Study of Surface Enhanced Raman Scattering of Single Molecule Adsorbed on the Surface of Metal Nanogeometries: Electrostatic Approach

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Abstract In this paper, we have studied the surface enhanced raman scattering (SERS) from a molecule adsorbed on coated and non-coated spherical shape metallic nanoparticles. We have accounted for the nonlocal dielectric response from the metal nanoshell by using a phenomenological model based on quasi-static domain. The calculation of the enhancement factor has been done keeping the outer radius of the shell fixed. The modal developed here suggests strong enhancement of the Raman signal due to plasmonic coupling effect of a nanostructure with a biological cell. This facilitates the detection of some particular biological cell for example cancer cell. The basic principle involves amplification of the Raman signal that carries characteristic signature of the cell using coupled resonance system of cell and nanostructure. We have also compared the two cases of coated and non-coated nanospheres to analyse the SERS enhancement factor, surface plasmon resonance (SPR) and extinction efficiency which results that the coated geometry shows better response over the non-coated. The parameters such as material, size, thickness of the shell, and molecule distance from the surface of nanogeometry have been optimized to achieve Raman enhancement signal of maximum signal strength. It has been concluded that a small particle size of 20 nm for Ag at shell thickness 12 nm shows greater enhanced Raman characteristics. The enhancement factor of the order of 10^{12} for core-shell (SiO2@Ag) system shows a lot of future prospects and applications that can be achieved using such a plasmonically coupled resonance system.

Keywords SERS mechanism · Enhancement factor · Coated and non-coated nanosphere · SPR

Introduction

The Raman effect in the context of molecule describes the inelastic scattering process between the molecule and the photon mediated by the vibrational and the rotational modes of the molecule. The energy exchange between the two partners (photon and molecule) results in the shifting of incoming photon energy by the characteristic energy of vibration of the molecule [1–3]. This kind of shift is in both directions depending upon whether the molecule is in a ground state or in excited state. In the first case, the molecule absorbs energy, and hence, shift will be in the lower frequency side and the corresponding line is known as the Stokes line. In the second case, when the molecule is in the excited state it releases energy, and hence, the energy of the photon increases that leads to the shifting in the frequency towards the higher side. As these transitions occur in between vibrational or in rotational states, the intensity of the signal corresponding to such transition is not enough to detect the huge amount of characteristic information present. This demands an urgent need of amplification in intensity of the signal. There are various approaches based on theoretical and experimental facts that have already been discussed in recent literatures [4, 5]. Out of these approaches, surface enhanced Raman scattering (SERS) is one of the significant ways to enhance the intensity signal according to our own requirements.

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SERS is an efficient vibrational spectroscopic tool which provides huge amplification in Raman intensity and reducing the traditional drawback of Raman scattering [6–8]. The enhancement or the amplification factor via SERS technique is high enough and is sufficient to allow even single molecule detection using Raman scattering [9, 10]. The SERS technique has a wide range of applications such as trace material analysis and cancer therapy, where the other techniques are inefficient to detect Raman signal [11–13]. The SERS technique pays much attention for the researchers since the past few decades due to its application in various fields of science and technology such as the plasmonic-based biosensor and molecular detection [14, 15]. There are two basic types of SERS enhancement mechanism; the first one is the chemical enhancement mechanism, and second is the electromagnetic enhancement mechanism. The electromagnetic enhancement occurs due to the interaction between incident field and Raman electromagnetic field on the metal surface under localized surface plasmon resonance. Out of these two types of enhancement mechanism, the electromagnetic enhancement mechanism is considered to be the main contributor to SERS phenomena [16–18]. The chemical enhancement mechanism is mainly due to the shifting of Raman scattering from non-resonance to resonance after the transformation of charges between the adsorbed molecules and metallic structures [19–21]. The magnitude of this enhancement mechanism is smaller as compared to the electromagnetic enhancement mechanism where a strong resonant field may enhance the strength of the signal manifold. But the chemical enhancement mechanism has its own potential in the field of plasmonic chemistry [22]. SERS mechanism is witnessed to have very strong electromagnetic enhancement in Raman signal in which the molecule is situated either on the surface or at a certain distance from the metallic geometry. This massive enhancement in Raman gain occurs due to the resonant interaction of electromagnetic field with the composite nanogeometry. Hence, metal nanostructures that support surface plasmon resonances are one of the strong candidates to study the SERS phenomena. In fact, the SERS enhancement mechanism can be realized in various nanogeometries; among them, core-shell is one of the key methods [23].

In this paper, we are interested in electromagnetic analysis where the interaction between the light and the metal nanoparticle is taken into account that results in the excitation of surface plasmon. We have used metallic nanoparticles that are capable to generate localized surface plasmons (LSP) [24–26]. When nanoparticle (NP) is excited by incident light, a huge electromagnetic field is confined near the surface of the nanoparticles after fulfilling the resonant condition [27]. By varying the geometrical parameters of a particle, like size and shape, the LSP resonance (LSPR) can be tuned over a wide range of electromagnetic spectrum [28, 29]. We have studied the SERS mechanism for a molecule adsorbed on a coated and non-coated metal nanosphere using the Gersten-Nitzan (GN) model. The calculation of polarizability for both coated and non-coated metal nanoparticles (MNPs) used in the GN model has been derived under quasi-static approximation. In case of coated sphere, a dielectric core and a silver metal shell have been taken into account. The optical constants of a core-shell material have been taken from the literatures [30]. We have found that the coated nanogeometry is more significant to obtain the enhancement of a SERS signal and tunability of a SPR peak as compared to non-coated nanospheres.

The SERS mechanism is twofold; first, the incident electromagnetic field E_o interacts with the Raman active system, exhibiting magnified scattered field E_s due to plasmonic effects. Second, these enhanced scattered fields again interact with the Raman active molecule and produce Raman scattering E_R which again interacts with plasmonic nanostructure and finally produces a SERS field (E_{SERS}), and its schematic diagram is shown in Fig. 1.

Theory

In order to understand the electromagnetic mechanism of SERS, we consider a single molecule adsorb on the surface of coated and non-coated MNPs. When the light is scattered by the molecule, the process is generally elastic and is called Rayleigh scattering. This can be treated classically by considering the molecule to act as a dipole which oscillates at the same frequency as the incident electric field.

The Raman cross section of coated and non-coated metal nanostructures can be obtained by using the GN model [11, 31] as

$$\sigma_{SERS} = \left(\frac{8\Pi}{3}\right)\left(\frac{\omega}{c}\right)^4 (\Delta C)^2 \left(\frac{\partial \alpha}{\partial C}\right)^2 \left|\frac{1}{1-\alpha G}\left[1 + \frac{2\alpha_{C,NC}}{(b+d)^3}\right]\right|^4 \quad (1)$$

$$G = \sum_l \frac{l+1^2}{b+d^{2l+1}}\alpha_{C,NC} \quad (2)$$

G is the geometry-dependent image field factor. Here, we have assumed that the molecule having constant polarizability is situated at a certain distance from the metal nanogeometry. Hence, the Raman enhancement factor for a composite system which contains both molecule and metallic nanogeometry can be expressed as

$$R = \left|\frac{1}{1-\alpha G}\left[1 + \frac{2\alpha_{C,NC}}{(b+d)^3}\right]\right|^4 \quad (3)$$

where α is the polarizability of the molecule taken to be constant equals to 10 A^3, $\alpha_{C,NC}$ is the dipolar polarizability of the coated and non-coated nanosphere. The polarizability expressions of coated and non-coated nanospheres are obtained by

Fig. 1 SERS mechanism of coated and non-coated metal nanospheres where the molecule is situated at a distance "d" from the surface of the nanosphere
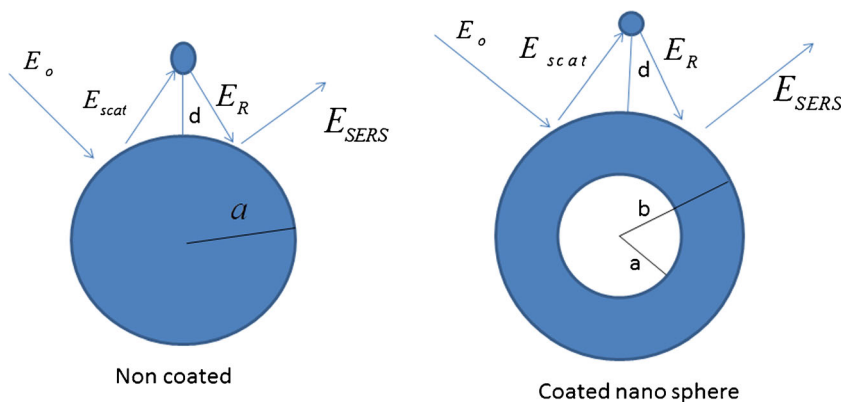
solving the Laplace equation under electrostatic approximation as [32].

$$\alpha_C = 4\pi b^3 \frac{(\varepsilon_p - \varepsilon_m)(\varepsilon_1 + 2\varepsilon_p) + f(\varepsilon_1 - \varepsilon_p)(\varepsilon_m + 2\varepsilon_p)}{(\varepsilon_p + 2\varepsilon_m)(\varepsilon_1 + 2\varepsilon_m) + f(2\varepsilon_p - 2\varepsilon_m)(\varepsilon_1 - \varepsilon_p)} \tag{4}$$

$$\alpha_{NC} = 4\pi a^3 \left(\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m} \right) \tag{5}$$

Once we have found the polarizability expression of chosen nanogeometry, we are able define the optical signature, like extinction, absorption and scattering of MNPs under quasi-static approximation which can be expressed as

$$C_{scat.} = \frac{k^4}{6\pi} |\alpha_{C,NC}|^2 \tag{6.1}$$

$$C_{absa} = k \operatorname{Im}(\alpha_{C,NC}) \tag{6.2}$$

$$Q_{ext} = \frac{(C_{scat} + C_{absa})}{\pi a^2} \tag{6.2}$$

where a is the radius of the sphere, ε_m is dielectric constant of the medium, ε_p is dielectric constant of the shell (Ag metal nano sphere), ε_1 is a dielectric constant of the core (silica), ω is frequency of incident light, and c is the velocity of light in free space [2, 33]. The size-dependent dielectric constant metal adopted from the Drude model that can be expressed as

$$\varepsilon(\omega) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + j\gamma_{bulk}\omega} - \frac{\omega_p^2}{\omega^2 - j\gamma\omega} \tag{7.1}$$

$$\gamma = \gamma_{bulk} + A\frac{v_f}{b-a} \tag{7.2}$$

$$\tau = 1/\gamma, \ \tau_{bulk} = 1/\gamma_{bulk} \tag{7.3}$$

where τ is the relaxation time of composite nano system, τ_{bulk} is the bulk metal free electron scattering time, $v_f (=1.38 \times 10^6$ m/s for silver) is the Fermi velocity of electron in silver MNP, A is the parameter that depends on the geometry whose value lies between 2 to 1, but we take $A = 1$ for isotropic scattering [34].

Results and Discussion

We have studied the SERS enhancement factor as a function of normalized incident light frequency for coated and non-coated metal nanostructures embedded in a medium with refractive index $N = 1$ as shown in Fig. 2. First, we have discussed the response of coated nanoparticles where the core is dielectric (SiO_2) and the shell is metal (Ag) as indicated in Fig. 2a. It is evident that there two plasmonic resonant modes (symmetric and antisymmetric) observed in different frequency domains with different Raman gain factors. The symmetric mode occurs at a longer frequency range, while the antisymmetric mode occurs at a lower frequency domain. Since the metal nanoparticle supports SPRs that have a wide range of tunability which depends on the size, core-shell thickness and dielectric environment. As we increase the core radii to 5 to 8 nm for a fixed value of $d = 1$ nm and the outer radii ($b = 10$ nm), symmetric and antisymmetric modes get red and blue shifted, respectively, with various magnitudes of R. The most interesting result noted is that thinner shells exhibit a greater enhancement factor at low frequencies as compared to a thicker nanoshell. For parameters $d = 1$ nm, $a = 8$ nm and $b = 20$ nm, we have found SPR frequency at 0.37 w_p and 0.85 w_p corresponding to antisymmetric and symmetric modes, respectively, with almost equal enhancement factor of the order of 10^{12}.

Now, we discuss the Raman enhancement factor of the non-coated silver nanosphere against the normalized incident light frequency as shown in Fig.2b. Four different radii ranging from 5 to 20 nm are taken into account to analyse the behaviour of plasmonic resonance and Raman gain with constant distance of molecule from the surface of nanosphere $d = 1$ nm. The result shows that the plasmonic resonances also split into two modes, one corresponding to the antisymmetric mode (higher frequency) and the other corresponding to the symmetric mode (lower frequency). If we increase the radii of metal nanosphere, the Raman gain factor increases consistently and its magnitude is more pronounced corresponding to the symmetric mode, but tunability of SPR peaks coincide at one
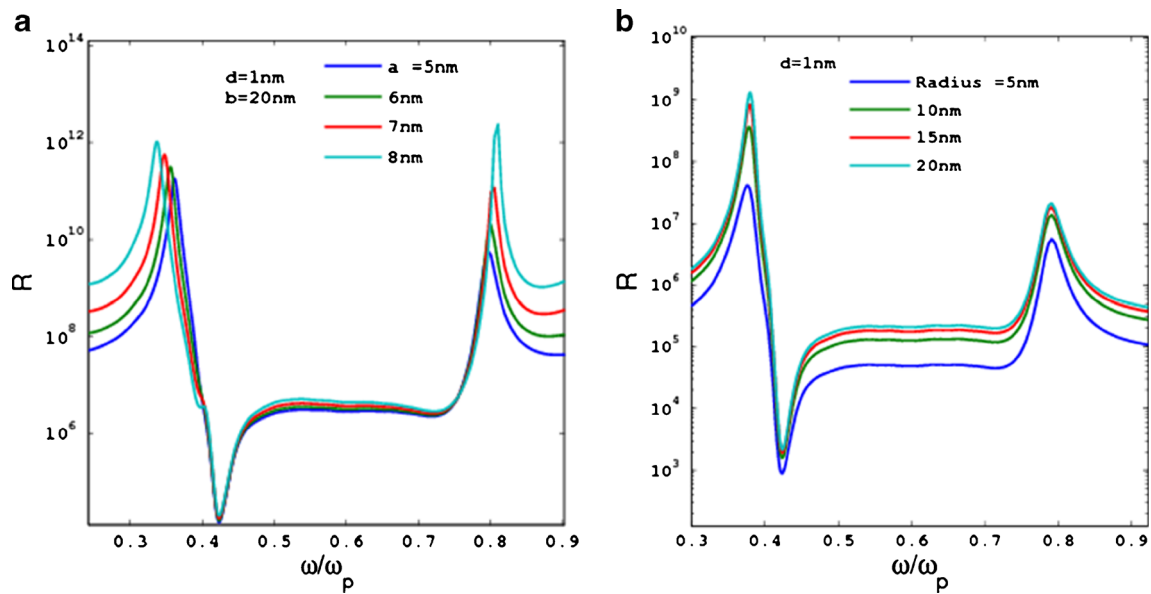
Fig. 2 SERS enhancement ratio (R) as a function of normalized plasmon frequency. **a** SiO$_2$@Ag core-shell MNPs with four different core radii and fixed outer radii $b = 20$ nm. **b** Non-coated Ag MNPs with four different radii ranging from 5 to 20 nm. In both cases, the distance of the molecule from the surface of nanosphere $d = 1$ nm, and embedding medium is air having refractive index $N = 1$

resonant frequency for all radii. For the 20-nm radius nanosphere (silver) and $d = 1$ nm, the observed order of Raman enhancement factor at resonance frequencies 0.35 w_p and 0.8 w_p are 10^9 and $>10^7$, respectively.

The variation of enhancement factor for coated and non-coated MNPs are plotted against the frequency with four different values of d (molecule distance from the surface of nanogeometry as shown in Fig. 3.). As we increase molecular distance from the surface of the coated nanosphere, both R and plasmonic resonances change which can be clearly seen in Fig. 3a. The SPRs do not have many influences in both the lower and higher frequency domains, but the magnitude of the Raman enhancement factor is inversely proportional to molecule distance from the surface of the coated nanosphere. Take
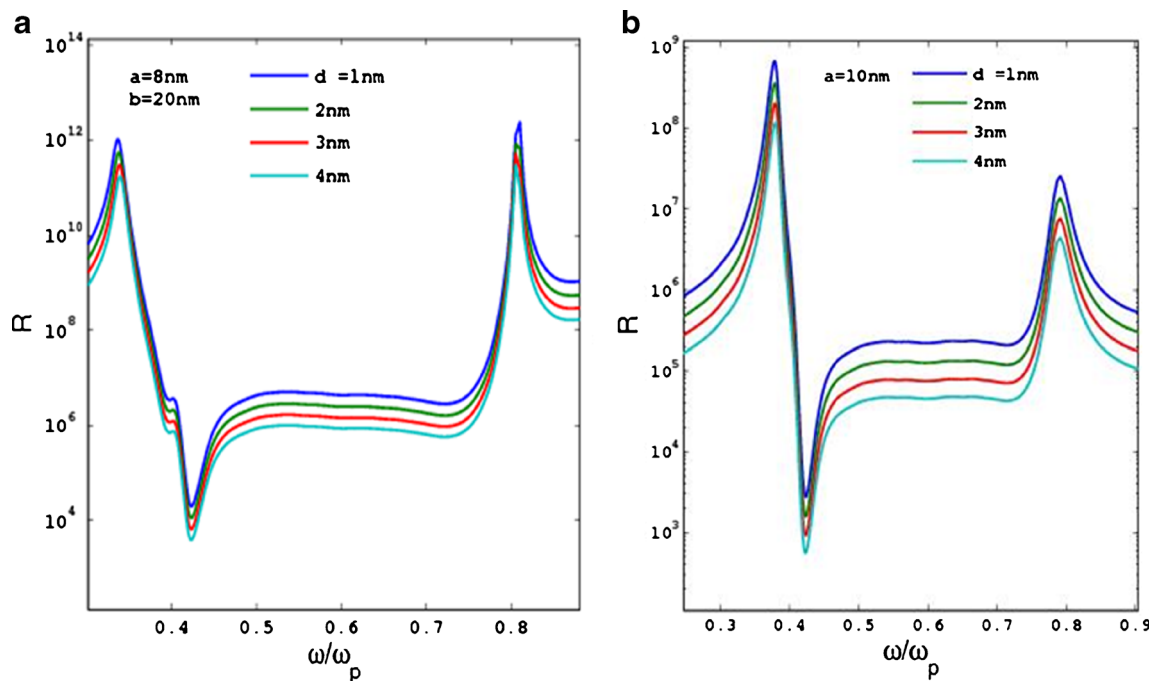

Fig. 3 SERS enhancement ratio (R) as a function of normalized plasmon frequency. **a** SiO$_2$@Ag core-shell MNPs with four different d values (1 to 4 nm) and fixed outer and inner radii $b = 20$ nm and $a = 8$ nm, respectively. **b** Non-coated Ag MNPs (radius $a = 10$ nm) with four different d values ranging from 1 to 4 nm. In both cases, embedding medium is air having refractive index $N = 1$
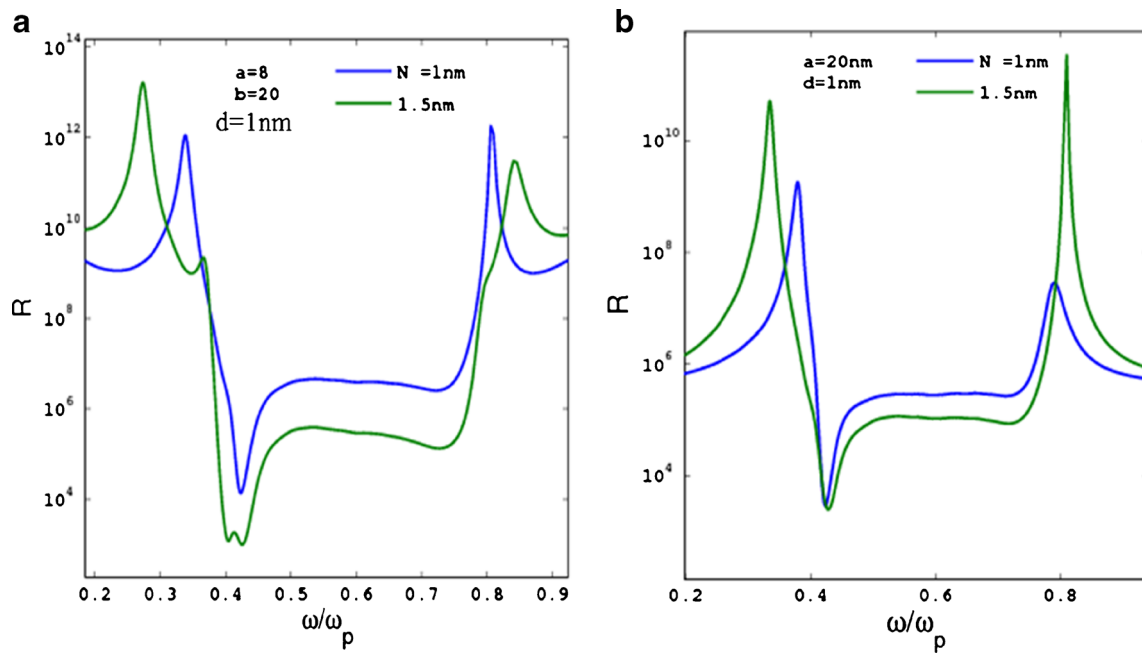
Fig. 4 Variation of SERS enhancement ratio (R) with normalized plasmon frequency having two different types of refractive indexes $N = 1$ and $N = 1.5$. **a** Coated nanosphere with $a = 8$ nm and $b = 20$ nm. **b** Non-coated Ag MNPs (radius $a = 10$ nm), and for both the cases, $d = 1$ nm

a particular case where inner radii $a = 8$ nm, outer radii $b = 20$ nm and molecular distance $d = 1$ nm. Observed Raman gain is nearly 10^{12} corresponding to both symmetric and antisymmetric modes. Figure 3b represents the frequency-dependent Raman enhancement factor of non-coated silver nanosphere for $a = 10$ nm various values of $d = 1, 2, 3$ and 4 nm, and whole system molecule and nanosphere are placed in air ($N = 1$). Silver nanosphere also exhibits two plasmonic modes in different regimes of frequency, but the magnitude of R is different corresponding to two different modes (symmetric and antisymmetric modes), and it is nearly more than 10

times smaller for the antisymmetric mode (higher frequency side) as compared to symmetric mode.

Figure 4 shows the variation of SERS enhancement ratio (R) (for coated and non-coated geometries of metal nanosphere) with normalized frequency (w/w_p). Both coated and non-coated nanoparticles embedded two different surrounding environments having index $N = 1$ and $N = 1.5$. Here, we have discussed how surrounding media (where the metal nanostructures and molecules are situated) influence the enhancement factor and plasmonic resonant peak positions. The coated nanosphere with $a = 8$ nm, $b = 20$ nm and $d = 1$ nm
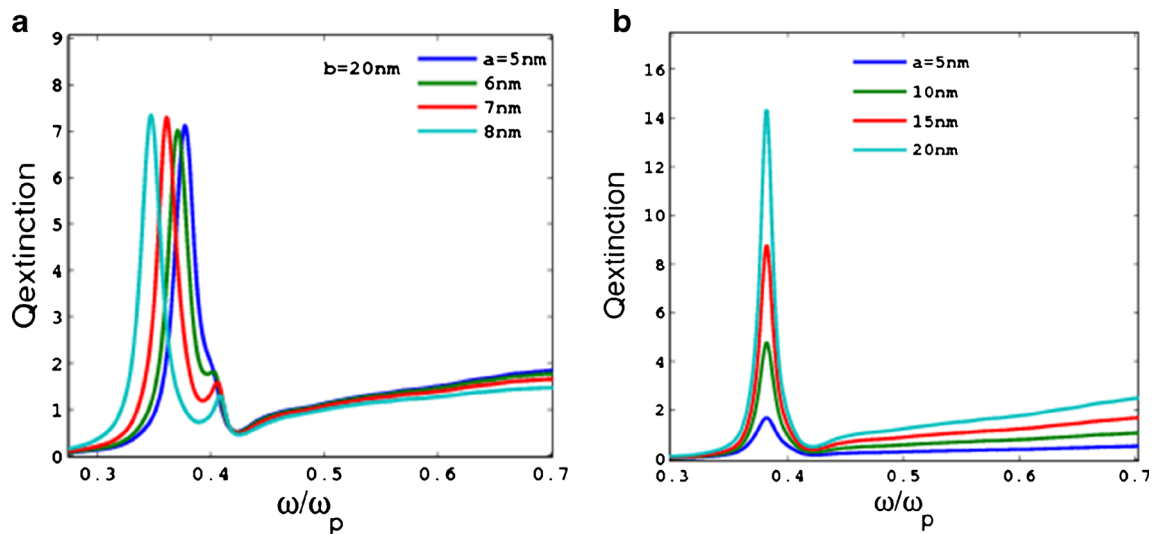

Fig. 5 Variation of Qextinction with normalization frequency of coated (SiO2@Ag) and non-coated silver metal nanospheres surrounded by air
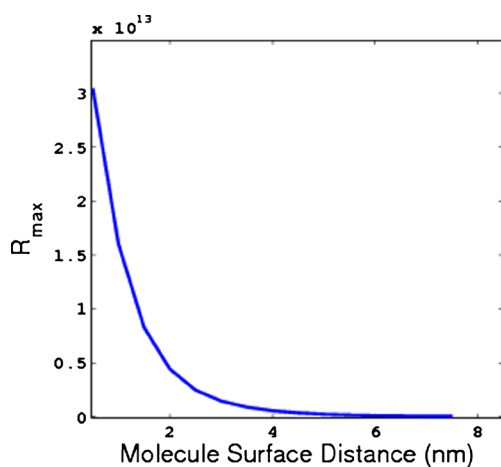
Fig. 6 Variation of maximal values of SERS enhancement (R_{max}) with molecule to surface distance for a SiO2@Ag (core@shell) MNP where $a = 12$ nm and $b = 20$ nm

embedded in air shows two resonant modes of equal Raman gain, while the same nanosphere embedded in the medium with $N = 1.5$ exhibits greater value of R at resonant frequency (0.28 w_p) and smaller R value corresponding to resonant frequency (0.86 w_p) as shown in Fig.4a. As we increase the refractive index of the medium from 1 to 1.5, SPR peaks get red shifted for the asymmetric mode and blue shifted for the symmetric mode. The same trends are followed by the non-coated nanosphere ($a = 10$ nm and $d = 1$ nm) as indicated in Fig. 4b. It also exhibits higher Raman gain corresponding to higher refractive index. The physics of high amplification for the higher ref. index medium is that the higher ref. index guides the optical signal effectively; hence, loss becomes smaller resulting in higher optical gain.

Extinction is basically the attenuation of electromagnetic wave by scattering and absorption as it propagates a particulate medium. In a homogenous medium, the dominant attenuation mechanism is usually absorption. Here, we have analysed the extinction spectrum of coated and non-coated silver spheres (embedded in a medium $N = 1$) against the normalized frequency. In Fig. 5a, we have studied the extinction spectrum of core/shell nanosphere where the outer radius is constant with various inner radii ranges from 5 to 8 nm for normalized frequency domain 0.3 to 0.7. The tunability of SPR comes into the picture as we change the core radius. Here, we observe that if the shell thickness decreases, the SPR peaks get red shifted. This all happens because of the higher interaction between the core and shell. Here, the core-shell nanosphere also exhibits the dual plasmonic peaks in two different regimes of frequency with different extinction magnitudes. If we take the particular case of coated sphere with inner radii 8 nm and outer radii 20 nm, two plasmonic resonances are observed at frequency 0.35 w_p and 0.41 w_p. In Fig. 5b, we have analysed the frequency dependence of extinction spectra for silver metal

nanoparticle embedded in air ($N = 1$) with various inner radii between 5 and 20 nm. Here, we see that the extinction peak increases with increase in radius.

Figure 6 shows the variation of maximal value of enhancement factor (R_{max}) with respect to the distance between the nanosphere and the molecule to be detected. The core-shell nanogeometry is taken to see the effects of maximum enhancement factor with core radius $a = 12$ nm and outer radius $b = 20$ nm. In this figure, we see that the R_{max} is maximum when the molecule is adsorb on the surface of the nanosphere, and it decreases when separation increases. Hence, it can be concluded that, for the detection of SERS signal, the distance between the sensing molecule and metallic geometries is taken to be quite small.

Conclusion

In this work, we have studied the surface enhanced Raman scattering from a molecule in the presence of coated and non-coated nanostructures under electrostatic approximation. We have found that coated nanogeometry plays a significant role in shifting of peaks as well as enhancing the Raman gain factor of SERS signal over the non-coated nanogeometry. We have confirmed that, at low (IR) frequency near the symmetric plasmonic resonance of a core-shell system, the SERS enhancement will in general be greater than that from a corresponding metallic sphere of the same size. The observed SERS enhancement in this study is due to the plasmonic effect, via various parameters such as core-shell geometry, thickness of the shell, molecular distance from metal nanogeometry, and surrounding environment. The present work furnishes the systematic study and comparison of two different types of metal nanostructures and its influences in the SERS enhancement mechanism that will off course be very helpful for research community.

References

1. Fleischmann M, Hendra PJ, McQuillan AJ (1974) Raman spectra of pyridine adsorbed at a silver electrode. Chem Phys Lett 26:163–166

2. Jeanmaire DL, Van Duyne RP (1977) Surface Raman spectroelectro chemistry: part I. Heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. J Electroanal Chem 84:1–20

3. Wustholz KL, Brosseau CL, Casadio F, Van Duyne RP (2009) Surface-enhanced Raman spectroscopy of dyes: from single molecules to the artists' canvas. Physical Chemistry Chemical Physics 11:7350–7359

4. Stiles PL, Dieringer FA, Shah NC, Van Duyne RP (2008) Surface-enhanced Raman spectroscopy. Annu Rev Anal Chem 1:601–626

5. Cao YC, Jin R, Mirkin CA (2002) Nanoparticles with Raman spectroscopic fingerprints for DNA and RNA detection. Science 297:1536–1540

6. Nie S, Emory SR (1997) Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. Science 275:1102–1106

7. Kneipp K, Wang Y, Kneipp H, Perelman T, Itzkan I, Dasari RR, Feld MS (1997) Single molecule detection using surface-enhanced Raman scattering (SERS). Phys Rev Lett 78:1667–1670

8. Emel'yanov VI, Koroteev TV (1981) Giant Raman scattering of light by molecules adsorbed on the surface of a metal. Sov Phys Usp 24:864–873

9. Pustovit VN, Shahbazyan TV (2006) Microscopic theory of surface-enhanced Raman scattering in noble-metal nanoparticles. Phys Rev B 73:085408

10. Kerker M, Wang DS, Chew H (1980) Surface enhanced Raman scattering (SERS) by molecules adsorbed at spherical particles: Errata. Appl Opt 19:4159–4174

11. Gersten J, Nitzan A (1980) Electromagnetic theory of enhanced Raman scattering by molecules adsorbed on rough surfaces. J Chem Phys 73:3023–3037

12. Schatz GC and Van Duyne RP, Electromagnetic mechanism of surface-enhanced spectroscopy, Handbook of Vibrational Spectroscopy, John Wiley and Sons, Ltd, 2006

13. Xu H, Wang XH, Persson MP, Xu HQ (2004) Unified treatment of fluorescence and Raman scattering processes near metal surfaces. Phys Rev Lett 93:243002

14. Yin YD, Gao L, Qiu CW (2011) Electromagnetic theory of tunable SERS manipulated with spherical anisotropy in coated nanoparticles. J Phys Chem C 115:8893–8899

15. Shalabney A, Khare C, Bauer J, Rauschenbach B, Abdulhalim I (2012) Detailed study of surface-enhanced Raman scattering from metallic nanosculptured thin films and their potential for biosensing. J Nanophoton 6(1):061605

16. Höfich K (2012) Plasmonic dimer antennas for surface enhanced Raman scattering. Nanotechnology 23:185303

17. Wang XT, Shi WS (2012) Surface-enhanced Raman scattering (SERS) on transition metal and semiconductor nanostructures. Physical Chemistry Chemical Physics 14:5891–5901

18. McMahon JM, Gray SK, Schatz GC (2009) Nonlocal optical response of metal nanostructures with arbitrary shape. Phys Rev Lett 103:097403

19. Jeanmaire DL, Van Duyne RP (1977) Surface Raman spectroelectro chemistry: part I. Heterocyclic aromatic, and aliphatic amines adsorbed on the anodized silver electrode. Electro anal J Chem 84:1–20

20. Xu H, Aizpurua J, Kall M, Apell P, Electromagnetic contributions to single-molecule sensitivity in surface-enhanced Raman scattering, Phys. Rev. E 624318–4324, 2000

21. Yamamoto YS, Ishikawa M, Ozaki Y, Itoh T (2014) Fundamental studies on enhancement and blinking mechanism of surface-enhanced Raman scattering (SERS) and basic applications of SERS biological sensing. Front Phys 9:31–46

22. Raza S, Wubs M, Mortensen NA (2011) Unusual resonances in nano-plasmonic structures due to nonlocal response. Phys Rev B 84:121412

23. Leung PT, Tse WS (1995) Nonlocal electrodynamic effect on the enhancement factor for surface enhanced Raman scattering. Solid State Commun 95:39–44

24. Pathak NK, Pandey GK, Ji Alok and Sharma RP, Study of light extinction and surface plasmon resonances of metal nanocluster: a comparison between coated and noncoated nanogeometry plasmonics, DOI 10.1007/s11468-015-9978-2, 2015

25. Xie HY, Chung HY, Leung PT, Tsai DP (2009) Plasmonic enhancement of FÄorster energy transfer between two molecules in the vicinity of a metallic nanoparticle: nonlocal optical effects. Phys Rev B 80:155448

26. Chung HY, Guo GY, Chiang HP, Tsai DP, Leung PT (2010) Accurate description of the optical response of a multilayered spherical system in the long wavelength approximation. Phys Rev B 82:165440

27. Bruzzone S, Malvaldi M, Arrighini GP, Guidotti C (2006) Near-field and far-field scattering by bimetallic nanoshell systems. J Phys Chem B 110:11050–11054

28. Wu DJ, Xu XD, Liu XJ (2008) Electric field enhancement in bimetallic gold and silver nanoshells. Solid State Commun 148:163–167

29. Rojas R, Claro F, Fuchs R (1988) Nonlocal response of a small coated sphere. Phys Rev B 37:6799–6807

30. Palik ED handbook of optical constants of solids, Academic, Orlando 1985

31. Westcott SL, Jackson JB, Radloff C, Halas NJ (2002) Relative contributions to the plasmon line shape of metal nanoshells. Phys Rev B 66:155431

32. Craig F. Bohren, Donald R. Huffman, Absorption and scattering of light by small particles, 1983

33. Noguez C J Phys Chem C Vol. 111 3806, 2007

34. Kreibig U and Vollmer M. Optical properties of metal clusters. Springer Berlin, 1995