A novel mechanism of DNA damage induction by K-shell resonance photoexcitations at nitrogen and oxygen as observed using an electron paramagnetic resonance spectrometer in SPring-8

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Many studies using soft X-rays (<10 keV) as fine probes of the energy deposition to biological systems have highlighted their unique biological effects due to the highly localized spatial properties on the scale of DNA [1]. In order to obtain more detailed insights into the physicochemical mechanism of DNA damage induction in terms of unpaired electron species, as intermediates of DNA damage, resulting from ionization, we have developed an X-band EPR spectrometer set up at a synchrotron soft X-ray beamline (BL23SU) in SPring-8, Japan [2]. This apparatus makes it possible for us to perform *in situ* observation of short lived unpaired species just appearing during irradiation.

Using this unique apparatus we have examined EPR signal of DNA thin films irradiated in the EPR cavity in a vacuum chamber [3]. Figure 1 shows the variation in EPR intensity (spin concentration of the unpaired electron species) for DNA thin films as a function of X-ray energy (red line). The right-hand axis in the figure shows X-ray absorption (blue line). The EPR intensities were significantly enhanced at energies slightly above the K-shell thresholds of nitrogen and oxygen. By normal K-shell ionization, two electrons emitted from nitrogen or oxygen atom in DNA, and the doubly charged parent cation will be produced (Auger effect). On the other hand, when the energy is slightly higher than the ionization threshold (σ* excitation energy), the post collision interaction (PCI), which is a deceleration of the ejected electron could be induced. The significant PCI effect leads the recapture of a photoelectron into an unoccupied orbital or a high-lying Rydberg orbital of DNA, which then produces unpaired electron species. In order to evaluate the PCI effect on the enhancement of the EPR intensities, the recapture cross section after the Auger effect in a DNA film was calculated using a semiclassical approximation. The calculated result shows the cross section increased sharply and then gradually decreased as X-ray energy above the ionizing threshold, which is similar to the significant enhancement of the EPR intensities was observed in this study. This indicates that only the enhanced spin concentration above the K-shell thresholds can be attributed to the recapture of a photoelectron.

The PCI effect is usually studied in the gas phase by photoemission spectroscopy, whereas our results may be the first observation of the PCI effect measured in a DNA, whose molecular weight is as large as a polymer, by EPR (Fig. 2). The result suggests that the DNA film itself forms unpaired electron species through the excitation of enhanced electron recapturing. Different from the well-known low photoelectron attachment to an electronegative site in DNA followed by dissociation [5] or the recombination of slow electrons with ion holes, the ionization process induced by the characteristic X-ray energy is a novel mechanism of DNA damage.

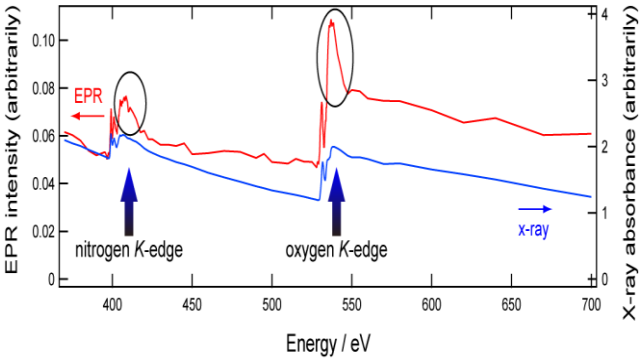

Fig. 1 Variation in EPR intensity for DNA thin film and X-ray absorbance as a function of X-ray energy. The EPR intensity significant enhances around both of nitrogen and oxygen K-edge as indicated by circle in the figure.

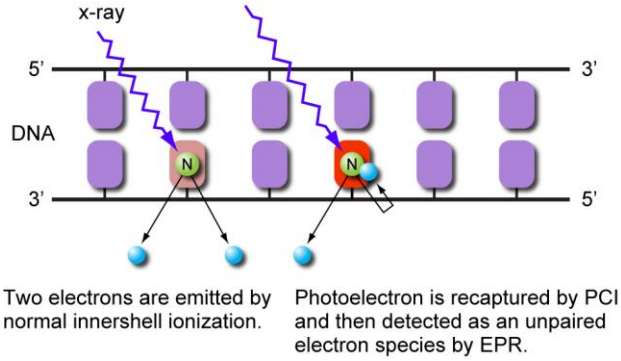

Fig. 2 X-ray absorption processes to the *K*-shell of specific atom in DNA. Photoelectron ejected from the DNA by irradiating X-ray with energy slightly higher than the ionization threshold decelerated and recaptured by PCI, and then detected as an unpaired electron species.

References

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