Identification of Peak near 200 nm in Absorbance Spectrum of Distilled Water upon Atmospheric-Pressure Plasma Jet Irradiation

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(Received 6 December 2011; Accepted 13 December 2011; Published 15 December 2011)

An argon atmospheric-pressure plasma jet was directly irradiated onto distilled water. As a result, a peak appeared at approximately 200 nm in the absorbance spectrum of the distilled water, and the peak intensity increased with plasma jet irradiation time. In the distilled water sample, the electrical conductivity increased and the pH decreased with increasing irradiation time. A comparison of the absorbance spectrum of the distilled water sample with that of nitrate ions (NO$_3^-$) in a sodium nitrate (NaNO$_3$) aqueous solution indicated that the peak near 200 nm was due to NO$_3^-$. This finding was also supported by the result of a capillary electrophoresis (CE) measurement. [DOI: 10.1380/ejssnt.2011.442]

Keywords: Plasma processing; Water; Liquid surfaces; Absorbance spectrum; Nitrate ion

I. INTRODUCTION

Research is ongoing on water purification by the decomposition of harmful organic compounds in water using discharges and plasmas, such as underwater pulsed streamer corona discharge [1, 2], underwater RF plasma within bubbles [3, 4], atmospheric-pressure pulse discharges on water [5, 6], and atmospheric-pressure plasma on water [7, 8]. Previously, we directly irradiated a plasma jet, which can be released into the atmosphere using our device [9], onto an aqueous solution containing methylene blue, a blue dye used as a model organic substance, and reported the resulting decolorization of the methylene blue aqueous solution [10]. In the subsequent study, we found that a peak appeared at approximately 200 nm in the absorbance spectrum of distilled water when a plasma jet was directly irradiated onto the distilled water at atmospheric pressure [11].

In this letter, we report the identification of the substance causing the absorbance spectral peak observed at approximately 200 nm from the measurement results of electrical conductivity, pH, the absorbance spectrum of sodium nitrate (NaNO$_3$) aqueous solution, and capillary electrophoresis (CE).

II. EXPERIMENTAL

Figure 1 shows a schematic of our experimental setup. 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. When a high AC voltage is applied, 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 argon 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 of the quartz tube [12], and its maximum diameter was approximately 6 mm. This plasma jet was directly irradiated for 1-10 min onto 10 mL distilled water (Wako Pure Chemical Industries, Ltd.) in a 60-mm-diameter glass petri dish. The distance between the end of the quartz tube and the surface of the distilled water sample was approximately 15 mm. The absorbance spectra of the distilled water in the wavelength range from ultraviolet to near-infrared were measured using a spectrophotometer (V-630, JASCO Corporation). The pH and electrical conductivity of the distilled water sample were measured using a multifunction water quality me-

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FIG. 1: Schematic of experimental setup.
ter (MM-60R, DKK-TOA Corporation). A CE system (G1600AX, Agilent Technologies) was used to identify the ions in the distilled water sample. The conditions were as follows. Capillary: fused silica, 80.5 cm × 50 μm I.D.; electrolyte: 8 mM chromic acid, 8 mM boric acid, 23 μM octadecyltrimethylammoniumbromide, pH=7 (adjusted using sodium hydroxide solution); applied voltage: −30 kV; detection: indirect UV, λ=372 nm.

III. RESULTS AND DISCUSSION

Figure 2 shows a plasma jet irradiated onto distilled water. A streamer discharge is generated in the plasma jet and appears to reach the surface of the distilled water sample.

Figure 3 shows the dependence of the absorbance spectrum of the distilled water sample on plasma jet irradiation time. Expanded spectra around 190-300 nm are shown in the inset.

Figure 4 shows the absorbance at 200 nm plotted against plasma jet irradiation time. The absorbance gradually increased with increasing irradiation time and reached 7 after 10 min of irradiation. This result indicated that the concentration of some type of ion that conducted electricity in the distilled water sample increased with increasing irradiation time.

Figure 5 shows the electrical conductivity of the distilled water sample plotted against plasma jet irradiation time. Before irradiation, the electrical conductivity was 0.496 mS/m; after irradiation, it gradually increased with increasing irradiation time, reaching 9.29 mS/m after 10 min of irradiation. This result indicated that the concentration of hydrogen ions (H⁺) in the distilled water sample increased upon plasma jet irradiation. Therefore, the ions that were generated in the sample as a result of plasma jet irradiation and conducted electricity were H⁺ or another substance that accompanied the generation of H⁺.

In a previous study, it was reported that ozone (O₃) and nitrogen oxide (NOₓ) were generated during a discharge in air because of the interaction between electrons and the nitrogen (N₂) and oxygen (O₂) molecules in air [13, 14] and that NOₓ reacted with water (H₂O) molecules to generate nitric acid (HNO₃) in water [15]. Here, HNO₃...
was ionized into $H^+$ and $NO_3^-$ in water.

Because a similar reaction occurred during the irradiation of the distilled water sample with the plasma jet in our experiment, it was considered that $H^+$ and $NO_3^-$ were present in the sample. Therefore, we hypothesized that $NO_3^-$ was the cause of the absorbance spectral peak near 200 nm upon plasma jet irradiation.

Thus, the absorbance spectrum of a $NaNO_3$ aqueous solution, which contains $NO_3^-$, was measured. Figure 7 shows the absorbance spectrum of $NO_3^-$ in the $NaNO_3$ aqueous solution. A spectrum with a peak at a wavelength of 201 nm was obtained. This wavelength was in agreement with the wavelength of the peak in the absorbance spectrum in Fig. 3, confirming that $NO_3^-$ was the cause of the peak observed at approximately 200 nm in the absorbance spectrum obtained when the plasma jet was irradiated onto a distilled water sample. As shown in Fig. 4, the absorbance at approximately 200 nm increased with increasing irradiation time, which was considered to be a result of the increase in $NO_3^-$ concentration in the distilled water sample with increasing irradiation time. When the $NO_3^-$ concentration in the sample increased, the $H^+$ concentration also increased, which is in agreement with the result in Fig. 6, where the pH of the distilled water sample decreased with increasing irradiation time.

To confirm that $NO_3^-$ was generated in the distilled water sample upon plasma jet irradiation, CE measurement was carried out. Figure 8 shows electropherograms of (a) a $NaNO_3$ aqueous solution, and distilled water samples (b) before irradiation, (c) after 5 min of irradiation, and (d) after 10 min of irradiation. In Fig. 8(a), a peak corresponding to $NO_3^-$ was observed at 9 min. In Fig. 8(b), no peaks were observed, indicating that no $NO_3^-$ was present in the distilled water sample before plasma jet irradiation. In Figs. 8(c) and 8(d), a peak was observed at 9 min and its intensity was greater after the longer irradiation time. This result indicated that $NO_3^-$ was generated in the distilled water sample upon plasma jet irradiation and that the $NO_3^-$ concentration increased with increasing irradiation time. Therefore, the substance generated in the distilled water
sample during plasma jet irradiation was NO$_3^-$.

IV. CONCLUSIONS

When an argon plasma jet was directly irradiated onto distilled water at atmospheric pressure for 1 min, an absorbance spectral peak was observed at approximately 200 nm and the peak intensity increased with increasing irradiation time. The electrical conductivity of the distilled water sample increased with increasing irradiation time from 0.496 mS/m before irradiation to 9.29 mS/m after 10 min of irradiation. This indicated an increase in the ion concentration in the sample. The pH of the distilled water sample decreased with increasing irradiation time from 5.8 before irradiation to 3.3 after 10 min of irradiation. In the absorbance spectrum of NO$_3^-$ in a NaNO$_3$ aqueous solution, a peak was observed at 201 nm. Therefore, the substance causing the peak near 200 nm upon plasma jet irradiation was identified to be NO$_3^-$. A comparison of electropherograms obtained from CE measurement also indicated that NO$_3^-$ was generated in the distilled water sample during plasma jet irradiation. It was considered that NO$_3^-$ was generated as a result of the reaction between the electrons in the plasma and the N$_2$ and O$_2$ in air. NO$_3^-$ then reacted with H$_2$O molecules in the distilled water sample to generate HNO$_3$, which was ionized to generate NO$_3^-$.

Acknowledgments

The authors are grateful to Professor R. Ohyama of Tokai University for his valuable advice.