

**TWO-DIMENSIONAL PLASMONIC HYBRID
MATERIALS FOR SURFACE ENHANCED RAMAN
SCATTERING**

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Two-Dimensional Plasmonic Hybrid Materials for Surface Enhanced Raman Scattering

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CERTIFICATE

It is to certify that the thesis entitled as “**Two-Dimensional Plasmonic Hybrid Materials for Surface-Enhanced Raman Scattering**” being submitted by **Ms. Preeti Garg (PHZ138481)** to the **Indian Institute of Technology, Delhi**, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. She has worked under our supervision and guidance and has fulfilled the requirements for the submission of this thesis, which to best of our knowledge has reached the requisite standard. The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree/diploma.



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ABSTRACT

The study and recent development of surface-enhanced Raman scattering (SERS) substrates have played a significant role in biosensing, single-molecule detection, analysis of forensic substances, and trace detection of explosive material. SERS is the enhancement in Raman intensity of analyte over conventional plasmonic nanostructures in a non-destructive way due to electromagnetic (EM) and chemical (CM) enhancement mechanism. The conventional plasmonic nanostructures constitute metal nanoparticles of Au, Ag, Cu, Al, Pt, etc. According to EM, the enhancement is because of localized surface plasmon resonance (LSPR) while CM is because of transfer of charge from analyte molecule to metal. With the continuous quest for new SERS substrates, two-dimensional (2D) materials like graphene, boron nitride, molybdenum disulphide (MoS_2) and graphene oxide have turned out to be a potential candidate. Apart from having remarkable properties, 2D materials, and their hybrid with noble metallic nanoparticles (NPs) are found to be ultra-stable and sensitive SERS substrates. Graphene has opened a new branch named Graphene Enhanced Raman Spectroscopy (GERS).

In present work, three different 2D materials including graphene, MoS_2 , and graphene oxide are prepared for SERS analysis and applications. Low-Pressure Chemical Vapour deposition (LPCVD) is utilized for synthesizing graphene over Cu, followed up with the transfer of graphene layers over Si substrates. The hybrid of Ag NPs and graphene has been fabricated over various kinds of graphene samples, having a different number of graphene sheets along with the dependence of SERS activity on the distinct number of graphene sheets. For Ag NPs enhanced single-layer graphene the SERS activity is maximum and biosensing of protein molecule has been carried out on them using micro-Raman spectroscopy. The protein molecules can be easily identified and detected over it even on diluting the aqueous solution of protein molecule up to femtomolar of concentration.

Further, Atmospheric Chemical Vapour deposition (APCVD) has been used for the direct growth of MoS_2 nanoflakes on Si substrates. The Ag and Au NPs are fabricated over three-layered MoS_2 nanoflakes, and SERS activity has been computed on them. The photoluminescence (PL) spectrum of MoS_2 has diminished on introducing Ag and Au nanostructures over it. Theoretical and experimental studies over the junction

of MoS₂ and metal suggest the transfer of charge carriers from the semiconductor to metal and hence the quenched radiative recombination of charge carriers in MoS₂ in its PL spectra.

In the next section, another 2D material, graphene oxide and its nanocomposite with Ag NPs have been synthesised through chemical means. Thorough characterisation including structural, optical, and electrochemical characterisation has been carried out. Because of the plasmonic coupling of Ag NPs with incident light, the Raman activity of the nanocomposite is higher than the bare graphene oxide with 532 nm laser excitation. The SERS substrate has been developed from the nanocomposite of graphene oxide and Ag NPs enabling the detection of explosive molecules to picomolar level of concentration.

Lastly, Ag nano dendrites over Cu foil are prepared through galvanic replacement chemical reaction and their evolution has been studied with time. Also, these Ag nano dendrites are spin-coated with graphene oxide leading to one order higher detection of methylene blue dye molecule as compared to its detection on Ag nano dendrites alone.

सार

सतह-संवर्धित रमन स्कैटरिंग (SERS) सब्सट्रेट्स के अध्ययन और हाल के विकास ने बायोसेंसिंग, एकल अणु पहचान, फोरेंसिक पदार्थों के विश्लेषण और विस्फोटक सामग्री का पता लगाने में महत्वपूर्ण भूमिका निभाई है। विद्युत चुम्बकीय (ईएम) और रासायनिक (सीएम) वृद्धि तंत्र के कारण गैर-विनाशकारी तरीके से पारंपरिक प्लास्मोनिक नैनोस्ट्रक्चर पर विश्लेषण की रमन तीव्रता में वृद्धि है। पारंपरिक प्लाज़्मोनिक नैनोस्ट्रक्चर में Au, Ag, Cu, Al, Pt आदि धातु के नैनोकणों का गठन होता है। ईएम के अनुसार, वृद्धि स्थानीय सतह प्लैसोन प्रतिध्वनि (एलएसपीआर) के कारण होती है, जबकि सीएम को धातु से आवेश के विश्लेषण के लिए अणु के विश्लेषण के लिए स्थानांतरण के कारण होता है। नए SERS सब्सट्रेट्स के लिए निरंतर खोज के साथ, ग्राफीन, बोरान नाइट्राइड, मोलिब्डेनम डाइसल्फ़ाइड (MoS_2) और ग्राफीन ऑक्साइड जैसी दो-आयामी सामग्री एक संभावित उम्मीदवार बन गई है। उल्लेखनीय गुण होने के अलावा, 2 डी सामग्री और उनके संकर महान धातु नैनोकणों के साथ अधिकतम स्थिर और संवेदनशील SERS सब्सट्रेट पाए जाते हैं। ग्राफीन ने ग्राफीन एन्हांस्ड रमन स्पेक्ट्रोस्कोपी (GERS) नाम से एक नई शाखा बनाई है।

वर्तमान कार्य में, SERS विश्लेषण और अनुप्रयोगों के लिए ग्राफीन, MoS_2 और ग्राफीन ऑक्साइड सहित तीन अलग-अलग 2D सामग्री तैयार की गयी हैं। कम दबाव रासायनिक वाष्प जमाव (LPCVD) का उपयोग Cu पर ग्राफीन के संश्लेषण के लिए किया गया है, इसके बाद Si सबस्ट्रेट पर ग्राफीन परतों का हस्तांतरण किया गया है। Ag नैनोकणों और ग्राफीन के हाइब्रिड को विभिन्न प्रकार की ग्राफीन नमूनों में विभिन्न परतों के साथ प्रसतूत किया गया है और इसकी SERS गतिविधि पर ग्राफीन की परतों की संख्या की निर्भरता निर्धारित की गयी है। मोनोलेयर ग्राफीन पर Ag नैनोकणों की SERS गतिविधि अधिकतम है और सूक्ष्म-रमन स्पेक्ट्रोस्कोपी का उपयोग करके उन पर प्रोटीन अणु की बायोसेंसिंग की गयी है। प्रोटीन अणुओं को आसानी से पहचाना जा सकता है और fM सांद्रता तक प्रोटीन अणु के जलीय घोल को पतला करने पर भी इसका पता लगाया गया।

इसके अलावा, वायुमंडलीय रासायनिक वाष्प जमाव (APCVD) का उपयोग Si सबस्ट्रेट पर MoS_2 नैनोफ्लेक्स के प्रत्यक्ष विकास के लिए किया गया है। Ag और Au नैनोकणों को तीन-स्तरीय MoS_2 नैनोफ्लेक्स पर गढ़ा गया है, और उन पर SERS गतिविधि की गणना की गई है। इसके साथ ही, Au और Ag नैनोस्ट्रक्चर की गढ़ना के बाद MoS_2 का फोटोलुमिनेसेंस (PL) स्पेक्ट्रम कम हो गया है। MoS_2 और धातु के जंक्शन पर

सैद्धांतिक और प्रायोगिक अध्ययन, सेमीकंडक्टर से धातु तक आवेश वाहकों के हस्तांतरण का सुझाव देता है और इसलिए अपने PL स्पेक्ट्रा में MoS₂ में प्रभार वाहकों के विकिरणित पुनर्संयोजन को रोकता है।

अगले खंड में, एक और 2 डी सामग्री, ग्राफीन ऑक्साइड और Ag नैनोकणों के नैनोकोम्पोसाइट को रासायनिक साधनों के माध्यम से संश्लेषित किया गया है। संरचनात्मक, ऑप्टिकल और विद्युत रासायनिक लक्षण वर्णन सहित पूरी तरह से लक्षण वर्णन किया गया है। नैनोकोम्पोसिट की रमन गतिविधि घटना विकिरण के साथ Ag नैनोकणों के प्लास्मोनिक युग्मन के कारण 532 nm लेजर उत्तेजना के साथ ग्राफीन ऑक्साइड से अधिक है। SERS सबस्ट्रेट को ग्रेफीन ऑक्साइड और Ag नैनोकणों के नैनोकोम्पोसिट से विकसित किया गया है, जो विस्फोटक अणुओं का पता लगाने के लिए एकाग्रता के पिको दाढ़ के स्तर को सक्षम करता है।

अंततः। Cu पत्री पर Ag नैनो डेंड्राइट गैल्वानिक रिप्लसमेंट केमिकल रिएक्शन के माध्यम से तैयार किए गए हैं और समय के साथ उसके विकास का अध्ययन किया गया है। इसके अलावा, ये Ag नैनो डेंड्राइट ग्रेफीन ऑक्साइड के साथ लेपित होते हैं, जो अकेले Ag नैनो डेंड्राइट्स पर इसके पता लगाने की तुलना में मेथिलीन ब्लू डाई अणु के उच्च क्रम का पता लगाते हैं।

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LIST OF SYMBOLS

E_g	Band gap energy
eV	Electron volt
ϵ_{metal}	Metal's dielectric constant
$\epsilon_{dielectric}$	Surrounding's dielectric constant
$M_{loc}(\lambda_i)$	Proportionality factor
E_i	Incident Electric field
E_{loc}	Localised Electric field
λ_i	Incident Wavelength
A	Polarizability
$E_{scatt}(\lambda_r)$	Scattered Electric field
E_{rad}	Radiated field
$M_{rad}(\lambda_r)$	Proportionality factor
ω	Excitation Frequency
ω_p	Plasmonic Frequency
I_{SERS}	Surface-Enhanced Raman Intensity of analyte
I_{NR}	Normal Raman Intensity of analyte
N_{SERS}	Number of analyte molecules in Surface-enhanced Raman condition
N_{NR}	Number of analyte molecules in normal condition
I_{gram}	Interferogram
ν	Wave number
I	Intensity transmitted
I_o	Background intensity
% T	Transmittance
F	Free exciton
D	Donor
A	Acceptor
e	Electron

h	Hole
d	Interplanar distance
θ	Angle of incidence
n	Integer
λ	Wavelength
V_{CPD}	Contact Potential Difference
ϕ_{tip}	Work function of AFM tip
ϕ_{sample}	Work function of sample
q	Electronic charge
I_{pc}	Cathodic peak current
I_{pa}	Anodic peak current
Z	Impedance
Z'	Real impedance
Z''	Imaginary impedance
Φ	Phase change
E	Sinusoidal Voltage
Γ	Brillouin Zone centre
K, K'	Brillouin zone corner
A	Laser excitation Area
h	Laser penetration depth
N_A	Avogadro number
ρ	Density of analyte
M	Molecular weight of analyte
C	Concentration of analyte
V	Volume of analyte
s	Area of analyte drop cast

LIST OF ABBREVIATIONS

LSPR	Localised Surface Plasmon Resonance
EM	Electromagnetic Mechanism
CM	Chemical Mechanism
SERS	Surface Enhanced Raman Spectroscopy
NPs	Nanoparticles
2D	Two- Dimensional
CCD	Charge Coupled Device
CVD	Chemical Vapour Deposition
LPCVD	Low Pressure Chemical Vapour Deposition
APCVD	Atmospheric Pressure Chemical Vapour Deposition
FE-SEM	Field Emission Secondary Electron Microscope
HRXRD	High Resolution X-ray Diffraction
AFM	Atomic Force Microscope
TEM	Transmission Electron Microscope
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
UV	Ultra Violet
TGA	Thermogravimetric Analysis
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
FWHM	Full Width Half Maximum
LOD	Limit of Detection
KPFM	Kelvin Probe Force Microscopy
PL	Photoluminescence
GO	Graphite oxide

rGO	Reduced Graphene Oxide
MWCNT	Multi Walled Carbon Nano Tube
GFET	Graphene Field Effect Transistor
GERS	Graphene Enhanced Raman Scattering
MS	Mass Spectroscopy
EDAX	Energy Dispersive X-Ray Analysis
NW	Nano Wire
HMX	Cyclotetramethylene-tetranitramine
RDX	Cyclotrimethylenetrinitramine
TNT	Trinitrotoluene
NDs	Nano Dendrites
DLA	Diffusion Limited Aggregation
OA	Oriented Attachment Growth
EF	Enhancement Factor
DI	De-ionised
mM	Milli Molar
μ M	Micro Molar
nM	Nano Molar
fM	Femto Molar
FDTD	Finite Difference Time Domain
DA	Dopamine
R6G	Rhodamine 6G
PLAL	Pulse Laser Ablation in Liquid
EBL	Electron Beam Lithography