

Shape-controlled Synthesis of Cu₂O Microstructures at Glassy Carbon Electrode by Electrochemical Method for Non-enzymatic Glucose Sensor

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In this work, the electrochemical deposition of Cu₂O microcrystals was investigated at glassy carbon (GC) electrode. Besides octahedral and microspherical Cu₂O, a novel superoctahedral structure was fabricated via controlling the reduction potential, and the transforming process from octahedral to microspherical structure was also examined. The possible growth mechanism was discussed here, and the growing rates played an important part on the morphology. The non-enzymatic glucose detection based on the as-prepared Cu₂O microspheres modified GC (Cu₂O-GC) electrode was also presented, which exhibited excellent operation stability and good linear dependence on glucose concentration from 10 μM to 5 mM and the calibration equation was $I (\mu\text{A}) = 4.56 + 5.01 \times 10^{-3} C (\mu\text{M})$ with a correlation coefficient of 0.9995.

Keywords: Cu₂O microcrystal, superoctahedron, electrochemical sensor, glucose

1. INTRODUCTION

Diabetes is a chronic disease that has affect hundreds millions of people, yet inclining to be double by 2030, and approximately 366 million people would suffered from the disease in the world [1]. As such, reliable and effective detection of blood glucose is of great significance. Among the various methods for glucose detection, electrochemical sensors have received great interest due to their outstanding features such as low detection limit, high sensitivity and relatively simple operating device [2]. Generally, electrochemical sensor has two kinds: enzyme-based and non-enzymatic sensor. The enzyme-based electrochemical sensor has received the focus of commercial application; however, it

has some critical flaws such as low stability of the immobilized enzyme, complicated fabrication process and unrepeatability [3-7]. As a result, many efforts have been made to fabricate novel non-enzymatic glucose sensor with nano/micro structure materials to solve these problems. The modification with metal particles to the electrode has been a hot topic coinciding with the development of nano/micro structure materials in the last decade.

Cu₂O, a kind of electrochemical active materials [8], has received particular interests in many fields, such as photovoltaic device [9], lithium ion batteries [10] and gas sensing [11]. A number of methods have been introduced for the preparation of cuprous oxide, like, fixture-reduction [12], microwave chemical route [13], thermal pyrolysis deposition [14] and electrodeposition [15]. Among these methods, electrodeposition acts as one of the most promising approaches due to its simplicity, low cost, facile fabrication processing allowing the fabrication of well-defined or complex structures in one [15] or two steps [11], and the shape control can be effectively achieved via controlling the deposition potential [16]. The properties of nano/micro structure materials are very diverse with respect to their morphology and size. As such, researchers have devoted to prepare different structures for the application and study. To date, many Cu₂O structures have been reported, such as porous nanowires [17], microcubes [8], pyramids, hexagonal nanotube [11] and multipod framework [18]. Although numerous Cu₂O structures have been produced, they were usually deposited on template and unavailable for the practical application, few papers reported the crystal structures in our work by varying the deposition voltage.

Ngan et al [15] fabricated the nanometer to micron size single crystals of Cu₂O on Au/Pd sputter-coated Si wafer and stainless steel substrates by electrodeposition. Several structures were observed which were transient shapes growing toward the octahedron, such as truncated octahedral shape, three and four-flower structure, by varying deposition voltage and deposition time. Guo et al [19] developed a templateless electrochemical method to deposit cuprous oxide on the surface of glass carbon (GC) electrode without any surfactant. Only two kinds of morphology were obtained, which were perfect Cu₂O octahedron and monodisperse colloid spheres. Here is the modification of the method developed by Guo et al, and six kinds of structure of Cu₂O were observed varying the deposition voltage. In addition, the Cu₂O microspheres modified GC (Cu₂O-GC) electrode has been employed for the glucose sensor successfully.

2. EXPERIMENTAL

2.1 Chemicals and solutions

D-(+)-glucose, Cu(NO₃)₂·3H₂O, L-ascorbic acid (AA), uric acid (UA), dopamine (DA), glutathione (GSH), and cysteine (CYS) were purchased from sigma. All other reagents were of analytical grade and used as received without any further purification. Deionized water (>18.4 M·cm⁻¹) was used throughout all the experiments.

2.2 Apparatus

The morphology characterization was performed on the scanning electron microscopy (SEM) (JSM6701F, Jeol, Japan) and operated at 3 kv with a special GC electrode for SEM. A CHI842c workstation (Austin, TX, USA) was employed for electrochemical measurements. The experiments were carried out using a conventional three-electrode system with a GC electrode (3 mm in diameter) as the working electrode, a platinum foil as counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference electrode, respectively. Prior to deposition, the GC electrode was polished with 1.0, 0.3 and 0.05 μm alumina powder and then rinsed by ethanol and deionized water, dried naturally at room temperature.

2.3 Deposition of Cu_2O microcrystals on GC electrode

In a typical method, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in water to form the 25 mM $\text{Cu}(\text{NO}_3)_2$ aqueous solution. NaOH was gradually added to $\text{Cu}(\text{NO}_3)_2$ solution with continuous stirring in ice-water bath until the sedimentation $\text{Cu}(\text{OH})_2$ completely dissolved. The resultant transparent deep blue solution was $\text{Cu}(\text{OH})_4^{2-}$. To fabricate the Cu_2O -GC electrode, the amperometric i-t technique was employed by applying appropriate potential to GC electrode in $\text{Cu}(\text{OH})_4^{2-}$ solution. Different shapes of Cu_2O structures were prepared by changing the potential from -0.48 V to -0.7 V for 15 min. while using for the electrocatalytic oxidation of glucose, -0.7 V was applied for 15 min.

3. RESULTS AND DISCUSSION

3.1 Electrodeposition of Cu_2O microstructures

As is known, the shape of crystal is determined by the crystallographic planes that form the surface. The crystal grows fastest in the direction perpendicular to the face with highest surface energy, thus the fastest growing faces shrink. The addition of organic or inorganic would change the surface energy during the crystal growth process, resulting in the change in the final crystal morphology [20]. Different geometrical crystal shapes can be attained by varying growth ratio, R, which is defined as the growth rate along the $\langle 100 \rangle$ direction to that along $\langle 111 \rangle$ direction. The octahedral structures with eight $\langle 111 \rangle$ facets are formed when the R is large than 1.73.

Different shapes of Cu_2O could also be synthesized by electrochemical method via controlling the potential [19]. Figure 1 shows the SEM images of Cu_2O structures electrodeposited at GC electrode at different deposition potentials. The electrodeposition potential, directly related the reaction rate, plays an essential role in the forming of different morphology. As can be seen in Figure 1, crystal growth was initiated from the 'core' and extended outwards and the orientation highly depended on the deposition voltage. When the applied voltage was higher than -0.6 V (a-c), the whole structure of Cu_2O seemed have octahedral framework, with the size of approximately 3 μm . Once the voltage was negative than -0.6 V (d-e), the crystal grew from the 'core' and along different directions, like stars,

and the size could large to 5 μm . With the applied voltage decreasing to -0.7 V (f), the star-like structure continued to grow ultimately to sphere.

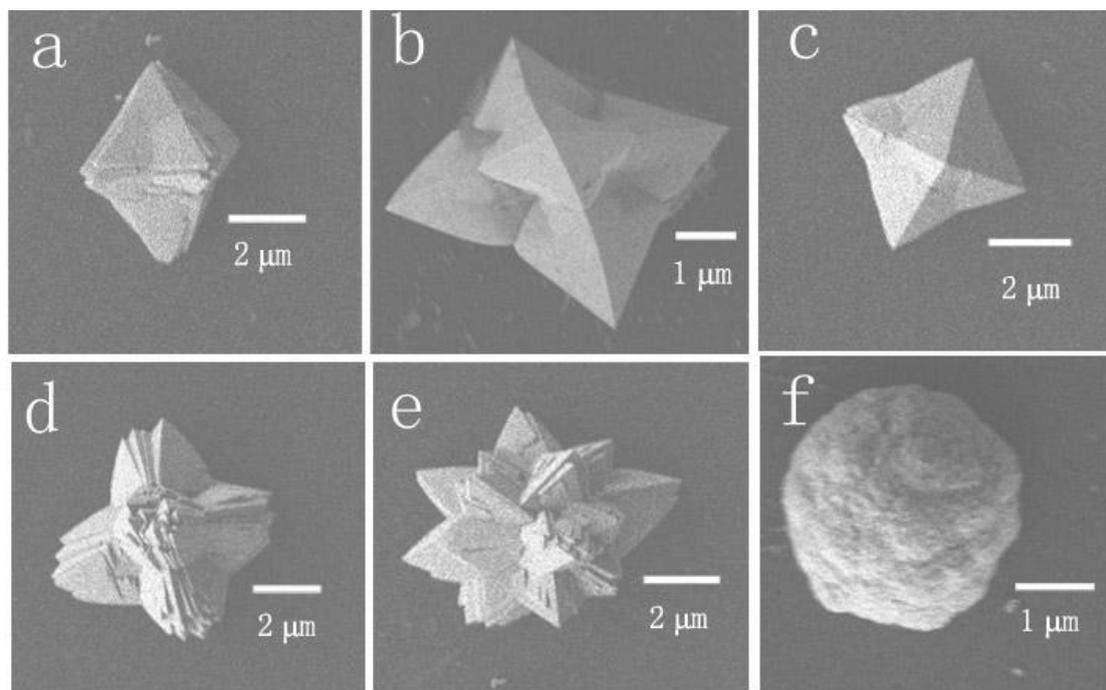


Figure 1. SEM images of the typical Cu_2O microcrystals electrodeposited in a solution of 25 mM $\text{Cu}(\text{OH})_4^{2-}$ for 15 min at different potentials. (a): -0.51 V; (b): -0.54 V; (c): -0.58 V; (d): -0.62 V; (e): -0.66 V; (f): -0.7 V.

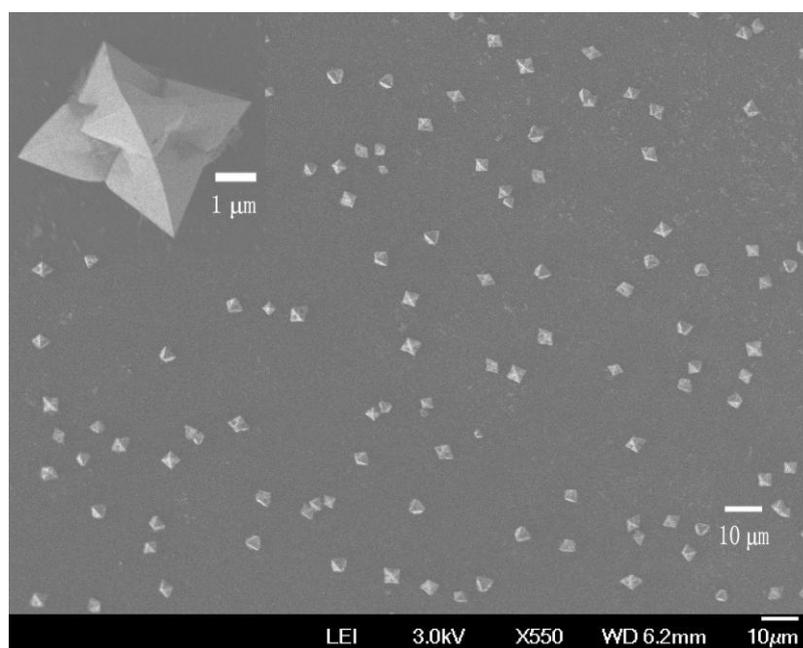
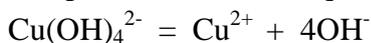


Figure 2. SEM image of Cu_2O microcrystals deposited on the surface of GC electrode at -0.54 V for 15 min. The inset picture shows the main crystal structure.

It was noted that uniform Cu₂O super-octahedron were deposited on the GC electrode surface at -0.54 V, as shown in Figure 2. It's visible that the Cu₂O particles have a size of about 3 μm. However, this novel Cu₂O super-octahedron was not observed at ITO electrode [19]. This may be caused by the difference of electrode surface between GC and ITO electrode, which suggesting that the electrode materials play an important role in the morphology of electrodeposited nanostructures.

The possible chemical equilibrium for the electrodeposition is as follows:



The Cu²⁺ ion was reduced to Cu₂O in an alkaline solution when applying negative potential. No particles were deposited on the surface of GC electrode with the deposition voltage higher than -0.48 V, indicating that the reduced potential range of Cu(OH)₄²⁻ to Cu₂O is lower than -0.48 V vs. Ag/AgCl. As such, the Cu²⁺ ion can be slowly reduced to Cu₂O in our system. Large quantities of OH⁻ existed around the GC electrode surface when the applied potentials were relatively high (-0.51 V - 0.6 V), leading to the preferential growth on certain facets. The possible growth mechanism may start from the nucleate crystal of Cu₂O and the growth towards two orthogonal <100> directions were preferential. As such, the octahedral structures would be formed on regular processing because of the large R.

According to Ngan's work [15], the structure in Figure 1 (b) was considered to be the transient structure growing towards the octahedron, which consisted of several smaller octahedral crystals. The grooves in the super-octahedron can be seen, and it seemed that the Cu²⁺ ion continued being reduced to Cu₂O which then filled the grooves to form octahedron, as shown in Figure 1 (c). No super-octahedron was observed when the applied voltage range from -0.51 V to -0.6 V. The anisotropic absorption of co-existing ion like OH⁻ and NO³⁻ on the Cu₂O facets might be the factors.

Figure 1 (d-e) shows the star-like structures of Cu₂O with different points under the deposition potential of -0.62 V and -0.66 V, respectively. When the applied voltage further decreased to -0.7 V, the microspherical shape Cu₂O was obtained, indicating the growth of Cu₂O might be kinetic control. The more negative potential would improve the reaction kinetic, resulting in the fast growing rate of Cu₂O. In this condition, the growth towards any direction was not preferential because of the fast growing rate and the anisotropic absorption of co-existing ion. As a result, the Cu₂O microsphere was finally produced.

Hence, from the previous discussion on Figure 1 and 2, we conclude that the Cu₂O structures would be super-octahedron at much higher deposition potential (-0.54 V), and then have star-like shapes with several points when applied more negative potentials (-0.6 V), and finally become microsphere under -0.7 V.

3.2 Electrochemical response of the modified electrode toward glucose

Traditional cyclic voltammetry (CV) and chronoamperometry (i-t) technique were used in this work to study the non-enzymatic electrocatalytic activity of the Cu₂O-GC electrode towards glucose. As Figure 3 shows, there was a strong electrocatalytic oxidation of glucose which began at +0.4 V and reached the peak current at +0.65 V in 0.1 M NaOH solution at the Cu₂O-GC electrode deposited at -0.7 V for 15min. That was in good agreement with the previous literature reported by Marioli and

Kuwana, where Cu(III) and hydroxyl radicals were involved [21]. Such strong electrocatalytic oxidation of glucose may be contributed to the high electroactive sites on the surface of the modified electrode provided by Cu₂O microspheres. The current tail over +0.8 V ascribed to breakdown of water [22].

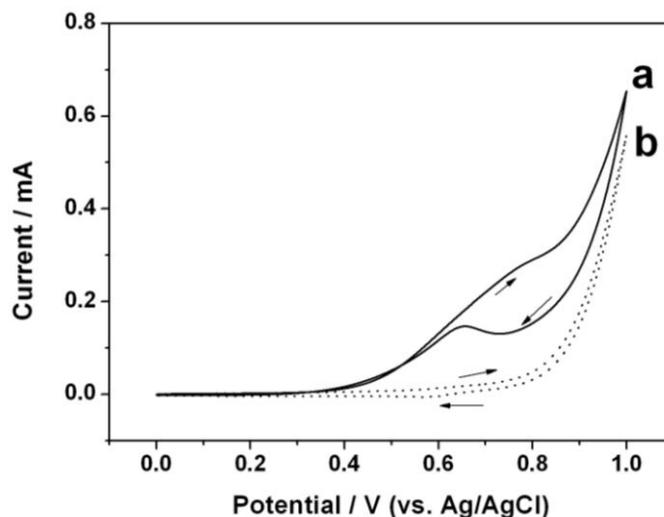


Figure 3. CVs of Cu₂O-GC electrode in 0.1 M NaOH solution in the presence(a) and absence(b) of 5 mM glucose.

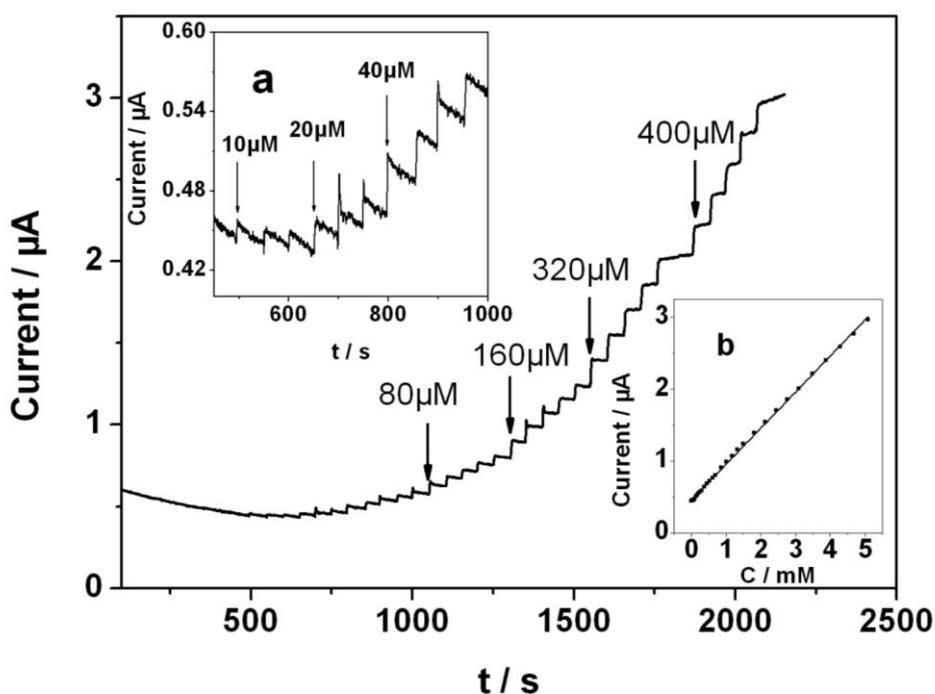


Figure 4. Current-time response curve of Cu₂O-GC electrode sensor with successive addition of glucose into 0.1 M NaOH, Inset: (a) the response at low concentration of glucose; (b) calibration curve.

Figure 4 shows the current-time response curve of the Cu₂O-GC electrode with successive addition of glucose into 0.1 M NaOH, the inset pictures are the response at low concentration of glucose and the calibration curve, respectively. At detection potential of +0.6 V, the Cu₂O-GC electrode presented a good linear dependence on the concentration of glucose from 10 μM to 5 mM and the regression equation was $I (\mu\text{A}) = 4.56 + 5.01 \times 10^{-3} C (\mu\text{M})$ with a correlation coefficient of 0.9995. The microsphere Cu₂O-GC electrode remained an excellent operation stability and quick response (< 10 s) if the addition concentration of glucose was not higher than 400 μM. The RSD for 10 successive detection of 100 μM glucose was 4.6%. The anti-interference property of the Cu₂O-GC electrode was also investigated in Figure 5.

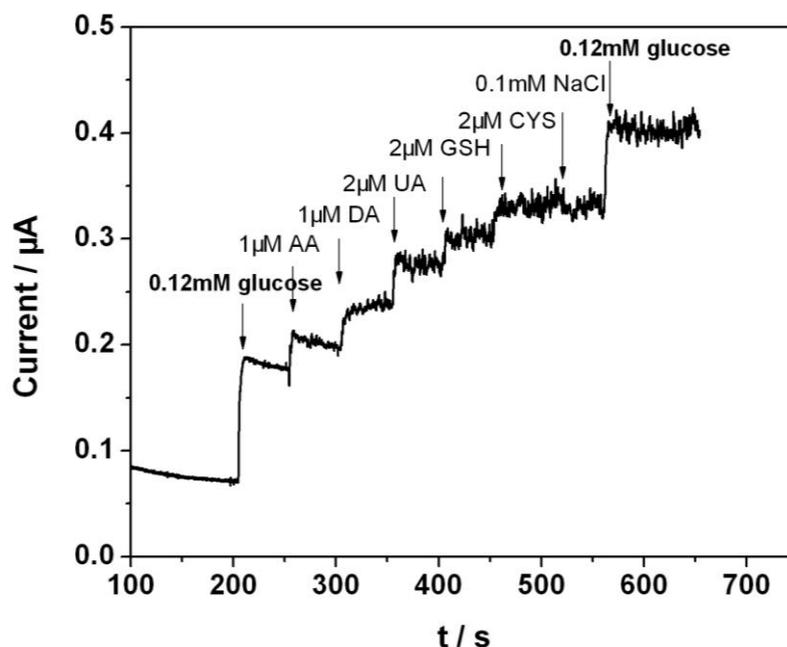


Figure 5. Interference test of Cu₂O-GC electrode in 0.1 M NaOH at +0.6V with 0.12 mM glucose in the presence of 1 μM AA, 1 μM DA, 2 μM UA, 2 μM GSH, 2 μM CYS and 0.1 mM NaCl.

The result shows that low concentration of co-existing interferences including AA, DA, UA, GSH and CYS, did not interfere significantly on the determination of glucose. The results demonstrate that the Cu₂O microsphere-based structure have great potential for glucose sensing.

4. CONCLUSIONS

Different shapes of Cu₂O microstructures from super-octahedral to octahedron and then to microspheres were fabricated by varying the deposition voltage at GC electrode. The anisotropic absorption of co-existing ion and the different growing rates on certain Cu₂O facets caused the forming of the different morphology. The presented Cu₂O microspheres exhibited high electrocatalytic activity toward glucose.

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