Surface-enhanced Raman scattering from silica core particles covered with silver nanoparticles

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In this paper we theoretically show that the Raman scattering by a core-shell micron or submicron particle with epsilon-near-zero metamaterial shell and silica spherical or cylindrical core can combine useful features of cavity-enhanced and surface-enhanced Raman scatterings. The cavity resonance together with the plasmon resonance lead to the giant enhancement of the field inside the metashell which is performed as a layer of silver or gold nanoparticles and is penetrable for molecules to be detected. This approach results in the significant increase in both effective volume in which molecules are affected by enhanced electric field and Raman gain averaged over this volume.

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I. INTRODUCTION

The role of the surface-enhanced Raman scattering (SERS) (Ref. 1) in the modern sensing, especially in molecular detection, is huge. The mechanism of SERS is related (in conventional SERS schemes) with plasmonic nanoparticles resulting from roughening the silver interface. The nanoparticles offer the resonant enhancement of the local field acting on molecules located near them in a liquid- or gas-host medium. The enhancement of the local field with respect to the incident wave field leads to the proportional increase in the molecule dipole moments at both excitation frequency ω_e and at Raman frequencies ω_R (e.g., Ref. 2). This effect is complemented by the similar increase in the radiation of a pair molecule plus nanoparticle at the Raman frequency (e.g., Refs. 2–4). The plasmon resonance experienced by a plasmonic nanoparticle (sphere or ellipsoid) is rather wide band. Usually, one of Raman frequencies radiated by a molecule (or both of them) is located within the nanoparticles resonance band as well as ω_e. Therefore the amplitude of the field scattered by the pair molecule plus nanoparticle contains the product of two coefficients: $\kappa(\omega_e)$ expressing the local-field enhancement and $\chi(\omega_R)$ which equals to the ratio of the nanoparticle and the molecule dipole moments. In the classical theory[2–4] it is shown that $\kappa(\omega)=\chi(\omega)$ when the nanoparticle polarization is dipole (the same as the molecule polarization). When the Raman shift is small, i.e., $\omega_R \approx \omega_e \approx \omega_{\mathrm{av}} \equiv \omega_e/2+\omega_R/2$ this equation results in the electromagnetic Raman gain (ERG) defined with respect to the scattered field amplitude $G_{\max}=\kappa_{\max}(\omega_e)\ \chi_{\max})(\omega_R) \approx \kappa^2_{\max}(\omega_{\mathrm{av}})$ of the order $10^{(1.5-2.5)}$ or in the Raman gain defined with respect to the intensity $G^{(I)}_{\max}=\kappa^4_{\max}(\omega_{\mathrm{av}}) \sim 10^{(3-5)}$.[2,5] This result corresponds to the optimal location of a molecule for the given position of the nanoparticle and wave incidence because only the radial (with respect to the nanoparticle center) field component is enhanced and because the enhancement holds only at small distances from the nanoparticle surface (less than the particle radius).[5,6] The chemical adsorption of the metal interface[5] and some quantum effects[6] bring additional increase in the molecule dipole moment at Raman frequencies, however below we consider only ERG.

The goal of the study is to find a mechanism of a very high (much higher than above) ERG in a structure that would be rather easy in fabrication and industrially adaptable. Known structures for which the huge ERG was obtained before either are characterized by the extreme locality of the field enhancement[7–10] or are very restrictive in the regularity of the plasmonic nanoarray.[11–14] The practical importance of the highest possible *averaged* ERG $G^{(I)}_{\mathrm{av}}$ and the way how to reach it were indicated in seminal work.[11] The averaging should be done over the whole surface of the substrate covered by metal nanoparticles or metal nanocorrugations. However, the amazing values of the averaged gain attainable in nanoarrays[12–14] require the extreme precision of nanofabrication. Statistical deviations from the regularity lead to the dramatic decrease in ERG.[12]

The present paper will, hopefully, pave the way to obtaining very high values of $G^{(I)}_{\mathrm{av}}$ (sufficient to detect separate molecules) in random nanoarrays of metal nanoparticles. These arrays are suggested to locate on the dielectric core. Such structures can be fabricated by the self-assembly widely used in the modern industry.[15] Very high averaged ERG $G^{(I)}_{\mathrm{av}}$ results from the theoretically revealed effect called in this paper the cavity-and-surface resonance (CSR). This resonance has features of both whispering-gallery (WG) resonance typical for a microcavity or a submicron cavity and collective plasmon resonance typical for dense arrays of metal nanoparticles. Usually the WG resonance corresponds to the field enhancement inside the optical microcavity. This effect has been used to obtain the strong Raman radiation of the cavity material.[16–23] This effect called the cavity-enhanced Raman scattering is not applicable for detecting molecules. It is considered in the literature in a form of the so-called stimulated Raman scattering which is promising for microlasers.[24]

In CSR the WG modes are located outside the cavity (more exactly, outside the solid core). Earlier a design when the field was enhanced outside optical cavities has been already found for arrays of touching cavities.[25] However the mechanism of this enhancement was different from CSR and the averaged ERG achieved in Ref. 25 was small ($G^{(I)}_{\mathrm{av}}=7$). Moreover, it is achievable only using special coupling elements to excite microcavities.

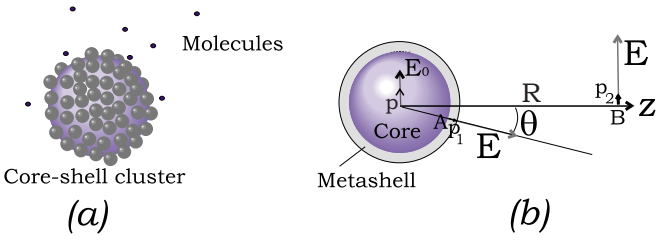

FIG. 1. (Color online) (a) A silica micron- or submicron-sized sphere (or a cylinder) covered with metal nanoparticles. (b) The same structure presented as a core-shell cavity. A point dipole p_1 located in the metashell (the radial component of the molecule dipole moment) creates at the observation point which equals to the radial component of the field produced at the center of the dipole p_1 by an auxiliary dipole $p_2=p_1$ placed at the observation point. E_0 is the amplitude of the field of the same auxiliary dipole in the absence of the core-shell cavity.

II. CORE-SHELL CLUSTERS WITH WHISPERING-GALLERY MODES

The structure suggested in the present paper is a core-shell cluster comprising a rather dense array of silver nanoparticles (e.g., spheres) randomly distributed on a silica core of submicron or micron size as shown in Fig. 1(a). We call these clusters as "templated particles" (TP). In prospective SERS schemes TP can cover a large area substrate. The advantages of such a structure compared to the usual SERS ones is not only the huge $G_{\mathrm{av}}^{(l)}$ which will be calculated below. It is also the increased effective surface at which the field is enhanced. The last feature was noticed in Refs. 26–28 where TP for SERS were already suggested, prepared, simulated, and tested.[26–28] The gain in the effective surface for spherical TP equals to 2π and for cylindrical ones it equals to π. However the best simulated and experimentally demonstrated $G_{\mathrm{av}}^{(l)}$ in these works was pretty the same as in conventional SERS.[28] This is because the effect of CSR was not used in these works and the analysis of the design parameters shows that they were far from those required for CSR.

In the present paper we consider TP with spherical or cylindrical geometry. Unlike the usual WG resonance the cavity is coupled to the host medium. This is very important for the industrial adaptation of SERS. In cavity-enhanced Raman scattering the electromagnetic coupling of an optical microcavity to outer space (i.e., to wave fields) is negligibly weak. The typical radiation quality is as high as $Q \sim 10^{(8-10)}$ and the WG modes are concentrated deeply under the surface. Thus, the simple pumping by incident waves is not efficient[18–21] and in cavity-enhanced Raman scattering schemes one uses special coupling elements (prisms or waveguides) with wave leakage between them and cavities.[18–23,25]

In the present structure the WG modes are efficiently excited by the plane waves. This is due to the presence of the metamaterial shell formed by metal nanoparticles. Due to the collective plasmonic resonance of this metashell it is possible to engineer some WG resonances so that the field is concentrated inside the metashell, i.e., at the core surface. This is what is called the CSR in the present paper.

The metashell can be presented with high accuracy as a layer of an effective continuous metamaterial as shown in Fig. 1(b).[29–31] In works[29] the homogenization model of the spherical metamaterial samples with radius $a=20-50$ nm (diameters of nanoparticles $d=3-6$ nm) was validated by additional calculations. In Ref. 30 the same was done for a metashell on a silica core. In Ref. 31 the high accuracy of the homogenization model for the metashell was confirmed by measured optical spectra where diameters of nanoparticles was either $d=15$ or $d=20$ nm and the core radius was $a=135$ nm. These results allow us to consider the TP as a bilayer sphere or a bilayer cylinder. Analytical calculations are based on the known solutions. The diffraction problems were solved for a concentric coated sphere in Ref. 32 and for a concentric coated cylinder in Ref. 33. Explicit expressions for the field in all regions can be found in Refs. 34 and 35, respectively. For a coated sphere the electric field in three regions (the core, the shell, and the outer space) is represented through vector spherical harmonics with corresponding Mie coefficients by formulas (1, 3, and 5) of Ref. 34. Formulas (7–14) were used to calculate these Mie coefficients. Similarly, for a coated cylinder, the electric field given by formulas (6, 8, and 10) of Ref. 35 contains Mie coefficients for all three regions. These coefficients were found as a solution of the linear system of equations [relations (22)–(29) of Ref. 35]. For both coated sphere and cylinder Mie coefficients for outer space coincide with those obtained in classical works.[32,33] The numerical results presented in Refs. 34 and 35 were also used for testing the MATLAB codes.

To calculate the metashell permittivity ε both Maxwell Garnett (as in Ref. 30) and Bruggeman (as in Ref. 31) models were used. For reliability the design parameters of the metashell (the silver nanosphere diameter $d=6$ nm and the averaged gap between nanospheres $\delta=1$ nm) were chosen so that they correspond to the case when both Maxwell Garnett and Bruggeman models overlap (give the same result). The host medium was assumed to be free space. The permittivity of fused silica was taken from Ref. 36 and that of silver from Ref. 37.

III. RESULTS AND DISCUSSION

Calculations showed that the electric field strongly concentrates inside the metashell when the WG modes are excited at the blue edge of the collective plasmon resonance of the metashell where its permittivity is close to 0. Only epsilon-nearly zero (ENZ) materials allow us to obtain this new resonance. With the shell of natural material two scenarios of the WG resonance are possible: the field of WG modes is concentrated inside the core; the field maxima are centered inside the shell but the modes are weakly localized and the enhancement is small. We need to strongly localize the field inside the narrow shell and this shell should be penetrable for molecules. This scenario becomes possible only with a ENZ metamaterial shell. ENZ materials form an important class of metamaterials which have been considered as promising for the modern optics since the publication of seminal work.[38]

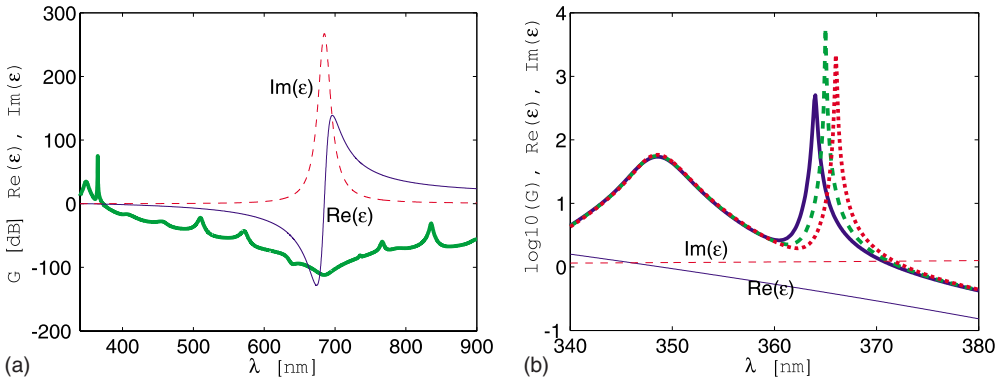

FIG. 2. (Color online) (a) Wide-band frequency plot of the averaged local-field intensity gain G (in dB) for spherical core with radius $a=323$ nm and of the complex permittivity of the metashell. (b) Same as (a) in a narrow band for three values of the core radius $a=322$ nm (solid line), $a=323$ nm (dashed line), and $a=324$ nm (dotted line).

It is important to stress that the formula $G_{\mathrm{av}}=\kappa_{\mathrm{av}}(\omega_e)\ \chi_{\mathrm{av}})(\omega_R)\approx\kappa^2_{\mathrm{max}}(\omega_{\mathrm{av}})$ or $G^{(I)}_{\mathrm{av}}(\omega_{\mathrm{av}})=\kappa_{\mathrm{av}}(\omega_{\mathrm{av}})^4$ holds not only for conventional SERS but also for TP under the condition $\omega_e\approx\omega_R\approx\omega_{\mathrm{av}}$. Let a molecule be located at a point A inside the metashell of the spherical core. The radial component of its dipole moment at the Raman frequency is denoted in Fig. 1(b) as p_1 (two other components of the dipole moment are not significant for ERG). This dipole creates at an arbitrary chosen observation point B located in the far zone the θ-polarized field of complex amplitude $E(B)$ that we can present in the form $E(B)=\chi(A)pF(R)$. Here $pF(R)$ (where F is the known function) expresses the field produced at point B in absence of the TP by the y-oriented dipole $p=p_1$ located at the same distance R from B as the TP center (see Fig. 1). From reciprocity $E(B)$ equals to the radial component of the field $\mathbf{E}'(A)$ produced at point A by an auxiliary y-oriented dipole $p_2=p_1=p$ located at B. Since the dipole p_2 is located very far from the TP the incident field from which the radial field $E(A)\equiv E'_r(A)$ results can be approximated as the field of a plane wave with amplitude $E_0=F(R)p$ at the sphere center. By definition the local-field amplitude enhancement is equal to $\kappa(A)\equiv|E(A)/E_0|$, where as we have seen $E(A)$ results from the plane-wave incidence. Therefore the amplitude radiation enhancement due to the presence of the TP defined as $|\chi(A)|\equiv|E(B)/pF(R)|$ equals to $|\chi(A)|\equiv|E(B)/pF(R)|=|E(A)/E_0|=\kappa(A)$. Since this result holds for an arbitrary point A, the radiated field enhancement and the local field enhancement are equivalent. Notice that the same speculation can be done for other field components and for a cylindrical TP as well.

So, instead of calculating the averaged amplitude of the local field and the averaged-radiated field amplitude we can simply average the intensity $|E(A)|^2$ over the metashell volume (for spherical and cylindrical cores it is a simple numerical integration of exact analytical expressions). Here $E(A)=\kappa(\omega_{\mathrm{av}},A)$ means the complex amplitude of the radial component of electric field if the TP is impinged by a plane wave of unit amplitude at frequency $\omega_{\mathrm{av}}\approx\omega_e$. This averaging procedure results in the amplitude ERG G_{av}. The intensity ERG is equal to $G^{(I)}_{\mathrm{av}}=G^2_{\mathrm{av}}$.

The result for G_{av} (in dB) versus light wavelength for the spherical TP (the core of radius $a=323$ nm) is shown in Fig. 2(a) together with the complex permittivity of the metashell. In the middle of the collective plasmon resonance band the losses in the metashell are very high and $G_{\mathrm{av}}\ll 1$. The CSR corresponds to the azimuthal and polar numbers of the WG mode $L=1$ and $N=9$, respectively. It holds at $\lambda=366$ nm where $\varepsilon=-0.1+i0.16$. Then $G_{\mathrm{av}}=5784$ and $G^{(I)}_{\mathrm{av}}\sim 4\cdot 10^7$. The optical quality of TP equals $Q\approx 5\times 10^6$ at this frequency. Cores with $a=322$ and $a=324$ nm still correspond to $G^{(I)}_{\mathrm{av}}\sim 3\times 10^7$, as we can see from Fig. 2(b), where ($\log_{10} G_{\mathrm{av}}$ is shown in more details for three values of the silica sphere radius. This result shows that the tolerances in the cavity fabrication are realistic.

It had been expected that the ERG should be higher at high-order WG resonances (when $a\geq 1$ μm) since the optical quality of cavities usually grows versus the resonance order. However, for spherical TP it is not so. The next CSR corresponds to $a=611$ nm ($L=1$, $N=18$), however $G^{(I)}_{\mathrm{av}}\sim 3$ does not improve since the WG resonance shifts to the red and the losses in the metashell reduce the gain.

For cylinders this shift was not found. The case shown in Fig. 3(a), i.e., the normal incidence of an axially polarized plane wave to an infinitely long cylinder of radius a covered with the same metashell was studied. There is only one component of the electric field $E=E_z$. In Fig. 3(b) the distribution

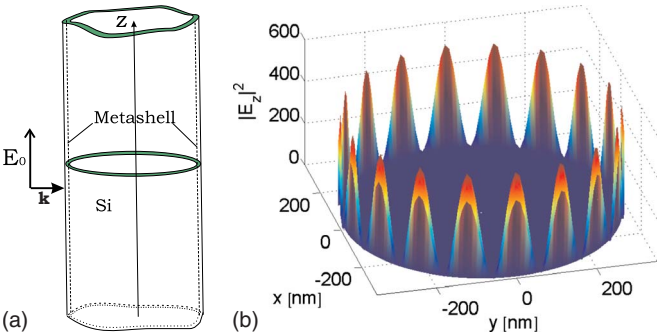

FIG. 3. (Color online) (a) Cylindrical silica core with the same metashell impinged by incident plane wave. (b) Electric intensity distribution in the structure with $a=337.5$ nm at $\lambda=353$ nm and $G_{\mathrm{av}}=202$.

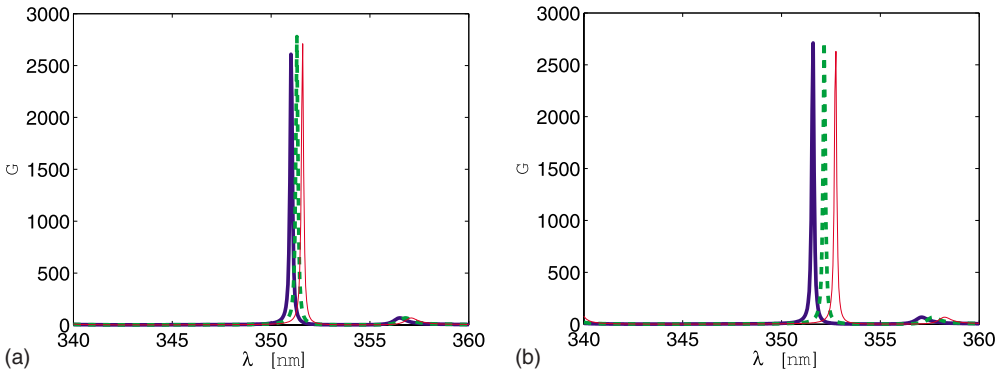

FIG. 4. (Color online) (a) Frequency dependence of G_{av} for three values of the cylinder radius $a=615.5,616,616.5$ nm (thick solid line, thick dashed line, and thin solid line, respectively). (b) Same as (a) where the metashell is an abstract dispersionless material with permittivity $\varepsilon_{const}=-0.08+i0.156$.

of the field intensity over the structure with $a=337.5$ nm at $\lambda=353.5$ nm is shown. The localization of the WG mode with azimuthal number $L=9$ within the metashell is clearly seen. Though $G_{max}=|E_z|^2_{max}$ exceeds 500, the averaging gives $G_{av}=202$, i.e., $G^{(I)}_{av}\sim 4\times 10^4$. Better results for cylinders were obtained for thicker cores. Figure 4(a) shows the frequency dependence of G_{av} for three values of the core radius $a=615.5,616,616.5$ nm corresponding to the WG modes concentrated inside the metashell. Then $G_{av}=2500\ldots2700$ ($G^{(I)}_{av}\sim 10^7$) within the band $\lambda=\lambda_{av}\pm 1$ nm, where $\lambda_{av}=352$ nm. In Fig. 4(b) the results are shown for a virtual metashell with dispersionless permittivity $\varepsilon_{const}=-0.08+i0.156$ which is equal to $\varepsilon(\lambda_{av})$. From this comparison it is clear that the dispersion of the metashell permittivity has no impact on the CSR.

Further increase in the cylinder radius allows us to obtain the higher gain, however too high values of $G^{(I)}_{av}$ correspond to very narrow resonance bands. Then the approximation $\omega_e\approx\omega_R\approx\omega_{av}$ is not anymore valid except the special case of molecules with very small Raman shift (less 1 cm^{-1} for wave numbers).

Exact analytical calculations were also done (for both spheres and cylinders) covered with a solid silver shell of same thickness $d=6$ nm. The WG resonances at which the field of WG modes is strongly localized (namely, concentrated at the inner interface between the silica core and the silver shell) were found. These resonances demonstrated tremendous G_{av} that attains even for submicron a values $G_{av}\sim 10^6$ ($G^{(I)}_{av}\sim 10^{12}$). This result also refers to CRS since the excitation of resonant WG modes by the plane wave is combined with the plasmon resonance of the solid metal shell. This core-shell structure can be applied in prospective *stimulated* Raman scattering schemes.

To conclude, in this paper a new resonance combining the resonant excitation of whispering-gallery modes and the collective plasmon resonance is theoretically revealed in core-shell templated particles and its unique features are discussed with respect to the prospective SERS schemes.

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