Attosecond Electron Delocalization in the Conduction Band through the Phosphate Backbone of Genomic DNA

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Partial density of states in the empty conduction band of the phosphate backbone sites in DNA was probed using energy-dependent resonant Auger spectroscopy. Results show that genomic DNA with periodic backbones exhibits an extended state despite separation of each phosphate group by an insulating sugar group. In antisense DNA with an aperiodic backbone, the equivalent state is localized. Remarkably rapid electron delocalization occurs at ca. 740 attoseconds for wet DNA, as estimated using the core-hole clock method. Such delocalization is comparable to the Fermi velocity of carbon nanotubes.

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In 1962, Brillouin [1], based on his theory, suggested that double-stranded sugar-phosphate backbones of genomic DNA form conduction bands because of their quasi-one-dimensional periodic structures. This suggestion is plausibly understood by the fact that electronic states are extended (Bloch states) in a periodic system. Charge and electron transport through such extended states is a key function for recognition, signaling, and repair of DNA damage [2]; it also underlies the hypothesis of cathodic protection of essential chromosomal domains [3] and is a current issue of debate related to electrical conductivity of a DNA molecular wire (see [4] for review). However, Bloch states in DNA backbone chains have never been explored experimentally, principally because most measurements specifically assess charge transport through the DNA π base stacks proposed by Eley and Spivey [5] in 1962. Consequently, whether or not charge and electron transport can occur through the DNA backbone remains an open question. To assess this question, we used x-ray absorption spectroscopy (XAS), which enables selective excitation of the phosphorus $1s$ core electron to an empty orbital of the DNA backbone [Fig. 1(a)]. Resonant Auger spectroscopy (RAS) is also used to monitor delocalization of an initially localized core-excited state around the absorption atom.

In our system, RAS spectra are interpreted based on two competing decay channels: core-hole decay and core-excited resonant electron delocalization. If the resonantly excited electron remains sufficiently long to be localized in the vicinity of a core-hole site during the core-hole decay, the decay process results in a final state of two holes with one electron ($2h1e$), known as ''spectator Auger decay'' [Fig. 1(b)]. In contrast, if it delocalizes to the conduction band prior to core-hole decay, the decay process results in a final state of two holes ($2h$), known as ''normal Auger decay'' [Fig. 1(c)]. Consequently, for the case in which the time scale of delocalization is comparable to the core-hole decay, both the spectator and normal Auger are visible. By quantifying the intensity ratio, one can measure the electron-delocalization time. This is the so-called ''core-hole clock'' method (see [6] for review), in which the core hole acts as a fast internal clock because its lifetime ranges from femtoseconds (10^{-15} s) down to even attoseconds (10^{-18} s) [7]. This method is supported theoretically by Ohno [8] and has been applied to studies of charge transfer from adsorbed atoms or molecules into substrates in the time scale of a few femtoseconds [9] to a few hundred attoseconds [10]. Such a short time period is difficult to analyze using traditional methods such as ultrashort-pulse laser pump-probe spectroscopy [11].

Information related to the degree of delocalization of the unoccupied conduction band is obtainable by plotting the spectator (localization) and normal (delocalization) Auger-electron intensities in RAS as a function of the photon energy. The normal Auger plots exhibit unoccupied partial density of states (DOS) near the Fermi level (E_F) in metal [12]. In fact, XAS is commonly recognized as reflecting unoccupied partial DOS, but it cannot distinguish localized and delocalized states. In this Letter, we present experimental evidence that a periodic backbone in DNA exhibits an extended state in the conduction band through comparison with an aperiodic backbone. The electron-delocalization time (τ_{ED}) has been measured in terms of the core-hole clock method to quantify the delocalization property of the band.

To examine the formation of extended Bloch-type orbitals along the backbone, we investigated two DNA backbone types. Double-stranded DNA sodium salt of fish sperm (Acros Organics) was used as an example of periodic backbones. A synthesized 10-mer single-stranded phosphorothioate DNA oligomer (PS-oligo, $d(G)_{10}$; Tsukuba Oligo Service Co., Ltd.) was used as an example of aperiodic backbones, where G indicates the DNA base guanine. The PS-oligo has one sulfur atom replacing a nonbridging oxygen atom in the phosphate backbone (Fig. 2). The substitution of one sulfur atom produces a

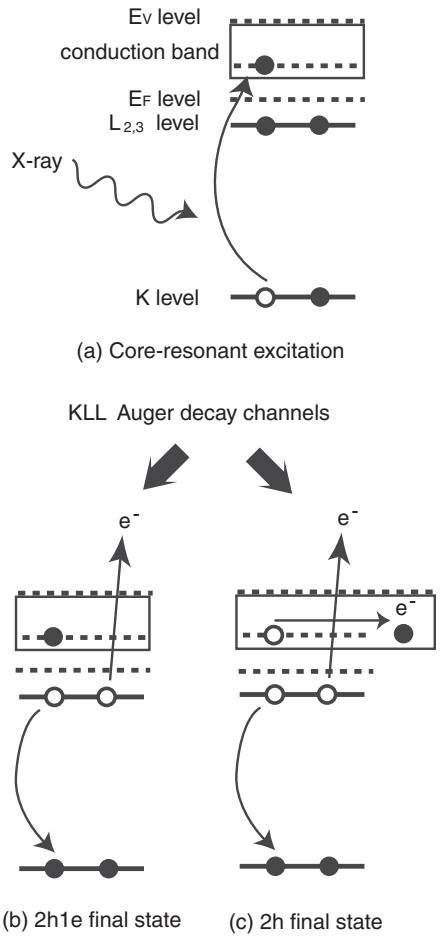

FIG. 1. (a) A phosphorus 1s core electron is excited into an unoccupied state in the conduction band. (b) Spectator Auger final state ($2h1e$) caused by localization of the electron to the core-hole site. (c) Normal Auger final state ($2h$) caused by delocalization of the electron to the conduction band coupling to the continuum.

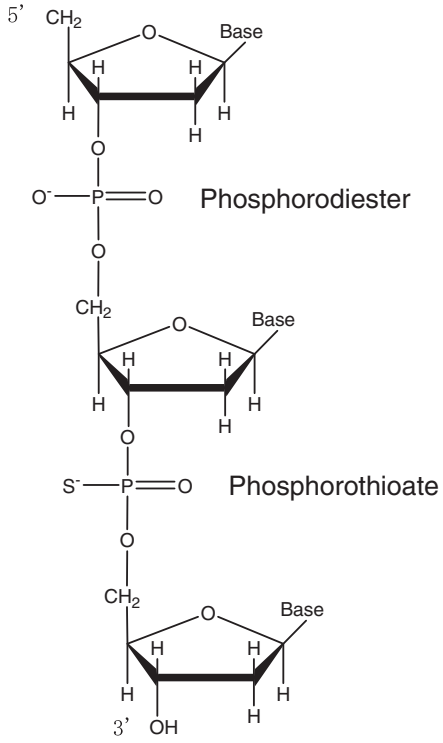

FIG. 2. Schematic representation of phosphodiester and phosphorothioate linkages.

chiral center at each internucleotide linkage of the PS-oligo. For that reason, P-S bonds cannot be aligned parallel to each other to give a mixture of 2^n diastereomers, where n is the number of phosphodiester bonds in the oligo. Both samples were prepared by firmly pressing them onto indium substrates. Wet DNA was measured to obviate the effect of interstrand interaction. It was prepared by mixing with water droplets on the dry DNA sample to produce a swollen amorphous film in which the distance between neighboring molecules increases by water layers [13].

Experiments were performed at beam line BL-27A of the Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba. The BL-27A is equipped with an InSb(111) double-crystal monochromator with energy resolution of 0.9 eV around the P K edge. The Auger spectra were measured using a hemispherical analyzer (CLASS-100; Vacuum Science Workshop) with pass energy of 44 eV. An electron flood gun was used to neutralize the charge on the DNA samples because DNA in solid state acts as an insulator. The XAS spectra were measured by monitoring the sample drain current with x-ray energies between 2150 and 2160 eV. Such energies were chosen to excite the P 1s core electron to an empty orbital t_2^* in phosphate groups. The t_2^* exhibits a strong contribution of both oxygen $2p$ and phosphorus $3sp^3$ hybrid orbitals [14]. It is noteworthy that XAS features of substituted phosphates (e.g., Na_3PO_4 and Na_3PO_3S) are very similar in spite of their symmetric distortions.

A typical P $KL_{2,3}L_{2,3}$ RAS of dry DNA at the t_2^* transition is shown in Fig. 3(a), where spectator [$(^1D_2)t_2^*$ and $(^1S_0)t_2^*$] and normal Auger peaks [$(^1D_2)$ and $(^1S_0)$] are observed. The observed structure is assigned by comparison with normal Auger spectra above the P1s ionization potential and by comparison with previous measurements [15]. The spectator Auger feature is shifted to higher kinetic energy compared to the normal Auger feature because of the screening interaction of a core hole with the localized spectator electron. This shift indicates that a spectator electron is caught in the localized empty t_2^* state during Auger decay. Following Auger decay, the final state is reached, which is the same as that produced in the normal Auger if the t_2^* electron delocalizes to an empty conduction band before the core-hole decay.

Partial yields for $2h1e$ and $2h$ Auger final states were obtained at each excitation energy from peak areas for the dominant $(^1D_2)$ and $(^1D_2)t_2^*$ Auger, respectively, as shown with the XAS in Fig. 3(b). Although there are other possible resonant decay pathways such as participant Auger,

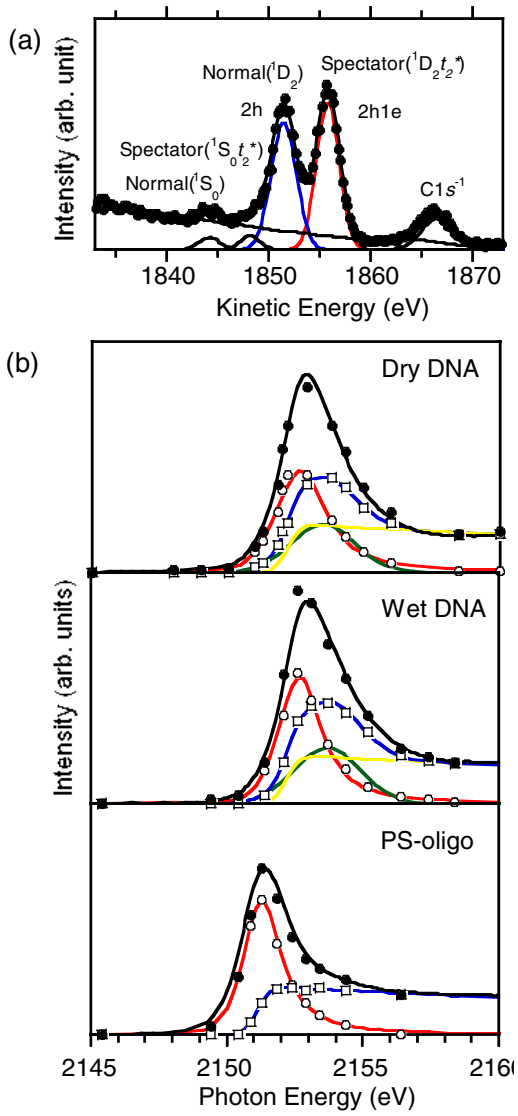

FIG. 3 (color online). (a) A typical P *KLL* resonant Auger spectrum of dry DNA at 2152.9 eV. Spectator Auger ($2h1e$, red line) and normal Auger ($2h$, blue line) features are visible. The dots and the solid lines, respectively, represent the experimental data and a least-squares fit. A C1s photoemission peak is also visible. (b) Integrated intensities of spectator (open circles) and normal (open squares) Auger components near the P K edge. Results of curve fitting for $2h1e$ and $2h$ spectra are shown, respectively, as red and blue lines. For dry and wet DNA, the $2h$ cross sections were decomposed into a Gaussian function (green line) for the conduction band and a Gaussian error function (yellow line) for the continuum. In PS-oligo, the $2h$ cross section was fitted by a Gaussian error function (blue line). The sum of $2h1e$ and $2h$ cross sections is shown as closed circles, which is similar to P1s XAS (black line).

the spectator Auger can be ascribed to the dominant decay pathway because the sum of normal and spectator contributions shows a clear resemblance to the XAS. The $2h1e$ yield spectra were expressed as a single asymmetric peak. The asymmetric shape is related to the balance between the experimental energy resolutions (Gaussian shape at lower energy side) and the lifetime of the intermediate core-excited state (Lorentzian shape at higher energy side). No significant shape differences were observed among samples, where a $2h1e$ yield spectrum corresponds to a localized component of partial DOS of t_2^* near E_F. In the $2h$ yield spectra, intriguing peaked features at ca. 2153.7 eV are observed for dry and wet DNA with periodic backbones, where a $2h$ yield spectrum corresponds to a delocalized component of partial DOS of t_2^* near E_F. A synthesized 10-mer single-stranded phosphodiester DNA oligomer, $d(G)_{10}$, shows a similar peaked feature (not shown). Such delocalized features confirm that the t_2^* orbitals are extended along the direction of the phosphate backbone. The extended state can survive even in wet DNA with structural disorder against Anderson localization [16]. Consequently, one-dimensional periodicity plays an important role in the formation of the extended states. On the other hand, the $2h$ yield spectrum of PS-oligo consistently shows a steplike continuum, which is characteristic of free atoms [17]. The lack of a delocalized peak in PS-oligo suggests that orbitals remain localized at each phosphate molecule. The step is not a genuine continuum, but rather a quasicontinuum in which autoionizing Rydberg states are embedded. Therefore, it is located in energy lower than the vacuum level (E_v). Here, the most important fact is that the insulating sugar group between each phosphate group does not interrupt the conduction band formation of the phosphate groups. This is consistent with the result obtained for band-structure calculations by Suhai [18]. Therefore, band-type conduction is probable through the backbone of the periodic DNA.

In comparison to semiconductor InP [15], DNA has a more localized conduction band state because the ratio of spectator to normal Auger intensity is larger in DNA than in InP. The conductive property of InP can be supported by the smaller spectator shift resulting from decreasing interaction between a spectator electron and two holes in the presence of conduction electrons. In general, if the spectator electrons lesser-couple to the two holes produced in the occupied states, the spectator shift is smaller [19]. The larger spectator shift of DNA is in agreement with a well-known characteristic that the genomic DNA has no conduction electrons (i.e., a wide band gap).

We examined the τ_{ED} of the core-excited electron to the empty conduction band using the core-hole clock method to explore the electron-delocalization rate in DNA. The relationship between the τ_{ED} and the relative intensity of $2h$ and $2h1e$ final states can be described based on previous studies [6,20] as $\tau_{\mathrm{ED}} = \tau(I_{2h1e}/I_{2h})$, where τ is the core-hole lifetime. Therein, I_{2h1e} and I_{2h} respectively represent intensities of spectator and normal Auger components. The P 1s core-hole lifetime of 1.25 femtoseconds corresponding to 0.53 eV [7] lifetime width is used for τ. The τ_{ED} for each sample is shown as a function of excitation energy in Fig. 4. The τ_{ED} shortens with increasing excitation energy. In the system, the energy dependence is expected to result

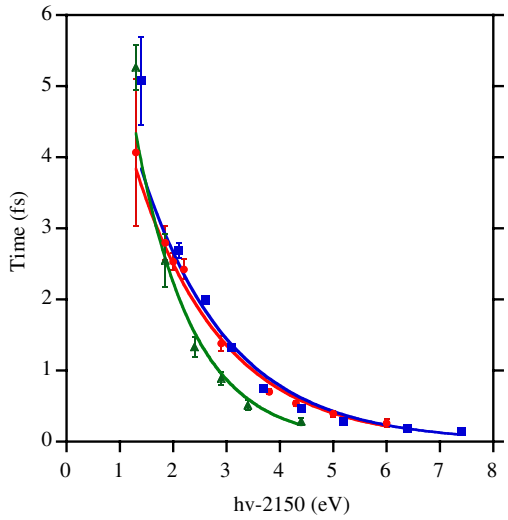

FIG. 4 (color online). Excitation energy dependence of electron-delocalization time for dry (circles) and wet (squares) DNA. The ionization time for PS-oligo is shown as green triangles. Error bars show $\pm 1\sigma$. Each solid line is obtained by an exponential fit.

from the tunneling barrier and density of states in the conduction band, based on the previous study [21]. In the case of PS-oligo, an obtained time can be attributed to the time scale of the excited electron tunneling into the continuum. This time scale is reasonably of the same order as the electron tunneling in atoms [22]. For wet DNA, the delocalization time was found to be ca. 740 ± 30 ($\pm\sigma$) attoseconds at the delocalized peak maximum (2153.7 eV), which is as fast as the charge-transfer time from an adsorbed atom or molecule to its substrate [9,10]. The time scales of DNA and PS-oligo are particularly similar at higher energies, resulting in their similarity of ionization above the continuum. However, their slopes of curves mutually differ, where solid lines show exponential fits to the measured data. A theoretical approach is necessary to interpret the obtained plots, but the slopes of curves might have some relation to the width of the continuum step or bandwidths of delocalized states. The more gradual slope of the curve probably corresponds to the wider conduction band state.

To assess the observed time, we tentatively assume that the electron delocalization occurs from one phosphate into the nearest-neighboring phosphate through a distance of ca. 0.3 nm (half the distance of P-P [13]). Therefore, a velocity of the conduction electron was estimated as ca. 4×10^5 ms^{-1}, which is comparable to the Fermi velocity of carbon nanotubes [23,24] and possibly a typical metal. This velocity is ca. 1000 times faster than the electron transfer rate through the π stack of the DNA base pairs [25].

In conclusion, we have observed the extended state in the periodic phosphate backbone of DNA and demonstrated that electron delocalization occurs along the backbone chains in the attosecond domain. To date, DNA base stacks have been widely accepted to explain the charge and electron transport through the DNA wire, but its mechanism remains unclear. Consequently, an interplay between the charge/electron transport through the base stacks and through the phosphate backbones might play a key role in explaining the mechanism. Finally, we emphasize that the core-hole clock method can serve as a new tool to probe attosecond electron-delocalization dynamics along one-dimensional molecular chains without electrodes.

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