Synthesis of carbon nanoparticles using various electrolyte concentrations in submerged glow discharge plasma

M S Ranjit and M R M Julaihi
Swinburne University of Technology Sarawak, Jalan Simpang Tiga, 93350 Kuching Sarawak, Malaysia
Email: 100073374@students.swinburne.edu.my

Abstract. This research aims to study the effects of the manipulation of the concentration of electrolyte on the synthesis and size control of carbon nanoparticles. Submerged glow-discharge plasma (SGDP) method was used which is a type of electrolysis. This method was proven to be both cost effective and eco-friendly in the synthesis of nanoparticles. Carbon nanoparticles generally range from 1 to 100nm and its small size gives it a high surface area to low volume ratio which gives it an edge over the sheet and bulk metals. They vary in their mechanical properties with respect to their sizes which makes it ideal for the manufacturing industry. The ability to control carbon nanoparticle size will give manufacturers the ability to obtain the desired mechanical properties. This research brings the potential of being able to control the size of carbon nanoparticles with a simple and cost-effective method by changing the concentration of electrolyte and plasma discharge voltage. The manufacturing industry in the future can benefit from this research as they will be able to manufacture materials with better mechanical properties at a cheaper cost.

1. Introduction
Synthesis and size control of nanoparticles require considerable amount of research. The main goal is being able to control the size of these nanoparticles depending on their applications. The method used here is the submerged glow-discharge plasma (SGDP) method. SGDP was proven to be simple to set up, does not require hazardous materials and cost effective [1]. The parameters that can be controlled in SGDP method are categorized into three categories (2):

1) Manipulating the concentration of the electrolyte.
2) Manipulating the depth of the cathode.
3) Manipulating the type of electrolyte used.

In this paper, a variety of electrolyte concentrations were used with the prospects of controlling the size of the synthesized carbon nanoparticles. Each of the carbon nanoparticles formed from the SGDP method is expected to show different mechanical properties based on the variation of their size with respect to the concentration of the electrolyte. Controlling the size of carbon nanoparticles can bring about controlling the properties of the nanoparticles produced. Being able to manufacture carbon nanoparticles by the numbers with a low starting cost shows the potential of this method being implemented in the future. Furthermore, SGDP is eco-friendly as no unwanted emission occurs except for water vapor when carrying out this process, which helps in the reduction of environmental pollution [2-3]. The manipulation of the depth of the cathode and the type of electrolyte used on the synthesis and size control of the carbon nanoparticles will be under the future
research section.

2. Submerged glow-discharge plasma method (SGDP)

The SGDP method is a form of electrolysis of water which comprises of four main stages; the electrolysis stage, vaporization stage, transition stage and plasma stage. It revolves around the collision of electrons and neutral atoms on the cathode surface which causes a spark which excites, ionize and dissociates with the emission of light “glow phenomenon” [4-5]. The schematic diagram summarizing the formation of nanoparticles by SGDP is shown in Figure 1.

![Figure 1. Submerged glow discharge plasma resulting in formation of metallic nanoparticles](image1)

2.1 Carbon nanoparticles

Carbon nanoparticles are particles which range from 1 – 100 nm. Carbon nanoparticles are made up of graphite which consists of intermediate crystalline structure. The range setting was done to differentiate nanoparticles and cluster particles.

2.2 Size control of carbon nanoparticles

The main focus for controlling the size of the carbon nanoparticles was to vary the concentration of the electrolyte. Different concentrations of electrolyte were expected to result in the change of carbon nanoparticles size and morphology. Using potassium carbonate (K₂CO₃) as the electrolyte, increasing the electrolyte concentration would increase the electrical current value as well. The high concentration of electrolytes indicates that there were higher numbers of free-flowing electrons in the solution. This in turn would increase the conductivity of the solution, subsequently increasing the current value at low voltages. This increases the number of substance in the solution [2]. In terms of size, it is predicted that a lower glow discharge voltage would decrease the size of the carbon nanoparticles produced [2,6].

The carbon nanoparticles formation on the cathode will vary in their sizes depending on the concentration of the electrolyte. A higher concentration electrolyte will provide more free-flowing electrons (e⁻), thus the probability of achieving glow-discharge voltage would be higher. At the same time more electron bombardment can occur on the cathode surface. Therefore, achieving the glow-discharge voltage or plasma initiation at a quicker rate will cause the sizes of the carbon nanoparticles to decrease. The electrolyte used here was potassium carbonate (K₂CO₃) which is a strong electrolyte. As a strong electrolyte, it has better electrical conductivity compared to weak electrolytes [7].

3. Methodology

3.1 Experimental setup

![Figure 2. Experimental setup for submerged glow discharge plasma](image2)
3.2 Experimental procedure

The apparatus was set as shown in Figure 3. An 800W DC power supply (Kikusui PWR800L) was used to generate a steady electrical current supply to the setup. A 100mm long graphite rod obtained from a mechanical pencil refill was used as the cathode and a 500mm coiled platinum wire was used as the anode. The concentration of the K₂CO₃ electrolyte was varied to 0.1M, 0.5M and 1.0M with different voltages applied. Scanning electron microscopy (SEM) was used to obtain images of the nanoparticles, while energy dispersive spectroscopy (EDS) was used to determine the elemental composition of the nanoparticles.

4. Results and discussion

The voltage and current measurements during plasma generation for each of the electrolyte is shown in Table 1.

| Concentration (M) | Sustained voltage (V) | Current (A) |
|------------------|-----------------------|-------------|
| 0.1              | 100                   | 1.5         |
| 0.5              | 75                    | 1.5         |
| 1.0              | 15                    | 4.5         |

The mass of the carbon nanoparticles are shown in Table 2. The mass of the nanoparticles were calculated as the difference in mass of the cathode before and after plasma discharge, assuming that any loss of the cathode mass was due to it converted into nanoparticles.

| Concentration, K₂CO₃ (M) | Initial mass of graphite, m₁ (g) | Mass of graphite after process, m₂ (g) | Nanoparticle mass, m₁ – m₂ (g) |
|--------------------------|----------------------------------|---------------------------------------|-------------------------------|
| 0.1                      | 125                              | 120                                   | 5                             |
| 0.5                      | 125                              | 114                                   | 11                            |
| 1                        | 125                              | 110                                   | 15                            |

As the electrolyte concentration increased, the mass difference of the graphite rod before and after plasma discharge became larger. This shows that the graphite rod was converted into carbon nanoparticles when the SGDP method was carried out. Higher concentrations lead to more bombardments of electron on the wall of the cathode which justified the decrease in the mass of the graphite rod.

| Concentration (M) | C (%) | O (%) |
|-------------------|-------|-------|
| 0.1               | 85.39 | 14.61 |
| 0.5               | 77.97 | 22.03 |
| 1.0               | 89.45 | 10.55 |

Table 3 shows the EDS results conducted on the particles that were obtained after SGDP process. It is clear that the elemental compositions for all of the nanoparticles show that they consisted of mainly carbon. The presence of oxygen showed the possibility that some of the nanoparticles were oxidized.
Figure 3. SEM images of carbon nanoparticles produced in 0.1M, 0.5M and 1.0M K₂CO₃

Figure 3 shows that the size of carbon nanoparticles produced varied with different electrolyte concentration. In 0.1M and 0.5M, the particles were quite large and were produced in small amounts compared to 1.0M electrolyte. Meanwhile, in at 1.0M concentration, there were numerous smaller nanoparticles compared to 0.1M and 0.5M concentrations. Here, the higher the electrolyte concentration and thus the lower the glow discharge voltage, the carbon nanoparticles were more uniform in shape and smaller in size.

Figure 4. Voltage-current relationship during plasma generation on graphite cathode

Figure 4 shows the voltage-current relationship during plasma generation for each of the electrolyte concentrations. For an electrolyte concentration of 1.0M K₂CO₃ the glow discharge voltage was achieved at 15V producing a current of 4.5A while the 0.1M K₂CO₃ electrolyte concentration which achieved its glow discharge voltage at 100V producing a current of 1.5A. According to Figure 4, the higher the concentration of the electrolyte, the higher the current flow in the aqueous solution. The glow-discharge voltage in turn was achieved at lower voltage.

The concentration of the electrolyte determines the number of free flowing electrons within the solution. More free flowing electrons meant that the glow-discharge voltage would be attained at a lower voltage. Having more free flowing electrons enabled more secondary electron bombardment on the walls of the cathode. This kept the plasma self-sustaining as well as producing large amounts of small sized carbon nanoparticles.

The main effect on carbon nanoparticles sizes formed was due to the electrolyte concentration influencing the glow discharge initiation voltage. This in turn affected the plasma sustaining voltage. The lower the glow discharge sustaining voltage the smaller the size of the carbon nanoparticles produced. The concentration of the electrolyte determines the number of electrons to bombard the walls of the cathode. More electrons being able to collide with the wall of the cathode to produce the self-sustaining plasma the lower the glow discharge initiation and sustaining voltage which prompts the release of smaller sized carbon nanoparticles.

5. Future research
Manipulating the depth of the cathode rod and the type of electrolyte used are two further parameters that are important in identifying the most optimal way of controlling the size of the carbon nanoparticles produced.
Manipulating the depth of the cathode rod while maintaining the concentration of the electrolyte in the solution is to test how the glow-discharge voltage will vary within this condition. Ideally, the increase in the surface area exposed to the electrolyte is expected to increase the glow-discharge voltage. This correlates to the production of carbon nanoparticles which depends on the plasma being able to keep its self-sustaining state. Having a larger surface area meant that the secondary electrons bombarding the walls of the cathode would be more scattered across the surface of the cathode, this is expected to cause the glow-discharge voltage to increase thus increasing the size of the carbon nanoparticles formed. A physical experimentation is to be done in order to verify this assumption.

Manipulating the electrolyte used will also indirectly influence the glow-discharge of voltage in the solution. In theory, using a stronger electrolyte will yield more accurate results as the electrolyte will completely ionize in water. Stronger electrolyte will have better electrical conductivity, thus is expected to decrease the glow-discharge voltage. This was confirmed through an experimentation carried out by Al Anbouri [4]. Despite this, not a lot is known on how to optimally control the size of the carbon nanoparticles through using the different types of electrolytes.

6. Conclusion

Submerged glow discharge plasma method was used to produce carbon nanoparticles. The carbon nanoparticles were found to be more uniformly shaped and smaller at 1.0M compared to 0.1M and 0.5M electrolyte concentrations. The increase in the concentration of the electrolyte affects the glow discharge voltage which controlled the size of the carbon nanoparticles formed. This breakthrough will be very beneficial to the manufacturing industry, as they will be able to control the size of the carbon nanoparticles through manipulation of the size of the electrolyte concentration and plasma discharge voltage. Furthermore, the SGDP method is also a simple and cost effective method of carrying out the production carbon nanoparticles.

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