Estimation of effective area of short-lived reactive oxygen species generated by an atmospheric-pressure helium microplasma jet

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Abstract: Here we investigated effective area of relatively short-lived reactive oxygen species (ROS), i.e., OH radicals and / or superoxide anion radicals (O_2^-•), generated by an atmospheric-pressure helium microplasma jet. Discoloration of methylene blue solution in a 3D printed micro-well was used for evaluation of the effect of short-lived ROS. It was also confirmed that there is no discoloration with longer-lived ROS and RNS such as H_2O_2, NO_2^-, NO_3^- and their mixed solutions. Our experimental results showed that short-lived ROS can be affected a large area about 16 mm in diameter.

Keywords: Short-lived ROS, Methylene blue solution, OH radical, Superoxide anion radical

1. Introduction

Non-thermal atmospheric pressure plasma (APP) technologies are widely used in biological and biomedical applications. It is strongly considered that the short-lived and highly reactive oxygen species (ROS) are the most important to induce biological reactions. Hydroxyl radicals (OH•), superoxide anion radicals (O_2^-•), singlet oxygens ($^1O_2$) and atomic oxygens are well-known short-lived and highly reactive ROS in plasma. Plasma jet is a well-known method to generate such ROS and to supply to biological target without thermal damage. Laser induced fluorescence (LIF), VUV absorption spectroscopy, and chemical probes associated with optical and / or magnetic method are used to detect the ROS. In general, however, it is necessary that the large scale of the experimental facility for short-lived ROS.

Methylene blue (MB) is a thiazine dye which is an organic compound containing a ring of one nitrogen, one sulfuric, and four carbon atoms. MB is commonly used in the laboratory as an indicator of chemical reactions molecule. In the early studies of wastewater treatment, plasma was suggested as a strong candidate to solve the issue and the decompose of MB molecules in water was an evaluation method. OH• is mainly supplied by dissociative process of water molecule in an interaction between plasma and humid air. It is expected sufficient OH• to be supplied by underwater discharge. Thus, underwater discharge was well developed for dissolving organic compounds in water. We used one of organic compounds e.g., MB to detect OH•. This result led to the conclusion that OH• is a major plasma species in the process of the MB decomposition. Spectrophotometry is a well-established method to determine the molecules in liquid solution and to evaluate the absolute concentrations as well. Likely, concentration of MB molecules in the water is also determined by the optical method in the visible range.

In this study, we investigated influence of well-known plasma generated long-lived RONS i.e., H_2O_2, NO_2^-, NO_3^- and their mixed solutions. Also, we investigate how MB concentration was affected by an increase of distance from the tip of plasma jet which irradiated on the plate acrylic surface. The tip of plasma jet is the end position of positively and negatively charged ionic species. We believe that the related results can lead to conclude the effective distance of plasma generated shorted-lived ROS as well as the effective lifetime of ROS.

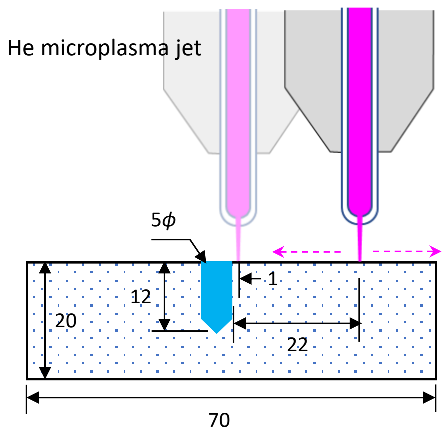

Fig. 1. Laboratory made a transparent acrylic well-plate for detecting reactive species delivered to the downstream of gas flow.

2. Experimental set-up

A non-thermal atmospheric-pressure helium micro-plasma jet was employed in this study. It consisted of a 150 mm long glass tube tapered from an inner diameter of 4 mm to 680 μm at the nozzle. The glass tube (borosilicate, Pyrex) has a 15 mm long metallic external ring electrode wound onto the glass tube at 50 mm from the end of the nozzle. Helium gas (99.98%, industrial grade) was fed into the glass tube with a fixed gas flow rate of 2.0 L/min. A capillary microplasma dielectric barrier discharge (DBD) was generated using a sinusoidal high voltage of 10 kV_{p-p}

(peak-to-peak) applied to the external electrode with a fixed frequency at 33 kHz. These operating conditions produced a plasma jet with a plume length of 12 mm and a gas temperature of 40 ℃ estimated by optical emission analysis of the N_2 second positive system. Plasma treatments were carried out a fixed distance at 10 mm where the plasma jet contacted the well-plate surface as shown in Fig. 1 and it appeared a-mm-spot on the surface. Treatment time was fixed 10 min.

A laboratory made well-plate was used to contain MB solution and enable to deliver ROS. A microwell was prepared in a-20-mm-thick acrylic plate. Volume of the well is around 230 μL. Unsaturated concentration of MB solution was prepared with 5 mg of MB pounder dissolved into 550 mL of deionized water. Plasma-well distance was varied from 1 mm to 22 mm. A dark room (closed space) was employed during the plasma treatment to minimize the effect of ambient air flow.

UV-vis-NIR spectrophotometer (UV-1900, Shimadzu) was employed to investigate the concentration of MB in solution. Disposable plastic microcuvette was used with mixed solution ~230 μL MB and 800 μL deionized water for a measurement. Standard solutions, hydrogen peroxide (H_2O_2), nitrate ($NaNO_3$), nitrite ($NaNO_2$), and their mixed solutions were used to make sure there are no effect on the decomposition of MB by long-lived ROS or RNS.

3. Results and discussion

First, we confirmed that how long-lived ROS and RNS are in the role of MB decomposition. Figure 2 shows relative concentration of MB solution (400 μL) which was mixed with standard solution (600 μL). The standard solutions, H_2O_2 (27%), $NaNO_2$ (1000 mg/L), and $NaNO_3$ (1000 mg/L) are known as ROS (H_2O_2) and RNS (NO_2^- and NO_3^-) in plasma activated water. It was reported that the ROS and RNS concentrations are in tens mg/L in case of higher concentrations with plasma jet. Considering the unchanged concentrations of MB solution after mixed with very high concentration of those standard solution. We could conclude long-lived ROS and RNS do not affect the decomposition of MB.

Next, plasma indirectly irradiated to MB solution as shown in Fig. 1. We see the absorption spectra of MB solution was decreased as a decrease of the plasma-microwell distance in Fig. 3. The absorption spectra showed a broad absorption spectrum profile in visible range between 500 and 750 nm, and strong absorption peaks at 615 nm and at 665 nm. Both absorption peaks are well represented MB_2^+ dimer and MB^+ monomer, respectively. It is clearly showed both intensities of MB_2^+ and MB^+ were linearly decreased as an increase of the distance. As consider the results in Fig. 2, short-lived and highly reactive ROS probably decompose MB solution at the downstream of gas flow in several mm.

When converted to concentration using the calibration curve, MB concentration was lower at near the plasma tip, i.e., highly affected by short-lived ROS, while it was higher at far. Interestingly, MB concentration did not decrease at

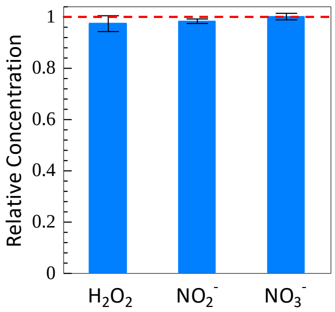

Fig. 2. Relative concentrations of MB solution were mixed with well-known long-lived ROS and RNS, H_2O_2 (27%), $NaNO_2$ (1000 mg/L), and $NaNO_3$ (1000 mg/L), respectively.

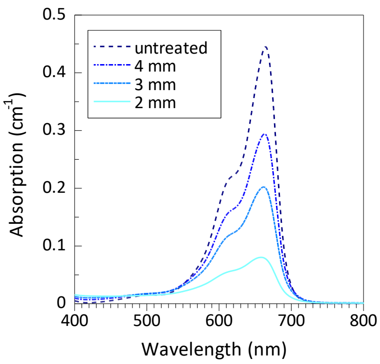

Fig. 3. Absorption spectra of MB solutions as depended on the distance between the microwell and plasma tip. Absorption peak intensity at 665 nm was decreased as in an increase of the distance.

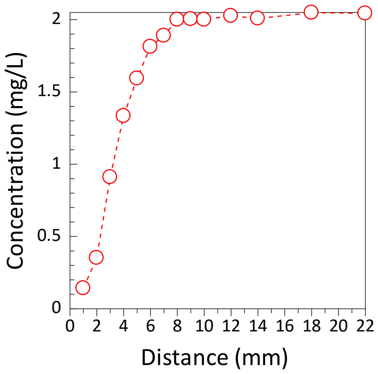

Fig. 4. Distance dependence on the concentration of decomposed MB.

a certain distance of around 8 mm. It seems that a boundary at 8 mm away from the plasma irradiation centre was existed. From the results so far, what kind of short-lived ROS was linked the MB decomposition. Assuming that the decomposition of MB is due to short-lived ROS, the effective area is less than 8 mm radius.

4. Conclusion

Using an atmospheric-pressure helium microplasma jet, we here investigated effective area of relatively short-lived reactive oxygen species (ROS) which can decompose methylene blue solution. It was also confirmed that there is no discoloration with longer-lived ROS and RNS such as H_2O_2, NO_2^-, NO_3^- and their mixed solutions. As result, we could estimate that short-lived ROS can be affected a large area about 16 mm in diameter.

Acknowledgement

This work was supported by JSPS/MEXT KAKENHI number JP19H01888.