Patterning surfaces with colloidal particles using optical tweezers

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A method for positioning colloidal particles on surfaces in any designed pattern is described. Optical tweezers are used to bring particles from a reservoir to the substrate where opposite surface charges are used to immobilize particles on the surface. Both chemical surface modification and polyelectrolyte coating of either substrate or colloids make the method generally applicable. We show that using this technique large, two-dimensional patterns can be created that can be dried without distortions by critical point drying. As an example we show the positioning of 79 nm radius metallodielectric particles and we show how two-dimensional patterns can be used to direct three-dimensional epitaxial crystal growth. The method is inexpensive, relatively fast, and can be fully automated. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1488690]

Colloidal particles are the building blocks for materials that find applications in many diverse fields of research. The typical particle sizes ranging from several nanometer to a few micrometers and the chemical tunability of particle morphology make colloids interesting for photonic,[1–3] electronic,[4,5] magnetic, and sensor[6] applications. The two-dimensional arrangement of colloids on a substrate is of interest for most of these applications. Several recent examples include the use of colloidal monolayers as microlense arrays[2] and arrays of closely spaced metal nanoparticles that can serve as subwavelength, plasmon-mode waveguides.[3,7] Two-dimensional colloid-patterned substrates also find use as calibration standards in techniques like near-field scanning optical microscopy, atomic force microscopy (AFM), and scanning tunneling microscopy. Furthermore, they can be used for further processing, like for example as a (deposition) mask for lithography,[7,8] or as a template in subsequent three-dimensional self-assembly.[9]

Recently reported techniques for arranging colloids in two-dimensional patterns that rely on self-organization, like template-directed self-assembly[1,2,10,11] and patterning of self-assembled monolayers,[12] offer a high processing speed, but lack local control over pattern structure. Direct single-particle patterning[13–16] does offer a much higher level of control over particle positions and composition of the structure, but the techniques reported so far are limited in particle number or particle morphology. In this letter we describe a method to create two-dimensional structures of any desired, locally well-defined pattern using optical tweezers that can be used on a large variety of particle morphologies and a wide range of particle sizes. The use of optical tweezers has the advantage that there is no need for contact with a probe, as is the case when a microrobot[15] or an AFM is used. Furthermore, the combination of the fact that particles are bonded through electrostatic interaction to oppositely charged substrates with the wide variety of available techniques for chemical and physical surface modification allows a large variety of particle sizes and morphologies to be used. Apart from examples of the use of our technique for micron- and submicron-sized particles, we will also show the application of these patterns in three-dimensional colloidal epitaxy.

In our setup, optical tweezers[17] are created by focusing a continuous-wave infrared laser beam (Spectra Physics 10 W, 1064 nm) to a diffraction-limited spot using a high numerical aperture objective (100×, numerical aperture=1.4, oil immersion), on an inverted optical microscope (Leica DM IRB). The position of the tweezers in the sample is controlled using acousto-optical deflectors (AOD) (IntraAction) or by moving a high-accuracy (0.5 nm) piezoelectrically controlled microscope stage (Physik Instr.). Apart from the possibility to position particles in a single-particle trap like in the examples shown later, the high scanning speed of the AODs (max. 100 kHz) also makes it possible to create a time-shared multiple trap, that can trap at least 100 particles simultaneously. The sample cell consists of a bottom glass cover slide and a top substrate with a surface charge opposite to that of the colloids, spaced approximately 10 μm apart. The whole sample can be imaged using bright-field or differential interference contrast (DIC) microscopy using a charge coupled device camera or by confocal microscopy (Leica TCS NT-2).

Particles are being selected and trapped in a reservoir and then brought to the surface for positioning. This reservoir can be created in two different ways, depending on the sedimentation coefficient of the particles. If this coefficient is large enough, sedimentation will naturally form a reservoir at the bottom glass plate of the sample. Otherwise, a reservoir has to be created that is displaced perpendicular to the optical axis with respect to the patterning area, e.g., by using a gradient in particle concentration. In the first case, where particles only have to be brought upwards after trapping, the optical tweezers can also be focused just at the upper plate. Now the potential field that creates the optical

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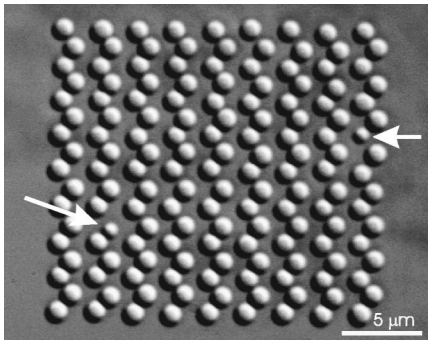

FIG. 1. Image of a pattern of 153 700nm radius silica particles arranged on a hcp(1100) lattice, taken with DIC microscopy in suspension. The arrows indicate two smaller particles that have been incorporated as defects in the pattern.

tweezers is used to drive a particle upwards to a position on the upper plate instead of moving a trapped particle. 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 particles in, e.g., a mixture of particle types. Because in all these cases image processing of the trapped sphere can take place at any stage of the patterning procedure, the process can be automated. In the present letter we used particles that can be trapped stable in three dimensions using a single-beam optical trap, but we want to remark that the technique mentioned last only requires two-dimensional (2D) stable trapping, resembling ''laser-driven particle propagation,'' [18] and that the conditions for three-dimensional stable trapping used in this letter improve the accuracy for positioning particles that can only be trapped stable in 2D.

The silica and metallo-dielectric particles shown in the examples below were all made following procedures described in the literature.[19,20] Particles were suspended in ethanol or water and particle concentrations were chosen such that if all particles were sedimented, they would cover approximately 20% of the bottom glass plate. A typical concentration was 10^7 ml^{-1}. Electrostatic interaction is used to immobilize particles on the top substrate. In case in suspension natural surface charges of either substrate or particles are too low or not of opposite sign, they can be changed by surface modification. Our glass cover slides were coated with 3-aminopropyltriethoxysilane (APS) (Fluka) following a previously reported procedure,[19,21] which renders the glass surface positively charged. We have also coated substrates and particles with a few nanometers thick layer of adsorbed polyelectrolytes (we used poly(allylamine hydrochloride) and/or poly(styrene sodium sulfonate)) using a layer-by layer assembly technique.[22,23] This technique has proven to work for a large variety of particles, including organic, inorganic, hybrid, and uncharged colloids (for a recent review see Ref. 23). Patterned substrates can be dried using critical point drying with liquid CO_2 (see Ref. 24 for details), the images shown below have all been taken in suspension.

Figure 1 shows a DIC-image of 153 silica particles of 700 nm radius patterned on a 3-APS coated glass cover slide. Particles have been placed with the symmetry of a (1100) plane of a hexagonally close packed crystal. The accuracy of

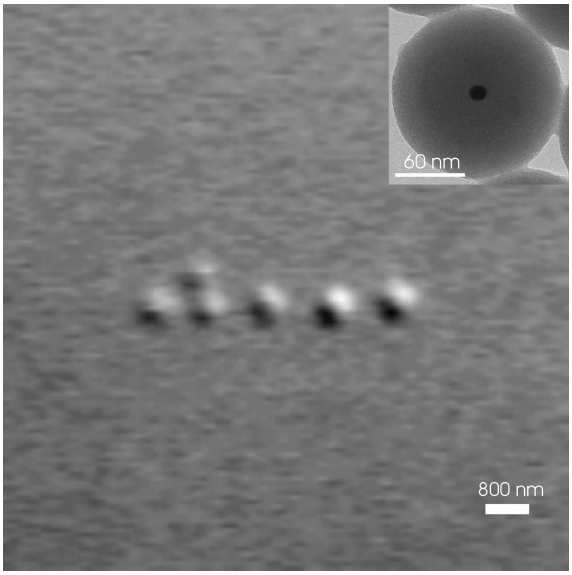

FIG. 2. Metallodielectric particles consisting of a 7.5 nm radius gold core coated with a silica shell with outer radius 79 nm, arranged in a line pattern. The interparticle spacing is 1 μm. A sixth particle has been placed above the second particle from the left. Image taken in DIC. The inset shows a TEM image of the particles used, with the gold core clearly visible.

positioning (root-mean-square deviation of actual versus designated position) was determined with image processing to be 73 nm. Note that in solution, particle excursions in the trap are limited to within several nanometers only. When the position of the trap is moved towards the glass surface, particle excursions increase due to reflections affecting the potential gradient in the trap. This can be improved considerably by using a counter-propagating beam, thus creating a more symmetric and stiffer trap over the interface, or by reducing reflections at the surface. As an illustration of how defects or a second type of particles can be incorporated into a structure, two smaller particles have been placed in the structure as indicated by the white arrows in Fig. 1.

Apart from the micron-sized silica particles shown in Fig. 1, we have also applied our method to 7.5 nm radius gold particles coated with a silica shell with a outer radius of 79 nm [see the transmission electron microscopy (TEM) image in the inset in Fig. 2]. Arrangement of functional particles in this size range in plasmon wire structures has been suggested as a route to high efficiency subwavelength waveguides.[3] Because of their smaller size compared to the 700 nm silica particles, a sample cell containing a particle concentration gradient was used, where particles were trapped in the high-concentration part of the sample and then moved towards the other end containing the patterned region. In Fig. 2 a line pattern of the metallodielectric core-shell particles is shown. The pattern consists of five particles spaced 1 μm apart, with a sixth particle arranged above the second one from the left. This demonstrates the range of particle sizes for which this technique can be used as well as its applicability for patterning particles with a functional morphology.

Finally, we want to show how this two-dimensional ''do-it-yourself'' organization can be used to direct three-dimensional self-organization by colloidal epitaxy. First, we patterned a structure consisting of a rectangular array of four

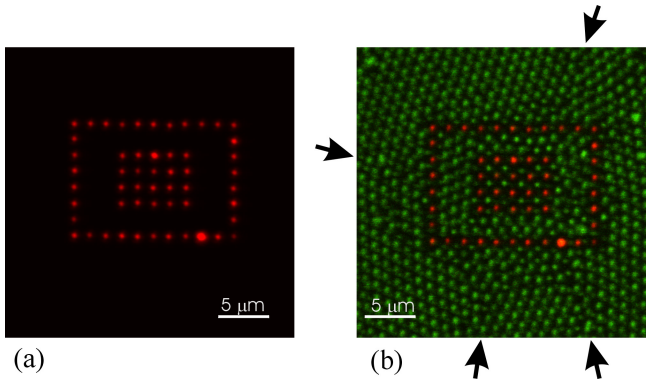

FIG. 3. (Color) Fluorescence confocal microscopy images of (a): a pattern of 500 nm radius silica particles labeled with RITC (red), (b): after addition of FITC labeled (green) particles. The image in (b) has been taken with the focus in between the first and the second layer so that in the central square particles from both the first (red) and the second (green) layer can be seen. The arrows indicate defect-lines in the surrounding crystal originating from the patterned structure.

by five particles surrounded by a rectangle of particles with equal interparticle spacing. The patterned 500 nm radius silica particles have a 100 nm radius core labeled with rhodamine isothiocyanide (RITC). Figure 3(a) shows a confocal microscopy image of this structure. After patterning, the sample cell was washed with water to remove excess particles, inverted and a small amount of particles with the same outer radius of 500 nm but labeled with a fluoresceïne isothiocyanide (FITC) dye (200 nm core radius) was added. Figure 3(b) shows both the initially patterned particles in red and the added FITC particles in green, 16 h after addition. The added FITC particles have crystallized in hexagonal sheets parallel to the glass wall, as is observed for a flat silica wall on which particles are free to diffuse. This is probably due to the fact that the APS-coated surface lost most of its positive surface charge by exposure to CO_2 in water (H_2CO_3) during the washing step, making an additional coating step[21] unnecessary. These FITC particles are slightly out-of-focus, causing the hexagonal lattice to be blurred out, so that the particles in the second layer above the square pattern could also be imaged. These particles are clearly visible as green particles in between the red particles and follow the square symmetry of the pattern, showing that a small grain can locally direct epitaxial growth. Similarly, the pattern could be made containing built-in defects (like in Fig. 1) in order to study the relaxation of defects in three-dimensional epitaxy. In Fig. 3(b) effects of the pattern on the in-plane crystallization can also be observed. First of all the distance between the array and the rectangular boundary has a clear impact on ordering of particles in between. By varying this distance and boundary structure the influence of confinement and boundary conditions on two-dimensional colloidal crystallization can be examined in a systematic way. Second, defect-lines in the surrounding hexagonal crystal, indicated by the arrows in Fig. 3(b), originate from the pattern. This again shows how with such patterns the role of defects in two- and three-dimensional crystal growth can be examined. Furthermore, by positioning particles on top of a crystal and subsequent further growth, e.g., by controlled drying,[25] defects can be created inside a three-dimensional crystal.

In conclusion, we have shown a method that enables the creation of large patterns of a wide variety of (functional) colloidal particles on surface-activated substrates with a resolution significantly below particle size using optical tweezers. Defects or impurities can be completely avoided or, if desired for a specific application, built into the structures at any desired position, which makes this procedure suitable for the creation of photonic, electronic, and magnetic materials. The structures can be dried without distortions using critical point drying. We have shown the application of such patterns in colloidal epitaxy, showing the possibility to both locally manipulate self-assembly as well as to study the evolution of defects in two- and three-dimensional crystallization.

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