

Theoretical study of coated spherical metallic nanoparticles for single-molecule surface-enhanced spectroscopy

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We investigate the possibility to use coated metallic nanoparticles for single-molecule surface-enhanced spectroscopy by extending the Mie theory. The aggregates of metalodielectric spheres of Au and Ag show a strong local intensity enhancement in the cavity between particles, which can result in up to a 10^{14} -fold increase for surface-enhanced Raman scattering. We also examine the thickness of the coating layer, the size of the core, and the incident wavelength that determine the enhancement. © 2004 American Institute of Physics. [DOI: 10.1063/1.1833570]

Single-molecule spectroscopy has been significantly focused recently due to both large potential of applications in life sciences and fundamental aspects of physics and chemistry in the statistical limit of single molecules.¹ An effective method to achieve the single-molecule limit is to use surface-enhanced spectroscopy,² which usually includes surface-enhanced Raman scattering (SERS)^{2,3} and surface-enhanced fluorescence.⁴ Single-molecule SERS have been well studied for dyes, proteins, and DNA bases.⁵ The SERS enhancement stems from the electromagnetic enhancement, which is the result of the enhanced local electromagnetic field in the excitation channel and the antenna effect in the emission channel. The chemical enhancement may also contribute to SERS in some special cases, but it is believed to be much weaker than the electromagnetic enhancement.³ In a resonant case, single-molecule SERS with an overlap of the fluorescence background can be observed when the electromagnetic enhancement factor is more than ten orders.⁶ With numerous theoretical studies, the electromagnetic mechanism of single-molecule SERS can be well understood.^{2,6,7}

However, spectra of single-molecule SERS reported in experiments were usually not stable, that is, with low reproducibility.⁵ This is probably caused by molecule jumping or some chemical reasons on the metallic surface. Apart from scientific interests, these instabilities may be serious obstacles for applications. Recently, scientists have started to apply coatings of metallic particles to solve these problems.^{8,9} The following properties of a coating layer are also merits for applications: (1) Functionalized coating layers can fulfill special requirements, for example, stability, biocompatibility, and biorecognition; (2) unlike bare metallic particles, coating layers can prevent the spill-out of free electrons, and block the interparticle tunneling current that reduces the local field in the cavity between particles; and (3) coating layers can also avoid the energy dissipation of an absorbed analyte molecule to metallic particles caused by the electron-hole-pair effect, hence the yield of the Raman emission can be increased.

In this letter, we investigate how the coating will affect the SERS enhancement and discuss the potential application in the single-molecule spectroscopy. The model system is based on close-packed core/shell metalodielectric spheres with an analyte molecule either embedded in a coating layer

or in a surrounding medium. The SERS enhancement factor G is simplified as the fourth power of the local electric field enhancement: $G = |E_{\text{loc}}/E_0|^4$. The local electric field out of coated particles can be expressed as the sum of the incident field \mathbf{E}_0 and a scattered field \mathbf{E}_s , generated by the response of the electromagnetic environment:

$$\mathbf{E}_{\text{loc}}(\mathbf{r}, \omega) = \mathbf{E}_0(\mathbf{r}, \omega) + \mathbf{E}_s(\mathbf{r}, \omega). \quad (1)$$

For N spherical core/shell particles, the scattered field can be expressed as

$$\begin{aligned} \mathbf{E}_s(\mathbf{r}) &= \sum_{i=1}^N \mathbf{E}_{s,i}(\mathbf{r} - \mathbf{r}_i) \\ &= \sum_{i=1}^N \sum_{n=1}^{\infty} \sum_{m=-n}^n A_{nm,i} a_{n,i} \mathbf{N}_{nm}^h(\mathbf{r} - \mathbf{r}_i) \\ &\quad + B_{nm,i} b_{n,i} \mathbf{M}_{nm}^h(\mathbf{r} - \mathbf{r}_i), \end{aligned} \quad (2)$$

where $\mathbf{E}_{s,i}$ is the scattered field from the i th sphere centered at \mathbf{r}_i , and \mathbf{N}_{nm}^h and \mathbf{M}_{nm}^h are spherical wave vectors. The superscripts j and h represent Bessel and Hankel forms, respectively. The coefficients $A_{nm,i}$ and $B_{nm,i}$, which depend on the incident polarization and the arrangement of the spheres, can be obtained in Ref. 10. The scattering coefficients $a_{n,i}$ and $b_{n,i}$ can be obtained using the generalized Mie theory, for details see Ref. 11. The local field inside the layer can be expressed as

$$\begin{aligned} \mathbf{E}_{i,\text{loc}}^l(\mathbf{r}) &= \sum_{n=1}^{\infty} \sum_{m=-n}^n A_{nm,i} [a_{n,i}^l \mathbf{N}_{nm}^h(\mathbf{r} - \mathbf{r}_i) + c_{n,i}^l \mathbf{N}_{nm}^j(\mathbf{r} - \mathbf{r}_i)] \\ &\quad + B_{nm,i} [b_{n,i}^l \mathbf{M}_{nm}^h(\mathbf{r} - \mathbf{r}_i) + d_{n,i}^l \mathbf{M}_{nm}^j(\mathbf{r} - \mathbf{r}_i)], \end{aligned} \quad (3)$$

where the scattering coefficients inside the coating layer $a_{n,i}^l$, $b_{n,i}^l$, $c_{n,i}^l$, and $d_{n,i}^l$ can be deduced according to Ref. 12.

Figure 1 shows the SERS enhancement factor G near two coated Ag spheres with a fixed separation $d=0.5$ nm. Silica is chosen as the coating dielectric material, since the coating techniques to Au and Ag are well developed.⁸ The dielectric functions of Ag and Au are based on experimental data in Ref. 13, and the multipoles are accounted to $N=60$ for enough convergence, same as the following. As shown in Fig. 1(a), the highest enhancement is close to 10^{12} in the cavity between Ag spheres. The details of the cavity are shown in Fig. 1(c). By comparing Fig. 1(a) and Fig. 1(b), it

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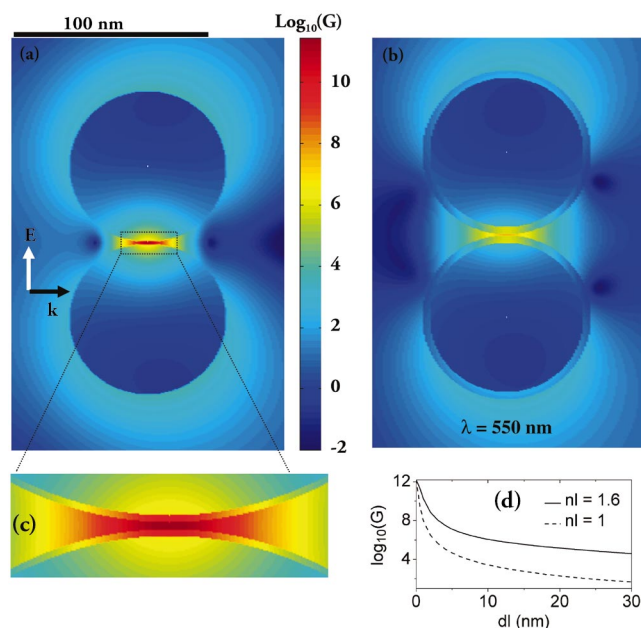


FIG. 1. (Color) Spatial distribution of the SERS enhancement G in a logarithmic scale (color) in the plane through the symmetric axis for (a) two coated Ag spheres with the core radius $r_0=40$ nm, the thickness of the layer $dl=0.5$ nm, the refractive index of the layer $nl=1.6$, the interparticle separation $d=0.5$ nm, and the refractive index of the surrounding medium $ns=1$; (b) same as (a) but with $dl=4$ nm; (c) an enlarged part of (a) in the cavity; (d) G versus dl with other configurations same as (a) for the solid line, and the dotted line shows the case for bare Ag cores. The excitation wavelength is $\lambda=550$ nm.

is clear that the coating layer obviously changes G . The maximum of G decreases about 10 000 times when the thickness dl of the coating layer increases from 0.5 nm in Fig. 1(a) to 4 nm in Fig. 1(b). Figure 1(d) shows that increasing dl will decrease the enhancement factor G . The reason is that the increase of dl will increase the separation between the metallic cores and decouple the surface plasmon resonance of the metallic cores.

The decrease of G with the increase of dl [the solid line in Fig. 1(d)] is much slower than that of the bare cores only (the dashed line). For $dl>0.5$ nm, G for the coated particles is 2–3 orders more than without the coating. This shows that a coating layer can maintain the surface plasmon coupling of metallic cores better than without a coating. One should be aware that a very thin coating ($dl<0.5$ nm) diminishes the effect of maintaining the surface plasmon coupling of the metallic cores. Such a coating effect is an accumulation effect, which can be shown by the ratio of G with/without coating. In Fig. 1(d) this ratio increases with increasing dl .

In order to obtain a higher enhancement, two core/shell metallodielectric particles can be arranged to touch, while the metallic cores are still separated by the dielectric layers to avoid the k -dependent local dielectric function¹⁴ and the strong energy dissipation^{6,15} that will largely diminish the increase of G for touching or nearly touching metallic particles. Figure 2 shows G at two different points versus the incident wavelength λ for two touching coated Ag spheres. Figure 2(a) shows G versus λ at the point in the cavity between these two core/shell particles and 0.25 nm away from the symmetric axis. The highest value of G can be reached to 10^{14} for a radius of the Ag core of $r=20$ nm at $\lambda=515$ nm. The peak enhancement can be larger than 10^{13} for other sizes of the Ag cores. As shown in the inset of Fig. 2(a), the peak

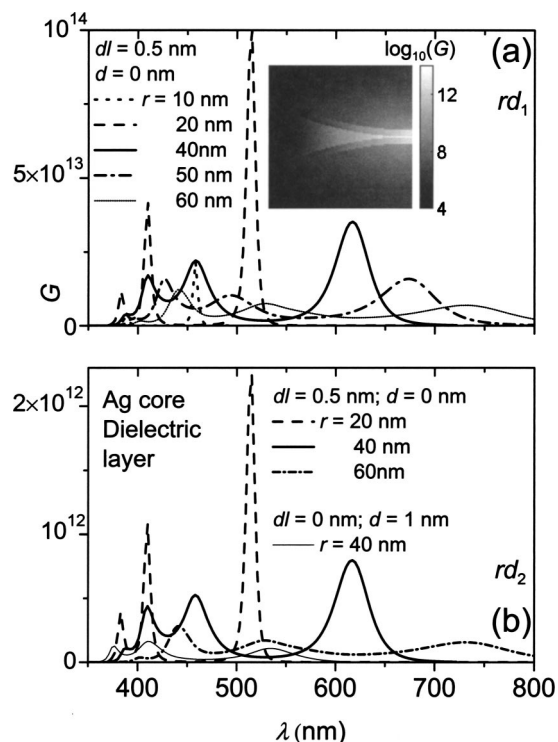


FIG. 2. SERS enhancement G (a) at the point rd_1 in the cavity between two touching coated Ag spheres and 0.25 nm away from the touching point and the symmetric axis, (b) at the point rd_2 inside the coating dielectric layer between Ag cores and 0.25 nm away from one Ag surface versus λ for the different radii r of the Ag core. The inset ($11\text{ nm} \times 10\text{ nm}$) in (a) shows the local distribution of G in the logarithmic scale at $\lambda=515$ nm for $r=20$ nm.

value is not a singularity at the touching point, but it has a considerable spatial distribution in the cavity between the two core/shell particles. For example, an enhancement factor of 5×10^{13} can be still obtained at a point 1.5 nm away from the symmetric axis. Such a high enhancement and a considerable large “hot” volume can be very beneficial for single-molecule SERS, even for colorless molecules; for example, DNA bases.

Inside the layer, as shown in Fig. 2(b), G is smaller than that in the cavity. It can be understood that the out-phased wave reflected by the outer surface of the dielectric layer can partly cancel the wave scattered by the metallic core. Even though G is still larger than that without coating [the thin line in Fig. 2(b)]. The peak wavelength also shifts to the red as the result of more retardation of multiscattering caused by the coating layer. Comparing the different sizes of the metallic core, the large size can also cause the red shift because of the retardation of multiscattering and the dispersion relation.¹⁶

Figure 3 shows the case for coated Au spheres. For a small size of the gold core, for example, $r=20$ nm, the SERS enhancement is 2–3 order less than for Ag, since the interband transition of Ag can contribute to the surface plasmon resonance in the short wavelength region.¹⁷ For larger sizes, however, the SERS enhancement for both Ag and Au is quite similar in the long wavelength region since both metals are more like the free-electron metal. For example, the peak enhancement in the red side for both coated Au and Ag particles with the radii of the core $r=40$ nm is about 3×10^{13} .

An interesting question is why core/shell metallodielectric particles can give such a high enhancement. The enhancement stems mainly from the surface plasmon resonance

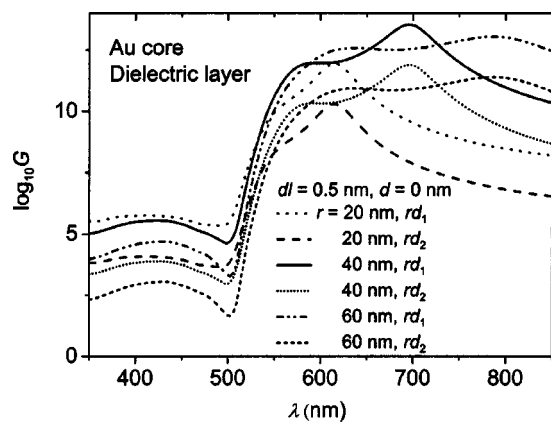


FIG. 3. Same as in Fig. 2 but for the Au core in a logarithmic scale.

of the metal cores, but a dielectric layer can modify the enhancement and refocus the light. In general, there are three reasons that a dielectric layer contributes to an additional enhancement factor. Firstly, a dielectric layer with a high refractive index can confine the light, similar to the optical fiber used in the optical communication. Secondly, the interference of the scattered light from the inner and outer interfaces partly diminishes the optical field inside the layer. Due to the energy conservation, a relatively larger enhanced field is focused at the outer surface of the dielectric layer. Thirdly, the multiscattering processes of the light scattered back and forth at the two curved surfaces of the dielectric layers can also contribute to a larger enhancement factor in the cavity. If a dielectric layer with a larger refractive index than silica, for example, diamond or SiC, is used, a further one or two orders of increase of the enhancement factor can be obtained.

As a summary, we report a huge SERS enhancement up to 10^{14} -fold in the cavity between coated Ag spheres, as calculated by the extended Mie theory, which can allow single-molecule SERS even for colorless molecules. Large coated

Au dimers can give a similar enhancement as for Ag at the red excitation. Compared with bare metallic spheres, the silica coating layer will result about two orders more SERS enhancement. Together with some other favored functions of the dielectric layer, coated metallic particles could be better substrates for single-molecule SERS.

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