Resonant Auger decays in nucleotide and DNA following core-to-valence resonant photoexcitation at the phosphorus K-edge

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Introduction
There has been great interest in the nature of thin films of DNA's as well as nucleotides on solid surfaces because of their potential applications to nanotechnology such as DNA tips and DNA computers. One of the fundamental problems to be solved is the information about the electric property of DNA thin films deposited on solid surfaces. Resonant Auger electron spectroscopy is one of the suitable methods to characterize electric properties in a localized site. It has been reported that the resonant photoemission spectra for DNA at the nitrogen K-edge photoexcitation shows that the charge hopping model is pertinent for the electric conduction in a DNA duplex [1]. Since the nitrogen atoms are included only in the bases, it is also important to elucidate the charge transport mechanism along the molecular skeleton. Here we report on the resonant Auger decay spectra for ATP and DNA molecules following the phosphorus K-edge photoexcitation in order to elucidate the charge transfer mechanism along one-dimensional chain in sugar/phosphate backbone.

Experimental
Experiments were performed at the BL-27A station. Samples were deposited on HOPG (highly oriented pyrolitic graphite) or embedded on a surface of an indium plate. The X-ray absorption spectra were measured by total electron yield mode.

Results and discussion
Fig. 1 shows the phosphorus KL2,3L2,3 resonant Auger decay spectra for DNA following phosphorus K-edge excitation together with the X-ray absorption spectrum. For higher energy excitation above the ionization threshold, the P KL2,3L2,3 Auger peaks with constant kinetic energy (marked A) are observed. These peaks are due to the normal Auger decays following the ionization of P 1s electrons. For the resonance excitation around 2153 eV, the Auger peak splits into two components. The higher energy peak marked B appears only around the resonance excitation energy (hν=2153 eV). It has been elucidated that the Auger peaks for insulator are split into two components; spectator and normal Auger peaks, while for semiconductors and metals only one Auger peak is observed [2]. In a spectator Auger process, a core electron is resonantly excited into a valence unoccupied orbital and another electron drops into the core hole, and then the other electron is emitted as an Auger electron. The energy splitting of the Auger peaks around the core-to-valence resonant excitation is observed only in insulator and the phenomenon is attributed to the localization of excited electrons in valence unoccupied orbitals during the Auger decay. Clear peak splitting in Fig. 1 suggests that the DNA molecules have insulating properties around the phosphate backbones. Another outstanding phenomenon seen in fig 1 is the energy shift of spectator Auger peaks (Fig.1(c)). The kinetic energy shift of spectator Auger electrons is due to the Auger resonant Raman scattering. It was reported that the energy widths over which the dispersions in resonant Auger peaks are observed are a measure of the localization of electrons in empty states [3]. The present data reveal that the DNA molecules are wide band-gap insulator in one-dimensional direction along sugar/phosphate backbone.

References

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