

DNA-Templated Fabrication of 1D Parallel and 2D Crossed Metallic Nanowire Arrays

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ABSTRACT

This paper reports a simple method for the fabrication of ordered nanostructures composed of metallic nanowires. Molecular combing was used to stretch and align linear λ -DNA molecules into parallel or crossed patterns. Subsequent metallization of DNA through electroless palladium deposition yielded 1D parallel or 2D crossed metallic nanowire arrays. This method has potential use in building interconnects between nanosized building blocks toward nanodevice construction.

This paper reports the fabrication of both 1D and 2D metallic nanowire arrays by a successful combination of molecular combing and DNA metallization. The preparation of ordered arrays of nanowires or nanotubes represents a major challenge in the assembly of nanoscale building blocks into functional devices and has attracted much research interest recently.^{1,2} Nanowires have been successfully aligned through flow or electric field alignment.¹ Recent work has shown the possibility of obtaining a 1D or 2D network of single-walled carbon nanotubes (SWNT) by controlling the direction of gas flow during a CVD synthesis.²

DNA molecules have been successfully employed either to organize nanoparticles into arrays via base pairing³ or as linear templates for the fabrication of metallic or semiconducting nanowires.⁴ One of the major advantages regarding DNA-assisted nanofabrication is the availability of various well-developed techniques concerning the synthesis, manipulation, assembly,⁵ and structure tailoring of DNA molecules. Thus, excellent control of the nanostructures derived from precursory DNA scaffolds is expectable. The DNA templated fabrication could be performed not only in solutions but also on surfaces. The latter is compatible with microelectromechanic system (MEMS) fabrication and allows the in situ generation of nanowires at desired locations,^{4c} which might enable electronic/magnetic communications between nanosized building units.

Here we demonstrate that a combination of molecular combing and DNA-templated metallization could generate ordered metallic nanowire arrays. Our strategy consists of three steps: (i) fluid flow is used to prepare parallel or crossed DNA arrays with a controllable direction and density;

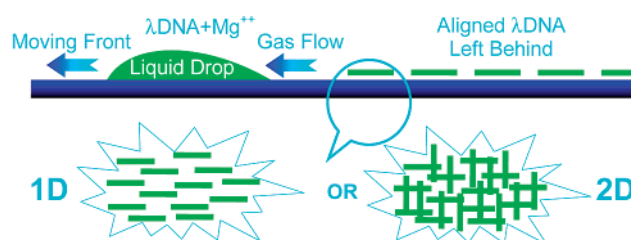


Figure 1. Schematic representation of the fluid-flow-assisted molecular combing of DNA molecules on a surface.

(ii) metal ions (Pd^{2+}) quickly absorb onto negatively charged DNA backbones; and (iii) chemical reduction of the absorbed metal ions (Pd^{2+}) produces palladium (Pd) nanowires. The resulting Pd nanowires follow the patterns defined by DNA molecules, producing parallel or crossed networks composed of Pd nanowires. Branches from nonspecific metal deposition are greatly reduced compared to that reported previously.^{4j,4k} The method reported here would be especially useful for the parallel assembly of nanosized building blocks into functional networks.

DNA molecules can be aligned and stretched with various molecular combing techniques.⁶ To get a unidirectional alignment of DNA molecules, which is necessary for the formation of well-organized metallic wire arrays, a modified literature method^{6e} was used to comb λ -DNA (New England Biolabs), as schematically shown in Figure 1. A 1.5- μL drop of DNA solution (40 $\mu\text{g/mL}$) in the presence of 0.45 mM $\text{Mg}(\text{Ac})_2$ was placed onto a glass slide or a freshly cleaved mica surface. Compressed air was then used to drive the solution to flow away along one direction. Stretched and parallel DNA chains were produced in the lane over centimeters, passed by the DNA solution. To create 2D DNA arrays, a second alignment was made along another direction.

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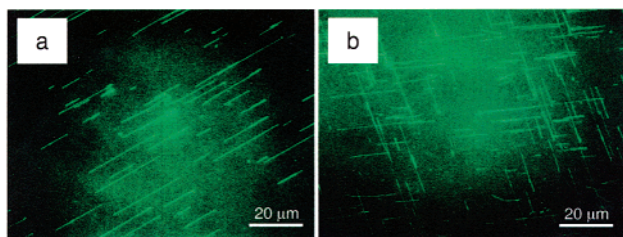


Figure 2. Fluorescence microscopy pictures showing (a) 1D- and (b) 2D-aligned DNA wires formed by fluid-flow-induced molecular combing.

Initially, we used a fluorescence microscope to characterize DNA samples on glass slides. We prestained DNA with YOYO-1 before molecular combing and used a DNA concentration of $0.5 \mu\text{g/mL}$ to get a DNA density suitable for fluorescence microscopy analysis. As seen from Figure 2, stretched and unidirectional DNA molecules were uniformly distributed on the glass surface.

Two factors have a critical impact on the resulting DNA networks. (i) Mg^{2+} , a divalent cation, fine tunes the DNA adhesion to glass and mica surfaces. At low Mg^{2+} concentration ($<0.05 \text{ mM}$), negatively charged DNA molecules cannot bind tightly to negatively charged glass or mica surfaces and will be swept away from the surface during the alignment process. However, a high concentration of Mg^{2+} ($>1 \text{ mM}$) will cause DNA molecules to form coils and random networks, and thus they cannot be well aligned (Supporting Information). (ii) The flowing velocity of a solution drop determines the straightness and density of the aligned DNA molecules. Both factors could be easily controlled experimentally. Our results showed that only with an appropriate interaction between the mica surface and the DNA molecules was it possible to achieve an excellent stretching (DNA strand should be almost free of kinks) and alignment (DNA orientations follow the flow direction well) of DNA chains, and this would substantially facilitate the following metallization step toward ordered nanowire networks.

Aligned DNA samples on micas were imaged with tapping-mode atomic force microscopy (AFM, Nanoscope IIIa), which clearly showed that DNA molecules were well stretched and aligned both in parallel and in crossed orientations (Figures 3b and 4b). The height of the DNA molecules aligned in this way is in the range of $0.3\sim0.4 \text{ nm}$, similar to reported values.

Metallization immediately followed DNA deposition. Ten microliters of a saturated $\text{Pd}(\text{Ac})_2$ solution, prepared by ultrasonically dissolving 10 mg of $\text{Pd}(\text{Ac})_2$ in 4 mL of doubly distilled water (ddH_2O) followed by centrifugation at $9000g$ to settle undissolved particles, was allowed to incubate with the patterned DNA molecules for 10 s . Then, the $\text{Pd}(\text{Ac})_2$ solution was removed either from the substrate edge with filter paper, leaving a “wet” mica surface, or blown away by compressed air. Ten microliters of a reduction bath, containing 250 mg/L sodium citrate, 250 mg/L 85% lactic acid, and 25 mg/L borane–dimethylamine (Aldrich), was then placed on the surface, allowing the reduction to happen within 15 s . The surface was rinsed afterward with ddH_2O .

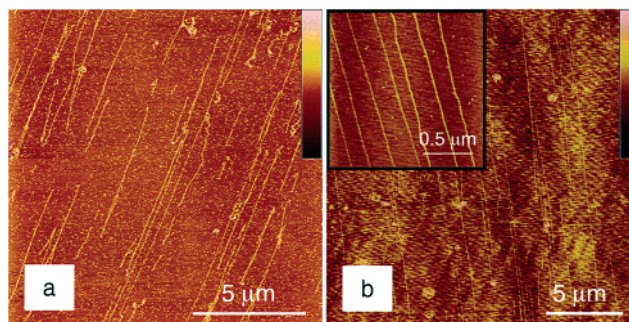


Figure 3. AFM images of (a) 1D-aligned Pd nanowires and (b) the corresponding precursory DNA molecules. The inset in b gives a detailed view of the parallel DNA duplexes. Height scale: (a) 15 nm and (b) 1.0 nm .

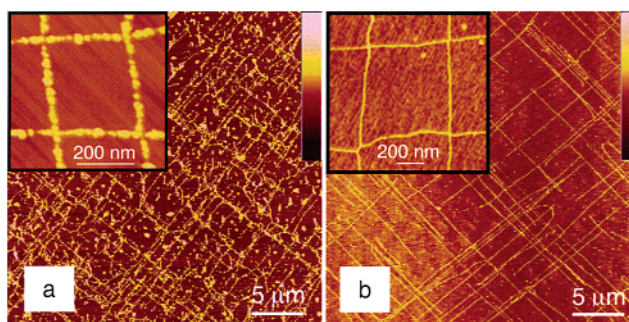


Figure 4. AFM images of (a) 2D-aligned Pd nanowires and (b) the corresponding precursory DNA molecules. The insets in a and b give enlarged views of 2D squares of metal nanowires and DNA molecules, respectively. Height scale: (a) 30 nm and (b) 3.0 nm .

Parallel or crossed metallic nanowires were produced on the mica surfaces. Figures 3a and 4a are typical AFM images of the 1D and 2D metallic nanowire arrays. The nanowires are composed of nanoparticles, and these wires are quite uniform with an average diameter of about 30 nm , bearing in mind that the actual diameter should be even smaller because of the limited lateral resolution of AFM. A section analysis (Figure 5, left) showed that these nanowires are about 5 nm in height, and this value may vary in the range of $4\text{--}10 \text{ nm}$ in different experiments. Figure 5 also presents an AFM image at high magnification showing a well-defined meshlike 2D Pd nanowire array.

The metallization of DNA commonly produces short branches due to random nanoparticle aggregation, as found in previous reports.^{4j,4k} We attributed this phenomenon to uncontrolled nucleation in solution and reasoned that restricting the metallization process on a surface might be helpful. Our experiments proved this hypothesis. After the activation of DNA by $\text{Pd}(\text{Ac})_2$, if the liquid drop of palladium solution was removed from the surface by compressed air before the reduction was done, then the resulting metal wires would exhibit quite uniform lateral dimensions as seen in Figure 3a. Samples prepared in this way are almost free of branches; otherwise, the nanowires will be abundant in branches (Supporting Information). However, during our experiments, molecular combing was primarily conducted using DNA solutions with low ionic strength, and this reduced DNA coiling and condensation. It is also noteworthy that the

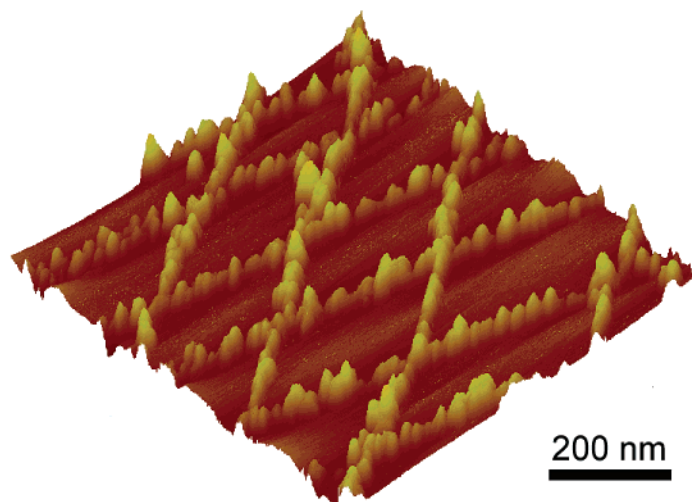
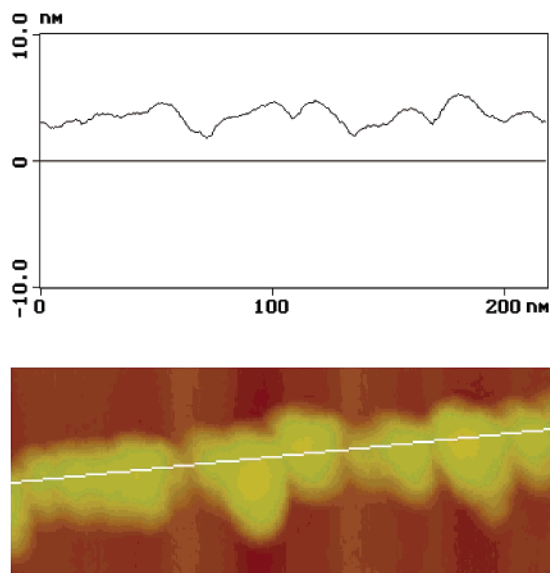


Figure 5. Left: high-magnification AFM image of a Pd nanowire; a section analysis of it shows an average particle height of about 5 nm. Right: high-magnification image of a meshlike 2D array of Pd nanowires formed by the metallization of a 2D-aligned DNA sample.

shortened incubation and reduction periods compared with those in previous reports minimized the distortions of the as-formed DNA patterns due to surface detachments but still allowed a complete metallization.

Although several methods have been developed to comb DNA molecules and to metallize DNA chains, it was not expected to be easy to combine them without a good understanding of these two separate processes and to control them efficiently because conventionally they are not compatible. We found that the combed DNA could detach from the substrate surface into the aqueous phase during the following metallization and that the previous DNA stretching and alignment techniques⁶ could not produce really unidirectional DNA patterns with reasonably strong attachment to the mica surface, which is necessary for a successful metallization. Our success in combining molecular combing and metallization for the fabrication of 1D and 2D nanowire arrays came from (i) the use of a modified gas-flow alignment technique that could easily generate a unidirectional alignment of DNA molecules suitable for metallization and (ii) shortened incubation and reduction times, which along with the use of a dry surface for electroless deposition avoided the detachment of DNA molecules and finally produced well-defined 1D and 2D nanowire arrays defined by the combed DNA molecules. The important difference between 2D and 1D patterns is not just the dimensionality itself but the formation of nanowire junctions that would open important opportunities for nanodevice research and is surely worthy of further pursuit.

In conclusion, we have demonstrated a simple method of fabricating parallel and crossed molecular networks of DNA and have successfully converted them into metallic nanowires through an efficient selective electroless deposition. The resulting nanowires are free from random branches and have a mean diameter below 30 nm. Although further improvements are still needed to remove some existing defects (e.g., some DNA molecules were not fully stretched, aggregated,

and overlapped), the method we developed here is controllable and will be promising for fabricating connecting wires in nanoscale electric circuits. In addition, the fabrication could be easily adapted for making ordered nanowire networks of other materials.

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Supporting Information Available: AFM images of randomly distributed Pd nanowires and DNA combed at high Mg^{2+} concentration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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