HIGHLY ANISOTROPIC METAL NANOSTRUCTURES FOR SERS-BASED TRACE-LEVEL MOLECULE DETECTION

ASHWANI KUMAR VERMA

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2023

© Indian Institute of Technology Delhi (IITD), New Delhi, 2023

HIGHLY ANISOTROPIC METAL NANOSTRUCTURES FOR SERS-BASED TRACE-LEVEL MOLECULE DETECTION

by

ASHWANI KUMAR VERMA

Department of Physics

Submitted
in fulfillment of requirements of degree of
Doctor of Philosophy
to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2023

Dedicated to my

Parents and Sisters

Who support me in every endeavour of my life

CERTIFICATE

This is to certify that the Thesis entitled "**Highly Anisotropic Metal Nanostructures for SERS-based Trace-level Molecule Detection**" submitted by **Mr. Ashwani Kumar Verma** to the Department of Physics, Indian Institute of Technology Delhi, New Delhi, for the award of the degree of "**Doctor of Philosophy**" is a record of bonafide research work carried out by him. He has worked under my supervision and guidance and has fulfilled the requirement for the submission of this thesis, which in my opinion, has reached the requisite standard.

It is certified that the work has not been submitted in part or full anywhere else for the award of any other diploma or degree of this or any other University.

Date:

Prof. R. K. Soni
Professor
Department of Physics
Indian Institute of Technology
Delhi
New Delhi – 110016
India

Prof. D. S. Mehta
Professor
Department of Physics
Indian Institute of Technology
Delhi
New Delhi – 110016
India

ACKNOWLEDGEMENTS

There are several people who contributed to this thesis in various ways, either by fruitful collaboration or constructive criticism and discussions. Firstly, I would like to thank the Almighty God for his blessings and guidance throughout my entire life.

I would like to express my sincerest gratitude to my supervisor, Prof. R. K. Soni, for giving me the platform, research insight, positive criticism, for his patience, motivation, and honest advice, without which none of this work would have been accomplished. He taught me how to become a good researcher as well as a better human being. I would also like to express my sincere gratitude to Prof. D. S. Mehta for his continuous support of my Ph.D. work, co-operation, encouragement, and valuable feedback, which helped me to improve my research abilities. His teachings will be gratefully remembered for all times to come.

Besides my supervisors, I would like to thank my Student Research Committee (SRC) members Prof. Joby Joseph (Dept. of Physics, IIT Delhi), Prof. G. Vijaya Prakash (Dept. of Physics, IIT Delhi), and Prof. Vamsi K. Komarala (Dept. of Energy Science and Engineering, IIT Delhi) for their continuous support, critical suggestions and insightful comments which widened my research perspective.

I would like to thank all the technicians and teaching assistants of TEM, HRTEM, SEM, FESEM, XRD, and Raman Spectrometer, who sincerely supported and devoted time to acquire information from my samples, which contributed highly to my thesis work. I would also like to thank the Central Research Facility (CRF) and Nanoscale Research Facility (NRF) of IIT Delhi for providing the characterization facilities. I extend my acknowledgement to JATC DRDO and DST-FIST UFO facility for Raman measurements.

My special thanks also go to my lab mates and friends: Dr. Rupali Das, Dr. Jaspal Singh, Govind, Arvind, and Lokesh for insightful discussion, constant support, unconditional help, and the little fun we had in between the stressful days. Working every single day with my lab mates here was a joyful experience, and they encouraged me for the betterment of my work. I also extend my gratitude to my friends Rajeev Gangwar, Sandeep Kumar, Chandra Prakash Verma, Rakesh Kumar, and Nanhe Kumar Gupta for their faith, care, support, and honest advice in each step making me a better person.

Most importantly, I am decidedly grateful to my loving family for their love and prayers. I am indebted to my Mother (Mrs. Asha Verma) and Father (Late. Mr. Panna Lal Verma) for their unconditional love and blessings giving me the strength to complete the work. I am blessed to have strong support from my sisters, Anjuli Verma and Priyanka Verma, in every phase of my life. I am more than thankful to my brother-in-laws Mr. Rakesh Kumar Verma and Mr. Charchit Verma, for their immense support, priceless advice, and moral to continue my Ph.D.

Date: **(Ashwani Kumar Verma)**

ABSTRACT

Plasmon-enhanced spectroscopy, like Raman spectroscopy, is extensively employed for the fingerprint identification of ultralow concentrations of analyte molecules due to its selectivity and sensitivity. In particular, surface-enhanced Raman spectroscopy (SERS) has proven its uniqueness as a sensitive, selective, non-destructive, and label-free spectroscopic technique for detecting trace-level concentrations of chemical and biomolecules in their individual as well as multiplexed form. The magnitude of Raman intensity enhancement can be efficiently optimized by the features of enhancing substrates through the morphology and composition of plasmonic nanostructures as well as their relative distribution over the substrates. The morphology of plasmonic nanostructures, especially the anisotropically engineered nanostructures exhibiting anisotropy in terms of morphology, composition, and distribution within the substrates, offers the possibility to efficiently tune the plasmonic response through generating intrinsic 'hot spots' and the larger surface area for the interaction of analyte molecules. Anisotropic metal nanostructures with highly branched morphology are attractive due to their fascinating plasmonic properties, which are related to their unique morphological features. The multi-component nanomaterials such as bimetallic ultrathin shell-wrapped core@shell NPs serve as active SERS substrates employing the strategy of "borrowing SERS activity" from the central metallic core. Moreover, shape-controlled nanostructures arranged in uniform assembly provide optimum intra-particle gaps and produce reproducible hot spot density over the larger-surface areas.

The vibrational modes of the vast category of analytes, including organic dyes, pesticides, explosives, and biomolecules, were assigned through DFT computations depicting close (~7-15 cm^{-1}) agreements between experimental and computed Raman bands. The plasmonic properties and near-field enhancements of the isotropic visible (Au and Cu) and UV (Pd, Rh, Sn, and In) active plasmonic materials were investigated employing COMSOL simulations. Isotropic Au and Cu monometallic NPs depict size-tunable plasmonic response in the visible region from ~520 nm to 570 nm and ~559 nm to 592 nm, respectively, with the increment of NPs' size from 10 to 100 nm. However, isotropic Pd, Rh, Sn, and In NPs exhibit the size-tunable plasmon wavelength from 208 nm to 446 nm, 205 nm to 413 nm, 202 nm to 386 nm, and 269 nm to 429 nm, respectively, depicting the plasmon tunability from DUV and visible spectral region, for increasing the NPs' size from 10 to 100 nm. The poor plasmonic activity of transition metal (TM) NPs efficiently improved by wrapping a TM shell over the highly-active AuNPs through utilizing long-range effect of localized electromagnetic fields. For core@shell Au@TM NPs, the blue-shifted dipolar plasmon wavelength for Au@Pd, Au@Rh, Au@Sn, and Au@In NPs and red-shifted dipolar plasmon wavelength for Au@Cu NPs are obtained. Interestingly, Au@TM NPs exhibit significantly improved relative electric field at the outer TM surface as compared to monometallic TM NPs through borrowing the SERS activity from the central core and thus exploring poor plasmonic TMs towards sensitive plasmonic platforms.

The chemically-synthesized silver stars and silver nanodendrites provide copious three-dimensional intrinsic hot spots at their sharp features as well as within nano-sized intra- and inter-branch gaps. Under optimized reaction parameters, the multi-branched morphology of silver nanodendrites enables comparatively higher enhancements than silver stars for different analytes, including MB, RhB, thiram, phosmet, 2,4-DNT, PNBA, and PA molecules with LODs down to the 10^{-18} M, 10^{-17} M, 10^{-19} M 10^{-15} M, 10^{-16} M, 10^{-16} M and 10^{-12} M concentrations, respectively. The combined effect of highly dense hot spots and the spectral modifications through chemical enhancement governs the overall reproducible (RSD ~ 10 %) intensity enhancements ~10^{10} and LODs ~10^{-19} M concentration. The multiplexed detection of pesticides and explosives from the complex mixtures of dye molecules was demonstrated. Moreover, sensitive detections of dyes and pesticides with apple juice, chili powder, and flexible substrates were investigated for real-life detection applications.

Liquid-assisted pulsed laser ablation (LA-PLA) technique was employed for green synthesis of different monometallic (Au and Pd) and bimetallic core@shell Au@TM (Au@Pd, Au@Rh, Au@Cu, Au@Sn, and Au@In) NPs. The size-controlled growth of monometallic NPs was performed by varying the laser fluence and evidently observed by red-shifted plasmon wavelength. The ultrathin (1-2 nm) TM shell-wrapped Au@TM core@shell NPs were successfully prepared employing single-step simultaneous laser ablation utilizing columbic attraction and self-assembly approach. The shifted LSPR response and the relatively higher electric fields at the outer TM shell surface depict good matching with the COMSOL simulated results. The SERS performance of the LA-PLA generated NPs was investigated by MB dye molecules and then targeted towards the highly reproducible (RSD ~ 10-20 %) detection of explosives AN and PA, and biomolecules adenine and L-tryp down to the 10^{-7}, 10^{-8}, 10^{-10}, and 10^{-7} M detectability, respectively. Moreover, the simultaneous detection of different concentrations of explosives AN and PA from the fixed background of MB dye molecules was achieved.

Laser direct writing has emerged as a powerful technique to control the distribution of micro/nano-structures through the optimization of fabrication parameters such as scanning line interval (pitch), scanning speed, and pulse energy to achieve a significant tip-to-valley ratio and surface roughness. Anisotropic (parallel lines) and isotropic (crossed patterns) texturing with variable pitch (100-250 μm) and scanning speed (50-300 μm/s) were fabricated on Sn and Pd substrates and employed for NIR (785 nm) and DUV (266 nm) SERS applications. Isotropically textured substrates (100 μm/s scanning speed and 150 μm pitch) depict regularly sharp conical-shaped morphological features and exhibit highly reproducible (RSD < 10%) intensity enhancements of the order of ~10^6 for MB molecules after AuNPs deposition. The SnTAu substrates exhibit comparatively higher reflection and consequently higher SERS performance as compared to PdTAu substrates with LODs down to the ~0.32 pM, 3.2 fM, 2.93 nM, 0.37 μM, 0.26 nM, and 0.14 μM concentrations for the MB, DTTCI, PA, AN, adenine and L-tryp molecules, respectively. The DUV SERS performance was explored with RhNPs coated isotropically textured Sn and Pd substrates with 100 μm/s scan speed and 150 μm pitch size. The efficient DUV LSPR of RhNPs enables the resonant excitation and exhibit EFs of ~10^5 for AN and adenine, and ~10^4 for PA and thymine molecules. The resonance excitation with the analyte's electronic absorption and LSPR band provides the detectability down to ~3.86 nM, 0.46 μM, 46.2 nM, and 0.45 μM for AN, PA, adenine, and thymine molecules, respectively, and thus demonstrated the trace detection capabilities. Therefore, the NIR and DUV SERS studies comprehensively demonstrated the applicability of laser-textured hybrid substrates for trace-level molecular detection.

सार

प्लास्मोन-संवर्धित स्पेक्ट्रोस्कोपी जैसे रॉमन स्पेक्ट्रोस्कोपी, अपनी चयनात्मकता और संवेदनशीलता के कारण विश्लेषण अणुओं क़ी अत्यंत-निम्न सांद्रता की फिंगरप्रिंट पहचान के लिए व्यापक रूप से प्रयुक्त होती है। विशेष रूप से, सऱफेस-इन्हैंस्ड रॉमन स्पेक्ट्रोस्कोपी (SERS) ने एक संवेदनशील, चयनात्मक, गैर-विनाशकारी और लेबल-मुक्त स्पेक्ट्रोस्कोपिक तकनीक के रूप में विशिष्ट तथा बहुभागी रूप में रासायनिक और जैव-अणुओं की ट्रेस-स्तरीय सांद्रता का पता लगाने में अपनी विशिष्टता साबित की है। रमन की तीव्रता में वृद्धि के परिमाण को संवर्धन सब्सट्रेट की विशेषताओ जैसे कि प्लास्मोनिक नैनोस्ट्रक्चर की आकृति और संरचना के साथ-साथ सब्सट्रेट पर उनके सापेक्ष वितरण के माध्यम से कुशलतापूर्वक अनुकूलित किया जा सकता है। प्लास्मोनिक नैनोस्ट्रक्चर की आकृति विज्ञान, विशेष रूप से अनिसोट्रोपिक रूप से इंजीनियर नैनोस्ट्रक्चर, जो आकृति, संयोजन और सब्सट्रेट पर वितरण के संदर्भ में अनिसोट्रॉपी का प्रदर्शन करते हैं, आंतरिक 'हॉट-स्पॉट' और विश्लेषण अणुओं की पारस्परिक क्रिया के लिए ज़्यादा पृष्ठ क्षेत्र को उत्पन्न करने के माध्यम से प्लास्मोनिक प्रतिक्रिया को कुशलतापूर्वक ट्यून करने की संभावना प्रदान करते हैं। अत्यधिक शाखित आकृति वाले अनिसोट्रोपिक धातु नैनोस्ट्रक्चर उनके आकर्षक प्लास्मोनिक गुणों जो उनकी अनूठी रूपात्मक विशेषताओं से संबंधित हैं, के कारण आकर्षक हैं । बहु-घटक नैनोमटेरियल्स जैसे कि द्विधात्वीय अल्ट्रा-थिन शेल आच्छादित कोर-शेल नैनोपार्टिकल्स केंद्रीय धातु कोर से " SERS गतिविधि उधार लेने" की रणनीति को नियोजित करने वाले सक्रिय SERS सब्सट्रेट के रूप में कार्य करते हैं। इसके अतिरिक्त, यूनिफ़ॉर्म असेंबली में व्यवस्थित आकार-नियंत्रित नैनोस्ट्रक्चर अनुकूलतम अंतर-कण अंतराल प्रदान करते हैं और ज़्यादा पृष्ठ क्षेत्रों पर पुनरुत्पादन योग्य हॉट-स्पॉट घनत्व उत्पन्न करते हैं।

कार्बनिक रंगों, कीटनाशकों, विस्फोटकों और जैवअणुओं सहित विशाल श्रेणी के विश्लेषण अणुओं के वाएब्रेशनल मोड को DFT संगणनाओं के माध्यम से प्रयोगात्मक और गणना किए गए रॉमन बैंड के बीच घनिष्ठ समानताओ (~7-15 सेमी$^{-1}$) को दर्शाते हुए निर्धारित गया था। COMSOL सिमुलेशन को नियोजित करते हुए आइसोट्रोपिक दृश्य (Au और Cu) और पराबैंगनी (Pd, Rh, Sn, और In) सक्रिय प्लास्मोनिक पदार्थों के प्लास्मोनिक गुणों और निकट-क्षेत्र संवर्द्धन की विवेचना की गई है। नैनोकणों के आकार में 10 से 100 nm की वृद्धि करने पर, आइसोट्रोपिक Au और Cu मोनोमेटेलिक नैनोकण दृश्य क्षेत्र में आकार-ट्यून करने योग्य प्लास्मोनिक प्रतिक्रिया को क्रमशः ~520 nm से 570 nm और ~559 nm से 592 nm तक दर्शाते हैं। हालांकि, नैनोकणों के आकार में 10 से 100 nm की वृद्धि करने पर, आइसोट्रोपिक Pd, Rh, Sn, और In

नैनोकण आकार-ट्यून करने योग्य प्लास्मोन तरंग दैर्ध्य क्रमशः ~208 nm से 446 nm, 205 nm से 413 nm, 202 nm से 386 nm, और 269 nm से 429 nm तक गहरे- पराबैंगनी और दृश्य वर्णक्रमीय क्षेत्र से प्लास्मोन ट्यूनेबिलिटी का चित्रण प्रदर्शित करते हैं। संक्रमण धातु (TM) नैनोकणों की तुच्छ प्लास्मोनिक गतिविधि स्थानीयकृत विद्युत-चुम्बकीय क्षेत्रों की लंबी दूरी के प्रभाव का उपयोग करके अत्यधिक सक्रिय Au नैनोकणों पर संक्रमण धातु शेल लपेटकर कुशलता से सुधरती है। कोर-शेल Au@TM नैनोकणों के लिए, Au@Pd, Au@Rh, Au@Sn, और Au@In NPs के लिए ब्लू-शिफ्टेड द्विध्रुवीय प्लास्मोन तरंगदैर्ध्य और Au@Cu NPs के लिए रेड- शिफ्टेड द्विध्रुवी प्लास्मोन तरंगदैर्ध्य प्राप्त होती हैं। दिलचस्प रूप से, Au@TM NPs केंद्रीय कोर से एसईआरएस गतिविधि उधार लेकर मोनोमेटैलिक संक्रमण धातु नैनोकणों की तुलना में संक्रमण धातु की सतह पर सार्थक रूप से बेहतर सापेक्ष विद्युत क्षेत्र का प्रदर्शन करते हैं और इस प्रकार तुच्छ प्लास्मोनिक संक्रमण धातुओं को संवेदनशील प्लास्मोनिक प्लेटफार्मों की ओर समन्वेषण करते हैं।

रासायनिक रूप से संश्लेषित सिल्वर स्टार्स और सिल्वर नैनोडेंड्राइट्स अपनी उच्च विशेषताओं के साथ-साथ नैनो-आकार के अंतः- और अंतर-शाखा अंतराल के भीतर प्रचुर त्रि-आयामी आंतरिक हॉट-स्पॉट प्रदान करते हैं। अनुकूलित अभिक्रिया मापदंडों के तहत, सिल्वर नैनोडेंड्राइट्स की बहु-शाखा आकारिकी विभिन्न विश्लेषणों MB, RhB, थिरम, फॉस्मेट, 2,4-DNT, PNBA और PA अणुओं के लिए सिल्वर स्टार्स की तुलना में उच्च वृद्धि तथा LODs क्रमशः ~10^{-18} M, 10^{-17} M, 10^{-19} M, 10^{-15} M, 10^{-16} M, 10^{-16} M और 10^{-12} M सांद्रता को सक्षम करती है। अत्यधिक घने हॉट-स्पॉट और रासायनिक वृद्धि के माध्यम से वर्णक्रमीय संशोधनों का संयुक्त प्रभाव समग्र पुनरुत्पादन योग्य (RSD ~ 10%) तीव्रता वृद्धि ~10^{10} और LODs ~10^{-19} M सांद्रता को निर्धारित करता है। डाई अणुओं के जटिल मिश्रण से कीटनाशकों और विस्फोटकों की बहुसंकेतन पहचान का प्रदर्शन किया गया है। इसके अतिरिक्त, वास्तविक जीवन का पता लगाने के अनुप्रयोगों के लिए सेब के रस, मिर्च पाउडर और लचीले सब्सट्रेट के साथ रंगों और कीटनाशकों की संवेदनशील पहचान की जांच की गई है।

लिक्विड-असिस्टेड स्पंदित लेजर एब्लेशन (LA-PLA) तकनीक को विभिन्न मोनोमेटेलिक (Au और Pd) और बाईमेटेलिक कोर-शेल Au@TM (Au@Pd, Au@Rh, Au@Cu, Au@Sn, and Au@In) नैनोकणों के हरित संश्लेषण के लिए नियोजित किया गया। मोनोमेटेलिक एनपी के आकार-नियंत्रित संवृद्धि को लेजर फ्लुएंस को परिवर्तित करके और स्पष्ट रूप से रेड- शिफ्टेड प्लास्मोन तरंग दैर्ध्य द्वारा पर्यवेक्षित किया गया। अल्ट्रा-थिन (1-2 nm) संक्रमण धातु शेल-लिपटे कोर-शेल नैनोकणों को कोलंबिक आकर्षण और सेल्फ-असेंबली

दृष्टिकोण का उपयोग करते हुए सिंगल-स्टेप समकालीन लेजर एब्लेशन को नियोजित करके सफलतापूर्वक तैयार किया गया। स्थानांतरित LSPR प्रतिक्रिया और संक्रमण धातु शेल सतह पर अपेक्षाकृत उच्च विद्युत क्षेत्र COMSOL सिमुलेटेड परिणामों के साथ अच्छे अनुकूलन को दर्शाते हैं। LA-PLA उत्पन्न नैनोकणों के एसईआरएस प्रदर्शन की जांच MB डाई अणुओं द्वारा की गई और फिर अत्यधिक पुनरुत्पादन योग्य (RSD ~10-20%) विस्फोटक AN और PA, और जैवअणुओं एडेनिन और एल-ट्रिप्टोफैन का पता लगाने के लिए क्रमशः ~10^{-7}, 10^{-8}, 10^{-10}, और 10^{-7} M डिटेक्टिविटी की ओर लक्षित किया गया। इसके अतिरिक्त, MB डाई अणुओं की निश्चित मात्रा से विस्फोटक AN और PA के विभिन्न सांद्रता का एक साथ पता लगाया गया।

एक अर्थपूर्ण टिप-टू-वैली अनुपात और सतह खुरदरापन प्राप्त करने के लिए स्कैनिंग लाइन अंतराल (पिच), स्कैनिंग गति, और पल्स ऊर्जा जैसे फैब्रिकेशन पैरामीटर के अनुकूलन के माध्यम से सूक्ष्म/नैनो-संरचनाओं के वितरण को नियंत्रित करने के लिए लेजर प्रत्यक्ष लेखन एक शक्तिशाली तकनीक के रूप में उभरा है। अनिसोट्रोपिक (समानांतर रेखाएं) और आइसोट्रोपिक (क्रॉस पैटर्न) चर पिच (100-250 μm) और स्कैनिंग गति (50-300 μm/s) के साथ Sn और Pd सबस्ट्रेट्स पर निर्मित किए गए और अवरक्त समीप (785 nm) और गहरे-पराबैंगनी (266 nm) SERS अनुप्रयोगो के लिए नियोजित किए गए। आइसोट्रोपिक रूप से निर्मित सबस्ट्रेट्स (100 μm/s स्कैनिंग गति और 150 μm पिच) नियमित रूप से तेज शंक्वाकार-आकार की रूपात्मक विशेषताओं को दर्शाते हैं और Au नैनोकणों के निक्षेपण के बाद MB अणुओं के लिए ~10^6 के क्रम की अत्यधिक पुनरुत्पादन योग्य (RSD <10%) तीव्रता वृद्धि प्रदर्शित करते हैं। SnTAu सबस्ट्रेट्स तुलनात्मक रूप से PdTAu सबस्ट्रेट्स की तुलना में उच्च परावर्तन और परिणामस्वरूप उच्च SERS प्रदर्शन MB, DTTCI, PA, AN, एडेनिन और एल-ट्रिप्टोफैन अणुओं के लिए LODs क्रमशः ~0.32 pM, 3.2 fM, 2.93 nM, 0.37 μM, 0.26 nM, and 0.14 μM सांद्रता प्रदर्शित करते हैं। गहरे-पराबैंगनी SERS के प्रदर्शन को Rh नैनोकणों निक्षेपित आइसोट्रॉपिकली टेक्सचर्ड Sn और Pd सबस्ट्रेट्स के साथ 100 μm/s स्कैन स्पीड और 150 μm पिच आकार के साथ समन्वेषित गया। Rh नैनोकणों का कुशल गहरे-पराबैंगनी LSPR रेसोनेन्ट उत्तेजना को समर्थ बनाकर AN और एडेनिन के लिए ~10^5, और PA और थाइमिन अणुओं के लिए ~10^4 EFs का प्रदर्शन करता है। एनालाइट के इलेक्ट्रॉनिक अब्सॉर्प्शन और LSPR के साथ अनुनाद उत्तेजना AN, PA, एडेनिन और थाइमिन अणुओं के लिए क्रमशः ~3.86 nM, 0.46 μM, 46.2 nM, और 0.45 μM तक सांद्रता का पता लगाने की क्षमता प्रदान करती है, और इस प्रकार ट्रेस-डिटेक्शन क्षमताओं का प्रदर्शन करती है। फलतः, NIR और DUV SERS अध्ययनों ने ट्रेस-लेवल मॉलिक्यूलर डिटेक्शन के लिए लेजर टेक्सचर्ड हाइब्रिड सबस्ट्रेट्स की प्रयोज्यता को व्यापक रूप से प्रदर्शित किया है।

CONTENTS

Certificate i
Acknowledgement ii
Abstract iv
Contents x
List of Figures xiv
List of Tables xxii
List of Symbols xxiii
List of Abbreviations xxv

CHAPTER 1: INTRODUCTION 1-26
- 1.1 Plasmonic Properties of Metals 2
- 1.2 Surface-Enhanced Raman Scattering 4
  - 1.2.1 Enhancement Mechanisms 6
  - 1.2.2 Visible-Near Infrared (NIR) Surface-Enhanced Raman Spectroscopy 8
  - 1.2.3 Ultraviolet Surface-Enhanced Raman Spectroscopy (UV-SERS) 16
- 1.3 Classification of SERS Substrates 18
  - 1.3.1 Isotropic Metallic Nanoparticles-based Substrates 18
  - 1.3.2 Anisotropic Metallic Nanoparticles-based Substrates 19
  - 1.3.3 Direct Fabrication of Nanostructures 19
- 1.4 Challenges for Ultrasensitive SERS Detection 20
- 1.5 Motivation and Scope of the Thesis 23
- 1.6 Overview of the Thesis 24

CHAPTER 2: EXPERIMENTAL DETAILS 27-53
- 2.1 Synthesis Techniques 28
  - 2.1.1 Chemical Reduction Method 29
    - 2.1.1.1 Introduction 29
    - 2.1.1.2 Silver Stars (AgSs) 30
    - 2.1.1.3 Silver Nanodendrites (AgNDs) 30
    - 2.1.1.4 Rhodium Nanoparticles (RhNPs) 31
  - 2.1.2 Liquid Assisted Pulsed Laser Ablation (LA-PLA) Method 31
    - 2.1.2.1 Experimental Setup 34
    - 2.1.2.2 Isotropic Mono- and Bi-metallic Nanoparticles Fabrication 36
    - 2.1.2.3 Strategy of Isotropic Core@shell Nanoparticles Fabrication 37
    - 2.1.2.4 Nanosecond (ns)-laser Texturing of Metallic Sn and Pd Substrates 38
  - 2.1.3 Materials 38
- 2.2 Characterization Techniques 40
  - 2.2.1 Morphological and Structural Characterizations 40
    - 2.2.1.1 Field-emission Scanning Electron Microscopy (FESEM) 40
    - 2.2.1.2 High-resolution Transmission Electron Microscopy (HRTEM) 41
    - 2.2.1.3 X-ray Diffraction (XRD) 42
  - 2.2.2 Elemental and Compositional Characterizations 43
    - 2.2.2.1 Energy Dispersive X-Ray Spectroscopy (EDX) 43
    - 2.2.2.2 Selected Area Electron Diffraction (SAED) 43

2.2.3 Optical and Spectroscopic Characterizations 44
    2.2.3.1 UV-Vis-NIR Absorption Spectroscopy 44
    2.2.3.2 Raman Spectroscopy 45
2.3 Surface-Enhanced Raman Spectroscopy (SERS) 48
    2.3.1 SERS Substrate Preparation 48
    2.3.2 Raman Intensity Enhancement Factor (EF) and Limit-of-detection (LOD) 50
    2.3.3 Analyte Molecules of Interest 52

CHAPTER 3: THEORETICAL AND SIMULATION DETAILS 54-87
3.1 Density Functional Theory (DFT) Calculations 54
    3.1.1 Theoretical Background: Density Functional Theory (DFT) 55
    3.1.2 Computational Details 61
    3.1.3 Ground-state Molecular Geometry Optimization and Vibrational Calculations 63
        3.1.3.1 Organic Dye Molecules – RhB, MB, and DTTCI 63
        3.1.3.2 Pesticide Molecules – Thiram, Phosmet, and HCB 64
        3.1.3.3 Explosive Molecules – 2,4-DNT, PNBA, PA, and AN 66
        3.1.3.4 Biomolecules – Adenine, Thymine, and L-tryptophan 69
3.2 COMSOL Simulations 70
    3.2.1 Theoretical Background: Electromagnetic Frequency Domain 71
    3.2.2 Simulation Details 72
    3.2.3 Optical Properties of Isotropic Nanoparticles 73
        3.2.3.1 Isotropic Monometallic (Au, Pd, Rh, Cu, Sn, In) Nanoparticles 73
        3.2.3.2 Isotropic Bimetallic Core@Shell Pd@Au and Au@TM (TM = Pd, Rh, Cu, Sn, In) Nanoparticles 76
    3.2.4 Near-field Enhancements 79
        3.2.4.1 Isotropic Monometallic (Au, Pd, Rh, Cu, Sn, In) Nanoparticles 79
        3.2.4.2 Isotropic Bimetallic Core@Shell Pd@Au and Au@TM (TM = Pd, Rh, Cu, Sn, In) Nanoparticles 82
3.3 Conclusion 86

CHAPTER 4: FABRICATION AND NIR-SERS STUDY OF HIGHLY-BRANCHED SILVER NANOSTRUCTURES 88-125
4.1 Growth of Silver Stars (AgSs) 89
    4.1.1 Effect of Molar ratio 89
    4.1.2 LSPR Response of AgSs 92
    4.1.3 Time-dependent Growth Mechanism 93
4.2 Growth of Silver Nanodendrites (AgNDs) 94
    4.2.1 Effect of Molar ratio 95
    4.2.2 LSPR Response of AgNDs 97
    4.2.3 Time-dependent Growth Mechanism 98
4.3 Near-Infrared (NIR) SERS for Chemical Sensing 100
    4.3.1 Fabrication of SERS Substrates 100
    4.3.2 SERS Performance of AgSs 101
        4.3.2.1 Detection of Dye Molecules 102
        4.3.2.2 Detection of Pesticide Molecules 104

4.3.3 SERS Performance of AgNDs 107
    4.3.3.1 Detection of Dye Molecules 108
    4.3.3.2 Detection of Pesticide Molecules 110
    4.3.3.3 Detection of Explosive Molecules 111
4.3.4 SERS Signal Uniformity and Repeatability 113
4.3.5 Comparative SERS Performance of AgSs and AgNDs 116
4.3.6 Effect of Morphology of Silver Nanostructures on SERS Performance 117
4.3.7 Multiplexed Analyte Detection 119
4.3.8 Real-life Analyte Detection 123
4.4 Conclusion 124

CHAPTER 5: FABRICATION OF METAL NANOPARTICLES BY LA-PLA FOR SERS-BASED DETECTION OF MULTIPLE ANALYTES 126-162
5.1 Isotropic Monometallic Nanoparticles 127
  5.1.1 Growth of Au Nanoparticles 127
    5.1.1.1 Plasmon Response of Au Nanoparticles 128
  5.1.2 Growth of Pd Nanoparticles 129
    5.1.2.1 Plasmon Response of Pd Nanoparticles 129
5.2 Isotropic Bimetallic AuPd and PdAu Nanoparticles 130
  5.2.1 Fabrication of Bimetallic Nanoparticles 130
  5.2.2 Plasmon Response of Bimetallic Nanoparticles 132
5.3 Isotropic Bimetallic Core@Shell Pd@Au and Au@TM (TM = Pd, Rh, In, Sn, Cu) Nanoparticles 132
  5.3.1 Fabrication of Core@shell Nanoparticles 132
  5.3.2 Plasmon Response of Core@shell Nanoparticles 135
5.4 Isotropic Mono- and Bi-metallic Nanoparticles for Chemical Sensing 138
  5.4.1 Fabrication of SERS Substrates 138
  5.4.2 SERS Activity of Mono- and Bi-metallic Nanoparticles 138
    5.4.2.1 Evaluation of SERS Performance 138
    5.4.2.2 Detection of Explosive Molecules 144
    5.4.2.3 Detection of Biomolecules 151
  5.4.3 SERS Signal Uniformity and Reproducibility 154
  5.4.4 Calculations of EFs and LODs 157
  5.4.5 Comparative SERS Performance of Mono- and Bi-metallic Nanoparticles 158
  5.4.6 Multiple and Multiplexed Analyte Detection 159
5.5 Conclusion 161

CHAPTER 6: FABRICATION OF TEXTURED METALLIC SURFACES USING NANO-SECOND LASER PULSES FOR NIR AND DUV-SERS 163-194
6.1 Laser-textured Sn Substrates 164
  6.1.1 Anisotropically-textured Sn Substrates 164
  6.1.2 Isotropically-textured Sn Substrates 166
6.2 Laser-textured Pd Substrates 169
  6.2.1 Anisotropically-textured Pd Substrates 170

6.2.2 Isotropically-textured Pd Substrates 171
6.3 Laser-textured Sn and Pd Substrates for NIR-SERS Detection 171
6.3.1 Fabrication of SERS Substrates 171
6.3.2 SERS Activity of Laser-textured Sn and Pd substrates 174
6.3.2.1 Evaluation of SERS Performance 174
6.3.2.2 Detection of Dye Molecules 175
6.3.2.3 Detection of Explosive Molecules 180
6.3.2.4 Detection of Biomolecules 181
6.3.3 SERS Signal Uniformity and Reproducibility 184
6.3.4 Comparative SERS Performance of Laser-textured Sn and Pd Substrates 185
6.4 Laser-textured Sn and Pd Substrates for DUV-SERS Detection 186
6.4.1 Fabrication of SERS Substrates 186
6.4.2 SERS Activity of Laser-textured Sn and Pd substrates 188
6.4.2.1 Detection of Biomolecules 188
6.4.2.2 Detection of Explosive Molecules 190
6.4.3 Comparative SERS Performance of Laser-textured Sn and Pd Substrates 192
6.5 Conclusion 193

CHAPTER 7: SUMMARY AND FUTURE PERSPECTIVE 195-199
7.1 Summary 195
7.2 Future Scope 198

REFERENCES 200
APPENDIX xxvii
LIST OF PUBLICATIONS xl
BIO-DATA OF THE AUTHOR xlii

LIST OF FIGURES

Figure 1.1 Schematic diagram illustrating the (a) surface plasmons (SPs) and (b) localized surface plasmons (LSPs). 2

Figure 1.2 The wavelength-dependent dielectric functions of different s- (yellow), transition (blue), and sp- (red) metals [solid and dashed lines represent the real $\varepsilon_1(\omega)$ and imaginary parts $\varepsilon_2(\omega)$, respectively]. 4

Figure 1.3 Schematic illustrations of the (a) electromagnetic (EM) and (b) chemical (CM) enhancement mechanisms contributing to SERS. 5

Figure 1.4 (a) Morphology of chemically synthesized silver stars, (b) SERS spectra of probenecid with silver stars, and (c) SERS spectra of crystal violet and fabrication of 3D forest-like dendritic micro/nanostructures. 10

Figure 1.5 (a) Schematic illustration for the fabrication of core@shell NPs via single-step laser ablation, (b) isotropic ultrathin tin-oxide shell wrapped Au@SnO_2 core@shell NPs, and (c) SERS spectra of organic phosphor molecule with core@shell NPs. 14

Figure 1.6 (a) Schematic illustration and SEM image of textured silicon surface and (b) concentration-dependent SERS spectra of rhodamine 6G dye; and (c) photograph, (d) laser microscopy image, and (e) SEM image of textured platinum surface; and (f) microscopy image, (g) SEM image, and (h) SERS spectra of 4-methylbenzenethiol molecules with textured silicon substrates. 15

Figure 1.7 (a) Schematic showing the process for the fabrication of gold triangular nanoprisms based on flexible SERS substrates, (b) schematic illustration of detection process and SERS spectra of benzenethiol molecules. 22

Figure 2.1 Flow diagram illustrating the experimental methodology employed. 28

Figure 2.2 Schematics showing the chemical reduction synthesis of (a) AgSs, (b) AgNDs, and (c) RhNPs. 29

Figure 2.3 Schematic showing the generation of NPs by nanosecond LA-PLA method: (a) irradiation with the front part of the laser pulse, (b) formation and expansion of the plasma plume, (c) different types of chemical reactions between plasma plume and surrounding environment, and (d) condensation and nanoparticle generation. 32

Figure 2.4 Schematic diagram illustrating the experimental laser ablation setup for (a) nanoparticle synthesis and (b) surface texturing. 35

Figure 2.5 Schematic illustration for the fabrication of bimetallic core@shell NPs using (a) sequential laser ablation method, (b) Single-step laser ablation method, and (c) the mechanism of the formation of the ultrathin shell through electrostatic self-assembly. 36

Figure 2.6 Schematic block diagrams of (a) Field Emission Scanning Electron Microscope (FESEM) and (b) High-resolution Transmission Electron Microscope (HRTEM). 40

Figure 2.7 Schematic diagram of Glancing-angle X-ray diffractometer (GAXRD). 42

Figure 2.8 Schematic diagram illustrating the optical path and components of UV-Vis absorption spectrometer. 45

Figure 2.9 Schematic diagram of a Raman Spectrometer used for Raman measurements. 47

Figure 2.10 Flowchart illustrating the fabrication procedure of SERS substrates. 49
Figure 2.11 Ground-state molecular structures of the different molecules. 51
Figure 3.1 DFT-optimized ground-state molecular structures of different analytes (a) organic dyes, (b) pesticides, (c) explosives, and (d) biomolecules. 60
Figure 3.2 The comparative DFT-calculated and normal Raman spectra of (a) RhB, (b) MB, and (c) DTTCI molecules. 62
Figure 3.3 The comparative DFT-calculated and normal Raman spectra of (a) thiram, (b) phosmet, and (c) HCB molecules. 65
Figure 3.4 The comparative DFT-calculated and normal Raman spectra of (a) 2,4-DNT, (b) PNBA, (c) PA, and (d) AN molecules. 67
Figure 3.5 The comparative DFT-calculated and normal Raman spectra of (a) adenine, (b) thymine, and (c) l-tryptophan molecules. 69
Figure 3.6 Calculated size-dependent extinction spectra of isotropic monometallic (a) Au, (b) Pd, (c) Rh, (d) Cu, (e) Sn, and (f) In NPs in the water medium. 75
Figure 3.7 Calculated extinction spectra of isotropic core@shell (a), (b) Pd@Au, (c), (d) Au@Pd, and (e), (f) Au@Rh NPs in the water medium. 77
Figure 3.8 Calculated extinction spectra of isotropic core@shell (a), (b) Au@Cu, (c), (d) Au@Sn, and (e), (f) Au@In NPs in the water medium. 78
Figure 3.9 Size-dependent relative electric field along X-axis for isotropic (a) Au, (b) Pd, (c) Rh, (d) Cu, (e) Sn, and (f) In NPs in the water medium under 785 nm excitation wavelength. 80
Figure 3.10 Electric-field contours for different sizes of isotropic (a) Au, (b) Pd, (c) Rh, (d) Cu, (e) Sn, and (f) In NPs in the water medium under 785 nm excitation wavelength. 81
Figure 3.11 Size-dependent relative electric field along X-axis for isotropic core@shell (a), (b) Pd@Au, (c), (d) Au@Pd, and (e), (f) Au@Rh NPs in the water medium under 785 nm excitation wavelength. 83
Figure 3.12 Size-dependent relative electric field along X-axis for isotropic core@shell (a), (b) Au@Cu, (c), (d) Au@Sn, and (e), (f) Au@In NPs in the water medium under 785 nm excitation wavelength. 84
Figure 3.13 Electric-field contours for different sizes of isotropic (a) Pd@Au, (b) Au@Pd, (c) Au@Rh, (d) Au@Cu, (e) Au@Sn, and (f) Au@In NPs; and core-sizes of (g) 30 nm and (h) 40 nm in the water medium under 785 nm excitation wavelength. 85
Figure 4.1 Schematic illustration of the NIR SERS study with multi-branched silver nanostructures (AgNSts). 88
Figure 4.2 SEM images of (a)-(g) the series of AgSs (from AgSsI to AgSsVII) samples, (h) SERS substrate, (i) UV-Vis-NIR spectra of the series of AgSs samples (under different reaction parameters, as listed in Table 4.1, and (j)-(m) SEM images for the growth mechanism of AgSsVI at different reaction times: (j) <10 s, (k) ~30 s, (l) ~1 min, and (m) ~5 min (longer times) fabricated by chemical reduction method. SEM images from 1(a)-(g) and 1(j)-(m) have the same scale bars. 91
Figure 4.3 SEM image of (a) AgSsVI, (b) individual branch at high magnification and (c) individual AgSsVI; (d) XRD pattern, and (e) EDX spectrum. 94

Figure 4.4 SEM images of (a)-(g) the series of AgNDs (from AgNDsI to AgNDsVII) samples, (h) SERS substrate, (i) UV-Vis-NIR spectra of the series of AgNDs samples (under different reaction parameters, as listed in Table 4.2, and (j)-(m) SEM images for the growth mechanism of AgNDsVI at different reaction times: (j) <10 s, (k) ~30 s, (l) ~1 min, and (m) ~5 min (longer times) fabricated by chemical reduction method. SEM images from (a)-(g) and (j)-(m) have the same scale bar. 96

Figure 4.5 SEM image of (a), (b) AgNDsVI, (c) individual AgNDsVI, and (d) individual branch at high magnification; and (e), (f) HRTEM images (g) XRD pattern, and (h) EDX spectrum. 98

Figure 4.6 Schematic illustration of the fabrication of AgNSt-based SERS substrates. 100

Figure 4.7 (a) The SERS spectra of 1 nM MB molecules with the series of AgSs (from AgSsI to AgSsVII)-based substrates and (b) variation of SERS intensity at 1625 cm^{-1} MB peak. Error bars are derived from the standard deviation values for five identical measurements for AgSs sample. 101

Figure 4.8 The comparative SERS, normal Raman, and DFT calculated spectra of (a) MB, and (d) RhB molecules; the concentration-dependent SERS spectra with AgS-based substrates of (b) MB, and (e) RhB molecules; and calibration curves of (c) MB, and (f) RhB molecules under 785-nm laser excitation wavelength. Error bars represent the standard deviation of five different measurements under similar experimental conditions. 104

Figure 4.9 The comparative SERS, normal Raman, and DFT calculated spectra of (a) thiram and (d) phosmet molecules; the concentration-dependent SERS spectra with AgS-based substrates of (b) thiram, and (e) phosmet molecules; and calibration curves of (c) thiram, and (f) phosmet molecules under 785-nm laser excitation wavelength. Error bars represent the standard deviation of five different measurements under similar experimental conditions. 106

Figure 4.10 Representation of the adsorption mechanism of DMDTC on the Ag surface. 106

Figure 4.11 (a) The SERS spectra of 1 nM MB molecules with the series of AgNDs (from AgNDsI to AgNDsVII)-based substrates and (b) variation of SERS intensity at 1623 cm^{-1} MB peak. Error bars are derived from the standard deviation values for five identical measurements for the AgSs sample. 107

Figure 4.12 The comparative SERS, normal Raman, and DFT calculated spectra of (a) MB and (d) RhB molecules; the concentration-dependent SERS spectra with AgNDsVI-based substrates of (b) MB, and (e) RhB molecules; and calibration curves of (c) MB, and (f) RhB molecules under 785-nm laser excitation wavelength. Error bars represent the standard deviation of five different measurements under similar experimental conditions. 108

Figure 4.13 The comparative SERS, normal Raman, and DFT calculated spectra of (a) thiram and (d) phosmet molecules; the concentration-dependent SERS spectra with AgNDsVI-based substrates of (b) thiram and (e) phosmet molecules; and calibration curves of (c) thiram and (f) phosmet molecules under 785-nm laser excitation wavelength. Error bars represent the standard deviation of five different measurements under similar experimental conditions. 110

Figure 4.14	The comparative SERS, normal Raman, and DFT calculated spectra of (a) 2,4-DNT, (d) PNBA, and (g) PA molecules; the concentration-dependent SERS spectra with AgND-based substrates of (b) 2,4-DNT, (e) PNBA and (h) PA molecules; and calibration curves of (c) 2,4-DNT, (f) PNBA and (i) PA molecules under 785-nm laser excitation wavelength. Error bars represent the standard deviation of five different measurements under similar experimental conditions.	112
Figure 4.15	SERS uniformity spectra of 1 nM thiram molecules from ten random spots of the silicon-supported AgSsVI-based SERS (a) substrate 1, (b) substrate 2, and 1 pM concentration (c) substrate 3, and (d) substrate 4 measured under 785 nm excitation wavelength.	114
Figure 4.16	SERS uniformity spectra of 1 nM thiram molecules from ten random spots of the silicon-supported AgNDsVI-based SERS (a) substrate 1, (b) substrate 2, and 1 pM concentration (c) substrate 3, and (d) substrate 4 measured under 785 nm excitation wavelength.	115
Figure 4.17	(a) Comparative SERS intensity and (b) intensity enhancement factors (EFs) of different analyte (MB, RhB, thiram, and phosmet) molecules with AgS- and AgND-based SERS substrates. Error bars represent the standard deviation of five different measurements under similar experimental conditions.	116
Figure 4.18	Schematic illustration of the formation of hot spots (a) stars and the dendritic nanostructures with (b) larger intra-branch separations and (c) relatively smaller intra-branch separations.	118
Figure 4.19	Multiplexed SERS spectra of analytes RhB, MB, thiram, and phosmet molecule with silicon-supported (a) AgSsVI and (b) AgNDsVI-based SERS substrates under 785 nm excitation wavelength. The multiplexed SERS spectra with different concentration combinations are given as: (i) RhB (5 μM), (ii) MB (5 nM), (iii) thiram (5 nM), (iv) phosmet (5 μM), (v) RhB (5 μM) + MB (5 nM), (vi) RhB (5 μM) + thiram (5 nM), (vii) MB (5 nM) + phosmet (5 μM), (viii) RhB (5 μM) + MB (5 nM) + thiram (5 nM), (ix) RhB (5 μM) + MB (5 nM) + phosmet (5 μM), and (x) RhB (5 μM) + MB (5 nM) + thiram (5 nM) + phosmet (5 μM).	120
Figure 4.20	Multiplexed SERS spectra of explosive (a) 2,4-DNT, (b) PNBA, and (c) PA molecules with AgNDsVI-based substrates under 785-nm excitation wavelength. The multiplexed SERS spectra with different concentration combinations are defined as: M1 (MB [1 nM] + explosive [1 μM]), M2 (MB [1 nM] + explosive [0.1 μM]), and M3 (MB [1 nM] + explosive [1 nM]).	121
Figure 4.21	Relative intensity from multiplexed SERS spectra of 2,4-DNT, PNBA, and PA molecules with AgNDsVI-based substrates under 785 nm excitation.	122
Figure 4.22	SERS spectra of thiram molecules (1 nM) (a) spiked with diluted (100 ×) apple juice, (b) flexible ITO-PET films, and (c) RhB in chili powder with solid silicon-supported AgNDsVI-based SERS substrates under 785 nm excitation wavelength.	124
Figure 5.1	(a) Schematic diagram for the fabrication of monometallic and bimetallic NPs using liquid-assisted pulsed laser ablation (LA-PLA) and (b)	126

schematic illustration for the fabrication of core@shell NPs via single-step laser ablation.

Figure 5.2 (a1) and (a3) HRTEM images, (a2) size-distribution histograms, and (a4) UV-Vis absorption spectra of the monometallic AuNPs; and (b1) and (b3) HRTEM images, (b2) size-distribution histograms, and (b4) UV-Vis absorption spectra of the monometallic PdNPs. 128

Figure 5.3 (a1), (a3) and (a4) HRTEM images, (a2) size-distribution histograms, and (a5) EDX spectrum of the bimetallic AuPdNPs; and (b1), (b3) and (b4) HRTEM images, (b2) size-distribution histograms, and (b5) EDX spectrum of the bimetallic PdAuNPs. 131

Figure 5.4 UV-Vis spectra of bimetallic (a) AuPdNPs and (b) PdAuNPs prepared with different laser fluences. 132

Figure 5.5 (a1), (a3) and (a4) HRTEM images, (a2) size-distribution histograms, and (a5) EDX spectrum of the bimetallic Pd@AuNPs; and (b1), (b3) and (b4) HRTEM images, (b2) size-distribution histograms, and (b5) EDX spectrum of the bimetallic Au@PdNPs. 133

Figure 5.6 (a1), (a3) and (a4) HRTEM images, (a2) size-distribution histograms, and (a5) EDX spectrum of the bimetallic Au@RhNPs; (b1), (b3) and (b4) HRTEM images, (b2) size-distribution histograms, and (b5) EDX spectrum of the bimetallic Au@CuNPs; (c1), (c3) and (c4) HRTEM images, (c2) size-distribution histograms, and (c5) EDX spectrum of the bimetallic Au@SnNPs; and (d1), (d3) and (d4) HRTEM images, (d2) size-distribution histograms, and (d5) EDX spectrum of the bimetallic Au@InNPs. 134

Figure 5.7 Experimental UV-Vis absorption spectra of bimetallic (a) Pd@Au, (b) Au@Pd, (c) Au@Rh, (d) Au@Cu, (e) Au@Sn, and (f) Au@In core@shell NPs; and the COMSOL simulated extinction spectra of (g) monometallic, (h) and (i) bimetallic core@shell NPs. 137

Figure 5.8 (a) Comparative Raman spectra, (b) comparative SERS intensities, and the concentration-dependent SERS spectra of MB molecules with LA-PLA fabricated (c) Au, (d) Pd, (e) AuPd, (f) PdAu, (g) Pd@Au, and (h) Au@Pd, (i) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 139

Figure 5.9 Calibrated SERS intensity of the maximum enhanced Raman peak (~446 cm^{-1}) of MB molecules with (a) Au, (b) Pd, (c) AuPd, (d) PdAu, (e) Pd@Au, and (f) Au@Pd, (g) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 141

Figure 5.10 (a) Comparative Raman spectra, (b) comparative SERS intensities, and the concentration-dependent SERS spectra of AN molecules with LA-PLA fabricated (c) Au, (d) Pd, (e) AuPd, (f) PdAu, (g) Pd@Au, and (h) Au@Pd, (i) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 145

Figure 5.11 (a) Comparative Raman spectra, (b) comparative SERS intensities, and the concentration-dependent SERS spectra of PA molecules with LA-PLA fabricated (c) Au, (d) Pd, (e) AuPd, (f) PdAu, (g) Pd@Au, and (h) Au@Pd, (i) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 147

Figure 5.12 Calibrated SERS intensity of the maximum enhanced Raman peak (~1043 cm^{-1}) of AN molecules with (a) Au, (b) Pd, (c) AuPd, (d) PdAu, (e) Pd@Au, and (f) Au@Pd, (g) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 149

Figure 5.13 Calibrated SERS intensity of the maximum enhanced Raman peak (~1337 cm^{-1}) of PA molecules with (a) Au, (b) Pd, (c) AuPd, (d) PdAu, (e) Pd@Au, and (f) Au@Pd, (g) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 150

Figure 5.14 Comparative Raman Spectra of (a) adenine, and (b) l-tryptophan molecules; concentration-dependent SERS spectra of (c) adenine, and (d) l-tryptophan molecules; and calibrated SERS intensity of (e) adenine, and (f) l-tryptophan molecules under 785 nm excitation wavelength. 152

Figure 5.15 Reproducibility SERS spectra of the 5 μM MB molecules recorded from 20 random detection sites of (a) Au, (b) Pd, (c) AuPd, (d) PdAu, (e) Pd@Au, and (f) Au@Pd, (g) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 153

Figure 5.16 Intensity bar graphs from uniformity SERS spectra of the 5 μM MB molecules Raman bands at 446, 1391, and 1620 cm^{-1} recorded from 20 random detection sites of LA-PLA fabricated (a) Au, (b) Pd, (c) AuPd, (d) PdAu, (e) Pd@Au, and (f) Au@Pd, (g) Au@Rh, (j) Au@Cu, (k) Au@Sn, and (l) Au@In NPs-based substrates under 785 nm excitation wavelength. 155

Figure 5.17 (a) RSD values for MB molecules with different monometallic and bimetallic NPs-based substrates, and (b) RSD values of MB molecules from 4 different batches of Au@CuNPs based substrates under 785 nm excitation wavelength. 157

Figure 5.18 (a) Comparative SERS intensity of MB, AN, and PA molecules, (b) Comparative EFs of AN (1043 cm^{-1}) and PA (1337 cm^{-1}) molecules, and (c) computed relative electric-field enhancements along the diameter of NPs under 785 nm excitation wavelength. 157

Figure 5.19 (a) SERS spectra of different analytes, and multiplexed SERS spectra of (b) AN+MB, and (c) PA+MB molecules with Au@CuNPs based substrates under 785 nm excitation wavelength. 160

Figure 5.20 Relative intensity variation from multiplexed SERS spectra of AN and PA molecules with Au@PdNPs based substrates, under 785 nm excitation wavelength. 161

Figure 6.1 Schematic illustration for the (a) NIR and DUV SERS measurements employing laser-textured substrates and (b) dynamics for the generation of micro/nano-structures. 163

Figure 6.2 FESEM images with different magnifications of the anisotropically laser-textured bare Sn substrates (SnTB) with 100 μm/s scanning speed and (a) 100 μm (A1), (b) 150 μm (A2), (c) 200 μm (A3), and (d) 250 μm (A4) pitch size. 166

Figure 6.3 FESEM images with different magnifications of the isotropically laser-textured bare Sn substrates (SnTB) with 100 μm/s scanning speed and (a) 100 μm (I1), (b) 150 μm (I2), (c) 200 μm (I3), and (d) 250 μm (I4) pitch size. 167

Figure 6.4 FESEM images of the laser-textured micro/nano-substrates (SnTB-I2) with 150 μm pitch size and different laser scanning speeds of (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 μm/s. 168

Figure 6.5 FESEM images of the laser-textured bare Pd substrates (PdTB) with 100 μm/s scanning speed and (a) ~3 mJ (single-scanning), (b) ~10 mJ (single-scanning), and (c) ~10 mJ (double-scanning) laser pulse energy. 169

Figure 6.6 FESEM images with different magnifications of the anisotropically laser-textured bare Pd substrates (PdTB) with 100 μm/s scanning speed and (a) 100 μm (A1), (b) 150 μm (A2), (c) 200 μm (A3), and (d) 250 μm (A4) pitch size. 170

Figure 6.7 FESEM images with different magnifications of the isotropically laser-textured bare Pd substrates (PdTB) with 100 μm/s scanning speed and (a) 100 μm (I1), (b) 150 μm (I2), (c) 200 μm (I3), and (d) 250 μm (I4) pitch size. 171

Figure 6.8 (a) HRTEM and size-distribution histogram and (b) UV-Vis absorption spectrum of laser-ablation generated AuNPs. 172

Figure 6.9 EDX mapping analysis of SnTAu substrate (a) EDX spectrum, (b) corresponding FESEM image, (c) layered overall mapped image, including elemental (d) tin (Sn), (e) gold (Au), and (f) oxygen (O). 172

Figure 6.10 EDX mapping analysis of PdTAu substrate (a) EDX spectrum, (b) corresponding FESEM image, (c) layered overall mapped image, including elemental (d) palladium (Pd), (e) gold (Au), and (f) oxygen (O). 173

Figure 6.11 Comparative SERS performance of 5 μM MB molecules with laser-textured (a) SnTB, (b) SnTAu, (c) PdTB, and (d) PdTAu substrates under NIR (785 nm) excitation wavelength (Insets in Figures (a) and (c) show the photographs of textured substrates). 175

Figure 6.12 Comparative Raman spectra of (a) MB and (b) DTTCI, concentration-dependent SERS spectra of (c) MB and (d) DTTCI, and calibrated SERS intensity of (e) MB and (f) DTTCI with SnTAu-I2 substrates, concentration-dependent SERS spectra of (g) MB and (h) DTTCI and calibrated SERS intensity of (i) MB and (j) DTTCI with PdTAu-I2 substrates under NIR (785 nm) excitation wavelength. 176

Figure 6.13 Comparative Raman spectra of (a) PA and (b) AN, concentration-dependent SERS spectra of (c) PA and (d) AN, and calibrated SERS intensity of (e) PA and (f) AN with SnTAu-I2 substrates, concentration-dependent SERS spectra of (g) PA and (h) AN and calibrated SERS intensity of (i) PA and (j) AN with PdTAu-I2 substrates under NIR (785 nm) excitation wavelength. 179

Figure 6.14 Comparative Raman spectra of (a) adenine and (b) L-tryp, concentration-dependent SERS spectra of (c) adenine and (d) L-tryp and calibrated SERS intensity of (e) adenine and (f) L-tryp with SnTAu-I2 substrates, concentration-dependent SERS spectra of (g) adenine and (h) L-tryp and calibrated SERS intensity of (i) adenine and (j) L-tryp with PdTAu-I2 substrates under NIR (785 nm) excitation wavelength. 182

Figure 6.15 Intensity bar graphs from uniformity SERS spectra of the 5 μM MB molecules Raman bands at 444, 1391, and 1620 cm^{-1} recorded from 20 184 random detection sites of SnTAu-I2 (a) Substrate_1 and (b) Substares_2 under NIR (785 nm) excitation wavelength.

Figure 6.16 Comparative SERS intensity of 5 μM MB molecules Raman bands at 444, 1391, and 1620 cm^{-1} with (a) anisotropically and (b) isotropically textured Sn (SnTAu) and Pd (PdTAu) substrates under NIR (785 nm) excitation wavelength. 185

Figure 6.17 (a), (b), and (c) HRTEM images, and (d) UV-Vis absorption spectra and size-distribution histogram of Rh nano-aggregates. 186

Figure 6.18 EDX mapping analysis of SnTRh substrate (a) EDX spectrum, (b) corresponding FESEM image, (c) layered overall mapped image, including elemental (d) tin (Sn), (e) rhodium (Rh), and (f) oxygen (O). 187

Figure 6.19 Comparative Raman spectra of (a) adenine and (b) thymine, concentration-dependent SERS spectra of (c) adenine and (d) thymine, and calibrated SERS intensity of (e) adenine and (f) thymine with SnTRh-I2 substrates under DUV (266 nm) excitation wavelength. 189

Figure 6.20 Comparative Raman spectra of (a) AN and (b) PA, concentration-dependent SERS spectra of (c) AN and (d) PA, and calibrated SERS intensity of (e) AN and (f) PA with SnTRh-I2 substrates under DUV (266 nm) excitation wavelength. 191

Figure 6.21 Comparative SERS intensity of 5 μM analyte (AN, PA, adenine, and thymine) molecules with (a) bare and (b) RhNPs deposited laser-textured Sn and Pd substrates under DUV (266 nm) excitation wavelength. 193

LIST OF TABLES

Table 1.1 SERS performance of different anisotropically branched silver nanostructures. 12

Table 2.1 Specifications of materials and chemical reagents. 38

Table 4.1 The overall concentrations of the chemical reagents and the average sizes of the series of AgSs fabricated by the chemical reduction method. 89

Table 4.2 The overall concentrations of the chemical reagents and the average sizes of the series of AgNDs fabricated by the chemical reduction method. 95

Table 4.3 The computed EFs for prominent Raman peaks of MB, RhB, thiram, and phosmet molecules with AgS-based SERS substrates under 785 nm excitation wavelength. 102

Table 4.4 The computed EFs for prominent Raman peaks of MB, RhB, thiram, and phosmet molecules with AgND-based SERS substrates under 785 nm excitation wavelength. 109

Table 4.5 The computed EFs for prominent Raman peaks of 2,4-DNT, PNBA, and PA molecules with AgND-based SERS substrates under 785 nm excitation wavelength. 113

Table 5.1 The computed EFs for main Raman peaks of MB molecules with monometallic and bimetallic Au-TM NPs based SERS substrates under 785 nm excitation wavelength. 143

Table 5.2 The computed EFs for main Raman peaks of AN molecules with monometallic and bimetallic Au-TM NPs based SERS substrates under 785 nm excitation wavelength. 143

Table 5.3 The computed EFs for main Raman peaks of PA molecules with monometallic and bimetallic Au-TM NPs based SERS substrates under 785 nm excitation. 147

Table 6.1 The computed EFs for main Raman peaks of MB and DTTCI molecules with SnTAu-I2 and PdTAu-I2 based SERS substrates under NIR (785 nm) excitation wavelength. 178

Table 6.2 The computed EFs for main Raman peaks of PA and AN molecules with SnTAu-I2 and PdTAu-I2 based SERS substrates under NIR (785 nm) excitation wavelength. 181

Table 6.3 The computed EFs for main Raman peaks of adenine and L-tryp molecules with SnTAu-I2 and PdTAu-I2 based SERS substrates under NIR (785 nm) excitation wavelength. 183

Table 6.4 The computed EFs for main Raman peaks of adenine and thymine molecules with SnTAu-I2 SERS substrates under DUV (266 nm) excitation wavelength. 190

Table 6.5 The computed EFs for main Raman peaks of AN and PA molecules with SnTAu-I2 SERS substrates under DUV (266 nm) excitation wavelength. 192

LIST OF SYMBOLS

$\varepsilon(\omega)$	Complex dielectric constant of metal
λ	Wavelength
ω	Incident angular frequency
ε_∞	Dielectric function
ε_o	Permittivity of free space
ω_p	Bulk plasmon frequency
γ	Damping factor
τ	Relaxation time of the free electron gas
$\varepsilon_1(\omega)$	Real part of the wavelength-dependent dielectric function
$\varepsilon_2(\omega)$	Imaginary part of the wavelength-dependent dielectric function
n	Free electron density
e	Charge of electrons
m	Effective mass of electrons
λ_L	Incident Wavelength
λ_R	Raman-shifted wavelength
E^I	Amplitudes of the incident field
E^{Loc}	Amplitude of the local field
M_1	Incident electric-field intensity enhancement
M_2	Scattered electric-field intensity enhancement
M^{n+}	Metal ions
M^0	Metal atoms
I_0	Intensity of incident light
I	Intensity of transmitted light through reference sample
$A(\lambda)$	Absorbance
l	Optical path length
$\epsilon(\lambda)$	Solute's molar absorbtivity
C	Concentration of metal nanoparticles
T	Transmittance
c	Velocity of light in vacuum
ρ	Incident polarization direction
σ	Scattered polarization direction
α_{mn}	Polarizability tensor
h	Plank's constant
ψ_m	Vibronic wave function of the initial ground state (m)
ψ_n	Vibronic wave function of the final ground state (n)
ψ_r	Vibronic wave function of the excited electronic state (r)
ν_0	frequency of incident light
I_{SERS}	Intensity of the prominent band in the SERS spectrum
I_{Ref}	Intensity of the corresponding band in the reference Raman spectrum
N_{SERS}	Average number of molecules in the scattering volume on SERS substrate
N_{Ref}	Average number of molecules in the scattering volume on reference substrate
NA	Avogadro number

V	Analyte volume deposited over the substrate
A_0	Laser spot area
A	Total area of the substrate
S_{LOD}	Minimum distinguishable signal
S_{BL}	Mean signal generated from blank for a specific Raman band
s_{BL}	Standard deviation of the blank
k	Number of blank measurements
μ_r	Relative permeability
k_0	Wave-vector
ε_m	Relative permittivity of the material
j	Imaginary unit number
σ	Electrical conductivity
E_0	Amplitude of the incident wave
n_m	Refractive index of the surrounding medium
σ_{sca}	Scattering cross-section
σ_{abs}	Absorption cross-section
σ_{ext}	Extinction cross-section
S_{sca}	Poynting vector of the scattered field
S_0	Power density of the incident field
Z_0	Characteristic impedance of the vacuum
Q_h	Total power dissipation density
x	Distance from the nanoparticle surface
M	Molar
mM	Millimolar
µM	Micromolar
nM	Nanomolar
pM	Picomolar
fM	Femtomolar
aM	Attomolar
zM	Zeptomolar

LIST OF ABBREVIATIONS

Ag	Silver
AgNDs	Silver nanodendrites
AgNSts	Silver nanostructures
AgSs	Silver stars
AlFON	Aluminum film-over nanosphere
APTMS	3-Aminopropyltrimethoxysilane
AN	Ammonium nitrate
Au	Gold
CM	Chemical enhancement mechanism
Cu	Copper
CV	Crystal violet
DDA	Discrete Dipole Approximation
DFT	Density functional theory
DI	De-ionised
DMDTC	Dimethyl-dithiocarbamate
DNA	Deoxyribosenucleic acid
DNT	Dinitrotoluene
DTC	Dithiocarbamate
DTTCI	3,3`-Diethylthiatricarbocyanine iodide
DUV	Deep-ultraviolet
EDX	Energy dispersive X-Ray spectroscopy
EF	Enhancement factor
EM	Electromagnetic enhancement mechanism
eV	Electron Volt
FCC	Face-centered cubic
FDTD	Finite difference time domain
FE	field emission
FEM	Finite element method
FESEM	Field-emission scanning electron microscopy
FWHM	Full width at half maxima
GAXRD	Glancing-angle X-ray diffractometer
HCB	Hexachlorobenzene
HRTEM	High-resolution transmission electron microscopy
L-tryp	L-tryptophan
LA-PLA	Liquid-assisted pulsed laser ablation
LOD	Limit-of-detection or detectability
LSP	Localized surface plasmon
LSPR	Localized surface plasmon resonance
IEDs	Improvised explosive devices
In	Indium
ITO	Indium tin oxide
JCPDS	Joint Committee on Powder Diffraction Standards
MB	Methylene blue
NA	Numerical Aperture

NCs	Nanocubes
NDs	Nanodendrites
NFs	Nanoflowers
NIR	Near-infrared
NPs	Nanoparticles
NRs	Nanorods
NSs	Nanostars
NTs	Nanotriangles
NWs	Nanowires
ns	Nanosecond
PA	Picric acid
PATP	p-aminothiophenol
Pd	Palladium
PDMS	Polydimethylsiloxane
PET	Polyethylene terephthalate
PLA	Pulsed laser ablation
PML	Perfectly matched layer
PNBA	p-Nitrobenzoic acid
PVP	Polyvinylpyrrolidone
R6G	Rhodamine 6G
RF	Radio Frequency
Rh	Rhodium
RhB	Rhodamine B
RhNPs	Rhodium nanoparticles
RR	Resonance Raman
RSD	Relative standard deviation
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy
SERRS	Surface-enhanced resonance Raman spectroscopy
SERS	Surface-enhanced Raman spectroscopy
Sn	Tin
SPPs	Surface plasmon polaritons
SPs	Surface plasmons
SSV	Sphere segment voids
TEM	Transmission electron microscopy
Thy	Thymine
TM	Transition metal
TNT	Trinitrotoluene
UV	Ultraviolet
UV-SERS	Ultraviolet surface-enhanced Raman spectroscopy
XRD	X-ray diffractometer