Abstract

Immunoglobulin (*Ig*) molecules play most important role in body's immune system, serving as a defense line against the harmful pathogens. Among the other classes of *Ig*s, *Ig*G is the most abundant one found in the blood serum, making it a potential biomarker for several oncological and inflammatory diseases. This leads to an utmost importance of examining the *Ig*G level in blood for diagnosis purpose. Apart from this, monitoring the glucose and H_2O_2 level in body fluids can also provide valuable insight regarding blood sugar regulation, whole body oxidative stress and metabolism system. Out of other conventional methods, electrochemical detection technique has been extensively used due to its simplicity, high accuracy and point-of-care detection strategies. The detection mechanism of *Ig*G includes the proper immobilization of the antibody molecules over the electroactive specimen called transducer, followed by quantification of the target *Ig*G molecules *via* electrochemical methods. On the other hand, the redox activity of some metal oxide nanoparticles towards glucose and hydrogen peroxide (H_2O_2) have opened up a convenient approach for non-enzymatic detection of such simple analytes. To design a high-performance electrochemical sensor, meticulous selection and designing of the transducer material is very crucial. In this regard, conducting polymers (*eg*., polyaniline, polypyrrole, Poly(3,4-ethylenedioxythiophene), etc.) are widely used as an electroactive material that can offer good conductivity, large surface area, and better stability. It has also been reported that composite of 2D layered nanostructures (graphene and its derivative, transition metal dichalcogenides (TMDCs), MXenes, graphitic carbon nitride (g-C_3N_4), hexagonal boron nitride (hBN), etc.) with conducting polymer holds high possibility for synergic tuning of several physico-chemical properties of the composite system, thereby expanding their range of functionalities for sensing applications. Apart from this, swift heavy ion (SHI) irradiation-based material modification can effectively modify the structural, morphological, electrical, optical and other spectroscopic behaviour of the target material. In polymer system, the SHI can introduce cross-linking and chain scissioning depending upon the energy, type and fluence of the ion beam used. It is anticipated that the electrochemical performance of the conducting polymer-based nanocomposites can be significantly improved through ion beam modifications.

In the present thesis, fabrication of both enzymatic and non-enzymatic electrochemical sensors has been carried out for sensing of biological analytes. In the first and second work, enzymatic detection of goat anti-mouse *Ig*G was performed by using

conducting polymer (CP) and 2D layered material based composite substrate decorated by electrodeposited gold nanoparticles (AuNPs). Here, fabrication of the immunosensor involves immobilization of the mouse *Ig*G antibody through glutaraldehyde cross-linking method and blocking of the non-specific sites using bovine serum albumin (BSA). Whereas, the third and fourth work explains the non-enzymatic electrochemical determination of glucose and H_2O_2 using metal oxide and 2D layered TMDC based hybrid system. Both, electrochemical and chemical synthesis routes were followed for fabrication of the sensor electrode throughout these works. In the last work, effect of 90 MeV C^{6+} ion on CP and TMDC based composite nanostructure have been studied at different fluences. Furthermore, the sensing activities of both the pristine and irradiated substrate-based immunosensors were compared to assess the impact of ion beam irradiation on the nanocomposite.

All the systems have been investigated by using several sophisticated analytical tools. Field emission scanning electron microscopy (FESEM) and Transmission electron microscopy (TEM) were employed for understanding the morphology of the synthesized nano systems. The conformational varieties of different systems have been examined through fourier transformed infrared spectroscopy (FT-IR). Structural information of these systems has been acquired by X-ray diffraction (XRD) spectroscopy technique. The electrochemical behaviour like redox activity, interfacial charge transfer impedance were understood by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The sensing of the target analytes have been accomplished by different electrochemical methods *viz.* transient capacitance plot, etc. and differential pulse voltammetry (DPV) technique. Based upon the variety of works, the present thesis is splitted into seven chapters.

Chapter 1

It includes the basics of electrochemical sensing mechanism and scope of the materials for development of enzymatic and non-enzymatic electrochemical sensor. The ion beam assisted material modification strategy is also discussed in this chapter. The essence of immunoglobulin, glucose and H_2O_2 detection for diagnosis and therapeutic purposes have also been included in this chapter.

Chapter 2

In this study, we utilized the electrochemical deposition technique to synthesize AuNP/GO/PEDOT-PSS based nanocomposite system. Subsequently, we developed an

immunosensor probe by immobilizing mouse *IgG* onto the composite substrate. The prepared immunosensor shows Langmuir adsorption isotherm behaviour. Direct measurement of goat anti-mouse *IgG* was performed by single frequency transient capacitance plot, which exhibited fast response towards the specific antigen with high sensitivity and detection limit of 49 ng/mL for 77 Hz.

Chapter 3

In this work, we have fabricated AuNP/PEDOT-MoS_2 composite based immunosensor system. The prepared biosensor exhibited a low LOD of 12.22 ng/mL or 81.46 pM with a sensitivity value of 1.8456 $\mu A.ng^{-1}$ $mL.cm^{-2}$ within a wide linear range of 7.7-263 ng/mL for selective determination of specific antigen. In addition, the calibration equation was estimated to be, y= 0.9228x+13.04. Such biosensors with a higher degree of sensitivity and selectivity have tremendous scope in diagnostics and also in point of care remedial measures.

Chapter 4

Here, CuO/PEDOT-MoS_2 derived non-enzymatic sensor was synthesized by electrochemical method. Different electrochemical parameters *viz*. diffusion coefficient (D), electroactive area (A) and heterogeneous rate constant (k_s) were estimated for the synthesized electrode towards the oxidation of glucose. Detection of glucose was performed by chronoamperometric technique in 0.1M NaOH solution. The proposed sensor exhibits a good selectivity towards glucose in a wide linear range of 30 µM-1.08 mM. The LOD and sensitivity of our sensor have been estimated to be, 0.046 µM and 829 $\mu A\ mM^{-1}cm^{-2}$; respectively.

Chapter 5

During this work, NiO nanosheet -MoS_2 based nanocomposite system was synthesized by simple hydrothermal route for the non-enzymatic electrochemical detection of glucose and H_2O_2. LOD and sensitivity value for detection of H_2O_2 are estimated to be 3.00 µM and 3.925 $\mu A.\ \mu M^{-1}.cm^{-2}$, respectively under the linear range of 5-455 µM in 0.1m PBS solution. For sensing glucose, the detection limit was calculated to be 3.53 µM with a sensitivity magnitude 1.880 $\mu A.\ \mu M^{-1}.cm^{-2}$ under 5-370 µM linear region in 0.1M NaOH solution.

Chapter 6

In this work, we report the hydrothermal synthesis of PPy-MoS_2 nanocomposite system followed by 90 MeV C^{6+} ion irradiation with different fluences *viz*. 1.0×10^{10}, 3.5×10^{11}, 1.0×10^{11} and 1.0×10^{13} ions/cm^2. Structural, morphological and electrochemical

characterization of the irradiated systems were performed by various techniques. It was found that, upon SHI irradiation the crystallinity of the PPy-MoS_2 derived system decreases at the highest fluence. Better electro-catalytic activity with low charge transfer resistance was achieved over $3.5x10^{11}$ ions/cm^2 of 90 MeV C^{6+} ion fluence. Also, electroactive area (A) is maximum (0.2684 cm^2) at this fluence. The sensing activity is better at the fluence of $3.5x10^{11}$ ions/cm^2 with a LOD and sensitivity value of 30.42 ng/mL and 10.00 $\mu A.ng^{-1}mLcm^{-2}$, respectively.

Chapter 7

It addresses the major conclusion remarks of all the chapters. Lastly, the future prospects for enhancing the performance of these systems have been incorporated.

Keywords: Immunoglobulin, point-of-care, cross-linking, limit of detection, immunosensor, rate constant, sensitivity