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Au–Cu Ratio Optimization In Co-Deposition For Superior Electrochemical Glucose Sensing On Screen-Printed Graphene Electrodes

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Abstract: *This study explores the influence of the gold (Au) ratio in Au-Cu co-electrodeposition on the electrochemical performance of a screen-printed graphene electrode (SPGE) for glucose sensing. By varying the Au content in the Au-Cu alloy, the electrode's current response was evaluated across five glucose concentrations: 55 nM, 110 nM, 165 nM, 220 nM, and 275 nM. The aim was to identify the optimal Au-Cu composition that enhances electron transfer and overall electrochemical activity. The experimental results revealed a non-linear relationship between Au ratio and current response. The most significant enhancement in current was observed at an Au ratio of 0.50, where the signal increased by approximately 100–250% compared to other compositions. This enhancement is attributed to the formation of a balanced Au-Cu alloy, which promotes efficient charge transfer, improved conductivity, and stable surface morphology. At lower Au ratios, excessive Cu content may lead to poor structural integrity and reduced catalytic activity, whereas higher Au ratios result in insufficient Cu to support the alloy's catalytic synergy, causing diminished current response. These observations confirm that the Au-Cu alloy composition plays a critical role in determining the electrode's electrochemical behavior. This work demonstrates that an Au ratio of 0.50 in Au-Cu co-deposition yields the most favorable electrochemical characteristics, making it a promising candidate for non-enzymatic glucose sensors, biosensors, and other electrocatalytic applications.*

Keywords: *Au-Cu Co-Deposition, Biosensor Optimization, Current Enhancement, Glucose Detection, Electrochemical Performance.*

1. INTRODUCTION

Electrochemical biosensors have emerged as a highly effective tool for detecting biomolecules due to their high sensitivity, rapid response, and cost-effectiveness. Among various biosensing applications, glucose detection has received significant attention, particularly for its role in diabetes management and biomedical diagnostics. The development of efficient and stable non-enzymatic glucose sensors has been a growing research focus [1-3], with metal-based electrodes offering enhanced electrocatalytic properties and durability [4, 5]. In particular, bimetallic alloys, such as gold-copper (Au-Cu) co-deposited electrodes [6-8], have shown superior catalytic activity due to their synergistic electron transfer capabilities, making them promising candidates for glucose sensing.

Gold (Au) is well known for its excellent electrical conductivity, chemical stability, and biocompatibility, making it a key component in biosensors [9, 10]. However, its high cost and limited active sites can hinder large-scale applications. Copper (Cu), on the other hand, provides high catalytic activity and affordability but suffers from poor long-term stability in electrochemical environments [11, 12]. By integrating Au and Cu into a bimetallic Au-Cu alloy, the resulting electrode can enhance charge transfer, increase active surface

area, and improve electrochemical performance, offering a cost-effective and efficient solution for glucose detection. Several studies have demonstrated the potential of Cu-based nanomaterials for glucose sensing. For instance, Pengjuan Ni et al. synthesized CuO nanowires (CuO NWs) from $Cu(OH)_2$ and reported a high glucose sensitivity of 1886.3 $\mu A \cdot mM^{-1} \cdot cm^{-2}$ [11]. Similarly, Zhenzhen Li et al. developed CuO NWs/CF-based sensors, achieving an even higher sensitivity of 2217.4 $\mu A \cdot mM^{-1} \cdot cm^{-2}$ [13]. Other researchers, such as Ensaf et al. and Kayyat et al., have explored Cu nanocomposites and CuO nanostructures [14, 15], demonstrating promising electrocatalytic properties. More recently, Haneen Ali Jasim et al. fabricated CuO nanorod (NR)-based glucose sensors [16], achieving sensitivities above 650 $\mu A \cdot mM^{-1} \cdot cm^{-2}$. These findings highlight the significant role of Cu-based nanomaterials in glucose detection and the potential advantages of combining them with Au to optimize sensor performance.

In this study, Au-Cu co-deposition was performed on screen-printed graphene electrodes (SPGE) using cyclic voltammetry (CV) electrodeposition to investigate the influence of varying Au:Cu ratios (0.1–0.9) on the microstructure and electrochemical properties of the electrode. Scanning electron microscopy (SEM) was used to characterize the morphology and elemental distribution of the Au-Cu alloy, while electrochemical techniques were applied to evaluate glucose detection performance at different concentrations (55–275 nM). The objective of this research is to determine the optimal Au-Cu composition that provides maximum current response and enhanced electrocatalytic activity. By analyzing the relationship between microstructure, alloy composition, and electrochemical behavior, this study aims to contribute to the advancement of cost-effective, high-performance glucose sensors. The findings could have broader applications in biosensing, medical diagnostics, environmental monitoring, and food safety analysis, paving the way for more efficient non-enzymatic electrochemical sensors.

2. MATERIALS AND METHODS

2.1. Materials and Procedures

The experiments were carried out using a screen-printed graphene electrode (SPGE) as the working platform. The SPGE includes a working electrode (WE), reference electrode (RE), and counter electrode (CE). Co-deposition of Au-Cu alloy was performed directly on the WE surface via cyclic voltammetry (CV) to modify the electrode with a bimetallic Au-Cu layer. The aim was to investigate how varying the gold (Au) content in the deposition bath affects electrochemical performance.

Table 1 presents the composition ratios of Au and Cu used in the electrodeposition process. The Au ratio was systematically varied from 0.10 to 0.90, with the corresponding Cu ratio adjusted to maintain a total metal ion concentration of 1.00. Thirteen different Au-Cu compositions were prepared, allowing for a detailed study of how the Au:Cu ratio influences the alloy structure and electrocatalytic activity. This approach enabled the identification of an optimal ratio that maximizes the current response during glucose detection.

Table 1 Composition Ratios of Au and Cu in the Electrodeposition Bath

Condition	Ratio of Au	Ratio of Cu
1	0.10	0.90
2	0.20	0.80
3	0.25	0.75
4	0.30	0.70
5	0.33	0.67
6	0.40	0.60

7	0.50	0.50
8	0.60	0.40
9	0.67	0.33
10	0.70	0.30
11	0.75	0.25
12	0.80	0.20
13	0.90	0.10

The gold solution (Au = 5 mM) was prepared using potassium tetrachloroaurate ($K[AuCl_4]$) in 5% sulfuric acid (H_2SO_4), while the copper solution (Cu = 0.4 M) was prepared using copper sulfate ($CuSO_4$) and sulfuric acid (H_2SO_4). The electrodeposition was performed under controlled potential conditions, scanning between -0.7 V to 0.9 V for 2 cycles at a scan rate of 0.1 V/s. This process ensured the formation of a uniform Au-Cu alloy layer on the WE surface. The process of Au-Cu co-deposition on SPGE for glucose detection is illustrated in **Error! Reference source not found.**.

The morphology and composition of the deposited Au-Cu layers were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

2.2. Glucose Detection Testing

The glucose detection capability of the Au-Cu-modified SPGE was evaluated by measuring the current response to glucose concentrations of 55, 110, 165, 220, and 275 nM. Electrochemical measurements were conducted using cyclic voltammetry (CV) in 1 M sodium hydroxide (NaOH) at room temperature. A three-electrode system was employed, where the modified SPGE served as the working electrode (WE), graphene as the counter electrode (CE), and Ag/AgCl as the reference electrode (RE). The glucose oxidation reaction was monitored by recording the current response over multiple CV cycles.

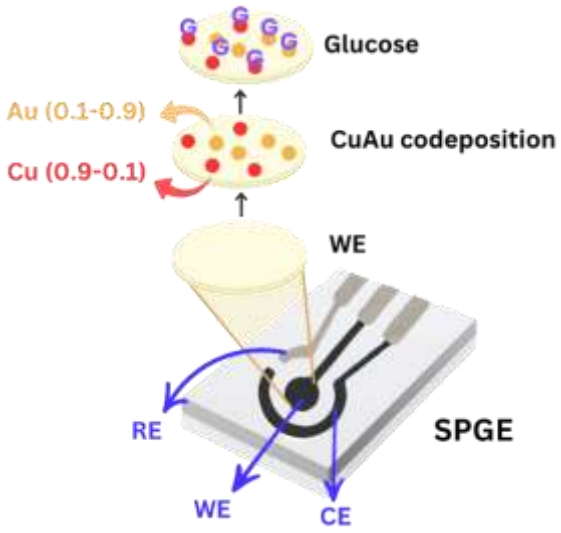

Figure 1. Schematic of Au-Cu co-deposition on SPGE for glucose detection, with varying Au:Cu ratios (0.1–0.9) modifying the working electrode (WE).

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3. RESULTS AND DISCUSSION

3.1. Microstructure of Au-Cu Co-deposition Electrode on SPGE (Au-Cu/SPGE)

The microstructural characteristics of the Au-Cu co-deposition electrode on the screen-printed graphene electrode (Au-Cu/SPGE) were analyzed using scanning electron microscopy (SEM) to examine the surface morphology and distribution of Cu and Au within the deposited alloy. The SEM image (**Error! Reference source not found.**), captured at a magnification of 6,000x, provides insight into the electrodeposition process and the formation of distinct structural features.

The SEM micrograph reveals a highly irregular and porous Cu matrix, characterized by plate-like and layered crystalline structures. These structures appear to be shrunken and fractured, which may be attributed to stress-induced contraction during the deposition process. The rough and uneven morphology of Cu suggests non-uniform nucleation and growth, potentially due to variations in the reduction rates of Cu and Au.

Dispersed throughout the Cu matrix are numerous small spherical Au particles, which appear bright and well-dispersed on the surface. The presence of these fine Au particles suggests a non-continuous deposition of Au, where Au nucleates in isolated regions rather than forming a uniform layer. This phenomenon is likely influenced by the relative electrodeposition potentials of Cu and Au, with Cu forming the primary structure and Au depositing as discrete nanoparticles. The distribution of Au across the Cu matrix indicates a heterogeneous alloy formation, which may enhance electrochemical activity by increasing the available active sites for electron transfer.

The observed microstructure suggests that the porous Cu framework and dispersed Au nanoparticles enhance catalytic performance, particularly for glucose sensing applications. The high surface area of the Cu matrix, combined with the electrocatalytic properties of Au, facilitates efficient charge transfer and improved glucose oxidation. These morphological insights highlight the connection between electrodeposition parameters, alloy structure, and electrochemical behavior. Energy-dispersive X-ray spectroscopy (EDS) analysis confirms the elemental distribution of the deposited Au-Cu alloy, showing that the shrunken matrix is Cu, while the dispersed particles correspond to Au.

Figure 2 SEM image of Au-Cu codeposition on SPGE (6,000x magnification), showing a porous Cu matrix with dispersed Au nanoparticles. Scale bar: 2 µm.

3.2. Effect of Au Ratio in Au-Cu co-deposition on Current

The effect of the Au ratio in Au-Cu co-deposition on current was investigated at different glucose concentrations (55 nM, 110 nM, 165 nM, 220 nM, and 275 nM), revealing a non-linear relationship between composition and electrochemical response. A distinct peak in current was observed at an Au ratio of 0.50, indicating that this composition provides the highest electrochemical activity (**Error! Reference source not found.**). This enhancement is likely due to the synergistic effect between Cu and Au, which optimizes electron transfer and conductivity. At lower Au ratios, the current level remains relatively low, likely due to Cu's dominant presence, which may limit catalytic activity.

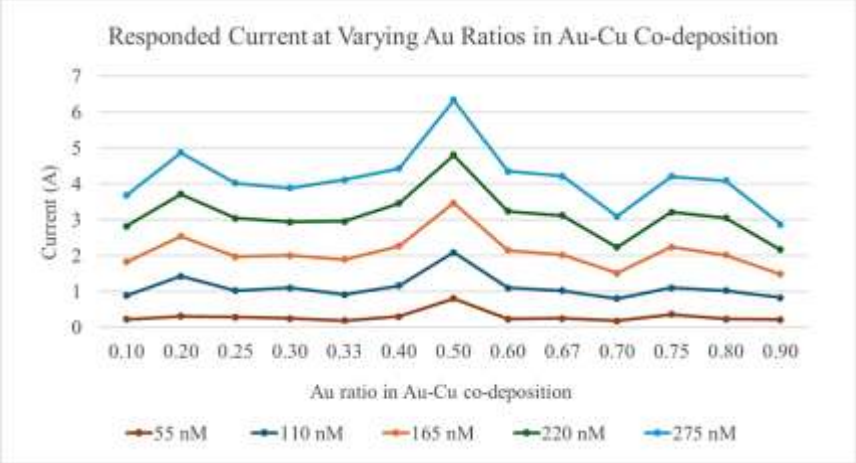

Figure 3 Current vs. Au Ratio in Au-Cu co-deposition at glucose concentrations 55–275 nM.

Conversely, at higher Au ratios, the current declines, suggesting that excessive Au reduces Cu's contribution to charge transfer and disrupts the alloy's structural stability. The optimal performance at Au ratio = 0.50 suggests that this composition maximizes the balance between catalytic activity, conductivity, and alloy stability, making it a promising candidate for applications requiring high electrochemical efficiency, such as glucose sensing.

These findings further emphasize the importance of precise control over the Au-Cu alloy composition during co-deposition. The observed non-linear current response, with a peak at an Au ratio of 0.50, reflects the delicate balance between catalytic enhancement and structural synergy. At this optimal ratio, the combined effects of Au's superior conductivity and Cu's high catalytic activity are maximized, leading to improved charge transfer and enhanced glucose oxidation. Deviations from this ratio, either with excess Cu or Au, disrupt the alloy's electrochemical equilibrium—resulting in reduced performance due to poor surface coverage or limited electron mobility. This behavior not only reinforces the value of bimetallic tuning for biosensor optimization but also suggests that Au-Cu co-deposition could be adapted for detecting other analytes, provided similar synergistic interactions are established. The strategic adjustment of alloy composition is, therefore, a key design parameter in advancing high-efficiency, cost-effective, non-enzymatic biosensors.

4. CONCLUSIONS

This study investigated the effect of Au ratio in Au-Cu co-deposition on the electrochemical performance of screen-printed graphene electrodes (SPGE) for glucose detection. The microstructural analysis revealed that Cu forms a porous matrix, while Au deposits as dispersed nanoparticles, contributing to an enhanced

surface area and improved charge transfer. Electrochemical studies demonstrated a non-linear relationship between the Au ratio and current response, with the highest current observed at an Au ratio of 0.50. This composition provides an optimal balance between catalytic activity, structural stability, and conductivity, resulting in enhanced glucose oxidation. At lower Au ratios, the current remains low due to Cu dominance, while at higher Au ratios, excessive Au reduces the alloy's synergistic effect, leading to a decline in performance. These findings highlight the critical role of Au-Cu composition in electrode optimization and demonstrate that the Au-Cu (0.50) electrode is a promising candidate for biosensing applications. Future studies should explore long-term stability and real-sample analysis to further validate the sensor's performance for practical applications.

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