Enhancement of Microplasma Generated in Water by Adding Carbon Nanotubes

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In this study, microplasma was generated in the distilled water, single-walled carbon nanotubes (SWCNTs) and graphite powder suspensions by using pulsed streamer discharge technique respectively. The phenomenon of microplasma in these suspensions was detected by using ICCD camera. Photograph of microplasma in the SWCNT suspension revealed that the microplasma was very stable and number of the discharge channel was dramatically increased, while the discharge in both of distilled water and graphite powder suspension were weak and unstable. It was experimentally concluded that the carbon shape and size have a direct effect on microplasma enhancement in water. Then the electric field at the tip of SWCNT was calculated by using simple plane to plane electrodes model. According to the theoretical results, the induced electric field was significantly enhanced when SWCNT exists on electrode. These results suggest that addition of carbon nanotubes in water could be useful for inception and activation of microplasma. In addition, enhancement of microplasma could represent an effective method for water purification processes such as sterilization and removal of organic pollutants and bacteria.

Keywords: microplasma, carbon nanotube, streamer discharge, aspect ratio, solubilization

1. Introduction

CNT is one of the very promising nanomaterials in variety fields. The poor solubility of CNTs in water or organic solvents limits their use in many potential applications, especially in biochemical science and composite material engineering. We have previously revealed that H_α and O^* radicals produced by microplasma (pulsed streamer discharge) in water played an important role in the water solubilization of SWCNTs [1]. A pulsed streamer discharge is a nonthermal plasma and can produce high energy electrons, a high electric field, active chemical species, ultraviolet rays and shock waves in water [2]. Sun et al. reported that the formation of chemical active species due to streamer corona discharge was very dependent on physicochemical parameters such as pH, conductivity of the water and additives [3]. We have also reported that the phenomena of microplasma and the radicals intensity were critically affected by solution electrical conductivity [4].

In the present study, effects of adding SWCNTs to water on microplasma phenomenon were investigated. In order to clarify effects of shape and size of carbon materials, graphite powders were also employed for comparison.

2. Experimental set-up

The microplasma was produced between a thin wire and plane electrodes which immersed in distilled water by using a home-made pulsed power generator based on a Blumlein transmission line as shown in Fig.1 [3]. The gap length between electrodes, applied pulse voltage, and pulse repetition rate were 14mm, 40kV, and 15Hz respectively.

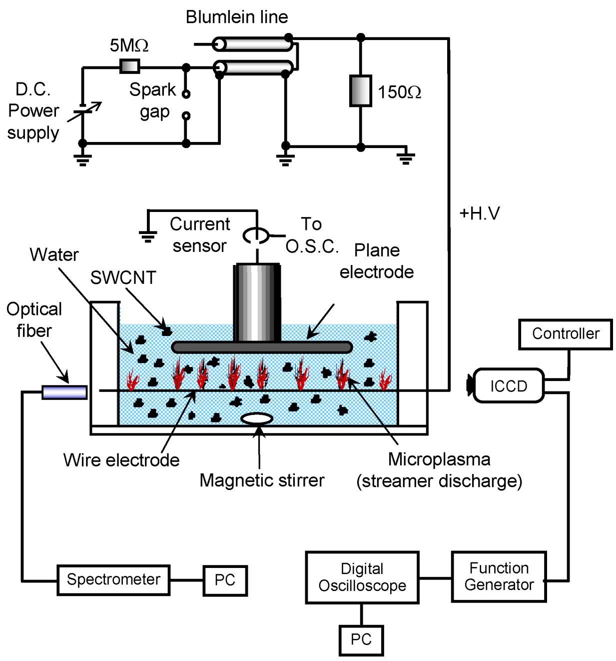

Fig.1 Experimental set-up.

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In order to clarify effect of adding small amount of carbon materials on microplasma enhancement, the SWCNTs or graphite powders were suspended in water at concentration varied from less than 1μg/mL to 10μg/mL. SWCNT had 1-2 nanometers diameter and 2-5 micro-meters of length, while the size of graphite powder typically ranges from the order of several micro-meters and up to sub mille-meters. An ICCD camera was used to detect microplasma in each case of water, graphite powders and SWCNTs suspensions at different concentrations. A spectrometer was used in order to measure the optical emission spectrum intensity from produced microplasma.

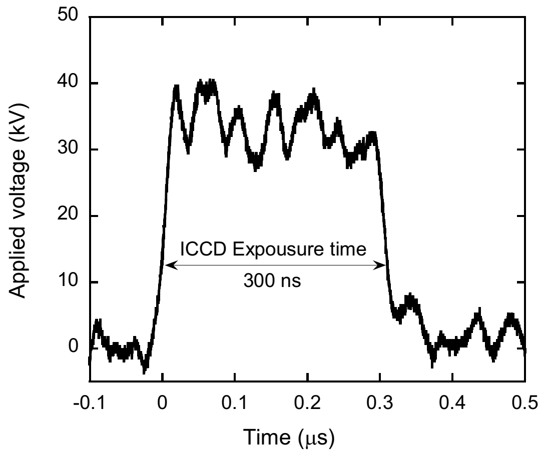

Fig.2 Applied voltage waveform.

3. Results and Discussion

The pulsed power generator could generate a square pulsed voltage, which was applied to a thin wire electrode. Fig.2 shows applied voltage waveform to wire electrode with a pulsed width of 300ns. The exposure time of ICCD camera was set at the same pulse duration time. First of all, it was observed from ICCD images that microplasma which produced in distilled water was very weak, unstable along the wire electrode, the number of microplasma channels were low and its length were very short as shown in Fig.3 (a). By adding a small amount of graphite powder of about 10μg/mL concentration to distilled water, microplasma developed and the number of streamer channels was little increased compared to distilled water case as shown in Fig.3 (b). When SWCNTs, of same concentration of graphite powder suspension, was added to distilled water, microplasma became stronger, streamer channels was dramatically increased, propagated vertically toward plane electrode and its length became longer as shown in Fig.3 (c). For more clarification, an Image-J software program was used in order to process images of microplasma photographs shown in Fig.3. The processed images are shown in Fig.4. It provides relationship between microplasma intensity and distribution of streamer discharge channels along the wire electrode and can distinguish the difference and stability of developed microplasma in each suspension. Moreover, it is possible to evaluate the number of streamer channels. Fig.5 gives a reasonable proof that number of streamer channels which were counted from Fig.4 was highly affected by adding carbon nanomaterials. Actually, a clear difference of microplasma enhancement by adding SWCNTs to water was confirmed at low concentrations which less than 1μg/mL. The number of channels, in case of SWCNTs suspension, was two or three times higher than that in case of graphite powder suspension under the same powder concentration in water.

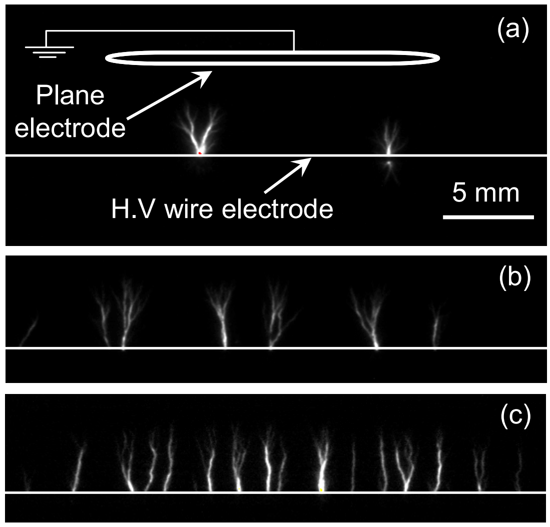

Fig.3 Typical ICCD images of microplasma in (a) distilled water, (b) Graphite powder suspension (10μg/mL) and (c) SWCNTs suspension (10μg/mL).

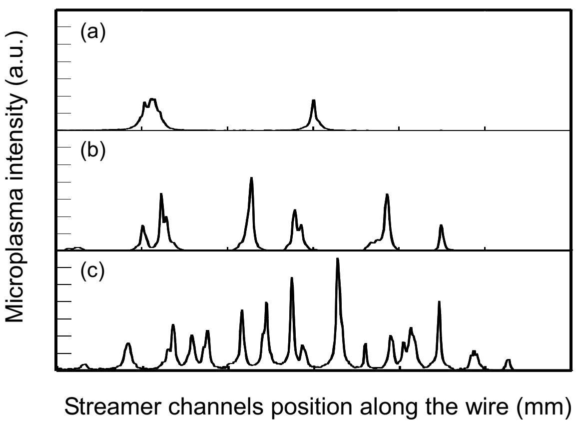

Fig.4 Image processed of microplasma intensity in (a) distilled water, (b) Graphite powder suspension and (c) SWCNTs suspension.

In order to verify the effect of treatment by microplasma on particle size of carbon nanomaterials, Fig.6 shows effective particle size distribution for both graphite powder and SWCNTs in water, which was obtained using an optical particle size analyzer (SALD-7100, Shimadzu, Japan) before and after microplasma treatment. The equipment analyzes an effective particle size according to diffraction and scattering optical elements assuming a spherical particle. It was previously reported that SWCNTs after the microplasma treatment had a well-dispersed mesh-like

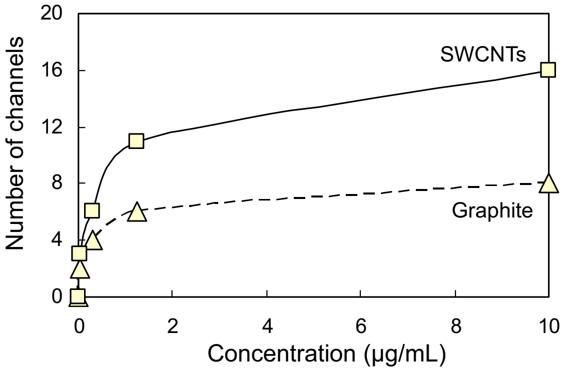

Fig.5 Relationship between SWCNTs and graphite powder suspension concentration and number of produced microplasma channels.

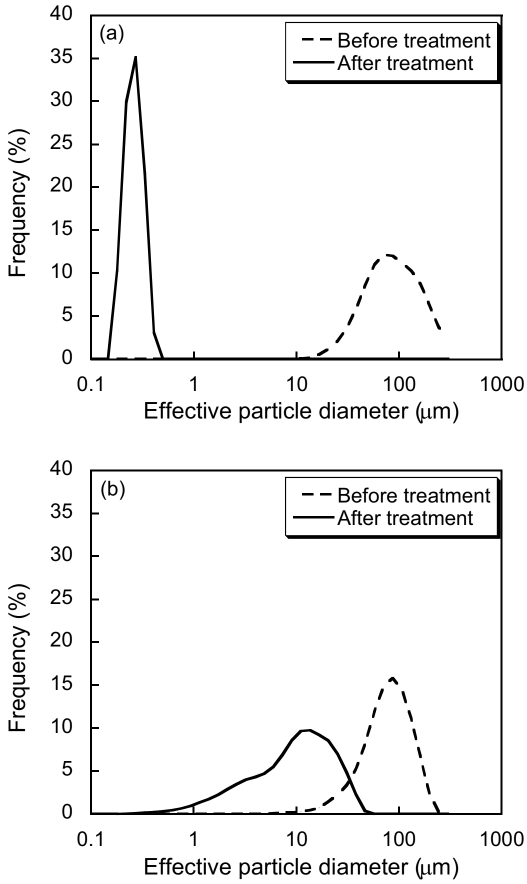

Fig.6 Effective Particle size distribution of (a) SWCNTs and (b) graphite powder in water before and after microplasma treatment respectively.

texture according to SEM and TEM observations [1,5,6]. From the results shown in Fig.6, it was clear that microplasma treatment effectively reduced the particle size of graphite powder and SWCNTs. Also, graphite powders had a larger effective particle size than SWCNTs even after microplasma treatment. It is clear that SWCNTs had smaller and intensive particle range after microplasma treatment compared to graphite powder particles. The initial effective particle size of treated graphite powder was reduced from ~100μm to ~10μm. While, the initial effective particle size of treated SWCNTs was reduced from ~100μm to ~0.3μm. This decrease on effective size of SWCNTs was due to the effect of water-solubilization of SWCNTs by the microplasma treatment [1].

Fig.7 shows optical emission spectrum of the microplasma in water and SWCNTs suspension. It has been found that emission intensity in distilled water was very weak. When a low concentration around 10μg/mL of SWCNTs powder was added into distilled water, emission spectrum intensity was increased significantly. This phenomenon would be due to strong electric field which could be built up by adding SWCNTs. It leads to produce higher electron energy which could enhance the excitation and ionization of water molecules and resultant formation of radicals such as H_α and O^*. The other reason which clarifies increasing spectrum intensity is due to increasing number and length of produced streamer channels once adding SWCNTs into water as shown before in Fig. 3 and 4. Mechanism of enhancement effect of microplasma by SWCNTs would depend on size effect of SWCNT and graphite powder. Due to that aspect ratio (length/diameter) of SWCNTs was very high and its ends were very sharp, so electric field might be enhanced by SWCNTs and consequently a high emission intensity of microplasma was generated compared to that of distilled water. Many parameters, including the aspect

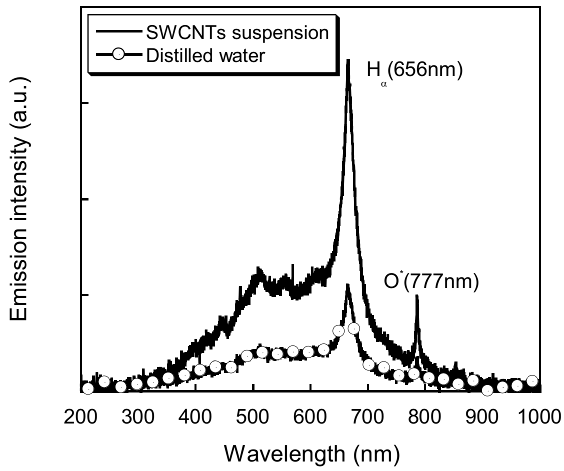

Fig.7 Emission spectrum in distilled water and SWCNTs suspension (10μg/mL).

ratio of nanotubes, the anode-cathode distance, CNT with open/close caps, intertube distance and so on, can influence the emission properties of the CNTs [7-15].

We discuss a possible enhancement effect of electric field by adding SWCNTs in water. Although a thin wire and plane electrodes were used in experiments, for simplicity of electric field calculation, we assumed a theoretical model consists of plane to plane electrodes system, in which SWCNT exists on a plane electrode. Electric field was calculated at tip of SWCNT. A simple formula to estimate the electric field enhancement, E at the apex of a single, straight SWCNT was given as the following expression [15]

$$E = \beta_0 * E_0 \tag{1}$$

where, E_0 *is* a uniform electric field and β_0 is the field enhancement factor which given by the following equation

$$\beta_0 = \frac{h}{\rho} + 3.5 \tag{2}$$

where, h is the SWCNT length, and ρ is its radius. The uniform electric field strength for the field between two plates can be calculated by

$$E_0 = V_a / d \tag{3}$$

where, V_a is the potential difference placed across plates and d is the gap length between electrodes. From equations (1)-(3) the electric field at the tip of SWCNT could be expressed by

$$E = \left(\frac{h}{\rho} + 3.5 \right) * \frac{V_a}{d} \tag{4}$$

Fig. 8 shows relation between electric field at tip of SWCNT, E and gap distance between electrodes, d with different aspect ratios of SWCNT. It shows a clear comparison between electric field calculations in case of SWCNT presence and electric field when SWCNT does not exist. From Fig.8, it was found that electric field when SWCNT exist between electrodes was higher compared to that without SWCNT. Electric field was very high at the tip of SWCNT and decreased gradually by increasing gap distance between electrodes. Also, electric field of high aspect ratio of SWCNT was higher than lower SWCNT aspect ratio. Therefore, induced electric field could be greatly enhanced if SWCNTs with large aspect ratio was added to water. These calculation results suggest that addition of SWCNTs into water enhances the electric field at the tip of SWCNT and enhanced electric field leads to the increase of intensity of microplasma and number of streamer channels.

One of the other significant effects when SWCNTs added in water on the discharge phenomena is increasing of conductivity of water. Fig.9 shows the relation between microplasma treatment time and water conductivity. The water was treated by microplasma for one hour treatment time, the applied pulsed voltage was 80kV and the concentration of SWCNTs was 0.1 mg/ml. The water conductivity without adding SWCNTs was increased with the treatment time because some ionic species such as NO_2^- and NO_3^- were produced in water by the discharge. On the other hand, the water conductivity was further increased during the discharge when the SWCNTs were added in water. This result indicated that the SWCNTs were well solubilized and dispersed in water by the discharge and in addition of production of ionic species mentioned above, many current passes by the dispersed SWCNTs would be formed in water. As the result, conductivity of water was increased.

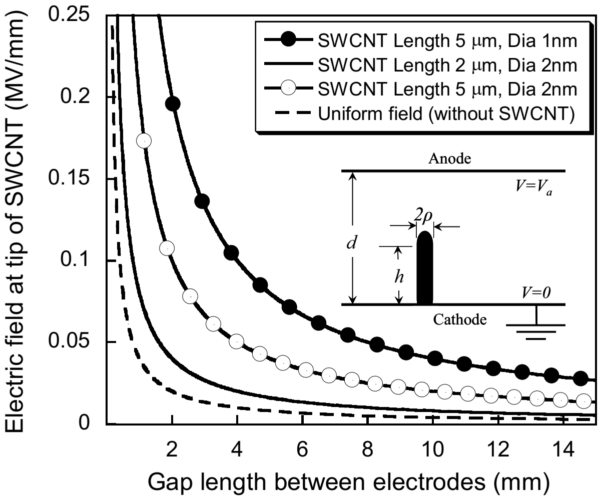

Fig.8 Relation between electric field at tip of SWCNT and gap length.

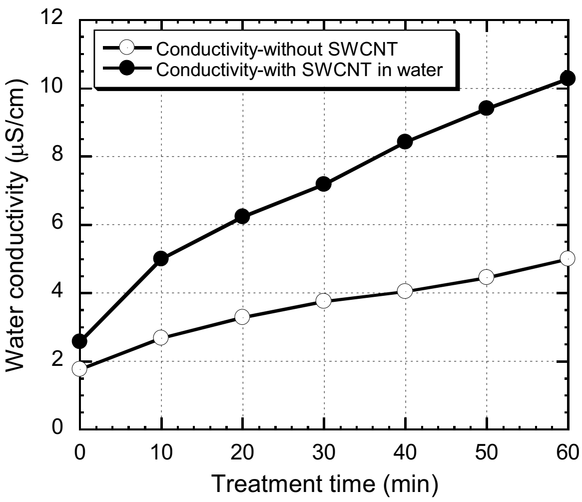

Fig.9 Effect of adding SWCNTs on the water conductivity.

4. Conclusions

This study presents an observation of microplasma phenomena when SWCNTs were added into distilled water. It was observed that the microplasma intensity and number of streamer discharge channels were stable and enhanced by adding a little amount of SWCNTs to the water. Therefore, it would be very useful to enhance the microplasma generation. In addition, theoretical analysis was revealed that the electric field was enhanced by adding SWCNTs compared to that without SWCNTs. These results are very important and suggest that the enhancement of microplasma could represent an effective method for many applications of microplasma treatment in water such as water purification processes and removal of organic pollutants and bacteria.

Acknowledgments

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