

Study on the Electric Conductivity of Ag-Doped DNA in Transverse Direction

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Abstract In this article, we reported a novel experiment results on Ag-doped DNA conductor in transverse direction. I - V characteristics were measured and the relative conductances were calculated for different silver ions concentrations. With the increase of the concentration of silver ions, the conductive ability of DNA risen rapidly, the relative conductance of DNA enhanced about three magnitudes and reached a stable value when Ag^+ concentration was up to 0.005 mM. In addition, Raman spectra were carried out to analyse and confirm conduction mechanism.

Keywords Ag-doped DNA · Gold electrode · Relative conductance · Increase · Raman spectra

Introduction

Deoxyribose nucleic acid (DNA) has taken centre stage in biophysical chemistry research during the past few decades. The elucidation of the molecular structure 50 years ago and the translation of the genetic code revolutionized the field of biotechnology. They sparked the creation of whole new industries based on this knowledge and on the various tools and technologies that have subsequently developed. Biologically, the function of DNA is to code functional proteins that are the expressed form of hereditary, genetic information. But in the past few years, the

discovery that DNA can conduct electrical current has made it an interesting candidate for other roles that nature did not intend for this molecule [1]. There has recently been an increased interest in charge transport in DNA, due to both its relevance in physiological reactions and its potential use in molecular electronics [2–4]. Previous studies have looked into the effect of the base sequence and structural distortions on charge transport and the interplay among different transport mechanisms [5–7]. However, much of the research so far has focused on how charge flows along the DNA helix axis. Very few experimental studies have looked into the transport properties of DNA in the transverse direction.

Electrical property of DNA has been investigated intensively for possible use in molecular devices [8–13]. There is a wide range of spectra in the previous results from Anderson insulator to superconductor [14–17]. To investigate the electrical property of DNA, other approaches may be needed. Chemical doping is a prominent strategy for controlling the electrical properties of materials, as demonstrated in semiconductors [18], electrically conductive polyacetylene [19] and high- T_c superconductors [20]. There have been a few previous studies on the electrical property of chemically doped DNA [10–12]. But few of them have paid attention to the electrical property of doped DNA in the transverse direction, which is expected to use in DNA sequencing through nanopore.

In this article, we report novel experimental results on chemical doping effect on Ag-doped DNA. We adopted Ag^+ as a dopant, which is expected to occupy the space between guanine (G) and cytosine (C) to form two rigid bonds [21, 22]. Ag^+ is substituted for H^+ which was previously bound to nitrogen atom in guanine. Then the Ag^+ takes an electron out of a double bond in cytosine and becomes $4d^9 5s^1 5p^1$ structure, which corresponds to hole

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doping. Under such experimental design, we have prepared Ag-doped DNA at different Ag^+ concentrations and measured their transverse conductance. On the basis of the transverse I - V measurement and the results of Raman spectra, we discuss the chemical doping effect on Ag-doped DNA conductor.

Materials and Methods

Materials

The calf thymus DNA was purchased in fiber from the Sigma Company and directly used without further purification. Silver nitrate (AR), ultrapure water and gold target (99.999%) were also used in our experiment.

Experimental Methods

Ag-doped DNA was prepared with different dopant concentrations as follows. Three mixtures were made by mixing 0.16 mg/L calf thymus DNA with 0.0005, 0.005, and 0.05 mM/L AgNO_3 according to 1:1 proportion (mixture I, II and III) and put into quartz cuvettes, respectively. UV-vis spectra were recorded using UV-3310 (Hitachi) to affirm that calf thymus DNA has integrated with silver ions and find out optimal concentrations of two reactants, respectively.

The I - V measurement was performed at room temperature under the 40% humidity. First, gold film electrode was grown on a piece of fresh cleaved mica, which was made by the technology of laser molecular-beam epitaxy with a high-quality target of gold. Second, according to the UV-spectra results, Ag-doped DNA that was made by mixing 0.16 mg/L calf thymus DNA with Ag^+ of 0–0.01 mM was stretched on the gold film, respectively. The last step was that the conductive diamond tips of AFM (NT-MDT CO.) were used as the other electrode to measure the transport properties of a single double-stranded

DNA and DNA bundles in the transverse direction. The tip switched from tapping mode to connect mode when the conversion operation of samples had been changed from scanning to curving. The setpoints at connect mode were determined by the F - Z curves. The DCP11 (NT-MDT) diamond tips were used in our experiment and their spring constant of the cantilevers was 5.5 N/m.

To determine the Ag binding site, we measure Raman spectra of Ag-doped DNA at confocal Raman microspectroscopy (British Renishaw) in the range of 400–1,800 cm^{-1} , with NIR 780 nm laser whose power was maintained at 25 mW and the spectral resolution was less than 2 cm^{-1} . Spectrometer scans, data collection, and processing were controlled by a personal computer. The liquid sample was put into a quartz glass capillary for Raman measurement and the ratio of Ag^+ to nucleotide of the sample was as same as mixture II.

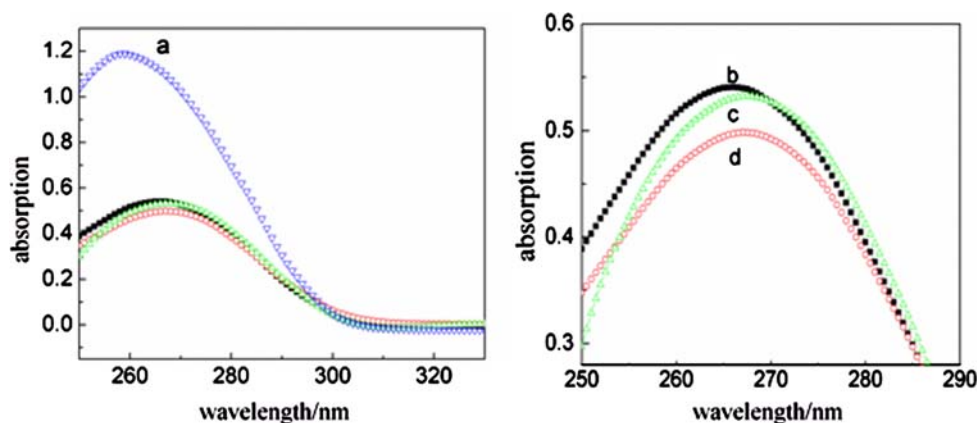
Results and Discussion

UV-Spectra

Generally speaking, the interaction between DNA and positive ions will be detected by absorption spectra. Figure 1 shows the UV-vis absorption spectra of the DNA solutions and mixture I, II, and III. The magnification of section cut is given on the right.

The UV-vis absorption spectra exhibit the absorption peak of native DNA at 258 nm, but the peak cannot be found from 250 to 330 nm for AgNO_3 . It is found that silver ions could cause a hypochromic effect on DNA. The peak of mixture I is at 264.5 nm, indicating that reaction occurs between silver ions and DNA. The peak of mixture II shifts to 268 nm and the mixture III almost has not any more shifts, marking that the combination between DNA and silver ions reaches saturation. So the maximum concentration of silver ions used in the next experiment was 0.01 mM.

Fig. 1 Absorption spectra of DNA in the absence and presence of Ag ions. a: pure DNA; b: mixture I; c: mixture II; and d: mixture III



Electrical Properties

Nature DNA was stretched onto the gold electrode surface and then the current–voltage (I – V) characteristic of molecule was measured as described in Sect. 2.2. The image of Ag-doped DNA samples at different Ag^+ concentrations and I – V measurement points by Atomic force microscopy (AFM) are shown in Fig. 2. Differences between nature and Ag-doped DNA were barely found from the AFM images. There is a line composed of seriate 30 points across this rope to avoid excursion of tips. The I – V curves

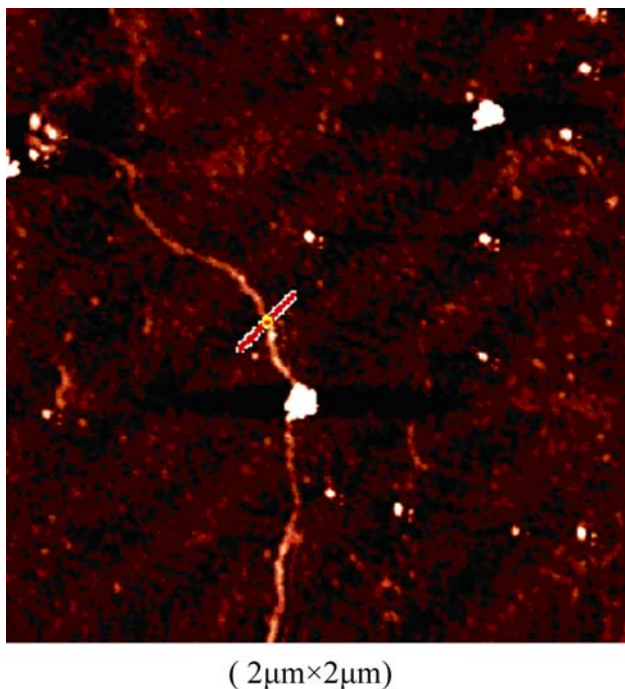
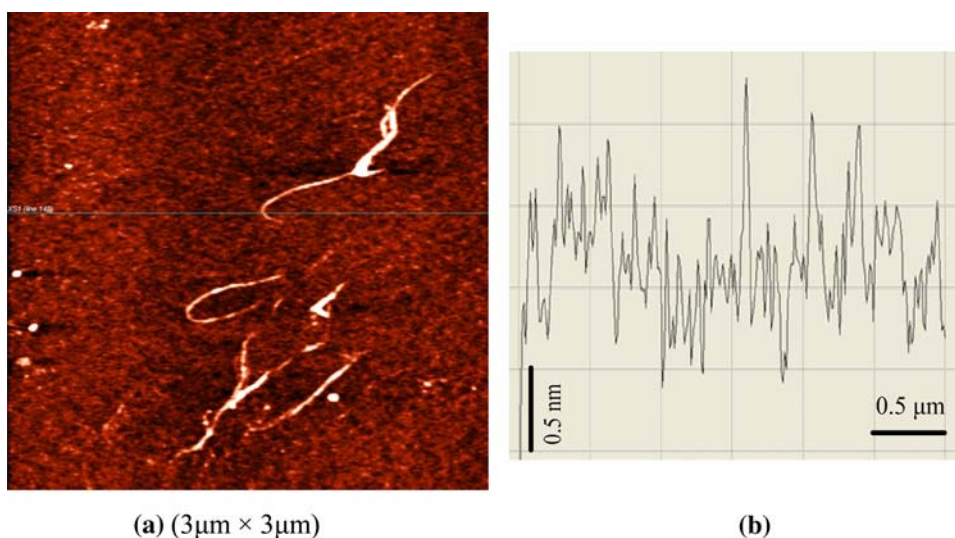


Fig. 2 Image of DNA rope stretched on the gold electrode surface

Fig. 3 **a** DNA image; **b** a height profile taken along the line marked in **a**



were obtained from each point existed along the line. When the tip touched the Ag-doped DNA rope, I – V curves from different points appeared. In our experiment, the single DNA rope was distinguished from DNA bundles by using the method shown in Fig. 3. Figure 3b is a height profile taken along the line marked in Fig. 3a. The difference in height between Ag-doped DNA and gold electrode is clear. The measured height of Ag-doped DNA is 1–2 nm. About 10% DNA bundles of 3–30 nm was also found in our AFM samples.

Figure 4 shows the I – V curves of DNA(a) and Ag-doped DNA(b–f) in transverse direction. The curves present almost linear and symmetric behavior in the bias range of -0.2 to 0.2 V. With the increase of the concentration of silver ions, the conductive ability of DNA rises rapidly and reaches a stable state at 0.005 mM. The calculated conductance of DNA and Ag-doped DNA with 0.01 mM Ag^+ were about 0.062×10^{-9} and 74.5×10^{-9} S, respectively. Moreover, any hysteresis was not found in all curves. In addition, we found that I – V curve of DNA showed a little excursion. The reason for this is studied further.

Considering the effects of electrodes, the relative conductance of Ag-doped DNA is calculated by I – V curve and is the average of many points on DNA for each Ag^+ concentration (The relative conductance is the ratio of the conductance of Ag-doped DNA ropes to the conductance of the loop which was composed of tip, gold electrode, and inner circuitry of AFM). The relationship between relative conductance of Ag-doped DNA and Ag^+ concentration is presented in Table 1 and pictured in Fig. 5a. This figure is interesting. First, the relative conductance of DNA is improved obviously and enhanced about three magnitudes after silver ions were added. Second, the conductance of Ag-doped DNA increases almost linearly and just stays at the same order of magnitude when the concentration of

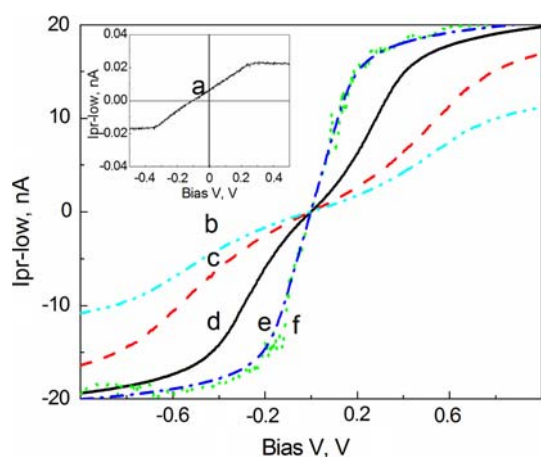


Fig. 4 Image of I - V curves of DNA (a) and Ag-doped DNA (b-f): a pure DNA; b-f, Ag-doped DNA with 0.0005, 0.001, 0.0025, 0.005, and 0.01 mM silver ions

silver ions ranges from 0.0005 to 0.005 mM. Third, there was rather little change in relative conductance when the concentration of silver ions is from 0.005 to 0.01 mM.

By Lagrange interpolation method, we can fit a curve as shown in Fig. 5b, its function is

$$c = 0.0006 + 152.94x + 289950x^2 - 1.71093 \times 10^8 x^3 + 3.15758 \times 10^{10} x^4 - 1.74268 \times 10^{12} x^5$$

where c and x stand for the relative conductance and the concentrations of silver ions, respectively. The fitted curve shows a good agreement with the available experimental result when the concentration is below 0.0025 mM.

We can also find that Ag-doped DNA bundles which were about 10% in our AFM samples showed almost non-Ohmic I - V behavior or as same as natural DNA. This result shows that the conductance was from single DNA and there was little electric current through DNA bundles.

It has been suggested that Ag^+ forms three types of complexes with DNA (type I, type II, type III) when $[\text{Ag}^+]:[\text{nucleotide}]$ ratio is greater than 0.5 [23–27]. In type I complex, Ag^+ binds to N7 positions of guanine and adenine. The metal ion forms interstrand bifunctional AT and GC adducts in type II complex and binds to other positions in type III complex. In our experiment, the ratio was more than 0.5 for the lowest Ag^+ concentration so that three complexes exist simultaneously, and then Ag^+ “bridge” would be build through DNA ropes in transverse direction between the electrodes. This “bridge” increases the conductance sharply.

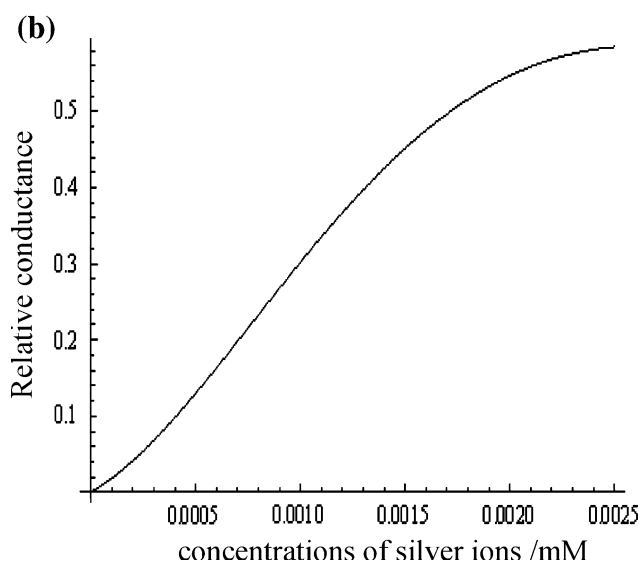
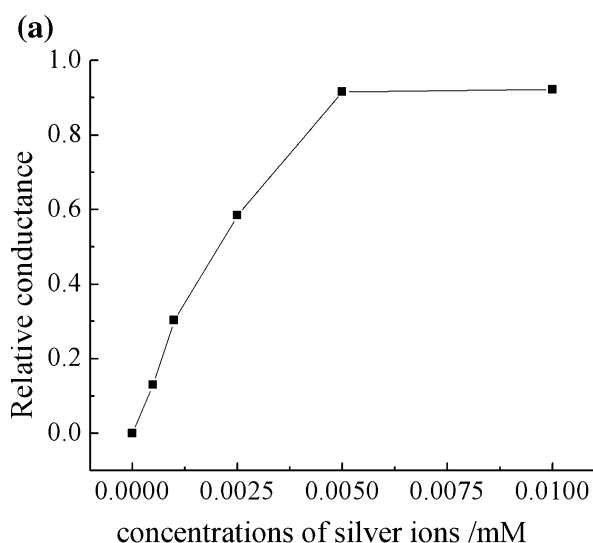


Fig. 5 The curves of the relative conductance varied with different concentrations of silver ions added in DNA. **a** The curve of experiment data. **b** The fitting curve which shows a good agreement with the available experiment result when the concentration is below 0.0025 mM

The Analysis of Conduction Mechanism by Raman Spectra

The Raman spectra of calf thymus DNA(a) and Ag-doped DNA(b) are presented in the Fig. 6. The frequency of Raman lines and their assignments are shown in Table 2. It is found that Raman bands assigned to guanine and adenine at 1,576, 1,487, 1,418, 1,375 and 727 cm^{-1} shift 4–9 cm^{-1}

Table 1 The Relative conductance varied with different concentrations of silver ions added in DNA

Concentrations of silver ions (mM):	0	0.0005	0.001	0.0025	0.005	0.01
Relative conductance:	0.0006	0.13009	0.30223	0.58505	0.91638	0.92164

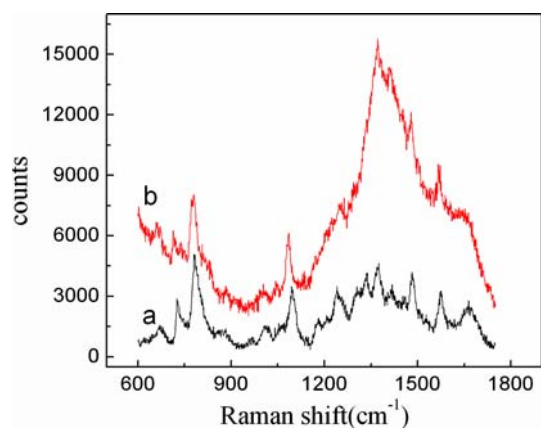


Fig. 6 Raman spectra of calf thymus DNA in aqueous solution a nature DNA, b Ag-doped DNA

Table 2 The assignment of Raman spectra of DNA and Ag-doped DNA

Raman shift/cm ⁻¹		Assignment
DNA	Ag-doped DNA	
1,665	1,666–1,650	G, A
1,576	1,569	G, A
1,487	1,480	G, A
1,418	1,409	A, G
1,375	1,371	T, A, G
1,249	1,249	T
1,091	1,085	O–P=O symmetric stretching vibration
1,047	1,047	Deoxyribose C–O stretching vibration
830	830	B-conformation
788	781	O–P–O diester symmetric stretching vibration
727	716	A

to lower wavenumbers after Ag⁺ combine with DNA. The bands at 1,091 and 788 cm⁻¹, assigned to the symmetric stretching vibration of O⁻P=O and O–P–O diester shift to 1,085 and 781 cm⁻¹, respectively. It is also noted that the band assigned to B-DNA has no change in frequency, but its intensity decreases sharply. Moreover, the band at 1,249 and 1,047 cm⁻¹ assigned to thymine and stretching vibration of C–O in sugar have no obvious shifts. The result suggests that binding of Ag⁺ caused the changes of DNA structure, especially in stacking of base pairs, hydrogen bond.

According to the Raman spectra analysis, the interaction between calf thymus DNA and Ag⁺ can cause monophasic transitions to the conformation of DNA. Ag⁺ interacts with DNA forming three distinct complexes marked I, II and III with progressively higher amounts of Ag⁺. Complex I has been assigned to a modified B conformation, whereas

complex II reflects a novel B-conformation in which the base pair tilt and roll significantly. It can also be noted that the intensity of the broad band from 1,371 to 1,569 cm⁻¹ raises obviously and the band at 1,665 cm⁻¹ becomes broad. It is expected that the changes are caused by type III.

Conclusion

In conclusion, we report the charge transport properties of double stranded Ag-doped DNA in the direction perpendicular to the backbone axis. The relative conductance of DNA is enhanced by three orders of magnitude. The origin of the novel results may be that a Ag⁺ bridge is build through DNA ropes in transverse direction. The results may give some references for the research of molecular devices and sequencing DNA through nanopore.

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