Solution Plasma Synthesis Process of Carbon Nano Particles in Organic Solutions

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Abstract—In this study, solution plasma process (SPP) was applied to synthesis carbon nanoparticles in organic solution. In the SPP process, carbon nanoparticles were formed by carbon atoms supplied by two different groups of organic solutions, sugar and aromatic hydrocarbon solutions. Glucose, sucrose and fructose were used as sugar solution, whereas benzene and toluene were applied for the aromatic hydrocarbon solutions. Within the same group of solution, the carbon structure and size distribution were found to be similar. On average, 100 ml sugar solution produced 15 mg of carbon by weight. The particles included hemisphere and sphere in shape, with a size distribution between 100 - 600 nm. For aromatic hydrocarbon solutions, 930 and 1000 mg of carbon could be generated, respectively, from 100 ml of pure toluene and benzene. The particles were spherical shape with a size distribution of 20 - 30 nm. Fundamental characteristics of plasma discharge including voltage and current waveforms, as well as active species generated were compared. The discharge in sugar solution occurred in three different phases: pre-discharge, the initiation and the formation of discharge, whereas the discharge in benzene happened in two main steps: pre-discharging and the formation of discharge. From the optical emission spectrum, the major active species obtained from sugar solution were H_α (656 nm), followed by atomic O (777 nm), H_β (486 nm) and relatively low intensity of atomic C (247 nm). For benzene and toluene solutions, the majority active species were observed to be C_2 (513 nm) and CH (431 nm) and followed by H_α (656 nm). The results indicated pure benzene might be suitable solution applied for the synthesis of carbon nanoparticles in solution plasma process.

Keywords—Solution plasma, carbon nano particles, sugar, aromatic hydrocarbon, benzene

I. INTRODUCTION

Recently, new types of carbon nanoparticles have been attracting attention due to several outstanding properties: high specific surface area, conductivity and electrocatalytic activity [1, 2]. This nano material can be used as electrode materials in fuel cells and rechargeable lithium batteries, catalyst support, supercapacitor electrodes, filler of nano composite due to its thermal stability, and their chain like structure [3-10]. Various synthesis methods, such as catalytic/non-catalytic chemical vapor deposition [7, 8], shock compression techniques, laser ablation [5], autoclave methodologies [13, 14], pyrolysis of carbon-metallic compounds [15] and electric arc [16] have been proposed throughout the years. Some studies have demonstrated successful conversion from organic substances such as saccharides (glucose, sucrose or starch) into carbonaceous microspheres [17-20]. It is supposed that the oxygen functionalities might help to construct the hollow sphere structure during formation of carbon particles [21]. More recent studies have shown promising results of producing carbon nanotubes [22, 23] and mono dispersed carbon nano-spheres [24] from liquid benzene. Beside benzene, other aromatic hydrocarbons were also proposed to use as a carbon source to generate carbon nano size particles [25].

Solution plasma process (SPP) was applied for the synthesis of carbon nanoparticles. SPP is the plasma process occurred in an aqueous solution. The application of electrical discharge in liquid has been studied for many years. The high voltage electrical discharge directly in liquid initiates both chemical and physical processes. It has been demonstrated to produce various radicals and ions depended on the choice of the solution. Previous studies showed the technique was capable of synthesis nanoparticles, including nanocolloidal particles, metal nanoparticles and carbon-rated materials, successfully [26-28]. Compared to the conventional methods, the process is superior to others in terms of the ease of handling, operation under atmospheric pressure and temperature and relatively short consumption time.

In this study, carbon nanoparticles were synthesized by solution plasma process. Based on the previous studies, two different types of organic solution, including sugar and aromatic hydrocarbon solution, were chosen as the carbon precursor. Glucose, sucrose and fructose were used as the representative of sugar solution, whereas liquid benzene and toluene were used as the carbon source in aromatic hydrocarbon solution.ar.

II. METHODOLOGY

A. Solution Plasma Process

The plasma discharge was produced by a bipolar pulsed power supply. A pair of Φ1.0 mm tungsten electrode was used as the electrodes and was insulated by

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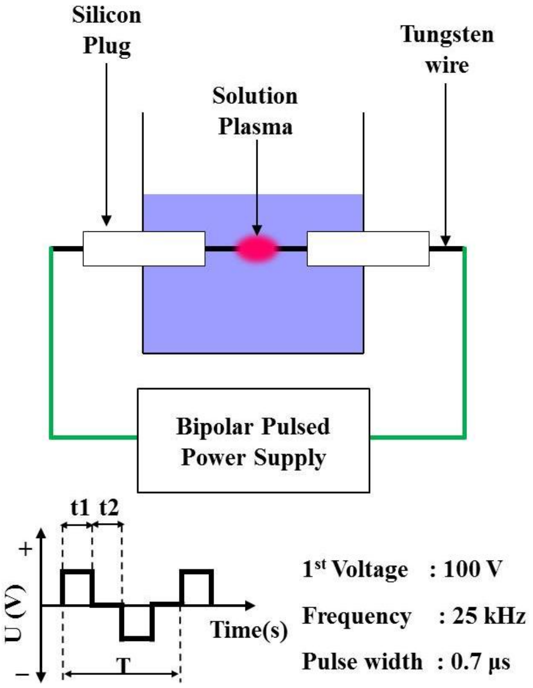

Fig. 1. Schematic of synthesis of carbon nanoparticles by solution plasma process.

ceramic tube. The solution included pure benzene and toluene as a representative of aromatic hydrocarbon. As for the carbohydrates, saturated concentration of glucose, sucrose and fructose were mixed with pure water. A small amount of KOH was added to improve the solution's conductivity. The conductivity was controlled in the range of 500 µS/cm, as we observed that discharge was most steady in this range of conductivity.

The parameters for plasma generation, applied voltage, pulse width, frequency and process time were strictly controlled to be 1 kV, 10~25 kHz, 2.0 µs, 1 mm and 20 minutes, respectively.

B. Experimental Apparatus

The morphology of nanoparticles was observed under several methods. Transmission Electron Microscopy (TEM) (JEOL JEM-2500SE) was performed at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) (JEOL JSM-6330F) was operated at an acceleration voltage of 5 kV. Fundamental characteristics (voltage and current) were measured by a digital oscilloscope (RIGOL DS 1202CA) via a high voltage and a current probe. An optical fiber/PC computer-based optical spectrometer (Ocean Optics Inst. Co. 200-1200 nm) was used to measure the optical emission spectrum through a horizontal Quartz lens window. The spectrum was set to take average of 10 shots, with a scanning time of 100 ms. The quartz window was located less than 0.5 cm away from the discharge. The schematic of SPP is shown in Fig. 1.

III. RESULTS AND DISCUSSIONS

A. Morphology of Carbon Nanoparticles Generated by Sucrose, Glucose and Fructose

After solution plasma process, the samples were centrifuged, filtered and dried at 80°C for 8 hours prior to the analyses of the generated carbon nanoparticles. The images of raw solution before and after SPP with centrifugation, as well as the dried carbon were shown, respectively, in Fig. 2 (a), (b) and (c). On average, 15 mg can be generated with a volume of 100 ml of sugar solution.

No significant difference was observed between the size distribution and the shape of the nanoparticles generated by sucrose, glucose and fructose. The nanoparticles were found to be mixed in two different shapes: hemisphere and sphere. The size distributions were approximately 100 - 300 nm and 100 - 600 nm for hemisphere and sphere nanoparticles, respectively. Under SEM, the morphologies of carbon nanoparticles formed by glucose, sucrose and fructose are illustrated in Fig. 3a, 3b and 3c. The ratio of hemisphere to sphere nanoparticles was not dependent on the type of sugar solution.

B. Morphology of Carbon Nanoparticles Generated by Benzene and Toluene

Dried carbon nanoparticles generated from pure aromatic hydrocarbon solution were obtained by the same procedures as mentioned in the previous section. Approximately 930 and 1000 mg of CNBs were generated, respectively, from 100 ml of benzene and toluene with 20 minutes of SPP treatment. The morphologies of carbon nanoparticles of benzene and toluene were illustrated in Fig. 4a and 4b respectively. TEM images showed the diameters of carbon nanoparticle were ranged from 20 nm to 30 nm in sphere shape and these carbon spheres were found to be chain-like morphology.

C. Fundamental Characteristics of Voltage and Current Waveforms in Sugar Solution Plasma Discharge

The discharge voltage and current waveforms were similar for glucose, sucrose and fructose. Typical waveforms are shown in Fig. 5. For the physical phenomena, the discharge were observed in three different stages: (I) the pre-discharge, (II) the initiation and (III) the formation of discharge. When voltage applied, joule heating started and the micro-gap spark discharge was initiated at the edge of both electrodes in the gas-liquid interface. Finally, the plasma discharge was formed with increasing applying voltage to approximately 100 V. The discharge processes were very similar to discharge under water [29-31]. The maximum current reached 9 A with an applied voltage of 1 kV. However, the discharge waveforms were slightly different than in the tap water. The waveforms might be

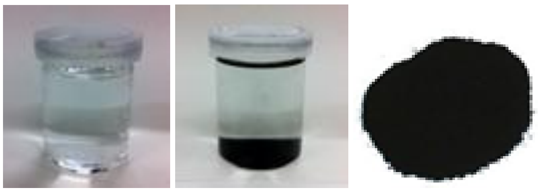
(a) (b) (c)

Fig. 2. Images of glucose solution (a) before plasma, (b) after plasma with centrifugation and (c) dried carbon.

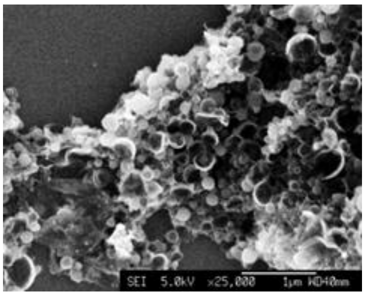

Fig. 3a. Carbon nanoparticle formed by glucose under solution plasma process

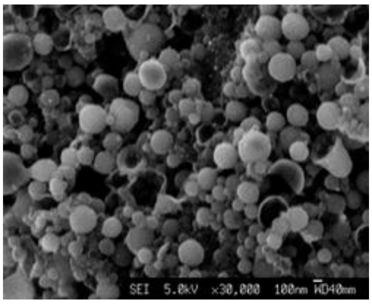

Fig. 3b. Carbon nanoparticle formed by sucrose under solution plasma process.

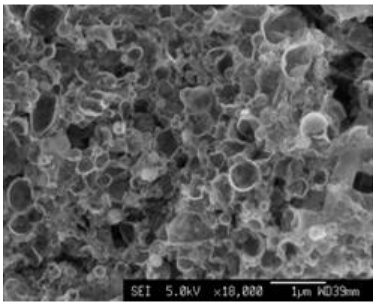

Fig. 3c. Carbon nanoparticle formed by fructose under solution plasma process.

affected by the present of sugar molecules and the solution conductivity.

D. Fundamental Characteristics of Voltage and Current Waveforms in Aromatic Hydrocarbon Solution Plasma Discharge

It had no significant differences between the discharge in pure toluene and benzene. However, the physical phenomena were quite different compared to the discharge in sugar solution. The discharge under aromatic hydrocarbon was observed only in two different stages: (I) pre-discharge and (II) formation of the discharge. The generation of micro bubbles was not observed between the pre-discharge and the formation of plasma. It is suggested the conductivity of benzene governed the discharge phenomena. Since benzene is a non-polar solution, almost no conductivity can be detected. No current can be conducted between the electrodes in the pre-discharge stage. Once the benzene

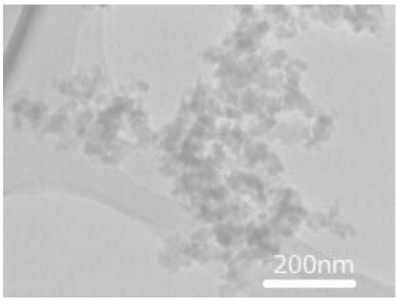

Fig. 4a. Carbon nanoparticle formed by toluene under solution plasma process.

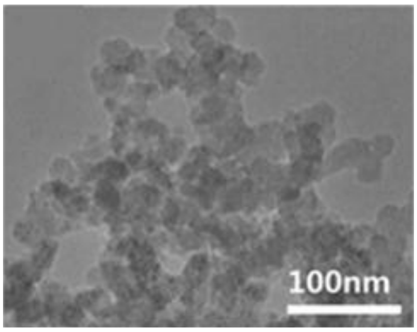

Fig. 4b. Carbon nanoparticle formed by toluene under solution plasma process.

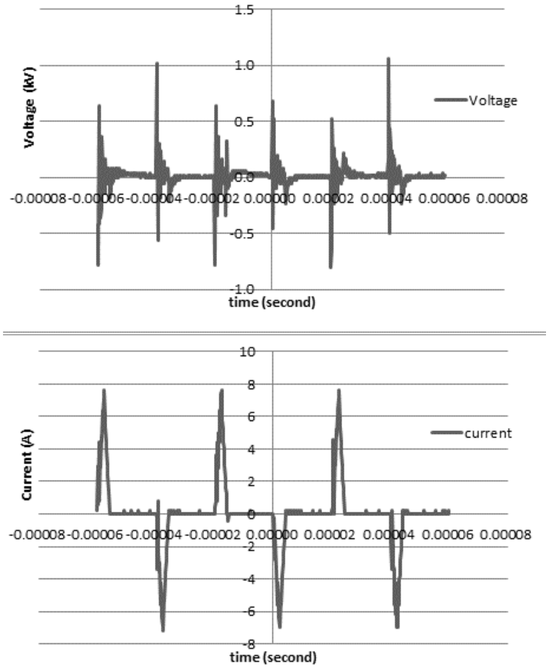

Fig. 5. Typical voltage and current waveforms during discharge in glucose solution with KOH.

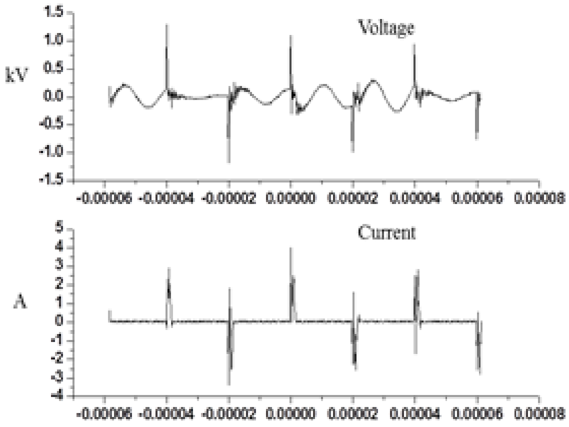

Fig. 6. Typical voltage and current waveforms during discharge in pure benzene.

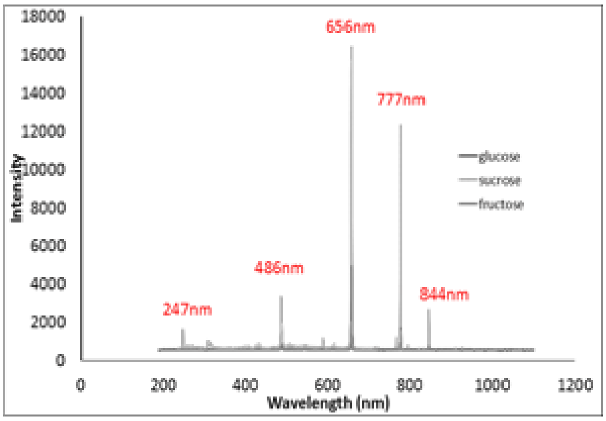

Fig. 7. Optical emission spectrum of discharge in glucose, sucrose and fructose.

was gasified with an applied voltage above 1 kV, the discharge started instantly and the discharge current increased simultaneously to 5 A. Typical discharge voltage and current waveforms of benzene are shown in Fig. 6. Detailed explanation and discussion of the discharge phenomena in aromatic solution is reported by Li *et. al.* [32].

E. Optical Emission Spectrum under Sugar Solution Plasma Discharge

Fig. 7 showed similar spectrums were obtained from the discharge occurred in glucose, sucrose and fructose. The majority of active species emitted were H_α at 656 nm and H_β at 484 nm, followed by atomic O radicals at 777 nm and 844 nm. Small speak of atomic C at 247 nm was observed as well. It is suggested the hydrogen and oxygen radicals were generated from water molecule instead of sugar compounds. The water chemistry and optical emission spectrum under plasma water discharge had been thoroughly investigated by previous studies [28-30], and indicated that water could be decomposed and formed these radicals. However, the formation of atomic C was obviously generated by the sugar compounds. The result indicated small portion of sugar molecules was decomposed and emitted atomic C inside the plasma channel.

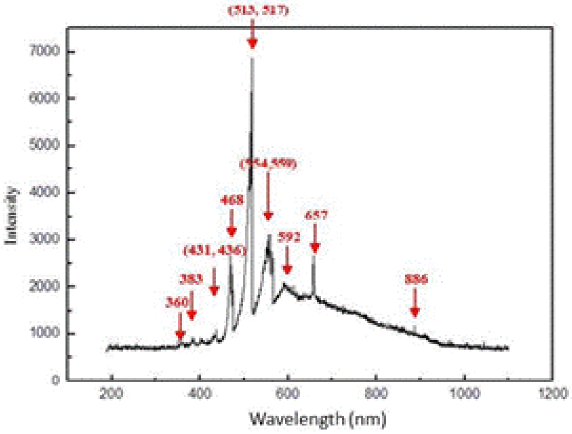

Fig. 8. Optical emission spectrum of discharge in benzene.

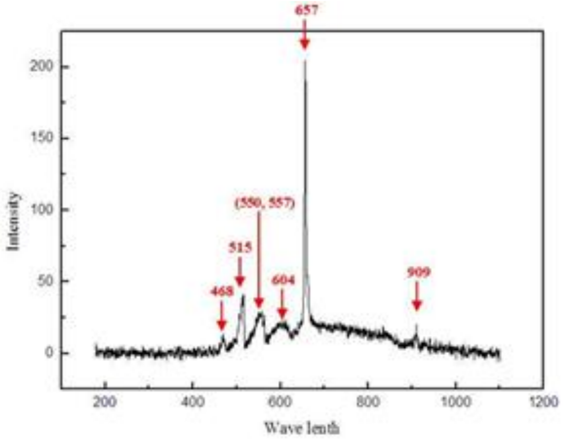

Fig. 9. Optical emission spectrum of discharge in toluene.

E. Optical Emission Spectrum during Aromatic Hydrocarbon Solution Plasma Discharge

The optical emission spectrums observed under plasma discharge in benzene and toluene are shown, respectively, in Figs. 8 and 9. For benzene, it was observed that the major emitted wavelengths were found in the range of 470 - 480, 510 - 520 and 560 - 565 nm. The spectrum was expected to belong to the excited C_2 emission spectrum [33]. A weaker intensity of wavelength between 430 and 435 nm were also inspected. It might be generated by the excited CH radicals [34-36]. The peak of 657 nm was possible contributed by active species of H_α. For toluene, the major species changed into Hα at 657 nm, followed by C_2 at 468 and 515 nm. The results showed that carbon molecules were more likely being created by the discharge in benzene. This proposal also agreed with the result observed from previous section. The amount of carbon nanoparticles generated from benzene was in higher amount compared to that from toluene. It is expected that benzene would achieving highest yield and quality of carbon nanoparticles since the decomposition of liquid benzene would give the greatest number of carbons for a given volume [37].

IV. CONCLUSION

The synthesis of carbon nanoparticles by solution plasma under various organic solutions has been investigated. It can be concluded that:

(1) On average, 15 mg of carbon particles was obtained from 100 ml saturated glucose, sucrose and fructose solution. The particles were observed to be hemisphere and sphere in shape, with a size distribution between 100 – 600 nm.

(2) For aromatic hydrocarbon solutions, 930 mg and 1000 mg of carbon could be generated, respectively, from 100 ml of pure toluene and benzene, the particles were spherical in shape with a size distribution of 20 - 30 nm.

(3) The discharge in sugar solution occurred in three different phases: pre-discharge, the initiation and the formation of discharge. Under optical emission spectrum, we observed the major active species obtained were Hα, followed by atomic O and atomic C. The discharge waveforms and optical emission spectrum were quite similar to that of tap water.

(4) For benzene and toluene solutions, the discharge happened in two main steps: pre-discharging and the formation of discharge. The majority active species were observed to be C_2 and CH. The dissociation of aromatic compounds were the source of the generation of these active species.

Based on these results, it is proposed that solution plasma process can synthesis carbon nanoparticles in one single step. The quality and quantity of generated carbon nanoparticles were highly depended on the type of solution applied the system. In this study, highest yield of carbon nano sphere was obtained from pure benzene as a carbon precursor.

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