Bismuth-based materials as a novel substrate for surface enhanced Raman spectroscopy

THESIS SUBMITTED IN PARTIAL FULFILLMENT
FOR THE AWARD OF DEGREE

DOCTOR OF PHILOSOPHY

By

ARTI SAROJ

Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005

Roll No: 18051005 **Year of Submission: 2023**

Dedicated to my Parents

CERTIFICATE

It is certified that the work contained in this thesis titled "***Bismuth-based materials as a novel substrate for surface enhanced Raman spectroscopy***" by "**Arti Saroj**" has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of comprehensive examination, candidacy and SOTA for the award of Ph.D. degree.

Dr. V. Ramanathan
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005, India

Dr. V. Ramanathan
Assistant Professor
Department of Chemistry
IIT (BHU), Varanasi-221005

DECLARATION BY THE CANDIDATE

I, **"Arti Saroj"**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the joint supervision of **"Dr. V. Ramanathan"** Department of Chemistry, from **"July, 2018 to November, 2023"**, 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 havenot willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available on websites and have not included them in this thesis and have not cited as my work.

Date: 15/11/23

Place: Varanasi

Arti Saroj

(Arti Saroj)

CERTIFICATE FROM THE SUPERVISORS

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

Dr. V. Ramanathan
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi – 221005

Dr. V. Ramanathan
Assistant Professor
Department of Chemistry
IIT (BHU), Varanasi-221005

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

HEAD
रसायन विज्ञान विभाग
Department of Chemistry
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.वि.)
Indian Institute of Technology (B.H.U.)
वाराणसी–२२१००५ / Varanasi-221005

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: ***Bismuth-based materials as a novel SERS substrate for surface enhanced Raman spectroscopy***

Name of the Student: Arti Saroj

COPYRIGHT TRANSFER

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the **"Doctor of Philosophy"** degree.

Date: November 2023
Place: Varanasi

Arti Saroj
(Arti Saroj)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

Acknowledgement

First and foremost, I would like to express my sincere gratitude to my research supervisor **Dr. V. Ramanathan** for his incessant support, invaluable guidance during my Ph. D. work. Over the last five years, his attention to detail and interest in my research work during Ph.D. has been a great source of inspiration and encouragement that will always remain as treasured memories in my life. He never believed in the idea of spoon feeding and I cannot repay him for the way he has given me extremely good suggestions and the opportunities to develop new ideas in the research field.

I also express my sincere thanks to my RPEC members, Dr. Sunil Kumar Mishra (Department of Physics) and Prof. Dhanesh Tiwary (Department of Chemistry) for their motivation and insightful remarks.

I would also like to thank Head of Department of Chemistry, Prof. Y. C. Sharma and former Heads, Prof. Dhanesh Tiwary and Prof. R. B. Rastogi for providing research facilities in the Department that enabled me to complete my research works successfully.

I owe a lot of gratitude to Prof. D. Tiwary for his cooperation, continuous support, extending lab space, providing his lab facility for some of my research work during my Ph.D.

I am again thankful to my supervisor for giving opportunity to work with Dr. Brijesh Kumar Mishra (Division of Sciences, Krea University). It was a great pleasure to me to work with him and I learnt a lot about some of my research work.

I am also grateful to all faculty members of the Department of Chemistry, IIT (BHU), Varanasi for their help and motivation, and I would like to thank Dr. Santanu Das (Department of Ceramic Engineering IIT (BHU)) for his valuable inputs.

I express my sincere thanks to CIFC, IIT (BHU), Varanasi for help in carrying characterization of the prepared samples. I am also thankful to all the non-teaching staffs of my department for their kindness and continuous support. I gratefully acknowledge CSIR, and IIT (BHU) for providing me financial support for my research work.

I also like to thank my seniors Dr. Manish Kumar Tripathi, Dr. Suresh Kumar Pandey, and lab-mate Su Shri Poonam Bhadoria for their support throughout my Ph.D.

I am indebted to my friend Shweta Pal for her encouragement, support, and care towards me in all situations. I am extremely thankful to all my friends in the Department of Chemistry for their sincere help and unconditional support.

There are no words to adequately describe heartfelt gratitude to my parents Sri Ramesh Chandra and Smt. Reeta Devi for their endless support, love, faith, and blessing at each and every steps of my life. I would also like to express my heartfelt gratitude to my younger brothers Manish Kumar, Sandeep Kumar for their constant support and understanding, without their support and encouragement this journey would not be possible. I am also thankful to my masi Richa, my cousins and my all family members for their constant support and care.

I would also like to thank everyone, who has helped me directly and indirectly during my Ph.D. work.

Finally, I thank **GOD** for giving me strength and providing the path to achieve goal because of freedom to express my thoughts, and acceptance without any judgment!

Place: Varanasi **Arti Saroj**

CONTENTS

List of Figures

List of Table

Abbreviations

IUPAC	International Union of Pure and Applied Chemistry
1-Phisa	1-Phenylisatin
1-Ph-AA	1-Phenyl anthranilic acid
1-Misa	1-Methylisatin
4-NP	4-nitrophenol
5-Fisa	5-Flueroisatin
5-F-AA	5-Fluoro anthranilic acid
5-Iisa	5-Idoisatin
5-I-AA	5-Ido anthranilic acid
AA	Anthranilic acid
Ach	Acetylcholine
AR	Allura red
AM	Amaranth
CTAB	Cetyltriethylammonium bromide
CT	Charge transfer
CM	Chemical enhancement mechanism
DMAB	4, 4′-dimercaptoazobenzne
FT-IR	Fourier Transform Infrared Spectroscopy
EM	Electromagnetic mechanism
EF	Enhancement factor
FWHM	Full width at half-maximum
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
LSPR	Localized Surface plasmon resonance
MEL	Melamine
MO	Methyl orange
PATP	p-aminothiophenol
RhB	rhodamine B
RSD	Relative standard deviation

R6G	Rhodamine 6G
Ag	Silver
SEM	Scanning electron microscope
SuI	Sudan I
SY	Sunset yellow
SERS	Surface enhanced Raman spectroscopy
SPR	Surface plasmon resonance
$\boldsymbol{E_{ss}}$	surface state energy levels
TR	Tartrazine
Vis	Visible
Vit C	vitamin C
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction patterns

List of Symbols

ω	Angular frequency
Å	Angstrom
a.u.	Arbitrary unit
δ	Bending
µM	Concentration
ε	Dielectric constant
$\vec{E}$	Electromagnetic field strength
Eq	Energy after the collision
E_β	Energy of the molecule
ν_0	Frequency of incident photon
d	Inter planer spacing
$\vec{E}_0$	Maximum field strength
M	Mass of the molecule
Γ	out-of-plane bending
$\vec{P}$	Polarization
H	Planck's constant
$\vec{\alpha}$	Polarisability
%	Percentage
P	Rocking
N	Stretching frequency
^oC	Temperature
Θ	Theta
ν_m	Vibrational frequency
V	Velocity of molecule
v'	Velocity of the molecule after the collision
Π	Wagging
cm^{-1}	Wavenumber
λ	Wavelength