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Anomalous doping effect on Ag-doped DNA conductor

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Abstract

We report novel experimental results of chemical doping effect on Ag-doped DNA conductor. The prepared Ag-doped DNA samples were confirmed by EXAFS that Ag^+ was doped into π-way. In *I–V* measurements at room temperature, nonlinear *I–V* curves with hysteresis emerged and systematic change in electrical conductivity σ was observed from 10^{-10} to 10^{-6} Ω^{-1} cm^{-1} under doping condition $[Ag^+]/[\text{Base pair}] = 10^{-6}-10$. The relation between the conductivity and dopant concentration showed a weak dependence $\sigma \propto [Ag^+]^{0.5}$. This 'weakly doping effect' may be caused by the long-range correlated randomness of sequence in DNA, in contrast with usual doped organic conductors.

1. Introduction

The uniqueness of DNA originates in its structure, in which history of life and its functions are coded in the stacking of base pairs [1]. Because of the π-way arising from the stacking, DNA is considered to be a one-dimensional electron system [2]. Recently, electrical property of DNA has been investigated intensively for possible use in molecular devices [3–11]. There is a wide range of spectra in the results of the previous studies from Anderson insulator to superconductor. 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 [12], electrically conductive polyacetylene [13] and high-T_c superconductors [14]. A suitable dopant to the π-way may change the electrical property of DNA. There have been a few previous studies on the electrical property of chemically doped DNA [8–10]. However, no systematic investigation on the chemical doping effect of electrical property has yet been made. One of the main reasons is that it is very difficult to evaluate how much of the dopant binds to DNA on the level of a single molecule. We are convinced that bundles of orientated DNA molecular chains are really suitable for a study of chemical doping effect, because precise evaluation of the amount of the dopant bound to DNA will thereby be feasible.

In this Letter, we report novel experimental results on chemical doping effect on Ag-doped DNA conductor. We adopted Ag^+ as a dopant, which is expected to occupy easily the space between guanine (G) and cytosine (C) and forms two rigid bonds, as shown in Fig. 1 [15]. Ag^+ is substituted for H^+ which was previously bound to a nitrogen 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 doping. Under such experimental design, we have prepared Ag-doped DNA bundles at different Ag^+ concentrations and performed their *I–V* measurements. On the basis of the

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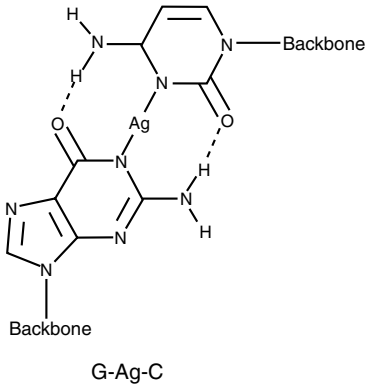

Fig. 1. Schematic representation of the binding site of Ag^+ in Ag-doped DNA [15]. Ag^+ forms two covalent bonds with two nitrogen atoms in G–C pairs and then takes electronic structure of $4d^9 5s^1 5p^1$.

experimental results, we discuss the chemical doping effect on Ag-doped DNA conductor.

2. Experimental

Ag-doped DNA bundles were prepared with different dopant concentrations as follows: Small bundles (<10 mg) of dry fibrous calf thymus DNA (SIGMA) were immersed into small amount (a few μL) of aqueous solutions of $AgNO_3$ (Wako) for ≈1 min under $[Ag^+]/[\text{Base pair}] = 0$ (non-doped), 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, 1 and 10, where $[Ag^+]$ and [Base pair] are defined as the numbers of silver ions and base pairs, respectively, obtained from weight of dry fibrous DNA. The ratio of $[Ag^+]/[\text{Base pair}]$ was determined stoichiometrically. The DNA bundles were then stretched and fixed to cover glasses (Matsunami Glass, Ind. Ltd.). The samples were dried at ≈26 °C for at least several hours. The prepared bundles were 50–100 μm-diameter in the center and ≈10 mm-length. We confirmed that rapid evaporation occurred at both ends of the DNA bundle in the dry process and then impurities including Ag^+ were accumulated there.

To determine the Ag binding site, we carried out an extended X-ray absorption fine structure (EXAFS) analysis for Ag-doped DNA at $[Ag^+]/[\text{Base pair}] = 0.1$ by a transmission method at Ag K-edge in BL01B1 of SPring-8 [16]. In this analysis, we used a software, REX2000J (Rigaku).

The *I–V* measurement was made by a two-probe method at room temperature under room humidity (30–80%). The bundles were put in a vacuum (≈10^{-6} Torr) to remove water. Then gold electrodes were deposited on both ends of the DNA bundles. A typical electrode gap was 30–50 μm. The bias voltage was swept between ±1 V. The average diameter and length of the bundles on the electrode gaps were measured by an inverted microscope IX-70 (Olympus) to obtain electrical conductivity. We confirmed that leakage current through the glass surface was $<10^{-13}$ A and can be neglected, and also that the electrical conductivity of the DNA bundle did not depend on the ambient humidity.

3. Results and discussion

3.1. EXAFS spectra

The binding site of Ag^+ in DNA was determined by an EXAFS analysis [17]. Fig. 2 indicates the Fourier transforms of the spectra at Ag K-edge of Ag-doped

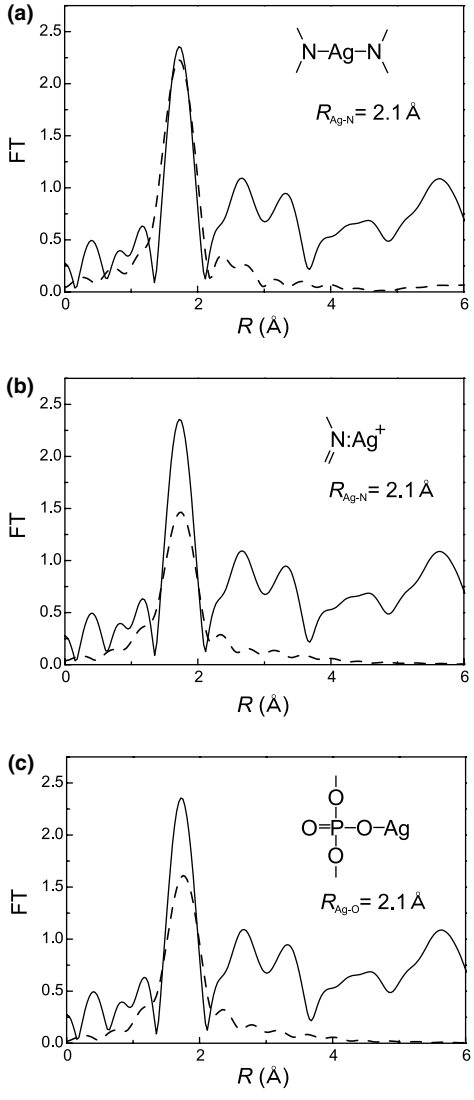

Fig. 2. Fourier transforms of EXAFS spectra at Ag K-edge of Ag-doped DNA at $[Ag^+]/[\text{Base pair}] = 0.1$. The solid line in each panel shows an identical experimental result. The main peak at 1.8 Å is due to the nearest neighbor(s) of Ag. The insets illustrate three possibilities of neighbor(s): (a) two nitrogen atoms (N–Ag–N); (b) a nitrogen atom (Ag^+: N, a coordination bond); (c) an oxygen atom in phosphate group (Ag–O). Dashed lines show their corresponding fitting results.

DNA at [Ag^+]/[Base pair] = 0.1. The distances of all peaks are displayed shorter than the actual values because of the phase shift [17]. The height of main peak at $R = 1.8$ Å, assigned to the nearest neighbor(s) of Ag, depends strongly on the kind and number of the nearest neighbor atom(s) [17]: i.e., two nitrogen atoms in G–Ag–C, a nitrogen atom in G (a coordination bond) and an oxygen atom in phosphate group (Ag–O). The fitting peaks are fixed at $R = 2.1$ Å from covalent radii and reference values, but their amplitudes are different. It is clearly shown that the fitting peak on G–Ag–C (Fig. 2a) is the best agreement among the three possibilities. Other possible configurations, including the formation of silver wire outside of DNA [18], are also ruled out from the EXAFS results. We have also found from EXAFS spectra that the amount of binding Ag^+ is proportional to [Ag^+]/[Base pair]. The details will be published separately.

3.2. Electrical properties

To evaluate the conductivity, we carried out the *I–V* measurements for various Ag-doped DNA bundles. Fig. 3 shows typical *I–V* curves of the non-doped and the Ag-doped DNA bundles at [Ag^+]/[Base pair] = 0.01 and 0.1. Nonlinear *I–V* curves with hysteresis were observed for all samples. Nonlinear conductions in DNA have been reported in previous studies on DNA conduction [6,8–10], but the hysteresis has not been reported to be very slight [10]. By analogy with the *I–V* curves in dielectrics [19] and charge–density-wave (CDW) [20,21], the clear hysteresis observed here reflects the existence of transient states in electrical conduction in the DNA bundles. Since guanine (G) is easily oxidized and then charged [11], DNA is a dielectrics consisting of an array of numerous G–C (charging site) and A–T (insulating site) pairs. Formation of bundle may enhance the hysteresis of a single DNA molecule.

We have also found other characteristics of the *I–V* curves: asymmetry of *I–V* curves and conductance fluctuations. The observed *I–V* curves are asymmetric with respect to the origin. These features have also been observed [6,10], but the reasons have never been discussed. Very recently, it has been shown that a symmetry/asymmetry of *I–V* curves of single organic molecules depend on *spatially*-symmetry/asymmetry of the organic molecule [22]. The asymmetric *I–V* curves observed here seems to be affected by the chirality of DNA. The conductance fluctuations, observed in junction arrays as single electron tunneling [23], have observed as small steps on the nonlinear *I–V* curves in Fig. 3a, similarity to that reported in [6]. The conductance fluctuations indicate that DNA also has the nature of a junction array. Asymmetric *I–V* curves and conductance fluctuations thus are important to understand the electrical property of DNA beside the chemical doping effect.

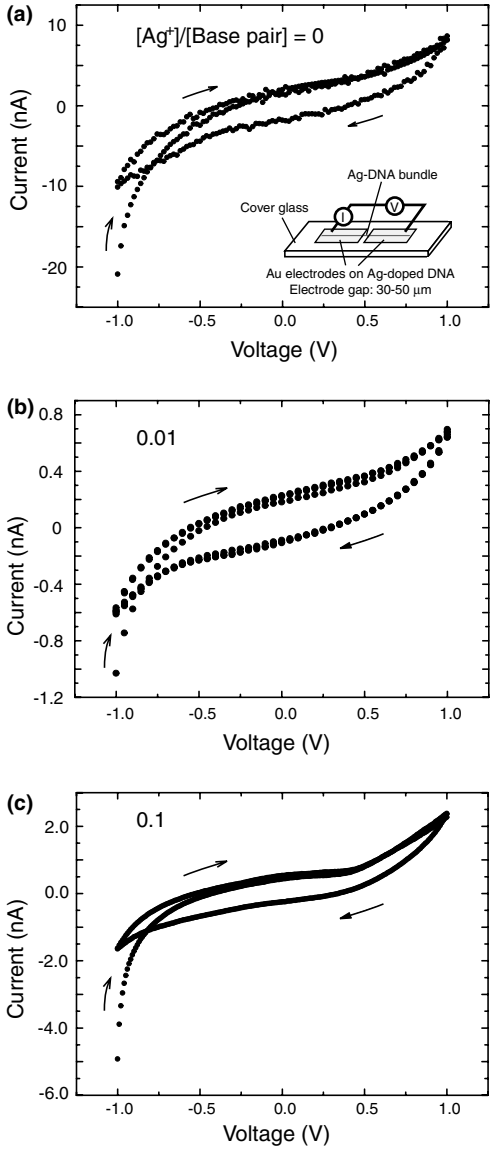

Fig. 3. Typical *I–V* curves observed in Ag-doped DNA at [Ag^+]/[Base pair] = 0 (non-doped DNA) (a); 0.01 (b); 0.1 (c) within ±1 V. Arrows indicate the direction of bias voltage tuning and the inset shows a schematic representation of a sample set.

Here, we emphasize that the electrical conduction arising from physical adsorption and chemisorption of Ag^+ can be denied from the view points of sample preparation (the rapid evaporation at both ends of the DNA bundles), EXAFS and the electronic structure of Ag compounds.

3.3. Chemical doping effect

To study the chemical doping effect on conductivity, we evaluated the electrical conductivity of non-doped and Ag-doped DNAs from the *I–V* curves. The conductivity σ was determined from the slopes of *I–V* curves at 0 V and sample size and then the dependence of σ on

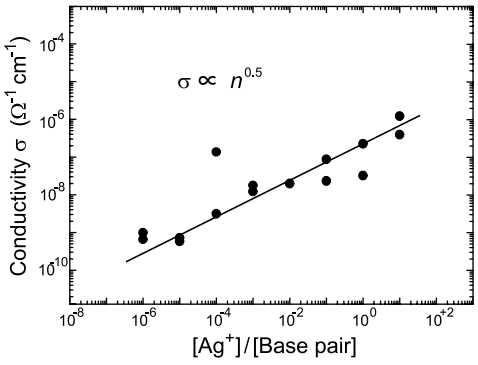

Fig. 4. Dependence of electrical conductivity of Ag-doped DNA on $[Ag^+]$. The solid line represents $\sigma \propto n^{0.5}$. The electrical conductivity of non-doped DNA is $(8.24 \pm 2.06) \times 10^{-10}$ Ω^{-1} cm^{-1}.

$[Ag^+]$ was evaluated. Fig. 4 illustrates the Ag^+ concentration dependence of σ, which systematically changes from 10^{-10} to 10^{-6} Ω^{-1} cm^{-1} within the range of $[Ag^+]$/[Base pair] from 10^{-6} to 10. The dependence of σ on $[Ag^+]$ is determined by a least-squares method within experimental error as

$$\sigma \propto [Ag^+]^{0.5}. \quad (1)$$

The scattering of data points in Fig. 4 primarily arises from the measurement of thickness of DNA bundles. The σ of non-doped DNA is $(8.24 \pm 2.06) \times 10^{-10}$ Ω^{-1} cm^{-1}, which agrees with that in a recent study [24] (not plotted in Fig. 4).

3.4. Conduction mechanism

To understand the conduction mechanism described by Eq. (1), we discuss the possibilities based on the doping effect in semiconductor including a critical behavior in metal-insulator transition, ionic conductions and organic conductors (π-electron system) as typical examples, as shown below.

First, we discuss the possibility of doped semiconductor. The doping effect in semiconductor is described by $\sigma \propto n$ [12], where n is the number of dopant. This indicates that DNA differs from a conventional semiconductor. Moreover, we compared with a critical behavior in metal-insulator transition of doped semiconductor [25], but Eq. (1) is quite different from that because the range in which Eq. (1) is satisfied is too wide as the critical behavior.

Next, we examine the possibility of an ionic conductions: whether Ag^+ moves along DNA chain. In this case, the mechanism is explained by ionic conductions in a strong electrolyte solution, where $\sigma \propto n$ [26], or solid state ionics, where $\sigma \propto [Ag^+]^x$, $x = +1.93$ and 1.64 for Ag–Ge–S and Ag–Ge–Sb–Se at 298 K, respectively [27]. In either case, the dependence is much stronger than in Eq. (1). Therefore, the ionic conductions can be disregarded in our problem.

Finally, we compare the doping effects between DNA and common π-electron system. The latter system such as polyacetylene, poly(*p*-phenylene) and poly(*p*-phenylene sulphide) exhibits a steep metal-insulator transition [28–30]. For example, in $[CH(AF_5)_x]_n$ the σ increases over eight orders from 10^{-5} to 10^{2} Ω^{-1} cm^{-1} at $x < 0.05$ [28], whereas the doping effect for DNA is much weaker. Therefore, the Ag-doped DNA is different from usual π-electron system. What is the origin of the difference between usual π-electron systems and DNA? The essential difference is *regularity* of their structures, because the π-system has a periodic structure, whereas DNA has a long-range correlated disordered sequence [31]. Very recently, Stanley and co-workers [32] have predicted that one-dimensional long-range correlated disorder electron system such as DNA shows a metal-insulator transition. Such a study would be necessary not only to understand the 'weakly doping effect' obtained here, but could also lead to a better understanding of DNA itself.

4. Conclusion

The novel experimental results of the chemical doping effect on Ag-doped DNA conductor are reported. Nonlinear *I–V* curves with clear hysteresis and conductance fluctuations are observed and the doping effect is determined to be $\sigma \propto [Ag^+]^{0.5}$, which is discussed in comparison with that in semiconductor, ionic conductions in a strong electrolyte solution and solid state ionics, and π-electron system. The origin of the 'weakly doping effect' may be discussed in terms of long-range correlated disordered sequence reflecting history of life.

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