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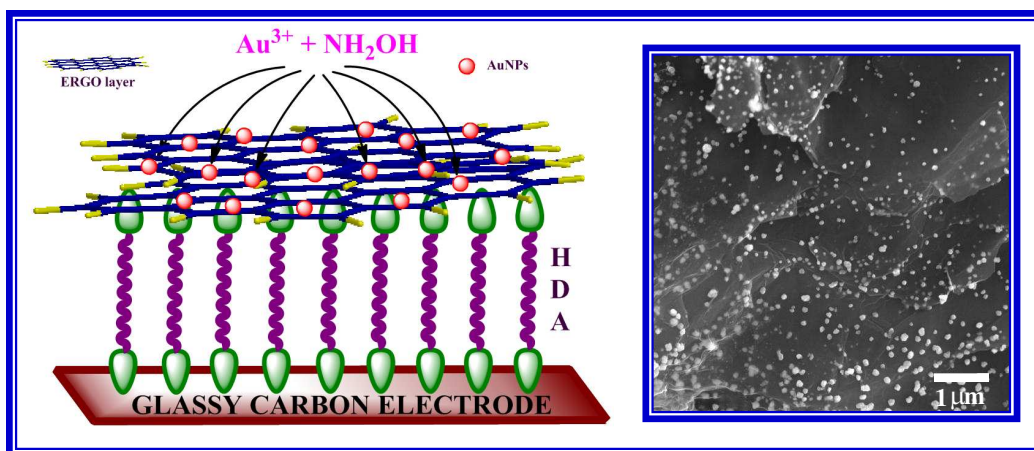


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Graphical Abstract

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ARTICLE TYPE

# Assembly of Gold Nanoparticles on Graphene Film via Electroless Deposition: Spontaneous Reduction of Au<sup>3+</sup> Ions by Graphene Film

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In this paper, electrochemically reduced graphene oxide-gold nanoparticles (ERGO-AuNPs) composite film was fabricated on glassy carbon electrode (GCE) by a simple electroless deposition method using a solution containing HAuCl<sub>4</sub> and NH<sub>2</sub>OH. The deposition of AuNPs on ERGO film was achieved via two different approaches. First approach involves the electroless deposition of AuNPs on graphene oxide (GO) modified GCE followed by the electrochemical reduction. The second approach is the electroless deposition of AuNPs on ERGO film modified GCE which was fabricated by self-assembling GO on 1,6-hexadamine modified GCE followed by the electrochemical reduction. The particle coverage estimated from cyclic voltammetry (CV) showed that the particle coverage of AuNPs deposited on ERGO film (22 %) was higher than that of GO film (17 %) and bare GCE (7%) under identical conditions. The obtained higher coverage is attributed ERGO film's ability to spontaneously reduce Au<sup>3+</sup> ions. Although AuNPs deposition was observed at ERGO surface in the absence of NH<sub>2</sub>OH, the particle coverage was much less (2 %) and hence the electroless deposition was carried out in the presence of NH<sub>2</sub>OH. SEM and CV studies showed that the particle coverage and density of AuNPs were increased while increasing the electroless deposition time.

## Introduction

Graphene comprises sp<sup>2</sup>-bonded carbon atoms, closely packed into 2D nanomaterials that has potential applications in nanoelectronics, sensors, biodevices, batteries and drug delivery.<sup>1-4</sup> Synthesis of composites of graphene received considerable attention in recent years mainly to expand the applications of graphene into different fields.<sup>5-7</sup> The inclusion of electron rich metal nanoparticles such as Au, Ag, Pt and Pd with graphene provides a new way to develop hybrid materials with potential applications in the field of surface enhanced Raman spectroscopy, field effect transistors, catalysis and biosensing.<sup>8-12</sup> These hybrid materials not only display the properties of metal nanoparticles and those of graphene but also exhibit novel properties due to the interaction between metal nanoparticles and graphene.<sup>13</sup> The interesting property of this composite material stems from the high surface area and superior electrical conductivity of graphene and greater reactive surface area of AuNPs.<sup>13,14</sup> Recent reports reveal that GO could be used to prepare graphene-AuNPs composite due to its solubility in various solvents.<sup>15-23</sup> Generally, solution based synthesis of graphene-AuNPs composite was achieved by the reduction of HAuCl<sub>4</sub> using a reducing agent in the presence of GO and reduced graphene oxide (RGO) suspension.<sup>15-23</sup> For instance, Muszynski et al. prepared a graphene-AuNPs composite by reducing HAuCl<sub>4</sub> with NaBH<sub>4</sub> in the presence of octadecylamine

functionalized graphene suspension.<sup>15</sup>

For creating nanopatterned structures on solid substrates, the composite nanostructures must be immobilized on them. Several methods have been used in the literature to fabricate graphene-AuNPs composite on electrode surfaces which include layer-by-layer assembly of graphene and AuNPs,<sup>24,25</sup> drop casting of graphene-AuNPs solution,<sup>16</sup> growth of graphene layers by chemical vapour deposition (CVD) followed by drop casting of AuNPs solution,<sup>26</sup> successive electrodeposition of AuNPs and graphene,<sup>27</sup> drop casting of amine functionalized graphene on electrode surface followed by the self-assembly of AuNPs,<sup>28,29</sup> electrodeposition of AuNPs on graphene modified electrodes and electrochemical co-reduction of graphene oxide (GO) and HAuCl<sub>4</sub>.<sup>30</sup> Careful examination of literature shows that mostly drop casting method has been used to fabricate graphene-AuNPs composite films. However, uniform film formation and reproducibility cannot be achieved by this method. To the best of our knowledge, no reports were available in the literature for the deposition of AuNPs on the self-assembled layers of graphene on electrode surface. Thus, the aim of the present study is to deposit AuNPs by electroless deposition method on graphene film modified GCE. The electrochemically reduced graphene oxide (ERGO) film was fabricated on GCE by self-assembly method<sup>31</sup> and it was used to anchor the deposited AuNPs.

The term 'electroless deposition' was coined by Brenner and Riddell and it is described as the spontaneous reduction of metal ions to the metallic state in the absence of external source of

electric current.<sup>32-34</sup> Electroless deposition is very simple in operation and cost effective compared to sputtering, CVD and electrodeposition.<sup>35-37</sup> It is applicable to various metal/substrate combinations such as metal on metal, metal on semiconductor and metal on insulator.<sup>34</sup> It generally describes any one of the two different processes: (i) direct electroless deposition, in which the metal is directly reduced by a reducing agent, or (ii) a galvanic displacement reaction where the electrons to reduce the gold ions are supplied by the dissolution of the substrate.<sup>38-41</sup> In the present work, direct electroless deposition method is used for the deposition of AuNPs on GO and ERGO films. The HAuCl<sub>4</sub> is used as a precursor and NH<sub>2</sub>OH is used as the reducing agent. It has been also shown that Au<sup>3+</sup>, Pt<sup>2+</sup> and Pd<sup>2+</sup> ions can be reduced by carbon nanomaterials such as single-walled carbon nanotubes (SWCNTs) and GO-carbon nanotubes composites in the absence of external reducing agent.<sup>42,43</sup> Although the AuNPs was deposited on carbon nanostructures by spontaneous reduction of Au<sup>3+</sup> ions, the particle coverage was much less. Hence, NH<sub>2</sub>OH is used as the reducing agent to improve the particle coverage of AuNPs on ERGO film in the present work. Usually, NH<sub>2</sub>OH and HAuCl<sub>4</sub> were used to enlarge the AuNPs which were preassembled on the electrode surface.<sup>44-48</sup> It has been suggested that the surface attached AuNPs catalyze the reduction of Au<sup>3+</sup> ions with the help of the mild reducing agent NH<sub>2</sub>OH.<sup>44-48</sup> The AuNPs attached on solid substrate act as the nucleation centre and hence the enlargement of AuNPs takes place at the surface.<sup>44-48</sup> In the present study, the ERGO film catalyze the reaction between Au<sup>3+</sup> ions and NH<sub>2</sub>OH and acts as the nucleation centre for the deposition of AuNPs because of its ability to reduce Au<sup>3+</sup> ions spontaneously. The AuNPs deposited GO and ERGO films were characterized by UV-visible spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray analyser (EDX), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV).

## 2. Experimental Section

### Materials

Graphite powder and 1,6-hexadiazine (HDA) were purchased from Alfa Aesar. Hydrogen tetrachloroaurate trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) and paracetamol (PA) were purchased from Sigma and were used as received. Hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) was purchased from Merck (India). 0.2 M phosphate buffer (PB) solution was prepared using Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>. All other chemicals were of analytical grade and were used as received. Double distilled water was used for preparing all the solutions. Indium tin oxide (ITO) plates were purchased from Asahi Beer Optical Ltd., Japan.

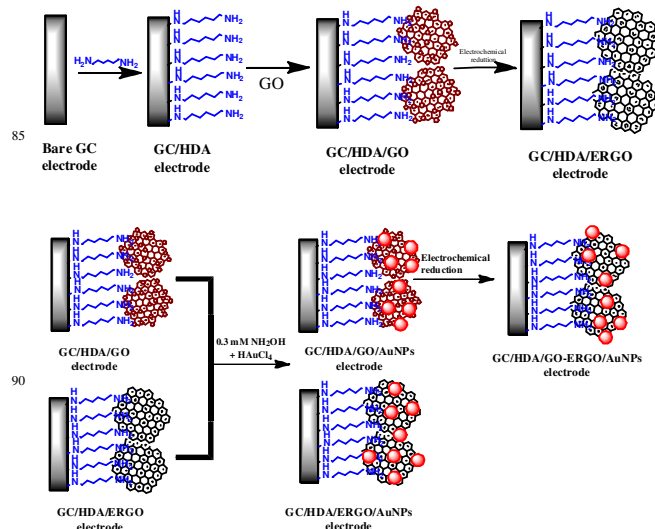
### Instrumentation

UV-visible absorption spectra were recorded with a JASCO V 630 UV-visible spectrophotometer. The electrochemical measurements were carried out with CHI electrochemical workstation (Model 643B, Austin, TX, USA). Raman spectra were recorded on a Bruker senterra dispersive Raman microscope with laser excitation wavelength of 532 nm. XPS measurements were carried out by using Shimadzu Axis 165 high performance multi technique analysis using an Al K<sub>α</sub> source with pass energy of 80 eV, where the pressure in the analysis chamber was lower

than 1 × 10<sup>-8</sup> Torr and the dwell time was 458 ms. The binding energies for identical samples were reproducible within ±0.10 eV. XPS PEAK41 software was utilized to analyze and deconvolute Au 4f region. Peak deconvolutions were performed using Gaussian components after a Shirley background subtraction. Scanning electron microscope (SEM) measurements were carried at VEGA3 TESCAN, USA. Energy dispersive X-ray analysis (EDX) was carried out at Bruker Nano, GmbH, Berlin, Germany. Electrochemical measurements were performed in a three electrode cell with GCE as a working electrode, platinum wire as a counter electrode and NaCl saturated Ag/AgCl as a reference electrode. For differential pulse voltammetry (DPV) measurements, amplitude of 0.05 V, pulse width of 0.06 s, sample width of 0.02 s and pulse period of 0.2 s were used. All the electrochemical experiments were carried out under nitrogen atmosphere at room temperature.

### Fabrication of ERGO Modified GCE

Initially, GO was synthesized using the Hummer's method with slight modification.<sup>49</sup> The ERGO was fabricated on GCE according to our recent paper.<sup>31</sup> Briefly, a well cleaned GCE was immersed into 1 mM solution of 1,6-hexadiazine (HDA) for 8 h. Then, HDA modified electrode was rinsed with water and subsequently immersed into exfoliated GO solution (1 mg/mL) for 12 h, followed by the electrochemical reduction of GO in PB solution (pH 7) for the removal of oxygen functional groups and to retain the aromatic lattice of graphene (Scheme 1).<sup>31</sup>



**Scheme 1.** Schematic representation for the fabrication of GC/HDA/GO-ERGO/AuNPs and GO/HDA/ERGO/AuNPs electrodes.

### Deposition of AuNPs on ERGO Modified GCE

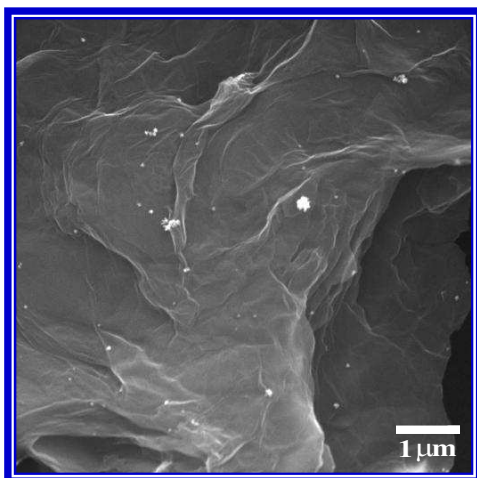
Two different methods were used for the deposition of AuNPs on ERGO modified GCE. First approach involves the immersion of GO film modified GCE into a solution containing 0.3 mM each NH<sub>2</sub>OH and HAuCl<sub>4</sub> for 30 min. Then, the electrode was washed with distilled water and electrochemically cycled between 0 to -1.4 V for 15 cycles in 0.2 M PBS to reduce the oxygen functional groups present on the surface of GO similar to the reduction of GO film modified GCE in the absence of GCE.<sup>31</sup> The second approach involves the immersion of ERGO film modified GCE into a solution containing 0.3 mM each NH<sub>2</sub>OH

and  $\text{HAuCl}_4$ . Scheme 1 illustrates the schematic representation for the electroless deposition of AuNPs on GO and ERGO films modified GCE. For UV-visible spectroscopy, SEM, EDX and XPS studies, the ITO substrates with similar modifications were used.

## RESULTS AND DISCUSSION

### Deposition of AuNPs on ERGO Modified GCE

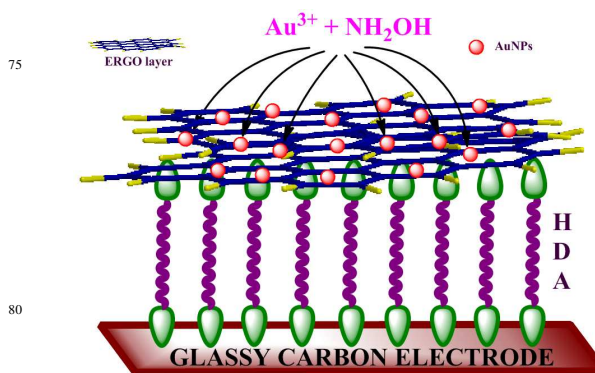
For the deposition of AuNPs on ERGO film modified GCE, electroless deposition method was used. It was achieved by the reduction of  $\text{Au}^{3+}$  ions using a mild reducing agent,  $\text{NH}_2\text{OH}$ . The mechanism for the deposition of AuNPs follows ERGO film assisted reduction of  $\text{Au}^{3+}$  ions by  $\text{NH}_2\text{OH}$ . It is known that  $\text{NH}_2\text{OH}$  is thermodynamically capable of reducing  $\text{Au}^{3+}$  ions to  $\text{Au}^0$ .<sup>50</sup> The ERGO film can accelerate the reduction of  $\text{Au}^{3+}$  ions due to its ability to spontaneously reduce  $\text{AuCl}_4^-$  ions. It has been already demonstrated that SWCNTs can spontaneously reduce  $\text{Au}^{3+}$  ions leading to the formation of AuNPs at the sidewalls of SWCNT.<sup>42</sup> In addition, Sun et al. reported the spontaneous reduction of  $\text{Pd}^{2+}$  ions at the surface of reduced GO-CNT composites.<sup>43</sup> According to these studies, the Fermi level, which is equivalent to the electrochemical potential of RGO is less than +0.25 V vs SHE<sup>42,51</sup> and this is above to the reduction potential of  $\text{AuCl}_4^-$  ions (+1.002 V vs. SHE).<sup>42</sup> The relative potential levels of RGO and  $\text{Au}^{3+}$  ions rationalize the spontaneous electron transfer from the graphene sheets to the metal ions and their reduction.



**Figure 1.** SEM image obtained for ERGO modified ITO substrates after immersing into a solution of  $\text{HAuCl}_4$  solution for 30 min.

The spontaneous reduction ability of ERGO film was confirmed by SEM analysis. Figure 1 shows the SEM image obtained for ERGO film modified ITO substrate after immersing into 0.3 mM  $\text{HAuCl}_4$  solution for 30 min. The SEM image shows the presence of AuNPs on ERGO film, confirming the reduction of  $\text{Au}^{3+}$  ions by ERGO film even in the absence of  $\text{NH}_2\text{OH}$ . The corresponding EDX spectrum shows the peaks at 0.23, 0.52 and 2.2 keV corresponding to C, O and Au, respectively (Figure S1). This reveals the surface catalyzing nature of ERGO film. As discussed earlier, the difference in the reduction potential between ERGO film and  $\text{Au}^{3+}$  ions leads to the spontaneous

reduction of  $\text{Au}^{3+}$  ions by ERGO film. On the other hand, the deposition of AuNPs was not observed at GO modified ITO substrate after immersing into the  $\text{HAuCl}_4$  solution suggesting that the spontaneous reduction of  $\text{Au}^{3+}$  ions is not feasible at GO film due to its insulating nature.<sup>52</sup> Although AuNPs deposition occurs on ERGO film by spontaneous reduction the density of AuNPs was much less. To improve the particle coverage, a mild reducing agent,  $\text{NH}_2\text{OH}$  was used. It is reasonably expected that the deposition of AuNPs at ERGO film will be more facile than that of GO film under identical conditions due to its ability to spontaneously reduce  $\text{Au}^{3+}$  ions. Even though GO modified substrate does not catalyze the spontaneous reduction of  $\text{Au}^{3+}$  ions in the absence of  $\text{NH}_2\text{OH}$ , AuNPs deposition was observed on GO film in the presence of  $\text{NH}_2\text{OH}$ . The oxygen functional groups of GO stabilized the gold nuclei, formed via in-situ reduction of  $\text{Au}^{3+}$  ions by the mild reducing agent  $\text{NH}_2\text{OH}$ . This is similar to the solution based synthesis of dendritic gold nanostructures on GO using  $\text{HAuCl}_4$  and  $\text{NH}_2\text{OH}$  reported by Jasuja and Berry.<sup>19</sup> It has also been reported that the Au surface facilitates the reduction of  $\text{Au}^{3+}$  ions in the presence of  $\text{NH}_2\text{OH}$ .<sup>50,53</sup> The initial deposition of AuNPs on GO and ERGO substrates autocatalyzes further reduction of  $\text{Au}^{3+}$  ions by  $\text{NH}_2\text{OH}$ . Scheme 2 illustrates the mechanism for the electroless deposition of AuNPs on ERGO film.



**Scheme 2.** Schematic representation for the reduction of  $\text{HAuCl}_4$  on GC/HDA/ERGO electrodes by  $\text{NH}_2\text{OH}$ .

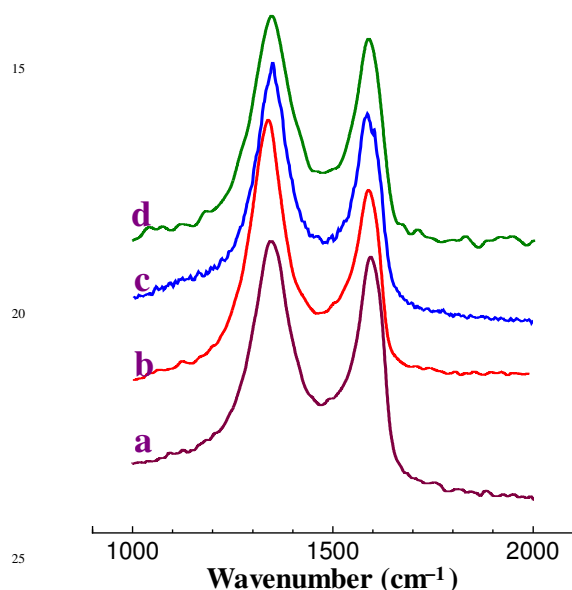
Figure S2 shows the electrochemical reduction of GO before and after the electroless deposition of AuNPs on GO film. The electrochemical reduction of oxygen functional groups of GO film modified GCE was observed at -1.15 V in 0.2 M PB solution (pH 7) (curve a). In the case of AuNPs deposited GO film modified electrode, the reduction of oxygen functional groups was observed at -1.0 V (curve b) which indicates that the AuNPs deposited on GO sheets modified GCE decreased the overpotential for the reduction of oxygen functional groups of GO.

### Characterization of AuNPs Deposited Electrodes by UV-visible Spectroscopy

Figure S3 shows the UV-visible spectra obtained for AuNPs deposited ERGO film modified ITO substrate prepared with electroless deposition time of 30 min, 1, 2 and 3 h. The surface plasmon resonance (SPR) band was observed at 559 nm for 30 min electroless deposition confirming the successful deposition

of AuNPs on ERGO film. For 1, 2 and 3 h deposition (curve a), the SPR bands were observed at 572, 581 and 602 nm, respectively. The shift in SPR band towards higher wavelength is due to the increase in the size of AuNPs while increasing the electroless deposition time. Figure S4 shows the UV-visible spectra obtained for AuNPs deposited GO film modified ITO substrate before and after electrochemical reduction. Before electrochemical reduction, it shows a SPR band at 567 nm, corresponding to the deposited AuNPs. After the electrochemical reduction, the SPR band becomes broad and shifted to 575 nm, indicating that the deposited AuNPs were not leached out from the surface of GO.

#### Characterization by Raman Spectroscopy

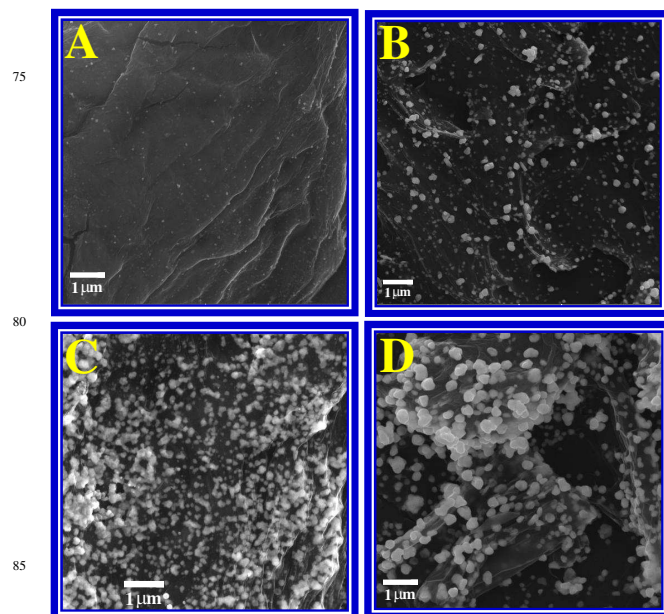


**Figure 2.** Raman spectra obtained for (a) AuNPs deposited GO film, (b) ERGO film and AuNPs deposited ERGO film prepared in the (c) presence and (d) absence of  $\text{NH}_2\text{OH}$  during  $\text{Au}^{3+}$  reduction

The characterization details of GO and ERGO modified ITO substrates were available in our previous study.<sup>31</sup> Figure 2 shows the Raman spectra obtained for AuNPs deposited GO, ERGO film, AuNPs deposited ERGO film in the presence and absence of  $\text{NH}_2\text{OH}$ . Similar to the Raman spectrum of GO film, AuNPs deposited GO film shows the D and G band at 1342 and 1587  $\text{cm}^{-1}$  and the  $I_D/I_G$  ratio was found to be 1.02. The AuNPs deposited ERGO film also shows the D and G bands and the intensity of D band is higher than that of G band indicating the decrease in the average size of  $\text{sp}^2$  domain upon the electrochemical reduction. The intensity ratios ( $I_D/I_G$ ) for AuNPs deposited ERGO film in the presence and absence of  $\text{NH}_2\text{OH}$  were found to be 1.28 and 1.24, respectively. During the reduction of  $\text{Au}^{3+}$  ions, ERGO film was slightly oxidized and the oxidation was more pronounced in the absence of  $\text{NH}_2\text{OH}$ . This result suggested that the  $\text{Au}^{3+}$  ions are not only reduced by  $\text{NH}_2\text{OH}$  but also reduced by ERGO film. The difference in the potential of ERGO film and  $\text{Au}^{3+}$  ions will be the reason for the spontaneous reduction of  $\text{Au}^{3+}$  ions by ERGO film.

#### Characterization of AuNPs Deposited Substrates by SEM and EDX

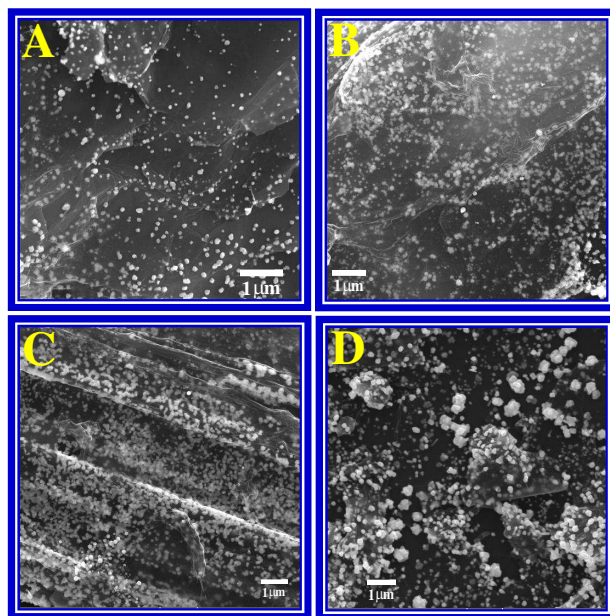
The surface morphology of AuNPs deposited GO and ERGO films modified ITO substrates was analyzed by SEM. Figure 3 shows the SEM images obtained for AuNPs deposited GO film prepared with a variable electroless deposition time. For 30 min deposition, SEM image shows the spherical AuNPs on the surface of GO layers. The density of AuNPs on GO layers was less and the size of AuNPs was found to be 21 nm (Figure 3A). While increasing the deposition time, the density and the size of deposited AuNPs on GO layers were increased. The size of AuNPs deposited on GO film was 40 and 75 nm for 1 and 3 h depositions, respectively (Figures 3B and 3C). The deposited AuNPs expected to act as a nucleation centre for the further reduction of  $\text{Au}^{3+}$  ions and hence the size of AuNPs was increased. On increasing the deposition time to 6 h, the size of AuNPs was further increased to 120 nm and the GO film was completely covered with AuNPs (Figure 3D). The AuNPs were not only deposited at the surface of GO layers but also intercalated into the layers of GO which is evidenced from the SEM image of AuNPs deposited ERGO film prepared with deposition time of 6 h (Figure 3D). From these results, it is concluded that increasing the electroless deposition time not only increases the coverage of AuNPs at GO layers but also increases the size of AuNPs.



**Figure 3.** SEM images obtained for AuNPs deposited GO films modified ITO substrates with (a) 30 min, (b) 1 h, (c) 3 h and (d) 6 h electroless deposition.

Figure S5 shows SEM image obtained for AuNPs deposited GO film modified electrode with an electroless deposition time of 1 h after electrochemical reduction of GO. It clearly showed that the deposited AuNPs were present at the surface of ERGO film and the particles were intercalated into the layers of ERGO. This indicates that the AuNPs were not leached out during the electrochemical reduction of GO. It is expected that the AuNPs stabilized by oxygen functional groups of GO might be leached out during electrochemical reduction. SEM studies showed that the AuNPs intercalated in between the layers of GO were not leached out during electrochemical reduction.

Figure 4 shows the SEM images obtained for AuNPs deposited ERGO film modified ITO substrates prepared by 30 min, 1, 2 and 3 h depositions. For an electroless deposition of 30 min, the AuNPs were deposited at the surface of ERGO layers and the size of AuNPs was found to be 28 nm (Figure 4A). The density of AuNPs on ERGO film modified substrate was higher than that of GO modified substrate for electroless deposition of 30 min. This might be due to the spontaneous reduction of  $\text{Au}^{3+}$  ions by highly conducting ERGO film besides the reduction of  $\text{Au}^{3+}$  ions by  $\text{NH}_2\text{OH}$ . The particle size and the density of AuNPs on ERGO film were increased while increasing the electroless deposition time similar to the deposition of AuNPs on GO film modified substrate (Figures 4B, C and D). In ERGO film, the deposited AuNPs were slightly aggregated due to the absence of any stabilizing functional groups. On the other hand, the AuNPs on GO film are not aggregated due to the presence of oxygen functional groups which may prevent the AuNPs from aggregation. The size of AuNPs on ERGO film for 30 min, 1, 2 and 3 h deposition was found to be 30, 64, 95 and 130 nm, respectively. These results indicate that the complete coverage of AuNPs on ERGO film requires 3 h whereas at GO layers it requires 6 h. The fast electroless deposition of AuNPs on ERGO film compared to GO film might be due to the spontaneous reduction of  $\text{Au}^{3+}$  ions by ERGO film besides the reduction by  $\text{NH}_2\text{OH}$ .

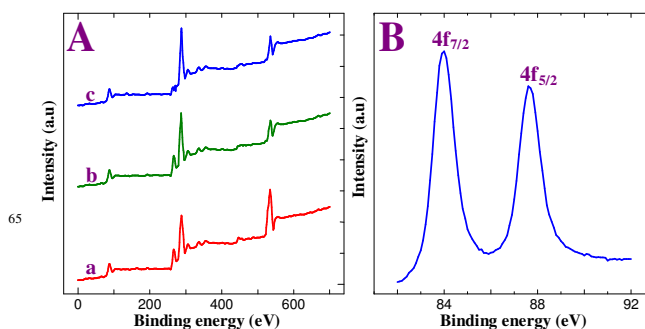


**Figure 4.** SEM images obtained for AuNPs deposited ERGO films modified ITO substrates prepared with (a) 30 min, (b) 1 h, (c) 2 h and (d) 3 h electroless deposition.

Further, the AuNPs deposited GO and ERGO films were also characterized by EDX analysis. Figure S6 shows EDX spectra obtained for AuNPs deposited GO layers before and after electrochemical reduction and ERGO film prepared with an electroless deposition of 1 h. The EDX spectra of them show peaks at 0.23, 0.52 and 2.2 keV corresponding to C, O and Au, respectively. The obtained other peaks might be due to the oxides of indium and tin. The EDX analysis also confirmed the successful deposition of AuNPs at GO and ERGO layers. The presence of Au peak at GO layers modified substrate after

electrochemical reduction further confirmed that the AuNPs were not leached out during the electrochemical reduction of GO. Although decrease in oxygen peak intensity was observed after electrochemical reduction of AuNPs deposited GO layers modified substrate (Figure S5B), it is not appropriate to determine C/O ratio quantitatively due to the possible interference caused by the oxides of indium and tin.

#### Characterization of AuNPs Deposited GO and ERGO Modified Substrates by XPS



**Figure 5.** (A) XPS survey spectra obtained for AuNPs deposited GO films (a) before and (b) after electrochemical reduction and (c) AuNPs deposited ERGO films modified ITO substrates prepared with an immersion time of 30 min during electroless deposition. (B) Au 4f region of AuNPs deposited ERGO films modified ITO substrate.

Further, the deposition of AuNPs on GO and ERGO films was confirmed by XPS. Figure 5A shows the XPS survey spectra obtained for AuNPs deposited GO film before and after electrochemical reduction and ERGO film modified ITO substrates. XPS survey spectrum of AuNPs deposited GO film shows the peaks at 286 and 531 eV corresponding to C 1s peak of  $\text{sp}^2$  carbon and O 1s spectrum of oxygen functional groups of GO, respectively. The peaks at 84 and 355 eV correspond to Au 4f and Au 4d regions of AuNPs deposited on GO surface (curve a: Figure 5A). After electrochemical reduction of GO, the intensity of O 1s peak at 533 eV was decreased due to the removal of oxygen functional groups of GO (curve b: Figure 5A). The presence of peak at 84 eV confirmed the presence of AuNPs. This result indicates that AuNPs were not leached out during electrochemical reduction. The increase in the C/O ratio from 1.12 to 4.04 confirmed the removal of oxygen functional groups of AuNPs deposited GO film after electrochemical reduction. Further, the XPS spectrum of AuNPs deposited ERGO film modified substrate was similar to that of AuNPs deposited GO layers modified substrate after electrochemical reduction (curve c: Figure 5A). Furthermore, Au 4f region shows two peaks at 83.7 and 87.4 eV for  $4f_{7/2}$  and  $4f_{5/2}$ , respectively with a difference of 3.7 eV (Figure 5B) which is consistent with the zero valent nature of Au.<sup>54</sup> XPS results confirmed that AuNPs were deposited at the surface of GO and ERGO film by electroless deposition and they were not removed after the electrochemical reduction of GO film.

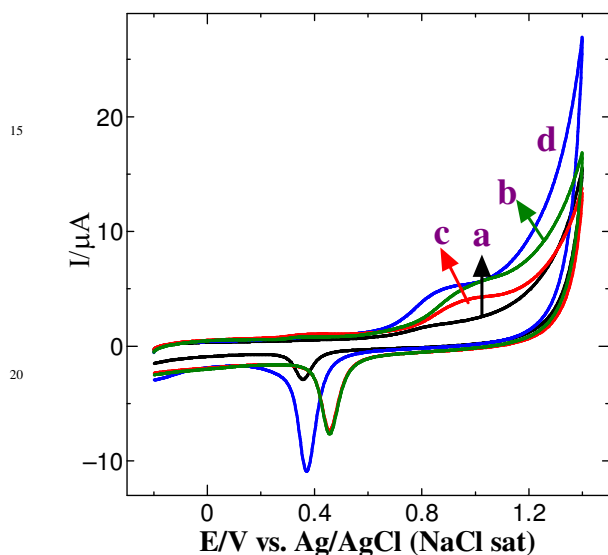
#### Characterization of AuNPs Deposited GO and ERGO Films Modified GCE by CV

Figure 6 shows the CVs obtained for AuNPs deposited on bare GCE, GO film modified GCE before and after electrochemical reduction and ERGO film modified GCE in 0.2 M PB solution

(pH 7). They show a broad oxidation peak was observed at +0.90 V and a reduction peak at +0.38 V, corresponding to the formation and subsequent reduction of gold oxide, respectively. Since the redox peak of AuNPs was surface sensitive, different redox potential was observed for AuNPs deposited on bare, GO and ERGO film modified electrodes. The surface coverage was calculated using the following equation.<sup>55,56</sup>

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

where, 723  $\mu\text{C}/\text{cm}^2$  corresponds to the charge of an electrochemically grown monolayer of gold oxide.<sup>56,57</sup>



**Figure 6.** CVs obtained for (a) AuNPs deposited GCE, AuNPs deposited GO films modified GCE (a) before and (b) after electrochemical reduction and (d) AuNPs deposited ERGO films modified GCE prepared with 30 min electroless deposition in 0.2 M PB solution (pH 7.2) at a scan rate of 50  $\text{mV s}^{-1}$ .

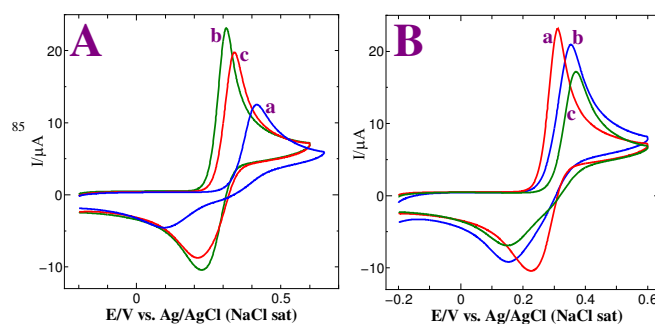
It was found that small amount of AuNPs were also deposited on bare GCE for the electroless deposition of 30 min (curve a). The particle coverages of AuNPs at bare GCE, ERGO and GO film modified GCEs were found to be 7, 22 and 18 %, respectively. The higher particle coverage was observed at AuNPs deposited ERGO film modified GCE (curve d) compared to that of bare and GO modified GCEs. This is consistent with the previous discussion regarding the spontaneous reduction ability of ERGO film compared to GO film. Although AuNPs were deposited at bare GCE, the surface coverage was very much less compared to other electrodes. The particle coverage values of AuNPs deposited GO film before (18 %) and after electrochemical reduction (17 %) were almost same (curves b and c) indicating again that the attached AuNPs were not leached out from the surface of GO film during electrochemical reduction. This is in accordance with the results of SEM, EDX and XPS. Further, the effect of electroless deposition time of AuNPs at ERGO modified GCE was studied. Figure S7 shows the CVs obtained for AuNPs deposited ERGO film modified GCE prepared with electroless deposition of 30 min, 1, 2 and 3 h in 0.2 M PB solution. The corresponding particle coverage values are 22, 26, 30 and 34 %. After 3 h, the particle coverage value was not increased due to the

complete coverage of AuNPs on ERGO film.

The ability of ERGO film to spontaneously reduce  $\text{Au}^{3+}$  ions was also confirmed by CV studies. Figure S8 shows the CV obtained for ERGO modified GCE after immersing into a solution of 0.3 mM solution  $\text{HAuCl}_4$  for 30 min in 0.2 M PB solution (pH 7). It showed the oxidation and reduction peaks at +0.9 V and +0.4 V, corresponding to the formation and subsequent reduction of gold oxide (curve a). The appearance of these peaks confirmed the spontaneous reduction of  $\text{Au}^{3+}$  ions by ERGO film. The particle coverage value of AuNPs deposited ERGO by spontaneous reduction was much less (2 %) compared to that of AuNPs deposition in the presence of  $\text{NH}_2\text{OH}$  (22 %).

#### Electrochemical oxidation of PA at bare, ERGO and ERGO-AuNPs modified GCEs

The electrocatalytic activity of ERGO and AuNPs deposited ERGO modified GCEs were examined by taking paracetamol (PA) as a probe. Figure 7A shows the oxidation of 0.5 mM PA (pH 7.2) at bare GCE, ERGO and ERGO-AuNPs modified GCEs. At bare GCE, the oxidation of PA was observed at +0.45 V (curve a). In the case of AuNPs deposited ERGO film modified GCE (electroless deposition time of 30 min), the oxidation of PA was observed at +0.31 V with enhanced oxidation current compared to bare GCE (curve b). To ascertain the enhanced catalytic activity is due to synergistic effect of ERGO and AuNPs film, the oxidation of PA was studied at ERGO film modified GCE alone. The oxidation of PA was observed at +0.34 V and the oxidation peak current was less (curve c) compared to that of AuNPs deposited ERGO film modified GCE. Hence, it is suggested that the increase in the oxidation current of PA at ERGO-AuNPs modified GCE might be due to the synergistic effect of AuNPs and ERGO film.



**Figure 7.** (A) CVs obtained for 0.5 mM PA at (a) bare GC, (b) GC/HDA/ERGO-AuNPs and (c) GC/HDA/ERGO electrodes prepared with an immersion time of 30 min during electroless deposition in 0.2 M PB solution (pH 7.2). (B) CVs obtained for 0.5 mM of PA at AuNPs deposited ERGO films modified GCE in 0.2 M PB solution prepared (a) 30 min, (b) 1 h and (c) 3 h electroless deposition.

Further, the dependence of electrocatalytic activity towards PA with electroless deposition time of AuNPs deposited on ERGO film was studied. Figure 7B shows the oxidation of PA at AuNPs deposited ERGO film modified GCE prepared with 30 min, 1 h and 3 h deposition. It was found that increasing the deposition time decreases the electrocatalytic activity towards the oxidation of PA at AuNPs deposited ERGO films modified GCE (curves a-c). Although the particle coverage increases with the increase in electroless deposition time, the electrocatalytic activity decreases due to increase in the size of AuNPs. The electrocatalytic activity



of ERGO film has been less pronounced due to the complete coverage of AuNPs at ERGO film which hinders the influence of ERGO film towards PA oxidation. The increase in the size of AuNPs with electroless deposition time is the reason for the decrease in the electrocatalytic activity. Hence, the synergistic effect of ERGO and AuNPs was pronounced only at the electroless deposition time of 30 min.

## CONCLUSIONS

The present work demonstrated the deposition of AuNPs on ERGO film modified GCE by electroless deposition method. Two approaches were used for the deposition of AuNPs on ERGO film. First approach is the direct electroless deposition of AuNPs on GO film modified GCE followed by the electrochemical reduction of GO and the second approach is the electroless deposition of AuNPs on ERGO film modified GCE. Although the ERGO film spontaneously reduce  $\text{Au}^{3+}$  ions in the absence of  $\text{NH}_2\text{OH}$ , the particle coverage of AuNPs was much less (2%). Hence,  $\text{Au}^{3+}$  ions were reduced to metallic Au with the help of the mild reducing agent,  $\text{NH}_2\text{OH}$ , on both GO and ERGO films. The reaction was accelerated by ERGO surface due to its ability to reduce spontaneously reduce  $\text{Au}^{3+}$  ions. This was confirmed from the CV and SEM studies which showed that particle coverage of AuNPs obtained at ERGO film was higher than that of GO film. The initial deposition of AuNPs on both GO and ERGO film autocatalyzes further reduction of  $\text{Au}^{3+}$  ions by  $\text{NH}_2\text{OH}$  and the size and the particle coverage increased with the increase in the electroless deposition time. SEM, XPS, EDX and CV studies confirmed that the AuNPs were not leached out from the GO film during electrochemical reduction. The prepared composite film modified electrode enhanced the oxidation peak current of PA due to the synergistic effect of ERGO film and AuNPs.

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## Notes and references

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