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**INVESTIGATIONS ON METAL (Ag, Au) / METAL OXIDES (ZnO, CuO)
NANOPARTICLES INCORPORATED ON CHITOSAN BLENDED
REDUCED GRAPHENE OXIDE NANOCOMPOSITES FOR
ELECTROCHEMICAL SENSING OF p-AMINOPHENOL AND
ANTIBACTERIAL & ANTICANCER APPLICATIONS**

THESIS

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CHAPTER VIII

SUMMARY OF RESULTS AND CONCLUSION

8.1 INTRODUCTION

The present work describes the influence of various concentrations of Metal (Ag, Au) / Metal oxides nanoparticles ensembled chitosan blended reduced graphene oxide nanocomposites on electrochemical detection of p-Aminophenol and biological applications. The structural, morphological and composition of prepared nanocomposites are characterized using standard analytical techniques like Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectroscopy (EDAX), High resolution transmission electron microscopy (HRTEM). The electrochemical sensing behaviour, antibacterial and anticancer activity of the prepared nanocomposites are investigated.

8.2 INFLUENCE OF CHITOSAN BLENDED REDUCED GRAPHENE OXIDE NANOSHEETS FOR THE ELECTROCHEMICAL DETERMINATION OF p-AMINOPHENOL

The graphene oxide is synthesized by modified Hummer's method and the chitosan functionalized reduced graphene oxide is synthesized by chemical reduction method. The synthesized rGO / CS nanocomposites are further characterized by FT-IR, XRD, SEM and EDAX analysis. The structural analysis showed that the sharp diffraction peak at 11.42° corresponds to (002) plane of graphene oxide and the broadening of the peak at 24° may be due to the amorphous nature of chitosan. SEM micrographs of rGO/CS nanocomposites showed that the formation of white patches on the surface of flat wrinkled leaf like structure of rGO. The electro-chemical behaviour for the prepared GO and rGO/CS nanocomposites is investigated using cyclic voltammetry. The electrodes are modified using GO and rGO/CS for better sensing. The electrochemical property reveals that the rGO/CS nanocomposites modified GCE exhibited high redox peak current $I_{pa} = 0.079\mu\text{A}$ and $I_{pc} = -0.09\mu\text{A}$ for p-AP compared to that of GO modified GCE. Due to high

adsorptive property and the high surface area, chitosan blended reduced graphene oxide resulted in the enhanced electrocatalytic activity of p-AP.

8.3 ELECTROCHEMICAL INVESTIGATION OF POLYMER FUNCTIONALIZED REDUCED GRAPHENE OXIDE / ZINC OXIDE NANOCOMPOSITES FOR THE DETECTION OF p-AMINOPHENOL

The various concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of rGO / CS / ZnO nanocomposites are successfully synthesized by chemical precipitation method and the nanocomposites are characterized using XRD, FTIR, SEM, EDAX, TEM and SAED analysis. The structural analysis revealed that the intensity of diffraction peaks of zinc oxide nanoparticles increases with decrease in intensity of chitosan peaks and the crystallite size is found to be about 27.3 nm, 33.4 nm and 34.9 nm for 0.006 M, 0.008 M and 0.01 M of ZnO nanoparticles. The surface morphology analysis revealed that the ZnO nanorods are entangled on the surface of rGO/CS nanosheets, thus the chitosan matrix helps the ZnO nanorods from aggregation and homogenous dispersion of nanorods on the surface of rGO/CS nanosheets. TEM images revealed that the average size of about 39 nm is distributed over the surface of rGO / CS. The distinct rings with discrete bright spots confirmed the polycrystalline nature of the prepared nanocomposites and the circular ring pattern ZnO nanoparticles is in good agreement with the XRD results.

The electrochemical behaviour of rGO/CS/ZnO nanocomposite towards the detection of p-AP at the modified glassy carbon electrode is studied. The prepared 0.008M of rGO/CS/ZnO nanocomposites has shown prominent electrochemical behaviour towards the detection of p-AP. The maximum redox peak current is observed for pH 7 is 0.06 μ A and the wide linear range of detection about 10 μ M to 180 μ M.

8.4 INFLUENCE OF COPPER OXIDE NANOPARTICLES ENSEMBLED ON CHITOSAN BLENDED REDUCED GRAPHENE OXIDE NANOSHEETS FOR THE ELECTROCHEMICAL DETECTION OF p-AMINOPHENOL

The various concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of copper oxide nanoparticles embedded on reduced graphene oxide / chitosan

nanocomposites is successfully synthesized by chemical reduction method. XRD revealed that for low concentration of copper II acetate monohydrate (0.002 M), no diffraction peaks of copper oxide nanoparticles is observed thereby indicating the strong binding of chitosan into the rGO. But by increasing the concentration of copper II acetate monohydrate from 0.004 M to 0.01M the intensity of diffraction peaks of copper oxide nanoparticles increases with decrease in the intensity of diffraction peaks of rGO/CS. It is observed that an average size of 17 nm of spherical shaped copper oxide nanoparticles are homogeneously distributed on the surface of rough, thin, wrinkled reduced graphene oxide/chitosan nanosheets. It is found that for higher concentration (0.01 M) of CuO nanoparticles, they are found to be aggregated. Due to heavy loading of copper oxide nanoparticles, chitosan loses its ability to form stable nanoparticles that leads to aggregation of nanoparticles on the surface of rGO/CS. Thus 0.008M concentration of copper II acetate monohydrate is chosen for the electrochemical detection of p-AP due to its large surface area with uniform distribution of copper oxide nanoparticles. The electrochemical performance of the prepared nanocomposites towards the detection of p-AP is studied using cyclic voltammetry. The rGO/CS/CuO nanocomposites showed a pair of well defined redox peaks at a potential of about about $E_{pa} = 0.036$ V and $E_{pc} = -0.038$ V with the redox peak current of about $I_{pa} = 0.07 \mu\text{A}$ and $I_{pc} = -0.16 \mu\text{A}$. The rGO/CS/CuO nanocomposite modified GCE showed excellent electrocatalytic activity towards the detection of p-AP due to its uniform dispersion of CuO nanoparticles on the large surface area of rGO/CS that leads to good electron transfer rate between p-AP and rGO/CS/CuO nanocomposite modified GCE. The maximum redox peak current of rGO/CS/CuO nanocomposite $0.18\mu\text{A}$ is observed for pH 5 and the linear range of detection is around $60\mu\text{M}$ to $150\mu\text{M}$.

8.5 EFFECT OF SILVER NANOPARTICLES ON POLYMER BLENDED REDUCED GRAPHENE NANOHYBRIDS AS A VERSATILE ELECTROCHEMICAL SENSOR FOR THE DETECTION OF p-AMINOPHENOL

The various concentrations (0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M) of rGO/CS/Ag nanocomposites are successfully synthesized by chemical

reduction method and are characterized by XRD, FT-IR, SEM, EDAX, HR-TEM and SAED analysis.. The crystallite size of the formed nanocomposites is about 17.5 nm, 21.4 nm, 23.5 nm, 23.8 nm and 25.6 nm for 0.002 M, 0.004 M, 0.006 M, 0.008 M and 0.01 M respectively. The crystallite size increases on increasing the concentration of Ag. The surface morphological studies revealed that the 0.006 M concentration of spherical shaped Ag nanoparticles are found to be uniformly dispersed onto the thin crumbled leaf like rGO/CS nanosheets indicating a strong interaction between the oxygen containing functional groups of reduced graphene oxide nanosheets and Ag⁺ ions. But for higher concentration of silver nitrate from 0.008 M to 0.01 M the particles on the surface of rGO/CS are found to be agglomerated leading to poor electrocatalytic property. The SAED pattern showed distinct circular rings and the dark spots revealed the crystalline nature of the synthesized silver nanoparticles. The 0.006 M of rGO/CS/Ag modified GCE electrode exhibited a high current for pH 6 of about 0.11 μ A and wide linear range of detection of 30 μ M to 160 μ M for p-Aminophenol. Thus the large effective surface area of the prepared nanocomposites allowed it to function as an electron transfer medium and enhances the charge transfer rate leading to good electrocatalytic activity towards the detection of p-Aminophenol.

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

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 are investigated using FT-IR, XRD, SEM, EDAX, HR-TEM and SAED analysis. The structural analysis revealed that the nanocomposites are of high crystalline in nature with the crystallite size of about 8.9 nm to 16.5 nm for 0.002 M to 0.01 M. The intensity of diffraction peaks of gold nanoparticles increases on increasing the concentration of gold (III) chloride trihydrate with decrease in the intensity of CS and rGO peaks. The morphological analysis revealed that 0.008 M concentration of gold (III) chloride trihydrate have large number of highly dispersed

gold nanoparticles, thereby increases the electron transfer rate between gold nanoparticles and rGO/CS nanosheets that leads to high electrocatalytic activity. The SAED reveals that the prepared nanocomposites are polycrystalline in nature and the obtained distinct rings are well indexed with highly resolved lattice planes (111) (200) (220) and (311) of gold nanoparticles. The electrochemical behaviour of p-AP for 0.008 M of rGO/CS/Au modified GCE is studied. Under optimized conditions, the maximum redox peak current is observed for pH 6 as 0.36 μ A with a wide linear range of detection as 10 μ M to 130 μ M and is found to be the most promising electrode material for the electrochemical detection of p-aminophenol in environment.

8.7 ANTIBACTERIAL AND ANTICANCER ACTIVITIES OF THE rGO/CS/METAL OXIDES (ZnO, CuO), METAL (Ag, Au) NANOCOMPOSITES

The different concentrations of Metal oxides (ZnO, CuO), Metal nanoparticles (Ag, Au) nanoparticles incorporated chitosan blended reduced graphene oxide nanocomposites possess potent bactericidal activity against Gram-positive (*B. subtilis* and *S. aureus*) and Gram-negative (*E.coli* and *K. pneumoniae*). The difference in bactericidal effect of Gram-positive and Gram-negative bacteria may be due to the differences in their cell structure, metabolism and degree of contact of bacteria with the prepared nanocomposites. Thus the positively charged nanocomposites attach to the negatively charged bacterial cell wall of electrostatic attraction thereby disrupting the cell membranes. The nanocomposites then enter into the bacteria by destroying the cell membrane. Thus the nanocomposites release ROS, which inhibits the ATP production and DNA replication thereby leading to cell death. Hence, due to high release of ROS from ZnO, rGO/CS/ZnO nanocomposites showed an excellent bactericidal activity compared to rGO/CS/CuO, rGO/CS/Ag and rGO/CS/Au nanocomposites.

The different concentrations (0.002M, 0.004M, 0.006M, 0.008M and 0.01M) of Metal oxides (ZnO, CuO), Metal (Ag, Au) nanoparticles incorporated chitosan blended reduced graphene oxide nanocomposites showed significant cytotoxicity and effective apoptotic activity against HepG-2 cancer cell line. cytotoxicity

increases on increasing the concentration of rGO/CS/Metal oxides (ZnO, CuO), Metal (Ag, Au) nanocomposites. The highest cytotoxicity rate observed for rGO/CS/Ag nanocomposites is 78.6% for 125 $\mu\text{g/ml}$. Thus the silver nanoparticles disrupt the normal cellular function and affect the membrane integrity by inducing various apoptotic signaling genes that leads to cell death. The rGO/CS/Ag nanocomposites can be used as a potential candidate for cancer therapy due to its high cytotoxic activity.

8.8 CONCLUSION

The Metal oxides (ZnO, CuO), Metal nanoparticles (Ag, Au) nanoparticles incorporated chitosan blended reduced graphene oxide nanocomposites shows tremendous advantages in this current research. The objective envisage in this work is to improve the electrochemical sensing and anticancer activity. The electro catalytic property towards the detection of p-Aminophenol is tested in this present study. The electrochemical studies revealed that gold nanoparticles doped chitosan blended reduced graphene oxide nanosheets exhibits high electrocatalytic activity which can be used as a promising electrode for the high electrochemical detection of p-Aminophenol. Moreover, the silver nanoparticles decorated chitosan blended reduced graphene oxide nanosheets exhibits excellent biocidal activity and cytotoxic activity. The metal nanoparticles decorated chitosan blended reduced graphene oxide nanocomposites can be used as a potent candidate for biomedical and environmental applications.