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Controlled nanocrystallites growth of plasma-treated Cu sheets

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Abstract. Controlling the growth size of nanocrystallites (NCs) has been a big challenge for previous researchers due to unpredictable growing rate and shape obtained during the synthesis. This paper demonstrates an efficient way to control the growth of copper (Cu) NCs using a combination of solution plasma, sunlight and water. The NCs are synthesized by using solution plasma method which has a lot of advantages in controlling NC growth sites. The material used in this paper is Cu sheet due to its antibacterial properties, high electrical and heat conductivity, and low cost. This method is followed by immersing the plasma treated Cu sheets in distilled water and exposing it to sunlight. This method is also known as submerged photosynthesis of crystallites (SPSC), which is a low-temperature and surfactant technique used for NCs fabrication. The photosynthesis-like method is used to allow for NCs growth. The NCs growth size and shape was observed using SEM and ImageJ software. The NCs shapes can be analyzed by observing the antibacterial properties of NCs which is related to the small size of the NCs. The beneficial outcomes of Cu NC shape with antibacterial properties are expected, which can be used in various applications without causing any environmental impact. In addition, using a combination of solution plasma and sunlight exposure, we demonstrated an easy and fast synthesis method to develop Cu NCs economically.

1. Nomenclature

NCs Nanocrystallites
NPs Nanoparticles
SEM Scanning Electron Microscopy
SPSC Submerged Photosynthesis of Crystallites

2. Introduction

In the past two decades, metallic nanocrystallites have been a huge subject for the in materials engineering field due to their special physicochemical and electrical properties. Research has been increasing for the nanomaterials that possess such special properties [1]. For instance, the physical properties of nanocrystallites can be improved in thermal stability and mechanical stiffness by using specialized synthesis methods [2]. The pure metals and alloy NPs have been used for some applications such as



magnetic, catalysis, optoelectronics and microelectronics. It is also used for conductive pastes, battery electrodes, and fuel cells. Among the different metals of NPs, copper NCs have gained a lot of attention because their applications in electrical devices such as multilayer ceramic and oriented circuit boards [3]. Cu is typically chosen because of its low cost and high conductivity [2].

The fabrication of the NPs is one of the most important topics of concern regarding nanotechnology since it is very important to have the ability to control the NPs shape, size and its distribution on the Cu sheet [4]. Also, there is a pressing need for a NC green synthesis methods which would result in their usage in different applications such as in the biomedical and antimicrobial usages [2].

Furthermore, Cu materials are commonly used methods since it shows high antimicrobial properties and cost-effectiveness compared with other metals with similar properties such as silver [2]. Typical methods to synthesize Cu NCs are pulsed sonoelectrochemical synthesis, microemulsion technique, polyol method, thermal decomposition method, laser ablation method and chemical reduction method [4]. In this paper, the method that was used is called solution plasma synthesis due to its simplicity to control size and morphology of the NCs [4].

3. Literature review

3.1 Plasma treatment and their applications

Firstly, plasma discharge is defined as the electrical unbinding of charged particles combined with free radicals generation. Since plasma discharge has multi-reactive constituents, its ability has the desirable effect such as materials surface modification [5]. The interaction of plasma-liquid produces energetic nucleation sites in materials surfaces. The usage of solution plasma rather than solid electrodes gives the ability to form the NPs on the surface of the plasma solution interaction region, rather than on the plasma layer itself which consists of ionized gases [6].

Usage of solution plasma in Cu NC synthesis is due to its low cost, simple process and the ease in controlling experimental parameters on the liquid surface [7]. The other advantages are the ease of experimental setup, simple mass production due to high yield, the availability of the metallic sheet used as raw materials for NPs synthesis and the use of the gas supply is not required [7].

3.2 Types of synthesis method

There are many methods used to synthesize the NPs and NCs divided into three types. The first type is the physical methods that break down bulk material into nanosized materials by cutting, scratching or grinding techniques as shown in Figure 1 [2]. Physical method is applied by physical strategies such as using the laser excision or vacuum discharge to synthesize the nanomaterials.

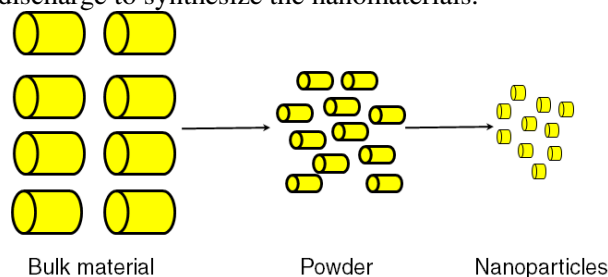


Figure 1. Physical synthesis methods of nanoparticles.

The other types of synthesis methods are the biological and chemical methods, which are used to develop the structure of NP atoms or molecules as shown in Figure 2 [2]. The chemical methods are

applied by using chemical reduction, electrochemical and microwave. Likewise, the other methods to synthesize NPs is biological synthesis, typically by extracting the enzymes or bacterium from the plant sources [2].

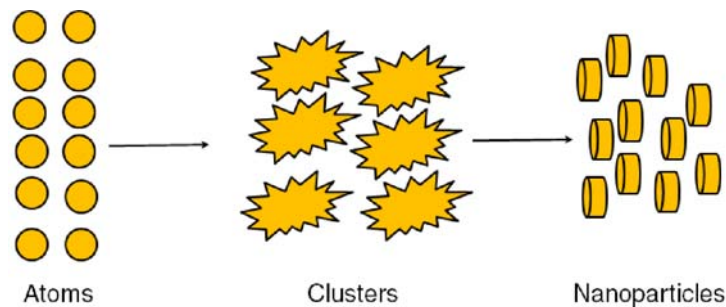


Figure 2. Chemical and biological synthesis methods.

However, some of these methods have high cost and complex setup. Also, some chemical and physical synthesis methods produce toxic by-products which are considered to be ecologically hazardous and it cannot be used in medical applications [2]. Therefore, the method used in this paper can be called a green synthesis method since its by-products are environmentally friendly.

Here, the proposed synthesis method is called solution plasma and the submerged photosynthesis of crystallites (SPSC) method, which means a surfactant-free, low temperature approach that is used for metal NCs fabrication [8]. SPSC is done by photosynthesis-like reaction with the irradiation treatment of UV light on the materials immersed in water to allow for NC growth. The NC growth was observed at room temperature without the need for additional chemicals besides water [8]. Apart from NC growth, another useful application of the SPSC method is hydrogen gas generation [8].

3.3 Effect of electrolyte concentration and plasma voltage on NC growth

A plasma field is maintained on the surface of the Cu sheets. The plasma layer is caused by heating of the solution plasma near the electrode, in this case Cu sheet, which is called “glow discharge” [7]. The glow discharge plasma causes nanosized surface protrusions to appear on the Cu sheet, increasing the surface roughness. We identified four parameters that could show effects on the surface morphology on Cu sheet during the experiment, namely plasma voltage, light intensity, time of light exposure and solution temperature [8].

However, in solution plasma method, the electrolyte concentration could affect the NC size as well. The higher the electrolyte concentration, the lower the voltage for glow discharge plasma initiation while the lower the electrolyte concentration, the higher the voltage needed for plasma initiation. A low plasma initiation voltage results in the appearance of smaller surface protrusions on the Cu sheets, and thus smaller NC size after undergoing SPSC process.

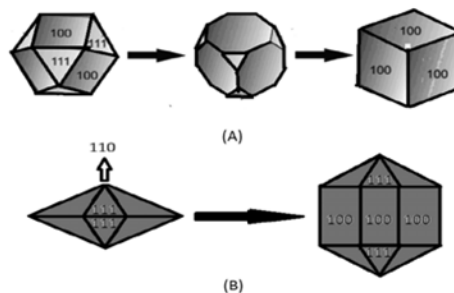
Table 1. Experimental observation condition and outcomes morphologies at 200 V [5].

Electrolyte(K_2CO_3) concentration	Electrolysis Time (min)	Morphology Shape
0.5M	60	Flower-like
0.1M	60	Flower-like
0.01M	60	Flower-like
0.001M	60	Flower-like

The table above shows that the NC can be maintained at a specific time which is 60 minutes at low electrolyte concentration in a high voltage as discussed in the previous literature. The observed shape is a flower-like shape in 200 voltages. Therefore, the NC growth size can be controlled by low electrolyte concentration in a fixed time at a high voltage [5].

3.4 Evaluation of NC growth size

The NCs growth size can be evaluated before and after the experiment by using scanning electron microscopy (SEM). The NC shapes such as whisker, pentagonal and tetragonal were mostly observed in high concentration electrolyte and extended time plasma treatment. On the other hand, the spherical shape and dendrite shape of the NPs were commonly observed during short plasma discharge times. [10].

**Figure 3.** The growth mechanism for (A) cube shape and (B) for rod-shape particles [11].

The NC size growth is related to its antibacterial properties [12]. In order to improve the antibacterial application, the NC size in a Cu sheet should be small to provide a high surface area to interact with microbial layers [12]. Therefore the obtained size range of the NC is 50 nm which is the size needed to allow antibacterial properties to appear on the SPSC treated Cu sheet. The NPs work to reduce the growth of the bacteria by destroying their outer layer [13-14].

Also, our experiment aims to obtain a certain shape of NC in order to impart antibacterial properties on the Cu sheet, namely the hexagonal shape [15]. Therefore, the size and shape should be taken into consideration while observing the NC in order to observe the antibacterial properties related to the small size and a specific shape.

4. Methodology

4.1 Experimental apparatus

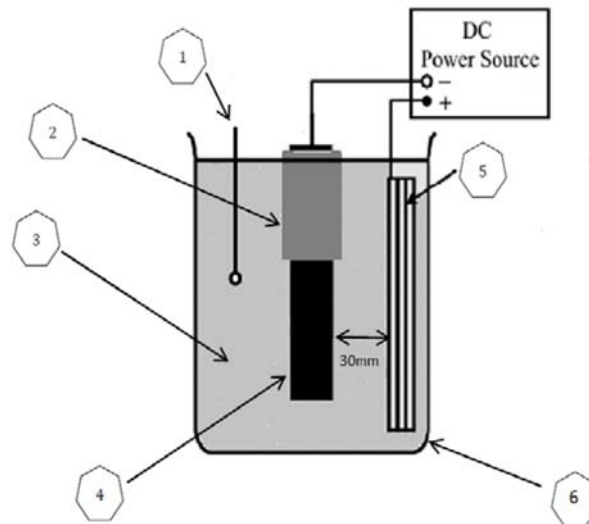


Figure 4. Diagram of experimental apparatus.

Table 2. Apparatus description.

No	Apparatus Description
1	Thermometer
2	Insulator
3	Electrolyte solution (K_2CO_3)
4	Cathode (Cu sheet with a size of 30×1×1 mm)
5	The anode of platinum wire with a diameter of 30 mm
6	Glass beaker with 250ml of capacity

4.2 Experimental procedure

4.2.1 Surface pretreatment. A Cu sheet was used as a cathode with a purity of 99.9% was cut into three pieces of 30×1×1 mm in size. The anode is a platinum wire 1 mm in diameter with purity of 99.9% curved into a coil shape. Both anode and cathode were washed with distilled water and then immersed in K_2CO_3 electrolyte. The contact area between Cu wire and Cu sheet is set with 20 mm of exposed area of Cu sheet. Firstly, the solution was preheated to 90 °C. After that, the applied discharge voltage was 140 V using DC voltage for 5 minutes to achieve plasma treatment on the sheet surface. Afterwards, the Cu sheet was collected and cleaned with distilled water and left to dry at ambient temperature. The surface pretreatment was repeated for subsequent Cu sheet specimens.

4.2.2 SPSC procedure. The Cu sheet placed inside glass test tubes filled with distilled water. Three Cu sheets were exposed to natural sunlight for 12, 24 and 36 hours respectively. After finishing exposure, the specimens were collected and let dry ambient temperature. The analysis of the surface morphology of NCs was observed using SEM.

5. Results and discussion

The results below show the SEM images of each of the plasma-treated Cu sheets after exposure to sunlight:

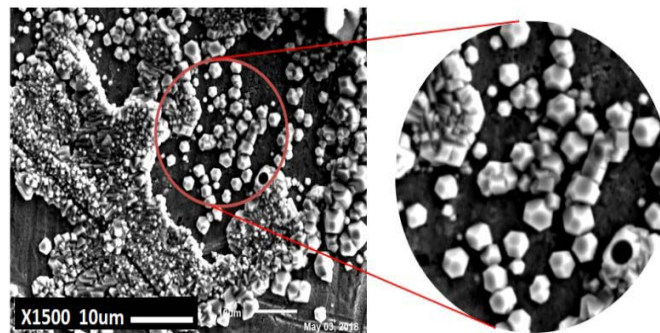


Figure 5. Surface of plasma-treated Cu sheet after 12 hours of SPSC.

According to the above figure, the growth of NCs occurred during the sunlight exposure. Using ImageJ software, the observed mean length of 20 NC shapes is around 293nm. Here, the NCs were shaped as tetrahedron-like after 12h of sunlight exposure.

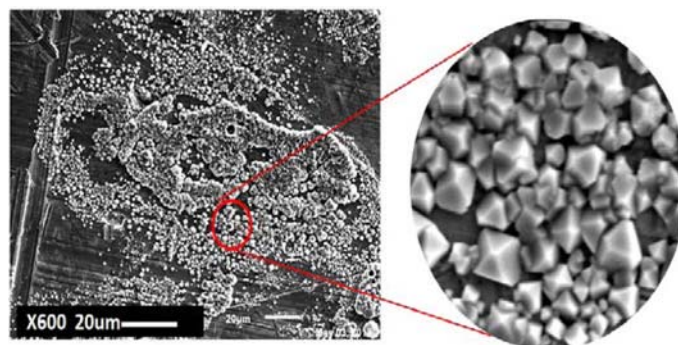


Figure 6. Surface of plasma-treated Cu sheet after 24 hours of SPSC.

After 24h of light exposure, the NCs length increased and the shape changed as well. The observed mean length of 20 NCs were around 3860 nm. The NCs shape changed to square pyramid-like after 24 hours of SPSC as shown in Figure 6.

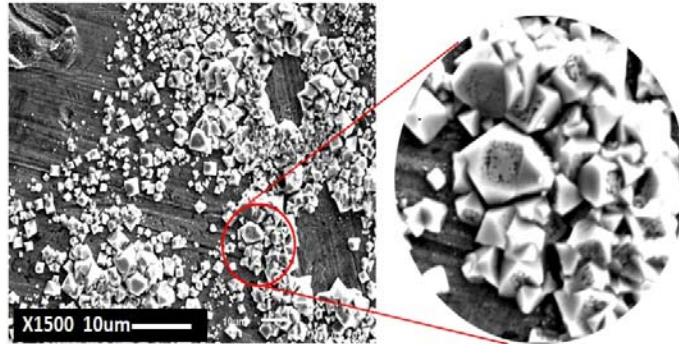


Figure 7. Surface of plasma-treated Cu sheet after 36 hours of SPSC.

In Figure 7, the NCs mean length of 20 NCs was around 4540nm after 36 hours of light exposure and the observed shape was decahedral-like shape.

Table 3. Summary of NC morphologies obtained.

Light exposure Times (hours)	NCs Mean Length (nm)	NCs Shape	Surface roughness
12	293	Tetrahexahedron-like	Fine
24	3860	Square pyramid-like	Fine
36	4540	Decahedral-like	Fine

The size and shape of NCs were highly dependent on the time of sunlight exposure to the plasma treated Cu sheets. There was a linear relationship between the exposure time and NCs size. Hence, the NCs growth can be controlled by adjusting the time of sunlight exposure. Also, the SEM images show that for each of the specimen the NCs have different shapes. The tetrahexahedron-like shape was observed in first 12 hours, square pyramid-like shape in 24 hours and decahedral-like shape in 36 hours of sunlight exposure. That means that as the NCs grow, the shapes also changed which allows for use in different applications depending on the shape and size requirements of the NCs. In addition, the plasma treatment of Cu sheet by using low electrolyte concentrations and high voltage resulted in fine structure and shapes of the NC nucleation sites, which in turn enhanced the growth of NCs.

A potential application of the Cu sheet after SPSC is that antibacterial properties can be obtained within the first 12 hours of SPSC, where showed the NCs size were around 293nm. The small size of NCs tends to have high surface volume, where they react to destroy bacteria by blocking the pores in bacteria layers. Thus the Cu NCs may possess antibacterial properties.

6. Conclusions

A new way of controlling NC growth size by using solution plasma and sunlight exposure in water has been successfully established. The size and shape of NCs depended on the time of sunlight exposure. The

small size of NCs can be obtained in short time of sunlight exposure, while the large size NCs can be obtained in a long time of sunlight exposure. Likewise, high voltage, low concentration of K_2CO_3 solution during surface treatments of Cu sheet delivered a fine structure and new crystallites shape after SPSC method. The used of distilled water during SPSC resulted in a fine surface of NCs. The small size of NCs in short exposure time was shown, which in turn imparts the antibacterial properties of Cu sheet. The experimental parameters resulted in a simple control of size and shape of Cu NCs. Moreover, the easy and fast synthesis method of Cu NCs has been successfully obtained.

7. References

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