Metallic Nanostructures

Molecular Lithography with DNA Nanostructures**

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The great success of photolithography results from its ability to accurately control the produced patterns. An alternative, bottom-up approach to build ordered patterns by self-assembly is promising and may supersede the traditional top-down lithography-based techniques for the preparation of nanoscaled patterns.[1–9] Among the many challenges in developing parallel and bottom-up techniques, the capabilities of controlling pattern topography and to scale-down feature dimensions are two central issues concerning their practical applications. One possible solution is to use tunable, self-assembled, supramolecular structures as lithography masks; DNA nanostructures appear to be ideal for this purpose.[10–16] Here we demonstrate that DNA nanostructures can be used as masks for molecular lithography. DNA nanostructures could be accurately replicated into metal nanostructures by metal evaporation followed by lifting off of the mask. The ease and flexibility of this reported technique make it suitable for producing defined and integrated nanopatterns, which represents a novel route to overcome the inabilities faced by traditional lithographic techniques.

DNA has found many applications beyond its original genetic interest.[7,8,10–20] DNA metalization to fabricate metallic or semiconductive nanowires is one example of how long DNA duplexes can be replicated. However, the metalization process results in a loss of the structural details of the DNA molecules. The resulting nanowires are at least 10-times thicker than the DNA templates.[17–19] More seriously, the resulting structures are exclusively linear structures, which is far removed from the structural complexities required for technological applications. The emergence and fast development of DNA nanotechnology makes it possible to construct complicated DNA structures through bottom-up self-assembly of engineered DNA motifs. The resulting DNA structures have been explored for performing molecular computations,[10] crafting nanomechanical devices,[13] and organizing other functional units.[15,20] These DNA structures would also provide an ideal means to meet the complexity requirement. It is conceivable that well-defined nanopatterns with designed DNA structures could be produced as masks for direct replication. Since it is possible to overcome the feature-size limitation of current lithographic techniques by the use of suitable molecules/macromolecules as masks, research on this topic may have fundamental influence on both nanoscience and nanotechnology. The molecular lithographic method we report here is a general and parallel method. The process consists of four steps (Figure 1), and can generate 1D and 2D metallic nanopatterns with feature sizes down to about 10 nm. With further elaborations, this method might be promising for making functional circuits, sensors, and display panels with highly controllable topography at the nanometer scale.

We assembled DNA arrays by slowly cooling equimolar mixtures of the corresponding component DNA strands from 95 °C to 22 °C, and depositing them onto freshly cleaved mica substrates. A 20-nm-thick gold film was then thermally evaporated onto the mica substrate. At the end of the evaporation, a drop of epoxy mixture was sandwiched and solidified between the gold film and a glass slide. The glass slide together with the gold film was then separated from the mica surface. The side contacting the DNA samples were exposed to air and contained the negative replica of the DNA structures. We analyzed the DNA structures and their metallic replicas by tapping mode atomic force microscopy (AFM).

We first demonstrated the principle with a one-dimensional (1D) DNA double crossover (DX)[14] array (Figure 2 and Supporting Information). There is an even number of half turns between any two crossovers in the 1D DX array (Figure 2a). Linear DX arrays could be easily resolved by AFM imaging. Section analysis indicated that the height of the 1D DX arrays was about 0.9 nm. Replication worked very well for this DNA structure. The gold film appeared to be an exact negative replica of the DNA molecules on the mica surfaces. The depth of the replicated grooves was about 0.6 nm. This lower value compared to the DNA masks was presumably a result of imaging artifacts. The 1D DX arrays were 4-nm wide and smaller than the radius of the AFM tip (10 nm). Thus, an AFM tip could not fully track down to the negative replicas. The apparent widths (measured as full-width at half maximum) of the DX arrays and their replicas were 13 nm and 11 nm, respectively.

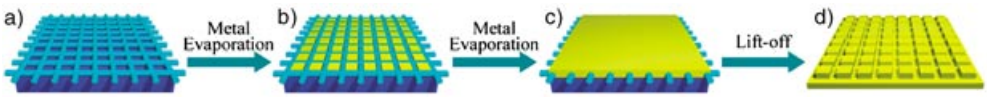

Figure 1. Schematic representation of the process of molecular lithography. a) DNA nanostructues are self-assembled in solution and deposited on mica. b) and c) Metal evaporates until a continuous metal film forms and covers the DNA mask on the mica surface. d) The metal film, after removal from the DNA/mica, exhibits a negative replica of the DNA mask.

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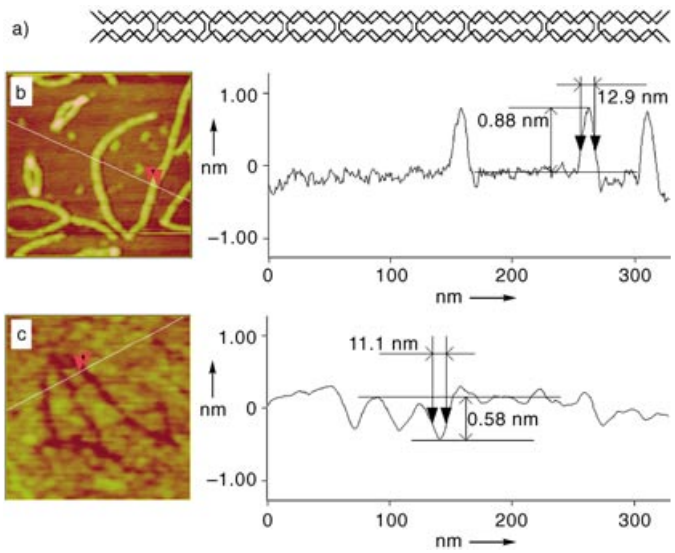

Figure 2. AFM analysis of the replication of DX 1D arrays. a) Schematic representation of a 1D DNA double crossover (DX) array. AFM images and section analysis of: b) the DNA arrays and c) their negative gold replica.

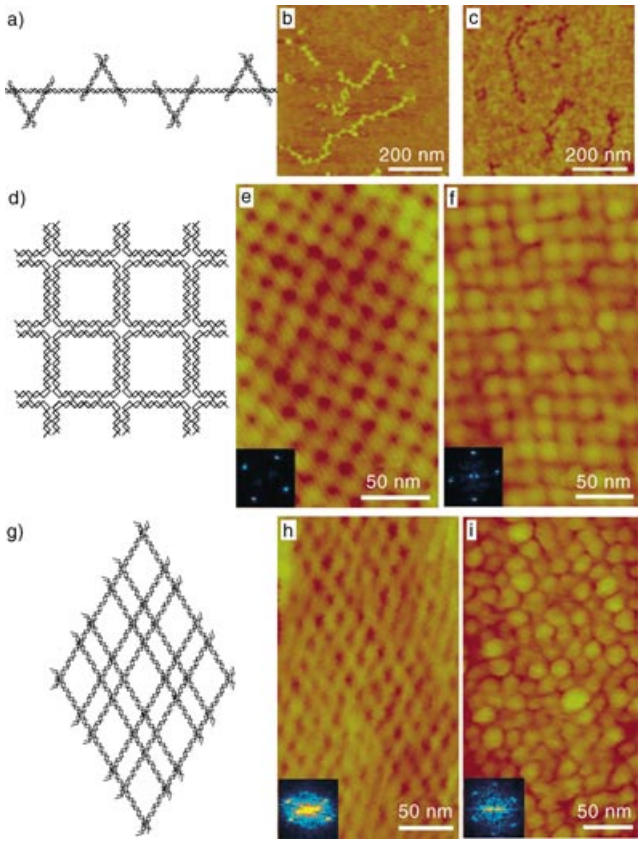

Figure 3. AFM images showing replications of three DNA nanostructures. a)–c) Replication of 1D DNA triangle arrays; d)–f) replication of a tetragonal 2D DNA array; g)–i) replication of a pseudohexagonal 2D array. a), d), and g) Schematic representations of DNA structures; b), e), and h) AFM images of DNA arrays; c), f), and i) AFM images of gold replicas of DNA arrays. The insets show the 2D Fourier transforms of the corresponding AFM images, which clearly show symmetry similarities between the DNA samples and their gold replicas. Height scales in all images are 5 nm.

We further analyzed the mica surface after the gold film had been peeled off. To our surprise, the DNA molecules remained on the mica surface and were intact (see the Supporting Information). We noticed that the height of the DNA samples became higher and could reach 3–4 nm. We suspected that this phenomenon was caused by heating during the evaporation stage, which could partially denature DNA molecules, especially the hydrogen bonds between sticky ends, and cause the spread DNA to contract into discontinuous, high bumps. However, this would not prevent DNA from serving as a mask for pattern replication, since the gold pattern layer of about 1 nm in thickness was formed at the very beginning of the evaporation process when no significant heat accumulated.

A 1D DNA triangle array[16] was also used as a template for molecular lithography. AFM images of the DNA samples and their replicas are shown in Figure 3a–c and in the Supporting Information. The DNA structure was an array of pearled-up DNA triangles with a regular spacing (27 nm) between all adjacent triangles. The vertex-to-vertex distance within each triangle was only about 12 nm, and our results showed an impressive resemblance between the DNA arrays and their negative replicas, which implies the great potential of this molecular lithography technique when dealing with extremely small lateral dimensions of around 10 nm.

The first two-dimensional (2D) DNA array that we chose to replicate was a tetragonal array (Figure 3d–f and Supporting Information).[15] A basic unit of the array had a cross-shaped structure, which contained four four-armed junctions pointing in four orthogonal directions. Figure 3e shows an image of the tetragonal 2D DNA array. The pitch of the DNA grids was measured to be about 18.0 nm, which is in good agreement with the estimated (17.6 nm) and the reported value.[15] The gold replicas showed negative patterns that were consistent with the DNA masks (Figure 3f). Since the DNA mask had a square grid structure, we would expect that the replicas would be an array of pillars with the same symmetry and periodicity as the mask. This expectation was verified by measuring the average distance between neighboring pillars. This distance was shown to be about 18.0 nm, which is almost identical to the periodicity of the corresponding DNA structure. The grid structure of the DNA mask and the pillarlike gold replica were more clearly represented by a 3D surface view of the AFM images (see the Supporting Information), which, together with the consistency in the periodicities and the similarity in the overall platelike shapes between the DNA arrays and their replicas (Figure 3e and f), unambiguously proved the high fidelity of our replication process.

A very appealing aspect of DNA nanostructures is that it is relatively easy to vary their structures: patterns with different symmetries are achievable. As a demonstration we have chosen a pseudohexagonal 2D DNA array formed by Holliday junctions (Figure 3g–i).[12] The basic unit of the array is a rhombus with an inner angle of approximately 62°. Thus, the DNA arrays have a pseudohexagonal symmetry. Con-

sequently, a hexagonal symmetry would be expected for their gold replicas. Figure 3h and i are AFM images of the Holliday junction array and its gold replica, respectively. The experimental results have clearly showed that self-assembled DNA nanostructures are suitable masks for making well-defined surface patterns.

In conclusion, we have successfully demonstrated that it is possible to use designed DNA nanostructures as molecular masks for the preparation of nanoscaled patterns. Masks with more sophisticated structures could be constructed by rational design and self-assembly of DNA motifs.[11] Following this approach and benefiting from the ease and accuracy of synthesizing and manipulating DNA, the wealth of enzyme tools for modifying DNA structures, and the availability of other evaporation materials besides metals as replication matrices, the construction of highly structured patterns for more realistic applications such as nanocircuits, nanosensors, nanofluidics, information storage, and super high resolution display panels with nanoscale pixels should be possible after further elaboration of the technique. Although the cost of preparing long DNA oligomers may become a concern, this technique is a cost-effective lithographic method because it doesn't require any special and expensive chemicals and facilities such as clean rooms and photoresists. It is very likely that this technique will merge with soft lithography[5,6] through the development of patterns on polymer substrates to obtain soft stamps, since the state-of-the-art soft lithographic technique can transfer patterns with vertical features as small as 2 nm, which can facilitate transfer and duplication of the replicated patterns.

Experimental Section

Construction of DNA structures: The design and construction of all DNA structures were reported previously.[12,14–16] DNA single strands were purchased from Integrated DNA technologies, Inc., and purified by denaturing polyacrylamide gel electrophoresis (PAGE). DNA nanostructures were formed by annealing equimolar mixtures of component DNA strands from 95 °C to 22 °C over 2 to 48 h.

Replication of DNA patterns: All the metal evaporations were carried out using a thermal evaporator (Turbo Vacuum Evaporator-EFFA). The evaporation speed was adjusted to 0.2 nm s^{-1}. After metal evaporation, a drop of premixed epoxy adhesive was then put on the gold film and immediately covered by a glass slide. After the epoxy was completely solidified, the metal replicas could be easily lifted off from the mica surfaces.

AFM imaging: A drop of DNA sample solution (2 μL) was spotted onto a freshly cleaved mica surface, and left for 10 s to allow strong adsorption to occur. The sample drop was then washed off with 10 mM $Mg(OAc)_2$ solution (30 μL) and dried with compressed air. DNA samples and their metal replicas were imaged by a tapping-mode atomic force microscopy on a Nanoscope IIIa microscope (Digital Instruments) with NSC15 tips (silicon cantilever, Mikro-Masch). For large area scans ($> 5 \times 5$ μm^2), the tip velocity was kept at 10 μm s^{-1}, otherwise a scan frequency of 1 or 1.5 Hz was used. The tip–surface interaction was minimized by optimizing the scan set-point.

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