Chapter VII

Synthesis, Characterization and Applications of 4α-MTAPcs-capped Gold and Silver Nanoparticles
7.1. Introduction

The synthesis of metal nanoparticles using different ligands for various applications has received huge interest for the past two decades because of their applications in catalysis, biosensing and optoelectronics [1,2]. The interesting properties of these nanoparticles originate from their quantum scale dimension [1]. The shape, size and morphology of the nanomaterials have significant roles in controlling their properties [2]. In general, metal nanoparticles with desired properties can be synthesized by tuning their shape, size and surface structure [3]. Owing to their high stability and ease in preparation, gold nanoparticles (AuNPs) received much attention to the researchers among the different nanomaterials [1,3]. It has been well documented in the literature that the ligand or capping agent plays an important role in the stabilization of AuNPs besides controlling their functions [1,4]. Recently, amine and thiol functionalized phthalocyanines (Pcs) were used as capping agents for the synthesis of Au, TiO₂, Ag and Rh nanoparticles [4-10]. The Au and TiO₂ nanoparticles capped with thiol substituted Pcs were formed a thin films on solid substrates and used as photosensitizers for photovoltaic applications [5,6]. In the first part of this Chapter, synthesis and characterization of 4α-Ni^{II}TAPc-AuNPs and their immobilization on Au electrode for the determination of hydrazine will be described.

Nanorods are widely used for optical sensing and they favored over nanoparticles because of their distinct absorbance and pronounced spectral shift
Among the different anisotropic particles, gold nanorods (GNRs) are primarily interesting from the point of view of their optical properties [12,13]. The GNRs show two absorption peaks corresponding to their transverse (~520 nm) and longitudinal (≥ 600 nm) plasmonic modes of absorption [14,15]. Since colour based imaging and tracking are important in biological and biomedical applications, GNRs have been explored as optical contrast agents in the field of molecular imaging [16-18]. Molecular assembly of these rods may produce novel materials with improved physicochemical properties, which are very useful in the fabrication nanoscale electronic devices [19]. Thus, the second part of this Chapter, synthesis of GNRs using 4α-NiI\textsuperscript{II}-TAPc-AuNPs as a seed solution will be described. Further, the immobilization of GNRs on sol-gel modified electrode for the determination of L-tyrosine will also be discussed.

In contrast to AuNPs, relatively less attention has been paid to the synthesis of silver nanoparticles (AgNPs). However, they received considerable attention recently because of their unique optical properties and strong surface enhanced Raman scattering activity [20,21]. In addition, they also found applications in catalysis, chemical and biochemical sensors [21-23]. In the final part of this Chapter, synthesis of non-peripheral amine functionalized manganese(III) phthalocyanine capped AgNPs (4α-MnIII-TAPc-AgNPs) and their self-assembly on glassy carbon electrode (GCE) for the determination of nitrite will be discussed.

Very recently, peripheral amine substituted cobalt(II) phthalocyanine (4β-Co\textsuperscript{II}TAPc) was used as a capping agent for the synthesis of Rh, Au and Ag nanoparticles [4,10]. Although 4β-Co\textsuperscript{II}TAPc was used as a capping agent to synthesize these nanoparticles, only Rh nanoparticles were used to fabricate a thin film on electrode surface by drop-casting for the determination of cytochrome c [4]. In the present study, we have attempted to use non-peripheral amine substituted nickel(II) phthalocyanine (4α-Ni\textsuperscript{II}TAPc) as a stabilizing agent to synthesize AuNPs and exploit the resulting AuNPs for the determination of hydrazine after attached them on Au electrode via 1,6-hexanedithiol (HDT) linker.

Hydrazine is widely used as a raw material in the manufacture of agricultural chemicals and a powerful reducing agent in fuel cells [24]. It is known as neurotoxin, carcinogenic and mutagenic agent, which create abnormalities and irreversible damage in the nervous system and DNA and it also affects liver and brain [25,26]. Considerable reports were available in the literature for the determination of hydrazine using various modified electrodes including MPcs [27-38]. Gold electrode modified with iron phthalocyanine complex [35], covalently attached multilayer film electrode containing cobalt phthalocyanine [36], glassy carbon electrode modified with polymeric cobalt phthalocyanine [37] and nickel
tetrasulfonated phthalocyanine immobilized on titanized silica gel modified carbon paste electrode [38] have been used for the determination of hydrazine. Although considerable articles were published for the determination of hydrazine including MPs modified electrodes [35-38], the fabrication of an electrochemical sensor using a simple procedure with high sensitivity and selectivity is still one of the challenging tasks for the researchers. In this section, the determination of hydrazine using Au electrode fabricated with 4α-Ni\textsuperscript{II}TAPc-AuNPs via HDT SAM will be discussed.

7.2.1. Characterization of the 4α-Ni\textsuperscript{II}TAPc-AuNPs

Synthesis of 4α-Ni\textsuperscript{II}TAPc-AuNPs was already discussed in Chapter 2 (Section 2.10). Figure 7.1 shows the UV-visible spectra of 4α-Ni\textsuperscript{II}TAPc and 4α-Ni\textsuperscript{II}TAPc-AuNPs in DMF. The 4α-Ni\textsuperscript{II}TAPc shows two Q-bands at 774 nm and 700 nm and two Soret bands at 475 nm and 334 nm (curve a). On the other hand, a new band was appeared at 528 nm for 4α-Ni\textsuperscript{II}TAPc-AuNPs and the absorption characteristics of 4α-Ni\textsuperscript{II}TAPc were almost disappeared for 4α-Ni\textsuperscript{II}TAPc-AuNPs (curve b). The band at 528 corresponds to the SPR band of the AuNPs. In addition to this band, a less intense band was appeared at 774 nm. This band may be due to the presence of excess 4α-Ni\textsuperscript{II}TAPc in solution. As mentioned earlier, when we used greater or lesser than 0.25 mM 4α-Ni\textsuperscript{II}TAPc, the formed AuNPs undergo aggregation. This suggests that an excess of 4α-Ni\textsuperscript{II}TAPc requires for the stabilization of AuNPs. The size and morphology of the AuNPs were
Figure 7.1. UV-visible absorption spectra obtained for (a) 4α-Ni\textsuperscript{II}TAPc and (b) 4α-Ni\textsuperscript{II}TAPc-AuNPs in DMF.

investigated by high resolution transmission electron microscopy (HR-TEM). Figure 7.2A shows the HR-TEM images obtained for 4α-Ni\textsuperscript{II}TAPc-AuNPs. It shows that they are roughly spherical in shape with a narrow distribution. The close view of the TEM image illustrates that the size of the 4α-Ni\textsuperscript{II}TAPc-AuNPs was 5 ± 2 nm (Figure 7.2B). The 4α-Ni\textsuperscript{II}TAPc contains four amine groups. It is expected that one of the amine groups was attached [10,34] with the AuNPs while the other amine groups are projecting away from the AuNPs surface. It is likely that the lone pair of electrons present in the nitrogen atom of the amine groups on the periphery of the benzene rings of the MPc stabilize the AuNPs by electrostatic repulsion (Scheme 7.1) besides the steric effect imposed by the macromolecule
parts in MPc [10]. The synthesized AuNPs remain stable for several months at atmospheric condition.

**Figure 7.2** (A) TEM and (B) HR-TEM image of 4α-Ni^{III}TAPc-AuNPs.

**Scheme 7.1**. Schematic representation of stabilization of AuNPs by 4α-Ni^{III}TAPc.
7.2.2. Characterization of Au/HDT/4α-Ni\textsuperscript{ll}TAPc-AuNPs Electrode

The synthesized 4α-Ni\textsuperscript{ll}TAPc-AuNPs were self-assembled on HDT modified electrode for the determination of hydrazine (Scheme 7.2). The attachment of AuNPs was confirmed by reflectance spectroscopy, SEM and cyclic

Scheme 7.2. Schematic representation for the fabrication of 4α-Ni\textsuperscript{ll}TAPc-AuNPs modified Au electrode.

Figure 7.3. Reflectance spectra for Au/HDT/4α-Ni\textsuperscript{ll}TAPc-AuNPs modified electrode.
voltammetry (CV). Figure 7.3 shows the reflectance spectrum obtained for Au/HDT/4α-Ni^{II}TAPc-AuNPs modified electrode. It shows absorption maximum at 534 nm corresponding to the SPR band of the immobilized AuNPs, confirming the successful attachment of AuNPs on HDT film. The attachment of AuNPs on HDT was further confirmed by SEM. The SEM image obtained for 4α-Ni^{II}TAPc-AuNPs immobilized on HDT modified Au plate is shown in Figure 7.4. It shows that most of the attached AuNPs were spherical in shape and uniformly distributed throughout the HDT film. The size of the AuNPs was found to be 7 ± 2 nm. The reflectance spectrum and SEM image suggest that the size of the immobilized 4α-Ni^{II}TAPc-AuNPs does not change appreciably after immobilized on HDT modified Au electrode.

![SEM images](image)

**Figure 7.4.** SEM images obtained for (A) bare Au plate and (B) Au/HDT/Ni^{II}TAPc-AuNPs.
CV of the reversible electroactive species, \([\text{Fe(CN)}_6]^{3+/4-}\) is a valuable and convenient tool for testing the kinetics barrier of the interface. Figure 7.5A shows the CVs obtained for bare Au, Au/HDT and Au/HDT/4α-NiII-TAPc-AuNPs modified electrodes in 0.2 M PB solution (pH 7.2) containing 1 mM K3[Fe(CN)6] at a scan rate of 50 mV s\(^{-1}\). Bare Au electrode exhibits a characteristic response for \([\text{Fe(CN)}_6]^{3+/4-}\) with a peak separation of 72 mV (curve a), whereas Au/HDT electrode blocked the redox response of \([\text{Fe(CN)}_6]^{3+/4-}\) (curve b). The absence of faradaic current at Au/HDT electrode suggests that the HDT film was densely packed on Au electrode surface. On the other hand, the redox reaction of

**Figure 7.5.** (A) CVs obtained for (a) bare Au, (b) Au/HDT and (c) Au/HDT/4α-NiII-TAPc-AuNPs modified electrodes at a scan rate of 50 mV s\(^{-1}\) in 0.2 M PB solution (pH=7.2) containing 1 mM K3[Fe(CN)6]. (B) LSVs obtained for the reductive desorption of (a) Au/HDT and (b) Au/HDT/4α-NiII-TAPc-AuNPs modified electrodes in 0.1 M KOH at a scan rate of 100 mV s\(^{-1}\).
[Fe(CN)₆]³⁻/⁴⁻ was restored with a peak separation of 85 mV (curve c) after the attachment of 4α-NiᴵᴵTAPc-AuNPs on Au/HDT electrode. The regeneration of electronic communication between [Fe(CN)₆]³⁻/⁴⁻ and the underlying Au electrode suggests the successful attachment of AuNPs. The redox current of [Fe(CN)₆]³⁻/⁴⁻ increases when increasing the immersion time of Au/HDT electrode onto 4α-NiᴵᴵTAPc-AuNPs and reaches maximum at 6 h immersion and after that no significant change was observed. Thus, the optimum time for the immobilization of AuNPs was found to be 6 h.

Figure 7.5B shows the typical linear sweep voltammograms (LSVs) obtained for the reductive desorption of Au/HDT and Au/HDT/4α-NiᴵᴵTAPc-AuNPs modified electrodes in 0.1 M KOH. The Au/HDT electrode shows a reductive desorption peak at -0.86 V (curve a) and the amount of charge was calculated as 88.2 ± 5 μC cm⁻² without subtracting the roughness of the electrode. The observed value is consistent with the monolayer coverage [39]. In the case of Au/HDT/4α-NiᴵᴵTAPc-AuNPs modified electrode, the reductive desorption peak current increases at -0.86 V (curve b) and the amount of charge was calculated as 122.84 ± 5 μC cm⁻². The obtained higher charge suggests that colloidal 4α-NiᴵᴵTAPc-AuNPs were covalently attached with the terminus -SH groups of HDT and reductively desorbs at the same potential where the bulk Au-S reduction occurs. This again confirms the successful attachment of 4α-NiᴵᴵTAPc-AuNPs on Au/HDT electrode.
7.2.3. Characterization of Au/HDT and Au/HDT/4α-Ni\textsuperscript{III}TAPc-AuNPs by Electrical Impedance Spectroscopy

Figure 7.6 shows the Nyquist and Bode plots obtained from EIS for bare Au, Au/HDT and Au/HDT/4α-Ni\textsuperscript{III}TAPc-AuNPs modified electrodes in 1 mM K\textsubscript{3}[Fe(CN)\textsubscript{6}] containing 0.2 M PB solution (pH 7.2) at scanning frequencies from 0.01 to 100000 Hz. Figure 7.6A shows the Nyquist plots obtained for different electrodes. The obtained Nyquist plots were best fit with Randles equivalent circuit model \([R_S (CPE-R_P)]\) (Figure 7.6A inset). The charge transfer resistance \((R_C)\) can be calculated from the semicircle obtained in the Nyquist plot [40]. The \(R_C\) value of the Au/HDT electrode (103670 \(\Omega\)) (Figure 7.6A, curve b) was much higher than that of bare Au electrode (12936 \(\Omega\)) (Figure 7.6A, curve a) suggesting the complete blocking of electron transfer reaction by HDT from the underlying Au electrode. However, after the attachment of AuNPs on Au/HDT electrode, the \(R_C\) decreases (17554 \(\Omega\)). This is due to the attachment of AuNPs and regeneration of the electron transfer reaction between K\textsubscript{3}[Fe(CN)\textsubscript{6}] and underlying Au electrode. The attached AuNPs act as an electron antenna to facilitate the electron transfer through HDT SAM. The Bode-phase angle plot is the plot of phase shift against frequency. Figure 7.6B shows the Bode-phase angle plot for the bare Au, Au/HDT and Au/HDT/4α-Ni\textsuperscript{III}TAPc-AuNPs modified electrodes. If the phase angle is greater or equal to 90°, the modified electrode behaves like an ideal capacitor indicating the insulating nature of the modified electrode [41]. If the
Figure 7.6. (A) Nyquist plots (B) Bode-phase angle plots and (C) Bode amplitude plots for (a) bare Au, (b) Au/HDT and (c) Au/HDT/4α-NiII-TAPc-AuNPs modified electrodes in 1 mM K₃[Fe(CN)₆] containing 0.2 M PB solution (pH = 7.2) at scanning frequencies from 0.01 to 100000 Hz. Inset: Equivalent circuit used to fit the impedance spectra.

Phase angle value is less than 90°, electron transfer reaction is facile due to the pinholes or defects in the SAM [42]. The Au/HDT electrode shows the maximum phase angle (θ = −86.09°) and hence approaches the nature of ideal capacitor.
However, Au/HDT/4α-NiII-TAPc-AuNPs shows less phase angle ($\theta = -79.89^\circ$) indicating that the electron transfer reaction is more facile and the attached AuNPs act like a conducting channel that facilitate the electron transfer reaction between the redox probe and underlying Au electrode compared to Au/HDT electrode ($\theta = -86.09^\circ$). Figure 7.6C shows the Bode amplitude plots for the bare Au, Au/HDT and Au/HDT/4α-NiII-TAPc-AuNPs modified electrodes. In the frequency range from $10^6$ to $10^3$ Hz, the $|Z|$ value is almost constant and equal for all the three electrodes indicating that the solution resistance ($R_S$) of the system is same for all the three electrodes. In the frequency range from $10^3$ to $10^0$, the $|Z|$ value starts to increase and the phase angle gradually decreases pointing to growing role of capacitive response for decreasing frequency. In the frequency range from $10^0$ to $10^{-3}$ Hz, the $|Z|$ value is almost constant and it is characteristic for the particular electrode. The $|Z|$ values are 12.93 k$\Omega$ for bare Au, 103.67 k$\Omega$ for Au/HDT and 17.55 k$\Omega$ for Au/HDT/4α-NiII-TAPc-AuNPs electrodes (Table 7.1). This denoted that the impedance is equal to the total resistance ($R_S+R_{CT}$) of the system [43]. Since the solution resistance is nearly same for all the three electrodes, it is observed from Figure 7.6C that the $R_{CT}$ increases after the attachment of HDT on Au electrode. At the same time, the $R_{CT}$ is slightly higher than that of bare Au electrode. The apparent electron-transfer rate constant ($k_{et}$) at the modified electrodes can be calculated using the following equation [44].

$$k_{et} = \frac{RT}{n^2F^2A}R_{CT}c^0$$  

(7.1)
Table 7.1. Impedance spectral data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bare Au</th>
<th>Au/HDT</th>
<th>Au/HDT /4α-NiII-TAPc-AuNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (kΩ)</td>
<td>0.211</td>
<td>0.120</td>
<td>0.110</td>
</tr>
<tr>
<td>CPE (F)</td>
<td>$4.288 \times 10^{-6}$</td>
<td>$7.092 \times 10^{-7}$</td>
<td>$5.868 \times 10^{-7}$</td>
</tr>
<tr>
<td>$R_{CT}$ (kΩ)</td>
<td>12.93</td>
<td>103.67</td>
<td>17.55</td>
</tr>
<tr>
<td>$k_{et}$ (cm s$^{-1}$)</td>
<td>$6.628 \times 10^{-4}$</td>
<td>$8.278 \times 10^{-5}$</td>
<td>$4.889 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

where, $R$ is the gas constant, $T$ is temperature (K), $F$ is the Faraday constant, $A$ is the electrode area (cm$^2$), $R_{CT}$ is the charge transfer resistance, $c^0$ is the concentration of the redox couple in the bulk solution (mol/cm$^3$) and ‘$n$’ is the number of transferred electrons per molecule of the redox probe (n=1 for the [Fe(CN)$_6$]$^{3-/-}$ probe). The apparent electron transfer rate constant ($k_{et}$) was estimated using the above equation and found to be $6.6 \times 10^{-4}$ cm s$^{-1}$ for bare Au, $8.2 \times 10^{-5}$ cm s$^{-1}$ for Au/HDT and $4.8 \times 10^{-4}$ cm s$^{-1}$ for Au/HDT/4α-NiII-TAPc-AuNPs. This confirms the fast electron transfer reaction at Au/HDT/4α-NiII-TAPc-AuNPs electrode compared Au/HDT electrode.
7.2.4. Electrocatalytic Oxidation of Hydrazine at Au/HDT/4α-NiIITAPc-AuNPs Electrode

One of the objectives of the present work is to determine hydrazine using the Au/HDT/4α-NiIITAPc-AuNPs modified electrode. Figure 7.7A shows the CVs obtained for bare Au, Au/HDT and Au/HDT/4α-NiIITAPc-AuNPs electrodes in 0.2 M PB solution (pH 7.2) containing 0.5 mM hydrazine. Bare Au electrode shows a broad oxidation wave for hydrazine at 0.45 V (curve a) whereas no oxidation wave was observed at Au/HDT modified electrode (curve b) due to the formation of compact HDT film on Au electrode. On the other hand, 4α-NiIITAPc-AuNPs modified electrode shows a sharp oxidation peak for hydrazine at 0.17 V (curve c) which is 280 mV less positive potential than at bare Au electrode. The 4α-NiIITAPc-AuNPs modified electrode does not show any response in the absence of hydrazine (curve d). Further, 2-fold higher oxidation current was observed at Au/HDT/4α-NiIITAPc-AuNPs modified electrode. The large surface area provided by 4α-NiIITAPc-AuNPs is the cause for the observed higher oxidation current for hydrazine at Au/HDT/4α-NiIITAPc-AuNPs modified electrode when compared to bare Au electrode. In order to find the influence of AuNPs on the oxidation of hydrazine, we have prepared the self-assembled monolayer (SAM) of 4α-NiIITAPc and studied the oxidation of hydrazine. The 4α-NiIITAPc SAM modified electrode shows an oxidation peak for hydrazine at 0.35 V (curve e) which is 100 mV less positive potential and one-fold higher current
Figure 7.7. (A) CVs obtained for 0.5 mM hydrazine at (a) bare Au electrode (solid: 1st cycle and dotted: 5th cycle), (b) Au/HDT, (c) Au/HDT/4α-NiII-TAPc-AuNPs (solid: 1st cycle and dotted: 5th cycles) and (e) Au/4α-NiII-TAPc SAM modified electrodes (solid: 1st cycle, dotted: 5th cycle) in 0.2 M PB solution (pH 7.2) at a scan rate of 0.05 V s⁻¹. (d) CV obtained for Au/HDT/4α-NiII-TAPc-AuNPs in 0.2 M PB (pH 7.2) solution. (B) LSVs obtained for 0.5 mM hydrazine at (a) Au/HDT/C-AuNPs and (b) Au/HDT/NiII-TAPc-AuNPs modified electrodes in 0.2 M PB solution (pH 7.2) at a scan rate of 0.05 V s⁻¹.

when compared to bare Au electrode. This shows that capping ligand also contributed to the electrocatalytic oxidation of hydrazine. However, when compared to Au/HDT/4α-NiII-TAPc-AuNPs modified electrode, the Au/4α-NiII-TAPc oxidizes hydrazine at 180 mV more positive potential with less oxidation current. Thus, the higher electrocatalytic activity of Au/HDT/4α-
Ni$^{II}$TAPc-AuNPs towards hydrazine oxidation was mainly contributed by the presence of AuNPs on the electrode. The obtained hydrazine oxidation peak was found to be highly stable at Au/HDT/4α-Ni$^{II}$TAPc-AuNPs indicating that the modified electrode prevents the surface fouling effect caused by the oxidation products of hydrazine. Further, the electrocatalytic effect of Au/HDT/4α-Ni$^{II}$TAPc-AuNPs towards hydrazine was compared with ~3 nm size citrate capped AuNPs (C-AuNPs) attached Au electrode prepared under identical conditions. Figure 7.7B shows the hydrazine oxidation was observed at 0.19 V (curve a) but the oxidation current was less when compared to Au/HDT/4α-Ni$^{II}$TAPc-AuNPs modified electrode (curve b). This may be due to the differences in particle coverage of 4α-Ni$^{II}$TAPc-AuNPs and C-AuNPs. The particle coverages ($\theta_p$) of 4α-Ni$^{II}$TAPc-AuNPs and C-AuNPs were calculated from the following equation.

$$\theta_p = \frac{\text{Au oxide reduction charge (\(\mu\)C)/723 (\(\mu\)C/cm$^2$)}}{\text{Au geometric area (cm$^2$)}} \times 100$$  

(7.2)

The particle coverage of Au/HDT/4α-Ni$^{II}$TAPc-AuNPs electrode was calculated by using the charge involved in the reduction of electrochemically formed Au oxide from the CV recorded in 0.2 M PB solution (Figure 7.8A), by assuming the charge density for the reduction peak of the Au oxide is 723 $\mu$C cm$^{-2}$ [45]. The particle coverage of 4α-Ni$^{II}$TAPc-AuNPs was found to be 35.7% whereas 26.8% was obtained for C-AuNPs under the experimental conditions employed in the present work. The obtained higher coverage of 4α-Ni$^{II}$TAPc-
AuNPs may be due to the facile attachment of 4α-Ni\textsuperscript{II}-TAPc-AuNPs in contrast to C-AuNPs.

Figure 7.8. (A) CVs obtained for (a) bare Au, (b) Au/HDT/C-AuNPs and (c) Au/HDT/4α-Ni\textsuperscript{II}-TAPc-AuNPs modified electrodes in 0.2 M PB solution (pH 7.2) at a scan rate of 0.05 V s\textsuperscript{-1}. (B) CVs obtained for 0.5 mM hydrazine at Au/HDT/4α-Ni\textsuperscript{II}-TAPc-AuNPs modified Au electrode in 0.2 M PB solution (pH 7.2) at scan rates of 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 V s\textsuperscript{-1}. Inset: Plot of hydrazine oxidation current vs. square root of the scan rate.

Figure 7.8B shows the effect of scan rate on the oxidation of hydrazine at Au/HDT/4α-Ni\textsuperscript{II}-TAPc-AuNPs modified electrode in 0.2 M PB solution (pH 7.2) containing 0.5 mM hydrazine. The oxidation peak currents of hydrazine were increased linearly with increasing scan rates from 0.05 to 0.5 V s\textsuperscript{-1}. The plot of peak current versus square root of scan rate is linear for the oxidation of hydrazine.
with a correlation coefficient of 0.9983 (Figure 7.8B Inset) suggesting that the oxidation of hydrazine at Au/HDT/4α-Ni\textsuperscript{II}TAPc-AuNPs was diffusion controlled process and not due to the adsorption process.

7.2.5. Determination of Hydrazine at Au/HDT/4α-Ni\textsuperscript{II}TAPc-AuNPs Electrode by Differential Pulse Voltammetry

![Graph showing differential pulse voltammetry results](image)

**Figure 7.9.** DPVs obtained for 10 µM of hydrazine at Au/HDT/4α-Ni\textsuperscript{II}TAPc-AuNPs modified electrode in 0.2 M PB solution (pH 7.2). Each addition of hydrazine increased concentration by 10 µM (b-k).

Figure 7.9 shows the DPVs obtained for hydrazine in the concentration range of 10-100 µM at Au/HDT/4α-Ni\textsuperscript{II}TAPc-AuNPs modified electrode in 0.2 M PB solution (pH 7.2). The peak current of hydrazine oxidation increases linearly with an increase in the concentration ranging from 10-100 µM. The plot of peak
current versus the concentration of hydrazine is linear with a correlation coefficient of 0.9986. The detection limit for hydrazine was found to be $5 \times 10^{-8}$ M (S/N = 3).

7.2.6. Stability and Reproducibility of 4α-Ni$^{II}$TAPc-AuNPs Electrode

The 4α-Ni$^{II}$TAPc-AuNPs modified electrode was highly stable when it was kept in 0.2 M PB solution (pH 7.2). Further, stability and reproducibility of 4α-Ni$^{II}$TAPc-AuNPs electrode was examined by series of 10 successive DPV measurements of 10 μM addition of hydrazine. The relative standard deviation was found to be 2.1%, indicating that the modified electrode showed good stability and reproducibility. The obtained higher stability of the present modified electrode is related to the chemical and mechanical stability of the HDT single dimension network film and the strong adsorption of 4α-Ni$^{II}$TAPc-AuNPs.

7.3. Synthesis of Gold Nanorods in Solution and on ITO and Au Substrates Using 4α-Ni$^{II}$TAPc-AuNPs as Seed

We have shown in the previous section that 4α-Ni$^{II}$TAPc-AuNPs were successfully synthesized in DMF medium. Since the size of the prepared AuNPs is ~4 nm, it is attempted to synthesize GNRs using 4α-Ni$^{II}$TAPc-AuNPs as the seed solution. Generally, many researchers have used the seed solution of ~4 nm size for the growth of GNRs in solution [46-51].

To the best of our knowledge, there are no studies related to the synthesis of GNRs using macrocycle metal complexes capped AuNPs as a seed solution.
Further, no report is available in the literature for the use of seed solution from different medium other than water for the growth of GNRs. In this section, we have investigated the synthesis of GNRs in both solution and on ITO and Au substrates using 4α-NiⅡTAPc-AuNPs as a seed solution. The growth of GNRs in solution was characterized by absorption spectroscopy and high resolution-transmission electron microscopy (HR-TEM). HR-TEM images of GNRs show the presence of cylindrical rods in addition to few dispersed spherical nanoparticles. We have also demonstrated the surface growth of GNRs on ITO and Au electrode surfaces by using (3-mercaptopropyl)-trimethoxysilane (MPTS) sol-gel as a linker. Very few reports are available in the literature for the attachment of GNRs on the solid substrates [40,52-54] which include the growth of GNRs directly on mica surface through surfactant-assisted seeded grown method [52], self-assembly of GNRs on 1,6-hexanedithiol modified Au electrode [40,53], and seed mediated growth of GNRs on Au and ITO substrates by using citrate-AuNPs as seed solution [54]. In the present study, an attempt is also made to grow GNRs by seed mediated growth method due to the less coverage obtained by direct attachment of GNRs on MPTS modified Au and ITO electrodes. For this, seed solution of 4α-NiⅡTAPc-AuNPs was initially immobilized on MPTS sol-gel modified electrode followed by the immersion of seed attached electrode into the growth solution. The surface grown GNRs were confirmed by reflectance spectroscopy, atomic force microscopy (AFM), cyclic voltammetry (CV) and
impedance spectral studies. Finally, the electrocatalytic activity of surface grown GNRs was examined by studying the oxidation of L-tyrosine (L-Tyr). The surface grown GNRs modified electrode shows higher electrocatalytic activity towards L-Tyr than bare Au electrode.

7.3.1. Characterization of GNRs Synthesized Using $4\alpha$-Ni$^{II}$TAPc-AuNPs as Seed Solution

The procedures for the preparation of $4\alpha$-Ni$^{II}$TAPc-AuNPs, GNRs growth solution and formation of GNRs in solution were discussed in Chapter 2 (section 2.11). As discussed in the previous section, the synthesized $4\alpha$-Ni$^{II}$TAPc-AuNPs show the characteristic SPR band at 528 nm (Figure 7.10 curve a). HR-TEM image shows that the particles are spherical in shape and size of the AuNPs was ~4 nm with a narrow size distribution (Figure 7.11A). It has been reported that the charge as well as the size play an important role in controlling the aspect ratio of the GNRs and compared to positively charged seeds, change in dimension was more pronounced in negatively charged seeds [47-49]. In most of the reports, the size of the seed solution used for the growth of GNRs was approximately 4 nm [46-51]. Since the size of $4\alpha$-Ni$^{II}$TAPc-AuNPs was ~4 nm, we used them as a seed solution for the growth of GNRs in a one step protocol. In order to avoid the secondary nucleation caused by decomposition of the excess NaBH$_4$, freshly prepared seed solution was used for the growth of GNRs throughout the experiments. On the addition of AA to the mixture of CTAB, HAuCl$_4$ and AgNO$_3$
solution, Au^{3+} ions are reduced to Au^{+} ion which is bound to the CTAB. When 12 μL of the freshly prepared solution of 4α-Ni^{II}-TAPc-AuNPs in DMF medium was added to the growth solution, the Au^{+} ions are reduced by the electron rich seed solution. The colorless growth solution was slowly changed into pink color within 20 min and the solution was kept undisturbed for 24 h for the growth of GNRs. The absorption spectrum of 24 h aged growth solution after the addition of seed solution shows two absorption bands at 526 and 761 nm due to transverse and longitudinal absorption bands of solution is in different medium, it has the tendency to reduce Au^{+} ions and results in the formation of GNRs in solution. Hence, the nucleation and controlled growth of GNRs are also possible with the

![Absorption Spectrum](image)

**Figure 7.10.** UV-visible absorption spectra obtained for (a) 4α-Ni^{II}-TAPc-AuNPs in DMF medium and (b) GNRs grown by using the growth solution containing 4α-Ni^{II}-TAPc-AuNPs as seed solution.
GNRs, respectively (Figure 7.11 curve b). In the present case, even the seed addition of seed solution prepared in organic medium. Further, to confirm the formation of GNRs, the 24 h aged growth solution was characterized by HR-TEM. Figure 7.11B shows the HR-TEM images of GNRs. It shows the presence of GNRs in addition to spherical AuNPs. The aspect ratio of GNRs was found

**Figure 7.11.** HR-TEM images of (A) 4α-NiII-TAPc-AuNPs, (B) GNRs grown by using 4α-NiII-TAPc-AuNPs as a seed solution, (C) selected area diffraction pattern of GNRs and (D) Histogram showing aspect ratio of GNRs.
to be 4.2 (Figure 7.11B inset). It can be seen from HR-TEM image that the yield of GNRs was less in the present method compared to the growth of GNRs using CTAB-AuNPs as seed solution [40,48,49]. The crystalline nature of the GNRs was evidenced from the appearance of concentric circles in the selected area diffraction pattern of GNRs (Figure 7.11C). The histogram for the aspect ratio of GNRs is shown in Figure 7.11D. It shows that most of the GNRs have the aspect ratio close to 4.5 ± 0.3. Compared to the absorption band of GNRs formed by CTAB capped AuNPs as seed solution, the intensity of longitudinal band was less when we use 4a-NiTTAPc-AuNPs as seed for the growth of GNRs. This indirectly indicates the low yield of GNRs.

7.3.2. Effect of Silver Ion

To know the role of silver ions in the growth of GNRs, it is attempted to synthesize GNRs without the addition of silver ions during the preparation of growth solution. The absence of characteristic longitudinal band for 24 h aged growth solution indicates that the GNRs are not grown in the solution in the absence of silver ion (data not shown). Hence, addition of silver ions into the growth solution is necessary for the growth of GNRs [48,55]. Further, the effect of concentration of silver ion on the growth of GNRs has been studied (Figure 7.12). The longitudinal SPR band was red shifted with increase in intensity while increasing the concentration of silver ions. This shows that the size of the GNRs can be tuned by varying the concentration of silver ions. When we compare the
present result with the growth of GNRs using CTAB-AuNPs seeds in the presence of different silver ions concentration, the intensity of longitudinal absorption band was less in all the silver ions concentration when we use 4α-Ni^{II}TAPc-AuNPs as a seed solution.

![UV-vis spectra](image)

**Figure 7.12.** UV-vis spectra obtained for the growth of GNRs by different volume (a) 50, (b) 100, (c) 150, (d) 200 and (e) 250 μL of 0.004 M the silver ion.

**7.3.3. Growth of GNRs on ITO and Au Surfaces**

The other objective of the present investigation is to attach GNRs on ITO and Au surfaces. First, we attempted to attach GNRs directly on the electrode surfaces by immersing the MPTS sol-gel modified electrode into the GNRs solution. Although GNRs were attached on the sol-gel modified electrode surface, the intensity of both transverse and longitudinal bands were very weak (Figure 7.3.3.1).
7.13A) suggesting that the amount of GNRs attached on the MPTS sol-gel modified surface was much less. This was further confirmed from the observed less pronounced redox response for $[\text{Fe(CN)}_6]^{3-/4-}$ (Figure 7.13B). The long alkyl chain moiety of CTAB on the surface of GNRs might hinder the attachment of GNRs on the -SH functionality of the MPTS sol-gel modified electrode.

![Graph A](image1.png) ![Graph B](image2.png)

**Figure 7.13.** (A) UV-vis absorption spectrum of colloidal GNRs directly immobilized on the MPTS sol-gel modified ITO plate. (B) CVs obtained for (a) bare Au and (b) direct attachment of GNRs on Au/MPTS at a scan rate of 50 mV s$^{-1}$ in 0.2 M PB solution (pH 7.2) containing 1 mM $\text{K}_3[\text{Fe(CN)}_6]$.

Hence, we have attempted to grow the GNRs directly by seed mediated growth method on Au and ITO surfaces. Since the 4α-Ni$^{II}$TAPc-AuNPs were successfully used as a seed solution for the synthesis of GNRs in solution, we have
used them as seed for the growth of GNRs on surface. For this, 4α-Ni$^{III}$TAPc-AuNPs were first immobilized on ITO and Au electrodes using MPTS as a linker. Then, the 4α-Ni$^{III}$TAPc-AuNPs modified electrodes were immersed into the growth solution. It is expected that the surface confined 4α-Ni$^{III}$TAPc-AuNPs can act as a seed for the growth of GNRs. The growth of GNRs on ITO plate was monitored by using UV-vis spectroscopy (Figure 7.14A). For this purpose, 4α-Ni$^{III}$TAPc-AuNPs were immobilized on ITO plate using MPTS sol-gel as a linker and then the seed attached ITO plate was introduced into a quartz cell containing the growth solution of GNRs. The growth solution does not have any characteristic absorption band in the region of 450 nm to 950 nm (curve a). The seed attached ITO plate shows a strong SPR band at 550 nm (curve b) suggesting that the seed was attached on MPTS sol-gel. After 10 min of immersion time, the intensity of peak at 550 nm was slightly increased and the peak becomes broader at higher wavelength (curve c). After 30 min, a new shoulder band at higher wavelength along with the SPR band at 550 nm was observed which typically reveals the growth of GNRs on the surface. As the immersion time increases, the intensity of both shoulder band and the peak at 550 nm were increased. The shoulder wave was shifted to longer wavelength for subsequent immersion and remained constant at 700 nm after 24 h. No significant change in the intensity of both bands at 550 nm and 700 nm was observed after 24 h. The observed bands at 550 nm and 700 nm might be due to the transverse and longitudinal modes of
absorption of GNRs grown on the surface of ITO plate. This confirms the growth of GNRs on the ITO substrate and taking 24 h for the complete growth of GNRs.

**Figure 7.14.** (A) Time-dependent UV-visible spectra of $4\alpha$-$\text{Ni}^{II}$TAPc-AuNPs seeds on the MPTS sol-gel film modified ITO plate immersed into the GNR growth solution. The UV-visible spectrum recorded for (a) growth solution and the spectra were recorded at time intervals of (b) 0, (c) 10, (d) 30, (e) 60, (f) 180, (g) 600, (h) 840, (i) 960, (j) 1080, (k) 1440 and (l) 1560 min. (B) UV-visible absorption spectra obtained for (a) bare ITO, (b) MPTS sol-gel film modified ITO, (c) Pc-AuNPs attached ITO/MPTS electrode and (d) ITO/MPTS/Pc-AuNPs electrode immersed into the GNR growth solution for 24 h.

Figure 7.14B shows the absorption spectra of bare ITO, ITO/MPTS and ITO/MPTS/$4\alpha$-$\text{Ni}^{II}$TAPc-AuNPs and ITO/MPTS/GNRs substrates. Bare ITO and ITO/MPTS substrates do not have any characteristic absorption band between 400
to 900 nm whereas $4\alpha$-Ni$^{II}$TAPc-AuNPs attached substrate shows a strong characteristic SPR band at 550 nm which confirms the attachment of $4\alpha$-Ni$^{II}$TAPc-AuNPs on ITO substrate. Then, $4\alpha$-Ni$^{II}$TAPc-AuNPs modified ITO plate was immersed into a GNRs growth solution. Since the complete growth of GNRs on ITO plate takes 24 h, the ITO plate was left undisturbed for 24 h and then washed with distilled water. The absorption spectrum shows two absorption bands at 551 and 700 nm due to the characteristic transverse and longitudinal absorption bands of GNRs. The appearance of two bands suggests that the GNRs were grown on the surface of ITO plate. Similar procedure was followed to grow GNRs on Au surface. The growth of GNRs on the Au electrode surface was confirmed by reflectance spectra. Figure 7.15 shows the reflectance spectra obtained for $4\alpha$-Ni$^{II}$TAPc-AuNPs modified Au surface and the surface grown GNRs on Au electrode. The seed attached Au surface shows the characteristic SPR band at 529 nm (curve a) whereas GNRs grown on Au surface shows two characteristic bands of GNRs at 525 nm and 771 nm which confirms the successful growth of GNRs on the electrode surface (curve b). The seed AuNPs and the surface grown GNRs on ITO substrate were characterized by AFM. Figure 7.16A shows the tapping mode AFM image of seed attached ITO substrate. It clearly shows the distribution of spherical AuNPs on ITO surface. Figure 7.16B shows the AFM image of the GNRs grown on the surface of ITO substrate. It illustrates that most of the spherical seed AuNPs were grown into GNRs with an aspect ratio of $2.7 \pm 0.3$.\[233\]
Figure 7.15. Reflectance spectra obtained for (a) Au/MPTS/4α-Ni^{II}TAPc-AuNPs electrode and (b) Au/MPTS/Pc-AuNPs-GNRs electrode immersed in the GNR growth solution for 24 hours.

Figure 7.16. (A) AFM image of spherical 4α-Ni^{II}TAPc-AuNPs adsorbed on the MPTS sol-gel film modified ITO plate (2 × 2 μm) and (B) AFM images of spherical 4α-Ni^{II}TAPc-AuNPs grown into GNRs with a length of 90-120 nm (2 × 2 μm).
with a length in the range of 90-120 nm and a width of 30-50 nm. The surface growth experiment was repeated for six times and the growth of GNRs is similar to those observed in Figure 7.16B.

![ATR-FT-IR spectrum](image)

**Figure 7.17.** ATR-FT-IR spectrum of surface-grown GNRs on the MPTS sol-gel film modified ITO substrate.

Further, the formation of GNRs was confirmed by ATR-FT-IR spectrum. It shows a weak symmetric and asymmetric stretching vibrations at 2890 and 2933 cm\(^{-1}\) corresponding to \(\nu\)C-H of the aliphatic -CH\(_2\) groups (Figure 7.17). In addition, a weak band at 903 cm\(^{-1}\) was appeared which corresponds to the C-N stretching vibration of aliphatic amine. This peak was similar to the FT-IR spectrum of solid CTAB in KBr pellet [54] which gives an indirect evidence for the growth of GNRs on the surface of the ITO plate.
7.3.4. Characterization of Au/MPTS/4α-Ni^{II}TAPc-AuNPs and Au/MPTS/GNRs Electrodes by Cyclic Voltammetry

Figure 7.18A shows the CVs obtained for bare Au, Au/MPTS, Au/MPTS/4α-Ni^{II}TAPc-AuNPs and Au/MPTS/GNRs in 1 mM K_3[Fe(CN)_6] containing 0.2 M PB (pH 7.2) solution at a scan rate of 50 mV s^{-1}. Bare Au electrode shows the characteristic reversible peak corresponds to the [Fe(CN)_6]^{3/-4} redox couple with a peak separation of 74 mV. No voltammetric response was appeared for the [Fe(CN)_6]^{3/-4} redox couple at MPTS sol-gel modified Au electrode due to the blocking of [Fe(CN)_6]^{3/-4} to the underlying Au electrode by the MPTS sol-gel. After the attachment of 4α-Ni^{II}TAPc-AuNPs, the redox response of [Fe(CN)_6]^{3/-4} was regenerated with a peak separation of 70 mV. The attached 4α-Ni^{II}TAPc-AuNPs act as an electron antenna which facilitate the electron transfer reaction between the [Fe(CN)_6]^{3/-4} solution and the underlying Au electrode. The surface grown GNRs electrode shows the characteristic voltammetric redox peak corresponding to the [Fe(CN)_6]^{3/-4} couple with less current as well as slight increase in the peak separation (75 mV) when compared to AuNPs modified electrode. This is due to the presence of long alkyl chain in the GNRs modified electrode which may hinder the electron transfer reaction between [Fe(CN)_6]^{3/-4} solution and the underlying Au electrode.

Figure 7.18B shows the linear sweep voltammograms (LSVs) obtained for the reductive desorption in 0.1 M KOH for Au/MPTS, Au/MPTS/4α-Ni^{II}TAPc-
Figure 7.18. (A) CVs obtained for (a) bare Au, (b) Au/MPTS (c) Au/MPTS/Pc-AuNPs and (d) Au/MPTS/Pc-AuNPs-GNRs electrodes at a scan rate of 50 mV s\(^{-1}\) in 0.2 M PB solution (pH=7.2) containing 1 mM K\(_3\)[Fe(CN)]\(_6\)]. (B) LSVs obtained for the reductive desorption of (a) Au/MPTS (b) Au/MPTS/Pc-AuNPs and (c) Au/MPTS/Pc-AuNPs-GNRs modified electrodes in 0.1 M KOH at a scan rate of 100 mV s\(^{-1}\).

AuNPs and Au/MPTS/GNRs electrodes. The Au/MPTS electrode shows the reductive desorption due to Au-S cleavage at -0.95 V and the amount of charge was calculated as 61 \(\mu\)C cm\(^{-2}\) (curve a). On the other hand, Au/MPTS/4\(\alpha\)-Ni\(^{ll}\)-TAPc-AuNPs electrode shows the reductive desorption at -0.99 V with increased current (curve b) and the amount of charge was calculated as 86 \(\mu\)C cm\(^{-2}\). The Au/MPTS/GNRs electrode shows the reductive desorption at -1.02 V with the slight enhancement of current and the amount of charge was calculated as

237
96 μC cm\(^{-2}\). This again confirms the successful growth of GNRs on Au electrode surface using MPTS sol-gel linker.

7.3.5. Characterization of Au/MPTS/GNRs by Impedance Spectral Studies

The GNRs attached electrode was further characterized by impedance spectral studies. Figure 7.19 shows the Nyquist and Bode plots obtained for bare Au, Au/MPTS, Au/MPTS/4α-Ni\(^{II}\)TAPc-AuNPs and Au/MPTS/GNRs electrodes in 0.2 M PB solution (PB 7.2) containing 1 mM K\(_3\)Fe(CN)\(_6\) solution. Figure 7.19A shows increase in the \(R_{CT}\) after the immobilization of MPTS sol-gel on Au electrode due to the complete blocking of electrochemical response between ferricyanide solution and the underlying Au electrode. After the immobilization of 4α-Ni\(^{II}\)TAPc-AuNPs seeds, the \(R_{CT}\) has been decreased which is due to fact that the attached seeds act as electron antenna to restore the electron transfer reaction. After the growth of GNRs on seed attached Au electrode, the charge transfer reaction has been slightly increased compared to 4α-Ni\(^{II}\)TAPc-AuNPs attached Au electrode due to the presence long alkyl chain in the CTAB molecule in the Au/MPTS/GNRs electrode. Figure 7.19B shows the Bode phase angle plots of bare Au, Au/MPTS, Au/MPTS/4α-Ni\(^{II}\)TAPc-AuNPs and Au/MPTS/GNRs electrodes. Compared to bare Au, Au/MPTS/4α-Ni\(^{II}\)TAPc-AuNPs and Au/MPTS/4α-Ni\(^{II}\)TAPc-AuNPs-GNRs electrodes, Au/MPTS electrode shows the maximum phase shift (θ= 85.52\(^\circ\)) between current and voltage which is due to complete blocking nature of MPTS sol-gel and hence approaches nature of ideal
Figure 7.19. (A) Nyquist plots (B) Bode-phase angle plots and (C) Bode amplitude plots for (a) bare Au, (b) Au/MPTS (c) Au/MPTS/Pc-AuNPs and (d) Au/MPTS/Pc-AuNPs modified electrodes in 1 mM K₃[Fe(CN)₆] containing 0.2 M PB solution (pH = 7.2) at scanning frequencies from 0.01 to 100000 Hz. Inset: Equivalent circuit used to fit the impedance spectra.

On the other hand, after the attachment of 4α-NiII-TAPc-AuNPs followed by the growth of GNRs, the electrodes show less phase angle compared
to Au/MPTS which is due to the conducting nature of the AuNPs modified electrodes. In the Bode’s frequency plot, the $|z|$ value was constant in the frequency region of $10^0$ Hz to $10^3$ Hz indicating that the solution resistance is same for all the electrodes. In the frequency range of $10^3$ to $10^0$ Hz, the $|z|$ value starts to decrease for all the electrodes which are due to the increasing capacitive response with decreasing frequency. In the frequency range of $10^0$ to $10^{-3}$ Hz, the $|z|$ value is constant and characteristic for the particular electrode

**Table 7.2. Impedance spectral data.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bare Au electrode</th>
<th>Au/MPTS electrode</th>
<th>Au/MPTS/Pc-AuNPs electrode</th>
<th>Au/MPTS/GNRs electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (kΩ)</td>
<td>0.306</td>
<td>0.212</td>
<td>0.304</td>
<td>0.556</td>
</tr>
<tr>
<td>CPE (μF)</td>
<td>3.50</td>
<td>1.05</td>
<td>0.604</td>
<td>0.865</td>
</tr>
<tr>
<td>$R_{CT}$ (kΩ)</td>
<td>27.14</td>
<td>139.75</td>
<td>34.50</td>
<td>50.53</td>
</tr>
<tr>
<td>$k_{ct}$ (cm s$^{-1}$)</td>
<td>$4.92 \times 10^{-4}$</td>
<td>$9.51 \times 10^{-5}$</td>
<td>$3.85 \times 10^{-4}$</td>
<td>$2.63 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

which denotes the total impedance of the system. Since the solution resistance is same for all the electrodes, it is evidenced from Figure 7.19C that the $R_{CT}$ was increased after the attachment of MPTS sol-gel than bare Au electrode and
decreased after the attachment of 4α-Ni\textsuperscript{II}TAPc-AuNPs. After the growth of GNRs on electrode surface, slight increase in $R_{CT}$ was observed which is due to the presence of long alkyl chain in the CTAB moiety. Further, the heterogeneous electron transfer rate constant ($k_{ct}$) was calculated using the equation (7.1). The estimated $k_{ct}$ values are $4.92 \times 10^{-4}$ cm s$^{-1}$ for bare Au, $9.51 \times 10^{-5}$ cm s$^{-1}$ for Au/MPTS, $3.85 \times 10^{-4}$ cm s$^{-1}$ for Au/MPTS/4α-Ni\textsuperscript{II}TAPc-AuNPs and $2.63 \times 10^{-4}$ cm s$^{-1}$ for Au/MPTS/GNRs electrodes. The impedance parameters are summarized in Table 7.2. These results indirectly give evidence for the growth of GNRs on Au surface.

7. 3.6. Electrocatalytic Oxidation of L-tyrosine

The electrocatalytic effect of surface grown GNRs modified electrode was examined towards L-Tyr oxidation. L-Tyr is a non-essential amino acid and associated with the inborn error diseases such as hereditary tyrosinemia type I [56,57]. Therefore, it is essential to determine the concentration of L-Tyr. Figure 7.20 shows the DPVs obtained for bare Au, Au/MPTS, Au/MPTS/4α-Ni\textsuperscript{II}TAPc-AuNPs and Au/MPTS/GNRs electrodes in 0.2 M PB solution (pH 7.2) containing 0.5 mM of L-Tyr. Bare Au electrode shows a broad oxidation wave for L-Tyr at 0.63 V (curve a) whereas no oxidation wave was observed at Au/MPTS electrode (curve b). The 4α-Ni\textsuperscript{II}TAPc-AuNPs seed attached Au electrode oxidized L-Tyr at 0.6 V (curve c) with higher oxidation current when compared to bare Au electrode as well as the Au/MPTS/GNRs electrodes. Although the GNRs has the greater
electrocatalytic effect compared to bare Au electrode, the oxidation current was
less compared to Au/MPTS/4α-Ni\textsuperscript{III}TAPc-AuNPs electrode which might be due to
the long alkyl chain moiety (CTAB) present in the GNRs which hinder the
electrocatalytic activity towards the oxidation of L-Tyr (curve d).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{DPVs obtained for 0.5 mM L-Tyr at (a) bare Au electrode (solid:
first cycle and dotted: after five cycles), (b) Au/MPTS, (c) Au/MPTS/4α-
Ni\textsuperscript{III}TAPc-AuNPs (solid: first cycle and dotted: after five cycles) (d)
Au/MPTS/GNRs modified electrodes (solid: first cycle and dotted: after five
cycles) in 0.2 M PB solution (pH 7.2).}
\end{figure}
7.4. Synthesis of Non-peripheral Amine Functionalized Manganese(III) Phthalocyanine Capped Silver Nanoparticles and Their Immobilization on Electrode Surface for the Determination of Nitrite

Nitrite ion is one of the most active intermediate agents in the nitrogen cycle and a useful indicator about the equilibrium state of the oxidative and reductive ways of this cycle [58]. It acts as a source of nitrogen, which is essential for environmental process in green plants. Eventhough nitrite was used as preservatives in food and beverages, there is much concern about their level in these materials because excess amount of nitrite leads to carcinogenic effects [59-61]. It is also used as additives in fertilizers in agriculture [62]. Therefore, its determination is much important for public health and environmental security. Since nitrite plays important role in both environmental science and in food chemistry, a reliable method must be developed for the determination of nitrite.

Electrochemical method is one of the very attractive methods for the determination of several molecules because it is less expensive, high selectivity and sensitivity. Direct reduction of nitrite ion on most of the electrode surfaces is thermodynamically favorable. One of the ways to improve the electron transfer process is to use modified electrodes as redox mediators to prevent the electrode from surface fouling. The electrocatalytic reduction of nitrite has been reported using different modified electrodes [63-67]. MPcs are well known electrocatalysts for chemical and biological molecules [68-70]. MPcs complexes have also been
employed for the oxidation of nitrite [71-74]. However, no report was available in the literature for the electrocatalytic reduction of nitrite using the MPc capped AgNPs modified electrode. In the final part of this Chapter, 4α-Mn$^{III}$TAPc-AgNPs are synthesized and immobilized on GCE for the determination of nitrite.

### 7.4.1. Characterization of 4α-Mn$^{III}$TAPc-AgNPs

Synthesis of 4α-Ni$^{II}$TAPc-AgNPs was already discussed in Chapter 2 (section 2.10). Figure 7.21A shows the UV-visible absorption spectra obtained for 4α-Mn$^{III}$TAPc and 4α-Mn$^{III}$TAPc-AgNPs. The 4α-Mn$^{III}$TAPc in DMF solution shows two Q-bands at 865 nm and 800 nm and two Soret bands at 550 nm and 350 nm (curve a). On the other hand, the 4α-Mn$^{III}$TAPc stabilized AgNPs show a new sharp band at 428 nm along with a less intense band at 865 nm (curve b).

![UV-visible spectra](image)

**Figure 7.21.** (A) UV-visible spectra obtained for (a) 4α-Mn$^{III}$TAPc NPs and (b) 4α-Mn$^{III}$TAPc-AgNPs NPs. (B) HR-TEM image of 4α-Mn$^{III}$TAPc-AgNPs. Inset: Selected area diffraction pattern of 4α-Mn$^{III}$TAPc-AgNPs.
Scheme 7.3. Schematic representation of stabilization of AgNPs by 4α-Mn$^{III}$TAPc.

In contrast to 4α-Mn$^{III}$TAPc in DMF, the Soret bands and the Q band at 800 nm were completely disappeared due to the formation of AgNPs. Further, the morphology and size of the 4α-Mn$^{III}$TAPc-AgNPs were examined by HR-TEM. The HR-TEM image shows that most of the AgNPs were roughly spherical in shape with a size of $8 \pm 2$ nm diameter and have a narrow size distribution (Figure 7.21B). The discrete dots in the diffraction pattern illustrate the crystalline nature of 4α-Mn$^{III}$TAPc-AgNPs (Figure 7.21B inset). Further, diffraction pattern image shows more bright spots indicating that the AgNPs have well defined crystalline lattices. The 4α-Mn$^{III}$TAPc contains four amine groups in the macrocycle. It is expected that one of the amine groups were attached on AgNPs while the other amine groups were projecting away from the AgNPs surface. It is likely that the lone pair of electrons present in the amine groups stabilize the AgNPs by electrostatic repulsion (Scheme 7.3) [10]. In addition, the steric effects due to
macromolecule parts in the MPc moiety efficiently stabilize the AgNPs from aggregation. The prepared AgNPs were kept at atmospheric condition and remained stable for several months.

7.4.2. Electrochemical Characterization of 4α-Mn$^{III}$TAPc-AgNPs Modified GCE

The presence of free amine groups in the surface of AgNPs were used to form a self-assembly of AgNPs on GCE [75,76]. Figure 7.22A shows the cyclic voltammogram (CV) obtained for the 4α-Mn$^{III}$TAPc-AgNPs modified GCE in 0.1 M H$_2$SO$_4$ (curve b). The silver oxide peak was observed at 0.23 V indicating the successful attachment of 4α-Mn$^{III}$TAPc-AgNPs on GCE. To ascertain the observed oxidation peak at 0.23 V was due to the oxidation of silver to silver oxide, we fabricate 4α-Mn$^{III}$TAPc SAM modified GCE under identical conditions and examined in 0.1 M H$_2$SO$_4$ (curve a). The absence of anodic peak at 0.23 V indicates that the obtained oxidation peak corresponds to the formation of silver oxide. Further, the attachment of 4α-Mn$^{III}$TAPc-AgNPs on GCE was confirmed by reflectance spectroscopy. The 4α-Mn$^{III}$TAPc-AgNPs modified GCE shows a characteristic SPR band at 478 nm which confirms the attachment of AgNPs on GCE (Figure 7.22B). As discussed earlier, the 4α-Mn$^{III}$TAPc-AgNPs contains free amine groups. The possible mechanism for the attachment of 4α-Mn$^{III}$TAPc-AgNPs on GCE surface is the formation of chemical bond between nucleophilic
amine groups capped AgNPs and olefinic bond on the surface of GCE (Scheme 7.4) [75,76].

**Figure 7.22.** (A) CVs obtained for (a) 4α-Mn\textsuperscript{III}TAPc and (b) 4α-Mn\textsuperscript{III}TAPc-AgNPs modified GCEs in 0.1 M H\textsubscript{2}SO\textsubscript{4} at a scan rate of 50 mV s\textsuperscript{-1}. (B) Reflectance spectrum obtained for 4α-Mn\textsuperscript{III}TAPc-AgNPs modified GCE.

**Scheme 7.4.** Schematic illustration of attachment of 4α-Mn\textsuperscript{III}TAPc-AgNPs on GCE.
7.4.3. Characterization of $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs Modified GCE by Electrical Impedance Studies

Figure 7.23 shows the Nyquist and Bode plots EIS for bare, $4\alpha$-Mn$^{\text{III}}$TAPc and $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs modified GCEs in 1 mM K$_3$[Fe(CN)$_6$] containing 0.2 M PB solution at scanning frequencies from 0.01 to 100000 Hz. Figure 7.23A shows the Nyquist plot for the bare, $4\alpha$-Mn$^{\text{III}}$TAPc and $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs modified GCEs. The obtained Nyquist plots were best fit with Randles equivalent circuit model [Rs (CPE-$R_p$)] (Figure 7.23A Inset). The $R_{CT}$ value was drastically decreased at the SAM of $4\alpha$-Mn$^{\text{III}}$TAPc (44219 $\Omega$) in contrast to bare GCE (107270 $\Omega$). On the other hand, the attachment of $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs on GCE, the $R_{CT}$ decreases (10067 $\Omega$) when compared to $4\alpha$-Mn$^{\text{III}}$TAPc modified GCE. This shows the facile electron transfer reaction at $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs modified GCE compared to bare and $4\alpha$-Mn$^{\text{III}}$TAPc modified GCEs. The Bode-phase angle plot is the plot of phase shift against frequency. Figure 7.23B shows the Bode-phase angle plot for the bare, $4\alpha$-Mn$^{\text{III}}$TAPc and $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs modified GCEs. The $4\alpha$-Mn$^{\text{III}}$TAPc modified GCE shows less phase angle ($\theta = 36.93^\circ$) when compared to bare ($\theta = 77.75^\circ$) and $4\alpha$-Mn$^{\text{III}}$TAPc ($\theta = 54.13^\circ$) modified GCEs. The decrease in phase angle at AgNPs modified GCE suggests that the attached $4\alpha$-Mn$^{\text{III}}$TAPc-AgNPs act like a conducting channel that facilitate the electron transfer reaction between redox probe and the underlying GCE. Figure 7.23C shows the Bode amplitude plot for the bare, $4\alpha$-Mn$^{\text{III}}$TAPc and
Figure 7.23. (A) Nyquist plots (B) Bode-phase angle plots and (C) Bode amplitude plots for (a) bare, (b) 4α-Mn$^{III}$TAPc and (c) 4α-Mn$^{III}$TAPc-AgNPs modified GCEs in 1 mM K$_3$[Fe(CN)$_6$] containing 0.2 M PB solution (pH= 7) at scanning frequency from 0.01 to 100000 Hz to 100000 Hz. Inset: Equivalent circuit used to fit the impedance data.

4α-Mn$^{III}$TAPc-AgNPs modified GCEs. In the frequency range from $10^6$ to $10^3$ HZ, the $|Z|$ value is almost constant and equal for all the three electrodes indicating that the solution resistance of ($R_S$) of the system is almost same for the three electrodes. In the frequency range from $10^3$ to $10^0$, the $|Z|$ value starts to increase
and the phase angle gradually decreases pointing to growing role of capacitive response for decreasing frequency. In the frequency range from $10^0$ to $10^3$ HZ, the $|Z|$ value is almost constant and characteristic for the electrode. The $|Z|$ values are

**Table 7.3. Impedance spectral data.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bare GC</th>
<th>GC/4α-Mn$^{III}$TAPc</th>
<th>GC/4α-Mn$^{III}$TAPc-AgNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (kΩ)</td>
<td>127.9</td>
<td>137.2</td>
<td>104.2</td>
</tr>
<tr>
<td>CPE (F)</td>
<td>$1.063 \times 10^{-5}$</td>
<td>$4.405 \times 10^{-5}$</td>
<td>$2.811 \times 10^{-4}$</td>
</tr>
<tr>
<td>$R_{CT}$ (Ω)</td>
<td>107270</td>
<td>44219</td>
<td>10067</td>
</tr>
<tr>
<td>$k_{el}$ (cm s$^{-1}$)</td>
<td>$8.006 \times 10^{-5}$</td>
<td>$1.940 \times 10^{-4}$</td>
<td>$8.525 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

127.9 kΩ for bare, 119.2 kΩ for 4α-Mn$^{III}$TAPc and 104.2 kΩ for 4α-Mn$^{III}$TAPc-AgNPs modified GCEs. Since the solution resistance is almost same for all the three electrodes, it is observed from Figure 7.23C that the $R_{CT}$ was high for bare GCE. After the attachment of 4α-Mn$^{III}$TAPc-AgNPs on GCE, the $R_{CT}$ is less when compared to both bare and 4α-Mn$^{III}$TAPc modified GCEs. The apparent electron-transfer rate constant ($k_{el}$) on the modified electrodes can be calculated using the equation 7.1. The apparent electron transfer rate constant ($k_{el}$) was estimated using above equation and was found to be $8.0 \times 10^{-5}$ cm s$^{-1}$ for bare GCE, $1.9 \times 10^{-4}$
cm s\(^{-1}\) for 4α-Mn\(^{III}\)TAPc and 8.5 \times 10^{-4} \text{ cm s}^{-1}\) for 4α-Mn\(^{III}\)TAPc-AgNPs modified GCEs (Table 7.3). The obtained higher k\(_{et}\) value suggests that the electron transfer reaction at 4α-Mn\(^{III}\)TAPc-AgNPs modified GCE is more facile than bare and 4α-Mn\(^{III}\)TAPc SAM modified GCEs.

7.4.4. 4α-Mn\(^{III}\)TAPc-AgNPs Modified GCE for the Reduction of Nitrite Ion

The 4α-Mn\(^{III}\)TAPc-AgNPs modified electrode was explored for the determination of nitrite. Figure 7.24 shows the CVs of bare, 4α-Mn\(^{III}\)TAPc and 4α-Mn\(^{III}\)TAPc-AgNPs modified GCEs in the presence of 1 mM sodium nitrite containing 0.1 M H\(_2\)SO\(_4\). Bare GCE does not show any response in the potential window between +0.2 V to -0.7 V (curve a). However, two irreversible peaks were obtained at -0.1 V and -0.4 V for nitrite reduction at the 4α-Mn\(^{III}\)TAPc-AgNPs modified GCE (curve b). The 4α-Mn\(^{III}\)TAPc modified GCE shows broad reduction peak with less current (curve c). The reduction current obtained at 4α-Mn\(^{III}\)TAPc was negligible in comparison with 4α-Mn\(^{III}\)TAPc-AgNPs modified GCE suggesting that the AgNPs on the GCE surface catalyzed the reduction of nitrite. The two reduction peaks obtained at -0.1 V and -0.4 V for nitrite were assigned to the conversion of Ag\(^+\)-NO\(_2\)^- to Ag\(^0\)-NO\(_2\)^- and Ag\(^0\)-NO\(_2\)^- to Ag\(^0\) + HNO\(_2\), respectively. In the absence of nitrite, the 4α-Mn\(^{III}\)TAPc-AgNPs modified GCE shows a characteristic silver oxide peak response at 0.23 V. This peak was also appeared in the presence of nitrite at 4α-Mn\(^{III}\)TAPc-AgNPs modified GCE.
Figure 7.24. CVs obtained for 1 mM nitrite at (a) bare, (b) 4α-Mn$^{III}$TAPc and (c) 4α-Mn$^{III}$TAPc-AgNPs modified GCEs in 0.1 M H$_2$SO$_4$ solution at a scan rate of 50 mV s$^{-1}$. (d) CV obtained for 4α-Mn$^{III}$TAPc-AgNPs modified electrode in the absence of nitrite in 0.1 M H$_2$SO$_4$ solution at a scan rate of 50 mV s$^{-1}$.

7.4.5. Determination of Nitrite

Figure 7.25 shows the DPVs obtained for nitrite in the concentration range of 20-100 μM at 4α-Mn$^{III}$TAPc-AgNPs modified GCE in 0.1 M H$_2$SO$_4$. The peak current of nitrite was linearly increased in the concentration of range of 20-100 μM with the correlation coefficient of 0.9986 and the detection limit was found to be $4.76 \times 10^{-7}$ M (S/N = 3). The reduction potential of nitrite was slightly shifted while increasing the concentration of nitrite.
Figure 7.25. DPVs obtained for the determination of nitrite at 4α-Mn$^{III}$TAPc-AgNPs modified GCE in 0.1 M H$_2$SO$_4$. Each addition increases the concentration of nitrite (a) 20, (b) 40, (c) 60, (d) 80, (e) 100 μM. Inset: Plot of peak current vs. concentration of nitrite.

7.5. Conclusions

In this chapter, we have demonstrated the synthesis of 4α-MTAPc capped AuNPs and AgNPs. In the first section of this Chapter, we demonstrated the synthesis of macrocycle capped AuNPs (4α-Ni$^{II}$TAPc-AuNPs) directly in DMF medium at room temperature (28°C). HR-TEM images show that the size of the 4α-Ni$^{II}$TAPc-AuNPs was 5 ± 2 nm. Then, they were immobilized on Au electrode using HDT as a linker. The immobilized AuNPs was successfully used for the determination of hydrazine in 0.2 M PB solution (pH 7.2). The DPV current
response was increased linearly in the concentration range of 10-100 μM hydrazine and a detection limit was found to be $5 \times 10^{-8}$ M (S/N = 3). We have also synthesized 4α-MTAPc capped AuNPs (M= Co(II) and Cu(II)) and their electrocatalytic activity differ towards hydrazine.

In the second section, we have synthesized 4α-Ni$^{III}$TAPc capped AuNPs in DMF medium and used as a seed solution for the growth of GNRs in solution. Although the seed solution is in organic medium, the growth of GNRs was observed which was confirmed by UV-vis spectroscopy and HR-TEM. The GNRs were also successfully grown on the Au and ITO electrodes by seed mediated method using MPTS sol-gel as a linker. UV-vis spectroscopy, reflectance spectroscopy and AFM confirm the growth of GNRs on the Au and ITO surfaces. Further, the GNRs grown electrodes were characterized by cyclic voltammetry and impedance spectral studies. The GNRs electrode was successfully used for the electrochemical oxidation of L-Tyr. Compared to bare Au electrode, the surface grown GNRs showed enhanced electrocatalytic activity towards L-Tyr.

The final section illustrates the synthesis of 4α-Mn$^{III}$TAPc-AgNPs in DMF medium. HR-TEM image shows that the size of the 4α-Mn$^{III}$TAPc-AgNPs was 8 ± 2 nm. Then, the 4α-Mn$^{III}$TAPc-AgNPs was successfully attached on the GCE surface using the free amine groups by SA method. The 4α-Mn$^{III}$TAPc-AgNPs modified GCE shows a characteristic SPR band corresponding to AgNPs which was confirmed by reflectance spectroscopy. Further, 4α-Mn$^{III}$TAPc-AgNPs on
GCE surface were characterized by CV and EIS studies. The 4α-Mn$^{III}$TAPc-AgNPs modified GCE was exploited for the reduction of nitrite. It shows enhanced electrocatalytic activity towards nitrite when compared to bare and 4α-Mn$^{III}$TAPc modified GCEs. The voltammetric reduction current of nitrite increases while increasing the concentration from 20-100 μM and the detection limit was found to be $4.76 \times 10^{-7}$ M (S/N = 3). We have also used non-peripheral amine functionalized phthloacyanine with different metal ion (Co(II) and Cu(II)) for the synthesis of AgNPs and their electrocatalytic activity differ from each other.
7.6. References


