

Generation of Ammonium Ions in Water by Atmospheric-pressure Argon Plasma Jet Irradiation at Room Temperature

by

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Abstract

Ammonium ions (NH_4^+) were generated in water irradiated with an atmospheric-pressure argon (Ar) plasma jet in air at room temperature. The concentration of NH_4^+ in the water was measured using a capillary electrophoresis (CE) system under different plasma irradiation conditions [plasma irradiation duration, 20–80 min; applied voltage, 8–10 kV; plasma irradiation distance (position of the water surface), 2–40 mm]. The NH_4^+ concentration in the water increased approximately in proportion to the plasma irradiation duration and applied voltage. The maximum NH_4^+ concentration was 43.2 μM when the applied voltage was 10 kV, the Ar gas flow rate was 10 L/min, the plasma irradiation distance was 10 mm, and the plasma irradiation duration was 80 min. The power consumption during plasma irradiation was ~ 20 W.

Keywords: Atmospheric-pressure plasma, Ammonium ions, Capillary electrophoresis

1. Introduction

Ammonia (NH_3) is used in the synthesis of various chemical products such as fertilizers, explosives, plastics, and synthetic fibers and resins¹⁻³. According to a research report of the United States Geological Survey (USGS), the annual world total production of NH_3 was ~ 96 million tons in 1995, ~ 104 million tons in 2000, ~ 131 million tons in 2010, and ~ 150 million tons in 2019, showing a yearly increase⁴⁻⁶. Approximately 80% of the produced NH_3 is used in the manufacture of fertilizers^{7,8}. NH_3 is a chemically synthesized product that is indispensable for producing the food essential for our survival. NH_3 is also expected to be used as a hydrogen carrier for fuel cells, which are necessary for the realization of a hydrogen-energy-based society, and as an easy-to-handle energy source that can be easily liquefied⁹⁻¹¹.

The current industrial synthesis of NH_3 is generally based on the Haber–Bosch process¹⁻³. In 1909, Haber succeeded in synthesizing NH_3 by reacting nitrogen gas (N_2) with hydrogen gas (H_2) using osmium (Os) as a catalyst at 500–600 °C and 200 atm¹². The industrialization of NH_3 synthesis was promoted by Bosch and coworkers at BASF in Germany, and in 1912, Mittasch and coworkers at BASF successfully synthesized NH_3 using a triiron tetroxide (Fe_3O_4) catalyst mixed with 2–6% alumina (Al_2O_3) and 0.2–0.6% potassium oxide (K_2O) instead of an Os catalyst at a decreased temperature (450 °C) and pressure (100 atm)^{13,14}.

The Haber–Bosch process is a high-temperature, high-

pressure process that consumes much energy, which led to a search for catalysts to lower the temperature and pressure in the synthesis process¹⁵. In 1971, Ozaki *et al.* achieved a reduced temperature (146 °C) and pressure (600 mmHg) using a ruthenium (Ru)-carbon (C)-potassium (K) catalyst instead of an iron-based catalyst¹⁶. In 2003, Yandulov and Schrock reported the synthesis of NH_3 at room temperature and 1 atm using a molybdenum (Mo) nitrogen complex with a triamide monoamine tetradentate ligand¹⁷. Since this report, many researchers have reported the synthesis of NH_3 at room temperature and 1 atm using various catalysts.

H_2 gas is used in the Haber–Bosch process and must be produced for the synthesis of NH_3 . H_2 gas is mainly produced by reforming natural gas. In plants for NH_3 synthesis, the production process of H_2 gas accounts for a large part of the entire process, and more than 90% of the total energy consumption of the NH_3 synthesis process is spent on the production of H_2 gas. The process of NH_3 synthesis including the production of H_2 gas makes up 1–2% of the total energy consumption by human beings¹⁸. Therefore, if NH_3 can be synthesized without using H_2 gas, energy consumption will be greatly reduced.

A method of NH_3 synthesis at room temperature without catalysts and H_2 gas was reported by Haruyama *et al.* in 2016¹⁹. By combining ultraviolet (UV) light irradiation and an atmospheric-pressure air plasma or N_2 plasma, they successfully generated NH_3 in water using water instead of H_2 gas.

An atmospheric-pressure plasma is generated under atmospheric pressure, as indicated by its name. Compared with low-pressure plasmas, atmospheric-pressure plasmas are characterized by an electron temperature being higher than the

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ion temperature in the plasma as well as a high electron energy^{20,21}). Research on the surface treatment of solid materials²²⁻²⁴), the purification of water^{25,26}), and the inactivation of bacteria and fungus^{27,28}) has been carried out using atmospheric-pressure plasmas. In particular, atmospheric-pressure plasmas have recently been used in biomedical applications^{29,30}), such as cancer treatment^{31,32}), and the intracellular introduction of genes and drug molecules^{33,34}), which has been intensively studied.

In our laboratory, we have been studying the decolorization of colored wastewater using an atmospheric-pressure argon (Ar) plasma jet³⁵⁻³⁷). We previously reported that hydrogen peroxide (H_2O_2)^{38,39}) as well as nitric acid (HNO_3) and nitrous acid (HNO_2)^{40,41}) were formed in distilled water irradiated with an atmospheric-pressure Ar plasma jet. In these studies, the possibility of nitrogen (N) radicals being formed through the dissociation of N_2 molecules in the air was discussed as a cause of the formation of HNO_3 and HNO_2 . NO_3 and NO_2 are formed because of the oxidation reaction of N radicals. oxygen (O) radicals, which are necessary for the oxidation reaction, should be formed by the dissociation of oxygen molecules (O_2) in air. It was considered that the N and O radicals combine to form NO_3 and NO_2 . The dissociation of N_2 and O_2 molecules is considered to be caused by high-energy electrons in the plasma. When the high-energy electrons collide with water (H_2O) molecules, the H_2O molecules are dissociated into hydrogen (H) and hydroxyl (OH) radicals. The OH radicals combine with each other to form H_2O_2 . Recently, we predicted that NH_3 can be produced when N and H radicals combine.

In this paper, we report that NH_3 is formed in distilled water irradiated with an atmospheric-pressure Ar plasma jet in air. The dependences of the concentration of ammonium ions (NH_4^+) in the distilled water on the plasma irradiation duration, applied voltage, Ar gas flow rate, and plasma irradiation distance were determined. The temperature of the distilled water during plasma irradiation was also measured using a thermocamera.

2. Experimental methods

Figure 1 shows a schematic of the experimental setup used in this study. In the unit that generates a plasma jet, a discharge electrode made of a copper tube (inner diameter, 4 mm; outer diameter, 6 mm) was inserted into a dielectric quartz tube (length, 50 mm; inner diameter, 6 mm; outer diameter, 8 mm) wrapped with copper foil (thickness, 0.05 mm; width, 10 mm) that functioned as the ground electrode. A high AC voltage was applied to the electrodes to induce dielectric barrier discharge inside the quartz tube between the electrodes and to convert the introduced Ar gas to plasma that was then ejected into air in the form of a jet. The plasma jet was generated at a frequency of 10 kHz and an applied voltages of 8-10 kV using a high-voltage power supply (LHV-10AC, Logy Electric Co., Ltd.). Distilled water (20 mL) in a glass Petri dish of 60 mm diameter was irradiated with the plasma jet at distances of 2-40 mm (from the end of the quartz tube to the liquid surface) for 0-80 min. Ar gas was adjusted the gas flow rate of 10 L/min using a gas flow meter (RK-1250, Kofloc). Voltage and current were measured using a digital oscilloscope (TDS1001B,

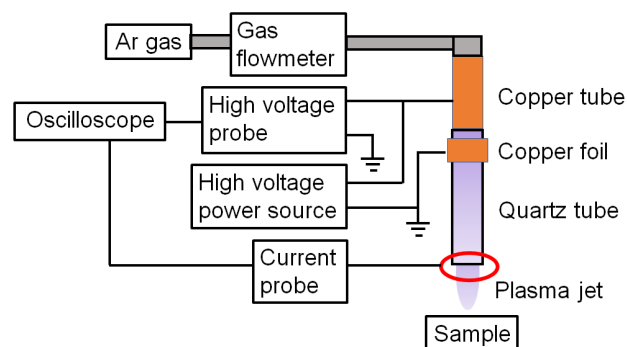


Fig. 1 Schematic of experimental setup.

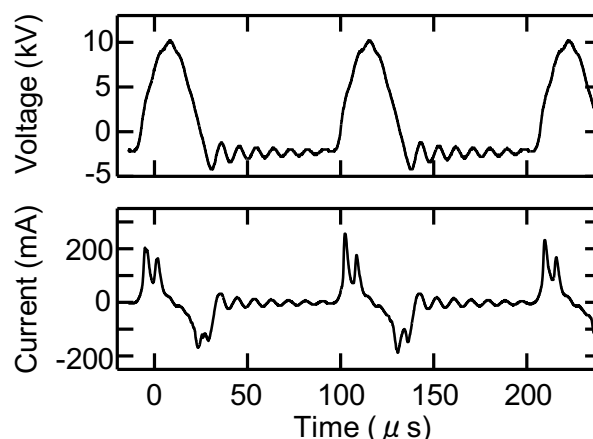


Fig. 2 Typical waveforms of voltage and current (applied voltage, 10 kV; irradiation distance, 15 mm).

Tektronix, Inc.), a high-voltage probe (P6015A, Tektronix, Inc.), and a current probe (A621, Tektronix, Inc.). Power consumption during plasma irradiation was measured using a watt monitor (TAP-TST8N, Sanwa Supply Inc.).

Nessler's reagent was used to confirm the presence of NH_3 in the distilled water. A capillary electrophoresis (CE) system (G1602A, Agilent Technologies Japan, Ltd.) was used to measure the NH_4^+ concentration in the distilled water. NH_3 is present as NH_4^+ in the distilled water. As the electrophoresis solution, a mixed solution of 10 mM imidazole, 5 mM lactic acid, and 0.5 mM 18-crown-6 was prepared, with the pH adjusted to 4.5 using 1 M acetic acid. Fused silica tubes with an inner diameter of 50 μm were used as the capillary tubes. The NH_4^+ was detected by the indirect absorbance method with an applied voltage of 30 kV, a detection wavelength of 310 nm (bandwidth of 20 nm), and a control wavelength of 215 nm (bandwidth of 10 nm).

A thermocamera (F30, NEC Avio Infrared Technologies) was used to measure the temperature of the distilled water during plasma irradiation.

3. Results and discussion

Figure 2 shows typical voltage and current waveforms during plasma irradiation. In the voltage waveform, a pulse with a maximum voltage of 10 kV and a maximum width of

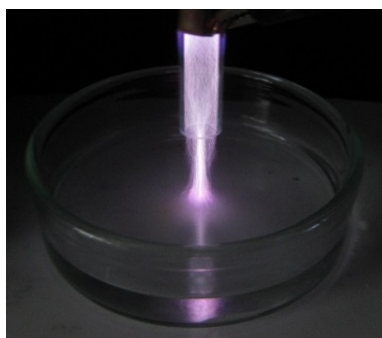


Fig. 3 Photograph of plasma jet ejected onto distilled water (applied voltage, 10 kV; irradiation distance, 15 mm).

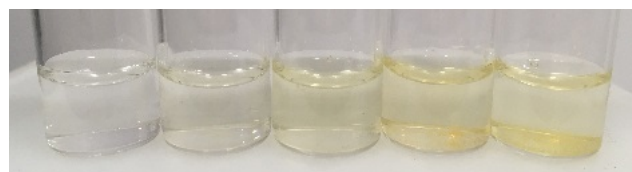


Fig. 4 Reaction of Nessler's reagent for different plasma irradiation durations (applied voltage, 10 kV; irradiation distance, 15 mm); (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min, and (e) 80 min.

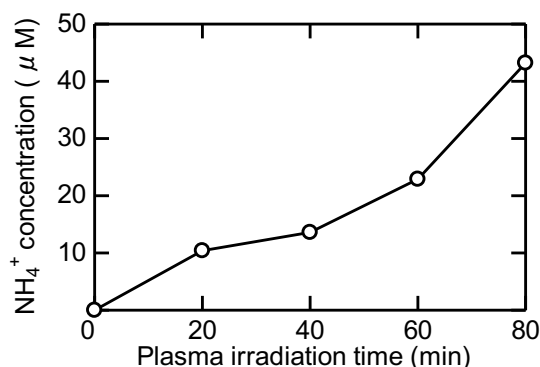


Fig. 5 Dependence of NH₄⁺ concentration on plasma irradiation duration (applied voltage, 10 kV; irradiation distance, 15 mm).

~33 μs appears once every 100 μs (because the power source frequency is 10 kHz). In the current waveform, the peaks were observed at the rise and fall of the voltage in the voltage waveform, and the maximum and minimum currents were 380 and -220 mA, respectively. This suggested that discharge occurred twice in 100 μs. The positive and negative currents were considered to be due to Ar⁺ ions and electrons, respectively. The time between the positive currents and the negative currents were ~25 μs. The power consumption during the irradiation of the plasma to the distilled water was ~20 W.

Figure 3 shows the plasma ejected onto the distilled water. There were many streamers in the plasma, which looked like white lines and collided with the distilled water. Therefore, it is considered that both Ar⁺ ions and electrons in the plasma reached the surface of the distilled water.

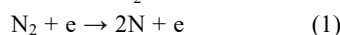
Figure 4 shows the reaction of Nessler's reagent for

different plasma irradiation durations. The color of the reagent was pale brown after 20 min of irradiation and became darker with increasing plasma irradiation duration. This result indicates that NH₄⁺ was present in the distilled water owing to plasma irradiation and that its concentration increased with the plasma irradiation duration.

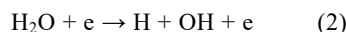
Figure 5 shows the dependence of the NH₄⁺ concentration in the distilled water on the plasma irradiation duration. The NH₄⁺ concentration in the distilled water increased almost in proportion to the plasma irradiation duration and was 43.2 μM after 80 min of irradiation.

Haruyama *et al.* used UV irradiation (185 and 254 nm) and an atmospheric-pressure N₂ plasma to produce 18 μM NH₄⁺ in water in 20 min¹⁹⁾. Although this concentration was ~1.7-fold higher than our result (10.4 μM) obtained by irradiation for 20 min, they had used N₂ gas instead of air. If we also use N₂ gas instead of air, the NH₃ concentration is expected to increase. However, we prefer to use air as it is.

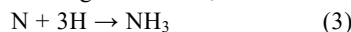
The following is a possible synthesis process of NH₃ and NH₄⁺ using an atmospheric-pressure plasma. High-energy electrons (e) in the plasma collide with N₂ molecules in air, which causes N₂ to be dissociated into N radicals^{42, 43)}.



In addition, the high-energy electrons (e) in the plasma also collide with H₂O molecules on the surface of the distilled water, causing H₂O to be dissociated into H and OH radicals^{44, 45)}.



The N and H radicals combine on the surface of the distilled water and generate NH₃ in air.



Part of this NH₃ diffuses into air and the remainder dissolves in the distilled water.

The H₂O in the distilled water is ionized into H ions (H⁺) and OH ions (OH⁻).



In the distilled water, NH₃ combines with H⁺ to form NH₄⁺.



The dissociation energies of N₂ and H₂O molecules are 9.1 eV⁴⁶⁾ and 5.1 eV^{46,47)}, respectively. If N₂ molecules are dissociated, the electrons in our atmospheric-pressure Ar plasma jet are considered to have a potential energy of ≥9.1 eV.

Haruyama *et al.* synthesized NH₃ in water by simultaneously irradiating the water with UV light and an atmospheric-pressure N₂ or air plasma and considered that the electrons in the plasma had a potential energy of ≥9.1 eV¹⁹⁾. Their result supports our discussion.

On the other hand, Ar atoms in the metastable state are considered to also exist in the Ar plasma. The Ar atoms in the metastable state have an energy of 11.5 eV^{48,49)}. They might have collided with N₂ and H₂O to dissociate these molecules.

Figure 6 shows the dependence of the NH₄⁺ concentration in the distilled water on the applied voltage when the irradiation distance was 15 mm and the irradiation duration was 60 min. With applied voltage of ≥8 kV, the NH₄⁺ concentration increased approximately in proportion to the applied applied voltage and was 23 μM for an applied voltage

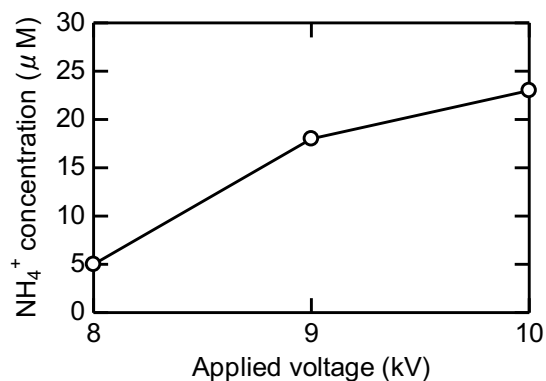


Fig. 6 Dependence of NH_4^+ concentration on applied voltage (irradiation distance, 15 mm; irradiation duration, 60 min).

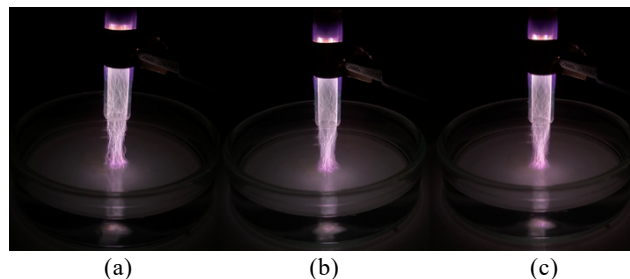


Fig. 7 Photographs of the plasma jet ejected onto the distilled water for different applied voltages when the irradiation distance was 15 mm; (a) 8 kV, (b) 9 kV, and (c) 10 kV.

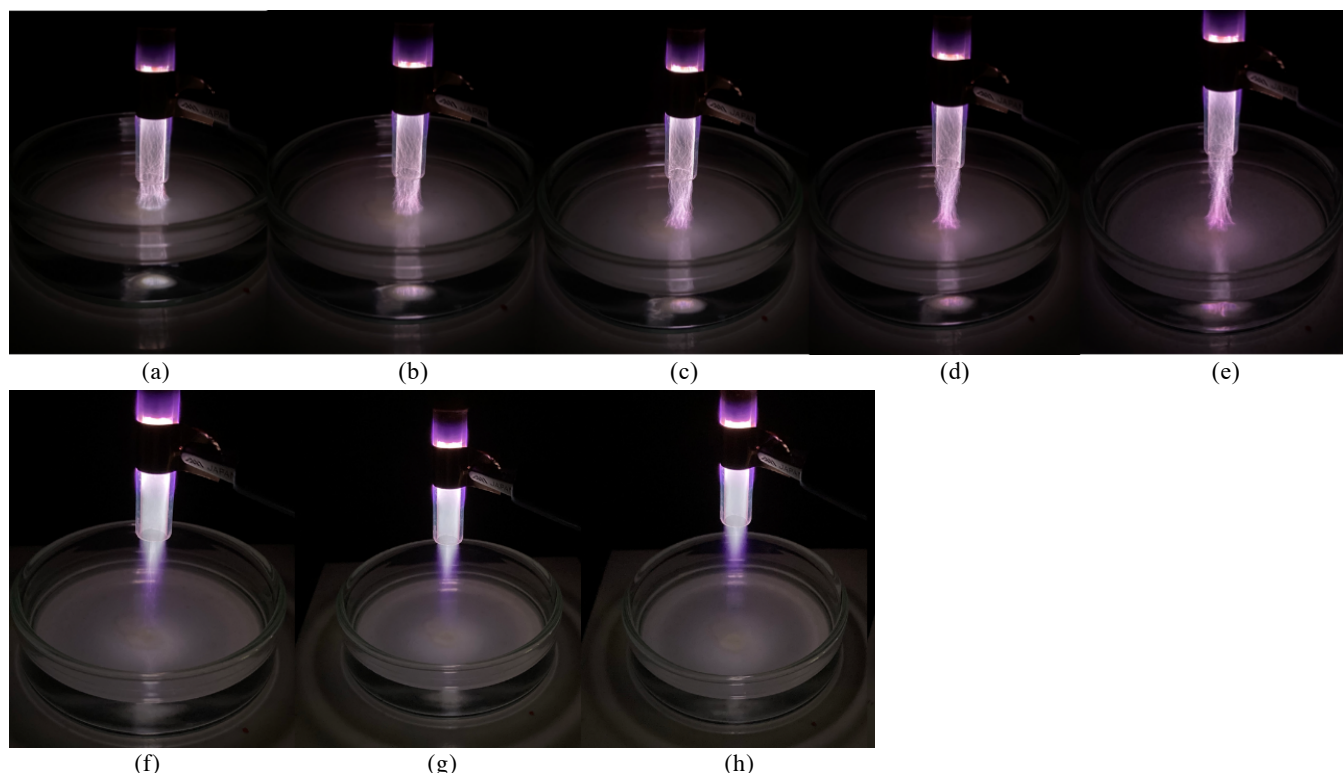


Fig. 8 Photographs of plasma jet ejected onto distilled water for different irradiation distances when the applied voltage was 10 kV; (a) 2 mm, (b) 5 mm, (c) 10 mm, (d) 15 mm, (e) 20 mm, (f) 25 mm, (g) 30 mm, and (h) 40 mm.

of 10 kV. This may be because the number of ionized Ar atoms increased with the applied voltage, which then increased the number of electrons and thereby the numbers of N and H radicals, resulting in an increased number of NH_3 molecules.

Figure 7 shows photographs of the plasma jet ejected onto the distilled water for different applied voltages when the irradiation distance was 15 mm. The streamers reached the water surface at all applied voltages. There were no differences in the behavior of the plasma jet when it came in contact with the water surface.

Figure 8 shows photographs of the plasma jet ejected onto the distilled water at different irradiation distances when the applied voltage was 10 kV. When the irradiation distance was 2 mm [Fig. 8(a)], the streamer traveled straight from the quartz tube and reached the water surface. When the

irradiation distance was 5-20 mm [Figs. 8(b)-8(e)], some streamers were slightly focused and they reached the water surface. When the irradiation distance was 25-40 mm [Figs. 8(f)-8(h)], the streamers were indistinct and did not appear to reach the water surface. From these results, we found that whether the streamers reach the water surface and the state of the plasma both depend on the plasma irradiation distance.

Figure 9 shows the dependence of the NH_4^+ concentration in the distilled water on the plasma irradiation distance. The NH_4^+ concentration was 12 μM for an irradiation distance of 2 mm, increased with irradiation distance to reach a maximum of 22 μM for 10 mm, and then decreased for 15-20 mm. The NH_4^+ concentration remained almost unchanged for 25-40 mm. These results indicate that the NH_4^+ concentration in the distilled water depends on the plasma irradiation distance and

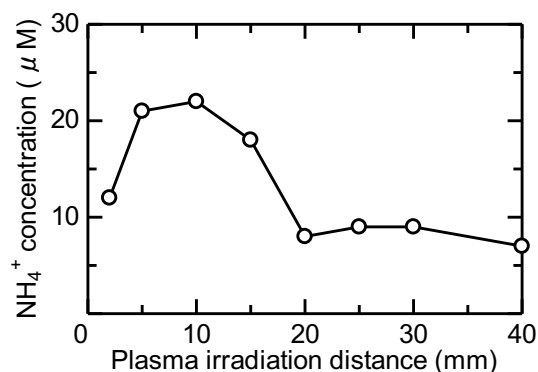


Fig. 9 Dependence of the NH_4^+ concentration in the distilled water on the plasma irradiation distance (applied voltage, 10 kV; irradiation duration, 60 min).

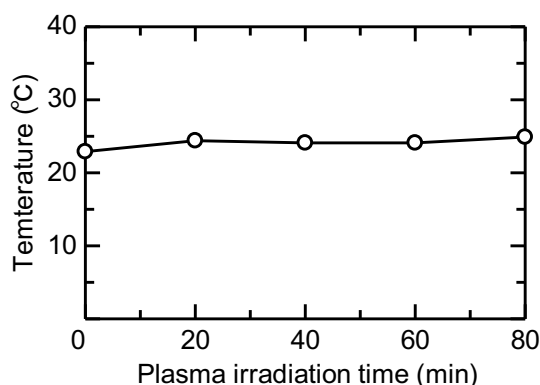


Fig. 10 Dependence of temperature of distilled water, determined by thermography, during plasma irradiation on plasma irradiation duration (applied voltage, 10 kV; irradiation distance, 15 mm).

reaches a maximum at an irradiation distance of 10 mm. The reason for this is considered to be as follows. Because the field of NH_3 synthesis expressed by Eq. (3) is in the vicinity of the water surface, the number of generated H radicals increases with decreasing plasma irradiation distance, resulting in an increased NH_4^+ concentration. However, the distance over which the plasma reacts with air is short when the plasma irradiation distance is excessively short. As a result, the amount of generated N radicals decreases and the NH_4^+ concentration also decreases. For an irradiation distance of 20 mm [Fig. 8(e)], the streamer reached the water surface. However, the NH_4^+ concentration for 20 mm was equivalent to those for other irradiation distances [Figs. 8(f)-8(i)] in which the streamers did not appear to reach the water surface. The reason for this remains unclear.

Figure 10 shows the dependence of the temperature of the distilled water, which was determined by thermography, during plasma irradiation on the plasma irradiation duration. The temperature of the distilled water was 22.9 °C at the start of plasma irradiation and was 24.9 °C after irradiation for 80 min. This result indicates that the temperature of the distilled water increased by ~1.5 °C owing to the initial plasma irradiation but remained almost unchanged at around room temperature during irradiation.

4. Conclusions

NH_4^+ were synthesized in distilled water irradiated with an atmospheric-pressure Ar plasma jet in air at room temperature. This is a result of N radicals dissociating from N_2 in air and H atoms dissociating from H_2O on the surface of the distilled water combining to become NH_3 , which dissolved in the distilled water and combined with H^+ in the water. The NH_4^+ concentration in the distilled water increased approximately proportionally to the plasma irradiation duration and applied voltage. In our experiment, the maximum NH_4^+ concentration of 43.2 μM was obtained when the applied voltage was 10 kV, the Ar gas flow rate was 10 L/min, the plasma irradiation distance was 10 mm, and the plasma irradiation duration was 80 min. The power consumption during plasma irradiation was ~20 W.

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