Splitting nucleation and growth potentials for controlling electrochemical deposition of Cu nanoparticles

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ABSTRACT

Uniformity in the size distribution of Cu nanoparticles plays an important role in enhancing the outstanding properties of Cu for diverse applications. This study proposes a simple method to control the size of Cu nanoparticles in an electrochemical deposition system using copper sulfate $CuSO_4$ as the copper source in a $LiClO_4$ electrolyte solution. The electrochemical kinetics of copper nucleation and growth on the ITO electrode were carefully analyzed using the LSV and CA processes combined with AFM characterization. Subsequently, the influence of pH conditions on the splitting factor of the nucleation and growth potentials was investigated, revealing that a pH value of 2.7 provides the optimal separation of potential for these two processes. The size of the deposited copper nanoparticles can be controlled by conducting two consecutive CA processes at distinct nucleation and growth potentials. Electrochemical deposition with an optimized pH approach provides a simple and straightforward method to synthesize copper nanoparticles with monodispersity and minimizes the risk of contamination by stabilizers.

Keywords: Copper nanoparticles; Size distribution control; Electrochemical deposition; Splitting Nucleation and growth potential; pH optimization; Monodispersity.

1. INTRODUCTION

In the field of material science, nanoparticles have attracted increasing attention from researchers due to their unique properties, such as high active surface area, enhanced mechanical properties, and optical and chemical reactivity. Recently, metals, metal oxides, ceramics, silicates, and polymer nanoparticles have been synthesized and employed in a variety of applications. Among them, metal nanoparticles have attracted considerable interest because of their fascinating ultraviolet-visible sensitivity and electrical, catalytic, thermal, and antibacterial properties [1].

Besides noble metal (i.e, gold or silver), copper nanoparticles are also potential candidates for applications in optics, electronics, medicine, conductive film manufacturing, and antimicrobial agents [1-3]. Advantages of using copper nanoparticles instead of silver and gold are due to the lower cost of copper, physical and chemical stability, catalytic activity, high conductivity, optical properties, light weight, and formability [4, 5]. The performance and efficiency of Cu nanoparticles depend heavily on their shape and size. Monodispersity is the key factor that determines the performance of copper nanoparticles and their suitability for various applications in diverse areas such as microelectronics and super-strong materials [5].

The synthesis of copper nanoparticles at the nanoscale is a challenging task because of their agglomeration nature and susceptibility to oxidation. Therefore, several studies have been conducted to propose the most advantageous method for synthesizing Cu nanoparticles. Physical fabrication methods include Pulse Laser Ablation Deposition [6] and Mechanical Ball Milling [7]. These processes provide excellent control, low time consumption, high quality, and high repeatability. However, the size and distribution of copper nanoparticles produced through these processes vary over a large range, and they also require expensive high-vacuum systems. Wet chemistry methods via chemical reduction reaction are among the most favorable approaches for synthesizing copper nanoparticles [8, 9]. These methods are straightforward, and it is simple to control the size and shape of the nanoparticles by manipulating the reaction conditions, such as by using stabilizing agents [10-12]. However, in such cases, the copper nanoparticles were contaminated with the additives, which led to a reduction in their efficiency as the active surface area was reduced by the occupancy of the stabilizers, which are quite difficult to fully eliminate. Reducing copper precursors by the electrochemical method is considered a solution to a contamination-free synthesis [13]. However, electrochemical approaches usually result in uncontrolled deposition of copper nanoparticles; their distribution over the electrode is non-uniform, and their sizes are polydisperse. Controlling the electrochemical system is essential to generate a more reliable process for the growth of copper nanoparticles.[14] Zhang et al. introduced a method to synthesize copper nanospheres by running chronoamperometry at a constant potential where the nucleation and growth processes took place [15]. Zhang controlled the deposition of Cu nanoparticles at low temperatures and obtained a homogeneous distribution with monodispersity, but his cooling system was still quite complex. [15]

This study proposes an easier way to synthesize copper nanoparticles with small size distributions and minimize contamination. By separating the nucleation and growth potentials during an electrochemical process, it enables to isolate of the formation of copper nuclei from their growth. Once the nucleation and growth processes are distinct, copper nanoparticles can be grown with a controlled size and monodispersity. The separation of these events rarely occurs under ambient conditions, but can be enhanced by modulating the environment of the cell, such as temperature, pH, type of working electrode, and precursor concentration. The kinetics of copper nanoparticle deposition were carefully studied using linear sweep voltammetry (LSV) and chronoamperometry (CA) processes. Under our optimized pH conditions, a uniform distribution of spherical copper nanoparticles was formed. Their size can be controlled by lengthening or shortening the time required to apply the growth potential to the system. The results of our project can be extended to modulate other metal particle deposition processes, such as gold, iron, and silver, for other research purposes.

2. MATERIALS AND METHODS

2.1. Materials

Indium tin oxide (ITO)-coated glass (1 mm thickness) from Lumtec-taiwan was cut into small pieces (1 cm × 2 cm) to serve as the working electrode. All chemicals and consumables, such as 95% H_2SO_4, $CuSO_4$, $LiClO_4$, NaOH, AFM tips (purchased from budget sensors), potentiostat (from Palmsens), and pH measurement (from inoLab) were obtained from the laboratory of Advanced Materials and Applications (AMA Lab) of USTH. All reagents were of analytical grade and used as received without any further purification. All aqueous solutions were freshly prepared using 2-time distilled water.

2.2. Methods

2.2.1. Electrochemical measurement procedure

a. Prepared experiment for investigating nucleation potential

The redox solution was prepared using $CuSO_4.5H_2O$ (10^{-3} M) and $LiClO_4$ (10^{-1} M) in distilled water. The reference electrode (RE) was a Saturated Calomel Electrode (SCE), and ITO pieces were used as the WE and CE. The WE surface was fixed using a hole-punched tape (2.0 mm^2, and the CE surface was fixed using a similar method at 4.6 mm^2. First, LSV measurements were conducted to obtain a broad view of the potential range where nucleation might occur, from the OCP value to the potential where the anodic current sharply increases. Then, CA processes in the obtained potential range were performed with a 0.01 V increment on several ITO electrodes. A potential was applied for 30 s for each sample. Subsequently, these samples were characterized using a Naio Nanosurf AFM machine. Five images were used per sample have been carried out to enhance the reliability of the results. The sample with the least negative potential, where copper seeds appear in all five images, was considered the nucleation potential. This potential is referred back to the position on the LSV line in the first step, so that for the following experiments where the pH changes, we can identify the nucleation potential by only performing LSV runs (without CA and AFM measurements).

b. Prepared an experiment for investigating of growth potential

A similar redox solution and electrochemical setup were used for this session, as mentioned in the previous task. First, LSV measurements were performed to investigate the growth potential range. Two LSV curves are required: the first curve onset potential indicates copper nucleation (copper-on-ITO deposition), while the second curve onset potential refers to the copper growth process (copper-on-copper deposition). Subsequently, the CA experiments were conducted in the growth potential range. Each ITO sample first undergoes a 30 s CA process at the nucleation potential to form copper nuclei over the surface. Then, growth-range potentials were applied to each sample for 30, 60, 90, 120 and 150 s. Topography AFM images were taken for each sample, and the set of samples with the least negative applied potential that showed a growing trend of copper nanoparticles on the ITO surface was considered as the growth potential. This potential is referred back to the position in the second LSV line in the first step, so that for the following experiment, where the pH changes, we can identify the growth potential by only performing LSV runs (without CA and AFM measurements).

2.2.2. Investigating pH influence on nucleation and growth potential

The initial redox solution contains $CuSO_4$ 10^{-3} M and $LiClO_4$ 10^{-1} M, with a pH value of approximately 4.95. H_2SO_4 and NaOH were used to adjust the solution pH. The pH of the final electrochemical solution was measured using an inoLab 7310 pH meter. Nucleation and growth potentials were recorded for each pH value by running two consecutive LSV lines. The splitting of these two lines indicates the separation of the nucleation and growth potentials. The pH value at which this splitting factor is maximized is recorded as the optimum condition for controlling the growth of the copper nanoparticles.

3. RESULTS AND DISCUSSION

3.1. pH influence on nucleation and growth potential

The pH value was adjusted, and the change in nucleation and growth potential was recorded to investigate the influence of pH on the nucleation and growth potential.

Figure 1 shows the LSV curve for a general view of copper deposition on the ITO electrode in a solution with controlled pH in the range of 1.6 to 5.7. The potential runs from the OCP value to negative values, where Cu^{2+} ions in the solution are reduced to Cu^0 atoms. The onset potential at the first scan, where Cu^0 starts to form, is considered the nucleation potential (copper-to-ITO deposition). The onset potential in the second scan is attributed to the growth potential of the Cu seed that formed after the first scan was completed.

At pH 5.1, it was quite close to the natural pH of the redox solution. Therefore, the nucleation and growth potentials of copper ions at pH = 5.1 are not well separated, similar to the initial solution pH = 4.9. When the pH increased to 5.7, the deposition current almost vanished. Moreover, the transparent solution turned into an opaque, light-blue suspension. This transformation was due to $Cu(OH)_2$ precipitation at a high pH. The precipitation of copper ions was the reason why the current disappeared in the LSV curves. In general, increasing the pH is not a good approach for separating the nucleation and growth potentials of copper ions.

In another approach, a lower pH range below the natural pH of the redox solution was investigated. Diluted H_2SO_4 was then added to the initial redox solution to reduce the pH value. The linear sweep voltammetry (LSV) curves for each pH value are shown in figure 2.

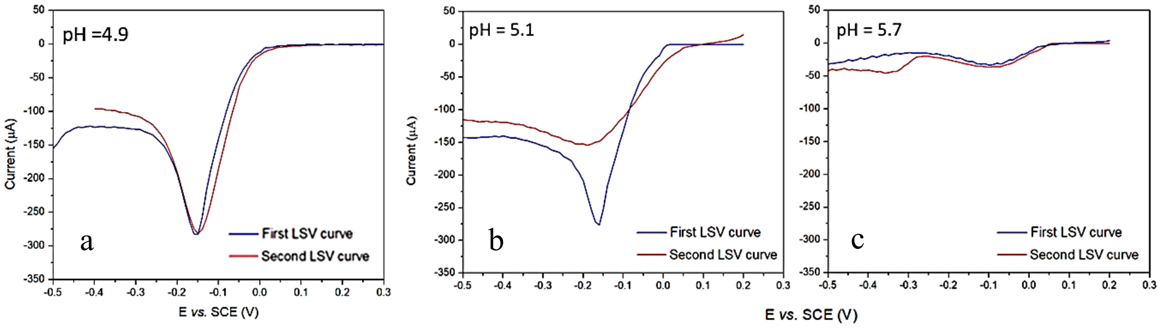

Figure 1. LSV curves for Cu deposition at initial pH values of 4.9 (a), 5.1 (b) and 5.7 (c).

Figure 2 shows a trend in which the separation factor increases at a low pH value, but it reaches a maximum and collapses when the pH is lower than 2.0. At pH 3.6, the nucleation and growth processes experienced a small shift compared with the separation at the initial pH. When the pH value decreased to 2.7, the largest separation between the two LSV curves was observed. With a further decrease in the pH value to 1.6, the separation was significantly reduced. After reproducing the experiment a couple of times, it can be concluded that the pH range around 2.3 and 2.7 has the best separation performance.

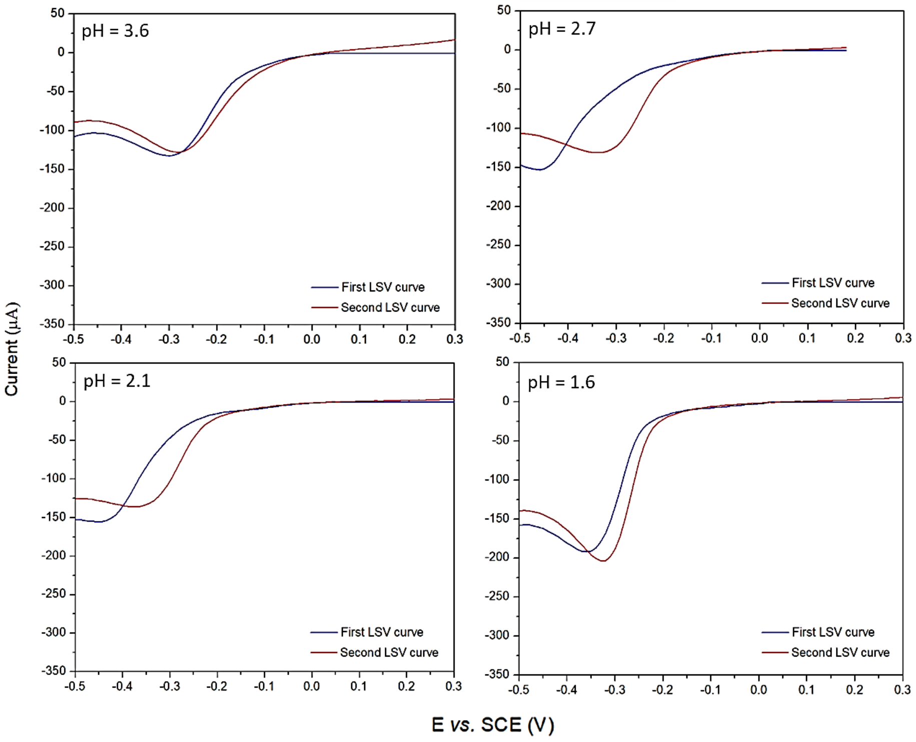

Figure 2. LSV curves for copper deposition at low pH values.

3.2. Control the growth of copper nanoparticles

An optimal pH value of = 2.7 is selected for controlling copper nanoparticle growth. As shown in figure 2b, the nucleation potential was approximately - 0.260 V, whereas the growth potential was - 0.190 V. All ITO electrodes underwent 30 s at - 0.260 V (nucleation potential), and the growth time for each sample increased from 30 s to 150 s (figure 3). The CA growth curves coincide quite well, indicating a similar growth rate for the five samples.

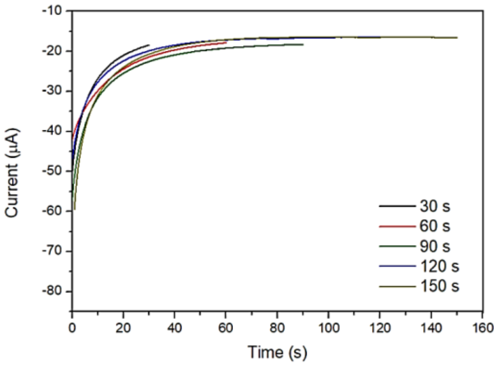

Figure 3. *CA curves for the growing process of copper nuclei with increasing time.*

After the electrochemical deposition, all five Cu/ITO samples were characterized using AFM. Figure 4 shows the topography images of the samples prepared under different growing times. The growth of the copper particles was visualized intuitively. One can see that the Expansion of these particles was observed when the growth time increased.

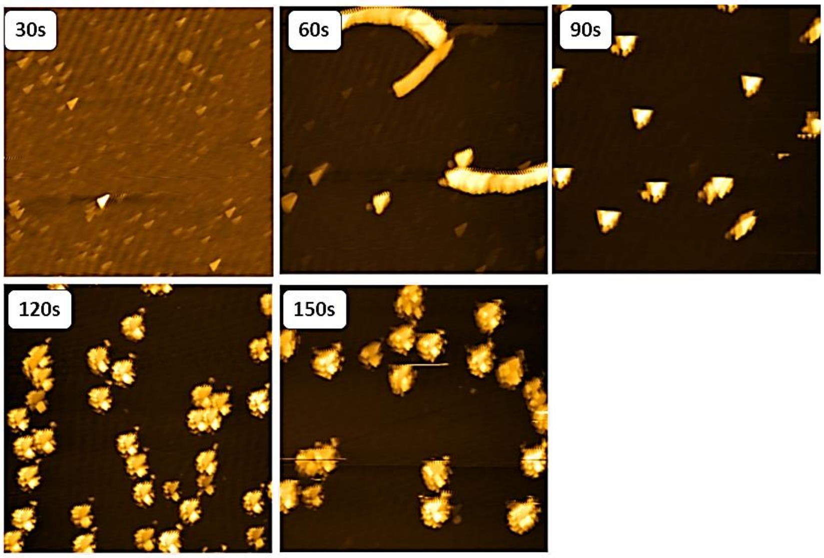

Figure 4. *AFM images of copper particles with increasing growing time.*
The image size is 20 μm x 20 μm.

This clearly shows a well-monodisperse surface for both samples. Almost no particularly small seeds were found among the large particles in the 120 s samples. We can conclude that the nucleation and growth processes were well-separated in this experiment. No new nuclei were formed during the growth of copper particles.

Even AFM tips have extremely poor lateral resolution owing to the tip effect; however, the analysis of particle size was carried out over five Cu/ITO samples. Figure 5 shows the relationship between the particle diameter and growth time when the nucleation time is fixed at 30 s. It clearly proves that Cu nanoparticle size gradually increases from 0.2 μm to 0.5 μm when the deposition time increases from 30 seconds to 150 seconds. This plot indicates that the growth time is directly linked to the size of the deposited nanoparticles. The shape of this plot is similar to our calculation of the radius of hemispherical nanoparticle growth in the model of multi-growing centers.

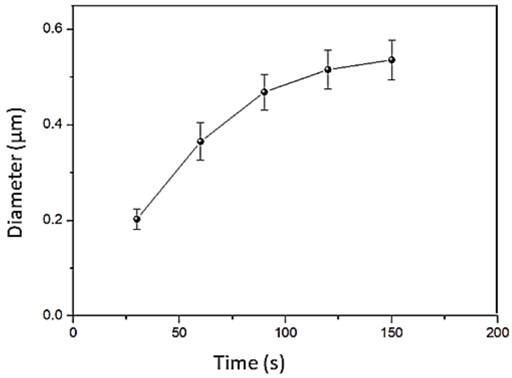

Figure 5. *Relation of copper particle diameter versus growing time.*

Overall, Cu particle sizes in the range of 200 - 500 nm were successfully deposited under the control of copper nuclei at a nucleation potential of 30 s, and varied with increasing growth time.

4. CONCLUSIONS

The electrochemical reduction behavior of Cu, along with its nucleation and growth kinetics on the ITO electrode, was systematically investigated. Linear sweep voltammetry (LSV), chronoamperometry (CA), and atomic force microscopy (AFM) characterization demonstrated that the nucleation and growth potentials of copper nanoparticles could be distinctly separated by controlling the solution pH within the range of 2.3 to 2.7, with optimal separation achieved in this interval. By performing CA at these discrete nucleation and growth potentials, precise control over the deposition of Cu nanoparticles on the ITO electrodes was achieved, resulting in a uniform size distribution. The particle size was tunable from approximately 200 to 500 nm by varying the growth time from 30 s to 150 s. These findings highlight the effectiveness of pH control in tailoring the nanoparticle characteristics during electrochemical deposition on ITO substrates.

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REFERENCES

[1]. Zhu, H., C. Zhang, and Y. Yin, *"Novel synthesis of copper nanoparticles: influence of the synthesis conditions on the particle size"*, Nanotechnology, 16, 3079, (2005).

[2]. Din, M. I. and R. Rehan, *"Synthesis, characterization, and applications of copper nanoparticles"*, Analytical Letters, 50, 50–62, (2017).

[3]. Maliki, M., I. H. Ifijen, E. U. Ikhuoria, E. M. Jonathan, G. E. Onaiwu, U. D. Archibong, and A. Ighodaro, *"Copper nanoparticles and their oxides: optical, anticancer and antibacterial properties"*, International Nano Letters, 12, 379–398, (2022).

[4]. Wu, S.-H. and D.-H. Chen, *"Synthesis of high-concentration Cu nanoparticles in aqueous CTAB solutions"*, Journal of Colloid and Interface Science, 273, 165–169, (2004).

[5]. Kart, H. H., H. Yildirim, S. Ozdemir Kart, and T. Çağin, *"Physical properties of Cu nanoparticles: A molecular dynamics study"*, Materials Chemistry and Physics, 147, 204–212, (2014).

[6]. Amendola, V. and M. Meneghetti, *"Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles"*, Physical Chemistry Chemical Physics, 11, 3805–3821, (2009).

[7]. Suryanarayana, C., *"Mechanical alloying and milling"*, Progress in Materials Science, 46, 1–184, (2001).

[8]. Hachem, K., M. J. Ansari, R. O. Saleh, H. H. Kzar, M. E. Al-Gazally, U. S. Altimari, S. A. Hussein, H. T. Mohammed, A. T. Hammid, and E. Kianfar, *"Methods of chemical synthesis in the synthesis of nanomaterial and nanoparticles by the chemical deposition method: a review"*, BioNanoScience, 12, 1032–1057, (2022).

[9]. El-Giar, E., R. Said, G. Bridges, and D. Thomson, *"Localized electrochemical deposition of copper microstructures"*, Journal of the Electrochemical Society, 147, 586, (2000).

[10]. Wang, J., X. Zhao, F. Tang, Y. Li, Y. Yan, and L. Li, *"Synthesis of copper nanoparticles with controllable crystallinity and their photothermal property"*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 626, 126970, (2021).

[11]. Jin, M., G. He, H. Zhang, J. Zeng, Z. Xie, and Y. Xia, *"Shape-controlled synthesis of copper nanocrystals in an aqueous solution with glucose as a reducing agent and hexadecylamine as a capping agent"*, Angewandte Chemie International Edition, 50, 10560–10564, (2011).

[12]. Lai, D., T. Liu, G. Jiang, and W. Chen, *"Synthesis of highly stable dispersions of copper nanoparticles using sodium hypophosphite"*, Journal of Applied Polymer Science, 128, 1443–1449, (2013).

[13]. Golden, T. D., M. G. Shumsky, Y. Zhou, R. A. VanderWerf, R. A. Van Leeuwen, and J. A. Switzer, *"Electrochemical deposition of copper (I) oxide films"*, Chemistry of Materials, 8, 2499–2504, (1996).

[14]. Grosse, P., A. Yoon, C. Rettenmaier, S. W. Chee, and B. R. Cuenya, *"Growth dynamics and processes governing the stability of electrodeposited size-controlled cubic Cu catalysts"*, The Journal of Physical Chemistry C, 124, 26908–26915, (2020).

[15]. Zhang, Q. B. and Y. X. Hua, *"Electrochemical synthesis of copper nanoparticles using cuprous oxide as a precursor in choline chloride–urea deep eutectic solvent: nucleation and growth mechanism"*, Physical Chemistry Chemical Physics, 16, 27088–27095, (2014).

TÓM TẮT

Điều khiển kích thước hạt nano đồng bằng phương pháp phân tách điện thế trong quá trình lắng đọng điện hóa

Tính đồng nhất về kích thước của các hạt nano đồng (Cu) đóng vai trò quan trọng trong việc nâng cao các tính chất ưu việt của Cu, phục vụ cho nhiều ứng dụng trong các lĩnh vực công nghiệp khác nhau. Nghiên cứu này đề xuất một phương pháp đơn giản nhằm kiểm soát kích thước của hạt nano Cu trong hệ điện hóa lắng đọng, sử dụng đồng sunfat ($CuSO_4$) làm nguồn cung cấp ion Cu trong dung dịch điện ly $LiClO_4$. Động học điện hóa của quá trình tạo mầm và phát triển hạt Cu trên điện cực ITO được phân tích cẩn thận thông qua các phép đo LSV và CA, kết hợp với đặc trưng bề mặt bằng AFM. Tiếp theo, ảnh hưởng của điều kiện pH đến hệ số tách biệt giữa thế tạo mầm và thế phát triển được khảo sát, cho thấy giá trị pH = 2,7 mang lại sự phân tách tối ưu giữa hai giai đoạn này. Bằng cách thực hiện hai quá trình CA liên tiếp tại các thế tạo mầm và phát triển khác nhau, kích thước của các hạt nano Cu lắng đọng có thể được điều khiển thông qua việc điều chỉnh thời gian áp dụng thế phát triển trong hệ. Phương pháp lắng đọng điện hóa với điều kiện pH được tối ưu hóa mang lại cách tổng hợp hạt nano Cu đơn tán một cách đơn giản và hiệu quả, đồng thời hạn chế nguy cơ nhiễm bẩn từ các chất ổn định.

Từ khoá: Hạt nano đồng; Điều khiển kích thước hạt; Phủ điện hóa; Tách thế tạo mầm và mọc hạt; Tối ưu pH; Đơn phân tán.