Proceedings of International Conference on Technology and Social Science 2017
Invited Paper

Space- and time-resolved optical diagnosis of discharge plasma generated in water vapor bubble formed in aqueous solutions

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Keywords: discharge plasma, aqueous solution, water vapor bubble, pulsed voltage, emission spectroscopy

Abstract. When a pulsed high voltage is applied to a gap between electrodes confined in aqueous solution, discharge plasma confined in a water vapor bubble forms between the electrodes. The plasma in water vapor bubble is expected to induce characteristic reactions applicable to many fields such as material processing, water treatments and medical surgery owing to the generation of large amounts of reactive chemical species in aqueous solutions. However, it has not been fully clarified that what kinds of chemical species in the plasma exist and how the physical parameters of the plasma, such as electron number density and temperatures, affect the generation and extinction of the chemical species. To measure these chemical species and physical parameters, we have developed a time- and space-resolved micro-spectroscopic imaging apparatus with a custom-made optical discharge cell. With the newly developed system, we estimated the plasma parameters and measured the spatial distributions of the reactive species and their temporal evolutions in the discharge plasma. The newly constructed instrument would provide a useful tool to investigate the physical and chemical properties of the plasma formed in water vapor bubble in aqueous solutions.

1. Introduction

When pulsed high voltage with a temporal duration of microseconds is applied to a micrometer gap between electrodes in aqueous solution, glow-like discharge plasma confined in a water vapor bubble generates between the gap [1]. In the discharge plasma, abundant water molecules are dissociated into hydrogen (·H) and hydroxyl (·OH) radicals by the collisions with free electrons accelerated Since the ·H and ·OH exhibit high reduction and oxidation activities, respectively, it is expected that the discharge plasma can be effectively applied for reduction and oxidation reactions for material syntheses, degradation of organic compounds and sterilization. Further, the plasma is formed and sustains in water vapor bubble under atmospheric pressure, many chemical reactions, which hardly occur under general conditions for the generation of plasma, i.e. under low pressure or in vacuum, are also expected to proceed effectively by the collision of ·H and ·OH to other chemical species dissolved in the surrounding aqueous solutions. Thus, the discharge plasma formed in aqueous solutions has been attracted attentions in many fields such as nanomaterialsprosessing, water treatments, and medical surgery. Actually, by utilizing the plasma formed in aqueous solutions, characteristic nanomaterials have been successfully synthesized [2]. In addition, the nanoparticles synthesized in the plasma formed in aqueous solution exhibit high dispersion stabilities in solution without adding any chemical dispersion stabilizer. As the origin of the high dispersion stabilities, it has been thought that the formation of surface OH groups by the reaction between the ·OH radicals generated in the plasma and the surfaces of the nanoparticles. Such ·OH radicals are also believed to play crucial roles in water treatments by the effective degradation of hazardous organic compounds in aqueous environments and in the infection prevention of surgical sites with a plasma scalpel.

Although the discharge plasma formed in water vapor bubble in aqueous solutions has been proved to provide effective reaction fields for many fields, its essential physical parameters, such as electron number density, electron temperature, and the excitation temperatures of reactive species, have not been fully understood. Furthermore, the spatial distribution and temporal evolution of the chemical species in the plasma and in water vapor bubble have also not been fully elucidated. Thus, an adequate spectroscopic apparatus for the measurements of such properties and chemical species has been desired.

In the present study, we report on the development of a microscopic imaging system with an optical discharge cell for monitoring the spatial distributions and temperatures of chemical species in the microscopic and heterogeneous plasma reaction field formed in water vapor bubble in aqueous solutions. We first present the measurement of the time-resolved emission spectra from the discharge plasma formed in the discharge cell. Second, the procedures for the estimations of electron number density, blackbody temperature, ·H electronic excitation temperature, and ·OH rotational excitation temperature are discussed.

2. Experimental

The discharge plasma in water vapor bubble was formed by applying a pulsed voltage to a gap between two electrodes fixed in a custom-made optical discharge cell. The plasma was spectroscopically investigated by combining the cell with instruments for the measurements of emission from the plasma. The schematic diagram of the system is shown in Fig. 1. Two holes were made on the sides of the cell and two ceramic insulator tubes were inserted to the cell through the holes. Two tungsten rods were inserted into the cell via the holes of the insulator tubes and used as the electrodes for discharge. An area of the bottom of the cell under the gap between the electrodes was made with a quartz plate. This is because that a quartz well transmits light in the wavelength region between 200 and 2000 nm, the emission spectrum ranging from UV to the near-IR region from the plasma formed in the gap between the electrodes can be measured. In addition, the optical cell minimizes the working distance, allowing us to combine an objective lens and the optical discharge cell to effectively collect the emission from the plasma.

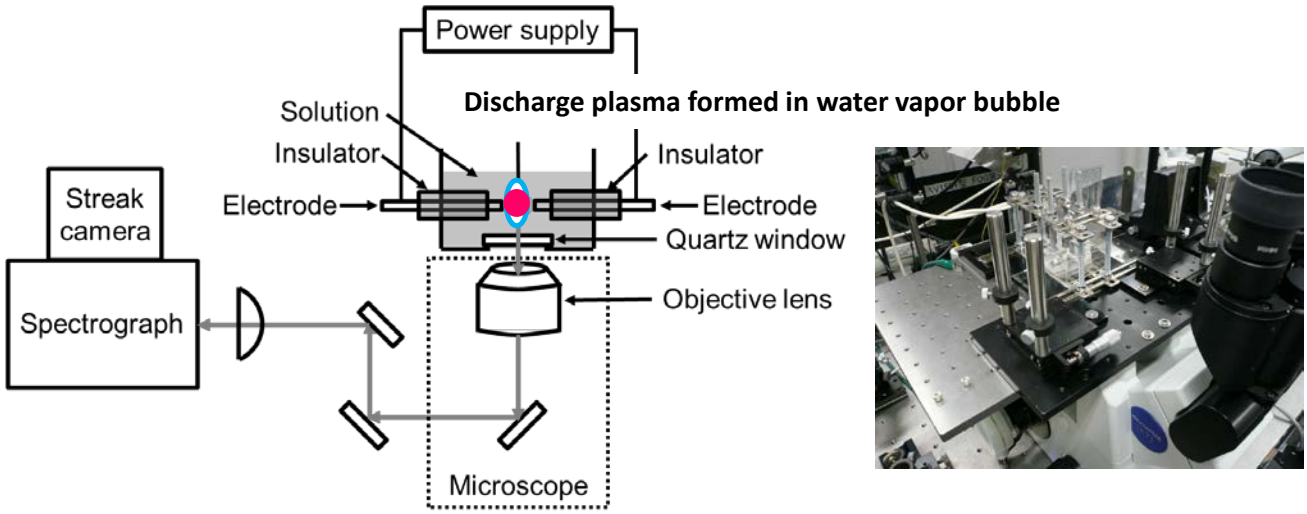

Fig. 1. Experimental setup for microscopic spectroscopy for the investigation of discharge plasma generated in water vapor bubble formed between the electrodes in aqueous solution. right panel shows the picture of the optical discharge cell loaded on the microscope.

The gap distance between the tip surfaces of the electrodes was set to 500 μm. The cell was filled with an aqueous solution of NaOH of 3 mmol dm^{-3} concentration. The discharge was induced by the application of a bipolar pulsed voltage with 0.7 μs duration. The amplitude and repetition rate of the voltage were 1.2 kV and 25 kHz, respectively.

The emission from the plasma, going through the optical window of the cell, was collected by a reflective objective lens installed in an inverted microscope. For the measurements of the spatial distributions of the radiative chemical species (free electrons, ·H, and ·OH), the emission was amplified by an image intensifier and their spatial distributions were detected by a CCD camera. A bandpass filter was located before the image intensifier for the selection of the wavelength for species-selective detection. To measure the temporal evolution of them, we measured the time-resolved emission spectra of them. The emission was introduced into a spectrograph and was detected by a streak camera. The detectors were temporally synchronized with the application of the pulsed voltage, which enabled us to measure the spectra with nanosecond temporal resolution.

3. Results and discussion

3.1 Spatial distributions of reactive species

We first obtained images of spatial distributions for free electrons, ·H, and ·OH. In the obtained image, shown in Fig. 2, the free electrons are found to be localized in the vicinity of the cathode. This result indicates that the free electrons are generated from the cathode by the collisions between the cathodic electrode and positively charged ions accelerated by the electric field applied between the electrodes, called secondary electron generation. As shown in Fig. 2, For ·H and ·OH, we measured that the spatial distributions are localized in the vicinities of the cathode, as well as the free electron. However, the spatial distribution for ·H is expanded in the plasma more than that for ·OH. This result may indicates that ·H is spatially dispersed faster than ·OH owing to the lighter weight. These results demonstrate that the developed apparatus enables us to measure the spatial distributions for the radicals and the free electron formed in the discharge plasma in water vapor bubble [3].

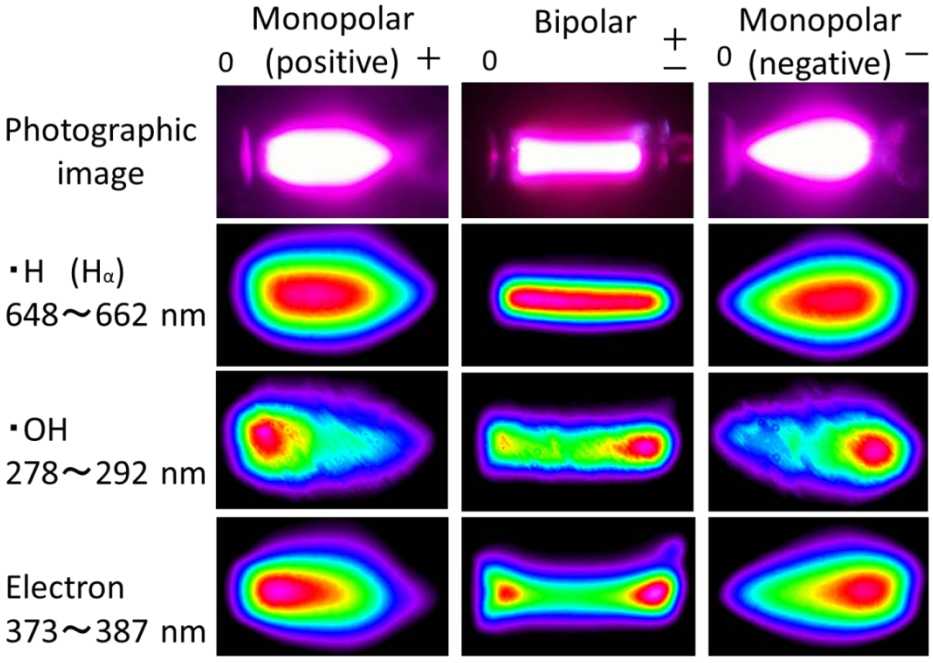

Fig. 2. Photographic image of the plasma (top) and images of the spatial distributions for · H (second top), · OH (second bottom), and free electron (bottom). The applied voltage was monopolar for the left and right columns, and bipolar for the center column.

3.2 Temporal evolutions of parameters for the discharge plasma in water vapor bubble

We next estimated the temperatures of the reactive species. By the curve fitting analyses of the emission spectrum from the plasma with theoretical calculation, the temperatures of ·H and ·OH were estimated successfully measured as 5,000 and 4,000 K, respectively. It is also revealed that the temporal evolutions of the radical temperatures correspond well with that of the electron number density and the temperature show the fluctuation between the duration of the application of the voltage (data will be presented in the presentation). The reason for the correlation between the temperature and the electron density was considered as follows. Since the plasma should be electrically almost neutral, when the electron number density is high, it is expected that the density of positively charged ions should be also high. The positively charged ions are then accelerated by the electric field applied between the electrodes and collide frequently with other particles including the radicals. By the collisions, the kinetic energies of the ions are transferred to the colliding particles. Due to the repetition of these acceleration-collision processes, the radical temperature should exhibit the correspondence with the electron number density. It is demonstrated that time-resolved optical emission spectroscopy combined with the newly developed optical microscope system provide a powerful method to investigate the temporal evolution and the temperature changes of the transient reactive species formed in the water vapor bubble [4].

4. Conclusion

For the diagnosis of the discharge plasma generated in a water vapor bubble formed in aqueous solution, an optical microscope system combined with a custom-made discharge cell and the space- and time-resolved optical emission spectrometer is developed. Microscopic images of transient reactive species such as ·H and ·OH radicals formed in the plasma were successfully obtained. Further, the excitation temperatures of the radicals were estimated as several thousands of kelvins. We also found that the radical excitation temperatures show strong correlations with the electron number density. The obtained information on the plasma will be useful for the designing of chemical reactions for various applications. Recently, we have also enhanced the system by adding gas-injection apparatus, where several kinds of gases can be introduced into the water vapor bubble directly [5]. The newly constructed system would contribute to the measurements, analyses and the control of the reaction fields utilizing plasma in water vapor bubble, that are going to be applied in material processing, medical surgery, and environmental detoxification.

References

[1] O. Takai, “Solution plasma processing (SPP)”, ***Pure Appl. Chem.***, Vol. 80, No. 9, pp. 2003-2011, 2008.

[2] M. A. Bratescu, O. Takai and N. Saito, “One-step synthesis of gold bimetallic nanoparticles with various metal-compositions”, ***J. Alloys Compds.***, Vol.562, pp.74-83, 2013.

[3] H. Yui, Y. Someya, Y. Kusama, K. Kanno and H. Takakuwa, “Microscopic Optical Discharge Cell for Micro-Spectroscopic Measurements Plasma in Solutions and Its Chemical-contrasted Imaging”, ***BUNSEKI KAGAKU,*** Vol. 62, No. 1, pp. 19-24, 2013.

[4] M. Banno, K. Kanno, Y. Someya and H. Yui, “Nanosecond time-resolved microscopic spectroscopy for diagnostics of an atmospheric-pressure discharge plasma formed in aqueous solution”, ***Jpn. J. Appl. Phys.,*** Vol. 54, No. 6, 066101, 2015.

[5] M. Banno, K. Kanno, H. Yui, “Development of direct gas injection system for atmospheric-pressure in-solution discharge plasma for plasma degradation and material syntheses”, ***RSC Adv.***, Vol. 6, Isss. 19, pp. 16030-16036, 2016.