Chapter V

Anisotropic growth of Au and Cu nanostructures on indium-tin-oxide electrode for surface enhanced Raman scattering and electrocatalytic applications
5.1. Introduction

In recent years, much attention has been directed towards the synthesis of anisotropic nanostructures (NS) such as rods, wires, prisms, pods, cubes and dendrites due to their optical and electronic properties \cite{1,2}. The peculiar properties of the metal NS mainly stem from their quantum size effects \cite{3}. The catalytic activity and selectivity of the NS are highly dependent on the type of facets exposed on the surface. This type of structural sensitivity has received significant interest in catalysis, plasmonics, sensors and surface enhanced Raman signalling \cite{1,2,4-6}. The unique shape-dependent properties and functionalities of anisotropic nanostructures can be utilized in many important diverse applications ranging from catalysis to sensing to optics \cite{7-10}. Recently, colloidal chemistry has been widely applied to synthesize the anisotropic NS which include triangular prisms, cubes, rods and wires \cite{8-13}. Different synthetic strategies like template synthesis, electrochemical, photoirradiation, ultrasonic irradiation, seed-mediated growth process have been widely employed for the synthesis of anisotropic NS in solution. However, synthesized anisotropic NS need to be immobilized on solid substrates for electrocatalytic applications and SERS. Instead, direct growth of the NS on electrode surfaces received considerable attention. Large efforts have been made by the researchers for the fabrication of anisotropic NS on solid substrates. Our research group also demonstrated the growth of Au nanorods on Au and ITO electrodes using (3-mercaptopropyl)trimethoxysilane as a linker by seed mediated growth process
using citrate and phthalocyanine capped AuNPs as seed particles and a facile electrochemical route using AgNO₃ as a shape directing agent [14-18]. However, the formation of different AuNS with peculiar morphologies by in-situ electrochemical method is not reported so far. Thus, the present study aims to grow different AuNS including spherical, bipyramidal and wires by in-situ electrochemical reduction of Au⁺ ions from the growth solution.

It has been already demonstrated that copper nanostructures (CuNS) found promising applications as heat transfer systems, sensors, surface enhanced Raman scattering and catalysts due to their high stability, excellent electrical conductivity, catalytic properties and low cost [12,13]. The electrochemical synthesis of different copper nanostructures on ITO electrode was achieved in this study by varying the deposition conditions. The surfactant free cubic, spherical, dendritic and prickly copper nanostructures were fabricated on ITO substrate by applying +0.1, -0.1, -0.3 and -0.5 V, respectively for 400 s in CuSO₄ containing 0.1 M H₂SO₄. Further, a detailed experimental study on the influence of SO₄²⁻, NO₃⁻, CH₃COO⁻, ClO₄⁻, and CO₃²⁻ anions on the morphology of CuNS was investigated. The influence of deposition potential, deposition time and pH of the electrolyte on the morphology of CuNS was also studied.

5.2. Direct growth of spherical, bipyramidal and wires of gold nanostructures on ITO substrate and their catalytic activity

5.2.1. Mechanism for the formation of AuNS

The preparation of growth solution and the electrochemical deposition of Au seeds are shown in Figure 5.1A. Initially, the colorless solution of CTAB was
turned to orange color while adding HAuCl₄, which is due to the formation of Au³⁺-CTAB complex and then 20 µM CuSO₄ was added to this solution. The addition of 300 µM AA turns the orange color solution to colorless, which is due to the reduction of Au³⁺-CTAB to Au⁺-CTAB by AA (Figure 5.1A) [19]. Since AA is a weak reducing agent further reduction of Au⁺ to Au⁰ is not possible under the present experimental condition. Therefore, Au seeds were

**Figure 5.1.** (A) Photographs of (a) CTAB and (b) before and (c) after the addition of AA into the CTAB-Au³⁺ solution. (B) DPV obtained for the reduction of growth solution at ITO substrate. (inset B: Photograph of the growth solution after the electrochemical deposition). (C) UV-vis absorption spectra obtained for the growth solution (a) before and (b) after electrochemical deposition and (c) AuNS grown ITO substrate.
Figure 5.1B shows the differential pulse voltammogram obtained for the reduction of Au$^+$ ions from the growth solution containing 20 μM CuSO$_4$. A cathodic peak was observed at -0.60 V due to the reduction of Au$^+$-CTAB complex and the color of the ITO electrode as well as the solution slowly turned to reddish-violet (Figure 5.1B, inset), indicating the growth of AuNS. This set-up was left undisturbed for 6 h. The reactions for the formation of AuNS are as follows:

$\text{Au}^{3+} + \text{CTAB} \rightarrow \text{Au}^{3+}\text{-CTAB (complex)}$ \hspace{1cm} (5.1)

$\text{Au}^{3+}\text{-CTAB} \xrightarrow{\text{AA}} \text{Au}^{+}\text{-CTAB (growth solution)}$ \hspace{1cm} (5.2)

$\text{Au}^{+}\text{-CTAB (growth solution)} \xrightarrow{\text{Electrodeposition}} \text{AuNS}$ \hspace{1cm} (5.3)

The deposited Au seeds on ITO substrate act as the nucleation centre to catalyze the reduction of Au$^+$ to Au$^0$. The added Cu$^{2+}$ in the growth solution assisted the nanoparticles to grow into different shapes and at some stages the facets were developed. The shape of the AuNS could be controlled by Cu$^{2+}$.

**5.2.2. Characterization of AuNS grown on ITO substrates by UV-visible spectroscopy**

The seed deposited ITO substrate was removed from the growth solution after 6 h and rinsed with water and then characterized by UV-vis spectroscopy. Figure 5.1C shows the UV-vis absorption spectra of growth solution before and after electrochemical deposition and AuNS grown ITO substrate. The UV-vis spectrum of growth solution before electrochemical deposition does not exhibit any characteristic SPR band for AuNPs in the region of 500-600 nm, indicating
that AA reduces Au\(^{3+}\) ions to Au\(^{+}\) only and further reduction of Au\(^{+}\) to Au\(^{0}\) does not occur in the growth solution before seeding (Figure 5.1C, curve a). While the UV-vis spectrum of the growth solution after electrochemical deposition shows two well defined absorption bands at 531 and 678 nm corresponding to the transverse and longitudinal plasmonic bands of AuNS, respectively (Figure 5.1C, curve b). On the other hand, the UV-vis spectrum of ITO substrate after electrochemical deposition of growth solution also shows similar bands (Figure 5.1C, curve c). This indicates that the AuNS were grown not only in the solution but also on the ITO substrate. The obtained results suggest that the electrochemically generated Au seeds induced the growth of the AuNS both in solution and on substrate.

### 5.2.3. Characterization of AuNS grown on ITO substrates by SEM

The time dependent growth of AuNS on ITO substrate was further monitored by SEM. Figure 5.2 shows the SEM images obtained for ITO/AuNS at different immersion time in the growth solution. The ITO substrate removed from the growth solution immediately after the electrodeposition of Au seeds shows spherical AuNPs with the average size of 10-20 nm (Figure 5.2a). After 1 h immersion of ITO in the growth solution, the size of the AuNPs was found to be increased to 60 nm and shows few elongated spherical structures (Figure 5.2b). The elongated spherical structures turned to bipyramidal structures while increasing the immersion time to 3 h in the growth solution (Figure 5.2c). Interestingly, it also shows few star like structures along with the bipyramidals (Figure 5.2d and e), suggesting that the facets of the AuNS were developed at
When the immersion time was further increased to 6 h, wire-like AuNS were grown over the ITO substrate (Figure 5.2f). Further, the grain size also increases while increasing the immersion time and the larger grains form the nanowires. Moreover, the population of the Au-nanowires on ITO is higher than the spherical, bipyramidal and star-like NS. This is due to surface diffusion followed by oriented growth of AuNS. While increasing the immersion time further, the already existing nuclei will grow onto the larger NS and the free nanoparticles diffused frequently toward the aggregate and then immobilized, forming a larger aggregate. The continuous attachment of AuNPs on the surfaces of larger AuNS in an oriented mode leads to the formation of different AuNS [7,20].
5.2.4. Effect of anion of the shape directing Cu$^{2+}$

As mentioned above, the spherical AuNPs could be directed to grow into different shaped AuNS with the assistance of Cu$^{2+}$ ions. Obviously, Cu$^{2+}$ ions play a critical role in controlling the reduction kinetics and thus, altered the morphology of the AuNS [19]. In addition, the role of anion present in the copper salt also could make an impact on the formation of AuNS. Hence, the effect of the counter ion of copper salt on the morphology of AuNS was also investigated. Copper salts of sulphate, nitrate, perchlorate and acetate were used with the concentration of 30 µM and the experiment was carried out under

**Figure 5.3.** SEM images obtained for AuNS grown ITO substrate (a) in the absence of Cu$^{2+}$ salt and in the presence of (b) CuSO$_4$, (c) CuNO$_3$, (d) Cu(CH$_3$COO)$_2$ and (e) Cu(ClO$_4$)$_2$. (f) Growth of Au-bipyramidal NS on [111] plane.
identical conditions. Figure 5.3 shows the SEM images obtained for ITO/AuNS in the absence and presence of different copper salts at an immersion time of 3 h. In the absence of Cu$^{2+}$ ions, only spherical particles with enlarged size were formed on seeding (Figure 5.3a). However, the presence of copper sulphate salt resulted the bipyramidal structure with sharp facets (Figure 5.3b). When copper nitrate was used, the elongated spherical AuNS were grown with pebbles like structure (Figure 5.3c). Very stumpy bipyramidal NS were grown on the surface in the presence of copper perchlorate salt (Figure 5.3d) whereas the acetate salt of copper aggregates the bipyramidal NS (Figure 5.3e). These results suggest that being a bivalent anion the sulfate ion acts as a bridging ligand between the deposited NS to form different AuNS and it shows well developed facets on the formed AuNS. The above results suggest that CuSO$_4$ is a better shape directing agent with well defined facets when compared to other copper salts.

The possible mechanism for the formation of AuNS was proposed based on the results obtained from the SEM analysis (Figure 5.2). Peculiar AuNS were observed only in the presence of Cu salt. Hence, Cu$^{2+}$ acted as an effective shape directing agent to form different shapes of AuNS. The plausible mechanism is as follows: (i) The primarily deposited AuNPs act as the nucleation centre, (ii) the well defined facets were developed by oriented growth on continuous nucleation and (iii) the Cu$^{2+}$ ions decrease the surface energy of the AuNPs to be deposited in all directions and the SO$_4^{2-}$ ions act as a bridge between the deposited AuNPs and (iv) continuous nucleation with decrease in surface energy followed by oriented growth leads to the formation of wire-like AuNS (Figure 5.4).
5.2.5. Characterization of AuNS in solution by HR-TEM

**Figure 5.4.** Plausible mechanism for the growth of different AuNS on ITO substrate.

**Figure 5.5.** HR-TEM images of electrochemically reduced growth solution after (A) 3 and (B) 6 h (insets A and B: SEM images of Au-bipyramidals and Au-nanowires grown on ITO substrate) and (C) SAED pattern obtained for AuNS in solution.

As evidenced from the UV-vis spectra (Figure 5.1C), the electrochemical reduction of Au$^+$ ions not only deposited the seed particles on the ITO substrate for the growth of AuNS but also generated them in the growth solution, which
leads to the growth of AuNS in solution. Figures 5.5A and B show the TEM images of AuNS grown in solution using the growth solution containing 30 µM of CuSO$_4$ at 3 and 6 h after electrochemical deposition. After 3 h, AuNS with bipyramidal structure were grown predominantly along with few elongated spherical AuNS similar to the one formed on the ITO substrate (Figure 5.5A). After 6 h, wire-like AuNS were grown in the growth solution along with spherical AuNS (Figure 5.5B). Figure 5.5C shows the SAED pattern of AuNS grown in the growth solution. The discrete dot in the diffraction pattern illustrates the crystalline nature of AuNS. The TEM images obtained for the growth solution match with the SEM images of AuNS grown on ITO substrates. This suggests that the in-situ generation of seed particles in solution can also lead to the formation of different AuNS similar to the AuNS on ITO substrate.

5.2.6. Characterization of ITO/AuNS by XPS, XRD and EDAX

The AuNS grown on ITO substrate after 3 h immersion in a growth solution containing 30 µM CuSO$_4$ was further characterized by XPS, XRD and EDAX. The XPS spectrum of ITO/AuNS shows two peaks at 83.6 and 87.3 eV corresponds to the 4f$^{7/2}$ and 4f$^{5/2}$ of Au, respectively (Figure 5.6A) [16,17]. The peak difference of 3.7 eV is consistent with the zero valent nature of Au.

Figure 5.6B shows the XRD patterns obtained for spherical, bipyramidal and wires of AuNS grown ITO substrates after 1, 3 and 6 h immersed in the growth solution (curve a-c). The XRD patterns exhibit four diffraction peaks at
34.97°, 44.35°, 55.73° and 74.08° which can be indexed to the {111}, {200}, {220} and {311} of fcc gold and indicating that the sample is composed of pure crystalline gold. It is important to note that the intensity ratio of the {200} and {111} diffraction peaks in the XRD pattern is 0.83, which is 1.7-fold higher than the value of a conventional powder sample (JCPDS file no. 04-0784). Hence, the grown AuNS bound by enlarged {111} facet which preferentially orient parallel to the substrate (Figure 5.3f) [13,19]. The two important parameters arrived from the peak width analysis are the crystallite size and lattice strain. Both these effects increase the peak width, intensity and shift the 2θ peak position accordingly. The crystallite size of the formed AuNS was calculated using Scherrer equation (equation 2.4). The calculated crystallite size values are 18.20, 59.34 and 66.62 nm for spherical, bipyramidal and wire-like AuNS, respectively. The obtained crystallite size values well matched with the values obtained from

**Figure 5.6.** (A) XPS of AuNS grown ITO substrate and (B) XRD patterns of (a) Au-spherical, (b) Au-bipyramidal and (c) Au-wires grown ITO substrate.
SEM analysis. On the other hand, lattice strain plays a crucial role on the properties of nanostructures [21]. The lattice strain on the surface of nanostructures can largely influence the surface free energy and the relevant mechanical properties, which is usually described as ‘‘smaller is stronger’’ [21,22]. The lattice strain ($\varepsilon$) of the formed AuNS on ITO substrate can be calculated by Williamson-Hall’s method (equations 2.5 and 2.6) [21]. The obtained $\varepsilon$ values are $0.3963 \times 10^{-3}$, $0.1214 \times 10^{-3}$ and $0.1041 \times 10^{-3}$ for spherical, bipyramidal and wire-like AuNS, respectively. It was found from the observed results that the lattice strain decreases with increasing the particle size. It is well established in the literature that the lattice contraction is induced by the effect of hydrostatic pressure arising from the surface stress and intrinsic compressibility [21,22]. In this case, the lattice strain was decreased upon continuous nucleation. This is due to the condensation of the deposited particles with the seeded particles during nucleation followed by the loss in surface energy. Moreover, the bond lengths of atoms at the edges and corners are relaxing with decrease in lattice strain compared with the center position.

![EDAX spectrum of AuNS grown ITO substrate.](image)

**Figure 5.7.** EDAX spectrum of AuNS grown ITO substrate.
The EDAX spectrum of ITO/AuNS shows peaks at 2.12 and 9.71 keV corresponding to characteristic Au peaks (Figure 5.7). The rest of the peaks correspond to the ITO substrate.

5.2.7. Characterization of ITO/AuNS by EIS and CV

In order to investigate the conducting nature of AuNS modified electrode, EIS study was carried out. Figure 5.8 shows the Nyquist plots obtained for bare ITO and Au-spherical, Au-bipyramidal and Au-nanowires fabricated ITO electrodes after immersed in the growth solution for 1, 3 and 6 h, respectively in 1 mM K₃[Fe(CN)₆] containing 0.2 M PB solution (pH 7.2) at scanning frequencies from 0.01 to 100,000 Hz. A Randles circuit model \([R_S(C-R_{CT})]\) (inset: Figure 5.8) was used to fit the impedance spectral data where \(R_S\) refers to the solution resistance and \(C\) refers to the capacitance. The obtained semicircle from the Nyquist plot can be used to calculate the charge transfer.

**Figure 5.8.** Nyquist plots for (a) bare ITO and (b-d) AuNS of spherical, bipyramidal and wires grown ITO substrates in 1 mM K₃[Fe(CN)₆] in 0.2 M PB solution (pH 7.2) at scanning frequencies from 0.01 to 100000 Hz. **Inset:** Equivalent electrical circuit used for fitting the impedance spectra.
resistance ($R_{CT}$). The bare ITO electrode shows a large semicircle of about 7.66 kΩ (curve a). The spherical and bipyramidal AuNS fabricated ITO substrates show the charge transfer resistance values of 5.41 and 3.31 kΩ, respectively (curves b and c). Interestingly, the Au-nanowires fabricated ITO electrode drastically decreased the interfacial charge transfer resistance to 2.06 kΩ (curve d) when compared to bare and other AuNS modified electrodes. The higher conductivity of the nanowires is attributed to the presence of large number of active sites containing lot of edges, corners and stepped atoms on their branches. These results reveal that the Au-nanowires fabricated ITO electrode shows lower charge transfer resistance than the other AuNS fabricated ITO electrodes. The obtained $R_S$, $C$, and $R_{CT}$ values are given in Table 5.1. The heterogeneous electron-transfer rate constant ($k_{et}$) was calculated using the equation 2.3 [23]. The calculated $k_{et}$ values are $3.47 \times 10^{-5}$ for bare ITO and $4.91 \times 10^{-5}$, $8.05 \times 10^{-5}$ and $1.29 \times 10^{-4}$ cm s$^{-1}$ for spherical, bipyramidal and wires of AuNS fabricated ITO electrodes, respectively. The obtained higher $k_{et}$ value for Au-nanowires fabricated ITO electrode indicates that the electron transfer reaction was faster at this electrode when compared to bare and other AuNS modified ITO electrode.

The AuNS modified ITO substrate was further characterized by cyclic voltammetry. Figure 5.9 shows the CV obtained for bare ITO and spherical, bipyramidal and nanowires of AuNS modified ITO substrate in 0.2 M PB solution at a scan rate of 50 mV s$^{-1}$. Bare ITO does not show any oxidation or reduction peak (Figure 5.9, curve a). The different AuNS modified ITO substrates exhibit
an anodic peak at +0.90 V corresponding to the formation of gold oxide and its subsequent reduction peak at +0.40 V (Figure 5.9, curves b-d), which confirms the successful formation of AuNS on ITO substrate. Among the different AuNS, the Au-nanowires fabricated ITO shows a well defined oxidation peak for the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bare ITO</th>
<th>ITO/AuNS</th>
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<tr>
<td></td>
<td></td>
<td>Spherical</td>
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<tr>
<td>$R_s$ (kΩ)</td>
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<td>31.89</td>
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<tr>
<td>$C$ (µF)</td>
<td>$2.30 \times 10^{-6}$</td>
<td>$6.92 \times 10^{-6}$</td>
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<tr>
<td>$R_{CT}$ (kΩ)</td>
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<td>5.41</td>
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<tr>
<td>$k_{et}$ (cm s$^{-1}$)</td>
<td>$3.47 \times 10^{-5}$</td>
<td>$4.91 \times 10^{-5}$</td>
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**Table 5.1.** Impedance spectral data of AuNS modified ITO substrates.

**Figure 5.9.** CVs obtained for (a) bare and (b-d) spherical, bipyramidal and wires of AuNS grown ITO substrates in 0.2 M PB solution (pH 7) at a scan rate of 50 mV s$^{-1}$.
gold oxide formation and higher reduction current for gold oxide reduction. This may be due to the higher population of Au-nanowires on the ITO substrate when compared to other AuNS as evidenced from SEM images (Figure 5.2a and b).

The surface coverage was calculated from the equation 2.1 [24,25] and it was found to be 1.8, 5.8 and 10.1 % corresponding to spherical, bipyramidal and nanowires, respectively. Further, the electrochemically active surface area (A) of the different AuNS modified electrodes was calculated from the Anson equation (equation 2.2) [27,28]. The electrochemically active surface area was found to be 0.42, 0.50 and 0.69 cm$^2$ for Au-spherical, Au-bipyramidal and Au-nanowires modified ITO electrodes. As evidenced from SEM analysis, while increasing the immersion time larger grains were oriented to form peculiar nanostructures. The obtained higher surface coverage and electrochemically active surface area for the Au-nanowires grown ITO substrate are due to the well ordered nanowire distribution. Besides, the long length nanowires are less vulnerable to dissolution and Ostwald ripening [22,29]. Further, the porous structure of the Au-nanowires can provide more active sites. Furthermore, the coarsening of the formation of AuNS is time dependent immersion process and the oriented attachment on immersion leads to the formation of NS with identical crystallographic configurations. When the crystallographic orientation is encountered, these nanoparticles merge together and this favorable process reduces the overall surface energy due to the elimination of energy associated with unsatisfied bonds [20,29]. The more populated growth of AuNS is due to decrease in surface and hence the electrochemical surface area of the electrode was increased.
5.2.8. SERS property of AuNS grown on ITO substrates

Surface-enhanced Raman scattering (SERS) has become a valuable but limited spectroscopic technique for the sensitive detection of molecules. Similar to normal Raman spectroscopy, SERS provides both chemical identification and structural information of a molecule based on its unique vibrational fingerprint [30,31]. Although Raman spectroscopy provides highly specific information regarding a molecule, its use is limited because of inherently low signal intensities and small molecular cross sections versus other spectroscopic techniques. In comparison to normal Raman scattering, SERS has been shown to increase the magnitude of the Raman effect for a given analyte by up to $10^6$ to $10^{14}$ orders of magnitude and has contribution from both chemical and electromagnetic enhancement effects [30,31]. Anisotropic AuNS exhibit strong SERS effects when molecules are adsorbed onto their surface due to coupling of the plasmon band of the metal with the molecules electronic states. Au nanorods and nanowires have enhanced electric fields at their tips, which would favour an increase of the SERS activity [7,31].

The SERS application of AuNS grown on ITO substrate was illustrated using 4-aminophenol (ATP) as a probe molecule. Briefly, the ITO/AuNS substrate was immersed into an ethanolic solution containing 1 µM ATP for 12 h and the ATP was self-assembled on the surface of AuNS through the formation of Au-S bond. Figure 5.10 shows the Raman spectrum of ATP on ITO substrate and SERS spectra obtained for ATP molecule assembled on AuNS grown ITO.
substrate. Raman spectrum of ATP exhibits peaks at 398, 1087 and 1583 cm\(^{-1}\) corresponding to \(\nu(C-C)\), \(\nu(C-S)\) and bending vibrational mode of \(\nu(C-S)\), respectively due to \(a_1\) vibrational modes of ATP molecule (curve a) \([32,33]\). It also exhibits a characteristic peak of \(b_2\) modes of ATP molecule at 1163 cm\(^{-1}\) \([34]\). When the ATP was adsorbed on the surface of AuNS grown ITO substrate, a noticeable change in the frequency was observed with enhanced intensity (curves c-e). The SERS spectra of ATP adsorbed AuNS grown ITO substrate shows the \(a_1\) vibrational modes at 391, 1081 and 1579 cm\(^{-1}\). The observed peaks were not only shifted towards less positive frequency region but also exhibit 15-fold enhanced intensity in contrast to the Raman spectrum of ATP, indicating a

**Figure 5.10.** (a) Raman spectrum of ATP self-assembled on ITO and SERS spectra of ATP self-assembled on (b) spherical, (c) bipyramidal and (c) wires of AuNS grown ITO substrates. **Inset:** Expanded view of 1000-1200 cm\(^{-1}\) region of the spectra.
strong chemical interaction ATP with AuNS. Moreover, the enhancement in SERS signals of b2 vibrational modes (1440, 1378 and 1132 cm\(^{-1}\)) of ATP on AuNS was also observed. As evidenced from SEM, the population of AuNS on ITO substrate increases with the increase in immersion time (Figure 5.2). Hence, it is clear from Figure 5.2 that while increasing the population of AuNS grown on ITO substrates, SERS signal was also enhanced. In other words, Au-nanowires show better enhancement in SERS signal when compared to spherical and bipyramidal AuNS. Further, the enhancement factor (EF) at wavelength 1081 cm\(^{-1}\) (since it is the strongest band in the spectra) (inset, Figure 5.10) was calculated using the following equation (5.4) [32].

\[
EF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}
\]  

(5.4)

where, \(I_{SERS}\) and \(C_{SERS}\) represent the intensity and concentration of enhanced Raman spectrum and \(I_{RS}\) and \(C_{RS}\) represent the intensity and concentration of normal Raman spectrum, respectively. The EF values were found to be \(4.6 \times 10^5\), \(6.2 \times 10^5\) and \(9.7 \times 10^5\) for ATP adsorbed spherical, bipyramidal and nanowires of AuNS modified ITO substrates. The higher enhancement in Raman signal observed at Au-nanowires may be due to high surface coverage and enhanced charge density localization at the longer nanowires. The anisotropic AuNS with high yield on ITO substrates were found to serve as a SERS-active substrate, indicating the AuNS grown ITO substrate will act as a potential candidate in clinical diagnostics, single molecular detection and bio-assays in future.
5.3. Fabrication of different copper nanostructures on ITO electrode and their shape dependent electrocatalytic activity

The surfactant free cubic, spherical, dendritic and prickly CuNS were fabricated on ITO substrate by applying +0.1, -0.1, -0.3 and -0.5 V, respectively for 400 s in CuSO$_4$ containing 0.1 M H$_2$SO$_4$. Further, a detailed experimental study on the influence of SO$_4^{2-}$, NO$_3^-$, CH$_3$COO$^-$, ClO$_4^-$, and CO$_3^{2-}$ anions on the morphology of CuNS was investigated. The influence of deposition potential, deposition time and pH of the electrolyte on the morphology of CuNS was also studied. The formation of different CuNS on ITO surface with respect to the above said parameters was monitored by scanning electron microscopy (SEM). The different CuNS modified ITO substrates exhibited shape dependent electrocatalytic activity towards the oxidation of glucose and hydrazine.

5.3.1. Electrodeposition of copper nanostructures

![Graph showing i-t curves](image)

**Figure 5.11.** $i$-$t$ curves obtained for different electrolysis potentials of (a-e) -0.1 to -0.5 V with 10 mM of CuSO$_4$ in 0.1 M H$_2$SO$_4$ for an electrolysis time of 400 s.
The relation between the morphology of the CuNS and the applied potential was first investigated. The morphology highly depends on the applied potential since it controls the electrochemical driving force in the constant potential mode [35]. More precisely, the applied potential via the Nernst equation controls the relative surface concentration of the electroactive species. Figure 5.11 shows the $i$-$t$ curves with different electrolysis potentials of -0.10 V to -0.50 V. From the curves, it is obvious that more negative potential resulted in the larger reduction current. During the electrolysis process, the applied potentials (-0.10 to -0.50 V) were sufficient for the reaction of $\text{Cu}^{2+} + 2e^- = \text{Cu}^0$ ($E^0 = 0.339$ V vs. SHE) to take place on the working electrode.

5.3.2. Characterization by SEM

![Figure 5.12](image)

Figure 5.12. SEM images obtained for ITO/CuNS at different deposition potential of (a) +0.10, (b) 0, (c) -0.10, (d) -0.20, (e) -0.30, (f) -0.40, (g) -0.50 and (h) -0.60 V at 400 s using CuSO$_4$. 
The SEM images of the copper deposited at different applied potentials with a fixed copper ion concentration of 10 mM and time of 400 s are shown in Figure 5.12. The SEM images show that the morphology of the deposited Cu varies while varying the applied potential. Cubic structures were formed when applying the potential of +0.10 V and the size of the copper cube is in the range of 200 nm (Figure 5.12a). It can be seen that the spherical nanostructures were grown along with some cubes when the applied potential is switched to 0.0 V (Figure 5.12b). At an applied potential of -0.10 V, the deposited CuNS contains mostly spherical particles with an average size of 100 nm (Figure 5.12c). When the applied potential is shifted to -0.20 V, copper dendrites were grown. But, the population of dendritic NS was less and each branch is in the range of 300 nm (Figure 5.12d). However, well defined dendritic structures with an average size of 100 nm were realized at an applied potential of -0.30 V (Figure 5.12e). When the potential is further switched to -0.40 V (Figure 5.12f), the population of dendrites was high but irregular. The prickly nanostructures were formed by splitting the dendritic nanostructures at applied potentials of -0.50 and -0.60 V with the average size of 100 nm (Figure 5.12g and h). From the above results, it is concluded that the formation of cubic, spherical, dendritic and prickly CuNS is favored at the applied potentials of +0.10, -0.10, -0.30 and -0.50 V, respectively with a deposition time of 400 s.
5.3.3. Characterization by XPS

Figure 5.13. X-ray photoelectron spectral profile obtained for ITO/dendritic-CuNS.

The oxidation state of CuNS was investigated by XPS. Figure 5.13 shows the XPS spectrum of ITO/dendritic-CuNS as a representative case. The Cu2p spectra of ITO/dendritic-CuNS substrate show two peaks at 932.5 and 952.8 eV, corresponding to $2p_{3/2}$ and $2p_{1/2}$ of elemental Cu, respectively [36]. The absence of peaks at 935 and 955 eV, suggest that the deposited CuNS does not contain Cu$^{2+}$ ions [36]. Although Cu$^+$ has the same binding energy with the Cu(0), it is distinguished from Cu(0) by the presence of two weak satellite peaks at 939-945 eV. These peaks are absent in the XPS spectrum (Figure 5.13), which confirms the absence of Cu$^+$. The XPS results clearly suggest that the copper present in the CuNS is in the form of Cu(0).
5.3.4. Characterization by XRD and EDAX

Further, the CuNS modified ITO was characterized by XRD and EDAX. Figure 5.14 shows the XRD patterns obtained for cubic, spherical, dendritic and prickly CuNS modified ITO electrodes (peaks represented by * are corresponding to ITO substrate).

Figure 5.14. X-ray diffraction (XRD) pattern of (a) cubic, (b) spherical, (c) dendritic and (d) prickly CuNS modified ITO electrodes (peaks represented by * are corresponding to ITO substrate).

Further, the CuNS modified ITO was characterized by XRD and EDAX. Figure 5.14 shows the XRD patterns obtained for cubic, spherical, dendritic and prickly NS at the deposition potentials of +0.10, -0.10, -0.30 and -0.50 V. Three major peaks were observed at 42.8°, 49.0° and 73.7°, corresponding to (111), (200) and (220) planes of Cu, respectively (JCPDS File No. 85-1326). The obtained characteristic peaks confirm the formation of crystalline CuNS. The peaks obtained at 22.7°, 30.2°, 35.6°, 38.3°, 40.1°, 46.4°, 50.7° and 67.1° are the characteristic peaks of ITO (JCPDS File No. 89-4599). It can be seen from Figure 5.14, the peak corresponding to the (111) plane is more intense than the other planes. The ratio between the intensity of the (200) and (111) diffraction peaks was much lower,
suggesting that (111) plane is the predominant orientation. Figure 5.15 shows the EDAX spectrum obtained for ITO/dendritic-CuNS substrate. The peaks at 0.92 and 8.0 keV are the characteristics of Cu. The peaks at 0.53, 3.29 and 3.44 eV are corresponding to oxygen, indium and tin, respectively.

**Figure 5.15.** EDAX spectrum obtained for dendritic-CuNS modified ITO substrate.

### 5.3.5. Characterization by EIS

It is well known that CuNS fabricated electrode facilitates the electron transfer between the electroactive species in solution and the underlying electrode [37]. Figure 5.16 shows the Nyquist and Bode plots obtained for bare ITO and cubic, spherical, dendritic and prickly CuNS fabricated ITO electrodes in 1 mM K$_3$[Fe(CN)$_6$] containing 0.2 M PB solution (pH 7.2) at scanning frequencies from 0.01 to 100,000 Hz. A Randles circuit model [$R_S$(CPE-$R_{CT}$)] (Figure 5.16A) was used to fit the impedance spectral data, where, $R_S$ refers to the solution resistance, CPE refers to the constant phase element. The charge transfer resistance ($R_{CT}$) can be calculated from the semicircle obtained in the Nyquist plot and it can control the interfacial electron-transfer rate of the redox probe between

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the solution and the electrode. Figure 5.16A shows the Nyquist plots obtained for the bare and cubic, spherical, dendritic and prickly CuNS fabricated ITO electrodes. The bare ITO electrode shows a large semicircle of about 4.939 kΩ (curve a). The cubic, spherical and prickly CuNS fabricated electrodes show the charge transfer resistance values of 1.486, 1.021 and 1.237 kΩ, respectively (curves b, c and e). Interestingly, the dendritic CuNS fabricated ITO electrode (at -0.30 V) drastically decreased the interfacial charge transfer resistance to 0.718 kΩ (curve d) when compared to bare and other CuNS modified electrodes. This is due to the porous structure of dendrites. These results reveal that the dendritic CuNS fabricated ITO electrode shows lower charge transfer resistance than the other CuNS fabricated ITO electrodes.

Figure 5.16B shows the Bode phase angle plot for bare ITO and CuNS fabricated ITO electrodes. It has been reported that if the phase angle is greater or equal to 90°, the electrode behaves like an ideal capacitor and less than 90°, allows the ions from the solution [38]. The phase angle value of 56° (Figure 5.16B curve a) was obtained for bare ITO electrode and it was decreased to 42°, 40°, 37° and 38° after modified with cubic, spherical, dendritic and prickly CuNS on ITO electrode (Figure 5.16B, curves b-e), respectively. This indicates the facile electron transfer reaction at CuNS modified ITO electrode.
Figure 5.16. (A) Nyquist, (B) Bode-phase angle and (C) Bode amplitude plots for (a) bare ITO, (b-e) cubic, spherical, dendritic and prickly CuNS modified ITO electrodes at the deposition potentials of 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 (A): Equivalent electrical circuit used for fitting the impedance spectra.

Figure 5.16C shows the Bode amplitude plots for bare and different CuNS modified ITO electrodes. The $|Z|$ value in the frequency range from $10^6$ to $10^3$ Hz is constant, suggesting that the solution resistance ($R_S$) is almost same for all the electrodes. The $|Z|$ value starts to increase and the phase angle gradually decreases at the frequency region of $10^3$ to $10^0$ Hz, which indicating the increasing role of capacitive response with decreasing frequency.
frequency. At lower frequency region of $10^0$ to $10^{-3}$ Hz, the $|Z|$ values are 4.939, 1.486, 1.021, 0.718 and 1.237 kΩ corresponding to cubic, spherical, dendritic and prickly CuNS fabricated ITO electrodes, respectively and the $|Z|$ value is equal to the total resistance of the system ($R_S + R_{CT}$) [39]. Since the $R_S$ is same for all the electrodes, it is clear from Figure 5.16C that the $R_{CT}$ value was decreased for the CuNS modified electrode compared to bare ITO electrode. After the fabrication of CuNS on ITO electrode, the $R_{CT}$ value was decreased, showing the conducting nature of CuNS modified electrode. The $k_{et}$ was calculated using the equation (2.3) [40]. The calculated $k_{et}$ values are $5.39 \times 10^{-5}$ for bare ITO and $1.79 \times 10^{-4}$, $2.77 \times 10^{-4}$, $3.70 \times 10^{-4}$ and $2.15 \times 10^{-4}$ cm s$^{-1}$ for cubic, spherical, dendritic and prickly CuNS fabricated ITO electrodes, respectively. The obtained higher $k_{et}$ value for dendritic CuNS fabricated ITO electrode indicates that the electron transfer reaction was faster at this electrode when compared to bare and other CuNS modified ITO electrode.

5.3.6. Electrocatalytic activity of different shaped CuNS towards the oxidation of glucose and hydrazine

The electrocatalytic activity of the different shaped CuNS was examined towards the oxidation of glucose and hydrazine. Since fast and reliable determination of glucose is of tremendous important in clinical diagnostics and food industries the development of electrochemical glucose sensors has attracted huge attention [41,42]. It has been well established in the literature that copper and its oxides show an excellent
electrocatalytic activity towards glucose oxidation because of their superior electrochemical activity, suitable surface charge and easily tunable surface structure [41,42-45]. Figure 5.17A shows the CVs of bare and CuNS modified ITO electrodes in 0.1 M NaOH in the absence and presence of 1.0 mM glucose. Bare ITO does not show any electrochemical response both in the absence and presence of glucose (curves a and c). The ITO/dendritic-CuNS electrode shows a broad reduction peak at +0.60 V in the absence of glucose (curve c), which corresponds to a Cu(0)/Cu(II) redox couple [43,44]. The

**Figure 5.17. (A)** CVs obtained for (a) and (b) bare ITO in the absence and presence of 1mM glucose, (c) ITO/CuNS in the absence and (d-g) cubic, spherical, dendritic and prickly CuNS modified ITO electrodes in the presence of 1mM glucose in 0.1 M NaOH at a scan rate of 50 mVs⁻¹. (solid and dashed lines 1st and 5th cycle). **(B)** CVs obtained for 0.5 mM hydrazine at (a) bare, (b) cubic, (c) spherical, (d) dendritic and (e) prickly CuNS modified ITO electrodes in 0.2 M PB solution (pH 7.2) a scan rate of 50 mVs⁻¹.
electrochemical oxidation of glucose was examined at different CuNS modified ITO substrates (curves d-g). Cubic CuNS modified electrode shows an anodic peak at +0.52 V (curve d) whereas the spherical CuNS show its oxidation at +0.54 V with enhanced current (curve e). When the electrode was modified with dendritic CuNS, the oxidation peak potential was shifted towards less positive potential with enhanced oxidation current when compared to cubic and spherical CuNS (curve f). It shows the glucose oxidation at +0.50 V with 2-fold increase in current when compared to other nanostructures. The enhanced electrocatalytic activity is attributed to the porous nature of dendritic CuNS which serves high specific surface area along with numerous active sites and sharp edges. When the prickly CuNS were modified on the electrode surface, the oxidation potential of glucose was shifted to more positive potential and the oxidation current also suppressed (curve g). This is due to the aggregated nature of the CuNS. The obtained results clearly indicated that the dendritic CuNS showed better electrocatalytic activity when compared to other CuNS. The anodic peak at +0.50 V at different CuNS electrode is due to the oxidation of glucose to gluconic acid (curves d-g). The above results are also consistent with the results obtained from the SEM and EIS studies.

We have also examined the electrocatalytic activity of the different CuNS towards the oxidation of hydrazine. Figure 5.17B shows the CVs obtained for bare and CuNS modified ITO substrates in the presence of 0.5
mM hydrazine in 0.2 M PB solution (pH 7.2) at a scan rate of 50 mV s\(^{-1}\). The bare ITO substrate shows hydrazine oxidation at 1.46 V (Figure 5.17B; curve a). In contrary, the oxidation peak of hydrazine was shifted towards less positive potential at CuNS modified ITO electrodes (Figure 5.17B; curves b-e). Among the different CuNS, dendritic CuNS showed higher electrocatalytic activity towards hydrazine by not only shifting its oxidation potential towards less positive potential but also enhanced its oxidation current (curve d).

Further, we have calculated the electroactive area of the different CuNS modified ITO electrodes according to the Randles-Sevcik equation (5.5) using glucose as a probe molecule [46].

\[
I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} \nu^{1/2} C
\]  

(5.5)

where, \(I_p\) corresponds to the oxidation peak current, \(A\) is the electroactive area of the modified electrode, \(D\) is the diffusion coefficient of the glucose molecule (6.70 \(\times\) \(10^{-6}\) cm\(^2\) s\(^{-1}\)), \(n\) represents the electron transfer number (\(n=2\)), \(\nu\) is the scan rate (50 mV s\(^{-1}\)) and \(C\) is the concentration of the probe molecule (1.0 mM). The \(A\) values for cubic, spherical, dendritic and prickly CuNS fabricated ITO electrodes are found to be 31.79, 47.01, 51.32 and 46.42 cm\(^2\), respectively. Among the different CuNS modified electrodes, the dendritic CuNS modified electrode showed higher electroactive area. This is attributed to the huge specific surface area which is evidenced from SEM studies.
The EIS and electrocatalaytic activity studies clearly demonstrated that dendritic CuNS showed faster electron transfer reaction, higher electroactive area and better electrocatalytic activity when compared to other CuNS. Therefore, the formation of dendritic CuNS with respect to electrolysis time, nature of the copper salt and pH of the medium was investigated. The dendritic CuNS formation with respect to the above parameters was monitored by scanning electron microscopy. The plausible mechanism will be proposed based on the results.

5.3.7. Formation of dendritic CuNS

(i) Effect of electrolysis time

In order to find the optimum time for the formation of dendritic CuNS with uniform morphology, the time dependent growth was carried out by keeping the applied potential of -0.30 V as constant. The growth of CuNS was monitored by SEM. At an electrolysis time of 100 s, the density of the deposited NS is very low and most of the particles obtained are

Figure 5.18. SEM images obtained for ITO/CuNS at the applied potential of -0.30 V for different electrolysis times of (a) 100 s, (b) 200 s, (c) 400 s and (d) 600 s using 0.01 M CuSO₄ in 0.1 M H₂SO₄.
spherical crystals with an average size of 100 nm without any dendritic morphology (Figure 5.18a). When the deposition time was increased to 200 s, the non-uniform quasi-dendritic structures with the average branch size of 200 nm were formed (Figure 5.18b). Further increasing the electrolysis time to 400 s, more uniform dendritic structures were grown on the ITO surface and the dendritic coverage on the ITO substrate was very high (Figure 5.18c). While increasing the deposition time to 600 s, the dendrites were grown as irregular shape and were highly dense and the size of the dendritic branch was increased to 600 nm (Figure 5.18d). This is due to the aggregation of dendrites. The obtained results reveal that 400 s is ideal for the deposition of well defined dendritic CuNS.

(ii) Effect of anion

The effect of the counter ion on the morphology of CuNS was investigated. Copper salts of nitrate, perchlorate, acetate and carbonate were used with the concentration of 10 mM in 0.1 M H₂SO₄ and the deposition was carried under identical conditions. Figure 5.19 shows the SEM images obtained for ITO/CuNS using different copper salts at an applied potential of -0.3 V for 400 s. The spherical agglomerated CuNS were grown on the surface of the ITO when copper nitrate was used (Figure 5.19a). On the other hand, when copper carbonate and copper acetate were used, the aggregated forms of CuNS were grown (Figure 5.19b and c). When copper perchlorate was used, very stumpy dendrites were grown on the surface (Figure 5.19e). These results suggest that
being a bivalent anion the sulfate ion acts not only as a bridging ligand between the deposited NS but also as a shape directing agent to form a dendritic CuNS.

Figure 5.19. SEM images obtained for ITO/CuNS at the applied potential of -0.30 V for 400 s using (a) Cu(NO$_3$)$_2$, (b) CuCO$_3$, (c) Cu(CH$_3$COO)$_2$, (d) CuSO$_4$ and (e) Cu(ClO$_4$)$_2$ in 0.1 M H$_2$SO$_4$.

It has been well established that the morphology will be rectangular or spherical in shape when there is no shape directing agent [47]. However, shape directing agents such as sulfates were added, and then one can achieve one dimensional NS [47]. Although the exact reason is not reported, it is believed that sulfate ions play a major role in the formation of one dimensional dendritic NS. They adsorb on the surface of the seed crystals of CuNPs and thereby decrease the surface energy of the seed
crystals in all directions except one direction [48]. In this particular undisturbed direction, further growth takes place by means of agglomeration or attachment with other seed layers. This process continues to give one dimensional dendritic NS.

To further understand the role of sulfate ion on the morphology of CuNS, CuSO$_4$ was dissolved in different acids and then carried out the deposition. The morphology of the deposited film was examined by SEM. When HNO$_3$ was used, only spherical CuNPs were grown on the ITO electrode whereas the aggregated form of CuNS were formed when HClO$_4$ was used as an electrolyte (Figure 5.20a and b). This may due to the less concentration of sulfate ion in the medium. On the other hand, while adding 10 mM Na$_2$SO$_4$ to 10 mM Cu(NO$_3$)$_2$ in 0.1 M H$_2$SO$_4$, the dendritic CuNS were grown (Figure 5.20c). These results confirm that sulfate ion influences the formation of dendritic CuNS. When the concentration of Na$_2$SO$_4$ was increased, the pH of the solution became basic and hence the

![Figure 5.20](image)

**Figure 5.20.** SEM images obtained for ITO/CuNS at the deposition potential of -0.30 V for 400 s using (a and b) 10 mM CuSO$_4$ in 0.1 M (a) HNO$_3$ and (b) HClO$_4$ and medium (c and d) 10 mM CuNO$_3$ in 0.1 M H$_2$SO$_4$ containing (c) 10 mM Na$_2$SO$_4$ and (d) 50 mM Na$_2$SO$_4$. 213
aggregated NS were grown on the surface (Figure 5.20d). The obtained results suggest that the solution pH influenced the formation of NS. Hence, the effect of pH on the morphology of CuNS was studied.

(iii) Effect of pH

The SEM images of ITO/CuNS obtained at different pH (pH 1 to 7) using 10 mM CuSO$_4$ at an applied potential of -0.3 V for 400 s are shown in Figure 5.21. The solution pH was adjusted using NaOH and Na$_2$SO$_4$.

**Figure 5.21.** SEM images obtained for ITO/CuNS at the electrolysis applied potential of -0.3 V for 400 s using CuSO$_4$ as an electrolyte at different pH of the electrolyte (a-f pH 2-7).

Well defined dendrites were formed at pH 1 (Figure 5.19d). However, when the pH was increased to 2, the particles on the dendrites were joined together to form aggregated dendrites (Figure 5.21a). At pH 3 and 4, the
particles from the aggregated dendrites were left to form a separated bunches (Figure 5.21b and c). When the pH was further increased to 5, well separated crystals of CuNS were formed (Figure 5.21d) and the crystals were further grown like pyramidal structures at pH 6 and polygon at pH 7 (Figure 5.21e and f). It is noticed that the porosity of the deposits decreases when the solution pH is raised. This is due to the precipitation and accumulation of hydrates and hydroxides of the deposits by migration and diffusion in the substrate when the pH of the solution is raised. The above results suggest that pH of the electrolyte also influences on the morphology of the CuNS. The acidic pH favors the dendritic CuNS formation due to the presence of high concentration of sulfate ion. On the other hand, while taking CuSO$_4$ in different acids such as HNO$_3$ and HClO$_4$, the SO$_4^{2-}$ ions of Cu salt may be hydrolyzed to form HSO$_4^-$, a fairly strong acid [49].

\[
H^+ + SO_4^{2-} \rightarrow HSO_4^- \quad (K_a = 1.2 \times 10^{-2} \text{ mol/L}) \quad (5.6)
\]

Thus, the concentration of SO$_4^{2-}$ ions is less in HNO$_3$ and HClO$_4$ acids and HSO$_4^-$ does not act as a bridging ligand to form dendritic CuNS (Figure 5.20a and b). In contrast, H$_2$SO$_4$ is a very strong acid, a weak base SO$_4^{2-}$ ion undergoes negligible hydrolysis in aqueous solution. Hence, the concentration of SO$_4^{2-}$ ions will be maintained and thus the sulfate ions act as a bridging ligand for the formation of dendritic CuNS.
(iv) Mechanism for the formation of dendritic CuNS

![Diagram showing the formation of dendritic CuNS](image)

**Figure 5.22.** Schematic representation of the possible mechanism for the formation of dendritic CuNS.

Based on the results obtained from the above experiments, the formation of dendritic NS involves the following five stages (**Figure 5.22**); (i) Cu$^{2+}$ is reduced to form Cu at an appropriate applied potential, (ii) large quantities of copper nucleus will be immediately formed at random positions due to the surface diffusion and a subsequent growth in which the free copper atoms from the solution will be captured by existing copper nuclei, (iii) the sulfate ions from the copper salt adsorb on the existing copper nuclei and decrease the surface energy of the CuNPs to be deposited in all directions and also act as a bridge between the deposited CuNPs, (iv) while increasing the electrolysis time, the already existing
nuclei will grow onto the aggregated CuNPs and the free nanoparticles diffused frequently toward the aggregate and further are immobilized, forming a larger aggregate and (v) beyond the particular electrolysis time, the newly arriving copper atoms are continuously attached onto the surfaces of the CuNS in an oriented mode of attachment which leads to the formation of dendrites.

5.3.8. Sensitive determination of glucose and hydrazine at dendritic CuNS/ITO electrode

![Graph of CVs obtained for 1 mM glucose at dendritic CuNS modified ITO electrode at different scan rates of 10-100 mV s⁻¹ (a-j) in 0.1 M NaOH. Inset: plot obtained for current vs. square root of scan rate. (B) DPVs obtained for each 20 µM addition of glucose in 0.1 M NaOH in 0.2 M PB solution (pH 7.2) at ITO/DCuNS electrode. Inset: Calibration plot of oxidation current vs. concentration of glucose.

CVs of ITO/dendritic-CuNS in 0.1 M NaOH containing 0.5 mM glucose at different scan rates are shown in Figure 5.23A. The anodic peak
current due to the oxidation of glucose was increased linearly while increasing the scan rates from 10 to 100 mV s\(^{-1}\) with the correlation coefficient of 0.9982 (Figure 5.23A, inset), suggesting that the oxidation of glucose at ITO/dendritic-CuNS electrode was a diffusion controlled process. Further, sensitive determination of glucose at the dendritic CuNS modified electrode was studied by differential pulse voltammetry (DPV). Figure 5.23B shows the DPVs obtained for each increment of 20 µM of glucose at ITO/dendritic-CuNS electrode in 0.1 M NaOH. The ITO/dendritic-CuNS electrode exhibits the oxidation peak at +0.45 V when adding of 20 µM of glucose. While increasing the concentration of glucose in the range of 20-300 µM, the oxidation peak current was increased linearly with a correlation coefficient of 0.999 (Figure 5.23B, inset).

**Figure 5.24.** Schematic representation for the mechanism of electrochemical oxidation of glucose at ITO/CuNS electrode.
Figure 5.24 shows the plausible mechanism for the electrochemical oxidation of glucose [42,45,50]. The metal Cu(0) was first oxidized into Cu(II) species such as Cu(OH)$_2$ under alkaline conditions at the onset of the potential scan [45,50,51]. Then, the Cu(II) species were electrochemically oxidized to Cu(III) species such as CuOOH or Cu(OH)$_4$\(^{-}\). Finally, glucose is catalytically oxidized by the Cu(III) species and produces gluconic acid [45,50,51].

Figure 5.25 (A) CVs obtained for 0.5 mM hydrazine at ITO/dendritic-CuNS in 0.2 M PBS at pH 7.2 at different scan rates from 10 to 100 mV s\(^{-1}\) (a-f). Inset: plot of oxidation current vs. square root of scan rate. (B) Plot of anodic peak potential of hydrazine oxidation vs. log scan rate (log \(v\)).

Figure 5.25A shows the CVs obtained for 0.5 mM hydrazine at ITO/dendritic-CuNS substrate in PB solution (pH 7.2) at different scan rates. The oxidation current of hydrazine was increased while increasing the scan rate. A good linearity between the anodic current of hydrazine and
square root of scan rate was obtained with a correlation coefficient of 0.9965 (Figure 5.25A, inset) at scan rates from 10 to 100 mV s\(^{-1}\). This indicates that the oxidation of hydrazine is a diffusion controlled process at dendritic CuNS modified ITO electrode. Since the oxidation of hydrazine is irreversible process, the oxidation peak potential (\(E_{pa}\)) was shifted towards more positive potential while increasing the scan rate. Further, \(E_{pa}\) is proportional to \(\log \nu\) and the slope is found to be 0.256 V with a correlation coefficient of 0.9958 (Figure 5.25B). The Tafel slope \((b)\) for the irreversible diffusion-controlled system is calculated using the following equation (5.7) [52].

\[
E_{pa} = \frac{b}{2} \log \nu + \text{constant} \quad (5.7)
\]

The Tafel slope \((b)\) was found to be 1.087 V at 10 mV s\(^{-1}\). This result is consistent with the voltammogram of hydrazine oxidation obtained at the scan rate of 10 mV s\(^{-1}\) and the rate limiting step is one electron transfer. Figure 5.26 shows the DPVs obtained for each increment of 20 µM of hydrazine at dendrite ITO/ dendritic-CuNS in 0.2 M PB solution (pH 7.2). The oxidation peak current of hydrazine increased linearly while increasing the concentration of hydrazine in the range of 20-300 µM/L with a correlation coefficient of 0.9971 (Figure 5.26, inset).
5.4. Conclusions

A simple, facile and fast method for the growth of anisotropic AuNS including bipyramidal and wires on solid and solution phases using in-situ electrochemical reduction of Au\(^+\) ions from the growth solution was demonstrated for the first time. The time dependent formation of different AuNS was monitored by HR-TEM and SEM and it was found that the spherical, bipyramidal and nanowires were grown on ITO substrate after 1, 3 and 6 h, respectively. The role of Cu\(^{2+}\) ions with different counter ions on the morphology of AuNS was examined and it was found that Cu\(^{2+}\) is an effective agent for controlled preparation of different shaped AuNS. The greater SERS enhancement was observed at the Au-nanowires grown.

Figure 5.26. DPVs obtained for each 20 \(\mu\)M addition of hydrazine in 0.2 M PB solution (pH 7.2) at ITO/DCuNS electrode. Inset: Calibration plot for current vs. concentration of hydrazine.
substrate when compared to spherical and bipyramidal NS due to higher surface coverage. On the other side, fabrication of surfactant-free cubic, spherical, dendritic and prickly CuNS on ITO surface by electrodeposition was described and investigated the role of applied potential, deposition time and pH on the morphology of dendritic CuNS. SEM images confirmed that cubic, spherical, dendritic and prickly CuNS were formed at the applied potentials of +0.10, -0.10, -0.30 and -0.50 V for 400 s, respectively in the presence of 10 mM CuSO$_4$ containing 0.1 M H$_2$SO$_4$. The catalytic activity of the different shaped CuNS modified ITO was examined towards the oxidation of glucose and hydrazine. The dendritic CuNS modified electrode effectively catalyzed the oxidation of glucose and hydrazine by not only shifting their oxidation potential towards less positive potential and also enhanced their oxidation current when compared other NS. Further, a detailed experimental study on the influence of SO$_4^{2-}$, NO$_3^-$, CH$_3$COO$, ClO_4^-$, and CO$_3^{2-}$ anions on the morphology of CuNS was investigated.
References


