

Building Two and Three-dimensional Structures of Colloidal Particles on Surfaces using Optical Tweezers and Critical Point Drying

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ABSTRACT

We describe a method for patterning substrates with colloidal particles in any designed two-dimensional structure. By using optical tweezers particles are brought from a reservoir to a surface that carries a surface charge opposite to that of the particles. Using this technique large, two-dimensional patterns can be created, where the pattern can be manipulated on a single particle level. We show that these structures can be dried using critical point drying thus preventing distortions due to surface tension forces. After drying patterned surfaces can be used for further processing, which includes repeating the procedure of patterning. We show some first results of three-dimensional structures created using this layer-by-layer method. The method is generally applicable and has been demonstrated for a variety of (core-shell) colloidal particles including particles that are interesting for photonic applications like high-refractive index (ZnS)-core – silica shell particles, metallodielectric (gold)-core – silica-shell particles, fluorescently labeled particles and small (several nanometers large) gold particles. Particle sizes used range from a few nanometers to several micrometers.

INTRODUCTION

Colloidal particles are the building blocks for materials that find applications in many diverse fields of research. The chemical tunability of particle morphology and typical particle sizes ranging from several nanometer to a few micrometers make colloids suitable for photonic [1-3], electronic [4], magnetic and sensor devices [5, 6]. Two-dimensional arrangements of colloids on substrates are of great interest for most of these applications and have in addition been used to create other nanostructures, e.g., by using them as a mask for lithography [7].

The techniques used for arranging colloids in two-dimensional patterns vary from template-directed self-assembly [2, 8, 9] and patterning of self-assembled monolayers [10], to direct single-particle patterning [11-13]. Clearly, this last category of methods offers the highest level of control over pattern structure, but it remains a challenge to find a technique that works for a large variety of particle sizes, particle morphologies and substrates and that furthermore can operate at relatively high speed and can be fully automated.

To our knowledge, Misawa and co-workers were the first to use optical trapping of micron-sized polymeric particles for assembling larger structures [14]. They recently described a technique to position polymeric particles on polymeric [11] substrates using optical tweezers and single-particle photothermal fixation. Local photopolymerization was used by Mio and Marr to fix particles arranged in the desired structure with time-shared optical tweezers against a glass substrate [13]. These techniques are limited in either particle type (polymeric) [11], particle size

(several hundreds of nanometers to micrometers) [11, 13] or pattern size [13]. Other techniques used involve a micro-robot in a Scanning Electron Microscope (SEM) chamber [12], and an Atomic Force Microscope, which both need a particle-tip contact limiting particle sizes and/or spatial resolution. Furthermore, the first method needs to be operated at high vacuum.

Recently we demonstrated a method for making two-dimensional patterns of colloids on substrates using optical tweezers [15]. Surfaces and or particles are first given an opposite charge if necessary and optical tweezers are then used to select, trap, position and stick the particle to the desired position. The method gives control over the structure on a single particle level. We have already shown that it is possible to direct three-dimensional crystallization of colloidal particles using these two-dimensional patterns as templates. For many applications however it is necessary to dry the structures before further processing. Drying by solvent evaporation easily destroys the structures, as surface tension forces can become much larger than the forces keeping the particles fixed to the surface.

In this paper we will first review our method for particle positioning and then describe how we successfully used critical point drying for removal of the solvent without disturbing the structures. Furthermore, we will show how by repeating the procedure of coating and patterning, three-dimensional structures can be build in a layer-by-layer fashion. We show some first results of three-dimensional structures made in this way.

EXPERIMENTAL DETAILS

In our setup optical tweezers [16, 17] are created by focusing an infrared laser beam (Spectra Physics CW 10W, 1064nm) to a diffraction limited spot using a high numerical aperture objective (1.4 NA 100x oil immersion) on an inverted microscope (Leica DM IRB). The position of the tweezers in the sample is controlled using acousto-optical deflectors (IntraAction) or by moving the sample using a high-accuracy (0.5 nm) piezo microscope stage (Physik Instrumente). The sample can be imaged in normal bright field mode or in Differential Interference Contrast (DIC) microscopy and a charge-coupled device (CCD) camera or by confocal microscopy (Leica TCS NT-2).

Figure 1 shows a drawing of the sample cell used. The cell consists of a bottom glass cover slide (Chance no.1) and a top substrate spaced approximately 10 μm apart. For particles with a high enough buoyancy sedimentation of particles in suspension naturally forms a reservoir at the bottom glass plate of the sample. Alternatively, in case of low buoyancy, a laterally displaced reservoir of particles in the sample was used. The optical tweezers are then used to trap particles in this reservoir and bring them to the top substrate. Alternatively, the optical trap can be focused just at the upper plate so that particles are guided upwards to desired, programmed positions on the upper plate. By leaving the beam focused at the top substrate and rapidly switching positions once a particle is immobilized, this allows for faster positioning, but in this way one cannot discriminate between different types of particles.

On the top substrate particles are immobilized by opposite electrostatic interactions. If necessary, the opposite charges were created using standard and very general surface modification steps. The silica particles used were made following procedures described in the literature [18, 19] and were suspended in ethanol (Merck, used as received). The substrates shown were glass cover slides coated with 3-aminopropyltriethoxysilane (APS) (Fluka, used as received) following a previously reported procedure [20], which renders the glass surface

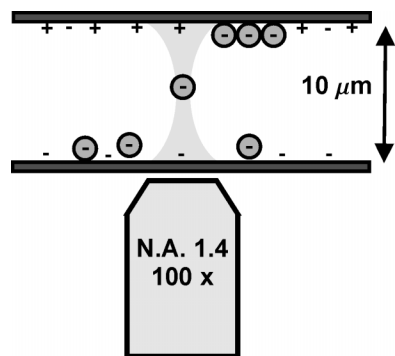


Figure 1 Schematic drawing (not to scale) of the sample cell used for making 2D and 3D structures. The sample cell consists of a colloidal suspension sandwiched between two cover slides of which the top one has an opposite charge from that of the colloids. Particles are freely diffusing on the bottom slide and are brought up using the optical tweezers.

positively charged. We have also patterned particles and substrates coated with a few nanometer thick layer of polyelectrolytes (we used poly(allylamine hydrochloride) and poly(styrene sodium sulfonate)) using a layer-by layer assembly technique [21, 22]. These techniques have proven to work for a large variety of particles, including organic, inorganic, hybrid and uncharged colloids (for a recent review see [22]).

The samples were dried in a Critical Point Dryer (Emscope cpd 750), which was filled with ethanol. After closing the chamber the sample was carefully flushed with liquid carbon dioxide for 10 min after which the sample was left for 10 minutes to ensure mixing of ethanol and liquid CO₂. These steps of flushing and soaking were repeated (typically two times) until no ethanol came out of the sample chamber. After the replacement of ethanol with liquid carbon dioxide the CPD sample chamber was heated resulting in an increase of the temperature and pressure above the critical point ($P_c=75$ bar; $T_c= 31.5$ C). With the carbon dioxide in its supercritical state the sample was let to equilibrate for 10 minutes after which the chamber was slowly depressurized taking care that the

temperature stayed constant and above the critical temperature.

For the positioning of a next layer the sample was kept at 80 °C for one night and the structure was recoated as described above. Scanning Electron Microscopy (SEM, Philips XL30 SFEG) with an acceleration voltage of 2 kV was used to image the dried structures.

RESULTS and DISCUSSION

Two-dimensional patterns

Figure 2 shows a bright field image of a two-dimensional pattern of silica particles with a radius of 700 nm in the wet environment of the sample cell. The structure was created on an APS coated silica cover slide using optical tweezers. Particles were brought up to the surface by focusing the tweezers on the positively charged top-surface. After a particle was trapped and bound the trap was turned off- with a beam shutter. The sample cell was then moved to the next position using a sample stage and the trap was turned on again. The distance over which the sample was moved is 5 micrometer.

The variety of particles that can be manipulated with optical tweezers is enormous. Materials that can be trapped include inorganic dielectric, metallic and biological materials. Particle sizes range from several nanometers to tens of micrometers. Structures we made using this method include particles that are interesting for photonic applications like high-refractive index (ZnS) core – silica shell particles, metallic (Au) core – silica shell particles, fluorescently labelled particles and small (several nanometers large) gold particles [15]. As described in the experimental section we also used the techniques developed by Decher and co-workers to coat the particles and/ or the substrate with polyelectrolytes. The combination of optical tweezers and

a simple coating step makes this a very general and powerful method for creating large two-dimensional patterns. During the whole procedure of particle capture and positioning image processing of the trapped sphere can take place, so that the process can be automated.

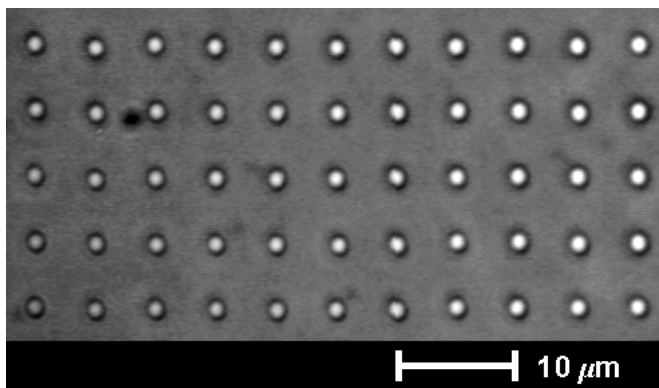


Figure 2. Bright field image of silica particles with a radius of 700nm positioned using optical tweezers on an APS coated surface. The particles were placed with a spacing of 5 micrometer.

Drying structures using Critical Point Drying

All structures created with our method are made in a wet environment. For most purposes however, removal of the liquid is necessary. Drying by solvent evaporation destroys the structures because surface tension forces become very large for small structures and these forces can easily overcome the forces keeping the particles attached to the surface. A method to dry the structure without surface tension forces is critical point drying.

Figure 3 shows a 2-dimensional pattern while it is still in solution (a) and after critical point drying (b). As can be seen upon comparison of figure 3a and 3b, critical point drying provides a way to dry the structures without destroying the pattern.

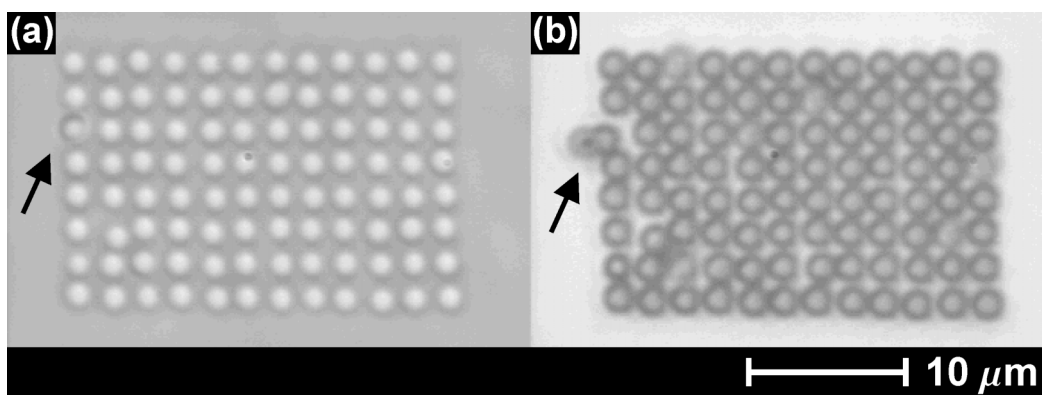


Figure 3. Bright field images of (a) 2D pattern of silica particles with a radius of 500 nm. The pattern is still in ethanol. The particle denoted with the arrow is a dumbbell that is standing out of the image plane. (b) the same pattern in air after critical point drying. Note that the structure was not affected by the critical point drying, but that the dumbbell fell over.

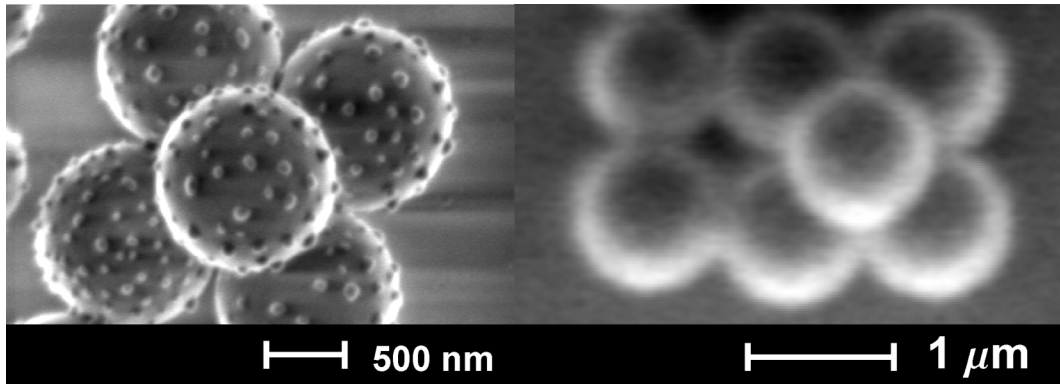


Figure 4. SEM images of three-dimensional structures made of colloidal particles

The particle denoted with an arrow is a dumbbell particle we incorporated in the structure (figure 3a). It was aligned perpendicular to the surface because of the optical scattering forces in the optical tweezers. Note that during the critical point drying the particle fell over to a more stable position (figure 3b).

Three-dimensional structures

Once a structure of particles is dried, it can be slightly ‘sintered’, recoated and patterned again. By repeating these steps it is possible to create 3-dimensional structures in a layer-by-layer fashion. Figure 4 shows the first structures made by this method. Although these are only preliminary results, they demonstrate that the method can be used to make large 3-D structures. For example, by placing layers of particles on top of the cubic structures shown in figure 3, an FCC crystal structure can be made. By using particles of different composition, for example silica and polystyrene (PS) and afterwards burning away the PS particles, a diamond structure can be made [23]. A photonic crystal with a diamond structure requires a relatively low contrast to achieve a full band gap and was considered impossible to make with colloids. Clearly, this method can also be combined with (directed) self-organization as well, for instance to dielectrically dope a photonic crystal in the bulk at specific lattice sites.

CONCLUSIONS

We developed a method to create large, two-dimensional patterns, with control on a single particle level. In this paper we have shown that these structures can be dried without disturbing the structures using critical point drying. By repeating the procedure of creating an opposite surface charge and patterning, three-dimensional structures can be build in a layer-by-layer fashion. Our first results of three-dimensional structures demonstrate the versatility of this approach. The method works for a large variety of (core-shell) colloidal particles that can be trapped in an optical tweezer; particles we used range in size from a few nanometers to several micrometers.

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