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Nanorobotic Manipulation of Microspheres for On-Chip Diamond Architectures**

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Controlled manipulation of particles can be used for the construction of macroporous structures. This would find an echo in different fields depending on the size of the particles involved. For instance, if the periodicity of the lattice is comparable with optical wavelengths, the crystals may show remarkable photonic effects.[1,2] Alternatively, for sizes around several tens to hundreds of micrometers, materials useful for tissue engineering might be found.[3] Indeed, porosity, pore size, and opening diameter of connecting windows are fundamental parameters for the control of cell or tissue induction within scaffolds[4] that can be made of biocompatible polymer blocks.[5]

A major target in materials science is the production of three-dimensional (3D) microporous structures that are periodic at an optical scale and have appropriate symmetry. Conventional lithography can be used to produce complex small-feature structures, not only in two dimensions.[6,7] Holographic lithography is quickly developing and has a great potential.[8] Colloidal techniques are attractive because they can produce very stable and robust structures with periodicity in the micrometer and submicrometer region. However, fabricated colloidal crystals have insufficient control of symmetry and produce mostly close-packed lattices.[9] Epitaxial growth of crystalline structures on patterned surfaces, gravitationally[10] or entropically driven,[11] and microfluidics[12] with layer-by-layer growth[13] present novel opportunities to build non-close-packed structures.

The trapping of micrometric spheres by radiation pressure[14,15] or manipulation of nanometer-sized particles with an atomic force microscope[16] have attracted attention in recent decades. The utilization of a nanorobot[17] attached to a scanning electron microscope (SEM) is particularly suitable for building 3D structures from microscopic objects of size above 100 nm. The probe can be controlled with high accuracy (a few nanometers) and used to pick and position the particles. This happens because electrostatic and van der Waals forces dominate the dynamics of micro-objects.[18]

However, assembling particles is subjected to a limitation. Regardless of lattice parameter or feature size, there is a condition that must always be fulfilled: the location where the particle is to be placed has to be mechanically stable. This is usually a problem when highly porous structures are used. Our work uses a sacrificial scaffold that can be eliminated when the structure has been assembled.

In this communication we describe the use of a nanorobot to assemble diamond-lattice crystals from silica microspheres, as an example of how our method can be applied. Such a material has potential as a biocompatible scaffold (for larger lattice parameters). Also the photonic bandgap community is very interested in this sort of structure because it can easily be made to sustain a full photonic bandgap.[19] The diamond lattice is a non-close-packed arrangement and, as a consequence, colloidal methods have so far failed to produce it. Inserting latex spheres that act as a temporary supporting scaffold has allowed us to build diamond-type lattices of silica microspheres by placing single microspheres in designated locations with the use of a nanorobot attached to an SEM. This method potentially enables fabrication of structures including line and point defects for optical circuitry.[20] Finite systems (as opposed to infinite crystals) are of great interest for theoretical approaches to the build up of photonic bands and as technological components of future photonic devices.[21,22] In particular, Ozin has invented[23] and adapted[24] techniques that enable the formation of planar opal-based microphotonic crystal chips with controlled shape, size, and orientation.

The idea of stacking spheres in a diamond lattice has been proposed recently.[25] It is conceptually based on two simple facts: first, a body centered cubic (BCC) lattice is formed by two interpenetrating diamond lattices,[26] and second, the BCC lattice is easier to grow since, in it, sphere sites are stable. Therefore, the proposed route comprises the assembly of a BCC lattice of mixed silica and latex spheres of equal diameter (mixed body centered cubic, mBCC hereafter) and subsequent removal of the latex set. Silica spheres would sit in the positions of one of the interpenetrating diamond lattices while latex ones would lie on the other sub-lattice. The resulting structure, after latex removal, is a diamond lattice of silica spheres.

To test the stability of the structure after latex removal, tentative samples were prepared using silica and latex submicrometer spheres. The beads were placed on a silicon substrate in a face centered cubic (FCC) disposition in two different orientations (Fig. 1a and b). The next step was to remove the latex spheres without disturbing the silica ones. Latex calcination was discarded for this purpose because it produced liquid latex, which dragged the silica beads by surface tension and the structure collapsed. Therefore, a more gentle method was used: oxygen plasma etching[27] at 65 mW cm^{-2} and 30 Pa. The

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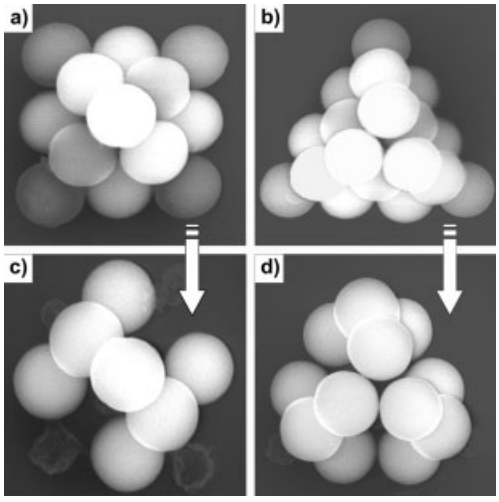

Fig. 1. Mixed FCC structures of latex and silica microspheres before and after plasma etching. Structures were grown in the: a) {001} and b) {111} orientation. Afterwards, latex spheres of (a) and (b) were etched: (c) and (d). Sphere diameter is 0.9 μm.

plasma selectively removes latex and hardly affects the silicon wafer or silica. Figure 1c and Figure 1d show the resulting structures after plasma etching.

For diamond structures, the previous fabrication of a patterned substrate on a silicon wafer consisting of an array of holes is essential for two reasons. First, to designate the positions where spheres must be laid and second, to ensure that the first layer is firmly attached to the substrate; this will prevent further layers deposited on top of this one from disarraying it. Photolithography and plasma etching provide the necessary tools for developing an arrangement of holes with convenient depth, diameter, and distances. The features of these holes will depend on the size of the spheres to be used and the desired crystallographic orientation. The spheres should be held in place by the rim of the holes and not touch the bottom to make sure that they will not move. To find an appropriate depth and diameter for the holes, two constraints must be taken into account. On the one hand, spheres must stick out enough to support those from the second layer that, otherwise, would lie on the substrate (and not have well-defined positions as a consequence). On the other hand, holes must be deep enough to provide a good anchorage for the beads. If these conditions are fulfilled the spheres fixed in the holes are extremely difficult to remove.

Growth should be easiest if high symmetry orientations are chosen; in particular directions such as {001} and {111} present free facets with very regular arrangements, the former being a square lattice whereas the latter is a hexagonal one. To grow a sample in the {001} direction two reservoirs (of latex and silica spheres respectively) were set apart by the template field chosen. The beads were picked one by one and placed at the predefined sockets on the patterned substrate (first layer) or at the appropriate position in a stable location among four supporting spheres from the layer underneath (other layers). The average time needed for each sphere was about 7 min. Figure 2a shows the final structure after setting 165 spheres of latex and 177 of silica (the sixth layer is composed only of silica spheres). Figure 2b shows the resulting diamond-lattice after plasma etching.

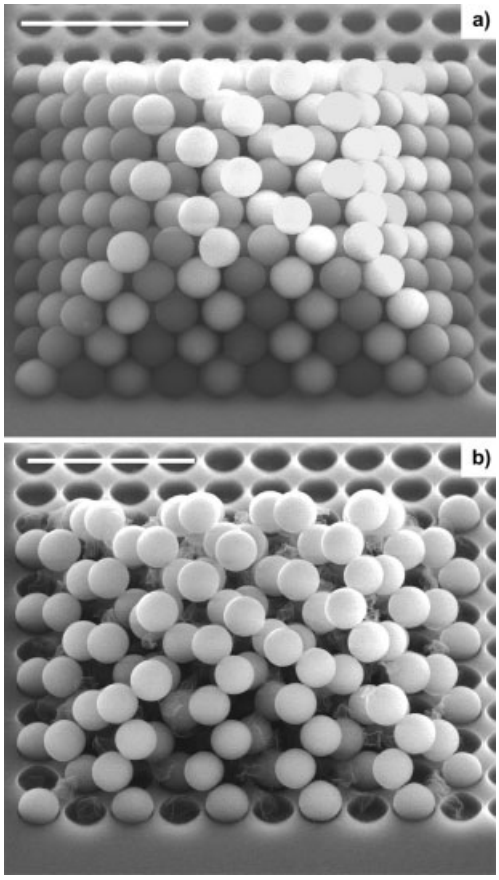

Fig. 2. Six-layer structure grown in the {001} orientation. a) mBCC made of 165 latex and 177 silica spheres. b) Same sample after plasma etching resulting in a diamond lattice. Sphere diameter is 1.18 μm. The pitch of the silicon template is 1.35 μm. Hole depth and diameter are 450 nm and 1.08 μm, respectively. Layer-to-layer distance is 680 nm. Pictures are tilted 45° to show {011} facets. Scale bars = 5.0 μm.

Owing to our nanorobot configuration,[17] one of the most time-consuming tasks was fetching spheres from a distant reservoir (more than 500 μm away) to the template field. In that sense, growing the mBCC lattice in the {111} direction presented an important advantage: unlike {001} oriented crystals, each layer was formed of one kind of spheres. This meant that the reservoir of silica could be placed right on the template itself. Under these circumstances, the average time was reduced to 2.5 min per silica sphere. Figure 3a shows a six-layer mBCC structure made of 133 spheres of latex and 274 spheres of silica. The first two layers are made of silica spheres, the next two layers are of latex, and the fifth and sixth layers are silica again. After plasma etching (Fig. 3b), a four-layer diamond lattice is obtained. It is interesting to highlight that the third layer of the diamond lattice lies exactly on top of the second one, in other words each sphere has only one point of contact with the layer underneath, but the structure is stable enough after etching.

So far, latex spheres have been used to scaffold a structure where minimum energy positions were available for the next

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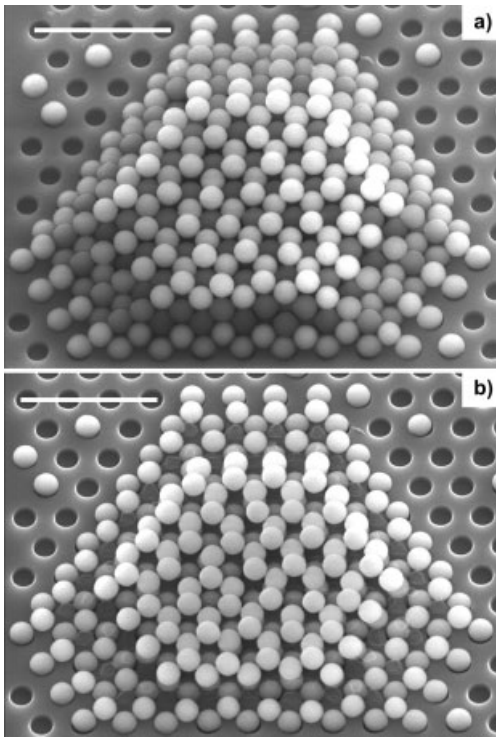

Fig. 3. Structure grown in the {111} orientation. a) Six-layer mBCC made of 133 latex and 274 silica spheres. Layer-to-layer distance is 300 nm. b) Same sample after plasma etching resulting in a four-layer diamond lattice. Sphere diameter is 0.9 μm. The pitch of the silicon template is 1.45 μm. Hole depth and diameter are 350 nm and 754 nm, respectively. Pictures are tilted 30°. Scale bars = 5.0 μm.

layer of beads. However, latex would be unnecessary if silica spheres could be glued to each other. For this purpose we took advantage of unintentional contamination produced by electron-beam-induced deposition.[28] It is well known among SEM microscopists that observation involves the formation of an amorphous carbon-rich contaminant film.[29] Silica spheres may become firmly fixed if the electron beam is focused on their junction for a few seconds. The contamination is deposited accurately in a small area around the contact point. Diamond lattices were grown in the {001} direction by means of this method (Fig. 4a). In our standard working conditions, the sample is tilted 45° with respect to the electron beam while manipulation takes place; {001} orientation is optimal because contact points between spheres are clearly observable, as shown in Figure 4b. Unfortunately, with the particular configuration of this experiment, the method is ineffective for the {111} growth direction because some spheres must be placed exactly on top of another. Consequently their contact point cannot be scanned at 45°. As an indication of the time required, the sample shown in this figure was finished in 10.5 h.

The structures shown in this work have a pyramidal shape to facilitate construction. However, vertical walls could be obtained using latex spheres as a lateral scaffold. This procedure would not involve any additional difficulty apart from needing to manipulate a larger number of spheres. Direct growth should allow it as well, although it has not been tested. Improvements such as optimizing the sample to e-beam orientation, better arrangements for bead supply, automatic arrangement of particles,[30] etc., could not only facilitate the manipulation but allow much larger defect-free samples to be made. We hope that this study will serve to foster the development of novel techniques that, with advances in microscopy and robotics, can end up in very promising practical applications in different research fields such as photonics or biomaterials technology.

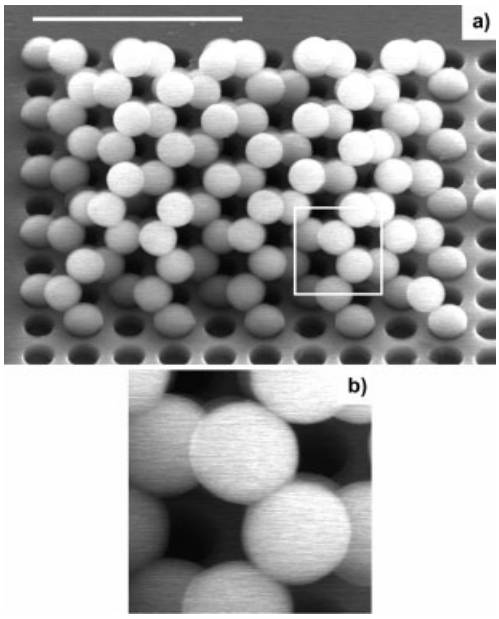

Fig. 4. Five-layer diamond lattice directly grown in the {001} orientation. a) Structure made of 165 silica spheres of 0.9 μm of diameter. b) Detail of a contact point between two silica beads. Contamination was used to glue them. The pitch of the silicon template is 1.05 μm. Hole depth and diameter are 450 nm and 770 nm, respectively. Layer-to-layer distance is 520 nm. Pictures are tilted 45° to show {011} facets. Scale bar = 5.0 μm.

In conclusion, diamond-type structures with micrometer size periodicity were fabricated by means of nanorobotic manipulation of microspheres. The method takes advantage of concepts and disciplines such as colloids, robotics, epitaxial growth, plasma etching, and photolithography. Results demonstrate the viability of this method for preparing macroporous lattices, open the way to controllable formation of a wide variety of microstructures, and provide a new route to the study of novel lattices with photonic properties.

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Lanthanide(III)-Doped Nanoparticles That Emit in the Near-Infrared**

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Luminescent nanoparticles attract a great deal of interest as components in light-emitting diodes (LEDs),[1] displays,[2] biological assays,[3] optoelectronic devices with nanometer dimensions,[4] and as a light source in zero-threshold lasers.[5] The materials employed are for instance semiconductor particles such as cadmium selenide[6] and indium arsenide,[7] and lanthanide(III)-doped oxide materials. The latter are of special interest due to their applicability in optical amplifiers and lasers.[8,9]

Lanthanide(III)-doped nanoparticles have been reported previously,[10] following procedures with high temperatures or bombarding experiments,[11] but these methods generally suffer from products with a low processability. Only a small number of redispersible nanoparticles have been reported that are doped with lanthanide(III) ions such as Eu^{3+} and Tb^{3+}, which emit visible light.[12–15] Processable nanoparticles doped with near-infrared (NIR) emitting lanthanide(III) would be of particular interest as the active material in polymer-based telecommunication components, polymer-based lasers, polymer displays, and polymer LEDs. An advantage of nanoparticles over organic complexes[16] is that the lanthanide ion is embedded in an inorganic matrix, yielding long luminescence lifetimes and high quantum efficiencies.

Here, we report the first redispersible lanthanide-doped nanoparticles that emit in the NIR and we show that these particles can easily be incorporated in polymer materials.

The colloids doped with the NIR-emitting Pr^{3+}, Nd^{3+}, Er^{3+}, Yb^{3+}, and Er^{3+} co-doped with Yb^{3+} ions were prepared according to a literature procedure.[13] More details can be found in the Experimental section. The particles were characterized by transmission electron microscopy (TEM); a typical image is shown of the $LaPO_4$:Pr particles in Figure 1.

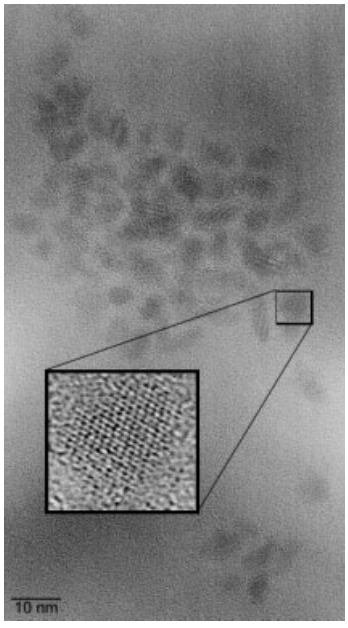

Fig. 1. TEM image of $LaPO_4$:Pr particles on a carbon-coated grid. The inset shows the high crystallinity of the particles

The picture shows that the particles are not ideally spherical and that the average size of the particles is about 5–7 nm.[17] The inset shows a magnification of some particles to illustrate the high crystallinity. The particles seem to cluster on the TEM grid but in solution they are present as single particles. This has been measured before with small-angle X-ray scattering.[12]

The elemental composition of the colloidal powders was determined by elemental analyses and by X-ray fluorescence (XRF), the latter being an excellent technique to distinguish between the different lanthanide ions. The elemental compositions obtained from elemental analyses and XRF are presented in Table 1. The molar ratio La^{3+}/Ln^{3+} is in all cases about 19:1, as was applied in the synthesis. Furthermore, the

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