Studies of Transition Metal Nanoparticles with Tetracyanoquinodimethane for Electrochemical Sensing Application

Thesis submitted in the partial fulfillment for the Award of Degree

Doctor of Philosophy

By

Kuldeep Kumar Maurya

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI - 221005
INDIA

Roll No. 19051010

2024

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It is certified that the work contained in the thesis titled **"Studies of Transition Metal Nanoparticles with Tetracyanoquinodimethane for Electrochemical Sensing Application"** by **Kuldeep Kumar Maurya** has been carried out under my supervision and this work has not been submitted elsewhere for a degree.

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Manisha Malviya

Dr. Manisha Malviya
(Supervisor)
Department of Chemistry,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi–221005

Dr. MANISHA MALVIYA
DEPARTMENT OF CHEMISTRY
IIT (BHU), VARANASI
U.P.-221005

DECLARATION BY THE CANDIDATE

I, **"Kuldeep Kumar Maurya"**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of **"Dr. Manisha Malviya"** from **"July-2019"** to **"May-2024,"** at the **Department of Chemistry, Indian Institute of Technology (BHU), 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 wilfully 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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Place: Varanasi

Kuldeep

(Kuldeep Kumar Maurya)

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Manisha Malviya

Dr. Manisha Malviya
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi- 221005

Dr. MANISHA MALVIYA
DEPARTMENT OF CHEMISTRY
IIT (BHU), VARANASI
U.P.-221005

Prof. Y. C. Sharma
Head of Department
Department of Chemistry,
Indian Institute of Technology
(Banaras Hindu University),
Varanasi- 221005

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Date:

Place: Varanasi **(Kuldeep Kumar Maurya)**

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List of Symbols/Abbreviations

AA	: Ascorbic acid
AFM	: Atomic force microscopy
3-APTMS	: 3-Aminopropyltrimethoxysilane
CPE	: Carbon paste electrode
CV	: Cyclic voltammetry
DPV	: Differential pulse voltammetry
DA	: Dopamine
EASA	: Electrochemically active surface area
EIS	: Electrochemical impedance spectroscopy
HR-TEM	: High-resolution transmission electron microscopy
HR-SEM	: High-resolution scanning electron microscopy
K_2PdCl_4	: Potassium tetrachloropalladate (II)
LOD	: Limit of detection
MNPs	: Metal nanoparticles
NPs	: Nanoparticles
NADH	: 1,4-Dihydronicotinamide adenine dinucleotide
NC	: Nitrogen doped carbon
NTA	: Nitrilotriacetic acid
PBS	: Phosphate buffer solution
PdNPs	: Palladium nanoparticles
PVP	: Polyvinylpyrrolidone
QCM	: Quartz crystal microbalances
R_{ct}	: Charge transfer resistance
SAED	: Selected area electron diffraction

SAW	: Surface acoustic waves
SPR	: Surface plasmon resonance
TCNQ	: 7,7,8,8-Tetracyanoquinodimethane
TTF	: Tetrathiafulvalene
UA	: Uric acid
XPS	: X-ray photoelectron spectroscopy
XRD	: X-ray diffraction
θ	: Angle (degree)
µ	: micro
µl	: microliter
µm	: micrometer
µM	: micromolar
mM	: millimolar
nm	: nanometer
µA	: microampere
s	: Time (second)
υ	: Scan rate
E	: Potential
V	: Volt
mV	: millivolt
eV	: electron volt
i	: Current
I_p	: peak current
E_{pa}	: anodic peak potential

E_{pc}	: cathodic peak potential
kΩ	: kiloohm
°C	: degree Celsius
cm^2	: square centimeter

Preface

Advancements in technology have heightened concerns over environmental and lifestyle-related health hazards. Such hazards can lead to a decrease in life expectancy and a rise in chronic conditions like diabetes, obesity, and hypertension. To address these challenges, there is a critical need for portable sensor devices capable of monitoring key biomolecules such as glucose, ascorbic acid, dopamine, and NADH in real time, especially in remote areas lacking medical infrastructure. The key focus areas for sensor device development include miniaturization, cost-effectiveness, and energy efficiency, with the potential to revolutionize daily healthcare by enabling bedside, regular, and remote monitoring of vital signs and health parameters.

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, high catalytic activity, ease of functionalization, better biocompatibility, selectivity, and sensitivity. Nanotechnology has made possible the miniaturization of devices into portable sensors. There are several diseases like Alzheimer's, Parkinson's, Schizophrenia, cancer, and neurological disorders, which if not identified at an early stage, may become severe and life-threatening. So, 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 the concentration of ascorbic acid, dopamine, and NADH. NADH helps in energy production and cellular metabolism. Dopamine functions on the brain to provide sensations of pleasure, contentment, and emotion. Ascorbic acid is necessary for wound healing as well as the repair and maintenance of bones and teeth. After the identification of the concentration of these biomolecules, we can find out the diseases, because when a disease is caused the level of

these biomolecules is increased or decreased. So, at present day, we need regular monitoring of our health which motivates us to fabricate sensors to identify levels of biomolecules. In the thesis, we are introducing a very facile method to fabricate an ascorbic acid sensor, dopamine sensor, and NADH sensor.

The thesis entitled, ***"Studies of Transition Metal Nanoparticles with Tetracyanoquinodimethane for Electrochemical Sensing Application"*** described the synthesis of various functional nanomaterials like palladium nanoparticles (PdNPs), cobalt tungstate nanoparticles ($CoWO_4$), cobalt N-doped carbon (Co@NC), and their composite with palladium metal nanoparticles for the enhancement of their catalytic properties and stability, like Pd-Co@NC. Further, the synthesized nanomaterials mixed with tetracyanoquinodimethane (TCNQ) and fabricated modified electrodes have been used for the sensing of different biomolecules such as ascorbic acid, dopamine, and NADH. The nanomaterials have a very crucial role in the improvement of the performances of the sensors in terms of their catalytic activity. Based on the findings the thesis has been divided into six chapters.

Chapter 1 describes the general introduction of biosensors, nanomaterials, the application of nanomaterials in biosensors, and the literature review.

Chapter 2 describes different experimental techniques that have been used for the physicochemical characterization of synthesized nanomaterials and electrochemical techniques to characterize fabricated sensors.

Chapter 3 describes the synthesis of palladium nanoparticles and fabrication of TCNQ-PdNPs modified carbon paste electrodes. This TCNQ-PdNPs modified carbon paste electrode was used for electrochemical sensing of ascorbic acid.

Chapter 4 describes the synthesis of $CoWO_4$ nanoparticles by hydrothermal method and fabrication of TCNQ@$CoWO_4$/CPE. This electrode is used for electrochemical sensing of dopamine and real sample analysis was performed in commercially available dopamine hydrochloride injections.

Chapter 5 describes the synthesis of Co@NC and Pd-Co@NC. By using TCNQ and Pd-Co@NC we have designed a low voltage TCNQ-Pd-Co@NC modified electrode and used it for electrochemical sensing of NADH.

Chapter 6 summarises the thesis work and highlights the future scope.