CHAPTER IV

Investigation on decoration of silver nanoparticles on polymer functionalized reduced graphene oxide nanosheets for electrochemical sensing applications

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INVESTIGATION ON DECORATION OF SILVER NANOPARTICLES ON POLYMER FUNCTIONALIZED REDUCED GRAPHENE OXIDE NANOSHEETS FOR ELECTROCHEMICAL SENSING APPLICATIONS

This chapter includes:

- Introduction
- Materials and methods
- Functional and structural characterization by FT-IR and XRD analysis
- Morphological analysis by FESEM and HRTEM
- Elemental analysis
- Electrochemical sensing studies by cyclic voltammetry
- Conclusion
- References

4.1. INTRODUCTION

Phenols and vicarious phenolic compounds in natural water gives a loathsome taste and odour to drinking water and have a toxic effects on animals, humans and plants even at a small concentrations [1]. Nitrophenols are more important chemicals widely used in industrial, agricultural and defence applications. Nitrophenols are used as an intermediate compound for the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, corrosion inhibitors and photographic chemicals [2]. These are produced as an intermediate by microbial hydrolysis of several organo-phosphorus pesticides such as during the photo degradation of pesticides [1]. Nitrophenol isomers pose an apparent health risk, since it is toxic to mammals, microorganisms and anaerobic bacteria. Toxicity of nitrophenol is due to the nitro group being easily reduced by enzymes to the nitro anion radical, nitroso and hydroxylamine derivatives [3]. These derivatives are responsible for the cytotoxic, mutagenic and carcinogenic

properties of nitro compounds. The detection and analysis of nitrophenols in both waste and potable water is most important. Nitrophenols are usually detected by chromatographic techniques sometimes coupled with mass spectrometry and spectrophotometry [4]. These approaches are relatively expensive, because of high analytical cost, lengthy sample preparation and analysis times, which are not advisable for in-situ measurements. Electrochemical methods are low on cost and depend on short analysis time in comparison with some of the known accustomed methods [1]. These techniques are also distinguished by high sensitivity, good selectivity, rapid response, and the instruments are roughly simple with the feasibility of miniaturization for in-situ measurements. Electrochemical analysis of nitrophenol on a bare electrode usually has the problem of fouling and low sensitivity [1].

There is need to sought for new materials that can be used as electrode modifiers in the bid to enhance the electrochemical reduction or degradation of phenol and minimisation of electrode fouling. Several nanocomposite materials are employed for the modification of electrode surface to enhance the sensitivity of the electrode towards the detection of nitrophenol. However, compared to other types of nanocomposite, the nanocomposite composed of silver nanoparticles, β-cyclodextrin polymer and reduced graphene oxide nanosheets offers good electrocatalytic behaviour with nitrophenol isomers. Graphene is a one-atom thick and two-dimensional closely packed honeycomb lattice. It has received plentiful inspections from both the experimental and theoretical scientific communities. Graphene is an excellent electrode material, due to the property such as large specific surface area, strong mechanical strength and excellent conductivity [5]. Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven, or eight glucopyranose units, which are toroidal in shape with a hydrophobic inner cavity and a hydrophilic exterior. CDs have enchanted great significance due to their ability to incorporate suitable guest molecules into the hydrophobic cavity [6]. Because of these unique properties of graphene and beta cyclodextrin (rGONS/β-CD) nanocomposite shows significantly improved electrochemical sensing performance compared to the unmodified graphene nanosheets [7].

Silver nanoparticle has high surface area and high electrocatalytic property which provides significant effect on the detection of nitrophenols [8-9]. The detection of nitrophenol isomers occurs by the accumulation of nitrophenol sites on the surface of

rGONS/β-CD/Ag nanocomposite modified GCE. Afterwards, it can be effectively sensed by electrocatalytic redox mechanisms between nitrophenol isomers and rGONS/β-CD/Ag nanocomposite. The large surface to volume ratio, high electrical conductivity, host-guest complexes along with synergistic effect of the nanoparticles are significantly enhances the sensitivity of nitrophenol.

In the present study, the β-cyclodextrin functionalized reduced graphene oxide nanosheets are prepared by facile chemical reduction method. The surface of the rGONS/β-CD nanocomposite is modified by the decoration with silver nanoparticles. The homogeneously dispersed silver nanoparticles along with high specific surface area and high electric conductivity of rGONS/β-CD nanosheet assist the detection of nitrophenol isomers in phosphate buffer solution. The detection of nitrophenol isomers are studied with respect to concentration of rGONS/β-CD/Ag nanocomposite, pH of the electrolyte medium, scan rate and concentration of nitrophenol isomers. The linear range of detection and sensitivity of the rGONS/β-CD/Ag modified GCE is calculated from the electrochemical analysis. The silver nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets could be effectively detect nitrophenol isomers (ortho-, para- and meta-nitrophenol).

4.2. MATERIALS AND METHODS

Graphene oxide (GO) is synthesized from natural graphite powder by modified Hummer's method [10]. The reduced graphene oxide nanosheets functionalized with β-cyclodextrin polymer is synthesized by chemical reduction method using hydrazine hydrate as a reducing agent [7] [11]. The loading of various concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of silver nanoparticles on the surface of rGONS/β-CD nanocomposite is accomplished via wet chemical method, by adding the dispersed silver nitrate ($AgNO_3$) solution into the dispersed rGONS/β-CD suspension followed by the addition of sodium borohydrate ($NaBH_4$) to reduce silver nitrate into silver nanoparticles. The reaction suspension is then dried at 60˚C for 4 hours to get a nanocomposite of silver nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets [11-12].

4.3. RESULTS AND DISCUSSION

4.3.1. FT-IR SPECTRAL ANALYSIS

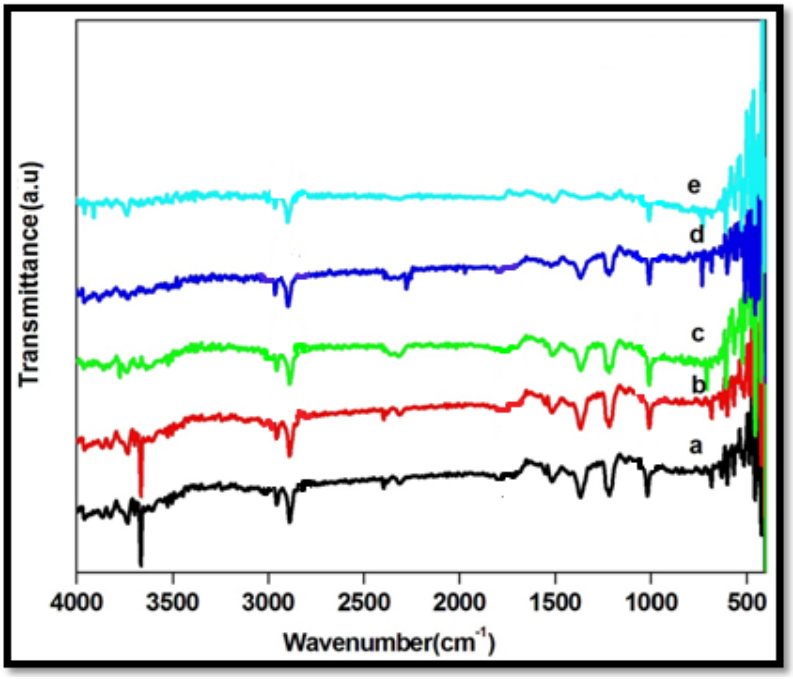


Figure.4.1. FT-IR spectra of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets using (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M concentrations of silver nitrate

The successful reduction of graphene oxide, chemical functionalization of β-cyclodextrin polymer and surface loading of silver nanoparticles in the synthesized silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets (rGONS/β-CD/Ag) using fiver different concentrations such as 0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M of silver nitrate is confirmed by FT-IR analysis and the obtained FT-IR spectra are shown in the Figure.4.1.(a-e). The FT-IR spectra of rGONS/β-CD/Ag nanocomposite presents the typical absorption bands of O-H stretching functional groups of reduced graphene oxide nanosheets and β-cyclodextrin polymer at 3668.21 cm^{-1} and 3732.92 cm^{-1} respectively. The bands observed at 1366.78 cm^{-1}, 1218.56 cm^{-1} and 1024.45 cm^{-1} are assigned to the coupled C-H/O-H bending, the coupled C-O-C stretching/O-H bending and the coupled C-O/C-C stretching functional groups of β-CD polymer. The C-H_2 bending functional group of β-cyclodextrin polymer is observed at 2919.62 cm^{-1} confirming the presence of reduced graphene oxide

nanosheets functionalized β-cyclodextrin polymer in the synthesized rGONS/β-CD/Ag nanocomposite [10]. The absorption band obtained at 1514.23 cm^{-1} may be attributed to the enhanced benzene ring vibrations of rGONS/β-CD, which suggests the reduction and restoration of layered structure of rGONS [12]. In addition to the absorption bands of rGONS and β-CD, the band appeared between 500 cm^{-1} to 700 cm^{-1} confirms the loading of silver nanoparticles on rGO/β-CD nanosheets.

The absence of FT-IR band around 1700 cm^{-1} corresponding to the COOH-functional group of graphene oxide nanosheets further confirms the formation of reduced graphene oxide nanosheets in the synthesized rGONS/β-CD/Ag nanocomposites [13]. The observed red shift in the O-H stretching absorption bands of rGONS and β-CD in comparison with that of FT-IR spectra of rGONS and typical β-CD polymer [10] [14] indicates the existence of strong hydrogen bonding between the oxygen containing functional groups of rGONS and β-CD polymer and which helps to form a complex rGONS/β-CD/Ag nanocomposite [10]. It may also enhance the water dispersion ability of reduced graphene oxide nanosheets by the inclusion of hydrophilic β-CD polymer, which helps to load silver nanoparticles into the surface of adjacent layer of reduced graphene oxide nanosheets. The decrease in the absorption band intensities (O-H, C-O, C-H_2, C-O-C, C-C and C-O) of rGONS and β-CD polymer with the increase in the concentration of silver nitrate from 0.002 M to 0.01 M further confirms the loading of silver nanoparticles on the surface of rGONS/β-CD. This may be due to the interaction between the oxygen containing functional groups of rGONS/ β-CD and Ag^{+} ions [15].

4.3.2. STRUCTURAL ANALYSIS

The loading of silver nanoparticles on the surface of β-cyclodextrin functionalized reduced graphene oxide nanosheet (rGONS/β-CD/Ag) is investigated by XRD analysis. Figure.4.2.(a-e) shows the loading of different concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of silver nanoparticles on the surface of β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets. The rGONS/β-CD/Ag nanocomposites shows the prominent diffraction peaks at 2θ values of 37.7˚, 43.9˚, 64.1˚, and 77.1˚ and are well matched with reference to the JCPDS card number 04-0783 [16]. The obtained diffraction peaks corresponds to the (111), (200),

(220) and (311) crystalline planes of face-centered cubic (fcc) phase of silver nanoparticles respectively [16-17].

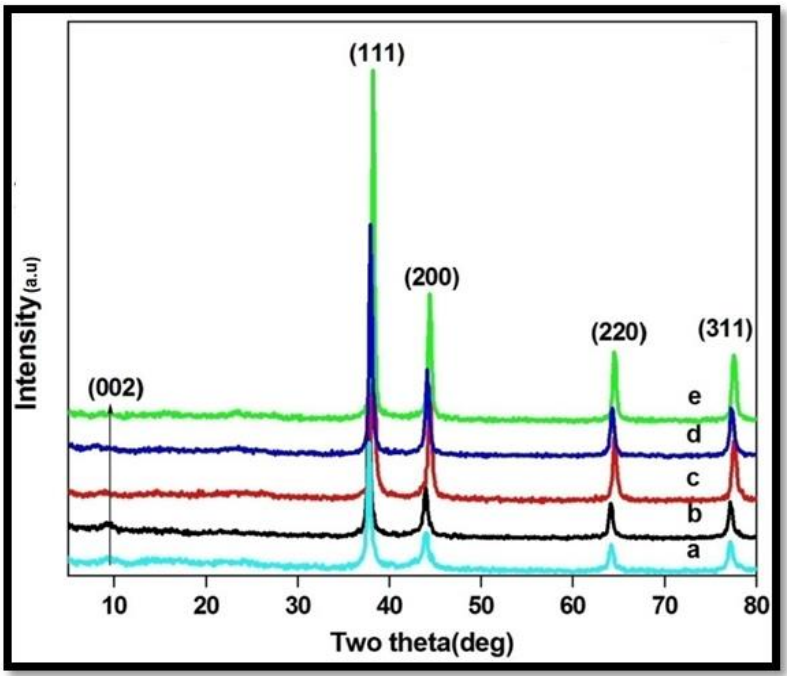


Figure.4.2. XRD spectra of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets using (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M concentration of silver nitrate

The diffraction peak intensity of reduced graphene oxide at 24.3˚ is observed to be disappeared in XRD spectra of rGONS/β-CD/Ag nanocomposite which may be due to the inclusion of silver nanoparticles on the rGONS/β-CD surface prevents the restacking of rGO nanosheets. This confirms that the silver nanoparticles are well dispersed and are attached onto the layers of rGONS/β-CD surface [18]. The sharp peak observed at 37.7˚ confirms that the synthesized nanoparticles are composed of pure crystalline silver nanoparticles [18]. A high intense diffraction peak (002) of graphene oxide has not been observed in the XRD spectra of 0.002 M to 0.01 M concentrations of rGONS/β-CD/Ag nanocomposites which may be due to the reduction of GO to rGONS [15].

It is observed from the XRD analysis that the diffraction peaks intensity corresponding to silver nanoparticles are increasing with the increase in the silver nitrate concentrations from 0.002 M to 0.01 M, thereby confirming the high crystalline

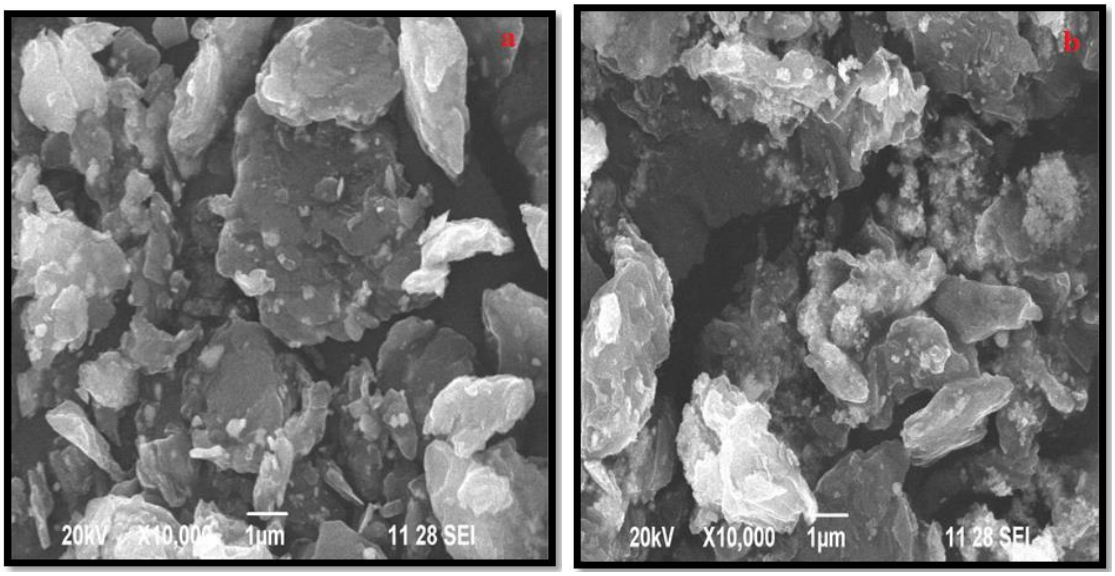
fcc structure of silver nanoparticles are loaded on the surface of β-cyclodextrin functionalized reduced graphene oxide nanosheets [13] [18]. The crystallite size of the silver nanoparticles are calculated by Debye-Scherrer equation [19]

$$D = K\lambda/\beta \cos\Theta$$

Where λ is the wavelength of the X-ray radiation (λ=1.5416 Å) used for the diffraction of atoms, K is the shape factor with the value of 0.9, β is the full width half maximum (FWHM) in radians and Θ is the Bragg's diffraction angle in degree [19]. The crystallize size of the silver nanoparticles are found to be 21.2 nm, 20.9 nm, 18.5 nm, 23.4 nm and 23.6 nm for 0.002M, 0.004 M, 0.006 M, 0.008 M and 0.01 M respectively.

It is also observed that at high loading of silver nanoparticles on the surface of β-cyclodextrin functionalized reduced graphene oxide nanosheet, the metal nanoparticles intercalate with rGONS, thereby increasing its d spacing, resulting in the broadening and decrease of rGONS peak intensity, indicating that the intercalation of silver nanoparticles with the oxygen functional groups of reduced graphene oxide nanosheet [12]. The functionalization of the rGONS surface with the β-cyclodextrin and silver nanoparticles prevents the restacking of graphene oxide nanomaterials [12] [16].

4.3.3. SEM ANALYSIS



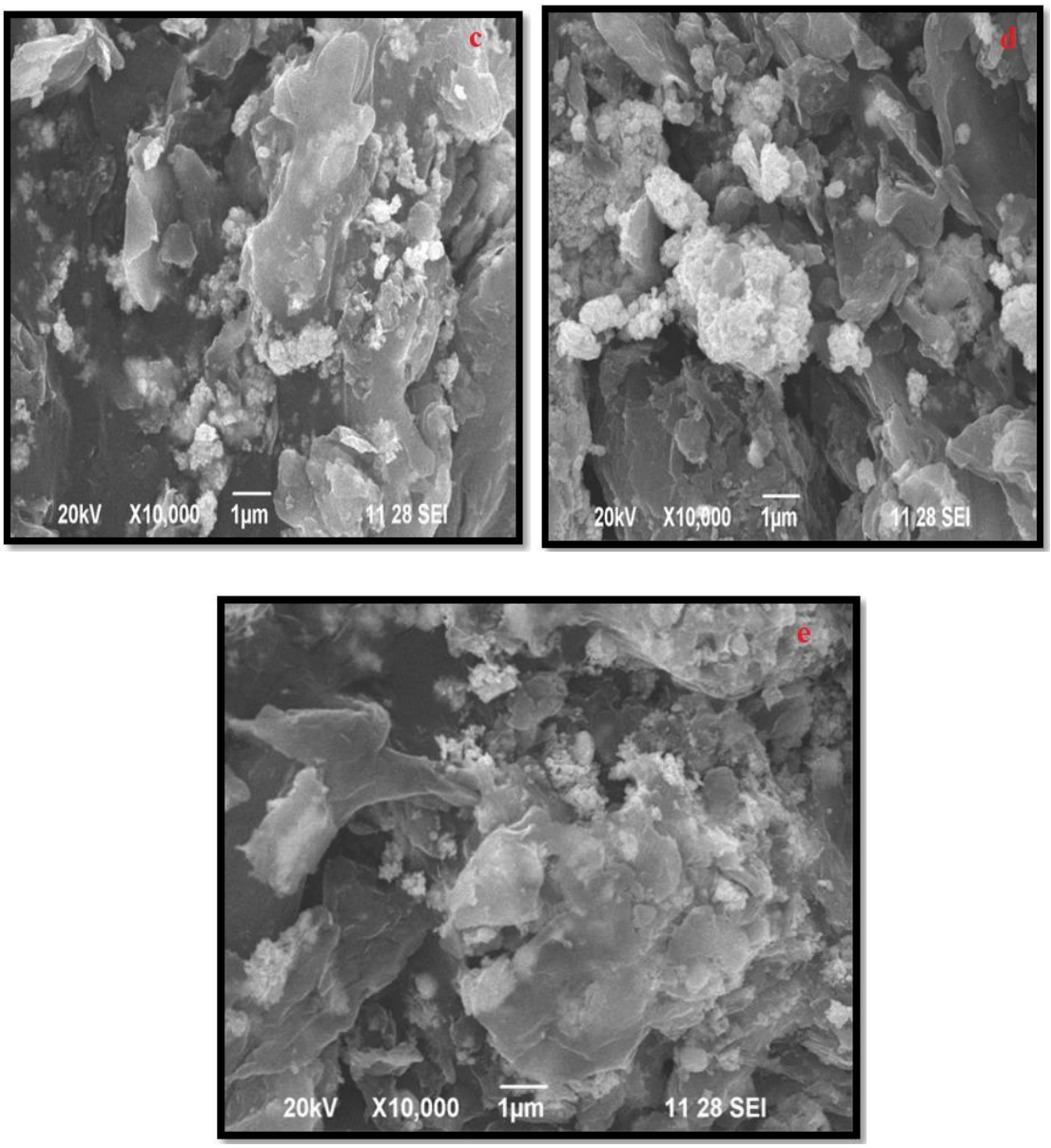


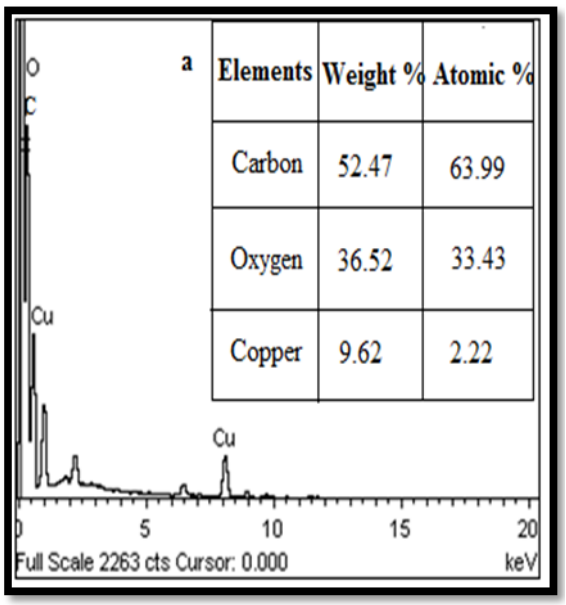
Figure.4.3. SEM images of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets using (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M concentrations of silver nitrate

Figure.4.3.(a-e) shows the SEM images of different concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanocomposites. It is observed from the Figure.4.3.(a-e) that the silver nanoparticles are well dispersed on the surface and edges of the rGONS/β-CD nanosheets, which indicates a strong polar interaction between oxygen containing functional groups of reduced graphene oxide nanosheets and silver nanoparticles [13]. The shape of the silver nanoparticles is found to be spherical in

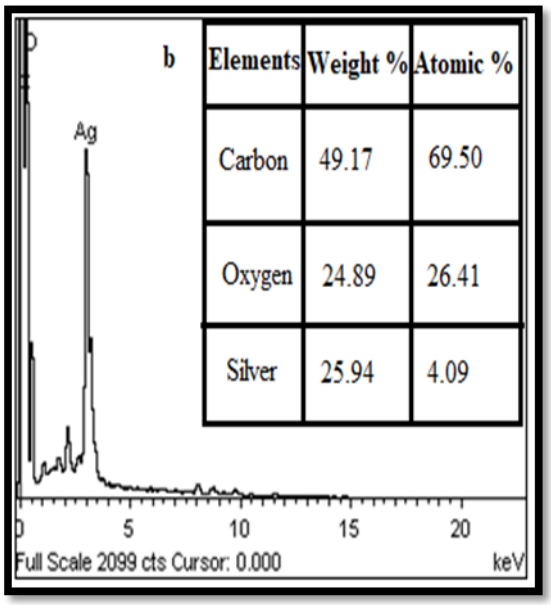
shape [18-19]. The SEM images in the Figure.4.3.(a-e) shows the rough and wrinkled morphology of the β-cyclodextrin functionalized reduced graphene oxide nanosheets presented in the rGONS/β-CD/Ag nanocomposite, which thereby confirms the formation of β-CD functionalized rGONS [20].

It is also observed that the numbers of dispersion of silver nanoparticles on the surface of rGONS/β-CD nanocomposites are found to be increased with the increase in the concentrations from 0.002 M to 0.006 M of silver nitrate due to the strong electrostatic interaction between the carbon-oxygen functional groups of rGONS/β-CD and silver nanoparticles [13]. It is further observed that for 0.008 M and 0.01 M concentrations of silver nitrate, the dispersion of silver nanoparticles on the surface of β-cyclodextrin functionalized reduced graphene oxide is found to be decreased and slightly aggregated which may be due to the enhancement in the mobility and re-crystallization of silver nanoparticles with rGONS/β-CD [13]. This indicates the loading concentration of silver nanoparticles on the rGONS/β-CD surface reaches its saturation, which could also be evidenced from EDAX analysis [15] [18]. By observing the SEM image of rGONS/β-CD/Ag nanocomposites, it is confirmed that the maximum dispersion capability of silver nanoparticles on the rGONS/β-CD surface is 0.006 M concentration of silver nitrate and continuous increment in the concentration of silver nitrate leads to the aggregation and thereby loses its electrocatalytic property. This helps to enhance the electrocatalytic activity and sensor sensitivity of synthesized rGONS/ β-CD/Ag nanocomposites [13] [18].

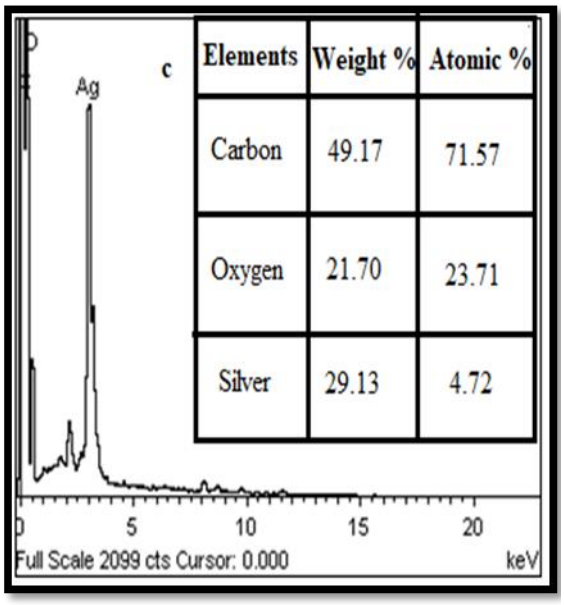
4.3.4. EDAX ANALYSIS



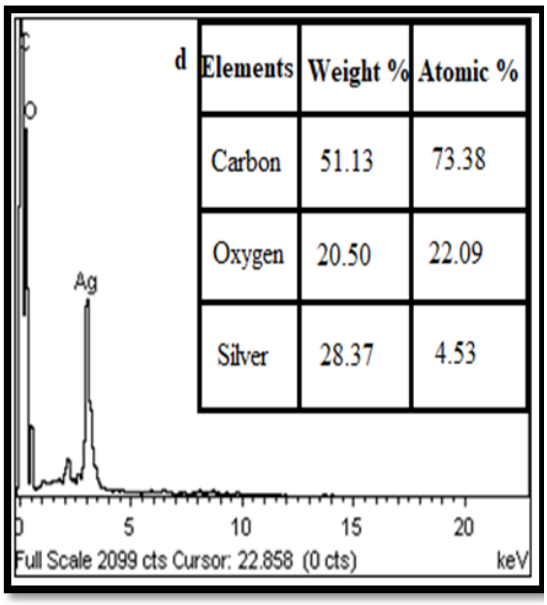
Elements	Weight %	Atomic %
Carbon	52.47	63.99
Oxygen	36.52	33.43
Copper	9.62	2.22



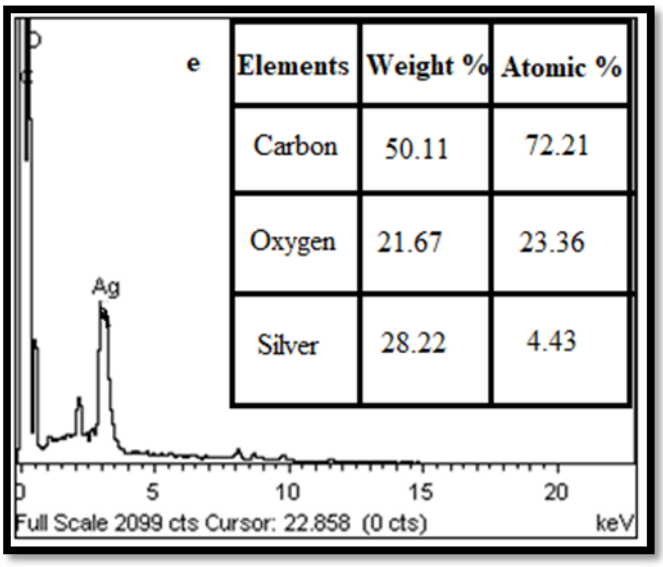
Elements	Weight %	Atomic %
Carbon	49.17	69.50
Oxygen	24.89	26.41
Silver	25.94	4.09



Elements	Weight %	Atomic %
Carbon	49.17	71.57
Oxygen	21.70	23.71
Silver	29.13	4.72



Elements	Weight %	Atomic %
Carbon	51.13	73.38
Oxygen	20.50	22.09
Silver	28.37	4.53



Elements	Weight %	Atomic %
Carbon	50.11	72.21
Oxygen	21.67	23.36
Silver	28.22	4.43

Figure.4.4. EDAX spectra of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets using (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M concentrations of silver nitrate

The EDAX analysis is used to determine the atomic percentage and composite formation in the produced nanomaterials. The EDAX spectra of 0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M concentrations of synthesized rGONS/β-CD/Ag nanocomposites are shown in the Figure. 4.4.(a-e). The EDAX spectra confirm the presence of carbon, oxygen and silver elements in the synthesized rGONS/β-CD/Ag nanocomposites. This analysis also confirms the presence of silver nanoparticles on the surface of rGONS/β-CD nanocomposites. The presence of oxygen peaks indicates that the oxygen functional groups are generated during the synthesis of rGO/β-CD nanosheets. The atomic and weight percentage of oxygen, carbon and silver in 0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M concentrations of rGONS/β-CD/Ag nanocomposites are listed in the table as a inset of the Figure.4.4.(a-e). It is confirmed from the EDAX analysis that with the increase in the concentration of silver nitrate from 0.002 M to 0.006 M, the number of silver atoms on the rGONS/β-CD surface increases and with the continuous increment in the concentration of silver nitrate above 0.006 M, the presence of silver atoms on the surface of rGONS/β-CD nearly the same as 0.006 M of silver nitrate, which could also be evidenced from SEM analysis [13] [18].

4.3.5. HRTEM ANALYSIS

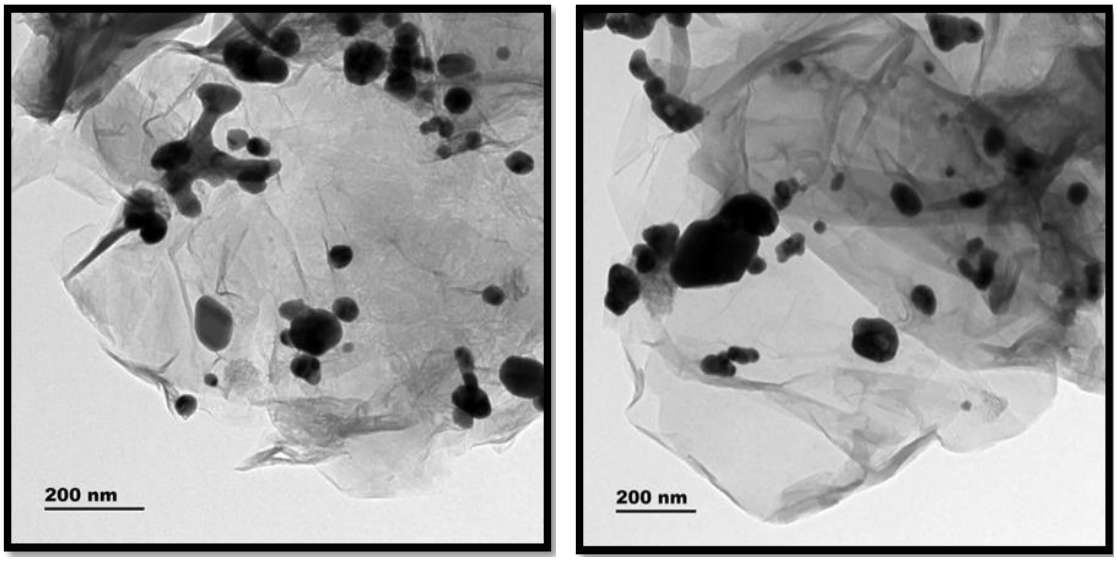


Figure.4.5. HRTEM images of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets using 0.006 M concentration of silver nitrate

The transmission electron micrographs of the synthesized rGONS/β-CD/Ag nanocomposite using 0.006 M concentration of silver nitrate are shown in the Figure.4.5. The HRTEM images depicts that the synthesized rGO/β-CD nanosheets are very thin, wrinkled and less trasparent which may be due to the impact of chemical functionalization of β-cyclodextrin with rGONS [10] [12]. The inclusion of β-CD across the basal plane of rGONS prevents the aggregations of reduced graphene oxide nanosheets [7] [16] . It is also observed from the Figure.4.5 that the black spots on the surface of rGO/β-CD nanosheets confirms the formation of well distributed silver nanoparticles on the surface of rGONS/β-CD nanosheets, which is also evidenced by the SEM analysis [16]. The distributions of silver nanoparticles are homogeneous without aggregation, which may be due to the impact of functionalized β-cyclodextrin polymer.

4.3.6. SAED ANALYSIS

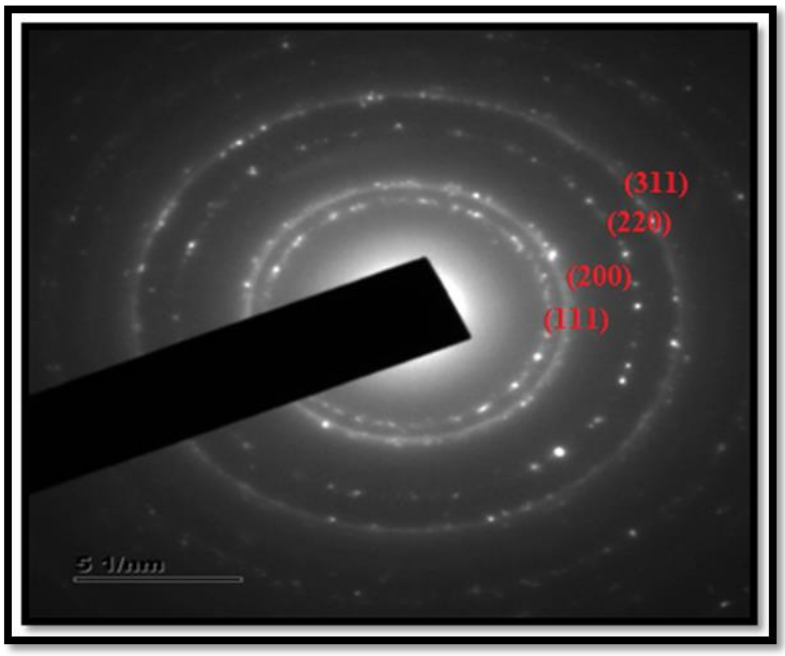


Figure.4.6. SAED pattern of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets using 0.006 M concentration of silver nitrate

The selected area electron diffraction pattern (SAED) of the synthesized rGONS/β-CD/Ag nanocomposites using 0.006 M concentration of silver nitrate is shown in the Figure.4.6. It is observed from the Figure.4.6. that there are four discrete bright rings corresponds to the well crystalline face centered cubic structure of silver nanoparticles on the surface of rGO/β-CD nanosheets. Each rings observed in the SAED patterns corresponds to the (111), (200), (220) and (311) diffraction planes of silver nanoparticles, which could also be evidenced from XRD analysis [20].

4.4. ELECTROCHEMICAL BEHAVIOUR OF MODIFIED ELCTRODES

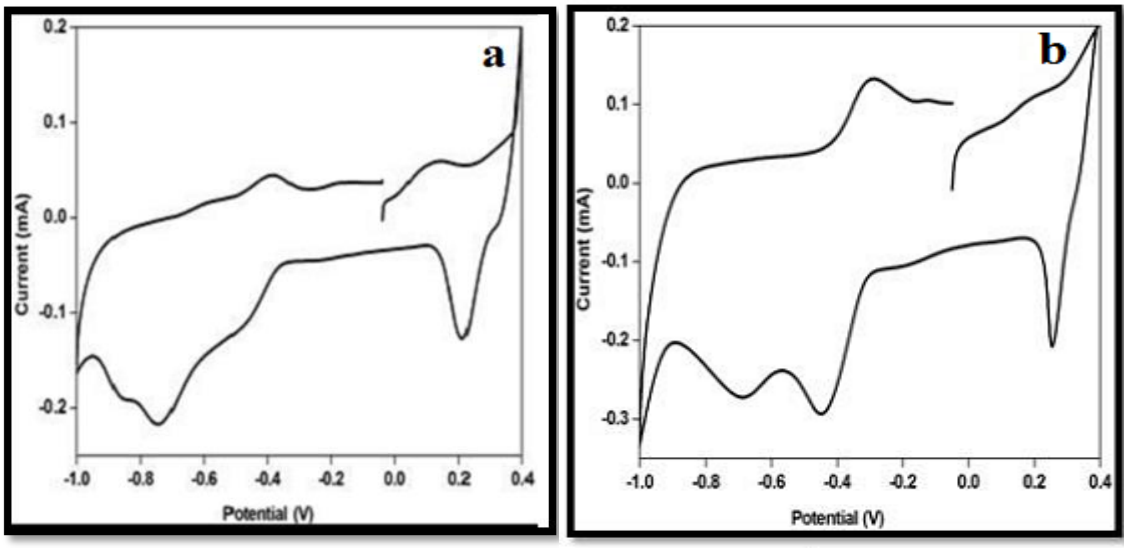


Figure.4.7. Cyclic voltagramm of 14 mM of o-NP at (a) rGONS/Ag/GCE (b) rGONS/β-CD/Ag/GCE in PBS solution at the scan rate of 10 mV/s

The electrochemical behaviour of ortho-nitrophenol (o-NP) is investigated using cyclic voltammetry in 0.1 M phosphate buffer solution (PBS) (pH 7.0). The well-defined electrocatalytic redox peaks are observed within the potential range from -1 V to +0.4 V as shown in the Figure.4.7.(a & b), which reveals that the ortho-nitrophenol shows a reversible electrochemical redox process on the modified electrodes [20]. The silver nanoparticles (Ag) loaded reduced graphene oxide nanosheets modified glassy carbon electrode (rGONS/Ag/GCE) showed the redox peak potential of o-NP at -0.75 V, -0.86 V and -0.41 V with the current value of -0.22 mA, -0.19 mA +0.05 mA respectively. It is observed from the results that the electrochemical behaviour of rGONS/Ag nanocomposite modified GCE is slightly greater than the rGONS/β-CD/GCE as discussed in the chapter 3 and this may be due to the large surface area and remarkable conductivity of rGONS and the catalytic ability of silver nanoparticles [20]. But for the silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheet modified glassy carbon electrode (rGONS/β-CD/Ag/GCE) showed the redox peak potential at -0.68 V, -0.42 V and -0.31 V with the current value of -0.29 mA, -0.31 mA and +0.14 mA respectively, which is higher than that of the rGONS/Ag/GCE. This enhancement in the electrochemical redox signal of ortho-nitrophenol may be ascribed to the formation of large number of uniformly loaded stable silver nanoparticles on the surface of reduced graphene oxide nanosheets in the presence of β-

cyclodextrin polymer as a stabilizing agent [16]. The β-cyclodextrin polymer provides large surface to volume ratio to accommodate more number of ortho-nitrophenol sites on the surface of rGONS/β-CD/Ag modified GCE electrode, which further enhances the electrochemical redox signal of o-NP [20]. The enhanced electrochemical performance may also be due to the large surface area and conductivity of rGONS and the synergistic effect and catalytic ability of Ag nanoparticles. It is revealed from the results that the rGONS/β-CD/Ag nanocomposite provides an efficient microenvironment for the electrochemical reduction and oxidation of ortho-nitrophenol and accelerates the electron transfer rate between the ortho-nitrophenol and modified electrode surface [20] [8]. Hence, rGONS/β-CD/Ag nanocomposite modified GCE is a good choice for the electrochemical sensing of ortho-nitrophenol. Further enhancement in the electrochemical property of rGONS/β-CD/Ag nanocomposites is achieved by the optimization of electrochemical sensing parameters such as concentrations of rGONS/β-CD/Ag nanocomposite, pH of the PBS solution and scan rate, etc.

4.5. ELECTROCHEMICAL DETECTION OF NITROPHENOL ISOMERS

The synthesized rGONS/β-CD/Ag nanocomposite is employed for the quantitative electrochemical detection of nitrophenol isomers such as ortho-, para- and meta-nitrophenol. The electrocatalytic activity towards the reduction and oxidation of ortho-, para-, meta-nitrophenol isomers are studied based on the various electrochemical parameters such as pH of the electrolyte medium, concentration of the rGONS/β-CD/Ag nanocomposite and the scan rate of electrochemical reactions.

4.5.1. Effect of rGONS/β-CD/Ag concentration on electrocatalytic activity

To optimize the concentration of rGONS/β-CD/Ag nanocomposite, the concentration of ortho-nitrophenol in the electrolyte medium is varied from 1 mM to 14 mM and the results show only the redox current response of 14 mM concentration of o-NP. The similar technique is carried out for the further optimization techniques.

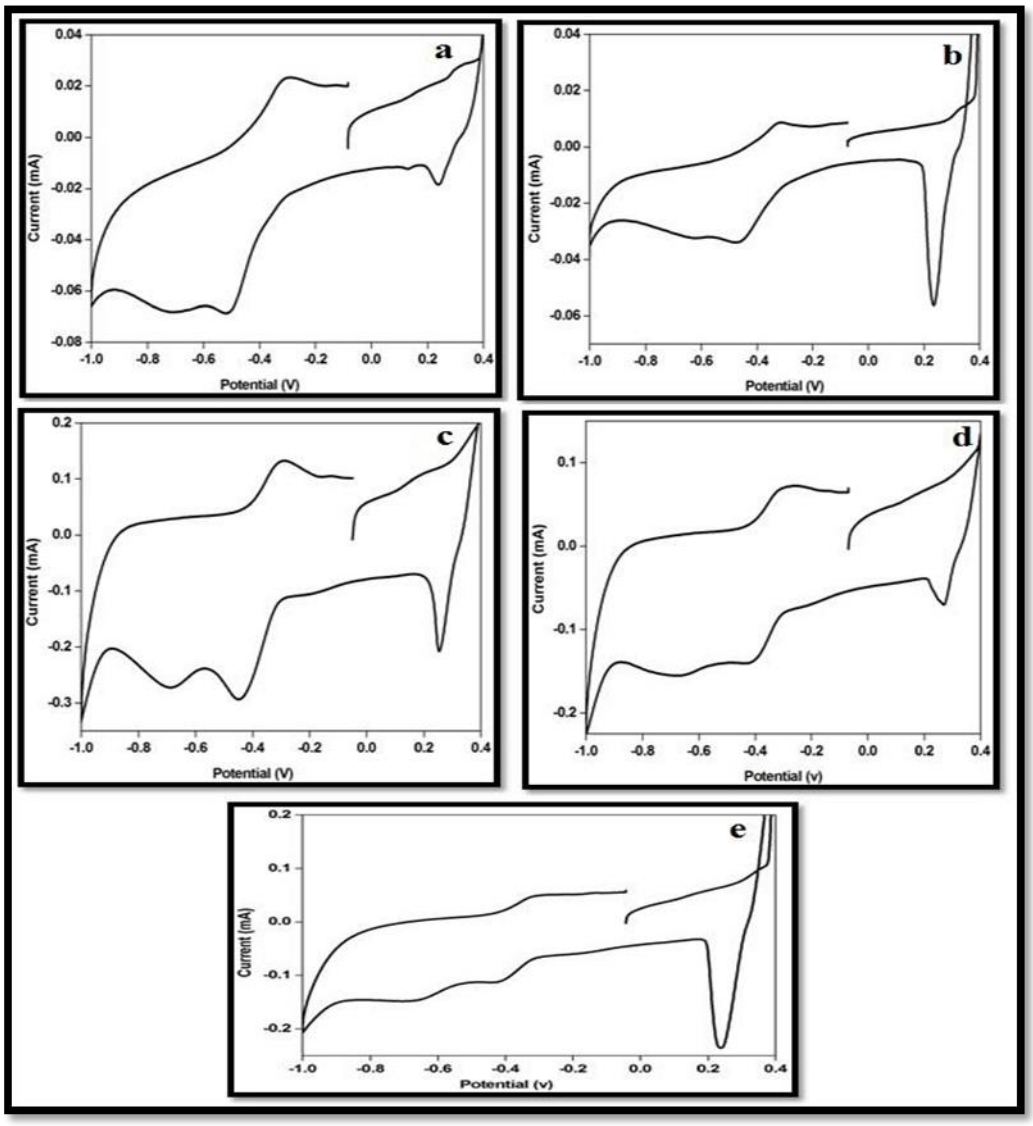
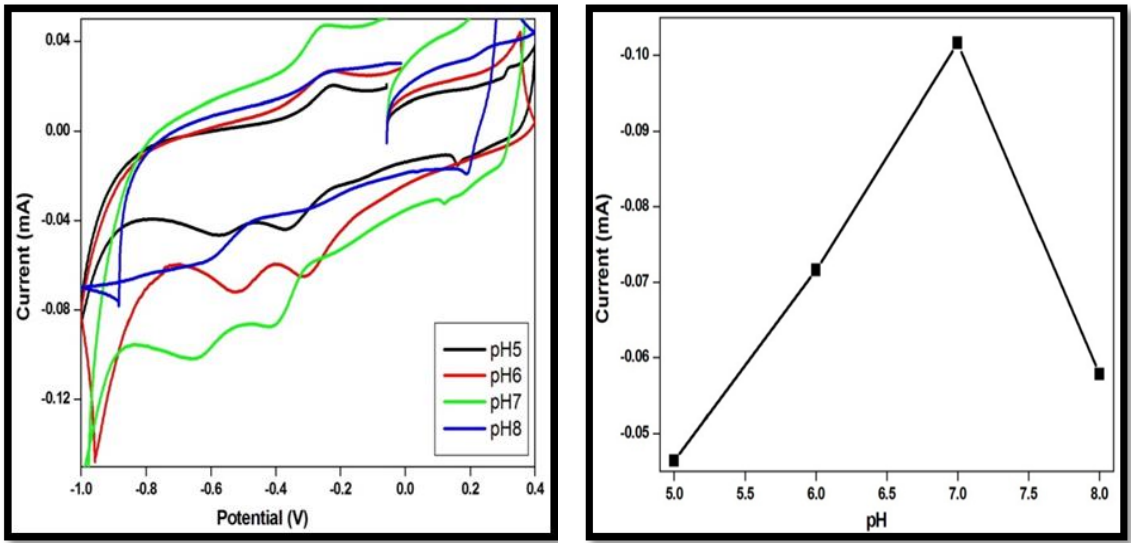


Figure.4.8. Cyclic voltagramm of 14 mM of o-NP at (a) 0.002 M (b) 0.004 M (c) 0.006 M (d) 0.008 M and (e) 0.01 M concentration of silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets in PBS solution

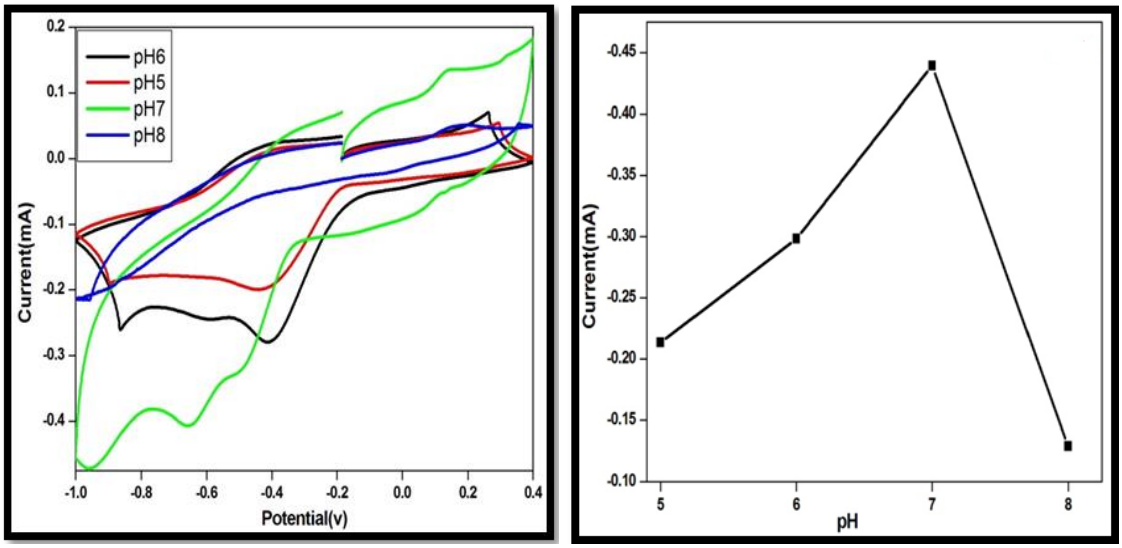
In order to obtain a maximum electrocatalytic activity towards the detection of ortho-nitrophenol, the effect of concentration of the synthesized rGONS/β-CD/Ag nanocomposite is studied and the results are given in Figure.4.8.(a-e). It shows the electrocatalytic behaviour of o-nitrophenol (o-NP) at the synthesized (a) 0.002 M, (b) 0.004 M, (c) 0.006 M, (d) 0.008 M and (e) 0.01 M of rGONS/β-CD/Ag nanocomposite modified GCE by cyclic voltammetry in 0.1 M of phosphate buffer solution (PBS) (pH.7.0) containing 14 mM of o-nitrophenol at the scan rate of 10 mV/s. It is observed from the Figure.4.8.(a-e) that, all the concentrations of silver nanoparticles loaded

β-cyclodextrin functionalized reduced graphene oxide nanosheets modified GCE shows the better electrochemical response towards the reduction and oxidation of ortho-nitrophenol. The cyclic voltagramm of 0.002 M of rGONS/β-CD/Ag/ GCE shows a low redox peak current with the redox potential around -0.51 V, -0.72 V and -0.38 V, due to its deficient electro-catalysis with the ortho-nitrophenol compound. This may be due to the amount of silver nanoparticles decorated on the surface of rGONS/β-CD is not sufficient for enhancing the electron transfer rate and this could also be evidenced from SEM and EDAX analysis [20]. But it is observed that by further increment in the concentration of silver nitrate from 0.002 M to 0.006 M, the rGONS/β-CD/Ag/GCE exhibits a higher reduction peak current, confirming the higher electrocatalytic activity of nanocomposites with the ortho-nitrophenol [16] [20]. This increase in the redox peak current may be attributed to the increase in the concentration of silver nanoparticles loaded on the rGONS/β-CD surface and also the excellent electrocatalytic activity of nanocomposites towards ortho-nitrophenol. Furthermore, with the continuous increment in the concentrations of silver nitrate for 0.008 M and 0.01 M, the redox peak current corresponding to o-nitrophenol is found to be decreased. This remarkable decrement in the redox peak current may be due to the aggregation and decrease in the number of silver nanoparticles loaded on the rGONS/β-CD surface as also evidenced from SEM and EDAX analysis [20]. It is further evident from the cyclic voltammetry analysis that the 0.006 M concentration of silver nanoparticles loaded rGONS/β-CD nanocomposites has better electrochemical behaviour and high redox peak current than the other concentrations of silver nanoparticles loaded rGONS/β-CD surface. Hence, the 0.006 M concentration of GONS/β-CD/Ag nanocomposite is further employed for the detection of all three nitrophenol isomers.

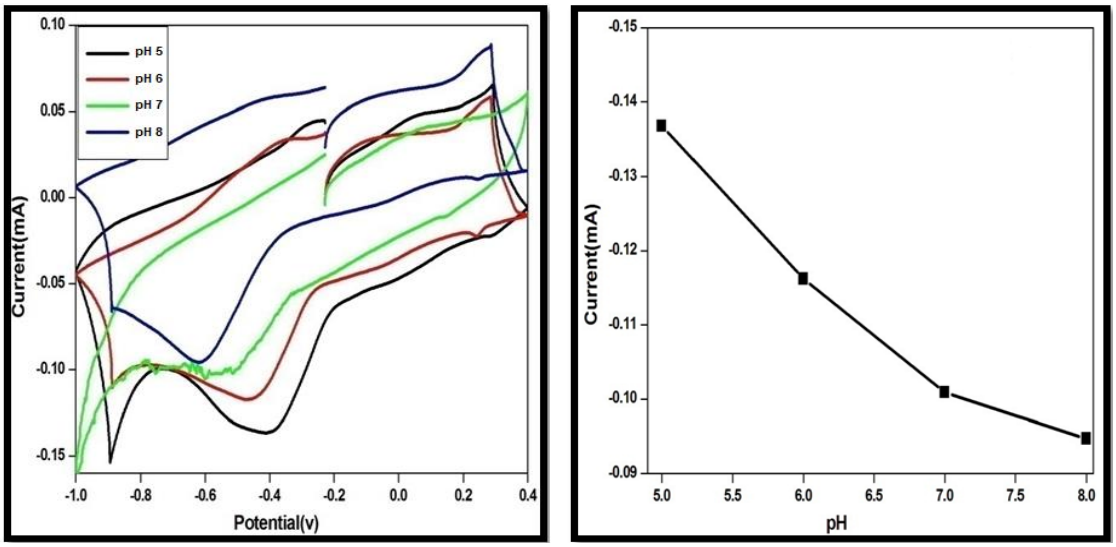
4.5.2 Effect of electrolyte pH



(a)



(b)

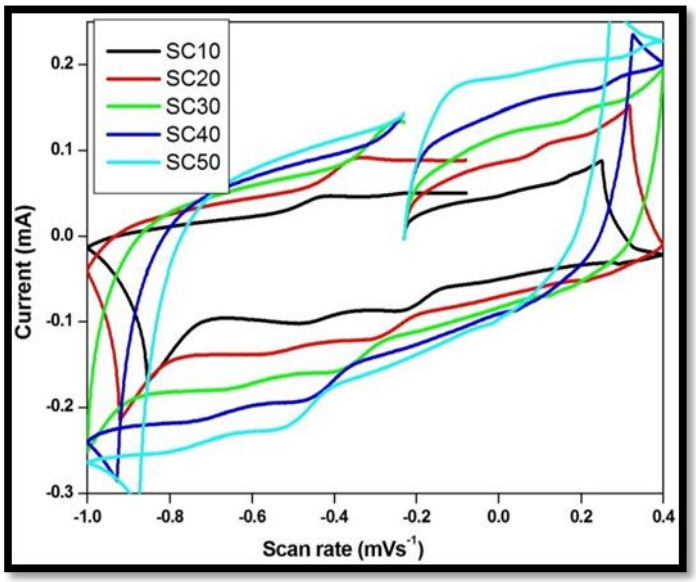


(c)

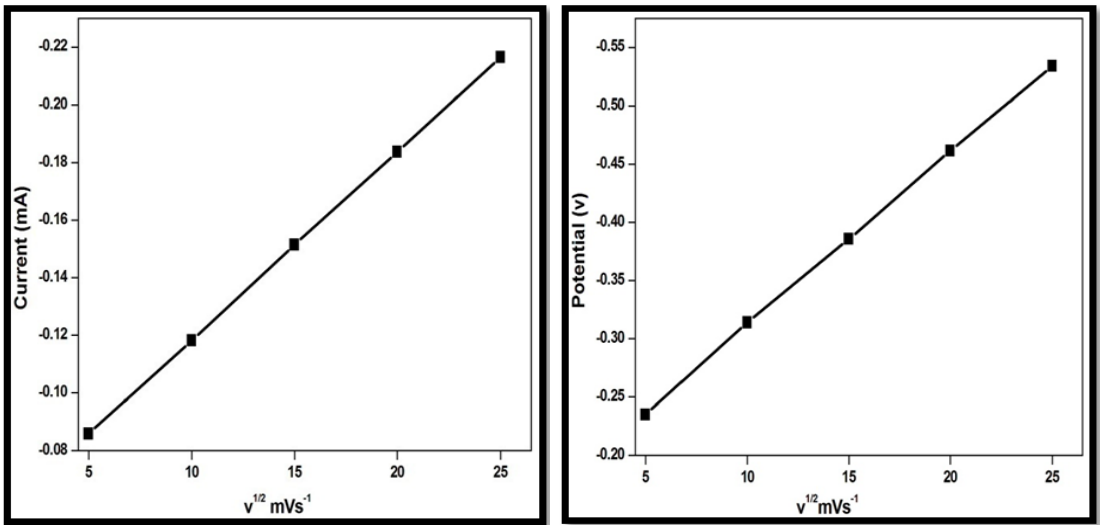
Figure.4.9. Effects of pH on the redox peak current of (a) 14 mM o-NP and its linearity (b) 25 mM p-NP and its linearity (c) 12 mM m-NP and its linearity in 0.1M of PBS solution at the scan rate of 10 mV/s

The effect of pH on the electrochemical behaviour of ortho-, para- and meta-nitrophenol isomers at the rGONS/β-CD/Ag modified GCE electrode is investigated with 0.1 M phosphate buffer solution in the pH range from 5.0 to 8.0 and the results are shown in the Figure.4.9.(a-c). The redox peak potentials of ortho-, para- and meta-nitrophenol isomers are shifted negatively with increasing the pH from 5.0 to 8.0, manifesting that the electrocatalytic reduction and oxidation process is accompanied with proton transport [8]. The calibration graph in the Figure.4.9.(a-c) reveals that the largest electrochemical redox peak current of ortho-, para- and meta-nitrophenol is obtained at pH 7.0, 7.0 and 5.0 respectively. Hence, phosphate buffer solution (PBS) of pH 7.0, 7.0 and 5.0 is used further for electrochemical investigation due to its best electrochemical response.

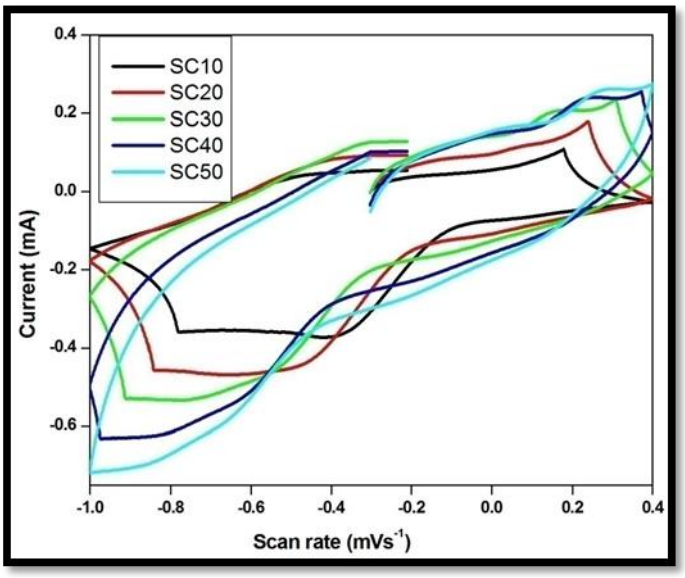
4.5.3. Effect of scan rate



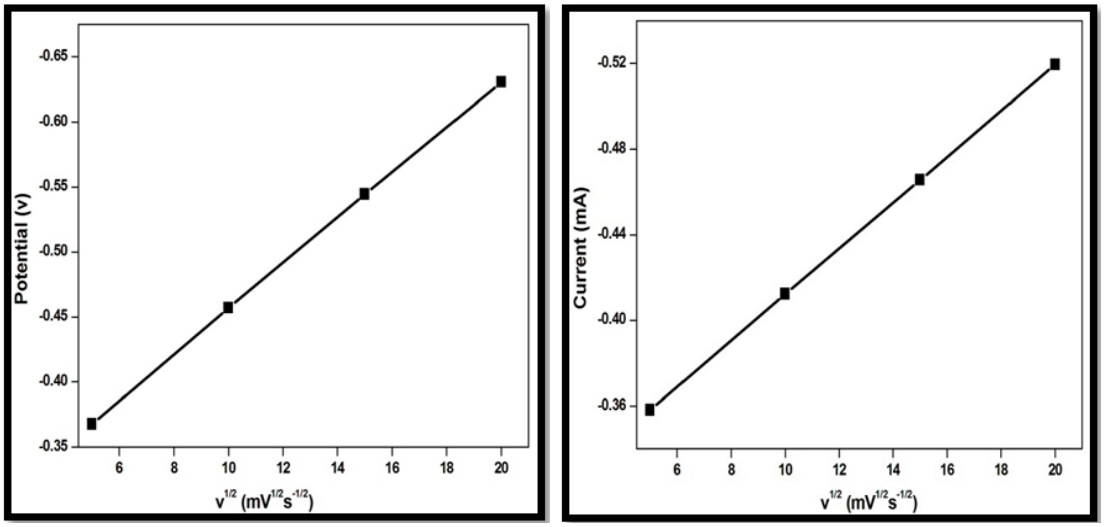
(a)



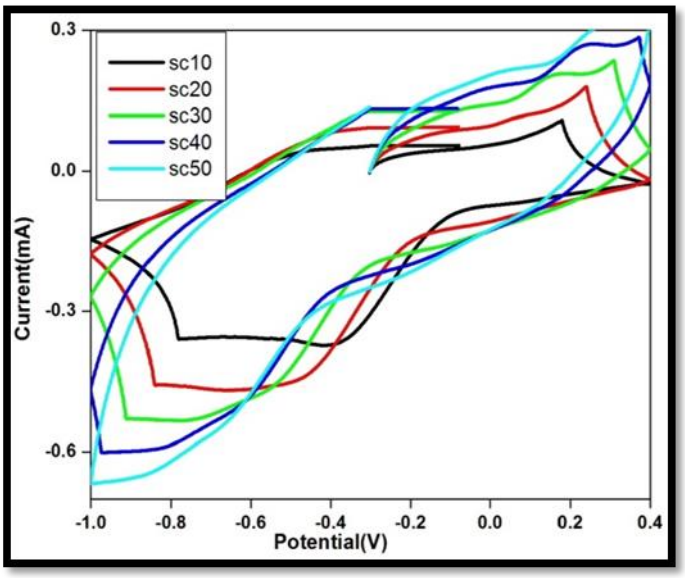
(b)


SC10
SC20
SC30
SC40
SC50
Current (mA)
Scan rate (mVs-1)

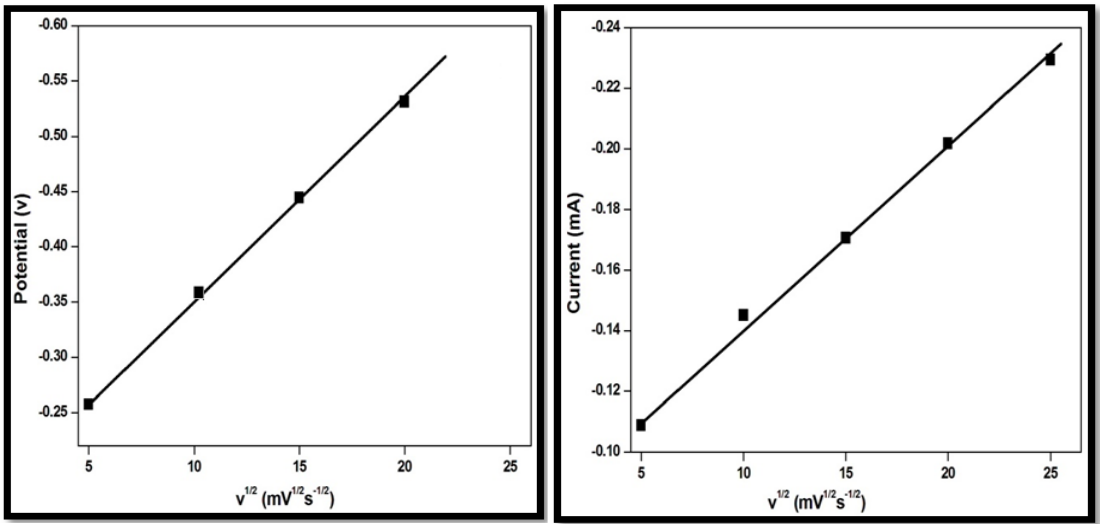
(c)


Potential (v)
v1/2 (mV1/2s-1/2)
Current (mA)
v1/2 (mV1/2s-1/2)

(d)



(e)



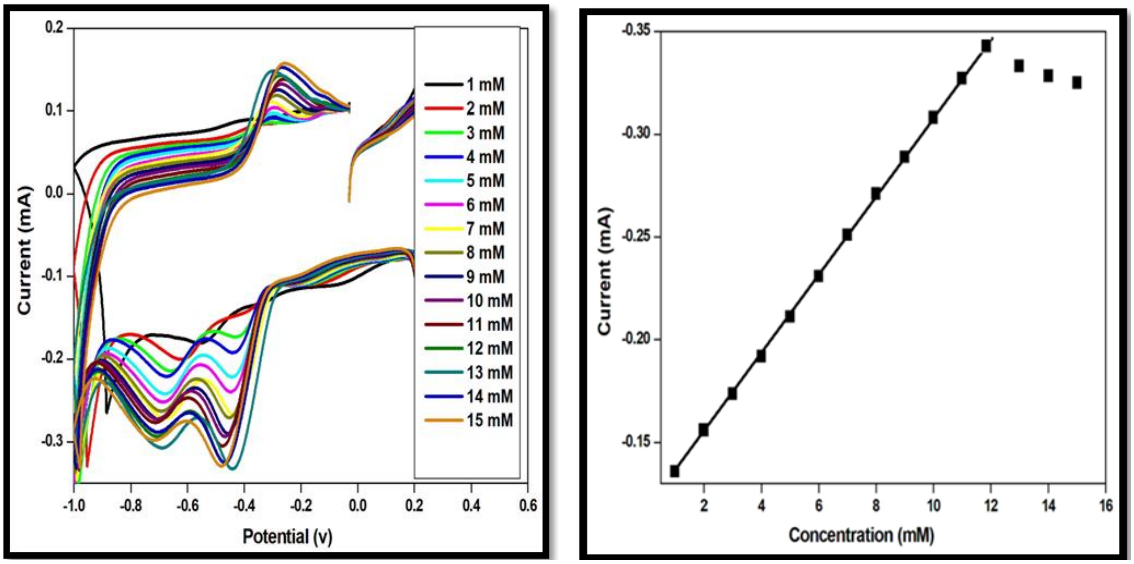
(f)

Figure.4.10. (a), (c) and (e) Effect of scan rate on the reduction current response for 14 mM, 25 mM and 12 mM of o-, p- and m-NP in 0.1 M PBS solution (b), (d) and (f) Linear relationship between E_{pa}, I_{pa} and square root of scan rate

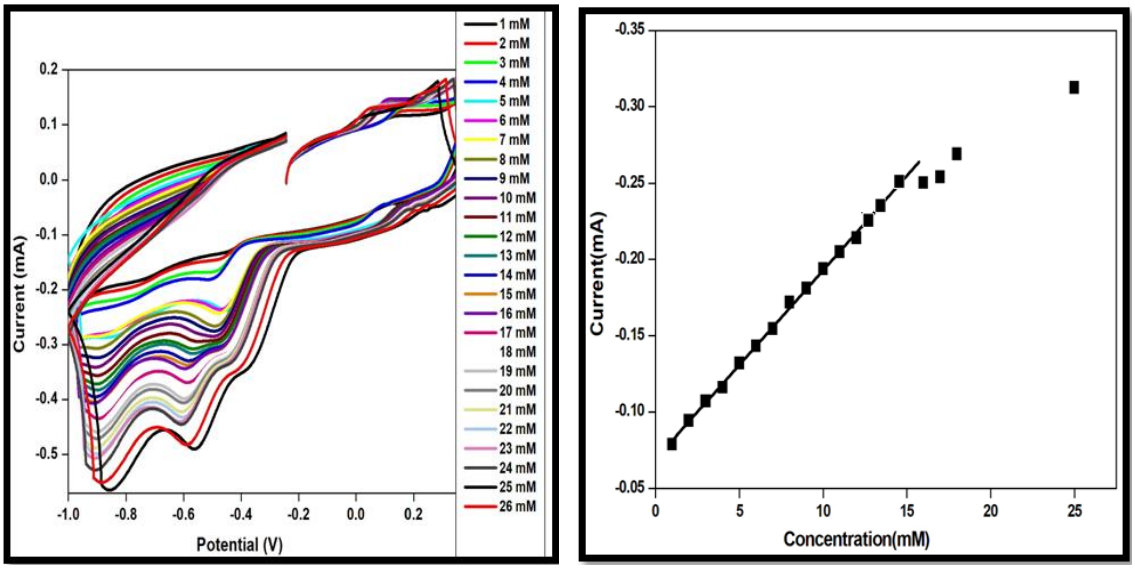
Figure.4.10.(a-e) shows the effect of scan rate (v) in 14 mM ortho-, 25 mM para- and 12 mM meta-nitrophenol at rGONS/β-CD/Ag/GCE by cyclic voltammetry (CV) analysis. It is observed from the electrochemical redox reaction results that, with the increase in the scan rate from 10 mV/s to 50 mV/s, the reduction and oxidation peak currents grow gradually and oxidation peak potentials shift positively. In contrast, the

reduction peak potentials shift negatively. The existence of both the oxidation and reduction peaks in cyclic voltagramm of Figure.4.10.(a, c and e), demonstrates that the electrochemical reduction and oxidation of ortho-, para- and meta-nitrophenol is a complete reversible redox process [16]. The results indicate that the electrochemical reduction and oxidation of ortho-, para- and meta-nitrophenol isomers at rGONS/β-CD/Ag/GCE are diffusion-controlled process.

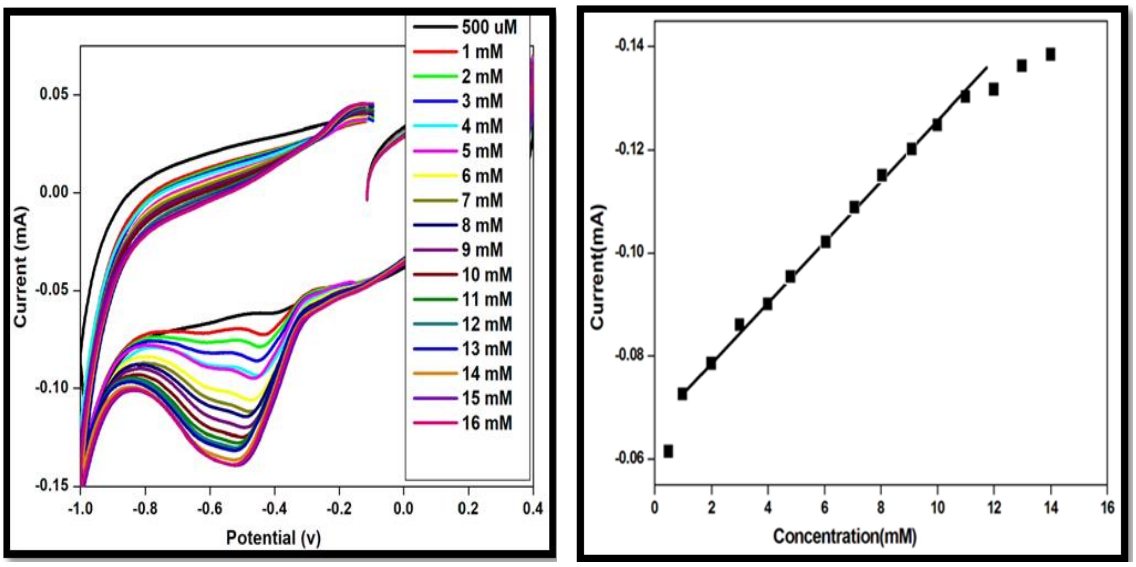
4.5.4. Effect of analyte concentration



(a)



(b)



(c)

Figure.4.11. Cyclic voltagramm of rGONS/β-CD/Ag/GCE in 0.1 M of PBS solution containing various concentrations of (a) o-NP, (b) p-NP and (c) m-NP

The cyclic voltammetry (CV) is carried out to examine the sensitivity of rGONS/β-CD/Ag/GCE towards the detection of ortho-, para- and meta-nitrophenol isomers. The detection of o-, p- and m-NP is performed in a series of solution containing different concentration of ortho-, para and meta-NP from 1 to 15 mM, 1 to 26 mM and 500 μM to 16 mM respectively. It is observed from the Figure.4.11.(a-c) that the voltammetric signals of nitrophenol isomers increases with the increase in the concentration of o-, p- and m-NP from 1 to 13 mM, 1 to 25 mM and 500 μM to 15 mM respectively and then decreases gradually, which confirms that the concentrations of nitrophenol sites onto the surface of rGONS/β-CD/Ag/GCE reaches its saturation state. The calibration graph (Figure.4.11.(a-c)) for ortho-, para- and meta-nitrophenol isomers show the linear range of detection and are tabulated in Table 4.1. The sensitivity values of the synthesized rGONS/CD/Ag nanocomposite are also calculated using the following formula and are also listed in the Table.4.1.

Sensitivity= Slope of the calibration graph / working area of the modified electrode

Table.4.1. Linear range of detection and sensitivity value of the rGONS/β-CD/Ag nanocomposite		
Nitrophenol isomers	**Linear range of detection (mM)**	**Sensitivity ($mAmM^{-1}cm^{-2}$)**
Ortho-nitrophenol	1 to 12	0.28
Para-nitrophenol	1 to 15	0.19
Meta-nitrophenol	1 to 11	0.09

It is revealed from the results that the linear region in the calibration graph of ortho-, para and meta-nitrophenol isomers are due to the diffusion process on the rGONS/β-CD/Ag layer covered on the surface of GCE. Hence, it is confirmed from the results that the synthesized rGONS/β-CD/Ag nanocomposite shows the good electrochemical behaviour towards the detection of ortho-nitrophenol with the linear range of detection from 1 mM to 12 mM and sensitivity value of about 0.28 mA mM^{-1} cm^{-2}.

4.6. CONCLUSION

This chapter describes the synthesis and decoration of rGONS/β-CD nanocomposites surface using different concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of silver nanoparticles and the ultrasensitive electrochemical detection of nitrophenol isomers (ortho-, para- and meta-NP). The XRD results revealed that the synthesized silver nanoparticles have high crystalline fcc structure and the average crystallite sizes of the silver nanoparticles are found to be from 18 nm to 23 nm. HRTEM and SEM analysis showed the spherical shapes of the silver nanoparticles that are loaded on the surface of rGONS/β-CD nanocomposites. Elemental analysis confirms the presence of silver, carbon and oxygen elements in the synthesized rGONS/β-CD/Ag nanocomposite. The electrochemical behaviour of the synthesized nanocomposites (rGONS/β-CD/Ag) is tested against three different nitrophenol isomers. The entire concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M, and 0.01 M) of rGONS/β-CD/Ag

modified electrode showed a good electrochemical performance for the sensing of nitrophenol isomers. The maximum redox peak current for the sensing of nitrophenol isomers are obtained for the concentration of 0.006 M of silver loaded on the surface of rGONS/β-CD nanocomposites. It may concluded from the different characteristic analyses that the nanocomposites synthesized using 0.006 M concentration of silver are more effective compared to other concentrations of silver loaded on the rGONS/β-CD surface. The synthesized 0.006 M concentration of rGONS/β-CD/Ag nanocomposites modified GCE exhibited an excellent electrocatalytic activity towards the reduction and oxidation of ortho-, para- and meta-nitrophenol isomers. It showed a wide linear detection range from 1 mM to 12 mM with the sensitivity value of 0.28 mA mM^{-1} cm^{-2} for the ortho-nitrophenol isomer than the other two nitrophenols. It can be concluded from the results that the synthesized rGONS/β-CD/Ag nanocomposite modified GCE is better for the electrochemical detection of ortho-nitrophenol than the other nitrophenol isomers.

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