BROADBAND PLASMONIC NANOSTRUCTURES FOR ULTRASENSITIVE SURFACE-ENHANCED RAMAN SPECTROSCOPY DETECTION

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

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DEPARTMENT OF PHYSICS

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CERTIFICATE

This is to certify that the thesis entitled, **"Broadband plasmonic nanostructures for ultrasensitive surface-enhanced Raman spectroscopy detection,"** *being submitted by* **Mr. Govind Kumar** *to the Indian Institute of Technology Delhi, New Delhi, for the award of the degree of* **Doctor of Philosophy in Physics** *is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the requisite standard.*

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

Surface-enhanced Raman spectroscopy (SERS) offers a reliable sensing platform capable of rapid detection and precise identification of hazardous compounds at ultra-low concentrations. SERS has become the preeminent spectroscopic technique for molecular detection due to its combination of various desired characteristics, including ultra-sensitivity, rapid acquisition speed, low cost, multiplexing capabilities, and portability. The development of SERS substrates with ultrasensitive detection capabilities is now undergoing a technological resurgence leveraging simple and cost-effective fabrication techniques. The detection capabilities of a SERS substrate are greatly enhanced by altering the composition, shape, and size of nanomaterials. However, the most critical aspect in influencing the detection sensitivity of a SERS substrate is the shape of the nanoparticles. The shape-anisotropic metal nanoparticles enable tuning their plasmon resonance wavelength over a broad spectral range and the generation of a high density of electromagnetic hot spots at corners or sharp edges. In addition to the enhancement of the SERS signal offered by plasmonic materials (mostly Ag and Au) in the visible and near-IR regions, harnessing the enhancement due to plasmon excitation in the UV is highly desirable. Employing the UV excitation wavelength in SERS produces a fluorescence-free and resonant Raman signal, making UV-SERS an attractive technique for molecular detection. This work focuses on the design and fabrication of SERS substrates with ultra-sensitive molecular detection capabilities using shape-tailored nanoparticles of different metals having a broadband plasmonic response in the deep-UV and visible to near-infrared regions.

FDTD simulations demonstrate the critical dependence of various important factors, including excitation wavelength, nanoparticle size, and corner curvature radius, on the optical properties of nanoparticles. A significant redshift in the dipolar LSPR peak wavelength (from 507 nm to 632 nm) and the emergence of higher-order multipolar plasmon modes are observed in the

FDTD-calculated Ag nanocube extinction spectra. The redshift (~449 nm) is more prominent in Ag nanoplates and only the in-plane excitations dominate the extinction spectra for large aspect ratio nanoplates. The Ag nanowire demonstrates a single plasmon peak at 413 nm for transverse polarization and Fabry-Pérot resonator characteristics for longitudinal polarization. Further, corner curvature has a significant impact on optical properties, resulting in drastic declines in field enhancement and a blue shift of the LSPR peak. In a dimer system, the strength of the near-field coupling, hence field enhancement, increases with decreasing interparticle separation and decreases with increasing corner roundness. However, in heterodimers, the nanoparticle size is crucial, deciding the degree of hybridization between all plasmon modes.

Shape-anisotropic Ag nanoparticles, including nanocubes, nanowires, and triangular nanoplates, are produced using chemical reduction-based synthetic techniques. Ag nanocubes show higher-order plasmon modes, while large aspect ratio nanowires exhibit exclusively transverse plasmon modes. Ag nanoplates exhibit a strong dipolar plasmon mode, tuned from visible to near-infrared wavelengths (698 nm to 1094 nm). Ag nanocube-based SERS substrate offers an enhancement factor (EF) as high as 3.6×10^{7} and is higher than the substrate based on Ag nanowire. SERS detection of molecules at ultralow concentrations (LODs of 3.8×10^{-17} M for PATP and 7.3×10^{-16} M for thiram) demonstrates the remarkable detection capabilities of the Ag nanocubes-based substrates. Trace level SERS detection of explosive molecules with EFs of 10^{7} for PA and 10^{5} for AN and LOD values of 2.3×10^{-11} M for PA and 3.1×10^{-8} M for AN display the superior field detection capability of the Ag nanoplate-based SERS substrate. The Ag-Au alloy nanocubes with 11.2% Au exhibit the highest EF of 1.9×10^{7} among the Ag-Au bimetallic nanocubes with varying Au contents generated by a simple galvanic replacement reaction. The Ag-Au alloy nanocubes-based SERS substrate displays remarkable detection sensitivity for explosive compounds, with LODs of 1.71×10^{-14} M for PNBA and 4.1×10^{-11} M for PA.

Three distinct shapes of Rh nanoparticles, triangular nanoplates (TNPs), rectangular nanoplates (RNPs), and concave nanocubes (CNCs), are synthesized using a modified polyol method to develop a deep-UV SERS platform. Rh CNCs have the highest deep-UV SERS activity with an EF of 4.5 x 10^5, as corroborated by FDTD-calculated extinction spectra and electric field distribution maps, in addition to near-field enhancement in Rh nanoparticle dimers. Further, the detection of trace explosives (LOD of 4.9 x 10^{-13} M for AN, 1.3 x 10^{-10} M for PNBA, and 1.1 x 10^{-7} M for DNT) demonstrates the excellent deep-UV SERS sensitivity of the cost-effective Rh nanoparticles substrate.

सार

सरफेस-एनहांस्ड रमन स्पेक्ट्रोस्कोपी (एसईआरएस) एक विश्वसनीय संवेदन मंच प्रदान करता है जो अत्यंत-कम सांद्रता में खतरनाक यौगिकों का तेजी से पता लगाने और सटीक पहचान करने में सक्षम है। अत्यंत-संवेदनशीलता, तेजी से अधिग्रहण की गति, कम लागत, मल्टीप्लेक्सिंग क्षमताओं और पोर्टेबिलिटी सहित विभिन्न वांछित विशेषताओं के संयोजन के कारण आणविक संसूचन के लिए एसईआरएस प्रमुख स्पेक्ट्रोस्कोपिक तकनीक बन गई है। अत्यंत-संवेदनशीलता संसूचन क्षमताओं के साथ एसईआरएस सबस्ट्रेट्स का विकास अब सरल और लागत प्रभावी फैब्रिकेशन तकनीकों का लाभ उठाते हुए एक तकनीकी पुनरुत्थान के दौर से गुजर रहा है। एक एसईआरएस सब्सट्रेट की संसूचन क्षमताओं को नैनोमटेरियल्स की संरचना, कण-आमाप और आकार में परिवर्तन करके बहुत बढ़ाया जाता है। हालांकि, एसईआरएस सब्सट्रेट की संसूचन संवेदनशीलता को प्रभावित करने में सबसे महत्वपूर्ण पहलू नैनोकणों का आकार है। आकार-अनिसोट्रोपिक धातु नैनोकणों एक व्यापक स्पेक्ट्रम रेंज के साथ-साथ कोनों या तेज किनारों पर विद्युत चुम्बकीय हॉटस्पॉट के उच्च घनत्व के उत्पादन पर उनके प्लास्मोन अनुनाद तरंगदैर्ध्य का समायोजन प्रदान करते हैं। दृश्यमान और निकट-अवरक्त क्षेत्रों में प्लास्मोनिक नैनोमटेरियल्स (ज्यादातर Ag और Au) द्वारा पेश किए गए एसईआरएस सिग्नल की वृद्धि के अलावा, पराबैंगनी प्रक्षेत्र में प्लास्मोन उत्तेजन के कारण आवर्धन का उपयोग करना अत्यधिक वांछनीय है। एसईआरएस में पराबैंगनी उत्तेजन तरंगदैर्ध्य को नियोजित करने से प्रतिदीप्ति-मुक्त और अनुनाद रमन सिग्नल उत्पन्न होता है, जिससे यूवी-एसईआरएस आणविक संसूचन के लिए एक आकर्षक तकनीक बन जाती है। यह कार्य अत्यंत-संवेदनशील आणविक संसूचन क्षमताओं के साथ एसईआरएस सबस्ट्रेट्स के प्रारुप और निर्माण पर केंद्रित है, जिसमें विभिन्न धातुओं के आकार-अनिसोट्रोपिक नैनोकणों का उपयोग किया जाता है, जिसमें गहरा-पराबैंगनी और निकट-अवरक्त से दृश्य क्षेत्रों में ब्रॉडबैंड प्लास्मोनिक प्रतिक्रिया होती है।

फाइनाइट डिफरेंस टाइम डोमेन (एफडीटीडी) अनुकार, नैनोकणों के प्रकाशिक गुणधर्मो पर उत्तेजना तरंग दैर्ध्य, नैनोकण आकार और कोने वक्रता त्रिज्या सहित विभिन्न महत्वपूर्ण कारकों की महत्वपूर्ण निर्भरता को प्रदर्शित करता है। द्विध्रुवीय एलएसपीआर शिखर तरंग दैर्ध्य (507 nm से 632 nm तक) में एक महत्वपूर्ण रेडशिफ्ट और उच्च-क्रम बहुध्रुवीय प्लास्मोन मोड के उद्भव को एफडीटीडी-परिकलित Ag ननौकयूब एक्सटिंक्शन स्पेक्ट्रा में देखा जाता है। Ag नैनोप्लेट्स में रेडशिफ्ट (~ 449 nm) अधिक प्रमुख है और बड़े अनुपात नैनोप्लेट्स के लिए एक्सटिंक्शन स्पेक्ट्रा पर केवल इन-प्लेन उत्तेजन हावी है। Ag ननौवायर अनुप्रस्थ ध्रुवीकरण के लिए 413 nm पर एकल प्लास्मोन शिखर और अनुदैर्ध्य ध्रुवीकरण के लिए फैब्री-पेरोट रेसोनेटर विशेषताओं को प्रदर्शित करता है। इसके अलावा, कोने की वक्रता का प्रकाशिक गुणधर्मो पर महत्वपूर्ण प्रभाव पड़ता है, जिसके परिणामस्वरूप विद्युत् चुंबकीय क्षेत्र आवर्धन में भारी गिरावट आती है और एलएसपीआर शिखर का ब्लूशिफ्ट होता है। एक नैनोकण डिमर व्यवस्था में, निकट-क्षेत्र युग्मन की ताकत, इसलिए विद्युत क्षेत्र आवर्धन, घटते अंतर-कण पृथक्करण के साथ बढ़ती है और कोने की गोलाई बढ़ने के साथ घटती है। हालांकि, हेटेरो-डिमर में, सभी प्लास्मोन मोड के बीच संकरण की प्रबलता तय करते हुए, नैनोकणों का आकार महत्वपूर्ण है। आकार-अनिसोट्रोपिक Ag नैनोकणों, जिनमें ननौकयूब्स, ननौवायर्स और त्रिकोणीय नैनोप्लेट शामिल हैं, रासायनिक अपचयन-आधारित कृत्रिम तकनीकों का उपयोग करके उत्पादित किए गए है। Ag ननौकयूब्स उच्च-क्रम प्लास्मोन मोड दिखाते हैं, जबकि बड़े पहलू अनुपात ननौवायर्स विशेष रूप से अनुप्रस्थ प्लास्मोन मोड प्रदर्शित करते हैं। Ag नैनोप्लेट्स एक मजबूत द्विध्रुवीय प्लास्मोन मोड प्रदर्शित करते हैं, जो दृश्यमान से निकट-अवरक्त तरंग दैर्ध्य (698 nm से 1094 nm) तक समायोजित किया जाता है। Ag ननौकयूब्स-आधारित एसईआरएस सब्सट्रेट 3.6×10^7 के रूप में उच्च आवर्धन कारक (ईएफ) प्रदान करता है और Ag नैनोवायर पर आधारित सब्सट्रेट से अधिक है। अत्यंत-कम सांद्रता पर अणुओं का एसईआरएस संसूचन (पीएटीपी के लिए 3.8×10^{-17} M के एलओडी और थीरम के लिए 7.3×10^{-16} M) Ag ननौकयूब्स -आधारित सबस्ट्रेट्स की उल्लेखनीय पहचान क्षमताओं को प्रदर्शित करता है। पिकरिक एसिड (पीए) के

लिए 10^7 और अमोनियम नाइट्रेट (एएन) के लिए 10^5 के ईएफ और पीए के लिए 2.3×10^{-11} M और एएन के लिए 3.1×10^{-8} M के एलओडी के साथ विस्फोटक अणुओं का अवशेष स्तर एसईआरएस संसूचन से Ag नैनोप्लेट्स-आधारित की बेहतर क्षेत्र संसूचन क्षमता प्रदर्शित होती है एक साधारण गैल्वेनिक प्रतिस्थापन प्रक्रिया द्वारा उत्पन्न 11.2 प्रतिशत Au के साथ Ag-Au मिश्र धातु ननौकयूब्स, विभिन्न Au मात्रा Ag-Au द्विधात्विक ननौकयूब्स के बीच 1.9×10^7 का सबसे बड़ा ईएफ प्रदर्शित करता है। Ag-Au मिश्र धातु ननौकयूब्स-आधारित एसईआरएस सब्सट्रेट विस्फोटक यौगिकों के लिए उल्लेखनीय संसूचन संवेदनशीलता प्रदर्शित करता है, जिसमें पीएनबीए (परा-नीट्रोबेन्जोइक एसिड) के लिए 1.71×10^{-14} M और पीए के लिए 4.1×10^{-11} M के एलओडी हैं।

Rh नैनोकणों के तीन अलग-अलग आकार, त्रिकोणीय नैनोप्लेट्स (टीएनपी), आयताकार नैनोप्लेट्स (आरएनपी), और अवतल ननौकयूब्स (सीएनसी) को एक गहरा यूवी-एसईआरएस प्लेटफॉर्म विकसित करने के लिए संशोधित पॉलीओल विधि का उपयोग करके संश्लेषित किया जाता है। Rh सीएनसी में 4.5×10^5 के ईएफ के साथ उच्चतम डीप-यूवी एसईआरएस गतिविधि है, जैसा कि Rh नैनोकण डिमर में निकट-क्षेत्र आवर्धन के अलावा एफडीटीडी-गणना एक्सटिंक्शन स्पेक्ट्रा और विद्युत क्षेत्र वितरण मानचित्रों द्वारा पुष्टि की गई है। इसके अलावा, अवशेष विस्फोटकों का पता लगाना ((एएन के लिए 4.9×10^{-13} M, पीएनबीए के लिए 1.3×10^{-10} M, और डीएनटी के लिए 1.1×10^{-7} M) लागत प्रभावी Rh नैनोकणों सब्सट्रेट की उत्कृष्ट डीप-यूवी एसईआरएस संवेदनशीलता को प्रदर्शित करता है।

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LIST OF ABBREVIATIONS

AN	Ammonium nitrate
AR	Aspect ratio
CCD	Charge-coupled device
CNC	Concave nanocubes
CT	Charge transfer
CTP	Charge transfer plasmon
CW	Continuous wave
DDA	Discrete-dipole approximation
DI	De-ionized
DNT	2,4-dinitrotoluene
DTC	Dithiocarbamate
EBL	Electron beam lithography
EDAX/EDX	Energy-dispersive X-ray spectroscopy
EF	Enhancement factor
EG	Ethylene glycol
eV	Electronvolt
FDTD	Finite-difference time-domain
FEM	Finite element method
FESEM	Field-emission scanning electron microscopy
FIB	Focused ion beam
FWHM	Full width at half maximum
gr/mm	Grooves/millimetre
HMTD	Hexamethylene triperoxide diamine
HOMO	Highest occupied molecular orbital
HRTEM	High-resolution transmission electron microscopy
LOD	Limit-of-detection
LUMO	Lowest unoccupied molecular orbital
MCA	Multichannel analyser
MW	Molecular weight
mW	Milliwatt
NIR	Near-infrared
PA	Picric acid
PATP	p-aminothiophenol
PETN	Pentaerythritol tetranitrate
PML	Perfectly matched layer
PMT	Photomultiplier tube
PNBA	p-nitrobenzoic acid
ppb	Parts-per billion
ppq	Parts-per quadrillion
PVP	Polyvinylpyrrolidone
R6G	Rhodamine 6G

RDX	Cyclotrimethylenetrinitramine
RhB	Rhodamine B
RIS	Refractive index sensitivity
rpm	Revolutions per minute
RNPs	Rectangular nanoplates
RS	Raman spectroscopy
RSD	Relative standard deviation
SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman spectroscopy
SHE	Standard hydrogen electrode
SPP	Surface plasmon polariton
SRS	Stimulated Raman spectroscopy
LSPR	Localized surface plasmon resonance
TATP	Triacetone triperoxide
TEM	Transmission electron microscopy
TFSF	Total-field scattered-field
TNPs	Triangular nanoplates
TNT	2,4,6-trinitrotoluene
TrEG	Triethylene glycol
TSC	Trisodium citrate
UV	Ultraviolet

LIST OF SYMBOLS

ω_p	Plasma frequency
n_e	Electron density
ε_0	Permittivity of free space
m_e	Effective mass of electron
e	Charge on electron
$\varepsilon(\omega)$	Dielectric function
γ	Collision frequency
f_k	Oscillator strength
γ_k	Bandwidth
ω_k	Resonance frequency
σ_{sca}	Scattering cross-sections
σ_{abs}	Absorption cross-sections
σ_{ext}	Extinction cross-section
V	Nanoparticle volume
λ	Wavelength of incident light
ε	Permittivity of nanoparticles
ε_1	Real part complex dielectric function
ε_2	Imaginary parts of complex dielectric function
ε_m	Permittivity of the surrounding medium
R	Radius of nanoparticle
ω_{LSPR}	Dipolar plasmon resonance frequency
l	Order of pole
Q	Quality factor
ω_0	Frequency of incident field
ω_R	Shifted frequency
ω_{vib}	Frequency of molecular vibration
k	Propagation constant
$E_0(\omega_0)$	Incident electric field
$E_{loc}(\omega_0)$	Local electric field
g	Enhancement averaged across the surface of the particle
g'	Enhancement factor corresponding to Raman-shifted wavelength
α_0	Raman polarizability of the isolated molecule
α_R	Raman polarizability of molecule adsorbed on metal nanoparticles
I_{Raman}	Raman-scattered intensity
I_{SERS}	SERS intensity
C_s	Original concentration of first metal
x	Variable distance from two metal interface
t	Time
$C(x, t)$	Concentration of first metal during the alloying process
D	Diffusion coefficient
E_{diff}	Energy barrier for diffusion
T	Temperature

A	Absorbance
I_0	Intensity of incident light
I	Intensity of transmitted light
ε	Molar extinction coefficient
C	Concentration
l	Path length
N_A	Avogadro number
V_m	Volume of analyte
N	Number of molecules per unit area on the substrate
N_{Raman}	Number of molecules deposited on bare silicon
N_{SERS}	Number of molecules adsorbed on the substrate under the laser spot area
A_{laser}	Area of laser spot
N_d	Number of nanoparticles per μm^2
σ	Surface area occupied by single analyte molecule
A_{NP}	Area of single nanoparticle
t_α^{n-2}	Critical value of the t-distribution
α	Significance level of the prediction interval
y_i	Measured values
y_i^p	Predicted values from regression
s_y	Normalized sum of squares of the difference between measured values and predicted values
μM	Micromolar
nM	Nanomolar
pM	Picomolar
fM	Femtomolar
λ_p	Plasma wavelength of the bulk metal
n_m	Refractive index of the medium
λ_{LSPR}	Plasmon resonance wavelength
$\Delta\lambda/\lambda$	Fractional plasmon shift
g	Interparticle nanogap distance
m	Coupling strength
τ	Decay constant
R^2	Correlation coefficient