Study of geometry dependent Raman enhancement factor of a single biomolecule

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Abstract

Optical properties of Au metal nanoparticle have been studied in terms of extinction (scattering+absorption) at the resonance wavelength from UV to IR region. For the spherical geometry having radius 10nm, local electric field intensity distribution were studied at wavelength 615nm. This enhanced field has been couples in the SERS where we increase the sensitivity of the surface to detect a single biomolecule which is adsorbed at the surface of metal nanoparticle. The field profile was studied using COMOL-5.2 which works on the principle of electrodynamics in which the solution of Maxwell's equation with certain boundary condition is solved. Optimized physical and geometrical parameters was suggested for the application in the field of chemical and biomedical instrument development for the purpose of drug detection and disease diagnosis for cancer detection at the early stage.

Keywords: Optical property, metal nanoparticles, extinction, SERS, SPR.

Introduction

The localized surface plasmon resonance supported by the noble metal nanoparticles MNPs are being used to enhance the scattering cross-section of the optical signal generated by the single molecule which is adsorbed at the surface of metal nanoparticle (MNP) under resonance condition in the polarisability of the nanoparticle. The material used for MNPs are Ag, Au, Cu etc. are called plasmonic material which has resonance wavelength in the visible range and can be tune over the range by changing the surrounding dielectric media. The wavelength at which resonance occurs is called resonance wavelength. This concept of resonance in the polarisability is exploited for the various applications. SERS is one of the most demanding field which has very high demand in biomedical and chemical engineering. Through the plasmonic coupled Surface enhanced Raman Scattering (SERS) called Raman plasmonics, sensitivity of the surface is enhanced for the detection of weak Raman signal which contain many physical and geometrical informations of molecule. The old technique called Surface Enhanced Raman scattering (SERS) was not very sensitive to detect single molecule situated near the surface. This branch of plasmonics (Raman plasmonics) deals with the issues related with the sensitivity of the device and tunability of detection range in terms of wavelength. The application of plasmonics in the Raman spectroscopy makes this field very fascinating and innovative in the various field like single molecule SERS (SMSERS), solar energy conversion, optical trapping, optical data storage etc. to the research community. The application of Raman plasmonics in the single molecule detection showed the real caliber of the technique in terms of huge enhancement in the sensitivity of the detection of biomolecule in biomedical and chemical field.

Theory

We discuss the Raman gain factor of single biomolecule absorbed at the Au metal nanosphere. The molecule which is chosen for the detection is assumed to be an equivalent dipole having constant polarisability. As the size of the nanosphere is smaller in comparision to the wavelength of incident light, electrostatic approximation could be employed to analyze the optical footprint. In this approximation, the Laplace equation $\nabla^2\Phi = 0$, have been solved for nanosphere to obtain the polarisability and field profile.[26, 27] Consider a sphere embedded in a uniform electric field E_0, the induced dipole moment per unit volume of particle $P = \varepsilon_0\varepsilon_m\alpha_s E$. Here α_s is the polarisability of metal nanosphere which can be expressed as

$$\alpha_s = 4\pi a^3 \left| \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \right| \quad (1)$$

Now we are interested in near field observation i.e. $\lambda_0 >> r$, where r is the distance to the point of observation and the λ is the wavelength of incident monochromatic light. Where, E is the induced field, ε_m is

the permittivity of surrounding medium, ε_0 is the permittivity of the free space, ε_1 is the permittivity of the silver metal sphere. The surface plasmon resonances in metal nanoparticles would occur due to the resonance in polarisability. When Frohlich condition ($\mathrm{Re}\,\varepsilon_1(\omega) + 2\varepsilon_m = 0$) is satisfied, the polarisability α_s will be maximum only. Under this condition, the field in the vicinity of the nanoparticle dramatically enhances that can be utilized for many purposes.

The scale dependent dielectric constant of metal nanoparticle has been derived using Drude model that can be expressed as [28]

$$\varepsilon(\omega) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + j\gamma_{bulk}\omega} - \frac{\omega_p^2}{\omega^2 - j\gamma\omega} \qquad (2)$$

Here $\gamma = \gamma_{bulk} + Av_f / a$ and $\tau = 1/\gamma$, $\tau_{bulk} = 1/\gamma_{bulk}$. where, "γ" is the modified damping factor when the material downshifted to the nanoscale, "γ_{bulk}" is the damping factor when the material is on bulk/large scale, "A" is the geometrical factor which depends on the geometry or the shape of the nanoparticle, "v_{fermi}" is the Fermi velocity of conduction electron which is of the order of the 10^6 m/sec, which depends upon the kind of material, and "a" is the radius of the nanosphere in the sphere dimer. The factor τ and τ_{bulk} are the modified and original relaxation time respectively.

The optical property of nanodimer can be expressed in terms polarisability as

$$C_{scat} = \frac{k^4}{6\pi}|\alpha_S|^2 ; k = \frac{2\pi}{\lambda_0}$$

$$C_{abs} = k\,\mathrm{Im}(\alpha_S)$$

$$Q_{ext} = \frac{(C_{scat} + C_{abs})}{\pi a^2} \qquad (3)$$

Here Q_{ext} is the extinction efficiency of nanodimer which is the ratio of sum of scattering and absorption cross section divided by geometrical cross section. [28-32]

The measure of interaction between the biomolecule and Aumetal nanoparticle is measured by Raman amplification factor R which is defiend by the formula [self paer]

$$R = \left| \frac{1}{1 - \alpha_{mol} G} \left[1 + \frac{2\alpha_{Geometry}}{(a+d)^3} \right] \right|^4 \qquad (4)$$

where $\alpha_{Geometry}$ is the polarizability of the nano geometry and α_{mol} is polarizabiliy of the olecule adsorbed at the surace of MNPs. G is called geometrical factor which depends upon the shape of the taken geometry. "a" is the effective radius of the geometry.

Results and discussion

Optical properties of metal nanoparticles can be very much analyzed by knowing the response of the light when it interacts with the MNPs. This response is being measured by knowing how much light absorbed and how much is being scattered. This total amount of light which is being absorbed and the light which is being scattered is called extinction (Q_{ext}), which is defined in the above eq.(3).

In **Fig. 1** for sphere nanogeometry Q_{ext} is very high and it is almost 0.4 and it decreases with decrease in radius with smallest value for 10 nm sphere. **Fig. 2** is the scattered field distribution for incident field polarization along Z- direction. The highest field intensity almost 5 unit is along the same direction as was applied along. At this high intensity region the possibility of single molecule detection is high while along X- direction it has least posibilty of detection.

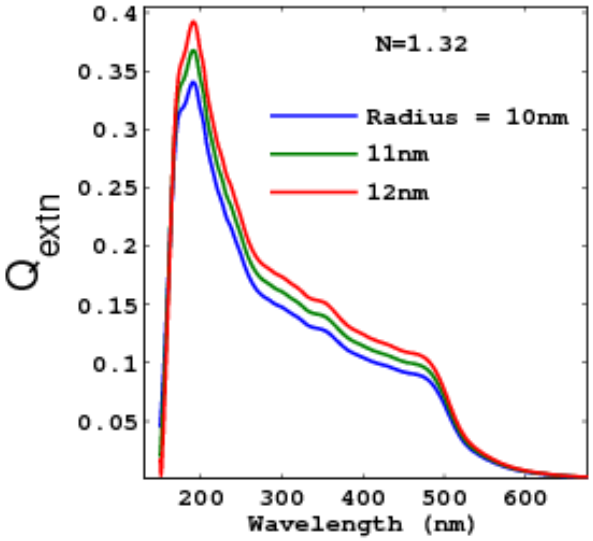

Fig. 1. Showing the variation of Q_{ext} for **sphere nanogeometry** with respect to the wavelength between 200nm to 700nm for the three different values of radii 10, 11, 12 nm respectively in water like surrounding medium.

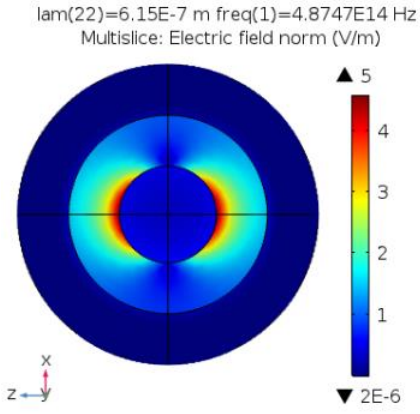

Fig. 2. Showing the intensity of scattered field in the vicinity of 10 nm radius Au nanosphere which is surrounded in the medium which has refractive index N=1.32 at wavelength 615nm.

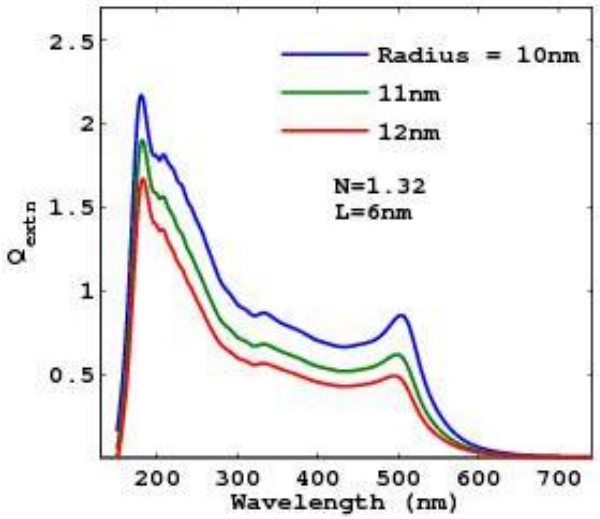

Fig. 3. Showing the variation of Q_{ext} for **spheredimer nanogeometry** with respect to the wavelength between 200nm to 700nm for the three different values of effective radii 10, 11and 12nm respectively in water like surrounding medium.

Fig. 3 explains how the Q_{ext} depends on the size as well as wavelength for the three different effetive radii 10, 11 and 12nm respectively for symmetric nanodimer with surface to surface distance 6nm between anospheres involved. We observed that Q_{ext} increases with decrease in radii.

Fig. 4 shows Raman gain factor (R) versus normalised frequency of sphere dimer where biomolecule adsorbed at a distance d=1nm. At radius 10nm the Raman enhancement factor more than 10^7 was found and smaller for higher value of efective radius when the system is put in the water like madium. When we increase the size of the geometry, the Ramman enhancement factor R decreases appresiably under same surrounding einvironment at the same resonence wavelength

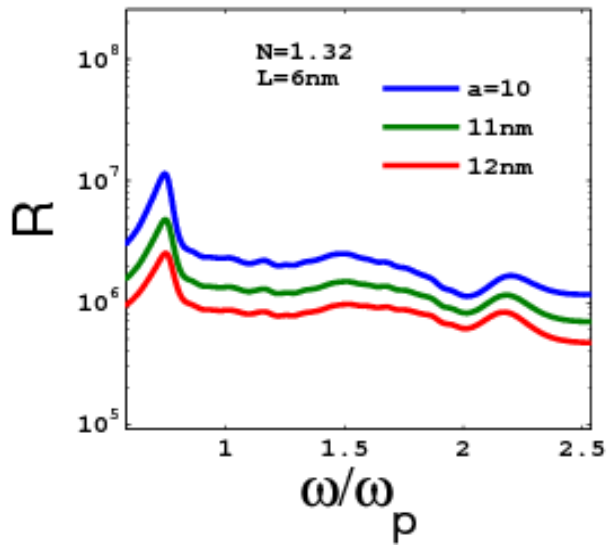

Fig. 4. Showing the variation of R (Raman enhancement factor) for **spheredimer nanogeometry** with respect to the normalized frequency (ω/ω_p) of effective radii 10, 11and 12 nm respectively in water like surrounding medium (N=1.32).

Conclusion

Optical properties of two different geometries have been studied for three different sizes and it was found that the extinction efficiency of dimer is many times higher than the extinction for the sphere geometry. If we compare the result of Q_{ext} for nanosphere and nanodimer, we find that first increases with increase in radius while in the case of second i.e. nanodimer it decrease with increase in effective radius. It was also found that the there are two resonance peaks coming in the dimer geometry, but in case of sphere no other resonance peak is observed. This implies that at other place there is a possibility of detection of biomolecule. For the **Au** nanodimer geometry the Raman enhancement factor (R) was very much dependent on radius and it decreases with increase in radius. These conclusions will certainly help to the research community.

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