

Electronic nanostructures templated on self-assembled DNA scaffolds

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Abstract

We report on the self-assembly of one- and two-dimensional DNA scaffolds, which serve as templates for the targeted deposition of ordered nanoparticles and molecular arrays. The DNA nanostructures are easy to reprogram, and we demonstrate two distinct conformations: sheets and tubes. The DNA tubes and individual DNA molecules are metallized in solution to produce ultra-thin metal wires.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It has been widely projected that, within approximately 10–20 years, traditional top-down lithographic methods for manufacturing microelectronics will reach their resolution limits. Anticipating this crisis, researchers in the field of nanoscience have begun developing bottom-up techniques for the molecular assembly of electronic circuits. However, few proposed approaches hold the potential for providing circuit layouts reaching the complexity that is available by lithographic methods. One potential approach is to use self-assembling DNA nanostructures as scaffolds for constructing and positioning molecular-scale electronic devices and wires [1].

DNA nanostructures provide a programmable methodology for bottom-up nanoscale construction of patterned structures, utilizing macromolecular building blocks ('DNA tiles') based on branched DNA, that self-assemble into periodic and aperiodic lattices [2]. The programmability is due to the highly specific hybridization of complementary DNA strands used to specify interactions both within and between DNA tiles. The process of self-assembly by hybridization entails simply heating a solution of properly designed oligonucleotides above their dissociation temperature and then cooling them very slowly to allow annealing with low error rates. An obvious advantage of DNA self-assembly for this application is that the fabrication will proceed in a massively parallel fashion such that millions of copies of a desired structure will be created simultaneously.

DNA nanostructures do not appear in themselves to have good properties as electrical conduits or devices [3].

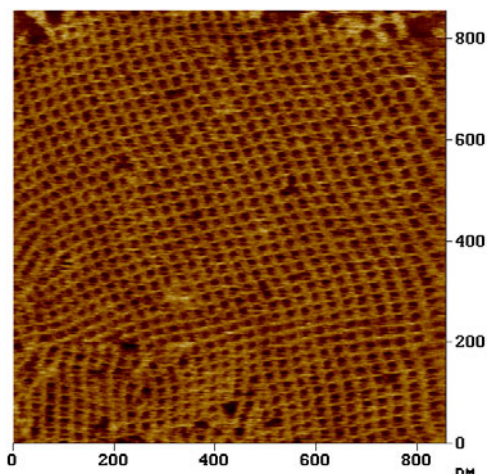


Figure 1. An AFM image of the self-assembled lattice based on our novel 4×4 DNA tiles.

Instead the significance of patterned DNA nanostructures lies in their application as scaffolds or templates for organizing and positioning other materials. In this paper, we discuss the fabrication and characterization of a novel class of nanostructures based on the DNA scaffolds. We work both with the unmodified double-strand DNA molecules and the complex DNA nanostructures based on DNA tiles, such as the self-assembled grid of figure 1 [4].

The two major fabrication schemes that we implement are:

- (i) functionalization of the DNA nanostructures through targeted attachment of organic and inorganic 'building blocks', and

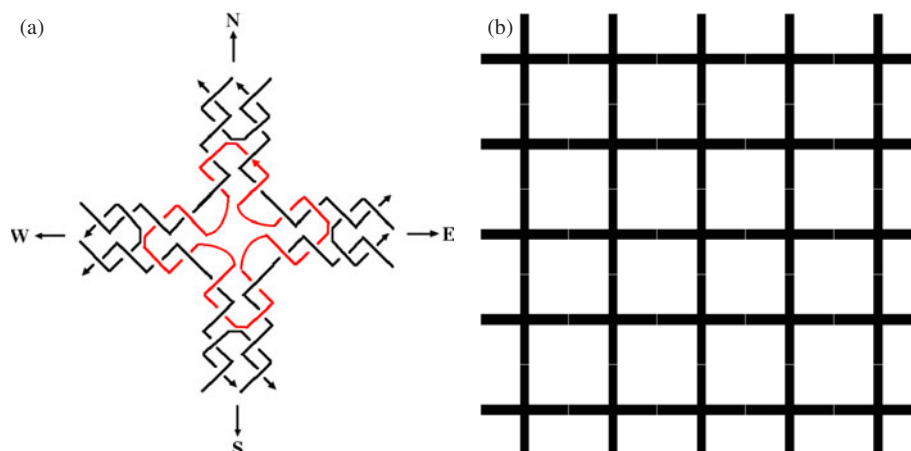


Figure 2. (a) Schematics of the 4×4 tile self-assembly. A 4×4 DNA tile is made from nine synthetic oligonucleotides. (b) 4×4 tiles assemble in a two-dimensional grid through the sticky-end association.

(ii) deposition of inorganic chemical compounds on DNA.

Using the first method, we have successfully used regular DNA arrays (such as that shown in figure 1) to guide the assembly of protein molecules and inorganic nanocrystals. Using the second approach, we have made the thinnest wires based on metallized DNA (figure 5). Our wires have a uniform width of ~ 20 nm, length of a few microns, and unlike many previous attempts have negligible granularity.

2. Main results

2.1. Self-assembled DNA lattices and targeted deposition

In our recent paper [4], we describe the design and construction of the 4×4 DNA tile (figure 2(a)) that contains four four-arm DNA branched junctions (hence the name 4×4 DNA tile). The tile has a square aspect ratio with four DNA ‘arms’ pointing in four directions (north, south, east, and west) in the tile plane. It is composed of nine strands, with the central strand participating in all four junctions (figure 2(a)). Bulged T_4 loops were placed at each of the four corners inside the tile core in order to decrease the probability of stacking interactions between adjacent four-arm junctions and to allow the arms to point to four different directions. This structure is sufficiently rigid to act as a building block in larger superstructures.

Based on the basic structure shown in figure 2(a), a modified version of the 4×4 tile with added DNA sticky ends was prepared. In solution, the tiles attach to each other through sticky end association (figure 2(b)), resulting in the formation of ordered lattices (figure 1), visualized by atomic force microscopy (AFM). The designed distance between adjacent tile centres is 4.5 helical turns plus two DNA helix diameters, totaling 19 nm. The AFM measured distance from centre to centre of adjacent tiles is ~ 20 nm, in good agreement with our design. Large lattice pieces, up to several hundred nanometers on each edge, were observed in which the tiles are perfectly ordered.

One major application of DNA nanotechnology is to use self-assembled DNA lattices as scaffolds for the assembly of other molecular components. The 4×4 DNA lattice displaying a square aspect ratio will be useful for forming regular arrays of other nanoscale ‘building blocks’. For example, the loops at the centre of each 4×4 tile can be modified with appropriate

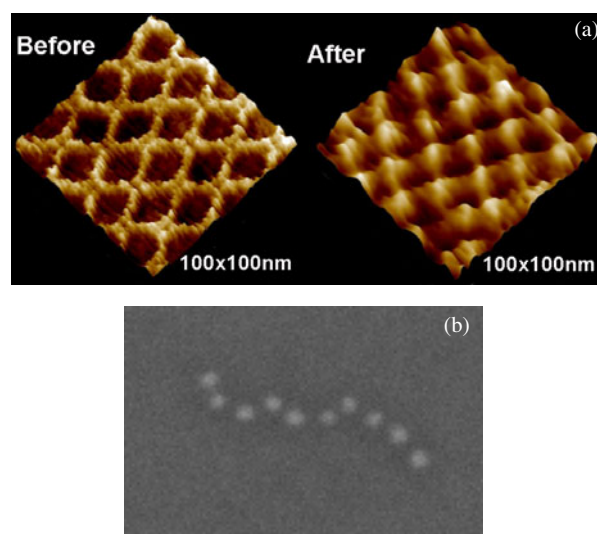


Figure 3. (a) $100 \text{ nm} \times 100 \text{ nm}$ AFM images of the self-assembled 4×4 DNA nanogrids before and after streptavidin was added to the solution. The streptavidin molecules are regularly attached to predetermined locations through the biotin-streptavidin attraction, resulting in bulging appearance. (b) SEM image of metal nanoclusters assembled in a 1D chain on a different tile array (TX tiles).

functional groups and used as a scaffold for directing the periodic assembly of desired nanoparticles or molecules. We have used the nanogrids to order the protein streptavidin into periodic arrays. The 4×4 DNA tile of figure 2 was modified by incorporating a relatively small biotin molecular group into one of the T_4 loops at the tile centre. By adding streptavidin to the solution of the self-assembled 4×4 DNA nanogrids, the interaction of streptavidin with biotin led to the formation of periodic streptavidin arrays (figure 3(a)). Streptavidin has a diameter of ~ 5 nm, so its binding to the DNA nanogrids generates bumps at the centre of the 4×4 tiles, which can be compared to the similar grid before streptavidin binding (figure 3(a)). We plan to further utilize this mechanism to assemble regular square arrays of metal nanoclusters marked with streptavidin. In fact, we have already succeeded in arranging such clusters in ordered linear chains based on a different type of DNA tile (TX tiles; see figure 3(b)).

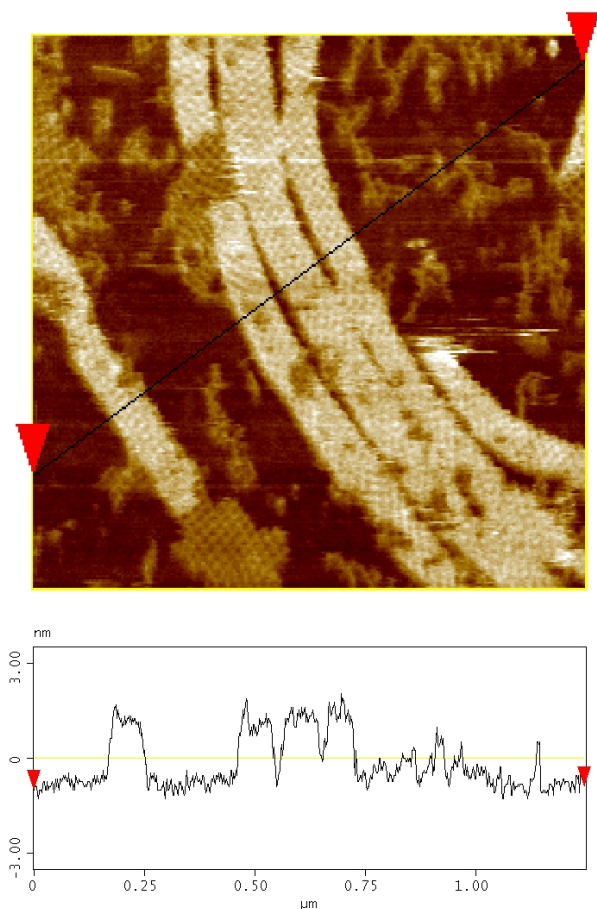


Figure 4. Top: a $1\ \mu\text{m} \times 1\ \mu\text{m}$ AFM image of the self-assembled DNA nanotubes based on the 4×4 nanogrids. The underlying 4×4 structure of the tubes is clearly visible. Bottom: height profile along the cross-section indicated on the top image.

A slight modification of the 4×4 tiles causes the DNA lattice to curve, eventually forming a tubular structure somewhat analogous to carbon nanotubes. Following placement of the sample on the substrate, the DNA nanotubes are observed to flatten, forming very regular ribbons 60 nm wide and many microns long (often $> 10\ \mu\text{m}$). Figure 4 shows an AFM image of several DNA nanotubes. In some parts of the image the nanotubes are damaged, revealing the underlying 4×4 grid structure. The height of the (flattened) nanotubes is twice as large as the height measured for a single layer of the DNA lattice. We have used the DNA nanotubes for templating highly conductive metallic nanowires [4].

2.2. DNA metallization

We have developed a novel electroless deposition technique to metallize DNA in solution. We applied it to coat double-stranded DNA molecules, both synthetic and natural (λ -bacteriophage) in silver on a Si/SiO₂ substrate. Figure 5 shows the resultant nanowires imaged by a scanning electron microscope (SEM). The metallized wires have a diameter down to 15 nm, which makes them an order of magnitude thinner than the previous DNA or protein-based metal wires ($\sim 100\ \text{nm}$) [5–11], and among the thinnest metal wires available to date by any method.

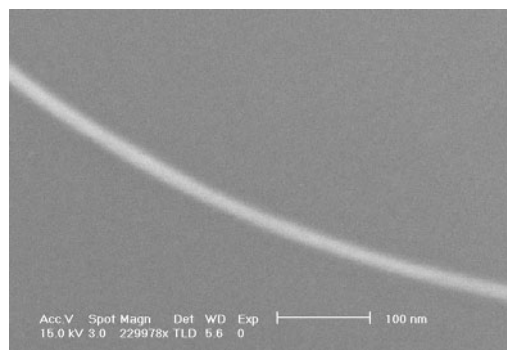


Figure 5. An SEM image of a 15 nm wide wire based on a double-stranded DNA molecule. Scale bar: 100 nm.

We have also metallized the 4×4 nanotubes of figure 4 with silver. The resulting structures have been characterized by AFM and SEM. The metallized nanotubes have heights and widths of 40 nm and lengths of up to $\sim 5\ \mu\text{m}$. Based on the AFM and SEM measurements of the width and height of the metallized DNA tubes and molecules, the thickness of the metallization layer is only $\sim 5\text{--}10\ \text{nm}$. We therefore expect the DNA nanotubes to stay hollow during the metallization process, forming hollow metal tubes only $\sim 40\ \text{nm}$ in diameter. Analytical experiments to examine this exciting hypothesis are planned. Such ‘nano-pipes’ may find applications in ‘nano-fluidics’ and targeted delivery of chemicals on a nanometre scale. Finally, we are currently working on metallizing the 4×4 flat DNA lattices in solution in order to fabricate metal grids with a pitch of just 20 nm.

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