CHAPTER VIII

Summary of results and conclusion

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8.1. INTRODUCTION

The present research work describes the synthesis of graphene oxide, polymer functionalized reduced graphene oxide and five different (Ag, Au) / metal oxide (ZnO, CuO) nanoparticles decorated polymer functionalized reduced graphene oxide nanosheets with various concentrations and their electrochemical performance towards the detection of nitrophenol isomers such as ortho-, para- and meta-nitrophenols. The prepared nanocomposites are characterized by the different analytical techniques such as FT-IR, XRD, SEM, EDAX and HRTEM with SAED analysis. The electrochemical study is carried out to investigate the electrochemical sensing performance against the nitrophenol isomers (ortho-, para- and meta-nitrophenols). The objective of the thesis work is accomplished successfully and the results are summarized as follows:

8.2. β-cyclodextrin functionalized reduced graphene oxide nanosheets

The cyclic voltammetry study is employed to investigate the electrochemical detection of ortho-nitrophenol using graphene oxide (GO), reduced graphene oxide nanosheets (rGONS) and β-cyclodextrin functionalized reduced graphene oxide nanosheets (rGONS/β-CD). The modified Hummer's and chemical reduction methods are successfully employed to prepare GO, rGONS, rGONS/β-CD nanocomposites and is confirmed by FT-IR, XRD, SEM and EDAX analysis. The synthesized nanocomposites are physically deposited on the surface of glassy carbon electrode (GCE) to modify the surface of GCE for the better electrochemical performance. It is evident from the SEM analysis that the surface of rGONS/β-CD nanocomposite is more wrinkled and less transparent than the GO and rGO nanosheet, thereby produces a large surface to volume ratio for the attachment of ortho-nitrophenol sites on the surface of modified GCE during the electrochemical analysis. The cyclic voltammetry results confirmed that the GO and rGO nanosheets modified GCE showed only low electrocatalytic performance towards the detection of ortho-nitrophenol. So, the β-CD polymer is chemically functionalized with the rGONS to improve the electrocatalytic

activity. The electrocatalytic performance is studied for the rGONS/β-CD nanocomposites modified GCE with 14 mM of ortho-nitrophenol in phosphate buffer solution at the scan rate of 10 mV/s. The results showed a well defined redox peak with the potential of -0.32 V and -0.74 V. This confirms the presence of chemically functionalized β-cyclodextrin polymer in the rGO nanosheets. The β-cyclodextrin contains numerous hydroxyl groups with high superamolecular recognition property, thereby forms the inclusion complexes with the ortho-nitrophenol site and modified electrode surface and thereby enhances the electrochemical reduction current of ortho-nitrophenol. Hence, the rGONS/β-CD/GCE exhibits an excellent electrochemical property compared to GO and rGO nanosheets.

8.3. Silver nanoparticles loaded β-cyclodextrin functionalized reduced graphene oxide nanosheets

The various concentration (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 nanosheets are synthesized via wet chemical method and examined for their electrochemical performance towards the detection of all three nitrophenol isomers (ortho-, para- and meta-nitrophenol). The SEM analysis showed that the number 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. With the increase in the concentration of silver nitrate from 0.008 M and 0.01 M, the dispersion of silver nanoparticles 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. Hence, the maximum dispersion capability of silver nanoparticles on the rGONS/β-CD surface is found to be 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. The β-CD polymer controls the aggregation and growth kinetics of silver nanoparticles on the surface of rGONS/β-CD nanocomposites. All these rGONS/β-CD/Ag nanocomposite exhibits good electrochemical behaviour towards the reduction and oxidation of ortho-nitrophenol. A low redox peak current is observed for the 0.002 M of rGONS/β-CD/Ag/GCE and this

may be due to the presence of less number of silver nanoparticles on the surface of rGONS/β-CD, as it is not sufficient for enhancing the electron transfer rate. With the further increment in the concentration of silver nitrate from 0.002 M to 0.006 M, a higher reduction peak current is observed and this may be attributed to the increase in the concentration of silver nanoparticles decorated on the rGONS/β-CD surface and also the excellent electrocatalytic activity of nanocomposites. But for the 0.008 M and 0.01 M concentration of silver nitrate, the redox peak current corresponding to o-nitrophenol is found to be decreased, which may be due to the aggregation and decrease in the number of silver nanoparticles decorated on the rGONS/β-CD surface. Hence it is observed that the 0.006 M concentration of silver nanoparticles decorated rGONS/β-CD nanocomposites has better electrochemical behaviour and high redox peak current than the other concentrations of silver nanoparticles modified rGONS/ β-CD surface. The electrochemical performance towards the detection of ortho-, para- and meta-nitrophenols are studied for the 0.006 M concentration of rGONS/ β-CD/Ag nanocomposite with different pH values from 4 to 8, different scan rate of 10 to 50 mV/s and different concentrations of o-, p- and m-NP. However, the maximum electrochemical reaction is attained at the pH values of 7.0, 7.0 and 5.0 at the scan rate of 10 mV/s for o-, p- and m-nitrophenol respectively. The cyclic voltammetry result showed that the linear segment ranges from 1 to 12 mM, 1 to 15 mM and 1 to 11 mM for ortho-, para- and meta-nitrophenol isomers respectively and this may be due to the diffusion process on the rGONS/β-CD/Ag layer covered on the surface of GCE. The sensitivity values of the ortho-, para- and meta-nitrophenol isomer are found to be 0.28 mA mM^{-1} cm^{-2}, 0.19 mA mM^{-1} cm^{-2} and 0.09 mA mM^{-1} cm^{-2} respectively. Hence, it is confirmed from the results that the synthesized rGONS/β-CD/Ag nanocomposite showed a 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}. But the synthesized electrode material showed a low sensitivity with linear range of detection in millimolar. To achieve a high sensitive and micro molar range of detection, the rGONS/β-CD surface is modified with different concentration of gold nanoparticles.

8.4. Gold nanoparticles encapsulated β-cyclodextrin functionalized reduced graphene oxide nanosheets

Wet chemical synthesis method is employed to prepare the various concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of gold nanoparticles encapsulated β-cyclodextrin functionalized reduced graphene oxide nanosheets (rGONS/β-CD/Au). The FT-IR analysis showed that the depth of the band corresponding to carbon-oxygen functional groups (C-O, O-H and C-H) of reduced graphene oxide nanosheets and β-cyclodextrin polymer decreases gradually with the increase in the concentration of gold (III) chloride trihydrate from 0.002 M to 0.01 M. XRD analysis showed that the diffraction peak appeared at 24.3˚ with the crystalline plane of (002) of rGO/β-CD nanosheet decreases with the increase in the concentration of gold chloride trihydrate from 0.002 M to 0.01 M, thereby confirms the encapsulation of gold nanoparticles concentrations on the surface of rGO/β-CD nanosheets.

The detection of nitrophenol isomers (o-, p- and m-NP) are examined with respect to the concentration of rGONS/β-CD/Au, pH, scan rate and concentration of analytes. The well defined redox peaks are observed for the 0.006 M concentration of rGONS/β-CD/Au nanocomposite modified GCE with the maximum redox peak current compared to other concentration such as 0.002 M, 0.004 M, 0.008 M and 0.01 M of rGONS/β-CD/Au nanocomposites. The electrochemical investigation towards the detection of ortho-, para- and meta-nitrophenol isomers are carried out using 0.006 M concentration of rGONS/β-CD/Au nanocomposite at the scan rate of 10 mV/s. The results showed the linear range of detection from 100 μM to 280 μM, 100 μM to 200 μM and 100 μM to 190 μM for ortho-, para- and meta-nitrophenol and the sensitivity values are of 8.87 mA μM^{-1} cm^{-2}, 1.92 mA μM^{-1} cm^{-2} and 1.02 mA μM^{-1} cm^{-2} respectively. The results confirmed that the synthesized electrode modification material showed a good linear range of detection and sensitivity for the reduction and oxidation of ortho-nitrophenol. Further enhancement in the sensitivity and micro molar range of detection is evaluated using metal oxide (zinc oxide, copper oxide) nanoparticles.

8.5. Zinc oxide nanoparticles embellished β-cyclodextrin functionalized reduced graphene oxide nanosheets

A simple and effective wet chemical method is employed for the synthesis of different molar ratios (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of rGONS/ β-CD/ZnO nanocomposites. XRD analysis revealed the effect of different molar ratio of zinc acetate dihydrate on the size controlled synthesis of wurtzite structure of zinc oxide nanoparticles with the crystallite size of 24.21 nm, 22.69 nm, 21.71 nm, 19.85 nm and 27.99 nm, respectively. The smaller and higher crystallite sizes are observed for the molar ratio of 0.008 M and 0.01 M which showed the significant effect on the electrochemical behaviour of rGONS/β-CD/ZnO nanocomposites. The morphological analysis showed that the zinc oxide nanoparticles with different morphologies on the surface of rGONS/β-CD can be synthesized by varying the molar ratios of Zn^{2+} ions on the surface of rGONS/β-CD. The spindle-like morphology of zinc oxide nanoparticles is not evident for the 0.002 M molar ratio of Zn^{2+} ions. This may be due to the insufficient amount of Zn^{2+} ions, the predominance of β-cyclodextrin polymer and the layered structure of reduced graphene oxide nanosheets. With the increase in the molar ratio of Zn^{2+} ions from 0.004 M to 0.008 M, the spindle like zinc oxide nanoparticles are effectively embellished on the rGONS/β-CD surface without agglomeration and this may be due to the presence of sufficient molar ratio of Zn^{2+} ions in the reaction system. But for the 0.01 M of Zn^{2+} ions, the spindle like morphology of ZnO nanoparticles with agglomeration is observed and this may be ascribed to the presence of more number of Zn^{2+} ions in the reaction system. The HRTEM analysis also further confirmed the spindle shaped zinc oxide nanoparticles are uniformly distributed on the surface of rGONS/β-CD without any agglomeration. The structural and morphological analysis revealed that the introduction of various concentrations of zinc acetate dihydrate into the rGONS/β-CD reaction system affected the crystallite size and morphology of zinc oxide nanoparticles and which shows the great impact on the performance of electrochemical detection. The electrochemical behaviour of rGONS/β-CD/ZnO nanocomposite is studied by cyclic voltammetry and the result showed a linear detection in the range from 10 to 210 μM, 10 to 240 μM and 40 to 240 μM and the sensitivity values are of 4.7 mA μM^{-1} cm^{-2}, 13.8 mA μM^{-1} cm^{-2} and 2.2 mA μM^{-1} cm^{-2} for o-, p- and m-nitrophenol respectively. The better electrochemical performance is

observed for the para-nitrophenol with the linear range of detection from 20 to 240 μM and sensitivity value of about 13.8 $mA\mu M^{-1}$ cm^{-2}. The sensitivity and linear range of detection is found to be high for the rGONS/β-CD/ZnO nanocomposite than the rGONS/β-CD/Au and rGONS/β-CD/Ag nanocomposites.

8.6. Copper oxide nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets

The different concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of copper oxide nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets (rGONS/β-CD/CuO) are prepared by wet chemical method and their physicochemical properties are investigated using various analytical techniques. The uniformly dispersed spherical shaped copper oxide nanoparticles are observed for the lower concentrations such as 0.002 M and 0.004 M of copper II acetate monohydrate. But for the higher concentration of copper II acetate monohydrate above 0.004 M, the dispersion of copper oxide nanoparticles on the surface of rGO/β-CD nanosheet is found to be aggregated, which indicates that the high loading concentration of copper oxide nanoparticles on the rGONS/β-CD surface leads to aggregation and thereby confirming the saturation accommodating ability of rGONS/β-CD. The concentration dependent analysis plays significant effect on the electrochemical behaviour of rGONS/β-CD/CuO nanocomposite towards the detection of ortho-, para- and meta-nitrophenol isomers. The uniformly dispersed and spherical shaped copper oxide nanoparticles decorated rGONS/β-CD nanocomposite are used to modify the surface of GCE and the result showed the good electrochemical performance for the detection of all three nitrophenol isomers. The sensing performance is also improved for the 0.002 M and 0.004 M concentrations and at the saturation condition such as above 0.004 M, the sensitivity is decreased. But for the 0.004 M concentration of rGONS/ β-CD/CuO nanocomposite, the linear detection range is obtained from 100 to 190 μM, 60 to 280 μM and 100 to 210 μM for ortho-, para- and meta-nitrophenol respectively. The sensitivity values are of 2.3 $mA\mu M^{-1}cm^{-2}$, 10.4 $mA\mu M^{-1}cm^{-2}$ and 3.0 mA μM^{-1} cm^{-2} for o-, p- and m-NP respectively. Hence, the synthesized rGONS/β-CD/CuO electrode material is good for the detection of para-nitrophenol with the sensitivity and linear range of detection of 10.4 $mA\mu M^{-1}cm^{-2}$ and 60 μM to 90 μM and 120 μM to 280 μM respectively.

8.7. CONCLUSION

The present thesis described a new dimension in the electrochemical detection of hazardous nitrophenol isomers using carbon based nanomaterials and proved to be reliable for sensing applications. The various physicochemical and electrochemical studies of synthesized nanocomposites revealed that the zinc oxide nanoparticles decorated β-cyclodextrin functionalized reduced graphene oxide nanosheets are the promising electrode material for the high sensitive detection of nitrophenol isomers. The molar ratios of metal/metal oxide nanoparticles embellished polymer functionalized graphene based nanocomposites may be varied and can be tested for food packing, water purification, cancer antigen detection and pesticides detection, etc.