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Study of molecular structure change of D- and L-glucose by proton irradiation using terahertz spectroscopy

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ABSTRACT

We investigated molecular structure change of D- and L-glucose by proton beam irradiation of 7.8 MeV, using terahertz time-domain spectroscopy. Both glucose pellets exposed to the irradiation of 10^{13}, 4×10^{13}, 6×10^{13}, and 8×10^{13} particles/cm^2 of the particle's fluence, were characterized using complex refractive indices in terahertz frequency region. We found that fingerprints of two types of glucose in terahertz frequency were disappeared above 8×10^{13} particles/cm^2. Crystallinity breaking and molecular structure change by proton irradiation was reaffirmed using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.

1. Introduction

Proton beam technology using accelerated protons of the hydrogen nucleus have attracted attention to improve quality of plant seeds and to develop new materials as well as a next-generation cancer therapy. The Bragg peak effect, a characteristic of the proton beam, allows the energy of the proton beam to be focused at a certain depth, rather than the radiant energy passing through the material, such as X-rays. This property allows the effect of the proton beam to reach only the target area, such as tumor, minimizing side effects by the radiation on surrounding normal tissue. In order to enhance the performance of the proton beam technology, it is necessary to study the structural change at the molecular level of the biomaterials by the strong proton beam irradiation. However, there is a severe lack of fundamental studies of such materials at molecular or atomic level, behind incredible growth of the proton beam technology. Recently, some handful studies have been implemented and focused on proton beam responses for several important molecules such as glucose and glutamine, which are very important in the metabolism of foods [1–3]. Glucose is, in particular, not only the most significant ingredient of food but also inevitable material to maintain the life as metabolite for photosynthesis and respiration. The glucose, molecular formula of $C_6H_{12}O_6$, can be structured in a chain form (Fig. 1(a)) or a ring form (Fig. 1(b)) and has its mirror-image structure, enantiomers such as D-glucose (Fig. 1(a), (b)) and L-glucose (Fig. 1(c)) [4]. D-glucose, monosaccharide which composes sugar, starch, and oligosaccharid plays important role as an energy source and a substance of organism. It is typically utilized for making ATP during glycolysis and electron transport system in mitochondria. While D-glucose is widely distributed in nature, however, its enantiomer, L-glucose has to be synthesized artificially [5]. These isomers have same physical and chemical properties but different optical properties. Using Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy, they can be distinguished each other, and also terahertz time domain spectroscopy (THz-TDS) can establish their differences in terms of both absorption coefficient and refractive index [6,7]. Especially, Terahertz wave, the electromagnetic wave that is laid between 0.1 and 10 THz (1 THz = 10^{12} Hz) in frequency domain and has 3 mm–30 μm wavelength, includes intra-molecular vibration mode such as weak hydrogen bonding of biomaterials [8,9]. THz spectroscopy thus allows to observe the structural difference of polymorphism and hydrogen state as well as quantitative measurement according to concentration of amino acid, avoiding any damage of the target sample due to its low energy (several meV), contrary to X-ray and ultraviolet [10–12]. Particularly, THz-TDS using the THz pulse makes it possible that complex optical constants are obtained directly without complicated data processing such as Kramer-Kronig relation used in FTIR

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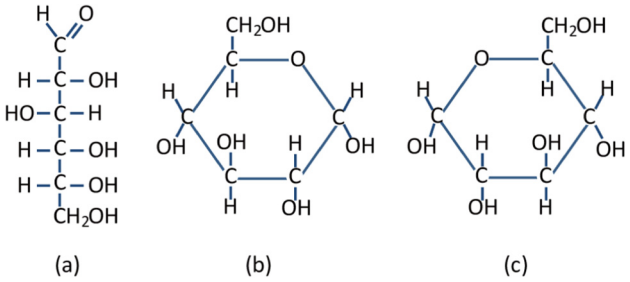

Fig. 1. Molecular structure of (a) open chain D-glucose, (b) ring form D-glucose, and (c) ring form L-glucose.

spectroscopy to extract them. In this report, we have observed the change of intra-molecular structures of D- and L-glucose before and after irradiation of proton beam with several dose using THz-TDS. THz-TDS results have been compared with X-ray diffraction (XRD) and FTIR spectroscopy results representing the change of crystallinity and molecular structure respectively.

2. Materials and methods

To perform the proton beam irradiation and THz spectroscopy experiments in transmission, D-glucose, L-glucose and high density polyethylene (HDPE) were prepared in pellet form. All samples were purchased as powder from Sigma Aldrich Co., then, prepared as pellet form. To make pellets, D- and L-glucose pellet samples were mixed at a ratio of 1:1 with HDPE which has low absorbance in THz frequency and compressed by oil hydraulic equipment with a pressure of 140 kg/cm^2 for 5 min. Pellet dimension is 8 mm in diameter and 650 μm in height. The sample was put in aluminum case with 1.5 mm thickness cover to irradiate proton beam. We used MC-50 cyclotron at Korea institute of radiological and medical science (KIRAMS). The irradiation was performed under current of 10nA and energy of 7.8 MeV. The particle fluence was 10^{13}, 4×10^{13}, 6×10^{13}, 8×10^{13} particles/cm^2 corresponded with irradiation time 102, 407, 611, 814, 1018 s, respectively.

The samples were measured by THz-TDS, X-ray diffraction (XRD), and FTIR. We use the TAS 7500SU at Advantest Co. for THz-TDS. Its frequency waveforms were from 0.5 to 7 THz with the frequency resolution of 7.6 GHz and dynamic range of 57 dB. XRD experiments were conducted using DMAX-2500 of Rigaku Co. in Korea institute of science and technology (KIST). The X-ray generator was 40 kV and 150 mA (6 kW) and source type was CuKα1 with the wavelength 1.5406 Å. Spectrum Two FTIR Spectroscopy from PerkinElmer Co. was utilized for FTIR spectroscopy in ATR mode. We scanned 400–4000 cm^{-1} region with the resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Optical properties of D-glucose and L-glucose in THz frequency range

The absorption coefficients and refractive indices of D-glucose, L-glucose and HDPE in the THz frequency range before irradiation of proton beam were shown in Fig. 2. While D-glucose has absorption peaks at 1.43, 2.08, 2.54, 2.66, 2.94, 3.33, and 3.77 THz, L-glucose has its peaks at 1.43, 2.09, 2.51, 2.67, 2.94, 3.35, and 3.77 THz. Absorption peaks of D-glucose are somewhat higher than those of L-glucose except 2.08, 2.94 THz. Refractive indices of L-glucose are higher than D-glucose in overall range. Whereas D-glucose has inflection points at 1.43, 2.08, 2.55, 2.67, 2.94, 3.34, and 3.75 THz, L-glucose has its inflection points at 1.43, 2.07, 2.55, 2.67, 2.94, 3.34, and 3.75 THz. These results are agreed with the previous data [7,13,14]. These observed absorption features can be accounted for intermolecular vibrational modes of the samples, dependent on the degree of crystallinity. HDPE which is used as control sample and buffer of glucose pellet has a refractive index of

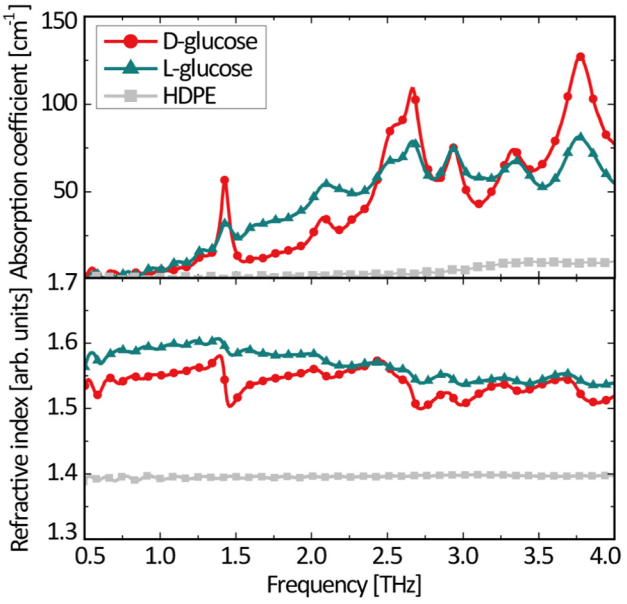

Fig. 2. The absorption coefficient and the refractive index of D-glucose, L-glucose and HDPE before proton beam irradiation.

1.39 and its slope is almost flat. HDPE is, consequently, almost transparent in the THz frequency even though its absorption coefficient was 10.2 cm^{-1} around 4 THz.

3.2. The structural changes of D-glucose and L-glucose in THz frequency range by proton beam

Fig. 3 shows photographs of D-glucose, L-glucose and HDPE pellets after proton beam irradiation. Target samples were irradiated by proton beam under various particle fluence of 10^{13}, 4×10^{13}, 6×10^{13}, and 8×10^{13} particles/cm^2, respectively. As the particle fluence of the proton beam increases, the color of pellet becomes darker except HDPE. Since the melting points of D- and L-glucose are known as 150–152 °C and 153–156 °C, somewhat higher than that of HDPE of 144 °C, it is inferred from that that the color changes for both glucose are caused by the molecular structure change rather than melting process.

Absorption coefficients and refractive indices of D- and L-glucose pellets after proton beam irradiation are shown in Fig. 4. The absorption peaks of D- and L-glucose gradually diminished as the particle fluence of proton increased and the peaks disappeared completely when particle fluence was raised to 8×10^{13} particles/cm^2. It showed the irradiation of proton beam changes the molecular structure of glucoses, associated with the broken crystallinity. This result is similar to the previous study in Ref. [14] which showed that when crystalline glucose became amorphous, certain absorption peaks decrease [14].

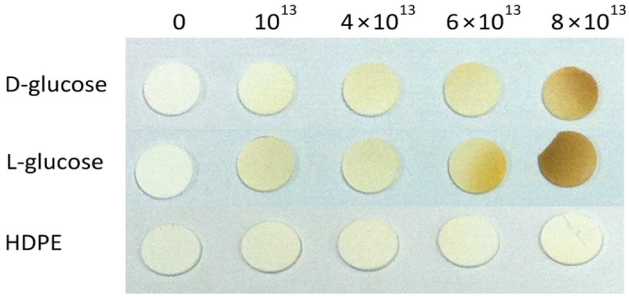

Fig. 3. Photograph images of D-glucose, L-glucose, and HDPE pellets. Particle fluence condition of the proton beam is 0, 10^{13}, 4×10^{13}, 6×10^{13}, 8×10^{13} particles/cm2 from left.

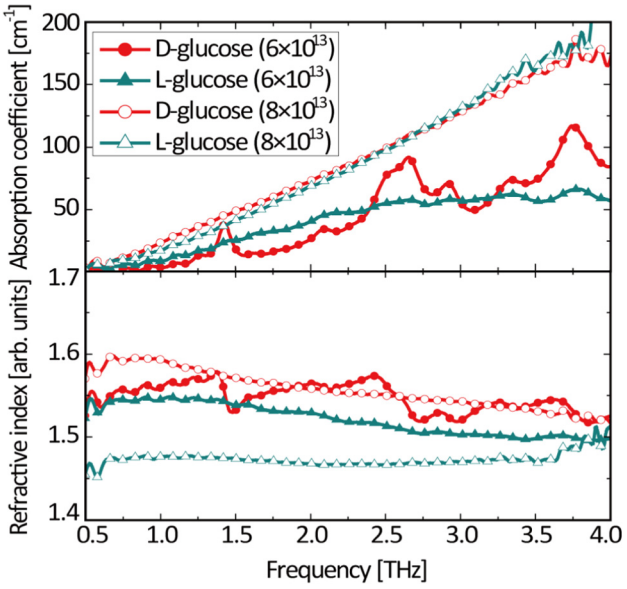

Fig. 4. Absorption coefficients and refractive indices of D-glucose, L-glucose after proton beam irradiation.

3.3. The XRD analysis of D-glucose and L-glucose irradiated by proton beam

To confirm the crystallinity breaking of glucose after proton beam irradiation, the XRD analysis was conducted. Fig. 5(a) and (b) showed each XRD pattern of D-glucose and L-glucose before and after irradiation. When the particle fluence increased from 6×10^{13} to 8×10^{13} particles/cm^2, several peaks in both glucoses disappeared and the XRD spectrums of both glucoses became like that of HDPE under same irradiation dose. Comparing with the XRD patterns of glucose and HDPE, the results reconfirmed the results of the broken crystallinity of glucose by proton beam irradiation.

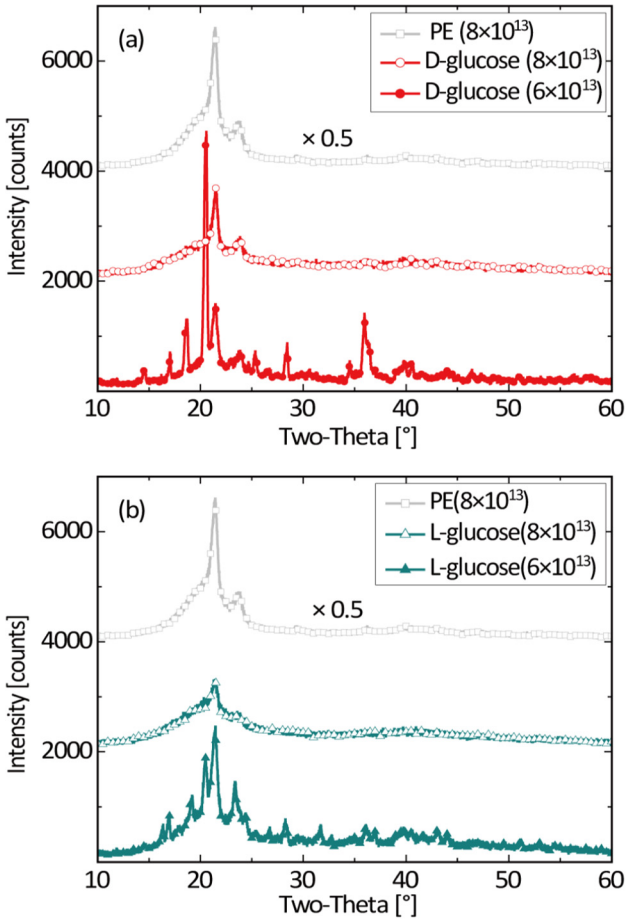

Fig. 5. XRD spectrums of (a) D-glucose, (b) L-glucose and HDPE after proton irradiation.

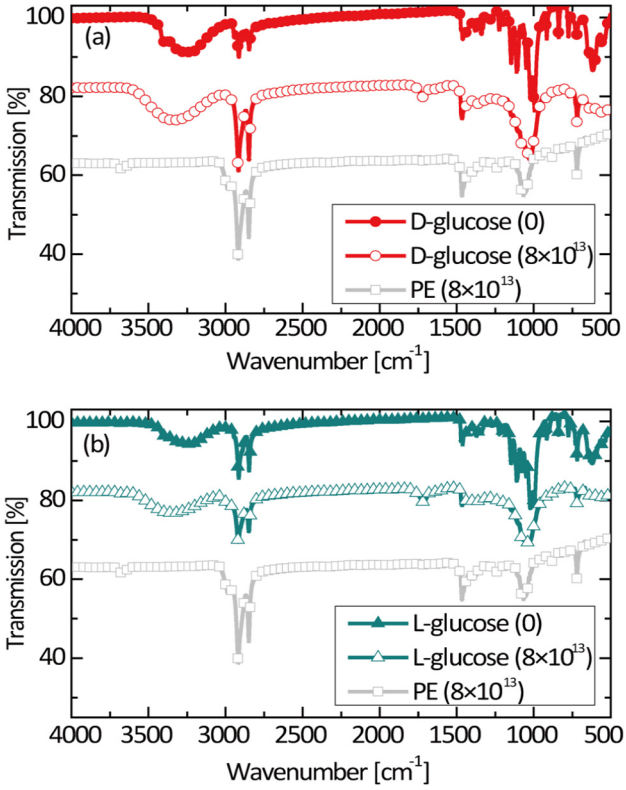

Fig. 6. FTIR spectrum of (a) D-glucose, (b) L-glucose and HDPE before and after proton beam irradiation.

3.4. The FTIR analysis of D- and L-glucose irradiated by proton beam

FTIR spectroscopy was also used to analyze the molecular structure based on the binding energy. Fig. 6 showed the FTIR spectrum of (a) D-glucose and (b) L-glucose before and after proton beam irradiation of 8×10^{13} particles/cm^2. Our FTIR spectrum of D-glucose without proton beam irradiation is similar with the previously published result of Ref. [15] Without proton beam irradiation on both glucoses, the vibration modes of C—O and C—C groups which were represented in 1500–600 cm^{-1} region and the stretching vibration of OH lies in the 3500–3000 cm^{-1} region were shown by the solid triangle line in Fig. 6 [15]. After proton beam irradiation, the considerable peaks in the 1500–600 cm^{-1} region lessened or completely vanished and the vibration modes in the 3500–3000 cm^{-1} was broadened and slightly blue shifted to 3600–3000 cm^{-1}. It implied that C—O and C—C binding would be messy and broken and the binding energy relevant with OH could be increased after proton irradiation. Furthermore, we found that the new peaks appeared in 1745–1690 cm^{-1} in both of glucose samples, which is associated with C═O stretching vibration. These results implied that the ring form of glucose (Fig. 1(b)) were not only fragmented but also transformed into its chain form (Fig. 1(a)) or some materials including C═O stretching vibration by the proton beam irradiation.

4. Conclusions

We investigated the structural changes on two types of glucose by the strong proton beam using THz TDS, XRD, and FTIR spectroscopy. THz spectrum shows directly the intermolecular changes of glucoses by proton beam irradiation. Under the same energy condition of 7.8 MeV, as particle fluence of proton beam gradually increased, the absorption peaks and inflection points of refraction were decreasing and disappeared at certain condition of 8×10^{13} particles/cm^2. It was confirmed that such intermolecular changes were caused by the crystallinity breaking by proton irradiation, confirmed by XRD analysis and FTIR spectroscopy. By checking the changes of functional group and molecular structure using two additional experiments, finally, we concluded that 8×10^{13} particles/cm^2 of proton beam could induce the chain form glucose or the materials with C═O stretching vibration break.

Declaration of interest

There is no conflict of interest to declare.

Acknowledgments

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