Template-Guided Self-Assembly of Colloidal Quantum Dots Using Plasma Lithography

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Quantum dots are building blocks in emerging applications such as diagnostics, imaging, nanoelectronics, nanophotonics, and energy.[1–5] Selective placement of colloidal quantum dots into large-area micro–nanopatterns, however, remains unresolved. We describe a nonconventional technique wherein selective plasma modification of a substrate guides self-assembly of colloidal quantum dots with features as small as 100 nm. In addition, we demonstrate plasma lithography applicability to diverse nanoscale building blocks, including fluorescent nanoparticles, gold nanoparticles, salts, and proteins.

Several methods currently exist for arranging colloidal quantum dots. These methods include molecular scaffold-based assembly,[6] microbead-based assembly,[7] and arranging free quantum dots from a liquid solution.[8,9] These techniques can yield useful nanoscale structures, but long-range order and control over the pattern and the ability to produce deterministic shapes necessary for a useable device can be lacking due to the nature of the processes. On the other hand, template-guided self-assembly on a solid substrate is a promising strategy for developing functional quantum-dot devices that can be integrated with other top-down-fabricated systems. Despite the recent development of quantum-dot self-assembly techniques,[10–12] complex and time-consuming steps are required to spatially arrange quantum dots on solid substrates. Few techniques are available for batch fabrication of quantum-dot-based structures that span the 100 nm to 1 cm scale and that are applicable to different substrate materials. Furthermore, the ability to modulate the density of the quantum dots over patterned areas, which has important implications in sub-wavelength nanophotonic integrated circuits and other coupled quantum-dot devices, are limited.[13]

One inherently rapid and effective method for surface patterning, which is compatible with a large variety of materials and top-down fabricated systems, is plasma surface modification. Using this patterning method, we have developed a technique, plasma lithography, that is suitable for guiding the self-assembly of nanoscale building blocks. The basis of using plasma lithography to guide the self-assembly of quantum dots is realizing a spatially selective plasma modification as a means to guide attachment of quantum dots to selective areas of a substrate. The fabrication method involves creating a nanoscale mold with 3D topography that when placed in contact with a substrate can shield selective areas of the substrate from the modification of a plasma, while allowing plasma surface treatment with other exposed areas.[14–16] This results in a spatial pattern of functionalized templates that can guide the attachment of quantum dots. The plasma-patterning technique uses a deformable mold to produce conformal contact with a surface, allowing patterning of both planar and nonplanar surfaces. Existing plasma-patterning methods typically use resist-defined masks or open-contact (stencil)-type masks where plasma contacts the substrate through holes defined in the masks. A deformable mold with topographically defined channels can achieve high-resolution structures without the need to create high-aspect-ratio structures or very thin masks, because it is not necessary to cut completely through the mask. The plasma lithography approach we have developed is a rapid, batch method that uses a simple, reusable master and is generally applicable to patterning a variety of nanoparticles and molecules onto a surface. The plasma surface modification can also be directly applied to modify a variety of substrate materials, and is one of the few techniques that can be specialized for functionalizing polymeric substrates that, due to their biocompatibility and tunable properties, are attractive for nanoscale and other applications.

To create templates for self-assembly of quantum dots, 3D molds were placed on polystyrene substrates during plasma treatment in order to spatially functionalize the polystyrene surface (Fig. 1a–d). Weights amounting to a pressure of ∼5–10 kPa were placed on top of the mold in order to ensure conformal contact between the deformable mold and the surface. The mold cavities provided for plasma treatment of selective areas of the substrate, which then spatially functionalized the surface. We have demonstrated that the plasma lithography technique can be applied for different substrate materials including polystyrene as well as glass, polydimethylsiloxane (PDMS), and other polymers (data not shown). For instance, the surface of polystyrene, which was used for most of the experiments, has phenyl functional groups, and is hydrophobic (contact angle ∼81°) in its untreated state.[17] After plasma treatment with atmospheric gas (air), it becomes hydrophilic (contact angle ∼10°), and presents oxygen-based functional groups[18–22] (see also Supporting Information Fig. S5). This type of plasma modification is transient over long periods of time (hours to days), as the contact angle will tend to return to its unmodified state over time with exposure to air post-plasma modification. For

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DOI: 10.1002/adma.200802122

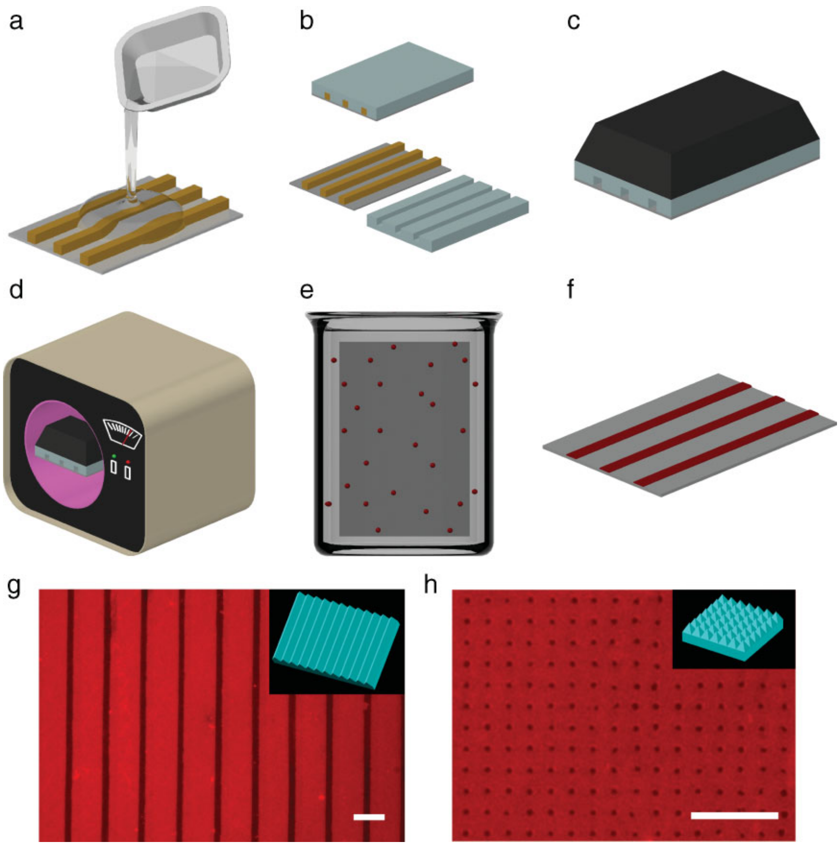

Figure 1. Quantum-dot assembly using plasma lithography. a) A micro- or nanoscale structure, such as a photoresist mold or optical grating, is used as the master for PDMS molding. b) The PDMS replica is removed from the master and placed on a substrate. c) A weight is placed on mold to ensure conformal contact with the substrate. d) The substrate–mold–weight assembly is treated in a plasma chamber for selective modification of the exposed areas. e) The mold and weight are removed from the substrate after the plasma treatment. The substrate can then be immersed in a quantum-dot solution for self-assembly. f) The substrate is removed from the solution, revealing quantum dots assembled onto the patterns. g and h) Fluorescence microscopy images of quantum dots arranged on a line and a grid pattern on polystyrene substrate. Insets: schematics of the mold used in plasma treatment. Scale bars: 20 μm.

the experiments conducted, the plasma-modified substrate was immediately placed into the quantum-dot solution, and no differences were noticed for typical air exposure times of 1–5 min seen by substrates before immersion in solution. The surface properties can also be preserved for weeks if stored in deionized (DI) water or phosphate-buffered saline (PBS) solution.

The patterned functionalization served as the guide for where the quantum dots would self-assemble once the substrate was placed in a solution of quantum dots (Fig. 1e and f). Fluorescent patterns could be detected within 15 min after the self-assembly process was started. In this study, substrates remained in the quantum-dot solutions for 24 h before being removed. Upon removal, the substrates were rinsed three times with DI water and then allowed to dry. Fluorescence microscopy was used to show the resulting patterns of quantum dots that were self-assembled onto the plasma-modified areas of the polystyrene substrate (Fig. 1g and h). The self-assembled structures were firmly attached onto the substrate, and were able to survive repeated rinsing cycles and soaking in DI water for up to a month with little change in fluorescence. Bright areas indicated that the amino-modified quantum dots preferentially assemble on hydrophilic, plasma-modified areas. In addition to the patterns shown, arbitrary geometry (data not shown) can be generated using this technique, as the resulting patterns are defined by the specifically created mold that is placed on the surface during plasma treatment. Pressure placed on the mold could also be varied as a means to produce different linewidths with high reproducibility and resolution (Fig. 2a), similar to an approach reported for creating tunable elastomeric nanofluidic channels.[23] This allowed for one mold to be used to produce self-assembled quantum-dot structures with different linewidths (Fig. 2b). The deformation behavior was observed to be repeatable for several cycles, and linewidths did not show any hysteresis between loading and unloading. The lines were also observed to retain their original geometries and not suffer any distortion, as the uniform loading meant that the PDMS mold would become pinned at its contact points with the surface. This provided a means to exercise precise, submicrometer control (Fig. 2c) over the creation of a number of patterns of varying linewidths with one mold. In addition, the same mold could be turned and plasma treatment repeated in order to produce more complex patterns with a single mold (see Supporting Information Fig. S2).

To further characterize the structures and estimate the resolution of the plasma lithography technique, SEM and AFM studies were performed on the self-assembled quantum dot structures (Fig. 3a and b). The analysis shows that the quantum dots self-assembled into a monolayer on the plasma modified surfaces and very few to no quantum dots were seen to have adhered to the areas that were protected from the plasma. It was observed that the quantum dots are not attracted to each other as evidenced by the lack of any stacking observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses. The step height of the structure was approximately 18 nm, which was consistent with the manufacturer-reported value for the quantum-dot diameter (Fig. 3c). Feature sizes as small as 100 nm, which were equivalent to about five quantum dots in width, could be produced. This resolution is comparable to other nanoscale lithography techniques, and it is likely that the resolution can be further reduced. Reduction could be achieved using a suitable mold with an appropriate aspect ratio and having a well-controlled pressure application system to press the PDMS mold into conformal contact with the substrate. At the same time, self-assembled structures in areas as large as 1 cm × 1 cm with few defects were repeatedly produced. These results indicate that plasma lithography offers a low-cost batch technique to generate

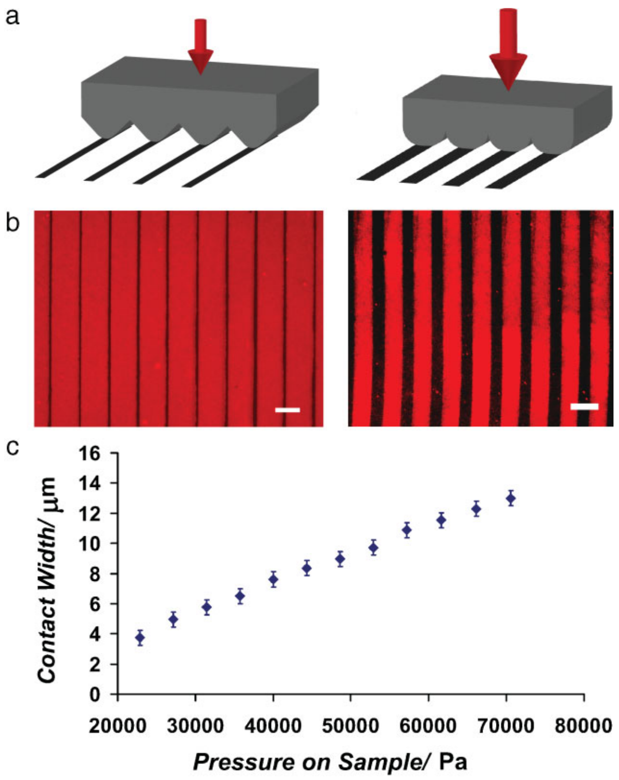

Figure 2. Linewidth adjustment by stress-induced deformation of the elastomeric mold. a) Schematic of the stress-induced deformation process: pressure at right is greater than at left. b) Different linewidths are obtained by applying different pressures on the PDMS mold during plasma treatment. Scale bars: 20 µm. c) Sub-micrometer linewidth control. The resulting linewidth could be changed by adjusting the pressure applied to the mold. The deformation behavior of the PDMS mold was linear, repeatable, and did not show any hysteresis when unloading.

templates for self-assembly of quantum dots with resolution much better than conventional photolithography.

We found that the density of the quantum dots can be effectively modulated by adjusting the concentration of the quantum-dot solution used in the self-assembly process. Deposition behavior of the process as seen in Figure 3d shows that increasing fluorescence relates to increasing concentration of the quantum dot solution, and an exponential relationship relating the surface coverage to the concentration is able to describe the self-assembly behavior of the quantum dots. The relationship between the concentration of quantum dots, time in solution, and solution parameters is in general agreement with other observations for colloidal particles adhering to a surface via diffusion in a quiescent solution.[24–26] These parameters determine how much of the surface area can be occupied by a particle, and how much of the surface area a particle can block against additional absorption. For our experiments, a maximum fluorescence signal was reached when a solution with a concentration of approximately 100 nM was used for the deposition soak. At higher concentrations, microscopic aggregation of quantum dots in the solution was observed, reducing the effective concentration in the solution. SEM analysis reveals that the quantum dots approach a maximum surface density of 1.3×10^{10} dots per cm^2 when increasingly concentrated solutions are used for the deposition process. The densely packed monolayer that can be achieved is likely to be the result of the high density of functional groups introduced on the surface. It is noteworthy that the self-assembly process is a dynamic balance between the particle–surface attraction and particle–particle repulsion,[11] and changing particle size or solution parameters can greatly influence the final outcome.[25,26] In the plasma lithography approach, surface functional groups are directly introduced on the substrates surface instead of utilizing an adhesion layer. The density of the functional groups obtained by plasma treatment is higher or similar to other polyelectrolyte or self-assembled monolayer (SAM) assisted assembly techniques.[10,11] In general, various functional groups have been reported to be introduced on the surface of polymeric substrates by plasma treatment,[27] offering a high degree of flexibility for functionalization. This low-cost, rapid, batch process can be generally applied to a variety of materials, taking advantage of the large selection of substrates and processing gases available for plasma surface treatment, rendering the use of plasma lithography amenable to the fabrication of different micro- and nanosystems.

In addition to guiding the self-assembly of quantum dots, we have also explored the use of the plasma lithography technique in a similar fashion to guide the self-assembly of other nanoscale building blocks. We have produced patterns of 20 and 200 nm fluorescently labeled particles, human α-thrombin, carboxyl-modified quantum dots, 20 nm gold nanoparticles, and aluminum potassium sulfate (alum) on polystyrene and glass surfaces (Fig. 4). The assembly processes are performed either in DI water or PBS (pH 7.4). Two distinct cases were observed to function as the sites that promoted the self-assembly process. One was when the protected, or nonplasma-modified areas promoted self-assembly, and the other was when the plasma-treated areas promoted self-assembly. Fluorescent particles, gold nanoparticles, and alum salt are observed to self-assemble on untreated areas, while human α-thrombin and quantum dots assemble only on functionalized areas. The mechanism behind the self-assembly process is driven by the change in surface free energy of the material to the plasma-modified surface, which occurs through the interaction of the differently functionalized areas with the materials in solution.[28] For quantum dots, the noncovalent interaction (see Supporting Information) between the polar groups on the quantum dot and the polar surface functional groups introduced by the plasma treatment is likely to play a dominant role in the assembly process.[10–13,29] The molecular interaction promotes adhesion between quantum dots and the modified surface areas, but not between individual quantum dots and the native, unmodified, nonpolar, polystyrene surface. For α-thrombin, fluorescent particles, and gold nanoparticles, hydrophobic and other van der Waals interactions between the material and the surface should also be credited as influential to the assembly process.[30] An additional mechanism that may promote adhesion or serve as a nucleation site is the fact that the plasma treatment increases the roughness of the polystyrene surface (see also Supporting Information Fig. S4). The increase in roughness (i.e., the increase in surface area and number of functional groups) may have served to further promote adhesion.

In conclusion, we have demonstrated the performance of plasma lithography as a unique technique to pattern different surfaces in order to guide the self-assembly of quantum dots as well as other nanoscale building blocks. Plasma lithography was seen to have several inherent advantages, including: i) as shown by fluorescence microscopy, SEM, and AFM investigations, pattern resolution of 100 nm to 1 cm in size can be achieved using simple procedures and equipment; ii) control over the resultant quantum-dot density (on the order of 10^{10} dots per cm^2) can be realized by varying the concentration of quantum-dot solutions in which the patterned substrate is soaked, and by other possible means such as control over the number of functionalized sites created by varying plasma power and treatment time; iii) the simplicity, rapidness (minutes), and compatibility of using plasma-based patterning for self-assembly of quantum dots should enable it to be a useful batch method for fabricating functional nanosystems; iv) the large selection of processing gases available for modifying polymeric substrates; v) the general applicability of one standard approach for self-assembly of a wide range of nanoscale building blocks. Based upon these characteristics of the process, we anticipate that the plasma lithography technique can be extended to a wide set of biomedical, material science, and nanophotonic applications that require the integration of a combined bottom-up and top-down approach to fabricate functional devices.

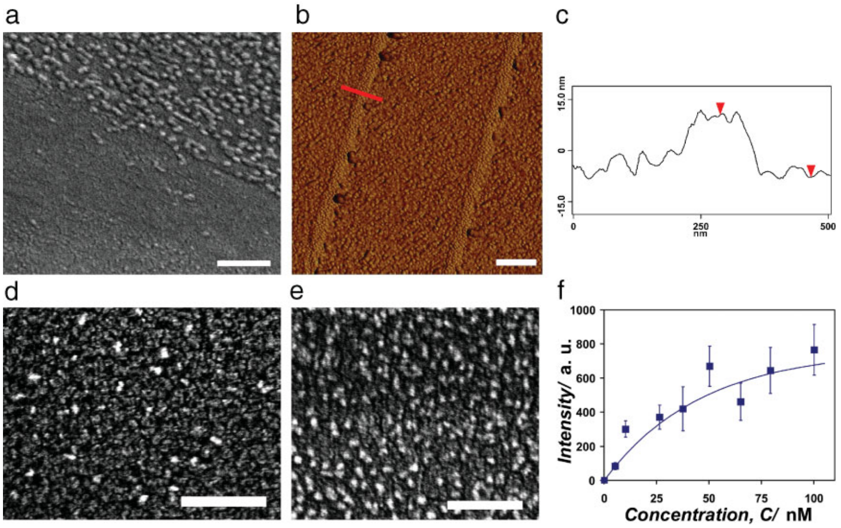

Figure 3. Resolution and deposition behavior of plasma lithography. a) SEM image of the edge of a patterned area as in Figure 1g. Scale bar: 100 nm. Quantum dots are white bumps in upper right hand section; dark area is polystyrene. b) Phase-contrast AFM image of 100 nm wide lines of quantum dots. Scale bar: 300 nm. c) AFM profile data corresponding to the red line in b). The height measurement between arrows is 18.4 nm, which corresponds to manufacturer's data for the size of quantum dots (15–20 nm). d and e) Images show typical surface coverage using less d) and more e) concentrated solutions. Scale bars: 100 nm. f) The concentration-deposition dependence of the self-assembly process of quantum dots characterized by fluorescence intensity. The solid line is an exponential curve fit and error bars are standard deviation.

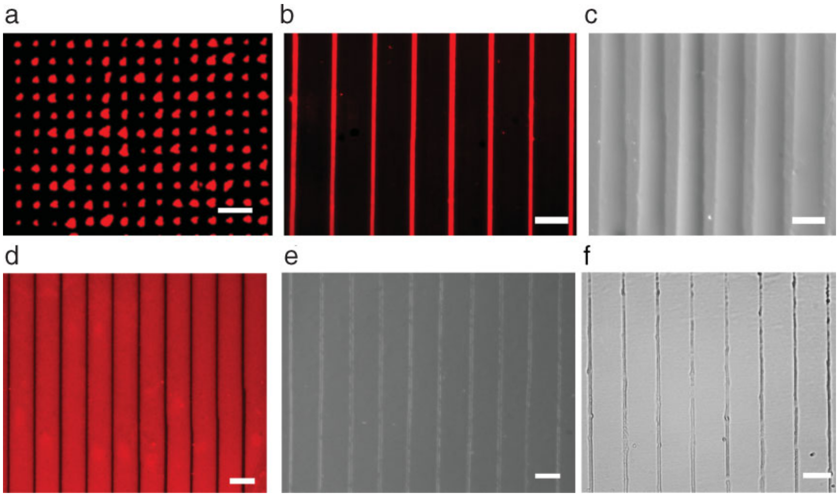

Figure 4. Applicability of the plasma lithography technique for self-assembly of different nanoscale building blocks. a and b) 20 nm diameter carboxylate-modified fluorescent polystyrene particles. c) Human α-thrombin. d) Carboxyl modified quantum dots. e) 20 nm gold nanoparticles. f) Aluminum potassium sulfate salt. Images a), b), and d) are fluorescent images, images c) and e) are dark-field images, and image f) is a bright-field image. All substrates are polystyrene. Scale bars: 10 μm for a) and 20 μm for b–f).

Experimental

Materials: Sterile polystyrene Petri dishes (Fisher Scientific) were used as substrates on which quantum dots were assembled. The Petri dishes used were subjected to plasma treatment as described below without further cleaning or modification. Glass microscope slides and PDMS (Sylgard 184, Dow Corning, Midland, MI) substrates could also be plasma treated and utilized for self-assembly, but all results shown were obtained using polystyrene as substrate. Quantum dots used for all experiments were amino [polyethylene glycol (PEG)] or carboxyl surface modified (Q21541MP and Q21341, Invitrogen, Carlsbad, CA). The quantum dots were suspended in PBS with concentrations raging from 5 to 150 nM. Several additional combinations of polar and nonpolar solvents were examined for suspension of quantum dots, but were not found to produce useable or reproducible results. All quantum dots used had an emission wavelength maximum of 605 nm. Gold colloid solution was obtained from Sigma (G1652). Fluorescently labeled particles of 20 and 200 nm were purchased from Invitrogen, Inc. and were suspended in DI water, as were colloidal gold particles. All other reagents were obtained from Sigma, unless otherwise specified.

PDMS Molding and Plasma Treatment: For template patterns, which govern final quantum-dot arraignment, optical gratings ranging in size from 833 nm to 25 μm were used. Casting off of the gratings produced the master 3D shape of the working molds. The casting was done using standard soft lithography, wherein liquid PDMS is poured over the master mold and allowed to cure. The PDMS used for this study was mixed in an 8:1 weight ratio, degassed in a vacuum chamber for 5 min, then cured at room temperature for 24 h before use. Substrates and working molds were placed in a plasma cleaner (PDC-001, Harrick Plasma) at room temperature and were subjected to air plasma treatment at 150 Pa with radio frequency (RF) power of 29.6 W for 10 min. The plasma was inductively coupled by means of a solenoidal coil and had a frequency of 8–12 MHz.

Imaging: Fluorescence images of the resulting quantum-dot patterns were obtained using a Leica inverted epifluorescence microscope (Leica Microsystems, Wetzlar, Germany) with a digital charge-coupled device (CCD) camera. Samples were illuminated with a band-pass excitation filter at a wavelength of 515–560 nm using a mercury vapor lamp, and images were recorded with a long-pass filter of 590 nm and a 580 nm dichromatic mirror. The native, background fluorescence of each substrate was subtracted from all images prior to data processing. SEM analysis was performed by sputter-coating samples with approximately 10 nm of platinum and imaging using a field-emission SEM (Hitachi S-4500/Thermo-Noran Digital Imaging/EDS, Tokyo, Japan). AFM was also carried out for the smallest resolution samples in tapping mode using an atomic force microscope (Veeco Instruments, Woodbury, NY) and a cantilever from MikroMasch (San Jose, CA).

Acknowledgements

The authors thank J. Keyes for technical assistance and Dr. X. Wu and Dr. J. Pyun for valuable discussions. This work was supported by the American Chemical Society Petroleum Research Fund (47507-G7). M. J. is partially supported by the Achievement Rewards for College Scientists and the University of Arizona TRIF Imaging Fellowship. Supporting Information is available online from Wiley InterScience or from the author.

Received: July 23, 2008
Revised: September 8, 2008

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