Fabrication and Electrocatalysis of Self-Assembly Directed Gold Nanoparticles Anchored Carbon Nanotubes Modified Electrode

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A self-assembly directed approach was adopted to modify glassy carbon electrode (GC) with gold nanoparticles incorporation and the electrocatalytic performance of self-assembly modified electrode, GC/SA-Au-ME was critically evaluated for the oxidation of ascorbic acid (AA). The modification involves the dispersion of multi-wall carbon nanotube (MWNT) and an inclusion complex, β-cyclodextrin-4-aminophenol on the surface of GC electrode in the presence of cetyltrimethylammonium bromide (CTAB). Gold nanoparticles were deposited into the self-assembled sites to fabricate the modified electrode, GC/SA-Au-ME. Another electrode (GC-Au-ME) was fabricated under similar conditions in the absence of CTAB. The electrocatalytic activity of the modified electrodes (GC/SA-Au-ME and GC-Au-ME) towards the oxidation of AA was critically compared. Cyclic voltammetry, chronocamperometry, and double potential chronocamperometry were used to evaluate the characteristics of the modified electrodes. The self-assembled electrode (GC/SA-Au-ME) shows excellent electrocatalytic activity over the other electrode, GC-Au-ME. Augmented current response, faster electron transfer kinetics (with a rate constant for electron transfer process as 3.25 × 108 cm3 mol−1 s−1), linear range of response for the analyte (1–50 mM with an extended detection limit to 1 μM), better sensitivity, and selectivity were witnessed for the self-assembly directed modified electrode.

Keywords: Self-Assembly, Gold Nanoparticles, Carbon Nanotube, Modified Electrode, Electrocatalysis.

1. INTRODUCTION

Materials composed of two- and three-dimensional self-assemblies of nanoparticles with narrow size distribution are becoming increasingly important in analytical and materials chemistry due to their practical applications in nanoelectronic and optoelectronic devices,1,2 chemical sensors, biosensors, and catalysts.3,4 Another wide field of technical applications, particularly in nanotechnology, is the development of new electro-analytical device applications. Electrostatic and covalent interactions of bi-functional groups on the substrates have been utilized for the self-assembly of individual nanoparticles into three-dimensional structures.5,9 It has been shown that the molecular dimension of self-assembled electrodes avoid slow diffusion of electroactive species towards the electrode surface and reduces the undesirable accumulation of species on or close to the electrode surface, which may lead to the electrode fouling. Additionally, fast electron transfer, good selectivity and high sensitivity can be easily achieved at the self-assembled electrodes.10,11

Gold nanoparticles have a large surface area and a good electronic property and are increasingly used in the construction of electrochemical sensors and biosensors.12,13 Au nanoparticles possess several advantages over other surfaces for self-assembly formation because of its intrinsic inertness in air and high conductivity. Self-assembled Au nanoparticles modified electrodes are usually fabricated by assembling Au nanoparticles electrode surfaces using organic linker molecules such as thiols and polymers.14-16 Monolayer protected Au nanoparticles possess a specific property of accumulating charge17-21 which makes them promising as new materials in the catalysis of electrochemical processes. Recently, carbon nanotubes (CNTs) have received much attention. The small
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dimensions, strength, and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications. The subtle electronic properties suggest that CNTs have the ability to promote electron-transfer reactions when used as an electrode in chemical reactions. CNTs possess good electrocatalytic activity compared with other carbonaceous materials such as glassy carbon, activated carbon, and pyrolytic graphite. An improved electrochemical behavior of catecholamine neurotransmitters, hydrogen peroxide, NADH, dopamine, epinephrine, ascorbic acid, uric acid, 3,4-dihydroxyphenylacetic acid, cytochrome c, glucose oxidase, azurin, hydrazine, and nucleic acid has been illustrated at CNT modified electrodes. There have been several studies on the dispersion of metal nanoparticles onto CNTs through impregnation or the electrochemical deposition method. These studies revealed that the pristine surface of CNT does not accommodate metal nanoparticles due to the hydrophobic nature of the surface. Chemical modification of the CNT surface is necessary to obtain good adhesion and dispersion of metal particles. Oxidation is an often-attempted method for functionalization where several oxidants such as H_2SO_4–HNO_3, HNO_3, K_2Cr_2O_7, and KMnO_4 have been used. Control of the particle size and dispersion of metal nanoparticles onto the surface of CNT are of prime importance and continue to receive attention as the metal nanoparticles distributed nanotube based composites are expected to find applications in catalysis, fuel cell, sensor etc.

In the present investigation, a novel self-assembly electrode was fabricated by depositing Au nanoparticles into the self-assembled units in the MWNT matrix. In the fabrication of the modified electrode, a mixture of an inclusion complex, \( \beta \)-cyclodextrin–4-aminothiophenol, and multi-wall carbon nanotube (MWNT), was self-assembled at the electrode/electrolyte interphase and used to anchor gold nanoparticles. The results revealed the successful fabrication of a self-assembled modified electrode with Au nanoparticles electrochemically deposited into the modified surface. The modified electrode thus fabricated is designated as GC-Au-ME.

2. EXPERIMENTAL DETAILS

2.1. Materials

Multi-wall carbon nanotubes (10–50 nm in diameter) obtained from CNT Co., Ltd, Incheon, Korea were rinsed with double-distilled water and dried. Cetyltrimethylammonium bromide, \( \beta \)-cyclodextrin, 4-aminophenol, auric acid, ascorbic acid, and dopamine of analytical grades were used as received. Double-distilled water was used throughout the experiments. Aqueous solutions of ascorbic acid were prepared in phosphate buffer (pH=7) refreshed at the time of experiments.

2.2. Fabrication of Self-Assembled Modified Electrode

Self-assembled modified electrode was fabricated through a sequence of steps.

2.2.1. Formation of Inclusion Complex

0.0626 g of 4-aminophenol (ATP) was dissolved in 10 mL of ethanol and added to an aqueous solution containing 0.5676 g of \( \beta \)-cyclodextrin (\( \beta \)-CD) in 40 mL of water. A homogenous solution was obtained after stirring. After distilling the solvents, under reduced pressure a white powder, inclusion complex of \( \beta \)-CD with ATP (CD-ATP-IC) (Scheme 1A) was collected. The powder was washed with acetone to remove the excess ATP and dried to obtain the powder of CD-ATP-IC.

2.2.2. Modification of Glassy Carbon Electrode

A suspension was prepared by mixing 1 mg of MWNT in 0.5 M cetyltrimethylammonium bromide and 1 mg of the inclusion powder (CD-ATP-IC). About 5 \( \mu \)L of the suspension was dropped on the surface of GC electrode and the electrode was kept at 60 °C for 12 h to evaporate the solvent. The electrode was washed with water and stored under nitrogen atmosphere. Au particles were electrochemically deposited into the modified surface from 0.5 M H_2SO_4 solution of HAuCl_4 by employing a repetitive potential scan from 1.1 V to 0.0 V (vs. SCE) and thus a self-assembled modified electrode (GC/SA-Au-ME). Au particles incorporated MWNT through a self-assembly of CD-ATP-IC (Scheme 1B), was fabricated and used. Formation of GC/SA-Au-ME is illustrated in Scheme 1. Also, another modified electrode was fabricated wherein MWNT and CD-ATP-IC were mixed and formed as a paste in the absence of CTAB. The paste was applied over the GC electrode. Au particles were electrochemically deposited into the modified surface. The modified electrode thus fabricated is designated as GC-Au-ME.

2.3. Electrochemical Measurements Using Modified Electrodes

Cyclic voltammetric measurements were performed using EG & G PAR 283 Electrochemical Analyzer. A conventional three-electrode assembly was used. Au nanoparticles modified electrode (GC/SA-Au-ME or GC-Au-ME) was used as the working electrode. SCE and platinum wire were used as reference and counter electrodes, respectively. Chronoamperometry experiments were carried out at an applied potential of 200 mV versus SCE under stirring (150 rpm). After the background current decayed to a steady value, aliquot amount of AA solution...
was added and the steady state current values corresponding to the electrocatalytic oxidation of AA were recorded.

3. RESULTS AND DISCUSSION

3.1. Formation of Self-Assembled Modified Electrode

The strategy of fabricating the modified electrode via self-assembly is as follows. In the fabrication of GC/SA-Au-ME, before the deposition of Au atoms, MWNT was dispersed in cetyltrimethylammonium bromide (CTAB), a cationic surfactant and mixed with an inclusion complex, CD-ATP-IC (Scheme 1A), and applied as a suspension over the surface of GC electrode. When the GC electrode covered with a mixture of MWNT in CTAB and CD-ATP-IC was placed in the electrolyte bath for the electro-deposition of Au atoms, the inclusion complex configured into a self-assembled structure (Scheme 1) at the surface of the electrode due to the micellar environment. In the micellar environment, the hydrophobic part of CTAB is expected to orient toward MWNT and the hydrophilic part of CTAB is expected to project toward the electrolyte phase. During the electrolysis of HAuCl$_4$, Au atoms are preferentially anchored into the –SH sites (Scheme 1B). Thus, a modified electrode with Au atoms distributed into the matrix of MWNT through a self-assembly of CD-ATP-IC, was fabricated. Attachment of Au atoms into self-assembled –SH groups is well known. AFM measurement (Fig. 1) was employed to investigate the attachment of Au nanoparticles on the surface of GC/SA-Au-ME. As shown in Figure 1, a relatively high-coverage of ordered monolayer of Au nanoparticles was observed with an average size of ~15–20 nm for Au nanoparticles. However, Au nanoparticles were observed as aggregates with a size much higher than 50 nm (figure not shown). Further, the presence of Au nanoparticles on the GC/SA-Au-ME was confirmed by XPS analysis. The XPS spectrum of GC/SA-Au-ME (Fig. 2) clearly shows the presence of doublet Au (4f$_{7/2}$ and 4f$_{5/2}$) peaks centered at 83.3 eV and 87.9 eV, respectively. The absence of aggregation of Au atoms at the surface of electrode, GC/SA-Au-ME, as inferred from AFM image of the modified electrode in which Au atoms were deposited in the presence of CTAB, (Fig. 1) clearly supports the incorporation of Au atoms in MWNT matrix through self-assembly of inclusion complex, CD-ATP-IC.

The self-assembly approach in the GC/SA-Au-ME induces few interesting features to the modified electrode. Generally, Au atoms could not be deposited uniformly in
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**Fig. 1.** AFM image of GC/SA-Au-ME.

**Fig. 2.** XPS spectrum of GC/SA-Au-ME showing the Au(4f 7/2) and Au(4f 5/2) double peaks.

GC electrode or dispersed into MWNT. This has been ascribed due to the hydrophobic environment in GC or MWNT. We have successfully deposited Au nanoparticles (15–20 nm) onto MWNT via the self-assembly of the inclusion complex and modified the GC electrode. However, when deposition of Au was performed on the GC electrode covered with CD-ATP-IC in the absence of CTAB, aggregates of Au atoms were witnessed. GC/SA-Au-ME is expected to have higher active area for electrocatalytic reactions than GC-Au-ME. The self-assembly directed Au deposited GC modified electrode is therefore expected to show superior performance in the electrocatalytic reactions, typically, oxidation of AA in the present study.

Cyclic voltammograms (CVs) of GC/SA-Au-ME and GC-Au-ME (Fig. 3) recorded in N₂ saturated 1 M H₂SO₄ solution informed that GC/SA-Au-ME has higher electroactive surface over the GC-Au-ME. Figure 3 provides evidence for the superior electrocatalytic performance of GC/SA-Au-ME over the other electrode, GC-Au-ME from the analysis of active surface area at these electrodes. The
active surface area was evaluated from the coulombic integration of the reductive waves of gold oxide. The active surface area for GC/SA-Au-ME was found to be three times higher than GC-Au-ME. It can be seen from Figure 3 that the active surface area of the GC/SA-Au-ME to GC-Au-ME is 3.1:1. It is to be envisioned that the surface sites for GC/SA-Au-ME is the consequence of uniformly distributed Au nanoparticles at the electrode surface due to the deposition of Au atoms through the self-assembly (Scheme 1).

We have compared the electrocatalytic performance of GC/SA-Au-ME over the GC-Au-ME by performing oxidation of ascorbic acid at these modified electrodes. CVs were recorded at the modified electrodes, GC/SA-Au-ME and GC-Au-ME, in a phosphate buffer (pH = 7). Figures 4A and 4B show the CVs of 7 mM AA at GC/SA-Au-ME and GC-Au-ME, respectively. GC/SA-Au-ME showed pronounced electrocatalytic effect for the oxidation of AA in comparison to GC-Au-ME. It can be seen from Figure 4B that the oxidation peak of AA is broad and observed at 275 mV at GC-Au-ME. In contrast, the oxidation current increased greatly and the peak potential shifted negatively to 202 mV at GC/SA-Au-ME (Fig. 4A). The increased peak current and the decrease in anodic overpotential of about ~70 mV for the electrooxidation of AA indicate the better electrocatalytic activity of GC/SA-Au-ME to AA than GC-Au-ME. The shift in the overpotential may be due to kinetic effect and in such a case, a substantial increase in the rate constant for electrocatalytic oxidation of AA is expected. This would improve the reversibility of the electron transfer processes. We hypothesize the following reasons for the enhanced catalytic activity for GC/SA-Au-ME over GC-Au-ME towards AA oxidation.

There can be two main reasons for the prominent electrocatalytic activity of GC/SA-Au-ME. Those are the crystal-like sizes of Au nanoparticles and the distribution of Au nanoparticles in the MWNT matrix. Smaller size (~15 nm) and uniform distribution of Au are evident from AFM topography (Fig. 1). The high surface area as evident from CV measurement is therefore due to the expected uniform distribution of Au nanoparticles, as the Au atoms are present at the sites directed from the inclusion complex (Scheme 1). The interaction between –SH group in CD-ATP-IC and Au prevents aggregation of Au nanoparticles. Few additional electrochemical characteristics of GC/SA-Au-ME were evaluated from cyclic voltammetry and amperometry studies.
CVs representing the electrooxidation of AA at GC/SA-Au-ME in phosphate buffer for different concentrations of AA are shown in Figure 5A. The oxidation peak current increases with an increasing concentration of AA (Fig. 5A). A linear correlation could be witnessed between the current response and concentration of AA in the range of 1–50 mM at the GC/SA-Au-ME.

The kinetic and transport characteristics of GC/SA-Au-ME were investigated by performing electrooxidation of AA by cyclic voltammetry for different scan rates (ν). It has been noted that the oxidation peak potential (Êp) for oxidation of AA shifts to a more positive values on increasing ν (Figure not shown), indicating a kinetic control for the oxidation of AA at the electrode. The influence of ν on the oxidation current of AA was also monitored. The anodic current showed square root dependence on ν in the range of 10–200 mV s⁻¹ (Fig. 6A) with a correlation coefficient of 0.9979 and suggested that the kinetics of the electrochemical processes might be diffusion controlled. In order to understand further on the rate-determining step for the electrode process, the Tafel plot of Êp versus log ν was made (Fig. 6B). The slope of the Tafel plot was determined (Fig. 6B) as 86 mV using the following equation for totally irreversible diffusion controlled process:51

\[ E_{\text{a}} = \frac{b}{2} \log \nu + c \]

where \( b \) is the Tafel slope and \( c \) is the constant. This slope correlates with a transfer coefficient (α) of 0.41 for the one electron oxidation of AA in the rate determining step.52 The value of anα (where \( n_α \) is the number of electrons involved in the rate-determining step) was calculated to be 0.36 for the oxidation of AA at GC/SA-Au-ME using the equation:

\[ \alpha n_\alpha = \frac{0.048}{E_p - E_{\text{a}/2}} \]

where \( E_{\text{a}/2} \) is the potential corresponding to \( I_{\text{a}/2} \). \( an_\alpha \) for GC-Au-ME was found to be 0.18, twice lesser than at GC/SA-Au-ME. This result clearly shows that GC/SA-Au-ME has less overpotential and faster electron transfer kinetic for the oxidation of AA in comparison to GC-Au-ME.

The response of pH on the voltammetric oxidation of AA at GC/SA-Au-ME electrode was investigated. It can be seen from Figure 7 that over the pH range of 1 to 4.1, a linear variation of peak potential (Êp) with pH was observed. Beyond ca. pH 4.1, the peak potential is insensitive to pH and this consistent with the reported pKₐ value (4.1) for AA at 25 °C.53

Amperometric response curves of the two electrodes (GC/SA-Au-ME and GC-Au-ME) for the successive additions of 1 mM AA at an applied potential of 200 mV are presented (Fig. 8A). Interestingly, GC/SA-Au-ME showed higher current response to oxidation of AA (curve a) in comparison to GC-Au-ME (curve b). Since an identical condition was used for the fabrication of GC/SA-Au-ME
Fig. 7. pH dependence on the oxidation peak of AA at GC/SA-Au-ME; Scans run at 50 mV s⁻¹.

and GC-Au-ME, an enhanced current response for GC/SA-Au-ME is attributed to arise from the Au deposition through self-assembly approach in GC/SA-Au-ME. The oxidation current at the GC/SA-Au-ME was proportional to the concentration of AA in the range from 1 to 20 mM and the detection limit was 1 µM (Fig. 8B). In addition, from Figure 8A, it can be seen that the time required to reach 95% of the steady-state current was less than 1 s after the addition of AA.

Double potential step chronoamperometry was employed to investigate the kinetics of electrochemical reaction at GC/SA-Au-ME. Figure 9A presents the double potential step chronoamperogram obtained at GC/SA-Au-ME in phosphate buffer (pH = 7) by setting the first and second working electrode potential at 700 and 200 mV (versus SCE), respectively, in the absence and presence of AA for various concentration of AA. Also, the current responses of different concentrations of AA at fixed times (5, 10, 15, 20, and 25 s) are presented in Figure 9B. It can be seen from the figure that an increase in concentration of AA was accompanied by an increase in anodic currents obtained for a potential step of 700 mV. For an electroactive material with a diffusion coefficient (D), the current corresponding to the electrochemical reaction

Fig. 8. (A) Chronoamperometric current response of different electrodes upon successive addition of 1 mM AA at 200 mV in phosphate buffer (pH = 7) at (a) GC/SA-Au-ME and (b) GC-Au-ME; (B) Relationship between Ia² and AA concentrations for (a) GC/SA-Au-ME and (b) GC-Au-ME.

Fig. 9. (A) Double potential chronoamperograms obtained at the GC/SA-Au-ME in the different concentration of AA (Inset: Plot of I versus t¹/₂); (B) the dependence of fixed-time current at different time after the first potential step on AA concentration (a-5, b-10, c-15, d-20, and e-25 sec).
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(under diffusion control) is described by Cortell’s law:  

\[ I = nFAD^{1/2}c_0/\pi^{1/2}t^{1/2} \]

where \( n \) is the number of electrons transferred, \( F \) is the Faraday constant (96484 C mol\(^{-1}\)), \( \gamma \) is the electrode surface area, \( c_0 \) is the bulk concentration, and \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)). The plot of \( I \) versus \( t^{1/2} \) is linear (Fig. 9A-inset) and from the slope, the value of \( D \) was calculated. \( D \) value was found to be \( 5.32 \times 10^{-6} \) cm\(^2\) s\(^{-1}\) for GC/SA-Au-ME and is close to the value of \( 5.5 \times 10^{-6} \) cm\(^2\) s\(^{-1}\) found by Prieto et al.\(^{55}\) using arrays of variable-sized channel micro band electrodes. \( 5.5 \times 10^{-6} \) cm\(^2\) s\(^{-1}\) measured via rotating disk electrode voltammetry\(^{56}\) and \( 6.7 \times 10^{-6} \) cm\(^2\) s\(^{-1}\) at a gold electrode.\(^{57}\)

Further, chronoamperometry was employed to evaluate the catalytic rate constant for the oxidation of AA occurring at the GC/SA-Au-ME using the method proposed by Galus:  

\[ I_{a} = I_{\gamma} = \gamma^{1/2}\pi^{1/2}\text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\sqrt{\pi} \]

where \( I_{a} \) is the catalytic current of AA at the GC/SA-Au-ME, \( I_{\gamma} \) is the limiting current in the absence of AA, and \( \gamma = kc_0 t \) (\( c_0 \) is the bulk concentration of AA) is the argument of the error function. When \( \gamma \) exceeds 2, the error function is almost equal to 1 and therefore the above equation can be reduced to:  

\[ I_{a}/I_{\gamma} = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kc_0 t)^{1/2} \]

where \( t \) is the time elapsed (s). Using slope of the \( I_{a}/I_{\gamma} \) versus \( t^{1/2} \) plot, \( k \) was obtained. Mean value of \( k \) was obtained as \( 3.25 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) for concentrations of AA in the range of 1–50 mM.

An attempt was made to determine the selectivity of electrooxidation of AA in the presence of interfering species (dopamine (DA)) at GC/SA-Au-ME. Figure 10 shows the differential pulse voltammogram (DPV) of AA and DA binary mixture at GC/SA-Au-ME in phosphate buffer (pH 7.0). As can be seen, the GC/SA-Au-ME resolve the overlapped voltammetric wave into two well defined voltammetric peaks at 203 mV and 328 mV, corresponding to the oxidation of AA and DA, respectively (Fig. 10). The separation between the two peak potentials is 125 mV, which is large enough for the selective determination of AA in the presence of DA, and also for the simultaneous determination of AA and DA in their mixture.

In order to demonstrate the practical performance of the GC/SA-Au-ME, selective determination of AA in vitamin C tablets (10 mg per tablet) in the presence of different concentrations of DA was performed. As shown in Table I, the determination of AA was not influenced by the presence of a wide range of the concentrations of DA. An average recovery of 99.5 % was obtained. This indicates the potential usefulness of the GC/SA-Au-ME for the practical determination of AA in real samples.

### 4. CONCLUSIONS

A self-assembly assisted synthetic strategy was successfully resolved to fabricate a modified electrode. In the modified electrode, Au nanoparticles were incorporated into MWNT via self-assembly. The self-assembly directed modified electrode exhibited enhanced electrocatalytic performance for the oxidation of ascorbic acid. Augmented current response, faster electron transfer kinetics, linear range of response for the analyte, better sensitivity and selectivity were witnessed for the self-assembly directed modified electrode. Thus, the new approach of fabricating the modified electrode is expected to have wider prospects in the applications of catalysis and sensors.

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### References and Notes

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