Visualization of the Two-dimensional Distribution of ROS Supplied to a Water-containing Target by a Non-thermal Plasma Jet

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Abstract—The supply mechanisms of reactive oxygen species (ROS) to a water-containing target by a plasma jet should be clarified. In this study, we investigated the two-dimensional distribution of ROS supplied to the target by a plasma jet using a gel reagent with iodine-starch reactions in atmospheric air and determined the effects of the irradiation distance and the addition of O₂ to He on the ROS distribution. Relative ROS concentration distributions were also obtained from visualized distributions by measuring the absorbance. In the He plasma jet, we clearly observed a doughnut-shaped ROS distribution on the target under certain conditions. The efficiency or local ROS supply to the target could be controlled by adjusting the irradiation distance. The results also indicated that short-lived species generated at the contact point between the He plasma jet and the target primarily supplied the ROS to the target. In contrast, in the O₂/He plasma jet, results indicated that the ROS distribution was influenced by the synergistic effect of long-lived species, for example O₃ generated in the gas phase over the target, along with the short-lived species.

Keywords—Atmospheric pressure non-thermal plasma jet, ROS distribution, gel reagent, plasma medicine

I. INTRODUCTION

The atmospheric pressure plasma jet has attracted increasing interest all over the world because of its special physical and chemical features [1]. It is well known that a plasma bullet is intermittently generated at the main discharge area of the plasma jet and it travels along the gas flow at high speed in atmospheric air [2]. To the human eye, many plasma bullets look like a plume. Therefore, the phrase “plasma plume” is often used [3]. In this study, a plasma jet is defined as a visible plasma plume. Various types of plasma jets have been developed and are expected to be applied in a wide range of fields. Recently, plasma jets have been actively studied and developed for biomedical applications because they can be directly irradiated to water-containing targets such as the human body and biological tissue in atmospheric air [3]–[9]. However, there are many questions regarding the interactions between plasma jets and targets such as these, where it is said that reactive oxygen and nitrogen species (ROS and RNS) play important roles [10]–[12]. In biomedical applications particularly, the ROS supply to water-containing targets by a plasma jet in atmospheric air is understood to be very important. However, we have no detailed understanding of its mechanisms currently.

In the gas phase, the spatiotemporal distribution of various active species has been studied using mainly optical measurements, e.g. spectroscopic analysis for excited species [8], [13]–[20], laser-induced fluorescence (LIF) for hydroxyl radicals (OH) [20]–[22] and ionized nitrogen molecules (N₂⁺) [19], two-photon absorption LIF for atomic oxygen (O) [15], [22]–[25], laser ablation spectroscopy for metastable helium atoms (He*) [19], mass spectrometry for ions [26], [27], UV absorption for O₃ [28], [29] and Thomson scattering for electrons (e) [30]. Simulations have also been performed to study dominant chemical species and reactions that play significant roles in the gas phase [25], [29], [31]–[34]. As mentioned above, there have been many reports on the gas phase. However, it seems that no group has addressed the ROS distribution on a target irradiated by a plasma jet, although there have been a few reports about this with respect to the area very near to the target surface [22].

Our group has used a gel reagent with iodine-starch reactions as a plasma-generated ROS detection method. Until now, the relative concentration distribution of the ROS supplied to the target in atmospheric air [35], [36] or in water [37] has been reported using this gel reagent. If the gel reagent comes in contact with the ROS, color reactions are induced at the contact point. These color reactions are caused by the oxidation of an iodine ion (I⁻) to molecular iodine (I₂) by the ROS. Furthermore, the relative ROS concentration distribution can also be obtained by measuring the absorbance of the color reactions, because the color of the gel reagent turns from translucent to blue when induced by the ROS. This gel reagent has been used to visualize the three-dimensional dose distribution of radioactive rays in the development of radiation therapy [38]; in this case, radiation-induced oxidation was detected. Iodine-starch reactions have also been used for the detection of the oxidation of I⁻ by the ultrasound sonochemical reaction [39].

In this study, we used the gel reagent with iodine-starch reactions as a water-containing target of a plasma jet in atmospheric air. The two-dimensional ROS distribution patterns could thus be visualized using the gel reagent. The effects of irradiation distance and the addition of O₂ to He on the ROS distribution and the relative ROS concentration distribution are reported here.
II. EXPERIMENTAL SETUP

Fig. 1 shows a schematic of the experimental setup. The plasma jet generator was made of a glass tube (Pyrex) with wrapped powered and grounded electrodes (width: 13 mm) separated by 20 mm on the tube. The outer and inner diameters (O.D. and I.D.) of the glass tube were 8 mm and 2.5 mm, respectively. A powered electrode was located 10 mm from the open end of the glass tube. He gas having 99.995% purity with and without 0.5% O₂ was supplied into the glass tube at a flow rate of 5.6 L/min. The plasma jet was generated at a high sinusoidal voltage of 16 kVp-p (3 kHz) using a function generator (Iwatsu, SG-4105) and an amplifier (Trek, 20/20C), and was irradiated to the target for 10 s. We varied the irradiation distance between the tip of the glass tube and the target from 5 mm to 50 mm.

The gel reagent for detecting the ROS was prepared prior to being used to serve as the target of the plasma jet in this study. The reagent contains 0.3% potassium iodide, 0.5% starch and 0.5% agarose [37]. It was gelled by adding agarose to fix the color reactions. Table I shows the oxidation potentials of a typical ROS that may play an important role in plasma chemical reactions. These ROS can be detected by the gel reagent used in this study because their oxidation potentials are higher than 0.54 V, which is the oxidation potential of iodine. That is, it is difficult to identify the reacted ROS because this reagent may react with several ROS. However, this reagent can easily detect many ROS supplied to the target at one try without any equipment. This is very important information for the application of plasma jets.

We also measured the absorbance proportional to the concentration to obtain the relative ROS concentration distribution from the color reactions. The absorbance measurement apparatus consists of a tungsten-halogen lamp, a collimating lens, an XY stage, a spectrometer and optical fiber cables.

III. RESULTS AND DISCUSSION

Absorbance can be measured within a radius of 35 mm from the center of a Petri dish. Fig. 2 shows the relationship between the maximum absorbance of color reactions obtained on the gel reagent and the irradiation time of the plasma jets to the gel reagent. The absorbance linearly increases with the irradiation time. This result indicates that the absorbance is a reliable to evaluate the amount of the reacted ROS with the gel reagent. Moreover, the linear relationship means that plasma-generated active species including the ROS do not decompose the gel reagent under experimental conditions in this study. The maximum absorbance is obtained around the contact point between the plasma jet and the gel reagent. If the active species decompose the gel reagent, the linear relationship cannot be obtained. All numerical data shown in this study are average values calculated after more than three measurements.

Fig. 3 shows the effects of the irradiation distance on the He plasma jet and the resulting ROS distribution. The irradiation distance was changed from (a) 5 mm to (f) 50 mm. The irradiation time was 10 s. The plasma jet fully reached the reagent at distances of 30 mm or less. At a distance of 40 mm, only the tip of the plasma jet made slight contact with the reagent. It seems that the plasma jet did not contact the reagent at a distance of 50 mm. These conditions had a great effect on the ROS distribution. The visualization at a distance of 5 mm, as shown in Fig. 3(a), clearly indicates a doughnut-shaped ROS distribution pattern. ROS were radially distributed from the boundary between the plasma jet and the surrounding air. An unreacted area was also observed around the center.

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidation potential [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl radical (OH)</td>
<td>2.80</td>
</tr>
<tr>
<td>Atomic oxygen (O)</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide (H₂O₂)</td>
<td>1.78</td>
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<tr>
<td>Hydroperoxyl radical (HO₂)</td>
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</table>
Fig. 3. Effects of irradiation distance on the He plasma jet and the resulting ROS distribution, as visualized by the gel reagent. The irradiation distance was changed from (a) 5 mm to (f) 50 mm. The applied voltage and irradiation time were 16 kV and 10 s, respectively. Points A and B are used in Fig. 4.

of the plasma jet. In the gas phase, it has been reported that doughnut-shaped distributions have also been observed in terms of the luminescence of a plasma jet [13], O [22], [24], [32], OH [21], O₃ [29], He⁺ [19] and N₂⁺ [19]. Judgments from those reports are that the active species generated in the gas phase were supplied onto the gel reagent in the doughnut shape and the color reactions were induced on the target. The result shown in Fig. 3(f) indicates that color reactions are not induced when the plasma jet does not make contact with the reagent. From this result, we assume that in the He plasma jet, the color reactions are primarily induced by short-lived species generated at a contact point between the plasma jet and the reagent with mixing the surrounding air. In the central area of the plasma jet, it is thought that the unreacted area appeared because the surrounding air was not mixed. The size of the unreacted area decreased with increasing irradiation distance in the range from 5 mm to 30 mm. The plasma jet is thought to have a cylindrical shape with a gradually closed tip.

To obtain the relative concentration distribution of ROS supplied to the gel reagent, we measured the absorbance of the color reactions shown in Fig. 3. Fig. 4 shows the relative ROS concentration distributions along the line AB of the color reactions shown in Figs. 3(a)-(f). Similar distribution patterns were obtained at distances of 5 and 10 mm. The maximum concentration obtained at a distance of 30 mm was about 2.5 times larger than those at 5 mm and 10 mm, but the distribution range (radius of about 5 mm) was similar. This result indicates that a high-efficiency ROS supply to the target can be obtained at a distance of 30 mm under the experimental conditions in this study. In other words, the ROS supply can be controlled without changing the distribution range by the irradiation distance. In contrast, although the ROS concentration was relatively low, a local ROS supply to the target can be obtained at a distance of 40 mm.

Fig. 5 shows the effects of the irradiation distance on the ROS distribution in the case of the O₂/He plasma jet. The irradiation distance was changed from (a) 5 mm to (f) 50 mm. The irradiation time was 10 s. The ROS were distributed in a wide-range area, and two-layered color reactions were observed. These two-layered color reactions are considered below (see Fig. 9). In the O₂/He plasma jet, it is thought that the color reactions were induced not only by short-lived species but also by long-lived species, for example O₃ had been generated in the gas phase over the target. This is because although the plasma jet did not reach the reagent at a distance of 50 mm, color reactions were induced, as shown in Fig. 5(f). Reportedly, O₃ concentration is increased by adding O₂ to the He gas [28], [31]. The gas flow advected the long-lived species towards and across the surface of the reagent, resulting in the observed color reaction over a wide range.
Fig. 5. Visualized ROS distribution in the O$_2$/He plasma jet. The irradiation distance was changed from (a) 5 mm to (f) 50 mm. Points A and B are used in Fig. 6.

Fig. 6. Relative ROS concentration distribution obtained by absorbance measurement along the line AB. Points A and B are shown in Fig. 5.

Fig. 7. Comparison of the maximum absorbance between the He and O$_2$(0.5%)/He plasma jets. Data shown in this figure were obtained from Figs. 4 and 6.

Fig. 8. Comparison of the relative ROS concentration between the He and O$_2$/He plasma jets. Data shown in this figure were obtained from Figs. 4 and 6.

Fig. 9. Possible reasons for the differences in ROS distribution.

- In the He plasma jet, the color reactions were induced not only by short-lived species generated at the contact point but also by long-lived species generated at the contact point but also by long-lived species.

- In the O$_2$/He plasma jet, the color reactions were primarily induced by short-lived species generated at the contact point between the plasma jet and the reagent with mixing the surrounding air. In contrast, in the O$_2$/He plasma jet, the color reactions were induced not only by short-lived species generated at the contact point but also by long-lived species.
species generated in the gas phase over the target. Therefore, in this case, the color reactions were induced by the synergistic effect of long-lived species along with the short-lived species. The higher absorbance was obtained by short- and long-lived species around the contact point, and the wide-range distribution is due solely to the long-lived species. This is the possible reason for the two-layered color reactions in the O$_2$/He plasma jet.

IV. CONCLUSIONS

In this study, we visualized the 2-dimensional distribution of the ROS supplied to a target using a gel reagent with iodine-starch reactions as the target of a plasma jet in atmospheric air. The effects of irradiation distance and the addition of O$_2$ to He on the ROS distribution patterns and the relative ROS concentration distribution were discussed. The ROS distribution depended significantly on the irradiation distance of the He plasma jet. The ROS supply to the target can be controlled by the irradiation distance. In this case, the color reactions are thought to be primarily induced by short-lived species generated at the contact point between the plasma jet and the gel reagent. In the O$_2$/He plasma jet, the ROS were supplied to the target in a wide-range area, and the distribution was divided into two layers. In this case, it is thought that the color reactions were significantly influenced by the synergistic effect of long-lived species, for example O$_3$ generated in the gas phase, along with the short-lived species.

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REFERENCES


