STM/STS Study of Electron Density of States at the Bases Sites in the DNA Alternating Copolymers

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Local electron density of state spectra at the bases sites in the two types (A–T pairs only and G–C pairs only) of double-stranded DNA molecules is measured with the use of STM/STS (scanning tunneling microscopy/scanning tunneling spectroscopy) technique. The difference of electronic structure between A–T pairs and G–C pairs is discussed in relation to the charge-transfer mechanisms in these molecules.

Charge (electron or hole) migration in DNA molecules is one of the important functions to keep them biologically stable or repairable from hazards, such as high energy irradiation. On the other hand, the structure of DNA with its π-electron system of four-kind bases stacked each other is reminiscent of certain molecular conductors and in this sense DNA could be a very unique element of certain molecular devices.[1–4] A lot of observations for its transport properties have been carried out; however, the actual magnitude of DNA conductivity as well as its physical mechanism is under debate. As one explanation models for its vague transport properties, Meggers et al. revealed some regularities in the motion of holes in DNA molecules by characterizing the bases-pair sequence dependence of the hole-transfer rate with biochemical methods.[5] In the general arguments on this type of problem and also for the elucidation of the Meggers's results, Ratner[6] pointed out that there are two types of charge-migration mechanisms, coherent superexchange and incoherent hopping, depending on the bases-pair configurations. In order to verify these models, transport measurement not in λ-DNA but in Poly(dA)–Poly(dT) or Poly(dG)–Poly(dC) has recently started out in some groups.[7,8] However, detail discussion for electronic structure of the DNA is difficult under each transport observation. In this study, we have directly measured the density of state spectra of double–strand (G–C pair DNA) and (A–T pair DNA) at the each bases site with the use of STM/STS technique and compared the energy-barrier-heights for holes in the DNAs.

The DNA samples used in this experiment were DNA alternating copolymers, Poly(dA–dT)–Poly(dA–dT) and Poly(dG–dC)–Poly(dG–dC), which were commercially available from Amersham Pharmacia Biotech. The 500 µg of each sample was dispersed in 500-µL distilled water and sonicated for 20 min. with an ultrasonic cleaner. The 30 µL of each dispersion was dropped and spread on an HOPG flake set on a spin-coater which was spinning at the rate of 3000 turns/min. The prepared samples were set in an ultra-high-vacuum scanning tunneling microscope, OMICRON, and observed in STM image mode and spectroscopic mode (STS) to obtain the spatially resolved spectra of the electron density of states at each base site. Every experiment was done in room temperature.

A typical STM image of Poly(dA–dT)–Poly(dA–dT) is shown in Figure 1a. Presumably a few double-helix copolymers were revealed with straight form. The individual image of the base has not been observed in this observation. It could be assumed that the electron density of state near 1 eV, applied bias-voltage, of the copolymer is slightly stormed by their assemble state or anything else.

Figure 1b shows a twin (or more) double-helix image of Poly(dG–dC)–Poly(dG–dC). The side-sectional view of the short arrow in the image is shown in the lower portion of the Figure 1b and its full length corresponds to the width of the DNA double-helix, 2.3 nm. The observed STM images usually reveals some aggregate forms in Poly(dG–dC)–Poly(dG–dC). Since this assemble form has hardly observed in the case of Poly(dA–dT)–Poly(dA–dT), this assemble state is one of the intrinsic feature of Poly(dG–dC)–Poly(dG–dC).

The STS results for Poly(dA–dT)–Poly(dA–dT) and Poly(dG–dC)–Poly(dG–dC) are shown in Figures 2a and 2b, respectively. It has been well known that the differential tunneling current of bias voltage, dI/dV (ordinate), is proportional to the elec-

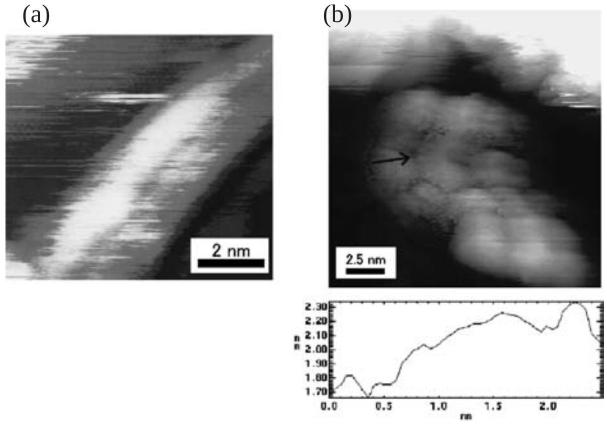

Figure 1. STM images of (a): Poly(dA–dT)–Poly(dA–dT) and (b): Poly(dG–dC)–Poly(dG–dC). These STM images, (a) and (b), were captured both under the 1.0 nA in setpoint-current, and 1 eV in bais-voltage. A few straight copolymers of A–T chains were observed in (a). On the other hand, some aggregate copolymers of G–C chains were revealed in (b). Most STM images of the G–C chains in this observation showed some aggregate form. An STM image of twin double-helices of and the cross-sectional height-view along the short arrow indicated in the upper picture in Figure b.

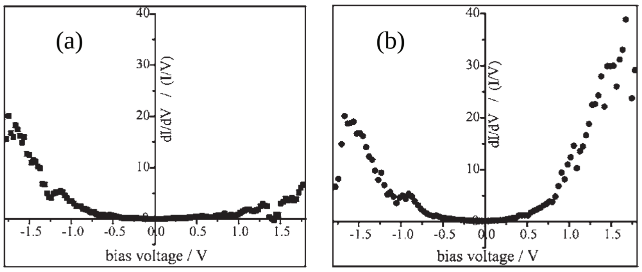

Figure 2. STS spectra of (a): Poly(dA–dT)–Poly(dA–dT) and (b): Poly(dG–dC)–Poly(dG–dC). These spectra were obtained in the average of each pair sites.

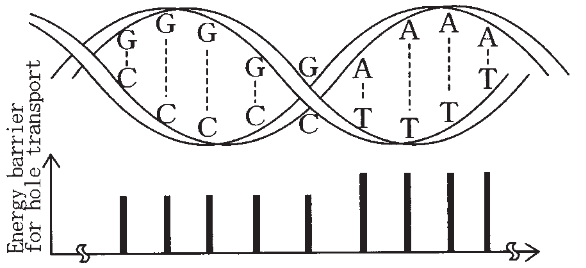

Figure 3. Schematic view of the λ-DNA and the energy diagram of the hole transport at each base site.

tron density of states of the target molecule and the bias-voltage, V (abscissa), is proportional to the energy-level (eV) of the electronic state. The STS measurements were carried out several times for each DNA cell to check the reproducibility. Although the noise levels of each spectrum were rather high, the averaged space-site resolved spectra at several relatively small areas showed reproducible results and the error bar in energy was about 0.1 eV. In Figure 2a, the graph indicates the dI/dV spectrum averaged over the several points of A–T chains. The apparent peak is located at around -1.2 eV in the spectrum, which may correspond to the electron energy level due to the A–T base-pairs in the valence band of Poly(dA–dT)–Poly(dA–dT) molecule. The spectra in Figure 2b were also obtained by averaging the signals in each G–C chain. The additional peak in the valence band in this case is located at around -0.9 eV in this spectrum. Thus these experimental results indicate that the electron energy level at G–C base-pair is higher by $\approx$0.3 eV than that at A–T base-pair site, and accordingly the barrier height for hole transport at G–C base-pair site in double-strand DNA is lower by $\approx$0.3 eV than that for A–T base-pair site.

Theses STM/STS experimental results obtained in this study are consistent with the biochemical experimental results on the hole migration in DNA molecules by Meggers et al.[5] which implied that the highest electron-energy level in the valence band at the G–C site is higher than that at the A–T site. With the consideration of these results, Figure 3 shows the schematic view of the situation of λ-DNA.

According to the STS observation, the holes transporting in the G–C sites have lower energy than that in A–T sites because of the smaller energy gap. Therefore, when A–T pairs are located between the G–C sites, it is considerable that the A–T pairs are energy barrier for the hole transport between the G–C sites. These results support the proposition on the hole-migration behavior in DNA molecules by Ratner[6] in which it was pointed out that there should be a significant contribution of the random walk of holes via the G–C sites to the long-range migration of holes in a DNA molecule. Furthermore, the obtained data are almost consistent with the data of redox-potential measurements.[9]

In summary, geological and electronic structures of the base-sites in a DNA alternating copolymers, Poly(dA–dT)–Poly(dA–dT) and Poly(dG–dC)–Poly(dG–dC), were revealed by means of STM/STS. It was observed that the electron energy level in the valence band for the G–C sites is higher by $\approx$0.3 eV than that for the A–T sites. This result supports the previously reported biochemical studies that the A–T site obstacles and the G–C site mediate the hole transport in DNA.

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