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Polyaniline Nanowires on Si Surfaces Fabricated with DNA Templates

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Abstract: It is essential to put individual, free-standing nanowires onto insulating substrates and integrate them to useful devices. Here we report a strategy for fabrication of conducting polymer nanowires on thermally oxidized Si surfaces by use of DNA as templates. The direct use of stretched and immobilized DNA strands as templates avoids the agglomeration of DNA caused by shielding of charges on DNA when polyaniline/DNA complexes formed in solution. Most importantly, the oriented DNA strands immobilized on the Si surface predetermine the position and the orientation of the nanowires. The approach described here is the first step toward uniting the programmable-assembly ability of DNA with the unique electronic properties of conducting polymers for high-density functional nanodevices. The conductivity of the nanowires is very sensitive to the proton doping—undoping process, suggesting that the nanowires hold great promise for sensitive chemical sensor applications.

Introduction

Like conventional silicon semiconductors, the electrical conductivity of conducting polymer materials can be reversibly controlled over many orders of magnitude. Certain conducting polymeric materials, for example, polyaniline, also have mechanical flexibility and environmental stability, which make the conducting polymer nanowires an ideal choice as building blocks of active circuit elements for the future ultraminiaturized nano-electronic devices. Furthermore, the conductivity of these materials can be controlled chemically, making conducting polymer nanowires also promising sensing materials for ultrasensitive, trace-level biological and chemical nanosensors. Despite recent advances,^{1–5} a functional nanodevice that uses individual conducting polymer nanowires has not yet been developed. This is largely due to the lack of an efficient method for producing nanowires that are compatible with practical aspects of device fabrication and the lack of a robust technique for integrating nanowires into functioning circuits.

To date, conducting polymer nanowires were obtained primarily with porous membrane as templates. In this approach, the dimension and the morphology of the polymer structures are defined by the porous support. Polyaniline nanowires with 3-nm diameter and polypyrrole nanowires of 30-nm diameter have been successfully fabricated by this method.^{1,2} However, the polymer nanowires may be destroyed or may form undesir-

able aggregated structures when they are released from the template. Isolated 10-nm polypyrrole nanowire arrays have been electropolymerized by use of step-edge defects on highly oriented pyrolytic graphite (HOPG) as templates, but transferring the nanowires to an insulating substrate has not been successful yet.³ Well-defined conducting polymer nanowires have been created on semiconducting and insulating surfaces with dip pen nanolithography.⁵ This method cannot be used for high-throughput applications due to the slow nature of the scanning probe microscopy (SPM) technique. Developing a reliable and scalable strategy for integrating individual nanoscale building blocks to functional devices with high density is the principal challenge facing the next generation of nanodevice development. Promising approaches have been advanced that exploit the properties of certain biomolecules.^{6–13} DNA, due to its excellent recognition ability, has been assembled into rather sophisticated and predesigned networks.^{14,15} It has also been used as “smart glue” to guide the self-assembly of nanostructures into functional circuits.^{16,17} Unfortunately, the absence of reasonable conductivity in native DNA molecules (still in a vigorous debate)^{18–24}

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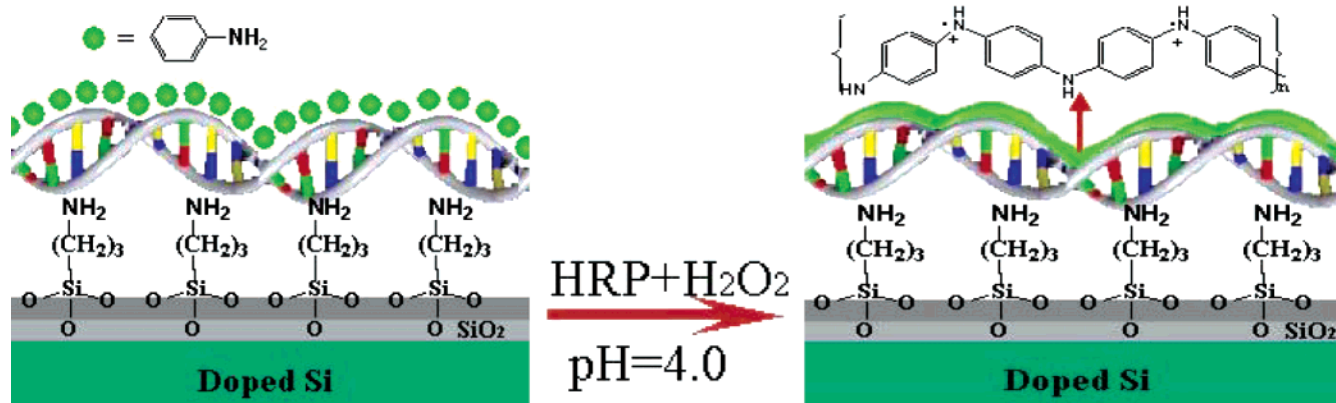


Figure 1. Fabrication of a polyaniline nanowire immobilized on a Si surface with stretched double-stranded DNA as a guiding template.

prevents their direct use in electrical circuits. One strategy to confer electrical conductivity to DNA molecules is to deposit metals along the DNA strands.^{9,10,25–28} Metal wires conduct electricity, but their conductance is not controllable, which restricts the application of metal/DNA nanostructures as active circuit elements. In this paper, we grant *controllable* electrical conductivity along individual DNA molecules by coating a thin layer of conducting polymer, polyaniline, along the DNA strands immobilized on a silicon chip.

Polyaniline is commonly synthesized by oxidizing aniline monomer either electrochemically or chemically^{29,30} in a strong acid environment, required to initiate the polymerization reaction. The harsh condition precludes the use of delicate biological-based materials as templates. It has been reported that the horseradish peroxidase (HRP) enzymatic approach³¹ is environmentally benign. The mild reaction conditions involved in the synthesis provide opportunities for the use of biological polyelectrolytes, such as DNA, as templates. It was found, however, that the products from the HRP enzymatic approach are typically a mixture of at least two structurally different types of polyanilines.^{32,33} The first is ortho- and para-substituted carbon–carbon and carbon–nitrogen bond structures, and the second is a benzenoid–quinoid (head-to-tail), which is the desired structure for higher conductivity. The presence of the highly branched ortho- and para-substituted polyaniline in the first type severely limits the degree of conjugation and hence the electrical and optical property of the resulting polymers.

To minimize branching, Samuelson and co-workers³⁴ developed polyelectrolyte-assisted polymerization of aniline. The polyelectrolyte acts as a template upon which the aniline monomers preferentially align and form a complex that leads to mostly para-directed synthesis, promoting extended conjugation of the resulting polyaniline chains with limited parasitic branching. Using this method, they have fabricated water-soluble, high molecular weight polyaniline complexes. They have also used DNA as a template to produce water-soluble DNA/polyaniline complexes,³⁵ in which the polyaniline was wrapped around the DNA matrix, and it could control reversibly the secondary structure of DNA in solution. However, after immobilization of the polyaniline/DNA complex by a freeze-drying method onto a freshly cleaved mica substrate, scanning probe and electron microscopic studies indicated that the formation of polyaniline causes the DNA–polyaniline strands to agglomerate,³⁶ which is not suitable for electronics. The possible reason that was reported is due to the concomitant shielding of charges on the phosphate groups of the DNA with the formation of polyaniline on the DNA templates. This shielding reduces the electrostatic repulsion between successive phosphate groups of DNA, leading to the formation of the overwound polymorph.³⁶ However, DNA agglomeration was not a problem in recent reports of DNA templates used to fabricate metal nanowires and to assemble gold nanoparticles.^{10,27}

In this paper, we describe our success in fabricating polyaniline nanowire arrays on Si substrates by using fully stretched DNA as growing templates while applying the gentle HRP enzymatic polymerization approach.

Experimental Section

The principle of the nanowire fabrication method is sketched in Figure 1. First, double-stranded λ -DNA is stretched, aligned, and immobilized on a thermally oxidized Si chip by the molecular combing method.^{37,38} Then the DNA templates are incubated in protonated aniline monomer solution to emulsify and organize the aniline monomers along the DNA chains. Finally, the aligned aniline monomers are polymerized

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enzymatically by adding horseradish peroxidase (HRP) and H_2O_2 successively to form polyaniline/DNA nanowires.

DNA Alignment. The thermally oxidized Si substrate was modified with (aminopropyl)triethoxysilane (APTES);³⁹ a vapor-phase method was used to provide a good adhesion between DNA strands and the substrate surface. A 2 μL drop of λ -DNA (48 500 bp, New England Biolabs Inc.) solution in TE buffer (10 mM Tris-HCl and 1 mM EDTA, pH = 8.0) was deposited onto the edge of a clean glass coverslip, and carefully placed onto the top of the APTES-modified Si surface. The weight of the glass forced the solution to spread into a thin layer. When the cover glass was slid away, the capillary force of the moving interface stretched and aligned the DNA in one direction.

Fabrication of Polyaniline Nanowires. Fabricating polyaniline nanowires was accomplished in three steps. First, the DNA templates were incubated in the aniline monomer solution (19 mM, pH = 4.0 adjusted by 0.1 M HCl). The electrostatic interaction between the protonated aniline and the phosphate groups in the DNA chains emulsified and organized the aniline monomers along the DNA chains.^{36,40} Next, free aniline monomers were removed by washing carefully with monomer-free electrolyte solution. Finally, the aligned aniline monomers were polymerized enzymatically in the same solution by adding horseradish peroxidase (HRP, 0.80 mM in 0.1 M KH_2PO_4 , pH = 4.7) and H_2O_2 successively.³⁶ To avoid the inhibition of HRP due to excess H_2O_2 , diluted H_2O_2 (3.5 mM) was added in three drops (25 μL) spaced 10 min apart. After the addition of H_2O_2 , the reaction was left for another 10 min, and then the sample was cleaned with Nanopure water (18.2 M Ω) to remove unreacted monomers and phosphate salts. Horseradish peroxidase (HRP, EC 1.11.1.7) type II (200 units/mg solid) was purchased from Sigma Chemical Co. Aniline (99.5%) was double-distilled and kept refrigerated under nitrogen prior to use. All other chemicals were of analytical-grade purity and were used as received from Aldrich Chemical Co. Inc. All solutions were prepared in Nanopure water, which was also used to rinse and clean the sample after polymerization and before any properties characterization.

Atomic Force Microscopy Studies. Atomic force images were obtained on a Nanoscope III A (Digital Instruments) in tapping mode operating in ambient air. A 125- μm -long rectangular silicon cantilever/tip assembly was used with a spring constant of 40 N/m, resonance frequency of 315–352 kHz, and tip radius of 5–10 nm. The applied frequency was set on the lower side of the resonance frequency. The image is generated by the change in amplitude of the free oscillation of the cantilever as it interacts with the sample. The height differences on the surface are indicated by the color code; lighter regions indicate higher heights.

Conductance Measurements. The conductance of the polyaniline nanowires was measured with a Keithley 6517 multimeter, and data were recorded by Yokogawa 708 oscilloscope. All the conductance measurements were carried out in a sealed glass chamber with two electrical feeds, one gas inlet, and one gas outlet. HCl and NH_3 gases were introduced into the chamber by nitrogen flowing through HCl or NH_4OH solutions and passing through a drying agent (3- \AA molecular sieve) to remove any water vapor in the gas flow.

Results and Discussion

AFM Characterization of Aligned DNA Strands and Polymer Nanowires. Figure 2 shows tapping-mode AFM images of the stretched DNA templates before and after polyaniline polymerization. The apparent height of the λ DNA is 0.3–0.4 nm (Figure 2a,b), much smaller than the expected 2-nm DNA diameter but consistent with the results of others.⁴¹ The discrepancy has been attributed to the deformation of DNA under the AFM tip, the adhesion force between DNA and the treated surface, the roughness of the Si surface, and most importantly, the presence of buffer salts, which increases the background significantly.⁴² The apparent widths of the DNA

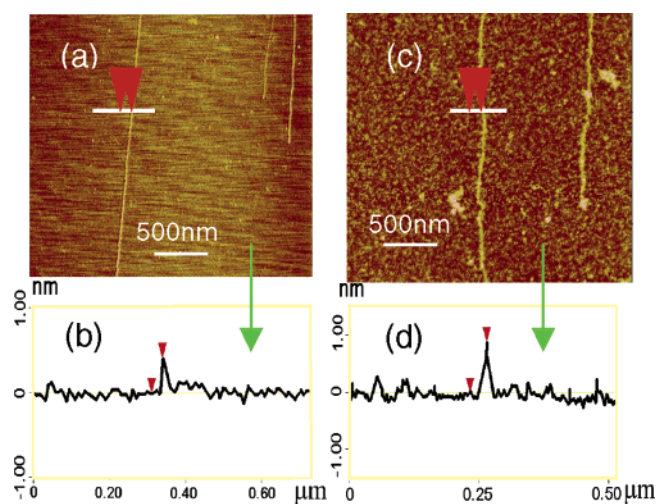


Figure 2. Tapping-mode AFM images of stretched DNA immobilized on an oxidized Si surface premodified with APTES. (a) Before polymerization; (b) cross-section of a DNA chain, indicated by arrows; (c) after polymerization; (d) cross-section of the wire indicated by arrows.

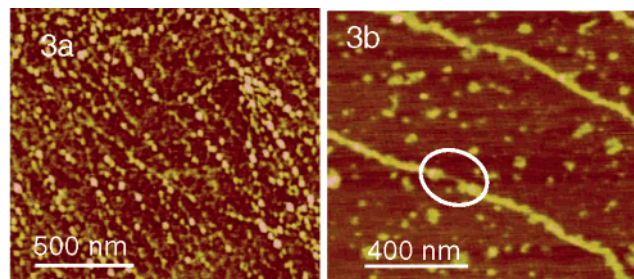


Figure 3. (a) Polyaniline particles formed along the DNA strands in the electrolyte solution of pH = 5.0. (b) Polymerization in pH = 3.2 solution resulted in incomplete coating of polyaniline along DNA strands.

molecules are much larger than the DNA diameter of 2 nm because of the convolution effect of the blunt AFM tip.

After the polymerization of aniline, the apparent height increases to 0.8–1 nm (Figure 2c,d), much higher than that of the bare DNA or the aniline monomer-adsorbed DNA (which has a height not detectably different by AFM from bare DNA). The height increase is therefore due to the formation of a thin layer of polyaniline along the DNA templates. The heights of the polyaniline/DNA complex nanowires are very similar in independent experiments (Figure 3b), demonstrating the reproducibility of this approach. The nanowires follow the shape and position of the DNA on the surface. Scanning probe and electron microscopy studies by Samuelson and co-workers³⁶ have indicated that the formation of polyaniline on the DNA templates in solution causes the DNA strands to agglomerate, due to the shielding of charges on the phosphate groups of the DNA. The complication from agglomeration of DNA strands seen in solution studies is not observed in our surface experiments.

pH Effects on Polymerization. The best wires were produced when the polymerization was run at pH 4.0. When the pH was raised to 5.0, we observed polyaniline particles deposited along the DNA strands (Figure 3a) instead of continuous wires. At

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pH 3.2, we found cases where the polymerization was incomplete (Figure 3b).⁴³ The strongly pH-dependent behavior may be explained by the critical pH dependence of the aniline molecules' alignment along the DNA templates and the catalytic activity of HRP.⁴⁴ Since the pK_a of aniline monomer is 4.6, a pH of 4 is sufficient to protonate the aniline monomers, and the electrostatic interaction between the positively charged aniline monomers and the negatively charged phosphate groups in the DNA promotes a preferential alignment of the protonated aniline along the DNA before polymerization. In higher pH solutions, the fraction of protonated aniline monomer was reduced, resulting in weaker net electrostatic interaction with the DNA and poor organization of the aniline monomer along the template. Since HRP polymerization is known to produce branched-chain and linear (head-to-tail) structures, the coupling that produces branched chains may become more dominant under these conditions, similar to enzymatic polymerization of aniline without a polyelectrolyte template.⁴⁴ In our experiment at pH 5.0, the polyaniline nanoparticle arrays formed along DNA templates may correspond to the parasitic branching polyaniline structures. A control experiment, at pH = 4.0 solution and without DNA template, results in similar particles.

Although lower pH is good for better organization and head-to-tail polymerization, the activity of the enzyme HRP decreased quickly. It is reported that the optimal pH for the catalytic activity of HRP is about pH 6.0.³⁴ The enzyme retains roughly 20% of the original activity after 20 min in pH 4.0 phosphate buffer solutions. In our experiments, para-directed polyaniline could be effectively synthesized at pH 3.2, but HRP was quickly denatured and lost its activity, resulting in partial coating of polyaniline along the DNA strands. The choice of pH 4.0 is critical to provide both adequate activity of the enzyme and electrostatic interaction, leading to the most para-directed synthesis. Samuelson and co-workers^{35,45} saw similar pH-sensitive changes in polyaniline morphology in their solution studies of polyelectrolyte templates.

The observations of the incomplete coating of polyaniline along the DNA chains at pH 3.2 are significant because inspection of the polymerization gaps provides further evidence that the polyaniline is in fact forming along the DNA strands. The circle in Figure 3b surrounds a thin section in a wire with a height (0.3–0.4 nm) that is consistent with our observations for uncoated DNA shown in Figure 2a,b. On either side of the thin span, the wire is 0.8–1.0 nm above the background, similar to our nanowire observations of Figure 2c,d. The fact that we can detect polymer-coated and bare DNA along the same wire supports our proposition that the polymerization occurs along the DNA template.

Conductance of the Polymer Nanowires. To measure the conductivity of the polyaniline nanowires, we first immobilized the DNA strands across an array of interdigitated gold electrodes with gaps of about 1.5 μm . The array consists of 10 pairs of

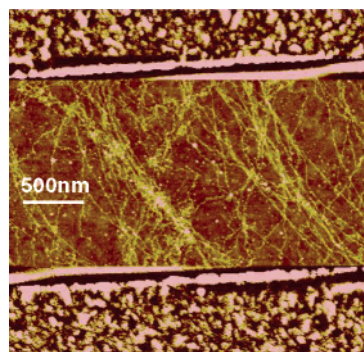


Figure 4. Typical TM AFM image of the polyaniline nanowires bridging the electrode gaps.

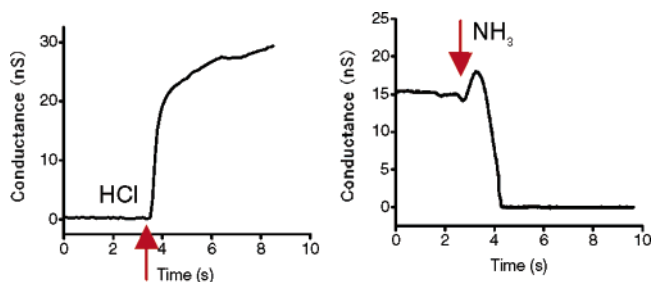
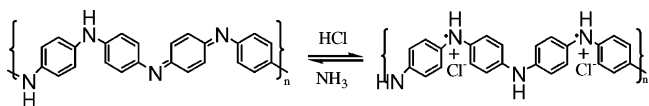


Figure 5. Conductance responses of the polyaniline nanowire arrays to vapors of (a) HCl and (b) HCl followed by NH_3 .

electrodes on a silicon substrate with a thermal oxide layer. Positioning of the DNA strands between the Au electrodes was obtained by placing a drop of DNA solution on top of the Si circuit and then removing it with a piece of filter paper perpendicular to the Au electrode lines. The capillary forces applied by the receding front of the evaporating DNA solution align the DNA chains perpendicular to the direction of the drying front. We used this method instead of the sliding glass/molecular combing method to avoid destroying the gold electrodes.

Then polyaniline nanowire arrays with built-in electrical contacts were fabricated by the same procedure as described above. The chip was cleaned with Nanopure water to remove unreacted aniline monomers and phosphate salts. Figure 4 shows a TM AFM image of the polyaniline nanowires arrays bridging one of the electrode gaps.

The conductivity of the nanowires was very low (Figure 5a), as expected, since cleaning the chip with Nanopure water removed the unreacted monomers and electrolyte salts, and it undoped the polyaniline nanowires since the pH of Nanopure water is around 7. Compared to other conducting polymers, polyaniline is unique in that it can be reversibly doped and undoped on the basis of simple acid/base chemistry,⁴⁶ and this property of polyaniline has been widely used for pH sensor applications. In acid or doped emeraldine salt form, polyaniline is conductive, and in the emeraldine base or undoped form, it is insulating. The two forms can be reversibly interconverted by the application of acid or base as shown below.



(43) When the polymerization was run at pH 3.2, occasional complete breaks (gaps with no polymer and no DNA) were observed in the nanowires that we suspect arise from infrequent damage to the DNA backbone. The breaks in DNA were seen in control experiments in which the aniline polymerization was skipped and the DNA templates were treated with 1 mM HCl or with 1 mM HCl and aniline monomers. The gaps are unlikely to arise from mechanical strain during the stretching and aligning process because far fewer breaks were observed at pH 4 and 5.

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When the wires were exposed to HCl vapor, a large current increase was observed (Figure 5a), which is due to the proton doping effect achieved by protonation of the imine nitrogens by HCl. The charge created along the backbone by this protonation is counterbalanced by the negatively charged chloride counterions. The change in conductivity is brought about by the formation of polarons that travel along the polyaniline backbone.⁴⁷ The conductance increase varied from device to device, depending on the density of the nanowires bridging the array electrodes.

No current increase was observed when NH₃ gas was introduced since the water-cleaned polyaniline nanowires had been undoped before the measurements. Introducing NH₃ gas in previously HCl-doped polyaniline nanowires caused a decrease of the conductance to almost zero (Figure 5b) (the initial increase and then decrease of the conductance was caused by mechanical interference when the NH₃ gas was introduced into the chamber). The conductance drop can be attributed to the deprotonation of polyaniline by the NH₃ gas. This typical proton doping–undoping phenomenon further confirmed the formation of polyaniline nanowire arrays and also demonstrated the potential for sensitive gas-sensing applications of the nanowires. Huang and co-workers^{48,49} showed that polyaniline nanofibers provided more sensitive detection of HCl and NH₃ vapors than the bulk materials. Tao and co-workers⁵⁰ recently reported that both the response time and sensitivity of a polyaniline/Au nanojunction sensor exceeded those of the polyaniline nanofiber-based sensor due to the small volume of the nanojunction. The response time of our polyaniline/DNA

nanowire array to HCl and NH₃ is within 1 s, 10 times faster than that of the polyaniline nanojunctions and 100 times faster than the polyaniline nanofibers due to the much smaller diameters of nanowires described here.

When the same experiments were performed for DNA arrays, no conductance change was measured. The bias voltage was slowly increased to 5 V and the currents observed remained at the noise level. Our results are in agreement with the results of De Pablo et al.,²⁴ Dekker and co-workers,⁵¹ and Braun and co-workers,^{9,10} who also found the absence of electronic transport through DNA.

Conclusion

Polyaniline nanowire arrays on Si chips were fabricated by using fully stretched DNA as growing templates. The pH value of the polymerization must be controlled around 4.0 to form continuous and conductive polyaniline nanowires because the pH value has a significant effect on both the catalytic activity of the enzyme and the formation of alignment of aniline monomer along the DNA templates. Conductance measurement from multiple nanowires demonstrates that the conductivity of the nanowires is sensitive to acid–base doping and undoping processes, indicating potential sensing application. To probe the intrinsic electrical property of individual nanowires and reveal the correlation between property and geometrical shape, defect structures of the nanowires are underway.

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