Production of reactive oxygen and nitrogen species in photoemission-induced atmospheric pressure DC air discharge

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Abstract: Atmospheric pressure DC discharge was generated in air flow without special discharge gases such as helium or argon by using a back-irradiated photocathode of gold nano-thick film and an excimer lamp at wavelength of 172 nm. Reactive oxygen and nitrogen species were analysed by UV absorption spectroscopy for the dissolved gas in water. When the discharge was operated, nitrate NO_3^- and hydrogen peroxide H_2O_2 appeared, and ozone O_3 further increased while some of it was produced by 172 nm UV alone.

Keywords: air discharge, plasma, atmospheric pressure, photoemission, RONS

1. Introduction

Low-temperature atmospheric pressure plasmas (LTPs) have been shown an interesting outcome in medical applications including, but not limited to, sterilization, wound healing, drug delivery, plasma dentistry, and cancer treatment [1-2]. These plasmas produce long-lived reactive oxygen and nitrogen species (RONS) when reacting with biological materials, such as hydrogen peroxide H_2O_2, hydroxyl OH, nitrite NO_2^- and nitrate NO_3^-. It has been reported that RONS could lead to cell death pathways by triggering cell signal cascades. Simultaneously, it has benefits for the growing process of plants [3]. The production of RONS from plasma is a key parameter for medical, biotechnological, and agricultural applications. The absence of a vacuum system in LTPs is considered as a motivation for medical applications because biological materials cannot tolerate low pressure or a vacuum environment. However, generating stable and uniform plasma in atmospheric pressure is still a challenging issue.

Based on Paschen's law, a small gap is suitable for easily igniting gas discharge at high pressure. Consequently, the volume of a discharge space decreases which leads to the reduction of the primary electrons supply from cosmic rays. Thus, it is effective to supply free electrons in such small space discharge either via field emission [4] or photoemission. Previous studies reported the generation of low-pressure plasma assisted by photoemission for carbon-based materials synthesizing [5-7]. The emission of photoelectrons from the cathode led to plasma generation in Townsend mode and glow-like mode. In the other studies, the application of photoemission had been used in electron beam lithography, electron guns, and optical fiber by back-illuminating a photocathode with ultraviolet (UV) light [8-10]. The photocathode of gold thin film deposited on the quartz glass is an alternative to produce stable photoemission even in atmospheric pressure conditions [11].

In this study, DC gas discharge generation was induced by UV back-irradiating a gold nano-film photocathode. The stability of the gas discharge generation was examined by measuring the voltage-current characteristic. Moreover, the production of RONS from gas discharge was evaluated through its UV absorbance.

2. Methods

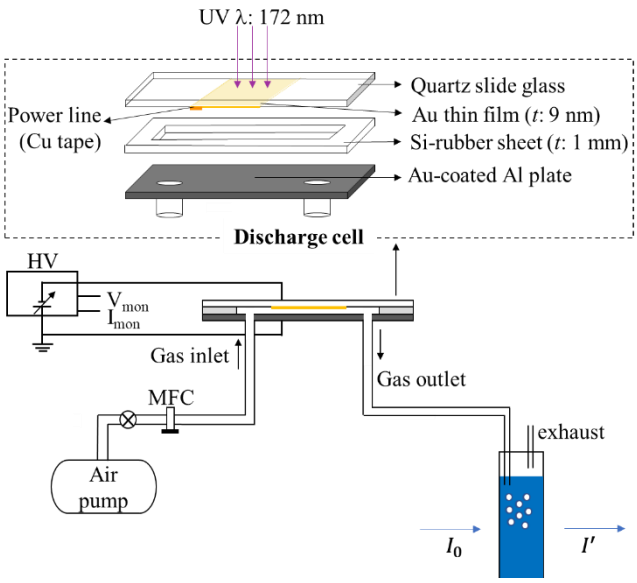

Fig. 1. Experiment set-up of photoemission-induced atmospheric pressure gas discharge.

Fig. 1. shows an experimental illustration of photoemission-induced gas discharge. A photocathode was fabricated by depositing gold thin film (25 mm x 26 mm) with a thickness of 9 nm on the quartz glass (76 mm x 26 mm x 1 mm). A silicon rubber sheet was inserted as a spacer between the photocathode and an anode plate of gold-coated aluminum plate to create a discharge cell with a gap of 1 mm, and a gas flow channel with a width of 15 mm. Air was flown from the air compressor into the discharge cell through a mass flow controller (MFC) at a flow rate of 250 sccm.

The photocathode was externally illuminated using an excimer lamp Xe_2* with a wavelength of 172 nm ($h\nu$: 7.2 eV) (ORC Manufacturing Co., Ltd.). The excimer lamp was operated at 37 kHz which resulted in the pulsation of the photoemission current and discharge current. However, the current was measured as the time-averaged DC. A high DC negative voltage was applied to the photocathode, and the anode was grounded. The voltage and current were obtained using the monitoring output of the power source.

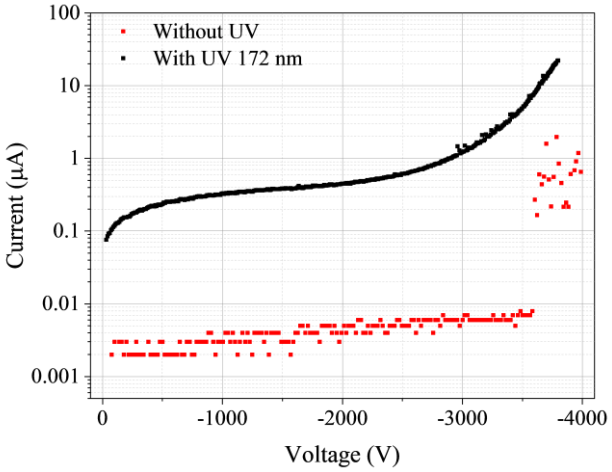

Fig. 2. Voltage-Current characteristic of photoemission-induced air discharge.

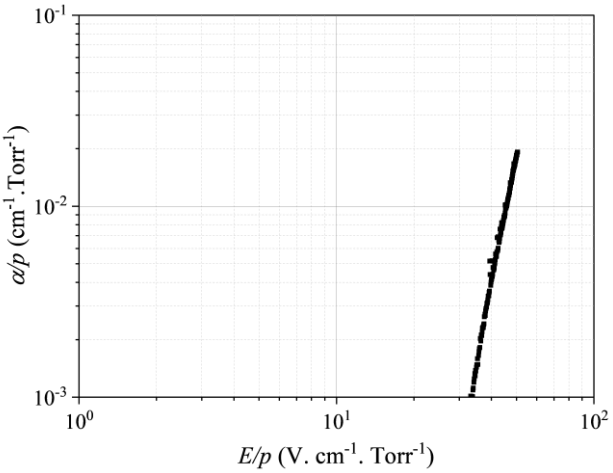

Fig. 3. Electron ionization coefficient α/p as a function of the field E/p for air.

The production of reactive species was examined by measuring the UV absorbance of gas discharge dissolved in deionized water (DI-water). The DI water of 3 mL was placed in cuvettes (Hellma Analytics QS-101) and then bubbled with the discharge gas. A conventional double-beam UV-VIS spectrophotometer (Hitachi U-3900) was used to measure the optical absorption in the UV region between 190 – 340 nm. The measurement was carried out with an optical path of 10 mm, a spectral resolution of 0.2 nm, and a scan speed of 120 nm/min. Deconvolution was performed on the obtained spectra to identify the details species then each concentration was estimated based on our previous studies [12-13].

3. Results and Discussions

The voltage-current relationship of photoemission-induced gas discharge of air is shown in Fig. 2. In the case without UV, no significant current was measured as bias voltage applied up to around 3700 V. Then, a sudden rising of current was observed around 1 μA owing to the spark discharge. It led to damage of the photocathode. In contrast, the utilization of UV resulted in current increases gradually which could be divided into three regions. First region, as the bias voltage increased up to around 1000 V, the current increased. It implies that electrons were emitted from the photocathode and moved to the anode under influence of an electric field in the discharge cell. Second region, the current was slowly increased, even almost saturated around 0.4 μA up to bias voltage around 2000 V. It suggests the enhancement of the emitted electron mobility to the anode, yet it was limited by the collision with air molecules. Third region, at the bias voltage 2000 V onward, the current increased exponentially up to around 30 μA. It indicates that photoelectrons finally gain sufficient energy to ionize the molecules. This process leads to electron avalanches which are similar to Townsend discharge of the α regime. Fig. 3 depicts the ionization coefficient per pressure α/p and the reduction of an electric field per pressure E/p, which were estimated from the I-V relationship. The ionization coefficient of air in this study has good agreement with the previous work [14].

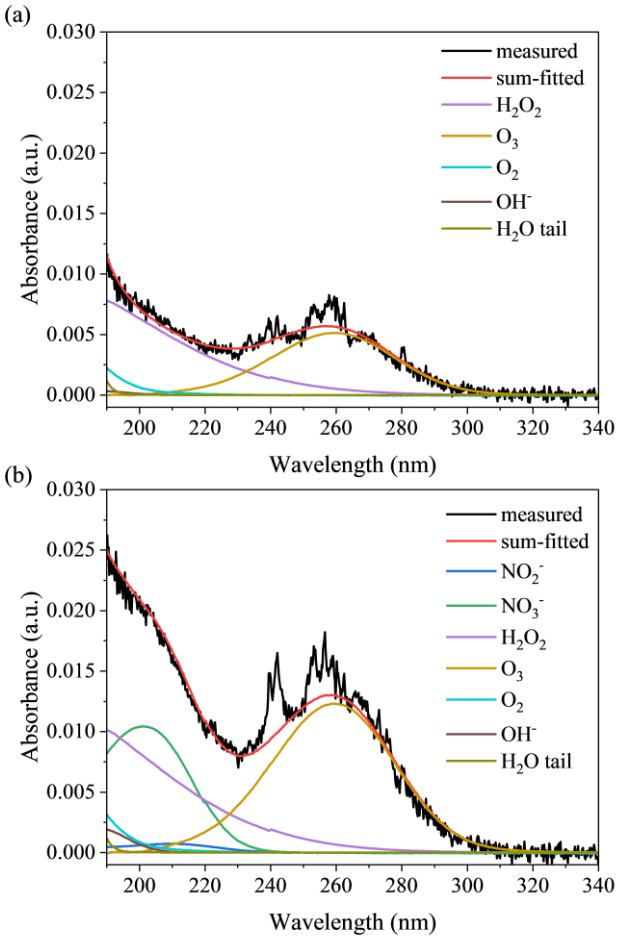

Fig. 4 Absorbance of gas discharge dissolved in water (a) excimer-irradiated gas (b) photoemission-induced air plasma

The generation of reactive oxygen and nitrogen species (RONS) was examined by comparing the UV absorption of

gas irradiated by an excimer lamp only (Fig. 4(a)) and gas discharge induced by photoemission (Fig. 4(b)). In the case of excimer-illuminated gas, a peak around 260 nm was found which corresponds to ozone O_3 diluted in the water. In addition, the tail of the peak at a wavelength below 220 nm was detected also. Deconvolution analysis showed that this peak can be assigned as hydrogen peroxide H_2O_2, oxygen molecule O_2, hydroxyl ion OH^-, and water tail which appeared due to water temperature change. These species are attributed as reactive oxygen species (ROS). On the other hand, for the absorbance spectrum of photoemission-induced gas discharge, a significant peak around 210 nm was found beside the peak at 260 nm. This peak corresponds to nitrite NO_2^- and nitrate NO_3^- which are known as nitrogen reactive species (RNS). A peak of hydrogen peroxide H_2O_2, molecule oxygen O_2, hydroxyl ion OH^-, and water tail were also detected.

Table 1. RONS concentration of air atmospheric pressure gas discharge.

RONS species	Excimer-treated gas (ppm)	Photoemission-induced plasma (ppm)
H_2O_2	1.0	1.3
O_3	0.05	0.12
O_2	0.4	0.6
OH^-	0.005	0.03
NO_2^-	-	0.01
NO_3^-	-	0.065

The details concentration of the reactive species is presented in Table 1. It is known that an excimer lamp with a wavelength of 172 nm produces ozone in the air. Thus, ROS was detected even in excimer lamp conditions only which was dominated by hydrogen peroxide then followed by oxygen and ozone, respectively. When a high voltage was applied with the power of 13 mW, the concentration of ROS was increased and RNS was detected which nitrite as the dominant species. It suggests that photoemission-induced plasma produces reactive oxygen and nitrogen species when interacting with liquid.

4. Conclusions

Production of the reactive oxygen and nitrogen species (RONS) from photoemission-induced atmospheric pressure DC air discharge was analyzed by measuring the UV absorbance of its dissolved in water. The UV absorbance spectra showed that RONS was generated which includes hydrogen peroxide H_2O_2, hydroxyl ion OH^-, nitrite NO_2^-, and nitrate NO_3^-.

5. References

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