Nano-Optical Investigation of Enhanced Field at Gold Nanosphere-Gold Plane Junctions

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The local field distribution around gold nanosphere-gold plane junction has been studied using the finite-difference time-domain (FDTD) electrodynamics calculation procedure. We find that both the in-plane and out-of-plane polarized excitation produce enhanced field strong enough to explain the observed SERS activities of the junctions. Comparison with a simple dipole-image dipole model shows that the enhanced field primarily originates from the multipole-image multipole interaction, which indicates that the detailed fine-structures of the nanoparticles also play a significant role in the SERS activities as well.

Key Words : Surface plasmons, Surface-enhanced Raman scattering, Finite-difference time-domain method, Metal nanoparticles, Dipole-coupling

Introduction

It is widely accepted that the local electromagnetic (EM) field enhancement at metallic junctions is mostly responsible for the single-molecule level surface-enhanced Raman scattering (SERS) signals.[1-3] However, microscopic structures of the usual SERS substrates such as self-assembled metal nanoparticles or roughened surfaces do not offer reproducibility and homogeneity in SERS activities that are required for the routine trace-level chemical analyses. Furthermore, definite nano-optical correlations among the SERS activities, local morphologies, and the local field intensity are hard to establish because of the stochastic structures of the commonly used SERS substrates. For these reasons, many different forms of the structure-controlled SERS active metal junctions, such as the rafts of nanowires,[4,5] hexagonally close packed nanospheres,[6] and nanosphere-plane junctions,[7-9] have been investigated for consistent SERS activities.

Here we examine the SERS activities of nanoparticle-molecule-plane junctions *via* numerical electrodynamics simulation of the local field. The nanoparticle-molecule-plane self-assembled nanostructure is a particularly attractive candidate because of the geometrical simplicity. Experimentally observed 10^5-10^7 fold enhancement of Raman signals from the particle-plane junctions appear significantly lower than those observed from the single nanoparticle-nanoparticle junction[3] (enhancement factors of 10^{12}-10^{14}), although these two types of junctions share similar physical origins of local field enhancement. In addition, the ensemble-averaged SERS measurements employed in-plane (parallel to the surface) polarization of the excitation light. However, far-field Rayleigh scattering spectra such as the ones measured by Porter and co-workers[10] indicate that the coupling between the particle and the surface may be negligibly small for in-plane polarized excitation.

Method

We attempt to resolve these seemingly contradictory experimental results by carrying out a 2-dimensional finite-difference time-domain (FDTD) electrodynamics simulation[11] of the localized field formed between the nanoparticle and the plane. In our simulation, the gold nanoparticle is modeled as a perfect sphere (radius = 100 nm) placed above a thin film of gold (thickness = 50 nm). The gap distance (d) between the particle and the surface is varied from 1 nm to 50 nm. A plane wave of 632.8 nm wavelength propagates along the z- or y- axis (see Figure 1), and the resulting local field distributions are evaluated after the full propagation of

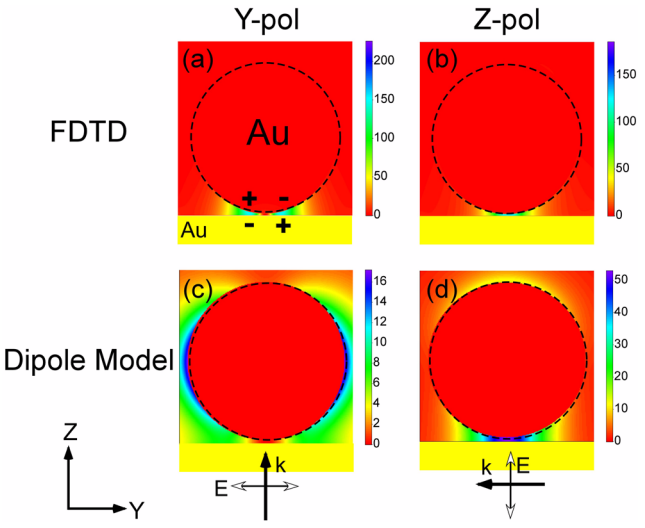

Figure 1. Local field intensity ($|E|^2 = E_y^2 + E_z^2$) distributions around nanosphere-plane junction (d = 5 nm) excited with y-polarized light (a and c) and z-polarized light (b and d). The (a) and (b) are the results of rigorous FDTD calculations. The (c) and (d) are the results from dipole-image dipole model calculations. Also shown are the propagation (k) and polarization (**E**) directions of the excitation field.

the input pulse through the system. The perfectly matched layer (PML) method[12] is employed as an absorbing boundary condition. In order to follow the essential physics of the local field enhancement, we also carried out a simplified dipole-image dipole coupling model.[13] In this model calculation, we consider the gold nanoparticle as an isotropically polarizable sphere and the dipole polarizability tensor is approximated by the quasi-electrostatic approximation of the perfect dielectric sphere. In the image dipole model, we assume that the coating is infinitely thick such that the surface can fully accommodate the image dipole.

Results and Discussion

In Figures 1a and 1b, we show the FDTD-simulated local field intensity distributions around a nanosphere-plane junction with gap-distance, d = 5 nm. The propagation and polarization directions of 632.8 nm plane wave are also denoted in the Figure 1. We find that both the in-plane (Figure 1a) and out-of-plane (Figure 1b) polarized excitations induce locally enhanced field. Analysis of vector directions (not shown) of the field reveals that the field is mostly polarized perpendicular to the gold plane (z-direction). In this particular configuration, we find the field enhancements (ratio of local field, E_{loc}, versus input field, E_0) of $|E_{loc}/E_0|$ = 12.2, and 11.2 for y- and z- polarized excitations, respectively. The z-polarized excitation leads to a uni-modal intensity distribution similar to those of the usual particle-particle junctions.[14] On the other hand, the y-polarized excitation induces a peculiar bimodal field distribution. A dipole model calculation (Figures 1c and 1d) of the same system provides a quasi-electrostatic interpretation of the local field induced by the y-polarized excitation: an induced dipolar charge distribution on the sphere creates (oppositely signed) image charge distribution on the plane. The Coulombic interaction between the real and image-charge distributions necessarily induces z-polarized local field. Although the approximate dipole-field and the rigorous FDTD-field have the same symmetry, the FDTD-derived field is more strongly enhanced within a smaller region than is predicted by the dipole-image dipole model. This difference indicates that the degree of field enhancement in nanoparticle-plane system cannot be quantitatively explained by the simplified dipole-image dipole interaction. Instead, particle-plane coupling occurs via the multipole-image multipole interaction. Additionally, FDTD calculation reveals that the local field strength is also influenced by the thickness of the film. Analogous calculation with the film thickness of 10 nm yield significantly weaker local field (data not shown).

We observe *equally strong* field enhancement with both y- and z- polarized excitation of the junction. This is in stark contrast to the nanoparticle-nanoparticle case in which the local field is sensitive to the input polarization direction.[14] The difference originates from the fact that flat metallic surface is indirectly excited via the image-charge formation, whereas the metallic particle is directly excited by the

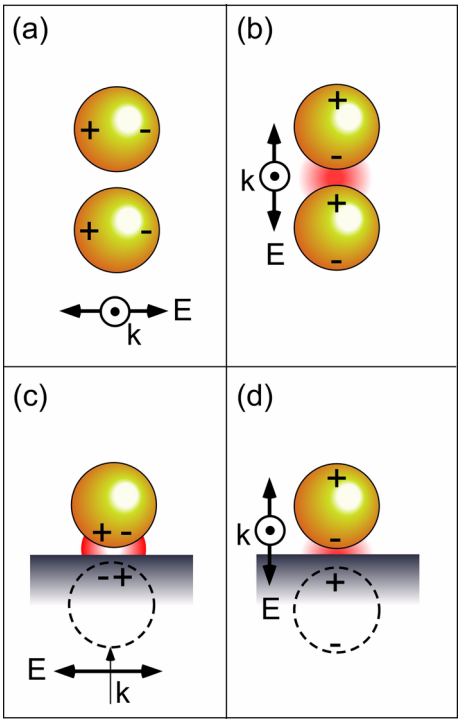

Figure 2. Comparison of particle-particle coupling (a and b) and particle-surface coupling (c and d) with two different excitation polarization directions. Also shown are the propagation (k) and polarization (E) directions.

excitation field. In addition, particle-particle coupling is dependent on the propagation direction as well as the polarization direction of the excitation beam.[15] This results in the in-phase oscillation (see Figure 2a) of the charges for particle-particle case (we assume that the propagation direction of the excitation beam is perpendicular to the inter-particle axis. An excitation beam with parallel propagation can lead to out-of-phase oscillation as pointed out by Kottmann *et al.*[15]), and out-of-phase oscillation of charges for particle-surface case (Figure 2c). In particle-particle coupling cases, the in-phase charge oscillation leads to weak and strong local field for excitation polarization perpendicular (Figure 2a) and parallel (Figure 2b) to the interparticle axis, respectively. On the other hand, in particle-surface cases, opposite charges are always brought close together (Figures 2c and 2d) irrespective of the excitation polarization direction, resulting in equally strong local field. Our results may seem contradictory to the results of far-field Rayleigh scattering experiment (white light plasmon scattering) by Porter *et al.*[10]

However, we note that the far-field Rayleigh scattering spectra only represent wavelength dependence of the *overall dipole polarizability* of the sphere-plane system.

As can be seen in Figure 1a, the localized electric field has two maxima that are 180 degrees out of phase with each other. Therefore, the contribution from the local field to the overall polarizability is cancelled, and hence the coupling induces negligible change on far-field scattering spectrum. On the other hand, the Raman scattering from the molecules

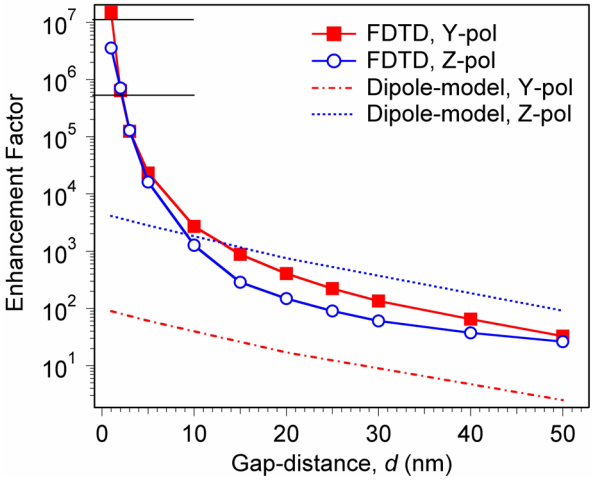

Figure 3. The Raman enhancement factor (EF = $|E_{loc}/E_0|^4$) versus gap-distance, *d*: solid squares (FDTD, y-polarized), open circles (FDTD, z-polarized), dash-dot line (dipole model, y-polarized) and dotted line (dipole model, z-polarized). Also shown (in black solid lines) are the experimental EF values of Orendorff *et al.*[9] (~10^7) and Kim *et al.*[8] (~5×10^5).

is an incoherent process. Therefore, the SERS radiation from the junction is not canceled and hence can be detected in the far-field region. Therefore, the observations of the strongly enhanced field, and the invariant far-field spectra[10] upon particle-plane coupling are not contradictory to each other. In fact, the independence of SERS and the far-field Rayleigh scattering has been already experimentally demonstrated by Michaels *et al.*[16] in particle-particle system.

According to the EM-mechanism proposed for the SERS, the effective cross section for the SERS process is proportional to the fourth power of the local field under which the molecules are situated, and therefore the SERS enhancement factor (SERS signal versus un-enhanced Raman signal, EF) should correspond to: $EF = |E_{loc}/E_0|^4$. Figure 3 displays the simulated SERS enhancement factors (EF) as a function of the particle-surface distance (*d*), obtained with y- and z-polarized excitation field, together with the experimentally measured EF values of Kim *et al.*[8] and Orendorff *et al.*[9] At the smallest gap-distance, d = 1 nm, we find that the EF values are 1.5×10^7 and 3.6×10^6 for parallel (y) and perpendicular excitation polarizations, respectively. These estimates are in reasonable agreements with the experimental EF values of 5×10^5 (Kim *et al.*[8]) and 1.2×10^7 (Orendorff *et al.*[9]), which verifies that both the in-plane polarized (y) and out-of-plane (z) polarized excitation of the junction indeed produce intense field sufficient to explain experimentally measured EF values. The EF values rapidly decay within the gap-distance of 5 nm, again confirming the multipolar nature of the particle-plane interaction (a dipole-image dipole coupling strength decays at the distance scale of the overall particle radius of ~100 nm. Also, see Figure 3).

Conclusion

In conclusion, we find that both the in-plane and out-of-plane polarized excitation produce enhanced field strong enough to explain the observed SERS activities of the junctions. The strength of the local enhanced field primarily originates from the multipole-image multipole interaction, which indicates that the detailed fine-structures of the nanoparticles may play a significant role in the SERS activities as well. In fact, Orendorff *et al.*[9] recently reported additional increase in SERS efficiencies with nanocube-plane junctions, corroborating our prediction. More systematic theoretical investigations of the particle-plane junctions, including the effects of the particle shape and film thickness on SERS efficiencies, are currently underway.

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