

**DEVELOPMENT OF 2D MATERIALS AND METAL
NANOPARTICLES NANOCOMPOSITES FOR SERS
BASED SENSING OF HAZARDOUS BIOMOLECULES
AND DISEASES DETECTION VIA GLAD BASED Ag
NANORODS**

Arvind



DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY DELHI

May 2025

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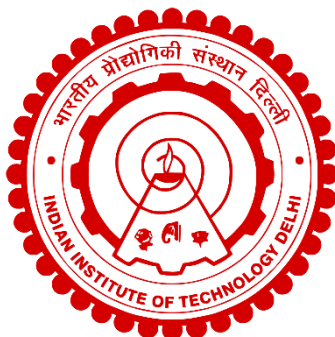
Arvind

Department of Physics

Submitted

***in fulfilment of requirements of degree of Doctor of
Philosophy***

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

Dedication

This dissertation is dedicated to my parents **Mr. Chander Dutt Sharma** and **Mrs. Chander Prabha**. Their support, blessings, encouragement, and constant love have sustained me throughout my life.

CERTIFICATE

I am satisfied that the thesis entitled “**Development of 2D Materials and Metal Nanoparticles Nanocomposites for SERS based Sensing of Hazardous Biomolecules and Diseases Detection via GLAD based Ag Nanorods**” submitted by **Mr. Arvind** is worthy of consideration for the award of the degree of **Doctor of Philosophy** and is a record of original and bonafide research work carried out by him under our supervision. The results contained in it have not been submitted in part or full to any other university or institute for the award of any degree/diploma.

Prof. J.P. Singh

Department of Physics

Indian Institute of Technology Delhi

New Delhi-110016, India

Date: 20th May 2025

ACKNOWLEDGEMENTS

The journey of this doctoral thesis might have been a fond illusion without the contribution and support from many inspiring individuals that create a productive environment for me to work in. Therefore, I would like to express my sincere gratitude to all the people who contributed to forming such a stimulating atmosphere that helped me over the years to complete my work successfully.

*Firstly, I wish to acknowledge my sincere gratitude towards my thesis supervisor **Prof. J.P. Singh**, who contributed significantly to shaping and guiding the direction for my thesis work. I am profoundly grateful to him for providing me with an environment where I learned from his knowledge, experience and wisdom that enabled me to complete this study. He has always inspired me with his endless patience, in-depth knowledge, and dedication to accomplish tasks at stipulated time. The allegiance with which he handles such a large group and is always willing to give new ideas and implement them is highly motivational. He has always motivated me and given me moral support in the most caring way during my thesis work.*

*I am highly obliged to **Prof R.K. Soni** for the valued support and suggestions which helped me in consolidation and realization of this work.*

*Besides my supervisors, I sincerely thank and appreciate the efforts of the SRC members, **Prof. A.K. Shukla**, **Prof. Sunil Kumar**, and **Prof. Vamsi Krishna Komarala**, for their ever-helping approach and supportive nature. I also express my sincere gratitude to **Prof. Amartya Sen** for his efforts in*

maintaining proper functioning of UFO lab and trusting me with the ability of handling the Raman system independently.

*I am thankful to **Prof. Ratnamala Chatterjee, Prof. Pankaj Srivastava and Prof. Sujeet Chaudhary** Head of the Department, Physics, IIT Delhi, for providing necessary facilities.*

*I express my deep gratitude towards **Dr. Neha Agrawal** (Department of Periodontics and Community Dentistry, Dr. Z. A. Dental College, Aligarh Muslim University, Aligarh), **Dr. Syed Aman Ali** (Aligarh Muslim University, Aligarh), **Dr. Prashant Bisht** (Sungkyunkwan University, Suwon 16419, Republic of Korea), **Dr. Sakshi Kapoor** (NRF, IIT Delhi) for providing who performed many experiments along with me and provided valuable suggestions on writing and understanding many aspects of research. I gratefully acknowledge the **Nanoscale Research Facility (NRF)** and **Central Research Facility (CRF)** at the Indian Institute of Technology Delhi for providing experimental facilities during this course of work.*

*I feel fortunate to be associated with GLAD and Nano-CVD Lab, which brings along an immense history of research and a tradition of dedication and innovation. I would also like to thank my seniors **Dr. Yogita Maithani, Dr. Sarjana Yadav, Dr. Jyoti Yadav, Dr. Jamal Ahmad Khan**, and my lab mates, **Sneha Senapati, Siddharth Rana, Shivam Singh, Vidya, Lakshay, Debottam, Simran, Deepali, Vandana and Priyanka** for their encouragement and scientific discussions.*

*I wish to extend heartfelt thanks to **Ms. Sneha Senapati** for being by my side during the peak time of my experimental work. I wish to extend a word of thanks to **Ms. Jyoti** who helped me in technical and non-technical aspects of research. I am much obliged to be associated with such a large group and helping colleagues at GLAD and Nano-CVD Lab.*

*Also, my profound acknowledgement to my friends **Mr. Arun, Mr. Sandeep, Mr. Dheeraj** and **Mr. Durgesh, Dr. Udit Pant, Dr. Viresh Mishra, Dr. Sajjan Sheoran, Dr. Taslim Khan, Dr. Vikas Dixit** for their constant presence. I must thank my friends at IIT Delhi **Dr. Gourav Choudhir, Dr. Hemant** for their encouraging discussions. Their friendship and support were a great source of encouragement and have spent the most enlightening time of my research life. I sincerely thank and acknowledge the useful comments and insightful discussions that have helped me throughout my doctorate journey. I also fondly recall my friends from the **Himalyan cricket team**, with whom I shared many joyful moments on the field. Our Saturday afternoon matches at the IIT ground were not just games, but a much-needed breather from academic pressure, recharging my spirit and preparing me for the next round of experimental challenges.*

*I am delighted to express my sincere appreciation to **my family** for their love, support and understanding that allowed me to nurture my dream and keep looking forward to more exceptional achievements in the future. I am incredibly grateful to my siblings **Ritu, Richa, Kavita, Mohit** and **Kirti** who encouraged and helped me at every stage of my personal and academic life and longed to see this achievement come true.*

I gratefully acknowledge the IIT Delhi for providing the funding support and Senior Research Fellowship for this study.

Above all, I owe it all to Almighty God for granting me the wisdom, health, and strength to complete this task and enabling me to compile it.

Arvind Kaushik

Date: 20-05-2025

Place: New Delhi

ABSTRACT

The term sensing invokes curiosity in the entire scientific community as it plays a crucial role in every field. It involves sensing the presence of different biomolecules, infectious bacteria, explosives, toxic pollutants, poisonous gases and many other hazardous or non-hazardous components through various techniques. For example, electrochemical sensing, fluorescence microscopy, chemiluminescence, colorimetric sensing etc. are employed for detection of the above-mentioned molecules of interest. In recent years, all these methods have been proved highly effective in dedicated sensing of various probe molecules. However, most of these methods involve difficult sample preparations, poor sensitivity at ultralow concentrations, etc. Here, Raman spectroscopy becomes extremely efficacious as it produces the highly specific, ultrasensitive signals which are molecular fingerprints of the detecting species. To enhance the small intensity signals of Raman spectra, surface enhanced Raman spectroscopy (SERS) is employed preserving all the critical features of Raman spectroscopy.

This study aims to develop and explore the 2D material and their nanocomposites with metal nanostructures for SERS applications along with real world application of SERS by employing silver (Ag) nanorods for distinction between different stages of oral cancer.

In the first work, different morphologies of MoS₂ were synthesized for potential SERS applications. The morphology tunability was achieved by varying the growth parameters during the facile solvothermal method. The SERS

substrate prepared with the nanoplate morphology MoS₂ structures shows excellent detection up to 10⁻⁹ M concentration of Rhodamine B (RhB) dye. The MoS₂-Ag nanocomposite SERS substrates successfully detect an ultralow concentration of 10⁻¹⁵ M of RhB dye with an enhancement factor of 9.2×10^7 . The contribution of Ag NPs to ultralow SERS detection is suggested in addition to a charge transfer mechanism between RhB molecules and MoS₂.

In next work, vertically oriented tungsten disulfide (WS₂) nanoflakes were synthesized on a silicon (Si) substrate using the pulsed laser deposition (PLD) technique. The fabricated nanoflakes of WS₂ were decorated with Ag NPs by employing thermal evaporation to enhance their SERS activity. The SERS performance of the WS₂-Ag nanocomposite was explored by using excitation lasers of 532 nm and 633 nm. Various environmental pollutant dyes such as Rh B (RhB), Methyl orange (MO), Methylene blue (MB) are detected at ultralow concentrations by using WS₂-Ag nanocomposite as SERS substrate. The detection limits achieved for RhB and MO are 10⁻¹⁶ and 10⁻¹⁷ M, respectively with 532 nm excitation laser, and 10⁻¹³ M is the detection limit for MB dye with 633 nm laser. The promising enhancement factors of the order of 10⁸ were achieved for WS₂-Ag nanocomposite substrate.

In the following work, MoS₂-Au nanocomposite is fabricated for SERS application with optimized concentration of Au nanoparticles. The nanocomposites of MoS₂ and Au NPs are successfully used as highly sensitive SERS substrates for the detection of hazardous dyes RhB and N719, and infectious bacteria of E. coli and S. aureus. The MoS₂-Au nanocomposite SERS substrate successfully detects the RhB and N719 dye up to 10⁻¹⁵ and

10^{-9} M. The highest enhancement factor obtained for RhB and N719 dye is 5.2×10^7 and 2.1×10^7 , respectively. Further, the nanocomposite substrate was employed for the sensing of infectious *S. aureus* and *E. coli* bacteria down to 10^2 cfu/ml.

In the final work of this thesis, glancing angle deposition-based label free Ag nanorods were employed for diagnosis of oral cancer in its pre-malignant phases, prior to its development into malignant tumors. All the SERS measurements were carried out on site in the field. The SERS spectra of pre-malignant and malignant samples exhibited distinct peaks corresponding to varying concentrations of inorganic metabolites and proteins. The multivariate analysis successfully separates the oral cancer positive and negative samples, as well as pre-malignant and malignant groups.

सार

संवेदन शब्द सम्पूर्ण वैज्ञानिक समुदाय में जिज्ञासा उत्पन्न करता है, क्योंकि यह प्रत्येक क्षेत्र में अत्यंत महत्वपूर्ण भूमिका निभाता है। यह विभिन्न जैव-अणुओं, संक्रामक बैक्टीरिया, विस्फोटक पदार्थों, विषैले प्रदूषकों, जहरीली गैसों और अन्य खतरनाक या गैर-खतरनाक घटकों की उपस्थिति का विभिन्न तकनीकों द्वारा पता लगाने की प्रक्रिया है। उदाहरणस्वरूप, इलेक्ट्रोकेमिकल संवेदन, फ्लोरेसेंस माइक्रोस्कोपी, केमिल्यूमिनेसेंस, और कलोरीमेट्रिक संवेदन जैसी विधियाँ उपरोक्त लक्षित अणुओं के विश्लेषण में प्रयुक्त होती हैं। हाल के वर्षों में, ये सभी विधियाँ विभिन्न खोजी अणुओं की समर्पित पहचान में अत्यंत प्रभावी सिद्ध हुई हैं। तथापि, इन तकनीकों में कठिन नमूना तैयारी, अत्यल्प सांद्रता पर कम संवेदनशीलता जैसी सीमाएँ होती हैं।

ऐसे में रमन स्पेक्ट्रोस्कोपी (Raman Spectroscopy) एक अत्यंत प्रभावी तकनीक बनकर उभरती है, जो विशिष्ट, अति-संवेदनशील संकेत उत्पन्न करती है जो विश्लेषण किए जा रहे अणु की आणविक पहचान होते हैं। रमन संकेतों की मंद तीव्रता को बढ़ाने के लिए सरफेस-एनहांस्ड रमन स्पेक्ट्रोस्कोपी (SERS) का प्रयोग किया जाता है, जो रमन स्पेक्ट्रोस्कोपी की सभी महत्वपूर्ण विशेषताओं को बनाए रखती है।

यह शोध, SERS अनुप्रयोगों के लिए द्वि-आयामी (2D) पदार्थों तथा उनके धातु नैनोसंरचनाओं के साथ बने नैनोसंयोजनों के विकास और अध्ययन पर केंद्रित है, तथा वास्तविक जीवन में SERS की उपयोगिता को भी प्रदर्शित करता है, विशेष रूप से चांदी (Ag) नैनोरोड्स की मदद से मौखिक कैंसर के विभिन्न चरणों के बीच अंतर करने के संदर्भ में।

शोध के पहले भाग में, MoS_2 की विभिन्न रूपाकार संरचनाओं को SERS अनुप्रयोगों के लिए संश्लेषित किया गया। यह रूपाकार परिवर्तन, सरल सॉल्वोथर्मल विधि के दौरान वृद्धि मापदंडों को बदलकर

प्राप्त किया गया। नैनोप्लेट रूपाकार वाली MoS_2 संरचना से तैयार SERS सब्सट्रेट ने Rhodamine B (RhB) डाई की 10^{-9} M सांद्रता तक उत्कृष्ट पहचान प्रदर्शित की। MoS_2 -Ag नैनोसंयोजन SERS सब्सट्रेट्स ने 10^{-15} M की अत्यल्प सांद्रता तक RhB डाई का सफलतापूर्वक पता लगाया, जहाँ संवर्द्धन गुणांक (enhancement factor) 9.2×10^7 रहा। इसमें Ag नैनोकणों का योगदान और RhB तथा MoS_2 के बीच चार्ज ट्रांसफर तंत्र की भूमिका प्रमुख रही।

अगले कार्य में, WS_2 नैनोफ्लेक्स को सिलिकॉन (Si) सब्सट्रेट पर पल्स्ड लेजर डिपोजिशन (PLD) तकनीक द्वारा लंबवत रूप से उगाया गया। इन WS_2 नैनोफ्लेक्स को थर्मल एवपोरेशन द्वारा Ag नैनोकणों से सजाया गया जिससे SERS क्रिया को बढ़ाया जा सके। WS_2 -Ag नैनोसंयोजन की SERS क्षमता का 532 nm और 633 nm उत्तेजना लेज़रों के साथ अध्ययन किया गया। विभिन्न पर्यावरणीय प्रदूषक डाई जैसे RhB, मेथिल ऑरेंज (MO), और मेथिलीन ब्लू (MB) की अत्यल्प सांद्रता पर पहचान संभव हुई। RhB और MO के लिए प्राप्त पहचान सीमा क्रमशः 10^{-16} M और 10^{-17} M रही (532 nm लेज़र के साथ), और MB के लिए 10^{-13} M (633 nm लेज़र के साथ)। इस सब्सट्रेट के लिए 10^8 के स्तर के प्रभावशाली संवर्द्धन गुणांक प्राप्त हुए।

इसके पश्चात, MoS_2 -Au नैनोसंयोजन को उपयुक्त Au नैनोकण सांद्रता के साथ SERS अनुप्रयोग हेतु विकसित किया गया। यह संयोजन RhB और N719 जैसे विषैले डाई, तथा E. coli और S. aureus जैसे संक्रामक बैक्टीरिया की पहचान के लिए अत्यंत संवेदनशील SERS सब्सट्रेट के रूप में प्रयुक्त हुआ। RhB और N719 की 10^{-15} और 10^{-9} M तक की सांद्रता की सफल पहचान हुई, जहाँ अधिकतम संवर्द्धन गुणांक क्रमशः 5.2×10^7 और 2.1×10^7 रहा। इसके अतिरिक्त, इस सब्सट्रेट द्वारा E. coli और S. aureus बैक्टीरिया की 10^2 cfu/ml स्तर तक पहचान भी संभव हुई।

शोध के अंतिम भाग में, glancing angle deposition तकनीक से निर्मित लेबल-फ्री Ag नैनोरोड्स का उपयोग मौखिक कैंसर के पूर्व-घातक चरणों का निदान करने के लिए किया गया, जो इसे पूर्ण रूप से घातक बनने से पहले पहचानने में सहायक है। सभी SERS मापन स्थल पर, क्षेत्र में ही किए गए। पूर्व-घातक एवं घातक नमूनों के SERS स्पेक्ट्रा में अकार्बनिक चयापचयों (metabolites) एवं प्रोटीन की सांद्रता में अंतर को दर्शाने वाले विशिष्ट शिखर (peaks) प्राप्त हुए। मल्टीवेरिएट विश्लेषण विधि ने कैंसर-सकारात्मक और नकारात्मक नमूनों के साथ-साथ पूर्व-घातक और घातक समूहों के बीच सफल पृथक्करण प्रदर्शित किया।

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ABBREVIATIONS

DOS	Density of states
EM	Electromagnetic enhancement
CE	Chemical enhancement
vdW	van der Waals
XRD	X-ray diffraction
FESEM	Field electron scanning electron microscopy
GLAD	Glancing angle deposition
OAD	Oblique angle deposition
XPS	X-ray photoelectron spectroscopy
SPR	Surface plasmon resonance
B.E.	Binding energy
MFC	Mass flow controller
PVD	Physical vapor deposition
2D	Two dimensional
3D	Three dimensional
EDX	Electron diffraction analysis
EPMA	Electron Probe Microanalyzer
TEM	Transmission electron microscopy
HRTEM	High-resolution transmission electron microscopy
AFM	Atomic force microscopy
TMDC	Transition metal dichalcogenides
PECVD	plasma-enhanced chemical vapor deposition
SERS	Surface enhanced Raman spectroscopy
OC	Oral cancer
JCPDS	Joint Committee on Powder Diffraction Standards
MO	Methyl orange
MB	Methylene blue
BPE	trans-1,2-bis(4-pyridyl)ethylene
EC	E. Coli
SA	S. Aureus
RhB	Rhodamine B

BSE	Backscattered electron
PLD	Pulsed laser deposition
PVD	Physical vapor deposition
PVA	Polyvinyl alcohol
EDS	Energy dispersive spectrometer
CB	Conduction band
VB	Valance band
SP	Surface potential
KPFM	Kelvin probe force microscopy
CCD	Charge coupled device
LOD	Limit of detection