Effect of Electrolyte Concentration during Solution Plasma on Copper Nanoparticle Size

To cite this article: M H S Al Anbouri et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 429 012084

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Effect of Electrolyte Concentration during Solution Plasma on Copper Nanoparticle Size

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Abstract. This research was conducted to investigate the effect of electrolyte concentration of solution plasma on copper nanoparticles size. Copper nanoparticles with the size between 1-100 nm have received a huge interest because of their optical, catalytic and electrical conducting properties. Electrolysis via solution plasma method has many advantages such as its cost effectiveness, simplicity, eco-friendliness, and less energy requirements compared to other methods. To synthesize copper nanoparticles via solution plasma, two wires of copper and platinum as cathode and anode respectively were immersed in a glass beaker of 300 ml of two electrolyte solution (K₂CO₃ and NaOH) with three different concentrations (0.1 M, 0.5M and 1M), and electrical current was applied similar to an electrolysis process. The images of the nanoparticles were obtained using scanning electron microscopy and their sizes were analyzed using ImageJ software. It was found that when the concentration of K₂CO₃ increased, the size of copper nanoparticle also increased. However, the size of copper nanoparticles decreased when the concentration of NaOH was increased. This research shows the potential of easily controlling size of copper nanoparticles by changing the electrolyte concentration used during solution plasma process.

1. Introduction

Nanoparticles are divided into two main groups, which are organic and inorganic. Organic nanoparticles mainly consist of carbon. Inorganic nanoparticles are split into three groups magnetic, metallic and semi-channel nanoparticles. Copper nanoparticles are classified under metallic group. Copper nanoparticles are recently becoming increasingly important due to their optical, catalytic and electrical conducting properties [1]. A variety of innovative application of nanoparticles has led to a variety of the copper nanoparticle’s shapes and sizes. Due to that reason, the study on how to control the shape and size of copper nanoparticles have gained importance. Figure 1 shows that there are many methods to synthesize copper nanoparticles which can be categorized into three approaches which are chemical, physical and biological [2].
During nanoparticles synthesis, the gases released and other emissions occurring tend to be polluting to the environment. As a result, green synthesis methods that do not involve toxic chemicals usage and are eco-friendly are needed to decrease the environmental pollution. Such green synthesis methods typically involve irradiation, polyoxometalates, toluene and biological methods which overcome the problem of using chemical agents. However, even these green synthesis methods present their own drawbacks. Such drawbacks are the selection of stabilizing and reducing nontoxic agents as well as the selection of solvent involved.

2. Solution plasma method

2.1 Advantages of selecting the synthesis method

There are many methods to synthesize copper nanoparticle, each of them requires different conditions and experimental setup. Among those methods, electrolysis via solution plasma method was chosen. Solution plasma is a type of hybrid liquid-gas phase plasma that is generated simply by conducting electrical current to the electrolyte.

Solution plasma process is a very simple and useful method for metal nanoparticles synthesis because it can provide extreme rapid reactions because of reactive radicals, chemical species and UV radiation generated in the atmospheric pressure plasma [3]. It can be applied to any metals or alloys. Also, it allows the control of nanoparticle size by changing the plasma initiation voltage or the electrolyte concentration. The nanoparticles produced from solution plasma process were usually in spherical shape [4]. This is a green approach of copper nanoparticles because it does not release any greenhouse gases and does not require any chemical addition. The process can be conducted under atmospheric pressure in an open system. Compared to chemical methods, it requires less processing time, low energy requirements as well as low cost. Because of all the advantages offered by solution
plasma, electrolysis via solution plasma is the most appropriate method for copper nanoparticle synthesis.

2.2 Factors affecting nanoparticle sizes
There are various factors that influence the synthesis, applications and characterization of nanoparticles. Some researchers have reported that time, environment and usage of catalysts can affect the dynamic nature of synthesized nanoparticles. There are other important factors that affect the size of synthesized nanoparticles including discharge time, concentration, voltage, temperature and the method used for synthesis.

In liquid phase processes, the liquid concentration is considered as a major factor on controlling the size of the nanoparticles synthesized. The concentration of the synthesis medium, in this case electrolytes, can influence the size and morphology of the produced nanoparticles. Conventionally, in order to control the size of nanoparticles, additives were added such as reducing agents, surfactants and electrolytes. Firstly, the concentration of added reducing agent can decrease the desired size of copper nanoparticles as long as the precursor concentration is maintained [5]. Moreover, surfactants were also tested upon using the liquid plasma method for copper nanoparticles. It was found that the size decreased when the concentration of the surfactants increased [1].

2.3 Advantages of controlling nanoparticles size related to application
Copper nanoparticles are being increasingly used in different applications on fields of engineering and science. The properties of nanoparticles are massively different from bulk materials, such as the emission of purple light from gold nanoparticles. Controlling nanoparticles size will assists in enhancing the properties of the desired element.

Controlling copper nanoparticles size would have many advantages to its real world applications. One importance of controlling copper nanoparticles size is to reduce the emission of nitrogen oxide in automobiles. Using biodiesels in vehicles engines has lowered the performance and caused a high rate of nitrogen oxide emission. Copper nanoparticles can replace some of the fuel additives in biodiesel. However, this requires copper nanoparticles with size between 40-50nm, which can be difficult to obtain consistently using conventional methods [6].

In addition, selection of catalysts depends on the ratio of surface-to-volume ratio and copper nanoparticles are being used as a catalyst because of this unique property [7]. They are applied as vapour detoxification and liquid-vapour catalyst. Since catalyst performance depends on the ratio surface-to-volume, controlling the size is an important factor to meet this requirement. Compared with noble metals, copper nanoparticles are low in cost and more conductive. Therefore, they are more appropriate for micro-fabrication technologies such as ink printing services.

2.4 Electrolytes selection
Electrolytes can be categorized as strong electrolytes and weak electrolytes. Strong electrolytes have an ability to completely ionize in water which means a 100% of the dissolved compound will break into anions and cations and they are good conductors of electricity. However, weak electrolytes are partially ionised and dissolved and they are considered as poor conductors of electricity. In addition, the weak and strong electrolytes are classified into three groups which are acids, bases and salts. In this paper, K₂CO₃ and NaOH were selected as the working electrolytes. Both are strong electrolytes that dissolve completely in water, ensuring consistent results throughout the experiments.

3. Materials and methodology
3.1. Materials
The following chemicals and materials were used to conduct the solution plasma synthesis:
1) Two types of electrolytes (NaOH and K₂CO₃)
2) Platinum wire with length of 1000mm and a diameter of 0.5mm
3) Copper wire with 1.0 mm in diameter and length of 20mm
3.2. Experimental setup
The nanoparticles were synthesized using electrolysis via solution plasma process. Figure 2 shows a glass beaker of 300 ml capacity in which the cathode used was a copper wire 1.0 mm in diameter and had 20mm immersion depth. Meanwhile, the anode consisted of a platinum wire which had a length of 1000mm and a diameter of 0.5 mm. The surface area of platinum wire (anode) was 50 times larger than copper wire (cathode); this required the anode to be shaped into a coil. Table 1 shows the electrolyte types and the concentrations used. It was important to ensure enough distance between cathode and anode to avoid any unnecessary material failure, electrical shocks or explosions.

![Figure 2. Schematic diagram of experimental setup of solution plasma for copper nanoparticle synthesis.](image)

<table>
<thead>
<tr>
<th>Electrolyte type</th>
<th>1st Concentration (M)</th>
<th>2nd Concentration (M)</th>
<th>3rd Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium carbonate (K$_2$CO$_3$)</td>
<td>0.1</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Sodium hydroxide (NaOH)</td>
<td>0.1</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

3.3. Experimental procedure
After setting up the experiment and all the wires are connected correctly, the DC power supply was turned on. Then the voltage increased in 5V increments every minute, warming the electrolyte, until the plasma in form of glow discharge plasma was reached. The glow discharge voltage was at least 110V. Then the voltage was maintained to sustain the plasma emission, allowing for the synthesis of nanoparticles. During this process, the current must be monitored closely to ensure it does not exceed 4A as it may result in excessive electrolyte bubbling. After 15 minutes, the electricity supply was turned off, and the glass beaker that contains the nanoparticles was left overnight to allow sedimentation of the suspended particles. This eased the process of collecting the nanoparticles synthesized and storing them into small centrifuged tubes to send them for further analysis.

3.4. Results reviewing
The images of the copper nanoparticles are obtained using a Scanning Electron Microscope (SEM). After the SEM images were obtained, the images were processed and the nanoparticles sizes were measured using ImageJ software. ImageJ is a publicly-available software that is recommended by the
National Institute of Health and has the ability to measure the size and angles of particles as well as evaluating the overall area of the sample.

4. Results

4.1. Using $\text{K}_2\text{CO}_3$ as electrolyte

Table 2. Experimental results using $\text{K}_2\text{CO}_3$ as electrolyte

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Concentration of electrolyte (M)</th>
<th>Voltage needed to reach glow (V)</th>
<th>Average size of copper nanoparticle (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>130</td>
<td>$6.99 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>115</td>
<td>$2.36 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>95</td>
<td>$2.85 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Figure 3. SEM images of copper nanoparticles using 0.1M $\text{K}_2\text{CO}_3$ electrolyte

Figure 4. SEM images of copper nanoparticles using 0.5M $\text{K}_2\text{CO}_3$ electrolyte

Figure 5. SEM images of copper nanoparticles using 1.0M $\text{K}_2\text{CO}_3$ electrolyte

4.2. Using $\text{NaOH}$ as electrolyte

Table 3. Experimental results using $\text{NaOH}$ as electrolyte

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Concentration of electrolyte</th>
<th>Voltage needed to reach glow</th>
<th>Average size of copper nanoparticle</th>
</tr>
</thead>
</table>

5
Table 1. Influence of NaOH electrolyte on production of copper nanoparticles

<table>
<thead>
<tr>
<th>(M)</th>
<th>discharge plasma (V)</th>
<th>nanoparticle (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.1</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>120</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>115</td>
</tr>
</tbody>
</table>

5. Discussion

5.1. Influence of glow discharge plasma on amount of produced copper nanoparticles

In order to produce copper nanoparticles, the cathode wire must undergo glow discharge plasma and sustain it for at least 10 minutes. Figure 9 shows the glow discharge plasma is luminous which can be generated when the electrons gain enough energy to produce visible light by repeated collisions that form photons. This happens due to the interaction of both cathode and anode in the solution plasma.
Figure 9. Glow discharge plasma

When the copper wire emits glow discharge plasma, the amount of copper nanoparticles produced will be optimal. It can be seen from Figure 10 that specimens 1 to 4 were highly eroded, while specimens 5 and 6 were slightly eroded after plasma emission. This was because specimens 5 and 6 did not reach full glow discharge plasma, only partial plasma emission compared to specimens 1 to 4. As a result, a smaller amount of nanoparticles were produced when 0.5M and 1.0M NaOH electrolyte concentrations were used.

Figure 10. Copper specimens after the experiment

5.2. Relationship between electrolyte concentration on nanoparticles size

The relationship between the electrolyte concentration and copper nanoparticles size was observed in this research. The concentration of the electrolyte solution can influence the size and morphology of the produced nanoparticles. When using K2CO3 as an electrolyte, it was observed that the size of the produced nanoparticles increased as the electrolyte concentration increased. This gave a linear relationship between copper nanoparticles size and the concentration of K2CO3, as shown in Figure 11.
However, in Figure 12, using NaOH showed an inverse relationship between the electrolyte concentration and the average nanoparticle size. Under this condition, in order to produce smaller copper nanoparticles, higher concentration of NaOH electrolyte was required. The reason behind this relationship was because of the lesser number of nanoparticles produced for 0.5 M and 1.0 M concentration of NaOH. Less nanoparticles produced would give a wider range of shape and sizes and thus accounting for the relationship.

5.3. Influence of electrolyte concentration and conductivity on voltage needed to reach glow discharge plasma

It is known that electrolytes are solutions which have dissolved ions and cations which are capable of conducting electric current since they liberate charged particle inside the solution. To generate and sustain glow discharge plasma emission, the electrolyte has to be conductive. The conductivity increases when the quantity of dissolved particles increases. Also, it is known that concentration is the amount of dissolved particles or substances inside a solution. This means that higher concentration needs higher amount of dissolved substance per unit volume. Thus, higher concentrations of electrolytes lead to higher conductivities since the amount of substance in the solution increases.

It was observed that when the concentration of electrolyte added increases, the conductivity will increase which will lead to lower voltage to reach glow discharged plasma formation. Figure 13
shows an inverse relationship between the voltage and the concentration for both electrolytes used. This is because the increased conductivity will increase the interaction between the cathode and anode, which would in turn decreases the effort needed to reach glow discharge plasma. As a result, the voltage needed to obtain glow discharge plasma decreased when higher concentration electrolytes were used.

Figure 13. Relationship between concentration and voltage needed to reach glow discharge plasma

6. Conclusions

This research aims to control the size of the copper nanoparticles by changing the concentration of the electrolyte used. Two types of electrolytes were used and investigated in this case to confirm the relationship between electrolyte concentration and the average size of copper nanoparticles. It was observed that when the concentration of K₂CO₃ increases, the size of the produced nanoparticles also increases. In contrast, the size of the copper nanoparticles decreases when the concentration of NaOH increases. Moreover, the intensity of glow discharge affected the amount of synthesized copper nanoparticles in which increases in the number will happen when the intensity increases. In addition, the conductivity showed a rise when both electrolyte are subjected to higher concentration which leads to lower glow discharge plasma initiation voltage.

The control of copper nanoparticle during solution plasma synthesis size allows them to be used in various applications. Copper nanoparticles can be used as a fuel additive in biodiesels where the required size is around 50 nm. Other applications include being used as a catalyst due to its unique high-surface-to-volume-ratio. Since copper nanoparticles size is affected by many factors, the research topic can be further extended to study the effect of the supplied voltage on copper nanoparticle sizes using the same method of synthesis. Other types of electrolytes can be investigated such as using acids and bases. Meanwhile, other metal nanoparticles such as silver and gold are widely used in different application. Therefore, the effect of various electrolyte concentrations reported here have the potential to be applied in the field of nanotechnology and nanomaterials.

References
Acknowledgements

The authors would like to thank Mr. Peter Yek Nai Yuh from University College of Technology Sarawak for conducting the SEM observation for the nanoparticle samples.