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Synergistic Effect of Au And Cu Co-Deposition on SPGE for Non-Enzymatic Glucose Detection

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Abstract
The development of non-enzymatic glucose sensors is essential for achieving high stability, cost-effectiveness, and long-term reliability. This study presents a Au-Cu electrode fabricated by direct co-electrodeposition on a screen-printed graphite electrode (SPGE) for glucose detection. The electrochemical performance of Cu, Au, and Au-Cu electrodes was evaluated, revealing that Cu alone exhibited negligible current, while Au generated 0.8 A, confirming its glucose detection capability. Notably, the Au-Cu co-deposited electrode showed the highest current response (1.6 A), surpassing both Cu and Au, highlighting a synergistic enhancement in glucose sensing performance.
The improved sensitivity of the Au-Cu electrode is attributed to the synergistic effect between Cu and Au, enhancing electron transfer and catalytic activity. While previous studies have focused on Cu and Au individually, the co-electrodeposition method for glucose sensing remains unexplored. This work further investigates the sensor's response to five different glucose concentrations (55 nM, 110 nM, 165 nM, 220 nM, 275 nM), demonstrating a clear correlation between glucose levels and current response.
The simple, scalable, and cost-effective fabrication method used in this study offers a promising alternative for high-sensitivity glucose sensors. With enhanced electrochemical response and practicality, the Au-Cu/SPGE electrode has significant potential for non-enzymatic glucose sensing in biomedical diagnostics and point-of-care monitoring.
Keywords: *Non-enzymatic glucose sensor, Au-Cu co-electrodeposition, Screen-printed graphite electrode (SPGE), Electrocatalytic activity, Bimetallic alloy sensor*

1. INTRODUCTION

Electrochemical biosensors have emerged as highly effective platforms for detecting biomolecules, offering advantages such as excellent sensitivity, rapid response times, and low production costs [1, 2]. Among various sensing targets, glucose detection has received particular attention due to its critical role in managing diabetes and advancing biomedical diagnostics. In recent years, the development of non-enzymatic glucose sensors has become increasingly important, as they provide greater operational stability and longer shelf-life compared to enzyme-based systems. Metal-based electrodes, particularly those utilizing bimetallic structures, have demonstrated enhanced electrocatalytic properties and durability in electrochemical applications [3, 4]. Gold (Au) and copper (Cu) are considered promising materials for electrochemical sensing owing to their complementary properties. Au exhibits excellent electrical conductivity, chemical stability, and biocompatibility, whereas Cu offers notable catalytic activity at a significantly lower cost [5, 6]. However, the high cost and limited surface reactivity of Au, alongside the poor electrochemical stability of Cu, have prompted increasing interest in their combination [7, 8]. This bimetallic approach aims to mitigate individual limitations and enhance the overall performance of electrochemical sensors. Alloying gold (Au) and copper (Cu) has shown significant potential for enhancing electrochemical sensor performance by improving charge transfer kinetics, increasing active surface area, and promoting synergistic electrocatalytic activity [9, 10]. Cu-based nanomaterials, such as CuO nanowires and nanorods, have demonstrated high sensitivity in glucose sensing due to their excellent catalytic properties [11-13]. When supported on conductive substrates like carbon fibers or combined with other functional materials, these Cu-based structures exhibit further performance improvements [14, 15]. Recent advancements have reported sensitivities exceeding 650 $\mu A \cdot mM^{-1} \cdot cm^{-2}$, highlighting the strong electrocatalytic potential of Cu. Integrating Cu with Au is expected to amplify these effects, offering a balanced combination of stability, conductivity, and catalytic efficiency for advanced non-enzymatic glucose sensors.

Although the individual application of Cu or Au in glucose sensors has been extensively studied, the direct co-electrodeposition of Au-Cu alloys remains relatively underexplored, particularly in the context

of optimizing non-enzymatic glucose sensor performance. This study presents the development of a high-performance glucose sensor based on the co-deposition of Au and Cu onto a screen-printed graphite electrode (SPGE). By systematically adjusting the Au:Cu ratio, the electrode's microstructure, electron transfer efficiency, and catalytic activity are enhanced, contributing to the advancement of cost-effective, sensitive, and stable glucose sensors suitable for biomedical applications.

2. Details Experiments

2.1. Materials and Procedures

A screen-printed graphene electrode (SPGE), comprising a working electrode (WE), reference electrode (RE), and counter electrode (CE), was employed as the sensing platform. Electrodeposition of Au, Cu, and Au-Cu alloy was carried out via cyclic voltammetry (CV) to compare their electrochemical performance. The Au deposition solution (5 mM) was prepared using potassium tetrachloroaurate ($K[AuCl_4]$) in 5% sulfuric acid (H_2SO_4), while the Cu deposition solution (0.4 M) was prepared using copper sulfate ($CuSO_4$) and H_2SO_4. Electrodeposition was conducted under controlled potential, scanning between -0.7 V and 0.9 V for two cycles at a scan rate of 0.1 V/s. This procedure facilitated the formation of a uniform AuCu alloy layer on the WE surface. The co-deposition process for glucose sensor fabrication is schematically shown in Figure 1. The surface morphology and elemental composition of the deposited layers were analyzed using Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS).

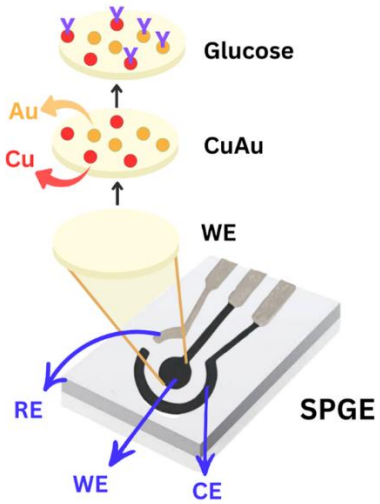

Figure 1 Schematic of Au-Cu co-deposition on SPGE for glucose detection modifying the working electrode (WE).

2.2. Glucose Detection Testing

The glucose sensing performance of the Au-Cu-modified SPGE was assessed by recording current responses at glucose concentrations of 55, 110, 165, 220, and 275 nM. Measurements were performed using cyclic voltammetry (CV) in 1 M sodium hydroxide (NaOH) at room temperature. A three-electrode configuration was used, comprising the Au-Cu/SPGE as the working electrode (WE), a graphene counter electrode (CE), and an Ag/AgCl reference electrode (RE). The glucose oxidation reaction was evaluated by monitoring the current changes across multiple CV cycles.

3. RESULTS AND DISCUSSION

3.1. Microstructure of Cu, Au, and Au-Cu deposition electrode on SPGE

The microstructures of Cu/SPGE, Au/SPGE, and Au-Cu/SPGE exhibit distinct morphological characteristics, reflecting the nature of each electrodeposition process. As shown in Figure 2a, Cu deposition results in large, rod-like crystalline structures distributed unevenly across the electrode surface, indicating directional growth and high surface roughness. In contrast, Au deposition (Figure 2b) produces well-defined flower-like crystals, suggesting nucleation-dominated growth that generates a texture and catalytic surface. Au-Cu co-deposition (Figure 2c) forms a highly porous and irregular Cu matrix, embedded with numerous small, bright Au nanoparticles. These differences arise from the intrinsic properties of Cu and Au, including their reduction potential and nucleation behaviors, and critically

influence the electrochemical performance of the modified electrodes. Detailed surface and pore characterizations are discussed in the following sections to further elucidate their role in enhancing glucose sensing efficiency.

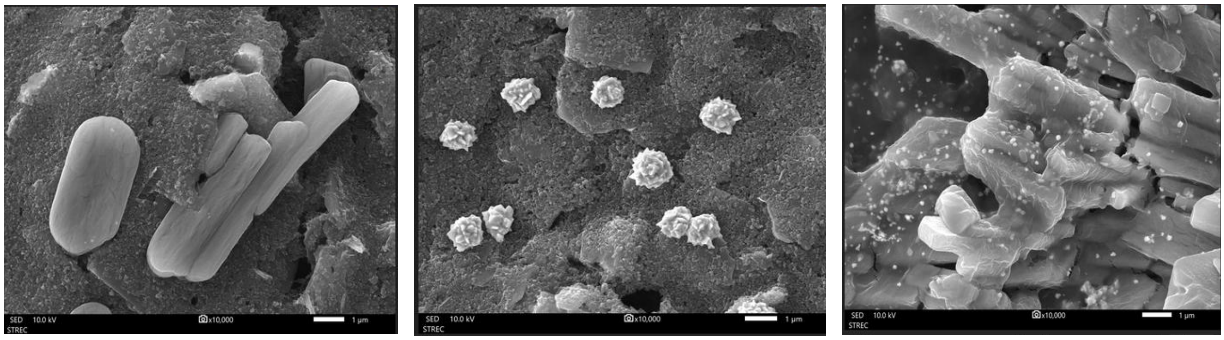

Figure 2 SEM images of (a) Cu-modified SPGE (Cu/SPGE), (b) Au-modified SPGE (Au/SPGE), and (c) Au-Cu co-deposited SPGE (Au-Cu/SPGE) at a magnification of 10,000X.

The SEM analysis reveals distinct morphological features for Cu/SPGE, Au/SPGE, and Au-Cu/SPGE electrodes. For Cu/SPGE (Figure 2a), the surface exhibits large, rod-like crystalline structures distributed unevenly across the substrate. This morphology indicates directional and rapid Cu growth during electrodeposition, resulting in a rough and porous structure that can increase the available surface area for electrochemical reactions. In contrast, Au/SPGE (Figure 2b) displays well-defined flower-like crystalline clusters, suggesting a nucleation-dominated growth process that produces a highly textured surface. The flower-like morphology of Au provides abundant catalytic sites but with a more compact structure compared to the porous Cu matrix.

For Au-Cu/SPGE (Figure 2c), a highly porous and irregular Cu matrix is observed, featuring layered and fractured structures, within which numerous small, bright Au nanoparticles are dispersed. This heterogeneous morphology results from the co-deposition behavior of Cu and Au, where Cu preferentially forms the main porous framework while Au nucleates as discrete nanoparticles due to differences in their reduction potentials.

Energy-dispersive X-ray spectroscopy (EDS) confirms that the porous matrix predominantly consists of Cu, with the bright dispersed particles corresponding to Au. The combination of a high-surface-area Cu scaffold and finely distributed Au nanoparticles enhances electron transfer and provides abundant active sites, directly contributing to the superior glucose oxidation performance of the Au-Cu modified electrode.

3.2. Electrochemical Response toward Glucose Oxidation

The cyclic voltammetry (CV) results, presented in Figure 3, illustrate the glucose oxidation responses of bare SPGE, Cu-modified SPGE (Cu/SPGE), Au-modified SPGE (Au/SPGE), and Au-Cu co-deposited SPGE (Au-Cu/SPGE). The bare SPGE (blue line) shows minimal current across the potential range, confirming that the unmodified electrode lacks significant catalytic activity toward glucose oxidation. The Cu/SPGE (green line) displays a slight current increase compared to the bare SPGE, indicating that Cu alone possesses some electrocatalytic activity but remains insufficient for efficient glucose detection. The low current response may be attributed to the limited electrochemical stability of Cu in alkaline media and the relatively fewer active sites available for glucose adsorption and oxidation. Au/SPGE (yellow line) exhibits a markedly enhanced current response, reaching a peak current of approximately 0.8 mA. This improvement is due to Au's excellent catalytic activity, high conductivity, and strong affinity for glucose molecules, facilitating more efficient electron transfer. The flower-like Au structures observed in SEM contribute to a moderately high surface area, enhancing the electrode's sensitivity.

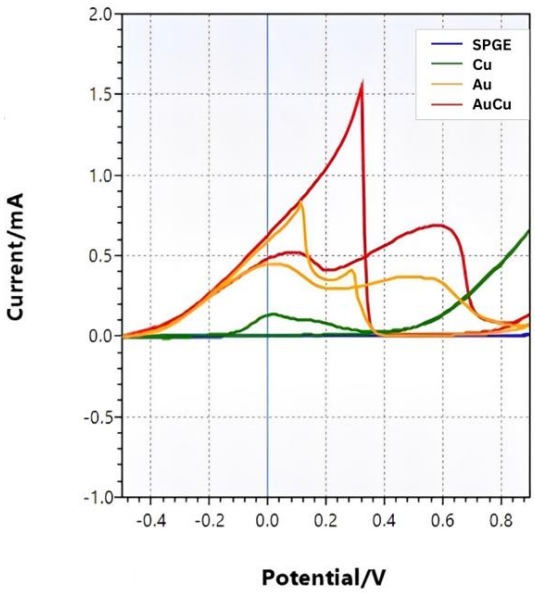

Figure 3 Current responses for glucose detection using bare SPGE (blue), Cu/SPGE (green), Au/SPGE (yellow), and Au-Cu/SPGE (red) in 1 M NaOH.

Significantly, the Au-Cu/SPGE (red line) achieves the highest current response, peaking at around 1.6 mA — roughly double that of the Au-modified electrode. This pronounced enhancement is attributed to the synergistic interaction between Cu and Au. The co-electrodeposition process results in a porous Cu framework that provides an extensive surface area for glucose adsorption, while the finely dispersed Au nanoparticles serve as highly active catalytic centers. The difference in reduction potential between Cu and Au promotes a heterogeneous nucleation process, leading to this optimized microstructure. The combined presence of a conductive, high-surface-area Cu matrix and catalytically active Au nanoparticles enhances electron transfer kinetics, increases the density of reactive sites, and reduces the activation energy barrier for glucose oxidation. This synergistic effect is key to the superior performance observed in the Au-Cu electrode, underscoring the advantage of bimetallic co-deposition strategies over single-metal modifications. Thus, the Au-Cu/SPGE demonstrates not only the highest sensitivity but also a more efficient and stable glucose oxidation process, validating the potential of Au-Cu co-electrodeposition as a powerful approach for developing non-enzymatic glucose sensors.

The structure of the electrode plays a critical role in determining its electrochemical performance toward glucose detection. The large, rod-like structures observed in Cu/SPGE provide limited active surface area, resulting in a relatively low current response. In contrast, the flower-like crystalline morphology of Au/SPGE offers more catalytic sites, leading to a significant increase in current. However, the Au-Cu co-deposited electrode exhibits a highly porous Cu matrix embedded with finely dispersed Au nanoparticles, creating a synergistic structure that maximizes both surface area and catalytic activity. This porous framework enhances glucose adsorption, while the uniformly distributed Au nanoparticles facilitate rapid electron transfer and lower the activation energy for glucose oxidation. As a result, the Au-Cu/SPGE generates the highest current signal, clearly demonstrating that an optimized microstructure with high porosity and well-dispersed catalytic centers is essential for achieving superior glucose sensing performance.

CONCLUSIONS

This study successfully demonstrated the fabrication of a non-enzymatic glucose sensor based on Au-Cu co-deposition on a screen-printed graphene electrode (SPGE). Morphological analysis revealed that the Au-Cu-modified electrode exhibited a highly porous Cu matrix decorated with uniformly dispersed Au nanoparticles, providing a large active surface area and abundant catalytic sites. Electrochemical measurements confirmed that the Au-Cu/SPGE delivered a significantly higher current response compared to electrodes modified with Cu or Au alone, highlighting the strong synergistic interaction between the two metals. The enhanced electron transfer kinetics and glucose oxidation activity observed in the Au-Cu electrode are directly attributed to the optimized microstructure achieved through co-deposition. These findings demonstrate that Au-Cu co-deposition offers a simple, scalable, and highly

effective strategy for developing cost-efficient, high-performance non-enzymatic glucose sensors suitable for biomedical and point-of-care applications.

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