DNA deposition on carbon electrodes under controlled dc potentials

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Abstract

The native calf-thymus DNA molecule fully dispersed in solution was deposited onto highly oriented pyrolytic graphite, carbon fiber column and disk electrodes under controlled dc potentials. X-ray photoelectron spectroscopy, atomic force microscopy and electrochemical investigations indicated that network structures of DNA could be formed on various carbon electrode surfaces resulting in significant surface enlargement. The conformation, conductivity and stability of the deposited DNA layer largely depended on the concentration of the DNA deposition solution, the applied dc potential and the mode of electric field. The optimal condition for deposition of the DNA on carbon fiber disk electrode was determined as a deposition potential of 1.8 ± 0.3 V versus 50 mM NaCl–Ag/AgCl and a deposition DNA solution of 0.1 mg ml$^{-1}$. Under this condition, the DNA was covalently bonded on the electrode surface forming a three-dimensional modified layer, generating a 500-fold enlarged effective electrode surface area and similarly enlarged current sensitivity for redox species, such as Co(phen)$_3$$^{3+}$.

A possible mechanism for the formation of DNA networks is proposed.

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Keywords: DNA networks; Carbon electrodes; dc Potential; Electrochemical biosensor

1. Introduction

The DNA molecules have been the focus of great interest for many years. The double helix structure of DNA molecules has been demonstrated to be conductive, although the mechanism and related biological functions of it still remains an open question (Fink and Schönenberger, 1999; Murphy et al., 1993). The long chain molecule can be doped with electron donor and acceptor moieties for measuring the conductivity and investigating the related chemical and biochemical functions (Paroggaman et al., 1988). Bipolar ac potential has been applied for stretching the long chain molecule and immobilizing it on interdigitated electrodes (Holzel et al., 2003). However, the stretching of the molecule may disrupt the base stacking, which would be unfavorable for its conductivity (Treadway et al., 2002). The direct measurements of electric current across an individual DNA molecule positioned between nano-sized electrodes by electrostatic trapping indicated an efficient conduction through the molecule (Porth et al., 2000; Bezryadin and Dekker, 1997). The applied dc (direct current) potential may result in the compression of DNA chains (Kim et al., 2002); however, neither the morphology of DNA on the electrode surface nor the conductivity between DNA and the electrode has been discussed in detail.

In this report, the native calf-thymus DNA was successfully immobilized from water solutions onto several kinds of carbon electrodes under controlled dc potentials for study. The potential resolved phenomena provided new insight into the investigation of DNA morphology and conductivity, which should be important for better understanding the biological functions of DNA in living system (Treadway et al., 2002). The results indicated that the DNA molecules can form a highly conductive network stable in pH 14 alkaline solutions and stable in boiling water. The DNA modified layer on carbon fiber disk electrode could lead to 500- to 1000-fold enlargement of the effective surface area and similarly enlarged voltammetric responses to redox species, such as Co(phen)$_3$$^{3+}$. It could provide a new type of biosensors and may find wide applications in the fields of DNA-based devices.
2. Experiment

2.1. Materials

Calf thymus double strand DNA (ct-dsDNA or ct-DNA) from Sino-American Biotechnical Co. (A260/A280 ≥ 1.8, average length of about 8 μm, ~23,000 bp) was used as received. The electrolyte used was 5 mM pH 7.1 Tris–HCl buffer (denoted as THB) containing 50 mM NaCl. The compound of [Co(phen)₃](ClO₄)₃ was prepared from buffer (denoted as THB) containing 50 mM NaCl. The electrolyte used was 5 mM pH 7.1 Tris–HCl buffer (denoted as THB) containing 50 mM NaCl. The compound of [Co(phen)₃]Cl(O₄)₃ was prepared from THB solution thoroughly, ready for electrochemical re-examination. A piece of carbon fiber of about 2 cm long was placed in a meddle of a glass capillary (1.1 mm OD and 0.8 mm i.d.), which was pulled to seal at a horizontal glass micropipet puller (model PN-30, Narishige, Tokyo, Japan) under electric heating. A piece of copper wire and a drop of silver glue were used to lead out the electricity from the inner end of the fiber, and a drop of epoxy was used to seal the conjunction gap between the glass capillary and the protruded carbon fiber, forming the CFCE. For preparing the CFDE, the protruded fiber column of the CFCE was insulated by covering a thin-layer of electro-polymerized film of phenol and 2-allylphenol, and then, the column was cut perpendicularly to expose a disk surface. The HOPG working electrode was prepared by embedding a piece of HOPG sample in a teflon block, which was leading out using a piece of copper wire.

2.2. Apparatus

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on CHI 660A workstation (CHI, USA). Three-electrode system was used for general electrochemical studies. An Ag/AgCl wire quasi-reference electrode and a platinum wire counter electrode were used. However, two-electrode system was used when carbon fiber disk electrodes were used for preparation of carbon fiber disk electrodes. All other chemicals, NaCl, Tris, HCl, NaOH, were reagent grade. All solutions were prepared in double distilled water and deaerated with high purity nitrogen.

The highly oriented pyrolytic graphite (HOPG, ZYH grade) was purchased from NT-MDT Co., Russia. It was freshly cleaved prior to each experiment. Poly acrylonitrile (PAN)-based carbon fibers (6 μm in diameter, 0.65 M2/g) came from the Jilin Carbon Company LTD (Shanghai), which was re-refined in acetone for 8 h before use. The resistivity of the fiber after the treatment was measured as 0.68 MΩ/m, High purity Ag conductive glue was purchased from SPI supplies (USA).

2.3. Fabrication of the electrodes

The CFCE and CFDE were fabricated as reported (Stein and Ewing, 1992; Lin et al., 2003). A piece of carbon fiber of about 2 cm long was placed in a meddle of a glass capillary (1.1 mm OD and 0.8 mm i.d.), which was pulled to seal at a horizontal glass micropipet puller (model PN-30, Narishige, Tokyo, Japan) under electric heating. A piece of copper wire and a drop of silver glue were used to lead out the electricity from the inner end of the fiber, and a drop of epoxy was used to seal the conjunction gap between the glass capillary and the protruded carbon fiber, forming the CFCE. For preparing the CFDE, the protruded fiber column of the CFCE was insulated by covering a thin-layer of electro-polymerized film of phenol and 2-allylphenol, and then, the column was cut perpendicularly to expose a disk surface. The HOPG working electrode was prepared by embedding a piece of HOPG sample in a teflon block, which was leading out using a piece of copper wire.

2.4. DNA deposition and electrochemical characterization

The ct-dsDNA deposition was conducted in a dilute ct-dsDNA solution under controlled dc potentials. To preserve DNA physiological pH and to avoid DNA-strand splitting or strong condensation, a pH 7.1 solution with a small ionic strength of 50 mM NaCl + 5 mM Tris–HCl buffer was used as the electrolyte for DNA dissolution. A dilute DNA concentration of 0.1 mg/ml-1 was found to be most suitable. After DNA deposition, the electrode was dipped into a THB blank solution for 10 min to remove any unadsorbed or weakly-adsorbed DNA. The prepared DNA modified electrodes was characterized by CV and DPV techniques in THB containing 0.3 mM Co(phen)$_3$Cl(O$_4$)$_3$ as an electrochemical indicator. The effective surface area of an electrode was calculated form the charging current ($i_C$) on its CV curves, according to the equation $i_C = CV_{eff} A_{eff}$, where $A_{eff}$ is the effective surface area, $V$ is the scan rate, and $C_{eff}$ is the differential capacitance of the electrode, assuming the C is the constant before and after the surface modification.

The stability of the modification was characterized by alkaline treatment and thermal treatment. For the alkaline treatment, the modified electrode was immersed in 1 M NaOH solution for 10 min at ambient temperature, rinsed with THB solution thoroughly, ready for electrochemical re-examination in 0.3 mM Co(phen)$_3$Cl(O$_4$)$_3$. For the thermal treatment, the modified electrode was soaked in boiling THB solution for 3 min, chilled in icy water, ready for electrochemical re-examination.

2.5. AFM characterization

AFM images were obtained on mica, HOPG and CFCE, respectively. The DNA samples on mica was prepared by spotting 2 μl DNA solutions onto a piece of freshly cleaved mica and leaving statically for 1 min, then, the DNA residues...
were gently blown off from the mica and dried for AFM imaging. As for electrochemical deposition of DNA samples on HOPG, CFCE and CFDE, 1 ml of desired DNA solution was placed in the electrochemical cell with the electrode under desired electrode potential for a desired time. The obtained modified electrode was rinsed with water to remove any unadsorbed and weakly-adsorbed DNA, dried under air flow. All images were recorded with the tapping-mode operation at height-mode. Typical imaging parameters were: (1) work frequencies, 120–140 KHz (2) work oscillation amplitude, 0.5–1.0 V (3) scan rate, 0.5–1.0 Hz. Images were processed offline by flattening to remove the background slope, and the contrast and brightness were adjusted. The height feature of the interest area was calculated by subtracting the background height for the bare electrode. The mean values of 30–60 measurements were used to calculate heights of the DNA cover layer.

3. Results and discussion

3.1. XPS spectra

XPS spectra of the DNA modified CFCE are presented in Fig. 1A. The C, N, O, P peaks were observed, showing the evidence that the DNA has been immobilized on the surface. It was noted that the P peak did not show for the deposition potentials lower than 0.9 V, however, it was well shown for 1.8 V (Fig. 1B). In comparison of N1s spectrum (Fig. 1C) and P2p spectrum (Fig. 1B, 3), the N/P ratio of 3.8:1 can...

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Fig. 1. XPS spectra of ct-dsDNA/CFCE prepared at 1.8 V. (A) The individual spectrum of P2p obtained at 0.8 V (B1), 0.9 V (B2) and 1.8 V (B3). The individual spectrum of N1s obtained at 1.8 V. (C) The deconvolution spectra of the C1s obtained at 1.8 V. (D) The high resolution peak of O1s obtained at 1.8 V.
be estimated for the deposition at 1.8 V. This ratio is in good agreement with the theoretical N/P ration of 3.7:1 for the ct-dsDNA with (G + C)/(A + T) = 39:61 (Schildkraut et al., 1962), verifying the immobilization of ct-dsDNA. Furthermore, Fig. 1D shows the deconvolution spectra of the C1s spectrum, which indicate the presence of C-C (284.60 eV), C-O (286.00 eV), C=O (287.05 eV), and COOH (288.60 eV) surface functional groups. These oxygen containing groups are attributed to the anodic oxidation processes (Runnels et al., 1999; Edmonds, 1985). In addition, the high-resolution O1s peak at 532.25 eV (Fig. 1E) indicates that a large amount of the surface oxygen was present in the form of C=O bonds most likely of a phenolic or hydroquinone type (Kamau et al., 1985). Although the phenolic-like groups are also present in the bases of the DNA, the strong O1s peak suggests that the DNA molecules could be linked to the carbon surface by the C–O–C bonds.

3.2 AFM images

The surface deposited DNA layer was imaged by AFM in tapping mode, by which the molecules loosely attached to the substrate could be observed under conditions which the sample was less disturbed. Fig. 2A and B) present the images of freely-adsorbed ct-dsDNA on mica. The DNA formed very fine networks with an average height of 2.0 ± 0.5 nm and mesh size of about 1 μm. Some white spots observed on the DNA chains may be the remnants of the salts from the DNA solution. The AFM images suggest that the ct-dsDNA in the THB solution before the deposition was well extended and well separated, such that the long chain DNA molecule appeared extended even after the free adsorption onto the mica surface. The large amount of cross-linkages between DNA chains played an important role in the three-dimensional netting. The overlapping and superimposing of the DNA chains can be seen on the images, which may be attributed to randomly occurring processes during the aggregation. Since mica has a hydrophilic surface, with negative charges, which could be compensated by the monovalent Na⁺ ions. Thus, a firm attachment of the DNA molecules to the mica surface occurred (Cai et al., 2000; Tanaka et al., 2001; Müller et al., 1997). Furthermore, hydrogen bonds could be formed between the hydroxyl groups on mica and the phosphate backbone of the DNA (Maur et al., 1998). However, the conformations of free adsorbed DNA on mica was much less complex than that on HOPG (Brett and Chioreca, 2003), and thus can be used for evaluating the existing state of DNA in the solution.

The morphology of the ct-dsDNA electrochemically deposited on HOPG under 1.8 V dc potential (Fig. 2C) differs significantly from that on mica. Many bead-like nano-blocks appeared to be periodically distributed along the strands. These nano-blocks were probably resulted from the aggregation and superimposition of the double helix chains of about 2.6 nm in diameter (Saenger, 1984). The network loops of about 40 nm width shown in Fig. 2D was likely due to the convolution effect of the tip radius. Because the bases in DNA could stack closely in the electric field (Tao and Shi, 1994), this could lead to an increase of molecular conductivity of DNA. The morphology on HOPG obtained under 1.8 V certainly shows the compression effect along the DNA chains.

Both HOPG and mica with cleavage planes are relatively chemically inert and atomically flat over hundreds of nano-meters, which are therefore ideal supports for AFM imaging (Müller et al., 1997; Arscott et al., 1989). While a quantitative description of AFM observations on carbon fibers is usually unavailable. However, we still tried to image the DNA modified CFCE in unprecedented detail, and provided new insight into the investigation of DNA morphology. The DNA molecules electrochemically deposited on the surface of CFCE aggregated into a much thicker layer with thickness of about 50–100 nm, in which the DNA chains aggregated into thick blocks of about 50 nm in diameter (Fig. 2E and F) and the mesh holes became unrecognizable. In comparison with the case on HOPG, the enlargement of the effective surface area for the DNA modified CFCE (DNA/CFCE) was larger than that for the DNA modified HOPG (DNA/HOPG). The thicker layer should be generated due to the faster mass transport on the micro-cylindrical surface. To verify this suggestion, a 10-times diluted DNA solution of 0.013 mg ml⁻¹ was used, a reticulate structure of about 30 nm mesh size and 8 nm thickness was obtained (Fig. 2G and H). The DNA chain is about 10–20 nm in width with no thick blocks. Obviously, lower DNA concentration was likely to form a basically two-dimensional thin film with network structure in which the DNA chains were extending and separating, while higher concentration was apt to form a three-dimensional condensation with the DNA chains aggregated into thick blocks.

For the sake of comparison, the AFM images recorded by tapping mode of bare electrodes were presented in Fig. 2I and J. Fig. 2I shows a rather flat surface with expected terraces that are characteristics of cleaved graphite surfaces. The typical features of ravines and traces on the carbon fiber surface were shown in Fig. 2J, which were formed during manufacture processes. No topographical features appearing similar to the DNA structures were observed.

3.3 Electrochemical characterization of DNA modified carbon electrodes

Along our consideration, the semi-spherical diffusion and electric field mode should be even more suitable for three-dimensional immobilization of DNA than the cylindrical and plain modes, since the DNA long chain molecules would be gathering from every direction along
Fig. 2. Tapping mode AFM topographic images and corresponding three-dimensional graphics of ct-dsDNA: freely adsorbed on mica from 0.1 mg ml\(^{-1}\) ct-dsDNA THB (A and B); deposited on HOPG at 1.8 V from 0.1 mg ml\(^{-1}\) ct-dsDNA THB (C and D); and deposited on the column surface of CFCE at 1.8 V from 0.1 mg ml\(^{-1}\) ct-dsDNA THB (E and F); and deposited on the column surface of CFCE at 1.8 V from a 0.013 mg ml\(^{-1}\) ct-dsDNA THB (G and H). The tapping mode AFM images of the bare HOPG (I) and CFCE (J).

the semi-spherical field vector, resulting in more significant in-situ concentrating effect, and much more perpendicular planting of the DNA chains would occur. Based on this idea, the CFDE was employed as a substrate for DNA deposition. AFM images of the disk surface on the top of the DNA modified CFDE (DNA/CFDE) was not successfully recorded since the CFDE thin fiber could not possibly stand up firmly on the testing platform for AFM imaging. Electrochemical techniques were used to verify the supposition.

The charging currents of these electrodes were measured for calculation of the effective surface area in the potential range where no redox reaction occurs (Bard and Faulkner, 1980), e.g. at −0.3 V in our case. Electrochemical char-
results were consistent with the AFM observations. The square root of the scan rate up to 150 mV s\(^{-1}\) showed that the CV peak current was proportional to the species. However, the scan rate dependence experiment at the CV curve showed exhaustion electrolysis of surface fer from the cobalt species to the deposited ct-dsDNA layer. Under these conditions, the higher fluency of electron transfer from the cobalt species to the deposited DNA layer, which may be generated from the electrode surface, and indicates the conductivity of the DNA modified layer. This is attributed to both the electrocatalytic activity and the conductivity of the DNA modified layer. Under these conditions, the higher fluency of electron transfer from the cobalt species to the deposited DNA layer, then to the carbon electrode resulted in a highly effective sensing electrode.

As is well known, the CV anodic-to-cathodic peak separation (\(\Delta E_p\)) is a conventional criterion for characterization of the reversibility and the ohmic drop of an electrode. Therefore, both the DPV peak current enlargement and \(\Delta E_p\) were used as factors to characterize the prepared DNA/CFDE. As seen in Fig. 4B, a minimum \(\Delta E_p\) is appeared for the electrode prepared under the DNA deposition potential of 1.8 V. Even more clearly, the DPV current enlargement (Fig. 4C) presents a maximum value at about 1.8 V. The threshold of the 1.8 V dc potential can also be seen on the deposition current-time curves, shown in Fig. 4D. The deposition currents were very small for deposition at 1.5, 1.6 and 1.7 V. For the deposition at 1.8 V, the current increased quickly in the first 7 min from zero to a maximal value then remained almost constant for the next 23 min. For the potential higher than 1.8 V, a current intercept at time zero was appeared for 1.9 V and became very serious at 2.0 V, indicating a significant corrosion of the carbon electrode. The surface corrosion may have altered the DNA immobilization mechanism, thus resulting in a decreased DPV peak enlargement and increased \(\Delta E_p\).

The DNA/CFDE prepared at 1.8 V was stable and could withstand treatment with both alkaline solution and boiling water. After immersing in pH 14 NaOH solution for 10 min, the CV curves of Co(phen)\(_3\)\(^{3+}\) at the DNA/CFDE had almost no change, as seen in Fig. 4E. This indicates that the DNA molecules deposited at 1.8 V were covalently bonded to the CFDE surface, since any non-specifically adsorbed DNA molecules should be removed by NaOH, whereas only covalently bonded molecules should still remain immobi-
lized (Hellas et al., 2002). And it also excluded a possibility of forming phosphate ester or carbonic ester which can be easily hydrolyzed in alkaline solution. This electrode was also soaked into boiling THB solution for 3 min and then chilled in icy water. After the treatment, the redox current of Co(phen)\(_3\)\(^{3+}\) was reduced to about 20–40%, indicating that thermal denaturation of the immobilized dsDNA
occur. However, the charging current of the electrode was doubly enlarged, so that nearly 1000-fold enlargement of the effective surface area in comparison with the original bare CFDE was obtained (Fig. 4F). The thermal denatured ct-dsDNA should still remain firmly attached on the CFDE surface and electrically conductive. Since the thermal decoupling of dsDNA followed by a fast cooling procedure is an irreversible process (Shen and Wang, 1989, Higher Education Publishing Company, China) and the hybridization reaction is usually carried out at 42°C (Cai et al., 2003), the renaturation/hybridization of the denatured-DNA/CFCE at room temperature is negligible. Certainly, the response of Co(phen)$_3$$^{3+}$ at the thermal denatured-DNA/CFDE was virtually stable for a week, storing in the tris buffer at room temperature. Clearly, the DNA/CFDE could be applied in wide pH ranges and thermal conditions.

The deposition time was limited to 30 min since a longer deposition time did not increase the enlargement factor. It is most likely that excess DNA molecules deposited during prolonged deposition periods do not become covalently

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**Fig. 4.** (A) CV curve of Co(phen)$_3$$^{3+}$ at ct-dsDNA/CFDE prepared at +1.8 V in comparison with the CV curve at the original bare CFDE (insert) (B) peak-to-peak separation of the CVs as a function of the dc depositing potential (C) the DPV peak current enlargement as a function of the dc deposition potential (the fitting line was generated by Lorentz fit of OriginPro 6.1) (D) current–time dependence curves during DNA deposition on CFDE (E) CVs of Co(phen)$_3$$^{3+}$ at ct-DNA/CFDE before (1) and after (2) dipping in NaOH of pH 14 for 10 min (F) CVs of Co(phen)$_3$$^{3+}$ at ct-DNA/CFDE before (1) and after (2) dipping in boiling THB for 3 min, followed by chilling in icy water. All the depositions were conducted in 0.1 mg ml$^{-1}$ ct-dsDNA THB solution for 30 min. CVs and DPVs data were obtained at 50 mV/s and 50 mV pulse height, respectively.
linked to the carbon surface and are therefore easily washed off after a simple treatment.

It is worth noting that not only ct-dsDNA but also short synthetic DNAs were also explored in our work and similar enlargement results were obtained. This indicates that such an immobilization approach by controlled dc potential was universal to different types of DNA. Such a DNA-modified micro probe may find wide applications in storage and controlled release of charge, energy, and drugs, and in electrochemical sensing of analyte molecules that can specifically interact with the DNA layer. Preliminary application of this electrode was made for sensing some small molecules such as catecholamine neurotransmitters in mimic biological conditions. Similar enlargement effect was also observed for dopamine but much less enlargement for ascorbic acid and uric acid. This is probably due to electrostatic repulsion of the polyanionic sugar–phosphate backbone of DNA. This simple molecular recognition effect provided a tolerance ratio of ascorbic acid for the dopamine determination higher than 1000 (Lin et al., in press). An extension of the study has been currently underway in our group.

3.4. Mechanism of DNA Immobilization on the carbon substrate

The applied positive dc potential generates an electric field across the carbon – solution interface. The conventional characteristic thickness ($\kappa^{-1}$) of the double layer at the electrode/solution interface can be estimated according to the Gouy–Chapman theory (Bard and Faulkner, 1980).

$$\kappa = \left( \frac{2n^0z^2e^2}{\varepsilon_0kT} \right)^{1/2}$$

where $n^0$ is the number concentration of each ion in the bulk, $z$ is the magnitude of the charge on the ions, $e$ is the quantity charge on the electron, $\varepsilon_0$ is the permittivity of free space, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. For the dilute aqueous solution ($e = 78.49$) and 25 °C, in the Tris–HCl buffer system containing 50 mM NaCl, the characteristic thickness of the diffuse layer was estimated as 1–2 nm.

However, it is expected that the conventional structure of the double layer should be significantly changed due to the presence of the electrically conductive double-helix DNA molecules. For the freely dispersed ct-DNA 8 μm long chain, the electric field in the solution due to current flow induces dipoles on its two ends of the DNA and tends to align the chain by attracting the negative end and pushing away the positive end. The electric double layer should be changed suddenly as soon as the negative end of a DNA chain is touched to the electrode surface and leads the charges from the electrode along the chain to its far end. This may result a formal dispersion of the compact double layer along the normal axis of the electrode surface and accelerates the deposition process, which is certainly evidenced as shown in Fig. 4D, the initial 5 min rising region of the current–time curve of the deposition at +1.8 V.

Due to the molecular conductivity the extended ct-DNA long chain in the field would be polarized, than directed and driven by the field force to touch the carbon surface via its one end, which could be subject to the electrostatic force generated at the negatively charged phosphate groups on the backbone and the induced dipole moments on the two ends of the double helix (Porschke, 1997). Due to the high charge density on the helix, the induced polarity on the negatively charged end would be so strong that the sudden discharge at the moment of contact would possibly link the end to the electrode surface through a C–O bond. This covalent binding is evidenced by the deposition current (Fig. 4D) and the formation of the bond is evidenced by the XPS results (Fig. 1D). In addition, the specific potential of 1.8 V was characteristic for the surface oxidation of carbon electrodes to generate aromatic free radicals (Kepley and Bard, 1988). It is most probable that joining of the carbon electrode to the 3′-OH of DNA through this linkage minimizes steric hindrances (Maeda et al., 1994). This covalent bonding ensured the conductive and stable immobilization of the DNA molecules on the surface. The advantage of deposition on CFDE would be to allow in situ aligned DNA chains to become more condensed and more perpendicularly planted on the surface instead of lying along the surface happened for the macro-HOPG electrode. On the other hand, the closely stacked bases of DNA in the electric field would cause the molecule to shrink and become compressed along its long axis (as evidenced from the AFM images obtained under dc potentials) and increase the conductivity of the DNA modified layer.

4. Conclusions

The network structure is an interesting feature of the native ct-dsDNA in solution. It seems to crosslink together by randomly superimposing and overlapping. It is also possible to relate this phenomenon to the existence of small molecule impurities in native DNA and in solution, which may interact with DNA chains. However, a full understanding of this process is rather lack at the present time. On the HOPG plane surface, the deposited DNA thin layer of less than 10 nm of average thickness typically generated six-fold enlarged effective electrode surface area. On the CFDE surface, the immobilized DNA layer generated 500-fold enlarged effective electrode surface area may have thickness of about 400 nm. The formation of DNA network can thus be controlled by designing the mode of mass transport and electric field across the electrode/solution interface. It is an advantage for the enhancement of effective surface area without significant increase...
of the electrode dimension. Furthermore, the nano-netting DNA intertexture fabricated on CFDE is stable in alkaline solution and in boiling water. This should be expected to find wide applications in the fields of DNA-based electrochemical biosensing, as well as in the design of charge/energy storage and drug storage/controlled release devices.

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