CHAPTER III

Synthesis and characterization of β-cyclodextrin functionalized reduced graphene oxide nanosheets for electrochemical detection of Nitrophenol

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SYNTHESIS AND CHARACTERIZATION OF β-CYCLODEXTRIN FUNCTIONALIZED REDUCED GRAPHENE OXIDE NANOSHEETS FOR ELECTROCHEMICAL DETECTION OF NITROPHENOLS

This chapter includes:

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

3.1. INTRODUCTION

Nitrophenol isomers such as ortho-, para- and meta-nitrophenols are appraised to be a dangerous waste by the U.S. Environmental Protection Agency [1]. It has a giant environmental effect due to its toxicity. Unluckily, nitrophenols are widely employed as intermediates in the manufacturing of pesticides, dyestuffs, and pharmaceuticals. In addition, nitrophenols can also be employed as an acid-base indicator and leather fungicide [2]. Therefore, nitrophenols will unavoidably be released into the environment to produce pollution in the process of manufacturing and applications. Hence, it is necessary to develop facile and reliable technique for the detection of nitrophenol isomers in environments [3]. So, the scientists are trying to fabricate the suitable nanomaterials for sensing nitrophenol isomer in environment using nanotechnology.

The application of nanomaterials can able to enhance the charge transfer between the surface of working electrode and the reaction medium through their large surface areas. Various types of nanomaterials (metal oxides, carbonaceous materials, doped metal oxides, and other nanomaterials and their nanocomposites) are employed for electrochemical sensing applications. Among the various types of nanomaterials, graphene oxide and its derivatives have large surface-to-volume ratios and thus graphene oxide nanomaterials are highly sensitive and cost-effective [4]. Additionally, graphene oxide nanosheets are highly selective for functionalization with polymer. The polymer functionalized reduced graphene oxides have many advantages including high electro catalytic efficiency, enhanced adsorption capacity, high surface-to-volume ratio and efficient surface reaction activity and thereby contributes in the remarkable electrical and optical features [5]. These results confirmed the successful applications of polymer functionalized reduced graphene oxide nanosheets in increasing the loading concentrations of nitrophenol isomers on the modified electrode surface. The polymer coating can able to reduce the aggregation of layers of reduced graphene oxide nanosheets and thus improves the electrocatalytic property of rGONS. Among many polymers, β-cyclodextrin acts as a stabilizing agent during the preparation of rGONS and improves the accumulation of nitrophenol sites on the electrode surface. The β-cyclodextrin polymer is macrocyclic oligosaccharide compound with seven glucose units in a toroidal configuration [6]. It has a hydrophobic interior and a hydrophilic exterior cavity. Because of this hydrophilic nature, it can easily interact with a large number of nitrophenol sites after the immobilization on the electrode surface through the formation of stable host–guest inclusion complexes [7].

The present work describes the synthesis of a graphene oxide (GO), reduced graphene oxide (rGO) and β-cyclodextrin functionalized reduced graphene oxide (rGONS) nanosheets via facile wet chemical method. The synthesized nanocomposites are investigated for the electrochemical detection of nitrophenol.

3.2. MATERIALS AND METHODS

Graphene oxide (GO) is synthesized from natural graphite powder by modified Hummer's method. The β-cyclodextrin functionalized reduced graphene oxide nanosheets are synthesized by taking 50 mg of graphene oxide and 0.6 g of β-CD in a 50 ml of water and dispersed well in an aqueous medium. The dispersed β-cyclodextrin

solution is then added into graphene oxide suspension followed by the addition of hydrazine hydrate and ammonia and stirred for 4 hours at 60˚C. The reaction suspension is then washed thoroughly using deionised water and dried at 60˚C for 4 hours [8].

3.3. RESULTS AND DISCUSSION

3.3.1. FT-IR SPECTRAL ANALYSIS

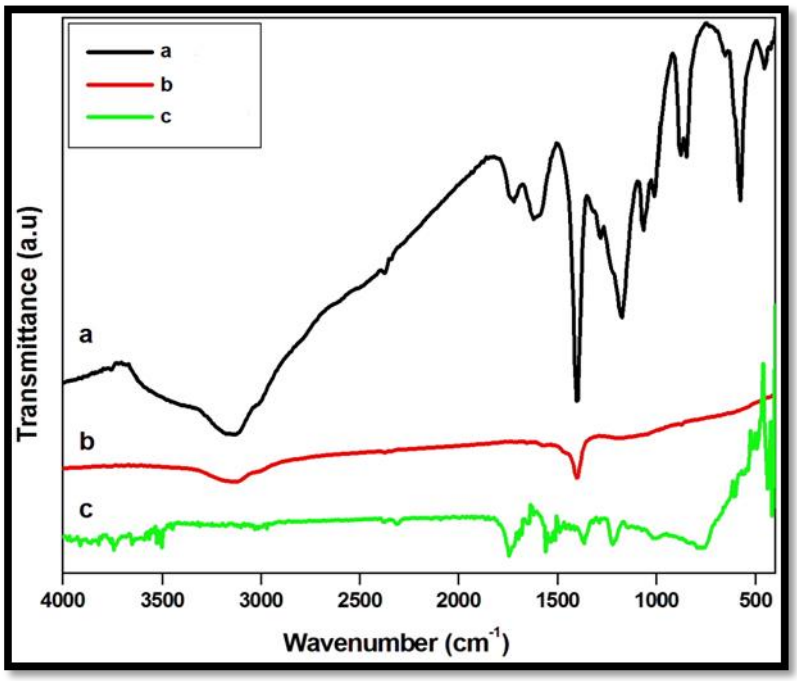


Figure.3.1. FT-IR spectra of (a) Graphene oxide (b) reduced graphene oxide (c) β-cyclodextrin functionalized reduced graphene oxide nanosheets

FT-IR is a characterization technique used to investigate the bonding interaction and functional groups of synthesized materials. Figure.3.1.(a) shows the FT-IR spectra of synthesized graphene oxide (GO). The characteristic band observed at 1061.31 cm^{-1}, 1182.66 cm^{-1}, 1394.60 cm^{-1}, 1606 cm^{-1}, 1727.14 cm^{-1} and 3160.38 cm^{-1} may corresponds to the alkoxy C-O, epoxy C-O, O-H stretching vibrations of water molecules, aromatic C=C groups of unoxidized sp^2 hybridized carbon atoms, carboxyl C=O group and stretching vibrations of O-H functional groups respectively [9-13]. The existence of O-H, C-O and C=O functional groups in the FT-IR spectra of graphene oxide confirms the incorporation of O-H water molecules and oxygen containing functional groups into the layers of graphene oxide during the oxidation of graphite powder by modified Hummer's method which confirms the successful synthesis of

graphene oxide [12-13]. It is observed from the FT-IR spectra of graphene oxide that some of the unoxidized graphite structures are still retained even after the completion of oxidation mechanism by showing the C=C vibrational functional group at 1606 cm^{-1} [11] [13]. The results of FT-IR spectra confirmed the successful synthesis of graphene oxide.

The FT-IR spectra of synthesized reduced graphene oxide are shown in the Figure.3.1.(b). It shows significantly low intense FT-IR bands at 1403.6 cm^{-1} and 3160.4 cm^{-1} which may be attributed to the O-H stretching vibrations of water molecules. This significant decrease in the intensity of the FT-IR band may be due to the removal of oxygen containing functional groups from the basal planes of graphene oxide during the chemical reduction of graphene oxide into reduced graphene oxide [14]. In comparison with that of FT-IR spectra of graphene oxide (Figure.3.1.(a)), the characteristic bands corresponding to the carbon-oxygen functional groups and aromatic C=C groups are not observed in the Figure.3.1.(b), which is also evidences the successful reduction of graphene oxide into reduced graphene oxide using a strong reducing agent such as hydrazine hydrate [14].

Figure.3.1.(c) shows the FT-IR spectra of rGO/β-CD nanosheets which exhibits the typical β-CD functional group bands along with reduced graphene oxide bands. The functional group of C=C and CH_2 observed at 1633 cm^{-1} and 2985 cm^{-1} confirms the presence of β-cyclodextrin polymer in the rGO/β-CD nanosheets [15-16]. The bending and stretching vibrations of O-H and C-O-C, C-C functional groups at 3627.43 cm^{-1} , 1140 cm^{-1} and 1026 cm^{-1} indicating the presence of reduced graphene oxide nanosheets [15]. It is observed from the Figure.3.1.(c) that the shift in the O-H stretching vibrational groups of reduced graphene oxide from its typical vibrational positions confirms the chemical functionalization of β-cyclodextrin polymer with the reduced graphene oxide nanosheets [15-16]. The observed shift in the vibrational position of water molecules is may due to the hydrophilic exterior cavity of β-cyclodextrin polymer changes the dispersion ability of reduced graphene oxide nanosheets [15-16]. It is confirmed from the FT-IR spectra of rGO/β-CD nanosheet that the β-cyclodextrin polymer are chemically blended with reduced graphene oxide nanosheets.

3.3.2. STRUCTURAL ANALYSIS

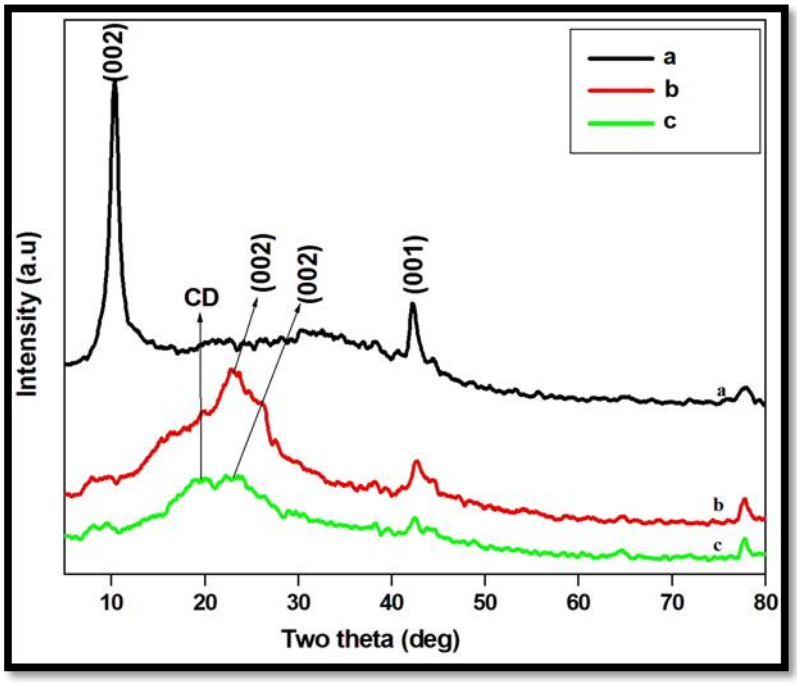


Figure.3.2. X-ray diffraction pattern of (a) Graphene oxide (b) reduced graphene oxide (c) β-cyclodextrin functionalized reduced graphene oxide nanosheets

X-ray diffraction analysis is the most widely used technique for the determination of general crystalline properties of materials. It is employed to measure the average spacing between the inter layers of synthesized graphene oxide (GO). The X-ray diffraction spectrum of synthesized graphene oxide in the Figure.3.2 (a) showed a very strong peak at 10.3˚, which is mainly due to the oxidation of graphite powder by modified Hummer's method [9] [12]. The typical diffraction peak of unoxidized graphite corresponds to the (002) diffraction plane is generally obtained at the angle of 26˚ with an inter layer spacing of 0.34 nm [9]. But as in the Figure.3.2.(a), the peak corresponds to (002) diffraction plane of pure graphite is shifted to the lower angle of 10.3˚, with the increase in the inter-layer spacing value to be 0.85 nm [9] [12]. This shift and the increase in the interlayer spacing value confirm the successful oxidation and exfoliation of graphene oxide [12]. This increase in the interlayer spacing between the consecutive basal planes of carbon is may due to the inclusion of high number of oxygen containing functional groups, water molecules and also due to the formation of weaker vanderwaals bonding by hydroxyl, carbonyl and carboxyl groups on the basal planes [9] [14-15]. Typically, the inter layer spacing of graphene oxide are controlled by

the degree of oxidation of graphite and the amount of intercalation of water molecules into the layers of GO sheets [14-15].

Figure.3.2.(b) shows the X-ray diffraction pattern of synthesized reduced graphene oxide (rGO). It show the broad diffraction peak of reduced graphene oxide at 23.7˚ having an interlayer spacing value of 0.3 nm along the (002) orientation [14] [16]. It is observed from the X-ray diffraction analysis that the sharp peak appeared at 10.3˚ in the Figure.3.2.(a) is found to be disappeared and shifted to the angle of 23.0˚, thereby confirming the successful synthesis of reduced graphene oxide. The shift and the decrease in the interlayer spacing value of diffraction peaks in reduced graphene oxide is attributed to the reduction of oxygen containing functional groups from the basal planes of the graphene oxide resulting in the disorder and restacking of the reduced graphene oxide [14].

The X-ray diffraction results of β-cyclodextrin functionalized reduced graphene oxide nanosheets are shown in the Figure.3.2.(c). The typical diffraction peak of β-cyclodextrin is usually obtained at 19.5˚ corresponding to the amorphous pattern of β-cyclodextrin [17]. The broad diffraction peaks around 19.5˚ and 23.0˚ which may be attributed to the β-cyclodextrin and reduced graphene oxide nanosheets respectively; confirming the formation of β-cyclodextrin functionalized reduced graphene oxide nanosheets. The broadness in the diffraction pattern may be due to the disorder restacking nature of reduced graphene oxide nanosheets. It is also observed that the diffraction peak intensity of the β-cyclodextrin functionalized reduced graphene oxide nanosheets is found to be very low compared with that of graphene oxide. This suggests that the beta cyclodextrin molecules are well incorporated into the layers of reduced graphene oxide [18]. The incorporation of β-cyclodextrin polymer into the reduced graphene oxide surface restricts the restacking and agglomeration nature of the reduced graphene oxide nanosheets. In the Figure.3.2.(a-c), the diffraction peak appeared at 42.1˚ corresponds to the (001) orientation and is due to the incomplete oxidation of graphite materials during the synthesis of GO, rGO and rGO/β-CD nanosheets.

3.3.3. SEM ANALYSIS

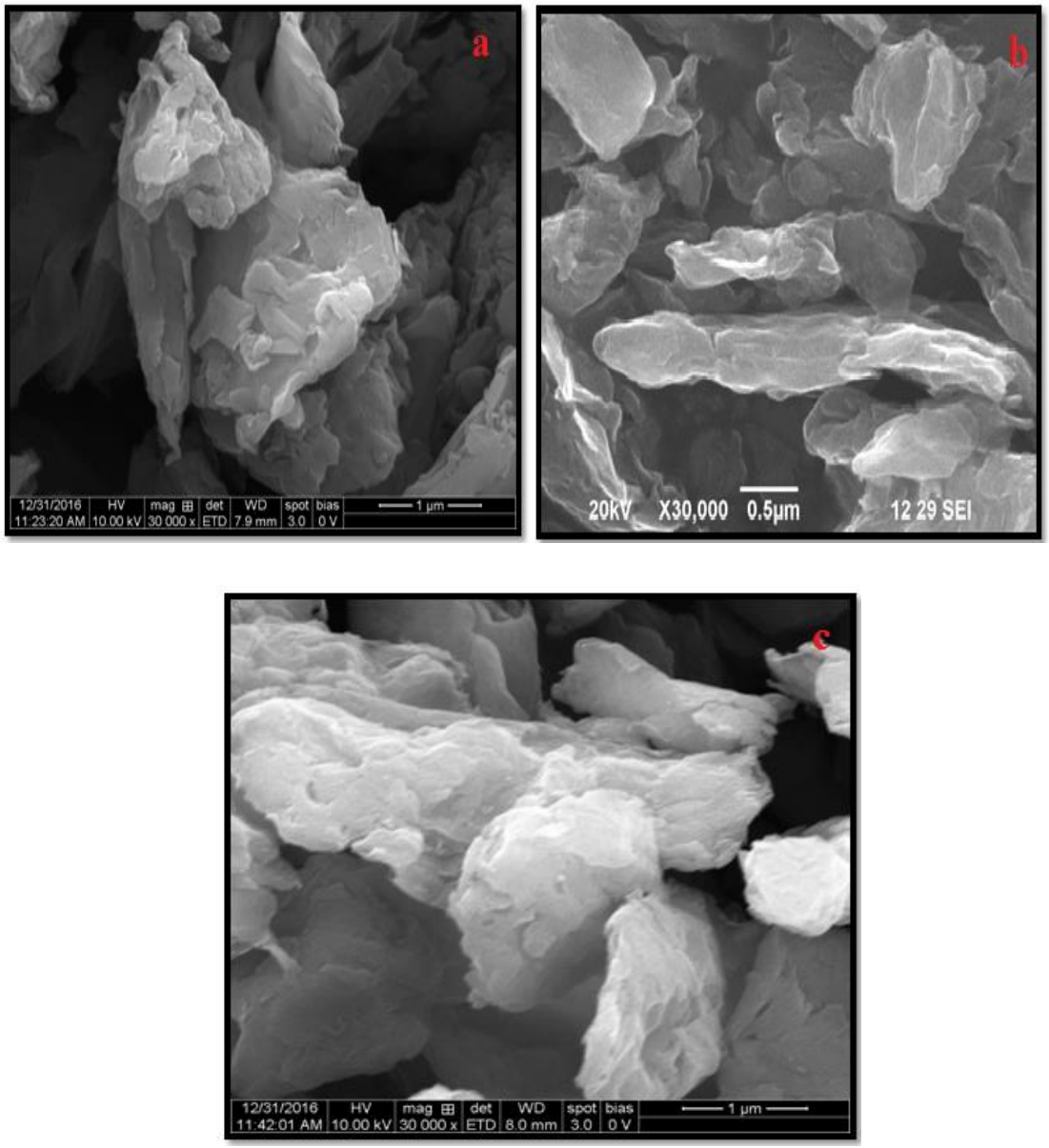


Figure.3.3. SEM images (a) Graphene oxide (b) Reduced graphene oxide (c) β-cyclodextrin functionalized reduced graphene oxide nanosheets

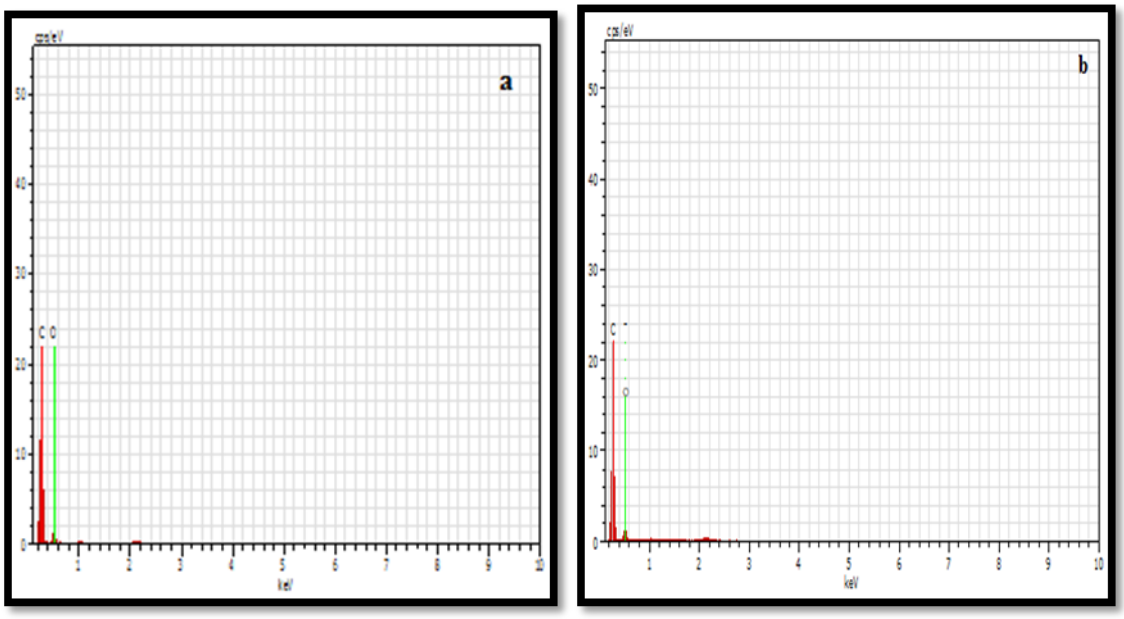
Scanning electron microscopy technique is used to investigate the morphology and shape of nanomaterials. Figure.3.3.(a) shows the scanning electron micrograph of synthesized graphene oxide with the magnification of 30,000. It is observed from the Figure.3.3.(a) that the synthesized graphene oxide has a layered or wrinkled structure. The layers of graphene oxide contain numerous ultrathin and homogenous graphene sheets and such sheets causes continuous, wrinkled or folded like morphology. It is

possible to discriminate the edges of the wrinkle shaped graphene oxide via chemical reduction method using strong reducing agents [19].

Figure.3.3.(b) shows the scanning electron micrograph of the synthesized reduced graphene oxide. It shows the typical two dimensional single or few layers of wrinkled structural morphology of reduced graphene oxide [16]. The morphology of the synthesized reduced graphene oxide is as similar as the morphology of synthesized graphene oxide, but the surface and edges of the reduced graphene oxide (rGO) is observed to be smooth folded [14] [20].

SEM images of the synthesized β-cyclodextrin functionalized reduced graphene oxide nanosheets is shown in the Figure.3.3.(c). It is observed from the SEM analysis that the sheets of rGO/β-CD sample are highly wrinkled than that of graphene oxide sample, which is mainly due to the functionalization of β-cyclodextrin with graphene oxide. In comparison with that of graphene oxide and reduced graphene oxide, the surface morphology of the β-CD functionalized reduced graphene oxide is more wrinkled as well as less transparent thereby confirming the successful functionalization of β-cyclodextrin with the reduced graphene oxide samples [21].

3.3.4. EDAX ANALYSIS



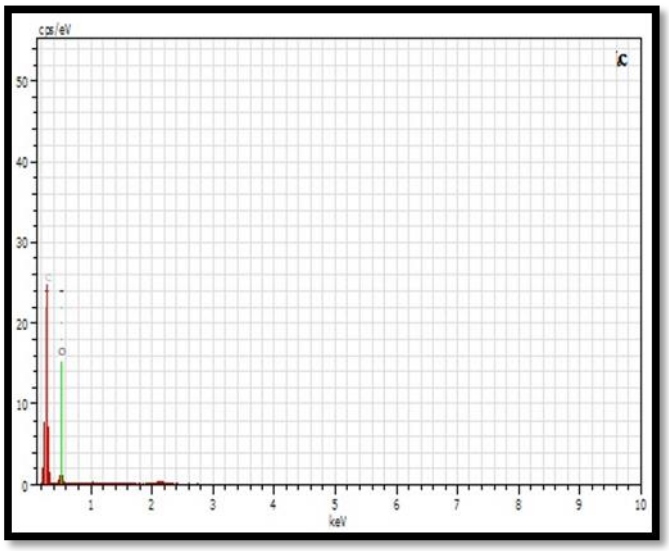


Figure.3.4. EDAX spectra of (a) Graphene oxide (b) Reduced graphene oxide (c) β-cyclodextrin functionalized reduced graphene oxide nanosheets

The EDAX spectrum of graphene oxide, reduced grapheen oxide and β-cyclodextrin functionalized reduced graphene oxide nanosheets are shown in the Figure.3.4.(a-c). It reveals that EDAX spectra of graphene oxide, reduced graphene oxide and β-cyclodextrin functionalized reduced graphene oxide nanosheets mainly consists of elemental peaks of carbon and oxygen which confirms the successful synthesis of GO, rGO and rGONS/β-CD without any impurites. The elemental atomic and weight percentage of carbon and oxygen in the EDAX spectra of GO, rGO, and rGONS/β-CD is listed in the Table.3.1.

Table.3.1. Elemetal percentage of GO, rGO, rGONS/β-CD

Element	Weight %		Atomic %	
	Carbon	Oxygen	Carbon	Oxygen
GO	75.70	24.30	80.95	19.05
rGO	83.56	16.44	87.21	12.79
rGONS/β-CD	84.20	15.80	88.74	11.26

It is observed from the Table.3.1. that the percentage of oxygen element in the rGONS is comparatively less than in the graphene oxide, thereby the removal of oxygen containg functional groups during the reduction of graphe oxide into reduced graphene oxide nanosheets is evidenced. But for the synthesized rGONS/β-CD nanocomposites, the percentage of carbon and oxygen elements ratios are higher than the rGONS and this may be due to the presence of β-cyclodextrin polymer, thereby confirming the succesful inclusion of β-CD polymer with the rGO nanosheets [17].

3.3.5. ELECTROCHEMICAL BEHAVIOUR OF MODIFIED ELCTRODES

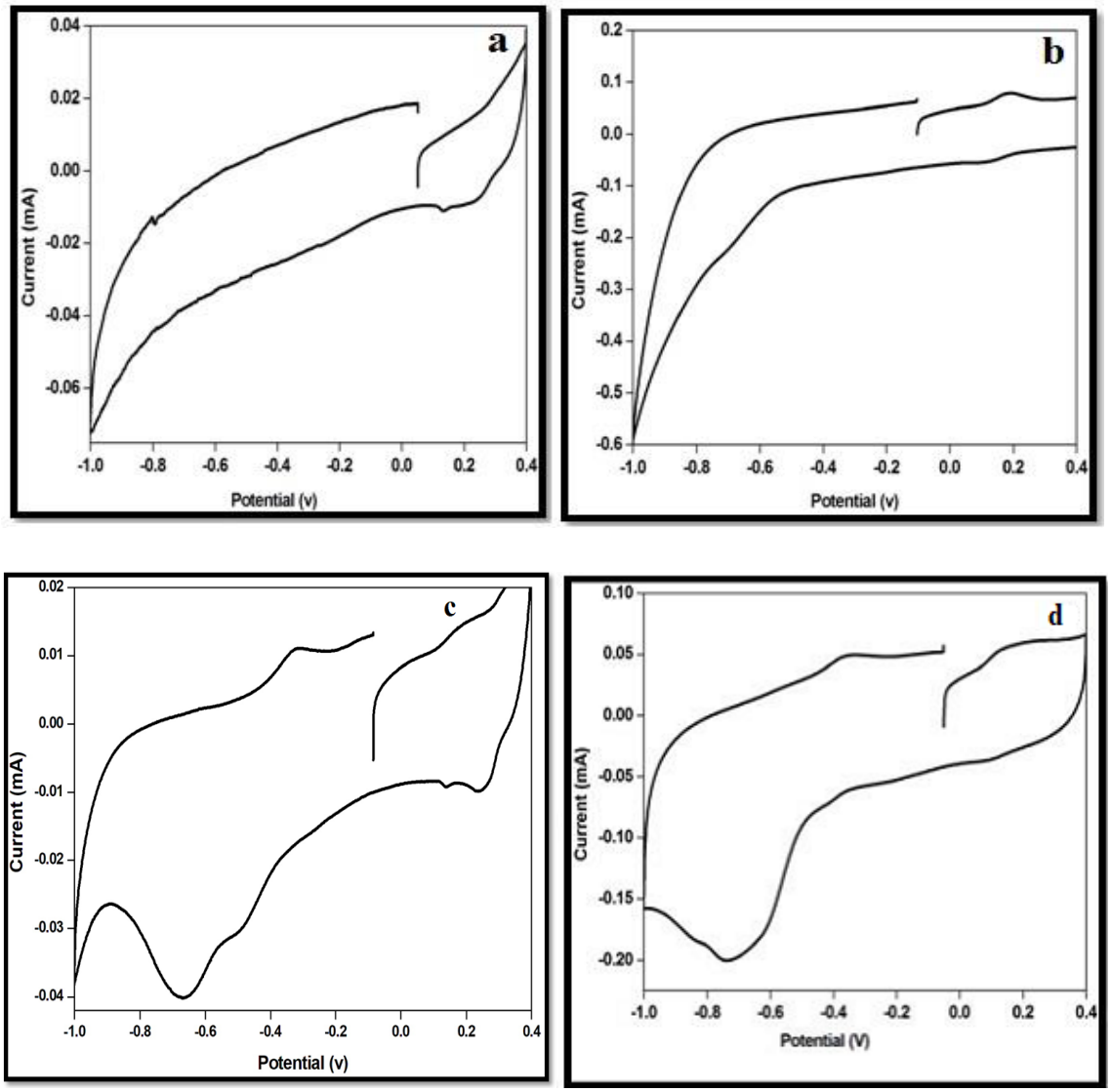


Figure.3.5. Cyclic voltagramm of 14 mM of o-NP at (a) bare GCE (b) GO/GCE (c) rGONS/GCE and (d) rGONS/β-CD/GCE in 0.1 M PBS solution (pH 7.0) at the scan rate of 10 mV/s

The voltammetric behaviour of 14 mM ortho-nitrophenol (o-NP) at the (a) bare GCE, (b) GO/GCE, (c) rGONS/GCE (d) rGONS/β-CD/GCE, are investigated in 0.1 M of pH 7.0 phosphate buffer solutions (PBS) at the scan rate of 10 mV/s and are shown in the Figure.3.5.(a-c). It is observed from the Figure.3.5.(a and b) that there is no significant oxidation and reduction peaks corresponding to o-nitrophenol for the bare and GO modified GCE, thereby confirming that there is no remarkable electro-active behaviour between bare GCE and o-nitrophenol. But the rGONS modified GCE as shown in Figure.3.5.(c) shows the better electrochemical behaviour for the sensing of o-nitrophenol molecules than the bare and GO modified GCE, which may be attributed to the excellent conductivity and large surface area of reduced graphene oxide nanosheets [22]. The rGONS/β-CD nanocomposites modified GCE shows the remarkable peak currents for the sensing of o-nitrophenol at the oxidation and reduction potential range around -0.32 V and -0.74 V. The observed oxidation and reduction peak current of o-nitrophenol is significantly higher than the other three electrodes such as bare GCE, GO/GCE and rGONS/GCE. This may be due to the presence of reduced graphene oxide nanosheets and β-CD in the synthesized rGONS/β-CD nanocomposites. Reduced graphene oxide in the rGONS/β-CD modified GCE can enhances the redox peak current intensity, because of its excellent electrical conductivity nature and it has the ability to reduce the electrical conductivity resistance of the nanocomposite modified on the surface of GCE. On the other hand, the enhancement in the reduction current of ortho-nitrophenol may be attributed to the presence of chemically functionalized β-cyclodextrin polymer. The β-cyclodextrin is a cyclic oligosaccharides molecule containing numerous hydroxyl groups with high superamolecular recognition property. Due to this excellent property, it can be able to form inclusion complexes with the ortho-nitrophenol site and modified electrode surface, which thereby increases the number of ortho-nitrophenol sites accumulated on the surface of rGONS/β-CD modified GCE, which further enhances the electrochemical reduction current of ortho-nitrophenol [22-23]. Hence it is evident from the results that the rGONS/β-CD exhibits an excellent electrochemical property by combining the property of reduced graphene oxide and β-cyclodextrin polymer.

3.4. CONCLUSION

In this chapter, the glassy carbon electrode surface modified with reduced graphene oxide and reduced graphene oxide based polymer functionalized nanocomposite is prepared for the sensitive detection of ortho-nitrophenol via simple, efficient and cost effective electrochemical method. The graphene oxide, reduced graphene oxide and β-cyclodextrin functionalized reduced graphene oxide nanosheets are successfully synthesized by modified Hummer's and chemical reduction methods. The synthesis and functionalization of reduced graphene oxide with β-cyclodextrin polymer is effectively studied by various characterization techniques such as FT-IR, XRD, FESEM and EDAX analysis. It is observed from the FT-IR spectra of rGO/β-CD nanosheets that the shift observed in the O-H stretching vibrational groups of reduced graphene oxide from its typical vibrational positions confirms the chemical functionalization of β-cyclodextrin polymer with the reduced graphene oxide nanosheets. The XRD pattern of GO and rGONS/β-CD nanocomposites indicate the formation of GO and polymer functionalized reduced graphene oxide nanosheets with the sharp and broad diffraction peak at 10.3˚ and 23˚ respectively.The morphological study confirms the formation of graphene oxide, reduced graphene oxide and β-cyclodextrin polymer functionalized reduced graphene oxide nanosheets with wrinkled surface morphology. It also confirms the chemical functionalization of β-cyclodextrin polymer with reduced graphene oxide nanosheets and it prevents the agglomeration and restacking of graphene layers. The electrochemical detection of ortho-nitrophenol at bare GCE, rGO/GCE and rGONS/β-CD/GCE is performed and the result shows the higher electrochemical performance for rGONS/β-CD/GCE than the other modified and bare GCE. This signifies the role of β-cyclodextrin polymer towards the enhancement of electrocatalytic property of reduced graphene oxide nanosheets and also the presence of β-CD polymer on the surface of rGONS effectively increases the surface area of rGONS. It also confirms the effect of supramolecular recognition capability of β-CD polymer on the formation of host-guest complexes with ortho-nitrophenol. It is concluded from the above results that the glassy carbon electrode surface modified with rGONS/β-CD nanocomposite exhibited a better electrochemical property towards the detection of ortho-nitrophenol. A better electrochemical behaviour can be achieved by further modification of rGONS/β-CD surface with some nanomaterials such as

metal/metal oxides than rGONS/β-CD nanocomposite and employed for the detection of all three nitrophenol isomers.

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