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## XPS Spectral Simulation of Chitosan in Thermal Decomposition Process

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We simulated XPS spectra of chitosan in thermal decomposition process. The simulation of thermal decomposition for chitosan has been performed by a quantum molecular dynamics {QMD (molecular dynamics with semiempirical MO methods)} using the model dimer molecules. In the MD calculation, we controlled the N ose-Hoover thermostats in the thermal energy range of 0.6 ~ 1.0 eV, and the sampling position data at a time step of 0.5 fs were evaluated up to 5000 steps with semiempirical MO method. The valence photoelectron spectra of chitosan dimer were simulated at initial, 1000, 2000, 3000, 4000, and 5000 MD steps in the energy range of 0.69, 0.78, and 0.86 eV by Amsterdam density functional (ADF) program.

### 1. Introduction

Chitosan is especially known as a most powerful adsorbent of natural origin and it widely used for the prevention of water pollution by highly toxic chlorinated aromatic compounds and metal ions [1]. Chitosan is inexpensive, environmentally benign, harmless to humans, and a hugely obtainable biomass which makes it very promising and attracting for use in many applications. Then, we think that ion beam irradiation is a useful method for modification of surface properties, such as wear resistance, corrosion resistance and biocompatibility for the biopolymers. Thus, we demonstrated that Kr<sup>+</sup> ion irradiation or bombardment is applied to the surface modification of chitosan.

We already described chitosan for study of C-13 NMR and X-ray photoelectron spectra (XPS) to clarify the electronic structure in the formation of properties of biological molecule, and to understand the changes in adsorption behavior of chemically modified biopolymer chitosan (crosslinked biopolymer) [2].

In the present study, we aim to analyze the valence XPS of chitosan with Kr<sup>+</sup> ion beam irradiation. In order to simulate the experimental valence electron spectra of the chitosan due to the ion irradiation effects, we calculated the thermal decomposition process

of chitosan dimer using the molecular dynamics with MO method, and simulated the valence spectra of the fragment results at 1000, 3000 and 5000 MD steps in the thermal composed process using Amsterdam density-functional (ADF) program [3].

### 2. Computational Method

#### (1) MD Calculation with MO method

The thermal decomposition of chitosan was simulated using the dimer model by QMD with semiempirical AM1 MO method [4]. Geometry and energy optimized results of the dimer by MO calculations were used as the initial MD step of QMD calculations. The thermal energy was controlled with the N ose-Hoover thermostats [5, 6] and the sampling position data were carried out up to 2.5 ps (5000 steps). The equations of nuclear motions were integrated using 5-values Gear method [7] as a predictor-corrector algorithm [8] with a time step of 0.5 fs.

#### (2) Valence Electron Spectra Simulation at the MD steps

In order to obtain the accurate vertical ionization potentials (VIPs) in the valence region, we use statistical averaging of orbital potentials (SAOP) [9] in ADF program. The SAOP method reproduces a Kohn-Sham exchange-correlation potential which includes

the orbital dependent Krieger-Li-lafrate (KLI) response potential [10] as the orbital relaxation effect. For VIP values, we calculated the ground state of the molecule using the TZP bases for C, O, N and H atoms in the SAOP. The intensity of valence XPS was estimated from the relative photo-ionization cross section for Mg  $K\alpha$  radiation using the Gelius intensity model [11]. For the relative atomic photo-ionization cross-section, we used the theoretical values from Yeh [12].

### 3. Experimental

We used commercially available chitosan (Wako Chemical co., Inc). Kr-ion bombardment was carried out at energy of 150 keV with fluences of  $1.0 \times 10^{15}$  ions  $\text{cm}^{-2}$  in the base pressure of less than  $4.0 \times 10^{-4}$  Pa at room temperature using a RIKEN 200 kV low current implanter. The beam current density used was about  $0.2 \mu\text{A cm}^{-2}$  to prevent the specimen from heating. Experimental photoelectron spectra of the samples were obtained on a JEOL JPS-9010 MC spectrometer using Mg- $K\alpha$  (1253.6 eV) radiation. The applied power was operated at 15 kV, and 20 mA. The base pressure of the analysis chamber was less than  $8.0 \times 10^{-7}$  Pa. Energy scale calibration was achieved using the Au  $4f_{7/2}$  (83.8 eV) transition. Dispersion compensation yielded an instrumental

resolution of 0.5 eV from full width at half-maximum for the Ag3d line of silver. Multiscan averaging on a multichannel analyzer was used for the valence band region, although a very low photoelectron emission cross-section was observed in this range.

### 4. Results and Discussion

With Kr ion-bombardment the energy loss to the chitosan is considered to be due to inelastic collision, since the Kr-ion is an inert gas element. We, then, think thermal effects may be more important. We, thus, calculate the thermal decomposition process of chitosan dimers to simulate valence XPS of chitosan due to  $\text{Kr}^+$  irradiation effects.

(1) Fragments of the chitosan model at MD steps by QMD calculation

We simulated the thermal decomposition process of chitosan dimer molecule by QMD program. The Nose-Hoover thermostat for the dimer was controlled in the energy range of 0.69, 0.78, and 0.86 eV and the sampling position data with a time step of 0.5 fs were carried out up to 5000 steps. As an example of data for chitosan dimer, Fig. 1 shows the thermal decomposed data of the dimer model at the initial, 1000, 3000, and 5000 MD steps with 0.78 eV energy control. It can be seen from the figure that the smaller fragments exist with the increasing sampling data steps in Table 1

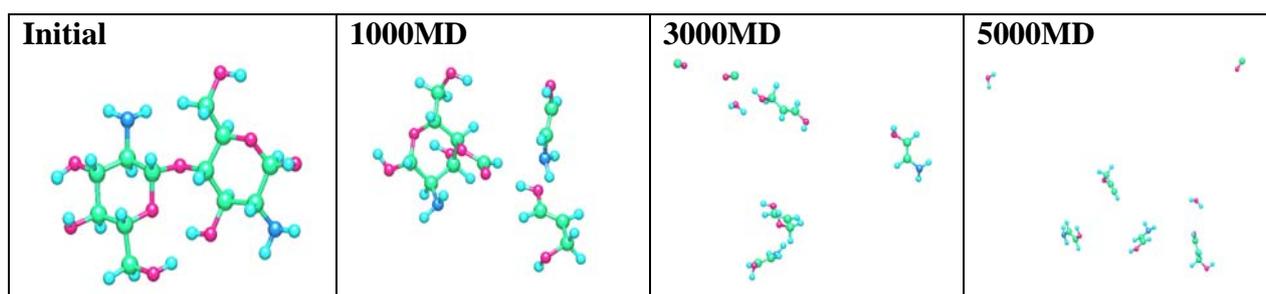


Fig. 1. MD snap shots of chitosan dimer in the energy range of 0.78 eV.

Table 1. Fragments of dimers at each MD in energy of 0.78 eV

1000 MD	3000 MD	5000 MD
$\text{C}_7\text{O}_6\text{NH}_{13}$	$2\text{C}_3\text{O}_2\text{H}_6$	$\text{C}_3\text{O}_2\text{H}_6$
$\text{C}_3\text{O}_2\text{H}_6$	$2\text{C}_2\text{ONH}_5$	$\text{C}_3\text{OH}_4$
$\text{C}_2\text{ONH}_5$	$2\text{CO}$	$2\text{C}_2\text{ONH}_5$
	$\text{H}_2\text{O}$	$2\text{CO}$
		$2\text{H}_2\text{O}$

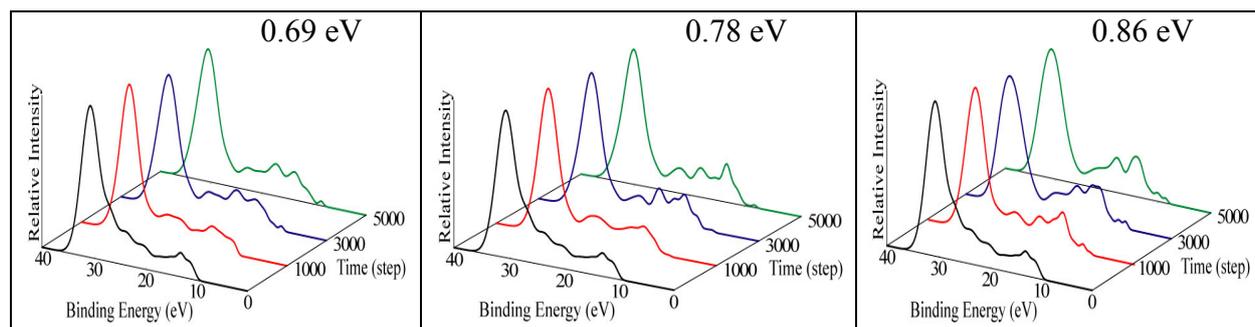


Fig. 2. Valence XPS in each MD step in the energy range of 0.69, 0.78 and 0.86 eV.

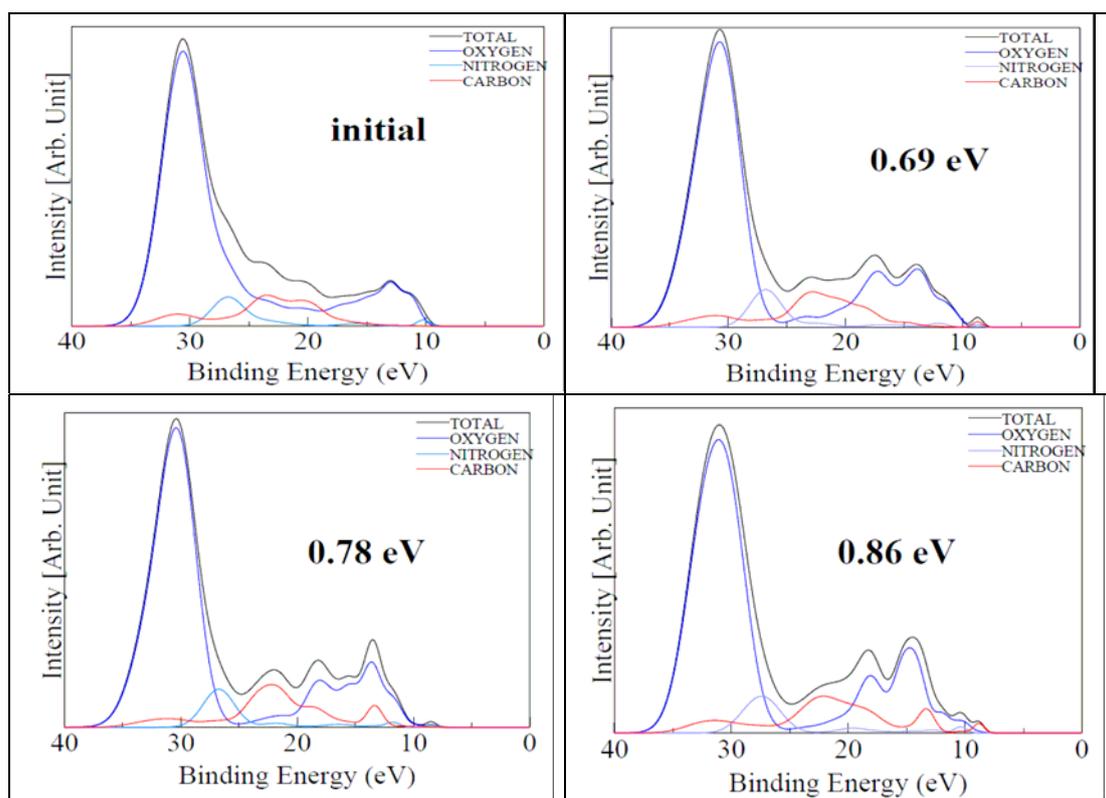


Fig. 3. Each atom contribution for valence XPS at 5000 MD in energy ranges of 0.69,0.78, and 0.86 eV

Table 2. AO, orbital nature of VXPS at 5000 step in 0.78 eV

VIP (eV)	AO Contribution	Orbital nature
32.8-29.8	O2s	$s\sigma(\text{O}2s\text{-C}2s)$
26.8-26.7	N2s	$s\sigma(\text{C}2s\text{-N}2s)$
23.5-18.3	C2s	$s\sigma(\text{C}2s\text{-C}2s)$
	O2s	$s\sigma(\text{C}2s\text{-O}2s)$
	O2p	$p\sigma(\text{C}2s\text{-O}2p)$
13.3-12.3	C2s	$s\sigma(\text{C}2s\text{-O}2s)$
	O2s	$p\pi(\text{C}2p\text{-O}2p)$
	O2p	$p\pi(\text{Lone Pair})$
11.9-11.8	O2p	$p\pi(\text{Lone Pair})$

## (2) Simulated valence X-ray electron spectra at the MD steps

We considered thermal decomposition process of the chitosan dimer using the molecular dynamics with MO method, in order to simulate the experimental valence electron spectra of the biopolymer due to the Kr ion irradiation effects. We, then, simulated the valence spectra of all fragment results at initial, 1000, 3000 and 5000 MD steps in the thermal composed process in the energy range of 0.69, 0.78, and 0.86 eV using Amsterdam density-functional (ADF) program in Fig. 2. Fig. 3 shows valence electron spectra with the photoelectron contributions of C, N, and O atoms at 5000 MD step in energy dependency of thermal decomposition. From the spectra in Figs. 2 and 3, we can see that the larger are the decomposition energies and the MD step, the more become the decomposed fragments of chitosan dimers. For the decomposed energy of 0.78 eV, valence photoelectron spectra in Fig. 2 and 3 reflect the smaller fragments in Table 1. The smaller fragments of gas molecules (CO

and H<sub>2</sub>O) indicate the p- $\pi$  bonding (lone-pairs) contributions of the spectra in the energy range of 10-15 eV.

(3) Analysis of experimental valence spectra due to Kr<sup>+</sup> ion irradiation

For the comparison between the calculated electron spectra for dimer model and experimental spectra of chitosan, we must shift each computed VIP( $I'_k$ ) by a quantity  $WD$  as  $I_k$  ( $= I'_k - WD$ ), to convert to VIP( $I_k$ ) relative to the Fermi level [13, 14]. Then, the simulated valence spectra after 4.2 eV shift as the  $WD$  value were shown with experiment ones in the initial state and due to the Kr<sup>+</sup> ion irradiation in Fig. 4. For simulated spectrum at 5000 MD step of 0.78 eV, we omitted contributions of H<sub>2</sub>O and CO, because the gases were excluded in the experimental vacuum apparatus. The simulation results correspond well to the observed ones. It, thus, indicates that H<sub>2</sub>O and CO are eliminated due to dissociation of chitosan on the most surface layer with the Kr<sup>+</sup> ion irradiation.

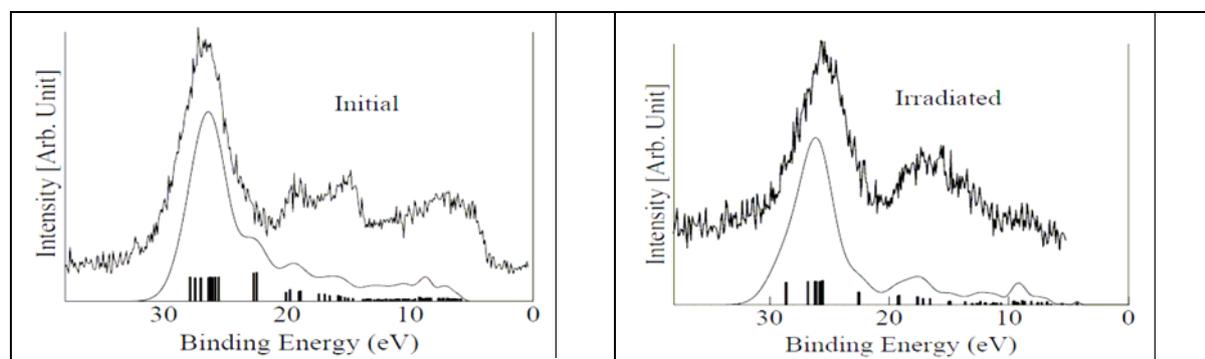


Fig. 4. Simulated valence electron spectra with observed ones.

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