Multibubble plasma production and solvent decomposition in water by slot-excited microwave discharge

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Intense microwaves are injected from a slot antenna into water partly filling a metal vessel. When the vessel is evacuated to saturated vapor pressure ($\sim 5\times 10^3$ Pa) of water, microwave breakdown gives rise to plasmas in many bubbles in the boiling water. Gas bubbling technique enables production of multibubble plasmas in water even at atmospheric pressure. Optical emissions from the exited species are investigated to identify radical species in water. In order to demonstrate application to purification of polluted water, methylene blue and trichlorethylene solution in 8 l water were observed to rapidly decrease with multibubble plasma treatment. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2783209]

Recently, much attention has been given to plasma production in liquid, from its potential applications point of view: purification of industrial effluent including trichlorethylene (TCE) pollution and synthesis of nanomaterial such as carbon nanotubes. To date, discharges in liquid have been one of the classical topics in plasma physics and applications. In general, electrical breakdown in liquid such as water and oil requires extremely high voltage and electric field. Thus, high voltages of dc or rf were applied to metal electrodes in liquid for plasma production.[1–6] Recently, microwave irradiation from metal rod antenna fed through a coaxial cable was also demonstrated to produce fuel gas or polycrystalline silicon carbide in liquids.[7,8] However, all these methods often have a problem of metal contamination in liquid due to sputtering or arcing of metal electrodes. In addition, these methods will meet difficulty in producing wide-area plasmas needed for high throughput in practical applications.

In contrast, slot-antenna excited microwave discharge enables metal-free plasma production since the metal slot antenna can be covered with dielectrics. Furthermore, one can easily produce large-area plasma in meter scale in gas phase at pressures from 1 Pa to atmospheric pressure, as already reported.[9,10] In this letter, we report microwave plasma production in water with a slot antenna immersed in water, together with its possible applications to purification of contaminated liquid.

A schematic view of the experimental apparatus is shown in Fig. 1. Pure water partly fills a cylindrical metal vessel of 300 mm in diameter and 155 mm in length. Microwaves at 2.45 GHz with power <3 kW are guided along a rectangular waveguide of TE_{10} mode filled with quartz, and injected into water through a slot antenna. The slot antenna of 1 mm in width and 56 mm in length is installed at the end of quartz-filled waveguide. The microwave generator can be operated either in continuous mode or pulsed mode (50 Hz–80 kHz). In the present work, the experimental data obtained in the pulsed mode are described at the repetition frequency of 20 kHz (unless stated) and duty ratio of 35%, with peak power of <3 kW. A thermocouple is inserted into the water to monitor the temperature. Various kinds of gas (argon, helium, and air) can be injected into the water to externally generate bubbles, through a nozzle via mass flow controller. Optical emission of the plasma viewed from a port in front of the slot antenna was measured through an optical fiber using a compact spectrometer (EPP2000-UVNb, Stellar Net, Inc.) covering a range of wavelength of 250–850 nm.

Microwave discharge in water easily occurs without gas injection when the vessel is evacuated down to the saturated vapor pressure of water, $\sim 5\times 10^3$ Pa at room temperature. At such reduced pressures, many small bubbles appear in water due to boiling, where the plasma is considered to be created in each bubble by gas phase ionization. When the operating pressure is higher than $\sim 5\times 10^3$ Pa, a gas bubbling technique is needed to continuously obtain stable multibubble plasma in liquid.

Figure 2 shows an example of optical emission image of multibubble plasmas in water produced at pulsed power of 800 W and pressure of $\sim 5\times 10^3$ Pa without gas injection. The slot antenna is located in the center of the bright region. Many bubble plasmas spread over a sheetlike region parallel to the slot-antenna plane. Examples of optical emission spectra of multibubble plasmas at 700 W and $\sim 5\times 10^3$ Pa are

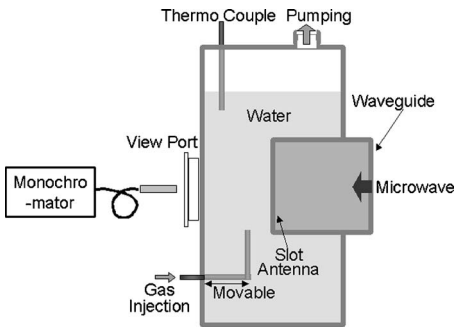

FIG. 1. Side view of the experimental apparatus.

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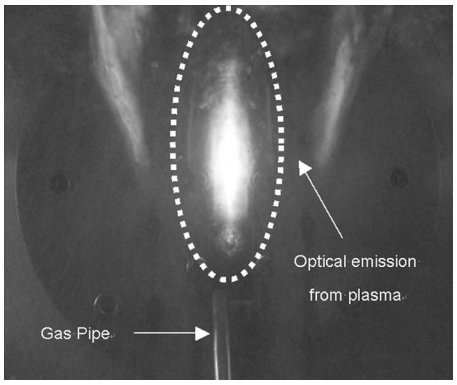

FIG. 2. Optical emission image of multibubble plasma produced by pulsed 800 W discharge at $\sim 5\times 10^3$ Pa.

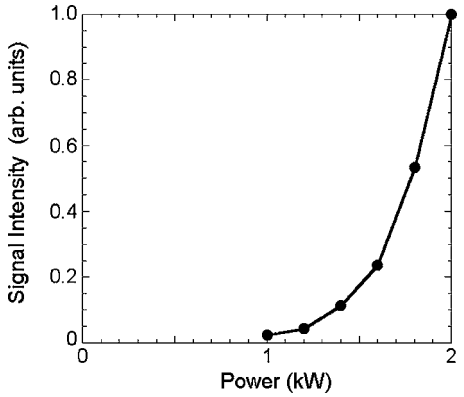

FIG. 4. Microwave power dependence of OH emission intensity at 308 nm at atmospheric pressure with air injection.

shown in Fig. 3. The line spectra of H_α(656 nm), H_β(486 nm), and O I (777 and 844 nm) were clearly observed in a wavelength range from 250 to 850 nm. On the other hand, 306.4 nm system of molecular OH transitions ($A\ ^2\Sigma^+$-$X\ ^2\Pi$) (Ref. 11) were observed with the strongest peak at 308 nm. These observed spectra suggest that water vapor (H_2O) contained in bubble is dissociated into OH, O, and H radicals by plasma in the bubble. The OH radical has the highest oxidation potential among OH (2.85 V), O_3 (2.07 V), and H_2O_2 (1.78 V) radicals, where OH and O radicals are effective for purification of water polluted with TCE.[12]

At pressures well above the saturated vapor pressure, no bubbles are observed and the microwave discharge hardly occurs in the present range of incident microwave power. Even in such condition, multibubble plasma could be generated up to atmospheric pressure by gas bubbling technique where air, argon, or helium gas is externally injected at the typical flow rate of 7 SLM (SLM denotes liter per minute at STP), thus producing bubbles near the slot antenna. The optical emission spectroscopy again revealed strong emission lines of H, O, and OH radicals. As for the spectra originated from the bubbling gas, a number of Ar I spectra were confirmed in case of Ar gas bubbling; however, He I spectra were hardly detected in case of He gas bubbling, probably because of the extremely high excitation level (>21.2 eV) for He I emission.

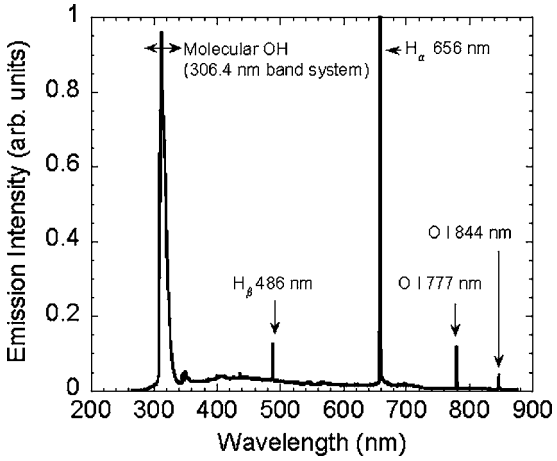

FIG. 3. Optical emission spectra for pulsed 700 W discharge at $\sim 5\times 10^3$ Pa.

In case of air bubbling, the large peaks of the second positive molecular nitrogen series ($C\ ^3\Pi_u$-$B\ ^3\Pi_g$ transitions) (Ref. 11) were detected at 337, 358, 381, 406, 434 nm, while the 317 nm spectrum of nitrogen molecular nitrogen series is overlapped by the OH molecular band spectrum. However, the first positive series of molecular nitrogen transitions ($B\ ^3\Pi_g$-$A\ ^3\Sigma_u^+$) and the atomic nitrogen line spectra were hardly detected in a range from 500 to 850 nm.

Figure 4 shows the microwave power dependence of OH (308 nm) emission intensity measured at atmospheric pressure with air injection at the flow rate of 7 SLM, where the emission intensity was normalized by the value at 2.0 kW. The produced plasma was stable for the microwave power higher than 1 kW. The OH emission intensity nonlinearly increases with increasing the microwave power, probably because of the increase in the number of bubble plasma and increase in the plasma density in each bubble.

In order to examine the chemical activity of multibubble water plasma, methylene blue solution in 8 l water at concentration of 10 mg/l was exposed to microwave discharge. The methylene blue concentration was evaluated with 650 nm light transmission, comparing the measured transmission intensity with that of known methylene blue concentration. Multibubble plasma was produced by the pulsed microwave discharge (peak power of 700 W, repetition frequency of 1 kHz) at pressure from 5×10^3 to 1.1×10^4 Pa, where the methylene blue concentration is almost uniform because of convection flow by gas bubbling. The time evolution of methylene blue concentration after discharge is shown in Fig. 5. After 75 min, the methylene blue concentration decreased to 0.3 mg/l with input power energy density of 1.4×10^5 J/l, which corresponds to 97% decomposition by multibubble plasma. Thermal plasma[6] has $\sim$0.5 mg/min treatment speed at the input energy density of 2.5×10^5 J/l, while nonequilibrium rf plasma provided a $\sim$0.4 mg/min treatment speed with 80 W rf power deposition in a 4 cm diameter vessel.[5] In comparison with these data, the present multibubble plasma technique gives a much faster treatment speed of $\sim$1.25 mg/min.

As an example of application to purification of polluted liquid, water containing TCE was treated by multibubble plasma (peak power of 700 W, repetition frequency of 1 kHz) where the TCE concentration in water was measured by a gas detector tube system (Gastec, 132L, 132LL). The TCE solution of 8 l was treated in three modes: (a) vacuum pumping mode without microwave injection, (b) multibubble

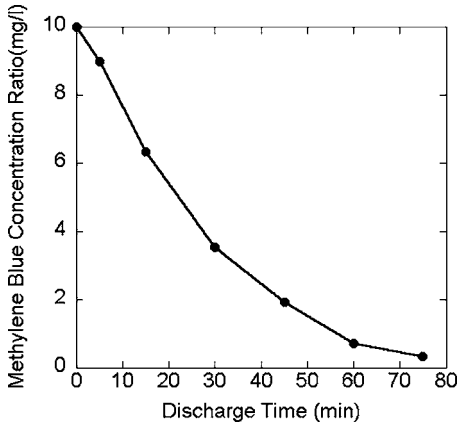

FIG. 5. Methylene blue concentration as a function of discharge time.

plasma mode at $\sim 5 \times 10^3$ Pa, and (c) multibubble plasma mode with O_2 gas bubbling at its partial pressure of $\sim 0.7 \times 10^3$ Pa in the total pressure of $\sim 5 \times 10^3$ Pa. In the present experiments, the initial concentration of TCE was different in the three modes: (a) 5.7 mg/l, (b) 6.6 mg/l, and (c) 10.25 mg/l. In order to compare the treatment efficiency, the measured TCE concentration in each mode was normalized by its initial concentration. Time evolutions of the relative TCE concentration during 60 min treatment are shown in Fig. 6. In mode (a), the TCE concentration decreased to 60% of the initial concentration after 60 min pumping. Such concentration reduction takes place by simple evaporation of TCE from water solution, since the vapor pressure of TCE is lower than that of water at the same temperature. Furthermore, the temperature of 8 l water increases in time from the initial temperature ($\sim$290 K) by 23–25 K after 60 min microwave injection in the 700 W pulsed mode. In mode (b), the multibubbled plasma effect markedly reduced the TCE concentration compared with the vacuum pumping mode (a). In mode (c), the concentration was further reduced by O_2 addition in the multibubble plasma, in particular, at

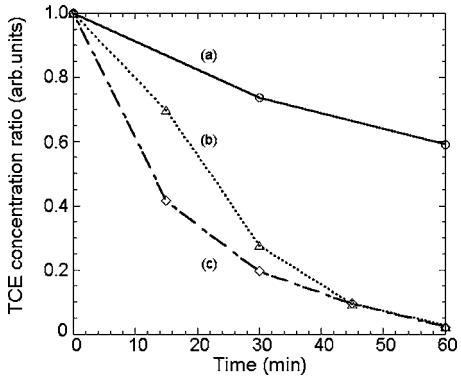

FIG. 6. Relative TCE concentration as a function of time in (a) pumping mode, (b) multibubble plasma mode, and (c) multibubble plasma mode with O_2 injection.

$\sim$10 min. In case of TCE, decomposition mechanism is tentatively understood as follows: TCE solved in water vaporizes into bubbles and it is oxidized reacting with O and OH radicals produced in the bubble. The reaction products are CO, CO_2, H_2, and HCI which can be easily treated. However, we cannot deny production of other hazardous materials in the purification process. In addition to gas phase process described above, liquid phase reactions might be possible such that TCE solved in water directly reacts with OH and O radicals solved in water, in spite of no evidence at present.

In case of TCE case, we could not find any previous report about plasma treatment. So far, purification of underground water containing TCE and other volitile organic compounds (VOCs) has been industrially treated in the following way: VOCs in water is firstly vaporized through shower to air, and they are absorbed by activated carbons which are eventually burred in the ground, thus leaving harmful materials without decomposition. There have been some attempts to decompose VOCs by combination of H_2O_2, VUV radiation and ozone,[13] and by application of intense supersonic waves.[14] However, their decomposition efficiencies are too small for industrial use, and hence innovative technologies have been desired for treating huge amount of soiled underground water.

In conclusion, multibubble plasma is produced by microwave injection into liquid at reduced pressures as well as atmospheric pressure. We are now constructing a meter-size multibubble plasma source to increase a treatment speed and capacity.

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