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SURFACE-ENHANCED RAMAN SPECTROSCOPY: A REVIEW

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ABSTRACT

Surface Enhanced Raman Spectroscopy is an offshoot of Raman Spectroscopy offering improved characteristics like compound specific Raman fingerprint for the identification of substances, rendering information on chemical and physical characteristics. Further the technique is non-destructive, highly sensitive and has expanded scope in research fields of analytical, bioanalytical, biophysical and life sciences. This review presents the basics of SERS theory, the prevalent Raman principles, and the mechanisms of SERS enhancement. In any SERS application, SERS substrate plays a pivotal role. A brief description of different SERS substrates, their fabrication method has been presented. Lastly, the related enhanced techniques like Tip-enhanced Raman scattering (TERS), Shell-isolated NP-enhanced Raman scattering (SHINERS), etc., have been mentioned.

KEYWORDS: SERS, SERS enhancement, TERS, SHINERS.

INTRODUCTION

Raman Spectroscopy

Raman Spectroscopy is an analytical technique which is used to measure vibrational energy levels of sample via scattered light. Raman spectroscopy furnishes unique Raman fingerprint for the identification of substances; provides chemical, structural information as well. The Raman spectroscopic study is governed by Raman scattering.

When a beam of light is incident on a system/sample, it absorbs the electromagnetic radiation which causes either an increase in the internal energy of the system or its electrons get activated which leaves it in a higher energy state. This leads to the formation of a short-lived complex between the photon and molecule which is generally called the virtual state of the molecule. This state is unstable and the photon is re-emitted spontaneously as scattered light.

However, approximately 1 in 10 million photons undergo Raman scattering. Raman scattering is an inelastic scattering process where a transfer of energy between the molecule and scattered photon is observed. It is explained in terms of Stokes Raman Scattering and Anti-Stokes Raman Scattering.
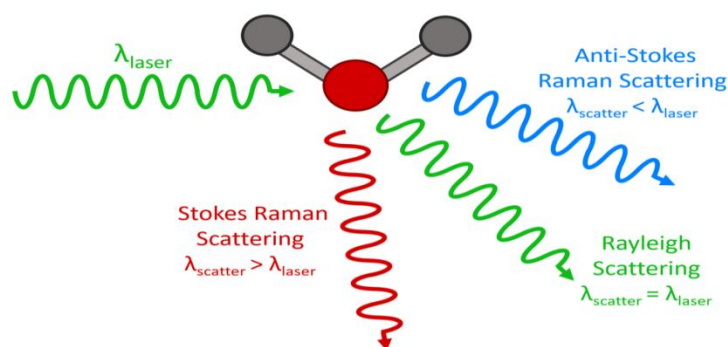

Fig. 1: Three types of scattering processes that can occur when light interacts with a molecule.

If the molecule gains energy from the photon during the scattering (the electrons get excited to a higher vibrational level) then the scattered photon loses energy and its wavelength increases; which is called Stokes Raman scattering. Likewise, if the molecule loses energy by relaxing to a lower vibrational level, the

scattered photon gains the corresponding energy and its wavelength decreases; which is called Anti-Stokes Raman scattering. Stokes scatter is the statistically

more probable process and is always more intense than the anti-Stokes, which is why always the Stokes Raman scatter is measured in Raman spectroscopy.[1]
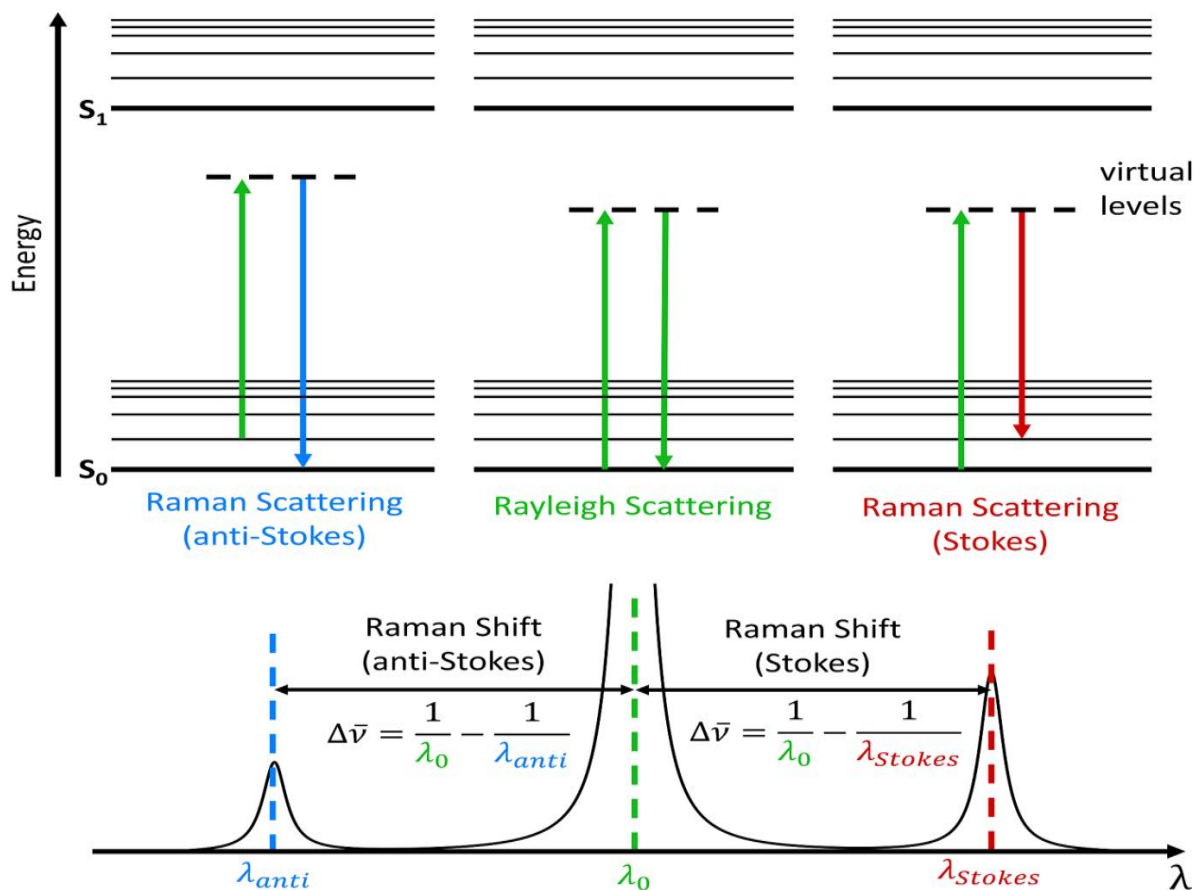

Fig. 2: Jablonski Diagram showing the origin of Rayleigh, Stokes and Anti-Stokes Raman Scatter.

Raman Shift
The wavelength of the Raman scattered light depends on the wavelength of the excitation light. Raman shift is the difference in the energies of incident light and excitation light; Raman scatter of molecular vibrations are studied in association with the Raman shift and therefore is independent of the incident light wavelength.

$$\Delta \bar{v}(cm^{-1}) = \left(\frac{1}{\lambda_0 \, (nm)} - \frac{1}{\lambda_1 \, (nm)} \right) x \, \frac{(10^7 nm)}{(cm)}$$

$(\Delta \bar{v})$ is the wavenumber of Raman shift in cm^{-1}
λ_0 is the wavelength of the excitation laser in nm
λ_1 is the wavelength of the Raman scatter in nm.

Surface Enhanced Raman Scattering (SERS)
Raman spectroscopy is a weak process (one in a million photons of light undergoes Raman scattering). Therefore concentrated solutions of samples have to be used. This drawback is overcome by making advancements in the electron trapping which would give amplified results.

Surface-enhanced Raman scattering (SERS) spectroscopy is based on the large increment of Raman scattering of molecules adsorbed on the surface of suitable metallic (mainly silver and gold) nanostructures. Two mechanisms contribute to the SERS enhancement:
- Electromagnetic mechanism (based on resonance excitations of surface plasmons in the metal)
- Chemical / molecular mechanism (based on increasing the polarizability of the molecule).

Average enhancement aspects are about 10^4 –10^6 but even values about 10_{11} can be achieved in some cases.[2]

Electromagnetic mechanism
This is a prime enhancement effect based on amplification of the EM field due to resonance excitations of surface plasmons (SPs). Surface Plasmon is a stationary electron wave at the surface of nanostructures which generates a strong electric field. This type of resonance is named dipolar localized surface plasmon resonance (LSPR) and can be derived from surface plasmon extinction-SPE otherwise called extinction spectrum (called surface plasmon extinction—SPE).
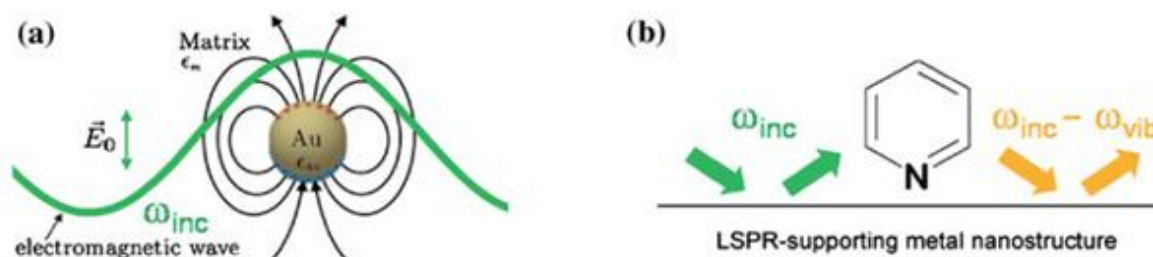
Fig. 3: Electromagnetic enhancement mechanism of SERS. a. A gold NP acts as a nanoantenna by excitation of a dipolar localized surface plasmon resonance (LSPR). b. Both the "incoming" field (ω_{inc}) and the "outgoing" field ($\omega_{inc} - \omega_{vib}$) are enhanced by elastic light scattering off the LSPR-supporting metallic nanostructure.

The resonance frequency ω_{max} of plasmons in the metallic nanostructure depends majorly on the dielectric functions of the metal ε_{metal} (ω) and the surrounding medium ε_m (ω). Firstly, the coupled state of the photon and LSPs is characterized by enhanced amplitude of the EM field close to the roughened metal surface. The molecule adsorbed at the surface is thus subjected to much stronger Electric field. Secondly, molecular dipole radiates Raman Scattering in close proximity of metal and not in free space. The frequency-shifted Stokes RS radiation at $\omega_s = \omega_{inc} - \omega_{vib}$ for one particular vibrational mode itself can excite a LSPR of the metallic nanostructure.

Chemical Mechanism
The chemical (or molecular) mechanism is characterized by increased molecular polarizability tensor $\alpha_{molecule}$ and subsequently Raman cross-section. This mechanism has a number of requirements, such as the existence of "active sites", metal-adsorbate chemical bond formation (sometimes referred to as a first-layer effect). The incident light frequency ω_{inc} gets in resonance with a charge-transfer transition of the newly formed complex of surface and adsorbate. Then the electron relaxes back to the metal. If the electron stays in the molecule for long enough, scattered photon ($\omega_s = \omega_{inc} - \omega_{vib}$) will carry information about a vibrational state of the molecule (ω_{vib}).[3]
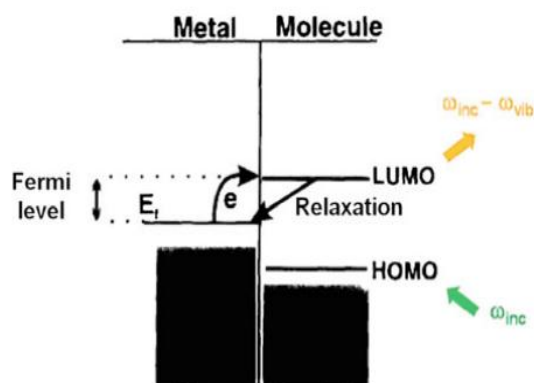

Fig. 4: Charge Transfer mechanism of SERS; LUMO the lowest unoccupied molecular orbital; HOMO the highest occupied molecular orbital.

SERS Substrates
SERS substrates can be classified in three basic categories:
1. NPs in suspension
2. NPs assembled and immobilized on solid substrates (bottom-up approach)
3. Nanostructures fabricated directly on solid substrate (top-down approach).

Metallic NP Hydrosols
The preparation of metallic NP hydrosols is simple and inexpensive without the need of using any specialized equipment. These colloids are formed by suspending metallic NPs with various shapes and diameters (about 5–200 nm). However, for successful preparation high purity of chemicals and glass vessels are to be used to not compromise the stability. Such Ag and Au hydrosols are prepared by techniques such as laser ablation or wet chemistry (reduction of $AgNO_3$ or $HAuCl_4$ with appropriate reduction agent). Widely used reduction agents used in such hydrosols preparation include sodium borohydrate (Creighton et al. 1979)[4] trisodium citrate (Lee and Meisel 1982)[5] hydroxylamine hydrochloride (Leopold and Lendl 2003)[6] and ethylenediaminetetraacetic acid (EDTA) (Heard et al. 1983)[7] The one noticeable problem of chemically prepared hydrosols is the presence of ions and surface organic contaminants that arise as products of chemical reduction which can superimpose on the SERS spectra of studied analyte (Yaffe and Blanch 2008)[8] This problem can be overcome by using chemically pure hydrosols prepared with laser ablation of a metal foil in ultrapure water by a pulse laser (Fojtik and Henglein 1993)[9] (Procházka et al. 1997a)[10] Ag-coated Au NPs and Au-coated Ag NPs can be prepared by growing Ag or Au on citrate-reduced Au or Ag NPs followed by chemical reduction of the corresponding salt.

NPs and Nanostructures on Planar Supports Fabricated by Bottom-Up Techniques
Stability and spectral reproducibility of metallic NPs can be significantly improved by bottom up techniques.

- *NPs Self-assembled in Planar Supports*
In this approach rationally designed NPs are self-assembled or immobilized on planar solid supports giving enhanced reproducibility. Different techniques

employed to assemble metallic NPs with various sizes and shapes are summarized in several reviews: Fan et al. (2011)[11] Guo and Dong (2011)[12] Romo-Herrera et al. (2011)[13] Preparation procedures include chemical attachment of NPs via small molecules or bifunctional polymers (Freeman et al. 1995)[14] inverse micelle polymer film (Jang et al. 2013)[15] Orendorff et al. 2005,[16] Baia et al. 2008)[17] solvent-induced evaporation (Wang et al. 2007)[18] electrostatic interaction between NPs and surface (Han et al. 2008)[19] layer-by-layer assembly (Zhang et al. 2007)[20] external field driven assembly (Wu et al. 2010a)[21] and liquid-liquid interface Langmuir-Blodgett (LB) assembly (Tao et al. 2008).[22]

- *Metallic NR Arrays Fabricated by Angle Vapour Deposition*

This technique is otherwise called oblique (or glancing) angle vapour deposition (OAD or GLAD). The angle deposition of Ag or Au from electron beam evaporation system is used for fabrication of NPs arrays on solid substrate (Negri and Dluhy 2013).[23]

Nanostructures Fabricated Using Nanolithographic (Top-Down) Techniques

This approach is generally classified as top-down and mainly covers the preparations of highly ordered metallic nanostructures by electron beam lithography (EBL) and chemical etching techniques.

- *Ion Beam Lithography (IBL) and Electron Beam Lithography (EBL)*

In these techniques, an array of highly ordered structures is produced by a focused electron or ion beam drawing patterns over the resist wafer in a serial manner with nanometre resolution (Kahl et al. 1998).[24]

- *Nanoimprint Lithography (NIL)*

NIL is a perspective method to produce batches of the substrates with identical properties. This method involves preparation of a mould of desired nanostructure by EBL, then aligning and pressing into the photoresist covering on the substrate. Once curing is done, the mould is lifted off and the substrate is deposited with metal. After the photoresist removal, a highly ordered nanostructures such as nanodots (Li et al. 2007)[25] or plasmonic crystals formed of precisely controlled nanostructural arrays (Yao et al. 2010)[26] over a large area can be fabricated. NIL has advantages of offering high efficiency and low-cost nanostrucures, but problems such as weak coupling and low enhancement effect still exist.

Highly Ordered Metallic Nanostructures Fabricated by Template Techniques

SERS sensing applications with enhanced uniformity and spectral reproducibility require control over the morphology of the metallic nanostructures. The use of templates that allow the deposition of metals with controlled geometry is one of the most promising approaches to overcome such challenges. These techniques are figuratively much easier, cheaper and faster than EBL and IBL. The template directed approach can be considered as bottom-up techniques described above.

- *Nanosphere Lithography (NSL)*

NSL—often called colloidal lithography (CL)—is an effective technique using self-assemblies of polystyrene (PS) micro- or nano-particles on solid surfaces as 2- or 3-dimensional masks for metal deposition (Zhang et al. 2010)[27] The size and shapes of the close-packed nanospheres and the holes between them, in addition to the metal deposition conditions, such as evaporation angle or specific deposition technique (e.g., sputtering, thermal deposition), influence the achieved metallic patterns.

1. Vapour deposition of 100–200 nm metal layer surface forms the "film over nanospheres" (FON) (Baia et al. 2005)[28]; (Baia et al. 2008).[17]
2. Removing of a PS mask gives a periodical nanostructure array. In 1995, Hulteen and Van Duyne (1995)[29] reported the preparation of periodic Ag triangle arrays with areas of 4–25 μm2 using double layer PS sphere mask.
3. Formation of nanostructured film containing a structured hexagonal array of metallic nanoholes, nanoislands or nanovoids by electrochemical deposition of metal followed by removal of PS mask (Abdelsalam et al. 2005).[30]

"Hole Mask" Colloidal Lithography (HCL)

The HCL technique is based on a sacrificial layer combined with a thin film mask with nanoholes (thus the name "hole mask") which in evaporation and/or etching steps defines a pattern and the sacrificial layer is used to remove the "hole mask" after processing (Fredriksson et al. 2007)[31] The sequence of steps is described below.

- A polymer film such as poly methylmethacrylate (PMMA) is spin-coated onto a glass or Si wafer surface followed by deposition of a colloidal solution containing PS beads.
- A thin film that is resistant to reactive oxygen plasma etching is then deposited onto the surface.
- The PS beads are tape-stripped away, leaving nanoholes in the plasma-resistant film ("hole mask") resting on the sacrificial PMMA layer.
- The average spacing and diameters of the holes are thus regulated by the separation distance and size of the removed colloidal particles.
- Reactive O_2 plasma etching is applied to selectively remove the PMMA exposed underneath the nanoholes in the masking film. At this stage the mask resembles the ones produced with EBL. The "hole mask" can then either be used as a metal deposition mask or etching mask, or both.
- After metal deposition, the double-layer film ("hole mask" + polymer) is lifted off. Different kinds of large array areas (several cm²) can be fabricated such as: (a) array of identically oriented elliptical Au nanostructures; (b) Au nanocone array; (c) binary

arrays of Au–Ag nanodisc pairs, (d) embedded nanodiscs with overall sizes currently down to 20 nm and occupying 10–50 % of the total surface area.

Electrochemical Depositions

For the fabrication of highly reproducible SERS substrates, the electrodeposition of metal on anodic alumina oxide (AAO) nanopore templates has been developed. The sequence of steps is described below.

- The AAO template can be obtained by dissolution of alumina in acidic solutions at alternating current deposition at 10– 25 V, which results in regular hexagonal packing of pores of tens of nanometres.
- The dissolution of the alumina layer in phosphoric acid releases metallic arrays of NRs or nanowires (NWs) (Tian et al. 2002).[32]

It is also possible to find commercial AAO membranes. Polycarbonate membranes with pore diameters varying in the range of 20–500 nm can be used as templates for the electrodeposition of nanowires and nanotubes. The 50 nm Au NWs provide SERS EF of 1.3×107 (Batista et al. 2009).[33]

Related Enhanced Techniques

Plasmon-assisted RS works by deposition of bare Au NPs as a film on a solid support and the molecules to be probed are in direct contact with the metal surface. This contact mode also applies to transition metal-coated NPs, extending the SERS application to other wavelength regions and transition-metal catalyzed reactions.

Tip-enhanced Raman scattering (TERS) work in a noncontact mode: the Au tip, acts as the signal amplifier. The Au tip and the probed molecules on the surface are separated from each other. Any substrate can be probed with this powerful approach at the nanometre scale.

TERS spectroscopy combines atomic force microscopy (AFM) and confocal SERS microscopy (Pettinger 2006).[34] A metal-coated nanotip scans the surface of the sample and SERS spectra are successively measured from the spots of the sample that is in contact with the tip, where the SERS enhancement is localized. This approach provides ultrahigh spatial resolution (better than $\lambda/20$).

Shell-isolated NP-enhanced Raman scattering (SHINERS) (Li et al. 2010)[35]; (Li and Tian 2014)[36] operates in the noncontact mode by using Au NPs protected by a 2 nm ultrathin glass shell. The glass shell isolates the Au surface from the probed molecules and therefore prevents a potentially disturbing interaction rendering a significant SERS signal compared to the contact mode. This approach is very flexible; it can be applied to virtually any surface by adapting to the surface topography and therefore the simultaneous interrogation of the entire surface is possible by spatial multiplexing.

Fluorescence (which is a special case of luminescence) in the vicinity of plasmonic metal can be both surface-enhanced and surface-quenched (Weitz et al. 1983)[37] The fluorescence is a stepwise process involving first absorption which is enhanced by EM mechanism. For the second step (emission), the presence of metal modifies the decay rates giving modified fluorescence lifetimes of the fluorophore but mainly to quantum yield or radiative efficiency (Le Ru and Etchegoin 2009).[38]

CONCLUSION

SERS spectroscopy is banked on the extensive enhancement of a Raman signal from molecules on or close to a metallic nanostructure principally silver and gold. Of the two enhancement mechanisms contributing to the total enhancement: the electromagnetic one has been recognized theoretically and experimentally as the dominant one. Since the discovery of SERS, a broad band of metallic substrates have been prepared and employed as an enhancing medium that would enable even detection of single molecules. However the spectral reproducibility is poor and cannot be used as a routine analytical method. The balance between the sensitivity and reproducibility is essential in any real time SERS analysis of compounds. The technique is becoming widespread and is finding new and varied applications in the field of analytical chemistry, biophysical and biomedical engineering.

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