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Chemical reaction of unsaturated fatty acid induced by atmospheric-pressure plasma
大気圧低温プラズマを照射した不飽和脂肪酸の反応について

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Atmospheric-pressure plasma has been used for attractive applications, for example, in sterilization and polymerization, but the effect of the plasma on organic materials is not clear enough. We have investigated oxidation reaction of linoleic acid, one of unsaturated fatty acids by the atmospheric-pressure plasma jet. Formation of malondialdehyde (MDA) through oxidation of linoleic acid was observed in helium and oxygen mixed atmosphere. We suppose that some active oxygen species produced by the plasma jet oxidize unsaturated fatty acid if oxygen is included in atmosphere.

1. Introduction

Recently, technologies of atmospheric-pressure nonthermal plasma have been developed intensively and its applications attract remarkable attention. Atmospheric-pressure plasma can produce valuable chemically active species, and this type of plasma is desirably applied to soft materials like polymeric biomaterial and human body as medical device [1].

It is required to clarify the effect of atmospheric-pressure plasma on organic materials. In this study, we focus on lipid as one of biomacromolecules. Unsaturated fatty acid in lipid is oxidized to lipid peroxide by some oxidant stress. After successive decomposition reactions of lipid peroxide, malondialdehyde (MDA) is formed. Ohkawa *et al.* reported that thiobarbituric acid (TBA) reacted with MDA and produced red pigment [2]. The amount of red pigment, i.e. optical absorbance at 532 nm is an indicator of oxidation degree of unsaturated fatty acid.

In this experiment, the plasma jet was exposed to linoleic acid, one of unsaturated fatty acids in the atmospheric-controlled chamber to investigate oxidation reaction by TBA tests.

2. Experimental Setup and Methods

A schematic view and a photograph of the plasma jet and the chamber are shown in Fig. 1. A glass tube on the top of the chamber was used for a supply of helium gas. Two ambient gases in the chamber were tested. In helium and oxygen mixed (He + O_2) atmosphere, oxygen gas was supplied from the side port of the chamber and the other port was used for exhaust, as shown with red arrows in Fig. 1-a. In pure helium atmosphere, both side ports were used for exhaust (blue arrows in Fig. 1-a). The flow rates were controlled with mass flow controllers (KOFLOC, 8500MC); 3 L/min for helium and 0.5 L/min for oxygen.

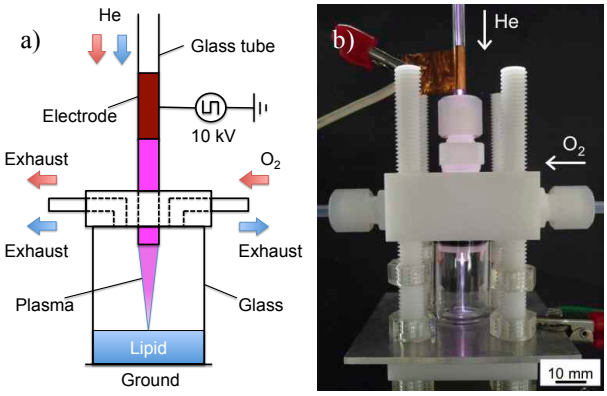

Fig. 1 A schematic view (a) and a photograph (b) of the atmospheric-pressure plasma jet and the chamber. Gas flows are indicated with red arrows for He + O_2 mixed atmosphere and blue arrows for pure He atmosphere.

The chamber was composed of a glass cup sealed by O-ring. After purging the ambient gas

in the chamber with the gas flows for 3 min, the plasma jet was exposed to 500 µL of linoleic acid in the cup. High voltage (~10 kV) with low frequency (~10 kHz) was applied to the single-sided electrode [3].

In preparation of TBA test, the following five solutions were mixed with 50.0 µL of each linoleic acid sample; (1) 400 µL of 2 mM ethylenediaminetetraacetic acid (EDTA) aqueous solution, (2) 100 µL of 8.1% sodium dodecyl sulfate (SDS) aqueous solution, (3) 750 µL of 0.1 M acetic acid solution, (4) 750 µL of 0.8% TBA aqueous solution, and (5) 25.0 µL of 0.8% dibutylhydroxytoluene (BHT) acetic acid solution. The mixed solutions were heated at 95˚C for 60 min and cooled with ice. After 500 µL of water and 2.50 mL of *n*-butanol:pyridine (15:1, v/v) were added to the solutions, they were centrifuged at 3000 rpm for 10 min. The organic phase extracted from the solutions was measured with UV-VIS spectrophotometer (JASCO, V-630). In oxidation of unsaturated fatty acid, not only MDA but also other aldehydes are released. Other aldehydes have an influence on TBA tests because the reaction is promoted with a small amount of iron ions [4]. EDTA solution inhibits the reaction aldehydes with TBA, so EDTA was used in this study to evaluate the amount of MDA, i.e. to investigate oxidation degree of linoleic acid.

3. Results and Discussion

Absorbance spectra of the red pigment in the linoleic acid exposed by the plasma jet in helium and oxygen mixed (He + O_2) atmosphere increase with the exposure time of the plasma in Fig. 2. As shown in Fig. 3, absorbance at 532 nm changes with the exposure time in the plasma with and without O_2 mixture. According to literature [2], oxidation degree is evaluated from absorbance at 532 nm. In Fig. 3, absorbance at 532 nm in He + O_2 atmosphere increased with the exposure time, while there was little change in absorbance in pure He atmosphere.

Since the plasma jet oxidizes unsaturated fatty acid and produces MDA in He + O_2 atmosphere, but the plasma jet does not oxidize unsaturated fatty acid in pure He atmosphere, unsaturated fatty acid is oxidized effectively by some active oxygen species with the plasma jet exposure. Therefore, it is supposed that lipid which is mainly consisted of unsaturated fatty acid should be oxidized by the plasma jet if oxygen is included in atmosphere.

4. Conclusion

Investigation on the oxidation reaction of linoleic acid exposed by the plasma jet indicates that oxidation reaction is promoted in unsaturated fatty acid with active oxygen species by plasma-induced chemical reaction in liquid if oxygen is in ambient atmosphere.

Finally, affect of plasma irradiation to human for hemostasis, disinfection, wound healing etc. in the research area of plasma medicine should be evaluated for the optimization of positive effect and the safety of negative effect. It is important subject to figure out the reaction of plasmas to biomolecules considering plasma-induced chemical processing in solution.

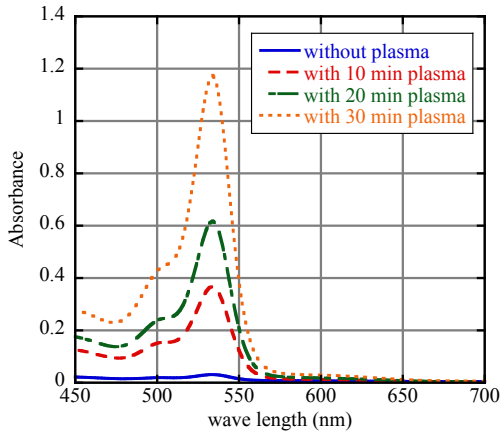

Fig. 2 Absorbance spectra of red pigment produced by reaction of the linoleic acid samples with TBA. The linoleic acid was exposed by the atmospheric-pressure plasma jet in helium and oxygen mixed (He + O_2) atmosphere.

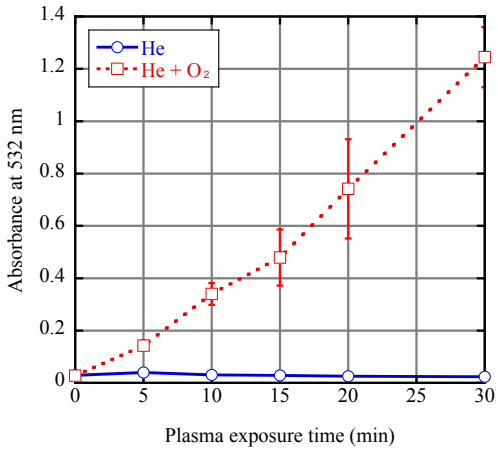

Fig.3 Changes of absorbance at 532 nm in the exposure time of the plasma jet (n = 3).

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