Declaration

hereby declare that the thesis entitled "**Development of conducting polymer, 2D layered naterial nanocomposite based enzymatic and non-enzymatic electrochemical sensors, ınd ion irradiation effects**", submitted to the School of Sciences, Tezpur University in partial fulfillment of the requirements for the award- of the Doctor of Philosophy in Physics, is a record of original research work carried out by me. Any text, figures, theories, results or designs that are not of my own creation are appropriately referenced in order to give owing credit to the original author(s). All the sources of assist have been assigned due acknowledgement. I also declare that neither this work as a whole nor a part of it has been submitted to any other University or institute for any degree, diploma, fellowship or any other similar title or recognition.

Date: 10-06-24

Place: Tezpur.

Ankush Medhi.

(Ankush Medhi)
Department of Physics
School of Sciences
Tezpur University
Tezpur-784028, Assam, India

Tezpur University

Certificate

This is to certify that the thesis entitled "**Development of conducting polymer, 2D layered material nanocomposite based enzymatic and non-enzymatic electrochemical sensors, and ion irradiation effects**", submitted to the School of Sciences, Tezpur University in partial fulfilment of the requirements for the award of the Doctor of Philosophy in Physics, is a record of original research work carried out by **Mr. Ankush Medhi** under my supervision and guidance.

All help received by him from various sources have been duly acknowledged.

No part of the thesis has been submitted elsewhere for award of any other degree.

(Prof. D. Mohanta)
Designation: Professor
School: School of Science
Department: Physics
Date: 10-june-24
Place: Tezpur-784028, Assam, India

Declaration

I hereby declare that the thesis entitled "**Development of conducting polymer, 2D layered material nanocomposite based enzymatic and non-enzymatic electrochemical sensors, and ion irradiation effects**", submitted to the School of Sciences, Tezpur University in partial fulfillment of the requirements for the award- of the Doctor of Philosophy in Physics, is a record of original research work carried out by me. Any text, figures, theories, results or designs that are not of my own creation are appropriately referenced in order to give owing credit to the original author(s). All the sources of assist have been assigned due acknowledgement. I also declare that neither this work as a whole nor a part of it has been submitted to any other University or institute for any degree, diploma, fellowship or any other similar title or recognition.

Date:

Place:

(Ankush Medhi)
Department of Physics
School of Sciences
Tezpur University
Tezpur-784028, Assam, India

Tezpur University

Certificate

This is to certify that the thesis entitled "**Development of conducting polymer, 2D layered material nanocomposite based enzymatic and non-enzymatic electrochemical sensors, and ion irradiation effects**", submitted to the School of Sciences, Tezpur University in partial fulfilment of the requirements for the award of the Doctor of Philosophy in Physics, is a record of original research work carried out by **Mr. Ankush Medhi** under my supervision and guidance.

All help received by him from various sources have been duly acknowledged.

No part of the thesis has been submitted elsewhere for award of any other degree.

(Prof. D. Mohanta)
Designation: Professor
School: School of Science
Department: Physics
Date:
Place: Tezpur-784028, Assam, India

Dedication

I dedicate this thesis to my beloved parents

ACKNOWLEDGEMENTS

First and foremost, I want to convey my deep gratitude to my former supervisor, Late Prof. Ashok Kumar. Throughout my journey as a Ph.D. candidate, Prof. Kumar had been a constant source of intellectual stimulation, invaluable guidance and encouragement. His extensive expertise and keen insights into electrochemistry, coupled with his unyielding commitment to rigorous research, have left an indelible mark on my academic journey. It goes without saying that I am immensely indebted to him for his unwavering support and guidance.

It gives me immense pleasure to convey my profound appreciation to my esteemed supervisor, Prof. Dambarudhar Mohanta, for his dynamic and meticulous guidance, motivation, and boundless inspiration throughout my Ph.D. journey. Without his persistent involvement, thoughtfulness, and relentless commitment, completing this thesis on schedule would have been a greater challenge. I will forever value the mentorship provided by Prof. Mohanta, as it has consistently propelled me towards the realization of my long-cherished academic goals.

I extend my heartfelt thanks to the members of my DRC committee, Prof. Pritam Deb and Prof. Pabitra Nath, from the Department of Physics, Tezpur University, for their inspiration, motivation and enriched discussions throughout my Ph.D. journey. My profound appreciation also goes to all the dedicated faculty members of the Department of Physics for their active engagement and timely assistance, which have been instrumental in facilitating my research endeavors.

I extend my sincere appreciation to Dr. C. A. Betty, Scientist, BARC, for granting me the opportunity to work in her lab during the critical phase of my Ph.D. I consider myself truly fortunate to have her mentorship which played a pivotal role to enrich my understanding and experimental expertise.

I am truly grateful for the remarkable opportunities afforded to me at Tezpur University. The outstanding facilities at Tezpur University have played a significant role in this journey. I would like to appreciate the technical and administrative staff of Department of Physics for their prompt assistance in various aspects of my work. I am beholden to all the technical staff of SAIC, Tezpur University for their co-operation in characterization of the samples.

I am thankful to Inter University Accelerator Center (IUAC), New Delhi for their financial support through the project (BTR-66303). I would like to convey thanks to the past and present members of GPS laboratory, Nanoscience and Soft-Matter Laboratory and Material Research Laboratory, Department of Physics, Tezpur University, for all the support, help and motivations. I am fortunate enough to have labmates like them who have cheered me on during both the highs and lows of the research journey. I would like to express my heartfelt gratitude to all my friends specially Sritam, Sunny, Mahesh and Biswa who have been an integral part of my academic and personal life during this journey. The support, encouragement, stimulating discussions and the countless moments of laughter and relaxation have helped me to navigate the challenges of this endeavor. Their presence has made this academic pursuit more enjoyable.

I would like to express my deepest gratitude to Maa, Deuta, Priyanka and Dada for their constant support, encouragement, and sacrifices that have made this academic achievement possible. Their belief in my abilities have been my guiding lights throughout this journey. I could not have reached this milestone without their love, guidance, and support.

Ankush Medhi

List of tables

Table	Caption	Page No.
Table 1.1	Comparision of conductivity values of some common CPs.	10
Table 1.2	Electron mobility comparision of some 2D materials.	14
Table 2.1	Fitted parameters of EIS spectra for the pristine, binary and ternary electrode.	52
Table 2.2	Fitted parameters of the EIS spectra for the ternary electrode (AuNP/GO/PEDOT-PSS) based sensor after every process step during sensor fabrication.	53
Table 3.1	Fitted EIS parameters for PEDOT, PEDOT-MoS_2 and AuNP/ PEDOT-MoS_2 electrodes.	73
Table 3.2	Fitted EIS parameters for AuNP/PEDOT-MoS_2 sensor electrode during different steps of the sensing experiment.	74
Table 4.1	EIS derived physical parameters obtained after proper fitting.	87
Table 4.2	Estimated electrochemical parameter of the three system electrodes.	92
Table 4.3	*LOD* and sensitivity values estimated from the three repeated experiments.	96
Table 4.4	% recovery of the current response of the sensor after multiple experiments.	97
Table 4.5	Comparison of real and estimated glucose concentration in the ORS samples.	98
Table 5.1	Fitted parameter of the Nyquist plot for the sensor electrode.	108
Table 5.2	Detection of H_2O_2 and glucose in artificial urine and ORS samples.	112
Table 6.1	EIS derived parameters of the pristine and irradiated samples.	128
Table 6.2	Electroactive area corresponding to pristine and irradiated systems.	132
Table 6.3	LOD and sensitivity values of pristine and irradiated systems.	135
Table 7.1	Comparision of sensing parameters of as designed sensors.	141

List of Figures

Figure	Caption	Page no
Figure 1.1	Basic components of an electrochemical sensor	3
Figure 1.2	Interaction mechanism of enzyme with the target analyte	4
Figure 1.3	Interaction mechanism of antibody with the target analyte	5
Figure 1.4	Schematic diagram of the H_2O_2 reduction mechanism by NiO based electrode	7
Figure 1.5	Schematic band structure of conducting polymer, and chemical structure of some common CPs	10
Figure 1.6	Different types of 2D layered materials and their lattice structures	12
Figure 1.7	Scheme of top-down and bottom-up synthesis procedures of 2D nanostructures	13
Figure 1.8	Schematic layered structure of GO and MoS_2	15
Figure 1.9	Ion-matter interaction in SHI irradiation	20
Figure 1.10	Schematic of the major components of FT-IR	29
Figure 1.11	Schematic of the major components of SEM	30
Figure 2.1	(a) Electropolymerization of PEDOT-PSS-GO over ITO, (b) Electrodeposition of AuNP over PEDOT-PSS-GO/ITO film	39
Figure 2.2	Illustration of immobilization of antibody over the surface of AuNP/GO/ PEDOT-PSS/ITO electrode by glutaraldehyde cross-linking	40
Figure 2.3	Effect of variation of pH; in case of AuNP/GO/PEDOT-PSS substrate electrode	41
Figure 2.4	XRD patterns of PEDOT-PSS, GO/PEDOT-PSS and AuNP/ GO/PEDOT-PSS on ITO electrode	42
Figure 2.5	FT-IR spectra of PEDOT-PSS, GO/PEDOT-PSS and AuNP/GO/ PEDOT-PSS on ITO electrodes	44
Figure 2.6	SEM micrograph and EDX response of (a) PEDOT-PSS, (b) GO/ PEDOT-PSS, and (c) AuNP/GO/PEDOT- PSS on ITO	45

Figure 2.7	(a) Schematic representation of band bending phenomena on electrode-electrolyte junction, (b) Mott-Schottky plot of PEDOT-PSS/ITO	47
Figure 2.8	(a) CV plots of PEDOT-PSS, GO/PEDOT-PSS, AuNP/GO/ PEDOT-PSS on ITO; Cyclic voltammetry of the (b) GO/ PEDOT-PSS and (c) AuNP/GO/PEDOT-PSS sensor after each process step with a total Antigen (*IgG*) concentration of 23.47 µg/mL in 0.05 M PBS buffer	49
Figure 2.9	(a) EIS plot of PEDOT-PSS, GO/PEDOT-PSS, AuNP/GO/ PEDOT-PSS on ITO; Impedance response of the (b) GO/ PEDOT-PSS and (c) AuNP/ GO/PEDOT-PSS sensor after each process step with a total Antigen (*IgG*) concentration of 23.47 µg/mL	51
Figure 2.10	C_p vs. time plots of PEDOT-PSS at (a) 77 Hz, (b) 1 kHz frequency, and (b) C_p vs. time plots of GO/PEDOT-PSS based sensors at (c) 77 Hz, and (d) 1 kHz frequency with various concentration of antigen injections	54
Figure 2.11	C_p vs. time plots of AuNP/GO/PEDOT-PSS sensor with various antigen injections in ng/mL concentrations at different frequencies, (a) 77 Hz, and (b) 1 kHz	55
Figure 2.12	Change in capacitance vs. antigen concentration in AuNP/ GO/PEDOT-PSS sensor electrode at (a)77 Hz, and (b)1 kHz; (c) Linear regression fitting for 1/ change in antigen concentration vs. $1/\Delta C_p$ at 77 Hz, and (d) at 1 kHz	56
Figure 2.13	Conductance transient vs. time plot of Au/GO/PEDOT-PSS at (a) 77Hz and (b) 1kHz	57
Figure 2.14	Photograph of the functionalized electrodes on ITO after sensing experiment (1) PEDOT-PSS, (2) GO/PEDOT-PSS, (3) Au/GO/ PEDOT-PSS	58
Figure 3.1	Schematic illustration of the immunosensor fabrication and detection mechanism	60

Figure 3.2	(a) XRD pattern, and (b) FT-IR response; of PEDOT, PEDOT-MoS_2 and AuNP /PEDOT-MoS_2 systems. The zoomed in view of FT-IR response of MoS_2 is shown in Figure (c)	63
Figure 3.3	FESEM micrograph and EDX spectra of (a) PEDOT, (b) PEDOT-MoS_2 and (c) AuNP/ PEDOT-MoS_2	65
Figure 3.4	CV response of (a) PEDOT, PEDOT-MoS_2 and AuNP/PEDOT-MoS_2 electrodes, and that of (b) PEDOT, (c) PEDOT-MoS_2 and (d) AuNP/PEDOT-MoS_2 sensor electrodes at different process steps throughout the sensing experiments	67
Figure 3.5	Cyclic voltammetry responses taken by varying scan rate for (a) PEDOT, (b) PEDOT-MoS_2 and (c) AuNP/PEDOT-MoS_2 electrodes. Peak potential (v) vs root of scan rate ($v^{1/2}$) plot of the CV responses of (a.1) PEDOT, (b.1) PEDOT-MoS_2 and (c.1) AuNP/PEDOT-MoS_2. Anodic peak potential (E_{pa}) vs. log (scan rate) plot of (a.2) PEDOT, (b.2) PEDOT-MoS_2 and (c.2) AuNP/ PEDOT-MoS_2 electrode systems	69
Figure 3.6	(a) Scan rate variation plot, (b) anodic peak current (I_{pa}) vs (scan rate)$^{1/2}$ plot, (c) anodic peak potential (E_{pa}) vs log (scan rate) plot, (d) E_{pa} vs. log (scan rate) plot, (e) log_e (I_{pa}) vs (E_{pa}-E_o) plot; for BSA/Antibody/Glu/AuNP/PEDOT-MoS_2 bioelectrodes	70
Figure 3.7	EIS responses of (a) PEDOT, PEDOT-MoS_2 and AuNP/PEDOT-MoS_2 electrodes, (b) PEDOT, (c) PEDOT-MoS_2 and (d) AuNP/ PEDOT-MoS_2 sensor electrodes at different process steps throughout the sensing experiment	72
Figure 3.8	(a) DPV response of Antigen/BSA/Antibody/Glu/AuNP/ PEDOT-MoS_2 sensor upon addition of different concentration of antigen, (b) Langmuir fitting of ΔI *vs [C]* plot, (c) $1/\Delta I$ *vs* $1/[C]$ plot, (d) Linear fitting of ΔI *vs [C]* plot, (e) selectivity test for BSA/ Antibody/Glu/AuNP/PEDOT-MoS_2 immunosensor, (f) comparison of LOD and selectivity estimated from three repetitive experiment	76

Figure 3.9	Detection of goat antimouse *IgG* via (a) BSA/Antibody/Glu/ PEDOT and (b) BSA/Antibody/Glu/PEDOT-MoS_2 bioelectrode	77
Figure 3.10	Repeatability test for BSA/Antibody/Glu/AuNP/PEDOT-MoS_2 bioelectrode (where the repeated experiments have been denoted as (i) and (ii))	78
Figure 4.1	Schematic diagram of the glucose oxidation mechanism by as-synthesized CuO/PEDOT-MoS_2/ITO electrode	81
Figure 4.2	(a) XRD patterns, and (b) FT-IR spectra of as-synthesized CuO, PEDOT, CuO/PEDOT, PEDOT-MoS_2, and CuO/ PEDOT-MoS_2 systems	83
Figure 4.3	FESEM micrograph of (a) CuO, (b) PEDOT, (d) CuO/PEDOT, (d) PEDOT-MoS_2, and (e) CuO/PEDOT-MoS_2 along with the EDX spectra shown on the right-hand side	85
Figure 4.4	(a) Cyclic voltammetry (CV) response, and (b) electrochemical impedance spectroscopy (EIS) plots of CuO only, CuO/PEDOT and CuO/PEDOT-MoS_2 electrodes. A magnified view of the segment in -Z" vs. Z' plot as well as equivalent RC circuit are also shown as inset in (b)	87
Figure 4.5	CV responses of (a) CuO/ITO, (b) CuO/PEDOT and (c) CuO/ PEDOT-MoS_2 at different concentration of glucose varying from 0.1 to 0.5 mM, (d) chronoamperometric response of CuO/PEDOT-MoS_2 sensor over different glucose concentration at +0.6 V dc potential	88
Figure 4.6	(a) Amperometric (*i-t*) response in presence and absence of 0.2 mM glucose, (b) Cottrell plot *(i vs $t^{-1/2}$)*, (c) current vs. voltage response with scan rate variation in cyclic voltammetry (CV), (d) Randle- Sevcik (i_p *vs* $v^{1/2}$) plot, (e) E_p vs *log* | *(scan rate)* | plot and (f) Peak potential (E_p) vs (scan rate) plot; for (I) CuO only, (II) CuO/PEDOT, and (III) CuO/PEDOT-MoS_2 electrode systems	90

Figure 4.7	(a) Merged amperometric (*i-t*) response of CuO, CuO/PEDOT and CuO/PEDOT-MoS_2 electrode, (b) selectivity test of CuO/PEDOT-MoS_2, (c) amperometric response of the CuO/PEDOT-MoS_2 with inset magnified portion, (d) change in (*i-t*) current (ΔI) vs. change in concentration ($\Delta[C]$) plot	93
Figure 4.8	Stability test for CuO/PEDOT-MoS_2 sensor electrode	94
Figure 4.9	(a) Repeatibility tests for the CuO/PEDOT-MoS_2 sensor electrode, change in current (ΔI) vs. concentration ($\Delta[C]$) plot for chrono-amperometric (b) response-1 and (b) response-3, and histograms of the (d) LOD and (e) sensitivity values	95
Figure 4.10	CV responses of CuO/PEDOT-MoS_2 (a) in presence and absence of glucose, (b) on different days. (c) Histogram plot of oxidation current response of the sensor on different days	96
Figure 4.11	Chronoamperometry response of CuO/PEDOT-MoS_2 sensor electrode for determining glucose concentration in commercially available ORS solution	98
Figure 5.1	(a) XRD, (b) FT-IR, (c) EDX, elemental mapping responses, (d, e) FESEM images, (f) TEM micrograph, (g) SAED pattern and (h, i) HRTEM images of the NiO-MoS_2 nanocomposite system	103
Figure 5.2	Cyclic voltammetry response of NiO-MoS_2 sensor electrode in (a) 0.1M PBS solution, (b) 0.1M PBS solution with varying H_2O_2 concentration, (c) 0.1M NaOH solution, (d) 0.1M NaOH solution with varying glucose concentration	105
Figure 5.3	EIS response of NiO-MoS_2 sensor electrode in (a) 0.1 M PBS solution and (b) 0.1M NaOH solution, with an inset Nyquist plot showing the magnified view of the high frequency region	108
Figure 5.4	Chronoamperometric response of NiO-MoS_2 sensor electrode in (a) 0.1M PHS solution, (b) 0.1M NaOH solution. (c) ΔI vs. $\Delta[C]$ plot for H_2O_2 sensing, (d) ΔI vs. $\Delta[C]$ plot for glucose sensing	109

Figure 5.5	Selectivity feature of NiO-MoS_2 based sensor for (a) H_2O_2 sensing and (b) glucose sensing. Detection of (c) H_2O_2 in artificial urine sample and (d) glucose in ORS sample	111
Figure 5.6	Repeatability test of NiO-MoS_2 based sensor for the detection of (a) H_2O_2, and (b) glucose	113
Figure 6.1	(a) XRD patterns of MoS_2, PPy and PPy-MoS_2, and (b) FT-IR characteristics of PPy and PPy-MoS_2 systems	118
Figure 6.2	(a) XRD and (b) FT-IR, responses of pristine system and irradiated systems with fluence 1.0×10^{10}, 3.5×10^{10}, 1.0×10^{12} and 1.0×10^{13}, ions/cm^2	120
Figure 6.3	Magnified diffraction pattern of the (002) peak of pristine and irradiated PPy-MoS_2 system	121
Figure 6.4	FESEM micrograph of (a.1, a.2) PPy-MoS_2 (pristine), and irradiated PPy-MoS_2 nanocomposites when subjected to fluences of (b.1, b.2) 3.5×10^{11} ions/cm^2, (c.1, c.2) 1.0×10^{13} ions/cm^2 at different magnifications	123
Figure 6.5	TEM micrograph of (a.1-a.3) PPy-MoS_2 (pristine), and irradiated PPy-MoS_2 composite systems at a fluence of (b.1-b.3) 3.5×10^{11} ions/cm^2, (c.1-c.3) 1.0×10^{13} ions/cm^2 and at different magnifications	124
Figure 6.6	Comparison of the CV responses of (a) PPy and PPy-MoS_2 system, (b) PPy-MoS_2 (pristine) and samples irradiated with different fluences	126
Figure 6.7	Comparison of the EIS spectra of (a) PPy, and PPy-MoS_2 composite, (b) PPy-MoS_2 (pristine) and irradiated samples	127
Figure 6.8	Scan rate variation plot with inset i_p vs $v^{1/2}$ graph of PPy-MoS_2 nano-composite system, (a) without (pristine), and with irradiation at a fluence of (b) 1.0×10^{10}, (c) 3.5×10^{10}, (d) 1.0×10^{12} and (e) 1.0×10^{13}, ions/cm^2	130

Figure 6.9 E_{pa} *vs* (scan rate) plot of PPy-MoS_2 composite system (a.1) without irradiation and irradiated with fluence of (b.1) 1.0×10^{10}, (c.1) 3.5×10^{11}, (d.1) 1.0×10^{12}, (e.1) 1.0×10^{13}, ions/cm^2 and, *ln* (I_{pa}) *vs* (E_{pa}-E_o), plot of PPy-MoS_2 composite system (a.2) without irradiation and irradiated with fluence of (b.2) 1.0×10^{10}, (c.2) 3.5×10^{11}, (d.2) 1.0×10^{12}, and (e.2) 1.0×10^{13}, ions/cm^2 131

Figure 6.10 DPV response, ΔI vs [C] plot and $1/\Delta I$ vs $1/[C]$ plot of PPy-MoS_2 composite system (a) without irradiation and irradiated with fluence of (b) 1.0×10^{10}, (c) 3.5×10^{11}, (d) 1.0×10^{12}, and (e) 1.0×10^{13} ions/cm^2 134

Figure 6.11 (a) CV and (b) EIS responses of the MPy:2 system monitored throughout the sensor fabrication and sensing experiment, (c) repeatability test for the MPy:2 system 136

Figure 6.12 (a) DPV response with inset ΔI vs [C] plot, and corresponding (b) $1/\Delta I$ *vs* $1/[C]$ plot, for MPy:2 system 137

Abbreviation	Meaning
W.E.	Working electrode
R.E.	Reference electrode
C.E.	Counter electrode
CP	Conducting polymer
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
LOD	Limit of detection
MO	Metal oxide
SHI	Swift heavy ion
AuNPs	Gold nanoparticles
TMDC	Transition metal di-chalcogenide
GO	Graphene oxide
EDOT	Ethylene-dioxy thiophene
PPy	Poly-pyrrole
PSS	Polystyrene sulfonate
ITO	Indium-tin-oxide
PBS	Phosphate buffer saline
BSA	Bovine serum albumin
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
DPV	Differential pulse voltammetry
EDX	Energy dispersive X-ray
NS	Nanosheet
M-S	Mott-Schottky
kD	Kilo-Dalton
ORS	Oral rehydration solution
NMP	N-Methyl-2-Pyrrolidone
PVDF	poly-vinylidene fluoride
PVP	polyvinylpyrrolidone
EG	Ethylene glycol
SEI	Solid-electrolyte interface
UA	Uric acid

Symbol	Meaning
Ig	Immunoglobulin
D	Diffusion constant
A	Electroactive area
k_s	Rate constant
R_s	Solution resistance
C_{dl}	Double layer capacitance
R_{ct}	Charge transfer resistance
W_z	Warburg impedance
CPE	Constant phase element
υ	Scan rate
I_p	Peak current
E_p	Peak potential
Z'	Real part of impedance
-Z"	Imaginary part of impedance
F	Faraday's constant
Ab	Antibody
An	Antigen