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Effects of Metal Ions on Conductivity and Structure of Single DNA Molecule in Different Environmental Conditions

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Abstract We design a novel nano-gap electrode to measure the current of DNA molecule, by which the current–voltage characteristics of individual native DNA, Ag-DNA and Ni-DNA molecules are obtained, respectively. The results show that the voltage gap of Ag- and Ni-DNA is higher than that of native DNA, and the conductance is lower than native DNA in neutral environment. The structure transition from B- to Z-DNA is observed in the presence of high concentrations of nickel ions and Ag-DNA appears chaos state by STM image and U-V spectra characterization. But in alkaline environment, the conductance of Ni-DNA rises and the voltage gap decreases with the increasing of nickel ion concentration denotes that the conductive ability of Ni-DNA is higher than that of native DNA.

Keywords DNA · Metal ions · Nano-gap electrode · Conductivity · Structure

Introduction

With the development of high-speed processing technology, more integrated silicon devices will be expected to reach a new level. Consequently, some new materials worked in nano-scale are strongly desired. In this aspect, DNA has received some attentions [1–3]. During the past few decades, DNA has taken center stage in biophysical chemistry research. The elucidation of the molecule structure 50 years ago and the translating of genetic code revolutionized the field of biotechnology. Biologically, the function of DNA is to code functional proteins that are the expressed form of hereditary information. But its unique double helix structure and nearly parallel base-pairs with overlapping π-electron systems make it a good candidate for long-distance and one-dimensional charge transport, which nature did not intend for this molecule. In recent years, charge transfer properties of DNA have attracted much attention among physicists, chemists and scientists in materials to exploit DNA in functional nanoelectronic devices [4–7]. Some reports consider that DNA may be a good linear conductor [5, 8], while other experimental measurements on DNA molecule showed that it seems to be an insulator [6], even a superconductor at low temperature [9].

To improve the electrical property of DNA, other approaches may be needed. Chemical doping is an effective way for improving the electrical properties of materials, as demonstrated in semiconductors [10] and electrically conductive polymers [11]. There have been a few studies on the electrical property of chemically doped DNA [12–15], denotes that metal-DNA (M-DNA) could be formed by metal ions, such as Cu^{2+}, Zn^{2+}, Ni^{2+}, binding into nucleobases, deoxyribose, or phosphodiester backbone and have provided potential applications to the areas of nanomaterials and biosensors. Some reports have showed that the conductive ability of M-DNA is better than that of native DNA [14, 16, 17], while other group reported the conductivity of M-DNA decreases [18]. Therefore, a thorough understanding of the charge transfer properties of doped DNA is crucial in developing the future DNA-based nanoscale devices. At the same time, the effect of metal ions on the structure of DNA is not clear, and no

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topological structure has been reported by now. In this paper, we have reported the measurement results about the I-V characteristics and structures of native DNA, Ag-DNA and Ni-DNA, respectively, and have discussed the effects of metal ions on conductive ability of single DNA molecules in different environmental conditions.

Materials and Method

Materials

Calf thymus DNA in fiber and Tris were purchased from Sigma–Aldrich USA, and DNA was directly used without further purification. Silver nitrate (AR) and $NiCl_2$ were from Zhengzhou Paini Chemical Reagent Factory (China). Millipore ultrapure water and gold target (99.999%) were also used in our experiment.

The Fabricating of Nanogap Metal Electrodes

The nanogap metal electrodes with a sandwich structure were fabricated by the technology of Laser Molecular-Beam Epitaxy 300 (LMBE-300) under 10^{-7} Pa high vacuum condition. It involved the successive deposition of Au (200 nm), Al_2O_3 and Au (200 nm) on the Si substrate, followed by cleaving the piece of Si to get nanogap (Al_2O_3) on the cleavage plane. The width of nanogap could be controlled by adjusting the thickness of Al_2O_3. No current was found between two electrodes when bias voltage was applied, denotes that nanogap is insulating.

Scanning Probe Microscopy Measurements

The current–voltage curves of DNA were measured by connecting two electrodes with the interior circuit of SOLVER-P47 scanning probing microscopy (NT-MDT, Moscow, Russia), operating in air under the relative humidity of 30% at room temperature. Top Au electrode is connected with the interior circuit by scanning probe. The inset part of Fig. 1a is the schematic diagram of electrodes arrangement for transport experiment. The conversion operation of samples had been changed from scanning to curving by the conductive diamond tips of AFM (DCP11, NT-MDT, CO.) switched from tapping to contact mode, in which the spring constant of the cantilevers was 5.5 N/m. The set points at contact mode were determined by F-Z curves. STM tip employed in this study were mechanically cleaved. STM images were obtained in the constant current mode with the set point currents in the range from 0.1 to 1.0 nA.

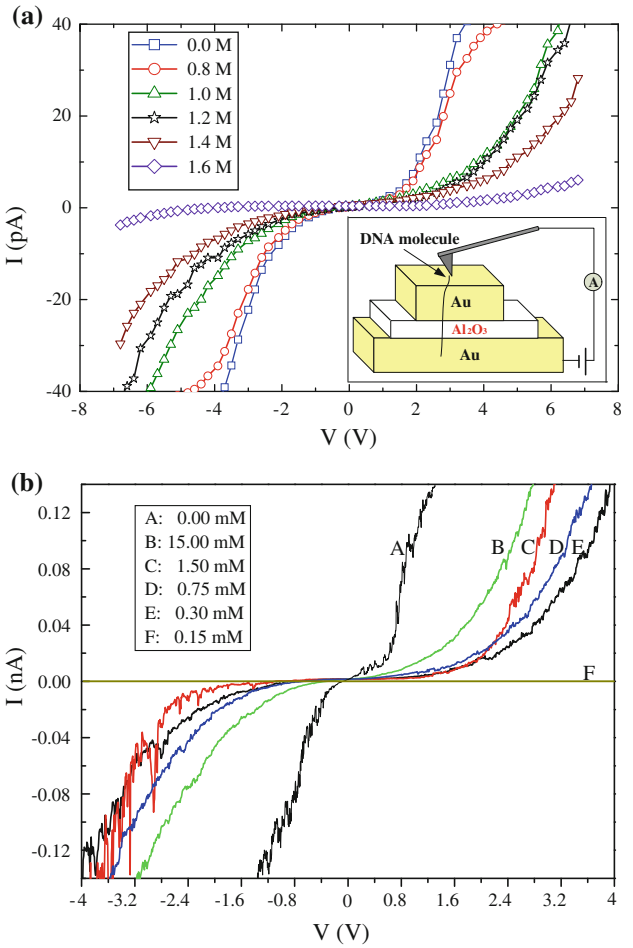

Fig. 1 I–V curves of single DNA molecular at different concentrations of Ni (**a**) and Ag (**b**) ions in neutral environment. The inset of (**a**) is the schematic diagram of electrode arrangement for transport experiments

Results and Discussion

The Effects of Metal Ions on Conductive Ability and Structure of DNA in Neutral Environment

The Effects of Ni Ion on Conductivity of DNA

5 ng/μl DNA solution was prepared firstly, and then Ni-DNA was formed by mixing 10 μl DNA with 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 M $NiCl_2$ solution according to 9:1 proportion in neutral environmental condition, respectively. After 10 μl of mixed solution was dropped on one of the gold electrode for 1 h, which was treated in 5 mM cysteamine for 30 min, it was blown to another electrode with nitrogen gas, in which the width of nanogap was about 27 nm. It can be observed by AFM that well-spread DNA molecules was fixed on the gold film uniformly, and the number of DNA molecules in unit length was the same (about 1 molecule in every 2 μm) after taking

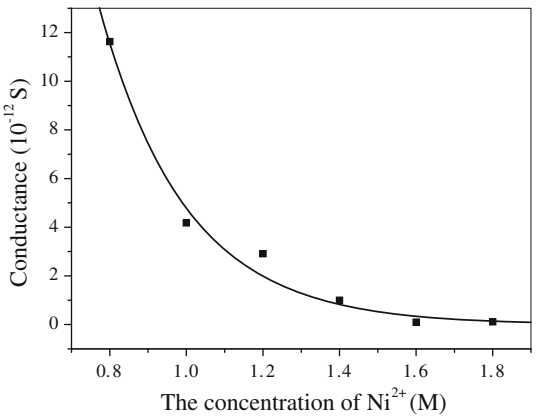

Fig. 2 The conductance curves of DNA at different concentrations of nickel ions in neutral environment. *Square dots* are the experimental data, and *solid curve* is the calculated results by Eq. (1)

measurements many times at different areas. I–V curves were measured after DNA was fixed on the gold electrode for 1 day. The contact resistance between DNA molecule and electrodes will always exist. The discrepancy of contact resistance can be eliminated by the same joining method and repeated experiments. The current–voltage data of single DNA molecule could be obtained according to the size of the electrode and shown in Fig. 1a. Conducting SPM analysis reveals that DNA is a semiconducting biopolymer. The voltage gap increases, and the conductance decreases with the increasing of nickel ions. The conductive ability decreased rapidly when the concentration reached 1.6 M, indicated that the great change occurs in structure of DNA. The conductance of DNA at different concentrations of nickel ions was obtained from the experimental results and shown in Fig. 2. It can be found that it satisfied an exponential decay function

$$y = A\exp(-\beta x), \tag{1}$$

where y is the conductance of DNA, x is the concentration of nickel ions, $A = 90$ and $\beta = 4.4$ are fitting parameters. The fitted curve shows a good agreement with the present experiment data when the concentration of nickel ions is above 0.8 M.

The Effects of Ag Ion on the Conductive Ability of DNA

In order to contrast the effects of other metal ions on the conductive ability in neutral solution, we measure I–V curves of DNA and Ag-DNA under nanogap of about 17 nm. First, DNA was dissolved in ultrapure water, and Ag-DNA was prepared by mixing 42 ng/μl DNA with 0.0005, 0.015, 0.15, 0.3, 0.75, 1.5, 15 mM $AgNO_3$ according to 1:1 proportion for 15 min, respectively. Second, a drop of specimen was deposited between two electrodes. It can be found by AFM that the number of DNA molecule spread on Au electrode is about 1 molecule in every 4 μm. I–V curves of individual DNA and Ag-DNA molecules can be obtained and shown in Fig. 1b. It can be found that the voltage gap of native DNA is about 0.4 V and smaller than Ag-DNA. Ag-DNA presents insulating behavior when the concentration of Ag ions is under 0.0005 mM, indicated that the conductive ability of native DNA is better than that of Ag-DNA, and a small quantity of Ag ion could bind to site between base pair and destroy the π-stack, in agreement with the function of Ag ion sterilization [19]. With the increasing of Ag^+ concentration, the voltage gaps decreases, and the current increases, so that the conductive ability rises when Ag^+ is in the range of 0.3–15 mM, denoted that a new conductive tunnel forms. This tunnel maybe results from the binding of Ag^+ to phosphate group, so that the charge will mainly be transfer by phosphate backbone, instead of π-stack, as reported in Ref. [20]. But the superfluous Ag can be found by AFM if Ag^+ concentration increases further.

The Effects of Ag and Ni Ions on Structure of DNA

(1) UV–Visible spectroscopy measurements

UV–Vis spectra of DNA were measured on UV-3310 spectrophotometer (Hitachi, Tokyo, Japan) in order to investigate the effects of Ni and Ag ions on DNA structure. Fifty-microlitre of DNA of 600 ng/μl was added to 1 ml $NiCl_2$ solution of nine kinds of concentrations 0, 0.4, 0.8, 1.2, 1.4, 1.6, 1.7, 1.8 and 2.0 M, respectively. The absorption spectra were recorded after 4 h at room temperature and shown in Fig. 3a. It can be observed that the absorption peak of native DNA was about at 260 nm. The red shift of absorption peak mostly happens in the concentration range of 1.6–1.8 M. The peak shifts to 266 and 279 nm when the concentration of nickel ion increases to 1.6 and 1.7 M, respectively, indicates that the transition from B- to Z-DNA happens, in agreement with Klump's results [21]. The peak shifts to 283 nm at 1.8 and 2.0 M, denotes that the B-Z transition has completed, in agreement with the phenomena of the weaker conductive ability at above 1.6 M in Sect. 3.1.1.

Figure 3b shows the effect of Ag^+ on UV–Vis spectra, which is different from the Ni^{2+}. A very small quantity of silver ions could cause a blue-shift and hypochromic (i.e. a decrease in intensity) effect to DNA, denotes that a small number of Ag^+ could bring a remarkable change to DNA structure, in agreement with the experimental results from I–V curves in Sect. 3.1.2.

(2) The STM images of native DNA, Ni-DNA and Ag-DNA

The effects of metal ion on topological structure of DNA could be approved by STM image, further. A drop of mixed solution corresponding to 0 and 1.8 M Ni^{2+} was

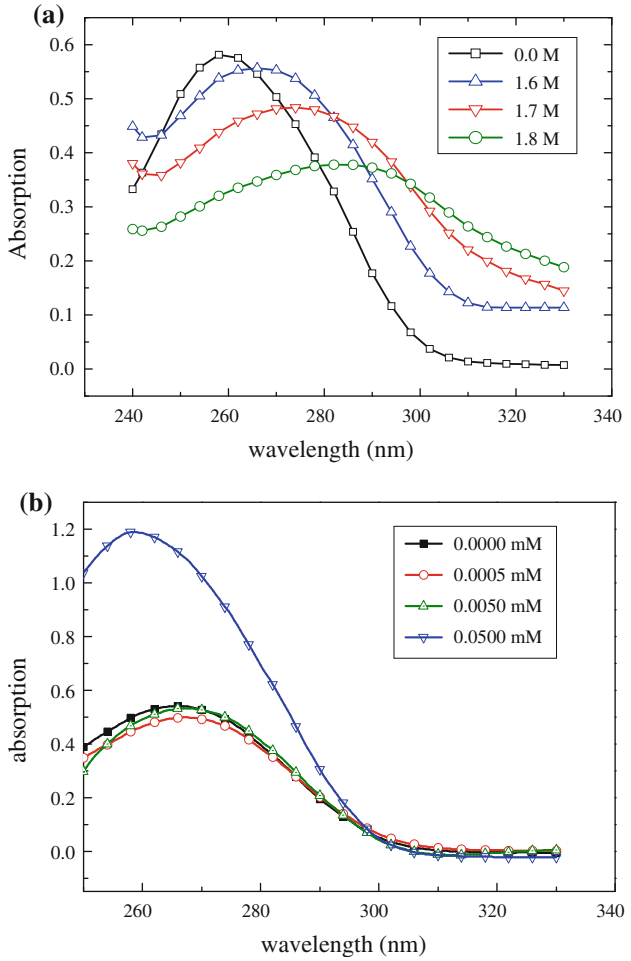

Fig. 3 UV–Vis spectra of DNA at difference concentrations of Ni (**a**) and Ag (**b**) ions in neutral environment

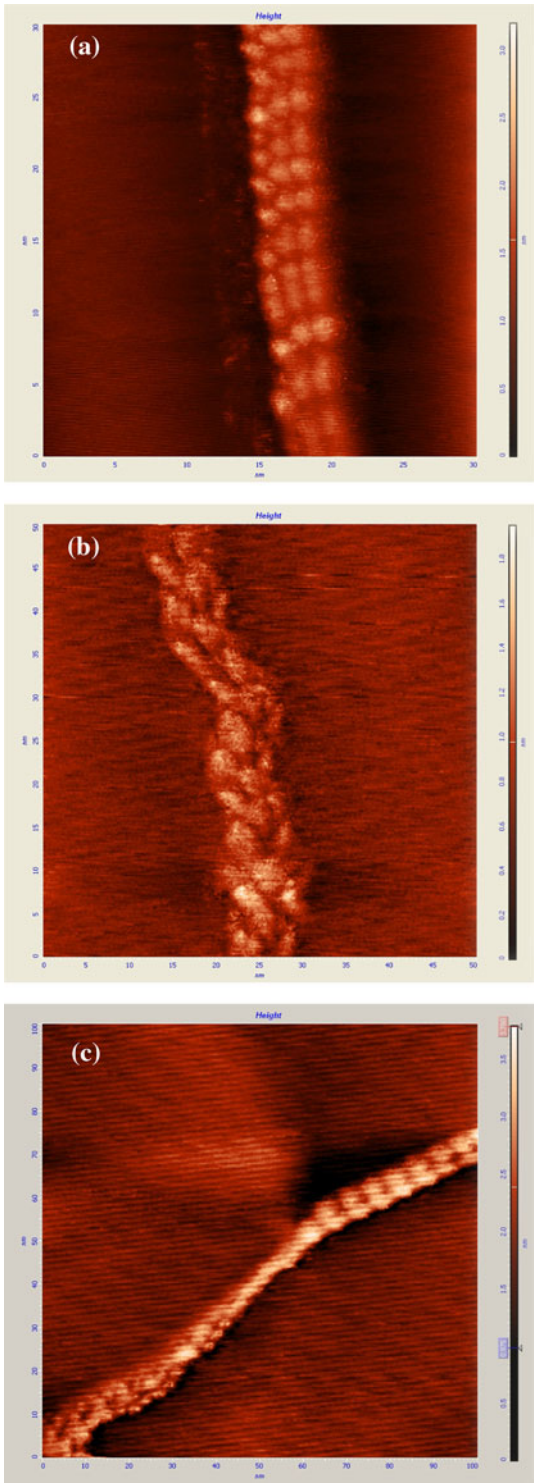

Fig. 4 The STM images of single DNA molecule stretched on HOPG. **a** The right-handed A-DNA (30 × 30 nm). **b** Left-handed Z-DNA (50 × 50 nm). **c** DNA in melting and chaos state (100 × 100 nm)

spread on highly oriented pyrolytic graphite (HOPG) surface according to the method of Arscott [22]. Figure 4a presents STM image of native DNA. The regular protuberances are deoxyribose of DNA, and the major and minor grooves cannot be identified. The right-handed helix structure is tight, and the diameter is about 2.4 nm by height analysis, in agreement with results derived from X-ray diffraction (2.3 nm) [23]. The image of left-handed Z-DNA is shown in Fig. 4b at high concentration of nickel ions. The helical diameter of Z-DNA was about 2 nm and only slightly bigger than that from X-ray diffraction (1.8 nm) [24]. The major and minor grooves are obvious, unwinding and disordering region can be found. But in accordance with previous studies, the major and minor grooves for DNA are unconspicuous [22]. This is because Arscott's DNA is uniform (C–G) sequence, so that major and minor grooves are unobvious, while calf thymus DNA is a random sequence in present work.

The analysis from STM images showed that the fall in conductance of DNA in high concentration of nickel ions maybe come from two reasons. (1) The backbone and base-pair were destroyed in some degree. (2) Great structure changes occurred after DNA underwent B-Z transition,

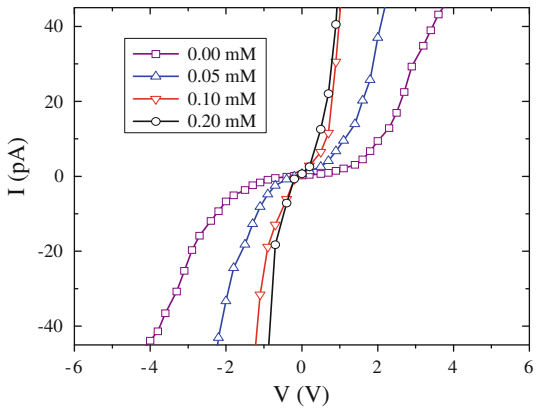

Fig. 5 The I–V curves of single DNA at different concentrations of nickel ions in alkaline environment

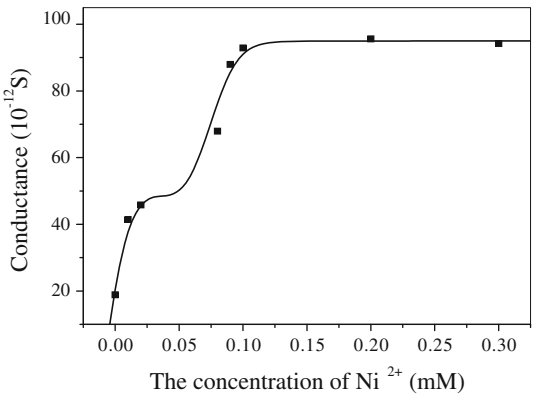

Fig. 6 The conductance of DNA at different concentrations of nickel ions in alkaline environment. *Square dots* are the experimental data, and *solid curve* is the calculated results by Eq. (2)

such as obvious major and minor grooves, local unwinding and disordering region. Consequently, DNA molecules were in chaotic state so that few current passed through DNA molecules even high bias voltage was applied.

Figure 4c shows the STM images of Ag-DNA that is prepared by mixing 0.1 ng/μl DNA and 0.01 mM Ag^{+} according to 1:1 proportion. It can be found that a part of DNA strand is melting and appears chaos state, indicating that DNA structure is destroyed by silver ion, in agreement with the above result which the conductivity of Ag-DNA is less than native DNA.

The Effects of Ni^{2+} on the Conductive Ability of DNA in Alkaline Environment

To contrast the effects of metal ions on the conductive ability of DNA in different condition, we measured I–V curves of DNA at different Ni^{2+} concentrations in alkaline environment. DNA solution of 5 ng/μl and nine kinds of $NiCl_2$ solution from 0 to 0.3 mM were mixed according to 9:1 proportion, respectively. Tris was used to control pH value of DNA solution at 8.5. I–V curves of single DNA, and Ni-DNA are obtained and shown in Fig. 5, in which the nanogap is about 27 nm. It can be observed that both DNA and Ni-DNA show semiconductor properties. The voltage gap of DNA is about 0.8 V. The conductance of Ni-DNA rises, and the voltage gap decreases with the increasing of Ni^{2+} concentration, which is about 0.6, 0.4, 0.4 V at 0.05, 0.1, 0.2 mM, respectively. The results indicate that the lowest electric transport energy of DNA [8] was changed after nickel ions insert to base-pair of DNA. In order to clarify the effects of nickel ions itself on current, we also measured I–V data of nickel ion solutions after they were dried on the nanogap of gold electrode. No current was detected even if high bias voltage was applied.

Figure 6 presents the conductance of single DNA molecule at different Ni^{2+} concentrations in alkaline environment and shown in Table 1. A fitting curve between the conductance and concentration of Ni^{2+} is given by

$$y = 95\tanh[-0.35 + 25x + 0.57\cos(43x)] \quad (2)$$

It can be found that the fitted curve shows a good agreement with the experimental data. The conducting mechanism of Ni-DNA in alkaline environment can be demonstrated as follows. When small amount of nickel ions was added to DNA solution (<0.01 mM), they firstly combine with the phosphate groups so that electron doping of DNA occurs [14] and the conductance remarkably increases. At the range of 0.01–0.05 mM, the nickel ions bonding to phosphate backbone are nearly saturated, meanwhile, few ions intercalate into base pairs so that the increase of conductance becomes slowly. And the conductance increase remarkably again when the concentration was above 0.05 mM, indicating that nickel ions intercalate into base pair and bind to N3 and N1 of Thymine and Guanine. Therefore, not only a π-stack but also an intercalated metal ion channel forms for Ni-DNA so that the conductance could be improved, in agreement with Ref. [14]. But the conductance did not change when the concentration was above 0.1 mM, denotes that the combination between Ni^{2+} and DNA approaches to saturation.

Table 1 The conductance of individual DNA at different Ni^{2+} concentrations in alkaline environmental condition

Ni^{2+} (mM)	0	0.01	0.02	0.05	0.08	0.09	0.1	0.2	0.3
Conductance (10^{-12}S)	18.9	41.45	45.8	52.37	67.98	87.97	92.93	95.63	94.25

Conclusions

In this work, we have obtained the I–V curves and topological structure of individual native DNA, Ni-DNA and Ag-DNA molecule at different environmental condition, respectively. The results showed that the conductive ability of native DNA is higher than that of Ag- and Ni-DNA in neutral environment. The conductance decreases, and the voltage gap increases with the increasing of Ni^{2+} concentration. Moreover, the structure transition from B- to Z-DNA occurs in high concentrations of nickel ions. The insulative behavior of Ag-DNA results from the appearance of chaos state. But Ni ion could enhance the conductive ability of DNA in alkaline environment. These results denoted that the effects of different metal ion on the conductive ability of DNA exist some distinction, and the conductivity of M-DNA has a close relation to the environmental condition.

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