throughout the sample cell, and had to be carefully tuned to allow the silica spheres to adhere to each other before becoming permanently attached to the glass cell wall. The advantage of our approach, i.e. using a dissolved polymer to induce depletion interactions, is that the low diffusion rate of the polymer allows us to confine it to a small region of the sample cell. As a result, the cell remains viable and construction may continue for several hours. The exact concentrations of polymer used are also less critical, provided that we exceed the levels required to induce adhesion that are listed in Table 1.

All of the structures shown above were built manually i.e. the spheres were guided into position one at a time by an operator. The process is currently quite laborious. It was found that the translation distance required to bring each sphere from the aqueous region to the production area was the critical factor controlling the rate of assembly of the structures. By reducing this translation distance, or by having a plentiful supply of microspheres nearby, the manufacturing time can be greatly improved. Another option currently being explored is to automate the building process: image recognition and computer controlled movements of the traps would also result in improved accuracy in the positioning of each sphere.

The accuracy of the PBG templates constructed may also be improved by controlling the polydispersity in the diameter and shapes of the microspheres. Ideally the variation in the diameter of the microspheres used in the crystals should not be greater than $\pm 1\%$.

In the work presented here, spheres with diameters of 800 nm, 2 and 3 μm have been used. The 2 and 3 μm spheres are easy to control independently; neighbouring beams do not interfere too greatly and the traps are strong enough to mitigate the effects of Brownian motion. However, the 800 nm spheres are at the limit of what we might expect to work when using an 800 nm trapping laser. We may reduce the effects of Brownian motion by increasing the concentration of polymer in the production area, but ultimately our attempts to construct PBG templates are limited by the trap diameter and hence by the wavelength of the laser. The scale invariance of Maxwell's equations suggests that smaller spheres may be manipulated into crystals if the wavelength of the laser is reduced accordingly. In the present case, a shorter wavelength would have been an advantage, since the trapping volume of the DHA was too great to permit the construction of an FCC structure from the 800 nm spheres.

5. Conclusions

We have demonstrated a simple and robust technique for the construction of 3-dimensional photonic crystal templates using directed assembly in the DHA. The technique relies on the use of depletion interactions, induced by the presence of high molecular weight polymer molecules, to cause silica and polystyrene spheres to adhere to each other. A variety of FCC and simple cubic structures have been demonstrated, using spheres of 800 nm, 2 and 3 μm diameter, which, on infilling with silicon, would form inverted opal PBG materials. The method enables the inclusion of cavities, waveguides, non-linear materials and quantum dots in a PBG material.

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