Micro-processing of fiber-type biomaterials by using infrared free electron laser

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Cellulose is a biopolymer that is polymerized via β1-4 glucoside bonds, and the cellulose fibers can be used as functional biomaterials. Furthermore, cellulose is most biomass in the earth and its degradation product, glucose, is used for the bioethanol production. Therefore, the processing technology of the cellulose polymers will be expected to lead to generation of novel functions of materials and sustainable system for the next-generation energy society. We propose here a novel physical approach using infrared free electron laser (IR-FEL) for the laser processing of the cellulose fiber materials.

The IR-FEL is a synchrotron-radiation based wavelength-variable laser from 3 to 100 μm and has pico-seconds pulse structure. The laser power is ranged from 1 to 10 mJ, and the beam diameter was set to about 100 μm above the sample surface by using focused lens. The cellulose fibril (10 mg) was irradiated in a glass tube by the IR-FEL for 10 min at room temperature. After those irradiations, each soluble fraction was subjected to electron-spray ionization mass spectroscopy (ESI-MS) and synchrotron-radiation infrared microscopy (BL15 beam line).

The MS profile measurement showed the fragmentation of mass peaks was observed after the IR-FEL irradiation tuned to 3.5 μm (νC-H), 7.2 μm (δH-C-O), and 9.1 μm (νC-O) compared to the non-irradiation sample (**Fig. 2**). From the mass chromatogram analysis, two mass peaks from glucose and cellobiose were observed after those irradiations. In case of irradiation at 3.0 μm (νO-H), no mass peak of glucose was observed, which indicates that the excitation of O-H bonds is not effective for the release of glucose. Synchrotron-radiation based infrared microscopy analysis revealed that absorption intensity around 1061 cm^{-1} that resonates with C-O stretch vibrational mode was decreased and the band width at 3400 cm^{-1} was shortened after the irradiations at 9.1 μm, 9.1 μm following 7.2 μm and 3.5 μm. These spectral changes indicated the cleavage of the glucoside bonds in the cellulose aggregated. The above all data demonstrated that the glucoside-bond selective irradiation by the IR-FEL can take out glucose unit from the cellulose fibril.

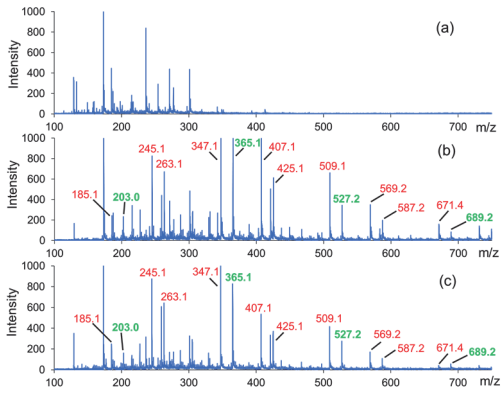

Fig. 1. ESI-MS profiles of non-irradiation (a), after serial irradiation at 9.1 following 7.2 μm (b), and after serial irradiation at 9.1 following 3.5 μm (c). Green characters mean mono-, di-, tri-, and tetra-saccharides, in descending order.

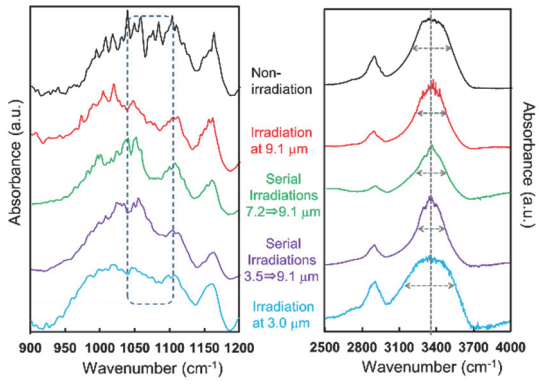

Fig. 2 SR-IRM spectra of cellulose aggregate before the laser irradiation (black) and after the irradiation at 9.1 μm (red), 9.1 μm following 7.2 μm (green), 9.1 μm following 3.5 μm (violet), and 3.0 μm (blue). Double-headed arrow: the half width of the infrared absorption peak.

References

(1) T. Kawasaki, T. Sakai, H. Zen, Y. Sumitomo, K. Nogami, K. Hayakawa, T. Yaji, T. Ohta, K. Tsukiyama, and Y. Hayakawa, *Energy & Fuels*, May 8, **2020**.