Generation of reactive nitrogen radicals in air plasma and their stability in liquid

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1. Introduction

Atmospheric-pressure nonthermal plasma (APNP) has been recently investigated for various application in bio related and medical areas [1]. Many groups reported that main key factors of plasma therapy are reactive oxygen species (ROS) and reactive nitrogen species (RNS) [2-3]. It is well known that ROS have a cell signalling role in many biological systems from bacteria to mammalian cells. Various reactive oxygen and nitrogen species in nonthermal plasma may actively provide a curing mechanism with which to treat these incurable diseases. ROS and RNS such as hydroxyl radicals (OH), hydrogen peroxide (H_2O_2), superoxide anions ($O2^{*-}$), as well as nitrogen oxide (NO) species can be generated on a bio-solution surface by means of APNP jet bombardment. These reactive species may provide beneficial effects in cells, although the exact pathway of the reactive molecules inside the cells is not yet known.

Under *in vivo* conditions, living cells and tissue are surrounded by a liquid environment. Recently, the reactions of plasma with liquid and stability of radical generated by plasma in liquid are very interesting topic in plasma medicine research field.

In this study, we analysed the characteristics of nitrogen plasma at atmospheric-pressure and evaluated the stability of nitrite (NO_2^-) and nitrate (NO_3^-) generated by plasma in deionized water.

2. Experimental

A schematic drawing of the micro-discharge jet is shown in Fig. 1. The underwater discharge system consists of a high-voltage electrode, ground electrode, dielectric tube, high-voltage power supplier, and developed reactor. The power supply used in this experiment was a commercially available 60 Hz transformer, and it was connected to the high-voltage electrode and ground electrode. The inner electrode shown in Fig. 1 was made of an 18 gauge stainless steel needle, and gas was injected through a hole with a diameter of about 0.2 mm. It was enclosed within a quartz tube with a diameter of 3 mm as the dielectric material. The ground electrode was a pencil-type electrode and was hollowed out for the inner electrode and dielectric. The outlet of the micro-discharge jet consisted of a hole with a diameter of 0.7 mm, and the plasma discharged into the water under the surface. In the region of plasma generation, the tip of the quartz tube had a 1-mm protrusion as the discharge gap against the tip of the inner electrode, and it was in contact with the outer electrode, as shown in Fig. 1. The discharge gap could be adjusted by controlling the distance between the tips of the quartz tube and the inner electrode. The plasma jet in the present work was produced from a discharge in the 1-mm gap. The discharge gas was fed through the injection needle and was ejected underwater via the discharge region. Once the discharge gases were introduced through the inner electrode and high-voltage ac power was applied, a discharge was fired in the gap between the electrodes and a long plasma jet that could reach distances of up to several centimetres was ejected into the open air or underwater, as shown in Fig. 2.

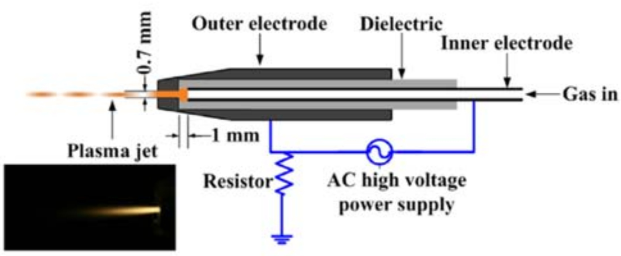

Fig. 1. Schematic drawing of the micro-discharge jet

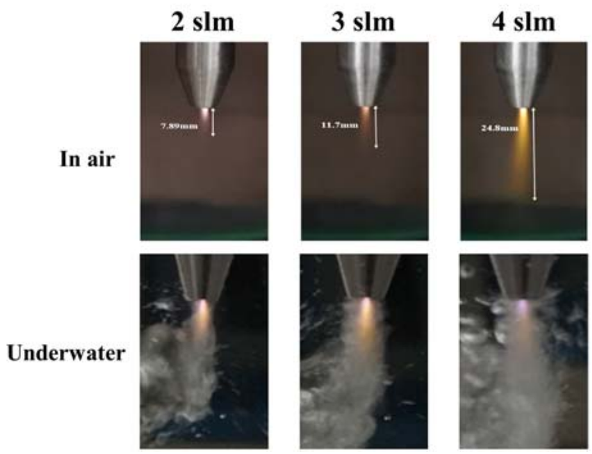

Fig. 2. Photo images of nitrogen micro-discharge

3. Results and Discussions

In order to explore generation of RNS by plasma, we analysed optical emission spectra of air plasma. Fig. 3 exhibits the optical emission spectra obtained to identify various excited plasma species produced by the air plasma jets over a wide range of wavelengths (200–950 nm). It is also shows a comparison of the intensity of radicals produced in open air and in water. Fig. 3 shows the optical emission spectrum obtained from the microdischarge jet at an air flow of 4 slm. The emission spectrum is dominated by the presence of excited nitrogen species, and it can be divided into the N_2 2nd positive system, N_2 1st negative, and N2 1st positive systems in the ranges of 320–360 nm, 370–430 nm, and 460–690 nm, respectively. A strong NO_γ band at 200–271 nm and atomic nitrogen peaks also appear at 747, 822, and 868 nm. The peaks at at 777 and 844 nm clearly show that highly reactive atomic oxygen exists in the plasma jet. The hydroxyl radical (A2Σ+–X2Π) and Balmer γ of hydrogen were also detected at 306–312 and 434 nm. From this results, we confirmed that the air plasma jet generated enough RNS underwater condition.

It is well-known that nitric oxide (NO) and nitrogen dioxide (NO_2) hydrolyze in water to form nitrous acid and nitric acid. The concentrations of NOx gas from the plasma were about 350 ppm of NO and 135 ppm of NO2 at flow rate of 4slm. After passing through the water, the concentration decreased by 20–50 ppm.

Fig. 4 shows the concentrations of NO_2^- and NO_3^- measured by the ion chromatograph. Both NO_2^- and NO_3^- were produced by the microdischarge jets with air, and they readily dissolved in water. At the optimized air flow rate of 4 L/min, the NO_2^- and NO_3^- concentrations gradually increased with time, and the NO_3^- concentration was about three times that of the NO_2^- concentration.

In order to evaluate stability of NO_2^- and NO_3^- generate by plasma in water, we measured the concentration of NO_2^- and NO_3^- for 1 month. The D.I water was treated by nitrogen plasma for 30 min. and the pH of D.I water was about 3.5. Fig. 5 shows the measured results of NO_2^-/NO_3^- concentration and pH by date.

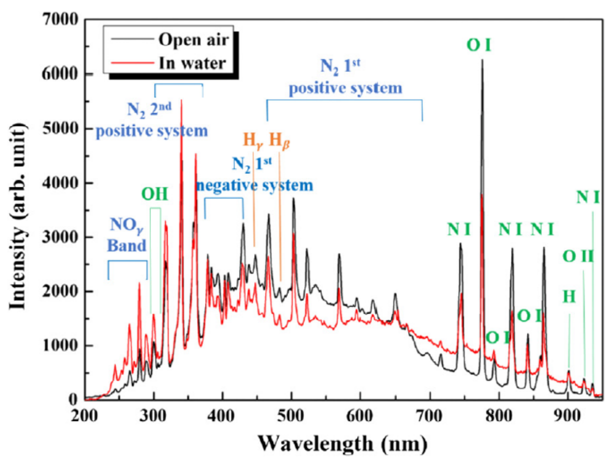

Fig. 3. Optical emission spectra of air plasma jet.

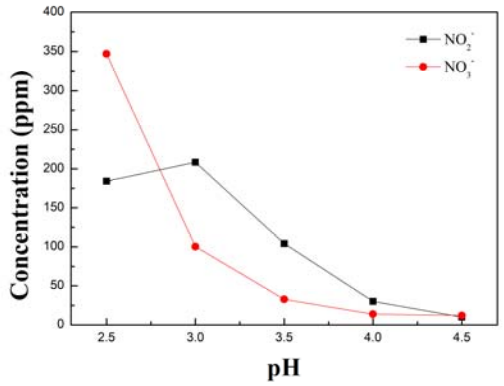

Fig. 4. The concentration of NO_2^- and NO_3^- in water according to discharge time.

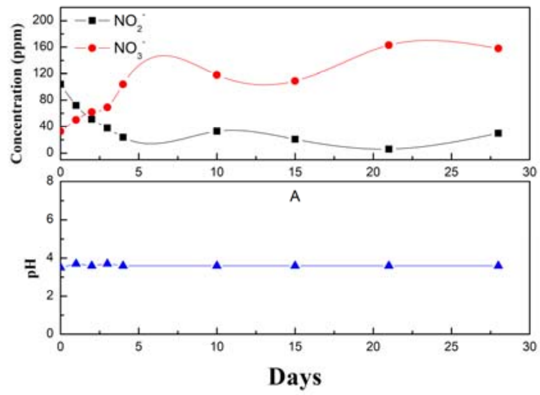

Fig. 4. The concentration of NO_2^- and NO_3^- in water and pH value by date.

The concentration of NO_2^- was decreased while concentration of NO_3^- was increased. However the pH value was constant. From these results, we confirmed that the NO_2^- ions were converted into NO_3^- ion such as $ONOO^-$.

4. Conclusion

In this study, we analysed the characteristics of nitrogen plasma at atmospheric-pressure and evaluated the stability of NO_2^- and nitrate NO_3^- generated by plasma in deionized water. And the NO_2^- ion generated by plasma in water was converted into NO_3^- ion according to time flow of time. The nitrogen ions generated plasma in water were maintained for 1 month.

5. References

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