Communication

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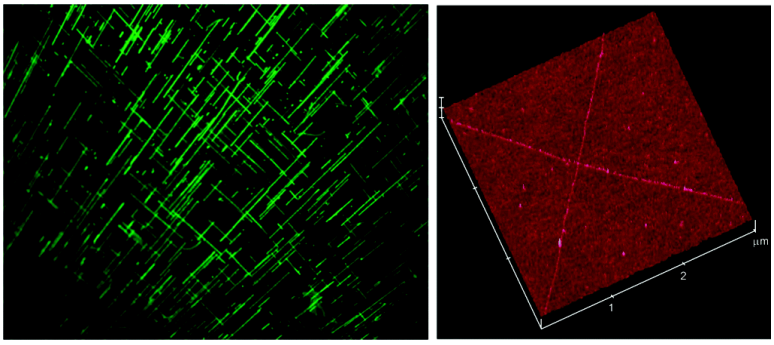

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Transfer-Printing of Highly Aligned DNA Nanowires

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The abilities to control the size of nanomaterials and to manipulate them on a nanometer scale are priority subjects in the field of nanotechnology. Some of the most promising near term realizations of nanotechnology are at the interface of physical and biological systems. Because many biomolecules have specific binding properties in self-assembly processes, they are attractive materials for nanotechnology. One such promising construction material for growing a well-defined nanostructure is DNA, due to its π-electron core and predictable recognition attributed to the specificity of Watson−Crick base-pairing. DNA has already been studied as a nanomaterial for DNA-based computation[1−4] and DNA nanowires.[5,6] Specifically, several methods for assembling metal on a DNA template were successful in yielding conduction wires.[7−10] The method of molecular lithography[7] has been expected to be a potential way to overcome the current limit of optical lithography. However, it is difficult to manipulate DNA molecules from their natural random-coil state into an extension state. The ability to reproducibly create and align well-stretched DNA onto surfaces is important for not only realizing nanoscale electronics but also utilizing the optical mapping method[11−13] to analyze the precise gene location on DNA. Although numerous methods have been developed to manipulate DNA molecules, they require special equipment.[14−17]

We developed a simple method of reproducibly creating highly aligned DNA nanowires, which enabled us to straighten and fix DNA molecules on surfaces without any surface modification or special equipment. As shown in Figure 1, the procedure was as follows. A solution of 5 μL of λ-DNA in TE buffer (10 mM Tris-HCl and 1 mM EDTA, pH = 8.0) prestained with YOYO-1 (Molecular Probes) was deposited on a poly(dimethylsiloxane) (PDMS) sheet,[18,19] and then its droplet was sucked up by a pipet. When a droplet of DNA solution on a surface is sucked up, the surface tension at the moving air−water interface is sufficient to stretch the molecules along the central direction of the droplet.[20] Next, the surface of the PDMS sheet onto which DNA molecules had been stretched and fixed was pressed onto a coverslip or mica without surface modifications. The PDMS sheet was in contact with the surfaces for 5 s and then removed. In this process, the applied force was estimated at 23 N/m^2. Consequently, DNA molecules initially present on the PDMS sheet were transferred onto another surface using this transfer-printing (TP) procedure.

Figure 2 shows fluorescent microscopic images of DNA molecules deposited on surfaces before and after TP. We previously reported a simple method for reproducibly stretching DNA molecules on surfaces using a polymer coating.[20] With polymers containing π-conjugation units (polyphenazasiline, PPhenaz and poly(vinylcarbazole), PVCz), many DNA molecules were stretched nicely and fixed on surfaces. Even though there were somewhat fewer DNA molecules deposited on PDMS than on PPhenaz and

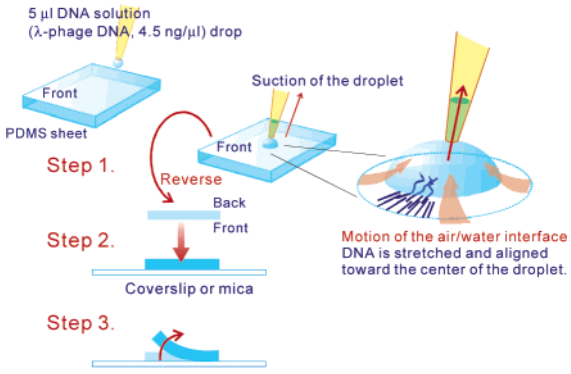

Figure 1. Procedure of transfer-printing for aligned DNA molecules.

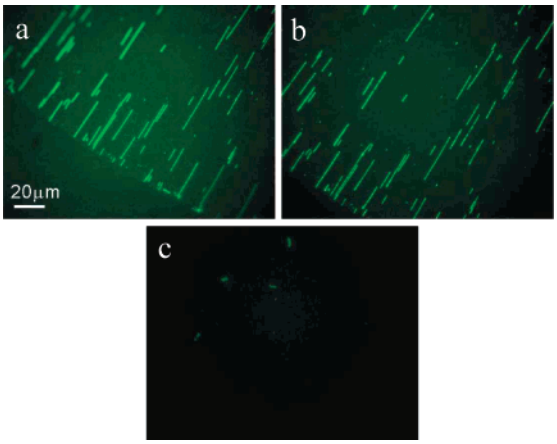

Figure 2. Fluorescent microscopic images of DNA molecules on surfaces before and after TP. Images are (a) DNA on PDMS before TP, (b) on coverslip after TP, (c) on PDMS after TP. Image a was observed through the coverslip covered on the PDMS sheet. The coverslip was carefully removed, and after image c was observed. Images a and c were at the same place on the PDMS sheet. Image b was observed from the removed coverslip.

PVCz, those shown in Figure 2a were sufficiently stretched and highly aligned on the surface. Allemand et al. have reported the pH-dependent fixation of DNA molecules on a hydrophobic surface.[21] The protonation to phosphate groups on DNA molecules affects the fixation of those on hydrophobic surfaces. Thus, further optimizations of pH or ion strength in DNA solution are necessary to allow more efficient fixation in our method. A comparison of the images shown in Figure 2a and b reveals that nearly every DNA molecule deposited on PDMS was transferred onto the glass surfaces. As far as we observed in several areas including characteristic edge positions shown in Figure 2, all DNA molecules on PDMS after TP were transferred (Figure 2c). Thus, the percentage of transferred DNA molecules was nearly 100% in this case. Furthermore, DNA molecules after TP remained straight and aligned. Glass or mica surfaces have stronger polar groups than

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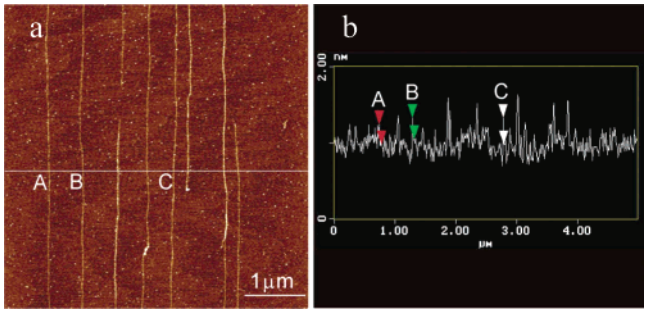

Figure 3. (a) AFM image of aligned DNA molecules transferred onto mica. (b) Section profile along the white line of the AFM image.

hydrophobic surfaces of PDMS. Therefore, DNA containing hydrophilic groups is easily transferred from PDMS surfaces to glass surfaces.

Although an atomic flat surface such as mica is necessary to directly observe DNA molecules with atomic force microscopy (AFM), unfortunately it is not enough to straighten and fix the DNA molecules. Thus, surface modifications with silane compounds or a multivalent cation are often required for mica surface. Our method does not require such modifications and alleviates choosing and pretreating substrate as required by various analytical equipment. AFM observation also revealed that many stretched DNA molecules were highly aligned on bare mica after TP (Figure 3a). The lowest height (diameter) of the observed DNA molecules was ~0.4 nm. For example, DNA molecules A, B, and C in Figure 3a had a apparent heights of 0.267, 0.285, and 0.353 nm (Figure 3b). These heights were smaller than a single double-strand DNA (~1.0 nm)[20,22] imaged by AFM in a previous study. The deviation may be attributed to the compression of DNA molecules by TP, which decreased the height significantly.

The main advantage of our method is that stretched DNA molecules can be easily aligned into a certain position, which is identical to the concept of microcontact printing (μCP). μCP has been often employed for patterning biomolecules such as protein.[23] Our method is novel in the point of directly printing stretched DNA molecules. Although μCP can in principle be used to pattern surfaces with sub-100 nm features, our method enabled the formation of molecular patterns with ~2 nm originated from the diameter of DNA. Furthermore, by repeating TP onto the same substrate, it is also possible to realize a two-dimensional (2D) assembly of DNA nanowires. We demonstrated the TP of 2D DNA patterns onto surfaces. To assemble the patterns, we first transferred DNA molecules onto the substrate and then overlapped the other PDMS sheet to which DNA molecules were fixed onto the first one. AFM images of 2D DNA molecule patterns are shown in Figure 4. The arrow marked "1st" notes the direction of the first TP, and the arrow marked "2nd" notes the direction of the second TP. In Figure 4a, the first TP of DNA molecules remained aligned, even if an additional TP was overlapped onto those. Therefore, DNA molecules are stably fixed once they are aligned on surfaces. Figure 4b is a magnified image extracted from the "*" area in Figure 4a.

In summary, we developed a simple method for reproducibly creating highly aligned DNA nanowires on various substrates. A combination of this method and several methods of metallizing DNA could enhance the advantages of DNA as future electronic circuits. This method will also be helpful for clarifying some of the interesting phenomena[24,25] such as quantum effects, observed in electric properties of native or metallized DNA molecules. By creating the appropriate relief-pattern on PDMS and surface modifications of the substrate, it is possible to achieve higher-ordered patterns of DNA nanowires. This could open the door to realizing nanoscale electronics using DNA.

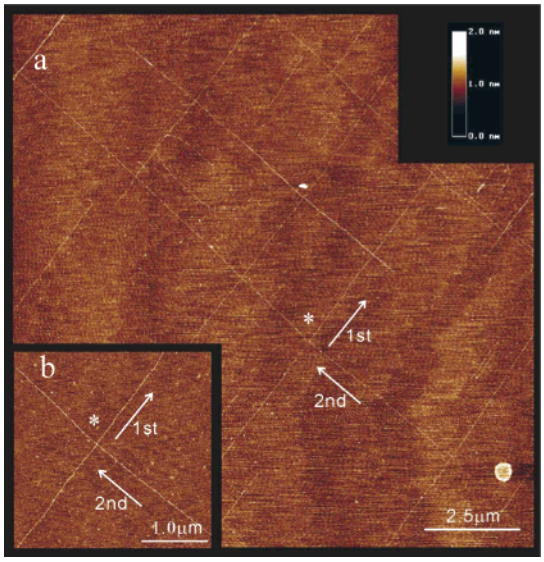

Figure 4. AFM images of a 2D DNA pattern aligned on mica after TP. (a) 2D DNA pattern in a large scan range. (b) Magnified image extracted from the "*" area.

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