

**DEVELOPMENT OF CONDUCTING POLYMER, 2D  
LAYERED MATERIAL NANOCOMPOSITE BASED  
ENZYMATIC AND NON-ENZYMATIC ELECTROCHEMICAL  
SENSORS, AND ION IRRADIATION EFFECTS**

**A thesis submitted for the partial fulfillment of the  
requirements for the degree of  
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# Chapter 7

## Summary, Conclusions and Future prospects

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*This chapter outlines the comprehensive conclusions drawn from each chapter highlighting important findings and limitations therein. The future directions and scope are also mentioned at the end.*

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### 7.1. Summary

The present thesis deals with the synthesis, characterization, and electrochemical studies of the conducting polymer and 2D layered material-based systems for their potential application in electrochemical sensing as well as biosensing. Further, an attempt has been made to explore the effect of swift heavy ions (SHI) on conducting polymer-based electrodes and consequently, in their electrochemical sensing performance. The major findings drawn throughout the entire work can be summarized below:

Firstly, AuNP/GO/PEDOT-PSS film was fabricated over ITO coated glass substrate via an electrodeposition technique. The CV and EIS responses suggested that the AuNP/GO/ PEDOT-PSS system was electrochemically stable and offered a low  $R_{ct}$  value of 34.08  $\Omega$  in 0.05 M PBS solution. The negative slope of Mott-Schottky plot indicates the presence of  $p$ -type carrier in the PEDOT-PSS system. However, a flat band potential ( $V_{fb}$ ) of 0.394 V was estimated from the M-S plot which was further used for assigning the dc bias potential in the transient capacitance response, during sensing experiment. Fabrication of immunosensor was performed by immobilizing mouse *IgG* (M.W.  $\sim$  150 kDa) antibody over the as prepared electrodes via glutaraldehyde cross-linking method. Sensing of the specific antigen (goat anti-mouse *IgG*) was performed through transient capacitance response captured at two frequencies *viz.* 77 Hz and 1 kHz, at 0.8 V dc bias potential. The decrease in capacitance value upon addition of antigen in the solution indicated the formation of antibody-antigen (*An-Ab*) complex over the immunosensor. The change in capacitance vs. added antigen concentration plot suggested that the adsorption process that would take place in the immunosensor system can follow Langmuir adsorption isotherm. The *LOD* value estimated from the calibration curve was found to be 49 ng/mL corresponding to the frequency of 77 Hz within the concentration range of 9-363 ng/mL. To overcome the drawbacks of AuNP/GO/PEDOT-PSS immunosensor, an amperometric

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sensing strategy was adopted by doing little modification on the transducer by functionalizing AuNPs over the PEDOT-MoS<sub>2</sub> film. All the electrochemical measurements of the synthesized nanosystem in PBS solution containing 5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] as redox probe. The detection of the target analyte was carried out by using an immunosensor based on AuNP/PEDOT-MoS<sub>2</sub> derived transducer. This modified biosensor exhibited a low LOD of 12.22 ng/mL (or, 81.46 pM) and having a sensitivity value of 1.8456  $\mu\text{A}\cdot\text{ng}^{-1}\cdot\text{mL}\cdot\text{cm}^{-2}$  under a wide linear range of 7.7–263 ng/mL for selective detection of specific antigen.

To address the limitation of enzyme-based sensors, a non-enzymatic sensor was developed by using CuO/PEDOT-MoS<sub>2</sub> based electrocatalyst system for detection of glucose. Here, all the electrochemical experiments were performed in 0.1 M NaOH solution. The CV and EIS responses showed that incorporation of PEDOT and MoS<sub>2</sub> as a substrate component can offer better electrochemical performance to the CuO NPs along with better interfacial charge transport. The glucose oxidation current was monitored at +0.6 V upon addition of glucose in the solution which was further used as a dc bias potential in the chronoamperometric response. The detection of glucose was performed through chronoamperometry technique, conducted at +0.6 V dc bias potential in 0.1 M NaOH solution. The change in glucose concentration ( $[\Delta C]$ ) vs. change in amperometric current ( $\Delta I$ ) plot corresponding to CuO/PEDOT-MoS<sub>2</sub> electrode displayed a good linear response under a concentration range of 30  $\mu\text{M}$  to 1.06 mM. The CuO/PEDOT-MoS<sub>2</sub> based non-enzymatic sensor exhibited good stability and better reliability for detection of glucose offering a low detection limit of 0.0467  $\mu\text{M}$  along with a high sensitivity value of 829  $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ . To add further advancement in non-enzymatic sensing protocol, NiO-MoS<sub>2</sub> nanosheet based system was fabricated for detection of multiple analytes. The prepared composite specimen exhibited good redox activities towards H<sub>2</sub>O<sub>2</sub> and glucose. The LOD and sensitivity for detection of H<sub>2</sub>O<sub>2</sub> were estimated to be 3  $\mu\text{M}$  and 3925  $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ , respectively under the linear range of 5–455  $\mu\text{M}$  in 0.1 M PBS solution. Similarly, the LOD and sensitivity for sensing glucose was estimated to be 3.53  $\mu\text{M}$  and 1880  $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$  respectively under the linear range of 5–370  $\mu\text{M}$  in 0.1 M NaOH solution.

Lastly, the impact of material modification via ion beam irradiation and their effect in sensing performance was studied. For this, the hydrothermally synthesized PPy-MoS<sub>2</sub> based composite systems were irradiated with 90 MeV C<sup>6+</sup> ion beam using fluences viz.  $1.0\times 10^{11}$ ,  $3.5\times 10^{11}$ ,  $1.0\times 10^{12}$  and  $1.0\times 10^{13}$  ions/cm<sup>2</sup>. Several phenomena, like formation of amorphized ion track, cross-linking and chain scissioning are expected to appear in the composite system at different fluences which results in the change in structural,

morphological, and spectroscopic behaviour of the irradiated samples. Here, all the electrochemical measurements of the pristine and irradiated specimens were carried out in 0.1 M PBS solution containing 5 mM  $K_3[Fe(CN)_6]$  as redox probe. The CV and EIS responses of the pristine and irradiated samples showed that better electrochemical performance, lower  $R_{ct}$  value (490  $\Omega$ ) along with higher electroactive area of 0.4485  $cm^2$  can be observed in case of the system exposed to moderate ion fluence ( $3.5 \times 10^{11}$  ions/ $cm^2$ ). Both pristine and ion beam modified PPy-MoS<sub>2</sub> based composite systems were subjected to immunosensor fabrication for detection of goat anti-mouse IgG by DPV technique. It has been obtained that the immunosensor probe irradiated with  $3.5 \times 10^{11}$  ions/ $cm^2$  could offer the lowest LOD (0.203 nM) and the highest sensitivity value (10.00  $\mu A ng^{-1} mL cm^{-2}$ ) among all the studied electrodes. This study elucidated that ion beams at a moderate fluence can beneficially manifest the spectroscopic and well as electrochemical features of the PPy-MoS<sub>2</sub> based composite systems for their potential application as biosensor.

### 7.2. Conclusions

To conclude, we initiated research by fabricating an immunosensor based on AuNP deposited PEDOT-PSS and GO-based transducer material. The composite system was designed taking advantage of combinatorial effect of the individual properties of each component. The AuNP/GO/ PEDOT-PSS based sensor offered a fast, and label free sensing of the target analyte via impedimetric technique. Besides, there was still some room for advancement of the transducer for high signal amplification and easy detection strategy. Later, the AuNP/PEDOT-MoS<sub>2</sub> based modified transducer system had effectively addressed the limitation of the earlier system resulting in a better sensing activity. This immunosensor offered a low *LOD* and moderate sensitivity upon amperometric detection of the target analyte. But the vulnerability of biomolecules leads to the essence for the development of non-enzymatic sensing protocol. In this regard, CuO/PEDOT-MoS<sub>2</sub> based sensor probe was designed for effective amperometric detection of glucose. This non-enzymatic sensor facilitated sensitive and selective determination of glucose with high precision. In addition, this work was further extended by fabricating a NiO-MoS<sub>2</sub> nanosheet based system having 2D morphology of NiO. This electrocatalyst exhibited a very high sensitivity for detection of both H<sub>2</sub>O<sub>2</sub> and glucose indicating high signal amplification of the transducer. The proposed non-enzymatic sensors can meticulously quantify H<sub>2</sub>O<sub>2</sub> and glucose in artificial urine and commercially available ORS samples; respectively. This underscores the better reliability of the sensor for real samples. The modification of the

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transducer performed by traditional methods still lacks some room for improvements that can be executed via ion beam irradiation method. So, the effect of 90 MeV C<sup>6+</sup> ion beam on a simple polymer-TMDC (PPy-MoS<sub>2</sub>) based system have been studied. The study showed that the ion beam at a select fluence has an advantageous impact on the PPy-MoS<sub>2</sub> based system for its rewarding effectiveness as a transducer for immunosensor application. This whole study basically covers the design and fabrication of both enzymatic and non-enzymatic sensor probes, and the effect of transducer modifications in the sensing performance. Moreover, the impact of ion beams on a polymer-based transducer system is an interesting study added to this thesis. Given below is a table presented to compare the effects of transducer modification on sensing phenomena. Here, a low *LOD* of 12.22 ng/mL has been obtained in case of AuNP/PEDOT-MoS<sub>2</sub> based immunosensor upon amperometric detection of the specific antigen. On the other hand, a PPy-MoS<sub>2</sub> based immunosensor system has offered a high sensitivity of 10.00  $\mu\text{A ng}^{-1} \text{ mL cm}^{-2}$  when modified with energetic ion beams. In case of non-enzymatic determination of glucose, the CuO/PEDOT-MoS<sub>2</sub> sensor exhibited a low *LOD* of 0.046  $\mu\text{M}$ . While the NiO-MoS<sub>2</sub> based layered system showed a comparatively high sensitivity of 1880  $\mu\text{A mM}^{-1} \text{ cm}^{-2}$ , indicating high accuracy and good signal amplification.

**Table 7.1:** Comparison of sensing parameters of as designed sensors.

Sensor	Technique	Target analyte	<i>LOD</i>	Sensitivity	Linear range
AuNP/GO/PEDOT-PSS	Impedimetric	goat anti-mouse <i>IgG</i>	49.2 ng/mL	--	9-363 ng/mL
AuNP/PEDOT-MoS <sub>2</sub>	Amperometric	goat anti-mouse <i>IgG</i>	12.22 ng/mL	1.845 $\mu\text{A ng}^{-1} \text{ mL cm}^{-2}$	7.7–263 ng/mL
CuO/PEDOT-MoS <sub>2</sub>	Amperometric	Glucose	0.0467 $\mu\text{M}$	829 $\mu\text{A mM}^{-1} \text{ cm}^{-2}$	30 $\mu\text{M}$ to 1.06 mM
NiO-MoS <sub>2</sub>	Amperometric	H <sub>2</sub> O <sub>2</sub>	3 $\mu\text{M}$	3925 $\mu\text{A mM}^{-1} \text{ cm}^{-2}$	5-455 $\mu\text{M}$
		Glucose	3.53 $\mu\text{M}$	1880 $\mu\text{A mM}^{-1} \text{ cm}^{-2}$	5-370 $\mu\text{M}$
PPy-MoS <sub>2</sub>	Amperometric	goat anti-mouse <i>IgG</i>	30 ng/mL	10.00 $\mu\text{A ng}^{-1} \text{ mL cm}^{-2}$	5-190 ng/mL

### 7.3. Future prospects and directions

The present thesis is a compilation of diverse approaches of electrochemical sensing phenomena using carefully chosen composites of inorganic-organic and all inorganic materials. Both enzymatic and non-enzymatic processes were considered independently for sensing purposes. In this regard, impedimetric and amperometric techniques have been deployed for analytical characterization. The performance of conducting polymer and 2D layered nanostructure-based sensor is believed to be improved significantly by synthesizing nanocomposites with different interesting materials.

- (i) Exfoliated TMDC materials namely, MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub> etc. can be opted for with specific volume dispersion and number of layers. Use of two anionic ternary systems e.g., MoSSe may also add value to electrochemical sensing response while facilitating interfacial charge transfer.
- (ii) The sensing performance can be further enhanced by using novel materials such as, MOFs, MXenes, etc. To be mentioned, MOFs are essentially porous organic-inorganic microstructure which can offer very high surface area as compared to many other materials. On the otherhand, MXenes are hydrophilic in nature, possesses high conductivity with 2D morphology usually suitable for catalysis.
- (iii) In future, one may intend to develop the whole device in the form of gazette to execute fast, reliable sensing. This can be done by using Arduino circuits and programming them as per our experimental conditions and calibration equations. A screen-printed electrode will be a suitable choice for developing the sensor probe which can directly fit in the device.
- (iv) Molecularly imprinted polymers (MIPs), a type of biomimetic material can be used for developing low-cost, reusable sensors having high physico-chemical stability. MIPs have significant selectivity towards protein-based targets and could be effectively applied for selective detection of several biomarkers, including nucleic acids, proteins, lipids, saccharides, and other small molecules.