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SURFACE ENHANCED RAMAN SCATTERING: NEW CONCEPTS IN MECHANISMS AND MODELING

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Abstract: The use of modeling and advanced theory has become necessary to understand SKRS as a fundamental phenomenon and to correctly interpret and predict experimental results obtained under different conditions and environments. This is valid for SM/single particle level SKRS as well as for ensembles containing few or many molecules/particles. Theoretical modeling of SKRS intensities and spectra has a long history and has been reviewed many times [8-15]. Researchers have now established that the overall enhancement factor (CF) is the electromagnetic (EM) enhancement associated with plasmon excitation in the metal particles serving as the SKRS substrate, and often during the formation of metal-molecule bonds to the metal particles and the target molecules. It has been suggested that the combination of chemical (CHEM) enhancement depends on the ability to transfer electrons in the excited state.

Key words: surface, enhancement, scattering, mechanism, modeling, concept.

Introduction

Noble-metal nanoparticles (NPs) have attracted extensive research interest due to their unique physical and chemical properties compared to all their counterparts, one of the most interesting aspects being their optical properties. These nanoparticles (NPs) exhibit strong absorption in the visible part of the spectrum, which is due to collective electron vibrations in the conduction band known as surface plasmons in response to the electric field of the incident light. A common spectroscopic technique used for this phenomenon is Surface-Enhanced Raman scattering (SERS), which has attracted much attention since its discovery in 1974.

SERS uses an electromagnetic field scattered on metal NPs or uneven metal surfaces to significantly amplify molecule-specific Raman signals, which is an ultrasensitive, nondestructive, and powerful analytical tool for real-time detection. It becomes possible to amplify the signal with a high order of magnitude and is widely used in the fields of sensing, molecular electronics, and single-molecule spectroscopy. In addition, SERS can be combined with other advanced techniques such as in vivo imaging and microfluidics. Despite the rapid development of this field, the creation of renewable and usable SERS substrates is complex, ranging from chemical procedures using colloidal metal solutions and reverse micelles to methods such as Nanosphere Lithography (NSL), Nanoimprint Lithography (NIL) and Electron Beam Lithography (EBL). has been a task. Many substrates produced by such methods are limited by air sensitivity and general instability (e.g., silver-based), and their production requires nanoparticle synthesis expertise or highly specialized equipment. The inhomogeneity in size and shape of NPs due to different preparation recipes can lead to inconsistencies and unreliable SERS performance.

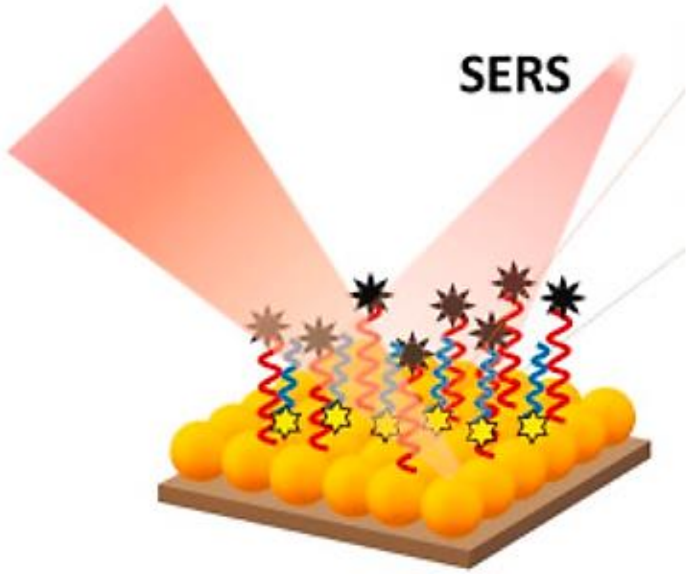

Figure 1. Raman signal enhancement at the surface.

The Raman signal is formed from the absorption of an incident photon with a frequency ωtush (see Fig. 1), which is related to the internal degree of freedom of the molecule (ωteb is formed by the re-emission of the molecular vibrational frequency at different frequencies ωem = ωtush ± ωteb, where the sum/difference, respectively leads to anti-Stokes/Stokes Raman scattering.Therefore, the process consists of three inelastic transitions (absorption, vibrational excitation, and re-emission); the vibrational excitation is via the chemical interaction discussed above occurs with a probability that depends on the environment, while the other two processes are controlled by the presence of photonic states at the positions of the molecules. i.e., the area of the incident beam where the incident photons are effectively converted to emitted Raman photons) has a quantification of ∼10–11–10–15 nm2 depending on whether the process is resonant or non-resonant Raman scattering (i.e. whether the incident light resonates with the transitions between the ground and excited electronic states of the molecule). The low intensity of Raman scattering is insufficient for many practical applications, and therefore it is often worthwhile to find means to improve the Raman scattering process. Such devices are provided with high amplification of the optical field created by suitable resonant structures. In particular, the initial absorption process is directly proportional to the intensity of the local electric field in the molecule, which can be dramatically enhanced by plasmons in metal nanostructures compared to the incident light intensity. Although it is possible to obtain SKRS by strengthening the electric field on single nanoparticles, it is useful to use a more complex structure, for example, placing molecules in nanometer-sized gaps between two metal particles (hot spots), which is usually up to KF ~ 105-106 allows to reach the intensity [6-9].

Hot spots can appear not only in the gaps between nanoparticles, but also at junctions between nanoparticles and flat metal surfaces that support plasmon resonances. The resulting field strength depends on the gap spacing and other geometric details. In particular, the amplitude of the electromagnetic field has an approximately inverse relationship to the gap. From the point of view of classical electromagnetism, the main characteristics of the Ugandan SKRS hot spot with a gap size in the range of 2-10 nm are satisfactorily described, if non-local effects are ignored, only the frequency-dependent dielectric functions of the materials in the structure are will be considered. When the nanoparticle spacing is reduced from 1 nm, non-local effects appear, which requires more complex processing of the optical results. Moreover, the amplification of EM fields at such small distances is so large that the optical response can be nonlinear (ie, the threshold for nonlinear effects decreases inversely with increasing field). In this strong binding mode, the internal properties of the molecule-nanoparticle system can change significantly, which in turn affects the SKRS intensity. For example, triggering or catalyzing chemical reactions, changing the photophysical or photochemical properties of the adsorbed molecule, generating hot electrons that can change the excitation dynamics and molecular opto-mechanical effects on the nanoparticle surface. includes. In the extreme binding regime (for example, a single molecule inside a nanometer-sized cavity or a picocavity), classical models are invalid and must be supplemented by descriptions based on quantum-mechanical approaches. Therefore, specific and accurate modeling of Raman scattering and competing processes at subnano- and nano-scale hotspots is essential to develop substrates with the desired SKRS response to support or interpret experimental results.

EXPERIMENTS AND MECHANISMS

MECHANISMS OF SURFACE ENHANCED RAMAN SCATTERING: ELECTROMAGNETIC FIELD AMPLIFICATION.

The electromagnetic field enhancement factor is the subject of many studies, usually using electrodynamic calculations to determine the enhanced electric field amplitude E(ω) that occurs when plasmons are excited in the SKRS substrate at frequency ω; E(ω) is then evaluated at the molecular positions. The SKRS gain is usually estimated by averaging |E(ω)|4/|E0|4 over the illuminated molecules, where E0 is the incident (laser) field amplitude. In fact, this analytical result neglects the Stokes shift, which can be introduced by a slightly more accurate expression: |E(ω)|2|E(ω')|/|E0|4, where ω' is the Raman scattering frequency. A somewhat more accurate approximation is also obtained by correcting the factor |E(ω')|2 to properly account for inelastic emission dipole emission (sometimes called dipole reradiation [10]). Another important problem is related to the significant field gradients that often arise from the strong spatial localization of the plasmon-enhanced field [11,12] ; these gradients contain non-dipolar components, which can provide effective SKRS including dipole-quadrupole and quadrupole-quadrupole input-output polarizations; These effects are stronger for transitions involving more spatially delocalized electronic states in the molecule. Calculations based on dipole backscattering and field gradient effects are rarely performed because nanoparticle structures are not known precisely enough to warrant this level of detail in the analysis. Indeed, in most cases the expression |E(ω)|4 gives good results as an approximate quantity. In fact, 10 years ago, Schatz and Van Duyne used this level of theory in their research on nanoparticle clusters, and found that the electromagnetic amplification factor for nanoparticle clusters often peaks at wavelengths where plasmon resonances are "dark" (experimentally ~ 109) showed that (ie, at wavelengths corresponding to a decrease rather than a maximum in the extinction spectrum) [13,14]. Dark plasmon modes, often of quadrupole character, can nevertheless generate strong electric fields at the electromagnetic points between nanoparticles [14]. Furthermore, at wavelengths where the plasmon resonance is dark, dipole reradiation can sometimes lead to stronger far-field (far-field Fig. 2) intensities than expected.

found that the dipole field of adsorbed molecules can more effectively excite quadrupole and higher-order multipole resonances than light plane waves.

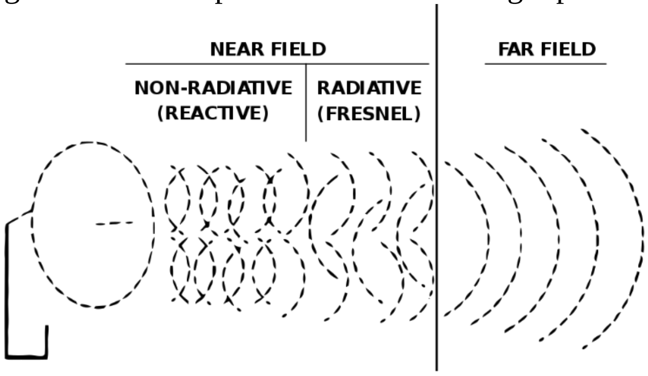

Figure 2. Near and far field view

Although most numerical simulations of electromagnetic amplification are limited to relatively simple geometries or at most a few particles, ensemble effects can be very important when dealing with real large-scale SKRS samples. In a recent example, state-of-the-art electromagnetic computing techniques were used to simulate nanoparticle-based SKRS substrates composed of hundreds of randomly arranged gold nanoparticles. The authors unexpectedly concluded that it is the nanoparticle surface morphology that provides significant enhancement at the individual particle level, for example, nanostars are not enhanced when separated into densely packed arrays; in contrast, simpler morphologies (such as spheres or stars) lead to a significant increase in SKRS as their surface density approaches full coverage (Figure 2) [9].

In addition to electromagnetic field enhancements that can be calculated by solving Maxwell's equations for specific nanostructures (such as spheroids) [15], more qualitative calculations of enhancement factors based on simple model structures have been developed and in good agreement with experimental data, ultraviolet (UV) of aluminum, gold or silver in a wide range of wavelengths from near infrared (NIR) was used to understand the SKRS for randomly uneven surface substrates [16].

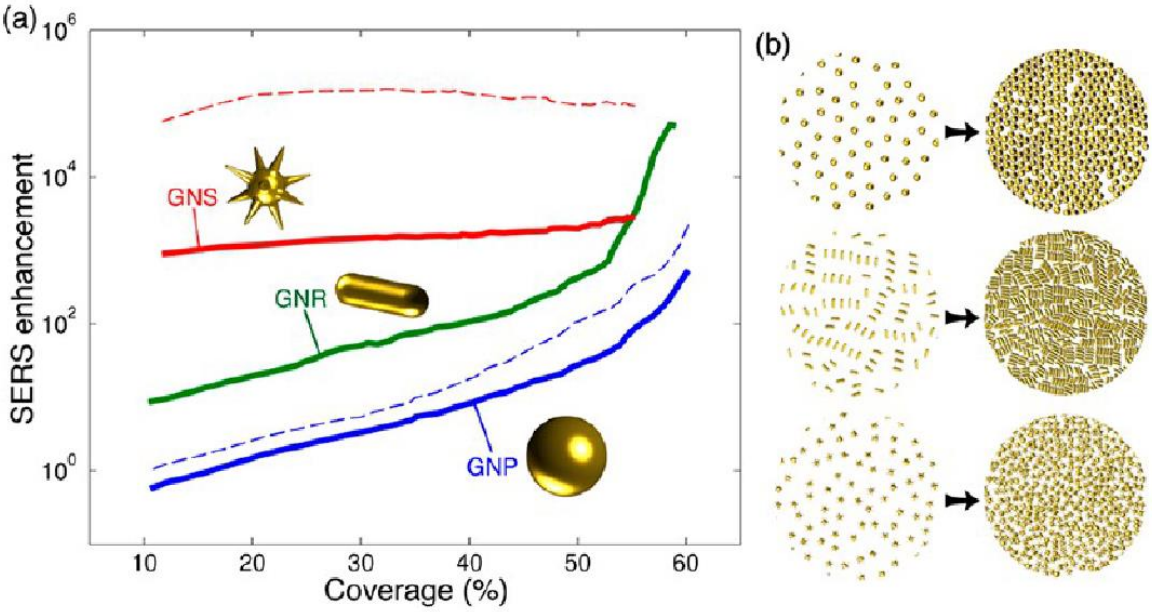

Figure 3. Predicted SKRS enhancement as a function of surface coverage for monolayers of gold nanoparticles of different shapes (a).

Solid curves obtained for excitation at 785 nm light wavelength (resonance with 65x21 nm nanostages); Dashed curves obtained for 633 nm (resonance with 51 nm nanospheres) and 900 nm (resonance with nanostars: 20 nm core, 10 nm branches). Schemes in (b) depict low and high density nanoparticle surface coating. Copyright 2017 American Chemical Society [9].

The prediction of plasmonic properties of nanoparticles with random morphology has also recently been simplified by deriving analytical expressions based on parameters derived from numerical modeling [17,18] . Non-local effects can also play a role in the electromagnetic mechanism; for example, even though electromagnetic hotspots that dominate SKRS measurements occur in the spaces between nanoparticles (leading to SM sensitivity), non-local effects may also play a role in the electromagnetic mechanism [19,20]; for example, gaps between nanoparticles lead to electromagnetic hotspots that dominate SERS measurements (resulting in SM sensitivity [21]), although classical electromagnetic enhancements predict that they should vary inversely with gap size [22], for gaps with dimensions significantly below 1 nm, electron tunneling quantum effects between nanoparticles are important, significantly changing the dominant plasmon energy, which usually leads to a weakening of the electric field [11,23 ,24].

MECHANISMS OF SURFACE ENHANCED RAMAN SCATTERING: CHEM.

The chemical mechanism of SKRS contributes to Raman scattering that does not rely on an electromagnetic field (e.g., plasmon excitation), as it is often associated with the transfer of electrons between adsorbed molecules and the nanoparticle substrate. This can occur through two pathways, corresponding to electron transfer and excited states of the molecule-metal system. The EF associated with the previous mechanism can be determined in terms of the derivatives of the static polarizability of the molecule-metal system [25], which can be calculated using electronic structure theory using a cluster model for a metal particle, in which the particle is replaced by a small cluster of metal atoms. This type of calculation produces a result that is nominally independent of frequency, reflecting the change in the polarization derivative due to charge transfer by a molecule adsorbed on the nanoparticle metal. Valley et al obtained values from such calculations for several substituted benzene thiolates adsorbed on silver and gold substrates and compared them with measured KF [26].

We note that the measurement of the Ag-CO KZRS can also be performed by observing the CO vibrational frequency change instead of the Raman intensity as a function of the potential shift.

CONCLUSION

Since the substrates were the same for all molecules considered, the change in KF for different molecules was entirely due to changes in chemical enhancement. Theory and experiment were in agreement within a factor of 2, and values showing a change of ∼10 for the molecules considered corresponded to chemical enhancements in the range of 10–100. Although the static polarization derivative provides a simple way to model the chemical effect, the charge transfer in the optical frequency characteristic should be fully understood [27,28]. However, charge transfer is difficult to assess because charge transfer states cannot be accurately described by standard density functional theory (DFT) methods and are strictly coupled to plasmonic excitations in models that bind molecules to metal clusters. . Thus, the charge transfer effect cannot be strictly separated from the plasmon excitation. One way forward involves the use of semi-empirical molecular orbital methods such as INDO/S, the parameters of which Ag is properly chosen to give optimal plasmonic properties. With this approach, charge transfer effects can be accurately described and the charge transfer and plasmonic contributions to SKRS can be separated for molecule/cluster models.

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