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SURFACE ENHANCED RAMAN SPECTROSCOPY

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ABSTRACT:

Surface-enhanced Raman spectroscopy (SERS) is a spectroscopic technique that simultaneously combines fingerprint recognition capabilities, typical of vibrational spectroscopies, and very high sensitivity (down to single molecule), owing to the enhancement provided by plasmonic effects. SERS inherits the rich chemical fingerprint information on Raman spectroscopy and gains sensitivity by Plasmon-enhanced excitation and scattering. In particular, most Raman peaks have a narrow width suitable for multiplex analysis, and the measurements can be conveniently made under ambient and aqueous conditions. SERS applications in bio analysis involve the complex interactions of plasmonicnanomaterials with biological systems and their environments. We then introduce the current understanding of the interaction of nanomaterials with biological systems, mainly living cells, to guide the design of functionalized SERS nanoparticles for target detection. In the end, we give an outlook of the key challenges in bio analytical SERS, including reproducibility, sensitivity, spatial and time resolution. The last section illustrates the applications of SERS in several fields of sensing, like the detection of chemical warfare agents, environmental pollutants, food contaminants, and illicit drugs; the use of SERS in art preservation, forensic science, and medical diagnosis.

Keywords: SERS, Plasmon's, Enhancement, Nanoparticles, Resonance, Finger printing

INTRODUCTION:

The weak Raman of surface-enhanced Raman scattering (SERS) spectroscopy. It was accidentally discovered in 1974 by Fleischmann, Hendry and Mcquillan of the University ofSouthampton, UK when they tried to do Raman with an adsorbate of very high Raman cross-section, such as pyridine (Py) on the roughened silver (Ag) electrode. SERS is a technique for molecular detection and characterization that relies on the enhanced Raman Scattering of molecules that are adsorbed, or near, SERS- active surfaces, such as Nano structured gold or silver. [1]

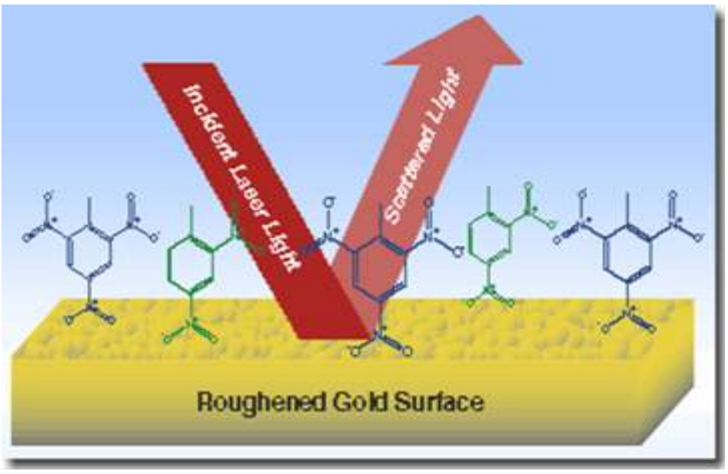

Figure: 1 Roughened gold surface

1.1. Principle:

The technique is so sensitive that even a singlemolecule can be detected. SERS consists inusing thelarge

Localfield enhancements can exit atmetallic surfaces to boost the Raman scatteringsignal of molecules at the

Surface. [2]

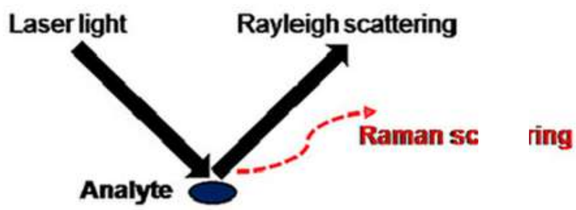

Figure: 2 Raman technique

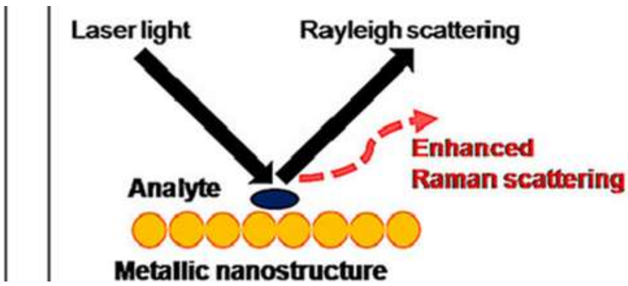

Figure: 3 SERS technique

1.2 Mechanisms:

There are many forms of SERS substrates depending on the purpose they are used for different applications.[3,4]SERS was first observed on the roughened surface of electrodes.[5,6] The Raman spectrum of pyridine was enhanced to almost more than million times in SERS on metal colloids. [7] This phenomenon was called SERS and it was realized that the nature of the substrate plays an important role in the enhancement. [8] Nano substrates from metals such as gold, silver, and copper exhibit enhancement of Raman spectra.[9] Figure 3 shows TEM image of silver nanoparticles. Every material has a characteristic plasmon (collective oscillations of electrons) associated with it, which is size dependent. When the mean free path of the electron exceeds the size of the structure; 10 nm to 100 nm, the plasmon is mostly associated with the surface. When a light matching the plasmon frequency of the nanostructure is incident on it, it excites the surface plasmon of the Nano substrate. This is called surface plasmon resonance.[10] The excited surface plasmon produces an oscillating dipole leading to the generation of the source, producing a local electromagnetic electromagnetic (EM) radiation matching the excitation enhancement very close to the surface (~1 nm of the nanosubstarte). When a molecule is in the proximity of the surface of such a nanostructure, the Raman signals enhanced due to the increase of the EM field because of resonant plasmons, leading to the phenomenon of SERS.[11] There are two proposed mechanisms for SERS enhancement, electromagnetic enhancement and chemical enhancement.[12]

The amplifications of Raman scattering in SERS effect generally generated by two mechanisms.

1.2.1. Electromagnetic field enhancement.

1.2.2. Chemical or electronic enhancement.

1.2.1 Electromagnetic field enhancement:

The collective excitation of the electron cloud of a conductor is called a plasmon; if the excitation is confined to the near surface region it is called a surface plasmon. EM enhancement is a consequence of the interaction of incident electric field (from incident radiation) with the electrons on the metal surface, which causes excitation of surface plasmons and, thus, enhancement of electric field at the metal surface. This mechanism was proposed by Jeanmarie and Van Duyne in 1977. Electromagnetic enhancement arises from the presence of surface plasmons on the substrate, Figure 4.

• Surface plasmons are electromagnetic waves that propagate along the surface parallel to the metal/dielectric interface.

• Surface plasmons are generated when the incident light excites the electron gas of the metal.

• When a substrate is placed in the proximity of the plasmon, it experiences an enhanced electromagnetic field and produces an enhanced scattered Raman field.

• Excitation of surface plasmon tends to form specially localized "hot areas".

• The magnitude of enhancement ~106-107 times for single colloidal silver, and ~108 for the gap between two coupled particles.

- ❖ Increase of the electric field near the metal surface where the molecule adheres. [13]
- ❖ Nano scale roughness
- ❖ Enhancement factor-10^4
- ❖ Long range:2-4nm

1.2.2 Chemical or electronicenhancement:

It results from an increase in molecular polarizability, due to the charge transfer between metal and sample molecule and due to specific interactions, forming charge-transfer complexes. When molecules are adsorbed to the surface, their electronic states can interact with the states in the metal and produce new transitions which cause enhancement of Raman signal. It was proposed by Albrecht and Creighton in 1977. It involves charge transfer between the chemisorbed species and the metal surface. The magnitude of chemical enhancement ~10-100 times. Figure 5

- ❖ Increase the molecular polarizability by formation of chemical bond with metal[13].

- Atomic scale roughness.
- Enhancement factor-10^2
- Short range:1-5A^0

Figure: 4 Em-enhancement

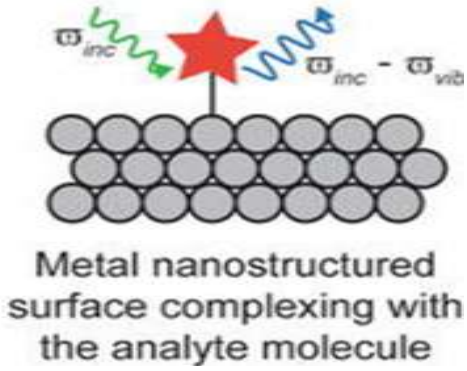

Figure: 5 Chemical enhancement

INSTRUMENTATION:

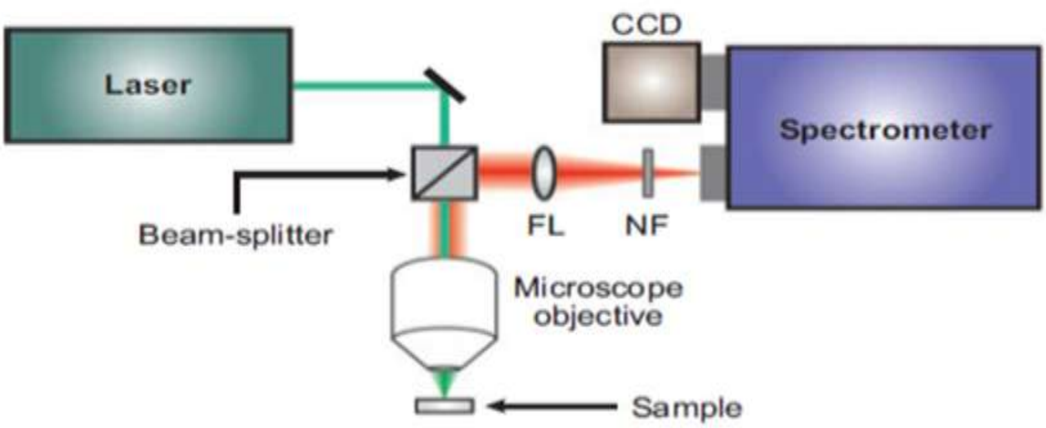

Figure:6 SERS Instrument

Instrumentation consists of

- Laser source
- Beam splitter
- Filters
- Detectors
- Sample holder

TheLaser light isbothfocusedand Raman light iscollected by a large collecting lens. The light is then passed throughthesame high numerical–aperture objective, after which the scattered light is passed through a notch filter (NF) for the removal of Rayleigh-scattered light. Finally, the light is focused by the focusing lens (FL)and directed to a spectrometer and detected using a liquid-nitrogen-cooled charged-coupled device (CCD) camera (Figure:6). The instrumental approach showing is typically used for experiments requiring low spatial resolution and high raw SERS intensity.

SERS activity strongly depends on the nature of metal and surface roughness. Therefore, SERS active substrate fabrication is a very important field in SERS research. The two most common SERS active substrates are metal colloids of coinage metals of Au, Ag and Cu obtained from chemical reduction, and the metal electrode surfaces roughened by one or more electrochemical oxidation–reduction cycles [1]. The recent advancement of nanotechnology has been utilized to fabricate various nanostructures from nanoparticles to nanowires, which can be used as SERS active substrates.

3. SERS Applications for pharmaceuticals:

- ❖ SERS methods are widely used for obtaining qualitative and quantitative information of different structures including pharmaceuticals. SERS line-widths are relatively narrow which allows for higher discrimination between samples with similar spectral profiles.
- ❖ Raman mapping and imaging of samples may provide data about the distribution andrelative amounts of active agent, additives, and binders present. [14]
- ❖ SERS were obtained using a small cuvette by using a volume ratio of three portions aqueous methimazole solution to one portion of nanoparticles dispersion. The data acquisition time was 20 seconds with one accumulation for collection with each SERS spectra. The SERS spectra were obtained in the range from 400-2000 cm^{-1}. [15]
- ❖ This method shows a higher sensitivity than that of conventional backscatter Raman spectroscopy and enables chemical information to be obtained from different depths within the sample.
- ❖ Davies, et al. Reported many polymeric materials and drug delivery systems. With high-quality spectra, drugs like promethazine, diclofenac, theophylline, and

indomethacin were monitored down to the 5% (w/w) concentration level in inert polymer matrices such as sodium alginate. [16]

❖ Raman spectroscopy has been applied to the analysis of Chinese medicines. Feng, et al. and Huang, et al. Reported a methodology for the detection of some traditional Chinese drugs by SERS. [17]

❖ Intense SERS bands were observed due to the strong interaction of the drugs with the silver colloid. Thus, SERS technique has a great potential for quick, effective, accurate, and non-destructive analysis.

❖ Huang, et al. Reported a method for collected confocal micro-Raman spectra of chick embryo vasculature with and without the antiangiogenic drug thalidomide.[17]

❖ Comparing with several methods, SERS has the advantages of being more sensitive and simple method for analysis without the need for tedious sample preparations.

❖ The method was reported with a good coefficient of determination, R^2 = 0.998 with a physical detection limit of 10 pM. [18]

❖ This method shows a higher sensitivity than that of conventional backscatter Raman spectroscopy and enables chemical information to be obtained from different depths within the sample. Davies, et al. reported many polymeric materials and drug delivery systems.[19]

❖ The reported results indicated relative Raman intensity variations for some characteristic peaks. The reported results indicated the effectiveness of the Raman method in detecting the mechanism of vascular changes. Comparing with several methods. [20-25]

CONCLUSIONS:

Surface-enhanced Raman scattering (SERS) revolutionised the Raman spectroscopy in the last decade. SERS is based on the marked enhancement of Raman signals of certain molecules when they are placed in the proximity of certain nanostructured metallic surfaces. Two types of mechanisms (Electromagnetic and Chemical Enhancement) are currently used to explain the SERS phenomenon. SERS has advantages of (i) High sensitivity, (ii) Specificity and Valuable tool for analysing mixtures, (iii) Low-power lasers and low magnification optics are suitable to acquire SERS spectra in very short acquisition times (typical ~10 s), and (iv) Many applications including drug analysis, manufacturing, and quality control.

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