Manipulation of Electrolyte Concentration and Cathode Morphology to Control the size of the Carbon Nanoparticles

M S Ranjit*, B L Y Yang and M R M Julaihi
Swinburne University of Technology Sarawak, Jalan Simpang Tiga, 93350 Kuching Sarawak, Malaysia

Email: 100073374@students.swinburne.edu.my

Abstract. The research aims to study the effects of concentration of the electrolyte and morphology of the cathode rod on the synthesis and size control of the carbon nanoparticles. The research was conducted using the submerged glow discharge plasma (SGDP) method. Potassium carbonate a strong electrolyte was used to maintain the accuracy of the results. The glow discharge voltage and any instabilities were recorded and monitored to obtain trends during the synthesis of carbon nanoparticles. Moreover, the shapes and sizes of the carbon nanoparticles formed were also observed and analyzed. The SGDP method is both eco-friendly and cheap to conduct. Carbon nanoparticles range from 1 – 100 nm. The small size of these nanoparticles gives it a high surface area to its volume ratio over sheet and bulk metals. The nanoparticles have different mechanical properties with respect to their sizes. The ability to control the sizes of the nanoparticles will enable manufacturers to obtain the mechanical properties they desire. The research conducted was able to determine the factors which enables the control of the sizes of carbon nanoparticles formed. At higher electrolyte concentration and higher cathode thickness, the size of the carbon nanoparticles decreased.

1. Introduction
A considerable amount of research is required in the synthesis and size control of carbon nanoparticles. Controlling the sizes of the carbon nanoparticles will have an effect on the mechanical properties of the carbon nanoparticles. The SGDP method was selected as it is easy to set up, requires no hazardous materials and cost effective to carry out [1]. The two main parameters controlled during the experimentation are manipulating the concentration of the electrolyte and manipulating the morphology of the cathode [2].

In this paper, the electrolyte concentration was varied to observe the relationship in the size of the carbon nanoparticles formed with respect to the number of free moving electrons in the solution. The morphology of the cathode is varied through manipulating the thickness of the carbon rod used. This is to investigate the relationship between the surface area and the size of the carbon nanoparticles formed.

2. Background
2.1 Submerged Glow Discharge Plasma Method (SGDP)
The submerged glow discharge plasma method (SGDP) is an electrolysis of water-based experiment. This method comprises of four main stages; electrolysis stage, vaporization stage, transition stage and plasma stage. The formation of the nanoparticles revolves around the collision between the electrons and neutral atoms on the surface of the cathode. The collision causes a spark which ionizes, dissociates and excites the electrons with the emission of light called the “glow phenomenon”. The nanoparticles are formed during the plasma stage through an electrical discharge in liquid [3].
During the transition phase, vapor bubbles are produced on the surface of the cathode separating the layer between the cathode surface and liquid. When plasma is formed, a pressure difference will exist between these two layers. High pressure on the surface of the cathode enables the nanoparticles to be discharged out in molten form. These particles in molten form falls to the bottom of the beaker and when cooled will turn into nanoparticles.

2.2 Breakdown Voltage ($V_b$), Glow Discharge Voltage ($V_d$) and Plasma Intensity

The breakdown voltage, $V_b$ is the maximum point at which the curve obeys Ohm’s law. When the voltage is increased at this point, gaseous bubbles begins to form with a current drop to signify a breakdown of normal electrolysis. As the voltage increase the gaseous sheath around the cathode will slowly stabilize. The current will continue to decrease until light emission is detected. This voltage point is called the glow discharge voltage, current onwards will slowly start to increase again [4]. Plasma formation occurs at the glow discharge voltage, nanoparticles are discharged out during this phase. At a higher applied voltage, the nanoparticles formed will increase in size due to the plasma intensity [5]. The plasma intensity is proportional to the excitation of electron temperature which occurs during the initiation of plasma on the cathode.

2.3 Size Control of Carbon Nanoparticles
In this research, the formation of the carbon nanoparticles occurs during the plasma stage when the glow discharge voltage, $V_d$, is achieved. This shows that at different $V_d$ values the shape and size of the nanoparticles formed would vary from one another.

With potassium carbonate ($K_2CO_3$) as the electrolyte, manipulating the concentration of electrolyte will vary the number of free-flowing electrons in the solution. A higher concentration would have more free-flowing electrons in the solution which will increase the conductivity in the solution. This will decrease the glow discharge voltage as the collision intensity between the electrons and neutral atoms increases [6]. The current concentration spots on the cathode will increase, thus will cause the discharge of smaller nanoparticles.

![Figure 3](image3.png)

**Figure 3.** Current concentration spots increases with electrolyte concentration and voltage.

The morphology of the carbon nanoparticles will be studied through varying the thickness of the cathode. This will increase the surface area of the cathode exposed to the electrolyte. Under fixed condition where by the concentration of the electrolyte and depth of the cathode are kept constant, a larger amount of current is now required to initiate the plasma formation [7]. The glow-discharge voltage is expected to change depending on the amount of surface area exposed to the electrolyte. To reach plasma stage, requires higher amounts of energy in the form of heat for thicker rods.

### 2.4 Electrode Reactions

The SGDP method consist of a combination of both physical and chemical reaction occurring simultaneously during the synthesis of the carbon nanoparticles. The reaction takes place on the cathode surface.

$$H_2O + e^- \rightarrow OH^- + H^+ + e^-$$

The formation of the nanoparticles is due to the reaction between the metal ion and the hydrogen radicals which are high energy state [8]. At the plasma zone, the high voltage supplied to the aqueous solution during the electrolysis phase will release the hydrogen radicals. The voltage excites the hydrogen radicals cause them to accelerate towards the cathode. The acceleration of the hydrogen radicals towards the cathode is what causes the bombardment of electrons on the wall of the cathode. This bombardment causes the temperature to increase due to the immense heat from the collision on the cathode surface. The plasma layer is formed with a high temperature and electro-conductivity region. There is an electro-thermal instability which occurs due to the current concentrated at the cathode [9]. This will form the carbon nanoparticles through the difference in pressure between the cathode surface and the solution.
2.5 Mechanism of the SGDP, Hydrodynamic Instabilities and Plasma Turbulence

From figure 2, the point at which \( V_b \) occurs gives the maximum current required for the vapor formation. The power density for the formation of the vapor layer is denoted by \( W_v \) (W/cm\(^2\)). An increase in the temperature of the solution will result in a decrease in the conductivity of the solution. Beyond this point the current will slowly decrease as the temperature in the solution increases [4]. Upon plasma formation, the electric power is reduced to enable the plasma to self-sustain. Moreover, when the solution has high amounts of resistance the power density required will be higher. Once vapor is formed, current will stabilize and the glow–discharge plasma can be obtained stably. The amount of power \( W_m \) (W/cm\(^2\)) required to form the plasma can be obtained from the product of the average current (I) and voltage (V) per surface area, A (cm\(^2\)) of the cathode exposed to the electrolyte at which the glow–discharge is maintained at.

\[
W_m = I \times \frac{V}{A}
\]  

(1)

If the \( W_m \) obtained is less than the \( W_v \) will suggest that higher amounts of power is required to initiate the plasma formation.

The morphological aspects in the evolution of gas is distinguished between the electrode potential and current. During normal electrolysis, separate bubbles are formed when the temperature in the solution is increased with respect to the voltage. When \( V_b \) is achieved at the transition phase, the electrode will be covered by a gaseous blanket moving in a violent motion. This results in a drop in the current and the electrode potential is increased [10]. The cathode will be enclosed by a continuous gaseous envelope (plasma layer). The stability of the plasma layer is dependent on the relative speed between the counter flowing gas and liquid streams. If the relative speed is too high, rapid small disturbance will grow and break the contiguous streams at the boundary layer. This small disturbance is directly related to the plasma turbulence.

\[\text{Figure 4. Instability during the glow – discharge.}\]

2.6 Carbon Nanoparticles

Carbon nanoparticles are carbon particles that are nanosized. These particles have a diameter of less than 100nm. The carbon nanoparticles consist of an intermediate crystalline structure of graphite and an amorphous state. This can be described as a turbostatic structure that has a different bulk graphite crystal in an ABAB order [11].

![Image of plasma formation and evolution](image-url)
3. Methodology
The submerged glow discharge plasma (SGDP) method was used to synthesis the carbon nanoparticles.

3.1 Experimental Setup

3.2 Experimental Procedure

a. Preparation of electrolyte

The mass of K$_2$CO$_3$ required by the system was calculated using the formula:

$$\text{Mass of } K_2CO_3 \ (g) = \text{Volume} \ (l) \times \text{Concentration} \ (\frac{mol}{l}) \times \text{Molar mass } K_2CO_3 \ (\frac{g}{mol})$$

$$\text{Mass of } K_2CO_3 \ (g) = 0.3l \times 0.05 \ (\frac{mol}{l}) \times 138.205 \ (\frac{g}{mol})$$

$$\text{Mass of } K_2CO_3 \ (g) = 2.073 g$$

The mass of K$_2$CO$_3$ in powdered form was weighted to obtain the mass calculated. The powder form K$_2$CO$_3$ was transferred to a beaker and distilled water filled up the beaker to 300 ml. The beaker was then heated on a hot plate before continuing the experiment. The steps were repeated to obtain mass for electrolyte concentration of 0.1M, 0.2M and 0.3M.

![Figure 5: Experimental setup for submerged glow discharge plasma](image)

![Figure 6: Flow chart to conduct the experiment](image)
b. Manipulating the electrolyte concentration
The apparatus was set as shown in Figure 4. A DC power supply was used to supply an amount of electrical current to the system. Carbon rods of 0.6cm was used as the cathode at a depth of 1.0cm in the electrolyte and a 10cm long platinum wire was used as the anode. The concentration of the K₂CO₃ electrolyte was set to 0.05M. The power supply was switched on and the voltage and current values were recorded. The voltage follows an increment of 5V every 30 seconds. The cathode rod was observed closely at every voltage increment until the formation of sparks (partial plasma). The voltage was further increased until the formation of full plasma. The voltages for both partial plasma and full plasma were recorded down as the glow-discharge voltage. At the glow-discharge voltage, the experiment was left to run for 30 minutes to produce more nanoparticles. The experiment was repeated with electrolyte concentration of 0.1M, 0.2M and 0.3M.

c. Manipulating the morphology of the cathode
The experimental setup is the same as experiment in (b). The changes are the concentration of electrolyte was fixed to 0.1M and the thickness of the cathode was changed to 0.5mm. The power supply was switched on and the voltage and current values were recorded. The voltage follows an increment of 5V every 30 seconds. The cathode rod was observed closely at every voltage increment until the formation of sparks (partial plasma). The voltage was further increased until the formation of full plasma. The voltages for both partial plasma and full plasma were recorded down as the glow-discharge voltage. At the glow-discharge voltage, the experiment was left to run for 30 minutes to produce more nanoparticles. The experiment was repeated with cathode thickness of 1.0mm, 2.0mm and 10.0mm. For both (b) and (c) if the solution volume decreases due to evaporation, a dropping funnel is used to add distilled water into the solution to maintain the solution volume.

d. Centrifuging
After conducting the experimental procedures in (b) and (c), the nanoparticles in the beaker were left overnight inside a covered box for sedimentation. The next day, the solution in the beaker was slowly reduced to around 50ml. The nanoparticles inside the remaining solution were transferred into a centrifuge tube and placed into the centrifuge machine. The machine was set to 6000rpm for 15 minutes per cycle. Three cycles were carried out and at the end of every cycle the remaining electrolyte solution were removed and refilled with distilled water. The nanoparticles were then transferred to another centrifuge tube and sent for SEM viewing.

e. Size analysis of carbon nanoparticles through ImageJ
The carbon nanoparticles obtained from SEM imagery were measured using the ImageJ software. Based on the given scale on the SEM image, the software helps to measure the size of the nanoparticles on the image by adjusting the scale to fit the line drawn on the diameter of selected particle on the actual image.
4. Results

**Figure 7.** Current-voltage curve for the discharge voltage at different concentration at constant cathode thickness of 0.6mm.

**Figure 8.** Current-voltage curve for discharge voltage for different cathode thickness. The boxes in white indicate formation of partial plasma and boxes in yellow indicate formation of full plasma.
**Figure 9.** SEM imagery from a) to c) indicate the CNP’s formed through change in electrolyte concentration. SEM imagery from d) to f) for indicates the CNP’s formed through change in cathode thickness.

**Table 1.** Size of nanoparticles with respect to concentration at constant cathode thickness of 0.6 cm

| Concentration (M) | Power to initiate glow discharge, P (W) | Surface area of the cathode, A (cm²) | Power to form the plasma per unit area, Wm (W/cm²) | Average size of Carbon nanoparticles, CNPs (nm) | Standard deviation of sizes of CNPs (nm) |
|-------------------|----------------------------------------|-------------------------------------|-----------------------------------------------|-----------------------------------------------|------------------------------------------|
| 0.05              | 204                                    | 2.4504                              | 83.3                                          | 121                                           | 26.53                                     |
| 0.1               | 209                                    |                                     | 85.3                                          | 98.7                                          | 22.21                                     |
| 0.2               | 270                                    |                                     | 110.2                                         | 80.6                                          | 12.78                                     |
| 0.3               | Unable to form                         |                                     |                                               |                                               |                                          |

**Table 2.** Size of carbon nanoparticles with respect to cathode thickness at constant electrolyte concentration of 0.1 M

| Thickness, t (mm) | Power to initiate glow discharge, P (W) | Surface area of the cathode, A (cm²) | Power to form the plasma per unit area, Wm (W/cm²) | Average size of Carbon nanoparticles, CNPs (nm) | Standard deviation of sizes of CNPs (nm) |
|-------------------|----------------------------------------|-------------------------------------|-----------------------------------------------|-----------------------------------------------|------------------------------------------|
| 0.5               | 76                                     | 0.16                                | 472                                          | 128.7                                         | 28.49                                     |
| 1.0               | 110                                    | 0.33                                | 334                                          | 123.4                                         | 29.17                                     |
| 2.0               | 117                                    | 0.69                                | 169                                          | 110.9                                         | 23.83                                     |

**Figure 10.** Size of CNP’s formed at different electrolyte concentration.
5. Discussion

5.1 Current – voltage curve relationship for change in electrolyte concentration and size of carbon nanoparticles

The results obtained from Figure 7 shows the initiation of glow – discharge plasma for varying electrolyte concentration. Due to the volatility of the system and to prevent injuries from explosion of carbon rod, the nanoparticles were left under partial plasma condition. At higher concentration the glow – discharge voltage, $V_d$ is lower. The amount of power required to initiate the glow – discharge also increases with the increase in the concentration of the electrolyte as seen in Table 1. This is due to the increase in the number of free moving electrons in solution. More electrons within system would require higher amounts of energy to excite the electrons to bombard neutral atoms on the wall of the cathode (Carbon). The higher energy required to initiate the glow - discharge, the more vigorous the movement of vapor bubbles in the plasma layer.

From the results obtained in Figure 10, the sizes of the carbon nanoparticles formed decreases when the concentration of the electrolyte increases. In addition to that, the glow – discharge voltage was found to be lower when the sizes of the carbon nanoparticles discharged out decreases [6]. However, the drop-in voltage corresponds to a higher current output indicating a higher amount of output power. The current concentration spots around the cathode increases with the increase in the number of free – moving electrons within the system. When the number of current concentration spots around the cathode increases, the tendency for these current concentration spots to overlap on the surface of the cathode increases. Due to this, there will be a higher amount of pressure difference on the surface of the cathode where the current concentration spot overlaps compared to other section of the cathode where there is no overlap in the current concentration spots. The higher amounts of pressure difference coupled with the overlapping current concentration spots causes the discharge of smaller carbon nanoparticles. The intensity and frequency of the current concentration spots determines the sizes of the carbon nanoparticles formed. This also relates to an observation made during the experimentation whereby the intensity of the plasma discharge was observed to be more intense at higher electrolyte concentration.

At 0.3M in Figure 7, shows the dissipation in the formation of the vapor gas. The dissipation in the vapor gas prevents the glow – discharge from occurring. In order to form the glow – discharge, a plasma

![Figure 11. Size of CNP’s formed with respect to different cathode thickness. Figure 12: Plasma intensity for varying electrolyte concentration](image)
layer must first be developed from the vapor gasses which is supposed to form gaseous sheath on the surface of the cathode.

5.2 Current – voltage curve relationship for change in the morphology of the cathode and size of the carbon nanoparticles

The results obtained from Figure 8 shows the variation in the initiation of glow – discharge when the morphology of the cathode in terms of its thickness was manipulated. Unlike the experiments conducted for 0.6cm carbon rod, the 0.05cm, 0.1cm and 0.2cm carbon rods were able to achieve full plasma discharge. The system was discovered to be less vigorous compared to the experiment with the 0.6cm carbon rod. The glow - discharge voltage at the initiation of plasma and full plasma stage in Figure 8 shows little variation in terms of when the formation of carbon nanoparticles occurs. However, there is a variation in the power required to initiate the glow – discharge. From Table 2 an increase in the thickness of the cathode will result in higher power required to form the glow – discharge. For a fixed number of free moving electrons in the solution, when the surface area of the cathode exposed to the solution is increased more energy is required to excite and drive the electrons to collide against the neutral atoms at the wall of the cathode. During the experiment, the vigorousness of the vapor bubbles in the system increases with respect to the amount of power required for the formation of the glow – discharge. The amount of power required to form the glow – discharge is dependent on the surface area exposed to the solution at constant electrolyte concentration.

From the graph plotted in Figure 11 the size of the carbon nanoparticles formed decreases when the thickness of the cathode increase. The amount of power required for the initiation of plasma also increases with respect to the thickness of the cathode. The high amount of power is enough to drive electrons around the surface of the cathode. There is a high amount of energy around the current concentration spots formed from the high energy levels within the system which causes heat to diffuse around the current concentration spot. Higher amounts of heat energy when the cathode thickness increases would cause the current concentration spot to increase and overlap one another on the cathode surface. The overlap in the current concentration spots is expected to not be as intense when compared to the experiment conducted with varying electrolyte concentration. This can be seen through comparing the amount power required to initiate the plasma discharge in Table 1 and 2. The power required to initiate the partial plasma discharge corresponds to the amount of plasma intensity and the heat energy from within the system.

5.3 Plasma turbulence, formation and shape of carbon nanoparticles

Not all the carbon nanoparticles formed observed in Figure 9 have a spherical shape. The shapes of some of these nanoparticles are irregular. The irregularity in the shape of the carbon nanoparticles formed is due to the presence of plasma turbulence. These turbulences exist in the plasma layer located in between the cathode surface and solution. It was noticed from the SEM imagery in Figure 9, the frequency of being able to obtain perfectly spherical carbon nanoparticles decreases with respect to both the increase in electrolyte concentration and increase in the thickness of the cathode.

The amount of power required to initiate the partial plasma formation increases with the increase in the electrolyte concentration and cathode thickness. The increase in power indicates an increase in the plasma intensity and heat energy within the system. When the system is experiencing a drop in current, a gaseous blanket will form around the cathode [10]. When the amount of energy in the system increase, the intensity and vigorousness of the movement of vapor bubbles increases as well. As mentioned, the stability of the plasma layer is highly dependent on the speed of the counter flowing gas and the relative liquid flow stream. If the system can maintain a stable plasma layer, the carbon nanoparticles discharged out from the cathode will be more spherical in shape. When the energy in the system is high, the movement of the counter flowing gas against the relative liquid flow stream will be high. This creates disturbance (turbulence) within the plasma layer. The consistency of the current concentration spots will decrease as the disturbance begins to grow with time. The pressure difference on the surface of the cathode will vary from each location on the cathode which cause the discharge irregularly shaped carbon nanoparticles. Being able to form perfect spherical carbon nanoparticles at both higher concentration and cathode thickness is due to the plasma layer being highly stable at the start of the experiment. But as the energy from the increase in power of the system increase, the disturbance begins to grow and
eventually breaking the plasma layer thus stopping the submerged glow discharge plasma from forming anymore carbon nanoparticles.

The experiment conducted at 0.3M in Figure 7 is unable to form the plasma layer as the speed of the vapor gas flow is flowing too high causing the high amount of disturbance which prevents the plasma layer from even forming the gaseous sheath.

5.4 Size of the carbon nanoparticles and cluster formations

The sizes of the carbon nanoparticles vary from one another through a standard deviation of around 12.78nm and 29.17nm. This shows that submerge glow discharge plasma method is able to control size of the carbon nanoparticles. However, it was noticeable that there were a lot of carbon cluster formation from the SEM images in Figure 9. This is due to carbon being less dense compared to water which causes the nanoparticles to float around the surface of the solution. If left unattended these carbon nanoparticles will form into carbon sheaths thus making it difficult to measure individual spherical carbon nanoparticles. The clusters of carbon if exposed to sunlight will form carbon crystals.

From Figure 9, the carbon nanoparticles have formed agglomerates and fractal structure. The formation of the fractal structures is due to the presence of attractive van der Waals forces. The carbon nanoparticles will attract one another with the aid of the van der Waals forces forming the agglomeration and reducing the accuracy in terms of the sizes of the carbon nanoparticles formed. The presence of agglomerates can reduce the effectiveness of the carbon nanoparticles in terms of its electrical conductivity [12].

6. Conclusion

The synthesis and size control of the carbon nanoparticles was able to be verified through the research conducted. It was found that at higher electrolyte concentration and higher cathode thickness the size of the carbon nanoparticles formed is smaller. The increase in the power required to initiate the partial plasma formation will affect the size of the carbon nanoparticles formed as the nanoparticles was found to be smaller in size. In short, the lower the glow discharge voltage, the smaller carbon nanoparticles formed. Controlling the size of the carbon nanoparticles brings about enhancing the mechanical properties of materials which would be beneficial in the future for material manufacturing industry.

References

[1] M. Ishigami, J. Cumings, A. Zettl, and S. Chen, “A simple method for the continuous production of carbon nanotubes,” Chem. Phys. Lett., 2000.
[2] P. N. Y. Yek, M. R. M. Julaihi, M. S. Osman, T. C. Tiong, W. H. Lee, and C. L. Lee, “Submerged Glow-Discharge Plasma: An Economical Approach to Convert Construction Scrap Metal into Nanomaterials,” in E3S Web of Conferences, 2018.
[3] M. R. M. bin Julaihi, S. Yatsu, M. Jeem, and S. Watanabe, “Synthesis of stainless steel nanoballs via submerged glow-discharge plasma and its photocatalytic performance in methylene blue decomposition,” J. Exp. Nanosci., 2015.
[4] S. K. Sen Gupta, “Contact glow discharge electrolysis: its origin, plasma diagnostics and non-faradaic chemical effects,” Plasma Sources Sci. Technol., p. 63001, 2015.
[5] G. Saito and N. Sakaguchi, “Solution plasma synthesis of Si nanoparticles,” Nanotechnology, vol. 26, no. 23, pp. 1–8, 2015.
[6] P. N. Y. Y. and M. R. M. J. M H S Al Anbouri, B W M Yii and S winbunre, “Effect of Electroyte Concentration during Solution Plasma on Copper Nanoparticle Size,” Eff. Electrolyte Conc. Dur. Solut. Plasma Copp. Nanoparticle Size, 2018.
[7] G. Saito, Y. Nakasugi, and T. Akiyama, “Generation of solution plasma over a large electrode surface area,” J. Appl. Phys., vol. 118, no. 2, 2015.
[8] P. Pootawong, N. Saito, and S. Y. Lee, “Discharge time dependence of a solution plasma process for colloidal copper nanoparticle synthesis and particle characteristics,” Nanotechnology, 2013.
[9] M. R. M. bin Julaihi, “Synthesis of metallic oxide nanoballs via submerged glow-discharge plasma and their photocatalytic effect,” Synth. Met. oxide nanoballs via Submerg. glow-discharge plasma their photocatalytic Eff., no. March, 2015.
[10] B. Mazza, P. Pedeferri, and G. Re, “Hydrodynamic instabilities in electrolytic gas evolution,”
Electrochim. Acta, vol. 23, no. 2, pp. 87–93, 1978.

[11] J. Kang, O. L. Li, and N. Saito, “Synthesis of structure-controlled carbon nano spheres by solution plasma process,” Carbon N. Y., 2013.

[12] X. Deng, Z. Huang, W. Wang, and R. N. Davé, “Investigation of nanoparticle agglomerates properties using Monte Carlo simulations,” Adv. Powder Technol., 2016.