Surface-Enhanced Raman Spectroscopy for Water Quality Monitoring

Surface-Enhanced Raman Spectroscopy for Water Quality Monitoring

Edited by

Tanuj Kumar, Vinamrita Singh
and Jyoti Malik

Cambridge
Scholars
Publishing

Surface-Enhanced Raman Spectroscopy for Water Quality Monitoring

Edited by Tanuj Kumar, Vinamrita Singh and Jyoti Malik

This book first published 2024

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-1-0364-0861-9
ISBN (Ebook): 978-1-0364-0862-6

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION TO SERS

UDAI BHAN SINGH AND SHIVANI CHAUDHARY

Deen Dayal Upadhyaya Gorakhpur University Gorakhpur, Uttar Pradesh, 273009

Summary

Molecular structures and chemical details may be investigated with unprecedented sensitivity and accuracy using surface-enhanced Raman spectroscopy (SERS), which combines theoretical physics with practical knowledge. Basic concepts and processes, such as electromagnetic enhancement and chemical enhancement, are discussed in this chapter as they pertain to SERS theory. Nanostructured metal surfaces or plasmonic nanoparticles emitting exciting localized surface plasmon resonances (LSPRs) are the basis of the EM enhancement method. High electromagnetic fields, or "hot spots," are created by the resonance phenomena surrounding these structures, which boost Raman scattering signals from neighbouring molecules. Chemical amplification, where charge transfer and molecule interactions with a metal substrate strengthen the Raman signal, is also discussed in this chapter. SERS's sensitivity is greater than that of conventional spectroscopy because of the method's complicated electromagnetic and chemical amplification mechanisms. SERS has a wide range of applications, from analysis in the chemical and materials sciences to studies in medicine and the environment. It demonstrates SERS's future as a powerful analytical tool and its ability to alter these fields.

1.1. Introduction

1.1.1 Historical Background of SERS

The origins of Surface-Enhanced Raman Spectroscopy (SERS) can be traced back to 1928, when Sir C.V. Raman discovered the Raman effect [1, 2]. Raman spectroscopy relies on the inelastic scattering of photons caused by the interaction of incident light with molecules [3, 4]. For the analysis of the vibrational characteristics that molecules exhibit, Raman spectroscopy has become a potent analytical tool. However, in a scenario of a Raman Effect characterized by only a minuscule fraction of dispersed photons undergoing a frequency shift or samples exhibiting feeble light scattering, the obtained signals might prove excessively faint for discernment. For many years, this limitation hindered the practical application of Raman spectroscopy [3, 5].

In the 1970s, it was discovered that when specific molecules were adsorbed onto roughened metal surfaces or nanostructured substrates, their Raman signals could be significantly boosted [5-8]. SERS, or Surface-Enhanced Raman Spectroscopy, has brought about a paradigm shift in numerous scientific domains, encompassing the realms of chemistry, biology, materials science, and environmental monitoring. By enabling the investigation of molecular structures and interactions at the nanoscale, SERS has bestowed upon us invaluable insights. Surface-Enhanced Raman Spectroscopy (SERS) is a sophisticated analytical method that is based on the fundamental concepts of electromagnetic field enhancement and vibrational spectroscopy [5, 6, 9]. The phenomenon under consideration exploits the interplay between input photons and metallic nanostructures, resulting in the emergence of localized surface plasmon resonances that give rise to highly concentrated electromagnetic fields sometimes referred to as "hot spots" [10, 11]. The aforementioned regions of high intensity, located in close proximity to the metal surface at a scale of nanometers, result in a significant increase in the magnitude of Raman scattering signals emitted by molecules in close proximity to the nanostructures [12, 13]. The mathematical description of this phenomenon may be achieved by using Maxwell's equations and the Mie theory. These theoretical frameworks provide insights into the complex relationship among incoming light, plasmonic resonance, and the amplified Raman signal [14]. Surface-enhanced Raman spectroscopy (SERS) not only offers exceptional sensitivity for detecting trace levels of substances, but it also gives a unique capacity to investigate molecular structures [15]. This technique yields a vast amount of valuable information on the chemical composition and conformation of molecules [16]. The extensive use of SERS across several scientific fields, ranging from surface science to biosensing, highlights the significant influence it has had in the arena of contemporary physics and spectroscopy [13, 17].

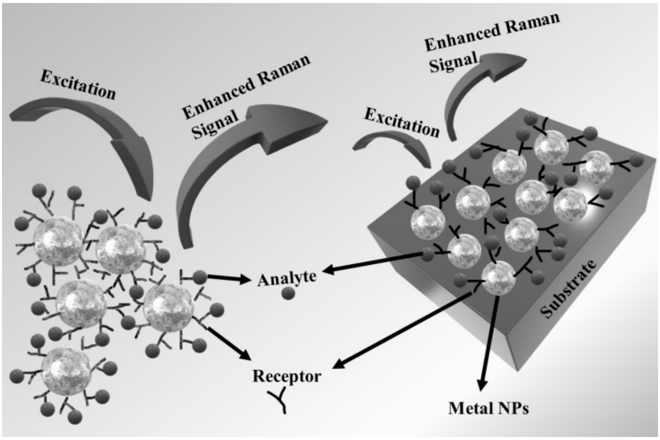

Figure 1: Illustration of Basic Principle of SERS

In this introductory chapter, we will explore the fundamental principles of SERS, its mechanisms, and the significance over other analytical techniques in modern science and technology.

1.2 Basic Principles and Mechanisms

In order to fully comprehend the underlying principles of Surface-Enhanced Raman Spectroscopy (SERS), it becomes imperative to embark upon an exploration within the domain of quantum mechanics. Quantum mechanical frameworks, such as density functional theory (DFT) and time-dependent DFT, offer valuable perspectives into the electronic and vibrational phenomena associated with SERS [18]. These models provide a comprehensive understanding of the alterations in molecular electronic structure and vibrational modes that arise from the intricate interplay between the metal substrate and the intensified electromagnetic fields [19, 20]. Or in other words, it is possible to elucidate the fundamental concept of surface-enhanced Raman spectroscopy (SERS) as follows: Upon illumination with specific wavelengths, noble metal nanoparticles, such as gold or silver, undergo coherent electron oscillations on their surface, resulting in the generation of confined electromagnetic fields. The aforementioned domains, commonly known as surface plasmons, demonstrate remarkable strength in immediate vicinity to the metal's surface and possess the capability to significantly enhance the Raman signals emitted by neighboring molecules. The enhancement effect has the potential to escalate to various levels, thereby making SERS an exceptionally sensitive technique for molecule detection and analysis.At its fundamental essence, SERS is predicated upon the intricate interplay of two mutually dependent enhancement mechanisms: electromagnetic (EM) enhancement and chemical enhancement, which are inherently grounded in the fundamental tenets of condensed matter physics.

1.3 Electromagnetic Enhancement Mechanism

Electromagnetic (EM) amplification, according to theoretical physics, seems to be substance-neutral. In contrast, chemical enhancement (CE) relies on a chemical reaction between the probe and the metal surface [5]. Surface-enhanced Raman scattering (SERS) increases are mostly attributable to the electromagnetic (EM) enhancement process, which is induced by the roughness of noble metal surfaces [21]. The nanostructure may be produced by either modifying the substrate or depositing nanoparticles of a noble metal. The 10-100 nm size of metal nanoparticles is responsible for their interaction with excitation light. The tiny dimensions of the metal nanoparticles give rise to distinctive evidence of light-induced electric polarization, which is uniquely accessible to their surface electrons [22]. The surface plasma oscillations, also known as collective oscillations, arise from the interaction between the electrons and the alternating electric field of the incident light wave. At a specific frequency, the plasmon oscillations exhibit resonance with electromagnetic radiation, thereby resulting in an amplification of the electric field intensity and an augmentation of the Raman scattering originating from the molecules that are affixed to the nanostructures. The conventional Drude model, which depicts metal as a lattice of ions submerged in the "gas" consisting of free electrons, may be used to calculate the surface electron oscillations in metal nanoparticles [23, 24]. The internal field of the metals, created by the displacement of free electrons, acts as a shield against the external electric field in a static electric field. Therefore, the electric field within the metal cannot be generated by the external electrostatic field. When metals are subjected to electrostatic fields, their dielectric permittivity is not easily defined. The dielectric permittivity quantifies the difference between the electric field inside a material and that of a vacuum. However, when a high-frequency electric field is applied, the freed electrons within the metal cannot perfectly synchronize with the oscillations of the high-frequency electric field. It causes metal to function as a dielectric at extremely high frequencies, allowing it to transmit the electric field of incident light. The calculation of the surface plasmon frequency ω_{sp} in small spherical metal nanoparticles involves the incorporation of the volume plasma frequency ω_p and the permittivity of the dielectric medium in which the nanoparticles are located [25].

$$\omega_{sp} = {\omega_p}\Big/{(1 + 2\epsilon_d)^{1/2}} \qquad (1)$$

Consequently, at the resonant frequency $\omega_{sp} = \omega$, based on Equations (1) and (2),

$$\in_m = -2 \in_d \qquad (2)$$

According to Eq. (2), metals should have negative permittivity. A Raman dipole with an oscillation frequency of $\mu = \alpha E$ is induced in a molecule by monochromatic light with frequency ϑ_0 and electric field E. The far-field Raman signal is detected at the frequency, where the oscillating Raman dipole emits a power proportional to $|\mu|^2$. SERS fits the same phenomenological description. However, the following changes take place when a nanostructured metal surface is present [26-28].

a) A local field enhancement may occur as a consequence of a significant rise in the electromagnetic field at the metallic surface.
b) The metallic surroundings influence the Raman dipole's (μ) radiation characteristics, which may lead to an amplification of radiation.

1.3.1 Plasmonic Resonances

The fundamental mechanism attributing to the electromagnetic amplification in surface-enhanced Raman spectroscopy (SERS) is the stimulation of localized surface plasmon resonances (LSPRs) [29, 30]. Plasmons, the coherent oscillations of free electrons localized at the interface of nanostructures composed of noble metals (typically gold or silver), appear as strong resonances within the electromagnetic spectrum [10]. The core of the SERS is the tunability of these resonances, which is based on the size, shape, morphology, interparticle distance, constituent material of the nanostructures, metal NPs concentration and dielectric constant of the surrounding medium. This provides a wide range of possibilities for scientific exploration within the realm of plasmonic. Plasmonic materials commonly regarded as highly favorable contenders for prospective implementations in optoelectronics, photovoltaics, and photonics [17]. These applications encompass a wide range of devices such as flat-screen televisions, electronic book readers, optical computing systems, optical data storage devices, all-optical switches, organic thin film transistors, organic photovoltaic devices, biosensors, optical telecommunications systems, solid-state lighting solutions, as well as harmonic generation and photodynamic therapy techniques. Ultrafast all-optical switching devices serve as pivotal constituents in the forthcoming era of broadband optical networks.

In the context of LSPR, the phenomenon of light interaction occurs with particles that possess dimensions significantly smaller than the incident wavelength [31, 32]. This gives rise to a plasmon that exhibits localized oscillations in the vicinity of the NP, characterized by a frequency referred to as the LSPR. When the incident electromagnetic radiation frequency aligns with the localized surface plasmon resonance (LSPR) frequency, a notable enhancement of the electromagnetic field appears in the immediate proximity of the nanostructures [33]. This enhanced field, referred to as a "hot spot," can be orders of magnitude stronger than the incident field, leading to the augmentation of Raman scattering cross-sections for nearby molecules [33, 34].

1.3.2 Hot-spot Formation

The electromagnetic enhancement observed in surface-enhanced Raman spectroscopy (SERS) exhibits non-uniform distribution throughout the substrate, instead arising in localized regions known as "hot spots" [10]. The emergence of these hot spots is based on variables such as the dimensions, morphology, and configuration of the nanostructures [11]. We embark on an exploration of the physics underlying the formation of hot spots, delving into the complex realm of plasmonic coupling, the resonant behavior of plasmonic dimers and aggregates, and the complex distribution of the electromagnetic field within these localized regions [11, 35]. Quantum mechanical models, such as the Mie theory, elucidate the fundamental principles dictating the intensities of hot spots and the shifts in their spectral characteristics.

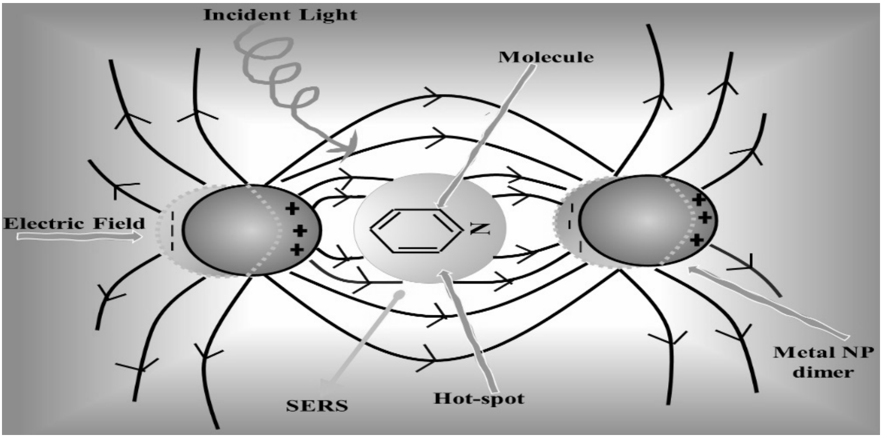

Figure 2: Surface-enhanced Raman scattering (SERS) illustration based on the electromagnetic (EM) effect.

1.4 Chemical Enhancement Mechanism

While electromagnetic enhancement is the predominant mechanism in SERS, chemical enhancement plays an important role in certain instances. Chemical enhancement in SERS is intricately influenced by these three distinct contributions: The resonance Raman effect, the charge-transfer effect, and the non-resonant chemical effect, each exerting its influence within their respective contribution ranges.

1.4.1 Resonance Raman effect (RR)

The Resonance Raman (RR) Effect, which affects the overall chemical enhancement (CE) within a specific range, occurs when incident light aligns with an electronic transition within the molecular entity under investigation[36]. The RR Effect entails the formation of a surface complex involving both the metal substrate and the analyte molecule, resulting in alterations to the molecule's characteristics, including the potential for resonance Raman scattering. It is traditionally regarded as a molecular attribute, but its inclusion as a mechanism in Surface-Enhanced Raman Spectroscopy (SERS) acknowledges that the presence of the metal substrate can influence the positioning of this resonance. This effect is typically considered a molecular attribute and is incorporated into Surface-

Enhanced Raman Spectroscopy (SERS) as the presence of a metal surface can influence the resonance's location [37].

1.4.2 Charge Transfer Effect

The charge-transfer effect, which occurs when the incident light resonates with a metal-molecule or molecule-metal transition, plays a crucial role in shaping the chemical enhancement[38] or CT effect becomes apparent only when the molecule and metal are in close proximity, allowing for a substantial overlap of their wave functions.. This leads to electron tunneling between the metal and adsorbate molecules, resulting in the formation of a negative ion. Enhancement occurs when the energy of this negative ion resonates with the incident photon. This mechanism is explained by treating the molecule and metal system as a unified entity, with the Fermi level of the metal layer lying between the molecular ground state and one or more excited states of the molecule [39]. The charge transfer mechanism operates over short distances (typically 0.1–0.5 nm) and is strongly influenced by geometric factors, bonding, and molecular energy levels[40, 41].

1.4.3 Non-resonant chemical (CHEM) effect

Conversely, the Chemical (CHEM) Effect is the least explored and challenging to quantify experimentally due to its minor contribution to overall enhancement. The non-resonant chemical (CHEM) Effect, which occurs when there is an overlap in ground-state orbitals between a molecule and a metal surface, emphasizes the importance of ground-state interactions in influencing CE. This mechanism is especially relevant for molecules that can chemisorb onto metal surfaces and endure charge transfer processes[42].

1.5 Instrumental Systems Pertaining to the Analysis and Imaging of SERS

The principle underlying surface-enhanced Raman scattering (SERS) spectroscopy is to increase the effectiveness of Raman scattering by a factor of 10^6 by adsorbing a chemical onto or near certain metal surfaces [43].Two very sophisticated systems have been developed for detecting objectives [43]. The acquisition of sensitive and repeatable Raman signals has been made possible by advancements in portable Raman systems and commercially available fragile Raman spectrometers [19]. The expanding range of SERS imaging applications is driven by advancements in SERS nanotags, scanning modes, and spectrum analysis methodologies [44]. This section compares and contrasts confocal and portable Raman systems, highlighting their unique features and benefits.

These systems allow for the use of several recording methods: (i) capturing the spectral information of specific locations, and (ii) obtaining a complete image of the full two-dimensional hybridization array plate [44].

a) Optical or transportable Raman imaging

The confocal Raman system consists of optical components, an automated sample stage, a computer control unit, a two-dimensional array charge-coupled device (CCD) detector, and a narrow-band laser [45]. It offers high-detection sensitivity and spectrum resolution, improved picture quality through X-Y mapping [46]. However, it has inconvenience and exorbitant costs [45].

Portable Raman devices, on the other hand, provide more versatile and affordable measurements due to fiber optics technology. The simplified structure allows for quick real-time detection and is easily transportable [45]. However, automated Raman mappings have limitations, such as mechanical sample stages and less performance of the CCD [46].

Both confocal and portable Raman devices have various applications, including basic lab research, field testing, substance identification, real-time detection, quick diagnostics, and intraoperative surgical guiding [45, 46].

b) Methods for imaging

Imaging based on scanning and imaging with a broad field of view are the two primary approaches of Raman imaging [46]. The most common method of pixel-by-pixel point scanning requires a lengthy acquisition time but yields highly resolved spectra at each pixel by use of a mechanical stage [47, 48]. An example of a specific point-scan mode, DuoscanTM uses two galvo mirrors to speed up imaging without using mechanical sample stage motions by enabling laser beam scanning throughout a mapping region [46].

In order to improve imaging efficiency and perhaps avoid laser-induced sample damage, line scanning employs a linear laser beam to acquire spectra from a series of sites [46]. Methods such as rapid line-scan Raman imaging and slit-scanning illustrate this approach, demonstrating how deep learning has improved temporal resolution and image quality.

A 2D detector array is used in wide-field imaging to light up and pick up emitted photons over a large region [46, 49]. Taking pictures over a single wavelength channel allows for the wavelength scan to happen. By combining spatial and spectral data in a single image, multifocal imaging mode may decrease the number of necessary spectra and the total collection time [47, 48]. Nevertheless, it is crucial to strike a careful equilibrium between spatial and spectral resolution.

Scanning and wide-field imaging modes are both available on confocal Raman systems and portable Raman readers based on fiber optics [46, 47]. The wide-field method has the ability to image huge regions faster, but it isn't often used since a longer integration time is needed to get a good signal [48, 49]. To augment the wide-field scanning approach and further improve picture speed, brighter SERS nanotags are essential [49].

c) The examination of spectra

SERS spectra provide valuable information on bio-substances' spatial distribution, but comprehensive data processing is necessary due to undesired interference or complicated mixes [47, 49]. Preprocessing techniques like smoothing, baseline correction, and normalizing refine the signal and reduce background interference [50]. Univariate imaging shows a unique Raman peak's intensity or integral area at each pixel, making it easier to demonstrate the location and concentration of analytes [50, 51]. Advanced multivariate approaches, including feature extraction and selection algorithms, demultiplexing algorithms, and classification methods, are used for complex biological materials. Artificial intelligence (AI) technology, such as multivariate curve resolution algorithms and machine learning, could improve spectrum categorization by improving Raman encoding capacity and reducing interference from fluorescent background [44]. Improving Raman detection skills is a long-term goal of AI-assisted SERS imaging, leading to better feature extraction and spectrum categorization in the near future [44].

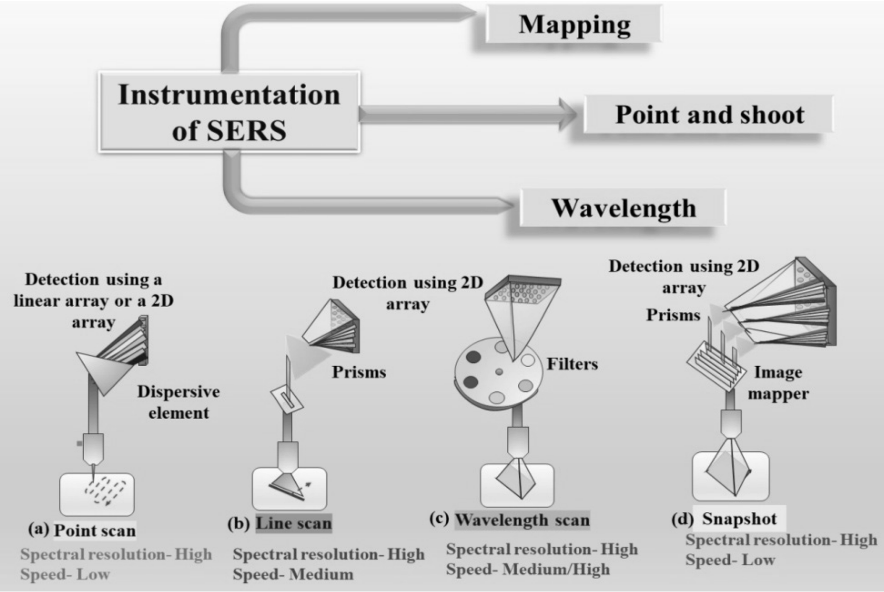

Figure 3: Standard methodologies employed in spectral imaging include in SERS instrumentation (a) point scan, (b) line scan, (c) wavelength scan, and (d) snapshot.

1.6 Advantages of SERS over other Analytical Techniques

Surface-Enhanced Raman Spectroscopy (SERS) has a number of distinct advantages over other analytical techniques, making it a potent and versatile instrument for a wide variety of applications. Here are some of the most significant benefits of SERS:

SERS provides exceptional sensitivity, enabling the detection of molecules at extremely low concentrations, frequently down to the level of a single molecule. This level of sensitivity is typically difficult to obtain with other spectroscopic approaches [36]. It has the inherent capacity to deliver data that is particular to individual molecules. It has the ability to accurately separate complicated mixtures into their component parts, such as chemical species, isotopologues, and structural isomers [52].The multiplexed analytical skills shown by SERS make it possible to detect and identify a large number of analytes in a single experiment. When analyzing complicated sample matrices, such those found in biomedicine, environmental monitoring, and materials research, this function is essential [35, 53]. Within the domain of analytical methodologies, Surface-Enhanced Raman Spectroscopy (SERS) emerges as an extremely powerful technique, characterized by its non-invasive nature. The aforementioned technique possesses the capability to perform sample analysis without inducing any alterations or impairments, thereby establishing itself as the favored option for investigating intricate biological specimens, valuable substances, and artifacts of historical significance. SERS operates at the speed of light, enabling real-time monitoring and swift sample analysis. This attribute is useful for dynamic systems and processes, as it expedites the acquisition of data. SERS is very amenable to small sample sizes, requiring just extremely low volumes for analysis. This quality is especially useful when working with rare or expensive samples since it lowers consumption and waste. SERS exhibits remarkable versatility in its ability to analyze liquids, solids, and gases with equal ease[54]. Its flexibility in analytical settings stems from its compatibility with a broad variety of substrates and experimental setups.SERS is particularly useful for studying surfaces with submicron-scale characteristics because of its great spatial resolution. The fields of materials science, nanotechnology, and surface characterization all greatly benefit from having this quality. The development of portable and field-deployable devices has allowed SERS to be used in both laboratory settings and in the field. Long-term monitoring and kinetic investigations are made possible by the extraordinary stability of SERS signals. This reliability increases its value for monitoring evolving processes and responses. SERS may be easily used with other analytical methods, like as chromatography and mass spectrometry, to get complementary insights. Accurate measurement of analyte concentrations is crucial in quantitative analysis, and SERS displays its quantitative competence via thorough calibration and data analysis[55].By allowing the observation of targeted biomolecules inside biological samples, SERS expands the scientific field of bioimaging. It has the potential to revolutionize fields including cancer diagnostics, medication delivery research, and cellular imaging [56].

Within the domain of analytical sciences, Surface-Enhanced Raman Spectroscopy (SERS) emerges as a remarkable combination of accuracy, perceptiveness, and versatility. Its ability to reveal molecular complexities and illumine the invisible world of molecules elevates it to the domain of the most sophisticated analytic methods. From quantum physics to analytical chemistry, SERS emerges as an irreplaceable gem destined to shape the future of scientific exploration.

1.7 Conclusion

Synergy between physics, chemistry, and nanoscience is on full display in Surface Enhanced Raman Spectroscopy. In addition to shedding light on SERS's extraordinary sensitivity, a deeper understanding of the physics and mechanics underpinning it reveals the technique's potential for ground-breaking findings in a wide range of scientific fields. As we go through this chapter, we set the stage for the upcoming chapters, where we'll delve into real-world applications and cutting-edge advances. This chapter is structured to provide a comprehensive need to know about SERS, from the very basics to the most recent and innovative applications. The theory, experimental methods, and practical applications of SERS are all discussed in detail across the several chapters. Readers will finish this book with a thorough understanding of SERS and its possible applications across a wide range of scientific fields. The next chapters will go into the theory behind SERS, the many applications that make SERS such an important tool in contemporary science and industry.

References

[1] C. Raman, K. Krishnan, A new class of spectra due to secondary radiation. Part I, (1928).
[2] C.V. Raman, A new radiation, Indian Journal of physics, 2 (1928) 387-398.
[3] E.C. Le Ru, E. Blackie, M. Meyer, P.G. Etchegoin, Surface enhanced Raman scattering enhancement factors: a comprehensive study, The Journal of Physical Chemistry C, 111 (2007) 13794-13803.
[4] R. Krishnan, R. Shankar, Raman effect: History of the discovery, Journal of Raman Spectroscopy, 10 (1981) 1-8.
[5] M. Moskovits, Surface-enhanced Raman spectroscopy: a brief perspective, in: Surface-enhanced Raman scattering: physics and applications, Springer, 2006, pp. 1-17.
[6] E.J. Blackie, E.C. Le Ru, P.G. Etchegoin, Single-molecule surface-enhanced Raman spectroscopy of nonresonant molecules, Journal of the American Chemical Society, 131 (2009) 14466-14472.
[7] J.R. Lombardi, R.L. Birke, A unified approach to surface-enhanced Raman spectroscopy, The Journal of Physical Chemistry C, 112 (2008) 5605-5617.

[8] M. Fleischmann, P.J. Hendra, A.J. McQuillan, Raman spectra of pyridine adsorbed at a silver electrode, Chemical physics letters, 26 (1974) 163-166.

[9] B. Barbiellini, Enhancement of Raman scattering from molecules placed near metal nanoparticles, Low Temperature Physics, 43 (2017) 159-161.

[10] G. Demirel, H. Usta, M. Yilmaz, M. Celik, H.A. Alidagi, F. Buyukserin, Surface-enhanced Raman spectroscopy (SERS): an adventure from plasmonic metals to organic semiconductors as SERS platforms, Journal of Materials Chemistry C, 6 (2018) 5314-5335.

[11] R. Pilot, R. Signorini, C. Durante, L. Orian, M. Bhamidipati, L. Fabris, A review on surface-enhanced Raman scattering, Biosensors, 9 (2019) 57.

[12] K. Kneipp, H. Kneipp, H.G. Bohr, Single-molecule SERS spectroscopy, in: Surface-enhanced Raman scattering: physics and applications, Springer, 2006, pp. 261-277.

[13] V. Bochenkov, J. Baumberg, M. Noginov, F. Benz, H. Aldewachi, S. Schmid, V. Podolskiy, J. Aizpurua, K. Lin, T. Ebbesen, Applications of plasmonics: general discussion, Faraday discussions, 178 (2015) 435-466.

[14] U.B. Singh, D. Agarwal, S. Khan, M. Kumar, A. Tripathi, R. Singhal, B. Panigrahi, D. Avasthi, Engineering of hydrophilic and plasmonic properties of Ag thin film by atom beam irradiation, Applied surface science, 258 (2011) 1464-1469.

[15] P.L. Stiles, J.A. Dieringer, N.C. Shah, R.P. Van Duyne, Surface-enhanced Raman spectroscopy, Annu. Rev. Anal. Chem., 1 (2008) 601-626.

[16] P. Jasrotia, B. Priya, R. Kumar, P. Bishnoi, T. Kumar, SERS Detection of Rhodamine-6G on Ion Beam Nanostructured Ultra-Thin Gold (Au) Films: A Correlation between Fractal Growth, Water Contact-Angle and Raman Intensity, ECS Journal of Solid State Science and Technology, 12 (2023) 027005.

[17] T.J. Moore, A.S. Moody, T.D. Payne, G.M. Sarabia, A.R. Daniel, B. Sharma, In vitro and in vivo SERS biosensing for disease diagnosis, Biosensors, 8 (2018) 46.

[18] P. Jasrotia, B. Priya, R. Kumar, P. Bishnoi, A. Vij, T. Kumar, A correlation between fractal growth, water contact angle, and SERS intensity of R6G on ion beam nanostructured ultra-thin gold (Au) films, Frontiers in Physics, 11 (2023) 1125004.

[19] G. McNay, D. Eustace, W.E. Smith, K. Faulds, D. Graham, Surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS): a review of applications, Applied spectroscopy, 65 (2011) 825-837.

[20] E. Le Ru, P. Etchegoin, M. Meyer, Enhancement factor distribution around a single surface-enhanced Raman scattering hot spot and its relation to single molecule detection, The Journal of chemical physics, 125 (2006).

[21] S.K. Saikin, Y. Chu, D. Rappoport, K.B. Crozier, A. Aspuru-Guzik, Separation of electromagnetic and chemical contributions to surface-enhanced Raman spectra on nanoengineered plasmonic substrates, The Journal of Physical Chemistry Letters, 1 (2010) 2740-2746.

[22] P. Jasrotia, B. Priya, R. Kumar, I. Sulania, R. Gupta, A.S. Verma, D. Kanjilal, T. Kumar, Surface nanostructuring and wettability of low energy Ar+ irradiated Au/V2O5/Au multilayer system for SERS detection of rhodamine-6G, Radiation Physics and Chemistry, 215 (2024) 111333.

[23] L. Mahmudin, E. Suharyadi, A.B.S. Utomo, K. Abraha, Optical properties of silver nanoparticles for surface plasmon resonance (SPR)-based biosensor applications, Journal of Modern Physics, 6 (2015) 1071.

[24] M. Dressel, M. Scheffler, Verifying the Drude response, Annalen der Physik, 518 (2006) 535-544.

[25] R. Gordon, Surface plasmon nanophotonics: A tutorial, IEEE Nanotechnology magazine, 2 (2008) 12-18.

[26] C.Y. Deng, G.L. Zhang, B. Zou, H.L. Shi, Y.J. Liang, Y.C. Li, J.X. Fu, W.Z. Wang, Local electric field enhancement of neighboring Ag nanoparticles in surface enhanced Raman scattering, Advanced Materials Research, 760 (2013) 801-805.

[27] D. Cialla, J. Petschulat, U. Hübner, H. Schneidewind, M. Zeisberger, R. Mattheis, T. Pertsch, M. Schmitt, R. Möller, J. Popp, Investigation on the second part of the electromagnetic SERS enhancement and resulting fabrication strategies of anisotropic plasmonic arrays, ChemPhysChem, 11 (2010) 1918-1924.

[28] E.J. Zeman, G.C. Schatz, An accurate electromagnetic theory study of surface enhancement factors for silver, gold, copper, lithium, sodium, aluminum, gallium, indium, zinc, and cadmium, Journal of Physical Chemistry, 91 (1987) 634-643.

[29] A. Verma, A. Srivastav, A. Banerjee, D. Sharma, S. Sharma, U.B. Singh, V.R. Satsangi, R. Shrivastav, D.K. Avasthi, S. Dass,

Plasmonic layer enhanced photoelectrochemical response of Fe2O3 photoanodes, Journal of Power Sources, 315 (2016) 152-160.

[30] M. Kumar, P. Rajput, P.K. Singh, A. Yadav, S. Pradhan, V. Baranwal, U.B. Singh, S. Jha, F. Singh, Luminescence properties of BaMgAl10O17: Mn2+ nanophosphors, Journal of Alloys and Compounds, 799 (2019) 556-562.

[31] R. Panneerselvam, G.-K. Liu, Y.-H. Wang, J.-Y. Liu, S.-Y. Ding, J.-F. Li, D.-Y. Wu, Z.-Q. Tian, Surface-enhanced Raman spectroscopy: bottlenecks and future directions, Chemical Communications, 54 (2018) 10-25.

[32] X.-M. Lin, Y. Cui, Y.-H. Xu, B. Ren, Z.-Q. Tian, Surface-enhanced Raman spectroscopy: substrate-related issues, Analytical and bioanalytical chemistry, 394 (2009) 1729-1745.

[33] Y. Zheng, L. Rosa, T. Thai, S.H. Ng, S. Juodkazis, U. Bach, Phase controlled SERS enhancement, Scientific Reports, 9 (2019) 744.

[34] A.I. Pérez-Jiménez, D. Lyu, Z. Lu, G. Liu, B. Ren, Surface-enhanced Raman spectroscopy: benefits, trade-offs and future developments, Chemical science, 11 (2020) 4563-4577.

[35] J. Zhu, J. Zhou, J. Guo, W. Cai, B. Liu, Z. Wang, Z. Sun, Surface-enhanced Raman spectroscopy investigation on human breast cancer cells, Chemistry Central Journal, 7 (2013) 1-5.

[36] S. Schlücker, Surface-Enhanced raman spectroscopy: Concepts and chemical applications, Angewandte Chemie International Edition, 53 (2014) 4756-4795.

[37] H. Ueba, S. Ichimura, H. Yamada, Where are we in the study of SERS? Role of chemisorption and charge transfer, Surface Science, 119 (1982) 433-448.

[38] J. Kim, Y. Jang, N.-J. Kim, H. Kim, G.-C. Yi, Y. Shin, M.H. Kim, S. Yoon, Study of chemical enhancement mechanism in non-plasmonic surface enhanced Raman spectroscopy (SERS), Frontiers in chemistry, 7 (2019) 582.

[39] J. Mock, M. Barbic, D. Smith, D. Schultz, S. Schultz, Shape effects in plasmon resonance of individual colloidal silver nanoparticles, The Journal of Chemical Physics, 116 (2002) 6755-6759.

[40] K.N. Kanipe, P.P. Chidester, G.D. Stucky, M. Moskovits, Large format surface-enhanced Raman spectroscopy substrate optimized for enhancement and uniformity, ACS nano, 10 (2016) 7566-7571.

[41] L. Cui, D.-Y. Wu, A. Wang, B. Ren, Z.-Q. Tian, Charge-transfer enhancement involved in the SERS of adenine on Rh and Pd demonstrated by ultraviolet to visible laser excitation, The Journal of Physical Chemistry C, 114 (2010) 16588-16595.

[42] S.K. Saikin, R. Olivares-Amaya, D. Rappoport, M. Stopa, A. Aspuru-Guzik, On the chemical bonding effects in the Raman response: Benzenethiol adsorbed on silver clusters, Physical chemistry chemical physics, 11 (2009) 9401-9411.

[43] S. Fornasaro, F. Alsamad, M. Baia, L.A. Batista de Carvalho, C. Beleites, H.J. Byrne, A. Chiadò, M. Chis, M. Chisanga, A. Daniel, Surface enhanced Raman spectroscopy for quantitative analysis: results of a large-scale European multi-instrument interlaboratory study, Analytical chemistry, 92 (2020) 4053-4064.

[44] L. Lin, X. Bi, Y. Gu, F. Wang, J. Ye, Surface-enhanced Raman scattering nanotags for bioimaging, Journal of Applied Physics, 129 (2021).

[45] L. Opilik, T. Schmid, R. Zenobi, Modern Raman imaging: vibrational spectroscopy on the micrometer and nanometer scales, Annual Review of Analytical Chemistry, 6 (2013) 379-398.

[46] Y.W. Wang, N.P. Reder, S. Kang, A.K. Glaser, J.T. Liu, Multiplexed optical imaging of tumor-directed nanoparticles: a review of imaging systems and approaches, Nanotheranostics, 1 (2017) 369.

[47] B. Durrant, M. Trappett, D. Shipp, I. Notingher, Recent developments in spontaneous Raman imaging of living biological cells, Current opinion in chemical biology, 51 (2019) 138-145.

[48] H. He, M. Xu, C. Zong, P. Zheng, L. Luo, L. Wang, B. Ren, Speeding up the line-scan Raman imaging of living cells by deep convolutional neural network, Analytical chemistry, 91 (2019) 7070-7077.

[49] L. Gao, L.V. Wang, A review of snapshot multidimensional optical imaging: measuring photon tags in parallel, Physics reports, 616 (2016) 1-37.

[50] C.L. Morais, K.M. Lima, M. Singh, F.L. Martin, Tutorial: multivariate classification for vibrational spectroscopy in biological samples, Nature Protocols, 15 (2020) 2143-2162.

[51] C.L. Morais, M. Paraskevaidi, L. Cui, N.J. Fullwood, M. Isabelle, K.M. Lima, P.L. Martin-Hirsch, H. Sreedhar, J. Trevisan, M.J. Walsh, Standardization of complex biologically derived spectrochemical datasets, Nature protocols, 14 (2019) 1546-1577.

[52] L. Furini, C. Constantino, S. Sánchez-Cortés, J. Otero, I. López-Tocón, Adsorption of carbendazim pesticide on plasmonic nanoparticles studied by surface-enhanced Raman scattering, Journal of colloid and interface science, 465 (2016) 183-189.

[53] K. Xu, R. Zhou, K. Takei, M. Hong, Toward flexible surface-enhanced Raman scattering (SERS) sensors for point-of-care diagnostics, Advanced Science, 6 (2019) 1900925.

[54] K.A. Willets, Surface-enhanced Raman scattering (SERS) for probing internal cellular structure and dynamics, Analytical and bioanalytical chemistry, 394 (2009) 85-94.

[55] D. Radziuk, H. Moehwald, Prospects for plasmonic hot spots in single molecule SERS towards the chemical imaging of live cells, Physical Chemistry Chemical Physics, 17 (2015) 21072-21093.

[56] D.-K. Lim, K.-S. Jeon, J.-H. Hwang, H. Kim, S. Kwon, Y.D. Suh, J.-M. Nam, Highly uniform and reproducible surface-enhanced Raman scattering from DNA-tailorable nanoparticles with 1-nm interior gap, Nature nanotechnology, 6 (2011) 452-460.

CHAPTER 2

WATER CONTAMINATION, ITS SOURCES AND IMPACT ON HUMAN HEALTH: AN OVERVIEW

AJAY KUMAR[1], MAYANK SUMBRIA[2]
AND SATVIK DUB[2] AND SUMIT SHARMA[2]

[1]Department of Physics, Govt Degree College, Chintpurni, Himachal Pradesh, India-143001.

[2]Department of Physics and Astronomical Sciences, Central University of Jammu, Samba, Jammu & Kashmir-180012

Summary

The safe usage of groundwater for drinking has been seriously questioned by the advancement of human civilization. One of the main issues in metropolitan cities and industrial areas are the problem of heavy metal-related ground water pollution. There could be bioaccumulation, bio magnification, and geo-accumulation as a result of these hazardous metals entering the ecosystem. It has been observed that mining and associated activities cause ground water to become contaminated with heavy metals like Arsenic, Copper, Lead, Magnesium, Chromium, Cadmium, Antimony and zinc in many parts of the world. One of the significant compounds that, depending on their concentration in natural and manmade sources, can have both positive and negative effects on the human body is heavy metals. There is a fine line between consuming these heavy metals in excess and within the proper limits. Exposure to heavy metals has been linked to developmental retardation, various cancers, kidney impairment and in extreme cases, death have all been related to very high exposure.

2.1 Introduction

"We drink water, but we're never sure of its quality." Even if plenty of water is abundant nearby, it still seems to be heavy burden on our pockets to obtain fresh, drinkable water [1]. As a vital support system for everyday life and the growth of industry, supplying fresh water constantly is crucial. According to the United Nations Human Rights Council (UNHRC), every citizen has a fundamental right to clean, safe drinking water and sanitation conditions for a long-lasting, and healthy environment. The Council commits to provide clean water assistance to every person on the earth by 2030 in order to promote equity for social and economic development. While some developed countries are already getting beneficial benefits from such reforms and targets, but it appears that developing countries face considerably more difficult circumstances. According to reports, around 90% of the garbage dumped in oceans comes from developing nations like China, India, Sri Lanka, Egypt, Malaysia, Nigeria, Indonesia, Philippines, Bangladesh, etc. [2]. Two million tons of sewage and other garbage are dumped into water bodies every day; this equates to eight million fatalities annually, the direct cause of which is untreated water intake [3].

Out of all the water on Earth, only around 2.5 percent is available as non-saline freshwater but unfortunately, this is constantly getting contaminated, which leads to a water crisis. Surface and ground water supplies are under stress and pollution as a result of increased industrial activity, originating from domestic sources, agricultural, and industrial sources [4]. For accurate chemical detection in water bodies, it is critical to understand how surface morphology has changed over past [5]. Numerous contaminants, ranging from large amounts of trash to nano-sized substances, contaminate these bodies of water and render them unsafe for human consumption. In addition to these factors, other factors that have contributed to the freshwater problem include the exploding population, unsustainable water use, climate change, increased industrial demand, the agricultural and residential sectors, and shifting consumption patterns. According to reports, water use has been rising by roughly 1% annually since the 1980s. If this trend continues, water demand is anticipated to rise by roughly 20% to 30% by 2050 [6]. As the results of human interference, water contamination has been classified by World Economic Forum as one of the largest global hazards for 2019 [7]. According to the reports, a sixth of the world's population suffers from a lack of freshwater [8].

Both natural and artificial sources can contaminate water. Geological materials from sedimentary rocks, floods, volcanic eruption, etc., along with a variety range of elements like magnesium (Mg), calcium (Ca), copper (Cu), lead (Pb), iron (Fe), etc. are example of natural pollutants. In moderation, these are vital to human health; but in excess, they have immediate negative consequences on health [9,10]. By-products petroleum, dye, chemical, oil, battery, and food industries are examples of artificial pollutant. The primary cause of these waterborne illnesses are listed by the Centres for Disease Control and Prevention as the following: perfluoroalkyl substances (PFAS), fluoride ions, heavy metals like As, Pb, Cd, Hg, Cr, Zn, nitrates, carbonates; Salmonella, norovirus, *Escherichia coli,* Hepatitis A virus, chlorinated solvents, and pesticides [11].Guidelines have been established by various international organisations, including the USEPA, WHO, EPA, and EU, to determine the maximum allowable quantity of heavy metals in drinking water [12].

Furthermore, this area is further enhanced by the application of fertilisers, herbicides, and insecticides in agricultural operations [13]. Water pollution is also caused by pathogens and parasites, which are dispersed by human and animal waste. However, their proportion of toxins is far lower than that of manmade and natural sources.

Chronic diseases like cholera, fever, vomiting, diarrhoea, dysentery, and gastroenteritis are also linked to volatile organic compounds (VOCs), which include chemicals like toluene, styrene, phosgene, adhesives, petrol additives, and microorganisms like Shigella, Vibrio cholera, and Salmonella [14, 15].

Generally, polluted water typically results in a variety of health issues for aquatic life, plants, and human also (both directly and indirectly). According to Kumar et al. (2018), exposure to these toxic wastes causes chronic poisoning that is characterised by liver damage, neurological, gastrointestinal, and cardiovascular issues [12].

Although fluoride in water is necessary to prevent bone deterioration but concentration rises above 0.5 mg/L leads to fluorosis. Large-scale use of Cu-contaminated water can lead to fever, diarrhoea, liver, and kidney damage. PFAS exposure has been linked to thyroid issues, cancer, rise cholesterol, and problems with fertility.

Kidney and bone damage may result from long-term exposure to cadmium through food crops irrigated by effluents [16]. If Infants and pregnant ladies drink water contaminated with Lead (Pb), they may get developmental delay, abdominal pain, birth abnormalities, hypertension, and preeclampsia. Lead (Pb) poisoning affects the blood, central nervous system, and kidneys and is found in drinking water from pipes, solder, and residential plumbing systems. In this sense, Flint, Michigan, serves as an example.In 2014, the city authorities made the decision to temporarily use the Flint River as a substitute point water supply. The new water pipeline was constructed, it was not treated with any anti-corrosive agent to prevent lead contamination. Studies revealed that this carelessnesscause blood lead levels by a factor of two, three, or more, which in turn leads to a number of skin-related problems [17].

Metallic mercury is an allergen that can harm the central nervous system and produce oral lichen. The most well-known instance of a high concentration of mercury discharge into Minamata Bay is the Minamata case. Approximately 2000 people were poisoned, and hundreds of cases of Minamata sickness—a disease caused by eating fish contaminated with methyl mercury—were reported [18]. Long-term exposure to high levels of arsenic (As) metal can cause bone marrow depression, hemolysis, melanosis, polyneuropathy, and other conditions.

The accumulation of heavy metals has an impact on aquatic flora and fauna as well, posing a threat to public health when contaminated species are consumed. The World Health Organisation (WHO) stated in 2019 that over 48,000 people die each year from diseases spread by contaminated water, including cholera, polio, pneumonia, typhoid, and diarrhoea [3]. Water pollution not only harms people's health but also negatively impacts on plants. Lack of nutrients in the water ecosystem, overuse of pesticides in agriculture, etc. poisons the plant, and also hinders plant growth.

Even though technology has advanced over the past few decades, thousands of rural villages lack access to safe drinking water due to improper pre-treatment and usage practices. According to WHO report, Two million individuals were exposed to contaminated groundwater, including radium, fluoride ions, and arsenic. It is not surprising that thousands of communities could not afford to filter these contaminants out and continue to drink the same contaminated water [19]. Here, it should be noted that the main cause of water deterioration is heavy metal contamination.

This chapter covers each of the above mentioned aspects and divided in sections. The general introduction to water quality is addressed in the first section. For a more in-depth analysis, the second section highlights the several sources of the primary contaminant, which is heavy metal pollution of groundwater. This chapter's third section adds to the category of pollution. The focus of this section is contamination from heavy metals. We have discussed the impact of heavy metal contamination on human health in the fourth segment. The fifth and sixth sections include information on current approaches to heavy metal remediation and water pollution mitigation. We have discussed the future plans that various governments have adopted and suggested certain actions to get rid of these exudates from the water. Lastly, this chapter concludes with future expects and conclusions drawn.

2.2 Sources of Heavy Metal Contamination

Pollutants can enter the water bodies from various sources, where they are subsequently transported along the stream-line. Water discharge bodies are contaminated by both legal and illegal factory discharges, leaks and spills in subterranean oil pipelines or during transit, hydraulic fracturing operations, and sewer overflows. Radiation leaks from nuclear power plants and methods used to disinfect drinking water are other potential sources.

This falls within the general category of pointed and non-pointed sources. Pollutants that enter a waterway through traceable sources, such as domestic sewage outlets, or industrial outlet pipes, are referred to as pointed sources. It should be mentioned that untreated waste discharge and human interaction are the main causes of these pointed sources. Non-pointed sources are activities that cause diffused contamination of water bodies, such as leaching, littering, and are difficult to trace and therefore difficult to monitor and control. In addition, there are anthropogenic and natural sources of heavy metal pollution in water. Figure 1 provides a quick discussion of these.

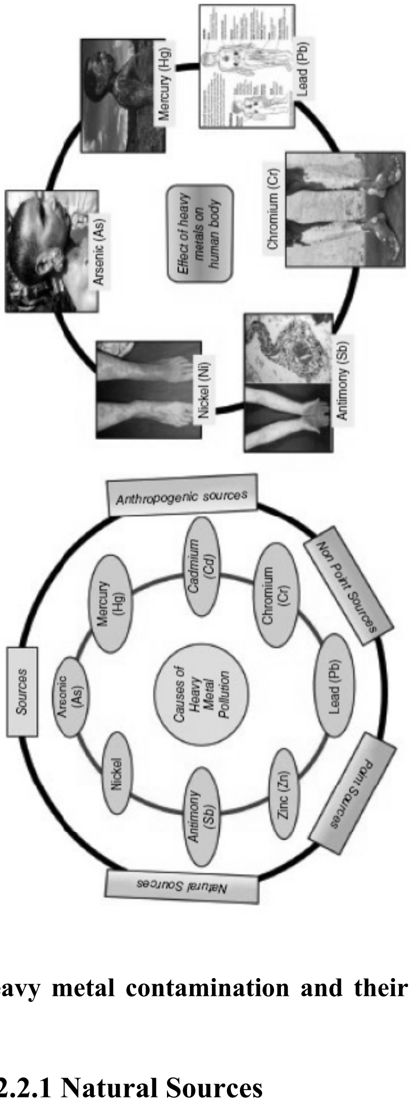

Figure 1: sources of heavy metal contamination and their effects on humans.

2.2.1 Natural Sources

Natural processes that are known to contribute to water source contamination include geothermal, volcanic, and rock weathering. Because rainwater, like acid rain, dissolves air contaminants and transports them into groundwater, it is also a common source of contaminated water. In