BL-27A/2013G707

Irradiation effect of soft X-ray to SAM-DNA double-layer immobilized on inorganic surface

Ayumi Narita[1,*] Kentaro Fujii[2], Akinari Yokoya[2], Yuji Baba[2] and Iwao Shimoyama[2]
[1]Advanced Industrial Science and Technology, Umezono, Tsukuba, Ibaraki 305-8568, Japan
[2]Japan Atomic Energy Agency, Tokai, Naka, Ibaraki 319-1195, Japan

1 Introduction

DNA damage induced by the excitation and the ionization of the atoms which compose DNA molecules is a significant research topics in radiation biology. Monochromatic soft X-ray is a powerful tool to control the initial process of DNA damage induction. It was revealed that the radiation damage yields of DNA including strand breaks and nucleobase lesions depend strongly on the soft X-ray energy tuned around *K*-edges of DNA constituent atoms, namely carbon (280 eV), nitrogen (400 eV) or oxygen (530 eV)[1]. In this report, however, few damage was confirmed because they used a DNA thick layer on a solid surface as a sample. We suggest a new DNA thin layer sample to investigate the mechanism of DNA damage. This new sample consists of two parts. One is the immobilization of oligonucleotide (OGN) through self-assembled monolayer (SAM). The other is the elucidation of the process for DNA damage caused by core electron ionization and Auger processes of the atoms composing DNA using synchrotron soft X-ray. In previous report, we demonstrated the immobilization of OGN molecules on the inorganic surface through the organic SAM [2]. This study investigates the irradiation effect of SAM-DNA double layer using a monochromatic soft X-ray.

2 Experiment

Mercaptopropyltrimetoxisilane (MPTS) molecules ($HS(CH_2)_3Si(OCH_3)_3$) was used to form organic layer between the substrate and the OGN. MPTS molecules have thiol group (SH) and silicon alkoxide ($Si(OCH_3)_3$) at the respective terminal sites of the alkyl backbone (Figure 1). MPTS molecules were adsorbed on sapphire single crystal by immersing the substrate in 10% ethanol solution. Then, 1 μM oligonucleotide dissolved in 10 mM Tris-HCl was dropped on the MPTS film. The samples were elucidated by XPS (X-ray photoelectron spectroscopy) and NEXAFS (near edge X-ray absorption fine structure). The irradiation experiments were performed at BL-23SU of SPring-8. The irradiation energy was fixed at 430 eV (6.7×10^{11} photons/s). The changes in chemical states of the layers after irradiation were observed by N *K*-edge NEXAFS measurements.

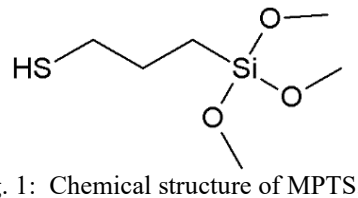

Fig. 1: Chemical structure of MPTS.

3 Results and Discussion

In previous report, we confirmed that the OGN molecules are strongly immobilized on the sapphire surface through the MPTS-SAM [2]. The thickness of the MPTS-SAM on the sapphire surface was estimated using XPS results. The thickness of the MPTS layer estimated was 3.1 nm. The OGN layer was calibrated using a simple calculation. An OGN film adsorbed on a thick MPTS layer was previously estimated to be 27.5 nm thick when 300 μl of a 2 μM OGN solution was dropped on an MPTS film. The total number of OGN molecules in the present experiment was one sixth of that in the previous experiment. The thickness of the OGN film was calculated to be about 4.6nm and thus the total thickness of the adsorbed layers (MPTS-OGN) was about 7.7 nm.

Concerning the irradiation effect of MPTS-OGN layers, the N *K*-edge NEXAFS spectra is shown in figure 2. Two peaks in the low energy region (395–403 eV) indicate resonances from the N 1s orbital to the π* unoccupied orbitals. After irradiation, the intensity of these two peaks decreased. This result means that the base of OGN was damaged by soft-X-ray irradiation because the N atoms are only in the bases. As a result, we observed radiation damage to the OGN molecules adsorbed on the MPTS film.

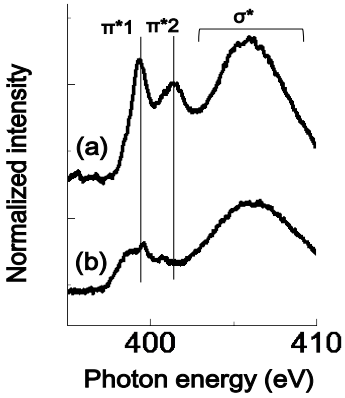

Fig. 2: N *K*-edge NEXAFS spectra of OGN-MPTS layer before (a) and after (b) X-ray irradiation at 430 eV for 30 min.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 25740020.

References

[1] K. Fujii, N. Shikazono, A. Yokoya, J. Phys. Chem. B **113**, 16007 (2009).
[2] A. Narita, K. Fujii, A. Yokoya, Y. Baba, I. Shimoyama, *Photon Factory Activity Report* 2013 **#31** (2014) B.

* a-narita@aist.go.jp