

Functional Nanomaterials Modified Transducers for Sensor Applications



Thesis submitted in partial fulfillment for the
award of degree

Doctor of Philosophy

By

Ravi Prakash Ojha

Supervisor

Prof. Rajiv Prakash

**SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI-221005**

Roll. No. 16111009

2022

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It is certified that the work contained in the thesis titled “**Functional nanomaterials modified transducers for sensor applications**” by “*Ravi Prakash Ojha*” has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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Prof. Rajiv Prakash
(Supervisor)
School of Materials Science & Technology,
Indian Institute of Technology,
Banaras Hindu University,
Varanasi-221005

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I, *Ravi Prakash ojha* certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of *Prof. Rajiv Prakash* from **July 2016 to December 2021** at the *School of Materials Science & Technology*, Indian Institute of Technology, Banaras Hindu University, Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports, dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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(Ravi Prakash Ojha)

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It is certified that the above statement made by the student is correct to the best of my knowledge.

Prof. Rajiv Prakash
School of Materials Science & Technology,
IIT (BHU), Varanasi

Coordinator
School of Materials Science & Technology,
IIT (BHU), Varanasi

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LIST OF ABBREVIATIONS

μA	:	Microampere
μL	:	Microlitre
A	:	Effective surface area
Ag	:	Silver
AgNPs	:	Silver Nanoparticles
Ala	:	L-Alanine
Asp	:	L-Aspartic acid
atm	:	Atmosphere
AuMoSe ₂	:	Gold decorated Molybdenum Diselenide
AuNPs	:	Gold nanoparticles
AuNRs	:	Gold Nanorods
AuNRs-g-C ₃ N ₄	:	Gold Nanorods decorated Graphitic Carbon Nitride
BSA	:	Bovine Serum Albumin
ChOx	:	Cholesterol Oxidase
Conc.	:	Concentration
Creat	:	Creatinine
CTAB	:	Cetyltrimethyl ammonium bromide
CuFe-PBA-NC	:	Cu-Fe Prussian blue analog nanocube
CV	:	Cyclic Voltammetry
Cys	:	L-Cysteine
DI	:	Deionised water
DPV	:	Differential Pulse voltammetry
EDS	:	Energy dispersive X-ray spectroscopy
EIS	:	Electrochemical impedance spectroscopy
ELISA	:	Enzyme-linked immunosorbent assay
eV	:	Electron volt

LIST OF ABBREVIATIONS

F	:	Faraday constant
FCC	:	Face-centered cubic
FESEM	:	Field emission scanning electron microscopy
FTIR	:	Fourier transform infrared
GC	:	Glassy Carbon Electrode
g-C ₃ N ₄	:	Graphitic Carbon Nitride
GCE	:	Glassy carbon electrode
Glu	:	L-Glutamic acid
Gly	:	L-Glycine
GOx	:	Glucose oxidase
GSH	:	Glutathione
h	:	Hour(s)
H ₂ O ₂	:	Hydrogen peroxide
HCys	:	Homocysteine
His	:	L-Histidine
HPLC	:	High performance liquid chromatography.
HRP	:	Horse Radish Peroxidase
INH	:	Isoniazid
K	:	Kelvin
K _m	:	Michaelis–Menten constant
LOD	:	Limit of Detection
Lys	:	L-Lysine
Met	:	L-Methionine
Min	:	Minute(s)
mM	:	millimolar
MOFs	:	Metal-organic frameworks

LIST OF ABBREVIATIONS

MoS ₂ -QDs	:	Molybdenum disulphide quantum dots
MoS ₂ -QDs-AgNPs	:	MoS ₂ quantum dots (MoS ₂ -QDs) stabilized AgNPs
MoSe ₂	:	Molybdenum Diselenide
nM	:	Nanomolar
nm	:	nanometer
NPs	:	Nanoparticles
°C	:	Degree Celsius
PBA	:	Prussian Blue analog
PBS	:	Phosphate buffer solution
Pro	:	L-Proline
R	:	Gas constant
R ²	:	Regression coefficient value
R _{ct}	:	Charge transfer resistance
SAED	:	Selected area electron diffraction pattern
S _b	:	Standard deviation
sec	:	Second
Ser	:	L-Serine
T	:	Temperature
TEM	:	Transmission electron microscopy
TMB	:	3,3',5,5'-tetramethylbenzidine
TMDs	:	Transition metal dichalcogenides
Try	:	L-Tryptophan
UA	:	Uric Acid
UV-Vis	:	UV Visible
V	:	Volt
V _{max}	:	Maximum velocity

LIST OF ABBREVIATIONS

XPS	:	X-ray photoelectron spectroscopy
v	:	Scan rate
μL	:	Microlitre
μM	:	Micromolar

Preface

Sensors play a decisive role in ameliorating the life of mankind with their extensive applications in the field of medical diagnostics, energy sources like fuel cells, batteries, and solar power, environmental monitoring, and exploring space. Sensors are the analytical devices that detect and translate their physical attributes into readable signals from their surroundings. The human body introduces itself as the best example of a complex system with numerous sensors capable of selective sensing a wide variety of physical, chemical, and biological quantities. There are particularly five principle sensors that relate to vision, hearing, smell, taste, and feel, that can be used in real-time control systems. In the field of medical diagnostics, sensors have ground in life-saving applications. The application ranges from the identification of types and stages of infection of different diseases in the patient, determining the narrow effective window for different drugs, and regular monitoring of the concentrations of the biomolecules in the biological fluids. As we head into a new decade, thoughts inevitably turn to the future and predictions of what our world will look like in another ten years' time. Technology is changing and growing at a more rapid pace than at any time in our history. With growing technologies and global competition, the risk to human lives and the environment becomes a prime aspect of concern. There is a loss of life expectancy due to environmental health hazards, lethal diseases, and pandemics. Therefore, the development of cost-effective, selective, reliable sensors is the need for hours. Nanotechnology in the field of sensors has played a pivotal role in designing advanced sensors with a low detection limit for the analytes as they have a large surface area that provides ease of functionalization and better biocompatibility, selectivity, and sensitivity. Nanotechnology has made possible the miniaturization of devices into portable sensors. There are several diseases like Tuberculosis, Dengue, and Cancer, which if not identified at an early stage, may become severe and life-threatening. So,

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there is a crucial demand for portable, cheap, and reliable sensors that can be used to identify them. Motivated by these facts, we are introducing an effective electrochemical technique to quantify a very lethal disease biomarker i.e. Dengue biomarker 'NS1'. After the identification of the diseases, there are challenges to monitoring the drug level as there is a narrow effective window for their action. Higher levels of the drugs may have several side effects and even results in organ failures, while low level makes them impotent and ineffective. In the thesis, we are introducing a very facile method with a portable device to quantify the anti-Tuberculosis drug 'Isoniazid'. Not only diseases but there are several biomolecules like cholesterol and L-Cysteine, glucose whose discrepancy may cause several fatalities like cardiac failure, diabetes, and many more. So, at present-day, we need regular monitoring of our health which motivated us to fabricate sensors to identify levels of biomolecules. In our thesis, we have presented the sensors for L-cysteine and Cholesterol.

The thesis entitled, "Functional nanomaterials modified transducers for sensor applications" comprises the synthesis of various functional nanomaterials like Molybdenum disulfide quantum dots (MoS_2 -QDs), Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), Molybdenum diselenide nanosheet (MoSe_2), and their composites with metal nanoparticles for the enhancement of their catalytic properties and stability, like MoS_2 -Qds stabilized silver nanoparticles, Gold nanorod decorated $\text{g-C}_3\text{N}_4$ nanosheet, gold nanoflower decorated MoSe_2 nanosheet, and synthesis of transition metals based metal-organic frameworks e.g. Cu-Fe Prussian blue analogue nanocube (Cu-Fe-PBA-NC). Further, the synthesized nanocomposites have been exploited for the sensing of different biological and chemical species like Dengue biomarker NS1, L-Cysteine, Cholesterol, and Isoniazid. The nanomaterials have a very crucial role in the

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improvement of the performances of the sensors in terms of their catalytic activity. Based on the findings the thesis has been divided into seven chapters.

Chapter 1 deals with the general idea and basic concepts about sensors, components of sensors, sensors types, nanomaterials and their importance, its composites with metal nanomaterials for various sensing applications, nanozymes as a substitute for natural enzymes. The literature survey presents detailed information related to the proposed research topic.

Chapter 2 describes different experimental techniques which have been used for the characterization of developed materials. The main techniques which have been employed in characterizations are Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray Diffractometer (XRD), Energy Dispersive Spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) used for the morphological and structural investigation. UV-Visible spectrometer has been used for spectroscopic characterizations and optical sensing of different analytes. Cyclic voltammetry (CV), Differential cyclic voltammetry (DPV) and Impedimetric technique (EIS) setup has been used for electrochemical characterization.

Chapter 3 In this chapter, we present a high-performance NS1 immunosensor based on gold nanorod decorated graphitic carbon nitride (AuNRs-g-C₃N₄) modified glassy carbon electrodes (GCE). AuNRs-g-C₃N₄ composite is synthesized, which possesses excellent electro-activity, fast electron transfer kinetics, and high catalytic property. NS1 antibody is immobilized onto the surface of the AuNRs-g-C₃N₄ modified GCE and used as an impedimetric sensing probe for the quantitative sensing of NS1 antigen through electrochemical impedance spectroscopy. We have chosen [Fe (CN)₆]^{3-/4-} as a

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redox couple to observe the respective changes in charge transfer resistance (R_{ct}) associated with antigen bonding with an antibody both in PBS buffer as well as in human serum. The prepared immunosensor shows an excellent electrocatalytic response for the quantitative determination of NS1. The analytical parameters obtained by using this immunosensor are found to be comparable or better to previously reported NS1 sensors and open new insights with great potential for the application of point-of-care besides application in the diagnosis of Dengue.

Chapter 4 In this work, we present an electrochemical biosensor assembled with gold nanoflower decorated molybdenum diselenide nanosheet ($AuMoSe_2$) and cholesterol oxidase enzyme for the detection of free cholesterol through Differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). $MoSe_2$ nanosheet has been synthesized through solvothermal technique and has been characterized using X-Ray Diffraction technique (XRD), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Transmission electron microscopy (TEM), and Energy Dispersive Spectroscopy (EDS). Further, gold nanoflower was insitu grown onto the surface of $MoSe_2$ modified glassy carbon electrode (GCE) by incubating it in the gold salt solution without any aid of a reducing agent. Cholesterol oxidase was immobilized onto the surface of the $AuMoSe_2$ modified GCE and used as a sensing probe for the quantitative estimation of cholesterol. $[Fe(CN)_6]^{3-/4-}$ was used as a redox couple to sense the respective changes in current and charge transfer resistance (R_{ct}) associated with the enzymatic reaction between cholesterol oxidase and cholesterol both in human serum as well as in PBS buffer. The fabricated biosensor shows a good electrocatalytic response for the sensing of cholesterol with a linear range from 60 μM to 10 mM and a detection limit of 3.2 μM in DPV, and 37 μM in EIS technique respectively.

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Chapter 5 deals with the hydrothermal synthesis of MoS₂ quantum dots and its application for the formation and stabilization of a nanocomposite with silver nanoparticles (AgNPs) in a single step. The composite was characterized by transmission electron microscopy and zeta potential measurements. It is found that this nanohybrid can be stimulated by mercury(II) ion and then exhibits excellent oxidase mimicking activity. The oxidase-like activity is demonstrated by the oxidation of 3,3',5,5'-tetramethylbenzidine by H₂O₂ which leads to the formation of a blue product. An assay was developed for the determination of cysteine (Cys) at the ultra-trace level because Cys inhibits the activity of the nanozyme via interaction with Hg(II). The Cys assay, best performed at a wavelength of 652 nm, works in the 1-100 μM concentration range and has a 0.82 μM detection limit. In addition, a portable Cys test kit is described that was applied to the determination of Cys in serum samples. The resulting colorations were compared with the color chart wheel. The method is simple, rapid, cost-effective, and sensitive.

Chapter 6. In this work, we present a colorimetric technique for the easy quantification of the Isoniazid (INH) in human urine. We have synthesized Cu-Fe Prussian blue analogue nanocube (CuFe-PBA-NC) using a simple precipitation method. The synthesized nanocube has been successfully characterized by FTIR, XRD, SEM, and XPS. The synthesized CuFe-PBA-NC act as an excellent oxidase mimic, having a very high affinity for TMB (3,3',5,5'-tetramethylbenzidine) furnishing a blue color compound with a characteristic absorbance peak at $\lambda_{\text{max}} = 652$ nm. Further, we have exploited the oxidase property of CuFe-PBA-NC for the colorimetric detection of the INH in human urine. The developed sensor shows very high sensitivity in the range of 1 to 100 μM with a detection limit of 0.44 μM. Furthermore, a portable kit was developed

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for the onsite detection of the INH concentrations in the test samples. The method is easy and cost-effective with sensitive detection of INH.

Chapter 7 includes the conclusive remarks and future prospects of the thesis.