CHAPTER VI

EMBELLISHMENT OF GOLD NANOPARTICLES ON THE SURFACE OF CHITOSAN BLENDED REDUCED GRAPHENE OXIDE FOR THE ELECTROCHEMICAL INVESTIGATION OF p-AMINOPHENOL

6.1. INTRODUCTION

Aminophenols are well known organic compounds that exist in three isomeric forms in which single amino group is located at para to the phenolic –OH group known as p-aminophenol (p-AP) [1]. It is an essential basic material commonly used for the production of dyes, polymers, photography etc., It is also used as an intermediate product for the preparation of paracetamol. Since the structure of p-AP is similar to aniline and phenol, it is considered as a highly toxic pollutant [2]. Moreover large amounts of p-AP are inevitably delivered into the environment as a pollutant. The exposure of p-AP causes serious nephrotoxicity and teratogenic effect that is harmful to humans, plants and animals. The accumulation of excess of acetaminophen causes severe fatal hepatoxicity, inflammation of the pancreas and skin rashes [3]. On account of its high toxicity, the United States and European pharmacopeias has limited the maximum content of p-AP in pharmaceuticals to 50 ppm. Hence, it is essential to detect p-AP in the environmental surroundings [4]. Thus it is important to develop simple, sensitive and accurate analytical methods for the detection of p-AP. During the last few decade researchers have been focused on electrochemical determination due to its good reliability, short time analysis, fast response, high sensitivity and selectivity [5].

Recently, graphene has attracted tremendous attention due to its extraordinary properties like mechanical stiffness, electronic transport and high electrical conductivity. It is composed of single-atom-thick sheet of carbon densely packed in a two dimensional honeycomb lattices [6]. Graphene oxide is one of the most important derivatives of graphene which has oxygen functional groups, carboxyl and epoxy groups on the basal planes and edges. Owing to their unique properties such as high specific surface area and fast ion diffusion process it has

tremendous applications in various fields such as energy storage devices , sensors etc., [7] Chitosan (CS) is a linear polysaccharide biopolymer composed of glucosamine and N-acetyl glucosamine linked with a β-1-4-glycosidic linkage. Since, chitosan consists of large amounts of amino and hydroxyl groups, it exhibits high adsorption capacity which can be applied in electrochemical sensors [8-9]. On incorporating metal nanoparticles onto the graphene oxide, the resulting nanocomposites are one of the most promising candidates and have been applied in various fields such as catalysis, dye removal, electrochemical sensors, batteries, fuels etc., Gold nanoparticles have attracted intensive attention due to their excellent biocompatibility, nontoxicity, optical, catalytic and electrical properties [10]. In this present work chitosan blended reduced graphene oxide /gold nanocomposites are synthesized by chemical reduction method. The prepared nanocomposites are tested for the electrochemical detection of p-Aminophenol and optimized using various pH and scan rate.

6.2. EXPERIMENTAL PROCEDURE

6.2.1. Reagents

Graphite powder, Conc.sulphuric acid (98% H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide solution (30% H_2O_2), sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH), gold (III) chloride trihydrate, sodium borohydride ($NaBH_4$) and aminophenol are of analytical grade, purchased from sigma Aldrich and are used as received without further purification.

6.2.2. Synthesis of reduced graphene oxide / chitosan / Gold nanocomposites

The rGO / CS/ Au nanocomposites are synthesized by dispersing 50 mg of rGO/CS solution in 25 ml of distilled water by ultrasonication for 1 hour to form the aqueous rGO/CS solution. About 0.002M of gold (III) chloride trihydrate is taken in 50 ml of distilled water and stirred for 1 hour separately. The stirred gold (III) chloride trihydrate solution is added dropwise into the above dispersed rGO/CS solution under constant stirring. Then 25mg of $NaBH_4$ is taken in 50 ml of distilled water and stirred for 1 hour separately. The stirred $NaBH_4$ solution is added drop wise into the above reaction mixture and is stirred for 4 hours at 60°C. Hence the

formed solution is left undisturbed for overnight and the resultant supernatant is filtered and washed rigorously by centrifuging at 8000 rpm. It is then dried in oven at 60°C for 4 hours and the sample is grinded finely to form the rGO/CS/Au nanocomposites [11-12]. The same procedure is followed to prepare various concentrations of (0.004 M, 0.006 M, 0.008M and 0.01M) gold (III) chloride trihydrate to form rGO/CS/Au nanocomposites.

6.3. RESULTS AND DISCUSSION

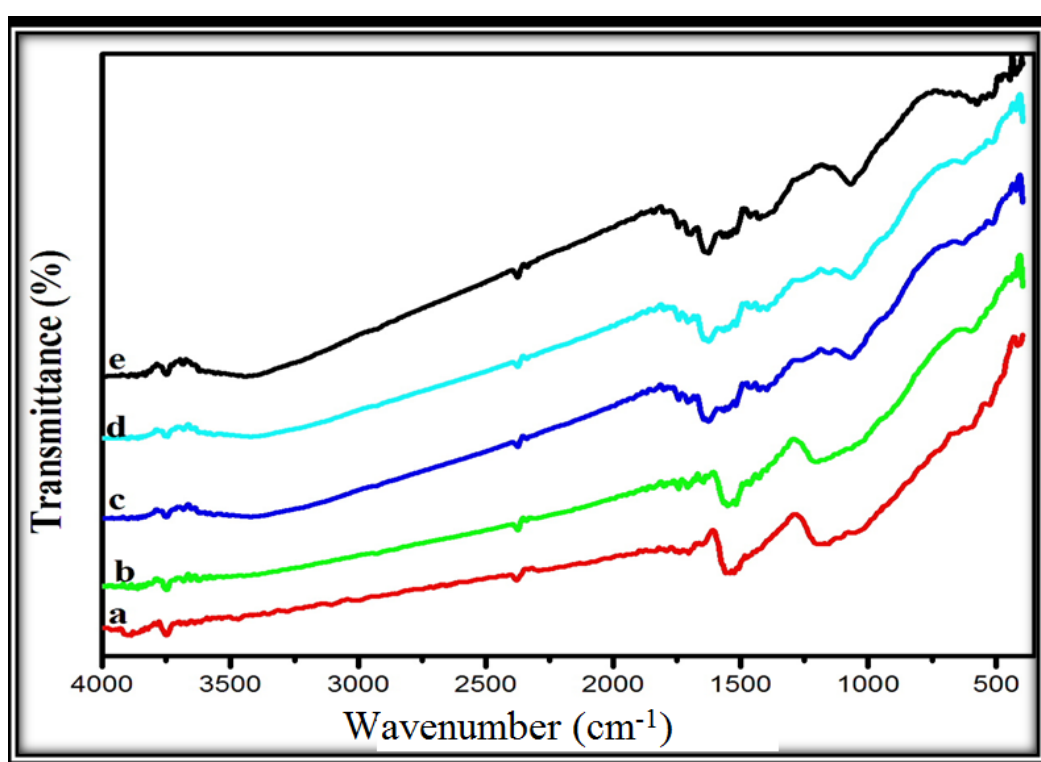### 6.3.1 FT-IR Spectral Analysis

Figure 6.1(a-e) FT-IR spectra for various concentrations (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M of gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites

Figure 6.1(a-e) shows the FT-IR spectra for various concentrations of (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites. The band at 3424 cm^{-1} corresponds to the O-H stretching vibrations of hydroxyl groups. The alkoxy C-O stretching vibrations are observed at 1066 cm^{-1}. The band at 1535

cm^{-1} can be assigned to the stretching vibrations of amine groups [13]. The presence of oxygen functional groups indicates that graphene oxide has been reduced into rGO. The characteristic band at 1644 cm^{-1} corresponds to the N-H stretching vibrations of amine groups. The band at 1413 cm^{-1} represents the C-OH stretching vibrations and the band at 586 cm^{-1} corresponds to the stretching of metallic vibrations of Au [14]. It is further observed that on increasing the concentration of gold nanoparticles the bands have been shifted to lower wavelength and this may be due to the synergistic effect of hydrogen bonding between reduced graphene oxide, chitosan and gold nanoparticles. The results show that gold nanoparticles are well interacted with the chitosan functionalized graphene nanosheets.
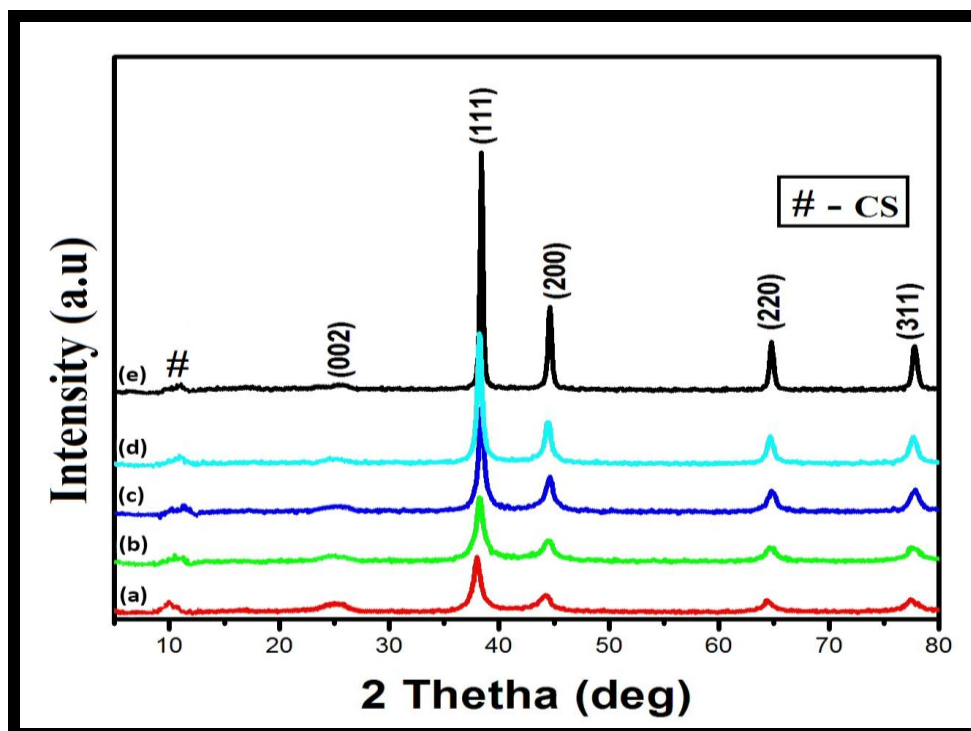
6.3.2 XRD Structural analysis

Figure 6.2 (a-e) XRD patterns for various concentrations (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M of gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites

The crystalline nature and the phase structure of the prepared nanocomposites is characterized using XRD analysis. Figure 6.2 (a-e) shows the XRD patterns for various concentrations of 0.002 M, 0.004 M, 0.006 M, 0.008 M

and 0.01 M of gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites. The small characteristic peak at 10.1° corresponds to the plane of chitosan which confirms the presence of chitosan in the prepared nanocomposites. The diffraction peaks positioned at 38.2°, 44.2°, 64.6° and 77.1° corresponds to the (111) (200) (220) and (311) planes of gold nanoparticles that are well matched with the JCPDS card number 04-0784. An additional broad peak at 24° corresponds to the (002) plane of reduced graphene oxide. The broadening of the peak at 24° is due to the amorphous nature of chitosan which increases its interlayer spacing of reduced graphene oxide nanosheets [15-16]. It is further observed that on increasing the concentration of gold nanoparticles from 0.002M to 0.01M, the intensity of diffraction peaks corresponding to gold nanoparticles increases thereby decreasing the intensity of CS and rGO peaks.

The crystallite size of the prepared rGO/CS/Au nanocomposites is determined using Debye-Scherrer equation ($D=K\lambda/\beta \cos(\theta)$).The calculated results from Scherrer formula indicate that the crystallite size is found to be about 8.9 nm, 9.82 nm, 11.14 nm, 14.1 nm and 16.5 nm respectively. It is also observed that the crystallite size of Au nanoparticles on the surface of rGO/CS nancomposites increases on increasing the concentration of gold (III) chloride trihydrate. These results clearly indicate the formation of gold nanoparticles into the rGO/CS nanocomposites.

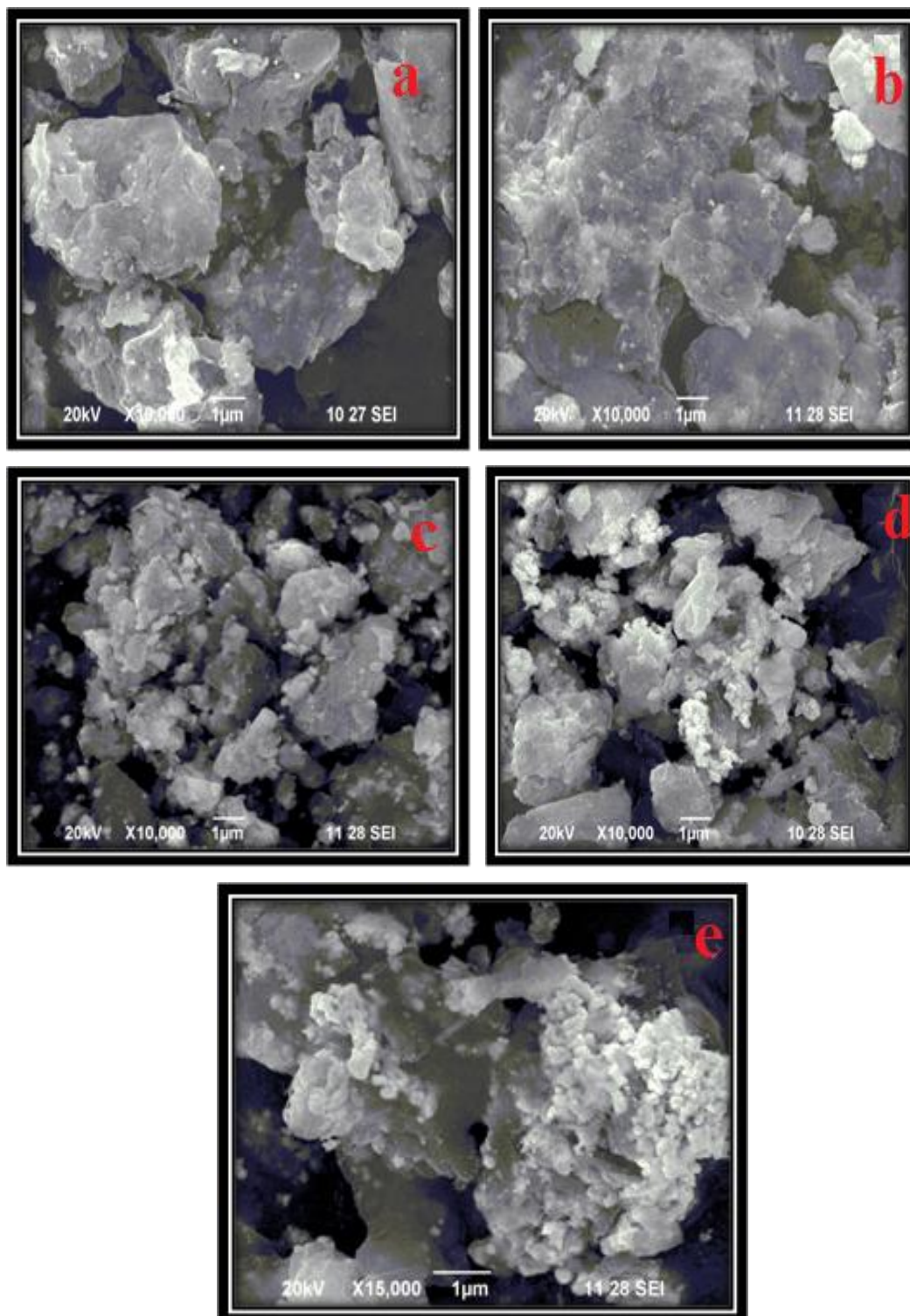## 6.3.3 Scanning Electron Microscopy Analysis

Figure 6.3 (a-e) SEM images for various concentrations of (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites

The surface morphology of the prepared nanocomposites is characterized using Scanning Electron Microscope analysis. Figure 3 (a-e) shows the SEM images for various concentrations 0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M of gold nanoparticles incorporaed on chitosan functionalized reduced graphene oxide nanocomposites. The SEM images of rGO/CS/Au nanocomposites reveals that the spherical shaped gold nanoparticles are homogeneously distributed and closely anchored onto the surface of rGO / CS nanosheets which indicates the strong electrostatic interaction between the reduced graphene oxide nanosheets and gold nanoparticles [17-18]. Thus the CS matrix acts as physical barrier which restricts the motion of nanoparticles and helps in uniform distribution of Au nanoparticles.

It is further observed that on increasing the concentration of gold nanoparticles from 0.002 M, 0.004 M, 0.006 M and 0.008 M, the number of nanoparticles on the surface of rGO/CS also increases. But for higher concentration 0.01M of gold, the CS matrix loses its tendency of making stable particles may be due to the aggregation of gold nanoparticles on the surface of rGO/CS nanocomposites as evidenced from XRD analysis. It shows that the gold nanoaparticles are well incorporated onto the surface of rGO/CS nanocomposites.
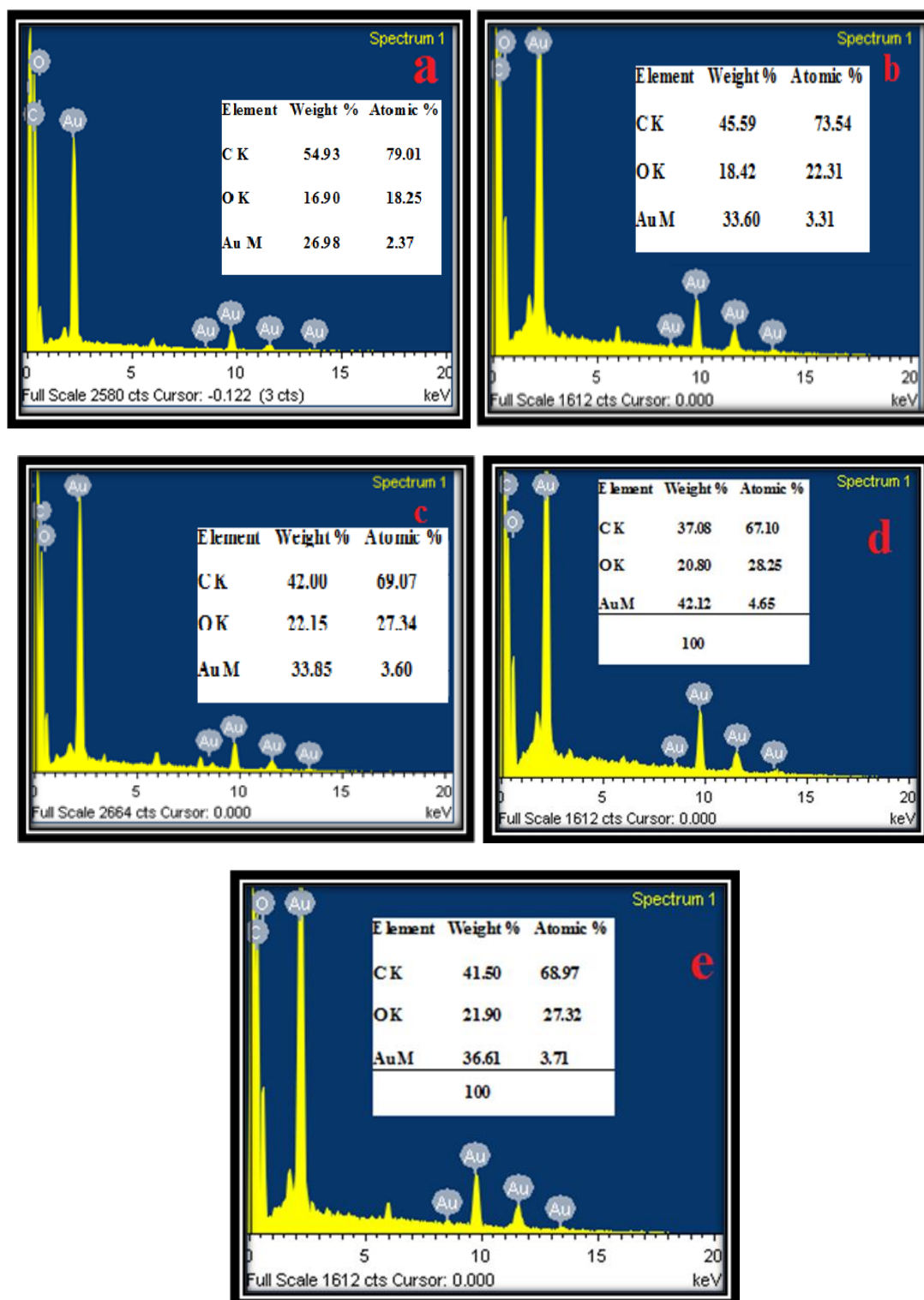
6.3.4 EDAX Analysis

Figure 6.4 (a-e) EDAX spectra for various concentrations (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M of gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites

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The elemental analysis of the prepared rGO/CS/Au nanocomposites is analyzed using Energy dispersive X-ray spectroscopic (EDAX) technique in the range between 0 and 20 KeV binding energy. Figure 6.4 (a-e) shows the EDAX spectra for various concentrations of 0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M gold nanoparticles decorated on chitosan functionalized reduced graphene oxide nanocomposites. The quantitative presence of carbon, oxygen and gold without any impurities confirms the formation of rGO/CS/Au nanocomposites along with the atomic and weight percentage of the elements are tabulated and shown in inset of Figure 6.4 (a-e) [19]. It is observed that on increasing the concentration of gold from 0.002M to 0.008M the atomic and weight percentage of gold nanoparticles also increases which attributes the strong electrostatic interaction between carbon-oxygen of rGO/CS and Au nanoparticles. It is further observed that for higher concentration of gold (0.01M), the atomic and weight percentage of gold nanoparticles decreases as rGO/CS nanosheets has attained saturation and it could not accommodate excess of Au nanoparticles.. These results clearly indicate the successful formation of rGO/CS/Au nanocomposites.
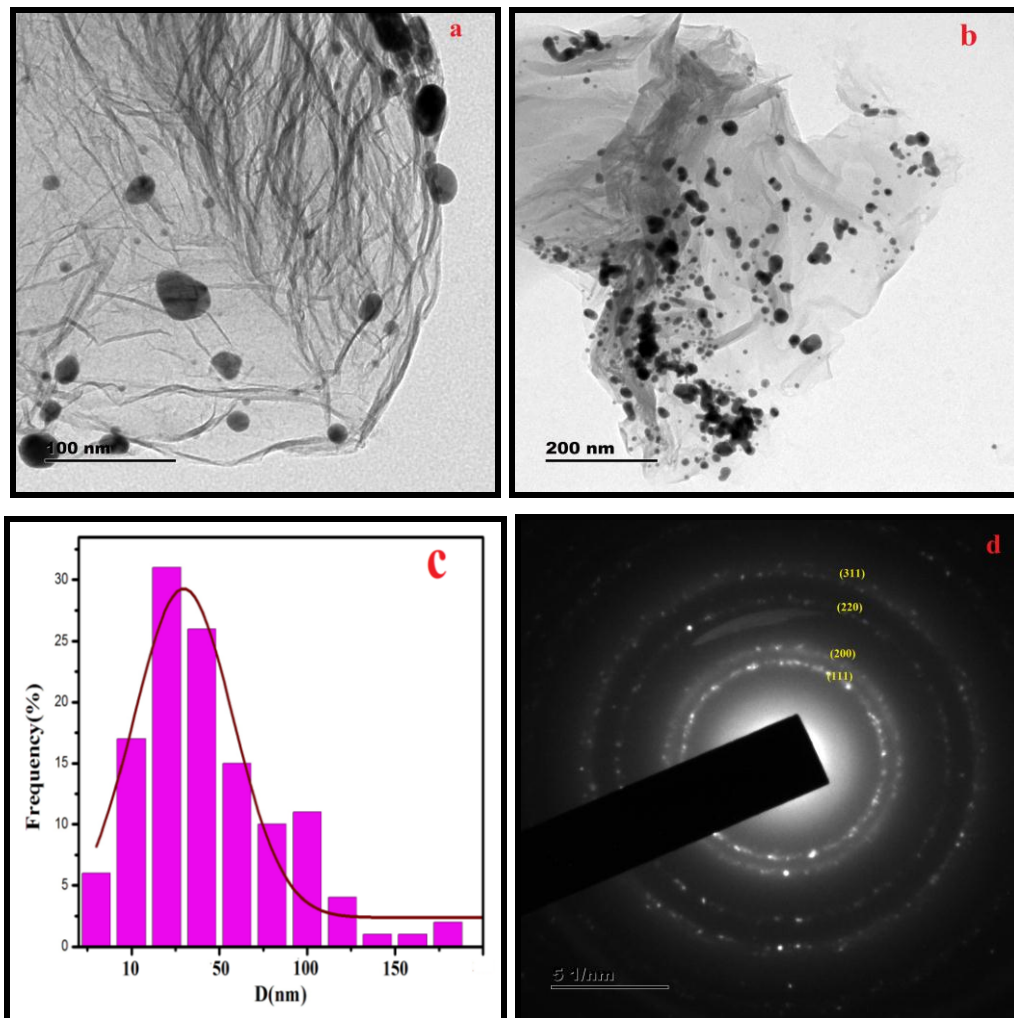
6.3.5 HR-TEM analysis

Figure 6.5 (a-b) TEM images for different magnifications and (c) Particle size distribution histogram of rGO/CS/Au nanocomposites (d) SAED pattern for 0.008M of gold nanoparticles incorporated on rGO/CS nanocomposites

Transmission electron microscopic analysis for 0.008 M of rGO/CS/Au nanocomposites is depicted in Figure 6.5 (a-b). HR-TEM analysis reveals that the formed graphene oxide is of extremely fine sheets and opaque the gold nanoparticles are of spherical shaped [20]. It is observed that the spherical shaped gold nanoparticles are loaded onto the surface of rGO/CS nanosheets. The size distribution of the Au nanoparticles is varied in the range of 10-50 nm with the mean diameter of 26 nm. The selected area electron diffraction (SAED) pattern for 0.008 M of rGO/CS/Au nanocomposites is shown in Figure 6.5 (c). It is observed from

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Figure 6.5 (c) that the obtained distinct rings confirm the polycrystalline nature of the prepared nanocomposites. The SAED patterns are well indexed with highly resolved lattice planes (111) (200) (220) and (311) of gold nanoparticles as evidenced from XRD analysis [21].

6.4 ELECTROCHEMICAL INVESTIGATION OF p-AMINOPHENOL

The prepared rGO/CS/Au nancomposites is tested for the electrochemical sensing of p-Aminophenol. Based on the characterization studies 0.008 M of Au nanoparticles decorated rGO/CS nanocomposites is chosen to be the electrode material for the electrochemical investigation of p-AP. The electrocatalytic effect of p-AP at 0.008 M of rGO/CS/Au nanocomposites is studied. Moreover various parameters such as the effect of electrolyte and effect of scan rate are also studied.

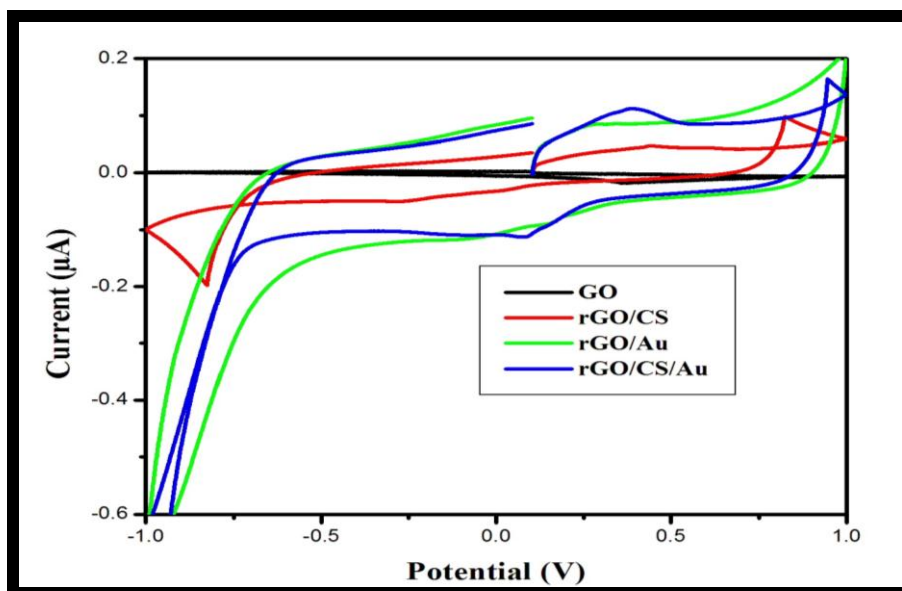### 6.4.1 Electrochemical behaviour of modified electrodes

Figure 6.6 (a-d) Cyclic voltagramm curve for (a) GO/GCE (b) rGO/CS/GCE (c) rGO/Au/GCE and (d) rGO/CS/Au/GCE in the presence of 50µM of p-APl in 0.1 M Phosphate Buffer Solution (PBS : pH 5) at a scan rate of 20 mV s^{-1}

The electrochemical behaviour of prepared rGO/CS/Au nanocomposites towards the detection of p-AP is investigated using cyclic voltammetry. It is carried out in PBS solution, at a potential range from −1 to1V with a scanning rate of 20 mV s^{-1}. Figure 6.6 (a-d) shows the Cyclic voltagramm curve for GO/GCE,

rGO/CS/GCE, rGO/Au/GCE and rGO/CS/Au/GCE in presence of 50μM of p-Aminophenol in 0.1 M of PBS at a scan rate of 20 mV s^{-1} with the pH maintained at 5. By the addition of 50μM of p-AP, no redox peaks is observed for GO modified GCE (GO/GCE) which indicates that GO is non-electro active. In contrary, a pair of weak redox peak current of p-AP is observed at a potential of about Epa=0.042V and Epc= -0.19V for rGO/CS modified GCE. Moreover for rGO/Au nanocomposites modified GCE, a pair of redox peaks is observed at potential of about Epa= 0.44V and Epc= -0.26V. But the addition of Au nanoparticles onto the surface of rGO/CS, a pair of well defined and quasi reversible peaks corresponding to the electrochemical reaction of p-AP is observed at a potential of about Epa= 0.38V and Epc= 0.08V for rGO/CS/Au modified GCE [22-24]. It is also observed that the current of rGO/CS/Au nanocomposites is slightly higher than that of both rGO/CS and rGO/Au nanocomposites. Since rGO/CS/Au facilitates to accommodate large number of active sites of p-AP that enhances the electrocatalytic activity of p-AP and this may be due to the π-π stacking interactions that exist between reduced graphene oxide nano sheets blended with chitosan and embedded with gold nanoparticles. These results clearly depicts that rGO/CS/Au nanocomposites showed good response towards the detection of p-AP.
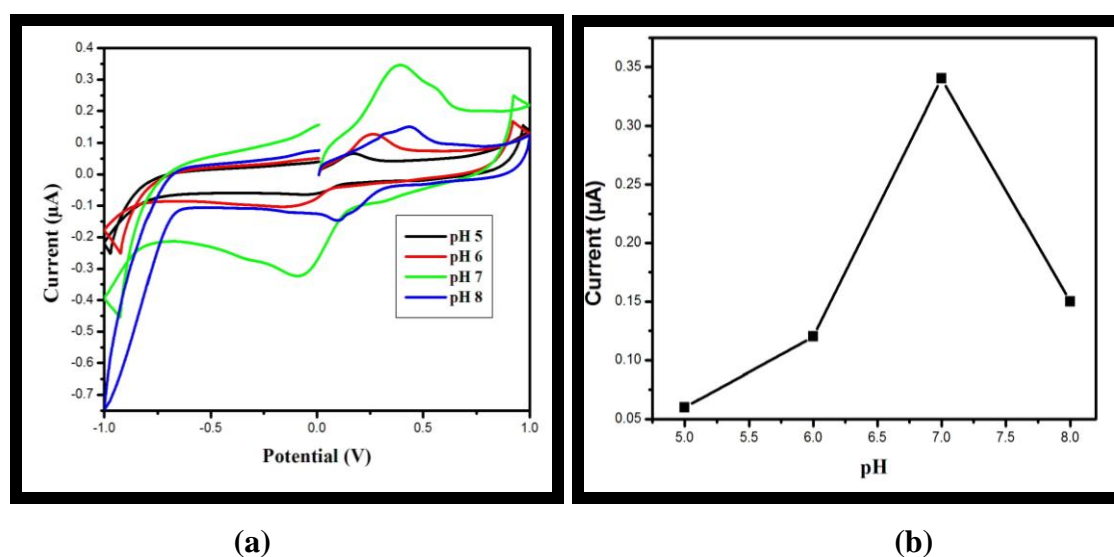
6.4.2 Effect of pH

(a)   (b)

Figure 6.7 (a-b) Effect of pH value of PBS on the redox peak current of 130 μM of p-Aminophenol and its linearity graph

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The electrochemical response of p-Aminophenol on the rGO/CS/Au/GCE is affected by pH value of PBS. Figure 6.7 (a-b) shows the effect of pH value of PBS on the redox peak current of 130 µM of p-Aminophenol and its linearity graph. In order to achieve the highest electrochemical response, the electrochemical reduction response of the modified electrode towards the detection of p-Aminophenol at different pH values ranging from 5 to 8 is investigated by cyclic voltammetry. It is observed from Figure 7(a-b) that the redox peak current of p-Aminophenol gradually increases with increasing the pH from 5.0 to 7.0. Moreover on further increase in the pH to 8.0 the redox peak currents of p-Ap decreases. Meanwhile, the oxidation peak potential sifts positively whereas the reduction peak potential shifts negatively [2]. This shifts in E_{pa} and E_{pc} clearly indicates that the electrochemical redox process is directly involved in proton transfer of p-Ap, at which equal number of protons and electrons are transferred during the electrochemical oxidation of p-AP on rGO/CS/Au nanocomposites.
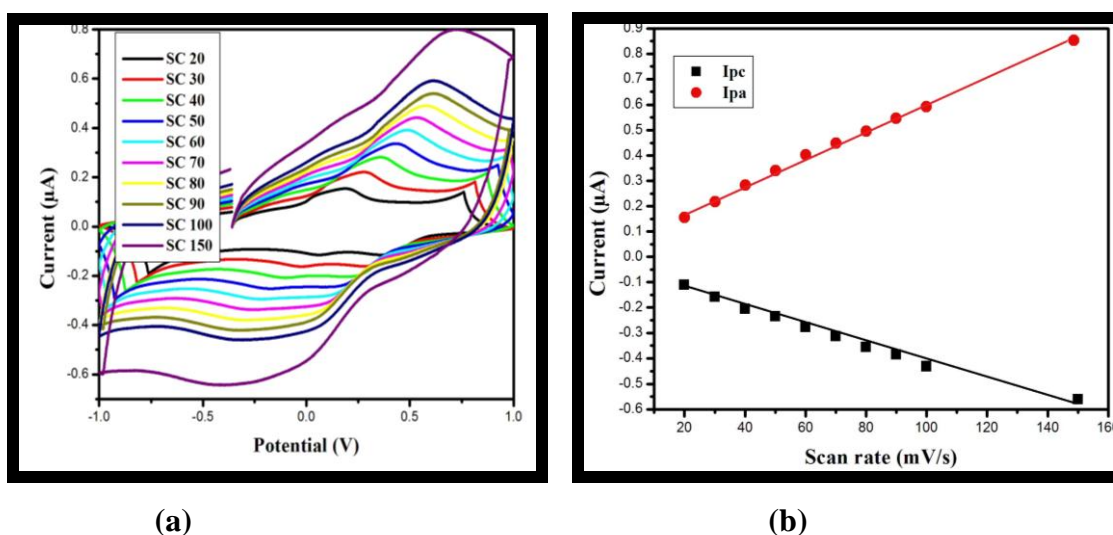
6.4.3 Effect of Scan Rate

(a)   (b)

Figure 6.8 (a-b) Cyclic voltagramm curves for effect of scan rate and its linear relationship for 150 µM of p-AP in 0.1 M of PBS solution (pH 7) at various scan rates.

The mechanism of the electrochemical reaction of p-AP is further investigated by the effect of scan rate on the cyclic voltammetric response of p-Aminophenol at 0.008 M of rGO/CS/Au modified GCE. Figure 6.8 (a-b) shows the

cyclic voltagramm curve for effect of scan rate and its linear relationship for 150 μM of p-aminophenol at pH 7 of PBS solution. It is observed from Figure 6.7 (a) that the redox peak current of p-AP increases with increasing the scan rate from 20 mV/s to 150 mV/s. By increasing the scan rate higher than100 mV/s, the shape of redox peaks gets distorted.   Moreover, the oxidation peaks shifts positively and the reduction peak shifts negatively [3]. It is clear from the plots of Figure 6.8 (b) that the intensity of redox peak current is linearly proportional to the scan rate. These results reveal that the redox reaction of rGO/CS/Au modified GCE towards the detection of p-Aminophenol is a surface controlled process.

6.4.4 Effect of Analyte Concentration

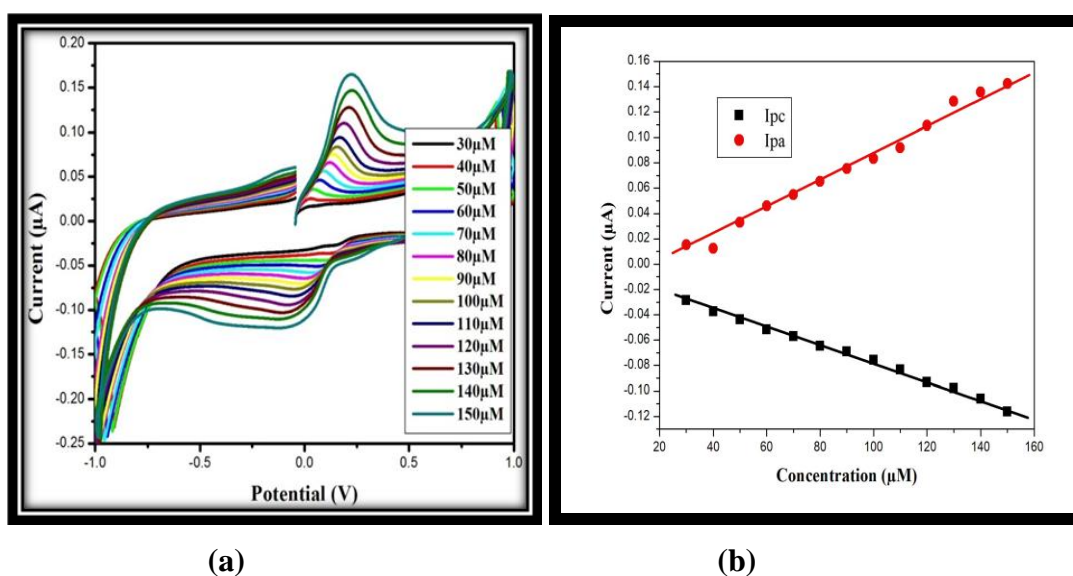| (a) | (b) |

Figure 6.9 (a-b) Cyclic voltagramm curves for 0.006M of rGO/CS/Au/GCE towards the detection of p-Aminophenol in 0.1 M of PBS solution (pH 7)

The electrochemical response of p-Aminophenol on 0.006M of rGO/CS/Au/GCE in 0.1 M of PBS solution (pH-7) at a scan rate of 20 mV/s is investigated by cyclic voltammetry. Figure 6.9 (a-b) shows the cyclic voltagramm curves for 0.008 M of rGO/CS/Au/GCE towards the detection of p-AP. It is observed from the Figure 6.9 (a) that on increasing the concentration of p-AP from 30 to150μM, the cationic and anodic peak current of p-AP increases linearly [4-5]. A good linearity is observed between the redoxpeak current and various concentration of p-AP as depicted in the Figure 6.9 (b). This significant increase in

the redox peaks can be ascribed to the good electrocatalytic activity and high surface area of the prepared nanocomposites which facilitates the accumulation of the p-Aminophenol at the surface of electrode and accelerates the electron transfer. These results reveal that rGO/CS/Au nanocomposites exhibit good electro catalytic activity towards the detection of p-Aminophenol.

6.5 CONCLUSION

The rGO/CS/Au nanocomposites are synthesized by chemical reduction method. The influence of various concentrations of (0.002M, 0.004M, 0.006M, 0.008M and 0.01M) of gold nanoparticles on the surface of rGO/CS/Au nanocomposites is investigated using FT-IR, XRD, SEM and TEM analysis. The interaction of functional groups between rGO, CS and Au is confirmed using FT-IR analysis. Stretching of metallic vibrations is observed at 586 cm^{-1}. XRD reveals that the nanocomposites are of high crystalline in nature with the crystallite size of about 8.9 nm to 16.5 nm. SEM and HRTEM analysis confirms that the spherical shaped gold nanoparticles are closely anchored onto the surface of rGO/CS nanosheets. EDAX analysis confirms the presence of carbon, oxygen and gold in the prepared nanocomposites. The electrochemical behaviour of p-aminophenol at rGO/CS/Au modified GCE is studied. The maximum redox peak current is observed for pH 6 of 0.008 M of rGO/CS/Au nanocomposite is 0.36μA and the linearity is about 10μM to 130μM and is found to be the most promising selectrode material for the electrochemical detection of p-aminophenol in environment.

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