Effect of Supporting Background Electrolytes on the Nanostructure Morphologies and Electrocatalytic Behaviors of Electrodeposited Gold Nanoparticles on Glassy Carbon Electrode Surfaces

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ABSTRACT: Electrodeposition is an electrochemical method employed to deposit stable and robust gold nanoparticles (AuNPs) on electrode surfaces for creating chemically modified electrodes (CMEs). The use of several electrodeposition techniques with different experimental parameters allow in obtaining various surface morphologies of AuNPs deposited on the electrode surface. By considering the electrodeposition of AuNPs in various background electrolytes could play an important strategy in finding the most suitable formation of the electrodeposited AuNP films on the electrode surface. This is because different electrode roughnesses can have different effects on the electrochemical activities of the modified electrodes. Thus, in this study, the electrodeposition of AuNPs onto the glassy carbon (GC) electrode surfaces in various aqueous neutral and acidic electrolytes was achieved by using the cyclic voltammetry (CV) technique with no adjustable CV parameters. Then, surface morphologies and electrochemical activities of the electrodeposited AuNPs were investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), CV, and electrochemical impedance spectroscopy (EIS). The obtained SEM and 3D-AFM images show that AuNPs deposited at the GC electrode prepared in NaNO₃ solution form a significantly better, uniform, and homogeneous electrodeposited AuNP film on the GC electrode surface with nanoparticle sizes ranging from ~36 to 60 nm. Meanwhile, from the electrochemical performances of the AuNP-modified GC electrodes, characterized by using a mixture of ferricyanide and ferrocyanide ions [Fe(CN)₆]₃⁻/⁴⁻, there is no significant difference observed in the case of charge-transfer resistances (Rct) and heterogeneous electron-transfer rate constants (k'), although there are differences in the surface morphologies of the electrodeposited AuNP films. Remarkably, the Rct values of the AuNP-modified GC electrodes are lower than those of the bare GC electrode by 18-fold, as the Rct values were found to be ~6 Ω (p < 0.001, n = 3). This has resulted in obtaining k' values of AuNP-modified GC electrodes between the magnitude of 10⁻² and 10⁻³ cm s⁻¹, giving a faster electron-transfer rate than that of the bare GC electrode (10⁻⁴ cm s⁻¹). This study confirms that using an appropriate supporting background electrolyte plays a critical role in preparing electrodeposited AuNP films. This approach could lead to nanostructures with a more densely, uniformly, and homogeneously electrodeposited AuNP film on the electrode surfaces, albeit utilizing an easy and simple preparation method.

INTRODUCTION

Electrodeposition of metal nanoparticles onto conductive solid electrode surfaces is a useful method in electrochemistry to produce chemically modified electrodes (CMEs) for electro-analytical and electrocatalytic applications. The main goal is to improve the electrochemical performances of the CMEs, in particular, the electrical conductivity of the modified electrodes. This method, which can be achieved either by applying a constant potential, current density, potential cycles, or pulse current, has been extensively employed in the synthesis of electrodeposited metal nanoparticle films. This method gives better control over surface morphologies such as the size, thickness, roughness, loading, and homogeneity of electrodeposited metal nanoparticles at the CMEs.

Various electrochemical techniques can be used for the electrodeposition of metal nanoparticles such as chronoamperometric, cyclic voltammetric (CV), or pulse current techniques. However, in our opinion, the simplest and most informative technique is CV. The CV offers potential benefits over other electrochemical techniques; for instance, the ability to control the thickness of the electrodeposited thin
films by gaining better control over particle nucleation and growth. This can be essentially achieved by controlling the CV scan rates, or the number of CV cycles. The CV technique can also provide us with a cyclic voltammogram for the electrodeposition of metals onto the electrode surface, which allows us to monitor both the oxidation and reduction peaks for dissolution and electrodeposition processes of metals and metal ions from the electrode surface. In the case of the electrodeposition of metal nanomaterials onto the electrode surfaces, the reduction peak is an indicator of the electrodeposition process, in which metal ions in the electrolyte solution are reduced to metal nanoparticles under the potential cycles by accepting the electron(s), thus producing electrodeposited metal nanoparticle films on the electrode surface.

Among the metal nanoparticles [such as platinum (Pt), gold (Au), silver (Ag), and palladium (Pd)], Au nanoparticles are the most commonly used metal nanomaterials in electroanalysis (electrochemical sensors and biosensors) and electrocatalysis due to their unique characteristics, such as high biocompatibility for the immobilization of biomolecules, in particular, via a self-assembly monolayer technique, electrocatalytic properties, high electroactive surface areas (ECSAs), and mass transport enhancement. Thus, gold-nanostructured forms offer enhanced electrochemical responses compared to the bulk Au electrodes as each Au nanoparticle electrodeposited at the modified electrode can perform as a tiny electrode, improving the electrical conductivity of the electrode surface. Essentially, the electrodeposited gold-nanostructured films on the modified electrode surfaces can be prepared with various nanostructure morphologies such as nanowires, nanocrystals, nanopores, and nanorings, where all these forms can be obtained by employing different electrodeposition techniques, and this has been greatly discussed in review papers by Tonelli et al. and Stine. However, in this current work, we employed the CV technique to obtain electrodeposited gold nanoparticle (AuNP) films on the glassy

Figure 1. Cyclic voltammograms for four cycles of 3 mM of HAuCl4 in (A) 0.1 M KNO3, (B) 0.1 M HNO3, (C) 0.1 M H2SO4, and (D) 0.1 M NaNO3 by cycling the potential from 0 to 0.9 V vs SCE at a scan rate of 0.025 V s⁻¹. (E) Cyclic voltammograms for 4 cycles of 3 mM of HAuCl4 in 0.1 M NaOH (as a control experiment), cycling the potential from 0.5 to −0.4 V vs SCE at a scan rate of 0.025 V s⁻¹. The geometric surface area of the GC electrode is 0.071 cm².
carbon (GC) electrode surfaces as the benefits of using CV have already been mentioned previously.

In addition to producing good electrodeposited metal films by CV, there are various experimental parameters which have to be considered such as the CV parameters during the electrodeposition process, electrolyte composition, pH, or addition of organic compounds. These factors are believed to be widely known to influence the nucleation and growth of nanoparticles that relates to the size, particle density, and morphology of the electrodeposited AuNP films on the electrode surface. Nevertheless, among the factors mentioned above, in this current study, we are only interested in investigating the effect of various background electrolyte solutions at different pH values on the nanostructure morphologies and electrochemical responses of the AuNP-modified GC electrodes by using a simple preparation method for obtaining electrodeposited AuNPs on GC electrodes. Exploring the use of background electrolytes in the electrodeposition of Au nanoparticles may offer major advantages during the electrodeposition process, in particular, improvement for the conductivity of the electrolyte solution, desolvation of AuCl$_4^-$ anions in the background electrolyte, solvation shell structure, electron-transfer kinetics of the metal reduction reaction, diffusional properties of metal ions in the solvent, and the double-layer structure that can alter the solvent adsorption.

Based on the intensive literature search, studies to date show that there are extensive publications on the applications of AuNPs in electroanalysis and electrocatalysis. Nevertheless, the aim of the present work is to highlight that the film of electrodeposited AuNPs on the GC electrode surface can be obtained as a better, uniform, and homogeneous film using the CV technique, and investigate the effect of different background electrolytes on the formation of the electrodeposited AuNP films. For broad applications of the electrodeposited AuNP film over the modified electrodes, a basic understanding of the preparation of the electrodeposited AuNP film in an electrolyte solution is required. This may help in tuning the electrodeposition conditions to acquire a better nanostructure morphology and the best electrochemical performance on the modified electrodes. Potassium nitrate (KNO$_3$), nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), sodium nitrate (NaNO$_3$), and sodium hydroxide (NaOH) are the background electrolytes used in this study. Preparation of the electrodeposited AuNPs on the GC electrode in a NaOH solution was chosen as the control experiment because the electrodeposition process may have similar thermodynamics, which has resulted in easier nucleation and growth of the AuNPs on the GC electrode surfaces.

Interestingly, the golden films on the surface of GC electrodes after the electrodeposition process can be observed by the naked eye. The shifting of the cathodic peaks to more positive values was observed after the fourth scan compared to the first scan in these voltammograms. The peak position shifted from 0.761 to 0.774 V for (A), 0.735 to 0.749 V for (B), 0.742 to 0.757 V for (C), and 0.742 to 0.753 V for (D). This shifting indicates that the electrodeposition of Au for the following scans occurred on the nanoparticle layer formed after the first scan. This peak shift is in agreement with the results obtained by Maringa et al. Besides, the cathodic currents are decreased in the second scan and then stabilized. This can be attributed to the fact that after the first scan the ECSA of the GC electrode has been fully covered by the electrodeposited AuNP film.

Based on these CV behaviors, as shown in Figure 1A–D, it is clear that there is no significant change in terms of the electrodeposition of AuNPs onto the GC surfaces using different background electrolytes. The reduction potential for all cyclic voltammograms was around 0.735–0.76 V versus SCE in neutral and acidic conditions. This indicates that the electrodeposition process may have similar thermodynamics, which has resulted in easier nucleation and growth of the AuNPs on the GC electrode surfaces. Additionally, it can be concluded that reaction R1 is pH independent. There are also no significant changes in the cathodic currents as shown in the CVs. Based on these data, we suggest that the electrodeposited AuNP films prepared in KNO$_3$, HNO$_3$, H$_2$SO$_4$, and NaNO$_3$ on the GC electrode surfaces may have the same surface morphologies for the Au nanostructures in terms of their nanoparticle sizes and densities. Nevertheless, a clearer understanding of the size and density of the AuNP deposits can only be found when analyzing morphological images for each AuNP film obtained through SEM analysis.

Meanwhile, as shown in Figure 1E, the electrodeposited AuNP film prepared in 0.1 M NaOH shows that the peak of the Au$^{+}$/Au reduction process is significantly shifted to a more negative potential from $-0.135$ V (first scan) to $-0.121$ V (fourth scan). Additionally, the cathodic currents are increased from the first cycle to the fourth cycle. This dictates that the proper growth of the AuNPs on the GC electrode occurs after the second cycle. However, the cathodic currents increase slowly because more electroactive surface sites of the GC electrode are still available. This can be seen more obviously when we discuss our results obtained from the SEM images.

**SEM Analysis.** SEM is one of the beneficial techniques to characterize the size and shape of electrodeposited metal nanoparticles. To investigate in-depth the formation and the surface morphologies of the electrodeposited AuNP films, SEM analyses were carried out. The analyses were done at two different magnifications; 30,000× (A) and 60,000× (B). Figure 2 shows the SEM images of the electrodeposited AuNP films prepared in different background electrolytes.

From the images (I–IV), it is obvious that the shapes of the obtained nanoparticles are hemispherically shaped Au nanoparticles with a variety of AuNP sizes and population densities. The AuNP sizes were also determined in the SEM analyses, using ImageJ software based on the analysis of 200 nanoparticles which showed the particle sizes ranging approximately from 65 to 290 nm for (I), 50 to 110 nm for (II), 60 to 126 nm for (III), 36 to 60 nm for (IV), and 230 to 500 nm for (V).

**RESULTS AND DISCUSSION**

**Electrodeposition of AuNPs onto the GC Electrode Surfaces.** Figure 1 shows the cyclic voltammograms of the electroreduction of 3 mM HAuCl$_4$ solution in different types of supporting electrolytes; (A) 0.1 M KNO$_3$, (B) 0.1 M HNO$_3$, (C) 0.1 M H$_2$SO$_4$, (D) 0.1 M NaNO$_3$, and (E) 0.1 M NaOH. The reduction peaks were observed in these voltammograms, indicating the reduction of Au(III) to Au(0). The reduction of Au is shown in reaction R1.

\[
\text{AuCl}_4^-(aq) + 3e^- \rightarrow \text{Au(s)} + 4\text{Cl}^- \quad \text{(R1)}
\]
585 nm for (V). The size distribution data patterns can be seen in Figure 3A−E. Interestingly, the surface morphology of the electrodeposited AuNP film prepared in NaNO₃ shows homogeneously distributed and well-dispersed Au nanoparticles compared to the other AuNP films, followed by HNO₃, H₂SO₄, KNO₃, and NaOH. Also, the electrodeposited AuNPs show higher particle population density with a smaller AuNP size. This data pattern is also very similar to the electrodeposited AuNP film produced in HNO₃. This result has been expected as the preparation of the electrodeposited AuNPs in the NaNO₃ solution, which contains NO₃⁻ ions, avoids coalescence phenomena (aggregated growth), as discussed by Evrard et al.¹⁹ This suggests that the electrodeposition of AuNPs in NaNO₃ may favor instantaneous nucleation and growth.¹¹,²¹ However, this is not the case for the electrodeposition of AuNPs in KNO₃ as this method led to the sparse deposition of AuNPs with a bigger nanoparticle size, as displayed in Figure 2IA,B, and may favor progressive nucleation and growth.¹¹,²¹ In addition to that, from the SEM images, the resulting Au nanostructures can also be described as irregular shapes that led to a substantial deviation from circularity due to the aggregated growth of two neighboring AuNPs or amorphous atom clusters. This result is also similar to the deposited AuNPs prepared in H₂SO₄. On the contrary, Figure 2VA,B shows that the shape of the deposited AuNPs in alkaline solution (NaOH) led to “popcorn-like” aggregates, leading to the increased particle diameter as the GC electrode surface is very sparsely populated with quite bigger isolated AuNPs. Besides, as shown in Figure 2VB, the image clearly shows that some regions of the GC electrode surface are largely absent of any AuNP deposits. This clearly shows that the GC electrode surface is not completely covered by the electrodeposited

Figure 2. SEM images of AuNP-modified GC electrodes, electro-deposited in different background electrolytes, at two different magnifications. (I) 0.1 M KNO₃, (II) 0.1 M HNO₃, (III) 0.1 M H₂SO₄, (IV) 0.1 M NaNO₃, and (V) 0.1 M NaOH (control experiment). The SEM images were taken at magnifications of (A) 30,000× and (B) 60,000×.

Figure 3. Particle size distributions for the electrodeposited AuNPs on GC electrode surfaces, analyzed using ImageJ software: (A) prepared in 0.1 M KNO₃, (B) prepared in 0.1 M HNO₃, (C) prepared in 0.1 M H₂SO₄, (D) prepared in NaNO₃, and (E) prepared in NaOH.
AuNPs. Thus, a poor AuNP population density was obtained. This occurrence could be due to the reduction of the \( \text{Au}^{3+} \) solution to deposited metal Au, which occurred at a more negative potential (lower cathodic overpotential).\textsuperscript{20} In addition, the electrodeposition mechanism may favor inconclusive nucleation and growth\textsuperscript{11} due to the distorting from the limiting nucleation mechanisms of Scharifker and Hills' models (instantaneous and progressive). This can be concluded that the nucleation and growth of the AuNPs did not follow either of the nucleation mechanisms and it may happen due to slower growth and faster growth of nuclei particles on the active sites being activated at the same reaction time during the reduction reaction. This leads to a high agglomeration and aggregation of AuNPs and random distribution on the GC electrode surface, as already shown in Figure 2VA,B. Nevertheless, this can only be verified through a theoretical study by conducting the electrodeposition process of the AuNPs using a chronocoulometric technique. However, this is beyond the scope of the current study. Based on these findings, we conclude that the improved and uniform dispersion of the AuNPs electrodeposited on the GC electrode surface is attributed to the nitrate ions (\( \text{NO}_3^- \)). A similar effect of \( \text{NO}_3^- \) anions in

\[
\text{KNO}_3 \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \quad \text{NaNO}_3 \quad \text{NaOH}
\]
background electrolytes on the nanostructure morphology of the SnO2 nanoparticles was reported by Raj et al. However, this is not the case for the deposited AuNP film synthesized in KNO3. This could be due to the effect of the zeta potential (ζ-potential), where it has been widely used as an indicator for the dispersion stability of nanoparticles. Thus, the distribution of AuNPs onto the surface of the GC electrodes during the electrodeposition process may also be affected by the ζ-potential, which has been influenced by the different types of the supporting electrolytes. In principal, a lower ζ-potential will result in a high degree of the dispersion, aggregation, and agglomeration of nanoparticles during the nucleation and growth processes. Hence, we expect that the ζ-potential magnitude during the electrodeposition of AuNPs in KNO3 may be smaller than that for the electrodeposition of AuNPs in NaNO3. This led to different dispersions, aggregations, and agglomerations of AuNPs as shown in the SEM analysis. Nevertheless, the ζ-potential analysis was not carried out as it is beyond the subject of the present study.

AFM Analysis. To get a further understanding of the AuNP-modified GC electrodes, AFM measurements are also conducted to investigate the layer thickness as depicted in 3D-AFM images, shown in Figure 4. Because there are varying surface morphologies of the deposited AuNP films from the SEM images, the AFM measurements were scanned at 10 μM × 8 μM. A smaller area of the scan was analyzed to yield a better representation of the surface via the 3D-AFM image. Through the AFM analyses, the maximum height profiles (Rpv) of the deposited AuNP films, the difference between the lowest point and the highest point from the deposited AuNP films, were obtained and are reported in Table 1. The Rpv can also be considered as the layer thickness of the electro-deposited AuNP film. Based on the 3D-AFM images and the Rpv values, the resulting patterns are in agreement with the SEM images. The largest nanoparticle size was shown for the control and AuNP-modified GC electrodes, thus a higher Rpv value was obtained. This can also be illustrated through the shades of blue color on the 3D-AFM image. The blue color represents the GC electrode surface. When there was very sparse deposition of AuNPs on the GC electrode surface, a more intense blue color appeared on the 3D-AFM image. Interestingly, it can be associated with the Rpv values of the deposited AuNPs. The Rpv values listed in Table 1 show a variety of Rpv values for all the electrodes. Thus, it can be concluded that a more intense blue color is seen in the 3D-AFM image, thus a bigger Rpv value is obtained. To investigate whether the obtained Rpv values alter the electrochemical performance of the modified electrodes, electrochemical characterizations utilizing CV and EIS techniques were conducted.

ECSA and Roughness Factor of AuNP-Modified GC Electrodes. As the Au oxide reduction peak of the process of cleaning Au in sulfuric acid (H2SO4) is obtained, as shown in Figure 5A,19 the Faradaic charge passed up during the reduction at a scan rate of 0.1 V s−1 can be obtained. By integrating the area under the reduction peak, the ECSA and electrode surface roughness (connected as the roughness factor, ρ) of the electrodeposited AuNP film can approximately be calculated using eqs 1–3, respectively

\[
\text{charge} \ (Q_{\text{real}}) = \frac{\text{integrated area under reduction peak}}{\text{scan rate of CV}}
\]

\[
\text{real electroactive surface area (ECSA)} = \frac{Q_{\text{real}}}{Q_{\text{theoretical}}}
\]

\[
\text{roughness factor} \ (\rho) = \frac{\text{ECSA}}{A_{\text{geo}}}
\]

where \(Q_{\text{real}}\) is the Faradaic charge passed up during the experiment, \(Q_{\text{theoretical}}\) is the theoretical charge density of Au given in the literature as 390 μC cm−2,24 and \(A_{\text{geo}}\) is the geometric surface area of the GC electrode. The calculated ECSA and ρ are then shown in Figure 5B,C, respectively. Although different surface morphology structures have been observed via the SEM images for the deposited AuNP films, there is no significant difference in the ECSAs of the AuNP-modified GC electrodes when electrodepositing AuNPs in KNO3, HNO3, H2SO4, and NaNO3, as depicted in Figure 5B. Nevertheless, there are significant differences in the deposited

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Table 1. Rpv Values for the Electrodeposited AuNP Films on the Control and AuNP-Modified GC Electrode Surfaces

| AuNP-modified GC electrode | Rpv (nm) |
|----------------------------|---------|
| prepared in KNO3           | 230.10 ± 4.50 |
| prepared in HNO3           | 137.33 ± 7.57 |
| prepared in H2SO4          | 175.55 ± 4.54 |
| prepared in NaNO3          | 78.36 ± 1.73 |
| prepared in NaOH (control electrode) | 624.61 ± 43.52 |

"Data shown as mean ± SD and n = 3."
AuNPs in NaOH (control experiment) when compared to the deposited AuNP films in KNO₃, H₂SO₄, and NaNO₃ (p < 0.001, n = 3) and HNO₃ (p < 0.01, n = 3). From the estimated ECSA, the roughness factor for each deposited AuNP film can be estimated, as shown in Figure 5C. As expected the same data pattern as the ECSA was obtained. From the results shown in Figure 5B,C, it can be concluded that preparing electrodeposited AuNPs on the GC electrodes in neutral and acidic solutions (KNO₃, HNO₃, H₂SO₄ and NaNO₃) does not significantly affect the ECSA and the roughness factors of the modified electrodes even though they have distinct surface morphologies of the deposited films as already shown by the SEM and AFM images. Additionally, it is clear that the electrodeposited AuNPs, synthesized in the NaOH solution, are not fully covered on the GC electrode surface, thus the data trends shown in Figure 5B,C have been expected. This is because we normalized the ECSA to the geometric surface area of the GC electrode (3 mm, 0.071 cm²). To accurately determine the ECSA provided by the deposited AuNPs, we then normalized the calculated ECSA to the mass of the electrodeposited AuNPs.42,43 As the reduction of the Au oxide layer involves a one-electron transfer, as illustrated in reaction R2.

\[
\text{Au(OH)} + e^- \rightarrow \text{Au}^+ \text{OH}^- \tag{R2}
\]

Then using the Faraday law \((Q = nmF)\), where \(n\) is the number of electron(s) transferred, \(m\) is the number of moles, and \(F\) is the Faraday constant, the mass of the electrodeposited AuNPs can be calculated. The calculated mass can be found in Table S1 (Supporting Information). This assisted us to normalize the current response and ECSA to the mass of electrodeposited AuNPs, as shown in Figure 6A,B, respectively. From the normalization, it is found that the normalized ECSAs (m² g⁻¹) for all the electrodeposited AuNPs are the same. This signifies that the variety of the supporting background electrolytes used in this study does not change the normalized ECSA but only affects the nucleation and growth processes, and distribution of AuNP deposits. Both the aspects could result in the agglomeration, aggregation, and dispersion of the electrodeposited AuNPs on the GC electrode surface.

**CV Responses in [Fe(CN)]₃⁻⁴⁻ Solution.** To investigate the performance of the AuNP-modified GC electrodes, the modified electrodes were measured in 100 mM [Fe(CN)]₃⁻⁴⁻ solution using CV, as shown in Figure 7A. There are two major significant changes observed from the cyclic voltammograms in the presence of the deposited AuNPs on the GC electrode. First, CV peak currents are drastically improved. The oxidation and reduction currents of the AuNP-modified GC electrodes are considerably increased compared to the redox currents from the bare GC and control electrodes, as shown in Figure 7B,C. The electrochemical performance of the control electrode (prepared in NaOH) will not be discussed in detail as more vacant spots are noticed. This is because the deposited AuNPs do not fully cover the GC electrode surface. Although the modified and control electrodes have had the same ECSA (m² g⁻¹), the increase of the CV peak currents can be explained by the good electrical contact of AuNPs within the films, which can significantly increase the electrical conductivity of the modified electrodes. However, this is not the case for the deposited AuNP film (control electrode) as more vacant spots within the AuNP film (shown in Figures 2VA and 4E) gave a poor electrical contact between AuNPs, resulting in the low conduction within the AuNP film and thus decreasing the electrical conductivity of the electrode surface. From the statistical analyses of \(i_p\) and \(i_c\) there are significant differences in the \(i_p\) and \(i_c\) of the AuNP-modified GC electrodes prepared in KNO₃, HNO₃, H₂SO₄ and NaNO₃ solutions when compared to the bare, GC electrode (p < 0.001, n = 3), and control electrode (p < 0.001, n = 3). However, there is no significant difference in the \(i_p\) and \(i_c\) of the bare GC electrode when compared to the control electrode.

Furthermore, the anodic and cathodic peak potentials, \(E_{pa}\) and \(E_{pc}\) of the AuNP-modified GC electrodes, are shifted to each other compared to the bare GC electrode. From the \(E_{pa}\) and \(E_{pc}\) values, the peak separation, the \(E_{pa} - E_{pc}\) for each type of electrode was obtained and are shown in Figure 7D. The \(E_{pa} - E_{pc}\) can be related to the electron-transfer kinetics of the electrode. If there is a reduction in the peak separation value in which the peak separation is getting closer, it means that the electrode facilitates the fast electron transfer of [Fe(CN)]₃⁻⁴⁻ ions.27 In contrast, if there is an increase in \(E_{pa} - E_{pc}\), this means that the electrode surface tends to undergo redox reactions with sluggish electron transfer.28,29

Moreover, in Figure 7D, there are significant differences in the \(E_{pa} - E_{pc}\) of the AuNP-GC electrodes when compared to the bare GC electrode (p < 0.001, n = 3) and control electrode (p < 0.01, n = 3). Thus, this exhibits that the AuNP-modified GC electrodes greatly facilitated the electron transfer of [Fe(CN)]₃⁻⁴⁻ and are better than the bare GC electrode although they have distinct surface morphologies. In other words, the AuNP-modified GC electrodes give faster electron-
transfer kinetics for $[\text{Fe(CN)}_6]^{3-/4-}$ compared to the bare GC electrode. Nevertheless, there is no significant change in the $E_{pa} - E_{pc}$ between the AuNP-modified GC electrodes. This concludes that the preparation of the electrodeposited AuNP films obtained in different background electrolyte solutions does not considerably affect the electrochemical performance of the AuNP-modified GC electrodes. Nevertheless, as previously discussed in the SEM and AFM analyses, this factor only affects the surface morphologies of the deposited AuNP films. To confirm this statement, we will discuss in detail in the next section when presenting our data on EIS spectra by showing Nyquist and Bode plots for each type of electrode. This leads to the heterogeneous rate of electron transfer ($k^*$) for reversible redox reactions of the $[\text{Fe(CN)}_6]^{3-/4-}$ ions to be calculated based upon charge-transfer resistance ($R_{ct}$).

Additionally, from the obtained $E_{pa}$ and $E_{pc}$ for each different type of electrode, the mid potential ($E_{mid}$) can be calculated and also compared, as shown in Figure 7E. For the $E_{mid}$ of the AuNP-modified GC electrodes (produced in HNO$_3$ and NaNO$_3$), there are significant differences when compared to the bare GC electrodes ($p < 0.01$) and control electrodes ($p < 0.05$). On the contrary, in the case of AuNP films electrodeposited in H$_2$SO$_4$, there is no significant difference when compared to the $E_{mid}$ of the bare GC electrode, control electrode, and AuNP-modified GC electrodes (prepared in

Figure 7. (A) Cyclic voltammograms (second cycle shown) of bare, control, and AuNP-modified GC electrodes in the 100 mM $[\text{Fe(CN)}_6]^{3-/4-}$ solution by cycling the potential from $-0.4$ to $0.9$ V vs SCE at a scan rate of 0.1 V s$^{-1}$. (B-E) Anodic current ($i_{pa}$), cathodic current ($i_{pc}$), peak separation ($E_{pa} - E_{pc}$), and mid potential ($E_{mid}$) of the bare, control, and AuNP-modified GC electrodes, respectively. Statistical analyses were performed using the post hoc Tukey test. Data are shown as mean ± SD; $n = 3$; and * denotes $p < 0.05$, ** denotes $p < 0.01$, and *** denotes $p < 0.001$. 

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Interestingly, for the \( E_{\text{mid}} \) of deposited AuNPs in NaNO\(_3\), there is a significant difference (\( p < 0.05 \)) when compared to deposited AuNPs prepared in KNO\(_3\). This result has been expected, as there is a significant difference in the nanostructure surface morphologies between the two deposited AuNP films. This dictates that the AuNP-modified GC electrode produced from the NaNO\(_3\) solution is more thermodynamically favorable for the redox reactions of the \([\text{Fe(CN)}_6]^{3-/4-}\) ions.\(^{30}\)

**EIS for AuNP-Modified GC electrodes.** EIS is an electrochemical technique that can be used to investigate the electron-transfer kinetics and diffusion coefficients of the \([\text{Fe(CN)}_6]^{3-/4-}\) ions on the AuNP-modified GC electrodes. There are two common plots used in EIS measurements, Nyquist plots and Bode plots. The Nyquist plot consists of the negative imaginary part \(-Z''\) versus the real parts \(Z'\) of the electrode impedance, as illustrated in Figure 8A. The semicircle and linear line in the Nyquist plot can monitor the charge-transfer resistance (\( R_{\text{ct}} \)) and diffusion process at the electrode/electrolyte interface, respectively. The \( R_{\text{ct}} \) essentially provides us with information about electron-transfer kinetics of \([\text{Fe(CN)}_6]^{3-/4-}\) on the electrode surface. In contrast, in a different physicochemical process, the diffusion process from the bulk solution to the electrode surface can be connected to the Warburg (\( W \)) constant element exhibited in a linear line in the Nyquist plot. Meanwhile, the Bode plot consists of the phase angle (\( \theta \)) versus log frequency (Hz) (Figure 8B). The Bode plot can also be used to study and support the data obtained from the Nyquist plot.\(^{31,32}\)

Thus, to further study the electrochemical behaviors for each type of electrodes, EIS measurements were conducted in a 100 mM \([\text{Fe(CN)}_6]^{3-/4-}\) solution and then compared with the bare GC and control electrodes. Figure 8A,B shows the Nyquist and Bode plots for the bare GC, control, and AuNP-modified GC electrodes.

Based on the Nyquist plots in Figure 8A, the semicircles of the AuNP-modified GC electrodes are getting smaller when compared to the bare GC electrode. This indicates that by the presence of the deposited AuNP films on the GC electrode surfaces, the \( R_{\text{ct}} \) values are significantly reduced.\(^{33}\) The decrease in the \( R_{\text{ct}} \) values led to the greater enhancement of the electron-transfer kinetics of the \([\text{Fe(CN)}_6]^{3-/4-}\) at the AuNP-modified GC electrode surfaces. This data trend is supported by the data observed in the Bode plots, as shown in Figure 8B. As shown in the Bode plots, the phase angles (\( \theta \)) of the AuNP-modified GC electrodes are shifted to a higher frequency compared to those of the bare GC and control electrodes. This indicates the enhancement of the electron-transfer kinetics with the AuNP-modified GC electrodes,\(^{34}\) resulting in the improvement of the electrical conductivity of the electrode surfaces through good electrical contact within the deposited AuNP films.

To obtain physical parameter values such as the \( R_e \) and \( R_{\text{ct}} \), the EIS spectra for the bare GC, control, and AuNP-modified GC electrodes were fitted to the equivalent circuits, as shown in Figure 8.
suggested in Figure 9A,B, respectively. The circuit shown in Figure 9A is employed to convergently fit the EIS spectra from

![Figure 9](image)

the bare GC and control electrodes. Meanwhile, the circuit shown in Figure 9B is employed to convergently fit the EIS spectra from the AuNP-modified GC electrodes. In the case of the control electrode, the EIS spectrum only convergently fits the equivalent circuit, as suggested in Figure 9A. This is because more vacant spots from the ECSA of the GC electrode are observed, as can be seen in the SEM and AFM images (Figures 2V and 4E). Hence, the electrochemical interface system may still be dominated by the ECSA of the GC electrode. Additionally, the $R_q$, $C_{dl}$, CPE, $R_{ct1}$, $R_{ct2}$, and $Y_o$ values were obtained over the EIS fittings, as shown in Tables S2−S7 (Supporting Information).

The obtained parameter values, $R_q$ and $R_{ct}$, are displayed in bar graphs, as shown in Figure 8C,D, respectively. There is no significant difference in the $R_q$ values for the AuNP-modified GC electrodes compared to bare GC and control electrodes. There is also no significant difference in the $R_q$ values when compared to each type of AuNP-modified GC electrodes. Meanwhile, as shown in Figure 8D, there are significant differences for AuNP-modified GC electrodes for the $R_{ct}$ values when compared to the bare GC electrode ($p < 0.001$, $n = 3$) and control electrode ($p < 0.001$, $n = 3$). The $Y_o$ values of the AuNP-modified GC electrodes are decreased significantly when compared to the bare GC electrode. This indicates that the presence of the deposited AuNP films has greatly enhanced the electron-transfer kinetics of $[\text{Fe(CN)}_6]^{3−/4−}$ ions through the improved electrical conductivity of the modified electrodes by the nanoparticles formed. Moreover, comparing the $R_{ct}$ values for each different type of AuNP-modified GC electrodes, there is no significant difference in the $R_{ct}$ values. This shows that having diverse surface morphologies for the electrodeposited AuNP films does not result in the superior alteration of the electrochemical performance of the modified electrode, particularly the electrode kinetics. This is because the deposited AuNP films have no significant difference in the normalized ECSA ($m^2\cdot g^{-1}$). This resulting pattern is in accordance with the data obtained from the CV measurements, where there is no significant difference in the $i_{pa}$, $i_{pc}$, and $E_{pa} − E_{pc}$ for the AuNP-modified GC electrodes.

As we have already obtained the $R_q$ value from the fitted EIS spectra, the $k_o$ value for a mixture of $[\text{Fe(CN)}_6]^{3−/4−}$ ions can be calculated by using eq 4. The equation only works when the concentration of the redox probe is in equimolar concentrations for oxidized and reduced species on the electrode surface.

$$R_q = \frac{RT}{n^2F^2AC_k^2}$$

where $R$ is the gas constant, $T$ is the temperature in K at room temperature, $A$ is the geometric surface area of the electrode, $n$ is the number of the electron(s) transferred in the redox reactions, $F$ is the Faradaic constant, $C$ is the concentration of $[\text{Fe(CN)}_6]^{3−/4−}$ solution in mol cm$^{-3}$, and $k_o$ is the heterogeneous electron-transfer rate constant of $[\text{Fe(CN)}_6]^{3−/4−}$ between the bulk solution and the electrode surface. The $k_o$ values for each type of electrodes were obtained from the analysis, as illustrated in Figure 10.

![Figure 10](image)

Based on Figure 10, there are significant differences in the $k_o$ values when compared to the $k_o$ values of the bare GC ($p < 0.001$) and control electrodes ($p < 0.001$). However, there is no significant difference for the $k_o$ values of AuNP-modified GC electrodes, although the obtained deposited AuNP films clearly show that they have different nanostructure morphologies. Comparing the obtained $k_o$ value of the bare GC electrode ($3.09 \pm 0.14 \times 10^{-4}$ cm s$^{-1}$) to the $k_o$ values of the AuNP-modified GC electrodes, the $k_o$ magnitudes between $10^{-3}$ and $10^{-2}$ cm s$^{-1}$ are obtained. This result shows that the electrodeposited AuNPs on the GC electrode surface greatly improved the electrode kinetics for redox reactions of the $[\text{Fe(CN)}_6]^{3−/4−}$ ions at the electrode/electrolyte interface by considerably improving the electrical conductivity of the modified electrodes to allow better electron tunneling at the interface. Essentially, for the modified electrode surface-based metal nanoparticles, the electron transfer from the modified surface to redox species in solution is via tunneling and heterogeneous electron transfer. By having deposited AuNPs on the GC electrode surface, more delocalized electrons surrounding the AuNP film will be achieved. This event provides energetic clouds of the delocalized electrons on the
electrode surface. Instantaneously, this improves the electrical conductivity of the modified electrode surface significantly and leads to an increase of electron tunneling, which subsequently enhances electron-transfer kinetics of $[\text{Fe(CN)}_6]^{3−/4−}$ on the AuNPs-modified GC electrode surface during the redox reactions. However, this is not the case for the control electrode as the electrical conductivity is still dominated by the GC electrode surface, although the normalized ECSA ($m^2g^{−1}$) of the control electrode is similar to the normalized ECSA of the AuNP-modified GC electrodes. This data trend is strongly supported by the fitted EIS spectra for the control electrode, where the equivalent circuit, as suggested in Figure 9A, was employed.

**CONCLUSIONS**

In summary, the electrodeposited AuNP films on the GC electrode surfaces, produced in different supporting background electrolytes (KNO$_3$, HNO$_3$, H$_2$SO$_4$, and NaNO$_3$) were successfully synthesized by using the CV technique. Through SEM analysis, sputtered-like AuNP with different surface morphologies and nanoparticle size distributions were observed for all the AuNP-modified GC electrodes. The SEM and 3D-AFM images showed that the AuNP-modified GC electrode prepared in NaNO$_3$ exhibited the best surface morphology with a uniform, well-dispersed, dense, and homogeneously deposited AuNP film. There has been no significant difference in the normalized ECSA ($m^2g^{−1}$) of all electrodeposited AuNPs based on the electrochemical characterization results from the measurements in 0.5 M H$_2$SO$_4$. Even though the modified and control electrodes have had the same ECSA ($m^2g^{−1}$), the electrochemical performances of the AuNP-modified GC electrodes are drastically improved compared to the control electrode when all the electrodes are investigated in $[\text{Fe(CN)}_6]^{3−/4−}$ solution by using CV and EIS. This has resulted in greatly enhanced electron-transfer kinetics of $[\text{Fe(CN)}_6]^{3−/4−}$ redox reactions, as shown by the obtained $R_\text{ct}$ and $k^*$ values from the EIS measurements. In contrast, there is no significant difference in the electrochemical performances between the AuNP-modified GC electrodes. Therefore, having the same ECSA for all the deposited AuNP films on the GC electrode surfaces shows that this is not the main factor for the great enhancement in the electrochemical performances of the electrodes. Nevertheless, we strongly affirm that the enhancement in the electrochemical performance of the modified electrode is mainly contributed by the good electrical conductivity of the electrode surface through better electrical contact within the AuNP films. This resulted in a significantly improved electrical conductivity of the modified electrode surfaces, which allows better electron tunneling at the electrode/electrolyte interface. However, this is not the case for the deposited AuNP film over the control electrode, as the deposited AuNPs are sparsely populated with quite bigger isolated AuNPs. Thus, more vacant spots within the AuNP film contribute to a poor electrical contact between AuNPs. This resulted in a decrease in the electrical conductivity of the electrode surface. Therefore, the fundamental findings in this study are greatly important to provide a key understanding of the electrodeposited AuNP films for CMEs, enabling the scientific community to rationally design their experiments for obtaining a well-deposited AuNP film for electroanalytical sensing platforms, electrocatalysis, and nanoelectronic studies.

**EXPERIMENTAL SECTION**

**Chemicals and Apparatus.** All the solutions for the electrochemical experiments were prepared using deionized water from a Millipore Direct-Q 3 water purification system. Gold(III) chloride trihydrate (99.9% purity), potassium nitrate (99.0% purity), sodium nitrate (99.0% purity), potassium chloride (purity 99%), nitric acid (65% purity), and sodium hydroxide (97% purity) were purchased from Sigma-Aldrich. Sulfuric acid (95−97% purity) was obtained from Fisher Scientific. Potassium ferrocyanide (purity 100%) and potassium ferricyanide (purity 100%) were purchased from Thomas Scientific. Ethanol (purity 99.9%) was purchased from QReC.

**GC Electrode Cleaning.** Prior to the electrochemical experiments, GC electrodes were freshly polished and cleaned to obtain a mirror clean surface. The GC electrode surfaces were polished with sandpaper (1200 grade) for 2 min, then using a lapping film (5 μm) for 2 min. GC electrodes were polished with 1.0 and 0.3 μm alumina powders on wet cloth polishing pads for 2 min, respectively. The polished surfaces were then subsequently rinsed with deionized water and ethanol solutions.

**Preparation of Au Electrodeposition Solutions.** 3 mM HAuCl$_4$·3H$_2$O was prepared by dissolving it in 0.1 M different electrolyte solutions (KNO$_3$, HNO$_3$, H$_2$SO$_4$, NaNO$_3$, and NaOH). The pH values of each supporting electrolyte were measured with a pH meter (Eutech Instrument) and the values are 6.76 for KNO$_3$, 1.93 for HNO$_3$, 2.22 for H$_2$SO$_4$, 7.11 for NaNO$_3$, and 13.07 for NaOH.

**Electrochemical Experiments.** All the electrochemical measurements, including CV and EIS, were performed by an Autolab PGSTAT204 potentiostat/galvanostat (Ecochemie) setup interfaced to a computer controlled by the NOVA 1.11 software package. The polished bare GC electrode, control, or AuNP-modified GC electrode acted as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All the electrochemical experiments were carried out at room temperature in a Faradaic cage.

**Electrodeposition of AuNPs onto GC Electrode Surfaces.** The electrodeposition of AuNPs onto the GC electrode surface was carried out using the CV technique with no adjustable CV parameters, in which the potential was cycled for four scans in the range of 0−0.9 V versus SCE at a scan rate of 0.025 V s$^{−1}$. In the case of electrodeposition of AuNPs in a NaOH solution (control electrode), the potential was cycled from 0.5 to −0.4 V versus SCE at a scan rate of 0.025 V s$^{−1}$ by continuously purging with N$_2$ gas. After the electrodeposition process was completed, the electrodeposited AuNP film on the GC electrode surface was gently rinsed with deionized water. Then, the AuNP-modified GC electrodes underwent a cleaning process in 0.5 M H$_2$SO$_4$ using CV at a scan rate of 0.1 V s$^{−1}$, cycling the potential from −0.2 to 1.2 V versus SCE.

**SEM and AFM Analyses.** The surface morphologies and layer thicknesses of the electrodeposited AuNP films at the GC electrodes were characterized by SEM and AFM. Removable GC electrodes with a head length of 5 mm were used for the SEM and AFM measurements.

**AFM analysis in this work was conducted using an XE-70 from Park System in the non-contact mode. The specifications of a PPP-NCHR cantilever were 2 nm radius and 125 μm length, with a force constant of 42 N/m and a resonance frequency of about 330 Hz. The measurement was conducted.
under ambient condition with a scan size of 8 μm × 10 μm, and scanning was achieved at a scan speed of 0.8 Hz. XEP software was used to adjust the feedback of parameters in real time, while electrodeposited AuNP films’ surface topography images and surface roughness (R_p) values were obtained using XEI software.

The surface morphologies and particle sizes were examined by SEM with a Quanta FEG 650, and xT microscope Server software was used to analyze the data. The head GC electrodes were placed in the SEM holder with double-sided electrically conducting carbon adhesive tape to prevent the surface charge forming from the samples when they were exposed to the electron beam at 15 kV. The particle size distribution was analyzed from the SEM images by counting 200 nanoparticles using ImageJ software.

Data Analyses. The electrochemical data were treated and analyzed using Origin 9.1 software. All the statistical differences between the data sets for bare GC, control, and AuNP-modified GC electrodes were analyzed using the post hoc Tukey test on GraphPad Prism 5.0. The EIS fittings were performed using NOVA 1.11 software (Metrohm Autolab). Data were presented as mean ± standard deviation (SD) and p < 0.05 was considered as significant.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02670.

Data for the mass of electrodeposited AuNPs and data for optimum fit parameters of EIS spectra (PDF)

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H.H.H. and N.D.Z. designed the experimental setup and methodology. N.D.Z., M.H.O., and N.N.A.K. conducted the preparation and electrochemical characterizations of the AuNP-modified GC electrodes. H.H.H., N.D.Z., M.H.O., T.S., and K.A.R. analyzed the data. N.D.Z., H.H.H., M.H.O., K.A.R., T.S., and V.B. prepared and edited the manuscript.

Notes
The authors declare no competing financial interest.

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