Generation of Nitric Acid and Nitrous Acid in Distilled Water Irradiated with Atmospheric-Pressure Plasma Jet

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An atmospheric-pressure argon (Ar) plasma jet was directly irradiated onto distilled water. Semiquantitative determination using test strips and flow injection analysis (FIA) revealed that nitric acid (HNO_3) and nitrous acid (HNO_2) were generated in distilled water by plasma jet irradiation for 1 min. The nitrate ion (NO_3^-) and nitrite ion (NO_2^-) concentrations in distilled water irradiated with a plasma jet, determined from the test strips, were in good agreement with those determined by FIA. The NO_3^- concentration in distilled water proportionally increased with the plasma irradiation time, whereas the NO_2^- concentration was almost unchanged. It is considered that high-energy electrons in the plasma jet collided with nitrogen molecules (N_2) and oxygen molecules (O_2) to generate nitrogen (N) and oxygen (O) radicals. Nitrogen oxide (N_xO_y) generated upon the reaction of the radicals is considered to react with water molecules (H_2O) in air and at the surface of distilled water to generate HNO_3 and HNO_2 . [DOI: 10.1380/ejsnt.2014.410]

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I. INTRODUCTION

The decomposition of organic compounds in wastewater using discharges and plasmas is a popular area of research. For example, researchers have reported the decomposition of phenol [1-3], organic dyes [4, 5], and acetic acid (as a model of persistent organic substances) [6] in water using on-water pulse discharge and the decomposition of organic dyes [7, 8] in water using on-water atmospheric-pressure plasma.

Previously, we examined the decomposition of methylene blue, used as an organic dye, in distilled water using an atmospheric-pressure argon (Ar) plasma jet [9]. In that study, we carried out measurements by absorption spectroscopy and capillary electrophoresis and reported that (1) nitric acid (HNO_3) was generated in distilled water irradiated with an Ar plasma jet, (2) the generated nitrate ions (NO_3^-) contributed to a peak at a wavelength of approximately 200 nm in the absorbance spectrum, and (3) the NO_3^- concentration increased with the plasma irradiation time [10]. However, the estimated NO_3^- concentrations were not reported.

In this study, we found that nitrous acid (HNO_2), in addition to HNO_3 , was generated in distilled water irradiated with an atmospheric-pressure Ar plasma jet. The dependences of the NO_3^- and nitrite ion (NO_2^-) concentrations in distilled water on the plasma irradiation time were semiquantitatively determined using test strips and then quantitatively determined by flow injection analysis (FIA) based on absorption spectrophotometry using naphthyl ethylenediamine and a Cu-Cd reduction column. The aim of this study is to clarify the phenomenon that always occurs when water is irradiated with an atmospheric-pressure plasma jet regardless of the presence of organic compounds in the water.

FIG. 1. Schematic of experimental setup.

II. EXPERIMENTAL

Figure 1 shows a schematic of the experimental setup used in this study. In this setup, a copper tube (inner diameter, 4 mm; outer diameter, 6 mm), used as a discharge electrode, is inserted into a dielectric quartz tube (length, 50 mm; inner diameter, 6 mm; outer diameter, 8 mm), around which copper foil (thickness, 0.05 mm; width, 10 mm) is wrapped as a grounding electrode [11]. When a high AC voltage is applied, a dielectric barrier discharge is induced in the quartz tube between these electrodes, and the inflowing argon gas is excited to form a plasma that is then released into the atmosphere.

A plasma jet was generated at an Ar gas flow rate of 10 L/min using a high-voltage power source (LHV-10AC, Logy Electric Co., Ltd.) with a frequency of 9 kHz and an applied voltage of 10 kV. Under these conditions, the plasma jet extended approximately 30 mm from the end

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FIG. 2. Plasma jet irradiated onto distilled water.

of the quartz tube and its maximum diameter was approximately 6 mm [12].

Ten milliliters of distilled water (Wako Pure Chemical Industries, Ltd.) in a 60-mm-diameter glass Petri dish was directly irradiated with an atmospheric-pressure Ar plasma jet for 1–30 min. The distance between the end of the quartz tube and the surface of the distilled water was approximately 15 mm.

To confirm the generation of NO_3^- and NO_2^- in distilled water, the following two methods were adopted. First, the NO_3^- and NO_2^- concentrations were semiquantitatively determined using test strips (Quantofix Nitrate Nitrite, Macherey-Nagel GmbH & Co. KG). These test strips can be used to semiquantitatively determine the NO_3^- and NO_2^- concentrations on the basis of the color change of the reagent-containing test strips ($5 \times 5 \text{ mm}^2$). Each test strip was immersed for 1 s in distilled water irradiated with a plasma jet and the NO_3^- and NO_2^- concentrations were determined from the resulting color. For each concentration, the average of three measurements was used.

Next, the NO_3^- and NO_2^- concentrations were determined by FIA. Two transfer pumps (DP-8020, Tosoh Corporation; PU-2080, JASCO Corporation) and a detector (UV-2075, JASCO Corporation) were used. Naphthyl ethylenediamine absorption spectrophotometry (detection wavelength, 530 nm) was used to detect NO_2^- . NO_3^- was reduced to NO_2^- using a Cu-Cd reduction column and detected similarly by absorption spectrophotometry. The NO_3^- concentration was calculated by subtracting the NO_2^- concentration calculated using the absorbance obtained before the reduction from the NO_2^- concentration after the reduction.

III. RESULTS AND DISCUSSION

Figure 2 shows a plasma jet irradiated onto distilled water. Streamer discharges are generated in the plasma jet and appear to reach the surface of the distilled water.

Figure 3 shows the color charts of the test strips and the changes in color of the NO_3^- and NO_2^- test strips immersed in distilled water irradiated with the plasma jet.

The test strips remained white before plasma jet irradiation, meaning that NO_3^- and NO_2^- were not present in the distilled water before plasma jet irradiation. The test strips became light pink after 1 min of irradiation, and the pink color darkened with increasing plasma irradiation time. These results indicate that NO_3^- and NO_2^- were generated in distilled water irradiated with the plasma jet for 1 min and that their concentrations increased with the plasma irradiation time.

Figure 4 shows the dependences of the NO_3^- and NO_2^- concentrations in distilled water on the plasma irradiation time determined from the color changes of the test strips. The NO_3^- concentration was 0 mg/L before plasma jet irradiation and proportionally increased with the plasma irradiation time: it was approximately 5 mg/L after 1 min of irradiation, 10 mg/L after 3 min of irradiation, 20 mg/L after 5 min of irradiation, 30 mg/L after 10 min of irradiation, 40 mg/L after 15 min of irradiation, 50 mg/L after 20 min of irradiation, and 70 mg/L after 30 min of irradiation. The NO_2^- concentration was 0 mg/L before plasma jet irradiation and increased with the plasma irradiation time up to 15 min. However, it decreased when the plasma irradiation time exceeded 15 min: it was approximately 1 mg/L after 1 min of irradiation, 3 mg/L after 3 min of irradiation, 5 mg/L after 5 min of irradiation, 7 mg/L after 10 min of irradiation, 10 mg/L after 15 min of irradiation, 7 mg/L after 20 min of irradiation, and 7 mg/L after 30 min of irradiation. These values were obtained by semiquantitative determination.

FIA was carried out to quantitatively determine the NO_3^- and NO_2^- concentrations. Figure 5 shows the dependences of the NO_3^- and NO_2^- concentrations in distilled water on the plasma irradiation time, as determined by FIA. The NO_3^- concentration was 0 mg/L before plasma jet irradiation and proportionally increased with the plasma irradiation time: it was 2.0 mg/L after 1 min of irradiation, 8.2 mg/L after 5 min of irradiation, 18.1 mg/L after 10 min of irradiation, 42.6 mg/L after 20 min of irradiation, and 76.5 mg/L after 30 min of irradiation. The NO_2^- concentration was 0 mg/L before plasma jet irradiation and increased with the plasma irradiation time up to 10 min. However, it decreased when the plasma irradiation time exceeded 10 min: it was 1.0 mg/L after 1 min of irradiation, 2.61 mg/L after 5 min of irradiation, 3.75 mg/L after 10 min of irradiation, 2.13 mg/L after 20 min of irradiation, and 0.61 mg/L after 30 min of irradiation. These results were in good agreement with the results obtained using the test strips.

Watanabe performed ion chromatography measurements of the concentration of negative ions generated in pure water subjected to a silent discharge. According to his report, NO_3^- was present but little NO_2^- was present in pure water after the discharge. Moreover, the NO_3^- concentration linearly increased with the discharge time [13]. However, the estimated NO_3^- concentrations were not reported.

Ikawa *et al.* reported that NO_3^- and NO_2^- were generated in distilled water irradiated with an atmospheric-pressure helium (He) plasma jet and that the $\text{NO}_3^- + \text{NO}_2^-$ concentration proportionally increased with the plasma irradiation time on the basis of the results of ion chromatography [14]. Their results were in good agreement with our results. However, they did not separately

FIG. 3. Color charts of test strips and changes in color of test strips immersed in plasma-jet-irradiated distilled water (Color chart: left, NO_3^- ; right, NO_2^- . Test strip: top, NO_2^- ; bottom, NO_3^-). (a) After 1 min of irradiation, (b) after 3 min of irradiation, (c) after 5 min of irradiation, (d) after 10 min of irradiation, (e) after 15 min of irradiation, (f) after 20 min of irradiation, and (g) after 30 min of irradiation.

FIG. 4. Dependences of NO_3^- and NO_2^- concentrations in distilled water on plasma irradiation time determined from color changes of test strips.

FIG. 5. Dependences of NO_3^- and NO_2^- concentrations in distilled water on plasma irradiation time determined by FIA.

determine the NO_3^- and NO_2^- concentrations.

From the results of ion chromatography, Huang *et al.* reported that NO_3^- was generated in pure water subjected to dielectric-barrier discharge and that the NO_3^- concentration increased with the discharge time [8]. However, no estimated NO_3^- concentrations were reported.

During atmospheric discharge, the following reactions occur [15-17].

Electrons (e) collide with nitrogen molecules (N_2) and oxygen molecules (O_2) in air to generate nitrogen (N) and oxygen (O) radicals. The O radicals react with O_2 to generate ozone (O_3). Through these reactions, nitrogen oxide (N_xO_y) is generated. Dinitrogen pentoxide (N_2O_5) and dinitrogen trioxide (N_2O_3) react with water molecules (H_2O) in air to generate HNO_3 and HNO_2 , respectively. Here, M is called the third body and absorbs the internal energy of the generated molecules to stabilize them and prevent their dissociation.

Braun *et al.* confirmed that O_3 , N_2O , N_2O_5 , and HNO_3 were generated in air by atmospheric discharge [15]. Miyazaki *et al.* found, using a gas detector, that

O₃, NO, and NO₂ were generated in a N₂-O₂ gas mixture upon pulse discharge [4]. Chen *et al.* reported that O₃, NO, and NO₂ were generated in air by atmospheric dielectric-barrier discharge. They also reported that the NO₂ concentration increased with the discharge time whereas the NO concentration was almost unchanged [18].

Similar reactions are considered to occur during plasma jet irradiation in air. In addition to the reactions with H₂O in air [reactions (12) and (13)], a reaction with H₂O at the surface of the distilled water may have occurred in our experiment. Therefore, we consider that HNO₃ and HNO₂ were generated in distilled water and ionized to H⁺ and NO₃⁻ [reaction (14)] and H⁺ and NO₂⁻ [reaction (15)], respectively.

From the above discussion, NO₃⁻ and NO₂⁻ are considered to be generated in distilled water irradiated with a plasma jet.

IV. CONCLUSIONS

An experiment using test strips and FIA based on absorption spectrophotometry using naphthyl ethylenediamine and a Cu-Cd reduction column revealed that HNO₃ and HNO₂ were generated and ionized in distilled water irradiated with an atmospheric-pressure Ar plasma jet. The NO₃⁻ and NO₂⁻ concentrations in distilled water irradiated with a plasma jet determined from the test strips were in good agreement with those determined by FIA.

The NO₃⁻ concentration in distilled water proportionally increased with the plasma irradiation time, whereas the NO₂⁻ concentration was almost unchanged. The NO₃⁻ and NO₂⁻ concentrations in distilled water irradiated with an Ar plasma jet for 30 min were 76.5 and 0.61 mg/L, respectively.

High-energy electrons in the plasma jet collided with N₂ and O₂ in air to generate N and O radicals. They reacted and produced N_xO_y. HNO₃ and HNO₂ are considered to be generated upon the reaction of N_xO_y with H₂O in air and at the surface of distilled water.

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