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ABSTRACT

This work presents a deposition of carbon thin films on the substrate from sucrose-containing-carbon source, that is, sugar, by using the two different plasma processes; one process is that the carbon particles are obtained from the sugar in the stable solution plasma reactor with external resistor, and the other process is that the carbon thin films are deposited on the substrate from the carbon particles obtained from sugar by using the atmospheric pressure plasma (APP) spray method. The carbon particles are obtained at a bipolar pulse waveform with a peak value of 1.5 kV and a frequency of 5 kHz under solution plasma, whereas the carbon thin films are deposited at a sinusoidal pulse waveform with a peak value of 12.5 kV and a frequency of 33 kHz under the APP spray method. Voltage probe, discharge current, and optical emission spectrometer (OES) techniques are used to analyze the plasma produced from the solution plasma reactor. Field emission scanning electron microscopy (FE-SEM) and ultraviolet–visible (UV-vis) spectroscopy techniques are used to analyze the carbon particles. FE-SEM results show that carbon materials from sucrose have a few ten to hundred nanometer size nanoparticles characteristics. The UV-vis and OES analyses show the characteristic graphene peaks with evidence that carbon sources from sucrose are broken due to discharge energy. This study contributes to a better understanding on the new synthesis method of carbon materials from renewable resource with low-cost, *i.e.* sugar cane.

1. Introduction

Over the past few decades, the research field of carbon nanomaterials has seen rapid development because of the unique optical, electrical, and catalytic properties of these materials [1–7]. Among the various methods for carbon materials synthesis, the use of plasma generation in solution is relatively new. Plasmas are one of the four fundamental states of

matter in addition to solids, liquids and gases, and they are closely connected with modern industry and human life. Plasmas via the ionization of neutral gases generally contain an equal number of positive ions and negative electrons with neutrals, metastables, reactive radicals, excited species, ultraviolet (UV) light, and electric field. Based on the flexible reactivity of the species in plasmas, gas-based reactive plasmas species are widely used in modern industries, such as the surface modification of materials and synthesis of new materials [8].

Recently, a new branch of plasma research, carbon nanomaterial synthesis using plasma–liquid interactions (PLIs), has been developing rapidly [8–14]. In PLIs, plasmas are over or inside liquids, providing plasma-liquid interfaces where many physical and chemical processes can take place, and these processes can be used to synthesize various carbon nanomaterials due to its intrinsic merits, such as simple implementation, low capital cost, and potential for high yield. The conventional methods for PLIs are classified as thermal plasma or arc plasma, requiring high energy to synthesize conductive carbon material under elevated temperature. Recently, a type of non-thermal in liquid method named the solution plasma process (SPP) has intensively studied for the synthesis of carbon-related materials [15–26]. Nonetheless, most plasma carbon materials grown using SPP tend to show poor film qualities, such as weak chemical stabilities and contaminations [16], which would inherently result from the use of plasma with unstable discharge in liquid condition. Moreover, it is difficult to obtain carbon nanomaterials with uniform size due to the unstable discharge via conventional SPP method with large voltage fluctuation. In order to synthesize the carbon materials using SPP, it is very important to produce the stable discharge and deposit the carbon materials on substrates without any contaminations from the liquid composition.

Therefore, in this study, we propose the advanced SPP reactor to produce the stable discharge during plasma synthesis of carbon materials from the sugar such as sucrose containing carbon source in SPP devices. In order to produce stable plasma with high plasma density, we use an external resistor with 1 kΩ to decrease the breakdown voltage with unnecessary current and to minimize the unstable discharge in SPP reactor. Furthermore, in order to deposit the pure carbon materials with uniform size on Si substrates, we use an APP spray method to eliminate the contaminations from solution materials such as water and raw sucrose by using additional plasma energy.

2. Experiment

Figure 1 shows the schematic diagram of solution plasma process (SPP) reactor and measurement setup employed in this study. The cylindrical glass tube (O.D. = 20 mm and I.D. = 18 mm) with height of 150 mm was used as a plasma reactor. The deionized (DI) water (Welgene, Inc., Resistivity = 18 MΩ) was used as solution with 15 mL, then sucrose 10 g (Sigma-Aldrich, ≥99.5%) was added into the DI water. The mixture was ultrasonicated for 10 min. As a result, the reagents were well dispersed in the solution. In order to synthesize the carbon materials using solution plasma process (SPP), two tungsten wires with a diameter of 1.2 mm, covered with the PTFE and glass tube, were used as electrodes at both sides of the plasma reactor. The gap between the two electrodes was set to 1 mm in the solution. The immiscible solutions were mixed by a magnetic stirring bar with a rotational speed of 1000 rpm in the reactor to reduce the particle aggregation. The bipolar pulse with 5 kHz of a frequency and depending on whether an external resistor (1 kΩ) was used or not, applied voltages of peak value were changed from 1.5 to 2.0 kV between two electrodes due to presence of external resistor. The detailed specifications of power sources for SPP are listed in Table 1. In the driving circuit, the inverter amplified the low primary voltage to reach a high
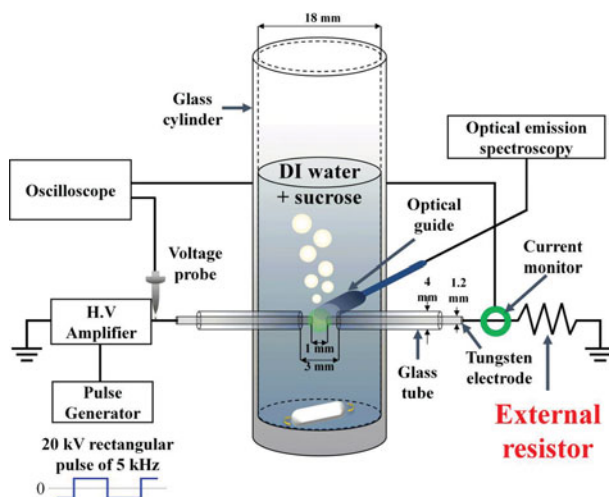
Figure 1. Schematic diagram of solution plasma reactor and measurement setup employed in this study.

secondary voltage. A high-voltage probe (Tektronix P6015A) and current probe (Pearson 4100) were connected between the power source via an inverter circuit and oscilloscope (LeCroy WaveRunner 64 Xi) to measure the applied voltage and total current, respectively. An optical emission spectrometer (OES, Ocean Optics, USB-4000UV-Vis) was employed to analyze the various reactive species in the solution plasma. In particular, the optical guide was used to measure the optical emission spectrum for minimizing the optical absorption from solution. All the photographs of the devices and plasma plumes were taken using a DSLR camera (Nikon D56300) with a Macro 1:1 lens (Tamron SP AF 90 mm F2.8 Di).

3. Results and discussion

3.1 Solution plasma process

Figure 2 shows the applied voltage including memory voltage and the discharge currents of unstable discharge characteristic without the external resistor (black line) and the stable discharge characteristics with the external resistor (red line). The memory voltage was determined by the sum of the externally applied voltage and the voltage internally induced by the accumulated charges. With conventional experimental setup condition without external resistor, it was difficult to produce stable discharge due to the high memory voltage, as shown in Fig. 2(a) [27]. In other words, the memory voltage variations were significantly increased in the case without external resistor, meaning that the unstable discharge could be produced relatively. However, when the external resistor was adopted, it was observed that the fluctuations of the memory voltage were extremely decreased, thereby producing the more stable discharge [27]. As a result, when adopting the external resistor in advanced SPP reactor, the voltage

Table 1. Power sources to generate bipolar pulse for solution plasma process.

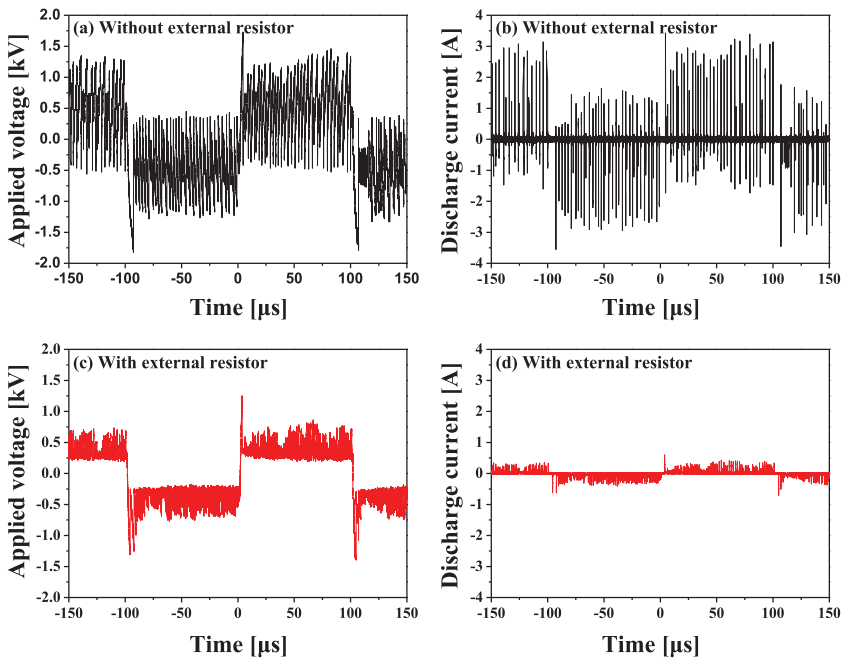| Equipment	Manufacturer	Model	Specifications
High-voltage amplifier	Trek, Inc.	20/20C-HS	gain: 2000 V/V slew rate: 800 V/μs
Pulse generator	Tektronix, Inc.	AFG-3102	amplitude: 40 m to 20 Vp-p rise time: ≤ 5 ns

Figure 2. (a) Applied voltage and (b) discharge current of unstable discharge characteristic without external resistor (black), and (c) applied voltage and (d) discharge current of stable discharge characteristic with external resistor (red).

fluctuations and currents were decreased, resulting in the production of the stable discharge and the reduction of the unnecessary current during plasma synthesis of carbon materials from the sugar such as sucrose containing carbon source in SPP devices shown in Fig. 1.

Figure 3 shows the color variations of the sucrose dispersed in the DI water using SPP with the external resistor under the various process times. When the process times were increased, the color of the solution changed from light-yellow to yellowish-brown color, indicating that some particles were synthesized from the sucrose mixture.

Figure 4 shows the UV absorption spectra in the pure DI water and sucrose dispersed in DI water using SPP with external resistor after 60 min plasma treatment using UV-vis spectroscopy (Eppendorf AG, BioSpectrometer, 200 nm – 830 nm). As shown in Fig. 4, no peaks were observed in the case of pure DI water. Whereas, in the case of sucrose dispersed in DI water, the UV-vis absorption peaks of graphene and graphene oxide were found in the peak
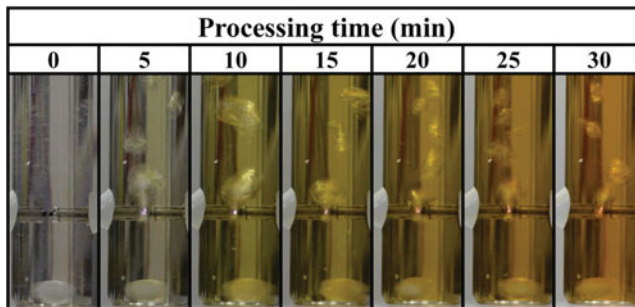

Figure 3. Changes in colors of sucrose dispersed in deionized (DI) water with external resistor relative to various process times using solution plasma process.
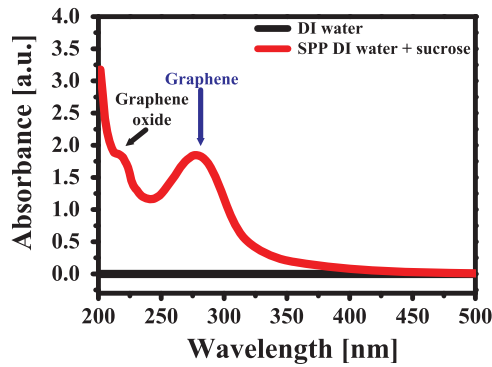
Figure 4. UV-vis absorption spectra in pure DI water (black) and sucrose dispersed in DI water (red) after 60 min plasma treatment using solution plasma process.

at 270 nm and 230 nm, respectively [28–30]. The UV-vis analysis shows the characteristics of graphene and graphene oxide peaks with evidence that carbon sources from sucrose were broken by discharge energy. Figures 3 and 4 indicate that the advanced SPP with the external resistor could be suitable for a sufficient fragmentation of the sucrose mixture and an efficient synthesis of new carbon materials.

Figure 5 shows the optical emission spectra measured between two electrodes of the solution plasma reactor during the discharge in pure DI water and sucrose dispersed in DI water, respectively. In the case of sucrose dispersed in DI water, the active species, such as Hα (656 nm) and H$_\beta$ (484 nm), were observed to be increased compared with those of the pure DI water case. In addition, small peak of atomic C (247 nm) was only observed as well in the case of sucrose dispersed in DI water, meaning that the sucrose molecules were decomposed to atomic C by the plasma. The hydrogen radicals were suggested to be generated from sucrose compounds with water molecule. Moreover, the formation of atomic C was obviously generated by the sugar compounds. These OES data show that the advanced SPP with the external resistor could be suitable for a sufficient fragmentation of the sucrose mixture and an efficient synthesis of new carbon materials.

The field emission scanning electron microscopy (FE-SEM, HITACHI SU8220) was employed to analyze the surface morphology. Figure 6 shows the top-view of SEM image of
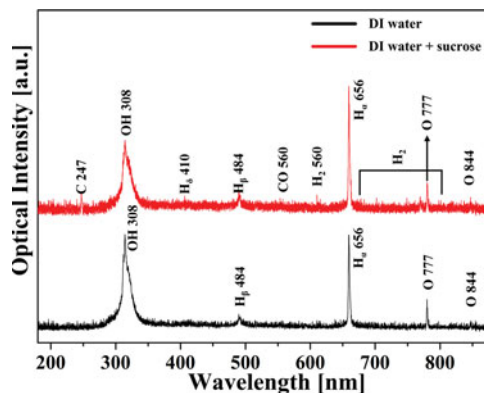

Figure 5. Optical emission spectra (OES) measured between two electrode of solution plasma reactor during discharge in pure DI water (black) and sucrose dispersed in DI water (red).
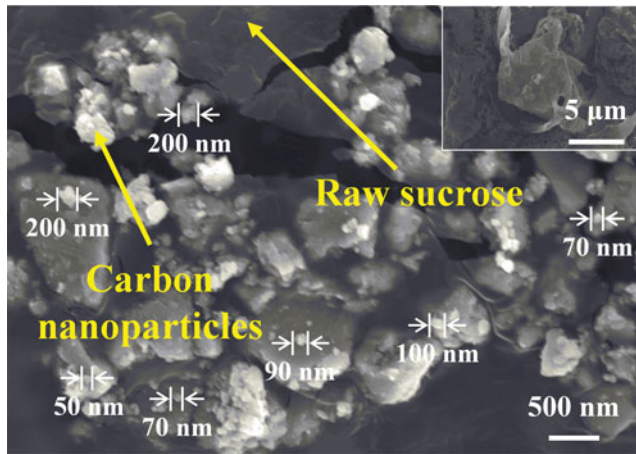
Figure 6. SEM image with high magnification of deposited carbon containing thin film using hot-plate deposition method after synthesis of carbon nanoparticles via solution plasma process. Inset represent the low magnification.

synthesized carbon nanoparticles by the SPP reactor with the external resistor using a hot-plate deposition method on a Si substrate. A sample of carbon materials from a synthesized sucrose solution mixture was prepared by drying a small drop on a Si substrate. The dropped carbon materials with sucrose mixture on Si substrates were placed on a warm hot-plate at 60 °C and the sucrose solution mixture was slowly evaporated to dryness. As shown in Fig. 6, many carbon nanoparticles were clearly observed, meaning that the carbon nanoparticles could be efficiently synthesized with the advanced SPP with external resistor. Nevertheless, in the case of hot-plate deposition method, raw sucrose surface contaminations were severely observed, meaning that the adoption of the hot-plate method cannot vaporize sufficiently the raw sucrose from the sucrose mixture with carbon materials during dryness process. There-fore, the methods for minimizing the surface contaminations were required additionally in order to synthesize the high purity carbon materials in conventional SPP reactor.

3.2 Atmospheric pressure plasma spray method

In order to eliminate the surface contaminations and obtain carbon materials with uniform size, the additional APP spray method was adopted to deposit the carbon materials on the various substrates. Figure 7 shows a schematic diagram of experimental setup for proposed APP spray method. The APP spray jet device consisted of single glass tube (O.D. = 5 mm and I.D. = 3 mm) and high voltage electrode. The high voltage electrode was twined around the single tube. The sinusoidal power supply was connected to the high voltage electrode with a peak value of 12.5 kV and a frequency of 33 kHz. The detailed specifications of power sources for APP spray method are listed in Table 2. A small quantity of synthesized carbon material

Table 2. Power sources to generate sinusoidal pulse for plasma spray method.

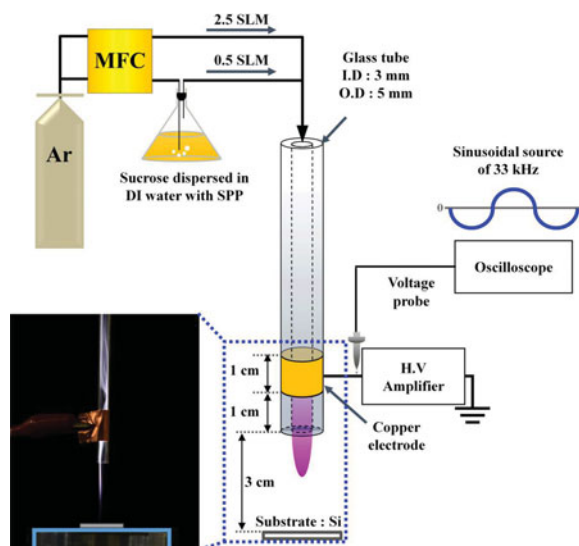| Equipment	Manufacturer	Model	Specifications
Plasma power generator	Information Unlimited Inc.	PVM500	Amplitude: 20 kV(40 kV pk-pk), 90 mA Frequency: 20 – 70 kHz
High voltage switching transformer	Information Unlimited Inc.	FLYPVM250+	2500 turns

Figure 7. Schematic diagram of plasma spray process and measurement setup employed in this study.

vapor was added to the gas, which flowed through the main tube by bubbling method of carbon materials with sucrose solution mixture synthesized by the SPP reactor. High purity argon (Ar) gas (99.999%) was used as the plasma discharge gas, the main gas and bubbling gas flow rates were fixed at 2500 Standard Cubic Centimeter per Minute (sccm) and 500 sccm, respectively. The intense Ar plasma was produced using APP spray method, which increased the charged particles and energy of the plasma with synthesized carbon material vapor in the nucleation region, thereby producing the more fragmentation of the synthesized carbon materials [31].

Figure 8(a) shows the top-view of SEM image of the carbon thin films deposited from the sucrose dispersed in DI water by directly using APP spray deposition method without any SPP method. Figure 8(b) shows the SEM image by using APP spray deposition method after the SPP synthesizing the carbon nanoparticles from the sucrose dispersed in DI water. As shown in Fig. 8(a), only a few nanoparticles were observed in the no SPP method case because the weak plasma was produced in the plasma region during APP spray deposition
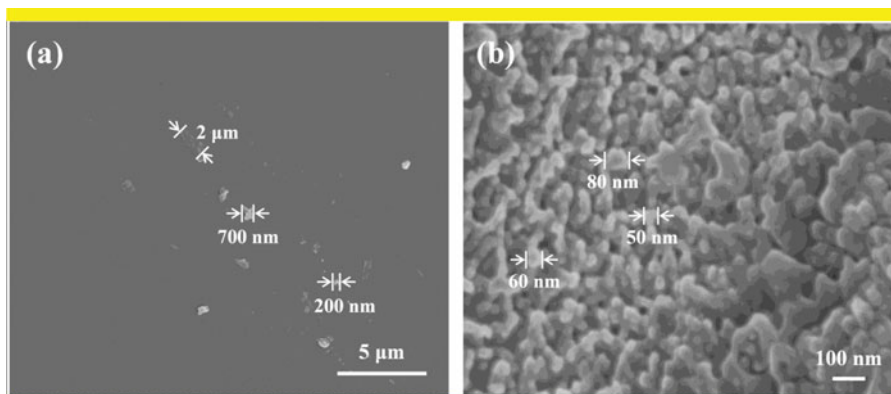

Figure 8. SEM image of deposited carbon containing thin film using plasma spray deposition method (a) without solution plasma process and (b) after synthesis of carbon nanoparticles with solution plasma process.

process. This means that the adoption of the APP spray deposition method without SPP cannot be suitable for sufficient fragmentation of the sucrose mixture. However, the presence of many carbon particles on the substrate in Fig. 8(b) illustrates that the combination of the APP spray deposition method with the SPP can efficiently synthesize the carbon nanoparticles and successfully deposits the carbon thin film with uniform size on the substrate without any contamination. In particular, it is important that no contaminations are observed when adopting APP spray deposition method. The lack of any contamination of sucrose can be attributed to the additional plasma energy in plasma nucleation region via APP jet. This means that the proposed APP spray method can be appropriate to remove contamination such as raw sucrose and water and produce carbon particles with uniform size. Consequently, these experimental results confirm that the proposed SPP device with the external resistor can obtain high purity of carbon nanoparticles without any contaminations. Furthermore, we expect that our carbon materials with nanoparticles can provide a unique advantage for future display, nanohybrid technology, optoelectronics, electrochemical, molecular electronics, and bio-nanotechnology applications.

4. Conclusions

This article investigates the synthesis of carbon materials from renewable resource such as sucrose containing carbon source by a stable solution plasma reactor with external resistor. In addition, the carbon materials were obtained by APP spray method that can deposit the carbon particles as thin film on Si substrate without any contaminations. A high-voltage probe and current probe were used to measure applied voltage and discharge current from the SPP and APP plasma devices, respectively. FE-SEM image shows morphology of synthesized carbon nanoparticles by the SPP, whereas UV-vis spectroscopy analysis shows the characteristic graphene peaks with evidence that carbon sources from sucrose are broken by discharge energy.

Funding

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