ROS/RNS generation by various discharge plasma

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1. Introduction

In recent years, plasma treated water has gained increasing attention, because reactive oxygen species (ROS) and reactive nitrogen species (RNS) in the plasma treated water play important roles in various fields such as plasma medicine(1) and agriculture.(2) These ROS/RNS are produced by dissolving species in plasma. To use the plasma treated water effectively and efficiently, it is important to control the ROS/RNS concentration.

In this work, we generated an Ar plasma jet, a positive DC corona discharge, a positive pulsed discharge and a packed-bed dielectric barrier discharge (PB-DBD), produced ROS/RNS in deionised water using these discharges, and then investigated the concentration and generation efficiency of the ROS/RNS in the water.

2. Experimental apparatus and conditions

Experimental apparatuses are similar to those used in previous works.(3-6) The Ar plasma jet is generated using a dielectric barrier discharge, and N_2-O_2 mixture gas is mixed into the plasma jet, and then deionised water is exposed to the plasma jet. The corona discharge and the pulsed discharge are generated above a water surface in N_2-O_2 mixture gas as a background gas. The PB-DBD is generated in N_2-O_2 mixture gas, and the off-gas of the PB-DBD reactor packed with soda-lime glass balls is sparged into deionised water. Samples of 1.2 mL from the water are taken.

The concentrations of H_2O_2, NO_2^- and NO_3^- in the sampled water are measured using High Performance Liquid Chromatograph (Shimadzu, Prominence, column: IC NI-424) in combination with an auto sampler. An eluent is the aqueous solution of acetic acid (3 mmol/L) and potassium hydroxide (1.9 mmol/L), and the wavelength of an absorbance detector is fixed at 220 nm.

3. Results and discussion

H_2O_2 is detected in the sampled water after the plasma exposure except in the case of PB-DBD, and these concentrations increase with input energies. H_2O_2 is mainly formed by the combination reaction of two OH radicals,(7) which are produced by the dissociation of H_2O. Although O_3 is detected in the off-gas from the PB-DBD reactor, no H_2O_2 is detected in the sampled water; therefore, O_3 does not contribute to H_2O_2 production. Consequently, the dissociation of H_2O by high-energy electron and excited molecules (atoms), such as metastable N_2 and Ar, may be dominant to OH production.

NO_2^- and NO_3^- are detected in the sampled water except for NO_2^- in the case of PB-DBD, so that it is necessary to generate plasma in the vicinity of water for NO_2^- generation. NO_2^- concentrations show tendencies to be constant or decrease with the increase of input energy, but NO_3^- concentrations are roughly relative to the input energy.

Table 1 shows the generation efficiency of H_2O_2, NO_2^- and NO_3^- in each discharge. The pulsed discharge has higher generation efficiency of H_2O_2 and NO_2^- than others, and PB-DBD off-gas sparging can only and efficiently generate NO_3^-.

Acknowledgement

This work was partly supported by JSPS Grants-in-Aid for Scientific Research Grant Number 24560320.

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Table 1. H_2O_2, NO_2^- and NO_3^- generation efficiency

discharge	generation efficiency [μg/Wh]		
	H_2O_2	NO_2^-	NO_3^-
plasma jet	10	20 ~ 50	60 ~ 90
corona	200	50 ~ 200	800 ~ 1400
pulsed	700 ~ 1500	< 350	650 ~ 1100
PB-DBD	—	—	800 ~ 2500